$1 50

Study and Interpretation of the Chemical Characteristics of Natural Water

By JOHN D. HEM

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1473

March 3, 1849

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1959

UNITED STATES DEPARTMENT OF THE INTERIOR

FRED A. SEATON, Secretary

GEOLOGICAL SURVEY

Thomas B. Nolan, Director

For sale by the Superintendent of Documents, US. Government Printing Office
Washington 25, D.C. - Price $1.50

CONTENTS

Page

Significance of properties and constituents reported in water analyses—Continued

ILLUSTRATIONS

TABLES

STUDY AND INTERPRETATION OF THE CHEMICAL CHARACTERISTICS OF NATURAL WATER

By JOHN D. HEM

ABSTRACT

The chemical composition of natural waters is affected by the soluble products of rock weathering and decomposition. Chemical analyses of representative water samples help indicate the nature and importance of some of the environmental factors to which liquid water may be exposed in the hydrologic cycle.

The United States Geological Survey utilizes standardized procedures in water sampling, analysis, and reporting of results.

More than 50 constituents or properties may be determined in water analysis, but the usual analysis includes only those considered essential, in the light of the use to be made of the data, by the agency requesting the analysis. Specific conductance is an approximate indicator of concentration of dissolved solids. Hydrogen-ion concentration, reported as pH, depends on the extent of hydrolysis of certain anions and cations in solution. Solid residue remaining after evaporation is a direct measure of dissolved-solids concentration in water of normal composition. Silica may be present in water as a form of undissociated silicic acid but may hydrolize in some waters to increase the pH. Iron in the ferric form is nearly insoluble in normal water, but in the ferrous form 10 ppm or more may *be* present. Manganese is rarer in water than iron, and, like iron, may be brought into solution by activity of micro-organisms. Aluminum is nearly insoluble in water in the pH range 5 to 9. Calcium carbonate is dissolved in water containing carbon dioxide and the resulting buffered system maintains the pH of most natural waters in the range 6 to 8. Magnesium is dissolved from igneous rock minerals and from carbonates and when in solution is less readily precipitated than calcium. Sodium salts are very soluble, and the more highly mineralized waters generally are high in sodium. In dilute waters which have been softened by base exchange or that have come from some types of siliceous igneous terranes, sodium may constitute a high percentage of the total cations. Potassium is less abundant in water than sodium because it is reconstituted into insoluble secondary minerals that are formed in the process of weathering.

Although alkalinity in water is expressed in terms of carbonate and bicarbonate ions, these values may actually represent not only the content of these ions but also all or parts of the effect of silicate, borate, and other anions which participate in hydrolysis. Acidity in water results both from hydrolysis involving cations, for example iron or aluminum, and from the presence of free acids. Sulfate is the form in which sulfur usually occurs in water. Weathering of sulfide-bearing rocks or direct solution of evaporate deposits may be important sources of sulfate. Chloride is present in many surface waters in amounts greater than could. come from windblown sea salt in rain water. Some chloride is dissolved from rocks and some may be associated with connate and juvenile water.

Fluoride concentrations in water are normally very low, but 30 ppm or more may occur in waters from certain environments. Nitrate may be added to water by organic pollution, or leaching of fertilized soils, but in some waters the presence of nitrate is not easily explained. Phosphate may be contributed by organic pollution and may be introduced in the treatment of public supplies, but is rarely present in amounts over 1 ppm. Boron is a component of some very stable minerals and in trace concentrations is widespread in soils and waters.

Traces of heavy-metal cations are present in most waters. The amounts of titanium, chromium, nickel, cobalt, copper, tin, lead, zinc, cadmium, and mercury that are normally present are not known. Analyses rarely include these determinations except for mine waters and sources which are suspected of pollution. Arsenic and selenium probably occur as anions and are of interest because of their toxic character, but rarely do unpolluted waters that are otherwise potable contain harmful amounts.

Nothing is known of the distribution of beryllium in natural water. Strontium is very similar in chemical behavior to calcium and minor amounts probably occur in many waters. Barium has a highly insoluble sulfate, and only traces of barium can be expected in waters where sulfate is present.

Lithium is probably common in amounts less than 1 ppm in water. Very little information is available about rubidium and cesium in water. Ammonium is found in water from some hot springs.

Many natural waters are weakly radioactive, owing to traces of natural radioactive disintegration products, especially radium and radon. Traces of uranium are common in natural waters.

Bromide and iodide are present in some natural brines and occur in trace amounts in other waters. Sulfite and thiosulfate are rarely found in natural water. Dissolved gases, especially oxygen and carbon dioxide, are important in the action of water as a biologic and geologic agent. Hardness in water is of interest in connection with practical water use. The reaction of water toward soil in irrigated areas may be best predicted by use of the sodium-adsorption ratio :

$$\frac{Na^{+}}{\sqrt{\frac{Ca^{++}+Mg^{++}}{2}}}$$

Tabulation of more than 50 analyses of waters from various streams and underground aquifers shows the wide range of concentration of the common constituents of natural waters.

Water analyses may be compared and interpreted by various techniques. These techniques range from inspection of the data to more intensive comparisons using ratios of one constitutent to another. Averages weighted by time or by discharge, and geochemical classifications made either mathematically or by graphic procedures are often used. The graphing systems in use include linear plots of two chemical variables, various types of bar graphs, radiating coordinates, multiple-axis pattern diagrams, linear pattern diagrams, subdivisions or distinctive shading of areas of fixed size or shape, and trilinear plots. Graphing procedures may be useful in showing relations of chemical variables to hydrologic variables, or to time. Such procedures include frequency diagrams, hydrographs, and rating curves. Areal study of water quality is aided by salinity profiles, and by symbol and isogram maps.

Quality of water is affected by many things besides mineral composition of the rock material associated with the water. When other factors are not of overshadowing magnitude, however, water from igneous terranes usually has a high proportion of dissolved silica. Water from resistate sediments is strongly influenced by solution of cementing material, water from hydrolyzates is often affected by connate salt and ion exchange, water from precipitates is usually porportionately high in calcium and magnesium bicarbonate, and water from evaporates is high in other dissolved salts. Waters may be considerably altered in composition by chemical precipitation, adsorption or ion exchange, reduction of sulfate, admixture of other waters, life processes of plants and animals, and activities of man.

Surface-water discharge can be measured by the behavior of injected "slugs" of salt and from the extent of dilution of continuous salt injection. These techniques can be applied in modified form to measure ground-water inflows to streams, rates of ground-water movement, and the volumes of underground water involved in mixtures of water from various sources.

Chemical quality standards for waters to be used for domestic, agricultural, and industrial purposes have been published by the U. S. Public Health Service, the Department of Agriculture and other agencies. Water that does not meet the published standards is used in some places, but the users of such water should recognize potential difficulties and be prepared to meet them.

INTRODUCTION

The study of water resources has always been an important part of the work of the U. S. Geological Survey. Beginning in the closing years of the 19th century and the early part of the 20th, many of these studies were made, especially in the newly settled areas of the West. Much of the work done during this period was of a reconnaissance type, and included studies of the quantities of water occurring in surface streams and in porous rocks underground. The quality of water from both sources was also determined so that the user might know which supplies were suitable for proposed uses. Independent areal investigations of this kind have been carried on to the present time.

With the fuller development of the Nation and the ever-increasing demand for larger and better water supplies, studies of water resources have become more comprehensive and detailed. New techniques have been developed and the science of hydrology has emerged as a separate discipline. Water analyses, when fully utilized by proper study techniques, are useful tools of the hydrologic investigator. As indicators of water quality for the prospective user, they also constitute an important phase of the integrated water-resources investigations which modern needs require. Intensified studies of water resources require the utilization of all possible avenues of investigation. One means by which a better understanding of the occurrence and movement of water can be gained is study of chemical analyses of the water and an increasing number of chemical-quality data are being used in this way.

PURPOSE AND SCOPE OF REPORT

The full value of quality-of-water studies in general or detailed hydrologic investigations often has not been realized, because few are familiar enough with the possible applications of quality-of-water data. This paper considers the importance of proper water sampling, discusses certain aspects of chemical analyses of water including the units of measurement commonly used, and surveys the basic chemistry of constituents and properties determined. The many possible means by which water analyses can be studied and applied in hydrologic investigations are touched upon. Specific examples of the use of analyses in studies appearing in the literature or with which the author is personally familiar are given in some instances to aid in understanding the techniques or because they may be helpful in suggesting similar or modified application elsewhere. The basic principles of the chemistry of natural waters need more thorough study before they can be fully presented, and they are not exhaustively discussed here. It is hoped, however, that some practical assistance in the interpretation of water analyses may be [illegible]rded in these discussions for geologists, engineers, and chemists active in the field of hydrology.

Natural waters acquire some of their chemical characteristics through direct solution of some of the solids, liquids, and gases with which they may come in contact in the various parts of the hydrologic cycle where water is in the liquid state. In addition, in the presence of water, chemical reactions may occur in which soluble products are formed. The final composition of a water is the result of a number of solutional and decompositional processes. The several chemical systems that are usually involved may present a very complicated combination, but one which may often be evaluated at least semiquantitatively by the use of principles of theoretical chemistry. Certain reactions—for example, the solution of carbonates and the exchange of cations between solutions and clay minerals—are reversible and may lend themselves fairly well to theoretical treatment. The chemical processes are affected by certain variables in the environments of natural waters. Some of these factors include the type of mineralogic and geologic environment, amount of water available, its rate of circulation, the activity of micro- and other organisms, and temperature and pressure. If the chemical reactions that are involved can be fairly well described and understood, the results as indicated in water analyses may give some basis for evaluating the environmental factors.

Much research in natural water chemistry remains to be done before a full realization of the value of water analysis as an interpretive hydrologic tool can be realized. This research will require the cooperative efforts of scientists in several different fields.

ACKNOWLEDGMENTS

As originally conceived, this report was to be a joint effort under the authorship of R. M. Jeffords, formerly of the Ground Water Branch of the U. S. Geological Survey, and the present author. A number of ideas and suggestions originated by Mr. Jeffords have been used in the present version of the report, although he was unable to participate actively in preparing it. The author also wishes to acknowledge the interest in the report and the generous assistance given by many of his colleagues in the Geological Survey.

This report was prepared under the supervision of W. F. White, chief, Chemical Quality Section, Quality of Water Branch, and under the general supervision of S. K. Love, chief, Quality of Water Branch.

PROPERTIES OF WATER

Water is a chemical compound of oxygen and hydrogen and in the gaseous state can be represented by the molecular formula 1120. Three isotopes of hydrogen and three isotopes of oxygen exist in nature, and if these are taken into account, 33 varieties of water are possible. Some consideration will be given to the isotopic varieties of hydrogen and oxygen later in this paper. The physical properties of liquid water are unique in a number of respects, and these departures from what might be considered normal for such a compound are of the greatest importance with respect to both the existence of life on earth and the operation of many geochemical processes. The boiling point and freezing point of water are both far higher than would be theoretically expected, considering the low molecular weight of the compound, and the range of temperature over which water exists as a liquid is wider than might be expected. An understanding of the reasons for these and other departures from "normal" behavior can be gained by more detailed consideration of the molecular structure of the compound.

Molecules and crystalline structures are often studied by the use of models, in which spheres of various sizes represent the atoms out of which the structure is built. Connecting devices of various kinds in these models represent the bonds that hold the structure together. Much information has been obtained, especially through the science of crystallography, as to the distances that separate the ions in crystals, and the effective size of the ions themselves. A model of the water molecule could be visualized as a single sphere representing the oxygen, to which two other spheres representing hydrogens are attached. The distance from the center of the oxygen to the center of each of the hydrogens is 0.9 angstrom unit. The spheres representing the ions coalesce to some extent, and the molecule might be thought of as a sphere having two rather prominent bubbles or "blisters" attached to it. The bonds connecting the hydrogens to the oxygen describe an angle of 105 , so that the two hydrogens are relatively close together on one side of the molecule.

Although this representation of the molecule is somewhat empirical, it helps to explain some of the features of the behavior of water. The molecule has dipolar properties because the positive charges associated with the hydrogen are concentrated on one side of the molecule, leaving a degree of negativity on the opposite side. Forces of attraction thus can exist between hydrogens of one water molecule and oxygens in other water molecules. These forces are called hydrogen bonds. They hold the molecules together in a fixed pattern in the solid state. In contrast to the orderly arrangement of molecules in a crystal of ice, the molecules of liquid water are in a chaotic condition of disorder. Hydrogen bonds still remain an important force, but their arrangement is continually shifting.

The cohesive forces represented by the hydrogen bonds impart to liquid water its high heat of vaporization. These forces also tend to prevent the passage of electric currents and impart to the fluid its high dielectric constant. The attraction between molecules of a liquid is shown at a liquid surface by the phenomenon called surface tension. The surface tension of water is 75.6 dynes per centimeter at 0°C and 71.8 dynes per centimeter at 25°C, which are very high values compared with many other liquids. When in contact with a surface to which the liquid particles are attracted, water is drawn into small openings with a force many times that of gravity, induced by the surface tension of the fluid. Water thus can penetrate small openings in rocks and come into intimate contact with minerals.

COMPOSITION OF EARTH'S CRUST

The average composition of the crustal material of the earth has been a subject of geochemical study for many years. For the present report, these averages are of secondary importance because mineral matter dissolved in waters is the primary consideration. However, this dissolved mineral matter originates in the crustal materials, and the composition of the crust is therefore worthy of brief consideration.

The literature of geochemical investigations contains many chemical analyses of rocks from all parts of the world. Compilations of these analyses and averages of those considered the most accurate were made by Clarke and Washington (1924) , and by Clarke (1924a). Later workers in the field of geochemistry have modified the original estimates of Clarke and Washington, particularly with respect to igneous rocks. Some of the more recent compilations (Fleischer, 1953, 1954) include elements present in trace quantities which were not covered in earlier studies. Data on concentrations of these trace constituents of rocks still are incomplete, and particularly so with respect to the sedimentary rocks, so that further modifications in the estimates of the composition of the crust can be expected.

Table 1 is based on data assembled by Rankama and Sahama (1950, p. 226) and gives the average concentrations of 38 of the elements in igneous and sedimentary rocks. These 38 elements are the ones which are of greatest present interest in water chemistry and which are discussed in this report. The column which deals with igneous rocks is based on data assembled by Goldschmidt (1937b) supplemented by more recent reported values from other writers. Data in columns relating to three of the classes of sedimentary rock are from Clarke (1924a) supplemented by newer results for the trace constituents obtained by other investigators. The data are believed the best estimates available.

TABLE 1.—*Average composition of igneous and some types of sedimentary rocks, with respect to certain elements dissolved in natural water (ppm)*

(After Rankama and Sahama, 1950]

Element	Igneous rocks	Sedimentary rocks		
		Resistates	Hydrolyzates	Precipitates
Si	277, 200	367, 500	272,800	24,200
Al	81,300	25,300	81,900	4,300
Fe	50.000	9,900	47.300	4,000
Ca	36,300	39, 500	22,300	304,500
Na	28.300	3,300	9, 700	370
K	25,900	11,000	27,000	2,700
Mg	20,900	7,100	14,800	47,700
Ti	4,400	960	4,300	
P	1,180	350	740	175
Mn	1, 000	trace	620	385
F	600-900		510	250
S	520	2.800	2,600	1,100
C	320	13,800	15,300	113,500
Cl	314	trace		200
Rb	310	273	300	0
Sr	300	<26	170	425-765
Ba	250	170	460	120
Cr	200	68-200	410-680	2
Zn	132	<20	200-1,000	50
Ni	80	2-8	24	0
Cu	70		192	20.2
Li	65	17	46	<26
N	46			
Sn	40		40	
Co	23	0	8	0
Pb	16	20	20	5-10
Th	11.5(?)	6.1	10.1	1.1
Cs	7		12	
Be	6(?)		<4	0
As	5			
U	4	1.2	1.2	1. 3
B	3	9-31	310	3
Br	1.62		<.2	
I	.3			.07-.55
Cd	.15	0	.3	
Se	.09		.6	<.1
Hg	08—.5	.1	.3	.03
Ra	1.3×10	$.7\times10$	$1.08\times10^{-}$	$.42\times10^{-6}$

According to Clarke and Washington (1924), 95 percent of the crust of the earth to a depth of 10 miles is igneous rock. Therefore, the average composition of the 10-mile crust closely approaches the average for igneous rocks. In the consideration of water and its relation to rock composition, however, the predominance of igneous rock is less significant. Most recoverable ground water occurs at depths of less than a mile below the land surface, and in this part of the earth's crust the sedimentary rocks are more prevalent than igneous rocks. As a rule, the igneous rocks are poor aquifers and do not, therefore, come into long, intimate contact with a large proportion of the ground water. In the headwater areas of many streams, igneous rocks are at the surface, and they may contribute solutes to surface waters directly and through leaching of partly decomposed rock present in the soil. The areas where such rocks are exposed to attack by surface streams are not a predominant part of the earth's surface. Therefore, the sedimentary rocks and the soil assume considerable importance as the immediate sources of soluble matter to be taken up by circulating ground and surface water. Reactions between water and the minerals of igneous rocks, however, are of fundamental importance in studies of geochemistry, and they have been considered at some length in this report.

The three classes into which sedimentary rocks are divided (table 1) are from Goldschmidt (1933b). This classification is based on chemical composition and the degree of alteration of the minerals making up the rocks. It probably is better suited to studies where chemical composition is involved than are the usual geologic classifications of these rocks by means of mineral character, texture, and stratigraphic sequence.

The three classes of sedimentary rocks for which data are given in table 1 may be defined as follows :

Resistate : A rock composed of residues not chemically decomposed in the weathering of the parent rocks.
Hydrolyzate : A rock composed of insoluble products formed by chemical reactions in the weathering of the parent rock.
Precipitate : A rock formed by chemical precipitation of mineral matter from aqueous solution.

A fourth rock type, the evaporates, may influence the composition of natural waters, but data available do not appear to be sufficient to permit quantitative estimates of the type included in table 1. Evaporates are rocks produced by deposition of solutes upon evaporation of the water in which they were dissolved.

In the practical application of these definitions, certain limitations of the system become apparent. The severity of chemical attack in weathering has a wide range. Under very rigorous conditions a residue consisting wholly of quartz sand might be produced from a given igneous rock. Under less severe attack an arkose containing feldspar and other mineral species less resistant than quartz might be produced from the same original rock. Under certain circumstances, a resistate could contain some of the ferromagnesian minerals that are not highly resistant to chemical attack.

Other important factors in determining the composition of sediments are the processes of comminution and mechanical sorting that accompany weathering. Resistates, as the term is applied here, are predominantly coarse grained. Some of the resistant residues, however, may be reduced to a fine powaer and be deposited with the naturally fine-grained hydrolyzates Chemical precipitation may occur in a highly saline environment so that evaporates and precipitates are mixed together in the rock-forming residue.

Because many of the sedimentary rocks contain mixtures of the weathering products, a division into classes must be somewhat arbitrary. Thus, although one might think of a pure quartz sand as typifying all ideal resistate, the class as used in this discussion also includes sandstones, conglomerates, arkose and even unconsolidated alluvium. Likewise, although clay might be considered a typical hydrolyzate, the class includes impure materials such as shale. The decision as to whether a given rock formation is a resistate or a hydrolyzate probably requires a decision as to whether it consists largely of comminuted fragments of relatively unaltered rock material, or if it consists mainly of chemical alteration products.

Carbonate rocks such as limestone and dolomite must be assigned to the precipitates, although most of them are aggregates of calcitic or dolomitic particles rather than original precipitates.

Goldschmidt recognized other types of sediments including those deposited as oxide, such as iron ores (oxidates), and organic or reduced residues (reduzates) such as coal or sedimentary sulfides. Data relating to the composition of these kinds of rocks and their total volumes seem to be insufficient to justify estimates of their average composition.

Statements of the composition of the hydrosphere are contained in the literature (Clarke 1924a, p. 36). The water and salt load of the ocean constitute a very large part of the hydrosphere and therefore the composition shown by Clarke is nearly the same as for the ocean. Table 2 shows the composition of the water of the ocean with respect to the elements listed in table 1. Clarke (1924b, p. 5) published data showing average composition of water of North American rivers, which have been widely quoted. In view of more complete data now available, Clarke's figures for river waters may need revision. Averages of this type are useful for comparative purposes. They show in

TABLE 2.—T[illegible] composition [illegible]

(After R[illegible] and S[illegible], 1950]

Constituent	Concentration (pp*
Cl	18,980
Na	10,560
SO_4	2, 560
M	1,272
C	400
	380
HCO_3	142
B	65
S	13
	4.6
	1.4
Rb	. 2
A	.16—1.9
L	. 1
Ba	. 05
	. 05
SiO_2	. 04—8. 6
	. 03—.9
Zn	. 005— . 014
Pb	. 004— . 005
S	. 004
A	. 003— . 024
C	. 001— . 09
Sn	. 003
F	. 002— . 02
C	~. 002
Mn	. 001— . 01
	. 001— . 10
Th	0005
Hg	. 0003
	. 00015— .0016
C	. 0001
Ni	. 0001 — . 0005
Ra	$8.\times 10^{-11}$
B	
Cd	
C	
Ti	T[illegible]

[illegible]

WATER AS A GEOCHEMICAL AGENT

THE ROLE OF WATER IN EROSION

[illegible]

important agent in the moving of disintegrated rock materials and minerals from place to place in the process of erosion. Water which runs off the land surface may frequently carry with it large quantities of sediment in suspension. This suspended matter often brings itself strikingly to the attention of man when deposited where it is unwanted, as in the deposits of mud left by flood water in river-bordering cities, or in the sediments which fill reservoirs intended for power development or for storage of water for irrigation or other purposes. The process of erosion by surface streams may produce other prominent effects, ranging from gullied farmlands to the spectacular Grand Canyon of the Colorado River.

Besides the materials carried in suspension, very large quantities are carried in solution, both in the water of surface streams and in ground water. The effects of erosion by solution are generally less evident than the effects of mechanical erosion but may be very striking. The salt beds and saline lakes which occupy the lower portions of some of the closed basins of the United States are the result of accumulation of the products of erosion by solution of the rocks of the surrounding areas. Deposition of minerals from circulating ground water has played a part in the production of commercially valuable mineral deposits. Ground water may dissolve and carry off rock material, producing limestone caverns, and the present-day topography of many areas is largely the result of extensive solution of underlying rocks.

The quantity of material removed in this process of "solvent denudation," as it is sometimes called, is large. Computations based on records of surface-water quality for the 1950 water year published by the Geological Survey show that from 70 to 86 tons of soluble matter were carried on the average in that year from each square mile of drainage area of the James River above Richmond, Virginia; the Iowa River above Iowa City, Iowa; the Colorado River above Grand Canyon, Arizona; and the Similkameen River above Oroville, Washington. Higher rates were observed for certain streams draining limestone terranes in humid areas, and lower rates are typical of certain streams in the Great Plains and in arid regions. A rate of 93 tons per year per square mile is reported for the Wind River basin of Wyoming by Colby, Hembree, and Rainwater (1956). A rate of solvent denudation of 80 tons per square mile per year is roughly equivalent to a lowering of the land surface of 1 foot in each 20,000 years by this process.

Water acts as a solvent, to some extent, on practically all minerals. The solvent action of water is greatly increased by the dissolved carbon dioxide, which is present in most natural waters. Rainwater may dissolve carbon dioxide from the air, and soil and ground waters receive even larger amounts from the decomposition of organic matter in the soil. A water solution of carbon dioxide is a weak acid. The humic acids in many waters as a product of decaying vegetation also may increase the solvent power of water.

Besides the importance of decay of organic matter in contributing the carbon dioxide that increases the solvent action of water on inorganic matter, the solution of organic matter is important in other ways. In many swamp and river waters a large part of the soluble load is dissolved organic matter as shown by the pronounced color of such waters. In densely populated areas, organic wastes may-constitute a large part of the dissolved and suspended load of streams. The importance of some of these organic substances in changing the solvent power of water is still incompletely understood.

CHEMISTRY OF WEATHERING PROCESSES

Since the last edition of F. W. Clarke's "Data of Geochemistry" (1924a), geochemical research has increasingly utilized basic principles of physical chemistry in explaining the chemistry of rock. An impressive amount of progress has been made in this direction, as shown by the newer texts on the subject of geochemistry. Geochemists working in the field of crystallography determined the arrangement and the effective size of ions in crystals, and this information was utilized to explain the substitution of one ion for another in minerals and many other features of the chemistry of rocks and minerals. The concept of "ionic potential," which is the ionic charge of an ion divided by its radius, was applied by Goldschmidt to explain why some ions are adsorbed and others tend to remain in solution in the ocean, and is an aid in other studies of the behavior of chemical elements in weathering.

Other investigators, for example, Garrels (1954) and Zobell (1946) , have been concerned with the evaluation of oxidation-reduction or "redox" potentials and pH of natural environments, and the use of such data in explaining and predicting the chemical reactions which are involved in the weathering of rocks and transport of soluble material in water.

By calculating the free energy changes involved in geochemical reactions (Chapman and Schweitzer, 1952) , a better understanding of factors involved in mineral stability has been gained. Chemical kinetics, the study of reaction rates, is another field that has broad applications in geochemistry.

Several fields of study offer considerable promise for improving our understanding of natural water chemistry. For example, values for ionic radii may often give useful indications as to the way ions from solutions may enter or attach to crystal structures. Ions having two or more oxidation states will affect the redox potential of solutions, or conversely the redox potential of the environment will determine the oxidation state of the ions that go into solution. Free energy data aid in predicting the reactions which may occur to add or remove dissolved ions, and provide a means for evaluating the strength of chemical bonds. Studies of reaction kinetics should help determine the degree to which equilibrium is achieved in natural systems. Unfortunately at this writing the literature of natural water chemistry contains relatively few examples of the application of these principles, but research now in progress, and that which will doubtless be undertaken soon, will improve this situation and help to give a better understanding of the chemistry of natural waters.

COLLECTION OF QUALITY-OF-WATER DATA

Water analyses have to be accurate and reliable to be useful in hydrologic studies. A vital phase of the data-collection procedure and one that is important to the accuracy of the final result is the obtaining of the water samples for analysis. This fact is often overlooked or insufficiently emphasized. Although water-sample collection does not constitute a part of interpretation, it seems appropriate to devote some space to the discussion of sampling, and to point out the possible effects of sampling techniques upon reliability of the results.

The types of sample containers used and conditions of storage of samples before analysis also may affect the results. These factors have been discussed by the U. S. Geological Survey (1958) in a report on laboratory procedures used in water analysis.

COLLECTION OF WATER SAMPLES

In any type of study in which only small samples of the whole substance under consideration may be examined, there is inherent uncertainty because of possible sampling error. The extent to which a small sample may be reliably considered to be representative of a large volume of material depends on several factors. These include first the homogeneity of the material being sampled, and secondarily the number of samples, the manner of their collection, and the size of the individual samples.

The sampling of a completely homogeneous body is a simple matter and would involve no error if the sample is large enough to contain a representation of all the components of the original. Because most materials are not entirely homogeneous, obtaining truly representative samples depends to a great, degree upon the sampling technique. A sample integrated by taking small portions of the material at systematically distributed points over the whole body should represent the material better than a sample collected from a single point.

The more portions taken, the more nearly the sample represents the original, but the total sample volume must be kept to a manageable size. As the amount of material in the sample increases, the potential error in sampling decreases and would reach zero if the sample equaled in volume the material being sampled.

Natural waters have properties which need to be considered in relation to the collection of samples. Water bodies generally are dynamic in the sense that they are in motion or have some internal circulation. Thus, although the water may be affected by localized additions of dissolved solids, there is a general tendency toward mixing and homogeneity. That such a tendency exists, however, is not sufficient ground for assuming that any water is so well mixed that no attention to sampling technique is required. Too great a reliance on the assumed homogeneity of a water body can lead to gross errors. The fact that many water bodies are moving makes the samples collected at a fixed point subject to differences resulting from water of different compositions passing the sampling point. Especially in studies of the quality of water of surface streams, changes in composition with the passage of time may be large and rapid.

SURFACE-WATER SAMPLING

The proper sampling of a flowing stream must take into account first the need for each sample, or set of samples, taken simultaneously to represent the whole flow of the stream at the sampling point at that instant, and second the need for enough samples distributed in time to define the changes which occur in the water passing the sampling point.

The homogeneity of a stream at a cross section is determined by physical factors, such as proximity of inflows and amount of turbulence in the channel. Locally, poor lateral or vertical mixing may be observed in places in most stream systems. Immediately below the confluence of a tributary there may be a distinct physical separation between the water of the tributary and that of the main stream, and particularly in large rivers this separation may persist for many miles downstream. The effect is more pronounced if the water of the tributary differs markedly from the water of the main stream in content of dissolved or suspended solids or in temperature. These effects may be of special interest in some investigations. If the average composition of the flow of a stream or its changes in total dissolved-solids content over a period of time are the factors of greatest significance, sampling locations where mixing is incomplete should be avoided. Figure 29 illustrates the lack of homogeneity of the water of the Susquehanna River at Harrisburg, Pa.

In theory, a sample representing the average composition might be obtained by combining depth-integrated samples of equal volume taken at places representing equal flow at several points across the stream. In practice on small or medium-sized streams, it is generally possible to find a sampling section at which the composition of the water is uniform with depth and across the stream. The problem of obtaining adequate samples is thus simplified and the cross section can be represented by one sample taken at or near midstream. For large streams, more than one sample may be required in the cross section.

Even when a sampling point has been found and procedure adopted which *assures* that each sampling represents adequately the water flowing at that instant, there remains the question as to how long the results of that sample can be considered to be representative. The composition of all surface streams is subject to change with time. Long-term changes may result from long rainfall or runoff cycles or changes in land or water utilization. Seasonal changes are to be expected from varying rates of runoff, evaporation, and transpiration typical of the seasons. Daily or even hourly changes of considerable magnitude may occur in some streams owing to flash floods or to regulation of flow by man, or dumping of industrial or other wastes.

In a complete study of surface-water quality, the samples should be collected at intervals such that no important cycle of change in concentration could pass unnoticed between sampling times. For some streams, especially those where flow is completely controlled by large storage reservoirs, or where flow is maintained by large constant ground-water inflows, a single sample may represent the flow accurately for several days or even weeks. Normally, however, one sample cannot be extrapolated over more than a day or two, and for some streams not more than a few hours. For the earliest intensive studies of quality of surface streams made by the Geological Survey, an interval of about 24 hours between samples was used. These studies were begun shortly after the turn of the century (Dole, 1909; also Stabler, 1911). Daily sampling of surface streams has been more or less standard practice for chemical-quality studies made by the Geological Survey since that time. However, this sampling schedule usually represents a compromise between funds available for data collection and the degree of accuracy required.

A complete analysis of each daily sample is not feasible because of the cost. Therefore, in most of these studies, the daily samples are combined into composite samples for analysis, and analytical work on the individual daily samples is held to the minimum required to provide the needed information. The composite samples usually include 10 daily samples but longer or shorter periods may be used at times. Because composite samples obscure day-to-day changes and do not indicate composition of extremes, samples of water that differ widely in conductance are usually not included in the same composite sample nor are samples collected at widely differing discharge rates. Procedures for preparing composite samples for analysis are discussed in a recent (1958) publication by the Geological Survey.

The range between high and low extremes of dissolved-solids concentration at a sampling point on a stream is rarely comparable in magnitude to the range between extreme high and low discharge rates. Maximum dissolved-solids concentrations 20 to 40 times as great as the minimum have been observed over long periods of record in some nontidal streams of the United States, but for most of the larger rivers the range is much narrower. Usually the changes in dissolved-solids concentration are somewhat related to the rate of discharge and the rate of change of discharge, but this relationship is complicated by other factors so that it cannot usually be directly utilized as a means of adjusting or extending data from samples collected infrequently. In the most extreme cases, a continuous record of specific conductance of a stream supplemented by sampling would be required to determine accurately the changes in water quality. In other instances, twice daily or more frequent sampling during changing discharge periods and daily or less frequent sampling at other times may be required.

Water-quality fluctuations in streams affected by oceanic tides present an especially complex pattern. Studies of such streams require special sampling and instrumentation techniques.

The Rio Grande above Elephant Butte Reservoir in New Mexico is a stream subject to rapid fluctuation in water quality at times. Figures 1 and 2 illustrate the extent of fluctuation in flow and specific conductance which are characteristic of the stream at different times of the year. In figure 1 the effect of large volumes of runoff from snow-melt during the spring months is indicated. Here the discharge ranges from a few hundred to nearly 10,000 cubic feet per second but the day-to-day change in conductance is comparatively minor and for the whole period, the maximum is only about double the minimum. Daily sampling in this period is evidently adequate to define these changes. During the summer, much of the runoff comes from flash floods in tributaries and the water may change rapidly in both amount and quality. Figure 2 is based on the results of sampling 1 to 5 times a day. On August 17th two samples a few hours apart showed a nearly 3-fold increase in concentration. Daily sampling in such a period is obviously not adequate to show all the changes that took place.

For streams whose discharge is controlled by reservoirs or by natural storage, the composition of the water may remain essentially constant for long periods and samples taken once a week or even once

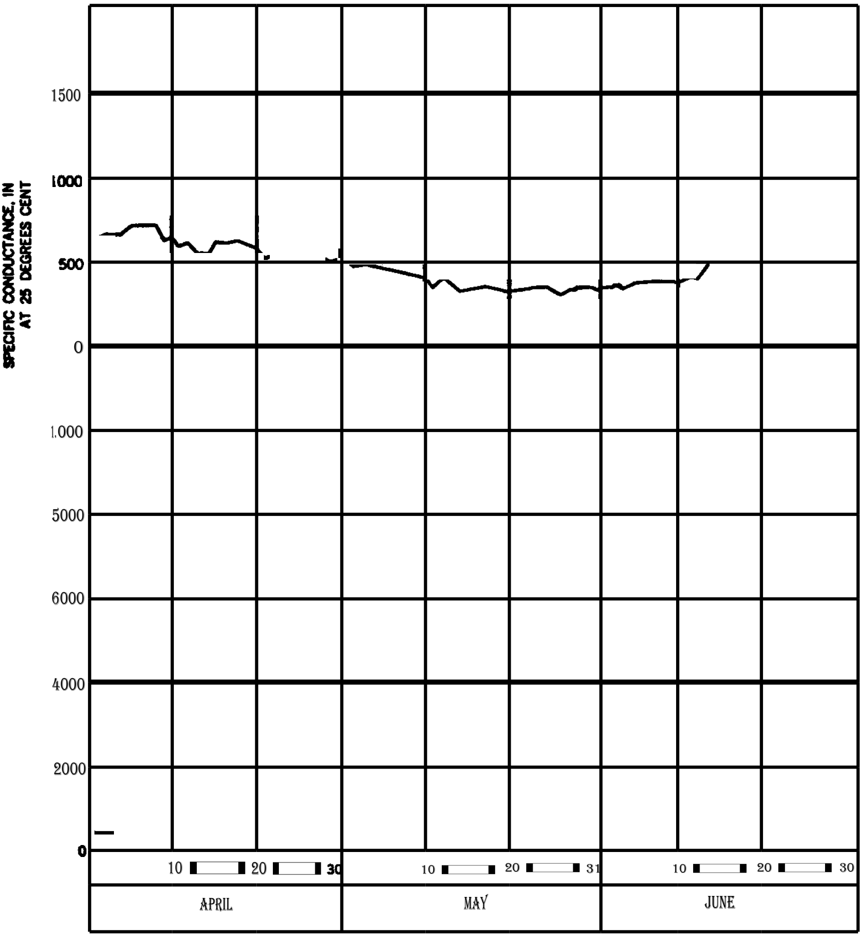


FIGURE 1.—[illegible] New Mexico, 1945.

[illegible]

[illegible]

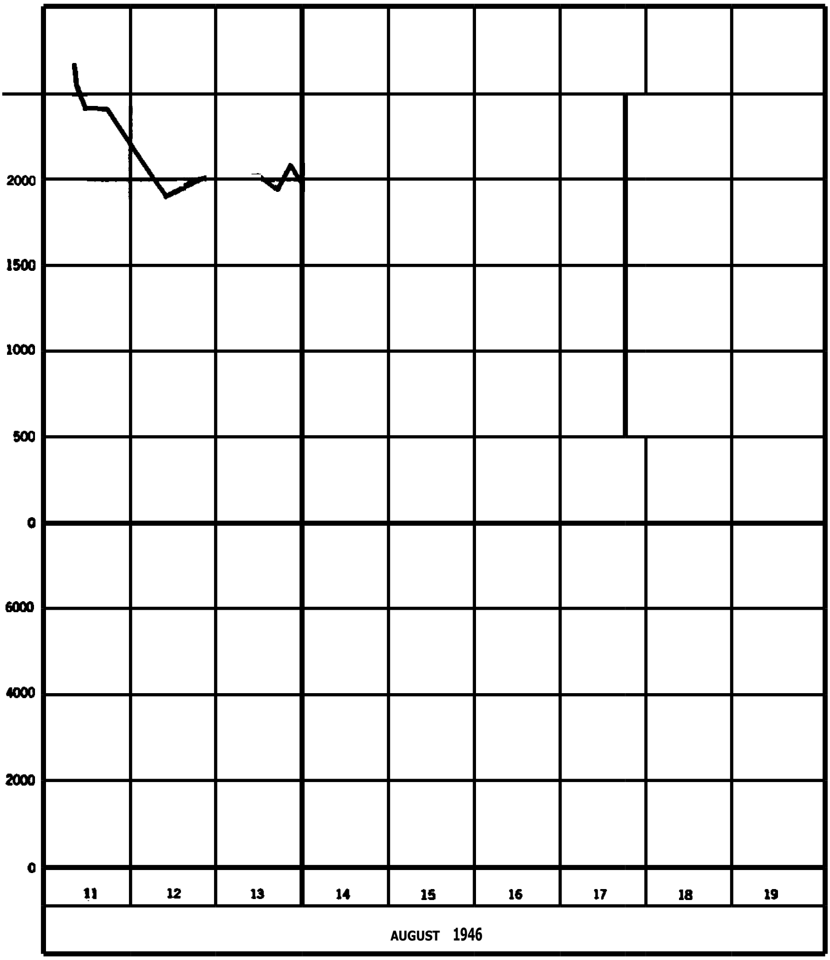


FIGURE 2.—Conductance and discharge at times of sampling of Rio Grande at San Acacia, New Mexico, under typical summer flow conditions.

may not be told at what point in a lake a sample was obtained or where the water level was. Sometimes the time of year is not stated. Analyses for streams may give no indication either as to means of sampling or to conditions of flow in the stream at the time the samples were obtained. Any interpretation or conclusion based on data such as these could be open to considerable question. For obvious reasons, therefore, the user of data relating to quality of surface waters should first satisfy himself that the sampling phase of the data-gathering program was carried out in such a way as to give reliable results. Various aspects of sampling surface streams have been discussed by the Geological Survey (1958).

GROUND-WATER SAMPLING

Most of the physical factors promoting mixing in surface-water bodies are much less effective or absent in ground waters. Experimental work by many investigators has shown that introduced saline water may move considerable distances through an aquifer without much mixing. The principles governing diffusion and mixing of soluble materials in underground waters need further study for a full understanding of the factors involved.

Considerable differences in composition of water may be found both vertically and laterally in ground-water reservoirs. Sampling programs are aimed at determining the content of dissolved matter in stored ground water throughout an aquifer, although a completely comprehensive answer is not usually practicable. From each well sampled, an indication is obtained of conditions at essentially a single point within a three-dimensional system. Collection of samples from many wells distributed areally over an aquifer generally will give the probable upper and lower limits of dissolved-solids concentrations in the ground-water body at that time and in a general way will show the distribution pattern of the water's quality.

Results of sampling a well should be interpreted in the light of the available knowledge of the characteristics of the well. If the well is constructed to admit water from all materials penetrated below the water table, the water from the well will represent only a rough average of the quality of water available throughout the depth of penetration, weighted by the characteristics of the well and the transmitting properties of the water-bearing materials at different depths.

When water of distinctly inferior quality is encountered in constructing a well, attempts are generally made to prevent it from entering the well. The effects of casing leaks which allow salt water to enter a well in small amounts may produce various effects on the quality of water produced when the well is pumped. Figure 3 is based on data obtained in pumping tests of a well at El Paso, Texas, in which a leak in the casing admitted salty water. (Sayre and Livingston, 1945, p. 174-188.) The chloride concentration of the water discharged increased rapidly after the pump was turned on, until the salty water which had leaked into the well during the preceding period of shutdown (nearly a year) had been removed and replaced with fresher water from the main aquifer. After about 14 days of pumping, the chloride had been reduced to about 300 ppm. Such a well might give a rather misleading sample if it were sampled only after a short period of pumping, and the sample was assumed to represent the water in the main aquifer. The interpretation of analyses of samples from wells must be made in the light of as much

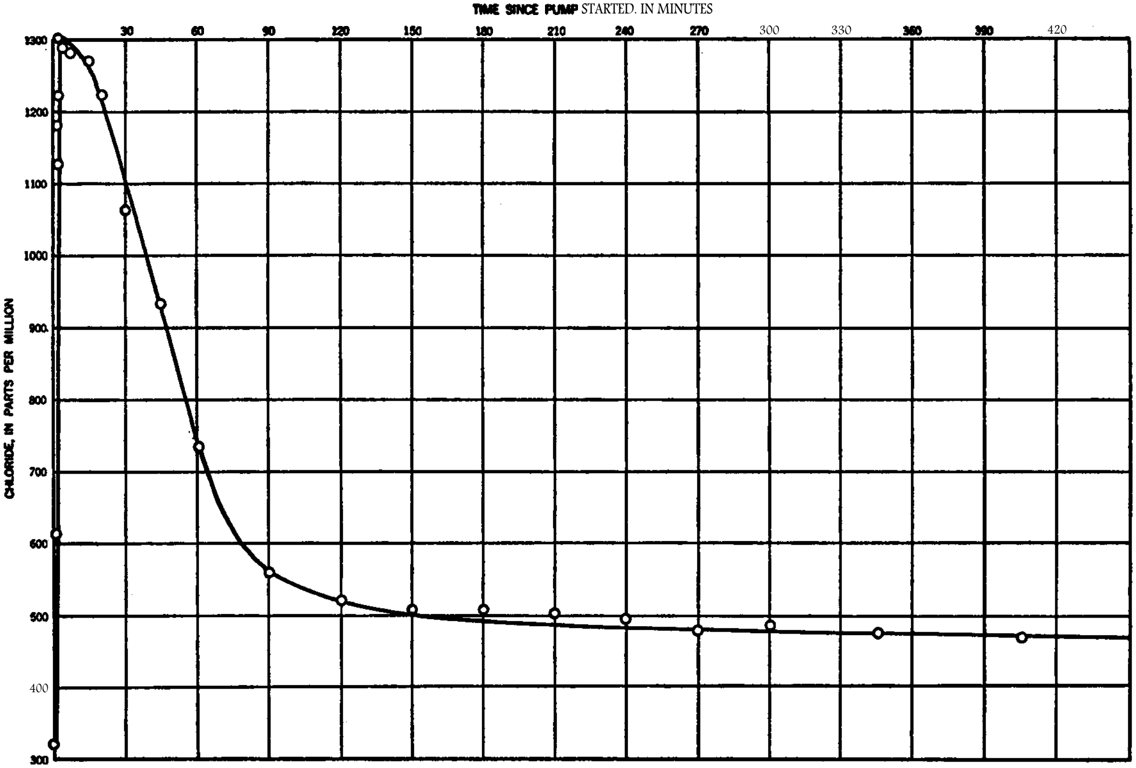


Figure 8.—Change in chloride concentration of water pumped from city well 1, El Paso, Texas, Aug. 28, 1939.

knowledge as can be obtained regarding the source. Electric logs are useful indicators of the possible presence of saline water and the points where such water may be found.

One can rarely be absolutely certain that a ground-water sample represents exactly the composition of water in the vertical section at that point, but by careful selection of sampling points, representativeness is reasonably assured. The results of sampling over the area give data that can be extrapolated in time with somewhat more confidence than can surface-water data.

In considering the variation of quality of ground water with time, it is probably better to think of aquifers as reservoirs subject to slow changes in quality as the water circulates, than to consider them as "pipelines" or watercourses through which water moves from one place to another. The latter concept may be valid to some extent for water moving through a system of relatively large channels such as those which may exist in cavernous limestone. The movement in any event is slow enough that changes in quality with time are much less significant in ground water than in surface water. Changes in ground-water quality can usually be followed satisfactorily by monthly, seasonal, or annual sampling schedules.

Several examples of seasonal or month-to-month changes in water quality are shown in figure 4. These curves are based on data obtained from a group of shallow observation wells driven in alluvial materials in the vicinity of the Gila River in the Safford Valley, Ariz. (Gatewood and others, 1950). Fluctuations shown in figure 4 are much more rapid than those observed in most ground waters, probably because of the exchanges of water between the surface stream and the ground-water reservoir in this environment.

A long-term building up of salinity in a ground-water reservoir is illustrated by figure 5 which shows the changes occurring over a 20-year period in two wells in the Wellton—Mohawk area along the lower Gila River in Arizona (Babcock, Brown and Hem, 1947).

COMPLETENESS OF SAMPLE COVERAGE

In areas where hydrologic studies are being made or are contemplated, a decision as to how many samples should be collected for chemical analysis is required. Except for administrative limitations in funds and manpower, this decision must be based on local conditions for each study, and should take into account the amount of data of this type already available, the hydrologic complexity of the area, the extent to which water of inferior quality is known or believed likely to occur, and possibly other pertinent factors. As a general rule, it is best to utilize as many sources as possible which are suitable for the collection of representative samples. The amount of laboratory work per sample should be sufficient to provide at least the minimum

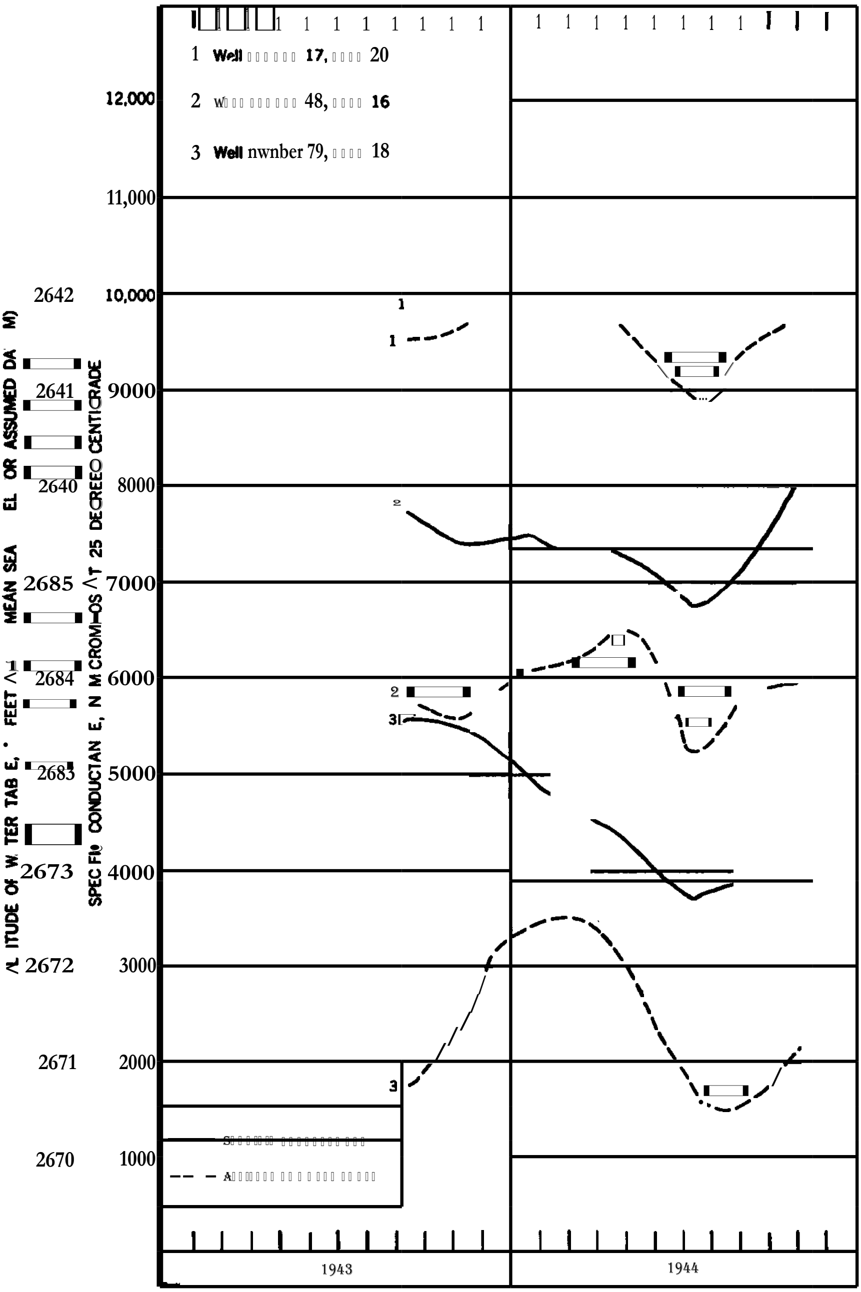


FIGURE 4.—Specific [illegible] **observation wells,** S[illegible] V[illegible], A[illegible].

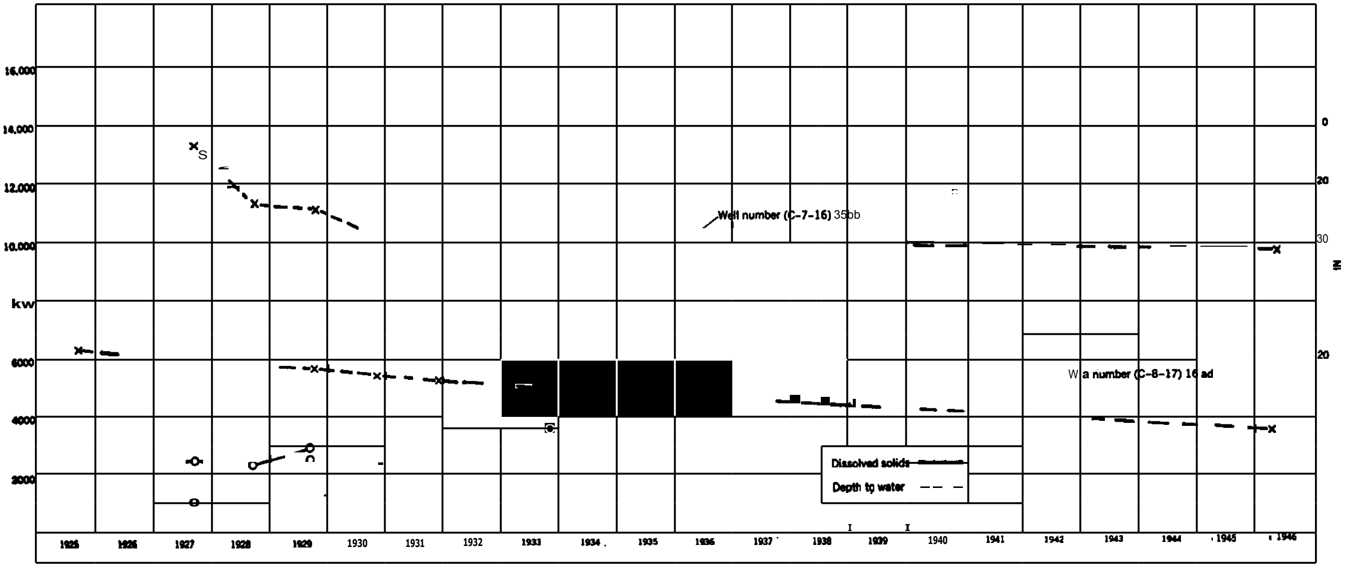


FIGURE 5.—Dissolved solids and depth to water in two irrigation wells, Wellton-Mohawk area, Yuma County, Arizona.

information needed to define the conditions in the area under study. If large numbers of samples are collected, the laboratory work can usually be arranged to make certain key determinations first. As the chemist becomes familiar with the water-quality conditions in the area, he can use these determinations to decide which samples are essentially the same and which may need more complete analyses to define the water quality hydrology. When this procedure is followed, the laboratory costs are held to a minimum, but complete data are available for concentration ranges in the various water sources, and detailed analyses which are made define the chemical composition at widely different concentrations. Carefully integrated planning of sampling and analytical work are amply repaid by superior data and lower overall costs.

ANALYSES OF WATER SAMPLES

The analysis of water for its dissolved components is a part of the work done by a large number of chemical laboratories, including many supported by Federal, State, and local governmental agencies as well as others under private sponsorship. Some of these groups have methods and equipment for making certain tests of water in the field as well as in the laboratory. This report does not include a detailed description of laboratory procedures because standard works on this subject are readily available for reference. However, some comments on the procedures for field analysis used by the Geological Survey and the general aspects of laboratory procedures are appropriate.

FIELD TESTING OF WATER

Examination of water in the field to determine its approximate chemical character is often useful. The procedures used range from determinations of specific conductance in streams, wells, and water bodies without removing a sample to rather extensive chemical analyses made with semiportable laboratory equipment mounted in a truck or trailer or temporarily placed in a fixed location in a building convenient to the work. The more comprehensive field setup may be essentially equivalent to a permanent fixed laboratory.

The usefulness of field tests was recognized early in the history of water investigations made by the Geological Survey. A manual on the subject was written many years ago by Leighton (1905) who recommended the use of tablets of reagents from which standard solutions could be made up as needed, thus reducing the need for carrying liquids in bottles. Leighton's manual is now of historical interest only. A discussion by Collins (1922) outlined methods suitable for use in a semipermanent laboratory which might lack certain facilities such as gas, distilled water, and analytical balances. These procedures also have been superseded to a great extent. Simplified kits of equipment were developed within the Geological Survey during the 1920's and 1930's to permit tests to be made at the point where samples were collected. For chloride determinations, the equipment included a pipette, a small dish, and stirring rod and dropping bottles filled with standardized silver nitrate solution and potassium chromate indicator. By counting the number of drops required to reach the end point and knowing the strength of solution and amount of sample taken, concentrations could be approximately determined in the field. Similar techniques and equipment were used to determine hardness of water using standard soap solutions. These tests were helpful in connection with pumping tests and in selecting sampling points for laboratory study.

Probably the most useful instrument for field studies of water quality is the fully portable wheatstone bridge for the measurement of conductivity. One model of this instrument was developed as early as 1896 for use in soils studies by the U. S. Department of Agriculture (Scofield, 1932). The conductivity equipment was powered by dry cells and included a calibrated slide wire with a buzzer arrangement to provide an interrupted current. A cell to which the water or saturated soil could be introduced was connected to the bridge and the balance point between the cell and the slide wire was detected by means of headphones. Units of this type were first utilized by the Geological Survey for field studies of water during the 1930's. Refinements eventually brought down the weight of the units, including cell and phones, to about 5 pounds. A lucite dipping-type conductivity cell and sample container reduced the possibility of breakage of essential parts. These units proved themselves sturdy and useful. Because they had a much lower accuracy than laboratory-type equipment, they were used to obtain comparative concentrations of various waters rather than to obtain absolute values of conductance.

Since 1945 commercial equipment for determining conductance in the field has become available. The more elaborate models, powered with flashlight-type dry cells, are calibrated to give readings directly in micromhos, automatically corrected to standard temperature, and null points are detected by a cathode ray tube rather than with earphones. The incorporation of conductivity cells into well-exploration equipment and sampling devices for use in surface-water bodies enables tests to be made in places not formerly accessible.

Portable laboratory kits containing all necessary glassware and solutions for simple chemical tests such as for chloride, hardness, and alkalinity also are available from several commercial sources. These kits are best used in a semipermanent installation. The colorimetric determination of hardness for which these kits provide is much better suited to determinations made in the field than is the soap method.

A rather fully equipped chemical laboratory can be set up in a truck or trailer which, if parked where needed utilities are available, is a suitable facility for complete water analyses. Such a portable laboratory is not field equipment in the meaning of this discussion. The Geological Survey has not developed complete mobile laboratories for water testing. Their greatest utility probably is for determining constituents which change rapidly after the sample is obtained and which therefore require undue and perhaps impossible speed in transporation to the central laboratory. Bacteriological examinations are sometimes made in mobile laboratories for this reason. Such examinations are not made by the Geological Survey, and other determinations made on water samples in the Survey usually do not require such immediate action after the sample is collected. Therefore, simply equipped semipermanent laboratories have been set up in the field when the volume of work required facilities of this type near at hand. For widespread, less intensive studies, laboratories of a more permanent type have been used to which samples may be shipped from a radius of several hundred miles if necessary.

The principal value of field testing in most water-resources studies lies in getting approximate data that can be used to plan a sampling program intelligently. The portable conductivity meter is most useful in this sort of work. Such testing equipment is also useful in the field as a means of checking quality of water encountered in the drilling of wells and locating ground-water inflows to surface streams. Field testing is inherently less accurate than work done in a central laboratory, and field tests should be considered supplementary to laboratory analysis.

ELECTRIC LOGS AS INDICATORS OF GROUND-WATER QUALITY

One of the most widely used means of geophysical exploration of subsurface conditions is electric logging of boreholes. There are several different types of electric-logging equipment, but essentially all determine as a part of the procedure the resistance to passage of an electric current of the formations penetrated by the borehole. As the electrode or electrodes are moved up or down the hole, the segment of which the resistance is measured changes. A recording device traces the resistance on a chart as the electrode moves. The result is a curve showing regions of high and low resistance below the surface of the ground.

The resistance of water-bearing material in place is a function of the resistance of the rock itself, the resistance of the water, and the length of the path through which the current passes in the water confined in the interconnected openings in the rock. Resistance of most dry rocks is very high, and essentially the resistance measured by electric logs is controlled by the water quality and the length of the current path. The resistance is expressed as "resistivity" (reciprocal of conductivity), usually in ohms per meter per square meter.

Values obtained for resistivity of aquifers through electric logging are therefore closely related to water conductivity and porosity of the rocks. The principal use of these logs has been as an aid in determining the physical properties of water-bearing formations and in correlating formations from well to well.

If the procedure is modified, the conductivity of the water in the formation can be considered the unknown, the other features of the aquifer which affect the resistivity data being computed on the basis of laboratory tests of drill cuttings from the formation, or on the basis of previous experience with the same aquifer. Used in this way, the electric log provides an indicator of water quality in place underground.

The reliability with which water conductivity can be determined from an electric log probably is highest for uniform granular aquifers and can be no better than the reliability of the available data for the average length of the path through which the current travels.

Some investigators have extended the water-quality data obtained from logs by using the conductivity values to compute hypothetical analyses in parts per million. Circumstances under which this may be done satisfactorily occur only where a large number of chemical analyses are available for water from the formation in question and where these analyses show a linear relationship between conductivity and each of the constituents for which the computation is made. Jones (1952) has described such computations for an area in Louisiana. The uncertainties involved in computing water composition from its conductivity alone are described on pages 39-42 where the conductivity determination is discussed.

Electric logs are highly useful indicators of the location of saline water in aquifers or parts of aquifers. For the most practical use of the logs, the large differences in resistivity between potable and saline water are easy to interpret, and exact figures for the composition of the waters involved are not needed.

LABORATORY PROCEDURES

The laboratory procedures considered generally acceptable and in widest use for water analysis in various laboratories in the United States are compiled in several different publications. The most widely known publication of this type has been prepared jointly by the American Public Health Association, the American Water Works

Association, and the Federation of Sewage and Industrial Waste Associations (1955). Other compilations widely used include those of the American Society for Testing Materials (1953), Association of Official Agricultural Chemists (1950), and U. S. Salinity Laboratory (1954). Methods used in the early years of water analysis in the Geological Survey were described by Collins (1928). These procedures have been extensively modified in more recent years. Methods currently in used in the Geological Survey laboratories are described in detail by the Geological Survey (1958). These procedures utilized by the Geological Survey are generally selected from standard methods described in the other references quoted above, with some additional procedures for components not usually included in water analyses, and modifications designed to speed the analysis of large numbers of samples.

EXPRESSION OF WATER ANALYSES

Various terms and units are commonly employed in the expression of data obtained from chemical analyses of water. An understanding of the more frequently used methods of expression is required for proper interpretation of these data.

ANALYSES REPORTED IN TERMS OF HYPOTHETICAL COMBINATIONS

Water analyses published before 1900 are practically all expressed in terms of concentrations of combined salts such as calcium sulfate or sodium chloride. This procedure is not commonly used today but occasionally one may still find analyses reported in this way. Probably the earlier analysts were attempting to express the composition of the dry residue remaining after evaporation of the water, and such information is important for some applications of water analyses. However, it is difficult to predict with certainty the composition of the residue that may be deposited from the same solution under different conditions, even if the amounts of the various substances in the solution are known.

The several recommended procedures for computation of results in terms of combined salts are based on conventional hypotheses regarding the compounds most likely to be formed, or which would be precipitated from solution first. Since several hypotheses have been used, however, the expression of the same data in terms of combined salts might be done differently by different analysts (Association of Agricultural Chemists, 1950, p. 548; Furman, 1939, p. 2087-88). In general, hypothetical combinations do not constitute the most accurate way of expressing the chemical character of water.

ANALYSES EXPRESSED IN TERMS OF IONS

For many years it has been known that most inorganic salts in solution in water are dissociated into charged particles or ions. A water analysis is intended to be a statement of the composition of a water solution, and it is therefore appropriate to use an ionic form of statement of the analysis. In accordance with the dissociation concept, water analyses are now generally expressed in concentrations of individual ions for those substances known to be dissociated in solution. Substances whose form in solution is unknown, or which may be suspected to occur in undissociated or even in colloidal form, are commonly reported either as an oxide or as an uncombined element.

DETERMINATIONS INCLUDED IN ANALYSES

Substances commonly determined in water analyses and expressed as ions include the cations (positively charged ions) calcium, magnesium, sodium, and potassium, and the anions (negatively charged ions) sulfate, chloride, fluoride, nitrate, and those contributing to alkalinity which are usually expressed in terms of an equivalent amount of carbonate and bicarbonate. Other substances, such as arsenic, barium, boron, bromide, chromium, copper, iodide, iron, lead, manganese, phosphate, selenium, silica, strontium, and zinc, some of which are determined as part of a routine complete analysis but most of which are not generally determined, are reported in ionic terms if the substances are known to occur in that form. Dissolved gases such as carbon dioxide and hydrogen sulfide, when determined, are usually reported in undissociated form.

Certain more general chemical and physical properties are reported in most water analyses. The acidity of a water may be expressed as concentration of hydrogen ions or in terms of the equivalent concentration of sulfuric acid. Hardness in water and sometimes alkalinity is conventionally expressed in terms of equivalent quantities of calcium carbonate. The properties frequently determined for a water and reported as a part of the analysis also include color, specific conductance, total dissolved solids, loss on ignition, specific gravity, suspended matter, turbidity, biochemical oxygen demand, and percent sodium. The significance of all these constituents and properties will be discussed in detail later in this report.

UNITS USED IN REPORTING ANALYSES

Over the years a wide variety of units have been used in reporting water analyses. Some progress toward standardization of these units has been made, but utilization of data from various sources and data in the older literature requires a general understanding of the units and systems which are used and which have been used in the past. The most commonly used systems generally report water composition in terms of weight of dissolved matter and weight of solution. Other systems which are commonly used, however, report composition in terms of weights per unit volume.

WEIGHT-PER-WEIGHT UNITS

For many years all water analyses made by the Geological Survey and most other laboratories in the United States have been reported in parts per million by weight (ppm). One part per million represents 1 milligram of solute in 1 kilogram of solution. The reader may be more familiar with data expressed in percentage, which is equivalent to "parts per hundred". For water analyses, percentage values usually would be far below unity and would involve cumbersome decimals, although sometimes analyses of brines are reported this way. One percent is equivalent to 10,000 ppm.

Parts per thousand sometimes are used in expressing analyses of set water. In this connection, the terms "chlorinity" and "salinity" have been defined in terms of parts per thousand (grams per Kg) for use in studies of sea-water composition (Rankama and Sahama, 1950, p. 287).

Some of the older chemical analyses are reported in terms of parts per 100,000. This unit is no longer in common use in the United States. For special work in trace constituents, data may be expressed in parts per billion which are equivalent to micrograms per kilogram.

WEIGHT-PER-VOLUME UNITS

Because water is a liquid, definite quantities for analysis are most conveniently obtained in the laboratory by use of volumetric glassware. The laboratory therefore usually obtains results which are in terms of weights of solute in a given volume of water. These data must be converted to a weight basis if the analysis is reported in parts per million. For most waters, this conversion is made by assuming that a liter of the water used weighs 1 kilogram, and that laboratory results in terms of milligrams per liter are equivalent, therefore, to parts per million. This is strictly true only for pure water at 3.98°C. The presence of dissolved mineral matter increases the density of water, and an increase in temperature decreases the density. For practical purposes, however, no serious error is introduced by assuming unit density unless the concentration of dissolved solids is more than 7,000 ppm. For highly mineralized waters, a density correction must be utilized in computing parts per million from milligrams per liter (U. S. Geological Survey, 1958). Differences in density caused by temperature are normally too small to be significant.

When the chemist is dealing with waters high in dissolved solids, it is simpler to report the results in terms of weight of solute per unit volume of solution, which avoids any need for density corrections. Many laboratories, especially in European and other countries where the metric system is standard, report all concentrations in terms of milligrams per liter. In the United States this procedure has not been widely adopted, although some favor its wider use.

In the United States and elsewhere that the English system of units is used, analyses are sometimes expressed in grains per gallon. The gallon that is meant must be specified, as the United States and Imperial gallons are unequal. Many are accustomed to thinking in terms of grains per gallon in considering hardness of water.

In considering the quality of irrigation water, the unit "tons per acre-foot" is commonly applied. The ton here used is 2,000 pounds. For moving streams, the dissolved-solids load may be reported in terms of tons per day.

TABLE 3.—*Conversion factors for quality-of-water data*

To convert	To	Multiply by
Grains per gallon	Parts per million	17.12
Parts per million	Grains per gallon	.05841
Parts per million	Tons per acre-foot	.00136
Parts per million	Tons per day	Second-feet X .0027
Parts per hundred thousand	Parts per million	10
Grams	Ounces (avoirdupois)	.03527
Ounces (avoirdupois)	Grams	28.35
Liters	Quarts (U. S.)	1.057
Quarts (U S.)	Liters	.9463
Second-foot days	Acre-feet	1.983471
Second-feet [2]	Gallons per minute	448.8
Second-foot days	Gallons per day	646,317
Acre-feet [3]	Gallons	325,851
Acre-feet	Cubic feet	43.560
Cubic feet	Gallons	7.481
Ca++	$CaCO_3$	2.497
$CaCl_2$	$CaCO_3$	.9018
BC Or	$CaCO_3$	.8202
HCOr	CO_3^{--}	.4917
Mg++	$CaCO_3$	4.116
$MgCl_2$	$CaCO_3$	1.051
Na_2CO_3	$CaCO_3$	.9442
Fe+++	H_2SO_4	2.634
NOr		.2259
	NOr	4.4266

1 second-foot day=1 cubic foot per second for 24 hours.
[2] 1 second-foot=1 cubic foot per second.
[3] 1 acre-foot=an area of 1 acre 1 foot deep.

Conversion factors which indicate the relationship of the various units to each other are given in table 3. Factors changing grains per gallon, or tons per acre-foot, to parts per million and the reverse, are based on the assumption of unit density of the water. This introduces no error of practical importance for waters containing less than about 7,000 ppm of dissolved solids. For more highly mineralized waters, the factor for converting parts per million to grains per gallon or tons per acre-foot should be multiplied by the density of the water in grams per milliliter.

Hardness values are sometimes expressed in degrees. Conversion factors for these units, which differ in different countries, are given later in the discussion of hardness in water.

EQUIVALENT-WEIGHT UNITS

A further refinement in units of expression may be desirable for some purposes, to help describe the composition of water and the relationships among the ions in solution. A commonly used system for expressing analyses takes into account not only the weight concentrations of ions but also the concept of chemical equivalence.

TABLE 4.—Conversion factors: Parts per million to equivalents per million

Ion	Multiply by	Ion	Multiply by
Aluminum (Al^{+++})	0.11119	Iron (Fe^{+++})	0.05372
Barium (Ba^{++})	.01456	Lead (Pb^{++})	.00965
Bicarbonate (HCO_3^-)	.01639	Lithium (Li^+)	.14409
Bromide (Br^-)	.01251	Magnesium (Mg^{++})	.08224
Calcium (Ca^{++})	.04990	Manganese (Mn^{++})	.03640
Carbonate (CO_3^{--})	03333	Manganese (Mn^{++++})	.07281
Chloride (Cl^-)	02820	Nitrate (NO_3^-)	.01613
Chromium (Cr^{6+})	.11536	Phosphate (PO_4^{---})	.03159
Copper (Cu^{++})	.03148	Potassium (K^+)	.02558
Fluoride (F^-)	.05263	Sodium (Na^+)	.04350
Hydrogen (H^+)	99206	Strontium (Sr)	.02282
Hydroxide (OH^-)	.05880	Sulfate (SO_4^{--})	.02082
Iodide (I^-)	.00788	Sulfide (S^{--})	.06237
Iron (Fe)	.03581	Zinc (Zn^{++})	.03059

Chemical equivalence may be introduced into the data by dividing each of the concentration values in parts per million or other units by the combining weight of that ion.[1] Table 4 contains the reciprocals of the combining weights of cations and anions generally reported in water analyses. Parts per million values may be converted to "equivalents per million" (epm) by multiplying ppm by the reciprocals of combining weights of the appropriate ions.

The terms "equivalents per million" is a contraction which has been generally adopted for the sake of convenience. In more exact language, these units are "milligram equivalents per kilogram" if derived from part-per-million data, or "milligram equivalents per liter" if derived from data expressed in milligrams per liter. Equivalent weights may be computed for use with any of the systems of expression of data.

In an analysis expressed in equivalents per million, unit concentrations of all ions are chemically equivalent. This relation aids in checking the accuracy and completeness of analytical work. When

---

[1] Combining weight = atomic weight of ion/ionic charge.

all major constituents have been determined, the total equivalents of cations should very nearly equal the total equivalents of anions.

Some techniques of interpretation require analytical data in terms of equivalents per million. The chemical behavior of water in dissolving and precipitating minerals can be better understood from analyses expressed in equivalents per million, and the results of mixing of waters are more accurately represented. To most chemists, the use of equivalents per million seems the best way of expressing a chemical analysis, and some laboratories have gone over to this system entirely. However, anything in solution in nonionized form is not normally reported in terms of epm. The system is therefore inadequate to show all characteristics of water which may be important, and for silica and iron and certain other constitutents, concentrations are generally expressed in parts per million or other weight-based units.

COMPOSITION OF ANHYDROUS RESIDUE

All means of expressing water analyses so far discussed are based on concentration of the dissolved substances in the solution. These concentration figures are often the deciding factors in the evaluation of waters for possible uses, but for studying the composition of waters with relation to rock types, some investigators have preferred to express the analysis in a form which gives only the relative amounts of the various ions present as computed from the anhydrous residue. In this form the analysis statement lists the percentage of the total dissolved solids that each ion or component comprises. Percentages based on parts per million include the supposedly nonionized matter such as silica or iron going to make up part of the dissolved matter. Dissolved gases and acids are not included, and bicarbonates are usually recalculated to carbonates.

Analyses expressed in terms of percentages of dissolved solids usually indicate total concentration of dissolved solids but do not report concentration values for individual ions. Many of the analyses in geochemical literature are expressed in terms of percentage of dissolved solids, for example in writings of F. W. Clarke (1924a, 1924b) where data of this kind are referred to as "percentage composition of anhydrous residue."

For some studies, it may be found better to compute analyses to percentages of total cations and anions in equivalents per million rather than of total dissolved solids in parts per million. An analysis expressed in this way gives a better indication of the chemical character of a water than the expression of percentage concentrations calculated from parts per million, and is particularly useful in comparing analyses with one another by graphical means. However, any substances not reportable in terms of equivalents per million cannot be considered in analyses reported in this form.

PARTS PER MILLION AS CALCIUM CARBONATE

The hardness of water is conventionally expressed in all water analyses in terms of an equivalent quantity of calcium carbonate. Such a procedure is required because hardness is caused by several different cations, present in variable proportions. It should be remembered that hardness is an expression in conventional terms of a property of water. The actual presence of calcium carbonate in the concentration given is not to be assumed.

Some laboratories, especially those associated with water treatment plants, express alkalinity in terms of an equivalent amount of calcium carbonate. The alkalinity as calcium carbonate should be divided by G.8202 to convert such data to parts per million in terms of bicarbonate. (See table 3.) Hardness or alkalinity values expressed in parts per million as calcium carbonate may be converted to equivalents per million by dividing by 50.

Some analyses express other constituents in terms of calcium carbonate. For analyses to be used in geochemical interpretations, this device is confusing. For such uses, it is essential to have a form of expression which comes as near as possible to showing in exactly what form the dissolved materials are present in the water.

TABLE 5.-*Analysis* of water sample expressed in five different ways

[Sample from flowing well 488 ft. deep. Water from Lance formation. NW¼ sec. 30, T. 57 N., R. 85 W., Sheridan County, Wyo., collected Aug. 3, 1946]

	(1)	(2)	(3)	(4)	(5)
Silica (9102)	7.9	---------	.40	---------	.46
Iron (Fe)	.17	---------	.01	---------	.01
Calcium (Ca)	37	1.85	1.87	6.1	2.16
Magnesium (Mg)	24	1.97	1.21	6.5	1.40
Sodium (Na)	611	26.58	30.80	87.4	35.69
Potassium (K)					
Bicarbonate (HCO_3)	429	7.03	11063	23.1	25.06
Sulfate (SO4)	1,010	21.03	50.90	69.2	59.00
Chloride (C1).	82	2.31	4.14	7.6	4.79
Fluoride (F)	.6	.03	.03	.1	.04
Nitrate (NO_3)	.0	.00	.00	.0	.00
Boron (13)	.2	---------	.01	---------	.01
Dissolved solids: Calculated	1,980	60.80	100.0	---------	115.65
Hardness as $CaCO_3$.					
Total	191	3.82	---------		11.16
Noncarbonate	0	.00	---------		0
Specific conductance (micromhos at 25° C).	2,880	2,880	2,880	2,880	2,880
pH	7.3	7.3	7.3	7.3	7.3

[1] As carbonate (CO_3).

1. Analysis in parts per million, usual form of expression of complete analyses made by Geological Survey.
2. Analysis In equivalents per million.
3. Analysis in percent of dissolved solids computed from parts per million.
4. Analysis in percent of dissolved cations and anions computed from equivalents per million.
5. Grains per U. S. gallon.

COMPARISON OF UNITS OF EXPRESSION

Table 5 shows a single water analysis expressed in parts per million, equivalents per million, percentages of total ions computed from parts per million and from equivalents per million, and grains *per* U. S. gallon. For this analysis, the part-per-million values are the same as milligrams per liter. All units shown in table 5 are in common use.

All analyses made by the Geological Survey are reported for **permanent** record both in parts per million and in equivalents per million. Some published reports, however, do not show the analyses in both forms. Although for certain special uses it may be desirable to express water analyses in other ways, the basic systems of parts per million and equivalents per million are the most generally applicable and can be used for computing the data to any other forms that may be desired.

As previously mentioned, the practice of expressing water analyses in terms of hypothetical combined salts is disappearing. Analyses expressed in this form generally must be recomputed to uncombined ions by means of molecular or atomic weights to make them readily usable. An example of the type of computation required is:

$$\text{ppm Ca} = \text{ppm CaCl} \; \frac{\text{at. wt Ca}}{\text{mol. wt CaCl}_2}$$

Part-per-million values thus obtained for calcium should be added to those obtained for calcium in other combinations, if any, and reported in the analysis. A similar procedure should be used to compute other cations and anions.

Most of the water analyses in this report are expressed in two forms, parts per million to show the weights of dissolved matter present, and in equivalents per million to show more clearly the chemical character of the water with reference to the dissociated ions.

SIGNIFICANCE OF PROPERTIES AND CONSTITUENTS REPORTED IN WATER ANALYSES

The properties and constituents which may be reported in water analyses have already been enumerated. In this section, they will be discussed in some detail to provide a better understanding of the nature of each constituent and to indicate possible sources from which it may be derived, its chemical behavior in solution, the accuracy with which it may be determined, and the range of concentration normally expected. Where appropriate, some discussions of a theoretical nature regarding the chemical properties of certain constituents and the bases of measurement of properties also are included. These discussions should aid in understanding the nature, usefulness, and limitations of chemical analyses.

Before discussing individual constituents that are contained in solution in natural water, it may be well to consider briefly some of the general theoretical aspects of solutions and the solution process in the light of present chemical knowledge.

The ionic-dissociation theory of Arrhenius published in 1887 explained the behavior of electrolytes in solution by assuming that these substances, when dissolved in water, are dissociated to some extent into ions, but that this dissociation is complete only at infinite dilution. Studies of the structure of crystalline inorganic salts later revealed that such crystals are actually made up of ions. Therefore, a solution of a crystalline strong electrolyte could not contain undissociated molecules, even though it might be evident from the behavior of the solution that not all the dissolved material was acting as one might expect dissociated ions to act.

Debye and **Hückel** suggested in 1923 that the cause of the anomalous behavior of solutions of strong electrolytes lay in forces of electrostatic attraction among the ions, which prevented them from moving about freely in the solution. As a result, the effective concentration, or activity, of the ions present is less than the actual concentration. The factor for conversion of actual concentrations to activities, the activity coefficient, for an ion can be computed from the relationship :

$$-\log f_g \quad Az_i \cdot \sqrt{\mu}$$

where f_i is the activity coefficient of the ion in question, z_i is the charge of that ion, and μ is the ionic strength of the solution.[2] If the solvent is water at 25°C, the constant A has a value of about 0.51. This form of the **Debye-Hückel** equation gives accurate results in studies of the behavior of electrolytes in solutions containing as much as about 1,000 ppm of dissolved solids, and, with modifications, approximate values for somewhat higher concentrations. It is not applicable to brines.

