methods. The residence times of the elements determined by Goldberg (1963a) are given in table 7. These range from 2.6×10^8 years for sodium to only 100 years for aluminum. Similar results were reported by MacKenzie and Garrels (1966).

In most respects, the concept of residence time in the ocean is more satisfying to the chemist interested in aqueous behavior of the elements than is the Goldschmidt model with its dependence on average igneous and sedimentary rock composition. As Barth (1961) has pointed out, the igneous rocks that lie near the surface of the continents, which are the ones available for collection of rock samples for analysis, represent material that has in all probability been reworked many times and may, therefore, have a composition very different from its original composition. The present compositions of rocks and the oceans represent the result of a long-continued process of fractionation, and the residence time of elements in the ocean is, therefore, useful as an index of their geochemical behavior. The elements whose chemistry definitely favors retention in aqueous species have long residence times, and those preferentially bound into solids have short residence times.

Processes of sea-floor spreading and plate tectonics can be viewed as the way in which the cycle of weathering is closed and the oceanic sediments are returned to the continental crust. However, the quantitative evaluation of such processes does not appear feasible at this time.

Cycles of some elements are interrelated. Lasaga (1980) evaluated some aspects of coupling between the cycles of carbon and oxygen, using concepts of thermodynamics of irreversible processes. This approach has interesting possibilities for future theoretical studies, be-

cause one can predict stable states that are not at thermodynamic equilibrium.

EVALUATION OF WATER COMPOSITION

The composition of natural water must be determined by physical and chemical means, usually by collection and examination of samples. The standard practice of collection of samples and later analysis in the laboratory is changing somewhat in response to the growing trend to use automatic sampling and continuous-sensing devices. It is with the study and interpretation of water composition, however the water is obtained, that we are principally concerned.

Collection of Water Samples

Sampling is a vital part of studies of natural-water composition and is perhaps the major source of error in the whole process of obtaining water-quality information. This fact is not well enough recognized, and some emphasis on it seems desirable.

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 considered to be reliably representative of a large volume of material depends on several factors. These include, first, the homogeneity of the material being sampled and, second, the number of samples, the manner of collection, and the size of the individual samples.

The sampling of a completely homogeneous body is a simple matter, and the sample may be very small. Because most materials are not homogeneous, obtaining

Table 7. Average residence time of elements in the ocean

[After Goldberg (1963a)]

Element	Residence time (yr)	Element	Residence time (yr)	Element	Residence time (yr)
Na	2.6×10^8	Rb	2.7×10^5	Sc	5.6×10^3
Mg	4.5×10^7	Zn	1.8×10^5	Pb	2.0×10^3
Li	2.0×10^7	Ba	8.4×10^4	Ga	1.4×10^3
Sr	1.9×10^7	Cu	5.0×10^4	Mn	1.4×10^3
K	1.1×10^7	Hg	4.2×10^4	W	1.0×10^3
Ca	8.0×10^6	Cs	4.0×10^4	Th	3.5×10^2
Ag	2.1×10^6	Co	1.8×10^4	Cr	3.5×10^2
Au	5.6×10^5	Ni	1.8×10^4	Nb	3.0×10^2
Cd	5.0×10^5	La	1.1×10^4	Ti	1.6×10^2
Mo	5.0×10^5	V	1.0×10^4	Be	1.5×10^2
Sn	5.0×10^5	Si	8.0×10^3	Fe	1.4×10^2
U	5.0×10^5	Y	7.5×10^3	Al	1.0×10^2
Bi	4.5×10^5	Ge	7.0×10^3		
Sb	3.5×10^5	Ce	6.1×10^3		

truly representative samples depends to a great degree on the sampling technique. A sample integrated by taking small portions of the material at systematically distributed points over the whole body represents the material better than a sample collected from a single point. The more portions taken, the more nearly the sample represents the whole. The sample error would reach zero when the size of the sample became equal to the original volume of material being sampled, but for obvious reasons this method of decreasing sampling error has practical limits.

One of the primary goals of a water-quality investigation may be to provide information that can be used to determine the composition of the whole volume of water within or available to a region. The object of study may be a slowly circulating mass in a lake or reservoir, the water in an aquifer, or the water carried by a river during some finite time period. Also, information may be required on the variations in composition at a point, or over the whole water body, with passage of time. For other types of studies, a synoptic evaluation of water composition in a river drainage system may be desired, with the goal of emphasizing spatial rather than temporal variations. The design of sampling programs that will accomplish all these objectives encounters different kinds of problems in surface- and ground-water systems, and rather careful attention to sample collection is required.

The purpose underlying a water-quality study largely governs the sampling procedures that should be followed. Commonly, the investigator wishes to know the composition of a cross section of a river at a specific time. For some purposes, however, only the composition that would occur at a fixed water-intake point is of interest, and in this case the procedure would be somewhat simpler to design.

Sampling of River Water

To determine adequately the instantaneous composition of a flowing stream, the sample, or set of samples taken simultaneously, must be representative of the entire flow at the sampling point at that instant. Furthermore, the sampling process must be repeated if the results of analysis are to be extrapolated in time, and the sampling interval chosen must represent adequately any changes that might occur. Changes occurring along the length of the stream can be evaluated by adding more sampling points.

The homogeneity of a stream at a cross section is determined by such physical factors as proximity of inflows and turbulence in the channel. Locally, poor lateral or vertical mixing can be observed in most stream systems. Immediately below the confluence of a stream and 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 kilometers downstream. The effect is more pronounced if the water of the tributary differs markedly from the water of the main stream in concentration of dissolved or suspended solids or in temperature. Where a river enters the ocean there is, of course, also a possiblity of seawater mixing incompletely with the flow. These effects may be of special interest in some studies, but if the average composition of the whole flow of a stream or its changes in composition over a period of time are the factors of principal significance, sampling locations where mixing is incomplete should be avoided.