When water comes into contact with a crystal of a soluble salt, the water molecules (being dipoles) orient themselves around exposed ions, the side of the molecule having a charge opposite to the ion being turned inward toward the ion. The result is that each exposed ion becomes surrounded by a shell of oriented water molecules that may be several layers deep. Because water has a high dielectric constant, the water shell acts as an insulator around the ion, and the ion's bonds to adjacent ions in the crystal are weakened and disrupted. The ion is thus brought into solution in a "hydrated" state and can move

---

The ionic strength of a solution is computed from the following equation :

$$\mu = \frac{C_1z_1^2 + C_2z_2^2 + C_3z_3^2 \ldots + C_nz_n}{2}.$$

where C_1, C_2, etc. are concentrations of ions in the solution in moles per liter and z_1, z_2, etc. are the charges on the ions.

about, being prevented by its shell of water molecules from uniting with unlike ions from the crystal which also may be present. The high dielectric constant of water is an important factor in keeping the dissolved ions apart. In very dilute solutions, the forces of attraction that may exist among them are negligible and the ions can move independently. As concentrations increase, the interionic forces exert a greater and greater influence on the behavior of the dissolved ions.

The relative solubility of simple crystalline solids would appear to depend upon the strength of the bond holding the crystal structure together, the distances the ions are separated in the solid, and probably other factors, and also upon the amounts and kinds of ions already present in solution. Most of the data in the literature for solubility of various compounds were obtained in pure water or in relatively simple solutions. Natural waters ordinarily are highly complex mixtures, and solubility data in the literature are not always directly useful in studies of the chemistry of natural waters.

In addition to the ions dissolved by the processes just described, water may contain larger segments of either crystalline or noncrystalline matter in colloidal suspension These colloidal particles also carry electrical charges and are surrounded by shells of oriented water molecules. The particles may range in size from near that of ions (a few angstrom units in diameter) up to about 0.2 micron (2 X 10 angstrom units). Particles much larger than this will generally settle from the solution by gravity. No exact boundary between the sizes of particles considered to be in solution and those in colloidal suspension can be given.

Some of the solute particles in natural waters may be essentially single molecules or crystal fragments so small that all the ions are accessible to participate immediately in chemical reactions. The silica content of most natural waters, for example, is postulated by Krauskopf (1956) to be in the form of monomolecular H_4SiO_4. Particles this size do not behave like colloids. Neither do these subcolloidal particles have the properties of charged ions. The terms "dissolved" or "in solution" are difficult to define in view of the different forms in which nonaqueous material occurs in natural water.

SPECIFIC ELECTRICAL CONDUCTANCE

Electrical conductance is the ability of a substance to conduct an electrical current. Specific electrical conductance is the conductance of a cube of the substance 1 centimeter on a side. This term is synonymous with "volume conductivity" (Handbook of Chemistry and Physics, 1953) and with the term "conductivity per centimeter" reported in analyses made by some laboratories. "Electrical conductivity" is defined by the American Society for Testing Materials

(1950) as equivalent to "specific electrical conductance" but the latter term probably is more widely accepted. The conductance of water solutions of mineral matter increases as the temperature of the solution rises; therefore, to make reported values comparable, they must all be referred to the same temperature.

UNITS FOR REPORTING CONDUCTANCE

Because conductance is the reciprocal of resistance, the units in which specific conductance is reported are reciprocal ohms or "mhos". Natural waters have specific conductance values much less than one mho, and in order to avoid inconvenient decimals, data are reported in millionths of mhos or micromhos. Before October 1, 1947, the specific conductance values reported by the U. S. Geological Survey were mhos X **10** . To convert these earlier values to micromhos, they should be multiplied by 10.

PHYSICAL BASIS OF CONDUCTANCE

Chemically pure water in liquid form has a very low electrical conductance. The presence of dissociated ions in solution, however, renders the solution conductive. A considerable amount of research has been done on the property of electrical conductance of solutions, and it is fully discussed from a theoretical standpoint in texts on physical chemistry (Glasstone, 1946, p. 884-919). Figure 6 illustrates the relation of conductance to concentration in ppm of a solution of the single salt potassium chloride. In simple dilute solutions of this type a linear relation exists between dissolved-solids concentration and conductance. As the concentration increases, however, the line will change in slope. The amount and direction of the change is different for different salts. The slope of the straight portion of the curve also is different for different salts.

Figure 7 illustrates another feature which has been mentioned. The solution of KC1 here is constant in concentration (746 milligrams per liter dissolved solids) but from 0° to 35°C its conductance more than doubles. This demonstrates the need for referring specific-conductance measurements to a single temperature. Most data for natural waters are referred to 25°C (77°F). However, a considerable volume of laboratory research data on solutions is referred to 18°C, and the literature, therefore, is not consistent. All data in this report are referred to 25°C, in accordance with general practice for water-quality work. The conductance increases approximately 2 percent for each increase in temperature of 1°C.

Natural waters are solutions of mixed salts, containing some undissociated substances reported as part of the dissolved solids. The dissociated salts have differing relations between concentration and

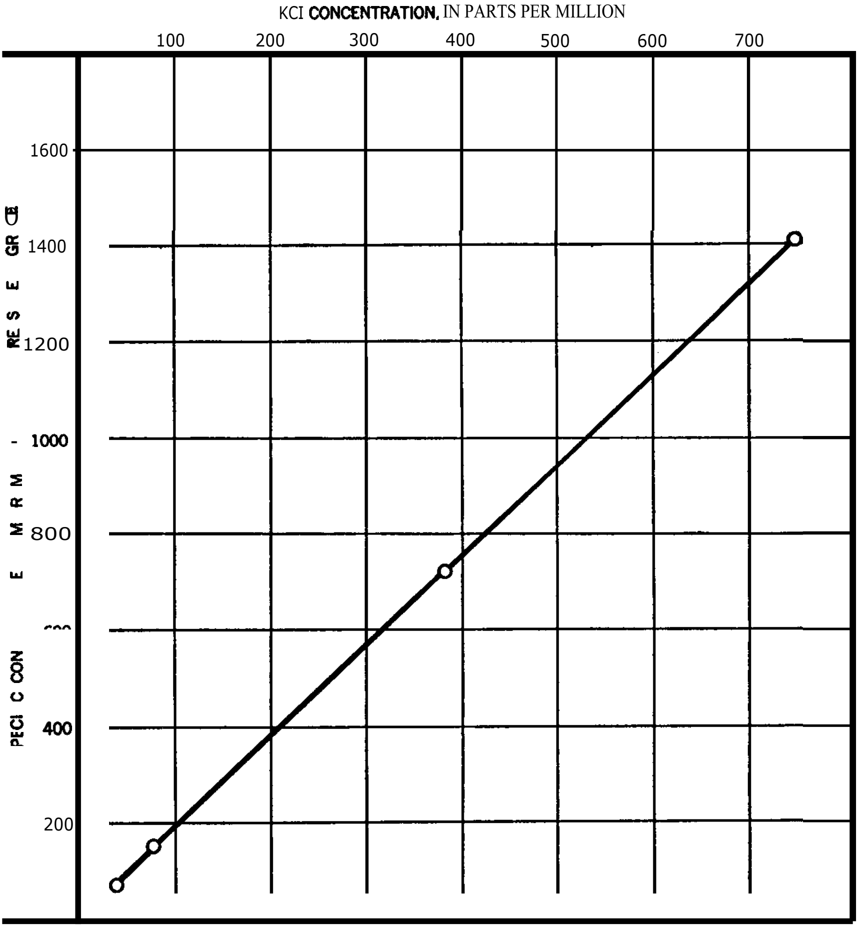


Figure 6.—Specific conductance of potassium chloride solutions.

conductance. The undissociated substances are nonconducting and tend to cause some aberrations in the dissolved solids-conductance relationship for natural waters. Waters with high concentrations of dissolved solids may have poorly defined dissolved solids—conductance relationships.

Research on conductance of solutions of electrolytes has been going on actively since the latter part of the 19th century. Although it might be supposed that a simple relationship should exist between ionic concentrations and conductance, this has not been found to be the case. Probably the most important factors in determining how well a given solution will conduct a current are the number and kinds of ions present, their relative charge and their "mobility." This last property is a means of expressing the relative freedom of ions to act

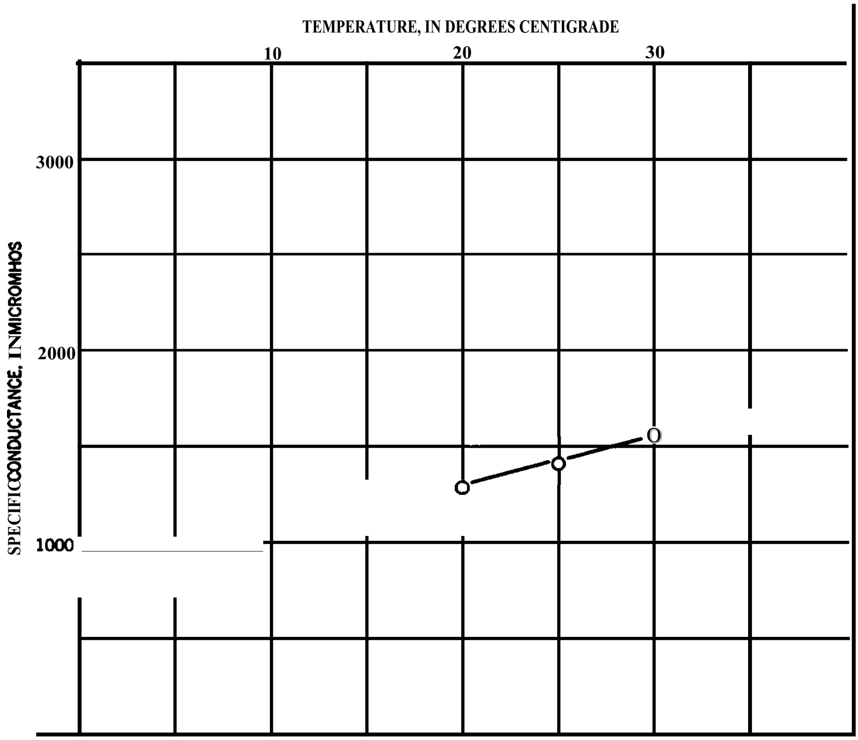


FIGURE 7.—Specific electrical conductance of a 0.01 normal solution of potassium chloride at various temperatures.

as conductors by movement through the solution and itself includes a number of factors, such as size and degree of hydration of ions, mechanical resistance to movement through the solvent, electrostatic forces caused by degree of concentration of ions, and perhaps other things. Some of these factors change with changes in concentration, and most or all are different for different ions.

In view of these complexities, it is not surprising that no exact relationship exists between conductance and dissolved solids in natural waters. In the relationship—

Specific conductance (μ mhos at 25° C) A=Dissolved solids (ppm)

the factor A has a value ranging from 0.5 to 1.0. For analysis 3, table 10, A has a value 0.54 and for analysis 3, table 8, A has a value of 0.96. Usually, however, A has a value between 0.55 and 0.75 unless the water has an unusual composition.

Figure 8 shows the relationship between specific conductance and dissolved solids for Gila River at Bylas, Ariz., for the period October 1, 1943 to September 30, 1944. The relationship does not deviate greatly from linearity throughout the range of concentration

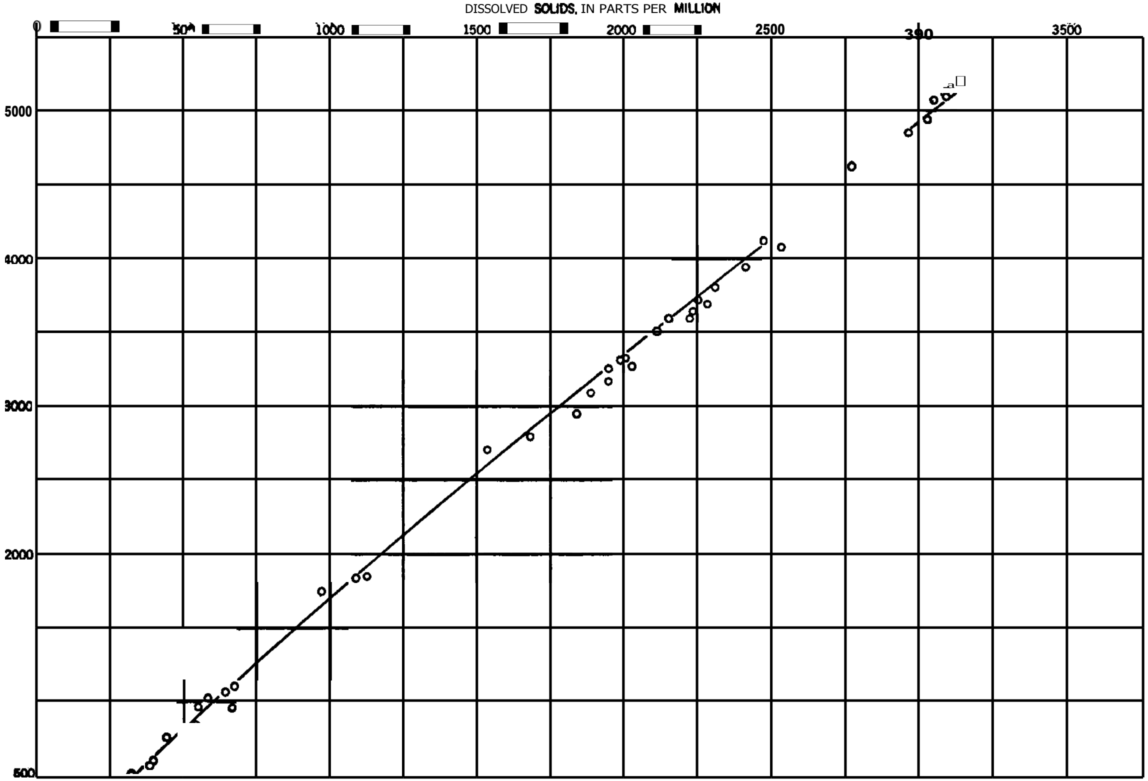


FIGURE 8.—Dissolved [illegible] conductance [illegible] composites [illegible], Gila River [illegible], Ariz., October 1, 1944, to September 30, 1944.

experienced during the period. At this sampling point, the base flow is maintained by ground-water inflows upstream which are high in sodium and chloride. Higher flows represent dilution of the base flow by direct runoff which is low in dissolved solids. Consequently, the water has a rather consistent dissolved solids-specific conductance relationship. In many streams, the relationship is less well defined.

Specific conductance is easily and conveniently determined. Conductance values may be used as a guide in selection of laboratory procedures for determining dissolved constituents and indicate the dissolved-solids content of waters closely enough for many other purposes. The determination is used in showing the short-term changes which occur in the quality of streamflow. Conductance data on large numbers of water sources in an area provide a basis for selecting sites for obtaining samples for more detailed chemical analyses. Determinations of conductance are conveniently made with portable field equipment, and the conductance of streamflow may actually be continuously recorded on a chart by instruments designed for that purpose. The use of conductance values in checking the accuracy of analyses has been suggested by Rossum (1949).

RANGE OF CONDUCTANCE VALUES

The specific conductance of the purest water that can be made in the laboratory is about 0.05 micromho (Glasstone, 1946, p. 891). Ordinary single-distilled water used in laboratory work generally has a conductance of 1 to 5 micromhos. The carbon dioxide content of ordinary distilled water is in equilibrium with the carbon dioxide in the laboratory air, and the water owes most of its conductivity to dissociated carbonic acid, which yields H^+ and HCO_3^-.

Rainwater has ample opportunity before touching the earth to dissolve gases from air and also may dissolve particles of airborne dust or other material. Rainwater is, therefore, less pure than distilled water and has a somewhat higher conductance. This is particularly true near large industrial cities, where the air contains sulfur dioxide and other industrial pollutants, or near the ocean where it may contain windblown salt from the sea. The conductances of surface and ground waters have a wide range throughout the United States and in some areas may approach those of the rain or snow from which they originated, or exceed that of the sea water. For natural surface waters in the United States, conductances range from 50 micromhos, or lower in some areas of abundant precipitation **and relatively insoluble rocks, to some 50,000 micromhos for ocean water. However, ground water approaching or greatly exceeding the conductivity of sea water occurs locally in most regions of the United States, and water from lakes in closed basins also may have a higher conductance than sea water.**

ACCURACY AND REPRODUCIBILITY OF CONDUCTANCE VALUES

In Geological Survey laboratories, emphasis has not been placed on obtaining the highest possible absolute accuracy of specific conductance values. Because of limitations of the apparatus and methods used in the laboratories, in the range of 10.0 micromhos up to about **50,000,** differences as high as **±5** percent on identical samples run on different sets of equipment could occur. Therefore, differences of **±5** percent or less in conductance in this range are found from one sample to another, but may not indicate actual differences in composition. For waters having a conductivity higher than 50,000 micromhos, the conductivity values should not be used as a basis for estimating dissolved-solids concentrations. The relationship between dissolved solids and conductance becomes indefinite for solutions approaching saturation.

Conductivity measurements made in the field on duplicate samples probably cannot be expected to agree among each other more nearly than about 10 percent. Primarily this is because the field apparatus is simplified and less precise than laboratory apparatus, and some of the conditions of measurement such as temperature cannot be controlled in fieldwork as effectively as in the laboratory. Differences of **a** magnitude of 10 percent, therefore, among field conductance results **or** between field and laboratory results should not be considered significant.

HYDROGEN-ION CONCENTRATION (pH)

Hydrogen-ion concentration is expressed in terms of pH units. The significance of pH values of natural waters cannot be explained without consideration of certain basic principles of physical chemistry upon which the pH concept is based.

As has been mentioned earlier, mineral salts dissociate into ions when they are dissolved in water. Pure water is itself dissociated into ions to a slight extent. Assuming for simplicity the existence of nonhydrated hydrogen ions, this dissociation takes the **form—**

$$H_2O \rightleftharpoons H^+ \quad OH$$

The chemical equilibrium in the preceding system can be mathematically expressed as follows :

$$\frac{A_{H}^{\cdot} \times A_{OH}}{A_{H_2O}}$$

The "A" terms in this expression represent "activities" of the ionized and nonionized portions of the water. The activity of an ion or molecule can be thought of as its effective concentration and is defined **as the product of concentration in moles per liter and the activity coefficient.** K is the equilibrium constant for this reaction.

The undissociated water is present in so large an excess that it can be considered constant for practical purposes. The activity coefficients for H+ and OH are approximately unity. For these reasons the product of the molar concentrations of the H+ and OH^{-} is equal to another constant, usually written as K. In terms of molar concentration then,

$$C_{H}^{+}\times C_{OH}=K_{w}$$

This is the derivation of the dissociation constant, or ionic product of water, which is useful in evaluating the conditions existing in aqueous solutions.

The value of K_{w} is known to be about 1 X 10^{-14} at 25°C, and increases about 8 percent per degree rise in temperature. In pure water one may assume neutrality and at neutrality CH+ must equal C_{OH} . Their product K_{w} is 10^{-14}. Hence, C_{n}+ and C_{OH} must both be 10^{-}i mole per liter. The exponent of the hydrogen-ion concentration is —7, or considered another way, the negative logarithm to the base 10 of the hydrogen-ion concentration is -1-7. This number is called the pH value. By definition, therefore, the pH value of a solution is the negative logarithm of the concentration of hydrogen ions in moles per liter.

If an excess of hydrogen ions is present in a water solution, the hydrogen ion concentration will exceed 10 , and in order to maintain K_{w} constant, the concentration of OH^{-} must be less by an equivalent amount. The negative logarithm of the hydrogen-ion concentration (pH) is lower than 7 in acid solutions and higher than 7 in basic solutions.

The pH of natural water is largely controlled by chemical reactions and equilibria among the ions in solution. The most important type of reaction affecting pH in natural water is hydrolysis, and because of the significance of the effect it is discussed further below.

HYDROLYSIS

When the neutral salt AZ goes into solution, it can be considered to divide into ions as follows:

$$AZ\rightleftharpoons A^{+}$$

Pure water contains 11+ and OH^{-} ions in equal amounts. When the salt is added, the cations tend to combine with OH^{-} and the anions with H+ from the water

$$A^{+}+OH\rightleftharpoons AOH \tag{1}$$

(2)

The extent of displacement of these two equilibria to the right depends upon the degree of dissociation of the acid or base that is produced. If the acid or base are both highly dissociated, the equilibria are shifted well to the left and the numbers of $H+$ and OH ions in solution remain about equal. A solution of sodium chloride is an example of this condition. It has a pH about the same as pure water.

If the original salt yields anions or cations which combine with $H+$ or OH from the water to give a product that is only partly dissociated, one or both of the equilibria may be shifted toward the right. This represents a chemical reaction between ions in solution and the water, and such a reaction is called hydrolysis. The effect of hydrolysis is generally to alter the pH of a solution either to the acid or basic side of neutrality.

The extent of the shift in pH depends on the difference in the degree of dissociation of the products ZH and *A*OH. In the case of the salt sodium carbonate, equilibrium (1) is shifted far to the left because the product NaOH is practically 100 percent dissociated. The 11_2CO_3 formed in equilibrium (2), however, is only very slightly dissociated and this equilibrium is shifted well to the right. In a sodium carbonate solution, therefore, a relatively large number of the $H+$ ions are rendered inactive and the pH is thereby raised above **7.**

In a solution of ammonium chloride, the position of equilibrium (1) is much farther to the right than equilibrium (2) ; hence the solution will tend to have a pH below 7. If the substances in solution tend to displace both equilibria to the right, as would be the case with ammonium carbonate, the final pH of the solution would still be governed by the difference in degree of dissociation of the products on the right-hand side of the equilibria.

In natural waters the hydrolysis due to carbonate and bicarbonate salts predominates in most instances. Hydrolysis due to phosphates, silicates, borates, fluorides, and a few other less common salts may also affect the pH. These all tend to raise the pH value above **7.** Substances giving an acid reaction upon hydrolysis, such as salts of iron and ammonium, are rarely present in large enough quantities to predominate in fixing the pH of natural waters.

BUFFERED SOLUTIONS

When a small volume of dilute acid is added to distilled water, the **pH** of the water will be greatly changed. The same volume of acid added to a natural water of moderate dissolved solids concentration may have a comparatively minor effect on the pH. Solutions whose **pH** tends to remain constant when small amounts of acid or base **are added** are called "buffered" solutions.

Buffering action is afforded in a solution by the presence of an acid, or base, which is only slightly dissociated and one of the salts.

of that acid, or base. When H^+ or OH^- ions are added to such a solution, they are first used up in converting undissociated acid or base to the salt or vice versa. Until this has been fully accomplished, there is little change in the pH of the solution.

Carbon dioxide gas, when dissolved in water, forms carbonic acid. A water which contains carbon dioxide and a carbonate or bicarbonate contains a weak acid (H_2CO_3) and its salt, and is therefore a buffered solution. Most natural waters contain this combination as the principal control of their pH. The carbon dioxide-bicarbonate system, however, is not stable if the system is subjected to an environment where carbon dioxide may escape from solution. In some waters, other substances may supplement or substitute for this buffer system. The bicarbonate—carbon dioxide system is effective in the control of pH in about the 4.5 to 8.0 range.

INTERPRETATION OF pH DATA

The pH value of a water represents the overall balance of a series of equilibria existing in solution. In the laboratory, the pH can be measured accurately, but it must be kept in mind that the result obtained depends upon conditions of sampling which cannot always be controlled and that the pH of water samples may change during storage. The carbon dioxide-bicarbonate-carbonate equilibrium and buffer system existing in most water samples is easily disturbed by loss of carbon dioxide. This is perhaps most important in sampling waters from confined underground sources. Where a source of carbon dioxide is available to such waters, they may become supersaturated with carbon dioxide with respect to atmospheric pressure. Immediately upon the release of confining pressure, as when such a water is brought to the land surface in a well or spring, carbon dioxide will be lost from solution until the amount equals that which will remain under the partial pressure of this gas in the atmosphere, and a new equilibrium will be established. Often a change in pH and precipitation of calcium cabonate and sometimes other compounds accompany the loss of carbon dioxide from solution.

If care is taken to insure that the sample bottle is tightly sealed, all the carbon dioxide that was in the water when the sample was collected can be retained, but it is essentially impossible to obtain laboratory pH data on such a water that will represent actual conditions within the aquifer because some carbon dioxide will be lost from the water before it is possible to get a sample. The carbon dioxide content can also be affected by temperature changes, for the solubility of carbon dioxide is lowered as the temperature rises.

Some of the ions in natural waters may occur in two or more valence states. The predominance of oxidized or reduced form depends upon the environment of the water. In contact with air, the reduced form may be oxidized, and in some instances, the pH of the solution may change as a result.

Uncertainties involved in assuming that laboratory determinations of pH represent natural conditions have caused some investigators to reject laboratory determinations in favor of field determinations made on the spot before some of the possible changes can occur. For many ground waters, determinations of pH in the field may have some advantages, but the laboratory data also have a place of importance. For surface waters and shallow unconfined ground waters, when samples are collected and stored with care, laboratory data probably represent field conditions closely enough for many purposes. In surface waters, the carbon dioxide content is regulated normally by the partial pressure of carbon dioxide in the atmosphere. Important changes in pH owing to loss of carbon dioxide during storage of samples would not be expected in such waters. Also, it should be kept in mind that values for pH determined in the laboratory may better represent conditions under which the water will be used than would field determinations.

Stevens (1934) has investigated the pH of solutions of silicate minerals. From his studies, it seems likely that high pH values in natural water may, at least in some instances, result from the action of water upon silicate rocks. In this connection, Stevens states:

> The effectiveness of silicate minerals as agents in determining the pH of aqueous solutions in geochemical processes seems to be clearly indicated by the experiments described in this paper, although it should be again pointed out that the abundance of carbonate rocks near the surface leads to their being the source of alkalinity in many natural waters. In deepseated waters, the silicates would have a major influence.

Values of pH often are used as a measure of the solvent power of water or as an indicator of the chemical behavior certain solutions may have toward rock minerals. However, one must not overlook the fact that pH values are only a means of stating the balance of certain chemical equilibria in water solutions. If a water of a low pH dissolves some solid material through reactions involving H^+ ions, a new equilibrium pH value will rapidly be reached and the reaction will stop unless the supply of low pH water is large compared to the solid phase material, or a continuing supply of soluble matter that lowers the pH is available. The investigator who utilizes pH data in his interpretations of water analyses should be 'careful to place pH values in their proper perspective.

In surface waters, the supply of water is ordinarily large in comparison with the solid material available for solution. The pH of the water, therefore, may not be greatly affected by the solution of all available ions. A ground water, on the other hand, may be considered to occur in an environment where solids available for solution are present in large excess compared to the water supply. Under these circumstances, recharge entering the ground-water reservoir will usually have ample opportunity to dissolve solid mineral matter, and the pH of water that has been in the ground-water reservoir will more closely reflect the influence of the solid material that was available. A discussion of pH and carbon dioxide equilibria related to lake waters is contained in a recent work by Hutchinson (1957).

RANGE OF pH VALUES

As stated previously, the pH of pure water is 7.0. Most ground waters found in the United States have pH values ranging from about 5.5 to slightly over 8. Waters with pH values considerably more than 8 or considerably less than 5.5 are occasionally found. In some places, particularly in humid regions, the pH of surface waters commonly is slightly below 7, but most surface waters range between 7 and 8. Waters containing an excess of dissolved carbon dioxide obtain hydrogen ions from the dissociation of carbonic acid and have pH values less than 7.0. Some bicarbonate ions may be present at pH levels down to about 4.5.

Natural waters with pH values lower than about 4.5 may contain free mineral acids added by volcanic gases or oxidation of sulfides, or may contain salts which on hydrolysis tend to give an acid reaction. Ferric salts and aluminum salts, for example, are likely to make water acid. Some waters containing organic matter may have rather low pH values owing to the presence of organic acids.

Analyses of waters having pH values ranging from 9.4 to 1.9 are contained in table 11. The effect of dissolved carbon dioxide present in excess is illustrated by the high bicarbonate content and relatively low pH in analysis 2 in that table. The pH of 9.4 reported for analysis 1 may be partly due to hydrolysis of silicates. The pH of the sodium carbonate brine from Wyoming (No. 3) probably is higher than any of those listed, but was not indicated in the published analysis. The low pH value given for analysis 4 in this table results from the presence of free sulfuric acid produced by oxidation of sulfur dioxide which is emitted by fumaroles in the vicinity.

Values are given for pH in most of the analyses in tables 6-10 and 12. The relationship of pH to alkalinity and acidity reported in other terms will be discussed later.

ACCURACY AND REPRODUCIBILITY OF pH VALUES

The pH of a water is generally determined by means of a calibrated potentiometer with glass and calomel electrodes immersed in the solution. This equipment permits an accuracy of a tenth of a pH unit, either in the laboratory or in the field. However, physical factors not related to instrumentation may affect the reproducibility of pH measurements and lower the significance of differences in pH which may be observed. Differences of several tenths must always be interpreted in the light of possible changes resulting from sampling and associated environmental changes. Most colorimetric methods of pH determination are better suited to laboratory than to field use and require more time than the pH meter method. Approximate values to about half a pH unit can be determined in the field or laboratory by use of commercially available test-paper sets.

COLOR

The extent to which a water is colored by material in solution is commonly reported as a part of a water analysis. The determination is based on a comparison of a column of the water sample with a column of equal height of an arbitrary standard whose color is rated at 500. This standard is made up from 1 gram of cobalt chloride and 1.245 grams of potassium chloroplatinate to which is added 100 milliliters of concentrated hydrochloric acid and the whole diluted to one liter with distilled water. Permanent standards in the form of colored glass discs are often used. Color in water is expressed in terms of units between 0 and 500 or more based on the above standard.

SOURCES AND SIGNIFICANCE OF COLOR IN WATER

Surface waters that leach decaying vegetation may be colored, and ground waters that pass through peat, lignite, or other buried plant remains may take on a deep color. The colored substances in these instances are organic compounds and may be partly ionized. Inorganic colored compounds may be added to water by industrial waste disposal.

Except for the possible significance of color in indicating the presence of organic ions that may have some bearing on solvent activity, or the possible presence of organic material in aquifers, the color determination has no great importance in geochemical studies of water analyses. The determination is mainly significant in the evaluation of drinking water supplies or for other uses where color is not desirable.

Water from swamps, where vegetation is abundant, may have color amounting to several hundred units on the cobalt-platinum scale, and some ground waters associated with peat or lignite beds may be colored even more.

RESIDUE ON EVAPORATION

The total concentration of dissolved material in water is ordinarily determined from the weight of dry residue remaining after evapora..

tion of an aliquot of the water sample. Total solids (TS), total dissolved solids, or dissolved solids are terms used more or less synonymously for this value. These terms, however, may also be used to designate computed rather than determined data. The computation procedure will be described later.

THEORETICAL BASIS OF DETERMINATION

Residue on evaporation is determined in the U. S. Geological Survey laboratories by evaporating an aliquot of the water to dryness in a dish on a steam bath and completing the process of drying by heating the dish and residue in an oven for 1 hour at 180°C. This final drying temperature was chosen to assure the complete conversion of bicarbonate to carbonate. A drying temperature of 110°C is commonly used in some laboratories in the determination of dissolved solids. If the residue contains much sodium bicarbonate, too low a drying temperature might fail to complete the conversion. For many waters, however, the different drying temperatures give results that are comparable within the limits of accuracy of this determination.

In an attempt to correct the residue on evaporation for water of crystallization and for organic matter not removed by the 180° drying, ignition at a higher temperature is sometimes resorted to. The ignition temperature is not closely controlled but is usually near or below dull red heat and is applied for 3 minutes. Even this ignition may not remove all the organic matter, and water of crystallization. Data for "loss on ignition" do not have much significance from a geochemical point of view and are no longer reported in analyses made by the Geological Survey.

The solid material deposited when a water is evaporated to dryness does not coincide completely with the material that was originally in solution. Dissolved gases which may have had an important bearing on the character of the water originally are driven off. In the drying process, bicarbonate is converted to carbonate with loss of carbon dioxide and H_2O and thus some chemically active material originally in the water is lost. Some of the solid salts deposited may be volatilized at the drying temperature. This effect is most important in waters high in magnesium, chloride, and nitrate. Some waters may deposit residues which contain water of crystallization not driven off at the drying temperature. This effect is most pronounced in highly mineralized waters and especially those from which crystalline gypsum is deposited, and may add to the residue something not chemically active in the solution.

Besides indicating the total concentration of dissolved matter, the results of the determination of residue on evaporation are often used in providing an approximate check on the accuracy and completeness of an analysis when they are compared with the results for "dissolved solids (sum)" for that analysis. Because of the limitations of the residue-on-evaporation determination, such a comparison can only be approximate.

RANGE OF CONCENTRATION

Natural waters in areas of high precipitation may contain 25 or 30 ppm of dissolved solids or less. Brines, on the other hand, may have 300,000 ppm of dissolved matter, and, rarely even more.

ACCURACY AND REPRODUCIBILITY OF RESULTS

The results of residue on evaporation for most waters having 100 to 1,000 ppm dissolved solids can be made to agree on duplicate samples to 5 or 10 ppm. On more dilute waters, somewhat closer agreement is to be expected. Errors of rather large magnitude are possible, however, in waters of certain types. The presence of water of crystallization in the residue or the loss of some of the residue by volatilization or decomposition are major possible sources of differences among results. Differences of the order of 5 percent or less among samples in this determination should not be considered significant in the interpretation of data. The discussion has pointed out that the concentration of dissolved solids determined by this method contains many uncertainties that cannot be readily evaluated. The absolute accuracy of the results may therefore be poor.

SILICA

It will be noted that silicon is the most abundant of the elements listed in table 1, both in igneous rock and in the resistates and hydrolyzates. Except for oxygen, it is the most abundant element in the earth's crust. In rocks, silicon may be in the form of the oxide silica ($Si0_2$). It is also combined with the metals in the form of silicates. The silicate minerals are particularly important in the composition of igneous and metamorphic rocks.

Mention is made of various silicate minerals in many places in this report in discussing sources of dissolved material in water. A full exposition of the structure and chemical composition of silicate minerals is not appropriate in this type of report. However, the reader will find it very helpful to him, if he has not already done so, to acquire some knowledge of this subject as an aid to understanding processes of decomposition of rocks and their relation to natural water composition. Modern theories of the nature of silicate minerals are based on structural concepts much like those involving carbon compounds in organic chemistry. The basic silicate unit is the tetrahedron formed by a silicon atom surrounded by four oxygen atoms oriented at about equal angles.

These SiO_4 tetrahedra are linked in five different ways to form five general classes of compounds. They may share valence bonds with bivalent cations, as in the case of the magnesium olivine, forsterite (Mg_2SiO_4). These compounds are called "nesosilicates." The tetrahedra may *be* connected in pairs that share one oxygen between adjacent tetrahedra, thus forming small groups of tetrahedra or ring structures—for example, beryl $(Be_3Al_2Si_6O_{18})$. This type is called *a* "sorosilicate." The tetrahedra may be further condensed so that each tetrahedron shares two oxygens with its neighbors. These silicates form long single-chain structures, as in the pyroxenes $(R_2(SiO_3)_2)$, or double chains may occur through cross linkage of two single chains as in the amphiboles $(R_7(OH)_2Si_8O_{22})$. R, in these formulae, represents various bivalent cations, usually Ca++, Mg++, and Fe++. These chain silicates are called "inosilicates." The tetrahedra may share three adjacent oxygens, forming sheet structures typical of the micas and of clay minerals such as kaolinite $(Al_2(OH)_4Si_2O_5)$. These are called "phyllosilicates." The fully condensed "tectosilicates" are made up of tetrahedra in which all four oxygens are shared with adjacent tetrahedra. This is the structure of quartz (SiO_2) and the feldspars, in which Al+++ ions substitute for part of the silicon.

The reader is referred to Mason (1952, p. 59-81) and to Hückel (1950, p. 740-755) for a more detailed discussion of the structure of silicates. A brief summary by Keller (1955) contains photographs of molecular models that show very well the different types of structures.

SOURCES OF SILICA IN WATER

Crystalline SiO_2 as quartz is a major constituent of many igneous rocks, and also constitutes the bulk of the grains in most sandstones. Quartz is one of the most resistant of all rock minerals to attack by water. For practical purposes, quartz can probably be ignored as *a* source of silica in the natural waters of temperate regions. The cryptocrystalline and amorphous forms of silica, such as chert and opal probably are considerably more soluble in water than is quartz. However, it is likely that the greater part of dissolved silica in water originates in the chemical breakdown of silicates in the processes of metamorphism or weathering.

The chemical reactions involved in decomposition of silicates are highly complex. In a general way they can be represented as hydrolysis reactions in which H+ from the water replaces metallic cations in the silicate lattice. The lattice is broken up and altered by this process. Clay minerals are formed from most of these reactions, and some of the silicon-oxygen groups of the original mineral are generally surplus to the new arrangement. The surplus silica and the replaced cations can be considered available for solution.

If the reaction is visualized as a simple hydrolysis, the removal of 11+ from the water would tend to raise the pH of the residual solution, the effect observed by Stevens (1934). Where carbon dioxide is contained in weathering solutions, it enters the reaction in two important ways. The dissociation of carbonic acid provides hydrogen ions to participate in the reaction, and the bicarbonate ions formed at the same time buffer the residual solution and prevent the pH from rising excessively.

The nesosilicates and inosilicates represent structures in which a relatively high proportion of the bonding is comprised of the linking of cations to oxygen. These bonds represent zones of weakness which can be disrupted relatively easily as compared to silicon-oxygen or aluminum-oxygen bonds. The ferromagnesian minerals, which belong largely to these two classes of silicate structures, are less stable to weathering attack than structures like the tectosilicates where silicon-oxygen bonding predominates to a greater degree. In weathering to clay minerals, however, the ferromagnesian minerals generally give up smaller amounts of surplus silica than do the tectosilicate feldspars. Under favorable circumstances, therefore, the weathering of feldspars could constitute an important source of silica for solution in natural water.

Analysis 2 in table 6, which shows a high proportion of silica, is of a water from rhyolitic rock, a type rich in alkali feldspar. The minerals that give up silica upon alteration by water are most common in igneous and metamorphic rocks but also may be found in incompletely leached resistate and hydrolyzate sediments and in lesser amounts in precipitates and evaporates. Much research remains to be done before the mechanisms of breakdown of silicates are fully understood. Factors such as temperature, amount of water available, and freedom of water movement through the rock affect the rate at which decomposition occurs and may also influence the type of clay mineral formed and the degree to which silica is taken into solution.

CHEMISTRY OF SILICA IN NATURAL WATER

Although it is an important constitutent of many natural waters, silicon does not hold a position in them comparable to that which it occupies in the composition of rocks. The actual significance of silicon concentrations in water has also been somewhat obscured because of uncertainty as to the form silicon takes in solution. For many years it has been customary to report the silicon present in water in terms of the oxide, silica ($Si0_2$). It is usually stated or implied in the older literature on the subject that the silica present in natural water is in finely divided colloidal form. The gravimetric method of determining silica in water recovers the silicon as the oxide.

In the anhydrous residue obtained by evaporating the sample to dryness, the silicon occurs as silica. In view of these facts, the assumption of colloidal silica seemed logical.

However, in recent years, a colorimetric procedure for determining silica in water has been widely adopted which would seem to depend for accurate results upon the silica being present, either in ionic state or something approaching it so closely that the individual particles act like ions in their readiness to take part in chemical reactions. For almost all waters, the colorimetric and gravimetric methods give the same result. This has prompted some authors to observe that essentially all the silica in water is present in ionic form as silicate (Mason, 1952, p. 149; Roy, 1945). There is, however, ample proof that the silica in natural waters is not in dissociated form. An acceptable hypothesis to explain the state of silica in solution in natural water must find some middle ground between the ionic and the colloidal states.

Der (1955) recently has prepared a monograph on silicate chemistry which helps considerably in explaining some of the observed features of the behavior of silica in water. From consideration of silicate mineral structure, one might anticipate that monomeric silica in water should consist of single silicon atoms having a coordination number of four. On hydration the equilibrium

$$SiO_2+2H_2O \rightleftharpoons Si(OH)_4 \text{ or } H_4SiO_4$$

occurs. Iler (1955, p. 19) suggests that silicion in solution actually has a coordination number of 6 and forms ions of the same type as the fluosilicate ion (SiF_6 —). This is equivalent to the metasilicate (SiO_3 —) ion plus three molecules of water.

Dissociation constants for metasilicic acid reported in the literature range from 1 X 10 to 10– for K_1, and are in the vicinity of 10 or 10 for K_2. Therefore, in order to contain appreciable amounts of dissociated SiO_3 — or $Si(OH)_6$ — ions the pH of the solution would have to be 11 or more. Natural waters do not attain this pH level. The existence of monovalent ions of the type $HSiO_3$ is possible under some conditions. Using a value of 10 for K_1, about half the silica might be in ionic form at a pH of 9. At a pH of 8, somewhat less than a tenth of the silica would be dissociated. If the lower value 10 is used for K_1, less than a tenth of the silica would be dissociated at a pH of 9. Only a few natural waters have a pH as high as 9. Theoretically, therefore, dissociated silicate ions must be rather rare in natural water.

Further indications may be gained from examination of some of the water analyses in this paper. Silicate anions would be involved in hydrolysis and contribute alkalinity that would be titrated and reported in terms of carbonate and bicarbonate. Analysis 1 in table 6

TABLE 6.-A

[**Analyses** by U. S. Geological Survey. Date below sample number **is** date of **collection**]

[Source of data: Nos. 1, 2, 4, 5, and 9 **unpublished** data, U. S. **Geol.** Survey files; No. 3, **Piper,** Robinson and Park, (1939) p. 117; No. 6, U. S. **Geol.** Survey Water-Supply Paper 1022, p. 266; No. 7, Lohr and Love, (1954) p. 286; No. 8, U. S. Geol. Survey Water-Supply Paper 1102, p. **400**]

	(1) Nov. 23, 1953		(2) Aug. 1, 1947		(3) Aug. 21, 1931		(4) June 13, 1952		**(5)** Apr. 18, 1952		(6) Apr. 11-19, 1944		(7) Oct. 12, 1951		(8) May 6, 1947		(9) Mar. 22, 1952	
	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm
Silica **(SiO₂)**	99		103				49		38		48		71		62		29	
Iron (Fe) **dissolved**	**.04**	-----	.0	-----	**0**		.01	-----	.24	-----	.03	-----	.0	-----	.01	-----	.33	----
Manganese (Mn)							.00	-----	00	------							00	----
Calcium (Ca)	2.4	.120	6.5	.324		.699	32	1.597	12	.599	43	2.15	32	1.597	22	1.098	17	.848
Magnesium (Mg)	1.4	.115	1.1	.090	**7.5**	.617	12	.987	6.6	.543	20	1.64	8.8	.724	4.4	.362	1.7	.140
Sodium (Na)	100	4.348	**40**	**1.729**	**1** □	1.783	30	1.305	7.2	.313	28	1.22	**42**	**1.826**	**20**	**.870**	**7.4**	**.323**
Potassium (K)	2.9	.074			**4.** □	.107	5.2	.133	3.1	.079	4.6	.12						
Carbonate (CO₃)	24	.800	0	**.0**		**.0**	**0**	**.0**	**0**	**.0**	**0**	.0	**0**	**.0**	**0**	**.0**	**0**	.0
Bicarbonate **(HCO₃)**	111	1.819	77	1.262	**4**	2.196	220	3.605	85	1.393	254	4.15	161	2.639	104	1.704	69	1.131
Sulfate **(SO₄)**	30	.625	15	.312	**4**	.291	11	.299	4.4	.092	8.3	.17	54	1.124	29	.604	6.9	.144
Chloride **(Cl)**	10	.282	17	.479	**4**	.677	7.9	.223	**1.2**	.034	28	.79	12	.338	.0	.000	1.1	.031
Fluoride (F)	22	1.158	1.6	084			.2	.011	.3	.016	.5	.03	.7	.037	.3	.016	.1	.005
Nitrate (NO₃)	.5	.008	.4	.006	**1.1**	.017	2.9	.047	.2	.003	.1	.00	.6	.010	1.4	.023	.0	.000
Boron (B)	.61	-----	.0	-----			.08	-----			0							
Dissolved solids																		
Calculated	**348**		222	-----		-----	259		115	-----	306		310		190		98	
Residue on evaporation						-----	257		114						158		98	
Hardness as CaCO₃	12		20				129		57		190		116		73		49	
Noncarbonate	0		0	-----			0		0		0		0	-----	0		0	
Specific conductance (**micromhos** at 25° C)	449		167			-----	358		136	-----	463	-----	404		198	-----	130	
pH	9.2	-----	6.7	-----			7.8	-----	7.9	------			7.9	-----	8.1		7.1	----
Color							10		8				2	-----			5	

1. Flowing well 7S 6E-9ba2, Owyhee County, Idaho, depth 800 ft. Temp. 122° F

2. Spring on Rio San Antonio, SW¼ sec. 7, T. 20 N., R. 4 E., **(unsurveyed)** Sandoval County, N. **Mex.,** temp. 101°F. Flow ±25 gpm. Water-bearing formation: Rhyolite.

3. Basque Spring. Lot 4, sec. 31, T. **26 S.,** R. 29 E., **Harney** County, Oreg. Water-bearing formation: Rhyolite and **possibly basalt.**

4. **Drilled** well, NW ¼ sec. 10, T. 2 N., R.32 E., Umatilla County, Oreg. **Water-bearing** formation: Columbia River basalt. Depth: 761 ft.

5. Flowing well, **SE ¼** sec. 16, T. 12 N., R. 17 E., Yakima County, Wash. Water-bearing formation: Basalt. Depth: 1078 ft. **Temp:** 63° F.

6. Eagle Creek at P-D pumping plant near Morenci, Greenlee County Ariz. Mean discharge for composite **period** 9.9 cfs. Drainage basin ±600 sq. mi. in which rocks exposed are essentially all extrusive volcanic rocks.

7. Main pump station, Albuquerque, N. Mex. Public supply. Seven wells 250 ft to 716 ft deep. Water-bearing formation: Santa Fe (valley **fill**).

8. **Middle** Loup River at Dunning, Nebr. Discharge 394 cfs. Drainage from Nebr. sand hills, flow maintained by ground water.

9. Well at Valdese Gen. Hospital, Rutherford **College,** Burke County, N. C. Depth: 400 ft. Water-bearing formation: Mica-schist. Temp. 59° F.

indicates the presence of 99 ppm of silica. If computed as metasilicate (SiO_3 —), this quantity would be 125 ppm, or 3.30 epm. The silicate ions would be titrated stoichiometrically in the conventional alkalinity determination, which for this water is reported as carbonate and bicarbonate in the amount of 2.619 epm. The assumption that all silica present as SiO_3^{-} is therefore not correct for this water, as it would give a higher alkalinity than was observed.

If $HSiO_3$ is postulated for all silica in analysis 1, table 6, the contribution to titratable alkalinity would be more reasonable, but this postulation still would give too high an alkalinity for analysis 2 in this table. In the titration of sodium silicate with acid, a double end point can be observed analogous to that found in the titration of carbonates. The parallel between these two systems indicates the possible existence of some form of bisilicate.

The theoretical data above ignore the possibility of polymerization of silica into dimeric or polymeric forms. Iler (1955, p. 20-28) suggests that dissociated silicate ions may polymerize and disappear from solution at pH levels where dissociation would be expected. At the concentrations of silica usually observed in natural waters, polymerization probably has not progressed very far. The rapid reaction of the dissolved silica in these waters with reagents added in the colorimetric silica determination indicates such silica cannot be present in large particles that would approach the colloidal size, because such particles could not be expected to react rapidly.

Krauskopf (1956) has reported the results of his experiments and studies of the recent literature which lead him to conclude that "amorphous" silica is taken up by water in both colloidal form and in solution as H_4SiO_4. The process of solution is slow and the portion of the silica present as a colloid is gradually converted to the hydrated dissolved molecules until the saturation point is reached.

White, Brannock, and Murata (1956) state that silica in hot-spring waters is in molecular solution, probably as H_4SiO_4. These investigators found that some springs yield supersaturated solutions of silica, in which there is a slow polymerization to colloidal silica. The colloidal silica reacted very slowly in the colorimetric determination.

On the basis of these studies, it certainly appears that the silica of most waters is present as particles of subcolloidal size. The presence of monomeric or dimeric silicic acid molecules is an attractive hypothesis.

Natural waters are occasionally found in which the silica is high (±100 ppm) and the pH also is high (9 or over). In waters of this type, it seems probable that some silica is present in the form of silicate ions. More studies are needed to evaluate the extent to which dissociated silicate may occur in such water.

High silica concentrations may also occur in acid waters. One would not expect dissociated silicates under these conditions.

RANGE OF CONCENTRATION

According to Lenher and Merrill (1917) , silica gel is soluble in pure water to the extent of 160 ppm of $Si0_2$ at 25°C and 426 ppm at 90°C. Krauskopf (1956) reports similar solubility values. Such high concentrations are rarely found in natural waters. Probably the presence of other substances in solution affects the solubility of silica, but the relatively high silica concentration in water from many hot springs does reflect the increase in solubility with temperature.

Sea water is normally very low in silica, and often contains less than 1 ppm, apparently because many marine organisms utilize silica in their shells and skeletons. In most natural waters, concentrations range from 1 to 30 ppm but concentrations up to 100 ppm are fairly common. Concentrations much over 100 ppm are relatively rare. Analyses in this report showing very high silica concentrations include Nos. 1 and 2, table 6; No. 4, table 11; and, Nos. 1 and 3 in table 13. Several of these are for water from hot springs, and two have a very low pH. In all the various types of waters shown in table 6, silica is a constituent of major importance. These waters are, for the most part, higher in sodium than in calcium. Goldschmidt (1954, p. 370) states that the presence of calcium bicarbonate reduces the solubility of silica in water. An inverse correlation between silica and calcium in natural waters could also be brought about by lack of soluble silica in rocks that constitute good sources for calcium.

ACCURACY AND REPRODUCIBILITY OF RESULTS

Glass is composed primarily of silicates, and the softer varieties of glass often used in manufacturing sample bottles may be attacked by the water of the samples stored in them (Collins and Riffenburg, 1923). Zabel (unpublished data, U. S. Geological Survey, 1954) reported that water samples increased slowly in silica concentration by dissolving silicates from the glass of the commonly used citrate of magnesia bottles. However, the contamination of water samples from this source can be minimized. Before they are put into use, new bottles should be allowed to stand full of water for a day or two to remove the most readily soluble film of silicate on the surface of the glass. Water samples should not stand in glass bottles in the laboratory or other places of storage for long periods before analysis.

Bottles made from Pyrex or other varieties of resistant glass have come into a wide use since the studies by Collins and Riffenburg

(1923) and are more resistant to solution by water than the ordinary prescription or pressure-seal bottles. Pyrex bottles are in extensive use in the Geological Survey laboratories for collection and storage of samples, although the other types of bottles also are much used. Polyethylene plastic bottles are essentially immune to attack by water, and in this respect are superior to glass as water-sample containers. The possibility of effects from solution of the sample container needs to be considered in **evaluating** silica-concentration data if the water has a high pH and has had an opportunity to remain in contact with glass a long time.

Values reported determined colorimetrically for silica are reproducible on duplicate samples to within about 2 ppm over the range from 10 to about 50 ppm, and more closely for values under 10 ppm. Above 50 ppm, the reproducibility probably is no better than 5 percent. For most waters, the standard procedures for silica all give the same results. For unusually high concentrations, especially in water from hot springs, the results obtained by different procedures may not be comparable.

IRON

The element iron (Fe) is one of the most abundant constituents of rocks and soils. The importance of determining small amounts of iron in evaluating the usability of a water for domestic and industrial purposes has led to the inclusion of an iron determination in all complete water analyses, even though the amount present may be a very small part of the total dissolved solids. In fact, the amounts of iron present in many waters are so small they are in the same range as trace constituents that are rarely determined.

SOURCES OF IRON IN WATER

Only oxygen, silicon, and aluminum are more abundant than iron in igneous rocks. It is more abundant in hydrolyzates than in resistates and precipitates. The silicate minerals of dark-colored igneous rock, such as the pyroxenes, the amphiboles, and the dark ferromagnesian micas, usually contain iron. The pyroxenes may be represented by the general formula

$$R_2[SiO_3]_2$$

and the amphiboles by the general formula

$$R_7[(OH)_2Si_8O_{22}]$$

where R is generally Mg^{++}, Fe^{++}, or Ca^{++}, although substitution of other cations can occur. Some anions (especially F^-) may substitute for **OH**. Biotite has the **approximate** formula

$$[R^{+}_{.70}R^{2+}_{2.10}][Si_{2.70}Al_{1.30}]O_{10}(OH)2K$$

Sulfide minerals, including the ferrous sulfide, pyrite and complex sulfides which include other metals besides iron, and oxides, particularly magnetite (Fe_3O_4), also are important iron-bearing minerals in igneous rocks. In sandstones, iron oxide, carbonate, and hydroxide are often present in the cementing material in appreciable percentages. Iron is present in the form of oxide, carbonate, and sulfide in shales and as a minor impurity in most carbonate rocks.

In addition to solution from such natural sources, iron may be added to ground water from contact with well casing, pump parts, piping, storage tanks, and other iron objects which may be in contact with the water. Suspended sediment in surface waters also may contain iron.

In order to obtain reliable information as to the quantity of iron a water contains in nature before it enters a well or is pumped or otherwise removed from a surface source, considerable care is necessary in sampling. Samples from wells should be taken as near to the pump discharge as possible, and should be taken from clear water delivered after the pumping equipment has been in operation long enough to remove water that might have been standing in the well in contact with the casing or pump, for the period since the well was previously pumped. Filtration at the time of collection may sometimes be necessary. Samples from surface sources should be obtained directly from the stream and allowed to settle until they become completely clear, or should be filtered so that they are free from suspended matter before the iron is determined. For purposes of evaluation of a water source for various uses, the iron added by contact with well casing and other similar influences may be significant, but it is not of interest for geochemical interpretation and may lead to erroneous conclusions.

CHEMISTRY OF IRON IN NATURAL WATER

Iron occurs in water at two levels of oxidation, either as bivalent ferrous iron or as trivalent ferric iron. The chemical behavior of the two forms is somewhat different, although both may be present in the same solution under certain circumstances. Under reducing conditions, iron in water will tend to be in the ferrous state. The ferrous salts, however, are unstable in the presence of oxygen or air, and are changed to the ferric state through oxidation when natural water containing ferrous ions is exposed to air.

The chemistry of iron in natural water is further complicated by a tendency for the formation of complex ions, and is influenced by certain kinds of micro-organisms.

In the pH range of 6 to 8, the amount of ferric iron in solution is theoretically limited by the solubility of ferric hydroxide, about

4 X 10 ^{0} to 5 X 10 mg of iron per liter (Mason, 1952, p. 141), which is below the limit of detection by ordinary laboratory methods. At a pH of 3, the solubility of ferric hydroxide is appreciable and increases rapidly as the pH decreases below 3. In natural waters, the influences of other dissolved constituents or the formation of complex ions may cause considerable deviation from the theoretical solubilities. However, it seems likely that any iron in the ferric state in alkaline and weakly acid waters is largely in a form other than dissociated Fe+++.

For ferrous iron, quite a different set of conditions prevail. If the solubility of Fe++ is controlled by the solubility of $Fe(OH)_2$, Larson and King (1954) report that at a pH of 8, the equivalent of 100 ppm of ferrous iron could occur in solution, and at a pH of 7, the theoretical maximum is about 10,000 ppm. In the presence of carbon dioxide, the solubility of ferrous iron is controlled by the solubility of ferrous carbonate and is greatly reduced but is still between 1 ppm and 10 ppm between pH 7 and 8 when 25 ppm of bicarbonate is present. Between pH 6 and 7, the solubility of ferrous iron may be much greater than 10 ppm even in the presence of more than 100 ppm of HCO_3. Probably the amount of ferrous iron that may dissolve from rocks also is determined by the reducing power of the environment of the water.

The oxidizing or reducing power of a system is conveniently expressed as the "redox potential" or Eh, in volts. The behavior of iron in natural water is related to both pH and Eh. A report by Hem and Cropper in preparation, discusses this relationship in detail. Hutchinson (1947, p. 691-726) also discusses this topic as it applies to lake waters.

When ground water containing iron in the ferrous state comes in contact with air, the following reaction can occur, assuming that ferrous and bicarbonate ions are present and that oxygen is available:

$$2Fe^{++}\quad 4HCO_3\quad H_2O+\tfrac{1}{2}O_2\rightarrow 2Fe(OH)_3+4CO_2$$

This oxidation reaction requires only 1 molecule of oxygen for each 4 molecules of ferric hydroxide produced. Some contact of natural waters with oxygen before or during sampling is almost unavoidable. The precipitation of ferric hydroxide is commonly observed in stored sample bottles which contain water that has ferrous iron in solution. Some air space is usually left when the bottles are filled, and this reaction could result from the small amount of air thus made available in the bottles. Conversion of iron to the ferric state may have a marked effect on the pH. Bicarbonate ions are removed from solution and replaced by carbon dioxide in the reaction above, which is the same thing that occurs when a water is titrated in determining alkalinity.

The activity of micro-organisms in dissolving and precipitating iron from water is worthy of mention. These organisms may be involved intimately in the processes of oxidation and reduction of iron. Certain types of bacteria, for example, exist without oxygen and promote a highly reducing environment favorable for taking iron into solution in the ferrous state. Other bacteria may actually derive the energy for their life processes from oxidation of ferrous iron to the ferric state. The latter type may aid in production of ore deposits and removal of ferrous iron from water.

Another factor involved in the chemical behavior of iron is the tendency of the ferric iron to form complexes with other ions in solution. The importance of inorganic complexes of iron is not yet fully explored, but the complexes with organic substances are important. Many waters containing organic solids that impart a color have iron in large amounts. Apparently this iron is bound to organic molecules or ions and is difficult to separate and determine by usual analytical procedures.

Many of the analyses of water that have been made by the Geological Survey report iron in two forms, "dissolved" and "total." The analyses for which only one iron value is reported usually give a value only for "dissolved" iron. Some of the analyses in the literature, particularly some of the older data, appear to give a high value for iron, and although usually no explanation is given, it may be that these data represent "total" iron. A few of the older analyses give a separate value for precipitated iron which represents iron not in solution when the sample was analyzed.

An explanation of the terms "dissolved" and "total" as they are applied in this connection is desirable, as they are not to be interpreted literally in every instance. "Dissolved" iron is the iron that appears to be in solution at the time the aliquot for the iron determination is withdrawn from the water sample in the laboratory. "Total" iron includes all the iron in solution and that which has precipitated in the sample bottle.

The "dissolved" iron determination often is not representative of conditions existing in the sample at the time of collection, because usually by the time the iron determination is started there has been opportunity for oxidation of ferrous iron and precipitation of ferric hydroxide. In some instances, the oxidation and precipitation will be complete, and in other instances they will be partial, depending on the length of time the sample has been in storage, the opportunity which has been afforded for dissolved carbon dioxide to escape, and various other factors which are not usually controlled. "Total" iron values, on the other hand, should represent more closely the actual concentration in the sample at the time of collection, but they will also include iron that was in suspension as well as what was in solution, unless the sample is filtered or otherwise clarified when it is collected. Usually a determination of suspended iron is not desired; hence, samples collected for "total" iron should be filtered at the time of collection if suspended iron is known or suspected to be present in the source.

In surface waters, the sediment normally present often includes some iron oxides that are formed in the process of weathering and are carried in colloidal suspension or as very small sediment particles. Incomplete separation of these particles from the water of surface streams during periods when much sediment is being carried will result in high values for iron from surface waters. Usually "total" iron is not determined for surface waters, but high values for "dissolved" iron in such waters may be the result of the presence of finely divided particles in suspension.

In 1957, the Geological Survey abandoned the reporting of "total" iron for most water samples. Unless otherwise indicated, values for iron reported in water analyses now represent amounts in solution at time of sampling. The older nomenclature is used in this report, however.

Industrial waste disposal and acid mine drainage are important contributors of iron to surface waters in some areas. The so-called waste pickle liquors" are waste solutions of iron sulfates and sulfuric acid which are sometimes disposed of by dumping into streams. The pH of these solutions is very low and the presence of both ferrous and ferric ions in large amounts in solution is possible under these conditions. Mine-drainage waters may contain similar solutions of sulfates and sulfuric acid derived from the oxidation of pyrite (ferrous sulfide) or other sulfides. Some of these wastes find their way into surface streams where the acidity is slowly dissipated as the water moves downstream by reactions between H+ and the dissolved matter in the stream water, carbonate minerals in the stream bed, and particles of sediment. Through oxidation the ferrous iron is converted to ferric hydroxide and is precipitated when a high enough pH has been attained.

Because it may be present in colloidal form and because of the possibilities for contamination, iron generally is not a good constituent on which to base conclusions in the geochemical interpretation of water analyses. Presence of large amounts of iron in ground water which can be definitely attributed to solution underground of ferrous iron, may have some significance in showing the minerals present in the aquifer and suggesting the chemical conditions under which the water existed in the aquifer.

RELATION TO pH

The reactions involved in waters containing ferrous and bicarbonate ions have been discussed and it has been pointed out that these reactions may tend to lower the pH. This effect is likely to be most noticeable in waters where an appreciable part of the HCO_3 present is removed when the iron is oxidized.

Ferric ions in solution tend to enter into hydrolysis reactions that in effect remove OH^- and lower the pH. A solution containing large amounts of Fe^{+++} and SO_4^{--} would have a pH well below 3. Ferrous ions also may enter into hydrolysis reactions to lower the pH. A water whose pH is controlled by hydrolysis involving iron rather than bicarbonate presents some problems which are discussed further in the section of this report dealing with acidity.

METHODS OF REPORTING IRON CONCENTRATION

For many years there has been disagreement among water chemists as to the best way of reporting iron concentrations. No universally satisfactory procedure has yet been devised. In the older literature, iron values are often expressed in terms of parts per million of oxide or as combined oxides (R_2O_3 where R may represent iron and aluminum). Apparently this form assigned iron to the colloidal state like silica.

In more recent data, iron is generally reported in terms of Fe in parts per million, often further classified in terms of the amount in solution when analyzed and the "total," as already discussed. These analyses usually do not attempt to show what portions may be in the ferrous or ferric states, and usually no attempt is made to show concentrations in terms of equivalents per million. Difficulties and uncertainties surround the reporting of iron in terms of equivalents per million which will not be cleared up until the chemistry of iron in natural waters is better understood. Even then it may be necessary to make some assumptions and reservations regarding the state of oxidation of iron in any specific water.

The presence of ferrous ions is usually postulated for alkaline waters high in total iron like analyses 3 and 9 in table 7. This form of iron is subject to oxidation and precipitation after the sample is collected, as has been described. If the sample stands for a time before analysis, the iron found in solution may drop nearly to zero as in analyses 3 and 9 in table 7. In the process, an amount of bicarbonate equivalent to the precipitated iron can be assumed to have been lost. If the water undergoes no change between the time the iron and the time the bicarbonate is determined, the equivalents per million values for cations and anions should balance, using values for iron in solution at time of analysis in computing this balance. Usually, this

TABLE 7.—*Analyses of waters containing iron*

[Analyses by U. S. Geological Survey. Date under sample number is date of collection]

[Source of data: Nos. 1-3, 5, 6, and 9, unpublished data, U. S. Geol. Survey files; No. 4, Lohr and Love (1954) p. 391; No. 7 U. S. Geol. Survey Water-Supply Paper 1022, p. 21; No. 8, Simpson (1929) p. 298]

	(1)		(2)		(3)		(4)		(5)		(6)		(7)		(8)		(9)	
	May 28, 1952		Mar. 8, 1952		Feb. 27, 1952		Aug. 31, 1951		Mar. 11, 1952		Jan. 30, 1952		Aug. 8, 1944		June 24, 1921		Oct. 26, 1954	
	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm
Silica (SiO_2)	20		12		26		41		9.1	------	8.1	----	21		23		7.9	----
Aluminum (Al)			1.2	-----	1.2	-----							29	3.23	------		.6	----
Iron (Fe) (in solution at time of analysis)	.08	----	1.2	-----	.13	-----			25				15	.81	------		.02	---
Iron (Fe) (total)	2.3	---	2.9	-----	10		8.1		32		.31	-----			4.8	----	11	
Maneanese (Mn)	.00	----					.00	----			.34		10	.36			.32	---
Calcium (Ca)	126	6.29	2.7	.135	8.8	.439	45	2.25	7,470	372.75	264	13.17	119	5.94	136	6.79	8.4	.419
Magnesium (Mg)	43	3.54	2.0	.164	8.4	.691	17	1.40	1,330	109.37	17	1.40	68	5.59	35	2.88	1.5	.123
Sodium (Na)	13	.56	35	1.522	34	1.478	[illegible]	2.74	43,800	1,940.59	52	2.26	17	.74	960	41.74	1.5	.065
Potassium (K)	2.1	.05	1.7	.044	2.9	.074			129	3.30	31	.80					3.6	.092
Bicarbonate (HCO_3)	440	7.21	100	1.639	65	1.065	208	3.41	76	1.25	61	1.00	0	.00	249	4.08	30	.492
Sulfate (SO_4)	139	2.89	5.6	.117	71	1.478	29	.60	47	.98	757	15.76	817	17.01	1,260	26.23	5.9	.123
Chloride (Cl)	8.0	.23	2.0	.056	2.0	.056	83	2.34	83,800	2,363.43	24	.68	22	.62	734	20.70	1.8	.051
Fluoride (F)	.7	.04	.1	.005	.3	.016	.2	.01	0		.8	.04	.1	.01	---		.1	.005
Nitrate (NO_3)	.2	00	.6	.010	.0	000	.6	.01	-------		.0	.00	.4	.01	7.5	.12	.4	.006
Dissolved solids:																		
Calculated	594		113		187	-----	389	----	137,000		1,280	----	1,260		3,280	----	47	
Residue on evaporation	571		101		180	-----	405	----	140,000		1,180				3,450		44	
Hardness as $CaCO_3$	490		15		56		182		24,200		730		845	----	484	----	27	
Noncarbonate	131		0		3		12		24,100	-------	679		845		280	----	2	
Specific conductance (micromhos at 25° C).	885		162	-----	264	-----	638	----	146,000		1,460	-----	1 780				63.8	----
pH	7.6	---	7.4	-----	6.4	-----	6.7	....	7.4	-------	7.5		3.0	-----			6.3	----
Color	1		23	-----	7		23		15	------	2		8	-----			3	
Acidity (total) as H_2SO_4													342					

1. Well 3, Nelson Road Water Works, Columbus, Ohio. Depth 117 ft. Water-bearing formation: Glacial outwash. Temp. 56° F.

2. Well 79:8-50, Public Supply, Memphis, Tenn. Depth 1310 ft. Water-bearing formation: Sand of the Wilcox formation. Temp. 72° F.

3. Well 5:290-1, 6 miles SE of Maryville, Blaunt County, Tenn. Depth 66 ft. Water-bearing formation: Chatanooga shale. Temp. 58° F.

4. Composite from city well filed, Elizabeth City, N. C. Depth 30 to 80 ft. Water-bearing formation: Coastal Plain deposits.

5. Brine produced with oil from well in NW¼ sec. 3, T. 11N. R. 12 E., Okmulgee County, Okla. Depth 2394 ft. Water-bearing formation: Gilcrease sand of local usage, Atoka formation.

6. Drainage at collar, drill hole 89, 7th level Mather A iron mine, Ishpeming, Mich. Temp. 59° F.

7. Shamokin Creek at Weighscale, Pa. Discharge 64.2 cfs affected by drainage from coal mines.

8. Flawing well, Mpls. St. Paul and Sault Ste. Marie R. R., Enderlin, Ransom County, N. Dak. Depth 613 ft. Water-bearing formation: Dakota sandstone.

9. City well 3, Fulton, Miss. Depth 210 ft. Water-bearing formation: Sand of the Tuscaloosa formation. Temp. 63° F.

amount of iron is small enough that it will have no effect on the balance, and it is usually ignored and not reported in equivalents per million at all. Small amounts of iron in the colloidal state still may be present, so one cannot be sure that what iron is still in solution is in a form that will affect the cation-anion balance.

For some purposes, a "reconstructed" analysis can be useful to represent more closely the composition of the water in its natural environment. If the sample is known to have included no suspended iron, the "total" iron value can be accepted to represent a measure of the iron originally in solution and reported as equivalents per million of ferrous iron. The cation and anion totals can be brought in balance by adding an amount of bicarbonate equivalent to the iron precipitated.

Waters that are strongly acid are usually more stable with respect to iron than those containing bicarbonate. For these waters, separate determinations of ferrous and ferric iron can be made and the results expressed in ppm and epm with greater confidence.

Analyses in this volume do not report equivalents per million values for iron unless the water is acid, in accordance with standard procedures used in the past. It is possible that these procedures need modification for some waters.

RANGE OF CONCENTRATION

Iron is normally present in fully aerated water of normal (slightly alkaline) pH in amounts of less than 0.50 ppm. Often the amount present in such waters is less than 0.10 ppm. Iron in these waters probably is in the ferric form. In acid waters having a pH of less than about 3.0, on the other hand, ferric iron may be present in amounts exceeding 100 ppm. Such waters are found in some thermal springs and in some surface waters strongly affected by disposal of wastes containing acids and iron. Iron in the ferrous state may occur in ground waters subject to reducing environments. Rarely, concentrations over 50 ppm may occur in waters with a pH of 5 to 8. Concentrations up to 10 ppm are common.

The analyses in table 7 show the chemical character of certain waters which are comparatively high in iron. Extremely high concentrations of iron as well as of manganese and aluminum are associated with very low pH in analysis 7. This water is from a surface stream in Pennsylvania affected by drainage of acid waters from coal mines. Similarly, high concentrations are often observed in low pH water from hot springs (analysis 4, table 11). High values for iron in the brine shown as analysis 5 in table 7 probably are associated with nontypical behavior of iron in such a concentrated solution of other materials. Analysis 6 in this table represents water from an iron mine, but which probably had entered the mine from other water-bearing formations and has not reached extremely high iron concentrations. Analyses 1-4, 8, and 9 represent waters from various sedimentary formations. These 6 waters contain alkalinity reported as bicarbonate and probably tend to precipitate iron from solution in accordance with the oxidation mechanism discussed earlier. The waters represented by analyses 3 and 9 in particular probably contained ferrous iron in their underground environment. As has already been stated, alkaline waters may contain large amounts of ferrous iron.

ACCURACY AND REPRODUCIBILITY OF RESULTS

The laboratory methods for iron are relatively accurate and precise for quantities from 10 to less than 0.10 ppm. However, the uncertainties of sampling where iron contamination is possible, and the changes which samples may undergo after collection, restrict the applicability of data for geochemical interpretation. Large differences of "dissolved" iron from one sample to another which are similar in other constituents, therefore, may not have any real significance.

MANGANESE

In its chemical behavior, and in its occurrence in natural waters, manganese resembles iron. Manganese is, however, much less abundant in rocks than iron. As a result, the concentration of manganese in water generally is much less than that of iron, and manganese determinations are often omitted from the water analysis, or if made, show only a very small quantity present.

SOURCES OF MANGANESE

In igneous rocks, manganese is comparatively rare and is distributed among the various minerals, usually as an impurity, and most frequently replacing part of the iron in the dark-colored silicate minerals such as the mica biotite and the amphibole hornblende (Rankama and Sahama, 1950, p. 645). Minerals containing larger amounts of manganese occur in metamorphic and sedimentary rocks. In the latter types, manganese oxides and hydroxides are concentrated through removal of more soluble minerals, and are found in the oxidates (often associated with oxides of iron) and hydrolyzates (clay minerals) . There also is a tendency for manganese to accumulate in soils as they are formed from rock weathering.

The manganese found in water is probably most often the result of solution of manganese from soils and sediments aided by bacteria or complexing with organic materials. Manganese occurs in sediment carried by streams in some areas. Such sediments deposited in reservoirs may yield manganese to the water in storage. This process is doubtless aided by the organic matter present in the sediments and by bacterial action. Manganese may give difficulty in water-supply reservoirs at certain seasons, owing to this effect. Amounts in excess of about 0.3 ppm of manganese are objectionable in public supplies.

CHEMISTRY OF MANGANESE IN NATURAL WATER

Like iron, manganese occurs in more than one state of oxidation. However, the oxidation states of manganese to be expected in water are the bivalent and the quadrivalent states, Mn++ and Mn++++. Manganese can also occur in more highly oxidized states, but is not normally encountered in those forms in natural water. Under reducing conditions, manganese can be taken into solution in water containing carbon dioxide as manganous bicarbonate in a manner analogous to the solution of ferrous bicarbonate. Manganous carbonate is reported by Haehnel (1924) to be somewhat less soluble in water in equilibrium with carbon dioxide at one atmosphere than is ferrous carbonate under the same conditions. In the quadrivalent form as MnO_2 or Mn (011)4, the manganese is nearly insoluble and probably is carried in colloidal suspension in a manner similar to ferric hydroxide in oxidized alkaline solutions.

An oxidation reaction for maganous bicarbonate analogous to that given for iron in the preceding section is

$$Mn^{++} + 2HCO_{o} + H_2O + \frac{1}{2}O_2 \rightarrow Mn(011)4+2002$$

This reaction requires oxygen from the air. Manganous bicarbonate is reported by Rankama and Sahama (1950, p. 647) to be more stable in waters containing carbon dioxide than is ferrous bicarbonate under similar conditions. This makes it easier to determine manganese concentrations in laboratory samples, although some of the same difficulties are experienced as those with the precipitation of iron when manganese is present in large amounts. The presence of organic materials in water is stated by Rankama and Sahama (1950, p. 647) to stabilize manganous bicarbonate solutions, perhaps owing to formation of complex ions or chelation by organic compounds.

Like iron, "dissolved" and "total" manganese are reported separately in most water analyses. The difference between the two is likely to be less significant for manganese than for iron, but the same problem exists in determining actual conditions in the aquifer on the basis of "dissolved" manganese values. The "total" manganese figures are better for determining these conditions, even though the manganese may be partly in the form of colloidal oxide and hydroxide by the time it is determined.

Manganese concentrations above 1 ppm may result where manganese-bearing minerals are attacked by water under reducing conditions or certain types of bacteria are active. Industrial waste disposal may add manganese to water, especially where iron is added by such wastes.

Manganese concentrations are normally reported in terms of parts per million as Mn. Because of uncertainty regarding extent of dissociation, epm values are not usually reported except for acid waters.

RANGE OF CONCENTRATION

In most natural waters, the amount of manganese is less than 0.20 ppm. Ellis and others (1946) state that the content commonly ranges from 0.05 to 0.22 ppm in natural water. Higher concentrations may be found in ground water and surface waters but do not often exceed 1.0 ppm unless mining or industrial wastes contribute manganese (Calif. SWPCB, 1952, p. 209).

Manganese in amounts greater than 1.0 ppm is reported in analysis 7, table 7 and in analysis 4, table 11. Both waters are strongly acid and high in iron. The alkaline water from the Michigan iron mine, No. 6 in table 7, contained about as much manganese as iron. Normally, manganese concentration is only a fraction of the iron concentration in alkaline waters.

ACCURACY AND REPRODUCIBILITY OF RESULTS

Laboratory procedures for manganese determination in the range below 1.0 ppm are accurate to 0.05 ppm or less, but as in the case of iron, sampling procedure and conditions in the source of the water must be taken into account in the interpretation. Manganese content, especially in surface sources, is likely to vary from time to time.

ALUMINUM

As indicated in table 1, aluminum is second in abundance of the metals both in igneous rock and hydrolyzates (shales and clays) and occurs in important amounts in the other two classes of rocks listed in the table.

SOURCES OF ALUMINUM

Aluminum may substitute for part of the silicon in certain silicate minerals. In general, this substitution is characteristic of the more condensed types of silicate structures. The feldspars, for example, are alumino-silicates of sodium, potassium, calcium, and other metals. The micas and clay minerals also are alumino-silicates.

In the process of weathering of primary minerals, the aluminum is generally left behind in the insoluble residue. In the weathering of feldspar, for example as already described, the clay mineral kaolinite may be produced which remains behind, while some of the silica and sodium (or other cations in the feldspar) are carried off in solution.

Under severe tropical weathering, the kaolinite may be leached of all its silica, leaving behind aluminum hydroxide generally with an admixture of iron oxide or hydroxide (Pirsson and Knopf, 1947, p. 179). Aluminum is therefore to be considered highly resistant to removal by solution during weathering and it remains behind persistently in the process of rock decomposition, to form the clay minerals in soils, and the greater part of shales and similar hydrolyzate sediments.

CHEMISTRY OF ALUMINUM IN NATURAL WATERS

Aluminum is a metal but is amphoteric in behavior. That is, it can appear in solution either as a cation or as part of a complex anion. Aluminum cations in solution in pure water hydrolyze strongly as follows:

$$Al^{+++} + 3H_2O \rightleftharpoons Al(OH)_3 + 3H^+$$

The aluminum hydroxide is very slightly dissociated and nearly insoluble; hence, the pH of a solution containing Al+++ ions is considerably below 7. The normal buffer system in natural waters, based on carbon dioxide, bicarbonates, and carbonates, tends to maintain a pH well above the level that would permit the presence of appreciable amounts of Al+++ in solution. It is only in waters where a pH below 5 is maintained that dissociated aluminum as Al+++ can be present in large amounts.

Aluminum can also form aluminate ions Al_2O_4 -, which hydrolyze in solution in pure water and raise the pH by forming essentially undissociated aluminic acid.

$$Al_2O_4 \quad + 2H_2O \rightleftharpoons H_2Al_2O_4 + 2011$$

The pH of solutions containing aluminates in measurable amounts theoretically would have to exceed 9, which is a level rarely found in natural waters. Hence, there is seldom opportunity for aluminum to be present as an anion in natural water.

Like iron, up to 1 ppm or so of aluminum can be present in colloidal form, probably as hydroxide dispersed in very small particles. It is also possible for small amounts to be present in solution, but not dissociated.

RANGE OF CONCENTRATION

Busch (1927) found aluminum hydroxide to be soluble in pure water to the extent of about 0.5 ppm as Al. Concentrations much over 1 ppm are not common, although in acid waters more than 100 ppm can occur. In such waters, the aluminum may have come from industrial wastes or mine drainage or may have been dissolved from rock materials by acid spring waters such as are found in some hot-spring areas. Data on solubility of aluminum in solutions of other ions are not available. Analysis 7, table 7, shows a high concentration of aluminum in water of low pH, as do analyses 4 in table 11, and 4 and 5 in table 13. No data on aluminum content of waters of high pH are available.

ACCURACY AND REPRODUCIBILITY OF RESULTS

In concentrations below 1 ppm, aluminum can be determined accurately to .1 ppm, and in concentrations up to about 20 ppm to the nearest part per million. However, the possibility of presence of colloids should be considered in evaluating the aluminum concentrations reported. In those waters which are strongly alkaline, there may be a possibility of aluminum being present as an anion. In this state, aluminum would be a contributor to the alkalinity and upon titration would be reported as an equivalent amount of bicarbonate, carbonate, or hydroxide. Inclusion of aluminum as a cation in the report of an analysis of such a water would be erroneous.

CALCIUM

Calcium is one of the alkaline-earth metals, a group in which beryllium, magnesium, strontium, barium, and radium also are usually included. The chemical properties of the members of the group are similar, but calcium is a more abundant constituent of natural water than any of the others, and is also much more abundant in rocks. Magnesium is the only other member of the group that has an importance in rocks and in water comparable to that of calcium. Magnesium is often lumped together with calcium in water analyses, as both contribute to the hardness of water. For the purpose of this report, however, and for interpretation of water analyses for geologic and hydrologic use generally, it often is important to consider calcium and magnesium separately. In some respects, their behavior toward water in the weathering process and their behavior in solution are significantly different.

Calcium is a major constituent of all rock types listed in table 1. The precipitates contain especially large percentages. Limestone is essentially composed of calcium carbonate, with impurities. Calcium is the most abundant cation in many surface and underground waters.

Calcium is normally present in natural waters in dissociated form as the bivalent ion Ca^{++}.

SOURCES OF CALCIUM

Calcium is a component of a number of the important silicate minerals. The plagioclase feldspar anorthite in pure form is calcium aluminum silicate. Usually it contains some sodium aluminum silicate (albite) in solid solution. The other principal complex silicates containing calcium are the pyroxenes and amphiboles. There are a number of simpler calcium silicates such as wollastonite $(CaSiO_3)$, but in general these are of lesser importance.

Nonsilicate minerals of calcium include, among many others, the carbonates, calcite and aragonite; the calcium-magnesium carbonate, dolomite; the sulfates, gypsum and anhydrite; and the fluoride, fluorite. Apatite $(Ca_5(PO_4)_3F, Cl)$ contains calcium, and there are many other calcium-bearing minerals of lesser importance.

Weathering of calcium-bearing silicate minerals such as calcium-bearing feldspars, pyroxenes, and amphiboles may yield soluble calcium that is carried off in solution leaving behind a residue of clay minerals.

The stability of anorthite toward attack by water is lower than that of feldspars not containing calcium (Rankama and Sahama, 1950, p. 194), and therefore the rocks where this type of feldspar occurs can constitute fairly important sources for calcium in water. Much more important sources, however, are the nonsilicate minerals, especially the' carbonates.

In sandstone and other detrital rocks, redeposited calcium carbonate is usually one of the principal constituents of the cementing material holding the rock grains together. Limestone is essentially a massive deposit of calcium carbonate. Calcium is also present in soils as carbonate and in other forms. Its presence adsorbed on clay-mineral particles is of great agricultural importance. Calcium in the form of sulfate minerals (gypsum and anhydrite) is often found in the evaporate sediments, and in some areas such rocks furnish large amounts of calcium to waters leaching them. Calcium sulfate goes into solution without undergoing chemical decomposition.

CHEMISTRY OF CALCIUM IN NATURAL WATER

Because of its widespread occurrence in rocks and soils, and its ready solubility, calcium is present in nearly all waters. High concentrations of calcium and sulfate in a water suggest the possibility of solution of gypsum or anhydrite, and low concentrations of calcium compared to sodium may indicate absence of readily soluble calcium minerals or the action of base exchange whereby calcium originally in the water has been exchanged for sodium.

In the presence of 11+ calcium carbonate is readily soluble in water.

$$CaCO_3+H^+\rightarrow Ca^{++}+HCO_3$$

The dissociation of carbonic acid is an important source of H^+ in most natural waters.

$$H_2CO_3\rightleftharpoons H^+ + HCO_3 \rightleftharpoons H^+ + CO_3^{=}$$

In the system $CO_2 + H_2O$ $CaCO_3$ so long as a sufficient supply of carbon dioxide is available, only the first dissociation step takes place and carbonate ions are not present in solution. Under these conditions calcium carbonate is attacked and calcium and bicarbonate ions are produced. The **11+** produced in the second step of the dissociation is not available for the reaction with calcium carbonate, however. If the pH of the solution reaches a high enough level for the production of CO_3^{--} in appreciable quantity, calcium carbonate will precipitate if its solubility product (about 1 X **10^{-}** **)** is exceeded. In most natural waters the carbon dioxide in the system is the critical factor: if carbon dioxide is being added to the system, solution continues; if it is removed from the system, deposition may occur.

Presence of large amounts of calcium and bicarbonate in solution is possible when a large amount of carbon dioxide is available. Such a solution can exist in stable form when under pressure sufficient to prevent the escape of the carbon dioxide. These conditions can occur in underground aquifers. Probably the amounts of carbon dioxide available for solution in such waters are generally insufficient to saturate them at the pressure involved. However, when such water rises to the water table or to the surface in a spring, it may be supersaturated with carbon dioxide at atmospheric pressure. Gas bubbles are often noticeable in the water of springs, and carbon dioxide will escape from samples of the water that is supersaturated unless special precautions are taken to retain the gas under pressure in the sample bottle by a tight bottle-closure device.

When the carbon dioxide escapes, the equilibrium in the solution is altered and calcium carbonate may precipitate until a point is reached where the carbon dioxide content at atmospheric pressure is in balance with the dissolved calcium bicarbonate. The deposits of travertine at spring openings where waters charged with carbon dioxide and calcium bicarbonate issue, result from this type of deposition. A rise in temperature of the water may also cause losses of carbon dioxide and result in carbonate deposition, and other factors such as evaporation, removal of carbon dioxide by aquatic plants or algae (Goldschmidt, 1954, p. 232) , and aeration also may cause calcium carbonate to precipitate.

Losses of calcium from water samples by precipitation during storage are a frequent occurrence. Usually such losses are readily detected by the presence of carbonate rings or coatings inside sample bottles, and the analyst is thereby warned that a reliable figure for the original calcium and bicarbonate content of the sample will be difficult to obtain.

In some instances where the sample was unstable after collection, there might have been some loss of calcium even before the sample was collected. The accumulation of carbonate deposits on well screens, for example, indicates this type of instability. **Probably the acccumu-**

lation is caused in most instances by head reduction associated with the accelerated movement of water in the immediate vicinity of wells being pumped. The reduction in head may cause some loss of carbon dioxide and deposition of calcium carbonate at the places where water moves into the well, (the head loss is greatest where the water moves most rapidly, generally in the screen openings themselves) and can become a serious problem in waters that are near saturation with calcium bicarbonate.

Surface waters, being in contact with air, are usually stable with respect to carbon dioxide and calcium carbonate. Their storage and handling are therefore usually less critical factors in the results of analysis. Samples from flood flows in streams may be rather high in sediment, however, and changes in the water composition during storage as a result of solution of sediment or deposition of materials in the sediment may occur. Very little is known about the nature and extent of such changes. The high-water marks of surface reservoirs are largely deposits of calcium carbonate. Few data on the extent of deposition of calcium carbonate during water storage are available. Howard (1954) reports that more than 9 million tons of this compound was deposited in Lake Mead from 1935 to 1949.

Analysis 2, table 11, represents ground water discharging into the Little Colorado River near its mouth. When it issues from spring openings, the water is supersaturated with carbon dioxide and Ca $(HCO_3)_2$ at atmospheric pressure and deposits travertine in large amounts when it reaches equilibrium with the air. These deposits occur at spring openings and in the river bed for several miles downstream. The pH of this water is 6.5 even though it has a high titratable alkalinity in terms of bicarbonate, illustrating the effect of large amounts of carbon dioxide in solution.

RANGE OF CONCENTRATION

The literature contains a great deal of data on the solubility of calcium carbonate in water in the presence of carbon dioxide at various pressures. According to Askew (1923), at 23°C freshly boiled distilled water will dissolve 13.4 mg of calcium carbonate per liter. This is equivalent to 5.4 ppm of calcium. These conditions are not attained in nature, as some carbon dioxide invariably is present in natural water.

Figure 9 is based on data compiled by Frear and Johnston (1929) which show the effect of carbon dioxide on the solubility of calcite in the absence of other salts. The solubility is greatly increased at high partial pressures of carbon dioxide. The data are all for a temperature of 25°C. Figure 10 shows the relationship of solubility of $CaCO_3$ to temperature, based on the data compiled by the afore-

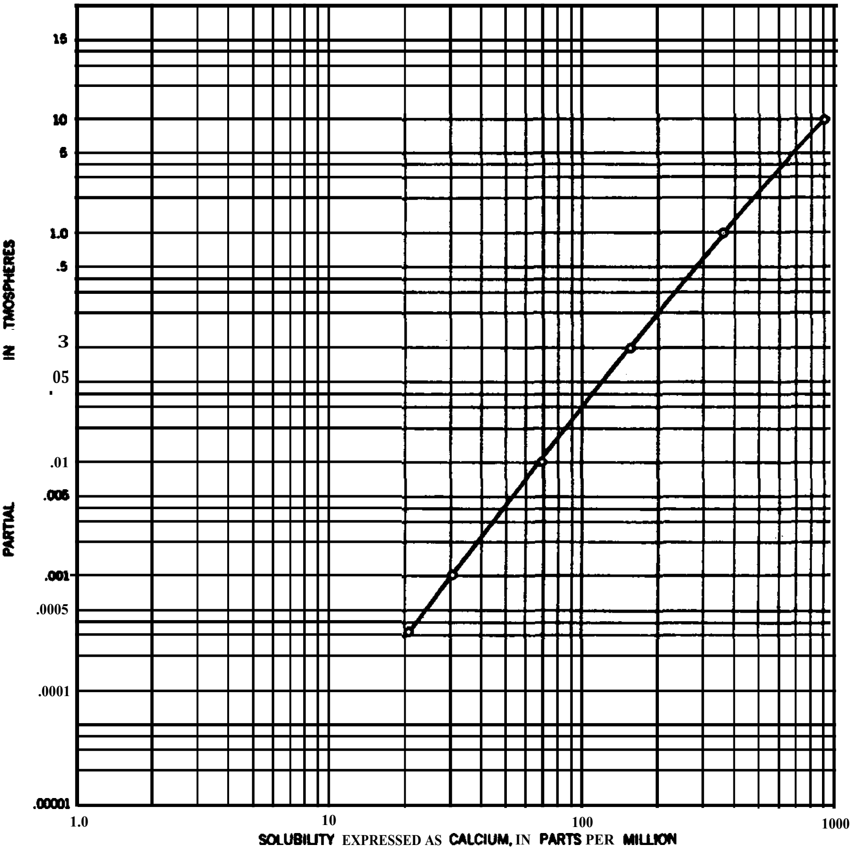


FIGURE 9.—Solubility of calcium carbonate (calcite), in water at 25° C in the presence of carbon dioxide.

named investigators, who state that, within the limits of the error of measurement, this relationship holds for any constant partial pressure of carbon dioxide from 0.0003 to 1 atmosphere.

The partial pressure of carbon dioxide in ordinary air is of the order of 0.0003 atmosphere, assuming 0.03 percent of carbon dioxide in air by volume. It is evident from figure 9 that, with no more carbon dioxide than is obtained from contact with the air, water would be a rather poor solvent for calcite and could contain only about 20 or 30 ppm of calcium at saturation. These data are for water containing no other salts in solution. The presence of sodium and potassium salts in the water increases the solubility of calcium carbonate. In the absence of carbon dioxide, the solubility of calcium carbonate in a solution of 600 ppm sodium chloride was about double the solubility in distilled water (Askew, 1923).

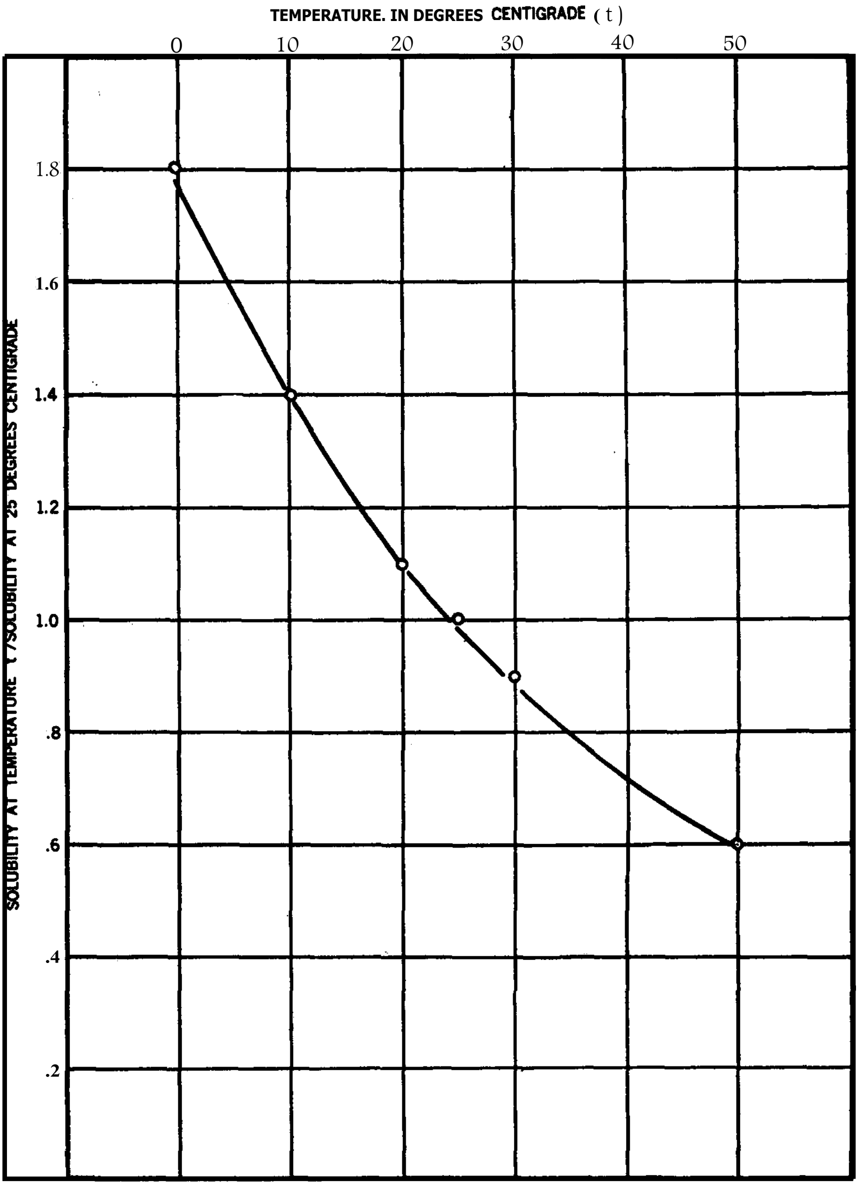


FIGURE 10.—Effect of temperature on solubility of calcium carbonate (calcite) in water in the presence of CO_2.

Water falling to the land surface as rain has an excellent opportunity to dissolve carbon dioxide from the air, and in passing through or over the soil where plants are growing, a considerably larger amount will be dissolved. Plant roots give off carbon dioxide to the air contained in soils above the water table. Decaying vegetation also contributes carbon dioxide to the soil air. Thorne and Peterson (1954, p. 22) state that 2 to 10 liters of carbon dioxide per day may be produced per square meter of soil.

The rate of production of carbon dioxide in the soil suggests that soil air could easily contain from 1 to 5 percent of carbon dioxide. Water in the soil would then *be* capable, according to figure 9, of dissolving from 70 to 110 ppm of calcium from calcite. Saturation often is not attained, however, so that water that has passed through the soil may be an excellent solvent for carbonate rocks.

Waters from limestone may contain more than 160 ppm of calcium. To attain such a high concentration in the absence of other salts, however, the water must theoretically have contained carbon dioxide under a partial pressure of more than 0.1 atmosphere, and thus may lose carbon dioxide and precipitate calcium carbonate when exposed to air. Analysis 2, table 8, is of a high-calcium water from limestone.

The theoretical data presented here with respect to solubilities of calcite are subject to certain limitations. As pointed out by Debye and Hückel, there are forces of attraction and repulsion among the ions in solutions of electrolytes. Water analyses give total concentrations of ions present; however, the amounts of these ions available to participate in chemical reactions like the solution and deposition of calcite are actual concentrations multiplied by activity coefficients. The ionic strength of many natural waters is high enough to make the activity coefficient considerably less than unity.

When considerable numbers of ions are present, as in a water of moderate or high dissolved-solids concentration, the solution of solid material therefore may not proceed in the manner that simplified theory would lead one to expect, and once in solution, the dissolved material may remain there when it should theoretically be precipitated.

Graf and Lamar (1955) have summarized many of the properties of calcium and magnesium carbonates, including solubility and related data, and give an extensive bibliography.

In some areas, calcium sulfate as gypsum or anhydrite is an important source of calcium in ground waters. Surface waters affected in this way occur in some areas of the United States (analysis 8, table 8). Water that has been in contact with gypsum contains large amounts of calcium because gypsum is fairly soluble in water and no carbon dioxide need be present. Data by Hulett and Allen (1902) indicate that water saturated with gypsum can contain about 600 ppm of calcium at ordinary room temperature. Waters approaching this concentration of calcium are common in areas where gypsum is an important rock type (analysis 3, table 8).

Posnjack (1940) made some experiments on solubility of gypsum in sea water. He reported that about 970 ppm of calcium would be

TABLE 8.—Analyses of waters in which calcium is a major constituent

[Analyses by U. S. Geological Survey. Date below sample number is date of collection. Source of data: Nos. 1-2, 4, 6, 9 and 10, unpublished data, U. S. Geol Survey files Nos. 3 and 5, Hendrickson and Jones 1952 ; No. 8, U. S. Geol. Survey Water-Supply Paper 1163, p. 360]

	1 Mar. 28, 1952		2 May 20, 1950		3 Nov. 25, 1949		4 Mar. 26, 1952		5 Jan. 26, 1948		6 June 23, 1949		7 May 19, 1952		8 1948 and 1949		9 June 7, 1954		10 Dec. 8, 1954	
	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm
Silica 8102	8.4		22		29		102				74		4.9	----	17		24		15	
Iron (Fe) dissolved ----	.04						(I)						.04	----			.02	----	[2].01	----
Manganese Mn																	.00	----	.01	----
Calcium (Ca) -------	46	2.295	144	7.19	636	31.74	73,340	3,659.68	99	4.94	277	13.82	25	1.248	394	19.66	88	4.39	96	4.790
Magnesium (Mg) -----	4.2	.345	55	4.52	43	3.54	9,477	779.36	28	2.30	64	5.26	3.9	.321	93	7.65	7.3	.60	19	1.562
Sodium Na	1.5	.065	29	1.24	17	.74	22,070	[illegible]	4.1	.18	53	2.29	4.5	.196	333	14.48	19	.83	18	.783
Potassium K	.8	.020					9,208	235.52					1.4	.036			2.8	.07	1.5	.038
Bicarbonate **(HCO₃)**	146	2.393	622	10.19	143	2.34	0	.00	287	4.70	85	1.39	90	1.475	157	2.57	320	5.24	133	2.180
Sulfate (SOO --------	4.0	.083	60	1.25	1,570	32.69	13	.27	120	2.50	113	2.35	12	.250	1,150	23.94	6.7	.14	208	4.330
Chloride **(Cl)**	3.5	.099	53	1.49	24	.68	200,100	5,643.46	6	.17	605	17.06	2.2	.062	538	15.17	13	.37	25	.705
Fluoride F	.0	000	.4	.02							.2	.01	.1	005			.3	.02	.4	.021
Nitrate (N0) --------	7.3	.118	.3	.00	18	.29	-------		2.8	.05	35	.56	1.9	.031	5.0	.08	4.6	.07	.4	.006
Dissolved solids:																				
Calculated ---------	[5]149		670		2,410	----	[6]320,000		401		1,260	----	100		2,610	----	323		[5]449	
Residue on **evaporation** ------------	139						325,600						99				322		468	
Hardness as **CaCO₃**	132		586		1,760	----			362		954		78		1,370	----	250		318	
Noncarbonate	12		76		1,650	----			127		884		5		1,240	----	0		209	
Specific conductance (micromhos at 25 C)---	250		1,120		2,510	----	[8]		651		2,340	----	172		3,540	----	543		690	
pH ----------------	7.0	----					5.29	------					6.7	----			7.5	----	7.8	----
Color --------------	5												5				2		3	

1. **Big Spring, Huntsville**, Ala. Water-bearing formation: Limestone. Temp. 61° F.
2. Spring on **Havasu** Creek near Grand **Canyon**, Ariz. **Water-bearing** formation: Limestone **in Supai** formation, 100 gpm. Temp. 67° F. Water deposits travertine.
3. Jumping Springs, SE¼ sec. 17, T. 26 S., R. 26 E., Eddy County, N. Mex. Water-bearing formation: Gypsum in Castile **formation**, 5 gpm.
4. Brine well 3 Monroe, SE¼ sec. 27, T. 14 N., R. 2 E., Midland, Mich. Depth 5,150 ft. Water-bearing formation: Sylvania sandstone. Temp. 115 F.+
5. Rattlesnake Spring, sec. 25, T. 24 S., R. 23 E., Eddy County, N. Mex. Water bearing formation: Alluvium, probably fed by Capitan limestone, 2,500 gpm.
6. **Irrigation** well, NE% sec. 35, T. 1 S., R. 6 E., Maricopa County, **Ariz.** Water-bearing formation: Alluvium. Temp. 78° F.
7. **Cumberland** River at **Smithland**, Ky. Discharge 17,100 cfs.
8. Pecos River near **Artesia**, N. Mex. Weighted average, 1949 water year mean discharge 298 cfs.
9. **City** well at Bushton, Rice County, Kans. Depth 99 ft. Water-bearing formation: Dakota sandstone.
10. Industrial well, Williamanset, Mass. Depth 120 ft. Water-bearing formation Chicopee shale. Temp. 54° F.

[1] Total iron 32 ppm.

[2] Total iron 1.0 ppm.

[3] Includes 1.0 ppm aluminum (Al).

[4] Includes strontium (Sr) 2,730 ppm, 62.31 epm, bromide (Br) 2,920 ppm, 36.54 epm, and iodide (I) 38 ppm, 0.30 epm.

[5] Includes .70 ppm lithium (Li) and .03 ppm zinc **(Zn)**.

[6] Density at 115°F, 1.275 **g/ml.**

in solution in normal sea water saturated with gypsum. In sea water diluted to half its normal concentration, about 850 ppm of calcium would be dissolved upon saturation with gypsum. Herman (1955) reports calcium sulfate to be soluble to the extent of about 2,400 ppm of calcium in a saturated solution of sodium chloride.

The 10 analyses in table 8 show the chemical character of different types of water which have calcium as their principal cation. Analysis 1 which represents a spring in limestone at Huntsville, Alabama is a calcium bicarbonate water of low concentration, a type of water commonly associated with calcareous rocks in humid regions. Analysis 7 is for the Cumberland River in Kentucky where fairly rapid leaching of carbonate minerals in rocks and soils is to be expected because of the humid climate. Analysis 2 (spring in Havasu Canyon, Ariz.) is for a water supersaturated with calcium carbonate, and which deposits travertine. Analysis 3 is for a spring water from New Mexico which owes its high concentration of calcium to solution of gypsum, as suggested by the predominance of calcium and sulfate. The water is nearly saturated with gypsum. Analysis 5 also shows the effect of gypsum, but to a much lesser degree, at another spring near Carlsbad Cavern. Analysis 8 is for the Pecos River in an area of New Mexico where gypsum and other evaporates are plentiful.

Analysis 10 represents a water of comparatively low dissolved solids in which calcium and sulfate predominate. This water is from shale in a humid region. Analysis 9 is for a calcium bicarbonate water from a sandstone in Kansas. Analysis 6 represents a well in southern Arizona that is probably affected by the return of residual irrigation water to the ground-water reservoir. It is unusual in that calcium and chloride are the principal constituents. Analysis 4 is for a calcium chloride brine from Michigan. This is probably a modified connate water.

ACCURACY AND REPRODUCIBILITY OF RESULTS

Calcium determinations on duplicate samples should agree within 5 to 10 percent for values below 10 ppm and within 2 to 5 percent for higher values, assuming that gravimetric or volumetric procedures are used.

In earlier years, the hardness of water was frequently determined by the use of standardized soap solutions. Some procedures for the determination of hardness by soap suggested that a point in the titration could be detected which would represent the hardness due to calcium alone. The results of soap hardness titrations were never very satisfactory even for total hardness, and any calcium values so determined are of little value. No determinations of calcium as such were made by the Geological Survey using this method, although the soap method was used widely for determinations of hardness. Titration with ethylenediaminetetraacetic acid has largely replaced the soap method in present-day use.

MAGNESIUM

According to data in table 1, magnesium is seventh in order of abundance of metallic elements in igneous rock. It is also an important component of other types of rock. Magnesium is abundant in the carbonate rocks, where it may occur as dolomite, the double carbonate with calcium, or as magnesite $(MgCO_3)$. All limestones contain some magnesium carbonate, but a rock is not termed a dolomite unless its composition is essentially $CaMg(CO_3)_2$.

As mentioned in the discussion of calcium, magnesium is the other major constituent causing hardness in water. This does not imply that calcium and magnesium components behave similarly toward water in all respects, although the solution of dolomite in water probably tends to give equal numbers of calcium and magnesium ions. Like calcium, magnesium normally is present in ionic form in solution.

Once in solution, magnesium has a stronger tendency to remain in that status than does calcium. This is indicated in a general way by the enrichment of magnesium in sea water where its concentration is second to that of sodium among the metallic ions. (See table 2.) Some of the calcium deficiency in sea water may be the result of extraction of calcium by aquatic organisms. Magnesium also is concentrated to a considerable extent in the evaporate sediments. Magnesium salts are among the last to be deposited in these sediments, for some of the magnesium salts are very soluble.

SOURCES OF MAGNESIUM

Magnesium is typically a component of the important silicate minerals in the dark-colored ferromagnesian and ultrabasic rocks. Among these minerals are olivine, the pyroxenes and amphiboles, the dark-colored micas, and others of less abundance.

A few nonsilicate minerals of magnesium exist of which the carbonate, magnesite, and the double carbonate with calcium, dolomite, are the most abundant. The oxide spinel is a fairly common magnesium mineral.

The magnesium silicates may be altered by water containing carbon dioxide. An example is the serpentinization of forste rite which may proceed—

$$5Mg_2SiO_4 + 4H_2O \quad 4CO_2 \rightarrow$$

(forsterite)

$$2H_4Mg_3Si_2O_9 + 4MgCO_3 + SiO_2$$

(serpentine)

Serpentinization is one type of metasomatism, a class of metamorphism defined as the process of forming new minerals from existing rock minerals through the *agency* of chemically active fluids, of which water is one of the most important.

Ultrabasic rocks are rich in minerals like olivine and are especially subject to the serpentinization reaction mentioned above, and yield silica and magnesium carbonate which may be dissolved in circulating water. Magnesium silicate minerals other than olivine also are similarly attacked, and magnesium can thus be made available for solution.

CHEMISTRY OF MAGNESIUM IN NATURAL WATER

The solubility of magnesium carbonate, like that of calcium carbonate, is increased by the presence of carbon dioxide. In the presence of carbon dioxide, the carbonate is converted to bicarbonate which is more soluble.

$$MgCO_3+CO_2+H_2O \rightleftharpoons Mg(HCO_3)_2$$

This reaction appears to be much less readily reversible and may be considered normally to be displaced farther to the right than the similar reaction for calcium carbonate.

Precipitation of calcium carbonate in water-sample bottles under conditions described in the preceding section often has little or no effect on the magnesium content of the water. Also, the analyses of travertine given by Clarke (1924a, p. 204) show a marked predominance of calcium carbonate. This would indicate a preferential deposition of calcium carbonate when travertine is formed and that part, or most, of the magnesium present is not deposited as carbonate under these conditions. Analysis 5, table 9, is for a pool in Carlsbad Cavern, New Mexico, which is replenished by water dripping from stalactites and other cave formations. The predominance of magnesium over calcium in this water suggests preferential precipitation of calcium carbonate. Water from limestone in this area normally contains much more calcium than magnesium.

In waters whose principal anion is bicarbonate or carbonate, magnesium concentrations may be controlled to some extent by the solubility of magnesium carbonate. In the absence of carbon dioxide, magnesium carbonate is not very soluble, although it is more soluble than calcium carbonate. Leick (1932, 1933) reports a solubility of magnesium carbonate equivalent to 18 ppm of magnesium at 100°C in the absence of carbon dioxide. The literature contains considerable data regarding solubility of magnesium carbonate in the presence of carbon dioxide. Data by Kline (1929) report a solubility of nesquehonite in terms of magnesium of about 190 ppm in equilibrium with carbon dioxide at a partial pressure of 0.0003 atmosphere at

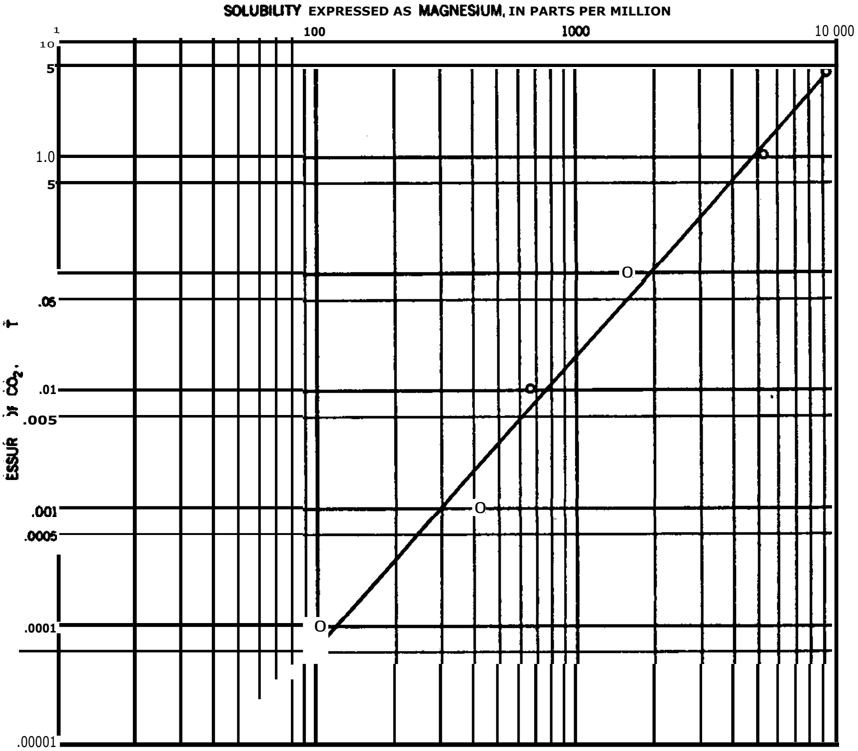


FIGURE 11.—S[illegible] $(MgCO_3 \cdot 3H_2O)$ in [illegible] 25 C [illegible] CO, (Kline, 1929).

25°C. These are conditions that could exist in water exposed to ordinary air.

Solubility over a wide range of carbon dioxide partial pressures is given in figure 11, which is based on Kline's data. A straight line has been drawn through the experimental points as an approximation. The scatter of points represent deposition of different kinds of solid-phase material.

It is evident from figure 11 that magnesium carbonate should remain in solution to a much greater degree than calcium carbonate in water exposed to the air. The graph of calcium concentrations against partial pressures of carbon dioxide (fig. 9) shows a solubility of only about 20 ppm calcium with a partial pressure of carbon dioxide of .0003 atmosphere, although about 190 ppm of magnesium will remain in solution under these conditions. These data help to explain why magnesium does not precipitate from water as readily in the form of carbonate as does calcium.

Magnesium carbonate is more readily dissolved by water containing sodium salts than by pure water. In the absence of carbon dioxide and the presence of about 11,000 ppm of sodium as the chloride at 23°C, the solubility of magnesium carbonate was about 3 times as great as in pure water under these conditions (Cameron and Seidell, 1904). An increase in the solubility of magnesium carbonate also was reported by these investigators in solutions of other sodium salts as compared with pure water.

On the basis of the differences between the solubility of calcium and magnesium carbonates, it would seem there should be a selective solution of magnesium carbonates from dolomite. Actually this does not seem to occur. Dolomite is less readily dissolved than limestone under ordinary weathering conditions (Clarke, 1924a, p. 580), and probably the double carbonate molecules go into solution as units. Waters from dolomite terranes often have about equivalent calcium and magnesium concentration. Analysis 1, table 9, is for water from a spring in the Knox dolomite of Tennessee. Analyses 2 and 9 in this table also may have been influenced by dolomite. The nearly equal concentration of calcium and magnesium in epm in analysis 1 is worthy of note. In a water from the Niagara dolomite, the magnesium is present in considerably larger amount than calcium (analysis 10, table 9) .

CALCIUM-MAGNESIUM RATIO

In most waters of low to moderate dissolved-solids concentration, magnesium content is considerably less than calcium even when computed on the basis of concentrations expressed in equivalents per million. The weight of a magnesium ion is only about three-fifths of that of a calcium ion; hence, equivalent concentrations of the two may appear quite different when expressed on a weight basis. The ratio of calcium-to-magnesium for natural waters computed from equivalents per million commonly ranges from about 5 to 1 to about 1 to 1. High values for the ratio suggest that the water obtained calcium from relatively pure limestone or other calcium carbonate precipitates or that gypsum was available for solution. Low values of the ratio may indicate that magnesium silicate minerals are being dissolved or that dolomitic rocks are being attacked. In some instances, a low value of the ratio may result from sea-water contamination. The ratio of calcium to magnesium for sea water is about 1 to 5. A low value for the ratio may in some instances result from precipitation of calcium carbonate either before or after the collection of the sample.

In general, it would appear from the data in table 1 that calcium is much more abundant than magnesium in sedimentary rocks. Since most waters obtain dissolved matter from such rocks and from soils, the difference in abundance of calcium and magnesium is probably

TABLE 9.—*Analyses of water in which magnesium is a major constituent*

[Analyses by U.S. Geological Survey except as indicated. Date under sample number is date of collection. Source of data: Nos. 1-3, 5-10, unpublished data, U. S. Geol. Survey files; No. 4, Waring (1915) p. 204]

	(1)		(2)		(3)		[1] (4)		(5)		(6)		(7)		(8)		(9)		(10)	
	Feb. 27, 1952		Apr. 11, 1952		Sept. 29, 1948		1900		Apr. 20, 1945		Feb. 7, 1939		May 21, 1952		Mar. 27, 1952		Mar. 11, 1952		Oct. 29, 1954	
	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm
Silica (SiO_2)	8.4	----	18	----	31	----	80	----	11				4.2	----	12		13	----	18	----
Aluminum (Al)	1.4	----													1.0	----			.2	----
Iron (Fe) in solution at time of analysis	.03	----	.04	----					.04	----			.13	----	.02	----	.01	----	03	----
Iron (Fe) total	.24	----	1.4	----			5.6	----							.03	----			.39	----
Calcium (Ca)	40	1.996	94	4.69	20	1.00	26	1.30	16	.80	97	4.84	18	.898	23	1.148	140	6.99	35	1.747
Magnesium (Mg)	22	1.809	40	3.29	42	3.45	614	50.49	71	5.84	38,300	3,149.70	8.5	.699	12	.987	43	3.54	33	2.714
Sodium (Na)	.4	.017	17	.74	19	.83	624	27.13	7.8	.34	43,900	1,908.80	2.5	.109	1.7	.074	21	[illegible]	28	1.218
Potassium (K)	1.2	.031	2.2	.06							2,090	53.50	2.4	.061	1.6	.041			1.3	.033
Carbonate (CO_3)	0	----	0	----	0	----			21	.70	----		0		0	----	0		0	.000
Bicarbonate (HCO_3)	213	3.491	471	7.72	279	4.57	4,090	68.26	320	5.25	1,380	22,60	90	1.475	127	2.081	241	3.95	241	3.950
Sulfate (SO_4)	4.9	.102	49	1.02	22	.46	6.0	.12	21	.44	222,000	4,619,80	9.5	.198	1.6	.033	303	6.31	88	1.832
Chloride (Cl)	2.0	.056	9.0	.25	7	.20	390	1100	8	.23	16,800	474.40	1.5	.042	2.0	.056	38	1.07	1.0	.028
Fluoride (F)	.0	000	.8	.04	.2	.01	----		1.0	.05	----		.0	.000	.0	.000	.8	.04	.9	.047
Nitrate (NO_3)	4.8	.077	2.4	.04	2.5	04	----		19	.31	----		.8	.013	.9	.014	4.1	.07	1.2	.019
Dissolved solids																				
Calculated	190	----	466	----	281	----	3,760	----	333	----	324,000	----	92		119	----	682	----	326	----
Residue on evaporation	180		527	----					321		379,000	----	106		108	----	701	----	329	----
Hardness as $CaCO_3$	190	----	400	----	222	----	2,590	----	332	----			80	----	107	----	526	----	224	----
Noncarbonate	16		13	----	0	----	0	----	34	----			6	----	3	----	329	----	27	----
Specific conductance (micromhos at 25°C)	326	----	764	----	458	----			570		(9		165	----	197	----	997	----	511	----
pa	7.4	----	6.7	----	8.2	----			8.3	----			7.0	----	7.6	----	7.4	----	8.2	----
Color	5		5	----									35		5				10	

1. Spring 2½ miles NW of Jefferson City, Tenn. Flow 5 000 gpm. From Knox dolomite. Temp. 58° F.

2. Well 5, City of Sidney, Ohio. Depth: 231 ft. Water-bearing formation: Niagara group Temp. 53° F.

3. Spring in Buell Park, Navajo Indian Res. Ariz. Water-bearing formation: Olivine tuff breccia, 18 gpm. Temp. 54° F.

4. Main spring at Cooks Springs, Colusa, Calif. Water-bearing formation: Serpentine. Temp. 64° F.

5. Green Lake in Carlsbad Cavern, N. Mex. Pool of ground-water seepage.

6. Test Well 1, SW14 sec. 24, T. 25 S., R. 26 E., Eddy County, N. Mex. Water from 142 to 195 ft.

7. Wisconsin River at Muscoda, Grant County, Wis. Flows through area of magnesian limestone.

8. Spring SW¼ sec. 26, T. 16 S., R. 7 E., Calhoun County. Ala. Supplies city of Anniston, Ala. Flow 46 cfs. Water-bearing formation: Quartzite. Temp. 64° F.

9. Oasis flowing well SW¼ sec. 15, T. 11 S., R. 25 E., Chaves County, N. Mex. Depth 843 ft. Flow over 9,000 gpm when drilled. Water-bearing formation: San Andres (limestone and dolomitic limestone with minor amounts sandstone, gypsum and anhydrite.)

10. Drilled well NW¼ sec. 6, T. 6 N. R. 21 E., Milwaukee County, Wis. Depth, 500 ft. Water-bearing formation: Niagara dolomite. Temp. 50° F.

[1] Analyst R. E. Swain.

Water contains 731 ppm carbon dioxide (CO,).

Contains .01 ppm manganese (Mn) and .9 ppm lithium (Li).

Density 1.345 g/ml.

enough to explain the common preponderance of calcium over-magnesium in waters.

RANGE OF CONCENTRATION

Natural waters have a wide range of concentration of magnesium.. Waters that have been subjected to complete softening by base exchange may contain essentially no calcium or magnesium. Amounts as much as 50 ppm or so of magnesium are common in waters from magnesian or dolomitic limestones. (Analyses 1, 2, 7, 9, and 10, table 9). Concentrations of magnesium more than equivalent to the calcium present are shown by analyses 3, 4, and 10, table 9. Concentrations of several hundred ppm of magnesium are sometimes found in waters which have been in contact with magnesian minerals.

Ocean water is high in magnesium, having more than 1,000 ppm (table 2). High magnesium concentrations in saline water in coastal areas may be indicative of contamination from the ocean.

In closed basins where salts may accumulate and reach very high concentrations, magnesian brines may occur. Analysis 6, table 9, is for a magnesium-sodium brine found near Carlsbad, N. Mex. During the formation of evaporate beds, sodium salts may crystallize out while magnesium remains in solution because of the greater solubility of magnesium sulfate and chloride. Evaporate beds with zones containing a high percentage of magnesium will result.

ACCURACY AND REPRODUCIBILITY OF RESULTS

The presence of large amounts of magnesium in water may tend to interfere with the calcium determination and lead to unreliable results for determinations of both elements unless special procedures are used. The standard methods that have been used to obtain data published by the Geological Survey can be expected to give results which agree on duplicate samples to about 10 percent for values below 10 ppm and to about 5 percent for higher concentrations. Short-cut procedures may give less precision and accuracy.

SODIUM

Sodium is one of the alkali metals. Other important members of this group are lithium, potassium, rubidium, and cesium. Sodium is by far the most important and abundant of the group in natural waters. In igneous rocks sodium is slightly more abundant than potassium but both are important constituents of these rocks. The amounts of sodium in resistates and hydrolyzates is relatively smaller and in carbonate rocks there is ordinarily very little Sodium. Sodium salts are very important in the evaporate sediments.

In general, sodium when leached from the rocks tends to remain in solution. It takes part in no important precipitation reactions like calcium and magnesium, because nearly all sodium compounds are readily soluble. Sodium-bearing waters may under some circumstances participate in base-exchange reactions whereby sodium replaces other cations in clay minerals or other materials. In these base-exchange reactions potassium differs considerably from sodium (p. 90). The two elements therefore should be considered separately in some aspects of interpretation of water analyses.

SOURCES OF SODIUM

According to Clarke (1924b, p. 6), the igneous rocks in general are composed to the extent of about 60 percent of feldspars. The feldspars are alumino-silicates of alkali- or alkaline-earth metals. Albite is the pure sodium feldspar and has the formula $Na\ Al\ Si_3O_8$. Feldspars in rocks seldom are pure compounds and a wide range of partially substituted forms may exist, with various proportions of sodium, potassium, and calcium.

According to Rankama and Sahama (1950, p. 194), albite and anorthite (sodium and calcium feldspar, respectively) are decomposed more easily than potassium feldspar. Upon attack by water containing carbon dioxide, the mineral albite decomposes to give silica, sodium carbonate, and a clay mineral. Undoubtedly this decomposition of feldspar is a major factor influencing the dissolved-solids composition of waters originating in areas where feldspars are a large part of the rock and soil. Feldspathoids—for example, nepheline ($NaAlSiO_4$)—also may be important sources of sodium. Most other silicates containing sodium are comparatively rare.

A few nonsilicate sodium-bearing minerals may occur in igneous rocks, but their importance as sources of sodium in water is usually minor.

In the resistates, the sodium may occur incorporated in unaltered silicate mineral grains, or it could be present as an impurity in the cementing material, or as crystals of readily soluble sodium salts deposited at the same time as, or after, the sediments were laid down. The soluble salts go into solution readily, and any appreciable quantity of them in a rock may impart high sodium concentrations to water passing through the rock. A low percentage of sodium compounds mixed with calcium carbonate cementing the mineral grains would go into solution at a rate comparable to that of the calcium carbonate because the sodium is protected from attack except at surfaces where it is exposed to water.

In the hydrolyzate sediments, some sodium may occur in unaltered silicates and some as salt laid down with the sediments. These sediments may also contain minerals capable of entering into base exchange, and these minerals may be saturated with sodium if they have been exposed to sea water or other highly saline water. Then, calcium or magnesium already in solution in water in contact with the mineral may be exchanged for sodium from the mineral. The exchange does not constitute a source of additional dissolved material but is merely a process which increases the proportion of sodium in the water. A water containing mostly calcium and bicarbonate, for example, could be altered to one containing sodium and bicarbonate. Many clay minerals have a capacity for base exchange. Besides their occurrence in hydrolyzate sediments, minerals capable of base exchange occur in lesser proportions in most other clastic sedimentary rocks and are important constituents of soils.

Carbonate rocks contain minor amounts of sodium as impurities either in the form of unaltered silicates or as evaporate residues. Normally waters associated with carbonate rocks are low in sodium concentration unless there is contamination from beds of evaporates associated with the carbonates.

Evaporates such as halite ($NaCl$) and mirabilite ($Na_2SO_4 \cdot 10H_2O$) are a source of sodium that is readily available for solution in water. High concentrations of sodium will be attained in waters which come in contact with beds of such material. More commonly, the minerals of evaporate sediments are scattered through rocks of other types, especially the finer grained sediments.

Sodium may be added to water in important amounts by discharge of sewage and industrial wastes.

CHEMISTRY OF SODIUM IN NATURAL WATER

In sea water (table 2), sodium is by far the most abundant cation. The high concentration of sodium in the oceans may be considered a demonstration of the tendency of this element to remain in solution in water once it has been dissolved.

The amount of sodium carried in solution by a water, both in terms of absolute quantities and in relation to concentration of other substances in the water, is a characteristic of major importance in the study of water analyses. For example, a water containing very large concentrations of sodium probably has been in contact with evaporate materials. Lesser amounts of sodium and a near or complete absence of calcium and magnesium may be the result of base exchange. Or, waters containing small amounts of dissolved material which consists mainly of sodium, bicarbonate, and silica may represent leaching of certain types of igneous rock.

RELATION TO pH

In those waters in which calcium is the predominant cation, the limited solubility of calcium carbonate tends to minimize the presence of carbonate ions (CO_3 —) in solution and in effect helps keep the pH below 8.2. When the predominant cation is sodium, however, this control over the pH is diminished because sodium carbonate is very soluble.

Soft alkaline waters may have pH values of 9 or more. However, there is usually some carbon dioxide present which gives a buffering effect that tends to lower the pH. Extremely high pH values in sodium-bearing waters may occur in circumstances where there is a lack of carbon dioxide. Such waters may also be obtained by leaching some types of soils in arid or semiarid regions. Sodium ions considered by themselves do not affect the pH directly.

RANGE OF CONCENTRATION

Essentially all waters contain some sodium. In some of the most dilute waters of humid regions where soluble rock minerals are largely leached away, the amount may be only 1 part per million or so. In other waters sodium may be a very minor part of the total dissolved solids. Water from pure limestones may have only 1 or 2 parts per million of sodium in a total dissolved solids of several hundred parts per million. Water from gypsum beds may contain as little as 10 parts per million of sodium in a total dissolved solids of several thousand. Waters from other sources having over 1,000 ppm dissolved solids usually will have more than 50 ppm sodium, however. Concentrations of sodium range widely from the moderate levels usually associated with resistate sediments to very high concentrations sometimes found in connate waters. Sea water contains about 10,000 ppm of sodium. Water found in contact with evaporate beds may be saturated with sodium chloride. Such a saturated salt brine can contain about 100,000 ppm of sodium.

ACCURACY AND REPRODUCIBILITY OF RESULTS

Many water analyses in the literature give a computed value for sodium. Such computed values are based on actual determination of the other constituents of the water believed to be present in important amounts. The difference between the sum of the determined anions in equivalents per million and the determined cations expressed in the same units is then assumed to be equal to the amount of sodium and potassium present. The computed value for sodium plus potassium is then reported in terms of an equivalent amount of sodium.

Although satisfactory for many purposes, such computed values have some basic deficiencies and limitations. Primarily, they contain the algebraic sum of errors in analysis, and errors due to possible omission of important determinations. With careful work such errors can be minimized, but they are never completely eliminated.

TABLE **10.** *Analyses* of water in which sodium is a major constituent

[Analyses by U. S. Geological Survey. Date below sample number is date of collection. Source of data: Nos. 1, 3, 7, 8, unpublished data, U. S. Geol. Survey files; No. 2, Riffenburg 1925 p. 44; No. 4, U. S. Geol. Survey Water-Supply Paper 1162, p. 457; Nov. 5 and 6, U. S. Geol. Survey Water-Supply Paper 1253, p. 205, 214; No. 9, **Griggs** and Hendrickson 1951, p. 1111

	1 June 3, 1952		2 July 24, 1023		3 May 13, 1952		(4) July 2-3, 1949		5 **1951-52**		6 **1951-52**		7 Dec. 8, 1951		8 Jan. **31,** 1938		(9) Oct. 15, 1947	
	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm
Silica **(SiO_2)**	22		13		22		**8.2**		18		**31**		45				13	
Iron (Fe) in solution at time of **analysis**	.03		.40		.00	----	04		.01		.01							
Iron (Fe) total	.20																	
Calcium (Ca)	2.5	.12	5.2	.26	49	2.45	40	2.00	48	2.40	**353**	17.61	496	24.75	597	29.79	30	1.50
Magnesium (Mg)	2.1	.17	1.8	.15	18	1.48	50	4.11	14	1.15	149	12.25	286	**23.52**	2,060	169.41	31	2.55
Sodium **(Na)**	[illegible]	.90	401	17.43	**168**	**7.29**	699	**30.40**	150	6.52	1,220	53.05	9,910	430.93	99,600	**4,331.00**	**279**	**12.**13
Potassium (K)			12	.31			16	.41	5.8	.15	9.8	.25	167	4.27	**3,060**	78.27		
Carbonate (CO_3)	30	1.00	0		0		26	87	0		0		0		**52**	1.73	0	
Bicarbonate **(HCO_3)**	412	**6.75**	964	15.80	202	**3.31**	456	7.47	153	2.51	355	5.82	1,490	24.22	33	.54	445	7.29
Sulfate **(SO_4)**	**3.5**	.07	7.2	.15	44	.92	1,320	27.48	50	**1.04**	1,000	20.82	882	28.36	9,650	200.90	303	**6.**31
Chloride (Cl)	9.5	.27	78	2.20	246	6.94	17	.48	223	6.57	1,980	55.84	15,900	448.43	156,000	4,399.70	80	2.26
Fluoride (F)	1.7	.09			.1	.01	1.0	**.05**	.4	.02	1.9	.10	--------				1.2	.06
Nitrate **(NO_3)**	.6	.01			2.2	.04	1.9	**.03**	2.4	.04	24	.39					17	.27
Boron (B)							**60**		.15		2.4	----	17					
Dissolved solids																		
Calculated	457		994		649		2,400		597		4,940		[1]**28,400**	-----	[2]271,000		973	
Residue on evaporation	452		1,010		651		**2,410**		**611**									
Hardness as **$CaCO_3$**	15		20		196		306		178		1,490		2,410				202	
Noncarbonate	0		0		**31**		0		52		1,200		1,190				0	
Specific conductance micromhos at 25°C	718				1,200		3,140		1,090		**7,620**		41,500		225,000	------	1,510	
pH	8.7	----			7.7	----	8.2						7.1	-----				
Color	1				2													

1. Well at Raleigh-Durham airport, Wake County, N. C. Depth 184 ft. water-bearing formation: Coastal Plain sediments.
2. Well in NE¼ sec. 3, T. 3 **S.,** R. 44 **E.** Rosebud County, Mont. Depth 178 ft. water-bearing formation: Fort Union (sandstone and shale).
3. Irrigation well in SE¼ sec. 3, T. **1** N., R. 5 E., Maricopa County, **Ariz.** Depth 500 ft. water-bearing **formation:** Valley fill. Temp. 69° F.
4. Moreau River at **Bixby,** S. **Dak.,** composite of two daily samples, mean discharge 1.7 cfs. Drains Pierre shale, Fox Hills sandstone, and **Hell** Creek formation.
5. Salt River below Stewart Mountain Dam, **Ariz.** Weighted average 1952 water year, mean discharge 362 cfs.
6. Gila River at Gillespie Dam, **Ariz.** Weighted average 1952 water year, mean discharge 71.1 cfs.
7. Spring entering Salt River at Salt Banks near Chrysotile, **Ariz.** Water-bearing formation: **Quartzite** and diabase. Temp. 70° F.
8. Test well 3 **in** sec. 8, **T. 24 S., R.** 29 E., Eddy County, N. Mex. Depth 292 ft. Brine from Salado and Rustler formations.
9. Well in SW¼ sec. 7, T 17 N., R. **26** E., San Miguel County, N. **Mex.** Depth **50** ft. Water-bearing formation: Shale of **Chinle** formation.

[1] Density 1.019 **g/ml** at 20° C.
[2] **Density** 1.21 g/ml.

Computed values of 10 ppm or more for sodium in two samples of the same water may differ by as much as 10 percent, and differences of this order of magnitude should not be given much weight in making comparisons of data. Calculated values below 10 ppm in waters containing several hundred ppm of dissolved solids may easily be in error by 25 percent. Because analyses containing computed sodium values cannot be checked, the user of the data should remember that the possibility of gross errors exists, and he must accept data of this type largely on the basis of the reputation for accuracy of the laboratory from which they came.

The custom of reporting computed sodium plus potassium values in water analyses has grown up because for many years all the available methods for direct determination of sodium and potassium were tedious, involved and expensive. The omission of these determinations greatly reduced the cost of water analyses. During the late 1940's, however, a simple technique for these determinations was introduced, using the newly developed flame photometer. It is now possible to make these determinations much more easily, and some laboratories have found that the flame-photometry technique can be used to reduce to a considerable extent the dependence upon computed values for Na + K.

Determined values for sodium are accurate to 3 to 5 percent Analyses for which sodium actually is determined generally are more reliable throughout than those which report computed sodium concentrations.

POTASSIUM

According to data in table 1, potassium is slightly less abundant than sodium in igneous rocks but is more abundant than magnesium. These relationships do not hold for relative amounts present in waters, however. Although sodium and potassium are both alkali metals and have a number of chemical traits in common, their behavior in the process of chemical weathering is different. Sodium remains in solution rather persistently when it is leached from the complex silicates of igneous rock minerals. Potassium, on the other hand, is easily recombined with other products of weathering, particularly the clay minerals of hydrolyzate sediments. This tendency is shown by the data in table 1 which indicate that potassium is present in hydrolyzate sediments in larger proportions than in igneous rock.

SOURCES OF POTASSIUM

The most common silicate rock minerals that contain potassium are the potash feldspars orthoclase, microcline, and others which have the chemical composition $KAlSi_3O_8$. Potassium is present also in feldspathoids and certain types of mica.

The potassium-bearing feldspars probably decompose in about the same way, but more slowly, than those containing sodium when they are attacked by water containing carbon dioxide. Micas may give up part of their potassium to solution in the weathering process, although part may be retained in clay minerals (Rankama and Sahama, 1950, p. 431). Although the minerals containing potassium are widespread in the sialic types of igneous rock, according to Goldich (1938) they are among the most resistant to decomposition by weathering. This may be one reason that sodium is normally present in water in larger amounts than potassium.

Potassium in resistate and hydrolyzate sediments is largely in the form of unaltered silicate minerals and clay minerals, respectively. In these forms the potassium is less readily available for solution in water than are the soluble sodium salts that often are found in the clastic sediments. Only in certain kinds of evaporates are large amounts of potassium salts available for direct solution in water. Potassium salts are highly soluble and are among the last to be separated as solutions are evaporated; hence, evaporates that contain much potassium are rather rare. Potassium in precipitate-type rocks probably is present mostly combined in clay-mineral impurities.

CHEMISTRY OF POTASSIUM IN NATURAL WATER

Most natural waters contain much more sodium than potassium, even though amounts of both that would appear to be available for solution are nearly the same (table 1). This disparity is of considerable interest in natural-water chemistry, but the explanation is not particularly difficult. It has already been shown that the sodium in most rocks is in a form that is more easily brought into solution than is the potassium. This fact alone may go a long way toward explaining the low concentration of potassium in many waters.

As soon as the potassium-bearing minerals break down under the influence of weathering, and go into solution, several processes tend to remove potassium selectively and return it to the solid phase. Base exchange or adsorption by clays is one means by which this can be accomplished. Potassium also tends to form micas or micalike minerals in some of the hydrolyzates. In this manner, potassium becomes refixed in new minerals which are resistant to chemical attack. Mason (1952, p. 136-137) states that the conversion of montmorillonite to illite (both clay minerals) is possibly the most important process in removal of potassium from natural waters.

Some writers have placed considerable emphasis on the role of plants in the concentration and transportation of potassium. The element is essential in plant nutrition and will be removed from soil solutions or from exchange media in the soil where plants are growing.

The potassium in the plant structure is returned to the soil, however, when the plant dies, unless the plant is removed. Agricultural soils must be replenished with potassium to remain productive. The effect of plants in the circulation of potassium is strictly cyclic, and with the possible exception of some cultivated areas is neither a source of potassium nor a major cause of reduced concentrations of potassium in water.

Sodium-potassium ratios may sometimes be useful indications of the types of rock environments to which waters have been subject. However, this computation has a rather limited value, owing to the tendency for potassium to be lost from solution by adsorption and other processes.

In analyses where a value for combined alkalies is reported, the potassium present is reported in terms of an equivalent amount of sodium. Because of the widespread use of this procedure, there are not as many data in the literature on potassium concentrations as there are for most of the other principal cations in natural water.

RANGE OF CONCENTRATION

In waters low in dissolved solids, the proportion of potassium to sodium may be nearly 1 to 1. This condition is probably most common in waters associated with sialic igneous rocks. Sodium concentrations much over 5 ppm, however, are usually accompanied by smaller relative amounts of potassium. The concentration of the latter seldom rises over 15 ppm in ordinary surface and ground waters and is usually 10 ppm or less. In brines, however, potassium concentrations of several thousand ppm can occur and some hot springs yield water containing 100 ppm or more. Analyses 7 and 8 in table 10 and analysis 4 in table 8 show rather large absolute concentrations of potassium. These are all strongly saline waters. Analyses 1, 7, and 8 in table 9 represent waters of low concentration where sodium and potassium are nearly equivalent to each other. Analysis 4, table 11 and 1 in table 13 represent hot springs and show rather large relative amounts of potassium.

ACCURACY AND REPRODUCIBILITY OF RESULTS

Potassium concentrations reported in the older analytical data were determined by a gravimetric procedure. At the low concentration of potassium usually found in natural waters, the accuracy of the method left something to be desired. In the older analyses, differences of 1 to 2 or even 3 ppm are to be expected in identical waters in the range below 10 ppm of potassium. Above 10 ppm, accuracy is of the order of 10 percent. Differences of this size should not be given serious weight in the interpretation of water analyses. More modern procedures aid in achieving greater precision in the usual concentration range, and are less time consuming.

ALKALINITY

The property of alkalinity in water is its ability to neutralize acid and is reported by the U. S. Geological Survey in terms of equivalent titratable amounts of bicarbonate, carbonate, or hydroxide ions. In many analyses made by others, alkalinity is reported in terms of equivalent amounts of calcium carbonate. In some analyses, alkalinity values are all reported in terms of equivalent amounts of carbonate, especially when concentrations are reported in terms of percentages of the dry residue. Conversion factors for computing data from one of these forms to another are given in table 3. Although some aspects of alkalinity have already been touched upon, it is important that the user of analytical data understand this property thoroughly; therefore, further consideration is in order.

The term "alkalinity" as used in water analyses is perhaps not in accord with generally accepted chemical terminology. In the discussion of pH, 7.0 was stated to be the neutral point. In water analysis, about 4.5 is the end point for titration of alkalinity. Thus, a water with a pH of 6 could be called "acid" on the basis of the pH, but might still have titratable "alkalinity." This introduces some confusion of terminology, and some water chemists prefer to avoid the general term "alkalinity" and speak of carbonate, bicarbonate and hydroxide instead. The determination of these ions, however, is an acid-base titration and does not. differentiate the ions that enter the reaction. "Alkalinity" has been used in this report as a general term to avoid lumping effects of diverse ions and assuming HCO_3 , CO_3 —, or OH^- to be the only ones present when one cannot be sure this is true.

SOURCES OF ALKALINITY

The anions that may contribute to the alkalinity are those which form acids that are only weakly dissociated in solution, and which thus enter into hydrolysis reactions. Chloride, sulfate, and nitrate ions do not affect the alkalinity. Cations that form weakly dissociated bases take part in hydrolysis reactions which tend to produce acidity rather than alkalinity. The presence of certain organic materials may have a considerable effect upon the alkalinity determination.

In general, because of the relative abundance of carbonate minerals and because carbon dioxide, which enters into equilibria with them in water solution, is readily available, bicarbonate and carbonate are to be expected in most waters. The presence of hydroxide ions in natural water in amounts sufficient to affect the alkalinity determination directly is very rare, unless artificial contamination has occurred.

Hydroxide may occur in water that has been softened by the lime process. Water in contact with fresh concrete may have an excessively high pH and apparent hydroxide alkalinity. The high pH of such water, however, may be due in part to silicates. Concrete may be a source of hydroxide alkalinity in samples from wells that are under construction. Its apparent presence usually can be taken as an indication of contamination and a nonrepresentative sample.

The user of water analyses should remember that under any system of reporting titrated alkalinity that is now in use, all the effects of the anions entering into hydrolysis reactions are lumped together and reported as an equivalent amount of a single substance, or as two more or less postulated ions. Thus, although alkalinity data may suggest the presence of definite amounts of carbonate, bicarbonate, or hydroxide, the ions have not been directly determined as such and the results may include the equivalent of all or part of such other anions as may tend to hydrolize. These ions include silicate, phosphate, borate, and possibly fluoride. Some other ions not ordinarily found in natural water, such as arsenate, aluminate, and certain organic anions which may occur in colored waters, also could increase the alkalinity.

CHEMISTRY OF ALKALINITY DETERMINATION

The alkalinity of water is determined in the laboratory by titration with standard acid to a definite pH. The theoretical background of the determination is as follows:

In the titration, conversion of dissociated carbonate ions (CO_3^{-} —) to undissociated carbonic acid takes place in two steps. In the first step, the carbonate ions in solution each take up one hydrogen and become bicarbonate ions (HCO_3). The hydrogen ions needed are supplied by the acid added in the titration. As the titration proceeds, the amount of unchanged carbonate decreases until the carbonate ions are nearly all changed over. At this point in the titration, a small addition of acid will produce a comparatively large reduction in pH and indicates the essential completion of the first step. This end point is usually considered to be at a pH of 8.2 and can be observed either with a pH-measuring device or an indicator that changes color in this range, such as phenolphthalein. Theoretically, at this pH level, the ratio of HCO_3 ions to CO_3 — ions is more than 100 to 1, as computed from dissociation constants for water and carbonic acid.

In the second step, each of the bicarbonate ions take up one hydrogen to form molecules of undissociated carbonic acid. This requires additional quantities of acid. When nearly all the HCO_3 ions have been taken care of, the addition of a small amount of acid again causes a large decrease in pH. At a pH of 4.5 the ratio of

H_2CO_3 molecules to HCO_3 ions is theoretically more than 100 to 1, and this is chosen as the end point. It can be detected by a pH-measuring device or by a suitable indicator such as methyl orange or methyl red.

In the interpretation of the titration, it is assumed that all alkalinity present in the water was in the forms of HCO_3, CO_3 –, and OH . If no OH^- is present, the acid required to complete step 1 is a measure of the CO_3 – content. The amount required for step 2, when corrected for any HCO_3 produced in the carrying out of step 1, is a measure of the original MCO_3 content. Waters containing OH , require more acid for step 1 than for step 2 and the magnitude of this difference is a measure of OH^- concentration. It is assumed throughout that OH^- and HCO_3 cannot exist in the same solution.

No matter what ions may be involved, if they are titrated stoichiometrically by lowering the pH to 4.5, alkalinity values in epm which give a cation-anion balance are obtained. The stoichiometric relation can be demonstrated theoretically or in actual experiments for the CO_3 HCO_3, CO_2 system which is the principal one in most waters. Silicate in the form SiO_3 – should not be present in waters in measurable amounts unless the pH is at least 11. The $HSiO_3$ form, however, might represent about half the silica present at a pH of 9 and about a tenth of it at pH 8. These theoretical data are based on dissociation constants for silicic acid quoted by Hückel (1950, p. 223), who states that K_1 and K2 for silicic acid are of the order of 10 and 10 respectively. Other authors give values for K_1 generally between 10 and 10^{-1}°. In view of this uncertainty, one can state only that dissociated silica can contribute to titrated alkalinity between pH values of 8 and 9, but the magnitude of the effect in this range is uncertain. Silicate ions in either of the above forms would be fully titrated in the regular alkalinity determinations. They would then be reported in terms of equivalent quantities of bicarbonate or carbonate. Other types of silicate ions also might affect the alkalinity.

Orthophosphate may occur in water in three forms, PO_4^{---}, HPO_4 –, and H_2PO_4 . The trivalent form is present in appreciable amounts only above a pH of 10. The HPO_4 – ion predominates from a pH of 7 to a pH of 2 (Calif. SWPCB, 1952, p. 324). The phosphate ions are not fully converted to orthophosphoric acid even at a pH of 1, but practically all the HPO_4 – ions would be converted to $H2PO4^-$ ions in an alkalinity titration stopped at a pH of 4.5. Waters that contain enough phosphate to affect the alkalinity appreciably are rare in nature. If such a water were titrated for alkalinity in the usual way, a part of the phosphate (about a third) would appear as an equivalent amount of bicarbonate or carbonate.

Borate ions also hydrolyze in water to affect the pH. Theoretically, these ions should all be converted to boric acid in the regular alkalinity titration. The form of such ions in solution in natural waters is not certain, however, and the effect of borates on alkalinity titration is difficult to evaluate fully. Waters are seldom found in which measurable alkalinity is contributed by borate ions because boron concentrations in water are normally very low. Borate in the dihydrogen form (H_2BO_3 is theoretically possible in the ratio of 1 part to about 17 parts of the undissociated acid at a pH of 8. At a pH of 7 and lower, dissociated ions are essentially absent.

Fluoride ions hydrolyze, but weakly, and probably they are rarely present in large enough amounts to affect the alkalinity.

The values given for dissociation constants in the literature hold for dilute solutions of single salts. Natural waters are not so simple, and exact conformance with theoretical behavior, therefore, is not to be expected. The computations, however, do give useful indications of the behavior of various ions that can take part in hydrolysis and contribute to alkalinity.

TABLE 11.—Analyses of *waters* having various alkalinity-acidity-pH relationships

[**Analyses** by U. S. Geological Survey Date under sample number **is** date of collection. Source of data: Nos. 1, 2 and 4 unpublished data, U. S. Geol. Survey; No. 3 U. S. Geol. Survey Circ. 235

	1 Sept. 9, 1954		2 June 14, 1950		3 December 1935		4 Aug. 31, 1949	
	ppm	epm	ppm	epm	ppm	epm	ppm	epm
Silica (SiO_2) -------	75		19				216	
Aluminum (Al) ----							56	6.23
Iron (Fe) **dissolved**-- -	.05		.01				33	L77
Manganese Mn	.08	-------				-	3.3	.12
Calcium (Ca)_	1.3	.065	264	13.17	0	[illegible]	185	9.23
Magnesium (Mg)-----	.3	.025	79	6.50	20	[illegible]	52	4.28
Sodium Na	72	3.131	513	22.31	21,700	943.6	6.7	.29
Potassium (K)	2.4	.061	23	.59	150	3.8	24	.61
Carbonate COs	38	1.266	0		17,000	566.5	0	
Bicarbonate (HCO_3)--	20	.328	964	15.80	4870	79.8	0	
Sulfate (SO_4)	32	.666	147	3.06	750	15.6	1,570	32.69
Chloride (Cl)	6.5	.183	815	22.99	10,100	284.8	3.5	.10
Fluoride F	16	.842	.2	.01	------		1.1	.06
Nitrate (NO,) ------	0	.0	3.2	.05			.0	.00
Dissolved solids:								
Calculated -------	254		2,340		52,100			
Residue on evaporation ----------	239							
Hardness as $CaCO_3$-	4		984		82			
Noncarbonate	0		194		0			
Specific conductance micromhos at 25°C -	328		3,940				4,570	-----
pH -------------	9.4	-------	6.5	-------			1.9	-----
Color -----------								
Acidity as H2SO4 (total) ----------							913	

L. Spring **NW¼** sec. 36, T. 11 N. ,R. 13 E. Custer County, Idaho. **Water-bearing** formation: Quartz monzonite. Temp. 135° F.

2. Spring discharging into Little Colorado River, 13 miles above mouth, Coconino **County,** Ariz. One of a group known as Blue Springs. Water-bearing formation: Redwall limestone. Water contains CO_2 and deposits travertine. Temp. 69° F. Discharge of group 200 cfs.

3. Brine well MFS 1 NW ¼ sec. 26, T. 18 N., R. 107 W., Sweetwater County, Wyo. Depth 439 ft **Water-bearing** formation: Evaporates.

4. Lemonade Spring, Sulfur Springs, Sandoval County, N. Mex. Water-bearing formation: **Volcanic** rocks. Temp. 150° F. Fumaroles emit H_2S and SO_2 in vicinity.

Analysis 1 in table 11 has a high proportion of alkalinity reported as carbonate. The high silica concentration of this water suggests the possibility of silicate ions contributing to the alkalinity. Analysis 1 in table 6 is similar. High alkalinity reported as bicarbonate in relation to other anions in waters whose principal cation is sodium are illustrated in analyses 1 and 2 in table 10. High values for bicarbonate concentration in the presence of much calcium are indicated in analyses 2 in table 8 and 2 in table 11. Bicarbonate in a magnesian water is illustrated by analysis 4, table 9. All these are ground waters.

RELATION TO pH

The alkalinity of a water is determined by titration to a prescribed pH as described in the foregoing section. Many users of chemical analyses are confused by the distinction between pH value and titratable alkalinity, especially because the titration for alkalinity is carried to a pH of 4.5, whereas at the same time a pH 7 is stated to be the neutral point.

If all the hydrolysis in a water is assumed to be due to the system $CO_3\ -\ {}^{H+}\ HCO_3\ {}^{H\ +}\ H_2CO_3$, the pH provides a means of deciding how far to the left the reaction is displaced. A pH below 8.2 indicates the absence of the normal carbonate phase and a pH below 4.5 indicates the absence of both the normal carbonate and bicarbonate phases, but otherwise the pH is only qualitative. By titration of the system with acid, a quantitative determination of the amount of each phase can be made, if the original assumption as to the ions present is correct. In order to complete this determination, the equilibrium must be shifted all the way to the right and the pH lowered to 4.5. In pure water at neutrality the pH is 7, but this represents an absence of ions that would take part in hydrolysis and is an entirely different condition.

RANGE OF CONCENTRATION

Alkalinity reported as hydroxide is ordinarily absent from uncontaminated natural water. Alkalinities reported as carbonate are common, particularly in waters that have a large amount of sodium in proportion to calcium and magnesium. This type of water generally occurs as ground water or as surface water concentrated by evaporation, rather than normal stream water. The usual stream water has no apparent carbonate alkalinity and in theory should have a pH below 8.2 if it contained an appreciable amount of calcium. However, some surface waters do have a pH greater than 8.2, either from CO_3 - or as a result of silicates or other anions in solution.

As a rule, alkalinity reported as carbonate is present in small amounts, generally less than 10 ppm. In waters high in sodium, higher values are sometimes encountered, but concentrations over 50 ppm are extremely unusual.

In acid waters there is, of course, no bicarbonate alkalinity. In alkaline waters, which for the purpose of this determination include all those whose pH is 4.5 or over, the range in alkalinity reported as bicarbonate is from zero up to more than 1,000 ppm. Concentrations much higher than 500 ppm, however, are unusual. In the ordinary calcium bicarbonate water having about 500 ppm of dissolved solids consisting mostly of these two ions, the bicarbonate concentration might be as high as 480 ppm. (The bicarbonate is converted to a lesser weight, specifically, 0.4917 of carbonate in determining dissolved solids.) Waters of limestone terranes do not commonly exceed this bicarbonate level unless much carbon dioxide is present. Waters highly charged with carbon dioxide may contain large amounts of alkalinity as bicarbonate. The reduction of sulfate to sulfide with the assistance of certain types of bacteria produces carbon dioxide as a by-product. This reaction will be discussed later in this report. It has probably affected analysis 2, table 10, and may cause high bicarbonate concentrations in waters associated with petroleum.

ACCURACY AND REPRODUCIBILITY OF RESULTS

It is evident from what has been said in the foregoing sections that for some waters, at least, the alkalinity data are largely empirical. The relative amounts of the different forms of alkalinity reported by analyses should not always be considered significant, as changes can easily occur from the time the sample is collected until the bottle is opened, and the alkalinity titration is made. The total alkalinity of a sample should be a reproducible figure, provided that similar conditions of sample treatment are followed. Agreement much closer than 2 to 5 percent, however, cannot be expected on duplicate samples, and differences this size should not be considered significant in making interpretations.

ACIDITY

As a corollary to the property of alkalinity just discussed, there is the opposite property of acidity which is found in some natural waters. In the discussion of pH, it was stated that a pH of 7 is considered a neutral point, but since bicarbonate ions theoretically can remain in solution down to a pH of 4.5, it is necessary to carry the titration for bicarbonate alkalinity down to that pH. If the usual "alkalinity" end-point is used, a water would not be reported as having acidity unless its pH is below 4.5.

This use of the terms acidity and alkalinity is widespread in the literature of water analysis and is a cause of confusion to those who are more accustomed to seeing a pH of 7.0 used as a neutral point. Unfortunately, there is no easy solution to the problem.

SOURCES OF ACIDITY OF NATURAL WATER

Free acids such as HCl or gases like SO_2 combine with water to form acid. Certain hot springs yield strongly acid water that has dissolved these substances. Free acids may also be added to streams or ground waters through waste disposal, or through oxidation of sulfides. The latter source is an important one in mining districts. Drainage from mines in areas where pyrite or other metallic sulfides occur in the ore, or in associated strata, may be strongly acid, containing not only free sulfuric acid but also iron and aluminum. This effect is especially noticeable in coal mining areas.

The oxidation of pyrite in air may be aided by some types of bacteria and can be written:

$$FeS_2 + H_2O + 7\,O \rightarrow FeSO_4 + H_2SO_4$$

The ferrous sulfate may be further oxidized to ferric sulfate which in solution gives:

$$Fe_2(SO_4)_3 \rightarrow 2Fe^{+++} + 3SO_4^{\prime}$$
$$Fe^{+++} + 3H_2O \quad Fe(OH)_3 + 3H^+$$

The hydroxide ions thus are removed from solution and the water becomes more acid through the process of hydrolysis. Aluminum cations in water also hydrolyze to give an acid reaction. These reactions have been discussed in the sections on iron and aluminum. A considerable oxygen supply is required for oxidation of pyrite, and ordinarily it would not take place very far below the water table, or in other situations where oxygen is deficient. Ferrous and ferric salts are added to surface streams in some types of industrial wastes.

Ammonium ions occasionally occur in natural waters. These ions are capable of hydrolysis, contributing to the acidity of samples. A buffer system involving ammonia gas and ammonium salts is theoretically possible in such waters, which in some instances might exert a control over pH somewhat analogous to the $CO_2—CO_3^{-}—HCO_3$ system in alkaline waters. The NH_4^+ ammonia system would probably be difficult to evaluate by titration but fortunately waters containing this system are rare in nature (analysis 2, table 13).

CHEMISTRY OF ACIDITY DETERMINATION

In those waters which have a pH below 4.5, the presence of acidity is reported. The acidity may be the result of actual free acids such as sulfuric or hydrochloric in solution. It can also be the result of the hydrolysis of certain cations in solution, just as certain anions are responsible for alkalinity. Normally the acidity in natural waters or those polluted by industrial or mine wastes is due in considerable part to hydrolysis involving iron. If the parallel between alkalinity and acidity determinations were exact, one might evaluate acidity in terms of iron and so report it, as is done for bicarbonate. However, the factors causing acidity are too complex to be dismissed so simply, and there is already a suitable direct procedure for iron determinations that is reliable and simple. Some sort of evaluation is required for the conditions existing in acid waters, however, and various means of accomplishing this evaluation have been used.

The so called free-mineral-acid determination is usually accomplished by titration with standard alkali to a pH of about 4.5 in the cold solution. An approximation of acidity can be obtained also by means of a calculation based on the pH. These two procedures give meaningful results only in the absence or near absence of iron and any other cations that might cause hydrolysis.

Total acidity generally has been determined by titration to the phenolphthalein end point (pH 8.2) at the boiling temperature. This supposedly gives the net effect of hydrolysis as well as the free-acid content. Actually the end point is somewhat arbitrary and may not be stoichiometric for all forms of iron or other cations involved in hydrolysis.

The Geological Survey (1958) has adopted some modifications in the acidity determination under which a practical evaluation can be made by titration with standard base to an end point pH of 7.0. This method is not intended to give a stoichiometric evaluation of substances involved in hydrolysis but the end point may sometimes be a more logical one to use as neutrality, so far as the user of the data is concerned.

None of these titrations can be depended upon to give meaningful results for all waters. When no free acid is present and no titratable alkalinity is present, cation-anion balance should be obtainable by reporting epm of iron in the ferrous and ferric states, as separately determined, and for other substances taking part in hydrolysis, especially aluminum and manganese. No method for accurate determination of free acid in the presence of salts which hydrolyze to lower pH has yet been described, and lack of cation-anion balance is to be expected in waters where these conditions exist.

Free acidity is commonly expressed in terms of units of H^+ ions. Total acidity is commonly expressed in terms of an equivalent amount of sulfuric acid.