An outstanding example of incomplete mixing across the stream is afforded by the Susquehanna River at Harrisburg, Pa. The stream at the highway bridge where samples were collected is about half a mile wide and is split into two channels by an island. The composition of the water is indicated by six samples spaced across the stream and is given in figure 2. More than 20 years of observations by the U.S. Geological Survey (Anderson, 1963) show that this pattern is always present in some degree, except at very high stages. The anthracite-mining region northeast of Harrisburg produces large volumes of drainage containing high sulfate concentrations and having a low pH. Tributaries entering the river from the west above Harrisburg, especially the Juniata River, are less influenced by mine drainage and usually carry alkaline water having much lower sulfate contents. Obviously, it is difficult to characterize the whole flow of the stream at Harrisburg, although samples at one point would indicate what an intake located there would obtain.

A composite sample that will represent accurately the water in a vertical cross section of a stream can be obtained by combining appropriate volumes of samples taken at a series of points along the cross section. At each point, samples should be obtained at enough different depths to compensate for vertical inhomogeneity. Obviously, it is physically impossible to obtain all these samples at one instant. The water in the stream is in motion at different rates in different parts of the cross section, and this further complicates the problem.

In practice, the collection of river-water samples is somewhat simplified by use of portable integrating sampling devices which allow water to enter the sample container at a rate proportional to water flow rate at the intake nozzle. The sampling device is raised or lowered from a selected position on a bridge or cableway to obtain a sample that will represent all the river flow at the particular point along the cross section. This process is repeated at other points along the cross section (commonly five or more) and the individual depth-integrated (or flow-rate-integrated) samples are combined.

Integrating samplers were developed beginning in the 1940's to obtain representative samples for calculating suspended sediment loads of streams. This sampling equipment and techniques for its use were described by

Guy and Norman (1970). The equipment may require modification to avoid contaminating samples collected for determining minor dissolved constituents.

If it is known or can be determined by field study that a stream at a proposed sampling site is uniform in composition at all flow stages, a single grab sample will satisfactorily represent the flow at the time it is collected. In earlier U.S. Geological Survey studies, efforts were made to establish river-sampling sites where homogeneity of solute concentrations across the stream was reasonably assured. For major solute constituents, some degree of homogeneity is common. For minor constituents that may be associated with suspended material, single grab samples may be very poor representations of the whole stream.

Some of the uncertainty in representativeness of individual samples was compensated for when samples were obtained at daily or shorter intervals. Most recent policy has been to obtain less frequent samples but to make a greater effort to be sure each represents the flow accurately. Sampling techniques used in studies made up to the mid-1970's were described by Brown and others (1970). Modifications of these procedures are required for unstable or trace constituents, and care must be taken to avoid contamination of samples by containers, preservatives, or sampling equipment. Some properties of water must be determined in the field. Detailed guidelines for sampling of river water have been set for U.S. Geological Survey studies by the technical memoranda circulated through the Water Resources Division. The major features of these guidelines are indicated above. Continuous sensing of specific conductance or other properties of the water supplements the periodic samples for detailed analysis.

Separate consideration of solution and solid phase portions of the sample is necessary, because free solutes and those associated with the solids will have very different physical and chemical behavior in the stream. Sampling and analytical procedures that do not make this separation adequately yield misleading and scientifically worthless results. At least a part of the sample generally must be filtered at the time of collection. Guidelines for filtration and preservation of samples were given by Brown and others (1970). Some aspects of sample treatment will be discussed later, as appropriate, in relation to specific solutes.

When a sampling point has been found and a procedure adopted that ensures that each sample adequately represents the water flowing at that instant, a decision generally is needed as to how frequently samples or measurements must be obtained. The composition of all surface streams is subject to change with time. Long-term changes may result from long rainfall or runoff cycles or from changes in land or in water use. 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, regulation of flow by humans, dumping of wastes, or biochemical changes.

Stream discharge commonly is computed in terms of mean daily rates. A strictly comparable water-quality observation would be the daily mean of a continuously determined property. A single grab sample, however, ought to be considered only to represent the instantaneous discharge at the time of sampling.

To determine the water-quality regimen of a river at a fixed sampling point, samples should be collected or measurements made at such intervals that no important cycle of change in concentration could pass unnoticed between sampling times. For some streams, where flow is completely controlled by large storage reservoirs or is
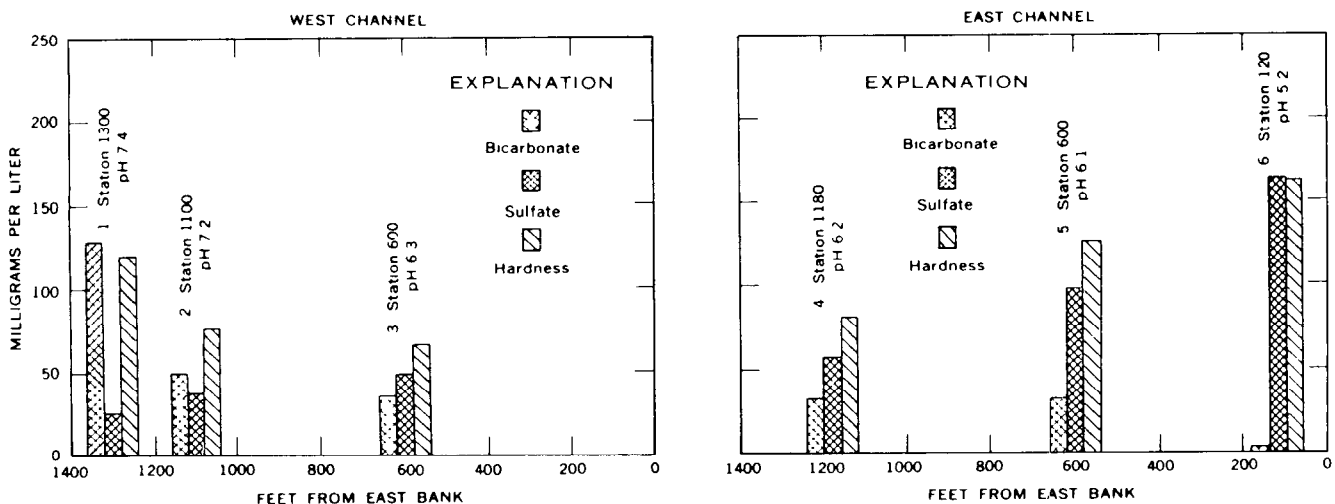