RANGE OF CONCENTRATION

Acidity can range from zero at the pH level that is taken as neutrality to several hundred parts per million as H_2SO_4 for pH levels around 2.5. Springs and waters strongly affected by mine drainage or industrial wastes may at times have lower pH values. The total acidity reported in terms of equivalent $H2SO_4$ has some significance in terms of treatment needed to remove acidity but is of less value in the representation of actual conditions in the water than reporting of alkalinity as carbonate and bicarbonate is for alkaline water.

Analysis 7, table 7, is a water that is acid because of drainage from coal mines. Analysis 4, table 11, is for an acid hot spring, as is analysis 3 in table 13. Analyses 4 and 5 in table 13 represent mine waters and contain large amounts of heavy metals.

REPRODUCIBILITY OF ACIDITY DATA

Because of the uncertainty regarding chemistry of acid waters, and their tendency to change in storage, the data on acidity should be interpreted cautiously.

SULFATE

Sulfur occurs in water largely in the completely oxidized form (S^{6+}) as sulfate (SO_4^{--}). Under some conditions, sulfur may be present as sulfide (S^{--}) as in the form of dissolved hydrogen sulfide, but other reduced forms are of minor importance. Surface waters subject to thorough oxidation are normally free from sulfide.

SOURCES OF SULFATE IN NATURAL WATER

In igneous rocks, sulfur is not usually a major constituent. The most common sulfur minerals are sulfides of heavy metals. Concentrations of these sulfides may constitute ores of economic importance. These minerals are in part oxidized in the weathering process to give soluble sulfates which are carried off in water. Sulfate is a component of certain igneous minerals of the feldspathoid group. Resistates and hydrolyzates may contain some unaltered sulfide minerals. Some shales contain considerable amounts of ferrous sulfide. The most extensive occurrences of sulfate minerals are in the evaporates where calcium sulfate in the form of gypsum and anhydrite is often abundant. Sulfate can accumulate in water to a rather high concentration because the cations taken into solution from rocks generally do not form insoluble compounds with sulfate.

CHEMISTRY OF SULFATE IN NATURAL WATER

Sulfates of most of the common metallic elements are readily soluble in water. The sulfate ion, once formed, is chemically stable in most of the environments to which natural waters are subjected. These two facts are of basic importance in governing the behavior of sulfate ions in water.

A variety of natural processes are involved in bringing sulfate into solution in natural water. Riffenburg (1925) reported that rainwater collected at Washington, D. C., contained 1 to 17 ppm of sulfate, and the data of the U. S. Weather Bureau quoted by Rankama and Sahama (1950, p. 313) indicate that considerably higher concentrations have been observed at times in rainfall at Mount Vernon, Iowa. Gorham (1955) has reported on the sulfate content of rain in the English Lake District, where he found from 1.1 to 9.6 ppm of sulfate in the rainfall over a period of 6 months.

The sulfate in precipitation in rural areas probably is largely dissolved from dust in the air which forms condensation nuclei for moisture, or which is washed down with the rain. Rainfall in arid regions or where soils are gypsiferous would be expected to contain considerable amounts of sulfate at times as a result of airborne dust. The activities of man may provide important sources of sulfate in rain waters. The combustion of coal and many industrial processes add sulfur dioxide and sulfur trioxide to the air, which may be dissolved in rainfall and brought down to the earth as a weak solution of sulfurous and sulfuric acids. The former is readily oxidized in air to sulfuric acid. Sulfur dioxide and sulfur trioxide may also be emitted from fumaroles and volcanoes and become sources of sulfate. Another source is the oxidation of hydrogen sulfide released to the atmosphere by decay of organic matter.

The total quantity of sulfate circulated in rainfall is undoubtedly large, even though concentrations are low. However, the other mechanisms which bring sulfates into solution are more important in most areas. In the upper oxidized layers of soil and rock, sulfides have largely been converted to sulfates and are gradually leached away by water. The rate at which the soluble sulfates are removed is largely dependent upon the water supply. In humid regions, the upper layers of soil and rock are kept thoroughly leached, and as fast as they are formed the soluble products are removed in the drainage water from the area in a dilute solution, because the amount of water is large in proportion to the available supply of soluble salts.

In semiarid regions, on the other hand, the soils are not fully leached and soluble salts produced by weathering may tend to accumulate in the soils. The amount of drainage water that leaves such areas is a small proportion of the total water supply from rainfall. Because of these factors, the supply of available soluble salt is large in proportion to the water volume in which it can be carried away, and as a result, surface and ground waters in some semiarid regions may be comparatively high in dissolved salts.

The above effect is often cited by writers seeking to explain high dissolved-solids concentrations in waters of the western United States. It is important, of course, in a general way, but is best applied to regions where the soil was derived from sedimentary rock that had a fairly large supply of soluble matter. The water of arid regions where soils are derived from igneous rock may be of very good quality.

Although low rates of runoff affect other constituents besides sulfate, this is the anion most commonly affected. Many surface and ground waters in regions of sparse runoff appear to show this effect—for example, analysis 4 in table 10 and analyses in the literature for other streams of the west, especially tributaries of the Missouri.

When an area of low rainfall is reclaimed for agriculture by construction of an irrigation project, the increased water supply has an immediate effect on the soil. Soluble matter which may have accumulated is leached out and appears in the drainage water leaving the irrigated area. This process is merely an acceleration of natural leaching processes, and will increase dissolved-solids concentrations and loads in the drainage return or residual water in the affected area at least temporarily. Sulfate concentrations will be involved in the general increase in relation to the extent to which the soluble matter in the soil consists of sulfates.

Continued irrigation tends to increase dissolved solids concentrations in residual waters in accordance with mechanisms that will be discussed later. Sulfate and chloride are the anions that are most strongly affected.

Gypsum and anhydrite are important components of many evaporate rock formations and are present in small amounts in a great many resistate and hydrolyzate rocks. Because of their relatively high solubility, these minerals are an important source of sulfate in water, even though in an individual formation they may be present only as a minor constituent. Analysis 3 in table 8 represents a calcium sulfate water associated with gypsum.

The fine-grained sediments may provide very poor opportunity for ground-water circulation, but over a large area of contact they may yield enough highly mineralized seepage to provide a considerable addition of sulfate to water in adjacent coarse-grained aquifers. The sulfate in water represented by analysis 8, table 7, may be partly derived from such a source. Extensively eroded terranes of fine-grained sediments, such as the badlands of certain areas in the western United States, provide a source of soluble matter that is constantly renewed as the insoluble detritus is mechanically removed by water running off the exposed rock surfaces, and fresh surfaces containing soluble material mixed with the insoluble components are exposed for future solution. Such a source is at least partly responsible for sulfate in water of the Moreau River represented by analysis 4, table 10, and water of the Rio Grande at times as shown in table 17. Salts also are brought to the surface of such beds through capillary action and surface evaporation (Colby, Hembree, and Jochens, 1953, p. 12).

Evaporate beds containing the more readily soluble sodium, potassium, and magnesium sulfates may provide a source for extremely high sulfate concentration in water. Analyses 6 in table 9 and 8 in table 10 illustrate waters of this type.

Sulfur is involved in the life processes of animals. These may add sulfate to water indirectly, or remove it rather directly through sulfate reduction. The latter process, in which hydrogen sulfide is usually produced, is promoted by bacteria and carbon or hydrocarbons.

$$CaSO_4+CH_4\rightarrow CaS+CO_2+2H_2O$$

$$CaS+2CO_2+2H_2O\rightarrow H_2S+Ca(HCO_3)_2$$

The presence of hydrogen sulfide and high bicarbonate concentration is a feature of some ground waters. Analysis 2, table 10 represents a water that probably was subject to sulfate reduction.

RANGE OF CONCENTRATION

Waters that contain barium in solution can have little sulfate, because barium sulfate is soluble to the extent of less than 2 ppm of sulfate. However, waters that contain barium are rather rare. Waters containing strontium, which probably are fairly common, can theoretically have about 60 ppm of sulfate (Kohlrausch, 1908) at saturation with respect to Sr SO_4. These data are for pure water, and strontium sulfate is somewhat more soluble in solutions containing other anions and cations (Gallo, 1935). Analysis 4, table 8, is for a strontium-bearing brine from Michigan, which has only 13 ppm of sulfate.

Calcium sulfate will dissolve in pure water to give, at saturation at ordinary room temperature, about 1,500 ppm of sulfate (Hulett and Allen, 1902). According to Herman (1955), in a saturated solution of sodium chloride gypsum is soluble to the extent of 5,800 ppm of SO_4. Magnesium sulfate and sodium sulfate are very soluble and waters containing large amounts of these components with little or no calcium may have sulfate concentrations in excess of 100,000 ppm. At the extreme, as much as 200,000 ppm may occur in certain types of brine, such as the magnesium brine represented by analysis 6, table 9.

ACCURACY AND REPRODUCIBILITY OF RESULTS

For the most part, sulfate values can be considered as accurate and precise as any determination in routine water analysis. In interpretation, differences of 5 percent or less in values over 100 ppm should not be given much weight. Results should be reproducible to ±2 ppm from 10 to 100 ppm and to 1 ppm or less in lower concentrations.

CHLORIDE

The element chlorine is a member of the halogen group of the elements. The other important members of this group are fluorine, bromine, and iodine. Chlorine, however, is by a wide margin the most important and widely distributed member of the group in natural waters. In dilute solutions it is present as dissociated chloride ions, but in concentrated brines, interionic effects and incomplete dissociation are to be expected.

SOURCES OF CHLORIDE

According to data in table 1, chloride is present in igneous rocks in somewhat smaller quantities than are the other major components of natural waters. Among the chloride-bearing igneous rock minerals are the feldspathoid sodalite, $Na_8[Cl_2(AlSiO_4)_6]$ and the phosphate mineral apatite. Shand (1952, p. 34) quotes data indicating that residual water contained in pores of granite or included within crystals in the rock may contain chloride. Available data on igneous rock composition may not dependably indicate the importance of such chloride. Kuroda and Sandell (1953) suggest that chloride replaces OH^- in biotite and hornblende and may be in solution in glassy rocks.

On the whole, however, igneous rocks at present appear to be a minor source for the chloride of natural waters. Much more important sources are associated with the sedimentary rocks, especially the evaporates. Chloride may be present in resistates as the result of inclusion of connate water, and is to be expected in any incompletely leached deposit laid down under the sea or in a closed basin where chloride was present. When porous rocks are submerged by the sea at any time after their formation, they are impregnated with soluble salts.

Chloride occurs in great abundance in the water of the ocean, where it is the predominant anion. Both in concentration and total volume, oceanic chloride is a large factor in chloride geochemistry.

Chloride is present in all natural waters, although in many areas the amounts are small. In most surface streams chloride is present in amounts considerably lower than sulfate or bicarbonate. Exceptions may occur where streams receive inflows of high-chloride ground water or industrial waste, or are affected by oceanic tides.

Chloride is present in rainwater in concentrations reported by investigators as 3.0 ppm on the average; (Riffenburg, 1925, based on data from several earlier investigations as well as his own) , 4.18 ppm in the Netherlands (Israel, 1934) ; 1.0 to 8.4 ppm in Victoria, Australia (Anderson, 1945) ; and less than 0.3 ppm (Collins and Williams, 1933) on the average over the United States. The latter investigators suggested that air contamination near cities and chloride blown inland from the sea in coastal regions are responsible for the higher values published in the literature and that such high values are not representative of conditions in inland rural areas. The chloride concentration of many natural waters in coastal areas, however, is doubtless considerably influenced by solid matter carried inland in the air from the seacoast and brought down in precipitation. Eriksson (1952) has published a summary of rainfall composition data from many areas.

Although igneous rocks, as indicated above, are generally low in chloride, volcanic gases and the water of many hot springs contain large amounts of chloride. Such magmatic sources of chloride are very important in their influence on the chloride content of waters of certain streams in the western United States. The Gila River system in Arizona has salt springs along the main stream and along the Salt River which yield more than 450 tons per day of sodium chloride (Feth, 1953). Analyses of some of these waters are given in table 11. No doubt, there are many more occurrences of this type throughout the world. In the Arizona case cited, it is uncertain what proportion of the chloride may be of magmatic origin, but there is little indication of any evaporate as a source for the chloride. Kuroda and Sandell (1953) believe a very large amount of chloride comes from magmatic sources each year.

Chloride is an essential element for plants and animals and both may constitute secondary or cyclic sources of chloride in water. *Tamarix gallica* (saltcedar) , for example, drops moisture containing sodium chloride on the ground from its leaves, in the process called guttation (Gatewood, and others, 1950, p. 80-81) , later to be leached to surface or underground waters. Chloride in domestic sewage may cause important increases in the chloride content in streams into which such wastes are emptied.

CHEMISTRY OF CHLORIDE IN NATURAL WATER

OCEANIC CHLORIDE

As indicated in table 2, the water of the ocean has a higher concentration of chloride than of any other ion. The order of abundance of anions in sea water is $Cl > SO_4 > HCO_3$. In the surface runoff to the ocean, on the other hand, the usual abundance of anions is the reverse; $HCO3 > SO4 > Cl$. These facts, and the very large quantity of chloride present in the oceans, have intrigued geochemists for many years, and a number of different explanations for them have been suggested.

Clarke (1924a, p. 141-143) observed that the excess of chloride in sea water was difficult to explain and quoted several theories offered by others. The extent of the excess of chloride in the ocean has been studied in some detail by more recent investigators. Goldschmidt (1933) calculated the total amount of igneous rock that would have to be eroded to release the amount of sodium now present in the ocean. Goldschmidt (1937a) also computed the amounts of other elements that would be contributed to the ocean by erosion of his computed amount of igneous rock. Rankama and Sahama (1950, p. 295) present data based in part on Goldschmidt's work, which show that the ocean contains more than 100 times as much chloride as could be obtained from the amount of average igneous rock needed to supply all the sodium.

Although some of these computations and basic assumptions may be subject to error and may need revision when more data are available, unless they are grossly erroneous it seems evident that a major source of chloride for the ocean other than weathering of igneous rocks is indicated. The explanation offered by most writers on this subject is that chloride in the form of hydrochloric acid or as volatile chloride salts in other forms has been added directly to the ocean in volcanic emanations (Suess, 1902) , and in juvenile or magmatic water which comes to the surface of the earth in gaseous form through fumaroles, or flows from geysers and hot springs. The hypotheses involving direct emanation of hydrochloric acid to the ocean are not particularly attractive from a chemical point of view, as they imply the ocean might have been acid for a good part of geologic time. However, there is little or no evidence on which to base speculations regarding composition of the ancient seas. Goldschmidt (1954, p. 584) suggests also that, owing to their volatile and soluble nature, the chlorides of the igneous rocks at the surface of the earth in its early history were soon lost and appeared in the ocean. It would seem that the soluble nature of chlorides generally is the important thing that would account for their early accumulation in the ocean. Modern igneous rocks near the surface would thus be lower in chloride than was the case in the early period of the earth's history if they have gone through several cycles of leaching and remelting during geologic time.

JUVENILE CHLORIDE

The question is often raised as to how much juvenile water occurs in hot springs; that is, whether the water is ordinary circulating ground water that has come into contact with hot rocks, or if it is wholly or in part newly released water formerly dissolved in igneous rocks or combined in rock minerals. The emphasis placed upon chloride as a constituent added to the ocean by such waters suggests that juvenile sources should be suspected for much of the chloride and at least a part of the water in those hot springs that yield water high in chloride. Those in Arizona, in the Gila-Salt River system, have been mentioned. Authorities differ with respect to the constituents that may be considered indicative of juvenile or meteoric origin. However, it seems possible that, locally at least, the natural waters of the earth are influenced considerably more than may be generally supposed by additions of juvenile water high in chloride. Kuroda and Sandell (1953) state that possibly as much as 10 grams of chloride per year is coming from juvenile sources.

CYCLIC CHLORIDE

The term "cyclic" is applicable to oceanic chloride that is recirculated by various mechanisms through the hydrologic cycle. The occurrence of chloride in rainwater has already been discussed briefly. Over the years there has been a considerable amount of discussion of this fact in the literature. It seems thoroughly established that some dissolved salt from the water of the ocean is carried up into the air in spray and is suspended in very small particles when the water that carried it evaporates. These salt particles may form condensation nuclei for water droplets in fog or clouds and be carried to the earth again in rain or snow. The greater part of the salt is, of course, returned directly to the ocean in rainfall over the water. However, winds carry some of the atmospheric salt inland where rains may carry it down to the land surface and increase the chloride content of the surface waters. Ground waters in such areas also could be influenced. The distance inland through which this effect may be important is probably small in most areas, but some investigators have suggested it may sometimes exert an influence far from the ocean. Unfortunately, the factual data available are insufficient to establish the importance or unimportance of windblown salt except in a few areas.

When the windblown chloride particles pass inland they are probably carried earthward rather rapidly. Jackson (1905) published maps showing a rapid landward decrease in the chloride content of waters along the coast in the northeastern United States. A level of 6.0 ppm is attained in an area a few miles wide along the coast of New York and New England, but in less than 100 miles inland the chloride concentration has decreased to 1.0 ppm or less. Windblown salt may be carried farther inland in arid coastal regions, because much of it would be expected to remain in the air until removed in precipitation. Not many data are available to show the importance of this effect in arid regions, although Goldschmidt (1954, p. 590) quotes a study in western Australia attributing salinity in that area to windborne salt. Anderson (1945) indicated a rather close resemblance of certain Australian surface waters to dilute sea water.

In recent years a revival of interest in the subject of rainfall composition and its relation to surface-water composition has occurred. Most of the recent work has centered in Australia and western Europe (Ericksson, 1952).

All these studies indicate that the effect of windblown oceanic salt extends farther inland in areas where the prevailing winds blow from sea to land. Along the eastern coast of the United States the prevailing wind direction is from the west to east and thus is not very favorable for importation of large amounts of oceanic salt. In western Europe, on the other hand, the direction of storms is more favorable.

No simple relationship exists between the composition of rainwater and the composition of sea water, even in regions where a considerable amount of oceanic salt might be present in the atmosphere. Jacobs (1937) prepared a table based on analyses of precipitation in northern Europe that had been published earlier by Kohler (1925). Jacobs demonstrated the relative amounts of the constituents in rainfall were similar to the relative amounts of the same constituents in the ocean.

Gorham (1955) reports fairly complete analyses for rainwater collected in England about 50 kilometers east of the Irish Sea which indicate a resemblance to ocean water with respect to the Na–Cl and Mg–Cl ratios. The rainwaters otherwise are very unlike ocean water. As air masses move inland, the oceanic salt they contain is lost by the washing effect of rainfall and the character of the soluble material changes as dust and other land-derived materials take the place of the salt.

The relative importance of airborne oceanic salt, especially chloride, in determining the composition of water in surface streams has been the subject of considerable debate in the literature. From time to time since Posepny first proposed it in 1877, statements have been made attributing essentially all the chloride in inland water to windblown salt from the ocean. Others have proposed that the salinity of lakes in certain closed basins has been influenced by or is entirely the result of oceanic salts in rainwater, even though such lakes have no chemical resemblance to the ocean. Clarke (1924a, p. 57) considered views such as these to be extreme. Mason (1952, p. 170) attributes all chloride in river waters to "cyclic" salt. The same assumption is made by Conway (1942) and by Sverdrup, Johnson, and Fleming (1942) and by various more recent investigators.

Chloride derived from sedimentary formations of all types could be considered cyclic in about the same sense as chloride carried by wind, so far as studies of the source of oceanic chloride is concerned. Geochemical literature does not always distinguish between chloride from rain and chloride leached from sediments, but may call both "cyclic" in the sense used by Mason, since in either instance the chloride probably came originally from the ocean.

For consideration of the problem of the evolution of the ocean, no distinction needs to be made, as any permanent addition of chloride must come from igneous rock or volcanic emanations. For the study of natural waters, however, a distinction between airborne and sedimentary sources may be significant. Sedimentary rocks are an important source of chloride in many, if not most, ground waters and inland surface waters.

According to Rankama and Sahama (1950, **p.** 317), the volume of annual precipitation on the land surface of the earth is 99 X 10 cubic kilometers, or 99 X 10^{15} liters. The literature provides a number of possible values for chloride concentration in this water. If one selects a concentration of 1.0 ppm of Cl as a compromise between the 0.3 ppm of Collins and Williams (1933) and the 3.0 ppm of Riffenburg (1925) already cited, the weight of chloride precipitation on the land each year would come to 99 X 10^{9} kg. Clarke's data (1924a) for annual dissolved load of the streams of the earth and their average chloride concentration would indicate that the surface streams carry to the ocean about 150 X 10° kilograms of chloride each year. Kuroda and Sandell (1953) give an estimate of 10 ^{3} g. per year of choride from juvenile sources.

The data available are as yet insufficient to permit any firm estimate of the quantities involved in chloride circulation in the atmosphere. The assumption that average rainwater contains about 1.5 ppm of chloride would bring the estimated amount in rain and the estimated amount returned by surface runoff to a point near equality, but some of the chloride in the rainwater will fall in closed basins or will be otherwise retained on the land surface, so that an excess in rainfall over the amount returned to the sea would have to be postulated if all chloride in river water is assigned to rainfall.

There may be more than 1.0 ppm of chloride in rainfall on the land in many places. However, there is evidence that in at least some large areas the chloride brought in from the ocean in rainfall must average far less than 1.0 ppm. Hoyt and Langbein (1944) have published a map showing average annual runoff in inches for the United States and southern Canada. This map shows that in a broad band covering large parts of Saskatchewan and the western tier of Plains States south to Texas, the runoff averages less than 1.25 inches, or **is one-**tenth to one-twentieth or less of the precipitation. To prevent chloride accumulation in this area, the runoff water should have a chloride concentration 10 to 20 or more times as high as the postulated rainfall. Streams in this area which are not extensively affected by evaporate sediments, or by the use of water for waste disposal or irrigation, have low chloride concentrations, as do most ground waters of the region.

Annual weighted-average values published by the U. S. Geological Survey (1947-50) for the Little Missouri River at Medora, N. Dak., show a range in chloride from 3.2 ppm to 0.5 ppm. For the Republican

River at Trenton, Nebr., the range is from 6.2 to 7.7 ppm. These values indicate either that the rainfall feeding these streams must have far less than 1.0 ppm of chloride or that chloride is accumulating in the soils or elsewhere and does not appear in the runoff. There is no evidence of chloride accumulation in this area. If any soluble material accumulates in the soils here, it is sulfate.

Of course, areas near the center of North America and far from the ocean may not represent average conditions better than do coastal regions. However, the lack of importance of airborne chloride in these inland areas is clearly indicated. Junge and Gustafson (1957) obtained average values of chloride in rainfall at many sampling points in the United States during 1955 and 1956. Their data show that only a small area near the coasts has as much as .5 ppm. of chloride in precipitation and that over most of the country, the average is less than .3 ppm.

Before any final conclusions can be drawn regarding the importance of rain-borne oceanic salts in determining the quality of surface waters, more data on the composition of rainwater and a better understanding of the processes by which soluble salts are added to or extracted from air masses are required. The collection of such data and their application in the study of specific areas is a field for research in both hydrology and meteorology.

Estimates of the world-wide average importance of wind-borne oceanic salt in stream water require reliance on average analyses prepared by Clarke (1924a). Many more data are available now than when Clarke computed his averages, and a comprehensive digest of more modern complete information would be helpful. Clarke's discussion of his estimates seems to indicate that he felt they could be improved when more data became available. Such a digest would be a large task but is another field where work is needed.

In summary, it may be said that a large part of the chloride in natural water is cyclic in the sense that it has been in the ocean at least once before. The path by which it circulates, however, is uncertain and the full understanding of it may be important in applying water-quality data to hydrologic studies.

RANGE OF CONCENTRATION

Chloride is present in all natural waters. Concentrations in dilute waters of humid regions, however, are low and usually do not exceed 5 ppm. Analyses of this type of water include Nos. 1 and 7 in table 8 and Nos. 1, 7, and 8 in table 9. These waters are associated with sedimentary rocks in areas of moderate to abundant rainfall. The low values of chloride for analyses in table 6 are typical of most igneous terranes without regard to climatic conditions.

Waters high in chloride usually are also high in sodium. This generalization is based on the fact that, in the most highly mineralized water, common salt (NaC1) is the main mineral in solution, and often in waters of intermediate concentration it makes up the greater part of minerals in solution. Six of the nine analyses of sodium-bearing waters in table 10 have chloride as the predominant anion.

Under some conditions, calcium chloride water such as the deep brine from Midland, Mich. (analysis 4, table 8), and the ground water from the area near Chandler, Ariz. (analysis 6, table 8), may occur. In the latter instance at least, base exchange probably has affected the relative cation concentration, and the chloride may have gone into the solution originally as sodium chloride.

In some areas where base exchange is relatively unimportant, the sodium, or sodium plus potassium, and chloride concentrations in waters tend to be practically equivalent, whether these components are present in large or small amounts. They may range from the minor amount in analysis 5, table 8, to a saturated salt brine like analysis 8, table 10 which occurs in the same general area. Concentrations of chloride in saturated sodium chloride brines are near 155,000 ppm. The chloride content of sea water is about 19,000 ppm.

ACCURACY AND REPRODUCIBILITY OF RESULTS

It is easy to determine chloride concentrations in the usual range from 1 ppm or more, fairly accurately. However, in most laboratories, chloride may be introduced into samples from the fumes often present in the laboratory air unless care is taken to prevent contamination. Differences of more than 1 ppm in chloride concentrations in the range to a maximum of 10 ppm can be considered significant in careful work. Differences of 2 to 5 percent between identical samples having from 10 ppm to 100 ppm chloride and about 2 to 3 percent at concentrations above 100 ppm are about the range of normal error in laboratory work.

FLUORIDE

Fluorine, like chlorine, is a member of the halogen group. Its behavior in rocks and in the weathering process is different, however, from that of the other halogens. Unlike the chlorides, most fluorides are low in solubility, and amounts which can be present in ordinary waters are therefore limited. For many years fluoride was not considered an important constituent in water, and fluoride determinations were rarely included in water analyses until the early and middle 1930's. About that time attention was focused upon fluoride in drinking water as the cause of dental defects, particularly mottled tooth enamel, observed among the residents of certain areas. The continued and intensive study of the physiological effects of small amounts of fluoride has produced a large amount of information relating to fluoride concentrations in water. In the course of these studies, a few natural waters have been found in which fluoride is one of the major anions, but such waters are relatively rare.

Data in table 1 indicate fluoride to be somewhat more abundant than chloride in igneous rocks. Considering the water of the ocean and the evaporates, however, the quantity of fluoride present in the earth's surface crust is far less than the quantity of chloride.

SOURCE OF FLUORIDE IN WATER

The principal independent fluoride mineral of igneous rocks is fluorite (calcium fluoride). This mineral is a source of fluoride in water but its solubility is low. There are a considerable number of complex fluoride-bearing minerals, the most important of which is apatite. Chloride may replace fluoride in this mineral. Fluoride is frequently found in igneous and metamorphic rocks as a component of amphiboles, such as hornblende, and of the micas and certain other minerals. In these minerals it replaces part of the OH groups in the mineral structure (Rankama and Sahama, 1950, p. 758). Alkalic rocks in general, and also obsidian, are stated by these authors to be higher in fluoride as a class than most other igneous rocks. Fluoride is often associated with volcanic or fumarolic gases, and in some areas is probably added to water by such emanations.

Resistate sedimentary rocks frequently contain fluorite as a minor constituent, and possibly other fluoride-bearing minerals may constitute part of the grain material of resistates, where chemical weathering has not been complete. Water from the Ogallala formation of the high plains of the United States contains fluoride that may come from this source. Some of the sedimentary rocks of this region include volcanic ash that may contain fluoride-bearing minerals. Cederstrom (1945) attributes fluoride in ground waters of the Virginia coastal plain to solution of micas which contain fluoride.

CHEMISTRY OF FLUORIDE IN NATURAL WATER

Fluoride is often a convenient constituent of water to utilize as a tracer in establishing paths of movement of water. It is sometimes possible to utilize fluoride-concentration data in differentiation between waters that have come from different rock formations.

Because hydrofluoric acid is only weakly dissociated in solution, fluorides present in water tend to hydrolyze to some extent. The effect is weak, however, and the small concentration of fluoride in most waters is not enough to contribute measurably to the alkalinity.

The solubility of calcium fluoride probably limits the concentration of fluoride in waters that have more than about 10 ppm of calcium in solution. According to **Auméras** (1927) , fluorite is soluble in pure water at 25°C to the extent of 8.7 ppm of fluoride. Data are not available to show the effects of common constituents of natural water on the solubility of calcium fluoride.

The complex fluosilicate ion (SiF —) appears to be much more soluble in the presence of calcium than is fluoride itself. The complex ions probably do not exist in most natural waters but their presence in some is possible. Most of the fluoride concentrations over 1 ppm in the analyses in this report are in sodium waters. Magnesium fluoride is considerably more soluble than calcium fluoride and sodium fluoride is very soluble in water.

RANGE OF CONCENTRATION

In general, fluoride concentrations of natural waters may range from almost 0 to 50 ppm or more. The highest concentrations in the analyses in this report are 32 ppm for a water from a flowing well near San Simon, Ariz. (analysis 1, table 12), and 22 ppm for water from a well in Idaho (analysis 1, table 6). Values in the literature with a maximum of 67 ppm in a water from the Union of South Africa are reported (Bond, 1946). Ordinarily waters having concentrations of 10 ppm or more are rare and surface waters seldom contain more than 1.0 ppm.

Fluoride in excessive concentrations is undesirable in waters used for drinking. It is stated in a comprehensive report by the California State Water Pollution Control Board (1952, p. 257) on water-quality standards ". . . that water containing less than 0.9 to 1.0 ppm of fluoride will seldom cause mottled enamel in children, and for adults concentrations less than 3 or 4 ppm are not likely to cause endemic cumulative fluorosis and skeletal effects." The inference that concentrations above 4 ppm may affect bone structure is clear, and although the literature on this subject is rather conflicting and inconclusive, it appears likely that concentrations of fluoride as high as those reported in the two analyses mentioned above (32 ppm and 22 ppm) may render a water undesirable for drinking by adults and farm animals as well as children. Mitchell and Edman (1953) have estimated that a daily intake of 15 to 20 milligrams of fluoride over a period of several years would be required to produce endemic fluorosis in an adult man. A daily intake of one quart of water having 22 ppm of fluoride would exceed this level.

ACCURACY AND REPRODUCIBILITY OF RESULTS

Fluoride determinations made by standard methods can be expected to give results accurate and reproducible to the nearest 0.1 ppm up to 1.0 ppm, and to about 0.2 ppm between 1.0 and 2.0 ppm. The methods

TABLE 12.—*Analyses of waters containing nitrate, fluoride, or phosphate in unusual amounts*

[Analyses by U. S. Geological Survey. Date below sample number is date of collection. Source of data: No. 1 Hem (1950 p. 87); Nos. 2-6 unpublished data, U. S. Geol. Survey files]

	(1) Apr. 29, 1941		(2) Aug. 14, 1952		(3) Sept. 16, 1947		(4) Jan. 31, 1946		(5) Oct. 25, 1954		(6) May 19, 1952	
	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm
Silica (SiO_2)			23	-------	27				13		18	
Iron (Fe) in solution at time of analysis									.01	-------	00	-----
Iron (Fe) total					.28	-------			.09	-------		
Manganese (Mn)									.00	-------	00	-----
Zinc (Zn)									.06	.002	-------	
Calcium (Ca)	5.5	.27	92	4.59	64	3.19	36	1.80	19	.948	42	2.10
Magnesium (Mg)	4.4	.36	38	3.12	19	1.56	18	1.48	5.1	.419	19	1.56
Sodium (Na)	157	6.81	110	4.80	114	4.96	102	4.44	4.4	.191	29	1.26
Potassium (K)					9.5	.24			3.2	.082	.7	.02
Lithium (Li)									.3	.043	.3	.04
Carbonate (CO_3)	58	1.93	0		0		0	-------	0	000	0	
Bicarbonate (HCO_3)	163	2.67	153	2.51	402	6.59	303	4.97	39	.639	65	1.07
Sulfate (804)	42	.87	137	2.85	74	1.54	34	.71	30	.625	114	2.37
Chloride (Cl)	10	.28	205	5.78	30	.85	32	.90	5.8	.164	13	.37
Fluoride (F)	32	1.68	.6	.03	.1	.01	.4	.02	.7	.037	5.0	.26
Nitrate (NO_3)			83	1.34	60	.97	68	1.10	15	.242	.3	.00
Phosphate (PO_4)									.0	.000	30	.95
Dissolved solids:												
Calculated	389	-------	764		596				116		303	
Residue on evaporation					578		440		114		318	
Hardness as $CaCO_3$	32	-------	386	-------	238		164		69		183	
Noncarbonate	0		260	-------	0		0		37		130	
Specific conductance (micromhos at 25°C)	660		1,320	-------	875		724		178		413	
pH					7.4	-------			6.9	-------	7.2	-----
Color									12		20	

1. Flowing well, NE¼ sec. 24, T. 13 S., A. 30 E., Cochise County, Ariz. Depth 850 ft. Water-bearing formation: Valley fill. Temp. 65° F.
2. Irrigation well, SE¼ sec. 25, T. 2 N. R. 2 W., Maricopa County, Ariz. Depth 275 ft. Water-bearing formation: Valley fill, 105 ft to 205 ft. Temp. 85 F.
3. Well, SE¼ sec. 21, T. 12 S., R. 10 W., Lincoln County, Kans. Depth 32 ft. Water-bearing formation: Alluvium, Temp. 58° F.
4. Well, NW¼ sec. 2, T. 8 S., R. 5 W., Maricopa County, Ariz. Depth 495 ft Water-bearing formation: Valley fill.
5. Drilled well, Willimantic, Windham County, Conn. (358 Jackson Street). Cased to 10 ft. Water-bearing formation: Willimantic gneiss of Gregory (1906) from 10 ft to 180 ft.
6. Peace Creek at State Highway 17 bridge, Salfa Springs, Fla., 140 cfs.

used in water analysis are intended for measuring quantities in this general range and for higher concentrations are accurate and reproducible to perhaps 10 percent.

Waters very high in fluoride are of interest as unusual specimens but differences of fluoride concentration among sources that are high in this constituent are not easy to interpret and fairly large apparent differences may not be particularly significant.

NITRATE

The element nitrogen is present in rather small quantities in igneous rocks and in the ocean. The greater portion of the amount on the earth occurs uncombined in the atmosphere. It is an essential part of living organisms in the structure of proteins. In water nitrogen may occur in several forms, depending on the level of oxidation. Ammoniacal nitrogen has the form N^{-} — — and occurs as ammonia (NH_3) or as ammonium ion (NH_4+). This form will be discussed briefly later under a separate heading. Organic or amino, sometimes called albuminoid, nitrogen is in the form N^{--}. Gaseous nitrogen is dissolved in water to some extent but has no significance in water quality. Nitrogen in this form has no ionic charge. In nitrite nitrogen $(NO_2\ \ )$ it has the form $N+++$ and in the completely oxidized state of nitrate $(NO_3\ \ )$ it has the form $N^{5}+$. This last form is the principal one in most natural water.

SOURCE OF NITRATE IN WATER

Very little information is available as to the manner in which nitrogen occurs in igneous rock, although Rankama and Sahama (1950, p. 577) suggest that it may be present in ammoniacal form and believe very little could be present as nitrate. Even the small amounts of nitrogen contained in igneous rock may provide some nitrate to natural waters in the process of weathering. All the nitrate compounds are readily soluble in water, and any formed in weathering will be found in solution. Except for volcanic emanations which may include ammonium chloride, igneous rocks appear to be a minor source of nitrate in water.

Nitrogen from the atmosphere is combined into nitric oxides by lightning discharges, and these oxides dissolve in rainwater to produce nitrous and nitric acids. This may be a source of nitrate in surface waters, although much of the nitrate in rainwater is doubtless left in the soil where it is available for use by plants. Riffenburg (1925) reports the average content of nitrate in rainwater to be 0.2 ppm.

The nitrate content of the subsoil is increased much more by other processes. Certain plants are able through bacteria on nodules on their roots to take nitrogen from the air and fix it in soil as nitrate.

These plants return more nitrogen to the soil than they take from it. The plants which perform this function are the legumes, a group which includes a number of plants native to desert regions.

In addition to that added by legumes, nitrogen in plant debris, animal excrement, and inorganic nitrate fertilizers is added to the soil. These additions, usually promoted by man himself, probably constitute a major source of nitrate in surface and underground water. Additional amounts are added to waters through discharge of sewage wastes. These wastes contain nitrogen in various forms; and microorganisms, either introduced during sewage treatment or naturally present in water or soil, convert the nitrogen to more highly oxidized. forms. Some nitrogen escapes as gaseous N_2 in this process, but eventually at least a part of the original nitrogen is converted to nitrate.

CHEMISTRY OF NITRATE IN NATURAL WATER

In the usual mineral analysis of water, the nitrate form of nitrogen is the only one determined, although the ammonium ion may be determined in the rather rare cases when it is present. Nitrate is reported in these analyses in terms of the content of NO_3 ions. In "sanitary" analyses, commonly made by health laboratories, all forms of combined nitrogen present in water are usually determined. In the studies for which these analyses are made, nitrogen in its various forms has considerable significance as an indication of pollution. In order to make the data for the forms of the element comparable, all are reported in terms of their equivalent concentration of elemental nitrogen.

The existence of two methods of reporting concentrations of nitrate is a source of considerable confusion to the users of water analysis data. The "sanitary" analysis may not always state directly that it reports NO_3^- concentrations in terms of the elemental N present, but this basis of reporting can be safely assumed for analyses of this type. Conversion factors for NO_3^- to N and vice versa are included in table 3.

Nitrate contains the most highly oxidized form of nitrogen and should probably be the most stable under conditions where plenty of oxygen is present as in the usual surface water. Nitrate also appears to be stable, however, under the conditions which normally exist below the water table. Because of its close relation to life processes, nitrate concentrations in water are likely to be strongly influenced by the activities of plants and animals. Bacteria play a particularly important role in connection with nitrate in water.

The occurrence of rather large amounts of nitrate in ground waters in certain localities has attracted the interest of several investigators. In some areas, these occurrences can be assigned fairly definitely to drainage of water through soil which has been repeatedly fertilized.

Irrigated areas such as the Salt River Valley area of Arizona are particularly likely to show such effects (analysis 2, table 12). In such areas, soluble nitrates and gaseous ammonia are widely used as fertilizers. A similar effect has been reported to occur on Long Island, N. Y. Fertilization of soils may contribute nitrate to surface runoff also.

Shallow ground waters in rural areas may be subject to pollution from barnyards and similar sources. Durum (in Berry, 1952) attributes the high nitrate of analysis 3, table 12 to surface pollution. Regarding the shallow ground waters of Kansas, Metzler and Stoltenberg (1950) state that some of the areas where high nitrate concentrations occur are so extensive they do not seem to be logically explained by barnyard pollution or fertilization.

Relatively high nitrate concentrations occur in the ground waters of certain areas where an explanation seems very difficult. Some of these areas are in desert basins where ground water occurs at considerable depth. Analysis 4, table 12, is from a deep well in an undeveloped desert area. It has been mentioned before that some of the plants native to the desert may fix nitrate in the soil. The leaching of soil and humus in old mesquite groves converted to irrigated farm land is suggested as the source of high nitrate concentrations in subsoil waters in the Coachella Valley, Calif. (Huberty, Pillsbury and Sokoloff, 1945, p. 14-15). It is possible that leaching of nitrate from existing soil horizons and possibly older buried horizons in basin-range type valleys or other areas containing successively deposited alluvial strata could be responsible for high nitrate concentrations in ground water in certain regions. Nitrate in some waters may be the result of volcanic emanations, but this source could be important only locally.

A discussion of possible sources of nitrate in the ground waters of Texas has been published by George and Hastings (1951). This paper expresses no definite conclusions as to sources, but suggests bacterial origin as one possibility. The suggestion is also made that nitrate may be lost from ground water at depth through anion exchange or the activity of nitrate-reducing bacteria.

It would appear from the state of the literature on this subject that further investigations of the behavior of nitrate in ground waters are required; although an organic origin is probably indicated for most such occurrences.

RANGE OF CONCENTRATION

Nitrate content in surface waters not subject to extensive pollution from sewage or other sources seldom is as high as 5 ppm, and often is less than 1 ppm. In ground water, however, the concentration may have a wide range, from practically zero to nearly 1,000 ppm. Clarke quotes an analysis for the holy well "Zem-Zem" at Mecca, showing 851 ppm of nitrate. Water of comparable nitrate concentration has been found in the Carlsbad Caverns of New Mexico where there apparently has been contamination by drainage from areas frequented by large numbers of bats.

Concentrations near 100 ppm occur in irrigated regions of Arizona near Phoenix as shown by analysis 2, table 12. Analysis 4 in this table also is of high-nitrate water. The conditions causing the high concentration in the Connecticut well are not known. The concentration of nitrate in water does not seem to have any consistent relation to the concentrations of the cations. In areas where nitrate is derived from organic pollution, the high nitrate may be accompanied by high chloride concentrations.

ACCURACY AND REPRODUCIBILITY OF RESULTS

The usual method of determining nitrate in water (by means of phenoldisulfonic acid) is best adapted for concentrations under 30 ppm. It is usually believed to be accurate to within a few parts per million at the upper end of this range and to the nearest tenth of a part per million at the lower end. This procedure is inaccurate if used for higher concentrations and may be less accurate than is generally supposed for the concentrations below 30 ppm. Owing to the uncertainties surrounding the source of nitrate in water, and the possibility of loss through bacterial action or consumption by plants, nitrate is probably not a desirable anion to use in tracing water movement or in correlating waters with their source using chemical analyses.

PHOSPHATE

The determination of phosphate is not generally included in the chemical analysis of a water. Except in unusual instances, the amount present is small and can be ignored without serious error.

SOURCES OF PHOSPHATE

In igneous rocks phosphate is largely concentrated in apatite which is a complex phosphate of calcium containing fluoride, chloride, and hydroxyl ions in varying proportions. Weathering of these rocks tends to release calcium phosphate, which is soluble to some degree in water containing carbon dioxide. However, the phosphates are usually redeposited in the hydrolyzates and do not remain in solution (Rankama and Sahama, 1950, p. 590).

Phosphorus is an essential element in the growth of plants and animals, and some sources that contribute nitrate, such as organic wastes and leaching of soils, may be important as sources for phosphate in water as well. These are cyclic rather than ultimate sources, however. The addition of phosphates in water treatment constitutes a possible source, although the dosage is usually small. In some areas, phosphate fertilizers may yield some phosphate to water. A more important source is the increasing use of phosphates in detergents. Domestic and industrial sewage effluents may therefore contain considerable amounts of phosphate.

CHEMISTRY OF PHOSPHATE IN NATURAL WATER

In routine water analysis, the phosphorus found is normally reported in terms of orthophosphate ions (PO_4^{---}). This form of statement implies a more exact knowledge of the state of the element in solution than is usually justified. Ions in which phosphorus has a lower valence are not normally to be expected, but several phosphate structures can occur.

The solubility of Ca, $(PO_4)_2$ in water under 2 atmospheres pressure of carbon dioxide is given as 140 ppm as PO_4 at 14°C by Ehlert and Hempel (1912). In the absence of carbon dioxide, the solubility is much less; however, data for solubility under these conditions are lacking. The monocalcium salt $CaHPO_4$ is soluble in carbon dioxide-free water to the extent of 96 ppm PO_4 at 25°C (Cameron and Seidell, 1904) and about four times as soluble in water saturated with carbon dioxide at this temperature (pressure not given). The HPO_4^{--} ion is probably the normal form for phosphate in the pH ranges of natural waters. Magnesium phosphate in the form $MgHPO_4$ is indicated as about as soluble as the calcium salt.

These solubilities are moderately high and are not the limiting factor that controls phosphate concentrations in most natural waters. Other factors are no doubt more important. These include the relative rarity of phosphate minerals as compared to carbonates or sulfates, and the redeposition of phosphates in hydrolyzates and elsewhere in the form of iron and calcium phosphates. Since phosphorus is essential in plant nutrition, it is likely that considerable amounts are withheld from water by vegetation.

Phosphate in water may add to the apparent alkalinity, as it undergoes hydrolysis similar to that of carbonate. If trivalent (PO_4^{---}) ions are present to start with, upon titration the ions are first converted to HPO_4^{--} and then to H_2PO_4 and finally to orthophosphoric acid, H_3PO_4. The final pH used for alkalinity titrations reported as bicarbonate (4.5) is about the point where all HPO_4^{--} has been converted to the monovalent form $(H_2PO_4^{-})$.

Probably few natural waters contain enough phosphate to affect the alkalinity measurably. However, the increasing use of polyphosphates in water conditioning increases the possibility of encountering such waters. A correction for the phosphate contribution to the titrated alkalinity should be made for waters high in phosphate, if equivalents per million values for the ion are reported; otherwise, there would be a discrepancy between sums of anions and cations. No sound basis for making such a correction presently exists, however.

RANGE OF CONCENTRATION

So few data are available on the content of phosphate in natural waters that little can be positively stated regarding the observed range of concentration. Probably the amount present is not often more than a few parts per million, however. A few waters are known which are high in phosphate. Analysis 6, table 12, represents a surface stream in Florida which shows an unusually large amount (30 ppm). This stream is in the part of the state where commercially important phosphate rock occurs in the form of pebbles, and mining activity may have affected the water.

ACCURACY AND REPRODUCIBILITY OF RESULTS

Phosphate can be determined with about the same degree of reproducibility as nitrate in low concentrations. Probably in the range from 30 to 100 ppm the determinations on duplicate samples should agree to ±2 ppm. However, because in most instances the data on occurrence of phosphate in water are incomplete, the value of the determination in comparing one water with another is not great at present. More study of phosphate occurrence in water is needed before any definite statement can be made as to accuracy of routine determinations.

BORON

The element boron is a minor constituent of rocks and of natural waters. It may be present also in volcanic emanations. The occurrence of boron in water has been studied rather closely in many areas of the western United States because small amounts of boron in irrigation water and soil are damaging to certain crops.

SOURCES OF BORON

Tourmaline is the most widely distributed igneous- or metamorphic-rock mineral in which boron is an essential component. Tourmaline is a complex silicate containing sodium, aluminum, fluoride, hydroxide, and sometimes lithium and magnesium as well as boron (Rankama and Sahama, 1950, p. 487). Typically it is a constituent of granitic rocks and pegmatites. It has been reported that boron may also be present in small amounts in basic rocks such as gabbro and in serpentine formed from ultrabasic rocks by metamorphism. In basic rocks, the boron is incorporated in minerals containing OH^-, such as biotite and the amphiboles. The decomposition of these minerals releases boron during the weathering process and the boron is carried off in solution. Tourmaline is very resistant to attack by water and persists in resistates and soils.

Boron may be liberated in volcanic gases as boric acid, H_3BO_3, or as halogenides such as BF_3. These are volatile at comparatively low temperatures. The gaseous BF_3 reacts with water to produce boric and hydrofluoric acids. The water of some hot springs and especially water from areas of recent volcanic activity may therefore be rather high in boron.

Certain evaporate deposits in the closed basins of southern California and Nevada contain notable amounts of borate salts, and waters that have come in contact with these evaporate beds may be rather high in boron concentration.

Boron may be added to water through disposal of waste materials, especially from cleaning operations where borates are used as detergents.

CHEMISTRY OF BORON IN NATURAL WATER

In the usual complete chemical analysis of water, boron is reported in terms of the element B as parts per million and no attempt is generally made to express the results in ionic form either in parts per million or equivalents per million. So long as the amounts present are minor, no serious error is introduced by leaving boron out of consideration in the cation-anion balance. Boron can be present in water in anionic form as a borate or as undissociated boric acid. Owing to hydrolysis the borates contribute to the titratable alkalinity and tend to raise the pH.

Theoretical data on the dissociation constants for boric acid (Handbook of Chemistry and Physics, 1953) indicate that essentially all the boron in water would be present as undissociated boric acid below a pH of 7. At a pH of 8 about 5 percent of the boron might occur as H_2BO_3 ions. At a pH of 9 these ions could constitute nearly 40 percent of the total boron. The HBO_3^{-} and BO_3^{--} ions would not be present in appreciable quantity when the pH is below 10 and would be dominant only at high pH levels not usually found in natural waters. The contribution of boron to titrated alkalinity is difficult to compute, and normally only a part of the boron would be reported in terms of equivalent carbonate or bicarbonate.

Agriculturalists are interested in boron concentrations in irrigation water because of the relationship of boron to plant growth. It is essential in trace quantities in plant nutrition but becomes toxic to some plants when present in amounts as small as 1.0 ppm in irrigating water. Most plants are somewhat more tolerant than this but many are damaged by concentrations of only 2.0 ppm. This subject has been covered at length in reports of the U. S. Department of Agriculture (Scofield and Wilcox, 1931, p. 9-10, Eaton, 1935) and detailed discussions are not pertinent here.

Colemanite (calcium borate, $Ca_2B_6O_{11}$ • 51120) is an important mineral among the evaporite deposits that contain boron. According to Mandelbaum (1909), at 30°C calcium borate (CaB_2O_4 • $4H_2O$) is soluble in pure water to the extent of 113 ppm of B. The hexahydrate CaB_2O_4 • 6H20 under the same conditions is soluble to the extent of only 64 ppm of B. These solubility data suggest that few natural waters reach a condition of saturation with respect to any calcium borate. In a very general way, however, the waters that are highest in boron concentration seem usually to be sodium waters, which might be expected because the sodium borates are more soluble.

The chemistry of boron in natural water is not fully understood, and the element is not always determined in water analyses. Aside from evaluations of waters for irrigation, boron concentrations may have some value as a means of evaluating the effect of hot-spring inflow containing boron on a surface stream. Boron in large amounts may be an indicator of juvenile or magmatic origin for at least *a* part of the water in which it is found.

RANGE OF CONCENTRATION

The boron content of natural waters may *range* from less than 0.01 ppm to 30 ppm or more. Concentrations above 10 ppm are, however, decidedly unusual, and most often occur in water from hot springs or in brines. Very high concentrations are indicated in analyses 1 and 2 in table 13. These data are for hot springs. Analysis 7, table 10, shows a concentration of 17 ppm in salt spring water from Arizona. Average sea water (table 2) contains 4.6 ppm of boron. Most waters of low to moderate concentration contain no more than a few tenths or hundredths of a part per million of boron.

ACCURACY AND REPRODUCIBILITY OF RESULTS

Boron determinations made by present standard procedures are considered accurate and reproducible to a tenth of a part per million in the 0 to 1.0 ppm range and to the nearest part per million up to about 20 ppm. Values above this level are rare and can be determined somewhat less precisely because the standard procedure is designed for small concentrations. Before 1948 data on boron concentrations in surface waters were published in Geological Survey reports in terms of BO_3^{-} — ions. Some of these determinations were made by a semiquantitative procedure that was subject to rather large errors.

TABLE 13.—*Analyses of waters containing heavy metals and other unusual constituents*

(Analyses 1,2, and 4-6 by U. S. Geol. Survey, 8 by Carnegie Inst. Date under sample number is date of collection. Source of data: Nos. 1-3, White and Brannock (1950); Nos. 4 and 5, Emmons (1917); No. 6, unpublished data, U. S. Geol. Survey files]

	(1) 1949		(2) ——		(3) About 1935		(4) About 1911		(5) About 1917		(6) Dec. 8, 1934	
	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm
Silica (SiO_2)	262	-------	67	-------	303	-------	56	-------	23	....	21	
Aluminum (Al)					1		433	48.65	12	1.32	-------	
Iron (Fe) ferrous							2, 178	77.99				
Iron (Fe) ferric					8	-------	0	-------				
Manganese (Mn)							.2	.01	-------			
Copper (Cu)							312	9. 82	-------			
Zinc (Zn)							200	6.12	345	10.55	-------	
Calcium (Ca).	8.7	.43	56	2.79	4	.20	68	3.39	260	12.97	452	22.55
Magnesium (Mg)	1	.08	57	4.69	2	.16	41	3. 37	49	4.03	555	45.6.4
Sodium (Na)	695	30.22	1,390	60.44	48	2.09	23	1.00	13	.57	1,900	82.65
Potassium (K)	74	1.89	68	1.74	80	.77	20	.51	3. 2	.08	17	.43
Lithium (Li)	5	72	-------									
Ammonium (NH_4)			543	30. 10	342	18. 96	-------					
Selenium (Se)											1.98	-----
Bicarbonate (HCO_3)	276	4.52	1,890	30.97	-------		0	-------	0	-------	476	7.80
Sulfate (SO_4)	156	8.25	1,980	41.22	1,100	20.90	6,600	138.65	1,650	34. 35	6,330	131.79
Chloride (Cl)	921	25. 98	489	13.79	5	.14	.1	.00	3.7	.10	288	8.12
Fluoride (F)	2.1	.11	-------									
Thiosulfate (S_2O_3)	14	.24	....									
Boron (B)	55		528		2.5	....						
Dissolved solids												
Calculated	[1] 2, 600		8,240	-------	[2] 1, 850		9,990		2,500	-------		
Residue on evaporation											[3] 10, 900	
Hardness as $CaCO_3$	26	-------	374								8,410	
Noncarbonate	0	....	0	-------								
pH	6. 3	....	7±	-------	3±	-------						
Acidity as H_2SO_4					59	-------	130	....	252	-------		

1. Hot spring at Steamboat Springs, Nev. Temp. 182°F.
2. Sulfur Bank Spring, Calif. Temp. 179°F.
3. Spring 33, Norris Geyser Basin, Yellowstone National Park, Wyo.
4. Water from first level below black copper workings, Burra-Burra mine, Ducktown, Tenn.
5. Water from Victor mine, Joplin district, Missouri.
6. New drainage ditch about 4 miles north of Mack, Colo.

Includes arsenate (AsO_4) 4.3 ppm, .09 epm, antimonate (SbO_3) 0.3 ppm.

[2] Includes arsenate (AsO_4) 0.9 ppm.

[3] Contains 224 ppm, 8.61 epm nitrate (NO_3).

TRACE OR MINOR CONSTITUENTS—CATIONS

In addition to the constitutents of natural waters thus far enumerated and discussed, there are a number of other cations that may be present. Usually the concentrations of these substances do not exceed 1 part per million, although in exceptional waters one or more of them may be present in comparatively large amounts and may for that particular water be a major component. The data available for the amounts of these seldom-determined constituents in waters are very incomplete. For special studies, such determinations may be useful but for general comparisons of natural waters they are not usually very helpful. These cations can conveniently be considered in four groups as follows:

Heavy metals
Alkaline-earth metals
Alkali metals
Radioactive elements

HEAVY METALS

The heavy metals include iron and manganese and, for the purpose of this discussion, aluminum, all of which have already been discussed. Additional metals of this group that are sometimes determined include titanium, chromium, zinc, nickel, copper, tin, cobalt, lead, cadmium, mercury, arsenic, and selenium. Special studies of the occurrence in water of some of the metals in this group have been made in connection with mineral prospecting (Lakin, Almond, and Ward, 1952).

TITANIUM

Table 1 indicates that titanium is present in igneous rocks in larger amounts than any of the other heavy metals listed for discussion in this part of this report. Rankama and Sahama (1950, p. 563-64) state that titanium is most common in the ferromagnesian rocks. Its principal mineral is ilmenite, a double oxide of iron and titanium.

There are practically no data on the occurrence of titanium in water. In the weathering process the titanium minerals are probably either left unaltered in the resistates or converted to hydrolyzate minerals, and very little titanium goes into solution. However, waters containing traces of titanium are probably common.

CHROMIUM

The element chromium is amphoteric and can exist in water in several different states. It is present in minor amounts in igneous rocks and, according to Goldschmidt (1937a), is much more abundant in basic and ultrabasic types than in the more silicic types of rock. In attack by weathering, chromium in cationic form (Cr^{+}) behaves somewhat like iron and is largely retained in resistates and hydrolyzates. Very little chromium goes into solution. Natural waters, therefore, would be expected to contain only traces of chromium as a cation, unless the pH were very low.

Chromium, under strongly oxidizing conditions, may be converted to the Cr^{6+} state and occur as chromate (CrO_4^{--}) anions. Natural cromates are rare, and when CrO_4^{--} is present in water, it is usually the result of pollution by industrial wastes. Fairly high concentrations of chromate anions are possible in waters having normal pH levels. An area of chromate contamination of ground water is reported to exist on Long Island, N. Y. (California State Water Pollution Control Board, 1952, p. 215). Concentrations of more than 0.05 ppm of Cr in the hexavalent form constitutes ground for rejection of a water for domestic use on the basis of the standards of the U. S. Public Health Service (1946). The Long Island supply mentioned above had 25 ppm of chromium in the hexavalent form upon one observation. Higher concentrations have been reported in ground water of industrial areas near Baltimore, Md.

ZINC

In rocks, zinc is most commonly present in the form of the sulfide sphalerite, which is the most important zinc ore. Zinc may replace iron or magnesium in certain minerals (Rankama and Sahama, 1950, p. 710). It may be present in carbonate sediments. In the weathering process, soluble compounds of zinc are formed and the presence of at least traces of zinc in water probably is common. The geochemistry of zinc has been discussed in some detail by Wedepohl (1953). Analyses 4 and 5, table 13, report zinc concentrations of 200 and 345 ppm, respectively. Both represent mine waters having low pH values. The present limit for zinc in potable water is 15 ppm as given by the U. S. Public Health Service (1946). Concentrations of 40 ppm impart a strong astringent taste to the water (California State Water Pollution Control Board, 1952, p. 407).

Zinc chloride and sulfate are very soluble in water but hydrolyze in solution to reduce the pH. If the pH is maintained by the presence of an excess of bicarbonates and other anions normally present in natural water, the solubility of zinc is likely to be controlled by the solubility of its carbonate and hydroxide. According to Ageno and Valla (1911), the carbonate is soluble in pure water at 25°C to the extent of 107 ppm of zinc. The hydroxide is reported by Oka (1940) to be soluble only to 0.2 ppm of zinc (temperature not stated). Levels higher than this by about a factor of ten are reported by Seidell (1940, p. 589) as determined by other investigators. The pH level at which zinc might precipitate as hydroxide is probably not reached in the presence of excess carbon dioxide in solution. At very high pH levels zinc may form anion complexes, but such conditions are not likely in natural waters.

Zinc is probably adsorbed to a considerable degree in hydrolyzate sediments and in soils and would not normally be expected in more than trace amounts in natural ground and surface waters.

NICKEL AND COBALT

Nickel and cobalt can be considered together, as they are very similar in chemical behavior. They are also closely related to iron. Both are present in igneous rocks in small amounts and are more prevalent in the basic and ultrabasic types than in silicic rocks. In the process of weathering, nickel goes into insoluble minerals of the hydrolyzates. Any nickel in water is likely to be in small amounts and could be in a colloidal state. Cobalt may be taken into solution more readily than nickel but is adsorbed to a great extent by the hydrolyzate or oxidate sediments (Rankama and Sahama, 1950, p. 684). Cobalt may be taken into solution in small amounts through bacteriological activity similar to that causing solution of manganese. However, so few data on the occurrance of either nickel or cobalt in natural water are available that only theoretical consideration is possible.

COPPER

The element copper is a fairly common trace constituent of natural water. Small amounts may be introduced into water by solution of copper and brass water pipes and other copper-bearing equipment in contact with the water, or from copper salts added to control algae in open reservoirs. Copper salts such as the sulfate and chloride are highly soluble in waters with a low pH but in water of normal alkalinity these salts hydrolyze and the copper may be precipitated. In the normal pH range of natural water containing carbon dioxide, the copper might be precipitated as carbonate. This copper salt is soluble to the extent of 1.5 ppm Cu in the absence of carbon dioxide and 89.7 ppm Cu at 1 atmosphere pressure of carbon dioxide (Seidell, 1940). Copper hydroxide, Cu (011)$_2$, is soluble to the extent of about 1.9 ppm Cu at 25°C (McDowell and Johnston, 1936). Copper is obviously more soluble than ferric iron and should remain in solution to a greater degree than ferric iron during the weathering and disintegration of rocks under oxidizing conditions. Copper, however, is dissolved and transported less readily than ferrous iron.

In rocks, copper occurs most commonly in the form of a sulfide. In weathering these rocks are oxidized. The copper may go into solution as sulfate, although in the presence of carbon dioxide, a considerable amount probably would be precipitated as carbonate.

The oxidized portions of sulfide copper ore bodies contain other copper compounds. The presence of large copper concentrations in mine water is common and some methods of copper recovery depend on the leaching of ores and removal of copper from the leaching solutions. Analysis 4, table 13 represents a copper-bearing water from a mine in the Tennessee copper district.

TIN

In nature, tin is a decidedly minor rock component and would not be expected to be found in natural water except in very minor traces. Stannous hydroxide Sn $(011)_2$ is reported to be soluble in water at 25°C to the extent of about 1.6 ppm Sn (Seidell, 1940). At pH ranges considerably below those normally found in natural water, a much higher concentration may be possible, and at a high **pH,** above normal ranges for natural water, tin may be part of an anion complex and so dissolve in greater amounts.

According to Rankama and Sahama (1950, p. 735), in weathering tin is not carried in solution to any great extent but is precipitated in hydrolyzates or remains in the resistate sediments. Tin may be added to water by industrial waste disposal. Very few data are available, however, to give any indication as to actual amounts that occur in water either naturally or as a result of pollution.

LEAD

Traces of lead in water usually are the result of solution of lead pipe through which the water has passed. Amounts of lead of the order of 0.1 ppm are significant, as this concentration is the upper limit for drinking water in the standards adopted by the U. S. Public Health Service (1946). Higher concentrations may be added to water through industrial and mine-waste disposal. Concentrations of 0.4 to 0.8 ppm are reported in natural waters as a result of solution of lead-bearing minerals (California State Water Pollution Control Board, 1952, p. 281). Lead occurs in rocks primarily as the sulfide, galena, and also in the form of oxides. It may replace certain ions such as calcium and can constitute an appreciable percentage of aragonite (Rankama and Sahama, 1950, p. 733). Lead carbonate is common in the oxidized zone of lead ores. Lead also occurs in potassium feldspars, where it replaces potassium (Rankama and Sahama, 1950, p. 733).

Lead in the form of sulfate is reported to be soluble in water to the extent of 31 ppm (Seidell, 1940, p. 1409) at 25°C. In the usual natural water this concentration would not be approached, however, since a pH of less than 4.5 would probably be required to prevent formation of lead hydroxide and carbonate. In natural waters containing bicarbonate and carbonate alkalinity, the concentration of lead could be limited by the solubility of lead carbonate, $PbCO_3$. It is reported (Pleissner, 1907) that at 18°C water free of carbon dioxide will dissolve the equivalent of 1.4 ppm of lead, and the solubility is increased nearly four-fold by the presence of 2.8 ppm of carbon dioxide in the solution. Presence of other ions may increase the solubility of lead. It is likely that lead is adsorbed by minerals in the hydrolyzate sediments and in soils so that observed concentrations rarely reach the theoretically possible level.

Techniques for determining lead in the 0.01-1.0 ppm range have been developed because of the high toxicity of this ion in domestic water supplies.

It is reported that lead may be dissolved from water pipes most readily by water which is low in hardness and bicarbonate, low in pH, high in dissolved oxygen, and high in nitrate (California State Water Pollution Control Board, 1952, p. 16).

CADMIUM

The element cadmium is present in rocks in quantities much less than those reported for zinc (table 1). Probably only minute traces are likely to be found in natural water, but cadmium may be introduced in amounts significant from a health standpoint by solution from containers or tubing, or by waste disposal. Cadmium in drinking water may be lethal, but definite limits have not been established.

Cadmium probably could be present only in small amounts in water with the normal alkaline pH range, because of the low solubility of the carbonate and hydroxide. The hydroxide is reported by Piater (1928), to be soluble to the extent of about 1 ppm Cd at 25°C. Exact data regarding solubility of the carbonate are not available. At pH levels below about 4.5 solubility of cadmium would be controlled by other factors and probably would be greater.

Presence of any more than trace quantities of cadimum in water is no doubt very unusual. However, data on the occurrence of cadmium in water are not available. Like zinc, cadmium probably is largely adsorbed from solution in natural water by the hydrolyzate and oxidate sediments and may also be removed by precipitation in the form of carbonate.

MERCURY

Mercury is a comparatively rare element and does not occur in many natural waters. A few hot-spring waters are known that deposit mercury (Ross, C. P., oral communication) in the form of cinnabar, HgS. Mercury may be introduced into water through mining and metallurgical or other industrial wastes. Because of its toxicity, mercury is an undesirable impurity in water, but dangerous concentrations are not likely to be reached in natural water that is potable in other respects.

Because of its volatility, mercury probably does not depend entirely upon solution in water for its removal from rock materials. Traces found in hot springs suggest heat may be an important factor in transporting the mercury. Mercuric sulfide (cinnabar) is reported to be soluble to the extent of only 0.1 ppm Hg at 18°C (Weigel, 1906, 1907). The oxide is reported by Seidell (1940) to be soluble to the extent of about 48 ppm Hg at 25°C and about 350 ppm Hg at 100°C. A possible mechanism for transport of the oxide by thermal water is indicated by these data. It is likely that mercuric ions are strongly adsorbed by minerals in hydrolyzates (Rankama and Sahama, 1950, p. 717) which prevents natural waters from carrying more than trace concentrations except under unusual circumstances.

ARSENIC

In rocks, arsenic is present in several forms, including the arsenides, as native arsenic in some mineral veins, and as oxides of arsenic. Arsenate (**AsO_4** ——) and arsenite (**AsO_2**) are anionic forms of arsenic. The former may replace phosphate in apatite. Arsenic is chemically related to phosphorus and the two elements have some traits in common.

In natural waters, trace quantities of arsenic may be fairly common. Although it is considered here as one of the heavy metals, arsenic in natural water is probably always present as an anion. Wastes from industry and mining activity, and residues from certain insecticides and herbicides, may constitute sources of arsenic in water. The U. S. Public Health Service drinking-water standards (1946) give a limit of 0.05 ppm of arsenic for potable water. However, concentrations up to 1.0 ppm in water apparently have had no serious effects when used for drinking, at least for short periods (California State Water Pollution Control Board, 1952, p. 185). Deaths among cattle as a result of drinking natural waters containing arsenic have been reported from New Zealand. There are local reports of similar deaths of cattle in the western United States, but presence of arsenic in the suspected water is not usually proved. About 20 mg of arsenic per pound of animal is a lethal dose.

Like phosphates, arsenates might affect the pH of water if they were present in large amounts, but it is unlikely that such an effect is important at the concentrations reached in natural water. Arsenic is reported as arsenate in waters from Steamboat Springs, Nevada in concentrations as high as 4 ppm $As0_4$ (analysis 1, table 13) and in minor amounts in other mineral wells and springs there and in other parts of the world, especially in Yellowstone Park (Clarke, 1924a).

Comprehensive data on natural occurrences of arsenic in water, however, are lacking.

SELENIUM

The element selenium is chemically similar to sulfur in a number of respects. In rocks, however, selenium is much less abundant than sulfur. Selenides often accompany sulfides in mineral veins. Selenium probably occurs in water in the fully oxidized state as the anion selenate (SeO_4^{--}), like sulfate. Selenium may be absorbed on hydroxide precipitates such as Fe $(OH)_3$ or on hydrolyzate sediments, and concentrations in natural water are normally very low.

Selenium is toxic in small quantities, and in some areas its presence in soils constitutes a problem in livestock management. Certain plants, particularly those of the genus *Astragalus*, take up selenium from the soil and concentrate it, sometimes to a level of over a thousand ppm in the dry plant. Animals grazing on such vegetation may take up enough selenium to suffer from chronic selenium poisoning or may even receive a lethal dose. The connection between selenium and the "alkali disease" or "blind staggers" of livestock was established by investigators of the South Dakota and Wyoming Agricultural Experiment Stations and by the U. S. Department of Agriculture in the early 1930's. Byers (1935, 1936) and his coworkers (Byers, and others, 1938; Lakin and Byers, 1941, 1948; Williams, Lakin and Byers, 1941) have issued a series of reports on the subject cf selenium in soils, water and vegetation, and data also have been published by Beath and others (1946), and by Knight and Beath (1937) which bear upon the occurrence of selenium.

From the work of the above investigators it has been established that selenium is most commonly found in rocks of Cretaceous age, especially shales, and in soils derived from them. The early investigations indicated that vegetation rather than water was the source of toxic quantities of selenium in such areas. Analyses of about a hundred samples of surface and ground water in the states of Colorado, Wyoming, Nebraska, and South Dakota indicated selenium concentrations in the waters sampled of less than 1 ppm Se in all cases, and generally much less (P. C. Benedict, Lincoln, Nebr., written communication). Analyses of samples from irrigation drains and other sources in the Grand Valley and adjacent area in Colorado in 1934 showed a selenium content somewhat over 1 ppm in some of the more highly mineralized water (analysis 6, table 13).

Selenium is believed to be highly toxic to man but limits for water based on factual data and experimentation are not yet established. The U. S. Public Health Service limit for potable water is given as 0.05 ppm (1946).

Quantities of selenium in water thus far found are small and the problem has been investigated largely because of the recurrent belief that certain waters may have dangerously large amounts for domestic or stock use. Theoretical solubility data for selenates (Handbook of Chemistry and Physics, 1953) indicate the amounts found in natural water are far below those theoretically possible. Adsorption or other factors not yet understood, as well as the relative scarcity of selenium in the rocks and soils, probably is important in maintaining observed low levels of selenium in natural waters. The established relationship of selenium to geology suggests the possible use of this constituent as a tracer to relate water and rock formations. However, the determination is complicated and time-consuming, and selenium is not readily carried in solution, so use of the element as a tracer is not particularly promising.

ALKALINE-EARTH METALS

Included in this group for the purposes of this discussion are calcium, magnesium, beryllium, strontium, and barium. The first two are important constituents of all waters and have already been discussed.

BERYLLIUM

Beryllium is a comparatively rare element. Although it is in the same group in the periodic chart of the elements as the alkaline earth metals, it has few properties in common with them. Beryllium replaces silica in the structure of some igneous rock minerals and is present as independent beryllium minerals in pegmatities. The most important of these is beryl, a double silicate of aluminum and beryllium (Rankama and Sahama, 1950, p. 444,445). In the weathering process, beryllium is concentrated in hydrolyzates, like aluminum, and does not go into solution to any appreciable degree. Beryllium is not likely to be found in natural waters in greater than trace amounts because of the relative insolubility of beryllium oxides and hydroxides at the normal **pH** range of such waters. The solubility of the oxide is reported as 0.07 to about 0.02 ppm in pure water at about 28°C (Remy, 1925). The sulfate and chloride of beryllium are very soluble, but would hydrolyze to lower the pll. In the presence of sodium hydroxide (high pH) the hydroxide is soluble (Seidell, 1940, p. 143). This probably results from the formation of anion complexes. The effects of other ions or cations on the solubility of beryllium are not known.

Some data on adsorption of trace quantities of beryllium in water by glass and plastic containers have been published by Thatcher and Singman (1954). These investigators found that at a pH of 3.5 there was no adsorption of beryllium by the container over a 3-month period. However, at pH 7 and 8 there was considerable adsorption. It is probable that adsorption of beryllium by naturally occurring minerals is an important cause of the low values in water, since such adsorption seems to proceed effectively at pH levels common in natural water.

Beryllium concentrations in the trace range may be important because of the high toxicity of this element. Exact tolerances, however, seem to be uncertain. Conceivably, beryllium could be added to waters by industrial waste disposal, although unless the water maintained a low pH, it seems unlikely that much would remain in solution.

STRONTIUM

Strontium is a typical alkaline-earth element, and both strontium and barium are similar chemically to calcium. Strontium is one of the most abundant minor constituents of igneous rock (table 1) and is important also in the carbonate sediments. Strontium can replace calcium or potassium in some of the common crystalline rock minerals, including feldspars, micas, apatite, pyroxenes, and amphiboles (Rankama and Sahama, 1950, p. 472-473). Data quoted by these authors (p. 476) indicate that strontium is more plentiful in syenitic and granitic rocks and occurs in very minute quantities if at all in ultrabasic rocks. Strontium sulfate (celestite) is a common component of carbonate sediments, and strontium may partly replace calcium in aragonite. Strontium carbonate (strontianite) also occurs. Kulp, Turekian and Boyd (1952) report a ratio of Sr : Ca of less than 1 : 1,000 in nearly all of a number of limestones, but that strontium is enriched in fossils.

Strontium is not often determined separately in the course of routine water analysis. The standard analytical procedures for calcium do not separate it from strontium. Any of the latter element present is reported as an equivalent amount of calcium. Strontium may be present in amounts up to a few parts per million much more frequently than the available literature indicates.

Strontium carbonate is dissolved in the weathering process by water containing carbon dioxide and can be carried in solution as bicarbonate in a manner analogous to calcium. At one atmosphere pressure of carbon dioxide Haehnel (1924) reported strontium carbonate soluble in water at 18° to the extent of 712 ppm Sr. If computed on the basis of equivalents per million, this is nearly the same solubility as shown in figure 9 for calcium with a similar condition of carbon dioxide pressure. In carbon dioxide-free water the solubility at 25°C is reported by Townley, Whitney and Felsing (1937) as 4.8 ppm Sr. When a sodium chloride solution of about 1,170 ppm was used in place of pure water, these investigators reported an increase of 40-percent in the solubility of strontium carbonate.

The solubility of strontium sulfate is much lower than that of calcium sulfate. Gallo (1935) reports the solubility of strontium sulfate in pure water at 20°C to be 132 mg per liter, equivalent to 63 ppm Sr and 69 ppm SO_4. Thus a solution containing more than 69 ppm SO_4 should, in theory, contain no more than 63 ppm Sr. However, the presence of certain other anions and cations such as Ca+ +, Na+, Cl , and NO,$^{-}$ is reported by the same investigator to increase the solubility of strontium sulfate. The solutions used were more concentrated than natural waters generally are.

Because so few determinations are available, little can be said concerning strontium concentrations in natural waters. Analysis 4, table 8 shows the presence of 2,730 ppm Sr in a chloride brine from Michigan. The sulfate concentration in this very highly mineralized water is 13 ppm. Alexander, Nusbaum, and MacDonald (1954) have published determinations they made for strontium in waters from 50 public supplies in the United States. None of the values they found were much over 1.0 ppm and most were much lower. Other analyses reporting Sr are scattered in the literature. Three wells in Waukesha, Wis. are reported to give water containing from 33 to 52 ppm of strontium. The water is not of unusual composition in other respects, and has from 336 to 506 ppm of dissolved solids (Lohr and Love, 1954). Strontium is present in sea water in about 1 : 30 the amount of calcium. In igneous rocks, however, the strontium to calcium ratio is 1 : 121 and in carbonate sediments about 1 : 670. It would appear, therefore, that in most natural waters the amount of strontium should be small in proportion to calcium. Abnormal concentrations of strontium in rocks associated with a water could, of course, give concentrations of strontium much more nearly equal to those of calcium, but such waters can hardly be common.

BARIUM

Barium is only slightly rarer than strontium in the earth's crust. Barium may replace potassium in some of the igneous rock minerals, especially feldspar. Barium sulfate (barite) is a common barium mineral of secondary origin. Barium is present in sea water in traces. In stream waters and most ground waters, only traces of the element are present.

The reason for the small amounts of barium in solution is the low solubility of barium sulfate. Because the usual natural water contains sulfate, barium will dissolve only in trace amounts. According to Kohlrausch (1908) barium sulfate is soluble in pure water at 20°C to the extent of 1.6 ppm of Ba and 1.1 ppm of SO_4. The solubility is reported by various investigators to be increased considerably by the presence of chloride and another anions and cations in dilute solutions. However, waters containing more than a few parts per million of sulfate cannot be expected to carry more than a few parts of barium.

Few data are available on the concentrations of barium in natural water. Barium sometimes occurs in brines, and analyses for a few of these from southern California are reported by Piper, Garrett, and others (1953). On the basis of the relative solubilities of the sulfates, it would seem likely that barium will usually be found in much smaller concentrations than strontium in natural water.

ALKALI METALS AND AMMONIUM

The alkali-metal group in the periodic system includes lithium, sodium, potassium, rubidium, and cesium. A sixth member of the group, francium, is an unstable disintegration product of actinium and need not be considered here. Sodium and potassium, which are major components of natural waters, have already been discussed. In addition to lithium, rubidium, and cesium, ammonium (NH_4^+) will be considered in this section, because it has some properties in common with the alkali metals.

LITHIUM

The element lithium is comparatively rare. It is concentrated in complex lithium minerals in granite and nepheline syenite pegmatites (Rankama and Sahama, 1950, p. 427), and may occur in deposits of evaporate sediments. It may partly replace magnesium in some of the dark-colored minerals of granitic rock, especially the micas.

Data concerning concentrations of lithium in water are scarce. It is not often determined in routine water analyses, but has been found to be present in waters of hot springs or highly mineralized brines, usually in amounts of less than 10 ppm. A concentration of 5 ppm is reported in water from Steamboat Springs, Nevada (analysis 1, table 13). Concentrations of 1 to 5 ppm may be more common in other areas than is generally supposed. Lithium is leached from rocks during the weathering process, and, because the simple compounds of lithium are readily soluble, they tend to remain in solution. The scarcity of lithium in rocks more than other factors probably is responsible for the relatively minor amounts of the element found in water.

Lithium should not be adsorbed or participate extensively in base-exchange reactions because all the common cations are reported to be able to dislodge lithium from base-exchange material (Kelley, 1948, p. 61). Any base-exchange reactions which might occur, therefore, should bring lithium into solution rather than remove it from solution.

RUBIDIUM

The element rubidium is about as abundant as strontium in igneous rocks (table 1). In these rocks it partly replaces potassium in some mineral structures such as the feldspars and micas, and minerals with fairly high concentrations of rubidium may occur in pegmatites. Rubidium is very seldom determined in water analyses. Rankama and Sahama (1950, p. 439) state that rubidium is commonly found in hydrothermal veins and in mineral waters of hot springs. Data available are not extensive enough to justify any definite statement as to concentration ranges, but rubidium in trace quantities may be a fairly common constituent of natural water.

Rubidium resembles potassium in its behavior in the weathering process. After removal from rocks through solution, it tends to be adsorbed by hydrolyzate sediments and soils. The difference in average concentration between sodium and potassium in water has been ascribed to the tendency of potassium to be adsorbed, and reconstituted in sedimentary minerals. Rubidium has an even greater tendency than potassium to be adsorbed (Rankama and Sahama, 1950, p. 440) and should therefore be present in water normally in amounts considerably smaller than potassium. The common rubidium salts are readily soluble in water, and concentrations in natural waters probably never reach saturation.

CESIUM

Cesium is a heavy alkali metal whose behavior in rocks and water is very similar to that of rubidium. It is much rarer than rubidium, however, and therefore should not be common in natural waters. As is the case with rubidium, there are very few data that could be used to give any indication of the normal distribution of cesium in water. It is found together with rubidium in minor amounts in the water from Owens Lake in California (Clarke, 1924a, p. 162), and in water of the ocean there are traces of both cesium and rubidium.

The tendency for cesium to be adsorbed by hydrolyzate sediments is doubtless a major factor in keeping its concentration in water at a low level, and since cesium is a decidedly rare element, it should not normally occur in water in quantities larger than traces.

AMMONIUM

Ammonia (NH_3) is a gas that is readily soluble in water to produce ammonium hydroxide NH_4OH. This substance is partly dissociated to give ammonium (NH_4^+) and hydroxyl ions. The nitrogen in this reduced state can be oxidized, especially with the aid of nitrifying bacteria, as mentioned in the discussion of nitrate. Ammonium ions may occur in surface waters or ground waters subject to direct pollution with organic waste products, but the nitrifying action generally converts the nitrogen from this state to free nitrogen or an oxidized form such as nitrate or nitrite.

The ammonium salts are volatile, and considerable quantities of ammonium ions can be contained in volcanic emanations and magmatic water. Water of hot springs may contain rather high concentrations of ammonium. Clarke (1924a, p. 198-200) quotes an analysis of a hot spring at Clear Lake, Calif. which shows 421 ppm of NH_4^+, and another for an acid water from Devils Inkpot in Yellowstone Park which shows 769 ppm of NH_4^+. In most waters only trace quantities of ammonium are likely to be found. Analysis 2, table 13 reports 543 ppm of NH_4^+ in an alkaline water from Sulfur Bank, Calif. and analysis 3 in that table reports 342 ppm in an acid water from Yellowstone.

Ammonium salts normally undergo hydrolysis in solution which tends to remove OH^- ions and to lower the pH. In most water the amounts present are very small and probably have no appreciable effect on the alkalinity. Where amounts of ammonium are large and carbonates are absent, the pH could be controlled by the ammonium hydrolysis, and would be in the acid range. Water containing both ammonia and ammonium ions may be buffered by this system. At pH levels in the normal alkaline range of natural water, ammpnium ions would easily be lost from solution by decomposing into gaseous ammonia. Waters containing both ammonium and carbonate ions could lose both carbon dioxide and ammonia when exposed to air at atmospheric pressure.

Ammonium ions are strongly adsorbed by natural exchange media. Adsorbed NH_4^+ in soils will probably be utilized by plants.

RADIOACTIVE COMPONENTS

The subject of radioactivity in water is too broad to be considered in detail in this report. Discussions of radioactivity which provide a basic exposition of principles and basic theories are included in books by Friedlander and Kennedy (1949) and by Glasstone (1950). A brief discussion of radioactivity in natural water has been prepared by Love (1950).

The property of radioactivity is the emission of radiant energy by the nuclei of certain atoms which disintegrate. This energy is given off in the form of alpha, beta, and gamma radiation. The alpha particles are positively charged helium nuclei. Beta rays are electrons, and gamma rays are electromagnetic waves of very short wavelength.

It has been known since the early years of the 20th century that some natural waters are radioactive. The radioactivity in water is the result of the presence of radioactive isotopes. For the most part, radioactive materials are dissolved ions, but a small amount of activity can be imparted by tritium (H) replacing normal hydrogen in some of the water molecules.

There exist in nature three isotopes of high atomic weight, *each* of which forms the starting point for a series of disintegrations which produce radioactivity. The disintegrations proceed in steps, each producing a different radioactive nuclide, until finally a non-radioactive isotope of lead is produced. These series begin with U^{288} (uranium series), Th^{232} (thorium series), and U^{235} (actinium series). Members of the first two series are responsible for most of the natural radioactivity in water. The actinium series is not very important as a source of radioactivity in water because natural uranium contains only a very small amount of the U^{285} isotope. A few other naturally occurring isotopes are radioactive—for example, K^{0} and Rb^{87}—but they constitute relatively small proportions of naturally occurring potassium and rubidium.

The alpha activity of water to date is essentially the result of disintegrations of nuclides in the naturally occurring radioactive series of elements. Isotopes of radium and radon are the most important alpha emitters. Beta and gamma activity also is evidenced by some of the members of these series, and also is characteristic of the naturally occurring isotopes K, and Rb^{87}. Many of the products of atomic fission are strong beta emitters. Sr^{89}, $Sr^{\circ\circ}$, I, Pu, Ca^{45}, and $Co^{6\circ}$ are among the artificially produced fission products having very high activity. Although these are absent from natural waters, they may be added in waste materials from atomic fission.

Measurements of the property of radioactivity in water are made by various types of instruments. The electroscope, which has been used by some investigators for this purpose, gives readings which may be standardized by the use of samples of known activity and thus referred to equivalent amounts of radium. Ionization chambers of various types are used in measurement of certain types of activity, especially that due to radon. Geiger-Müller tubes and scintillation tubes with electronic scaling circuits are used in measuring all three types of radiation.

Many of the published data report activity in terms of number of disintegrations observed per unit time. Data expressed in these terms are essentially qualitative. Any quantitative interpretation requires knowledge of amounts of sample used, counter efficiency, and various details of the conditions of measurement. To standardize these data and make comparison possible, radioactivity of water is usually expressed in terms of an equivalent quantity of radium or in terms of the rate of radioactive disintegration (curies). One curie is defined as 3.7 X 10 disintegrations per second, the approximate specific activity of a gram of radium in equilibrium with its disintegration products. This unit is very large for the purposes of studying the minute amounts of natural radioactivity occurring in water, and data are therefore often expressed in micromicrocuries (C × 10^{-12}) or something near this order of magnitude. Other units occasionally used include the Rutherford (2.7 X 10 curies), the Eman (1 X 10^{-10} curies per liter) and the Mache unit (3.6 X 10 ^{0} curies per liter).

Measurements of radioactivity in water may take the form of an assay of total activity not differentiated as to alpha, beta, and gamma, or separate assays of total alpha and total beta gamma activity. The measurements may be further refined to report activity due to a particular element or isotope in terms of curies, or they may report weight concentration of individual elements or isotopes contributing to the activity.

The Geological Survey has begun some studies of naturally occurring radioactive substances in water. These studies include determinations of gross beta-gamma activity in micromicrocuries per liter, radium in micromicrocuries per liter, and uranium in micrograms per liter.

At the present writing (1955) this work has not progressed far enough to permit statements regarding radioactive components as detailed as those for other constituents of water. The brief discussion here is mostly confined to what can be stated at present regarding the occurrence of uranium and decomposition products in the uranium series in natural waters. There are many published data on radioactivity of natural water in various parts of the world. Among the more recent is a compilation by Kuroda (1953) and studies of public supplies by Hursh (1954).

URANIUM

Natural uranium is composed of several isotopes of which U^{238} predominates. As previously mentioned, this is the starting point in a radioactive decay series which ends with the lead isotope Pb. The half life of U^{238} is very long (4.5 × 10° years), and it is not strongly radioactive. In the amounts in which it is normally found in water, it is best detected by chemical means.

Uranium is widely distributed in igneous rocks. It is present in much the largest amounts in the sodic granites and decreases as the proportion of ferromagnesian minerals increases, reaching a minimum in the ultrabasic rocks (Faul, 1954, p. 77). In sedimentary rocks uranium may occur as adsorbed ions, or be included in the cementing material of sandstones. It also seems to be deposited where organic matter has caused locally favorable conditions in the sediments.

Uranium may occur as $U^{4}+$ ions under reducing conditions, and these ions are soluble in water of low pH. In natural water, however, the uranium is usually hexavalent and may be present as uranyl (UO_2++) ions. At high pH levels, it may act as an anion and be present as uranate. Various complex anions and cations containing the uranyl group may occur under some conditions. The most important of these are carbonate anionic complexes (Bullwinkel, 1954) and sulfate complexes. The uranyl salts are nearly all readily soluble in water and are the ones to be expected in the presence of air. The rather high solubility of uranium and its readiness to form soluble complex ions are characteristics of considerable importance, which tend to disseminate the element widely.

Uranium is present in trace quantities in most natural waters. Concentrations in excess of 10 micrograms per liter (0.01 ppm), however, appear to be unusual, so far as is known at the time of writing. Higher concentrations are found in waters associated with disseminated uranium in sedimentary formations.

RADIUM

There are four naturally occurring isotopes of radium, Ra^{228}, Ra224, Ra226, and Ra^{228}. Two of these, Ra^{228} and Ra^{224}, are disintegration products of thorium, Ra is a disintegration product of U^{288}, and Ra^{223} is a disintegration product of U^{285}. Ra has a half life of some 1,600 years, much longer than any of the others. Probably the Ra^{226} isotope is the most common in natural water. All the radium isotopes are strongly radioactive. They can be determined in extremely small quantity by radiochemical procedures.

Radium is a member of the alkaline-earth group of elements. It has some points of chemical similarity to barium. The sulfate is almost insoluble in water. Although radium is produced by the disintegration of U^{238}, there is plenty of opportunity for the radium to be separated from the uranium. The different characteristics of the two elements with respect to solution in water aids this separation. It is not to be expected that many natural waters would contain equilibrium concentrations of the two elements. The chemical conditions in the waters and their environments that facilitate separation are not yet fully known. However, it appears that most natural waters should be better solvents for uranium than for radium.

The concentration of radium in most waters is far less than that of uranium, and generally is below 1 micromicrocurie per liter. Concentrations exceeding 9,000 micromicrocuries per liter have been reported for certain springs in the United States (Love, 1950) and still higher concentrations have been reported for waters in other countries. It seems possible, however, that some of these data were obtained by methods that did not distinguish between radium and radon (Stehney, 1955), and they should be discounted to some extent.

The maximum permissible concentration in drinking water is given by the National Bureau of Standards (1953) as 40 micromicrocuries per liter. Earlier suggestions as to this limit usually gave a considerably higher figure.

RADON

Radium$^{\text{[illegible]}}$ decays to radon^{222}. This element is a noble gas and is highly radioactive. It has a half life of less than 4 days; consequently, it reaches equilibrium with its parent rather rapidly. Radon is soluble in water to some extent. It is present in detectable amounts in rainwater, and in certain springs and underground waters rather large amounts may be present. Waters carry radon much more readily than they do radium, and thus a greater than equilibrium amount of radon may often be present. This radon decays and the radioactivity of the water decreases rapidly from the time the water leaves the point where the radon was added. Radon concentrations are best measured soon after sample collection. Kuroda and Yokoyama (1954) report the use of a field-type electroscope for study of short-lived radioactive isotopes in water. Others (Rogers, 1954) have utilized a conventional ionization-chamber system with a sensitive electrometer designed to be semiportable, which could be taken from place to place in a truck and used near the sampling area.

Radon^{220} (thoron) is produced in the radioactive disintegration series of thorium. This isotope may be fairly common in water but has a short half life (54.5 sec.)

THORIUM

According to data in table 1, thorium is much more plentiful in rocks than uranium. The two elements may occur together in some minerals such as the double oxide, thorianite. Their chemical behavior in the weathering process is not the same, however. Thorium tends to accumulate in the hydrolyzate sediments. At the pH levels of natural water, the concentration of thorium is probably controlled by the solubility of thorium hydroxide which is extremely low.

No methods suitable for routine determination of thorium in the concentrations that would be expected in water have yet been available. It is not possible, therefore, to make any statement regarding the amounts that may occur.

TRACE OR MINOR CONSTITUENTS-ANIONS

The amphoteric heavy metals and a few other ions already discussed as minor constituents may appear in water as anions under certain conditions. The only remaining anions that occur frequently enough to merit discussion are the heavier halogens, bromide and iodide, and the incompletely oxidized forms of sulfur.

BROMIDE

Igneous rocks contain only traces of the element bromine, but commercially important amounts of bromide salts occur in certain brines and evaporate beds. Compounds containing bromine are generally readily soluble in water; hence bromide resembles chloride in that it tends to be concentrated in sea water. The data available as to bromide concentration in natural water, however, are rather meager. The higher levels occur in brines where large amounts of chloride also are present. Some of the waters of this type whose analyses are quoted by Clarke (1924a) contain over 100 ppm of bromide. Analysis 4, table 8 represents a brine from which bromine is extracted commercially. It contains 2,920 ppm of bromide. Sea water contains-65 ppm of bromide (table 2). Probably trace amounts of bromide are of frequent occurrence in natural waters. They are included with chloride in the usual titration procedure and reported as chloride. Separate determination of bromide may be useful in establishing the relationship of one water to another, or to a source of salinity. The procedures for determination of bromide ion are somewhat less accurate at low levels of concentration than those for chloride. Bromide concentrations were used in studies of California ground waters to differentiate between sources of salinity (Piper, Garrett, and others, 1953, p. 91-92).

IODIDE

Iodine is considerably less abundant both in rocks and water than bromine. Both are found to some extent in soils, and iodine in particular is an essential trace element in nutrition of the higher animals. Iodide occurs in sea water to the extent of less than 1 ppm. Rankama and Sahama (1950, p. 769) report that a mineral water on the island of Java contains 150 ppm of iodide. Analysis 4, table 8 reports 26 ppm of iodide in a Michigan brine.

Iodide is apparently adsorbed more readily in the hydrolyzate sediments than bromide and also may be taken up by plants. Also, iodine is a less abundant element than bromine. These factors probably explain the relatively minor amounts of iodide present in most natural waters.

Rankama and Sahama (1950, p. 767) report iodide present in rainwater to the extent of 0.001 to 0.003 ppm and in river water in about the same amount. Goldschmidt (1954, p. 608-609) expressed the opinion that airborne iodide from the ocean is important in supplying the ion to water and soil. However, a content of 0.001 ppm of iodide in rainwater would require about 20 ppm of chloride to be present also if the relative proportions are to be held the same in the rain as they would be in the ocean. The amounts of chloride actually present in rain water already have been indicated probably to be in the 0.2 to 2.0 ppm range, which casts doubt on any possibility of the reported amounts of iodide in rainwater being a direct contribution from the ocean in inland areas. Data on amounts of iodide in water probably have a limited value in tracing sources of water. The concentration of iodide in water can be determined accurately by usual methods in the range of 0.02 to 2 ppm. Few waters will be found to contain much over 2 ppm.

SULFITE AND THIOSULFATE

A very few natural waters are known which contain sulfur in the form S++++ as sulfite or S++ as thiosulfate. Analysis 1, table 13 reports a small amount of thiosulfate in water from Steamboat Springs, Nevada. The occurrence of such anions is to be expected only where rather strong reducing conditions prevail, or where sulfide-bearing waters come into contact with air.

TOTAL DISSOLVED SOLIDS-COMPUTED

The measurement of total dissolved mineral matter in water by evaporating an aliquot to dryness and weighing the residue has been discussed. The specific conductance of a water provides another measure of the content of dissolved matter. An approximate measurement of dissolved solids can be obtained by determining the specific gravity. A fourth procedure for measuring dissolved solids consists of adding together the concentrations separately determined for all the anions and cations in the water. This computed value is possibly a more useful indication of total dissolved solids for certain types of water than is the residue on evaporation. However, in order to obtain a reasonably accurate value, a rather complete analysis is required.

CHEMISTRY OF DISSOLVED SOLIDS DETERMINATION

In developing standard procedures for computing the sum of dissolved constituents, the assumption has generally been made that this figure will be used either as a substitute for determined residue on evaporation or as a means of checking the analysis by comparison with results for that determination. In the determination of residue on evaporation the bicarbonates present are presumably converted to the carbonate form by heating. Therefore, the bicarbonate reported in the analysis is converted by computation (multiplying by 0.4917) to an equivalent amount of carbonate, and the carbonate figure is used in the computation of the sum. A value is thus obtained representing dry residue rather than the actual material in solution. The assumption that alkalinity represents only HCO_3 and CO_3 $^{--}$ ions is inherent in this computation. It has been pointed out that this assumption is not always correct, but that it is not far from correct as applied to most natural waters.

In those instances where the residue on evaporation may include water of crystallization, the computed dissolved solids may be a better value to use. Waters which on evaporation deposit gypsum are a good example. Even though the water of crystallization should in theory be fully removed from gypsum crystals by heating at 180°C, the residue on evaporation of such a water may exceed the computed dissolved solids by 100 ppm or more, owing to retention of water. Some waters may leave a residue that is unstable at the drying temperature—for example, waters containing magnesium along with chloride and nitrate in considerable amounts. The residue on evaporation may give a figure considerably lower than the sum for these waters, owing to decomposition of magnesium salts at the drying temperature. Some waters deposit a hygroscopic residue that is very difficult to weigh accurately. As a general rule of thumb, the computed dissolved solids are more reliable than the determined residue on evaporation for concentrations above 1,000 ppm.

In computing the dissolved solids, all the determined anions and cations are included as well as the components reported in terms of the element, such as iron and boron. Free acidity, however, is not included. Inclusion of elements and oxides whose state in solution is not known introduces some possibility of error. A part of the silica, for example, may have been titrated in the alkalinity determination and reported in terms of equivalent bicarbonate. Such errors will usually be small.

The computed dissolved solids is generally used in comparison with. the residue on evaporation as a check on the accuracy of the analysis. The computed dissolved solids will usually be slightly lower than the residue on evaporation. A difference in either direction of 10 to 20 ppm in waters containing 100 to 500 ppm of dissolved solids and a somewhat greater difference at higher concentrations can be anticipated as normal. Obviously, only gross errors in major constituents can be detected by this comparison.

ACCURACY AND REPRODUCIBILITY OF RESULTS

Because the sum contains the algebraic sum of all experimental errors, results on duplicate samples could differ by as much as 5 percent, and differences of this order of magnitude can be ignored in. interpretive work.

DISSOLVED GASES

Natural waters invariably contain dissolved gases as well as dissolved solids. The commonest dissolved gases include oxygen, nitrogen, carbon dioxide, hydrogen sulfide, methane, oxides of nitrogen, sulfur dioxide, and ammonia. Some of these gases are derived from the atmosphere and others may come from decaying organic matter, gaseous pollution of the air resulting from industrial or other operations, or the gases issuing from the earth in volcanic regions. Oil-field waters may contain large amounts of dissolved carbon dioxide, and hydrogen sulfide resulting from the reduction of sulfate. Chlorine gas in small amounts is often added in water treatment to destroy bacteria. An important source of dissolved oxygen and carbon dioxide is the metabolism of aquatic plants and animals.

The solubility of a gas in water varies inversely with temperature and directly with pressure. The solubility of gases is somewhat reduced by the presence of dissolved mineral matter, but this effect is not very important in the concentration range of most natural waters. High pressure existing far below the surface of the earth may permit larger amounts of gases to remain in solution in deep-seated waters underground than can long remain in such waters after they reach the surface. For the more common gases, the amounts which a water exposed to the atmosphere at normal temperatures may contain is small. Oxygen, for example, is usually present in amounts of 10 ppm or less in unpolluted surface waters.

Dissolved oxygen in surface water is necessary for the support of aquatic life, which in turn is necessary for the removal of organic pollution. Dissolved oxygen also is of significance in evaluating the corrosiveness of the water. Oxygen may also play an important role in the oxidation of inorganic components, as in the alteration of ferrous to ferric iron. The determination of dissolved oxygen is an essential part of sanitary analyses or in studies involving corrosiveness of water.

The other gases mentioned above (except nitrogen and methane) have a considerable effect on the solvent power of waters in which they are dissolved. Solutions of ammonia have a basic reaction and those of carbon dioxide and hydrogen sulfide are weakly acidic. The importance of carbon dioxide in the solution of carbonate rock and in stabilizing the pH of waters have already been discussed. Waters containing much sulfur dioxide or oxides of nitrogen may be rather strongly acidic. These gases occur in minute amounts in rainwater, but strong solutions of them are rarely found in nature.

Routine chemical analyses generally omit the determination of gases that do not ionize in solution. Determinations are made for hydrogen sulfide when the amount present is important. A strong odor is imparted by less than 1 ppm of H2S in water. Rarely water may contain much H2S and some dissociated HS^- ions. Amounts of carbon dioxide present can be computed on a theoretical basis when pH and titrated alkalinities are known. This computation involves some assumptions and is of questionable value for many waters, especially those of high dissolved-solids concentration.

Presence of several hundred ppm of carbon dioxide in water is not particularly uncommon. Most of the gases, however, are generally present in minor amounts.

BIOCHEMICAL OXYGEN DEMAND

In the so-called sanitary analysis or in analyses of wastes to be discharged to streams, a determination of biochemical oxygen demand (BOD) is usually included. This determination is a measure of the amount of oxygen required to remove organic matter from the water in the process of decomposition by aerobic bacteria. This determination has limited significance in mineral analyses of water and is not ordinarily made in Geological Survey laboratories. It provides an index of the degree of organic pollution of water.

HARDNESS

The concept of hardness as an evaluation of certain properties of water has become deeply imbedded in the literature of water analysis and in the habits of thought of almost everyone who is concerned with water quality. In spite of this wide usage, the property of hardness is difficult to define, or rather there are conflicting definitions in general use.

The terms "hard" and "soft" are contained in a discourse on water quality by Hippocrates (460-354 B. C.) quoted as follows by Baker (1949) : "Consider the waters which the inhabitants use, whether they be marshy and soft, or hard and running from elevated and rocky situations . . ." The use of the terms here implies a relation to the source of the water, which may have had local validity. Over the years, the property of hardness has generally been associated with the effects observed in the use of soap, or with the incrustations left by some types of water when they are heated. If the reactions with soap are the only ones included, one might say that hardness represents the soap-consuming power of a water. This results from the presence of cations which form insoluble compounds with soap. For over 100 years the hardness of waters has been measured by titration with standard soap solutions.

Because most of the effect observed with soap results from the presence of calcium and magnesium, hardness has been defined by some authorities in terms of these constituents alone (American Society for Testing Materials, 1954, p. 356). However, if the property of hardness is considered to be related to action with soap, this definition is not complete. Free acid, heavy metals and other alkaline earths yield insoluble products when they react with soap.

The constituents causing hardness may also contribute to incrustation but silica is an important part of the incrustants in many waters. Silica does not contribute to hardness.

Because hardness is a property not strictly allocable to any one constituent, a conventional procedure has been adopted for reporting hardness data in terms of an equivalent quantity of calcium carbonate. Total hardness supposedly represents the effects of all the substances which react with soap. Calcium, magnesium hardness, on the other hand, represents values computed from reported concentrations of these two cations alone. In much of the literature of water analysis, these terms are used interchangeably. The usual methods for calcium and magnesium, it is true, will not give separate values for other alkaline earths which may be present, but will include their effects as equivalent quantities of the reported calcium and magnesium. Consequently, calcium, magnesium hardness values are generally equivalent to the hardness due to all alkaline earth metals.

Carbonate hardness where reported includes that portion of the hardness which is equivalent to the carbonate and bicarbonate present in the water. Any hardness in excess of this amount is called noncarbonate hardness. The terms "carbonate" and "noncarbonate" have largely supplanted the terms "temporary" and "permanent" which formerly were used to describe these subdivisions of hardness.

Hardness values are reported in analyses made by the Geological Survey and most other laboratories in the United States in parts per million. However, some laboratories still report hardness as calcium carbonate in grains per United States gallon, and many old analyses are expressed in these terms. Analyses made in some European countries report hardness in "degrees" based on various systems. One French degree is equivalent to 10 ppm, one German degree is equivalent to 17.8 ppm, and one English or Clark degree is equivalent to 14.3 ppm, all in terms of calcium carbonate.

The soap procedure for determining hardness is being replaced to a large extent by the chelation procedure using the disodium salt of ethylenediaminetetraacetic acid. The latter procedure gives, in effect, the hardness due to alkaline earth metals, and a redefinition of hardness on this basis might be desirable. The property, however, cannot be considered a chemical entity. Although hardness data will continue to be valuable to the water user, they do not provide a good basis for evaluating the chemical properties of water.

UTILIZATION

Although one wishing to interpret water analyses in terms of hydrology or geology will find hardness data to have a limited value, a great deal of information on hardness of waters is available, because the determination is included as a part of most chemical analyses of water. For some interpretive purposes these data can be utilized by assuming that they represent the amount of calcium and magnesium present. Separate values for these two components are usually preferable if chemical resemblances of waters to one another are being studied, because the Ca: Mg ratio provides helpful information in many instances. However, a determination of hardness and determination of the principal anions will provide information sufficient for a computation of sodium, and analyses of this type may be highly useful as supplements to more complete chemical analyses.

RANGE OF CONCENTRATION

The adjectives "hard" and "soft" applied to water have an inherent lack of scientific exactness, an a number of writers have attempted to set up gradations of the terms based on part-per-million values of hardness. The value of such classifications is open to question because the connotations of the terms to different individuals may be quite different. A resident of New England or some other area where waters are normally low in dissolved solids might consider a water having a hardness of 100 ppm as "very hard," whereas water of the same level of hardness in Iowa or Illinois or New Mexico might be described by local residents as "soft."

Hardness of water to be used for ordinary domestic purposes does not become particularly objectionable until it reaches the level of 100 ppm or so. Hardness can greatly exceed this level, and in many places—especially where waters have come in contact with limestone or gypsum—few natural waters will be found to have a hardness of much less than 200 or 300 ppm. At these levels, hardness is decidedly noticeable and becomes increasingly troublesome as the concentration rises. In gypsiferous waters, hardness over 1,000 ppm is not uncommon.

Authors who discuss water analyses should avoid such terms as "moderately hard" in speaking of waters unless they make it abundantly clear to the reader what is meant by the term.

ACCURACY AND REPRODUCIBILITY OF RESULTS

Hardness was formerly determined by titration with standard soap solution. This procedure always left something to be desired so far as accuracy was concerned, and a good analyst could seldom check his results on duplicate samples with an error of less than 10 percent. Differences in soap-hardness values of this magnitude therefore should be considered insignificant. In recent years the ethylenediaminetetraacetic acid titration for hardness has largely supplanted the soap method and is much more dependable. This titration can be expected to give agreement on duplicate samples within about 5 percent.

PERCENT SODIUM

For the past 20 or 25 years a value for percent sodium has commonly been reported in chemical analyses of irrigation waters. The importance of sodium salts in causing alkali soils and the undesirable characteristics of such soils had been known for many years before that time. Gedroiz (1912) first pointed out the importance of base exchange in arid alkali soils. Those soils which have taken up sodium in exchange for calcium or magnesium are impaired in tilth and permeability.

When a soil containing exchangeable Ca^{++} and Mg^{++} ions is irrigated with water in which Na^+ greatly outnumbers other cations, the calcium and magnesium of the soil will tend to be replaced with sodium. If the irrigation is continued long enough, the soil may develop the undesirable properties mentioned above.

The extent to which an irrigation water might promote the loss of exchangeable Ca^{++} and Mg^{++} from the soil can be approximately predicted, on the basis of the sodium percentage and the total concentration of dissolved solids (Wilcox, 1948). The effect does not become important until the sodium percentage rises considerably above 50 because the soil exchange complex retains the bivalent ions preferentially. This effect is overcome as the relative abundance of sodium ions available for exchange increases.

SODIUM-ADSORPTION RATIO

In a recent discussion of the quality of irrigation waters and related topics issued by the U. S. Department of Agriculture (U. S. Salinity lab staff, 1954) a revised form of the sodium-percentage concept has been suggested, which involves computation of the "sodium-adsorption ratio" or "SAR." The ratio is determined by the following relation where ion concentrations are expressed in epm :

$$\text{SAR} = \frac{\text{Na}^+}{\sqrt{\frac{\text{Ca}^{++}+\text{Mg}^{++}}{2}}}$$

$$= \text{Na}^+ \frac{1}{\sqrt{\frac{\text{Ca}^{++}+\text{Mg}^{++}}{2}}}$$

The SAR value for a water is simply related to the experimentally determined adsorption of sodium by soil to which the water is added. As a means of estimating the possible results of using a water for irrigation, the SAR value therefore is more directly significant than the percent sodium.

In figure 43 which is modeled after a similar diagram developed by the U. S. Salinity laboratory (1954) a system of rating irrigation waters based on dissolved solids and SAR is given. It should be kept in mind that the SAR value is more or less empirical and of significance only in considering base-exchange reactions in soils and evaluation of irrigation waters. The percent-sodium value is useful in plotting analyses according to various systems described elsewhere in this report. It is useful also in direct comparisons of analytical data on various sources of water.

Percent-sodium values are generally computed from the sodium and total-cation concentrations, the latter including potassium. The literature on the subject of potassium in irrigation waters appears to indicate that adsorbed potassium in soils is not undesirable. Values for sodium alone are therefore preferable to computed Na K values in this computation. The SAR concept appears to ignore the effect of potassium. For most waters, the amount of potassium present is minor and probably is seldom significant.

DENSITY

The relationship between parts per million by weight and milligrams per liter in expressing analytical results has already been discussed and it has been pointed out that for practical purposes, the two systems are equivalent except for highly mineralized waters. In the laboratories of the Geological Survey, equivalence is assumed only for waters having a specific conductance below 10,000 micromhos. Above this concentration, the density of the water is determined and is reported with the analysis. The density value is chiefly useful in computing the weights of volumes of samples used in the laboratory determinations, so that correct parts per million values can be computed. For brines, however, the density may provide a useful measure of their concentration, and one that is easily applied either in the laboratory or in the field.

ORGANIZATION AND STUDY OF WATER-ANALYSIS DATA

To this point the report has been concerned with individual chemical analyses of water and the determinations which go to make up the analysis. In broad interpretation of water-quality data, the analyses must be correlated with one another and with related information.

The techniques for doing this range from brief inspection to careful statistical analysis of the data, and can include preparation of maps and graphs and other techniques to relate the chemical-quality data to other hydrologic factors.

EVALUATION OF WATER ANALYSES

Chemical analyses which indicate the quality of water in an area being studied usually are obtainable from several sources. For some areas, considerable published data from earlier studies may be available. There may also be unpublished analyses from various sources including Federal laboratories, State laboratories, waterworks laboratories, State health departments, commercial laboratories, and others. Generally, it is necessary to supplement these data by collecting additional samples for analysis. A first step in data interpretation is the evaluation of the available data, with respect to their completeness and their accuracy and reliability.

For surface-water sources, a long period of record is usually required to define accurately the continually changing quality of the water. Single samples from such sources have only a limited value. On the other hand, a single sample from a ground-water source may represent closely the quality of water from that source for many years. Resampling should be done, however, and some check determinations should be made before existing data relating to ground-water quality are accepted as representing present conditions.

Analyses made by organizations, the quality of whose work is not known, should be scrutinized carefully to ascertain their reliability for the use to be made of them. In some instances, the original accuracy requirement for an analysis may have been low because the use that was made of the data did not require a high order of accuracy. Such an analysis, even though adequate for its original purpose, is not suitable for use in hydrologic studies, especially if small differences between analyses will be used to distinguish between sources of water, or to reach some other significant conclusion.

The best indication of the reliability of a water analysis is first-hand knowledge of the accuracy standards of the organization that made the analysis. The analyses made by the Geological Survey are expected to be used for widely varying purposes, and standards of accuracy are observed which are satisfactory for most uses of the data. Most of the other organizations that publish data for general use observe similar standards.

The accuracy of a complete chemical analysis can be checked by several different procedures. When all the important anions and cations have been determined, the sum of the cations in equivalents per million should, for most types of water, be about equal to the sum of the anions expressed in the same terms. The difference between the two sums should not be greater than 1 percent of the total of anions and cations for the best work, although in waters where the total of anions and cations is less than about 5.00 epm larger percentage errors are sometimes unavoidable. If the analysis is found acceptable on the basis of this check, it can be assumed that the errors in the individual determinations will be of the order of magnitude indicated in the foregoing section of this report dealing with individual constituents.

The concept of equivalence of total cations to total anions in routine analytical work is based on several assumptions which should be considered. The first of these is that the water does not contain undetermined cations or anions in amounts large enough to affect the totals significantly. Some waters that are highly colored may contain organic anions which are not determined, and such waters may consistently fail to reach a cation-anion balance. In such instances, the values for constituents reported may be completely accurate, but the apparent error shows that something has not been determined. Waters containing large amounts of inorganic substances that are not usually determined could show the same effect, but such waters are rare.

The second assumption made in arriving at the cation-anion balance is that all anions participating in the hydrolysis which causes alkalinity are titrated by lowering the pH to 4.5. This is probably correct for nearly all alkaline waters. For acid waters, the parallel assumption would be that the titration of acidity measures all the effects of hydrolysis of cations. Unfortunately, this assumption does not always hold true. However, reporting the total amount of such cations in terms of equivalents per million cannot be expected to result in cation-anion balance either, because part of the determined amounts will represent undissociated molecules or colloidal particles. Acid waters also may contain ions that are not looked for and hence not determined. A lack of cation-anion balance for waters containing much iron and manganese and having a low pH is almost unavoidable.

Many analyses report a computed value for sodium or sodium plus potassium. These values are based on assumptions discussed earlier and contain the algebraic sum of any errors or omissions in the entire analysis. Analysis tabulations may not indicate whether the reported values for sodium were calculated or determined, but exact or near exact agreement between the sums of equivalents per million values for cations and anions for all the analyses in any array of data suggests strongly that sodium values were calculated.

Analyses where sodium values are calculated cannot be closely checked, although gross errors may sometimes be detected. The values for dissolved solids (sum) and residue on evaporation should agree within a few parts per million unless the water is of exceptional composition, as noted in the discussion of these values on page 143. If the sum of dissolved constituents is not reported, it can be computed so that this check can be made.

An approximate check is possible on the basis of conductivity and dissolved solids. The dissolved-solids value in ppm should be from 0.55 to 0.75 times the specific conductance in micromhos for waters of ordinary composition. Waters containing mostly bicarbonates or chlorides will have a factor near the lower end of the range. Sulfate waters will approach or exceed the upper end, especially waters affected by solution of gypsum, and highly siliceous waters also may have a high factor. The total of equivalents per million of anions (or cations) multiplied by 100 usually gives approximately the conductivity in micromhos. This relationship is not very exact but is somewhat less variable than the relationship of conductivity to dissolved solids in parts per million. The relationship of dissolved solids to conductance becomes indefinite for waters very high in dissolved solids (over about 30,000 ppm) and is not useful as a check of accuracy for analyses of such waters.

Analyses reporting zero concentrations for sodium or reporting values "less than"- a round number for sodium probably contain some analytical error which caused the total equivalents per million of cations to exceed the total for anions. Analyses reporting zero values for some other common major constituents also may be looked upon with suspicion, especially such combinations as zero calcium when some magnesium is present, or zero chloride except in very dilute water.

A concentration of 0 reported in a chemical analysis should be interpreted to mean that the amount present was less than 0.5 ppm and that better than one-place accuracy could not be obtained. A concentration of 0.0 implies two-place accuracy and a concentration of less than 0.05. These values of course do not mean complete absence of the constituent. Evaluation for probable accuracy should be made by a chemist experienced in water analysis.

Many analysts tend to report their data to 4 or 5 significant figures when only 2 or 3 are really justified. The discussions of accuracy of the various determinations give an idea of the number of significant figures that are meaningful.

TABULATION

For publication, water analyses are generally presented in tabular form. The tables should include all the analytical data and pertinent information regarding sample sources. The user of the data should be able to obtain from the tables and accompanying text all the pertinent information that was available to the author of the report.

Even in those reports that make extensive interpretations of the analyses, the reader is entitled to see the factual data for himself so that he can make any other interpretation he wishes. Placing the facts before the reader also provides a means of evaluating the soundness of the author's conclusions.

TABLE 14.—*Arrangement of chemical and related data in reports for transmittal and publication by Geological Survey*

- **Field Data**
  - **Date of collection**
  - **Time of collection**
  - **Gage height** — **Modify for reporting ground-water data**
  - **Water discharge (cfs)**
  - **Water temperature (°F)**
  - **Other climatological data**
- **Silica (SiO_2)**
- **Cations—Heavy metal ions**
  - **Aluminum (Al)**
  - **Iron (Fe), ferrous**
  - **Iron (Fe), ferric**
  - **Iron (Fe), total dissolved**
  - **Iron (Fe), (without qualifying statement, refers to iron in solution when sample collected)**
  - **Iron (Fe), in solution at time of analysis**
  - **Iron (Fe), total (All forms of soluble iron plus iron extracted from suspended materials (turbid samples) with acid.)**
  - **Manganese (Mn), (without qualifying statement, refers to Mn in solution when sample collected)**
  - **Manganese (Mn), in solution when analyzed**
  - **Manganese (Mn), total (See total iron.)**
  - **Titanium (Ti)**
  - **Chromium (Cr), trivalent**
  - **Chromium (Cr), hexavalent**
  - **Chromium (Cr). (total dissolved)**
  - **Nickel (Ni)**
  - **Copper (Cu)**
  - **Tin (Sn)**
  - **Lead (Pb)**
  - **Zinc (Zn)**
  - **Cobalt (Co)**
  - **Arsenic (As)**
  - **Selenium (Se)**
  - **Cadmium (Cd)**
  - **Antimony (Sb)**
- **Cations—Alkali earths and metals**
  - **Calcium (Ca)**
  - **Magnesium (Mg)**
  - **Strontium (Sr)** — **Earths**
  - **Barium (Ba)**
  - **Beryllium (Be)**
  - **Sodium (Na)**
  - **Potassium (K)** — **Metals**
  - **Lithium (Li)**
  - **Ammonia nitrogen as NH_4**
  - **Free acidity (H^+) (calculated to pH 4.5)**
- **Anions**
  - **Bicarbonate (HCO_3)**
  - **Carbonate (CO_3)**
  - **Hydroxide (OH)**
  - **Sulfite (SO_3)**
  - **Sulfate (SO_4)**
  - **Chloride (Cl)**
  - **Fluoride (F)**
  - **Bromide (Br)**
  - **Iodide (I)**
  - **Nitrite (NO_2)**
  - **Nitrate (NO_3)**
  - **Nitrogen (N), total dissolved**
  - **Orthophosphate (PO_4)**
  - **Phosphorus as PO_4**
  - **Cyanides as (CN)**
  - **Boron (B)**
- **Organic, nonionic, and calculated values**
  - **Phenolic material as C_6H_5OH**
  - **Oils and waxes**
  - **Organic matter (For example: humates, nitrobodies, detergents, weed sprays, and Insecticides)**
  - **Total solids (Dissolved and suspended)**
  - **Loss on ignition**
  - **Dissolved solids**
    - **Calculated**
      - **ppm**
      - **Tons per acre foot**
      - **Tons per day**
    - **Residue on evaporation at 180°C**
      - *ppm*
      - **Tons per acre foot**
      - **Tons per day**

TABLE 14.—*Arrangement of chemical and related data in reports for transmittal and publication by Geological Survey—Continued*

- Organic, nonionic, and calculated values—Continued
  - Suspended solids at 110°C
  - Hardness as $CaCO_3$
  - Noncarbonate hardness as $CaCO_3$
  - Alkalinity as $CaCO_3$
  - Saturation index (Langelier)
  - Immediate acidity (H^+) pH 7.0
  - Potential free acidity (H^+) pH 7.0
  - Total acidity (H^+) pH 7.0
  - Percent sodium
  - Sodium adsorption ratio
- Other data
  - Specific conductance (micromhos at 25 C)
  - pH
  - Color
  - Turbidity
  - Density at 20°C
  - Viscosity (centipoises at 20°C)
- Biochemical, dissolved gases, and related measurements
  - Odor
  - Biochemical oxygen demand
  - Dissolved oxygen
    - Percent saturation
  - Oxygen consumed
  - Free carbon dioxide (CO_2)
  - Sulfides as H_2
  - Chlorine (Cl_2)
- Radioactivity
  - Total alpha activity, micromicrocuries per liter
  - Total beta+gamma activity, micromicrocuries per liter
  - Radium (Ra), micromicrocuries per liter
  - Uranium (U), micrograms per liter
  - Radioisotopes (radioactive Sr, I, Co, etc.) micromicrocuries per liter

The techniques of tabulating data do not require extensive exposition here. Some compromise between legibility of the data and economy in printing cost may be required. In the most complete chemical analyses, the data to be reported require a considerable amount of space. Arrangements of tables conforming to present practice in the Geological Survey can be observed in the water-supply papers in recent members of the series "Quality of Surface Waters of the United States," and in other recent publications of the Survey containing water analyses. In general, the data regarding source of sample come first in the table, followed by oxides (silica), cations, anions, calculated values, physical data, biochemical data and dissolved gases, and radioactivity data. Table 14 is a listing of data in the order in which they are currently tabulated by the Geological Survey.

STUDY TECHNIQUES

Water analyses can be studied in various ways to demonstrate similarities and differences of composition. Some of these techniques will be discussed in this report and references will be made to reports where some of the techniques are described in greater detail. The basic methods, which may be subject to minor variations to adapt them better to conditions in a particular area, include inspection and simple mathematical treatment, and preparation of graphs, maps, and diagrams of various kinds.

INSPECTION AND COMPARISON

A simple inspection of a group of chemical analyses will generally make possible a separation of the analyses into subgroups. For example, it is easy to group waters together which have dissolved-solids concentrations falling within selected ranges. The consideration of dissolved solids, however, should generally be supplemented by that of other parameters.

It is common practice in literature on water quality to refer to waters or to classify them by such terms as "calcium bicarbonate water" or "sodium chloride water." These classifications are arrived at on the basis of the predominant cation and anion, from inspection of the equivalents per million reported. Classifications of this type can hardly be expected to be precise, and are useful only in a general way in the indication of the chemical character of a water and pointing out broad similarities between waters. If not used carefully, they may be misleading. A water probably should not be referred to as a sodium chloride water, for example, if the sodium and chloride ions constitute less than half the cations and anions, respectively. Waters in which one cation and one anion are not clearly predominant should be recognized as mixed types and identified by the names of all the important cations and anions.

USE OF RATIOS

Classifications of the kind just discussed are loose and approximate at best. More exact and quantitative methods are needed in most instances. Expression of the relationship of one ion to another or to the total dissolved solids in terms of a ratio may make resemblances or differences among waters stand out clearly. An example is given in table 15 where three hypothetical analyses are compared. All three of these analyses could be classified as sodium bicarbonate waters and they do not differ greatly in total concentration. The high proportion of silica in waters *B* and *C*, their similar Ca-Mg and Na-Cl ratios, and their similar proportions of SO_4 to total anions establish the clear similarity of *B* to *C* and the dissimilarity of both of them to *A*. For most comparisons of this type, concentration values expressed in terms of epm will give best results.

Inspection of a group of analyses may suggest which constituents might be used to compute ratios for comparison. The foregoing discussions in this report of the cations and anions in water may also aid in a logical choice of constituents to use. The ratio of calcium to magnesium, for instance, may be useful in comparing waters from rocks containing an abundance of ferro-magnesian minerals with waters from rocks having a different composition. This ratio may be useful also in separating waters of dolomitic rocks from those of lime-

TABLE **15.**—*Hypothetical chemical analyses compared by means of ratios*

[Date below sample letter is date of collection]

	(A) Jan. 11, 1950		(B) Feb. 20, 1950		(0) Mar. 5, 1950	
	ppm	epm	ppm	epm	ppm	epm
Silica (8100	12		33		30	
Calcium (Ca)	26	1.30	12	0.60	11	0.55
Magnesium (Mg)	8.8	.72	10	.82	9.2	.76
Sodium (Na Potassium	n	3.16	89	8.85	80	3 50
Bicarbonate OO₃)	156	2.56	275	4.51	250	4.10
Sulfate (804	92	1.92	16	.33	15	.31
Chloride (Cl)	24	.68	12	.34	12	.34
Fluoride F)	.2	.01	1.5	.08	1.2	.06
Nitrate O₃)	.4	.01	.5	.01	.2	.00
Dissolved solids:						
Calculated ppm	313		309		282	
Calculated tons/acre ft	.42		.42		.38	
Hardness as CaCO₃:						
Oa and Mg	101		71		66	
Noncarbonate	0		0		0	
Specific conductance (micromhos at 25°C)	475		468		427	
pH	7.7		8.0		8.1	

NOTE.—Comparison of analyses of the 3 samples.

	SiO₂ ppm	Ca epm	Na epm	804 epm
	Sum ppm	Mg epm	Cl epm	Total anions epm
A	0.038	1.8	4.6	0.37
B	.11	.73	11.3	.063
C	.11	.72	10.3	.064

stone, or for tracing sea-water contamination. The ratio of sodium to total cations (percent sodium) is useful in studies of natural base exchange. The ratio of chloride to dissolved solids or to a particular ion may be useful in determining the influence of solution of salt (sodium chloride) from aquifer materials or through contamination. The study of analyses by means of ratios as described above has many possibilities that have not been fully exploited. Some suggestions along this line have been made by Schoeller (1955) with special reference to water associated with petroleum. White (1957a, 195Th) has used ratios of constituents to help identify waters of magmatic or connate origin.

USE OF AVERAGES

When a large number of analyses for a single source are available, it may be easier to grasp their general significance by computing an average. To most people, an average of a number of observations of some variable which fluctuates with time, constitutes a sort of "normal" in the sense that averages of precipitation or temperature data may give some idea as to normal weather conditions at a particular place and time. The same concept may apply in a limited way to data other than weather observations, such as those relating to the chemical composition of water passing a fixed point on a river. However, it is inherently inexact to apply the idea of normalcy to these averages. The complex variables that determine the chemical content of stream waters rarely will be exactly equivalent, at any given time, to an average of those variables. For approximate generalization, however, comparatively simple averages are easier for the mind to grasp than are more voluminous statistics.

For some purposes, a simple arithmetical average is commonly used. If the variations throughout the period of record are large, most of the users of the data will also be interested in the extremes, and they may be more important than the average.

For a better understanding of many phases of hydrology as related to water quality, a discharge-weighted average may be useful. In making such a computation, the concentration reported for each chemical constituent for each sample is multiplied by the discharge at the sampling point for the period that sample represents. These products for the whole period of the average are added together. The sum is then divided by the total discharge for the year or for whatever period the average is to cover. If an average of this type is to be made, the composites of daily samples which are prepared in the course of studies of surface water quality should, if possible, also be weighted on the basis of discharge, by including, in the composite sample, amounts of each day's sample proportional to the discharge at the time of sampling.

The discharge-weighted average may be thought of as representing approximately the composition of all the water that passed the sampling point during the period covered by the average; it is approximately the result that would have been obtained if all the water had been caught in a reservoir and thoroughly mixed before analysis. Such an average, however, should not be assumed to represent actual conditions that would be encountered in storage of water, even if all the water were collected in a reservoir that was originally empty. Some water would normally be released from time to time during the year, some would evaporate, and certain chemical changes in the stored water might be expected, such as precipitation of carbonates and possibly silica, and solution of soluble matter in the reservoir.

The U. S. Bureau of Reclamation (1953) has outlined the procedures it uses in computing quality of stored water from chemical analyses of streamflow. These procedures are analogous to conventional reservoir-operation studies. By taking into account the effects of releases and inflows, a closer approximation to what water may actually be expected to be available at a given proposed reservoir can be made. This procedure requires a long water-quality record, and assumptions must still be made regarding extent of mixing and changes in composition due to storage; therefore, such a treatment of the data is an approximation, but one that is good enough for many purposes.

Inthe sense that weighted averages take into account actual quantities of water and solids, they are useful in other types of hydrologic study involving erosion rates, salt balance, and other kinds of quantitative applications.

Averages not weighted by discharge probably are most useful in evaluating water supplies for users whose daily demand for water is nearly constant. In some instances, a single large flood of a few days' duration may contribute water that is very much different from that which normally passes the measuring point. A discharge-weighted average will be strongly influenced by such events and thus *give* different information than is required by the water user whose withdrawals each day are about the same.

Averages of analyses of surface waters may be useful in geochemical studies if the data are complete enough to be significant, and discharge-weighting and other adjustments are judiciously applied.

Clarke (1924b) has discussed the chemical quality of surface waters in many streams, as indicated by averages of analyses, for a period of a year or so, and by single presumably typical analyses. The average values are apparently all computed on a basis of equal weight for each analysis. Only very general deductions as to geologic influence upon the streams can be made on the basis of such averages. More specific deductions are possible for small streams draining simple geologic terranes, where the type of water is likely to be fairly constant. For larger streams, different sources may bring in different types of water, and averages are likely to obscure these effects unless the period used for the average is carefully selected, and the method of averaging the data is suited to the application. It is well, also, to avoid so-called typical analyses for sources known to yield water of variable composition.

Important facts relating surface-water quality to the environmental influences may be brought out by averages. However, one should avoid a stereotyped approach using only one method of averaging and covering inflexible calendar- or water-year periods. The approach should always consider the individual characteristics of the data and follow methods calculated to bring out the points of interest. Some applications are suggested in the following paragraphs.

Tables 16 and 17 contain averages computed in various ways to show the characteristics of water of the Rio Grande at San Acacia, N. Mex. The Rio Grande drains a total area of 26,770 square miles above this station, although some of the area is noncontributing. The basin includes a wide variety of landforms and geologic terranes, and has areas of high and low average precipitation and runoff. San

Acacia is below a large area irrigated by diversions from the river and its tributaries. The water of the river fluctuates widely in chemical quality in response to these influences.

In normal years the flood runoff at San Acacia occurs in two rather well defined periods, the snow-melt period in the spring when the flow originates largely from the melting of the winter's accumulation of snow in the high mountains, and the summer storm period when the flow originates largely from violent local rainstorms mostly centered in the parts of the basin that are at lower altitudes. The snow melt water is characteristically low in dissolved solids. The runoff from storms in much of the lower part of the basin is comparatively high in dissolved solids, owing to the presence of soluble matter in some of the exposed rocks and in the soils in these parts of the basin. The amount of runoff during the snow melting period is normally a large part of the total for the year.

The periods selected for study included a period of heavy precipitation in 1941 and 1942 and of drought in 1945 and 1946. In table 16 averages computed by two methods are given, each covering a full water year. The discharge-weighted average is of course strongly influenced by the low concentrations experienced during the snow-melt period, when the discharge was greatest. Usually, at such times,

TABLE 16.-*Average* analyses computed by different methods for Rio Grande at San Acacia, N. Mex., for ***1941-42*** and 1945-48 water years

[**Analyses** by **U. S. Geol.** Survey. Date below sample number is date of collection. Source of data: **U. S. Geol.** Survey Water-Supply Papers 950 and 10501

	1		2		3		4	
	1941-42		1941-42		1945-46		1945-46	
	ppm	epm	ppm	epm	ppm	epm	ppm	epm
Silica (SiO_2)	23		26		**30**		31	
Iron (Fe) dissolved	.05	-------	.05	-------	06		.06	-----
Calcium (Ca)	45	2.246	53	2.64	76	3.79	84	4.19
Magnesium (Mg)	9.1	.748	10	.82	15	1.23	17	1.40
Sodium Na	34	1.478	47	2.04	78	3.39	98	4.26
Potassium K	3.7	.095	4.2	.11	5.9	.15	6.0	.15
Bicarbonate **(HCO_3)**	129	2.114	154	2.52	200	3.28	222	3.64
Sulfate **(SO_4)**	93	1.936	120	2.50	203	4.23	243	5.06
Chloride **(Cl)**	16	.451	23	.65	37	1.04	48	1.35
Fluoride F	.4	.021	.4	.02	.5	.03	.6	.03
Nitrate **(NO_3)**	1.8	.029	1.6	.03	1.6	.03	1.6	.03
Dissolved solids calculated	289		361		546		639	
Hardness as **$CaCO_3$**	**150**		173		251		280	
Noncarbonate	44		47		87		98	
Specific conductance **(micromhos** at 25 C	435		550		800		926	
Mean **discharge (cfs)**	**3, 255**		3,255		345		345	

1. Average of analyses of composites of equal volumes of daily **samples** weighted by discharge for composite period, Oct. 1, 1941 to Sept. 30, 1942.
2. Average of analyses of composites of equal volumes of daily samples weighted by number of days in composite **period,** Oct. 1,1941 to Sept. 30, 1942.
3. Average of analyses of **composites** of equal volumes of daily samples weighted by discharge for composite **period,** Oct. 1, 1945 to Sept. 30, 1946.
4. Average of analyses of composites of equal volumes of daily samples weighted by number of days in composite period, Oct. 1,1945 to Sept. **30,** 1946.

TABLE 17.—*Discharge-weighted average analyses for Rio Grande at San Acacia, N. Mex., representing periods in the 1941–42 and 1945-48 water years in which different sources of runoff predominated*

[Date below sample number is date of collection. Source of data: U. S. Geol. Survey Water-Supply Papers 950, 970, 1050, and 1102]

	(1) Nov. 1, 1941-Feb. 28, 1942		(2) Mar. 1-June 30, 1942		(3) July 1-Oct. 31, 1942		(4) Nov. 1, 1945-Feb. 28, 1946		(5) Mar. 1-June 30, 1946		(6) July 1-Oct. 31, 1946	
	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm
Silica (SiO_2)	27		22	------------	26	------------	32		33		21	
Iron (Fe) dissolved	.04		.05		.08		.04		.07		.04	-------
Calcium (Ca)	51	2.55	39	1.946	65	3.24	63	3.14	66	3.29	139	6.94
Magnesium (Mg)	10	.82	8.2	.674	12	.99	13	1.07	14	1.15	28	2.30
Sodium (Na)	46	2.00	25	1.087	63	2.74	60	2.61	68	2.96	161	7.00
Potassium (K)	3.7	.09	3.7	.095	4.3	.11	5.5	.14	5.6	.14	7.0	.18
Bicarbonate (HCO_3)	161	2.64	115	1.885	176	2.88	197	3.23	201	3.29	209	3.42
Sulfate (SO_4)	102	2.12	74	1.541	161	3.35	133	2.77	149	3.10	541	11.26
Chloride (Cl)	26	.73	11	.310	28	.79	32	.90	38	1.07	59	1.66
Fluoride (F)	.4	.02	.3	.016	.4	.02	.4	.02	.5	.03	.7	.04
Nitrate (NO_3)	1.3	.02	1.9	.031	1.7	.03	1.5	.02	1.4	.02	1.9	.03
Dissolved solids calculated	347	10.99	242	7.585	448	14.15	437	13.90	475	15.05	1,060	32.83
Hardness as $CaCO_3$	168		131		211		210		222		462	
Noncarbonate	36		37		68		49		58		291	
Specific conductance (micromhos at 25° C)	526		366		665		664		715		1,460	
Mean discharge (cfs)	1,610	--------	6,620		692		633		149		189	

1. Winter base-flow period, 1941-42. Large part of flow from ground-water inflow and irrigation return, following wet year.
2. Snow-melt runoff period 1942. Most of flow from melting of above-normal mountain snow pack.
3. Summer runoff period 1942. Most of flow resulted from summer rainstorms.
4. Winter base-flow period 1945-46. Flow from irrigation return and ground-water inflows, following year of about normal runoff.
5. Snow-melt runoff period 1946. Drought conditions, no snow melt reached station. Flow continued to be largely irrigation return.
6. Summer runoff period 1946. Most of flow resulted from summer rainstorms, curtailed by drought.

dissolved-solids concentrations are low. The time-weighted averages in table 16 were made by multiplying each constituent of each composite sample by the number of days represented in the composite and dividing the sums by the numbers of days in the year. This essentially represents the composition of a body of water that received equal inflow from the river each day of the year. The discharge-weighted average for each year gives a concentration much lower than the time-weighted average, although the difference in the dry period of 1946 was smaller. In 1942 the snow-melt runoff constituted about three-fourths of the total for the year, but in 1946 essentially no direct snow-melt runoff reached this station.

The period October 1—September 30, which is the water year in studies of streamflow, may not always represent the best period to use in study of stream-water quality. Differences in precipitation distribution within the year and various other factors may affect the water quality for long periods, but they may be obscured in averages covering as long a period as a full year. For the purposes of somewhat more detailed study, table 17 was prepared covering nearly the same period as table 16 but broken down into shorter periods.

The runoff at San Acacia comes from three major sources, each of which may be considered as normally dominant during a certain period of the year. The snow-melt period commonly begins in March and usually is over by the end of June. The period March 1 to June 30 was therefore selected to represent the snow-melt season. From July to the end of October is the season of summer storms which normally cause the larger part of the runoff during the summer. The period July 1—October 31 therefore was selected as the summer-storm runoff period. These two periods also represent the irrigation season in the area above the station. From November 1 to February 28 there is rarely any direct runoff from rain or snow and the streamflow is sustained by ground-water inflows. The water table has been raised in the irrigated area during the other two periods as a result of water applications, and the ground-water inflows to the river during the winter are thus essentially return flow from irrigation. The period may be called the "winter base-flow period."

In table 17 discharge-weighted averages for each period during the 1942 and 1946 water years are given. Although the periods fail by a month to match exactly the water years, the lack of congruence is negligible for this comparison. It will be noted that for 1942, the discharge-weighted average for the year (table 16) approaches most closely the average for the snow-melt period when most of the runoff during the year occurred. In 1946 the runoff during the normal snow-melt period was all derived from ground-water inflow. The averages for the first two periods (4 and 5 in table 17) resemble each other closely. The annual discharge-weighted average falls between the average of the first two and the third periods, as would be expected, but is nearer the value for the ground-water-inflow period, when most of the runoff occurred.

Comparison of corresponding periods for the two years in table 17 demonstrates the effect of drought conditions on water quality, especially for the periods of winter base flow and snow-melt runoff. The quality of runoff in the summer-storm period is partly controlled by the geographic distribution of the rainfall, as some tributaries produce more highly mineralized floodwater than others, and comparisons of data for this period require knowledge of factors other than those discussed here.

Data presented in tables 16 and 17 are intended to suggest possible means of using averages in interpretive reports. When averages are computed, the periods chosen for averages and the method of averaging should be selected on the basis of knowledge of conditions in the area under study.

PALMER'S GEOCHEMICAL CLASSIFICATION

A system of classifying analyses of water which had the aim of making it easier to compare analyses from various geologic environments was proposed by Chase Palmer (1911). Under this system, the analyses were expressed in terms of percentages of total concentration in equivalents per million, and the relative proportions of certain groups of cations and anions were then stated. The Palmer system still is used occasionally in the study of analyses by some investigators in the original form in which it was proposed. Within the Geological Survey, however, this system has been supplanted by other more convenient procedures. In some respects, the Palmer geochemical classification may be considered the parent of more modern procedures, and although it is now mainly of historical interest, an understanding of its principles is desirable. The following discussion is based on Palmer's description of his system.

Palmer believed that waters may have two general properties, 'salinity and alkalinity. Salinity is caused by salts that are not hydrolyzed, especially chlorides, sulfates, and nitrates. The full amount of salinity present in a water is obtained by doubling the sum of equivalents per million of chloride, sulfate, and nitrate. These values are doubled because any cations in combination with these anions would also be considered as contributing to salinity. Alkalinity is caused by hydrolysis of substances carried in solution. Palmer states that the full value of alkalinity is obtained by doubling the epm value of cations present in excess of the sum of chloride, sulfate, and nitrate. Essentially, this represents twice the value of titrated alkalinity in the usual water analysis.

Cations were divided by Palmer into two classes, the alkalies (Na and K) and the earths (Ca and Mg). To take care of acid waters, a third class was established for hydrogen. The properties of salinity and alkalinity are further subdivided on the basis of the cations present in the water as follows (data expressed in percent of total equivalents) :

1\. Primary (alkali) salinity :
(Na K), + equivalent amount of Cl + SO_4 + NO_3.

2\. *Secondary* salinity (that associated with earths) :
Cl SO_4 + NO_3 in excess of Na K (if any excess), + equivalent amount of Ca + Mg.

8\. Tertiary salinity :
Excess of Cl SO_4 + NO_3, over Na + K + Ca + Mg + equivalent amount of H.

4\. Primary alkalinity (that associated with alkalies) :
Excess (if any) of Na K over Cl + SO_4 + NO_3, + equivalent amount of HCO3 or CO_3.

5\. Secondary alkalinity (that associated with earths) :
Excess (if any) of Ca Mg over Cl SO_4 + NO_3 + equivalent amount of CO3 + HCO_3.

Certain of these properties are mutually exclusive, and a water can have no more than 3 of the 5 properties. An acid water (tertiary salinity), for example, could have no alkalinity either primary or secondary, and alkaline waters can have no acidity. Further, a water could not have both secondary salinity and primary alkalinity, since they represent opposite relationships between Na K and Cl + SO_4 + NO_3. The determination of the relative amounts of the three characteristic properties of a water is made by computing the percentage each ion constitutes of the total cations and anions; or by computing the percentage of the three properties present on the basis of the foregoing definitions.

The chemical principles on which the Palmer system is based have considerable value in defining general trends or resemblances of waters from similar rock types. Some constituents are lumped together that in some instances may not be closely related, and waters of unusual composition or those reported as acid cannot be very well represented. The system does not consider fluoride concentrations, which were not determined in water analyses made in Palmer's time. This and other minor anions can generally be lumped with Cl, SO4, and NO_3. The system has no means of taking silica concentrations into account, except for the part which may appear in the alkalinity. Several of the graphical procedures for classifying water analyses are closely related to the Palmer system, as will be pointed out later.

Table 18 presents the results calculated by the Palmer system of 9 analyses selected from the tables of this report. The first 6 analyses represent the averages from table 17. The snow-melt runoff represented by analysis 2 from this table is characterized by the highest secondary alkalinity of the group; while analysis 6, representing more saline summer-storm runoff, is characterized by the highest primary salinity. Also included in the table are 4 analyses of waters of different types which were selected from tables in this report and have been used throughout later sections of this paper to illustrate graphic methods of classification. The differences among these waters are shown fairly well by the Palmer classification procedure.

The Palmer classification system in its original form is out of date, and other methods of treatment of data probably accomplish the same results more easily. The revival of this procedure is not advocated.

TABLE 18.-*Analyses recomputed to show the geochemical classification as suggested by Palmer*

[Anions and cations In terms of percent of total epm Numbers in boxheads refer to table number and analysis number in table, as 17-2, table 17, analysis 2]

	17-1	17-2	17-3	17-4	17-5	17-6	5	6-6	9-1	11-3
Calcium	23.3	25.6	22.9	22.6	21.9	21.2	3.1	21.0	42.3	10.9
Magnesium	7.5	8.9	7.0	7.7	7.6	7.0	3.2	16.0	6.4	6.6
Sodium	18.3	14.3	19,4	18.8	19.7	21.3	[illegible]	11.9	1.2	
Potassium	.8	1.3	.7	1.0	.9	.5		1.1	.4	
Bicarbonate	24.0	24.9	20.4	23.3	21.9	10.4	11.6	40.5	44.2	14.8
Carbonate										
Sulfate	19.3	20.3	23.7	19.9	20.6	34.3	34.5	1.6	1.5	4.1
Chloride	6.4	4.1	5.6	6.5	7.1	5.1	3.8	7.7	1.8	30.9
Fluoride	.2	.2	.1	.1	.2	.1	.1	.2	.0	.0
Nitrate	.2	.4	.2	.1	.1	.1	.0	.0	2.2	.2
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Primary salinity	38.0	81.2	40.2	39.6	41.2	43.6	76.8	19.0	3.2	65.0
Secondary salinity	14.2	18.8	19.0	13.6	14.8	35.6	0	0	7.8	5.4
Tertiary salinity	0	0	0	0	0	0	0	0	0	0
Primary alkalinity	0	0	0	0	0	0	10.6	7.0	0	0
Secondary alkalinity	47.8	50.0	41.8	46.8	44.0	20.8	12.6	74.0	89.0	29.6

GRAPHICAL REPRESENTATION

The average reader of a technical report does not have time to delve deeply into the tables of factual data or to assimilate through careful study the mass of figures that constitute a table of water analyses. For these readers, chemical analyses in graphic form will save time, and if the subjects are carefully chosen will drive home many points that the author might otherwise have difficulty in making clear. In fact, most authors dealing with water-quality information will find it helpful to experiment with graphic procedures of data analysis so as to receive help in fully understanding their basic data before they write an interpretive report.

A wide variety of graphic methods of treatment of water analyses can be found in the literature. Some of the most useful types of graphs will be described and discussed in this report, but it is not practical or necessary to discuss all the many variations that exist. If a graphic method is used to present data in a report or for study, the system should be adopted which most clearly indicates the points it is desired to emphasize. Graphic procedures are not a universal solution for all problems related to water quality and should be considered in proper perspective with the other methods presented here for studying such problems.

SCATTER DIAGRAMS

In studying the chemical characteristics of repeatedly sampled single sources of water or of several sources known or suspected to be related, the so-called scatter diagram may be useful. In using such diagrams, the dissolved solids or specific conductance may be plotted as the independent variable and one or more constituents as dependent variables. This kind of treatment is commonly used in the study of records of surface-water quality. An example of a diagram of this type is figure 12, in which hardness, chloride, and sulfate are plotted against specific conductance for composites of daily samples from the Gila River at Bylas, Ariz.

Figure 12 shows that the relationship of chloride to conductance for this sampling point is well defined except at low concentrations and a similar relationship exists between sulfate and conductance, although a few of the points lie some distance off the curve. For hardness, the relationship is more poorly defined, but some correlation exists.

By mere inspection of these data, one may reach some tentative conclusions as to the reliability with which one may predict the composition of the water of the river at Bylas solely from the conductance. A more definitely stated evaluation of the accuracy of the prediction can be arrived at through the application of statistical procedures such as the computation of correlation coefficients. The example shown is for a series of analyses of surface-water samples, but the general principle has wider potential uses.

Figure 12 suggests that chloride is the main anionic constituent of the river water at the sampling point, at times when the water is high in specific conductance. The study of the water quality is carried a step farther in figure 13 which is based on the same period of record for the Bylas station used in preparing figure 12. In figure 13, chloride in equivalents per million is plotted on one axis and sodium in equivalents per million on the other axis. This type of treatment is a graphic representation of the ratio of sodium to chloride. A constant value for the ratio is indicated by a straight line. In the special case where the value of the ratio is unity, the line would have unit

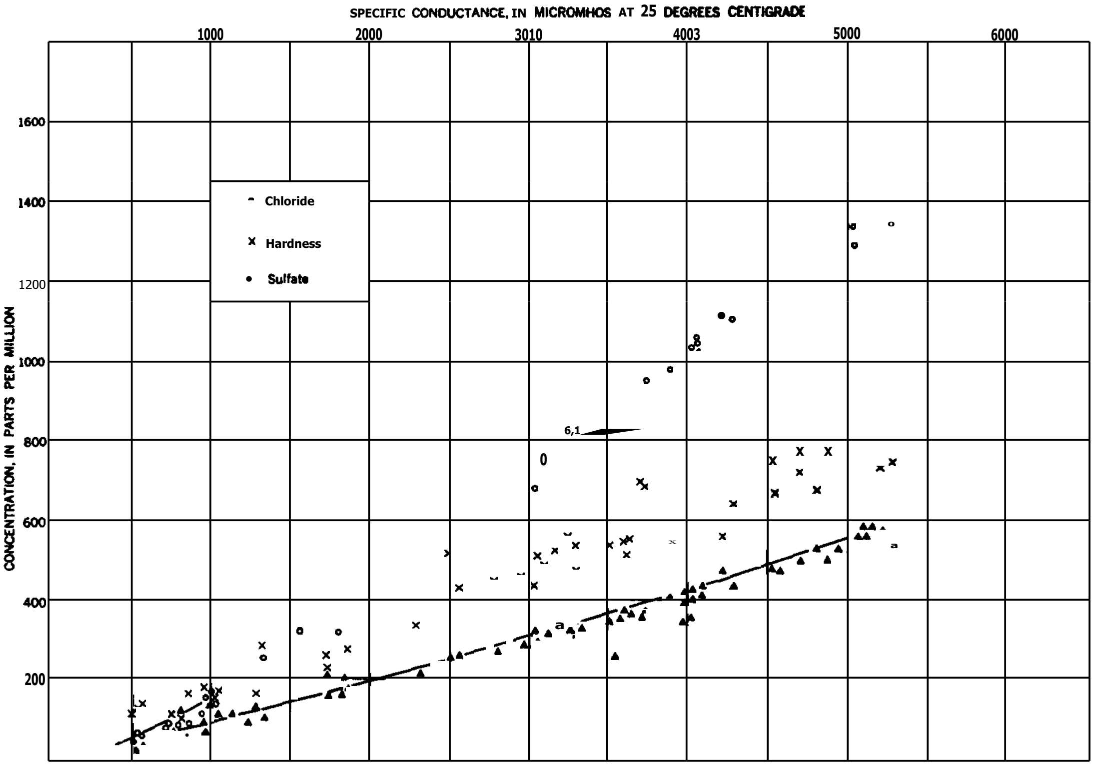


FIGURE 12.—Relation of conductance to chloride, hardness, and sulfate concentrations, Gila River at Bylas Ariz., October 1, 1943, to September 30, 1944.

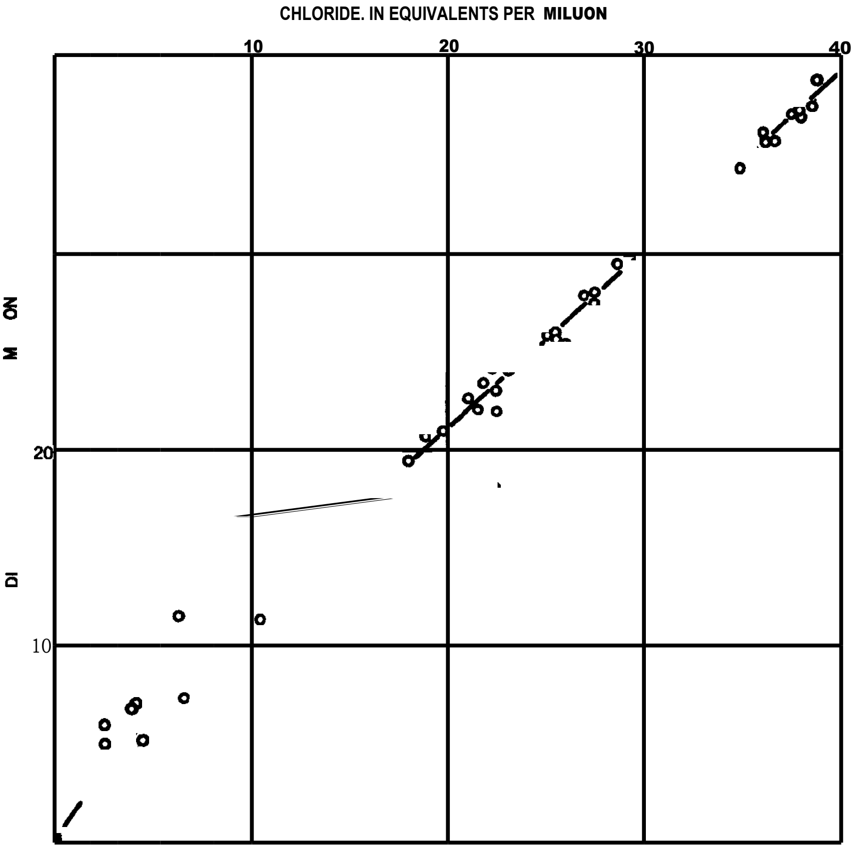


FIGURE 13.—Sodium-chloride relationship. Gila River at **Bylas,** Ariz., October 1, 1943, to September 30, 1944.

slope. In figure 13 the best line through the points would have a slight curvature near the origin, but is essentially a straight line of nearly unit slope above about 18 epm of each ion. In fitting regression lines like those in figure 12 and 13 to plotted points, the method of least squares generally should be employed.

Figures 12 and 13 illustrate several of the most significant chemical features of the water of Gila River at Bylas. It is evident that the water is strongly affected by inflows which are high in dissolved solids, and that sodium chloride predominates among dissolved salts in these inflows. The quality of the river water is affected at low concentrations (high river flow) by dilute direct runoff. The character of these flood inflows may vary somewhat, so that the linearity of the relation is less definite near the origin. The flood inflow appears to be somewhat higher in sodium than in chloride, suggesting solution of sodium salts other than chloride by such inflows.

Various treatments of data plotted on scatter diagrams are possible. Because factors other than those considered in the diagrams may affect the dependent variable, a good many of the plotted points may depart from any discernible linear relationship. For some data assemblages, a correlation coefficient may be calculated to express mathematically the degree of scatter and the confidence with which any relationship between the variables may be postulated. The reader is referred to standard texts on statistical analysis for means of treating data. The plotting of a line through points that are widely scattered should not be based on mere inspection.

Even though data may fail to give strictly linear plottings, the analyses may be found to fall within bounding curves or may tend to group about a point on the diagram. In fact, almost any systematic arrangement may have some significance.

For wide concentration ranges, logarithmic-log or semilog paper may be preferable to that having rectangular coordinates. In any event, the user of the method can choose the data to be used and the method of graphing to fit best the circumstances of his application.

IONIC-CONCENTRATION DIAGRAMS

In several of the various methods of graphical treatment of analyses, the total concentration of dissolved matter and the concentration of each important anion and cation are shown. Generally, the concentration is expressed in equivalents per million.

The system of graphic presentation of analyses most widely used in the United States probably is the one proposed by Collins (1923). Under this system, the analysis is represented by a vertical bar graph whose total height is proportional to the total concentration of anions or cations. The bar is divided into segments to show the concentrations of the cations and anions which make up the total. Usually, there are six subdivisions but more may be used if desired, and each is identified by a distinctive pattern or color. Cations are plotted on the left half of the vertical bar and anions on the right. An example of the Collins diagram is shown in figure 14 as applied to four analyses selected from tables 5, 6, 8, and 10 in this report. The graphing procedures are illustrated with the same four analyses throughout. Collins' diagrams with minor modifications are used later in this report in discussing relationships of water and rock composition.

A bar graph made by the procedure proposed by Reistle (1927) using parts per million is shown in figure 15. Reistle used this procedure for the study of oil-field waters. He recommended plotting on coordinate paper with the cations above and the anions below a baseline. A pattern or color system could be used to differentiate the anions and cations from one another on the graph.

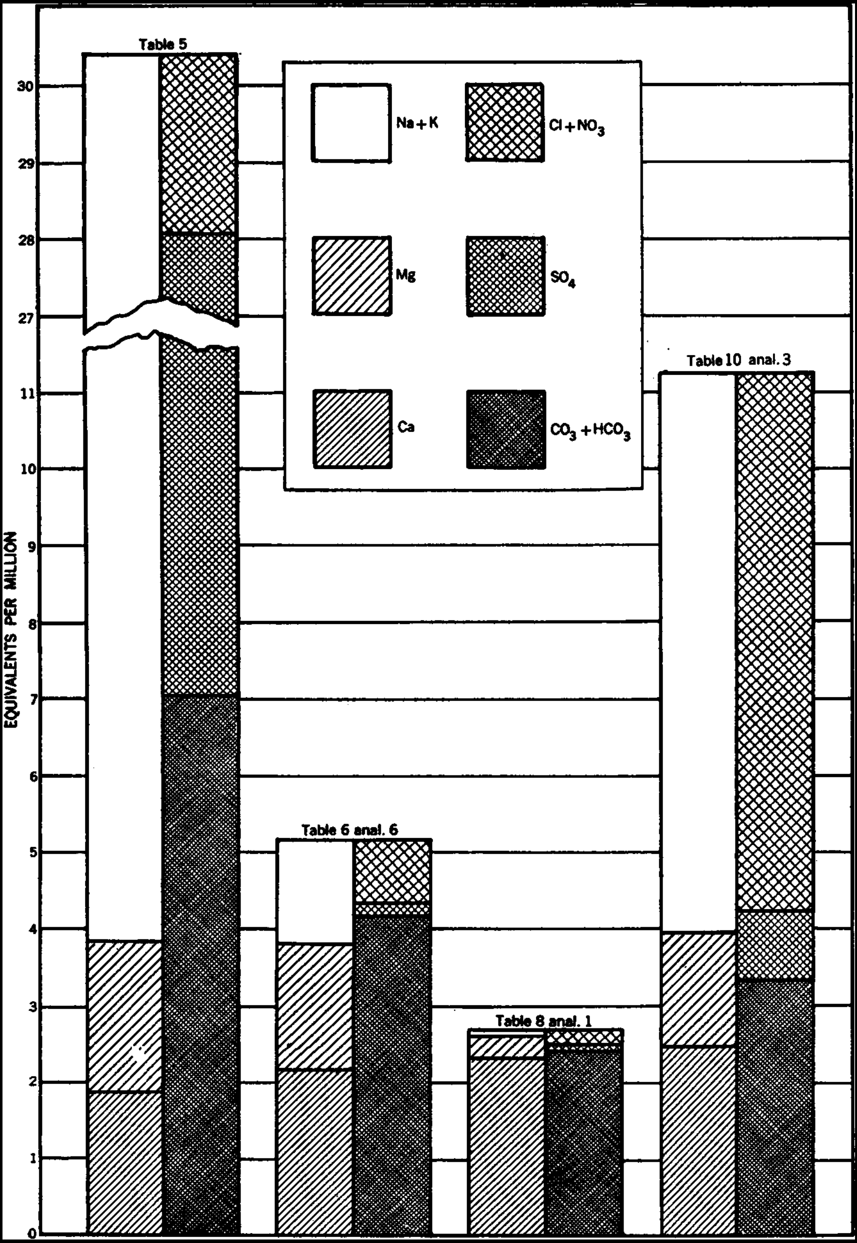


FIGURE 14.—Analyses represented by vertical bar graphs of equivalents per million.