Figure 2. Bicarbonate, sulfate, hardness (as $CaCO_3$), and pH of samples collected in cross section of Susquehanna River at Harrisburg, Pa., July 8, 1947.

maintained at a nearly steady rate by large, constant, ground-water inflows, a single sample or observation may represent the composition accurately for many days or weeks. For many streams, however, one sample cannot be safely assumed to represent the water composition closely for more than a day or two, and for some streams not for more than a few hours.

The U.S. Geological Survey began extensive investigations of the chemical quality of river water shortly after 1900 (Dole, 1909; Stabler, 1911), as a part of the agency's program for appraisal of water resources of the country. In these studies, samples were collected by a local observer once a day for a period of a year or more at each sampling site, which also was the site of a gaging station for measuring the flow of water. Once-daily sampling schedules were standard practice for many years in later work of this kind by the Geological Survey. Although this frequency of sampling might miss a few significant changes, it generally was thought to provide a reasonably complete record for most large rivers. After some records of this kind have been obtained, however, it is often possible to decrease sampling frequency and still maintain a useful, although less detailed, record.

A single daily sample usually was assumed to represent all the water passing the sampling point on the day it was collected and also to represent a discharge rate equal to the daily mean. The descriptive text accompanying the published river-water analyses for the early years of this century does not tell much about sampling methods and gives no reasons for the decision to obtain one sample each day. Continuous water-stage recorders were not in wide use at that time (Corbett and others, 1945, p. 191). It may be that investigators who were conditioned to accept once- or twice-daily gage readings as a basis for calculating mean daily water discharge felt that a once-daily sampling schedule was so obviously indicated that no alternative needed to be considered.

In recent years, equipment has been developed that can be installed on a streambank or a bridge to obtain various measurements of water quality every few minutes and to record or transmit the information to a central point. Developments in this field have been rapid, and such equipment obviously can provide much more detailed information than could be obtained by the old sampling methods. Some limitations of sampling remain, however, because the water on which measurements are made has to be brought to the instrument through a fixed intake. The site of the intake represents a fixed sampling point.

In the early studies mentioned above, the daily samples were combined into composite samples before the analysis was begun. The composites usually included 10 daily samples, and 3 composites were prepared for each month. In later investigations, a single determination, usually of specific conductance, was made for each daily sample before making the composite with the remaining water. One of the principal reasons for combining individual daily samples into composites was the need for a large volume of water for the analytical procedures that were then in use. Another reason, of course, was economic, as the analytical work was expensive. The composite samples usually included 10 to 30 daily samples, but shorter periods were used at times to avoid obscuring day-to-day changes and to study the composition of water at times of unusually high or unusually low discharge rate. Samples of water that differed widely in conductance usually were not included in the same composite, nor were samples representing widely different discharge rates; such samples were analyzed separately. In studies of streams in the Missouri River basin beginning in 1946, composites were prepared by using amounts of each daily sample proportional to the discharge rate observed at the time of sampling. That procedure yields discharge-weighted analytical results. Similar procedures were followed for some other streams, but for many streams, composites continuted to be made by equal volumes of each daily sample. The publications in the U.S. Geological Survey Water-Supply Paper series "Quality of Surface Waters of the United States," in which the results up to 1970 were released, describe compositing methods used. For various reasons there has been a trend in recent years away from daily sampling and compositing of samples for analysis. Depending on the requirements for information that the sampling program is expected to satisfy, the frequency of sampling may range from a few collections a week to once every 3 to 6 months. When comprehensive data on fluctuations are needed, these samples are supplemented by continuous automated records of conductivity and other properties.

In a statistical study, Sanders and Adrian (1978) developed a method for determining optimum sampling frequency for river-monitoring stations on the basis of water-discharge fluctuations. Stations in the Geological Survey's NASQAN network follow an operating schedule that includes once-a-day or continuous conductivity measurements and once-a-month or less frequent sampling for determination of major dissolved constituents. A similar schedule has been adopted for many other stream sampling stations operated by the Geological Survey.

The range between high and low extremes of dissolved-solids concentration at a sampling point on a stream is rarely as wide as that between high and low flow rates. Maximum dissolved-solids concentrations 20–40 times as great as the minimum have been observed over long periods of record in some nontidal streams in 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 water discharge and the rate of change of discharge,

but this relationship is complicated by other factors related to both the hydrology and the geochemistry of the system. For some streams, past records can be used directly to estimate water quality from discharge. For other streams, such estimates are too inaccurate to be of any value.

Automated or continous-recording equipment for conductivity and other solution variables, supplemented by properly designed sampling and chemical analyses, provides many details on water-quality regimens that are not attainable by sampling alone. This approach is particularly useful in streams having tributaries that supply water that varies extensively in composition, in streams having large actual or potential inflows of waste, and in streams influenced by oceanic tidal inflow.

From compilations of water-quality records obtained at properly chosen sites on a stream system, a hydrologist can put together a basin-wide or statewide summary of stream chemistry. For example, Wood (1970) summarized the composition of Michigan stream water using maps and selected analyses. Anderson and Faust (1973) made a much more detailed summary of water-quality and hydrologic factors that control it in a 762-square-mile area drained by the Passaic River in New Jersey.