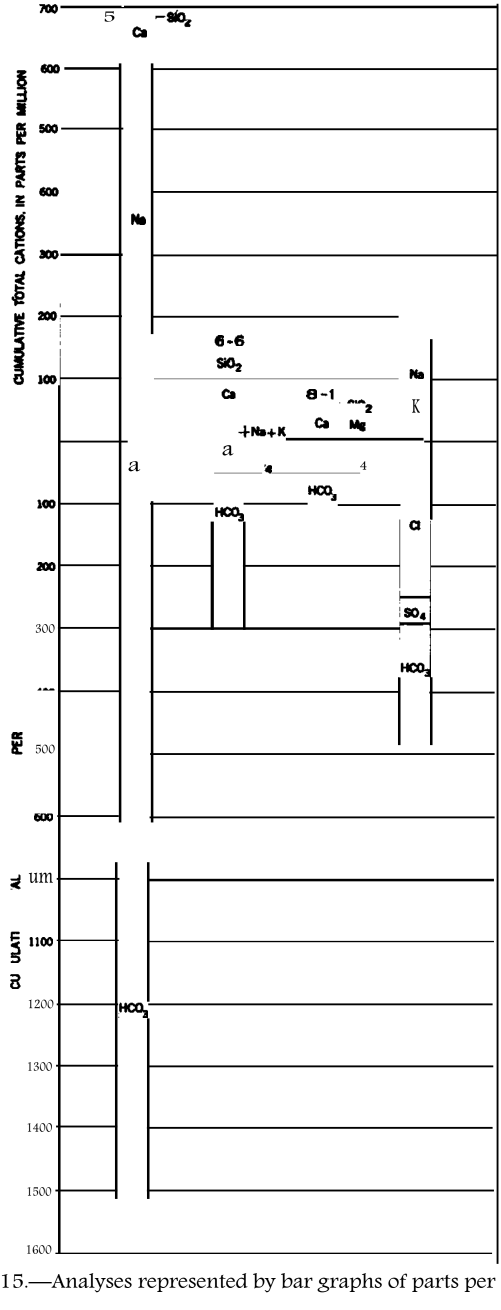


FIGURE 15.—Analyses represented by bar graphs of parts per million.

Figures 14 and 15 illustrate bar-graph systems which differ principally in that one is based on equivalents per million and the other on parts per million. Both show clearly the relative and total concentrations of dissolved matter present. For the usual general-purpose report, graphs clearly showing total concentrations are desirable because, for most water uses, the dissolved-solids concentration is a very important feature of water quality. A few Collins-type diagrams of analyses are included in most Geological Survey reports that deal with water quality. These diagrams generally are included to illustrate the resemblances or differences among waters discussed in the text and to show concentration ranges.

Graphs of analyses according to the Collins system are sometimes supplemented by a bar, bracket, or other indicating device drawn to equal the height of the calcium plus magnesium, with a scale indicating hardness values in ppm as $CaCO_3$ (figure 16). In figures 33–39 a supplementary bar representing silica concentrations in parts per million has been added. The graph may be subdivided to show concentrations of additional anions or cations in equivalents per million, at the option of the user.

The Collins procedure is recommended for general use in reports, especially for applications where considerable emphasis on the total concentration of dissolved solids is required. It is superior to the methods using part-per-million values for comparison of waters to

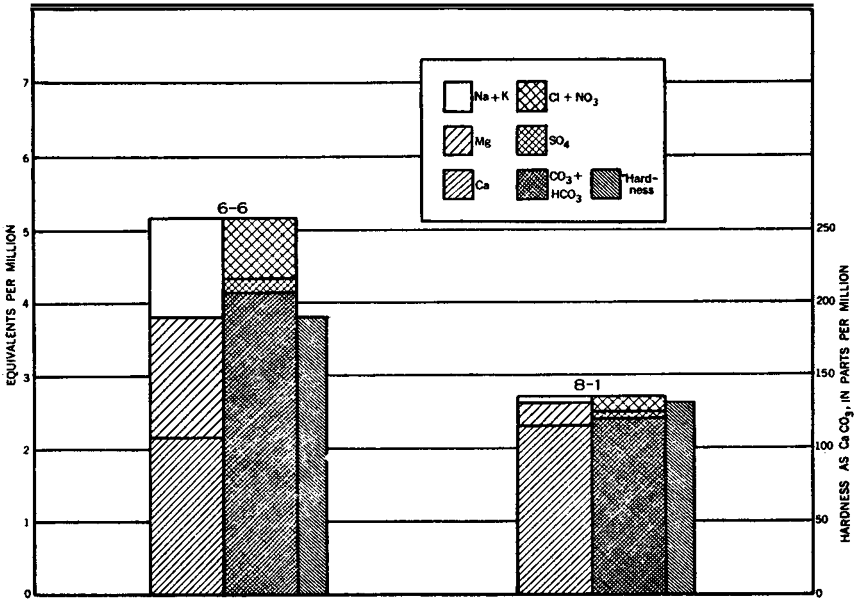


FIGURE 16.—Bar graph of equivalents per million which also shows hardness values in parts per million.

each other for presenting most clearly the chemical properties of a water. A bar diagram using a central zero line with cations plotted above and anions below may be useful for certain studies.

A system of plotting analyses using radiating vectors was proposed by Rezso Maucha in Hungary (1949). Such a system is illustrated in figure 17. The length of each of the six vectors from the center represents the concentration of that ion in equivalents per million. This system may have some merit in comparison of waters but has no particular advantage over the Collins system, especially since bar diagrams are in more common use in the United States and they are familiar to most users of hydrologic reports.

A system using four parallel horizontal axes and one vertical axis has been suggested by Stiff (1951) and used by him in studies of oil-field waters. Four cations can be plotted, one along each axis to the left of the zero point and four anions in a similar manner on the right. Concentrations are expressed in equivalents per million. When an analysis is plotted, a series of points result, one on each axis to the left and one on each axis to the right of the center zero. Connecting

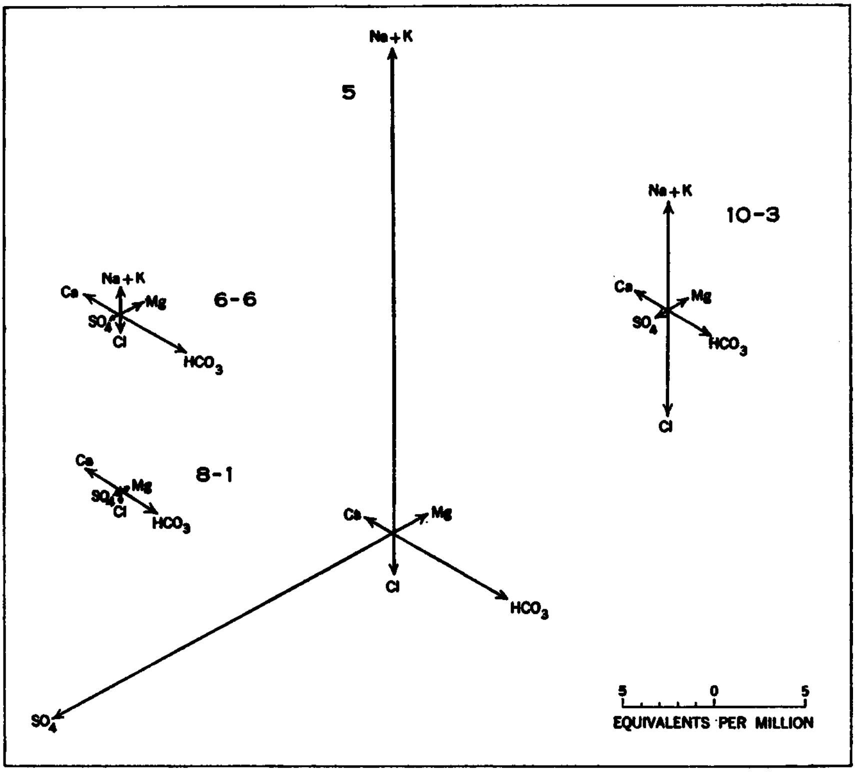


FIGURE 17.—Analyses in equivalents per million represented by vectors.

together the points representing anions and the points representing cations gives a closed figure or "pattern" whose shape is more or less characteristic of a given kind of water.

The procedure proposed by Stiff is illustrated in figure 18. Scales and ions shown can be varied to suit the need of the user. This plotting method is more or less related to other "pattern" procedures which, however, are usually based on percentage composition of the dissolved matter, and which are discussed as a group later in this report. Stiff's method may be useful in making comparisons of waters, especially highly mineralized ones, is simple to use, and can be varied to suit the waters being studied. It probably is better suited for study of data in the office than for illustration of reports, however, and is more applicable to ground-water data that are interrelated than to miscellaneous surface-water analyses.

PERCENTAGE-COMPOSITION DIAGRAMS

A considerable number of graphing methods emphasize or show only the relative proportions of the principal cations and anions present, usually in terms of the percentage of total equivalents per million that is represented by each. Some of these systems may show also the total concentration of dissolved solids, but they usually do not make differences in this property stand out as clearly as do the types of diagrams already described.

Among the principal types of percentage-composition graphs are certain pattern diagrams which represent the percentage composition of water by a characteristic pattern or figure, and the various trilinear plotting systems, some of which express an analyses by means of a single point.

PATTERN DIAGRAMS

The diagrams which may represent the chemical character of a water by means of a pattern are of various types. One type consists of a linear plot of the cumulative percentage of dissolved constituents as in figure 19. The data plotted here are in terms of percentage of total parts per million and hence can include concentrations of silica. Bicarbonate values have been converted to equivalent amounts of carbonate. Percentage of total equivalents per million could also be used in preparing a diagram of this kind. The shape of the plotted line is characteristic of the chemical composition of the water. However, only waters with major differences in composition will plot along widely divergent lines. Waters of similar composition plot essentially on the same line. This type of plotting is suitable only for considering major differences or where any minor differences may be ignored.

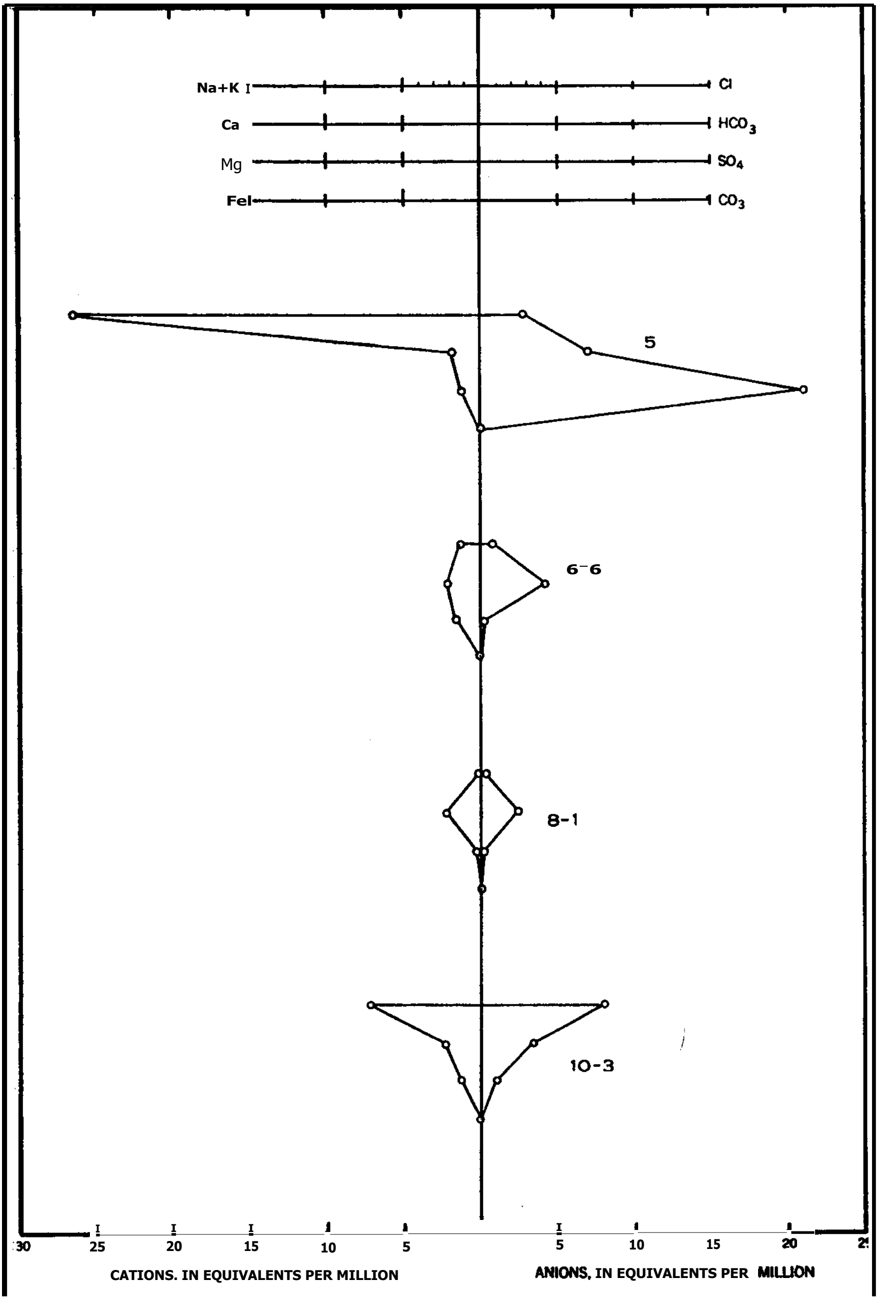


FIGURE 18.—Analyses represented by patterns based on equivalents per million.

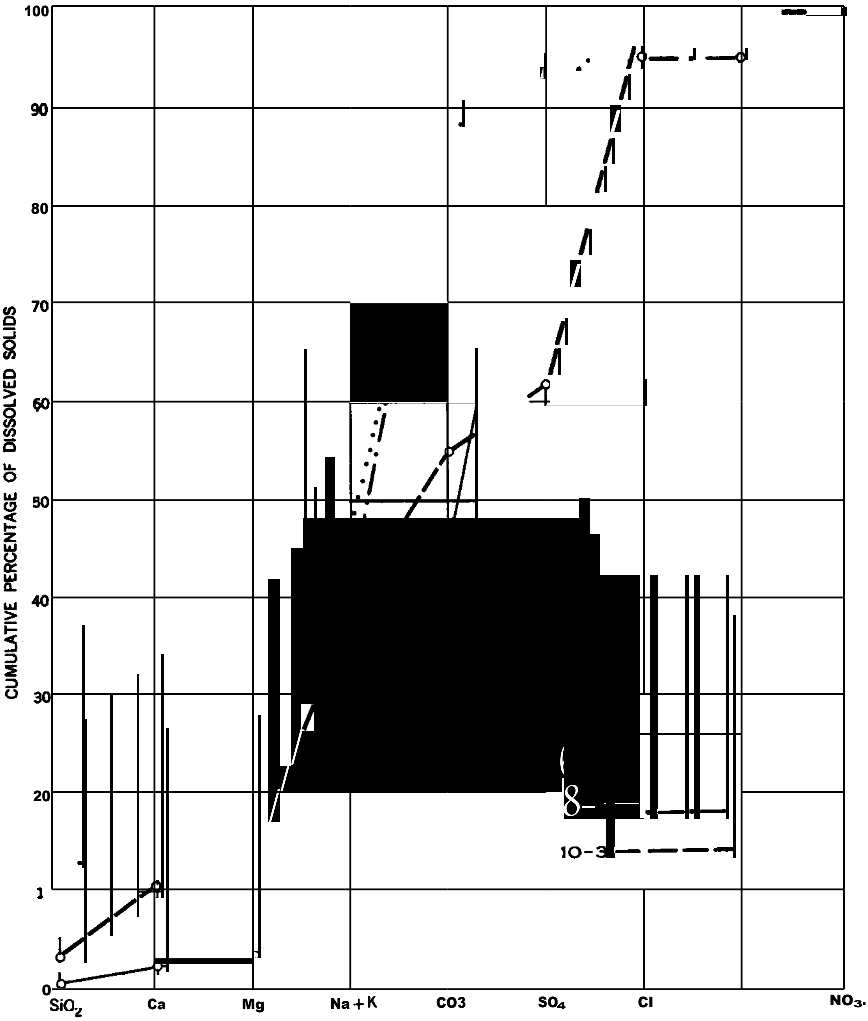
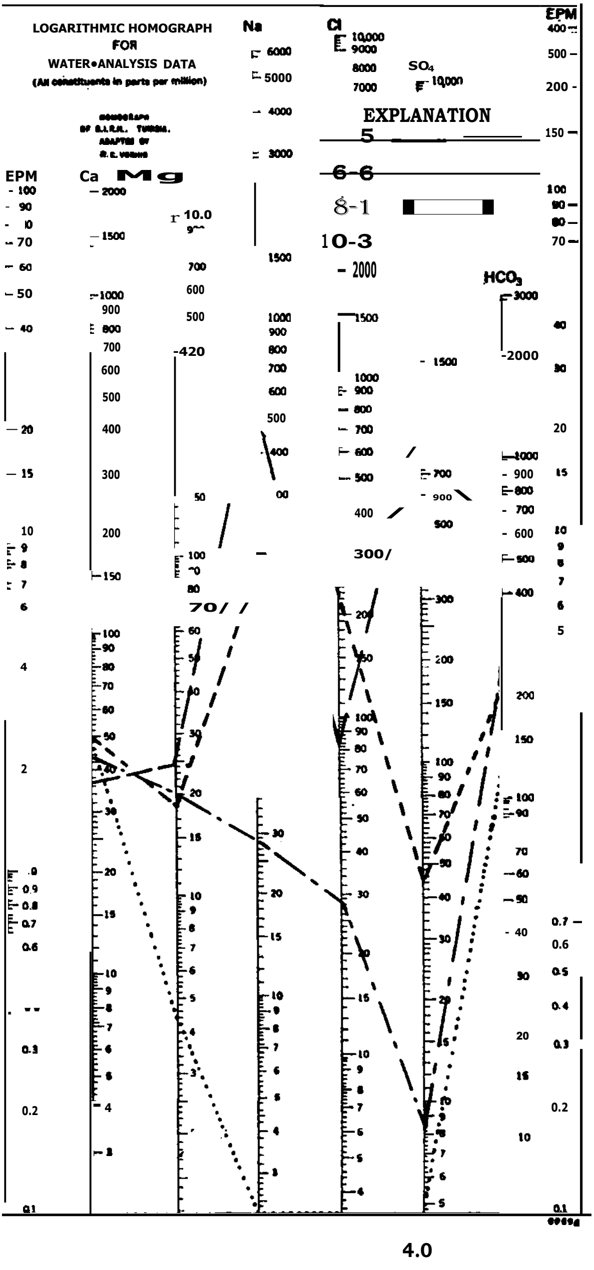


FIGURE 19.—Analyses represented bylinear plotting of cumulative percentage composition based on parts per million.

Figure 20 is another type of linear pattern diagram which is based on a system developed in part by the French investigator Schoeller (1935). The form given here is that used by the Bureau for the Inventory of Hydrologic Resources of Tunisia, with modifications suggested by R. C. Vorhis, of the Geological Survey. A line representing an analysis may be drawn on this diagram by connecting points representing gravimetric concentrations of ions. Concentration values are expressed on a series of logarithmic scales, so arranged that the sheet can serve as a nomogram for conversion of data to equivalents per million from parts per million or the reverse. The plotting of



4.0

Figure 20.—Analyses represented by logarithmic plotting of concentrations in parts per million.

data on a diagram of this type may be helpful in comparing analyses, and the diagram is very useful as a nomograph to show relationships between parts per million and equivalents per million for the major ions. The logarithmic scale has some disadvantages for water of low dissolved-solids concentration. The differences between concentrations of 0.1 and 1.0, for example, may not be as significant as differences between 10 and 100. Differences in slope of the lines representing two analyses may therefore be less meaningful in some parts of the diagram than in others.

Another type of pattern diagram is illustrated by figure 21. This is the so-called pie diagram, which represents the total concentration of the water by means of a circle. The scale for radii used in drawing the circles is intended to give areas proportional to the total concentration. The segments of the circle are indicative of the percentage composition. Diagrams of this type are probably most useful for indicating the composition of waters on a map or geologic section or column. In limited space, all the circles may have to be of one size

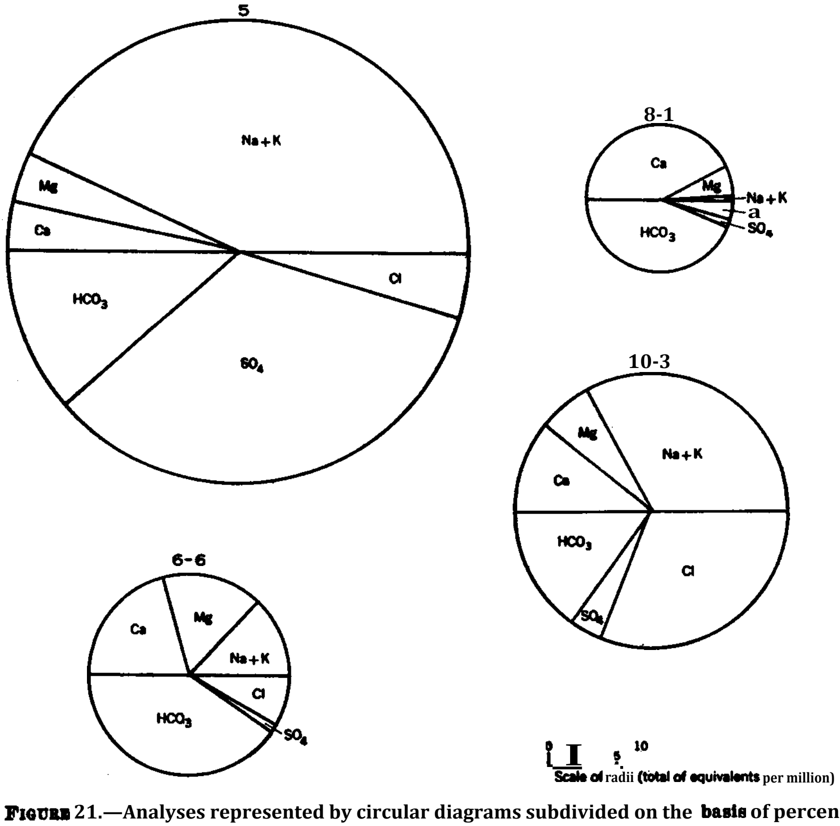


FIGURE 21.—Analyses represented by circular diagrams subdivided on the basis of percent of total equivalents per million.

and show percentage composition without regard to the total concentration, although numerical concentration values could be entered on the diagram.

Figure 22 illustrates another means of showing percentage composition. It is somewhat analogous to the Collins bar graph, but the total height of the graph is always the same. This type of diagram may be useful in supplementing illustrations of the conventional Collins pattern to show more clearly the relative proportions of dissolved material present.

The literature contains a reference to a pattern diagram suggested by Rezso Maucha (1934) of Hungary. This diagram consists of a

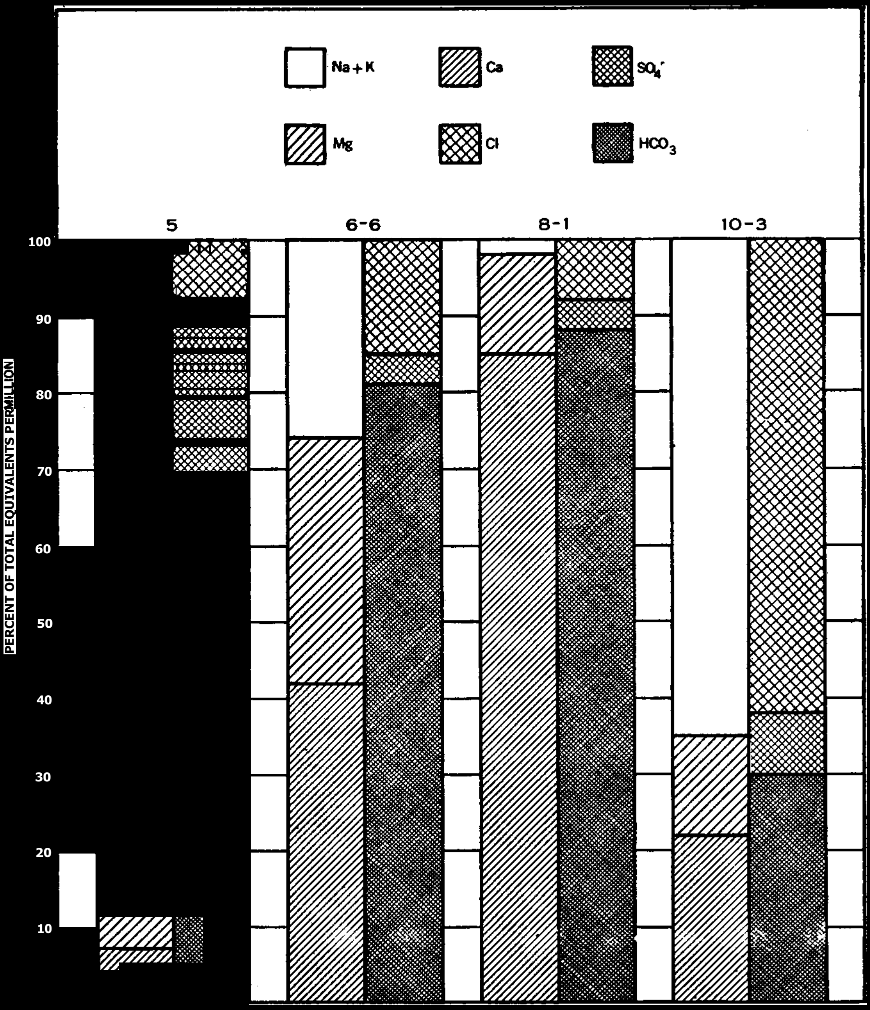


FIGURE 22.—Analyses represented by bar-patterns based on percent of total equivalents per million.

basic polygon, apparently of fixed size, divided into segments representing 8 ions. The percentage each ion represents of the total dissolved matter is indicated by shading a part of the segment for that ion. In some types of water where a few ions may comprise a very large percentage of the total, shading is carried to an adjacent area outside the basic polygon. It is believed this technique does not have sufficient advantages over those already described to be considered further.

Pattern diagrams representing water analyses may also be made using radial coordinates. Such a method is described by Tickell (1921) and is illustrated in figure 23. Six coordinates are drawn radiating from a common point. Five of these are used, 2 for cations, and the other 3 for anions. Distances are marked off on the coordinates away from the origin proportional to the percentage of that ion or group of ions included in the dissolved solids. The points thus formed are interconnected to give an irregular polygonal shape.

Pattern diagrams may aid the investigator to correlate water analyses. Especially to one not very familiar with water analyses, a resemblance between two analyses may not be evident until they are expressed graphically. The resemblances or differences among analyses which the investigator may wish to demonstrate in a report may best be brought out for the reader by means of one or two carefully chosen and prepared graphs or pattern-type diagrams.

TRILINEAR PLOTTING SYSTEMS

If one considers only the major dissolved constituents, and lumps together certain dissolved ions whose properties are similar, most natural waters can be represented as solutions of 3 cationic constituents, calcium, magnesium, and the alkali metals; and of 3 anionic constituents, sulfate, chloride, and those contributing to alkalinity. The composition of a water therefore can be represented conveniently by trilinear plotting.

The simplest trilinear plots utilize 2 triangles, 1 for cations and 1 for anions. Each vertex represents 100 percent of a particular ion or group of ions. The composition with respect to the cations is indicated by a point plotted in the cation triangle on the basis of the percentages of the three which are present. The composition with respect to anions is indicated by the position of a similar point in the anion triangle.

Emmons and Harrington (1913) used trilinear plots of this type to study water quality. Their application was the earliest found in surveying published literature for this report. However, Emmons and Harrington make no claim for originating the idea. In the form used by Emmons and Harrington, the cation triangle lumps calcium

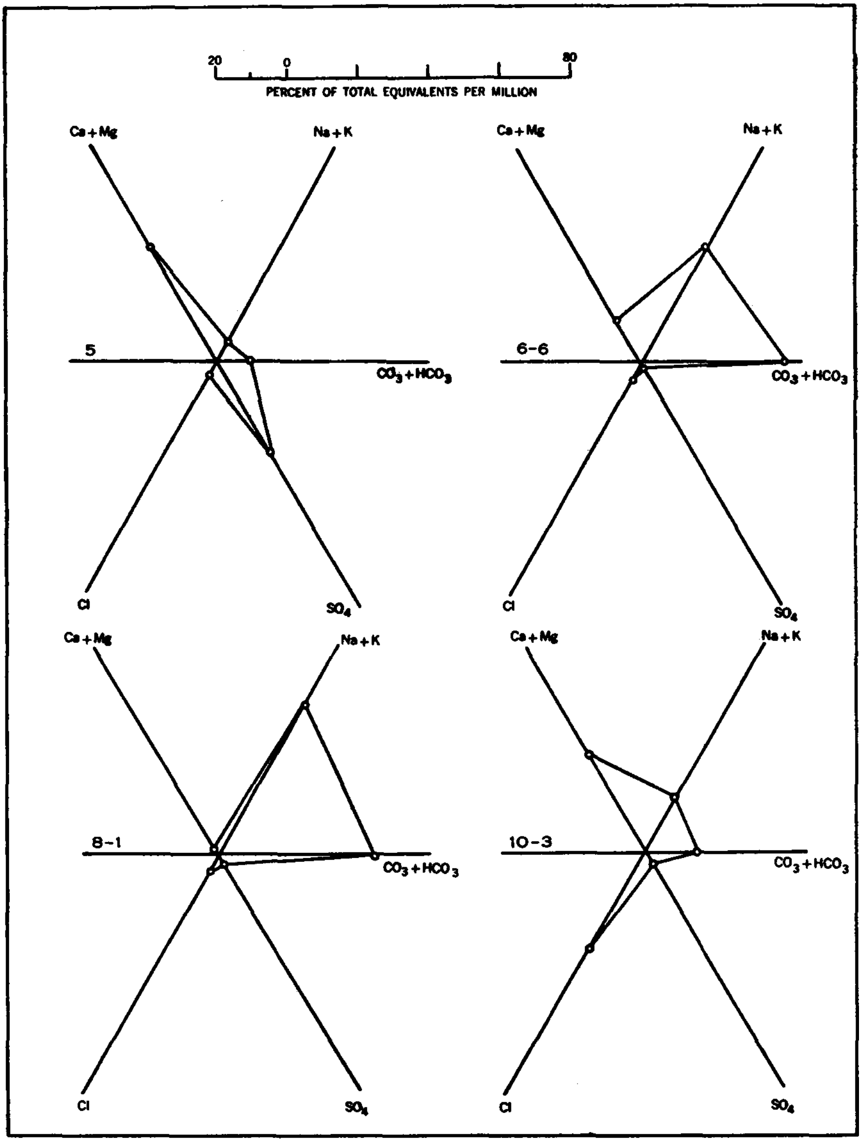


FIGURE 23.—Analyses represented by patterns drawn on radial coordinates.

with magnesium at one vertex and sodium with potassium at another. This leaves the third vertex for "other metals" which are seldom found in appreciable amounts in ordinary waters. These authors were particularly interested in mine waters where such metals are more common. Some lumping together of ions is required in waters of unusual composition if they are to be studied by trilinear plotting.

De la O. Carreño (1951, p. 87-88) has described a method of trilinear plotting used by his fellow countryman, Hermión Larios.

Under this system, the principal cations, Ca, Mg, and Na K, are plotted in one triangle and the anions bicarbonate, chloride, and sulfate in another. Each triangle is subdivided into 10 equal areas, numbered from 0 to 9. A 2-digit number then is used to characterize the water. The first digit is the number of the area of the cation triangle in which the water plots. The second digit is the number of the area in the anion triangle, where the plotted point falls.

In recent years a considerable number of publications have appeared in which trilinear plotting of water analyses is described and variations of the basic procedure are suggested. Admittedly the representation of a water analysis by two points each in a separate triangle is not very convenient. Several authors have suggested adding a third plotting field that represents a projection of the triangles into a common area where the analysis can be represented by one point. The position of the single point is dependent upon the relative concentration of one cation with respect to the sum of the other two, and of one anion with respect to the sum of the other two. Which cation and anion are singled out depends upon the arrangement of the plotting fields.

The first combination trilinear chart using this idea to appear in this country was published by R. A. Hill (1940). In the Hill diagram the anion and cation triangles occupy positions at the lower left and lower right with their bases alined vertically. The central portion of the diagram is diamond shaped. In using this diagram, the proportions of cations and anions, in percent of half the total equivalents per million, are computed and plotted as a single point in each of the lower triangles. Each point is then projected into the upper field along a line parallel to the upper margin of the field, and the point where the extensions intersect represents the composition of the water with respect to certain combinations of cations and anions.

The characterization here represents a concept analogous to Palmer's geochemical classification (1911) but expressed graphically rather than mathematically. Hill's original diagram however was so arranged that the sulfate was grouped with bicarbonate and carbonate rather than with chloride as in the Palmer system. Hill proposed a subdivision of the diamond-shaped field into 10 areas, and, depending upon where the analysis plotted, he classified the water in one of 10 types. In later discussions of his procedure, Hill (1941, 1942) suggested an alternate form of his geochemical chart which brought the groupings of anions and cations into conformance with the Palmer grouping.

Langelier and Ludwig (1942) suggested a rearrangement of the Hill diagram which could be placed on standard trilinear coordinate paper. The combinations of cations and anions represented in this diagram would coincide with the Palmer classification. Langelier (1944) proposed a rectilinear diagram in which the analysis would be represented by a single point based on the relation of Na K to HCO_3 + CO_3 and Ca + Mg to Cl + SO_4.

Piper (1944) suggested a somewhat different form of the trilinear diagram which is illustrated in figure 24 and which is extensively used by the Geological Survey. This diagram represents an analysis by three plotted points as does the Hill diagram. The third point, plotted in the diamond-shaped upper field, indicates the character of the water as represented by the relationships among the Na Ca + Mg, CO_3 + HCO_3, and Cl + SO_4 ions.

Recently some versions of the trilinear system of water analysis plotting have appeared in literature of other countries. Durov (1948) suggested a system that appears from a summary in Chemical Abstracts to be generally similar to that of Piper. Filatov (1948) suggested a 2-point system using cation and anion triangles with a common side.

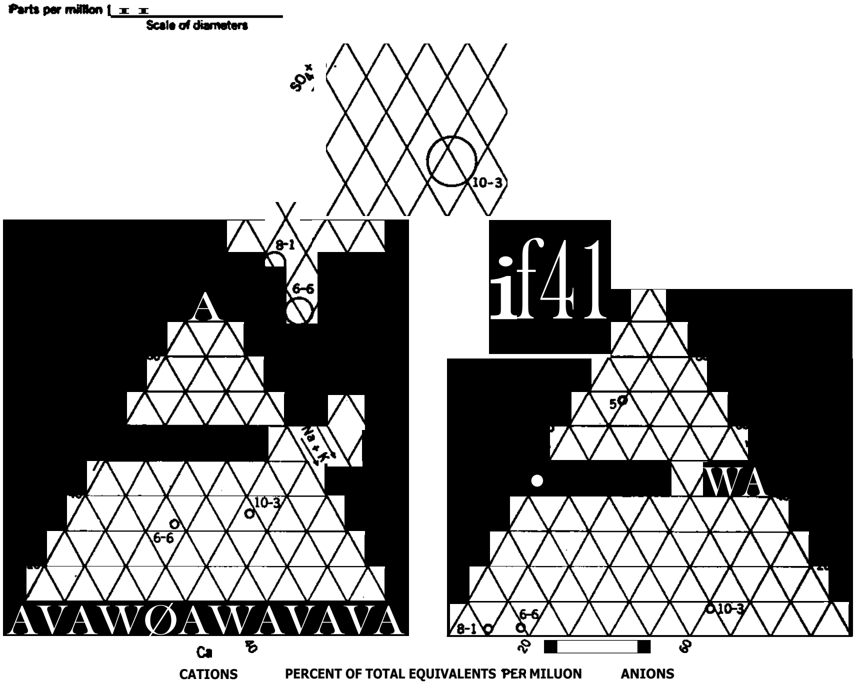


FIGURE 24.—Analyses represented by three points plotted in trilinear diagram (after A. M. Piper).

In his geochemical classification, Palmer expressed by means of three percentages the composition af alkaline waters with respect to primary and secondary alkalinity and primary and secondary salinity. In any such water, only three of these properties can be present, thus they present the possibility of being represented as a single point in either of two triangles having a common side. The diamond-shaped field in the Piper diagram can be divided horizontally into two equal triangular fields. Waters which the Palmer system would classify as having secondary salinity plot in the upper field, and those having the property of primary alkalinity plot in the lower field.

Trilinear diagrams constitute a very useful tool in water-analysis interpretation. Most of the other graphing procedures represent only a means of pointing up the differences or similarities among waters in a more impressive way than is possible with the numerical data alone. Most of the graphic procedures, therefore, are of value only in pointing out things about the analyses that need closer study, and do not in themselves constitute that closer study which will bring to light the explanation that is needed. By use of the Piper diagram and related trilinear systems the chemical relationships among waters may be brought out in more definite terms than is possible with any other plotting procedure.

Piper (1944) and the other writers who have proposed trilinear graphs have pointed out that, where analyses represent two original waters and a mixture, the analyses will plot on a straight line. For absolute proof of a mixture, the individual concentration values in the analyses must be in proper proportions, and the graphic method alone is not complete proof of a mixture. However, in many practical problems, this use of trilinear graphs is invaluable. There are many instances in which the possibility of mixtures needs to be explored, and this procedure is perhaps the simplest one to use in such work. For three-component mixtures, the analysis of the mixture should plot within a figure bounded by the components.

Piper suggests other applications of the diagram. Analyses of waters at different points in a system may plot on a straight line passing through a vertex of the plotting field. If for example 2 analyses line up with the vertex representing 100 percent Na and 100 percent Cl, 1 of the analyses could represent water that is the same as the other except for added salt, either from an inflow of water containing a high proportion of sodium chloride or from the solution of solid salt from the rock associated with the water. Orientation toward another vertex could represent, for example, a gain in calcium sulfate, or its loss through precipitation of gypsum.

In certain environments a water may exchange calcium and magnesium for sodium (base exchange) or exchange sulfate for alkalinity (sulfate reduction). Analyses of two waters that are the same except for one of these effects will plot on a straight line parallel to one of the bases of the central plotting field. The possibility of using these diagrams in quantitative hydrologic studies will be discussed later.

On the whole, trilinear plotting is a very useful interpretative tool. For presentation of data in reports where graphs serve only to illustrate differences among waters, trilinear-plotting procedures are subject to a number of limitations. All such methods emphasize percentage composition rather than total amount of dissolved solids. Concentrations of dissolved matter in individual waters can be represented on the graph by using circles of various sizes instead of points when the analyses are plotted, but it is evident that only large differences in concentration will be readily noticeable if this system is used. For those uses where emphasis must be placed upon concentration differences, some other plotting system is desirable as either a supplement or a substitute.

Minor changes in the arrangement of constituents on the trilinear plot may make it more useful for waters of unusual composition. Acid waters and waters that have high enough concentrations of iron, or other unusual cations or anions to be significant in the overall composition, cannot be shown adequately unless such changes are made. The single-point plotting is dependent only on four variables. In the Piper diagrams, these are the relative proportions of alkalies (Na , alkaline earths (Ca + Mg) , alkalinity (CO_3 HCO_3) and salinity ($SO4$ + Cl). Although these relationships are useful ones in classifying waters, for some conditions they may not be appropriate. The user may, however, show any grouping desired so long as there are 3 groups of cations and 3 of anions in the lower triangles. The variable represented at 100 percent at the lower inner vertex of each triangle appears unchanged in the central plotting field. The other two groupings of anions and cations are added to give the four variables represented by a single point in this central field.

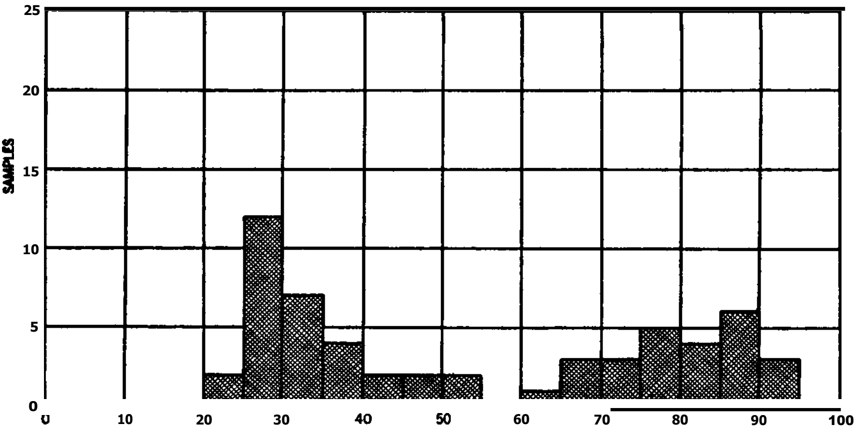
All the trilinear systems omit silica from consideration. Because of the importance of silicates in rocks, consideration of silica in water is often desirable where correlations between water analyses and kinds of source rocks are to be made. For some other types of interpretation, the omission of silica may not be important.

For a more complete discussion of the trilinear systems, the reader is referred to the articles by Hill (1940, 1941, 1942), Langelier and Ludwig (1942) and Piper (1944). A number of examples of applications of the Piper method are to be found in a publication by Piper, Garrett, and others (1953).

FREQUENCY DIAGRAMS

In the study of large numbers of analyses it may sometimes be helpful to consider the frequency of occurrence of certain values or relationships. Statistical methods for treatment of data have not been extensively used in water-quality work. The number of analyses available often is too small to make standard statistical procedures useful. However, some consideration of certain procedures may be worth while. Figure 25 was prepared from analyses for water samples from flowing wells of similar depth in alluvium in an area of the San Simon Valley, Ariz. The figure indicates that waters of two types are yielded by these wells. One type of water is low in sodium percentage and the other high. Further study of these data indicated a fairly definite geographic separation of the two types of water. A similar treatment of data might be used to demonstrate the difference in chemical character of water from different aquifers, or from different surface streams. The value used for preparing a frequency graph could be a percentage value such as percent sodium, a ratio of one ion to another, a concentration value for a single constituent, or whatever demonstrates best the thing about a group of analyses the investigator wishes to emphasize. The data treated by such procedures should have some known cohesive relationship, however, before this type of treatment is undertaken. Unless some hydrologic or geochemical relationships tie the data together, results obtained may be misleading.

Frequency diagrams may be highly useful in discussing and demonstrating the chemical character of surface waters. Figure 26 is a frequency diagram showing the percentage of time during which



nouns 25.—Number of samples having percent-sodium values within ranges indicated, San Simon artesian basin, Arizona.

certain conductivity values were observed on three major rivers near Pittsburgh, Pa. This type of frequency graph shows the range of conductivity and the extent to which the extremes depart from the most frequently observed range. It also shows differences in this characteristic from one stream to another. The value of this type of treatment of the data to a user planning daily water withdrawals is evident. Statistical analyses of this or a similar type would doubtless be of value in interpreting the records of quality of surface water in many other areas.

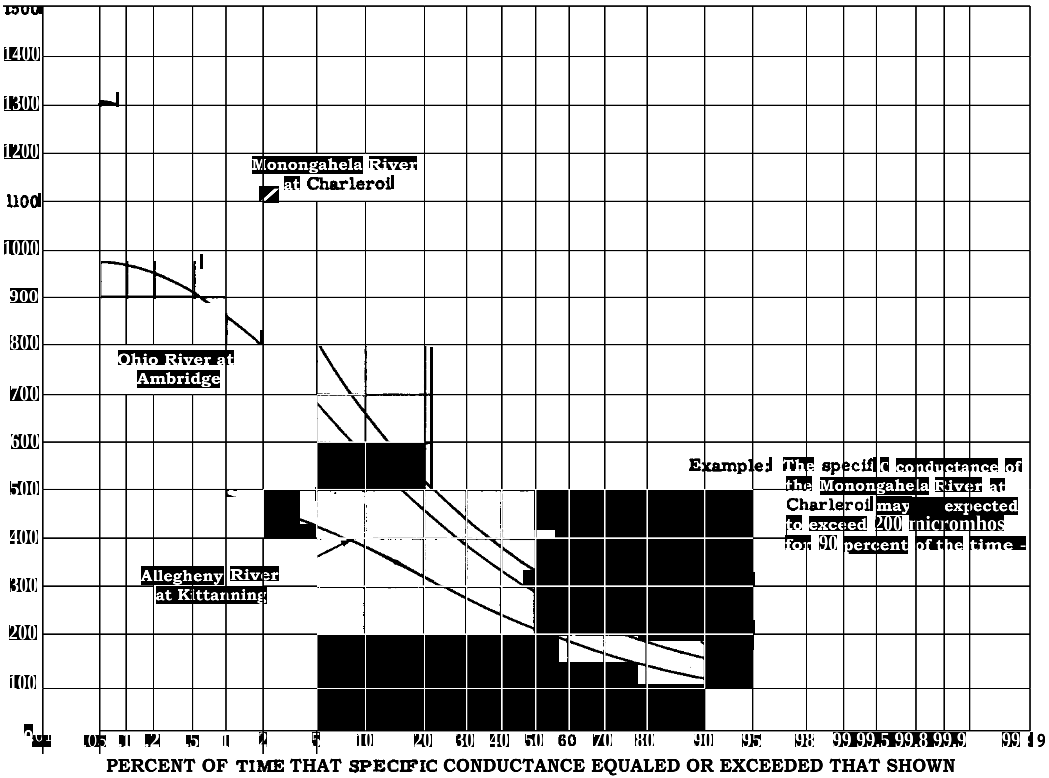
CHEMICAL ANALYSES PLOTTED AGAINST NONCHEMICAL VARIABLES

Most of the graphic methods discussed thus far have utilized only the chemical data themselves. The chemical analyses show the effects of various factors, usually either hydrologic or geologic in nature. Graphing techniques may be found helpful in determining and demonstrating the existence of such relationships. Variations in chemical composition usually are indirectly related to time because as time passes certain hydrologic factors are in operation that affect the quality of water. Chemical data may be shown to be related to the hydrologic factors by such factors as direct plotting of chemical properties against streamflow or ground-water pumpage, water level, or precipitation. Differences in chemical characteristics through horizontal or vertical distances in an area under study may be shown by salinity profiles. Maps showing the distribution of chemical properties or relationships are often useful, especially for ground waters. For specific problems, other characteristics of the area under investigation may be related to chemical data by graphic procedures.

HYDROGRAPHS

A graph showing the changes with respect to time of some property of water in a stream, or underground, is generally termed a hydrograph. Hydrographs of chemical quality may be useful to illustrate the characteristics of quality fluctuations with time. Figures of this kind are useful for surface streams because such sources often experience rapid changes in quality with the passage of time.

Day-to-day changes in specific conductance of the water of the Rio Grande at San Acacia, N. Mex., are comparatively small at some times and large at other times (figs. 1 and 2). By way of contrast, in streams that are completely regulated by reservoirs, such as the Colorado River below Hoover Dam, streams whose discharge is all or nearly all derived from ground-water sources, or streams which have a very large flow like the lower Mississippi, day-to-day quality fluctuations are small. The manner in which changes in quality are related to the rate of discharge of the stream may conveniently be shown by indicating the discharge on the same graph.



Example: The specific conductance of the Monongahela River at Charleroi may be expected to exceed 200 micromhos for 90 percent of the time.

FIGURE 26.—Cumulative frequency curve of specific conductance, Allegheny, Monongahela, and Ohio River waters, Pittsburgh area, Pennsylvania, 1944-50.

In ground waters, the changes of quality with time are usually comparatively slow. A long-term increasing trend of dissolved solids for a well in the lower Gila River valley near Wellton, Ariz. (fig. 5), is associated with withdrawals of water for irrigation and has obvious hydrologic and economic significance. Other types of fluctuation including seasonal changes, changes associated with above-normal precipitation or recharge, changes associated with water-level fluctuation, and possibly changes due to other factors occur in shallow wells in Safford Valley, Ariz. (fig. 4). Short-term changes in water quality when pumping was started in a well which had been shut down (fig. 8), shows how imperfect casing through a salt-water aquifer, and slow leakage of salt water into the well, raised the concentration of water standing in the well bore and in the main aquifer surrounding the well. When short-term fluctuations are observed they can usually be related to local conditions at or near the well. The associated changes in water-table elevation are usually of interest in normal quality fluctuations and these may be shown on the same graph. (See figs. 4 and 5.)

DISSOLVED-SOLIDS RATING CURVES

The concentration of dissolved solids carried in the water of a surface stream at a particular time can be considered to indicate the point of equilibrium of a variety of factors that affect the water quality at that point. The rate of stream discharge is one of the most important of these factors. The effect of direct surface runoff is usually to dilute the solutions of mineral matter added to the stream as a result of natural processes or the activities of man. For some streams, the discharge factor plays so important a role in determining the concentration of dissolved solids that a definite curvilinear relationship may be established between rate of discharge and concentration. A dissolved-solids rating curve of this type offers promise as a means of computing an approximate extended water-quality record for a stream that may have long gaging-station records but which has only been sampled for quality study for a briefer period. However, for most streams, other factors besides discharge must be considered in computing water quality, and often these other factors are not well enough known to be compensated for or evaluated.

A rating curve should be based on simultaneous and comparable values of discharge and concentration. The concentration of a representative sample is valid only for the instant of collection. To get instantaneous values of discharge, however, may require extensive restudy of gage-height graphs and is not always practicable. In the utilization of quality data, the concentration value for the daily sample is assumed to represent the discharge for the whole day, and presumably such values can be used with data on daily mean discharge that are readily available to prepare a rating curve having at least some validity. Basically, however, concentration figures comparable with daily mean discharge values ought to be used. Such figures would be obtained by continuously withdrawing water into a sample container each day at a rate proportional to the discharge; or by recording the conductance of the water continuously and computing an average from the record.

An indication of the nature of the discharge-conductance relationship for two streams in Arizona may be obtained from figure 27 and plate 1. Figure 27 is based on data obtained by analysis of daily samples from the San Francisco River at Clifton. Specific conductance of daily samples is plotted against daily mean discharge for the 1944 water year. A large part of the dissolved solids carried by the river at this point is contributed by the saline Clifton hot springs, a mile or two upstream from the sampling site. The variable amounts of dilution from direct runoff or from the relatively dilute base flow of the stream above the springs should, therefore, be a major factor controlling the concentration, and in theory, the quality of the water at the sampling station should be rather closely related to discharge.

The scatter of the plotted points in figure 27 is larger than might be expected for these conditions, although a fairly definite relation between the two variables is indicated. Some of the spread in the plotted points may have resulted from variations in the amount of hot-spring inflow. Hem (1950) has indicated there seemed to be a decrease in flow of the Clifton springs during 1944. Some of the spread could also have been caused by lack of homogeneity in the river water at the sampling point. Most of the scatter, however, probably is related to failure of individual samples to represent correct average concentration values for the day.

The San Francisco River is subject to flash rises, especially during the summer season in response to heavy local showers. These storms usually occur in the afternoons and evenings and cause many rises at night. Samples taken in daylight hours, as is the normal procedure, will usually represent flows well below peak stage and probably often below the 24-hour mean stage and hence would be above the concentration they should have to represent the daily average correctly. During the periods of changing discharge, the odds would be against a sample representing the average closely. The errors from this cause from day to day would tend to be only partly compensating in a long period of record. As indicated earlier, the use of instantaneous discharge values for the time of sampling should produce a better relationship, but such values cannot be obtained from published data.

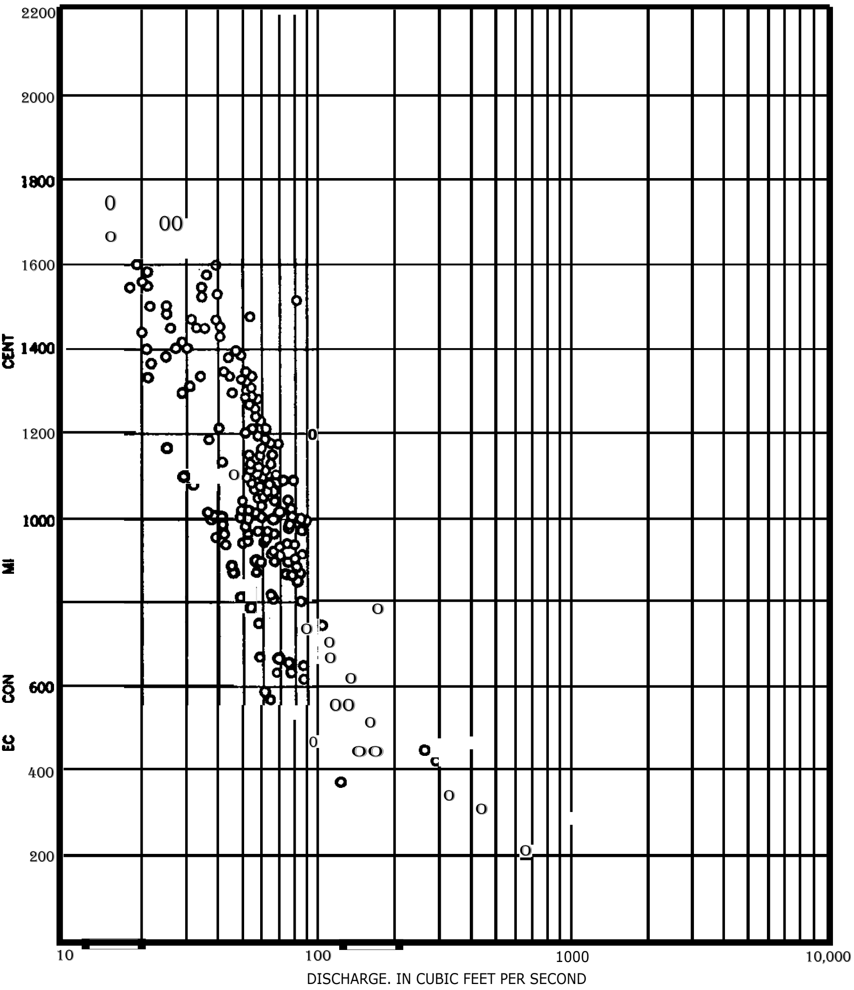


FIGURE 2T.—S[illegible], S[illegible] F[illegible] R[illegible] C[illegible], **Ariz.,** O[illegible] 1, 1948, [illegible] S[illegible] **30,** 1944.

P[illegible] 1[illegible] 1944 [illegible] G[illegible] R[illegible] B[illegible] **complex** [illegible]. I[illegible] 1 [illegible]. D[illegible] **SO** [illegible] B[illegible] **great** [illegible], [illegible] S[illegible] V[illegible]. T[illegible], [illegible]-[illegible], [illegible]. T[illegible]. I[illegible] places the water table may be drawn down so far that inflow to the river is temporarily stopped. During the nonirrigation season, amounts of inflows are increased, and the quality of some inflows may improve.

The dissolved solids in the river water are diluted by direct runoff which is from different sources and may itself vary somewhat in chemical composition as indicated by figures 12 and 13 which cover the same period for this station. The scatter of points in plate 1 is also partly due to the methods of sampling.

Like the San Francisco River, the Gila River at Bylas has a drainage basin of steep slopes conducive to rapid runoff from the high-intensity summer showers that provide much of the flow. More sustained runoff from general winter rains occurs in most years but had little effect during the period covered in plate 1. The larger area of the basin above Bylas reduces the likelihood of a preponderance of flood peaks occurring at night. Hence, although changes in quality are rapid, the sampling errors from assuming a daytime sample represents the 24-hour mean flow are probably compensating over a long period. Over a short period they may be large and can be expected to cause considerable scatter when used with accurately known mean discharge data to prepare a diagram like plate 1.

Use of instantaneous discharges for the sampling times is not a full answer to the preparation of a well-defined dissolved-solids rating curve for this station. When a sudden increase in discharge occurs above Bylas, a flood wave tends to pass downstream. The front of this wave consists of water that was in transit in the channel before the rise and usually is more highly mineralized than the dilute runoff water itself. The first water of a flood also picks up salt left by evaporation in the channel and may therefore be much higher in dissolved solids than water passing later. The amount of water contained in this wave, the height to which the channel may be filled, the composition of the water in the first rise, and the extent of mixing with more dilute flows are all subject to change from one rise to another. Under these conditions, the quality of the water taken at any instant cannot be expected to have any consistent correlation with discharge. The extent to which the quality of the water of a stream may change over short periods is not evaluated fully by daily sampling and should be studied by continuous recording devices in the more extreme cases, of which this sampling station is a good example.

That no simple relationship always exists between discharge and water quality is not to say that projected estimates of quality are impossible. Estimates may be made if all factors that are important are considered. By breaking a year into seasonal periods, for example, much more definite conductivity-discharge relationships may sometimes be established.

Durum (1953) in a study of the Saline River in Kansas used a number of graphic and other devices to compute amounts of dissolved solids contributed to the stream by groundwater discharge.

WATER-QUALITY PROFILES

The collection of simultaneous samples of water along a horizontal or vertical cross section of a stream or other body of surface water may reveal some differences in quality from point to point. These differences can be illustrated graphically by plotting distance from the bank or the surface along one axis and concentration along the other. Figure 28 illustrates such a salinity profile for the Susquehanna River at Harrisburg, Pa. The variation in composition in the cross section of the Susquehanna River mainly results from lack of mixing of tributary inflow from mining regions upstream. Usually a series of such profiles must be obtained before the overall significance of the variation can be evaluated, because the conditions in cross section may be different at different conditions of the flow. They are particularly useful in the study of salt-fresh water boundaries in estuaries. Vertical stratification of water in a lake or reservoir also may be illustrated by such profiles. Figure 29 is an example from Howard's discussion (1954) of the chemical composition of the water of Lake Mead, showing variation of dissolved solids and temperature with depth at two locations at different times of the year. Inflow to Lake Mead has a considerable range of concentration throughout the year and the degree of mixing in the reservoir is variable.

Salinity profiles for ground water reservoirs have not been widely used but may be an effective means of showing water-quality changes over short distances. Meinzer and Ellis (1916) utilized a diagram of this type to show the increase in salinity of ground water in an area near the lower end of Paradise Valley near Phoenix, Ariz. This area is crossed by the Arizona Canal which normally carries water considerably higher in dissolved-solids concentration than normal ground water in the vicinity. Seepage from the canal and irrigation near it influenced the quality of the ground water. A series of profiles of this type for a period of years may give valuable data on rates of saline encroachment.

QUALITY-OF-WATER MAPS

A useful procedure in the study of water-quality data is to enter the information on a map of the area under investigation. Such maps are most generally utilized in the study of underground waters in single, widespread aquifers, but they also have some value in surface-

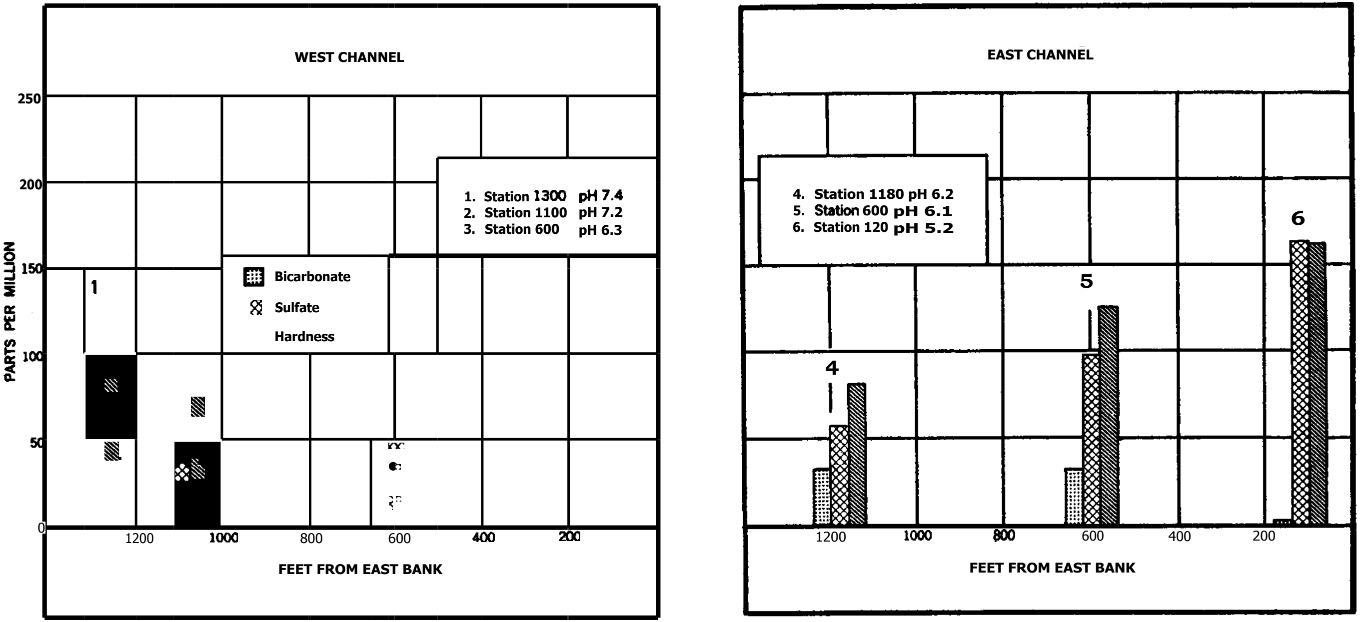


FIGURE 28.—Bicarbonate, sulfate, hardness, and pH of samples collected in cross-section of Susquehanna River at Harrisburg, Pa., July 8, 1947.

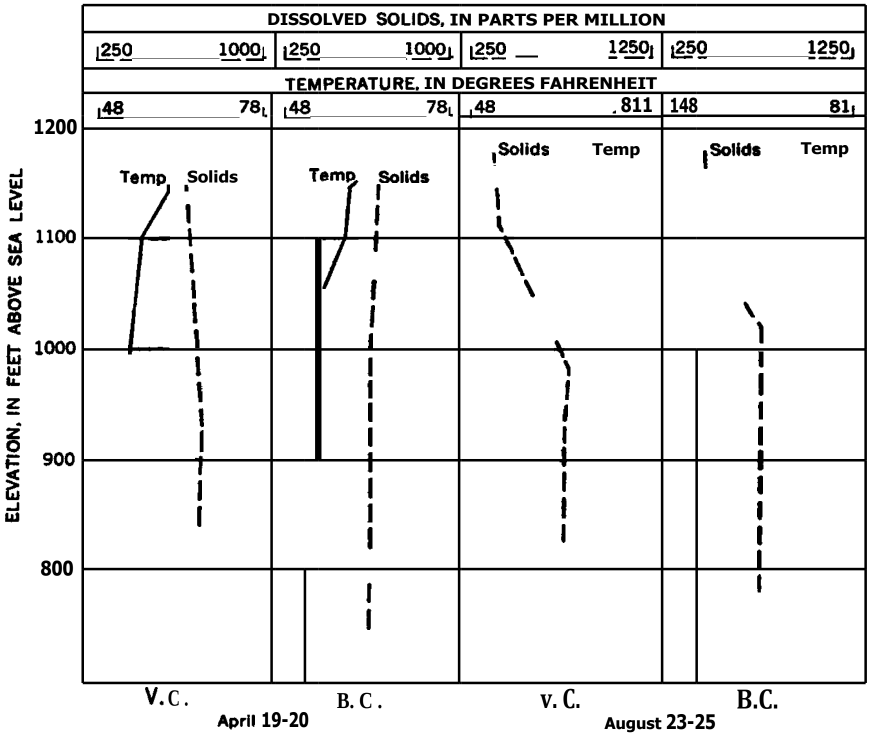


FIGURE 29.—Temperature and dissolved solids of water in Lake Mead, in Virgin and Boulder Canyons, 1948.

water studies. Where the areal distribution of water-quality features can be determined, correlations with other characteristics of the ground water can usually be made. It is a good technique to keep the data plotted on a study map that is kept up to date during the field phases of an investigation so that tentative correlations that may appear can be worked out as they come to light.

Usually a water quality map is prepared by entering numbers or symbols at well and spring locations to represent the concentration of dissolved solids or of individual constituents. The areal distribution of the water of various kinds can be observed on the map in a general way. If many of the available wells are open in more than one aquifer or the water in the principal aquifer of the area varies in quality with depth, it may not be possible to gain more than a very general indication. If these conditions exist, or if only a mall percentage (10 percent or less) of the existing sources have been sampled, no more detailed study is justified.

If, on the other hand, the area, has one aquifer system, or several separate systems having many wells that have been sampled, and the variations in quality with depth in a single aquifer are known to be minor, the preparation of an isogram map may be justified. This type of map extrapolates data between sampling points and shows areal characteristics more clearly than any other procedure.

When the data are incomplete, preparation of a map for study purposes may be helpful even though it may not be worthy of publication. Many conditions of possible hydrologic or geologic significance may be revealed by mapping water quality.

MAP SYMBOLS

One type of water-quality map is prepared by entering at each sampling location a symbol representing the dissolved solids or other characteristics observed in the sample obtained there. In the case of surface waters, for example, the symbol might be a small bar graph showing concentration and nature of dissolved solids. Or the entry could be the numerical value of one component of the water. A symbol map by itself indicates only the conditions observed at the sampling points and leaves any interpolation of the data to the user of the map, or to interpretation in the text of the report of which it is a part.

Figures 30 and 31 illustrate different types of symbol maps. A map showing quality of ground waters in the Milwaukee area, Wisconsin is included in a recent report on that region (Drescher, Dreher and Brown, 1953, p. 30).

ISOGRAM MAPS

The technique of mapping water quality characteristics by drawing lines of equal concentration of dissolved solids or single ions has been used in publications of the U. S. Geological Survey and other agencies for many years. A related procedure consists of using shading or colors to identify areas within which waters have a particular range of concentration.

The accuracy of this type of map is dependent upon two main factors: First, the homogeneity of quality in a vertical direction of water in the area or aquifer to be mapped, and second, the completeness and accuracy of sampling that is possible within the area. An isogram map is particularly helpful in the study of ground-water bodies in widespread uniform aquifers. In alluvial fill in the Basin and Range physiographic province of the Western United States, the water-bearing zones usually are of a lenticular nature but are usually closely enough interconnected to constitute single hydrologic systems over large areas. Isogram maps have been used successfully in several areas of this kind. In some instances, the procedure has been adapted to surface waters, and especially in the study of reservoirs and of the ocean.

Figure 32 represents the concentration of dissolved solids in ground waters in the Coconino sandstone in a portion of northeastern Arizona.

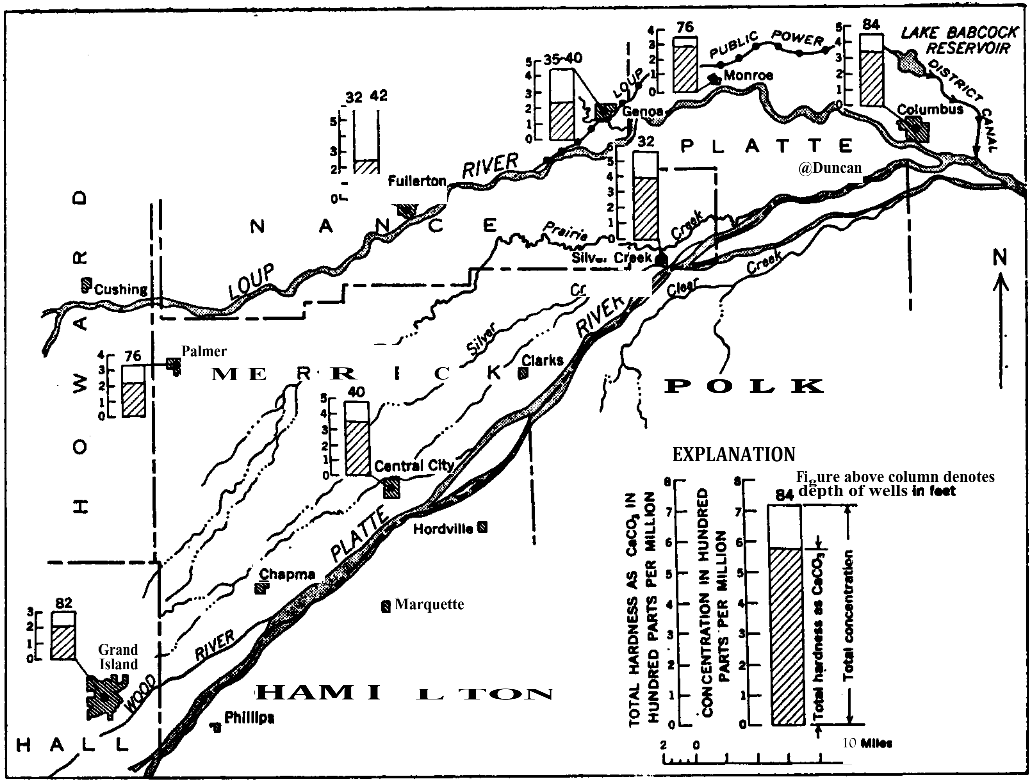


FIGURE 30.—Total concentration and **hardness** of water from deeper wells **in** Prairie Creek unit, Nebraska.

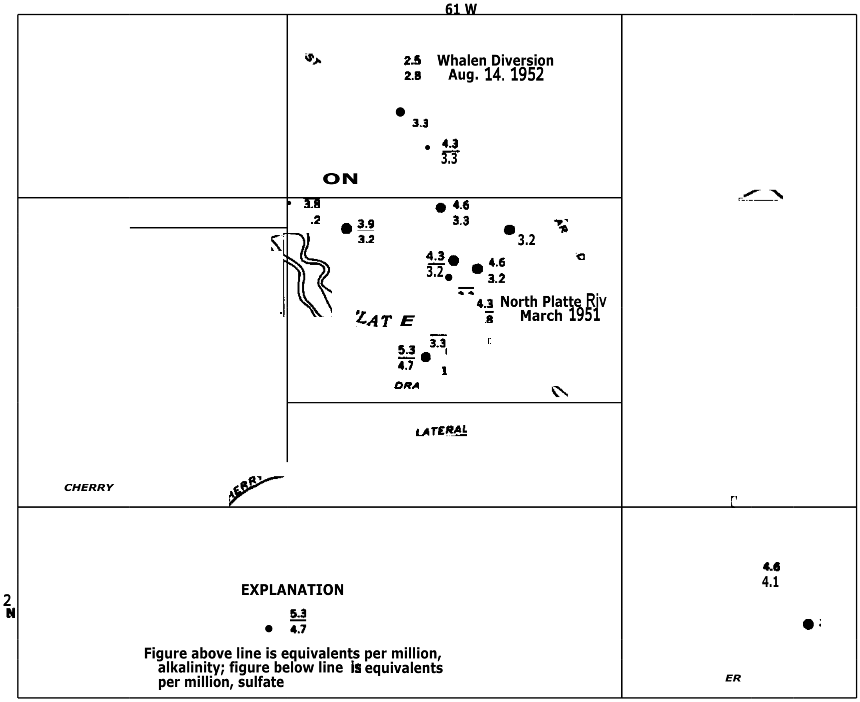


Figure 81.—Ratio of alkalinity to sulfate in water from unconsolidated deposits in the Torrington area, Nebraska.

The Coconino is tapped by a number of wells in this area, and is well suited to mapping by the method used. The shape of the body of more dilute water in the aquifer may be indicative of the path taken by most of the water moving from the area of recharge near the Mogollon Rim toward the areas of discharge along the Little Colorado River. This illustration was published in a report prepared by Babcock and Snyder (1947). McDonald, Walcott and Hem (1947) have published similar data for the Phoenix area, and Babcock, Brown and Hem (1947), for the Wellton—Mohawk area of Arizona. The quality of water in alluvium in these areas is shown by isogram maps in both reports. Drescher (1953) has prepared similar maps for an area near Green Bay, Wis. Less detailed maps were included in a report by Meinzer and Kelton (1913), to show water quality conditions in Sulfur Springs Valley, Ariz.

Detailed hydrologic studies in the lower part of Safford Valley, Ariz., were made in 1943-45 and are described by Gatewood and others (1950). Quality of ground water in the alluvial fill of Recent age in this area which lies adjacent to the Gila River is shown by a map in that report, a part of which is reproduced here (pl. 2). During the investigation, a large number of observation wells were installed

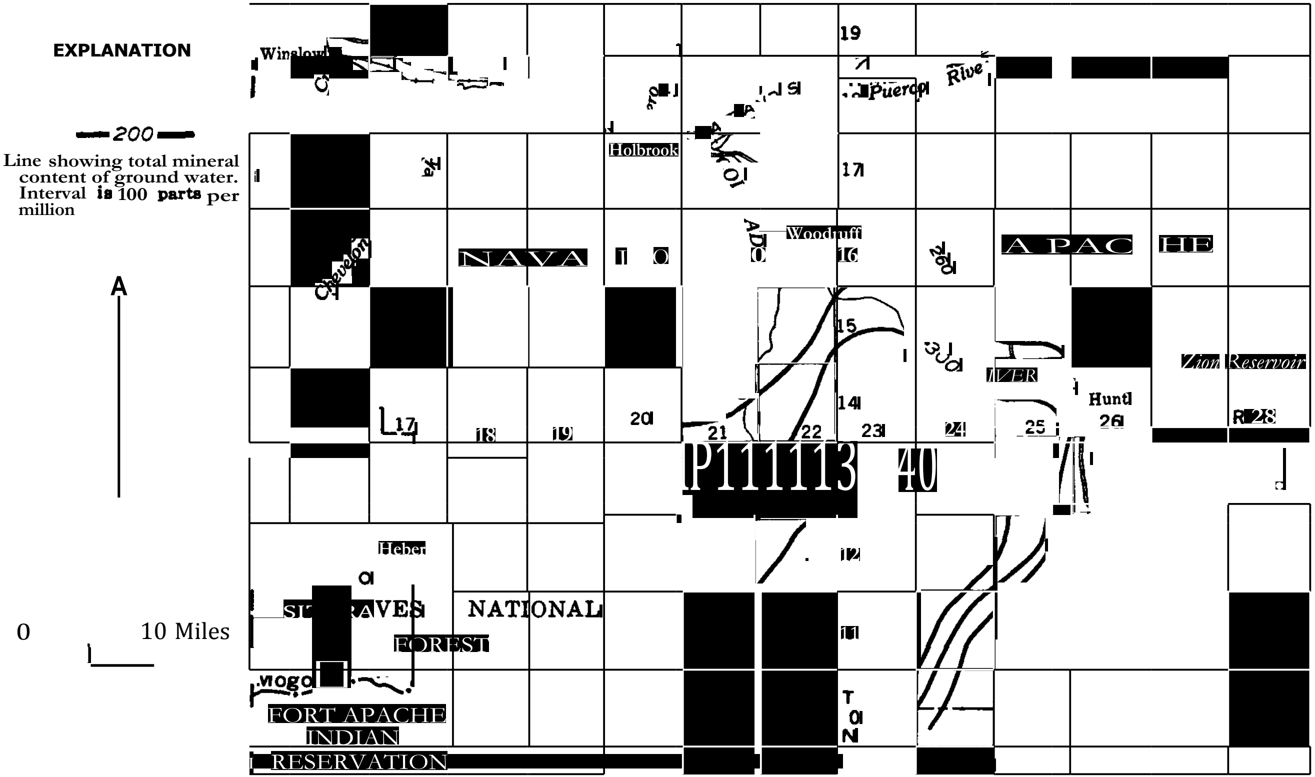


Figure 32.—Map of portions of Apache and Navajo Counties, **Ariz.,** showing mineral content of ground water in the Coconino sandstone.

in the river-bottom land, and the concentration of dissolved solids in shallow ground waters in the area can be accurately extrapolated over the short distances between wells. Plate 2 shows there is saline ground water throughout the river bottom area near Fort Thomas. Farther downstream in the vicinity of Geronimo the saline water is replaced by comparatively dilute water. The dilute water comes from underflow of Goodwin Wash and other ephemeral streams which drain large areas to the south. The effect of the underflow on water levels in the area is also marked, and when the water-level maps were interpreted along with the quality-of-water maps, a more complete understanding of hydrologic conditions in this area was gained than could have been obtained from either type of map alone.

Many different characteristics of water can be mapped. A report by Hill (1940) contains maps of the Coachella Valley, Calif., to demonstrate the variations of sodium percentage in the ground water. Lines showing equal chloride concentrations ("isochlors") were used in a report by Jackson (1905) to show the chloride content of water in the northeastern part of the United States, and the manner in which the chloride concentration decreases inland from the ocean. The maps are intended to show concentrations both in surface and ground waters, and are based on data for both. The purpose of isochlor maps of the type just described was to establish a base of normal" value for chloride in water. In the areas concerned, chloride concentration excessively above the normal could then be considered indicative of pollution.

SELECTION OF STUDY TECHNIQUES

From what has been stated, it is evident that a sizable kit of tools is available for use in the study and interpretation of water analyses. The particular tool or modification of it to be used with a set of data, however, should be selected carefully.

The extent to which quality-of-water data are complete for the area under investigation will often govern the methods of study that can be used to advantage. For an area where only scattered and more or less unrelated samples of water were collected, inspection of the analyses, noting the relationships of waters to one another or their differences, perhaps with the aid of ratios or other simple mathematical devices, may be about all the study that is justified. However, plotting analytical data on maps of the area is likely to be helpful in the study phases of the preparation of the report, even if such maps cannot be considered worthy of publication.

A systematic sampling program in an area will yield analytical data to represent most or all of the important sources of water in the area. These data should be carefully studied so that a detailed interpretation can be made. To begin with, the available data should be arranged so that related analyses are together. Surface-water analyses should be grouped so that data for each sampling point are together and in chronological order. Variations of water quality with discharge can then be noted and extremes of concentration for various time periods observed. Mean concentrations for a period of any length can be computed, either on a straight arithmetical average basis, or using discharge data as a weighting factor. Frequency graphs or hydrographs of concentrations against time, and similar plotting techniques may help to reveal the nature of the water at different points and the changes which may be expected.