Water-quality data for U.S. streams obtained after 1970 have been published in annual reports for each State in a series entitled "Water Resources Data for (State) _____ , Water Year _____ ," available from the National Technical Information Service, Springfield, Va. The data also are stored in computer data banks (WATSTORE and STORET) and can be located by the National Water Data Exchange (NAWDEX), U.S. Geological Survey, Reston, Va. These records provide an enormous volume of factual information and have many practical applications.

A basin-wide summary of water-quality characteristics can also be obtained by making simultaneous observations and measurements at many sites along the main stream and important tributaries. The synoptic overview thus obtained can be repeated at different times of the year to give an indication of the effects of discharge changes and seasonal variations. A broad-scale application of this approach to the Willamette River Basin in Oregon was described by Rickert and others (1976).

The way water composition changes at a specific sampling and measuring point can best be determined by continuous sensing of specific conductance or related variables. There may be gaps in such records owing to instrument malfunction, and the feasibility of extrapolating or interpolating such records depends on the hydrologist's knowledge of water-chemistry variation at that site.

The Rio Grande at the San Acacia gaging station in central New Mexico is an example of a stream exhibiting considerable fluctuations of discharge and quality. Figures 3 and 4 show the way in which discharge fluctuates and specific conductance of the water changes at different time of the year. Figure 3 covers the spring-runoff period when melting snow in the river's headwater region caused the flow to increase from a few hundred cubic feet per second in April to nearly 10,000 cubic feet per second in May. The flow decreased to low stages again in June. During this period, the conductance of the water declined and then rose, but the day-to-day change was minor; the maximum for the 3 months was only about double the minimum. Daily, or less frequent, sampling will define such a period adequately. During the summer much of the runoff passing San Acacia results from flash floods in ephemeral tributaries in which both the quantity and the quality of the water vary widely. In figure 4 the results of samples collected from one to five times a day during part of the month of August were plotted with discharge rates observed at sampling times. On August 17, two samples collected a few hours apart showed a nearly threefold difference in concentration.

During the snowmelt period, a relatively small uncertainty is introduced by extrapolation of specific conductance over several days. During the summer-runoff period, however, the water composition is obviously difficult to predict without frequent measurements.

The implication here that discharge or flow measurements should be available for sampling sites is intentional. Chemical analyses of river water generally require some sort of extrapolation, if only because the water sampled has long since passed on downstream by the time a laboratory analysis is completed. The discharge record provides a means of extrapolating the chemical record if the two are closely enough related. The discharge data also serve as a means of averaging the water analyses, give an idea of total solute discharges, and permit evaluation of the composition of water that might be obtained from storage reservoirs.

Comparability of Records

The U.S. Geological Survey has now compiled detailed but discontinuous records of water quality for a great number of river-sampling sites over a time span exceeding three-quarters of a century. These records have a potential for indicating trends in water composition. Comments regarding methods of detecting such trends will be made later. However, as the preceding discussion has noted, the protocols for sampling and analysis have changed significantly during the period of record, and the direct comparison of published data obtained at different times may give misleading results unless the effect of these changes is considered.

For a few sampling stations, records of daily determinations of specific conductance exist that span more than 40 years. Specific conductance was not determined routinely in Geological Survey analyses before about

1935. The daily conductivity records prior to about 1970 mostly were not published, but were stored in Geological Survey district office files. Prior to 1935, chemical analyses of composites of about 10 daily samples constitute most of the published records. Virtually no determinations were made on the daily samples before compositing. The composites generally were made by combining equal volumes of the daily samples. If flow rate and solute concentration in the stream vary substantially, this method of compositing introduces a bias and can cause errors in attempts to correlate water composition with stream discharge. Composites weighted by discharge were used for some stations beginning about 1946. This practice became more common later but was never used for all sampling points.

During the 1970's the practice of compositing daily samples before analysis was almost completely abandoned in favor of making complete analyses of single samples collected less frequently. Rigorous comparison of newer and older records entails going back to daily measurement records and extending or coordinating data from the differing types of analytical records. Although some studies of this kind have been made, it appears likely that the uncertainty in computed data will result in an exces-
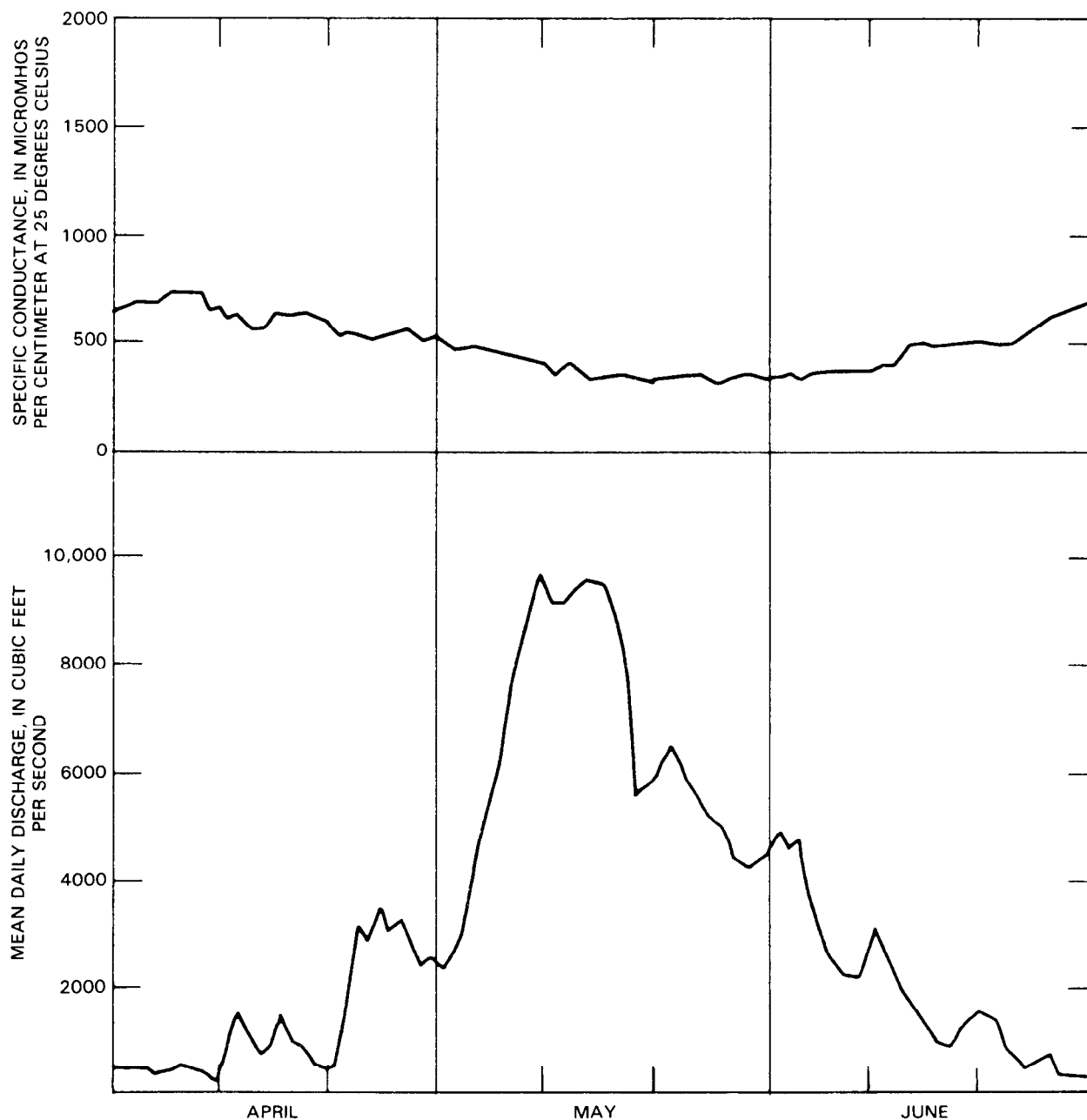

Figure 3. Conductance of daily samples and mean daily discharge of Rio Grande at San Acacia, N.Mex., 1945.

sively large noise-to-signal ratio that may mask the more subtle long-term changes in water composition.

Lake and Reservoir Sampling

Water stored in lakes and reservoirs commonly is not uniformly mixed. Thermal stratification and associated changes in water composition are among the most frequently observed effects. Single samples from lakes or reservoirs can be assumed to represent only the spot within the water body from which they come.

The effect of stratification on water composition is noticeable in concentrations of ions whose behavior is influenced by oxidation and reduction, the reduced species commonly increasing in concentration with depth below the surface and assuming particulate form in oxidizing shallower water. The components that are used by life forms in the water also are often considerably affected.
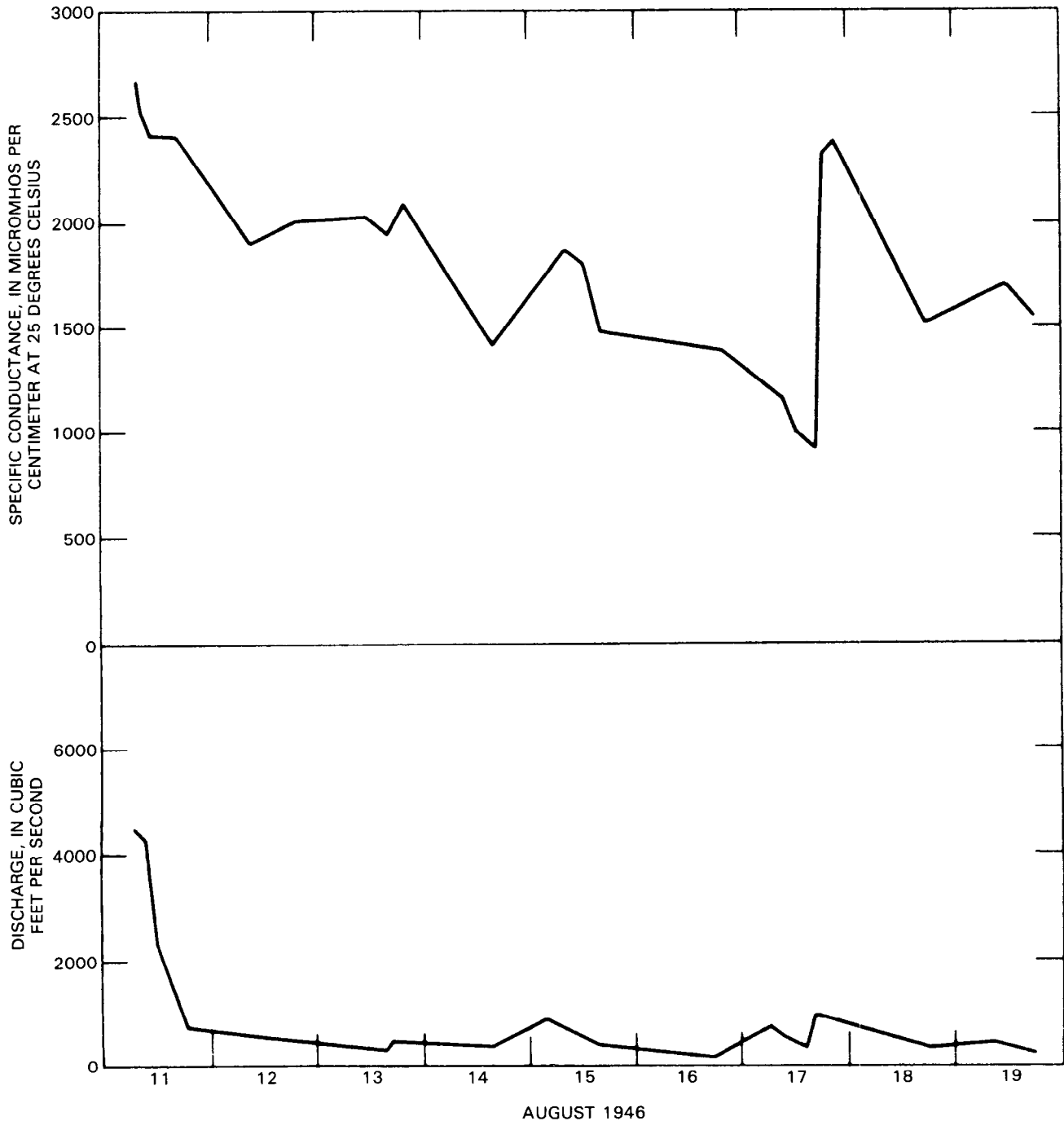