The relation between surface waters can be studied by use of bar graphs, patterns, or trilinear plotting. Changes in water quality in a downstream direction along a river can be related to hydrologic or geologic features, and resemblances of waters from areas of similar geology can be revealed by graphical or other methods. The effects of hydrologic, geologic, and climatologic factors on water quality in the region should be considered, and attention given to the effects of man's use of water or of pollution by waste disposal.

In many studies, the hydrologic relationship of surface waters to ground waters is important. The comparison of chemical analyses of waters from both surface and underground sources will often aid in establishing the existence and extent of such relationships. Graphical and mathematical procedures are helpful tools in such studies. They may be a means of estimating quantities of water, as will be described later.

In investigations which are largely concerned with ground waters, the first grouping of analysis data for study purposes should be according to aquifers. A study of the analyses for waters from each aquifer will then show how uniform the composition of water in the aquifer may be. Inspection of the data may reveal that some of the sources need to be reconsidered, and perhaps reinvestigated in the field, if the analyses indicate they may be getting all or a part of their water from an aquifer different from the one supposed. A study of the analyses, aided by mathematical or graphic treatment, will generally aid in verifying the sources of water obtained from wells and in identifying aquifers where uncertainty exists as to the source of water.

After the correlation of analyses with stratigraphy in the region, a consideration of the areal variation in water quality in each aquifer is usually desirable. This often is best accomplished through preparation of maps. A study of the quality of water maps will often give some indications as to hydrologic or mineralogic conditions in the aquifers.

The changes in ground-water quality which occur with the passage of time are not so rapid as such changes in surface-water quality and are less frequently the subject of detailed investigation. There are, however, a number of problems of quality deterioration over a period of time as a result of such factors as salt-water intrusion or irrigation development. Changes in quality of ground water with the passage of time have a hydrologic significance that should not be overlooked.

Consideration should be given to the specific problems of water use as affected by quality of the available supplies in the area. This is an important part of a water quality study, but it is not the purpose of this report to dwell extensively upon such interpretations. A subsequent section will discuss some aspects of water quality as related to use.

These are all general water-quality considerations. In most hydrologic studies, more specific particular problems *need* to be solved and modifications of the interpretive techniques are necessary to meet these needs. Some possible applications of the water-quality data to quantitative hydrology will be brought up later.

RELATIONSHIP OF WATER QUALITY TO GEOLOGIC CONDITIONS

Proper interpretation of the results of chemical analyses of water requires a general understanding of certain geologic conditions that can be expected to affect water quality. Not all such conditions can be considered in detail in this report, but in this section some of the most important ones will be discussed.

AQUIFER COMPOSITION

It has been stated that there should be a general relationship between mineral composition of a natural water and that of the solid minerals with which the water has been in contact. This relationship may be comparatively simple and uncomplicated, as in the case of an aquifer receiving direct recharge by rainfall and from which water is discharged without contacting any other aquifer or other water. Or the situation may be rendered very complex by influence of one or more interconnected aquifers of different composition, mixing of unlike waters, chemical reactions such as base exchange, adsorption of dissolved ions, and other factors. In surface waters and certain shallow ground waters, the soil composition and the factors involved in soil formation may have a considerable influence on water quality.

Most rocks are complex mixtures of minerals which differ widely in their stability toward or solubility in water. The bulk of all rocks except the evaporates, however, is made up of minerals that are not very soluble. The composition of a rock as indicated by its chemical or mineralogic analysis is mostly determined by these nearly insoluble substances. The things that most affect water quality are sometimes present only in traces in the rock. Igneous rocks, for example, consist mainly of relatively stable and insoluble siliceous minerals, but some such rocks may contain minor impurities of more readily soluble matter. The effect of soluble impurities occurring in such rocks on circulating water would be far out of proportion to the importance of such salts in the mineral composition of the rocks. Resistate and hydrolyzate rocks may contain remnants of highly mineralized connate water which may strongly affect the quality of ground water,. or of surface waters associated with such rocks.

In spite of the acknowledged difficulties, many investigators have wished for a classification system for waters which could be based on the chemical composition of the rocks from which the waters have dissolved their load of mineral matter. Regarding such a classification, Clarke (1924b, p. 8) states in discussing quality of surface waters in the United States:

> A classification of waters according to their origin is something quite different . . . its purpose is geologic and although no complete scheme for it has yet been developed, the analyses as arranged in this memoir give some suggestions as to what may be possible.

Clarke goes on to mention limestone and dolomitic waters and siliceous waters which he states "might be termed granitic or feldspathic, at least until a better name can be found."

Investigators since Clarke's time have not been able to develop any rigorous classification system to relate water to rock types on the basis of the dissolved matter in the water. Some who declare such a classification to be impossible, support their position by citing analyses of water from what seems to be entirely different kinds of rock, which have essentially the same kinds and amounts of dissolved matter. The author does not subscribe to this point of view. However, the differences in climate or other influences on the weathering process can produce very different types of water from essentially similar source rocks. The importance of these influences must not be overlooked. The determination of more trace constituents in water analyses may help differentiate waters that appear to be similar on the basis of less complete analyses. It is not likely that a completely satisfactory system of classifying water could ever be developed that was based entirely on composition of source rocks.

Although the study of the composition of natural waters and the principles of chemistry which are relevant can stand alone as a broad field of research, a full understanding of the field requires consideration of the influences which have been active in bringing about the observed chemical composition. One of these influences obviously of major importance is the nature of the rock material with which the water has been associated. Research in quality of natural waters will need to take into account not only the composition of dissolved solids but the nature of sources of these dissolved materials as well.

In this part of this report some analyses are presented in graphic form to illustrate the kinds of water which have been found to be associated with certain types of rocks. These data were selected partly on the basis of best agreement between the actual analysis and what would theoretically be expected in such an environment. The reader should not expect to find such clear-cut relationships between water and rock types in all areas because complicating factors may be present. The analyses are given as specific instances and are not to be interpreted as unvarying generalizations. In the study of specific areas other factors which affect the composition of water should be considered. Over some areas of the size normally included in hydrologic studies, these environmental factors may be essentially constant, so that they can be considered subordinate to the effects of source material. In any event, it is believed an understanding of the types of water that one might expect under ideal conditions in association with certain types of rock is worth cultivating.

IGNEOUS ROCKS

Rocks of igneous origin may be classified on the basis of their mode of origin as extrusive and intrusive. The extrusive rocks include those ejected at the land surface as lava flows and pyroclastic deposits resulting from explosive volcanic activity. The latter include such deposits as volcanic ash and cinders, tuff, and breccia. Some of these may be permeable enough to be good aquifers. The intrusive deposits include batholiths, stocks, dikes, sills, and other forms which are intruded below the surface of the earth and are usually dense and nonwater-bearing or nearly so. Both the extrusive and intrusive rocks are classified by geologists on the basis of chemical and mineral composition, texture, and other characteristics. The chemical composition is of principal importance in the relationships here to be discussed and classifications based on other characteristics will not be considered. Extrusive rocks and intrusives of the same chemical and mineral composition have different names.

In their mineral composition, with *respect* to major constituents, the igneous rocks may be considered to form a continuous series, the members of which grade into each other successively. At one end of the series are the rocks such as syenite which contain largely *alkali* feldspar, and granite which contain largely alkali feldspar and quartz. Further on in the series are rocks such as diorite which consist of mixtures of alkali and plagioclase (calcium and sodium) feldspars with quartz. Still farther on in the series are rocks like gabbro and basalt which contain mostly plagioclase feldspar and ferromagnesian minerals with no quartz, and finally at the other end of the series are rocks which contain only ferromagnesian minerals.

The rocks containing only or largely alkali feldspar and quartz are sometimes termed acid rocks or sialic rocks (from the importance of silica and alumina in their composition) and those high in ferromagnesian minerals are sometimes called basic, or ultrabasic if only ferromagnesian minerals are present. The rocks at this end of the system also are termed femic or mafic by some writers. A detailed discussion of rock classifications is not pertinent here but such a discussion is included in standard texts on geology and petrology (for example, Pirsson and Knopf, 1947, p. 117).

In considering igneous rocks in their relation to water the texture and structure of the rocks is of some importance. Ground waters may be recovered in large amounts from some of the extrusive igneous rocks, where there are shrinkage cracks or other joints, interflow zones, or other openings through which water may move. Most igneous rocks, however, are relatively impermeable. They may affect to some extent the composition of surface waters where streams flow over their exposures and through areas where soils are derived from them, but usually the ground waters are more effective solvents owing to slower movement of the water and more intimate contact between water and rock minerals.

Detrital material is derived from igneous rocks through the process of weathering and erosion. This process can be largely mechanical, so that the minerals in the igneous rock originally are not fully subjected to the chemical action of water. Subsequent circulation of water through this kind of detritus will give an assemblage of dissolved mineral matter similar to what might have been expected in water circulating through the original uneroded rocks. This type of detrital material is common in arid regions.

In discussing sources of silica in water, it was stated that certain silicate minerals yield silica when attacked by water containing carbon dioxide. Because igneous rocks in general are composed to a great extent of these silicate minerals one would naturally expect waters associated with igneous rocks to be comparatively rich in silica.

The silicate minerals differ considerably with respect to the amounts of silica released in their reactions with water. The decomposition of alkali feldspar already mentioned supposedly can occur in several different ways depending upon conditions of weathering. The same is true of other silicate minerals. The complex mixture of such minerals which makes up igneous rocks, and the fact that some minerals are much more readily attacked than others, all go to make impossible any close prediction of the amounts of silica that will be yielded by different types of rock. A better understanding of some of the processes involved, however, may be aided by further consideration of different minerals as sources of soluble silica.

Alkali feldspar can yield from 2 to 3 molecules of $\mathrm{Si0_2}$ for each sodium or potassium ion, according to Pirsson and Knopf (1947, p. 179) , although generally the smaller amount can be expected. Calcium feldspar, anorthite, could decompose to kaolinite and calcium bicarbonate with no release of silica at all. Olivine may yield one molecule of silica for each four magnesium ions released during the formation of serpentine. Pyroxenes such as hypersthene and augite may also be converted to serpentine by a similar process involving the action of water and carbon dioxide. Clarke (1924a, p. 614) states that for diopside, a principal variety of augite, 4 molecules of silica are released for each 3 calcium ions. In a general way, these reactions suggest that silicates rich in alkalies are likely to release more silica in the weathering process in proportion to the cations released than the ferromagnesian silicates or those containing much calcium. Although not all the silica released may be dissolved, these relationships may help explain why certain types of igneous-rock terranes yield soft waters high in pH and with relatively high silica concentrations. Other types of igneous terranes yield water that is hard, has a lower pH, and which may have a lower relative concentration of silica.

Figure 33 illustrates by bar diagrams the analyses of water from igneous rocks of various types. The silica concentration in parts per million is represented by a separate bar for each analysis. The highest silica concentration is in the waters having the highest sodium percentages, and the lower concentrations are in waters associated with rocks having higher proportions of ferromagnesian minerals.

Because silica is more soluble in hot water than in cold, the temperature of the water from the sources has some relation to silica content. The water represented by analysis 6-2 issues from the ground at a temperature of 101°F, which helps explain the high silica content. Water from the other sources represented in figure 33 are only a few degrees above the mean annual temperature of their localities.

To indicate the relative importance of silica in these waters more clearly, the silica concentration is also expressed in terms which are directly comparable to the equivalents per million values plotted in the bar graphs. In the reaction

$$2\ \mathrm{NaAlSi_3O_8} + 2\ \mathrm{H20} + \mathrm{CO_2} \rightarrow \mathrm{Al_2Si_2O_5(OH)4} + 4\ 8102 \qquad \mathrm{Na_2CO_3}$$

if the silica is assumed to be present in the final solution as $\mathrm{H_2SiO_3}$ in largely undissociated form, it is only necessary to increase the

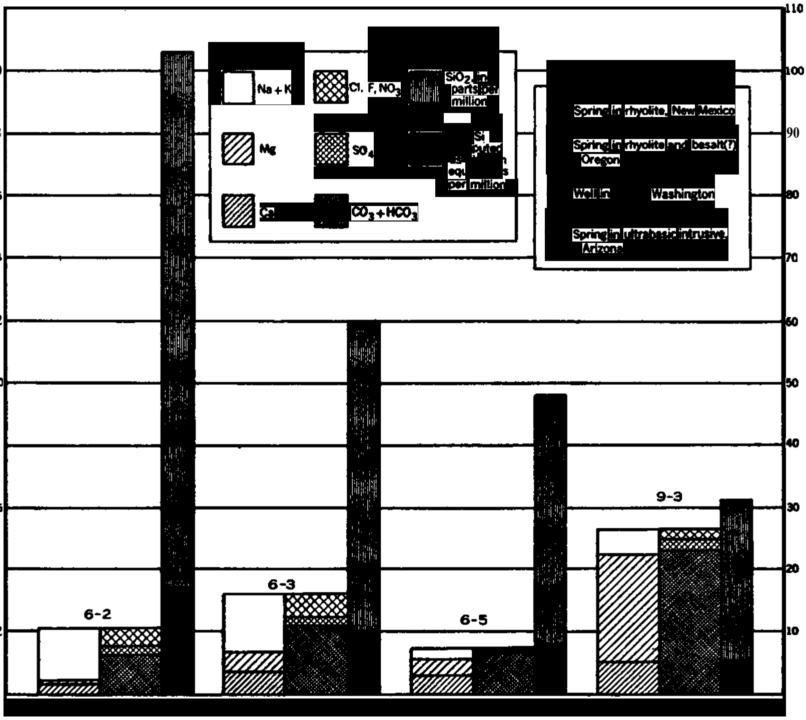


FIGURE 33.—Analyses of waters associated with igneous rocks.

amount of water entering the reaction to six molecules. The products will then include 4 H_2SiO_3 molecules or 4 potential SiO_3 ions for each 2 Na+ ions. A similar addition of water could be made to any such process that produces SiO_2 molecules. Unless the pH is very high, the SiO_3 — ions should remain undissociated and need not be considered in the ionic balance, although any part of them titrated as alkalinity would appear as an equivalent amount of CO_3 — or HCO_8 —, as discussed earlier.

The determined silica in ppm has been computed for the purpose of this illustration (figure 33) into an equivalent amount of SiO_3 — in epm. The lower hatched portion of the silica bar represents therefore the silica in terms equivalent to those used for the dissociated ions. It is not intended to imply that all or part of the silica is actually dissociated. Rather, this portion of the silica block represents the maximum possible amount of SiO_3 — that the SiO_2 content would produce if it were ionized.

For waters characterized predominantly by sodium and alkalinity, **an upper limiting value which could be expected for silica might be very roughly computed by assuming that 4 molecules of silica are produced for each 2 Na+ ions. This value is approached in analysis**

6-2. For waters like 6-3 and 6-5 which come partly or wholly from basalt, a portion of the silica is doubtless derived from alteration of ferromagnesian minerals and the proportion of silica is lower as would be expected since the reactions of water with such minerals releases fewer silica molecules for each cation. Basalt contains predominantly calcium-sodium feldspar and ferromagnesian minerals which on decomposition should give appreciable concentrations of sodium, calcium and magnesium.

Analysis 9-3 in figure 33 represents a water of unusual composition occurring in an area where olivine is abundant. In the serpentinization of olivine, 1 silica molecule is produced for each 4 magnesium ions. Hence, one would expect a 1 to 4 ratio of silica expressed in epm to magnesium, as a maximum, if all the silica came from this source. The ratio for this analysis is about 1 : 3.5. However, the outstanding characteristic of this water is the predominance of magnesium, which is due to magnesium minerals in the rocks with which the water was in contact.

SEDIMENTARY ROCKS

Several different systems exist for classifying sedimentary rocks. Chemical composition and grain size and other physical characteristics provide bases for these systems. Commonly, several broad classes are set up including the detrital rocks made up of fragments of various sizes resulting from weathering of consolidated material, the chemical precipitates such as carbonates, and the evaporates resulting from concentration of waters by evaporation. The latter include the readily soluble sulfates and chlorides.

A more exacting classification which gives greater weight to the chemical composition of the sediments is given by Rankama and Sahama (1950, p. 198) as adapted from earlier work by Goldschmidt. Some use of these terms already has been made in this report in considering the composition of the earth's crust and the sources of dissolved material in waters.

The sedimentary rocks which have been classified as resistates may differ considerably in chemical composition. Ideally, the bulk of resistates should consist of particles of relatively insoluble rock material, such as quartz grains and other highly resistant minerals like garnet, tourmaline, and zircon. However, the conditions of weathering may be as important in determining which minerals are attacked and which are not, as the composition of the minerals themselves. In many sedimentary rocks, classed as resistates, the chemical attack by weathering has not been strong enough to remove all the less resistant silicate minerals. Some sands and gravels are essentially comminuted fragments of the original rock. These fragments will be subject to later solution and attack by water. The consolidated resistate rocks such as sandstone have the spaces between the mineral grains partly or wholly filled with cementing material, usually deposited by water and therefore subject to re-solution. The cement of sandstone is generally the source of most of the dissolved matter found in water that is associated with that rock. Cementing materials are usually high in calcium carbonate. They may also contain silica, sulfates, ferrous carbonate, oxides, or hydroxides of iron, and minor impurities as well as insoluble clay minerals.

To cite a type of water that could be considered typical of resistate sediments is not possible, as a wide range of concentration and chemical character occurs. It is rare, however, for such a water to contain an important concentration of silica unless the rock still contains a substantial proportion of undecomposed silicate minerals.

Figure 34 contains analyses of four waters which were obtained from resistate rocks. A wide range of concentration is represented. Analysis 6-7 is for water from detrital material probably derived in considerable part from igneous rock under weathering conditions prevailing in an arid region. The proportion of silica to sodium in this sample suggests decomposition of alkali feldspar as the silica source, and the predominance of sodium and bicarbonate shows further resemblance to some of the analyses in figure 33.

Analysis 7-8 represents water from the Dakota sandstone in southeastern North Dakota. This water is characterized by high concentrations of sulfate and chloride possibly derived from connate water or saline residues in the formation taken into solution in the long distance this water has come through the sandstone. The sluggish circulation of water in this aquifer probably is responsible for the failure of these soluble salts to have been removed by flushing.

Analysis 8-6 represents a water from valley fill in the Chandler area near Phoenix, Ariz. The character of this water has been strongly influenced by irrigation return flow that contained much chloride. In this water the relationships among the cations may have been altered by a base-exchange process in the course of which sodium originally in the water has been exchanged for calcium. The rather high proportion of silica probably would correlate better with a water having a high sodium percentage as this one probably did have before base exchange occurred.

Analysis 8-9 represents a water from the Dakota sandstone in eastern Kansas where the formation has been more thoroughly flushed than it has in the Dakotas. The calcium and magnesium bicarbonate in this water probably came from normal solution of cementing material. Silica is about the same as in the highly mineralized water from the Dakota sandstone, 7-8.

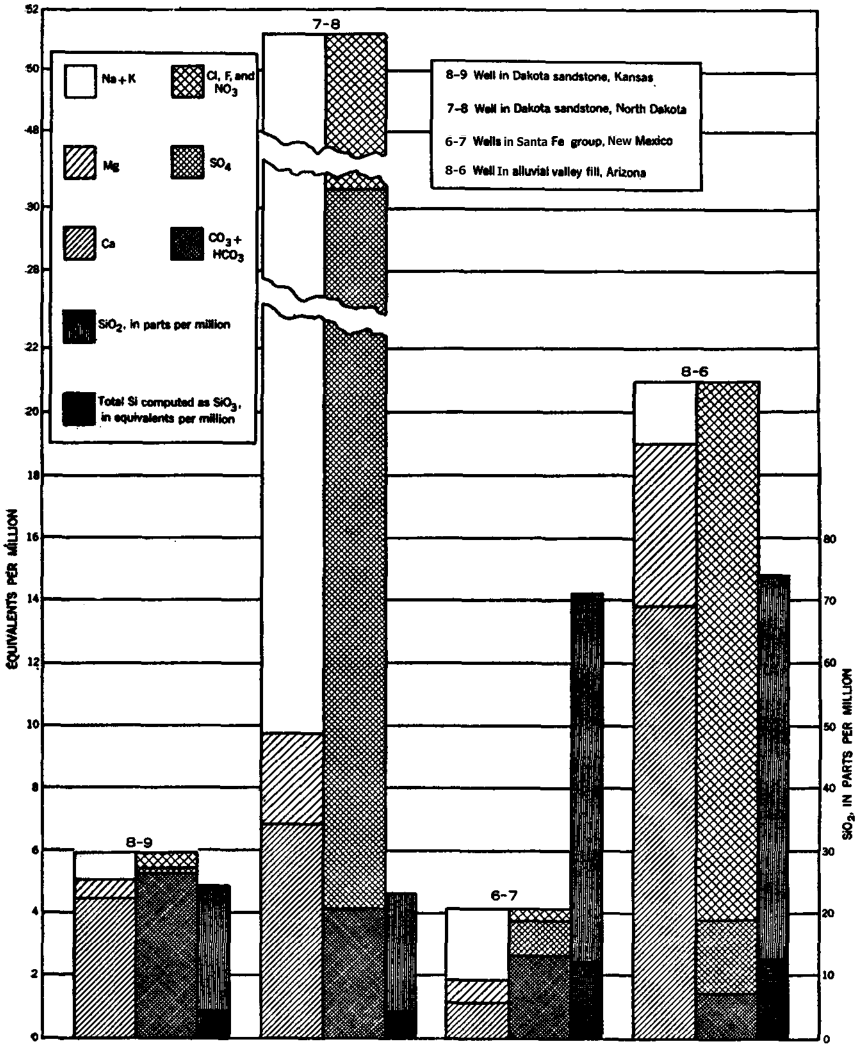


FIGURE 84.—Analyses of waters associated with resistate sediments.

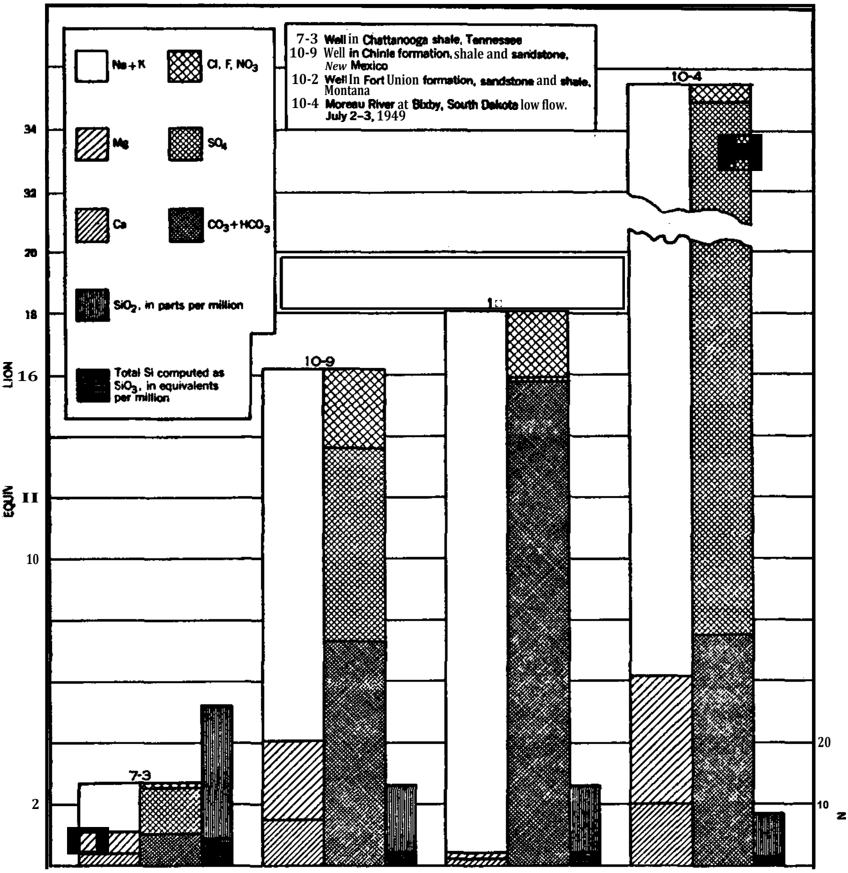
Hydrolyzaths are composed largely of particles which have already been altered by water. The shales and similar rocks of this type are porous but do not transmit water readily because the openings are very small. Movement of ground water through them therefore is very slow. In many instances the sediments were originally laid down in salt water and some of the water and its dissolved matter remains in the pore spaces and attached to the mineral grains. Because little circulation of water can occur, this connate water is removed very slowly, and water from shales may therefore be high in dissolved matter.

Although very little ground water may be directly recovered from wells in shale, it should be remembered that from a wide area of shale beds, the total amount of water may be appreciable. For example, an artesian aquifer of sandstone may be confined between shale beds hundreds or even thousands of square miles in area. The contribution of saline water from a shale surface of so large an area may be considerable if the artesian head fluctuates so that movement of water into and out of the confining shale can occur. Under water-table conditions, seepage from permeable material though an underlying shale into aquifers underlying the shale could be a major factor influencing the quality of water in the lower aquifers.

The effect of shale beds on the quality of surface runoff, even when it occurs as direct overland flow, may be of considerable importance as will be explained later.

Analyses in figure 35 represent four waters from shale or formations in which shale is an important phase. They share one dominant characteristic in that all are high in sodium in proportion to the other cations. However, this is not necessarily characteristic of waters in shale, as some are high in calcium. Shale beds may be expected to contain sodium-saturated clay minerals which tend to soften waters by base exchange. Analysis 7-3 represents water from the Chattanooga shale which occurs in a humid region. The rather high proportion of silica present in this water is anomalous and suggests that some other types of rock may be influencing the water, or that the shale contains unaltered silicate minerals. Analysis 10-9 represents a more typical rather highly mineralized water from shale in the Chinle formation in a semiarid region. Analysis 10-2 represents water from sandstone and shale of the Fort Union formation. This water has been subjected to softening by base exchange and to reduction of sulfate to give an increased bicarbonate content.

Analysis 10-4 shows the effect of soluble impurities in shale beds upon the quality of surface water in the Moreau River, South Dakota. The area of exposed shale beds containing soluble salts in the drainage basins of certain streams may be large. Each heavy rain on such exposed areas tends to remove some of the shale by mechanical action. The resulting sediments are carried off in the streamflow and the soluble salts they contain are available for solution in the flood waters. The effect is very marked in the Rio Puerco basin which is tributary to the Rio Grande in west-central New Mexico. Flood waters from this tributary are heavily laden with sediment and dissolved solids. Figure 36 shows by bar graphs the average analyses for normal low flow and for summer floods periods for the Rio Grande at San Acacia, N. Mex., below the mouth of the Rio Puerco. The difference between the averages is essentially the result of the effect described above.



FIGU 35.—Analyses of waters associated with hydrolyzate sediments.

Because of their susceptibility to erosion, shale deposits are also of importance in connection with suspended-sediment studies. Such considerations are outside the scope of this report, however. Colby, Hembree, and Jochens (1953) have discussed the relationship of geology to sediment loads and water quality in the Moreau River basin, South Dakota. Swenson (1953) has discussed relation of geology to chemical quality of water of the Powder River in Wyoming and Montana.

Precipitate sediments are essentially the result of chemical reactions and thus this type of sediment consists predominantly of a few comparatively pure compounds. The solution of limestone which has already been discussed at some length in the consideration of sources of calcium in water is a process of basic importance and waters from comparatively pure limestones may be characterized by analysis 8-1 in figure 37. Limestone may be expected to contain

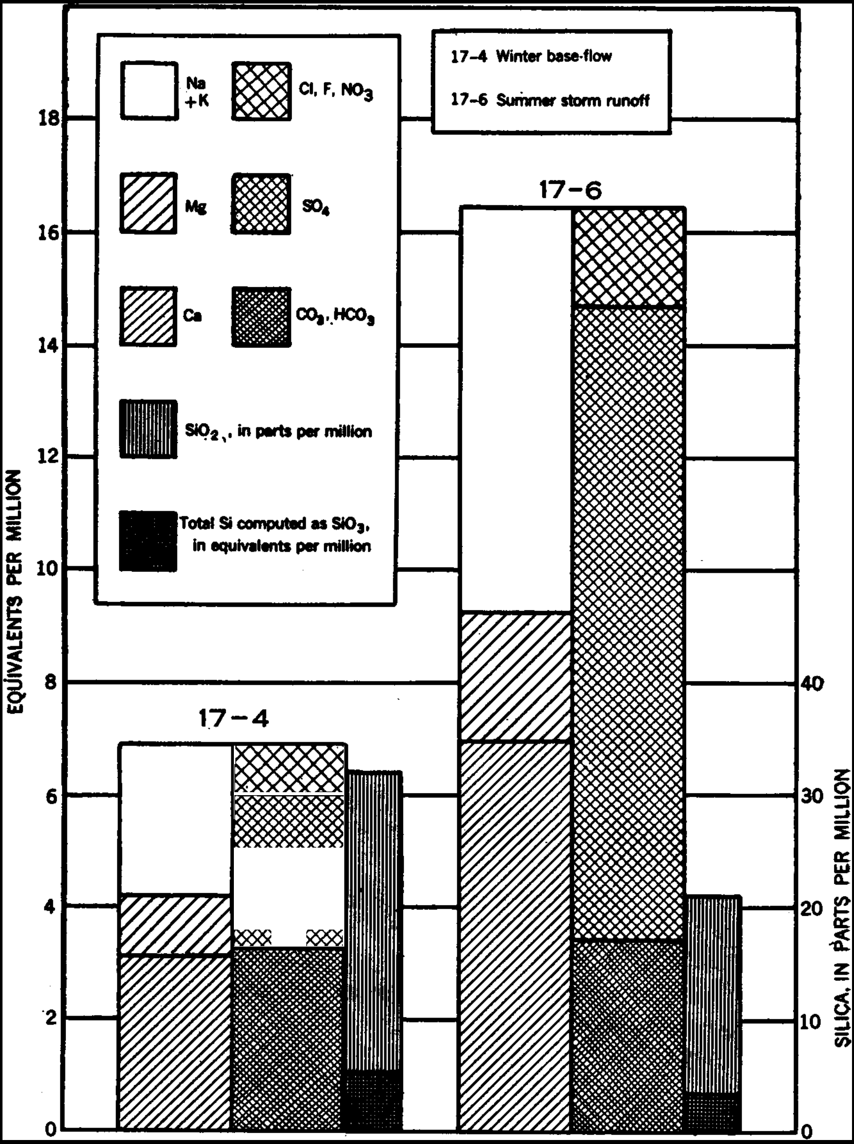


FIGURE 86.—Weighted average analyses for the Rio Grande at San Acacia, N. Mex., for two periods in the 1945-46 water year.

impurities; probably magnesium carbonate is the most common. The presence of some magnesium in a limestone water is therefore to be expected. Dolomitic waters should in theory contain equivalent amounts of calcium and magnesium. Water from limestone or dolomite usually contains bicarbonate in a much greater proportion than other anions, because it is through the mechanism of bicarbonate formation that the carbonates in the rock are rendered soluble. The presence of other anions in water from limestone is the result of impurities, connate water, or the influence of other types of rocks associated with the limestone. Silica is normally a minor constituent of waters from limestone.

Analysis 9-1 in figure 37 shows the nearly equivalent amounts of calcium and magnesium to be expected in water from dolomite. Analysis 9-9 represents water from impure limestone containing both dolomite and gypsum. Analysis 8-2 is of a supersaturated water from limestone. The water loses carbon dioxide to the air and deposits travertine.

Evaporates are deposited from highly concentrated natural brines and consist of readily soluble compounds The conditions of deposition may have caused only the least soluble materials such as gypsum or anhydrite to be deposited. Some evaporate beds include great quantities of the highly soluble sodium and potassium salts, as a result of more intense and long continued evaporation.

Gypsum, like limestone, may serve as an aquifer when solution channels or other contiguous openings exist through the bed. A water from gypsum is likely to be a saturated $CaSO_4$ solution and its composition is readily predictable (analysis 3, table 8).

Common salt is usually the principal component of the highly soluble phases of evaporate deposits, and a ground water in contact with the readily soluble alkali chlorides of evaporate beds becomes in most instances a saturated sodium chloride brine. The accessory components of natural brines depend upon the composition of the salt deposits, and may include minerals of economic value. Some of the materials commercially recovered from natural brines include magnesium, potassium, boron, lithium, and bromine. Figure 38 shows on a greatly reduced scale the composition of three natural brines. Analysis 10-8 is a sodium chloride brine from the Rustler formation in southeastern New Mexico. Analysis 9-6 is for a magnesium sulfate brine in the same area. Analysis 11-3 represents a sodium carbonate brine from Wyoming.

METAMORPHIC ROCKS

Rocks of any kind may be metamorphosed. All degrees of alteration exist from minor chemical or physical change to complete change and reassembly of minerals, and considering the wide possible variety of original rock, it is evident that few reliable generalizations regarding the possible chemical character of water from metamorphic rocks are possible.

Heat and pressure are among the most important metamorphic processes. If these forces are sufficiently intense, the rock may be completely changed to form a new igneous mass. Gneiss and schist

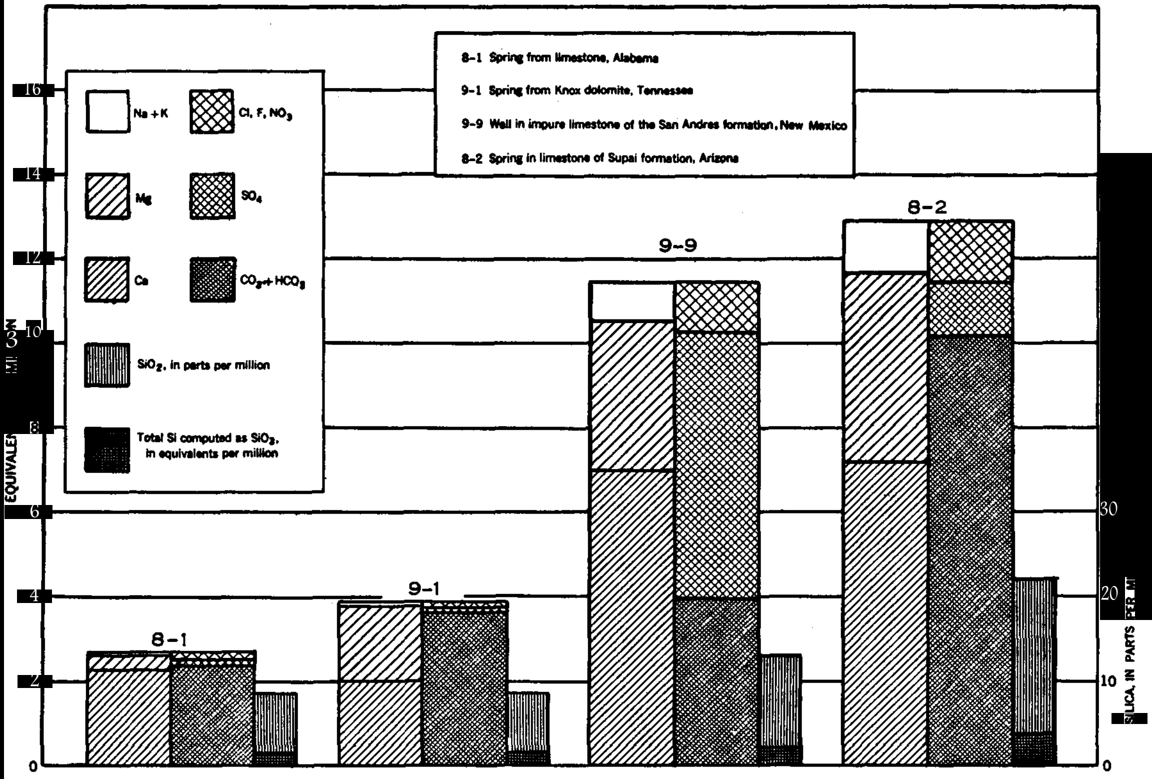


FIGURE 37.—Analyses of waters associated with precipitate-type sediments.

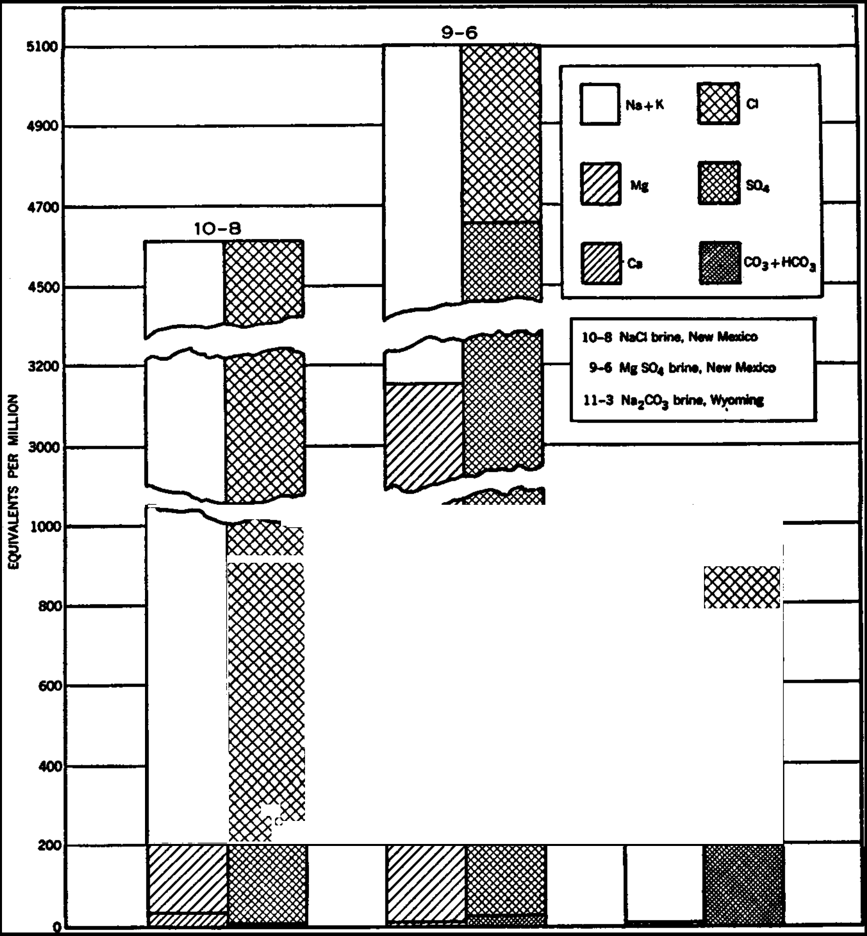


Figure 38.—Analyses of waters associated with evaporate sediments.

result from heat and pressure that do not go so far as to form a new igneous mass. These may be dense rocks that do not yield much ground water, but under some conditions, they are water bearing. The silicate minerals which usually comprise a large part of such rocks may be attacked by water, much as are similar minerals in igneous rocks, to give solutions similar to those associated with igneous rock. The dense structure of unweathered slates and quartzites prevents the contact of water over large surface areas such as occurs in unmetamorphosed shales and sandstones. The opportunity for water to pick up dissolved matter from the metamorphic forms of these rocks is therefore much less, and in general waters associated with quartzites or slates are likely to be low in dissolved-solids concentration. Limestone may be converted to marble without much chemical change, and in such marble the processes of solution are similar to those in limestone. Other marbles, however, may contain large proportions of minerals less soluble than calcite.

Attack by water is one process of metamorphism, which is exemplified by the alteration of olivine to serpentine. The process was mentioned earlier in this report as a source of magnesium in water.

Figure 39 shows 4 analyses for waters from metamorphic rocks. Analysis 6-9 represents water from schist in North Carolina. The large proportion of silica suggests solution of silicate minerals as in igneous rock. Analysis 9-8 represents a water from quartzite, comparatively low in dissolved solids. The water may be influenced by carbonate rocks in the vicinity or may derive its calcium and magnesium carbonates from minerals retained in the quartzite. Analysis 9-4 represents a spring in an area of serpentine in California. Part of the dissolved matter may come from other rocks, but it would appear that metamorphism by water may still be active here and the water itself may represent an active agent in the process. Analysis 12-5 represents water from gneiss, a strongly metamorphosed rock. The water is low in dissolved material.

CLASSIFICATION OF WATER BY ORIGIN

Many writers dealing with waters from wells and springs have attempted to classify the waters by ultimate source in two ways, first "meteoric" or "vadose" waters which are derived entirely from the atmosphere through precipitation, and second "juvenile" or "magmatic" waters which represent water vapor released from molten rock or otherwise produced far below the earth's surface. In addition, a third type, "connate" water, is sometimes proposed. This type of water is supposedly laid down in sedimentary rocks at the time of their formation.

Attempts to make this type of classification have given rise to considerable discussion among geologists and geochemists as to chemical criteria which might be used to indicate whether the water of a hot spring, for example, is wholly or partly of magmatic origin. Clarke (1924a, p. 214) reports that the French investigator Gautier believed vadose waters to be characterized by calcium, magnesium, bicarbonate, chloride, and sulfate, and magmatic waters by heavy metals, silicate, and alkalies. Other investigators quoted by Rankama and Sahama (1950, p. 266-268; 277-280) and Mason (1952, p. 176-177) seem to feel that large amounts of chloride and fluoride may be characteristic of magmatic water.

It seems unlikely that the ordinary chemical analysis will serve to differentiate between vadose and magmatic water in most instances.

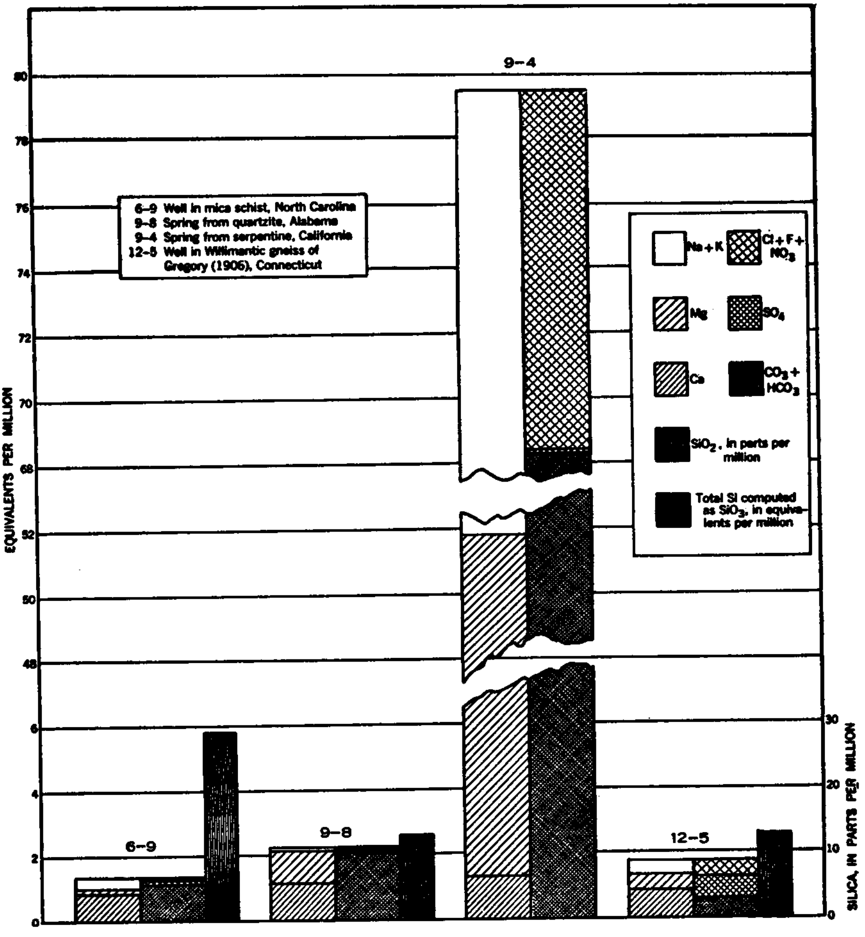


FIGURE 89.—Analyses of waters associated with metamorphic rocks.

White and Brannock (1950) believed that chloride, boron, and to a lesser extent sulfur and carbon dioxide are characteristic of water from magmatic sources. These investigators also made some computations based on the relative amounts of oxygen isotopes O and O^{--} present in the water. The ratio of these isotopes and the quantity of deuterium present in the water may give some indication regarding its origin. Studies relating to determining these properties of water have been made by Epstein and Mayeda (1953). These investigators report a relatively high proportion of 0^{18} in water condensed from a fumarole at Parícutin volcano in Mexico.

Tritium or H^{-} is a radioactive isotope of hydrogen formed naturally in the bombardment of the atmosphere of the earth by cosmic rays. It has a half life of 12.5 years. Recently, Libby (1954) has suggested that the tritium content of water would serve to indicate the length of time it had been out of contact with the atmosphere and could be used to determine rates of movement of ground water or perhaps proportions of magmatic water, because the latter would contain no tritium.

Under natural conditions the rate of tritium production has been constant for a long time, but man's nuclear experiments have released relatively large amounts to the atmosphere in recent years. These differences will need to be considered in study of tritium occurrence in the future. Tritium is not strongly radioactive and determining the small amounts present in natural water is not an easy task. However, the tritium atom is actually incorporated into water molecules which means it should be carried without loss in water moving through various environments. Hence, tritium may have promise for use as a ground-water tracer. Begemann and Libby (1957) have used tritium data to estimate rates of water circulation and research on the uses of this tool is continuing.

MODIFICATION OF CHEMICAL CHARACTER OF WATERS

When a natural water comes in contact with solid phase materials different from the ones it had been in contact with previously, or when unlike waters are mixed, chemical reactions may occur. Biologic factors also may alter the composition of waters. The more important kinds of reactions are considered here to help explain the composition of natural waters.

CHEMICAL PRECIPITATION

Natural waters may be modified in chemical character either underground or at the surface by losing certain constituents, as insoluble precipitates separate out. The reactions that cause precipitation may be chemical, as in the case of mineral matter already in solution reacting with ions dissolved from adjacent rock to form new insoluble compounds. Such reactions may be involved in the formation of vein deposits of minerals or in certain types of metamorphism. A possible example is the formation of fluorspar (CaF_2) by the reaction of fluoride in water with calcium derived from the country rock.

The deposition of substances from a solution may be caused by changes in temperature or pressure which affect the solubility of certain constituents of the water. The precipitation of calcium carbonate from a water on release of some of the dissolved carbon dioxide is a common example, although this may be considered at least in part a chemical decomposition. The release of carbon dioxide may result from a decrease in pressure, an increase in temperature, or both. The deposits of calcareous tufa, or travertine, which are built up around the orifices of springs in many areas are one of the more prominent results of this reaction. Deposition of silica by certain hot-spring waters also is of common occurrence. This deposition may be related to temperature changes and other factors.

Exposure to the air causes oxidation of dissolved substances in certain types of water. A common result of this oxidation is deposition of iron as ferric hydroxide from waters containing ferrous iron in solution.

The deposition of chemical compounds from a water also results from evaporation of all or part of the liquid. A wide variety of substances may be deposited in this way, depending upon the nature of the water and its temperature.

ADSORPTION

The surface of a solid which is in contact with a gas or a liquid is covered with a thin layer of molecules or ions taken up from the nonsolid phase. The layer is held to the solid surface by physical or chemical forces and in either instance is tenaciously retained. The phenomenon is called adsorption.

Finely divided solids may have a large surface area per unit volume and hence a considerable capacity for physical adsorption. Finely divided charcoal, for example, may be used to adsorb gases or organic compounds that produce colors or odors in water. The intermolecular or "Van der Waals" forces, between the solid surface and the adsorbed layer, cause the adsorbed material to be retained in a layer of the order of one molecule in thickness. The quantity of material which can be so adsorbed is a function of the surface area of the solid, but is different for different adsorbents and adsorbates. Natural waters may be exposed to various types of finely divided solids that can have an adsorptive capacity. In most instances, the physical adsorption is of minor importance so far as the major dissolved components of the water are concerned. Water molecules and substances like dissolved gases or organic matter not in ionic solution probably are the principal things adsorbed by the physical process just described.

Another type of adsorption exists in which the forces of chemical bonding between ions is involved rather than the physical forces mentioned previously. This type of adsorption is termed "chemisorption" and replacement of adsorbed ions by ions in solution is termed "ion exchange." The capacity for chemisorption is mostly a result of unsaturation of the chemical bonding in the crystal lattice of the solid having this capacity. In most of the important natural exchange media there is an excess of negative bonds in certain areas of the crystal lattice, and positively charged ions are attracted to these areas. Divalent cations are usually but not always held more tightly than monovalent ones, but the exchange process is essentially a reversible chemical reaction which obeys the law of mass action.

Most of the ion exchange reactions involve cations and are often referred to as base exchange. The process of anion exchange is mentioned by Reiche (1950, p. 33-35). Mineral structures capable of chemisorption of anions would have to have an excess of positive charges. Studies of anion exchange in soils have shown that some capacity for this process exists (Dean and Rubins, 1947) although the mechanisms involved are not yet fully understood. Not enough is known of the possible effects of anion exchange materials on water quality to justify further discussion of this subject.

The phenomenon of cation exchange in soils was discovered by the English agricultural chemists, Thompson (1850) and Way (1850). Way published several papers discussing the effect and considered it from a quantitative viewpoint. These early studies showed that when solutions of ammonium salts were passed through columns of soil, the ammonium ions were removed from solution and the leachate contained instead an equivalent amount of calcium.

In the years since this discovery, much research has been done on the nature of the exchange effect in soils, and the solid minerals and the ions involved. A discussion of ion exchange, especially as related to soils, has been published by Kelley (1948) who discusses in his book the history of studies of the exchange processes.

Although many natural minerals have some exchange capacity, certain of the clay minerals are especially important, both because of high exchange capacity and wide distribution in soils and sediments. The clays of the montmorillonite group are probably the most important, and these clays were discussed by Ross and Hendricks (1945). A voluminous and growing amount of literature on exchange properties of clays is now available. However, much of this material is related to natural water chemistry in only an indirect manner, and need not be completely covered in this report. A recent summary of the subject of clay mineralogy and related topics has been prepared by Grim (1953).

The effects of cation exchange on the composition of natural waters were pointed out by Renick (1925) in connection with studies he was making of ground waters in the state of Montana. Waters softened naturally, of the type he found there, are common in many parts of the world. Such waters may contain practically no calcium or magnesium. They have a wide range of dissolved solids concentration and among the anions bicarbonate, sulfate, or chloride, are present in many different proportions. The sodium bicarbonate type of water is probably the most common, however. Waters softened by ion exchange have been recognized in the Fort Union formation of Montana and North Dakota (Renick, 1925; Riffenburg, 1925), the sediments of the Atlantic and Gulf Coastal Plains (Stephenson, Logan, and Waring, 1928; Foster, 1937, 1939, 1950; Cederstrom, 1945; and Meyer and Turcan, 1955), the valley-fill deposits of the Basin and Range physiographic province (Halpenny and others, 1952), and in many other areas.

Because minerals having exchange capacity are widespread and abundant, their role in altering the composition of dissolved matter in water is very important.

The cations in solution in water and the adsorbed ions held by exchange material in contact with the water constitute a system in chemical equilibrium, provided contact is long enough. In the reaction $2\,\mathrm{Na}X + \mathrm{Ca}^{++} \rightleftharpoons \mathrm{Ca}X_2 + 2\mathrm{Na}^{+}$ (where X represents a unit of exchange capacity in the solid-phase material), the degree of displacement of the equilibrium to the right or left is governed by the law of mass action. Normally, calcium and magnesium ions from solution replace adsorbed sodium on the exchange material and usually the equilibrium is displaced well to the right. If, however, the water passing through this exchange material were changed in composition to a relatively highly mineralized sodium chloride brine, the reaction would be displaced to the left. The release of calcium and magnesium from exchange positions can be observed in some fresh-water aquifers that become contaminated with sea water. The zone of contact of fresh and salt water often contains water that is higher in calcium and magnesium than could be explained by assuming a simple admixture of sea water and fresh water. Such an effect can be explained by postulating ion exchange that releases previously adsorbed Ca^{++} and Mg^{++}. Piper, Garrett, and others (1953, p. 182) observed this effect in the Long Beach-Santa Ana area of California.

Properties of soil may be affected by ion exchange reactions between minerals in the soil and ions in solution in soil moisture. Where the soil moisture is provided through irrigation, the number of ions introduced may be large, and the possibility of exchange reactions is a factor to be considered in the evaluation of irrigation water supplies. The mechanisms of ion exchange reactions have been rather extensively studied and several different mathematical expressions have been developed. Kelley (1948, p. 40-50) gives a number of these equations and discusses their advantages and shortcomings.

The Freundlich adsorption isotherm was developed for adsorption of a gas by a solid and is written:

1.

Applied to cation exchange reactions, is the amount of cations taken up per given weight of adsorbent, p is the amount of cation remaining in solution, and k and n are constants. This relationship is useful over a limited range of concentrations. The Langmuir adsorption equation is somewhat more generally applicable and can be expressed:

2. $$\frac{x}{m}\quad\frac{ksc}{1\ kc}$$

where - is again the amount of cations taken up per weight of adsorbent, s is the exchange capacity of weight m of adsorbent, c is the concentration of cations in solution, and k is a constant.

Applying the mass-action law to the equilibrium $Ca^{++}+2NaX \rightleftharpoons CaX_2+2Na^+$ one could write

3. $$\frac{[CaX_2][Na^+]^2}{[Ca][NaX]^2}$$

where the bracketed quantities represent active concentrations and k is the equilibrium constant. The activity coefficients for the adsorbed ions involved in this equation are not easy to determine. Vanselow (1932) suggested the mole fractions of these adsorbed ions present in the exchange material should be proportional to their activities. The terms [CaX2] and $[NaX]$ could then be written

$$\frac{CaX_2}{NaX+CaX_2}$$

and $$\frac{NaX}{NaX\quad CaX_2},$$

in terms of concentration. Upon substitution into equation 3

$$\frac{[Ca++](NaX)^2}{[Na]^{-}(CaX_2)(NaX+CaX_2)}\quad k$$

where bracketed terms are active concentrations and terms in parentheses represent molar concentrations. According to Kelley (1948, p. 45), Vanselow reported that the application of this equation to mixtures of exchange material and water containing various concentrations of cations, gives constant values for k over a considerable range of concentration, when certain corrections are introduced.

Other investigators have developed equations for the ion-exchange reaction but none are applicable over a very wide concentration range.

In systems of interest in natural-water chemistry, many complexities are introduced because of the mixtures of exchange media involved, and changes in the solutions in contact with them also occur. Quantitative treatment of such systems, therefore, is difficult. Before such treatment could be attempted, a fundamental question to be answered is whether equilibrium is actually reached in such systems. The exchange process itself generally is a rapid reaction although the rate depends on the type of exchange material and other factors. Even if it were a rather slow reaction, in a uniform fine-grained aquifer through which movement of water may be only a foot or so a day, there should be a good opportunity for equilibrium to be established.

Few attempts seem to have been made to make a quantitative treatment of the exchange performance of aquifers. Such studies would be of considerable interest, however, and may be essential in understanding the capacity of aquifer materials to alter the cation concentrations in large volumes of water. The processes by which cations are transported through granular aquifers containing exchange material and the ability of solid-phase material to screen out foreign cations that might be added to ground waters in waste disposal are related topics needing study.

SULFATE REDUCTION

The chemical reduction of sulfur from the fully oxidized S^{+6} state in the form of sulfate ions to the **S** - or sulfide state commonly occurs in underground waters. The reactions postulated by Engler and Hofer (1909) are :

$$CaSO_4 \quad CH_4 \rightarrow CaCO_3 + H_2S + H_2O$$

or

$$CaSO_4 + CH_4\text{-)}CaS + CO_2 + 2H_2O$$

and are said to occur in the presence of certain types of bacteria. Water is probably required as a medium for the reactions and the solid products formed would have to be carried away to permit the reactions to go to completion. If sulfate reduction is presumed to occur in solution, the reaction could be written :

$$SO_4^{--} + CH4 \ ^{\text{(bacteria)}} HS^{-} + H_20 + HCO_3$$

The pH and the reducing power of the environment would determine the form of the anions produced. The ionic statement probably is a better way of representing the mechanism of sulfate reduction, but the reaction probably is more complex than is indicated by any of these statements. The methane here shown should be considered only as a possible oxidizable substance, and many other hydrocarbons would perform the same function. Rankama and Sahama (1950, p.341) suggest sulfate could be reduced by hydrogen released through the decomposition of organic matter by anaerobic bacteria :

$$CaSO_4 + 4H_2 \rightarrow 4H_2O \quad CaS$$

Conceivably, these reactions could produce free sulfur rather than sulfides. Many waters affected by sulfate reduction seem to have gained in carbon dioxide and bicarbonate as well, but other processes such as the decomposition of peat and lignite may add carbon dioxide to ground water (Foster, 1950). At any rate, the importance of bacteria in the sulfate-reduction reaction is definitely indicated. The waters of some oil fields are high in carbon dioxide and low in sulfate, and H_2S often occurs in the gases accompanying the oil and water. Sulfate reduction may be the explanation of these conditions. The reaction occurs on a small scale in closed water sample bottles which contain sediment that has a content of organic matter. During the reduction process, the sediment generally turns black, probably because of formation of sulfides and the water emits a strong odor of hydrogen sulfide.

Waters which have been subjected to sulfate reduction can be expected to contain some hydrogen sulfide unless conditions have existed which allowed the gas to escape or react with metals to form metallic sulfides. Many of these waters have a high content of bicarbonate and often of carbon dioxide which can be gained at the expense of sulfate. The chemical analysis of a water which has undergone sulfate reduction usually gives other evidence of the process (analysis 2, table 10) in its composition, even if the H_2S is no longer present.

Rankama (1954, p. 277-289) cites the work of several investigators who have studied the relative abundance of the sulfur isotopes S^{32} and S^{34}. The S^{32} to S^{34} ratio has a relatively low value in sulfates dissolved in water or deposited in sediments. The ratio in biogenic sulfur and sulfides is considerably higher. Some studies made in North Africa (MacNamara and Thode, 1951) showed a fractionation process occurred in sulfate reduction that caused a greater proportion of S^{32} in the reduced form.

SALINE-WATER ENCROACHMENT

Surface and underground waters are subject to saline contamination in those areas where salt water is in contact with fresh water or where opportunity for such a contact exists. These conditions are most common in coastal regions but exist also in some inland regions.

In coastal regions, the quality of surface and underground waters may be adversely affected by salt water from the sea. The zone in which fresh water flowing in a river mixes with sea water may extend for some distance upstream from the river's mouth as well as seaward from it, and will fluctuate in both size and position in response to certain factors. The zone of mixing extends farthest upstream in regions where the coastal plain is nearly flat and the lower reaches of rivers are tidal estuaries or submerged valleys whose bottoms are below sea level for some distance inland.

The energy of the fresh water flowing down the river tends to push a fresh-water front out into the estuary, and this force is continuous but fluctuates in response to the volume of flow. The cyclic effect of tides in the sea is opposed to the flushing action of the stream, with the result that periodically salt water is pushed back upstream as far as the tidal force can move it.

Because of its higher density, sea water tends to move along the stream bottom, while the fresh water remains nearer the surface. However, both flows are subject to turbulence which causes some mixing along the fresh-water interface. The effect of turbulence and other factors promoting mixing, such as channel obstructions, are probably more important than ionic diffusion in bringing about fresh-salt water mixing in tidal streams.

As a result of these effects, the water of a tidal stream varies in composition vertically and horizontally in the cross section at any point, and changes in quality with the passage of time in response to changes in streamflow and to tidal fluctuations. The general conditions that can be expected in the tidal zone can be predicted when the effects of these changes in that particular area have been evaluated. Study of tidal streams involves extensive sampling on horizontal and vertical cross sections and integration of the results with data on streamflow and tides. A number of such studies have been made. The techniques required have been discussed by Keighton (1954), who gives an annotated bibliography of papers on this subject.

The relation between sea water and fresh water in aquifers along the seacoast is the result of certain natural factors, although the effects of man's withdrawal of water from these systems may be of much greater relative importance than in surface-water systems.

The occurrence of fresh ground water in a small land body of moderate and continuous permeability which is nearly or entirely surrounded by sea water is governed by the socalled Ghyben-Herzberg principle. The European scientists W. Badon Ghyben and Alexander Herzberg found near the turn of the century that, under conditions of hydrostatic equilibrium, the fresh-water body under such a land body would assume a lens shape, essentially floating on the surrounding salt water. The position of the salt-fresh water interface is a function of the height of the fresh water above sea level and the density of the sea water. In accordance with Archimedes' principle, a floating body must displace a weight of fluid equal to its own weight. The difference between the density of sea water and fresh water is relatively small, and, therefore, for any given volume of fresh water to be maintained at a level above the sea, a much larger volume of fresh water must occur beneath it to give the necessary buoyancy.

Exact conformance with the Ghyben-Herzberg principle is not to be expected in nature because the equilibrium attained is dynamic, being subject to changing tides, changing amounts of fresh water, and outward movement of the fresh water. The interface, therefore, is not a sharp contact but a changing transitional zone from fresh through brackish to salt water.

Withdrawal of small amounts of fresh water may cause a relatively great upward movement of the interface below the point of withdrawal. Theoretically, a reduction in the fresh water head at a pumped well of only 1 foot might result in an upward movement of the fresh-salt water interface as much as 40 feet below the well. Thus, a relatively small rate of withdrawal from the system can result in salt-water contamination of a well.

Aquifers containing fresh water which extend seaward from the coast may be subject to sea-water contamination if they are open to the entry of salt water below the surface of the sea, when the hydrostatic head in the aquifer is lowered by withdrawals of water from the landward part of the system. If the head is lowered sufficiently, the salt water may move inland. The rate of movement of salt in the aquifer is governed by the hydraulic conditions in the system and probably is nearly the same as the rate of water movement. The rate of movement of some ions in the salty water may differ from the water-movement rate, however, owing to diffusion effects and adsorption or ion-exchange reactions occurring in the aquifer. These effects have not yet been studied closely enough to be fully evaluated and understood.

The problem of salt-water intrusion into highly developed aquifers is serious in many coastal areas, and can occur elsewhere if there is a system into which salt water may enter upon reduction of hydrostatic head of fresh water. It is important to be able to recognize incipient stages of salt-water intrusion so that steps can be taken to correct the situation.

The composition of average sea water is given in table 2. Chloride is a major component of sea water, and increasing chloride concentrations may well be the first indication of sea-water intrusion reaching a fresh water. In an area where no other source of saline contamination exists, high chloride concentrations close to the seashore can be considered fairly definite proof of sea-water contamination. Where chloride in important amounts could come from other sources, however, the establishment of a definite proof of seawater intrusion may be more **difficult.**

The use of other components of sea water to trace contamination is possible, but objections can be raised to most of them. Magnesium is present in sea water in a much greater proportion than calcium. A low calcium-to-magnesium ratio may sometimes be considered diagnostic of sea-water contamination. The presence of sulfate in proper proportion also may be diagnostic. However, because of possible base exchange and sulfate reduction in the aquifers where such a different type of water is introduced suddenly, the proportions of anions and cations in the first contaminated water to reach the sampling point should not necessarily be expected to be exactly those caused by simple mixing with a highly mineralized contaminant. It is indeed very likely that the observed mixture after passage through even a short distance of the aquifer may bear little superficial resemblance to the theoretical mixture. After the exchange capacity of the aquifer has been satisfied and equilibrium re-established, the observed and theoretical mixtures may be more nearly the same, but this condition is reached only in later stages of contamination.

TABLE 19.—*Analyses showing effects of sea-water contamination in Gaspur water-bearing zone, Dominguez Gap, Los Angeles County Calif.*

	(1) Jan. 8, 1923		(2) Apr. 4, 1928	
	ppm	epm	ppm	epm
Silica (SiO_2)			20	----------
Iron (Fe), dissolved			.97	----------
Calcium (Ca)	27	1.35	438	21.86
Magnesium (Mg)	11	.90	418	34.38
Sodium (Na)	82	3.57	1,865	81.10
Potassium (K)			56	1.43
Bicarbonate (HCO_3)	235	3.85	193	3.16
Sulfate (SO_4)	40	.83	565	11.76
Chloride (Cl)	40	1.13	4,410	124.38
Fluoride (F)			0.0	.00
Nitrate (NO_3)			1.8	.03
Dissolved solids calculated	318	----------	8,200	
Hardness as $CaCO_3$	113	----------	2,810	
Noncarbonate			2,650	

[1] In solution at time of analysis.

1. Well 4/13-35 M3 Southern California Edison Co. West Gaspur well, Los Angeles, Calif., before contamination by sea water.
2. Same well, water contaminated by intrusion of sea water, water-bearing formation: Gaspur water-bearing zone. Analyses from Piper, Garrett, and others (1953) p. 227.

The determination of minor constituents of sea water may aid in some instances in establishing sources of contamination after it has reached a substantial level. Incipient stages cannot be detected by these constituents. Piper, Garrett, and others (1953) report some success in distinguishing between sea-water and connate-brine contamination using iodide, boron, and barium determinations. These selections were related to the character of the connate brine which also could have caused contamination in the area under investigation.

Table 19 gives the analyses of water before and after contamination by sea water of a well in the Los Angeles area. The calcium in the contaminated water is higher than would be expected from a simple mixture, probably owing to some of the effects noted in previous pages.

A discussion by Revelle (1941) on the subject of chemical criteria for recognition of sea-water contamination at early stages points out the possibility of considering the chloride-to-bicarbonate ratio as diagnostic of sea-water intrusion. Sea water is low in bicarbonate, and an increase of the ratio might therefore be caused by something having a high Cl: HCO_3 ratio, such as sea water.

In any problem of salt-water intrusion, consideration needs to be given to all possible salt sources, so that remedial measures that are taken will be directed at the true source of trouble.

Banks, Richter and Harder (1957) have described remedial measures taken to stop sea-water intrusion into an important aquifer at Manhattan Beach, Calif.

CHANGES ASSOCIATED WITH LIFE PROCESSES OF PLANTS AND ANIMALS

All forms of life on the earth are dependent upon water for their existence. In return, the life processes of plants and animals have a considerable influence upon the composition of natural waters. Many of these processes, such as the precipitation of silica and calcium carbonate by plants and animals, occur in the ocean and saline lakes and in bodies of fresh water as well, and are important in controlling the amounts of silica and calcium in solution. For the purposes of this report, the ocean is not of direct interest, but many important processes occur on land which affect the composition of terrestrial water.

Probably the most important zone of the earth's crust for the land-dwelling animals and plants is the upper few inches, called the soil. In this zone, great numbers of bacteria exist in every cubic centimeter. Those in the upper layers are mostly aerobic; that is, they require cxygen in their metabolism. The ones occurring deeper in the earth may be anaerobic and derive energy for their life processes from such reactions as the reduction of sulfate or iron. Bacteria and fungi are involved in the production of carbon dioxide which is released to water and is important in the solution of minerals. Other varieties of plants and animals may act as links in the nitrogen cycle, in which nitrogen from the air is fixed in the soil and converted by plants to amino acids. These are consumed by animals and returned to the soil in nitrogenous waste, and then partly oxidized to nitrate, in which form nitrogen appears in most natural waters.

The role of plants in the reactions between water and minerals in the soil is important. The process of plant growth liberates carbon dioxide into the soil atmosphere, and carbon dioxide is derived also from decay of organic matter. Thorne and Peterson (1954, p. 22) state that under conditions of vigorous plant growth from 2 to as much as 10 liters of carbon dioxide per day per square meter of soil may be produced. A part of this carbon dioxide is no doubt dissolved in water in the soil, where it aids in the solution of calcium carbonate.

Keller (1955, p. 24-25) refers to several other processes that may be actively promoted by plant roots to lower the pH of the surrounding water in the soil and bring about chemical reactions that decompose silicate minerals and bring them into solution. He suggests also the possible importance of chelation by organic substances imparted to soils by plants and animals. The chelating agents are able to form complexes with cations which will remain in solution, but the chelated ion cannot take part in the chemical reactions it would be subject to if it were not chelated. The importance of chelation in natural water quality has not been studied extensively.

Besides their role in the various processes that put dissolved material into water when it. passes through soils and rocks, plants and animals play a part in removing these materials from solution. In surface waters, the presence of aquatic plants and animals helps preserve a balanced supply of dissolved oxygen and carbon dioxide. Some plants tend to remove directly, substances like calcium bicarbonate from solution, or by removing dissolved carbon dioxide promote calcium carbonate deposition.

The role of biologic agencies in controlling natural water quality with respect to organic pollution is well known. A great amount of study remains, however, before it will be possible to evaluate fully the importance of such agencies in controlling or influencing the amounts and kinds of inorganic substances carried by natural waters.

CHANGES RESULTING FROM MAN'S ACTIVITIES

Man's development of the water resources of the earth has brought about extensive changes in water quality. Some of these changes have come about because of natural forces man has knowingly or otherwise set in motion. Sea-water contamination of ground waters is a good example.

In point of quantities involved, irrigation is probably the largest use of water in which a large part of the water is consumed. Man's intervention in the normal hydrologic pattern in an area where he develops irrigation has a profound effect on behavior of both surface and underground waters and has a simultaneous effect upon the chemical quality of both. Because much water is evaporated and transpired in an irrigated area, there ,is a tendency for the residual water to carry increased concentrations of soluble salts, and this effect is usually noticeable in both surface and underground effluents.

Analyses in table 10 show the average quality of water of the Salt River above the irrigated area around Phoenix, Ariz., and the average quality for the same period for the residual effluent from the area in Gila River at Gillespie Dam. The Salt River water is the major source of irrigation supplies and the residual water is greatly increased in concentration through irrigation use. The increase of dissolved solids in ground water in the Wellton area of Arizona shown in figure 5 probably is related to irrigation in an area where the residual water was not allowed to escape.

A discussion by Cunningham, Haney, Bendixen, and Howard (1953) on the effects of irrigation has been published. These men considered a number of aspects of the effects of irrigation on water quality and give many references.

The fertilizers and soil amendments used in irrigated areas also tend to change the quality of effluent water. The concentration of nitrate in ground water is considerably increased in some areas because of agricultural activities (analysis 2, table 12).

The use of streams for waste disposal has a very important influence upon the composition of certain surface waters, especially in highly industrialized areas. Streams serve the function of removal of soluble waste material under natural conditions, and the removal of waste material contributed by man is a highly beneficial function. The use of a stream for this purpose should not be thought of as invariably undesirable. However, when excessively large amounts of wastes are put into streams, problems may be created, especially where others must use the waters farther downstream. The waters affected by waste disposal may contain substances not found in natural water, and study of polluted waters is a broad field itself which has not been considered here.

In some areas, ground waters are utilized for the disposal of undesirable mineral wastes. Usually only deep aquifers containing essentially stagnant salty water are satisfactory for such disposal procedures.

APPLICATION OF WATER-QUALITY DATA IN QUANTITATIVE HYDROLOGY

A number of methods of study and comparison of water-analysis data have been discussed in this report. Some of these methods have never been applied or have been only partly utilized in the determination of quantities of water involved in hydrologic systems. Most problems in modern hydrology are quantitative; that is, one needs to know the amounts of water involved. The changes in chemical composition of a water as it moves through a system can be considered at least an indication of quantities of water involved, provided that some of the quantities are known and complete data on chemical composition are available.

Corbett and others (1945, p. 88-90) describe two "chemical" methods of measuring water discharge, both of which have been utilized to some extent in measuring flow of surface streams. The first of these, the so-called salt-velocity method, depends upon measurement of the time of travel of a "slug" of strong salt solution suddenly introduced into a water-carrying channel. This procedure is of somewhat limited usefulness because a strictly quantitative application requires a channel of constant cross section. The second procedure is the so-called salt-dilution method, which involves the introduction at a constant rate of a salt solution of known and constant composition. At a point downstream where the water is completely mixed, a sample is collected and analyzed. From the composition of the mixture and the known rate and composition of the salt inflow, the stream discharge can be computed, using simultaneous algebraic equations.

In an experiment of this type, the water discharges are related as follows:

$$q_1+q_2=q_3$$

where q_1 is the discharge of the stream before the salt solution is added, q_2 is the discharge rate of the salt solution and q_3 is the discharge rate of the mixture. Also,

$$q_1c_1+q_2c_2=q_3c_3$$

where the three c quantities represent salt concentrations of each of the three discharges. When salt is added to measure the discharge, the quantity q_2 is known and all the c terms are determined by analysis. It is simple to compute the two unknown discharges when the other values have been determined.

The principle of this method of discharge measurement is not new but it appears capable of wider use than has been made of it in the study of natural waters, both on the surface and underground, with minor variations in technique to fit the situation. A simple example of a system that can be evaluated is a stream that receives inflow from a salt-water spring. If the spring is accessible for measurement, the procedure can be used just as described to determine the streamflow. If the spring is not directly measurable, a single streamflow measurement to evaluate q_1 or q_8, coupled with necessary sampling, will give a value for the spring discharge.

TABLE 20.—*Analyses of water from Clifton Hot Springs and from San Francisco River above and below Clifton, Ariz.*

[Source of data: Hem (1950). Date below sample number is date of collection]

	(1) Jan. 10, 1944		(2) Jan. 10, 1944		(3) Jan. 10, 1944	
	ppm	epm	ppm	epm	ppm	epm
Silica (SiO_2)					58	
Iron (Fe), dissolved [1]					.19	--------
Calcium (Ca)	44	2.20	72	3.59	860	42.91
Magnesium (Mg)	12	.99	13	1.07	41	3.37
Sodium (Na)	58	2.52	156	6.78	2,670	116.10
Potassium (K)					142	3.63
Bicarbonate (HCO_3)	204	3.34	206	3.38	109	1.79
Sulfate (SO_4)	17	.35	19	.40	153	3.19
Chloride (Cl)	70	1.97	270	7.62	5,800	163.58
Fluoride (F)	.8	.04	.8	.04	3.0	.16
Nitrate (NO_3)	.2	.00	.5	.01	7.5	.12
Dissolved solids calculated	302	---------	633		9.790	
Hardness as $CaCO_3$	160	----------	233		2.310	
Noncarbonate	0	---------	64		2,220	
Specific conductance (micromhos at 25° C)	547		1,160		16,500	
Discharge (cfs)	58 (calc)	---------	60 (meas)		2.1 (calc)	....

[1] In solution at time of analysis.

1. San Francisco River 2 miles above Clifton, Ariz.
2. San Francisco River at gaging station at Clifton, Ariz.
3. Clifton Hot Springs seep opposite Southern Pacific Lines depot. Temp. 110 F.

Such a condition occurs in the vicinity of Clifton, Ariz., where a zone of salt spring inflow occurs below the surface of water in the San Francisco River. Current-meter measurements above and below the zone of inflow are a standard means of evaluating such inflows, of course. In this instance, however, the amounts of flow in the river are normally so much larger than the salt-water inflow that the unavoidable errors in measurement would be of the same order of magnitude as the inflow. A measurement by difference would therefore have a low order of accuracy. The salt-dilution procedure gives a computed discharge whose accuracy is about the same as that of the single discharge measurement required.

In the study of the hydrology of this area, Hem (1950) utilized this method to determine the spring inflow at Clifton on several occasions. Base data and results for one set of measurements are given in table 20. The discharge below the spring zone was continuously measured by a stream gaging station.

In areas where ground-water reservoirs and surface streams are closely interconnected, one technique for evaluation of their relationship is the so-called "seepage run" in which successive measurements are made of the surface flow as it moves downstream. The observed gains and losses show the manner in which the stream is replenished by ground-water inflow and depleted as it recharges the ground-water reservoir.

Collection and analysis of samples at measuring points, and of observed inflows, provide an aid in the quantitative interpretation of seepage measurements. The data can be used to compute quantities of inflow to compare with values measured by differences in streamflow. They may help to indicate reaches of the stream where inflows occur that are partly or wholly offset by losses elsewhere in the reach. Gatewood and others (1950) and Hem (1950) used chemical data to aid in interpreting ground water-surface water relationships in Safford Valley, Ariz.

The general procedure can be extended to more complex mixtures of surface and ground waters either by treating the problem stepwise, as a series of successive two-component mixtures, or assuming a greater number of components and determining a sufficient number of discharges by other means.

The Piper trilinear diagram discussed earlier in this report can be an aid in computing the amounts of different components that make up a mixture (Piper, 1944). This use of the Piper diagram is essentially a graphical adaptation of the salt-dilution procedure, and to obtain values in terms of definite quantities of water, it requires the same base data as the algebraic solution.

The applications discussed so far relate to surface waters or to systems of interrelated surface and ground waters. In such systems, most or all of what is happening is visible and available for study at any point. It would be very helpful and convenient to be able to apply quantitative interpretations of water analyses in ground-water systems where mixing of different types of water occurs. In these systems, however, close study is hampered by the inaccessibility of the system. What cannot be seen must be inferred, and the samples on which inferences can be based cannot usually be obtained from all the places they are needed, with the assurance of representativeness afforded by a system at the land surface. Because of the effects of solid materials in aquifers, waters of different quality mixing in aquifers may yield water different from what might be anticipated. Also, quantities of water underground cannot be measured easily, and therefore, there may be no values to use for the q terms in the salt-dilution equations.

The accuracy with which water-quality data can be applied in the quantitative study of ground waters depends upon the extent to which complicating factors are absent or can be allowed for. Usually some assumptions must be made regarding the existence of a state of equilibrium and the relative importance of factors that have brought about the chemical composition that can be observed.

Factors that control the quality of ground waters have been considered in preceding sections. They may be classified for present purposes into those which are relatively constant and those which are dynamic. Factors that remain more or less constant include mineral composition of solid materials available for solution in soils and rocks, geologic structure affecting water movement, climatologic conditions which influence the chemical reactions occurring in rock weathering, and effects of plant and animal life in the soil and underlying material. These factors may be thought of as acting to **promote a relative** uniformity in the chemical composition of ground water of a particular aquifer with the passing of time, and can **usually be** assumed to have a tendency to reach equilibrium.