Figure 4. Conductance and discharge at times of sampling of Rio Grande at San Acacia, N.Mex., under typical summer-flow conditions.

A detailed study of these effects in water of a lake in the English Lake District was made by Sholkovitz and Copland (1982). The mechanics of stratification in lakes have been studied by many limnologists and will not be reviewed further here.

Many reservoir outlets are located in positions where they may intercept water that is depleted in dissolved oxygen. From a practical point of view, the water user is interested only in the composition of water available at the outlet, and most samples from storage reservoirs for which analyses are available come from released water.

Ground-Water Sampling

Most of the physical factors that promote mixing in surface waters are absent or are much less effective in ground-water systems. Even in thick sand of uniform permeability, the movement of water in the zone of saturation is slow and mixing is poor. In most sediments, the horizontal permeability is greater than the vertical permeability. This inhibits vertical movement of water, and water in a particular stratum may develop chemical characteristics that are substantially different from water in strata above or below.

Means of studying differing composition of water in different parts of the saturated zone are not entirely adequate. Wells commonly obtain water from a considerable thickness of saturated material and from several different strata. These components are mixed by the turbulent flow of water in the well before they reach the surface of the land and become available for sampling. Springs may obtain water from a lesser thickness of saturated material, but often the exact source is difficult to ascertain. Most techniques for detailed well sampling and exploration are usable only in unfinished or nonoperating wells. Usually, the only means of evaluating the quality of water tapped by a well is an analysis of a pumped sample. The limitations of a preexisting well as a sampling device are obvious but unavoidable. Observation wells specifically designed and installed for obtaining water-quality information may be necessary to avoid some of these problems.

Mixing of water from different strata in a well, and in some instances exposure of the water to the atmosphere, may bring about chemical instability, even though the original water in place was in equilibrium with its surroundings. This chemical instability may cause changes in certain constituents and requires sample preservation or onsite determination. This subject has been discussed by Wood (1976).

The differences in water quality with depth below the surface, and associated differences in lithology, are shown for three wells in the western part of Pinal County, Ariz., in figure 5. Water samples were obtained at several depths in each well during periods when the pumps were

not operating; the specific conductance of each sample is indicated on the diagram opposite the depth at which the sample was obtained. Kister and Hardt (1966), in whose publication the illustration first appeared, reported a range in specific conductance in one well from 1,480 μmho/cm at a depth of 300 ft. below land surface to 29,400 μmho/cm at 550 ft. Water pumped from the well had a specific conductance of 5,960 μmho/cm. As Kister and Hardt pointed out (p. 10), "Chemical analyses of water samples collected from the discharge pipe of a pumping well are not necessarily indicative of the quality of water throughout the sequence of sediments penetrated by the well."

Although the range of conductance is unusually great, the data show how water yielded by a well could change in quality in response to changes in pumping rate or regional drawdown of the water table. Many wells are influenced to some degree by water-quality stratification, and the interpretation of ground-water analyses must always consider the possibility of such effects. Electric logs may provide useful indications of the location of water of poor quality in the saturated material penetrated by wells.

Although one rarely can be certain that a sample from a well represents exactly the composition of all the water in the vertical section at that point, it is usually a useful indication of the average composition of available water at that point. Where a considerable number of wells reaching the same aquifer are available for sampling and show similar composition, the investigator usually is justified in assuming homogeneity in drawing some conclusions about the chemistry of the ground water in the aquifer. If a well penetrates a large, relatively homogeneous aquifer, the composition of the pumped water generally will not change much over long periods of time. Areal variations in ground-water quality are evaluated by sampling wells distributed over the study area as appropriate to the amount of detail that is desired.

Because rates of movement and mixing in ground-water systems are generally very slow, changes in composition of the water yielded by a well or spring with respect to time can usually be monitored by annual or seasonal sampling. Exceptions may occur in aquifers having large open channels (as in cavernous limestone) or where there is recharge or contamination near the well. Some fluctuations in composition may be artifacts related to well-construction defects, casing failure or leakage, that permit entry of small amounts of water of poor quality.

Some examples of month-to-month changes in very shallow ground water in the alluvium of the Gila River in Safford Valley, Ariz. (Hem, 1950, p. 15), are shown in figure 6. These fluctuations are more rapid than those usually observed in wells of greater depth, and because many factors such as changes in river discharge, rainfall,

irrigation pumping, and return flow may influence the water composition, no well-defined pattern of quality fluctuation can be discerned.

A long-term trend in ground-water composition is shown in figure 7. The two wells indicated in the graph were used for irrigation in the Welton-Mohawk area along the Gila River in southwestern Arizona (Babcock and others, 1947) before Colorado River water was brought into this area in the 1950's. The dissolved solids increased greatly over the period of record.