Ground-water systems are affected by other factors which can be considered as causing the quality observed at a point to change, or which may cause changes from place to place in an aquifer. These factors include changes in amount of water available, mixing of waters from different aquifers, intrusion of saline water, and other things which may change the equilibrium that might naturally be reached if the factor were absent. Investigators have made some quantitative interpretations in ground-water hydrology based on chemical-analysis data. Techniques have involved both the addition of "slugs" of dye or salt and the evaluation of natural dilution **or mixing effects. These methods are related to the salt-velocity and salt-dilution procedures discussed for surface waters.**

Addition of salt or dye to a ground water has been extensively utilized in order to evaluate directions and rates of movement of water in aquifers. Some of the early work along this line was done by Slichter (1902) , who refers to earlier similar work done in Europe by Adolph Thiem. Slichter used salt solutions and measured the length of time required for such solutions to travel from a well in which they were introduced to an adjacent observation well. Others have used fluorescein dye because it can be detected visually in low concentrations or have used radioactive isotopes which are detectable in minute traces. There has been a great need for data on rates of travel of underground water, especially in connection with artificial recharge, and considerable work in this field has been done. The California State Water Pollution Control Board (1954) has recently issued a report on a study of this type.

The basic assumption made in experiments where a substance is added to ground water to follow its movement is that the added material moves at the same rate through the aquifer as the water molecules do. In surface-water bodies where movement is relatively rapid, this probably is a relatively safe assumption. Ground waters almost invariably move much more slowly, and factors other than water movement influencing the rate of travel of the dissolved material may

have relatively great importance. Probably the two most important are molecular diffusion and adsorption.

Molecular diffusion is a slow process in undisturbed media. Relatively little is known about the rates of diffusion that could be expected in the tiny passages through granular water-bearing materials, and in experiments where salt is added to ground water one can only assume the effect to be small enough to be negligible.

When large amounts of dissolved material foreign to the system are suddenly added, adsorption of dissolved material on the large exposed surface area of granular aquifers may have a very important influence on rate of travel of ions. The normal effect is to retard the movement of the dissolved material, and may result in the apparent loss of such material en route or in exchange of one kind of ion for another so that the added material is not recovered. In ground-water environments where large open channels occur (cavernous limestone or volcanic rocks, for example), this effect is minimized. Where opportunity for adsorption exists, the more easily adsorbed substances cannot be used successfully. These substances include most of the cations and large molecules such as those of dyes. Ordinarily it is assumed that, of the ions commonly found in water in important amounts, chloride ions are the least likely to be adsorbed.

Conditions in which a "slug" of salt enters an aquifer may occur naturally, but usually where ground waters of different composition meet and are mixed, inflow is relatively continuous. Areas of mixing may therefore lend themselves to quantitative study by variations of the **salt-dilution** computation which was described for surface waters.

One of the simplest examples is that of the well which taps two aquifers that yield water of different composition. If sufficient data are available on the composition of the unmixed water from each aquifer, the proportion of each type of water can be readily calculated from the composition of the mixture. The most serious source of difficulty in this type of calculation lies in obtaining a representative analysis for each of the original unmixed waters, and of the final product.

In some types of aquifers, such as alluvium, the main body may be recharged in part by subsurface inflow from the sides through tributary aquifers. Such a system can be treated as if it were a surface system, at least as an approximation. If the composition of the side inflow differs from that in the main aquifer, an equation can be set up on the basis of the average composition of ground water in the main aquifer above and below the inflow, and that of the water in the tributary aquifer. This relationship will indicate the relative proportion of water contributed by the tributary inflow. If an estimated or assumed figure is taken for one of the quantities or flow rates involved, all these can be calculated, although in such a system there are likely to be complications that would make such figures only rough estimates.

In the Santa Cruz Valley below Tucson, Ariz., the main stem is joined by the large tributary Avra Valley. Both valleys are typical Basin-Range structural features containing deep deposits of alluvium and an interconnected ground-water body, moving slowly toward a downstream discharge point. The surface streams of the area are ephemeral. Turner and others (1942, p. 57) computed the quality of ground water moving down the Santa Cruz Valley above the Avra Valley junction by averaging analyses for wells on a line across the narrows of the basin near Cortaro. They computed in a similar fashion, the composition of water flowing down the Avra Valley and of the water in the valley fill below the junction. They assumed the latter to be a mixture of the average Santa Cruz and Avra Valley waters. From the known characteristics of the fill at the Cortaro narrows and the slope of the water table, a computation was made of the annual volume of ground water moving through the narrows. From these data, there were sufficient values for c and q terms to compute the amount of ground water entering the area from Avra Valley.

This type of computation involves some unverifiable assumptions and gives only an approximate answer. However, for many studies, such approximations are very useful, particularly if cross checked using other information.

The discussion of water-quality maps has indicated some of the features such maps may show. In places where a water-quality map indicates that a different type of water is entering the system, it should be possible to estimate quantitatively the effect of one inflow as compared to others by study of the isograms of dissolved solids. The rate at which such inflows mix with other water present in the aquifer and the relative volumes of water affected could be evaluated by means of the spacing of the isogram lines in a downstream direction from the point of the inflow and the slope of the water table in the area. The author is not aware of any area where this has been tried, however.

Larson (1949) has published a study of certain ground water-surface water relationships in the Illinois River Valley at Peoria, Ill. By scatter diagrams, similar to figure 12, he found a general linear relationship between hardness and sulfate and between hardness and alkalinity for the water of the river. Ground water unaffected by seepage from the river was assumed to be represented by a selected analysis for a particular heavily pumped well. Using these relationships, Larson computed the percentage of river water in the water pumped from this well at various times. Although this procedure is not highly precise, it is probably a useful approach to the problem of mixtures of water from different sources in the area studied.

Gatewood and others (1950) describe a method of computing water loss by transpiration and evaporation in Safford Valley, Ariz., on the basis of water-quality changes. The increase in chloride concentration of shallow ground water as it moved through areas covered by brush and trees was taken as a measure of the amount of water removed from the system by transpiration and evaporation.

Although efforts have been made to use water-analysis data in quantitative computations, the field remains largely unexplored. Further development of the methods here described or suggested should lead to a better understanding of the possibilities which lie dormant in these methods at present because they have not received the attention they deserve from workers in the field of hydrology. It is hoped that in the future there will be more interest in developing quantitative interpretations of this kind.

RELATIONSHIP OF QUALITY OF WATER TO USE

The most immediate purpose of the usual quality-of-water study is to determine if the water is satisfactory in quality for a proposed use. Accordingly, the subject of quality of water as related to use must generally be considered in any interpretation of the results of quality-of-water investigations. The discussion in this portion of this report is intended to provide some assistance to the authors of reports where such evaluations are required. Most readers of the Geological Survey's reports on water resources are likely to be interested in the use of a water for ordinary household or domestic purposes, for agricultural purposes, or for industrial processes. In addition to these three major classifications, some special uses may occur which might require mention in reports of some investigations.

The use of a water as a public supply entails a combination of all three main types of utilization. Therefore, the standards which must be used to evaluate the quality of a public supply are generally higher than would be applied to water to be used for small domestic or farm supplies, for example, though not necessarily higher than those which apply to many industrial uses.

The medicinal use of water, particularly water from mineral springs or hot springs, still receives a considerable amount of attention, but this subject is beyond the scope of reports of the Geological Survey..

DOMESTIC USE

It is important that water to be used in the home should be free from color and turbidity and should have no unpleasant odor or taste..

Harmful micro-organisms must be absent. These characteristics are not usually given much study in the course of Geological Survey investigations of ground water, and the Survey's laboratories do not make bacteriological examinations of water. The only standards, therefore, by which domestic supplies may be evaluated on the basis **of** chemical analyses made by the Survey are those related to dissolved mineral matter. A statement that these analyses do not indicate the sanitary condition of water is generally desirable to avoid any assumption by the reader that a water said to be chemically suitable for domestic use is necessarily safe bacteriologically.

Because of differences in individuals, different amounts of water used, and other factors, it is very difficult to establish safe limits for any of the mineral components usually found in water. The limits usually quoted in the United States for drinking water are based on the U. S. Public Health Service drinking-water standards. These standards were established first in 1914 to control the quality of water supplied by common carriers to passengers for drinking or for use in culinary processes. The standards have been revised several times, and those in current use date from 1946 (U. S. Public Health Service, 1946). According to these standards, the following substances should **not be present in excess of the concentrations shown as follows:**

	Ppm
Fluoride	1.5
Lead	1
Arsenic	05
Selenium	05
Hexavalent chromium	05

An excessive concentration of any of the above elements constitutes a basis for rejection of the supply. If the water is acceptable on the basis of the constituents mentioned, it is evaluated according to the following less restrictive upper limits for other constituents:

	Ppm
Copper	3.0
Iron and manganese (together)	.3
Magnesium	125
Zinc	15
Chloride	250
Sulfate	250
Phenolic compounds (as phenol)	.005
Total dissolved solids (good quality)	500
(Where no better water available)	1,000

Although these standards are widely quoted for drinking water, they are not directly applicable to every situation. In some sections of the United States, the quality of water available from most individual **domestic supplies and some public supplies does not meet the** standards in one or more respects. Nevertheless, many people in such areas have used these waters for their entire lifetime, and although detailed medical data are not available it would appear that the poor quality of their water supply, so far as dissolved solids are concerned, has had little visible effect. The limits for fluoride, lead, arsenic, selenium, and chromium as given by the Public Health Service standards should be followed as closely as possible. The effect of most other mineral constituents in the drinking-water supply has not been studied in detail.

Those constituents which are relatively toxic in low concentrations are rather rare, but should there be a good reason for suspecting the presence of dangerous amounts of these constituents, their determination should be included in the analysis. In general, where references are made to the Public Health Service standards in areas where many supplies do not meet the requirements of the standards, a qualifying statement has been made in many reports to avoid labeling as nonpotable waters that have been used extensively without obvious ill effects. In some areas, a comparison with quality of local public supplies may be helpful in providing a basis for evaluating domestic supplies.

About the time the last revision of the Public Health Service standards was in preparation, an investigation as to the effect of nitrate in water was reported (Comly, 1945). This and later investigations (Waring, 1949; Bash, 1950; Maxcy, 1950) seem definitely to link nitrate in domestic water supplies with methemeglobinemia, or cyanosis, in infants whose feeding formulas are mixed with these waters. This so-called "blue-baby" disease appears to be a possible hazard with waters containing more than 10 parts per million of nitrate expressed in terms of nitrogen (N). The analyses made by the Geological Survey report nitrate in ppm of NO_3, whereas in the usual "sanitary" analysis, the forms in which nitrogen may be found are listed in terms of the element (N) alone. The tentative limit when concentrations are expressed as NO_3 is, in round numbers, 44 ppm. Differences in ways of reporting nitrate concentrations have led to considerable confusion among water users concerning these limits.

Most of the more common constituents in drinking water appear to be objectionable only when they are present in such high concentration as to be noticeable to the taste. Because of differences between individuals, the concentrations that may be objectionable are difficult to state. A chloride concentration of 200 to 300 ppm in water containing an equivalent amount of sodium is enough to give a noticeably salty taste to most people. The presence of sulfate in similar concentrations will have a laxative effect on some of those who drink the water. If the dissolved matter is practically all calcium and bicarbonate, little taste will be noted up to the maximum concentrations of these substances which could be present in such a water. Calcium and sulfate give some taste, but waters containing over 1,000 ppm of these substances together have less taste than similar concentrations of most other substances. The temperature of a water has considerable effect on its palatability also, low temperatures improving the taste for most people.

The presence of small amounts of phenolic compounds may give a very disagreeable taste and odor to the water after chlorination. This effect is the result of a chemical reaction between the chlorine and the phenolic substances. Very small quantities of some other organic substances added through waste disposal may impart objectionable tastes and odors.

Because of the many inherent difficulties in evaluation of tastes, the tasting of a water is a poor substitute for chemical examination, and the reporting of observed tastes, while a guide to the analyst if mentioned in description of samples submitted, generally is not appropriate in a scientific report.

The presence of iron, manganese, and hardness in water to be used for laundry generally is objectionable. The iron and manganese leave stains of oxide or hydroxide on fabrics and other articles and on plumbing fixtures. Iron is often dissolved from piping by water which has corrosive tendencies.

The meaning of the term "hard" when applied to water is different in different areas, depending on the condition to which the water user is accustomed. As the hardness of a water increases, the desirability of the water decreases for most domestic purposes, especially cleaning, .cooking, and heating.

Tolerances with respect to radium in drinking water were considered in the discussion of radium earlier in this report, and tolerances for all radioactive materials are given in detail in a recent report by the National Bureau of Standards (1953).

The California State Water Pollution Control Board (1952) has issued a comprehensive publication on water-quality criteria which has been repeatedly referred to. It is based on a survey of published material on water quality as related to domestic, agricultural, and industrial uses, as well as for fish culture, recreational activity, and wildlife propagation. The data were summarized for the report by the California Institute of Technology. The reader is referred to this publication for discussions of the effect of a wide variety of mineral and organic substances not considered here which may be found in waters to be used for human consumption and other purposes.

AGRICULTURAL USE

The use of water on the farm for nondomestic purposes **includes** the water consumed by livestock, the irrigation of crops, and in operation of machinery.

Water to be used by stock is subject to quality limitations of the same type as those relating to quality of drinking water for human consumption. However, most animals seem to be able to use water considerably poorer in quality than would be considered satisfactory for human beings. The literature does not contain many references to quality standards for stock-water supplies. Range cattle in the western United States seem to be able to use water containing 5,000 ppm or more of dissolved solids, and animals that have become accustomed to highly mineralized water have been observed, in the course of investigations of water quality by the author, to drink water containing nearly 10,000 ppm of dissolved solids. A high proportion of sodium or magnesium and sulfate in such highly mineralized waters would make them very undesirable for stock use, however. Probably a supply of considerably better quality than the upper limit of tolerance is generally desirable for the best growth and development of the animals.

In a publication (1950) relating to practices in Western Australia, the officers of the Department of Agriculture of that State quote the following upper limits for dissolved-solids concentration in stock water:

TABLE 21.—Upper limits of ***dissolved-solids*** concentration in water to be consumed by ***livestock***

	Parts per ***million***		Parts per million
Poultry	2, 860	Cattle (dairy)	7, 150
Pigs	4, 290	Cattle (beef)	10, 000
Horses	6, 435	Adult sheep	12, 900

Waters in this region apparently are high in sodium and chloride. These data are quoted in the California Water Pollution Control Board report (1952) mentioned previously. That report also (p. 155) quotes other investigators who have found concentrations as high as 15,000 ppm to be safe for limited periods but not for continuous use. Some studies, on the other hand, indicate an upper limit of 5,000 ppm in water to be used by livestock.

Selenium has already been discussed briefly. It is known to be very poisonous to animals, but generally poisoning results from eating selenium-concentrating plants. A concentration of 0.4 to 0.5 ppm in water is reported nontoxic to cattle (California State Water Pollution Control Board, 1952, p. 351). Waters satisfactory in other respects but having selenium concentrations above 0.5 ppm could possibly occur, but the author knows of none.

The chemical quality of a water is an important factor to be considered in evaluating its usefulness for irrigation. Features of the chemical composition that need to be considered include the total concentration of dissolved matter in the supply, the concentration of individual constituents, and the relative proportions of some of the constituents present in water. Whether a particular water may be used successfully for irrigation depends on many factors not directly associated with water composition however. A discussion of some of these factors will show the complex nature of the water-quality problem in irrigation agricultrre.

The portion of irrigation water actually consumed by plants or evaporated is essentially free from dissolved salts. The growing plants retain a part of the mineral matter originally dissolved in this water, but the amount so retained is not large. Eaton (1954, p. 12) has conducted studies that show the amounts of soluble matter from irrigation water withheld by the crops is a minor fraction of the amount in the water, and consists mainly of calcium and magnesium salts. Therefore, most of the soluble matter originally in the portion of the water which is consumed largely remains behind in the soil or is dissolved in residual water. In either instance, this constitutes a disposal problem which must be solved in order to maintain the productivity of irrigated soil on a permanent basis.

The extent to which disposal of excess soluble salts is a problem in any irrigated area is dependent on several factors. Among these factors are the chemical composition of the water supply, the nature and composition of the soil and subsoil, and topography of the land, the amounts of water used and the method of applying it, the kind of crops grown, and the climate of the region, including the amount and distribution of rainfall.

In most areas excess soluble matter left in the soil from irrigation is removed by leaching the topsoil and allowing the resulting solution to pass downward into the ground-water reservoir. In those areas where the water table beneath the irrigated area can be kept depressed to a sufficient extent, this process of drainage will be effective in maintaining permanent productivity. The necessary leaching may be accomplished by rainfall in those areas where the amount of precipitation is sufficient to give rise to direct recharge. The process of leaching is also carried on by the use of irrigation waters, either with that purpose in mind or more commonly without that intent in an effort to store water in the soil to tide the plants over an expected dry period, or to utilize unusually large supplies of water at one time.

Eaton (1954) has developed formulas for use in computing leaching requirements.

In areas where natural drainage is poor, irrigation water that infiltrates below the root zone may eventually cause the water table to rise excessively, resulting in serious problems. "Seeped" (waterlogged) land, where irrigation has brought the water table to or near the surface of the land, has become common in many irrigated areas in the United States. Such land has little value for agriculture but provides instead a site for water-loving vegetation of little or no economic value. Transpiration by this vegetation, and direct evaporation from damp soil or open water surfaces, result in waste of a large and economically significant quantity of water; also, in time the soil of such areas becomes highly charged with salt from the water so discharged.

In most waterlogged areas, the quality of water available was not the primary cause of the abandonment of the land. The reason for failure of some of the ancient civilizations that practiced irrigation such as that of the Indians in the Salt River Valley of Arizona or of that in the Tigris-Euphrates Valley in what is now known as Iraq, is somewhat obscure, but lack of drainage to remove excess salts and water according to Eaton (1950) certainly played a large part in the decline of the area in Iraq and may have been important elsewhere, also.

In most large irrigated areas, it has become necessary to provide some means of facilitating the drainage of ground water into streams and thus keeping the water table far enough below the land surface. Open ditches or buried systems of drainage tile have been used, or a system of wells may be pumped to lower the water table. The drainage water extracted, provided no new water has entered the system, is smaller in quantity than the amount of irrigation water applied, but is higher in dissolved solids owing to the effects of concentration by evapotranspiration and the leaching of soluble matter from soil, and from fertilizer and other soil amendments.

For long-term successful operation of irrigation projects, essentially all the salts added in the irrigation water should be recovered and appear in the drainage water. The relation between salt inflow and outflow is called "salt balance" by Scofield (1940) and is considered "favorable" when outflow of salt equals or exceeds the inflow. A favorable salt balance must be maintained in an irrigated area if irrigation is to continue permanently. Since 1940, several modifications and refinements of Scofield's concept have been suggested; these will be discussed later.

In the more highly developed irrigated areas depending at least partly on surface supplies, such as the developments along the Rio

Grande from the San Luis Valley, Colo., to Fort Quitman, Tex., and those along the Salt and Gila Rivers of Arizona, the drainage waters returned to the stream by the upper irrigated areas are used again for irrigating the next lower area. The cycle of reuse may be repeated six times or more, until the drainage water is too small in quantity and too poor in quality for further use.

The deterioration in quality of water resulting from reuse of return flows is generally recognized, but it is probably accelerated in many places by the use of pumped wells to supplement surface supplies or for drainage. The water pumped from these wells usually is reused for irrigation in the immediate vicinity, and it does not, therefore, leave the area directly as gravity-drainage water normally would. The recirculation of the ground water through several cycles of irrigation in the same area tends to increase the concentration of dissolved solids in the ground water, by creating what is essentially a "closed basin" in the ground-water reservoir of that area. If withdrawals of ground water are so large that they dry up the natural drainage channels, the ground-water movement away from the area is stopped or greatly reduced, and the ground water eventually will be so concentrated that its use for irrigation will be impossible. Thus, excessive withdrawals of ground water may create a problem of quality as well as of declining water levels. The condition is illustrated west of Phoenix, Ariz., where use of ground water for irrigation, including some pumped for drainage, is largely responsible for the increasing dissolved-solids content of ground water (Halpenny and others, 1952, p. 147-149).

It probably is true that in many ground-water basins overdevelopment will lower the water table so rapidly that rising pumping costs will enforce a reduction in pumping before quality problems can become serious. However, the deterioration of quality of water resulting from reuse does limit the development in an irrigated area whether the water supply comes from ground water, surface water, or both. Attention is being given to this problem in several areas in the western United States where progressive "salting up" of ground water is occurring in the lower parts of irrigated valleys and threatens to require a curtailment of irrigated areas. It may be stated as axiomatic that serious difficulty eventually will result if a water supply is so fully developed for irrigation that the only water allowed to leave the area does so as vapor.

In addition to salinity problems caused by excessive amounts of the common constituents of the dissolved solids, certain specific constituents in irrigation water are undesirable and may be damaging when present in only small quantities. One of the most important of the constituents present in irrigation water in minor amounts is boron.

This element is essential to proper plant nutrition and is sometimes added to fertilizer in small amounts, because many soils in humid regions are deficient in boron. A small excess over the needed amount, however, is toxic to some types of plants. Among the plants most sensitive to excess boron are citrus fruit trees and walnut trees. Early work by Kelley and Brown (1928) established the relationship between boron and certain symptoms of injury to trees. Scofield and Wilcox (1931) stated that the critical concentration of boron in irrigation water for lemons and walnuts lies between 0.5 and 1.0 ppm.

Later studies have led to the inclusion of boron in standards for evaluation of irrigation waters on the basis of chemical quality. Such studies have also shown that certain crops including most deciduous fruit and nut trees and navy beans are sensitive to boron; a group including most small grains, potatoes, and some other vegetables and cotton are semitolerant ; and alfalfa, most root vegetables, and the date palm are tolerant to boron. These data were published by the U. S. Salinity laboratory staff (1954). The following table by Scofield (1936) to show permissible boron concentrations was given :

TABLE *22.—Rating of irrigation water for various crops on the basis of boron concentration in the water*

Classes of water		Sensitive crops ppm	Semitolerant crops ppm	Tolerant crops ppm
Rating	Grade			
1	Excellent	<.33	<.67	<1.00.
2	Good	33 to.67	.67 to 1.33	1.00 to 2.00.
3	Permissible	67 to 1.00	1.33 to 2.00	2.00 to 3.00.
4	Doubtful	1.00 to 1.25	2.00 to 2.50	3.00 to 3.75.
5	Unsuitable	>1.25	>2.50	>3.75.

Relative tolerances of a number of plants to boron are given in table 23.

It is to be anticipated that boron concentrations in water in the root zone will exceed the concentration in the irrigation water applied. The extent of the difference is affected by soil characteristics and irrigation practices, so that a range of concentration values in the water is given rather than a single value.

Experiments have shown that some of the common constituents of irrigation water are more toxic to plants than others present in the same concentration. Data reported by the U. S. Salinity laboratory staff (1954) indicate that for some plants sulfate is more toxic than chloride but that for others the reverse is true. Also, magnesium salts were found to be more toxic in equal concentrations than sodium or calcium salts, in the growth of beans. However, the effects of total concentration of soluble salts probably is more important than individual differences in the toxicity of anions or cations.

TABLE 23.—*Relative tolerance of plants to boron*

[After U. B. Dept. Agriculture Handbook 60, 1954. In each group, the plants first named are considered as being more sensitive and the last named more tolerant]

Sensitive	Semitolerant	Tolerant
Lemon	Lima bean	Carrot
Grapefruit	Sweetpotato	Lettuce
Avocado	Bell pepper	Cabbage
Orange	Pumpkin	Turnip
Thornless blackberry	Zinnia	Onion
Apricot	Oat	Broadbean
Peach	Milo	Gladiolus
Cherry	Corn	Alfalfa
Persimmon	Wheat	Garden beet
Kadota fig	Barley	Mangel
Grape (Sultanina and Malaga)	Olive	Sugar beet
	Ragged Robin rose	Palm (Phoenix canariensis)
Apple	Field pea	Date palm (P. dactylifera)
Pear	Radish	Asparagus
Plum	Sweet pea	Athel (Tamarix aphylla)
American elm	Tomato	
Navy bean	Pima cotton	
Jerusalem-Artichoke	Acala cotton	
Persian (English) walnut	Potato	
Black walnut	Sunflower (native)	
Pecan		

"Black alkali" or sodium carbonate is present in some soils and is derived from some types of water on evaporation. The pH of such soils is very high and the characteristic brown or black color of alkali crusts on the soil surface is the result of the solution of organic matter in the highly alkaline water from which the surface deposits of "alkali" result. So called "white alkali" deposits generally are composed mainly of sodium sulfate and chloride. A discussion of "black alkali" and its relation to sodium percentage in irrigation water is contained in a recent paper by Eaton (1950). An important side effect of high pH values in soils is the depression of the solubility of some of the plant nutrients. This may result in considerable plant injury as an indirect result of the presence of sodium carbonate in the soil.

Base exchange, the process by which cations dissolved in water are exchanged for others in solid form in a base-exchange medium, has been discussed elsewhere in this report. The principal significance of this reaction in irrigation is in the exchange of sodium from the water for calcium and other cations held by soil mineral particles. The reaction is a reversible one, and the direction in which it proceeds depends on the concentration of sodium and its relation to the concentration of the other cations in the water solution in contact with the soil particles. This relative concentration of sodium may be reported in chemical analyses as sodium percentage, which is computed as described elsewhere in this report (p. 148).

For the study of base-exchange effects in soil it has recently been suggested by the U. S. Salinity laboratory staff (1954) that the sodium-adsorption ratio (SAR) is more directly useful **and** expresses the situation better. The method of computation has already been mentioned. The SAR value is:

$$\text{SAR} \quad \frac{\text{Na}}{\sqrt{\frac{\text{Ca}+\text{Mg}}{2}}}$$

where all concentration values are expressed in equivalents per million. It was found by the U. S. Salinity laboratory staff (1954, p. 25-28) that the SAR value for water extracted from samples of saturated soil had a fairly definite straight-line relationship to the **exchnageable-sodium** ratio of the soil. The exchangeable-sodium ratio is expressed by the relation—

$$\frac{\text{exchangeable sodium (epm)}}{\text{cation-exchange-capacity (epm)— exchangeable sodium (epm)}}$$

Because of the above relationship, empirically demonstrated in soil-chemistry work, it is to be expected that there is a less definite but probably significant relationship between SAR values for irrigation water and the extent to which sodium is adsorbed in the soil on which the water is used. Such a relationship has not been established for percent-sodium values. The SAR values, therefore, are probably better expressions of the tendency an irrigated water may have to take part in base-exchange reactions in soil. An exact relationship cannot be expected, however, in all areas.

A soil high in exchangeable sodium is very undesirable for agriculture. It is deflocculated or "puddled," tends to have a hard crust, and may be nearly impermeable to water. This condition is promoted by waters of high SAR and is reversed by waters containing a high proportion of calcium and magnesium. Soil amendments such as gypsum or lime may correct the situation by increasing the available calcium. Similar effects may be produced by sulfur, sulfuric acid, or ferrous sulfate, which lower the soil pH and cause $CaCO_3$ in the soil to go into solution and to enter the exchange process in those soil particles which have exchange capacity.

Another factor in evaluation of irrigation waters has been suggested by Eaton (1950). It is Eaton's contention that water applied in irrigation may lose calcium and magnesium by precipitation as carbonates in the soil. If a water has enough carbonate and bicarbonate to precipitate all the calcium and magnesium present, it has a "possible sodium percentage" of 100 according to Eaton. He believes the presence of "black alkali" in certain irrigated soils may be due to this effect. The U. S. Salinity laboratory staff (1954, p. 75) and Kelley (1951, p. 101) do not believe that this reaction ordinarily goes to completion but that it may have an important effect in some instances. The SAR value of a soil solution that has lost calcium by precipitation is, of course, increased over the value of SAR for the water before the reaction took place.

The U. S. Salinity laboratory staff (1954, p. 75-76) reports an experiment of irrigating soil in pots which vindicates Eaton's suggestions at least for waters containing a considerable amount of dissolved solids, large excess of sodium over calcium, and an excess of bicarbonate over calcium. These writers (p. 81) suggest that waters containing more than 2.5 epm of "residual Na_2CO_3" are not suited for irrigation, those containing 1.25 to 2.5 epm are marginal, and those containing less than 1.25 epm are "probably safe." "Residual Na_2CO_3" is twice the amount of carbonate or bicarbonate a water would contain after an amount equivalent to the calcium and magnesium has been removed.

The original article by Eaton contained no experimental data. The experiment cited above used water containing no magnesium. One would not expect magnesium to precipitate as carbonate as readily as does calcium. Eaton (1954) , however, cites data indicating that calcium : magnesium ratios in irrigation drainage do not differ greatly from those in the original water supply. Further experiments along this line might be desirable.

It has been mentioned earlier that potassium does not behave the same as sodium in base exchange and adsorption reactions. Sodium-percentage values are therefore computed where possible on the basis of sodium alone, as related to the total cations including sodium and potassium. The SAR concept is based on theoretical differences in behavior of monovalent and bivalent cations in base-exchange reactions, but, as defined, the value of SAR does not consider potassium. Because the potassium content of irrigation waters is practically always minor, the potassium may be considered as not significant.

A widely distributed and utilized diagram for evaluation of irrigation waters on the basis of dissolved-solids concentration and percent sodium was published by Wilcox (1948). It may be considered to be largely superseded by a diagram suggested by the U. S. Salinity laboratory staff (1954, p. 80) which is reproduced in modified form as figure 40. This diagram uses SAR and conductance or dissolved-solids values as parameters for evaluation of the water.

Table 24 is based on data from the same source (p. 67), showing relative tolerance of crops to salinity of the water.

In a recent discussion of standards for evaluation of irrigation water, Doneen (1954) suggests abandonment of conductance as a

TABLE 24.—*Relative tolerance of crop plants to salinity*

[After U. S. Dept. Agriculture Handbook No. 60, 1954. In each column the plants first named under each class are most sensitive and the last named under that class the most tolerant]

Sensitive	Moderately tolerant	Tolerant
	FRUIT CROPS	
Avocado Lemon Strawberry Peach Apricot Almond Plum Prune Grapefruit Orange Apple Pear	Cantaloupe Grape Olive Fig Pomegranate	Date palm
	VEGETABLE CROPS	
Green beans Celery Radish	Cucumber Squash Peas Onion Carrot Potatoes Sweet corn Lettuce Cauliflower Bell pepper Cabbage Broccoli Tomato	Spinach Asparagus Kale Beets
	FORAGE CROPS	
Burnet Ladino clover Red clover Alsike clover Meadow foxtail White Dutch clover	Sickle milkvetch Sour clover Cicer milkvetch Tall meadow oatgrass Smooth brome Big trefoil Reed canary Meadow fescue Blue gramma Orchardgrass Oats (hay) Wheat (hay) Rye (hay) Tall fescue Alfalfa Hubam clover Sudan grass Dallis grass Strawberry clover Mountain brome Perennial ryegrass Yellow sweet clover White sweet clover	Birdsfoot trefoil Barley (hay) Western wheatgrass Canada wildrye Rescue grass Rhodes grass Bermuda grass Nuttall alkaligrass Saltgrass Alkali sacaton

TABLE *24.—Relative tolerance of crop plants to salinity—Continued*

Sensitive	Moderately tolerant	Tolerant
FIELD CROPS		
Field beans	Castorbeans Sunflower Flax Corn Sorghum (grain) Rice Oats (grain) Wheat (grain)] Rye (grain)	Cotton Rape Sugar beet Barley (grain)

measure of salinity hazard. In accord with Eaton, he believes that the carbonates of calcium and magnesium will be precipitated in harmless form in the soil and that a further amount of the dissolved matter in the water may tend to precipitate as calcium sulfate, or at least will not reach a damaging concentration. Doneen therefore suggests a classification system which gives a potential or "effective" salinity. This value is computed by assuming maximum possible precipitation of calcium and magnesium carbonates and calcium sulfate. By implication, these substances also could be left out of consideration in salt-balance computations.

It is very difficult to predict on the basis of water analyses what may take place in the complex mineral assemblages of most soils, where physical adsorption, base exchange, and the formation of complex salts may all occur when irrigation water is added. Those who use water analyses to evaluate irrigation supplies should not depend exclusively upon any classification system that takes only the composition of the water into account.

A recent report by the Geological Survey (1954, p. 9-14) summarizes the suggested criteria, published through 1954 for evaluation of irrigation waters, on the basis of their chemical quality.

INDUSTRIAL USE

The quality requirements for industrial water supplies range widely, and almost every industrial application has different standards. For some uses, such as single-pass condensing or cooling, or for the concentrating of ores, chemical quality is not particularly critical, and almost any water may be used. At the opposite extreme, water approaching the quality of distilled water is required for processes such as the manufacture of high-grade paper, pharmaceuticals, and the like where impurities in the water used would seriously affect the quality of the product. Modern maximum-pressure steam boilers may require makeup water less concentrated than the average distilled

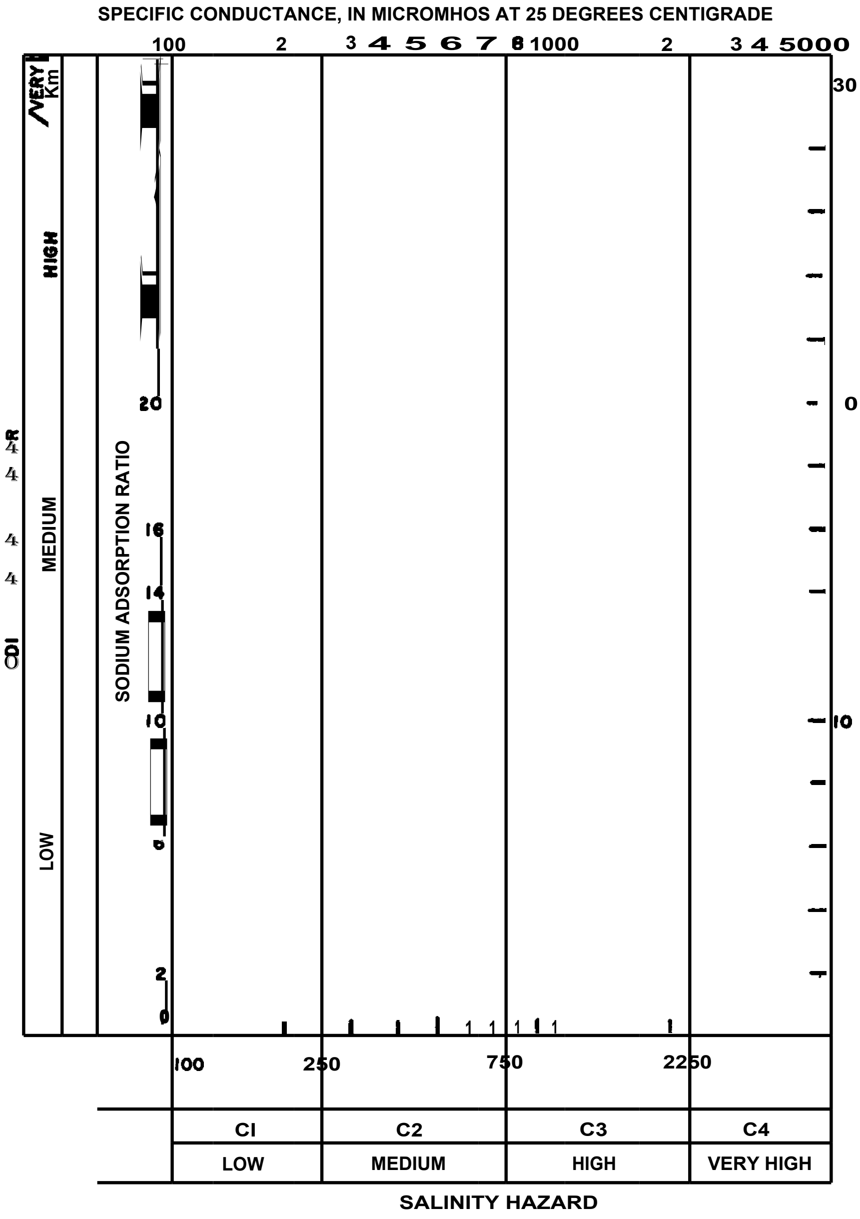


FIGURE 40.—D[illegible]. A[illegible] U.S. S[illegible] L[illegible]. S[illegible], D[illegible] soils, 1954. U.S. D[illegible]. A[illegible]. H[illegible] 60, [illegible]. 80.

water of commerce. It is not the aim of this report to quote many chemical-quality standards for industrial water, because of the wide variation from industry to industry. Further, reports intended for use by the general public probably should not emphasize the specialized needs of specific types of industry, but should present facts and interpretations of a general nature that can be further studied by those who have special requirements.

It is technically possible to treat any water to give it a composition that will be satisfactory for any special uses. If the water requires extensive treatment, however, especially if large amounts of water are involved, it may not be economically feasible to utilize the supply. In the future, most industries having large water requirements doubtless will be located with reference to water supplies which come closest to meeting their needs, in both quantity and quality.

Tables 25 and 26 are based on a report by Moore (1941) giving water-quality requirements for certain industrial uses. Detailed information on industrial standards are also contained in the report of the California State Water Pollution Control Board (1952) which has already been referred to.

Although water temperatures have not been given much consideration in this report, the temperature of a supply and the seasonal fluctuation of that temperature are major considerations in water used for cooling by industry. In some areas, ground waters are extensively used for this purpose because of their low and relatively constant temperature. In other areas, industries have recharged aquifers with cold water taken from surface streams during the winter and have withdrawn the cool stored water in the summer when the regularly used surface supply is too warm. In some areas, industrial plants located along the same stream have used and reused the water for cooling until the temperature of the water has been raised to far above normal levels for many miles of river.

Rapid increases in recent years in the amounts of water used by industry have contributed extensively to the increasing need for water in the United States. Much of the industrial use, however, is nonconsumptive. That is, the water is not evaporated or incorporated into the finished product, but is released by the industry in liquid form possibly with an increased load of dissolved material, or possibly very little different in composition from the original water. Many industries have resorted to re-use of water that in former years might have been allowed to flow down the sewer or into a surface stream. Recirculation introduces a factor of concentration of the dissolved material. Eventually the tendency to utilize water supplies more intensively will result in a higher average dissolved-solids concentration in industrial effluents, although the volume of such effluents may be reduced. In

TABLE *25.-Suggested water-quality tolerances*

'Allowable limits in parts per million. Source of data: E. W. Moore, (1940). **P, indicates** that potable water, conforming to **U.** S. Public Health Service standards **is** necessary. Iron as Fe limit given, applies to both **iron** alone and the sum of **iron** and manganese)

Industry or use	Turbidity	Color	Hardness as **CaCO₃**	Iron as Fe	**Manganese** as Mn	Total solids	Alkalinity as **CaCO₃**	Odor and taste	**Hydrogen** sulfide	Other requirements
Air conditioning				0.5	0.5	-----		Low	1	No corrosiveness, slime formation.
Baking	10	10	-------	.2	.2	-----		Low	.2	P.
Boiler feed										
Brewing:										
Light beer	10			.1	.1	500	75	Low	.2	P. **NaCl** less than 275 ppm (pH **6.5–7.0).**
Dark beer	10			.1	.1	1,000	150	Low	.2	P. **NaCl** less than 275 ppm (pH 7.0 or more).
Canning:										
Legumes	10		25-75	.2	.2	-----		Low	1	P.
General	10			.2	.2	-----		Low	1	P.
Carbonated beverages	2	10	250	.3	.2	810	50-100	Low	.2	P. Organic color plus oxygen consumed less than 10 ppm.
Confectionery				.2	.2	100	-----------------	Low	.2	P. pH above 7.0 for hard candy.
Cooling	50		50	.5	.5	-----			5	No corrosiveness, slime formation.
Food: General	10			.2	.2	-----		Low	--------	P.
Ice	5	5	------	.2	.2	-----		Low	--------	P. **SiO₂** less than 10 **ppm.**
Laundering			50	.2	.2	-----				
Plastics, clear, **uncolored**	2	2	-------	.02	.02	200	-----------------			
Paper and pulp:										
Groundwood	50	20	180	1.0	.5	-----				No grit, corrosiveness.
Kraft pulp	25	15	100	.2	.1	300	-----------------			
Soda and sulfite	15	10	100	.1	.05	200	-----------------			
High-grade light **papers**	5	5	50	.1	.05	200	-----------------			
Rayon (viscose):										
Pulp production	5	5	8	.05	.03	100	Total 50; **hydroxide** 8			**Al₂O₃** less than 8 ppm, **SiO₂** less than 25 ppm, Cu less than I ppm.
Manufacture	.3	------	55	.0	.0	-----				pH **.8** to 8.3.
Tanning	20	10-100	50-135	.2	.2	-----	Total 135; **hydroxide** 8.	-----		
Textiles: General	5	20	-------	.25	.25	-----				
Dyeing	5	5-20	-------	.25	.25	200	-----------------			Constant composition. Residual alumina less than 0.5 ppm.
Wool scouring		70	-------	1.0	1.0	-----				
Cotton bandage	5	5	-------	.2	.2	-----		Low	--------	

TABLE *26.—Suggested water-quality tolerance for boiler feed water* [1]

[Allowable limits in parts per million]

	Pressure (psi)			
	0-150	150-250	250-400	Over 400
Turbidity	20	10	5	1
Color	80	40	5	2
Oxygen consumed	15	10	4	
Dissolved oxygen	1.4	.14	.0	.0
Hydrogen sulfide (H2S)	55	3	0	0
Total hardness as $CaCO_3$	80	40	10	2
Sulfate-carbonate ratio (A. S. M. E.) (Na_2SO_4: Na_2CO_3)	1:1	2:1	3:1	3:1
Aluminum oxide (Al_2O_3)	5	.5	.05	.01
Silica (5100	40	20	5	1
Bicarbonate (HCO_3)	50	30	5	0
Carbonate (COs)	200	100	40	20
Hydroxide (OH)	50	40	30	15
Total solids	3,000-500	2,500-500	1,500-100	50
pH value (minimum)	8.0	8.4	9.0	9.6

[1] **Moore,** E. W., Progress report of the committee on quality tolerances of water for industrial uses: Jour. New England Water Works Assoc., v. 54, p. 263, 1940.

[2] Limits applicable only to feed water entering boiler, not to original water supply.

Except when odor in live steam would be objectionable.

Depends on design of boiler.

highly developed industrial areas, water-quality problems and waste-disposal problems can be expected to increase in complexity and severity as a result of the closer approach to maximum utilization of water.

Irrigation uses consume large proportions of the water applied, and intensive development results in reuse of the unconsumed residue. The effects of these factors on the quality of water supplies have already been pointed out. Increased industrial consumptive use and growing need for re-use of effluents may never create the type of salinization problem that has come into existence in some irrigated areas. Nevertheless, there is a limit to the extent to which a water supply can be reused. The apparent solution to a problem of deficient quantity of water that is offered by manifold reuse of what water is available may lead to an equally difficult water-quality problem.

Obviously, man still has much to learn before the optimum utilization of natural resources will be reached. The recurring problems of water supply, both with respect to quantity and quality, demonstrate that the knowledge in this field is far from complete. Optimum development of water supplies for beneficial uses can be attained only when the science of hydrology is more fully developed and applied.

SELECTED REFERENCES

Ageno, F. and Valla, E., 1911, Hydrolysis of carbonates : Atti Accad. Lincei, v. 20, II, p. 706-712.

Alexander, Geo. V., Nusbaum, Ralph E., and MacDonald, Norman S., 1954, Strontium and calcium in municipal water supplies : Am. Water Works Assoc. Jour., v. 46, p. 643-654.

American Public Health Association, American Water Works Association, and Federation of Sewage and Industrial Wastes Associations, 1955, Standard methods for the examination of water and sewage: New York, N. Y.

American Society for Testing Materials, 1954, Manual on industrial water: Am. Soc. for Testing Mat., Philadelphia, Pa.

Anderson, V. S., 1945, Some effects of atmospheric evaporation and transpiration on the composition of natural waters in Australia: Jour. Proc. Australian Chem. Inst., v. 12, p. 41-68; 83-98.

Association of Official Agricultural Chemists, 1950, Official methods of analysis of the A. O. A. C., 7th edition: Assoc. of Official Agri. Chemists, Washington, D. C.

Askew, H. O., 1923, Solubility and hydrolysis of calcium carbonate: Trans. New Zealand Inst., v. 54, p. 791-796.

Auméras, M., 1927, Equilibrium of calcium fluoride and dilute hydrochloric acid: Jour. Chim. Phys., v. 24, p. 548-571.

Babcock, H. M., Brown, S. C., and Hem, J. D., 1947, Geology and ground-water resources of the Wellton-Mohawk area, Yuma County, Ariz.: Ti. S. Geological Survey open-file report, 22 p.

Babcock, H. M., and Snyder, C. T., 1947, Ground-water resources of the Holbrook area, Navajo County, Ariz.: U. S. Geol. Survey open-file report, 27 p.

Baker, M. N., 1949, The quest for pure water: Am. Water Works Assoc., New York, N. Y.

Banks, H. O., Richter, R. C., and Harder, J., 1957, Sea-water intrusion in California: Am. Water Works Assoc. Jour., v. 49, p. 71-88.

Bash, H. N., and others, 1950, Methemeglobinemia and Minnesota well supplies: Am. Water Works Assoc. Jour., v. 42, p. 161.

Beath, O. A., Hagner, A. F., and Gilbert, C. S., 1946, Some rocks and soils of high selenium content: Wyoming Geol. Survey Bull. 36.

Begemann, F. and Libby, W. F., 1957, Continental water balance, ground-water inventory and storage times, surface-ocean mixing rates, and world-wide water circulation patterns from cosmic-ray and bomb tritium: Geochim. et Cosmochin, Acta, v. 12, p. 277-296.

Berry, D. W., 1952, Geology and ground-water resources of Lincoln County, Kans.: Kansas Geol. Survey Bull. 95.

Bond, G. W., 1946, A geochemical survey of the underground water supplies of the Union of South Africa: Union of South Africa Dept. of Mines, Geol. Survey Memoir 41,208 p.

Bullwinkel, E. D., 1954, The chemistry of uranium in carbonate solutions: U. S. Atomic Energy Comm. Topical Rept. RMO-2614 (unpublished).

Busch, Werner, 1927, The applicability of electrometric titration to the determination of the solubility of slightly soluble oxides; Zeitschr. Anorg. Chem., v. 161, p. 161-179.

Byers, H. G., 1935, Selenium occurrence in certain soils in the United States, with a discussion of related topics: U. S. Dept. Agriculture Tech. Bull. 482.

1936, Selenium occurrence in certain soils in the United States, with a discussion of related topics, 2nd rept.: U. S. Dept. Agriculture Tech. Bull 530.

Byers, H. G., Miller, J. T., Williams, K. T., and Lakin, H. W., 1938, Selenium occurrence in certain soils in the United States, with a discussion of related topics, 3rd rept.: U. S. Dept. Agriculture Tech. Bull. 601.

California State Water Pollution Control Board, 1952, Water-quality criteria: California State Water Pollution Control Board pub. 3.

——— 1954, Report on the investigation of travel of pollution: California State Water Pollution Control Board, pub. 11.

Cameron, F. K., 1904, Jour. Am. Chem. Soc., v. 26, p. 1460.

Cameron, F. K., and Seidell, A., 1903, Jour. Phys. Chem., v. 7, p. 588.

Cederstrom, D. J., 1945, Geology and ground-water resouces of the Coastal Plain in southeastern Virginia: Virginia Geol. Survey Bull. 63.

Chapman, C. A., and Schweitzer, G. K., 1947, Electrode potentials and free energy changes: Jour. Geol., v. 55, p. 43-47.

Clarke, F. W., 1924a, The data of geochemistry, 5th ed.: U. S. Geol. Survey Bull. 770.

——— 1924b, The composition of the river and lake waters of the United States: U. S. Geol. Survey Prof. Paper 135.

Clarke, F. W., and Washington, H. S., 1924, The composition of the earth's crust: U. S. Geol. Survey Prof. Paper 127.

Colby, B. R., Hembree, C. H., and Jochens, E. R., 1953, Chemical quality of water and sedimentation in the Moreau River drainage basin, South Dakota: U. S. Geol. Survey Circ. 270.

Colby, B. R., Hembree, C. H., and Rainwater, F. H., 1956, Sedimentation and chemical quality of surface waters in the Wind River Basin, Wyo.: U. S. Geol. Survey Water-Supply Paper 1373.

Collins, W. D., 1922, Field examination of water; U. S. Geol. Survey open-file report.

——— 1923, Graphic representation of analyses: Ind. and Eng. Chem., v. 15, p. 394.

——— 1928, Notes on practical water analysis: U. S. Geol. Survey Water-Supply Paper 596-H.

Collins, W. D., and Riffenburg, H. B., 1923, Contamination of water samples with material dissolved from *glass* containers: Indus. and Eng. Chemistry, v. 15, p. 48-49.

— 1928, Quality of water of Pecos River in Texas: U. S. Geol. Survey Water-Supply Paper 596-D, p. 67-68.

Collins, W. D., and Williams, K. T., 1933, Chloride and sulfate in rainwater: Ind. and Eng. Chem., v. 25, p. 944.

Comly, H. H., 1945, Cyanosis in infants caused by nitrates in well water: Am. Med. Assoc. Jour., v. 129, no. 2, p. 112-116.

Conway, E. J., 1942, Mean geochemical data in relation to oceanic evolution: Proc. Royal Irish Acad. 48B, no. 8, p. 119.

Cunningham, M. B., Haney, P. D., Bendixen, T. W., and Howard, C. S., 1953, Effect of irrigation runoff on surface-water supplies: Am. Water Works Assoc. Jour., v. 45, p. 1159-1178.

Corbett, D. M. and others, 1945, Stream-gaging procedure: U. S. Geol. Survey Water-Supply Paper 888.

Dean, L. A., and Rubins, E. J., 1947, Anion exchange in soils: Soil Sci., v. 63, p. 377-406.

De La O. Careño, Alfonso, 1951, Las provincias geohidrológicas de Mexico, (primera parte): Univ. Nac. de Mexico, Inst. de geologia, Bol. 56.

Dole, R. B., 1909, The quality of surface waters in the United States, pt. I, analyses of waters east of the one hundredth meridian: U. S. Geol. Survey Water-Supply Paper 236.

Doneen, L. D., 1954, Salination of soil by salts in the irrigation water: Am. Geophys. Union Trans., v. 35, p. 943-950.

Drescher, W. J., 1953, Ground-water conditions in artesian aquifers in Brown County, Wis.: U. S. Geol. Survey Water-Supply Paper 1190.

Drescher, W. J., Dreher, F. C., and Brown, P. N., 1953, Water resources of the Milwaukee area, Wisconsin: U. S. Geol. Survey Circ. 247.

Durov, S. A., 1948, Natural waters and graphic representation of their composition: Doklady Akad. Nauk SSSR, v. 59, p. 87-90.

Durum, W. H., 1953, Relationship of the mineral constituents in solution to streamflow, Saline River near Russell, Kans.: Amer. Geophys. Union Trans., v. 34, p. 435-442.

Eaton, F. M., 1935, Boron in soils and irrigation waters and its effect on plants with particular reference to the San Joaquin Valley of California: U. S. Dept. Agriculture Tech. Bull. 448.

1950, Significance of carbonates in irrigation waters: Soil Sci., v. 69, n. 2, p. 127-128.

1954, Formulas for estimating leaching and gypsum requirements of irrigation waters: Texas Agriculture Expr. Sta. Misc. Pub. 111.

Ehlert, H., and Hempel, W., 1912, Solubility of certain salts: Z. Electrochem., v. 18, p. 727.

Ellis, M. M., Westfall, B. A., and Ellis, Marion D., 1946, Determination of water quality: U. S. Dept. of Interior, Fish and Wildlife Service, Research Rept. 9.

Emmons, W. H., 1917, The enrichment of ore deposits: U. S. Geol. Survey Bull. 625.

Emmons, W. H., and Harrington, G. L., 1913, A comparison of waters of mines and of hot springs: Econ. Geology, v. 8, p. 653-669.

Engler, C., and Hofer, H., 1909, Das wasser in den Erdölgebieten: Das Erdöl, Band 2., p. 28.

Epstein, S., and Mayeda, T., 1953, Variation of O^{18} content of waters from natural sources: Geochim. et Cosmochim. Acta, v. 4, p. 213-224.

Eriksson, E., 1952, Composition of atmospheric precipitation II; sulfur, chloride, iodine compounds, bibliography: Tellus, v. 4, p. 280-303.

Faul, Henry, ed., 1954, Nuclear geology: John Wiley and Sons, New York, N. Y.

Feth, J. H., 1953, Preliminary report of investigations of springs in the Mogollon Rim region, Arizona: U. S. Geol. Survey open-file report.

Filatov, K. V., 1948, Graphic representation of chemical analyses of water: Doklady Akad, Nauk SSSR, v. 59, p.91-94.

Fleischer, Michael, 1953, Recent estimates of the abundance of elements in the earth's crust: U. S. Geol. Survey Circ. 285.

——— 1954, The abundance and distribution of the chemical elements in the earth's crust: Jour. Chem. Educ., v. 31, p. 446-455.

Foster, M. D., 1937, The chemical character of the ground waters of the South Atlantic Coastal Plain: Washington Acad. Sci. Jour., v. 27, p. 405-412.

——— 1939, Ground waters of the Houston-Galveston area: Indus. and Eng, Chemistry, v.31, p. 1031-1035.

——— 1950, The origin of high sodium bicarbonate waters in the Atlantic and Gulf Coastal Plain: Geochim. et Cosmochim. Acta, v. 1. p. 33-48.

Friedlander, G., and Kennedy, J. W., 1949, Introduction to radiochemistry, John Wiley and Sons, Inc., New York, N. Y.

Friedman, Irving, 1953, Deuterium content of natural waters and other substances: Geochim. et Cosmochim. Acta, v. 4, p. 89-103.

Furman, N. H., ed., 1939, Scott's standard methods of chemical analysis, 5th ed. 2 vs., D. Van Nostrand, New York, N. Y.

Gallo, G., 1935, Equilibrium of strontium sulfate and water at various temperatures: Ann. Chim. Applicata, v. 25, p. 628-631.

Garrels, R. M., 1954, Mineral species as functions of pH and oxidation-reduction potentials, with special reference to the zone of oxidation and secondary enrichment of sulphide ore deposits; Geochim. et Cosmochim. Acta., v. 5, p. 153-168.

Gatewood, J. S., Robinson, T. W., Colby, B. R., Hem, J. D., and Halpenny, L. C., 1950, Use of *water* by bottom-land vegetation in lower Safford Valley, Ariz.: U. S. Geol. Survey Water-Supply Paper 1103.

Gaum, C. H., 1953, In: The physical and economic foundation of natural resources, IV, Subsurface facilities of water management and patterns of supply-Type area studies : Interior and Insular Affairs Committee, U. S. House of Representatives, p. 94-104.

Gedroiz, K. K., 1912, Colloidal chemistry as related to soil science, I. Colloidal substances in the soil solution, Formation of sodium carbonate in the soil, Alkali soils and saline soils : Zhur. Opit. Agron., v. 13, p. 363-412.

George, W. 0. and Hastings, W. W., 1951, Nitrate in the ground water of Texas : Am. Geophys. Union Trans., v. 32, p. 450-456.

Glasstone, Samuel, 1946, Textbook of Physical Chemistry, 2nd ed. ; D. Van Nostrand, New York, N.Y.

1950, Sourcebook on atomic energy : D. Van Nostrand, New York, N. Y.

Goldich, Samuel S., 1938, A study in rock weathering : Jour. Geol., v. 46, p. 17.

Goldschmidt, V. M., 1933a, Grundlagen der quantatativen Geochemie : Fortschr. Mineral. Krist. Petrog., v. 17, p. 112.

1933b, Geochemie. In: Handworterbuch der naturwissenschaften, 2, Aufl. Bd. 4, p. 886. Jena.

1937a, The principles of distribution of chemical elements in minerals and rocks : Jour. Chem. Soc. (Great Britain) for 1937, p. 655.

1937b, Geochemische Verteilungsgesetze der Elemente IX die Mengenverhaltnisse der Elemente und der Atom-Arten : Skrifter Norske Videnskaps-Akad. Oslo. I Mat.-Naturv. Klasse, No. 4.

1954, Geochemistry [edited by Alex Muir] : Clarendon Press, Oxford, England.

Gorham, Eville, 1955, On the acidity and salinity of rain : Geochim. et Cosmochim. Acta, v. 7, p. 231-239.

Graf, D. L. and Lamar, J. E., 1955, Properties of calcium and magnesium carbonates and their bearing on some uses of carbonate rocks : Econ. Geology, 50th Anniversary, p. 639-713.

Gregory, H. E., 1906, The crystalline rocks (of Connecticut) : Connecticut Geol. and Nat. Hist. Survey, Bull. 6, p. 115.

Griggs, R. L. and Hendrickson, G. E., 1951, Geology and ground-water resources of San Miguel County, N. Mex. : New Mexico Bur. Mines and Min. Resources Ground Water Rept. 2.

Grim, R. E., 1953, Clay mineralogy : McGraw-Hill Pub. Co., New York, N. Y.

Haehnel, 0., 1924, Solubility of magnesium carbonate in water saturated with carbon dioxide at high pressures and the properties of such solutions : Jour. Prakt. Chem., v. 107, p. 165-176; v. 108, p. 61-74; p. 187-193.

Halpenny, L. C. and others, 1952, Ground water in the Gila River Basin and adjacent areas, Ariz. : A summary : U. S. Geol. Survey open-file rept.

Handbook of chemistry and physics, 1953, Chemical Rubber Publishing Co., Cleveland, Ohio.

Hem, J. D., 1948, Fluctuations in concentration of dissolved solids of some southwestern streams : Am Geophys. Union Trans., v. 29, p. 80-83.

——— 1950, Quality of water of Gila River basin above Coolidge Dam, Ariz.: U. S. Geol. Survey Water-Supply Paper 1104.

Hem, J. D. and Cropper, W. H., 1959, A survey of chemical equilibria and redox potentials : U. S. Geol. Survey Water-Supply Paper 1459-A, in preparation.

Hendrickson, G. E., and Jones, R. S., 1952, Geology and ground-water resources of Eddy County, N. Mex. : New Mexico Bur. of Mines and Min. Res., Ground Water Rept. 3.

Herman, R., 1955, La configuration chimique des eaux souterraines : Centre Belga D'Etude et de Documentation des Eaux No. 27, p. 37-45.

Hill, R. A., 1940, Geochemical patterns in Coachella Valley, Calif. : Am. Geophys. Union Trans., v. 21, p. 46-49.

1941, Salts in irrigation water : Am. Soc. Civ. Eng. Proc., v. 67, p. 975-990.

1942, Salts in irrigation water : Am. Soc. Civ. Eng. Trans., v. 107, p. 1478-1493.

Howard, C. S., 1954, Chemical limnology, *in* Lake Mead Comprehensive Survey, 1948-1949, pt. 7, Limnology, U. S. Geol. Survey preliminary report.

Hoyt, W. G., and Langbein, W. B., 1944, The yield of streams as a measure of climatic fluctuations : Geog. Review, v.34, p. 218-233.

Huberty, M. R., Pillsbury, A. F., and Sokoloff, V. P., 1945, Hydrologic studies in Coachella Valley, Calif. : California Univ., Coll. of Agriculture, Div. of Irrigation, preliminary rept.

Mickel, Walter, 1950, Structural Chemistry of inorganic compounds : Elsevier Publishing Co., New York.

Hulett, G. A., and Allen, L. E., 1902, The solubility of gypsum : Jour. Am. Chem. Soc., v. 24, p. 674.

Hursh, J. B., 1954, Radium content of public water supplies : Am Water Works Assoc. Jour., v. 46, p. 43-54.

Hutchinson, G. Evelyn, 1957, A treatise on limnology, v. 1, geography, physics, and chemistry : John Wiley and Sons, Inc., New York, 1010 p.

Iler, Ralph K., 1955, The colloid chemistry of silica and silicates : The Cornell Univ. Pres, 324 p.

IsraM, H., 1934, Über den Chlorgehalt des Regenwassers : Bioklimatische Beible. Meterol. Zeitschr., v. 1., p. 53.

Jackson, D. C., 1905, The normal distribution of chloride in the natural waters of New York and New England : U. S. Geol. Survey Water-Supply Paper 144.

Jacobs, Woodrow, 1937, Preliminary report on a study of atmospheric chlorides : Monthly Weather Review, v.65, p. 147.

Jones, P. H., 1952, Electric-logging methods, principles of interpretation, and applications in ground-water studies : U. S. Geol. Survey open-file report, 34 p.

Junge, C. E. and Gustafson, P. E., 1957, On the distribution of sea salt over the United States and its removal by precipitation : Tellus, v. 9, p. 164-173.

Keighton, W. B., 1954, The investigation of chemical quality of water in tidal rivers : U. S. Geol. Survey, open-file report.

Keller, W. D., 1955, The principles of chemical weathering : Lucas Bros. Publishers, Columbia, Mo.

Kelley, W. P., and Brown, S. M., 1928, Boron in the soils and irrigation waters of southern Calif. and its relation to citrus and walnut culture : Hilgardia 3: 445-458,1928.

Kelley, W. P., 1948, Cation exchange in soils : Reinhold Pub. Corp., N. Y.

1951, Alkali soils : Reinhold Pub. Corp., N.Y.

Kline, W. D., 1929, Solubility of magnesium carbonate (nesquehonite) in water at 25°C and pressures of carbon dioxide up to one atmosphere : Jour. Am. Chem. Soc., v.51, p. 2093-97.

Knight, S. H., and Beath, 0. A. 1937, The occurrence of selenium and seleniferous vegetation in Wyoming : Wyoming Agr. Expt. Sta., Bull 22.

Kohler, Hilding, 1925, Unterschungen über die elemente des Nebels under der Wolken Medd Statens Meteor. Hydrog. Anstalt 2, no. 5.

Kohlrausch, Fr., 1908, Saturated aqueous solutions of sparingly soluble salts: Zeitschr. Physik. Chem., v. 64, p. 121-169.

Krauskopf, Konrad B., 1956, Dissolution and precipitation of silica at low temperatures: Geochim. et Cosmichim. Acta, v. 10, p. 1-26.

Kulp, J. L., Turekian, K., and Boyd, D. W., 1952, Strontium content of limestone and fossils: Geol. Soc. America Bull., v. 63, p. 701-716.

Kuroda, P. K., 1953, Tables of the radioactivity of natural waters: Arkansas Univ. Inst. of Sci. and Tech., 58 p.

Kuroda, P. K., and Sandell, E. B., 1953, Chlorine in igneous rocks: Geol. Soc. America Bull., v. 64, p. 879-896.

Kuroda, P. K., and Yokoyama, Y., 1954, Determination of short-lived decay products of radon in natural waters: Anal. Chem., v. 26, p. 1509-11.

Lakin, H. W., Almond, Hy, and Ward, F. N., 1952, Compilation of field methods used in geochemical prospecting by the U. S. Geol. Survey: U. S. Geol. Survey Circ. 161.

Lakin, H. W., and Byers, H. G., 1941, Selenium occurrence in certain soils in the United States, with a discussion of related topics, 6th rept.: U. S. Dept. Agriculture Tech. Bull. 783.

——— 1948, Selenium occurrence in certain soils in the United States, with a discussion of related topics, 7th rept.: U. S. Dept. Agriculture Tech. Bull. 950.

Langelier, W. F., 1936, The analytical control of anti-corrosion water treatment: Am. Water Works Assoc. Jour., v. 28, p. 1500-1521.

——— 1944, Discussion of, A graphic procedure in the interpretation of water analyses; by Piper, A. M.: Am. Geophys. Union Trans. v. 25, p. 925-927.

Langelier, W. F., and Ludwig, H. F., 1942, Graphical methods for indicating the mineral character of natural waters: Am. Water Works Assoc. Jour., v. 34, p. 335-352.

Larson, T. E., 1949, Geologic correlation and hydrologic interpretation of water analyses: Illinois State Water Survey Div. circ. 27.

Larson, T. E., and King, R. M., 1954, Corrosion by water at low flow velocity: Am. Water Works Assoc. Jour., v.46, p. 1-9.

Leick, J., 1932, The solubilities of calcium carbonate and magnesium carbonate in water that is free from carbonic acid: Zeitschr. Anal. Chem., v. 87, p. 415-422.

1933, Equilibria in the transposition of sodium carbonate, calcium hydroxide, and trisodium phosphate with calcium and magnesium sulfate: Zeitschr. Anorg. Allgem. Chem., v. 210, p. 203-209.

Leighton, M. O., 1905, Field assay of water: U. S. Geol. Survey Water-Supply Paper 151.

Lenher, V., and Merrill, H. B., 1917, Solubility of silica: Jour. Am. Chem. Soc., v. 39, p. 2630.

Libby, W. F., 1954, Tritium in surface water: Am. Chem. Soc. 126th Natl mtg., September 1954.

Lindeman, H. B., 1954, Sodium carbonate brine and trona deposits in Sweetwater County, Wyo.: U. S. Geol. Survey Circ. 235.

Lohr, E. W., and Love, S. K., 1954a, The industrial utility of public water supplies in the United States, 1952, pt. 1, States east of Mississippi River: U. S. Geol. Survey Water-Supply Paper 1299.

——— 1954b, The industrial utility of public water supplies of the United States, 1952, Pt. 2, States west of the Mississippi River: U. S. Geol. Survey Water-Supply Paper 1300.

Love, S. K., 1950, The natural radioactivity of water: Am. Chem. Soc. 118th Natl mtg., September 7,1950.

Macnamarra, J., and Thode, H. G., 1951, The distribution of S in nature and the origin of native sulfur deposits: Research (Br.) v. 4, p. 582.

Mandelbaum, R., 1909, Calcium monoborates: Zeitschr. Anorg. Chem., v. 62, p. 370-382.

Mason, Brian, 1952, Principles of geochemistry: John Wiley and Sons, New York.

Maucha, Rezso, 1934, Graphic demonstration of composition of waters: Hidrol. Közlöny, v. 13, p. 117-118.

——— 1949, The graphic symbolization of the chemical composition of natural waters: Hidrol, Közlöny, v. 29, p. 28-30.

Maxcy, K. F., 1050, Report on the relation of nitrate concentrations in well waters to the occurrence of methemeglobinemia in infants: Natl. Research Council, Bull. Sanitary Eng. and Environment App. D.

McDonald, H. R., Walcott, H. N., and Hem, J. D., 1947, Geology and ground-water resources of the Salt River Valley area, Maricopa and Pinal Counties, Ariz.: U. S. Geol. Survey, open-file report.

McDowell, L. A., and Johnston, H. L., 1936, The solubility of cupric oxide in water and the second dissociation constant of cupric acid: Jour. Am. Chem. Soc., v. 58, p. 2009-14.

Meinzer, O. E., and Kelton, F. C., 1913, Geology and water resources of Sulphur Springs Valley, Ariz.: U. S. Geol. Survey Water-Supply Paper 320.

Meinzer, O. E., and Ellis, A. J., 1916, Ground water in Paradise Valley, Ariz.: U. S. Geol. Survey Water-Supply Paper 375—B, p. 51-75.

Metzler, D. F. and Stoltenberg, H. A., 1950, The public health significance of high nitrate waters as a cause of infant cyanosis and means of control: Kansas Acad. of &I. Trans., v. 53, no. 2, p. 194-211, fig. 1-4.

Meyer, R. R., and Turcan, A. N., Jr. 1955, Geology and ground-water resources of the Baton Rouge area, Louisiana: U S. Geol. Survey Water-Supply Paper 1296, p. 68.

Mitchell, H. H., and Edman, M., 1953, Fluorine in human nutrition: Jour. Am. Dietetic Assoc., v. 29, p. 24.

Moore, E. W., 1940, Progress report of the committee on quality tolerances of water for industrial uses: New England Water Works Assoc. Jour., v. 54, p. 271.

National Bureau of Standards, 1953, Maximum permissible amounts of radioisotopes in the human body and maximum permissible concentrations in air and water: Handbook 52.

Officers of the Department of Agriculture and Government Chemical Laboratories, 1950, Waters for agricultural purposes in Western Australia: Jour. of Agriculture of Western Australia, v. 27, ser. 2,156.

Oka, Y., 1940, Fundamental reactions in analytical chemistry, 9 Summary: Jour. Chem. Soc., Japan, v. 61, p. 311-20.

Palmer, Chase, 1911, The geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479.

Plater, J., 1928, The amphoteric character of cadmium hydroxide: Zeitschr. Anorg. Chem., v. 174, p. 321-41.

Piper, A. M., 1944, A graphic procedure in the geochemical interpretation of water analyses: Am. Geophys. Union Trans., v. 25, p. 914-23.

Piper, A. M., Garrett, A. A., and others, 1953, Native and contaminated waters in the Long Beach-Santa Ana area, California: U. S. Geol. Survey Water-Supply Paper 1136.

Piper, A. M., Robinson, T. W., and Park, C. F., Jr., 1939, Geology and ground-water resources of the Harney Basin, Oreg.: U. S. Geol. Survey Water-Supply Paper 841.

Pirsson, L. V., and Knopf, A., 1947, Rocks and rock minerals, 3d ed., John Wiley and Sons, New York.

Pleissner, M., 1907, Arb. Kais. Gesundheitsamt, v. 26, p. 384-443.

Posnjack, E., 1940, Deposition of calcium sulfate from sea water: Amer. Jour. Sci., v. 238, p. 559-568.

Rankama, K., 1954, Isotope geology: McGraw-Hill Book Co., New York.

Rankama, K., and Sahama, T. G., 1950, Geochemistry: Chicago Univ. Press, Chicago, Ill.

Reiche, Parry, 1950, A survey of weathering processes and products, revised.: New Mexico Univ. Publications in Geology, no. 3.

Reistle, C. E., Jr., 1927, Identification of oil-field waters by chemical analysis: U. S. Bureau of Mines Tech. Paper 404.

Remy, H., 1925, Conductivity measurements in very dilute solutions: Zeitschr. Electrochem., v. 31, p. 92.

Renick, B. C., 1925, Base exchange in ground water by silicates as illustrated in Montana: U. S. Geol. Survey Water-Supply Paper 520-D, p. 53-72.

Revelle, Roger, 1941, Criteria for recognition of sea water in ground waters: Am. Geophys, Union Trans., v. 22, p.593-97.

Riffenburg, H. B., 1925, Chemical character of ground waters of the northern Great Plains: U. S. Geol. Survey Water-Supply Paper 560-B, p. 31-52.

Rogers, A. S., 1954, The physical behavior and geologic control of radon in mountain streams: Utah Univ. PhD. thesis.

Ross, C. S., and Hendricks, S. B., 1945, Minerals of the montmorillonite group, their origin and relation to *soils* and clays: U. S. Geol. Survey Prof. Paper 205, p. 23-79.

Rossum, J. R., 1949, Conductance method for checking accuracy of water analyses: Anal. Chem., v. 12, p. 631.

Roy, C. J., 1945, Silica in natural waters: Am. Jour. Sci., v. 243, p. 393-403.

Sayre, A. N., and Livingston, P. P., 1945, Ground-water resources of the El Paso area, Texas: U. S Geol. Survey Water-Supply Paper 919.

Schoeller, Henri, 1935, Utilite de la notion des exchanges de bases pour la comparison des eaux souterraines : France Soc. Geol. Comptes Rend. Sommaire et Bull. Ser. 5, v. 5, p. 651-657.

1955, Geochemie des eaux souterraines : Revue de L'Institute Francais du petrole, v. 10, p. 230-244.

Scofield, C. S., 1932, Measuring the salinity of irrigation waters and soil solutions with the wheatstone bridge: U. S. Dept. of Agriculture Circ. 232.

——— 1940, Salt balance in irrigated areas: Jour. Agriculture Res. v. 61, p. 17-39.

Scofield, C. S., and Wilcox, L. V., 1931, Boron in irrigation water: U. S. Dept. Agriculture Tech. Bull. 264, p. 9-10.

Seidell, Atherton, 1940, Solubilities of inorganic and metal organic compounds, 3d ed., v. 1, D. van Nostrand, New York.

Shand, S. J., 1952, Rocks for chemists: Pitman Publishing Co., New York.

Simpson, H. E., 1929, Geology and ground-water resources of North Dakota: U. S. Geol. Survey Water-Supply Paper 598.

Slichter, C. S., 1902, The motions of underground waters: U. S. Geol. Survey Water-Supply paper 67.

Stabler, Herman, 1911, Some stream waters of the western United States, with chapters on sediment carried by the Rio Grande and the industrial application of water analyses: U. S. Geol. Survey Water-Supply Paper 274.

Stehney, A. F., 1955, Radium and thorium x in some potable waters: Acta Radiologica, v.43, p. 48-51.

Stephenson, L. W., Logan, W. N., and Waring, G. A., 1928, The ground-water resources of Mississippi: U. S. Geol. Survey Water-Supply paper 576, p. 22.

Stevens, R. E., 1934, Studies on the alkalinity of some silicate minerals: U. S. Geol. Survey Prof. Paper 185, p. 1-13.

Stiff, H. A., Jr., 1951, The interpretation of chemical water analysis by means of patterns: Jour. of Petrol. Tech., p. 15, Oct.

Suess, E., 1902, Hot springs and volcanic phenomena: Geol. Jour., v. 20, p. 520.

Swenson, H. A., 1953, Geochemical relationships of water in the Powder River Basin, Wyoming and Montana: Amer. Geophys. Union Trans., v. 34, p. 443-448.

Sverdrup, H. U., Johnson, M. W., and Fleming, R. H., 1942, The oceans, their physics, chemistry, and general biology: Prentice-Hall, New York.

Thatcher, L. L., and S[illegible], David, 1954, The determination of beryllium in water: U. S. Geol. Survey open-file report.

Thompson, H. S., 1850, On the absorbent power of soils: Royal Agriculture Soc. Jour., v. 11, p. 68-74.

Thorne, D. W. and Peterson, H. B., 1954, Irrigated soils, their fertility and management: The Blakiston Co., Inc., New York.

Tickell, E. G., 1921, A method for the graphical interpretation of water analysis: Rept. of California State oil and gas supervisor, v. 6, p. 5-11.

Townley, R. W., Whitney, W. B., and Felsing, W. A., 1937, The solubilities of barium and strontium carbonates in aqueous solutions of some alkali chlorides: Jour. Am. Chem. Soc., v. 59, p. 631-633.

Vanselow, A. P., 1932, Equilibria of the base exchange reaction of bentonites, permutites, soil colloids, and zeolites: Soil Sci., v. 33, p. 95-113.

U. S. Bureau of Reclamation, 1953, Reclamation manual, v. IV, pt. 2, Chap. 2.4 (revised).

U. S. Geological Survey, 1958, Methods for collection and analysis of water samples U. S. Geol. Survey Water Supply paper (in press).

U. S. Geological Survey-1954 Quality of surface waters for irrigation, western United States, 1951 U. S. Geol. Survey Water-Supply Paper 1264.

U. S. Geological Survey-Quality of surface waters of the United States. Annual reports as follows: 1942, Water-Supply Paper 950; 1943, Water-Supply Paper 970; 1944, Water-Supply Paper 1022; 1945, Water-Supply Paper 1030; 1946, Water-Supply Paper 1050; 1947, Water-Supply Paper 1102; 1948, Water-Supply Papers 1132 and 1133; 1949, Water-Supply Papers 1162 and 1163; 1950, Water-Supply Papers 1186-1189.

U. S. Public Health Service, 1946, Public Health Reports, reprint 2697.

U. S. Salinity Laboratory Staff 1954, Diagnosis and improvement of saline and alkali soils: U. S. Dept. of Agriculture Handbook no. 60.

Waring, F. G., 1949, Significance of nitrate in water supplies: Am. Water Works Assoc. Jour., v. 41, p. 147.

Waring, G. A., 1915, Springs of California: U. S. Geol. Survey Water-Supply paper 338.

Way, J. T., 1850, The power of soils to absorb manure: Royal Agriculture Soc. Jour., v. 11, p. 313-379.

Wedepohl, K. H., 1953, Untersuchungen zur Geochemie des Zinks: Geochim. et Cosmochim. Acta, v. 3, p.93-142.

Weigel, O., 1906, Behavior of sulfides of heavy metals in water solution: Math. Kl., Ges. Wiss. Gottingen, p. 525-48.

1907, Behavior of sulfides of heavy metals in water solution: Zeitschr. Physik. Chem., v. 58, p. 292-300.

White, D. E., and Brannock, W. W., 1950, The sources of heat and water supply of thermal springs with particular references to Steamboat Springs, Nev.: Am. Geophys, Union Trans., v. 31, p. 566-574.

White, D. E., Brannock, W. W., and Murata, K. J., 1956, Silica in hot-spring waters : Geochim. et Cosmichim. Acta, v. 10, p. 27-59.

White, D. E., 1957a, Thermal waters of volcanic origin : Geol. Soc. of America Bull., v. 68, p. 1637-1658.

——— 1957b, Magmatic, connate and metamorphic waters : Geol. Soc. of America Bull., v. 68, p. 1659-1682.

Wilcox, L. V., 1948, The quality of water for irrigation use: U. S. Dept. Agriculture Tech. Bull. 962.

Williams, K. T., Lakin, H. W., and Byers, H. G., 1940, Selenium occurrence in certain soils in the United States with a discussion of related topics, 4th rept.: U. S. Dept. Agriculture Tech. Bull. 702.

——— 1941, Selenium occurrence in certain soils in the United States, with a discussion of related topics, 5th rept.: U. S. Dept. Agriculture Tech. Bull. 758.

Zobell, C. E., 1946, Redox potential of marine sediments: Am. Assoc. of Petrol. Geol. Bull., v. 30, p. 477-513.

INDEX

U.S. GOVERNMENT PRINTING OFFICE 1960 O—563878