Completeness of Sample Coverage

In areas where hydrologic studies are being made, a decision is needed as to how many samples or other water-quality observations are required. Aside from administrative limitations in funds and personnel, this decision should be based on the conditions in the area to be studied. Factors to be weighed include the amount of information of this type already available, the hydrologic complexity of the area, the extent to which water of inferior quality is known or thought likely to be present, and other similar considerations. The aim of many water-quality investigations is to evaluate the resource as thoroughly as possible, and this usually requires many samples and field observations. The amount of laboratory work per sample often can be decreased if, by means of field determinations and laboratory determinations of certain key constituents, it can be shown that many of the

samples have similar composition. The experienced water chemist thus can determine the water quality of an area by the most efficient combination of complete and partial chemical analyses. The water chemist's place on the team of any hydrologic investigation is important beyond the actual performance of analytical determinations.

Analysis 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 State, Federal, and local governments, academic and research institutions, and private enterprise. The methods used in water analysis are fairly well standardized and will not be discussed here. There are certain procedures for field testing and exploration, however, that should be commented on.

Field Testing of Water

Examination of water in the field is an important part of hydrologic studies. Certain properties of water, especially its pH, are so closely related to the environment of the water that they are likely to be altered by sampling and storage, and a meaningful value can be obtained only in the field. Other properties of water, its specific conductance, for example, are easily determined in the field with simple equipment, and the results are useful in
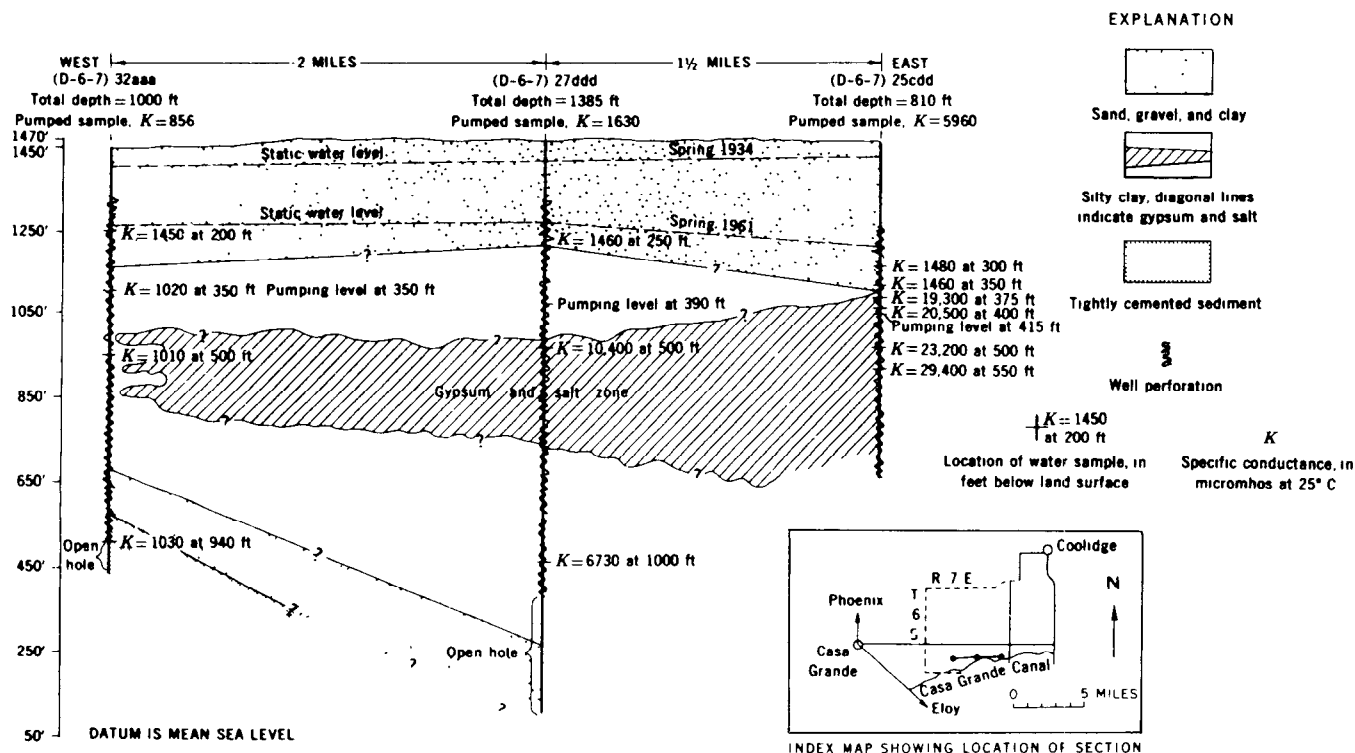

Figure 5. Changes in conductance of ground water, Pinal County, Ariz. Modified from Kister and Hardt (1966).
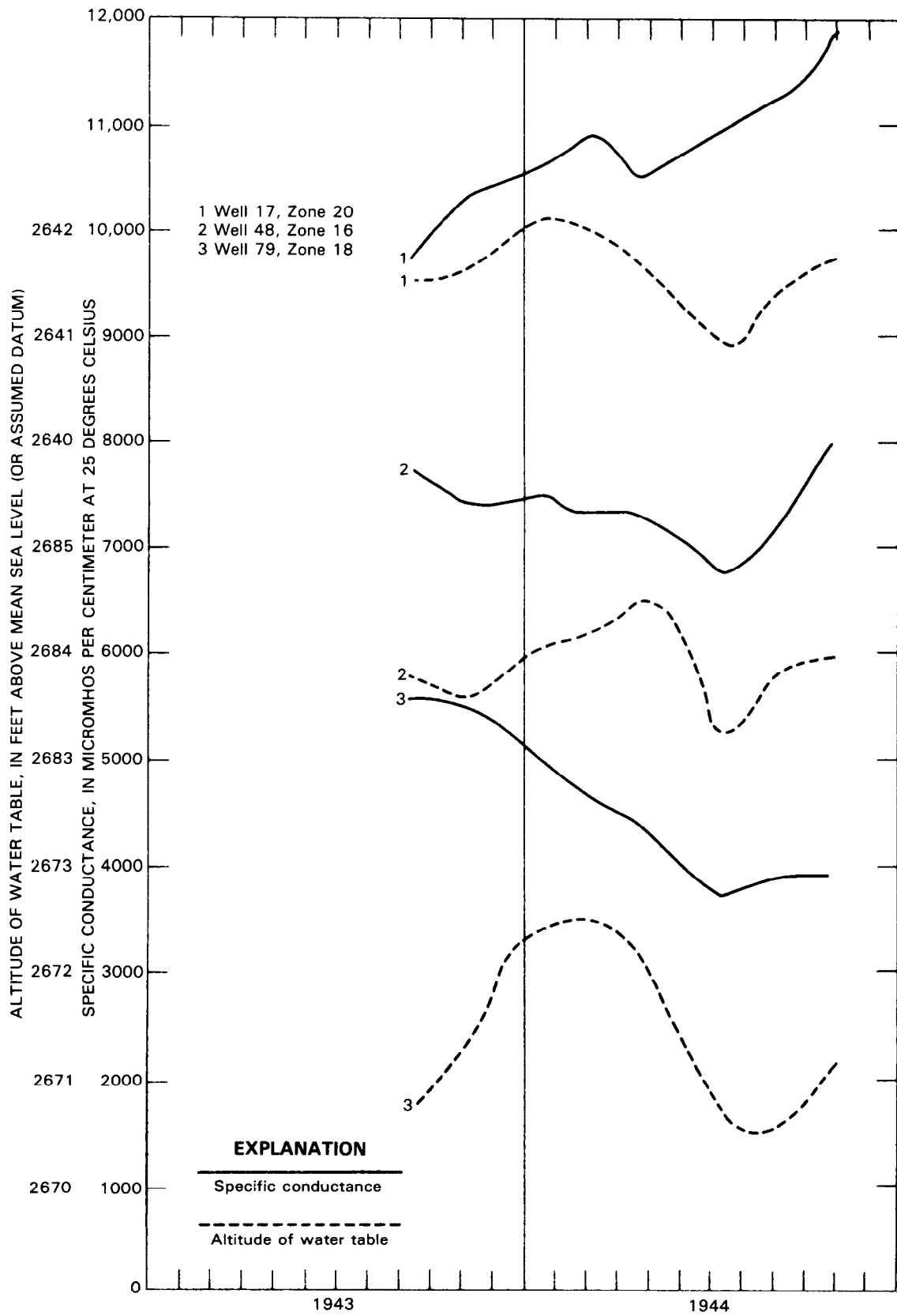
Figure 6. Specific conductance and altitude of water table for three typical observation wells, Safford Valley, Ariz. (Hem, 1950, p. 15).

supplementing information obtained from analyses of samples and as a guide to which sources should be sampled for more intensive study. Commercial equipment is available or can be adapted to field use, ranging from pocket-sized testing kits to trailer- or bus-mounted mobile laboratories. In the more elaborate units, almost any kind of standard analysis can be made.

The early history of field testing shows that its importance was recognized as long ago as the early 1900's, but equipment available then generally was rather crude. As early as 1896, a portable Wheatstone bridge for measuring the conductivity of water and saturated soil was being used by the U.S. Department of Agriculture (Scofield, 1932). The equipment for measuring water conductivity in the field has evolved into fairly sophisticated models that yield digital readings of temperature and specific conductance of samples. The units are battery powered, light, and easy to carry and give results nearly as accurate as those obtained in the usual laboratory installation. Sensing cells also can be incorporated in well-exploration equipment. Specific-conductance measurements and their meaning are discussed under that heading in a later section of this book.

A rapidly expanding application has been the continuous measurement of conductivity or other characteristics of river water with equipment installed at the sampling site. These units can be made to record results in a form that can be fed directly into an electronic computer. Power for operating the installation usually is best obtained from a 115-volt alternating-current line.

Any determination that can be made by potentiometric methods can easily be accomplished in the field or can be built into an onsite sensor. The pH of a water, for example, generally is determined by means of a sensitive electrometer and suitable reference and glass electrodes. For most ground water, the pH needs to be determined immediately after the water issues from the well or spring, if the value is to represent conditions within the system in which the water occurs (Barnes, 1964). Electrode systems for determining dissolved oxygen and many individual ions also are available.

Although almost any property or component of natural water can now be determined at a streambank location and probably could be automated if necessary, the cost of the most elaborate installations is high, and a real need must exist as justification.

Geophysical Indicators of Ground-Water Quality

One of the most widely used means of geophysical exploration of subsurface conditions is electric logging of boreholes. One of the principal determinations made as part of the logging procedure is the resistance to passage of an electric current through the formations penetrated by the borehole. One form of resistivity logging uses a pair of electrodes which are spaced a specific distance apart and held against the side of the uncased hole. As the electrodes are moved up or down the hole, the electrical resistance observed between them changes in response to environmental changes. A recording device traces the resistance on a chart as the probe moves in or out of the hole. The result is a curve showing resistance plotted against depth below the surface.

The resistance of water-bearing material in place is a function of the resistance of the rock itself, the resistance of the interstitial water, and the length of the path through which current passes in the water contained in the interconnected openings in the rock. Resistance of most dry rocks is high, and, in effect, the resistance measured by electric loggers is controlled by the water conductivity
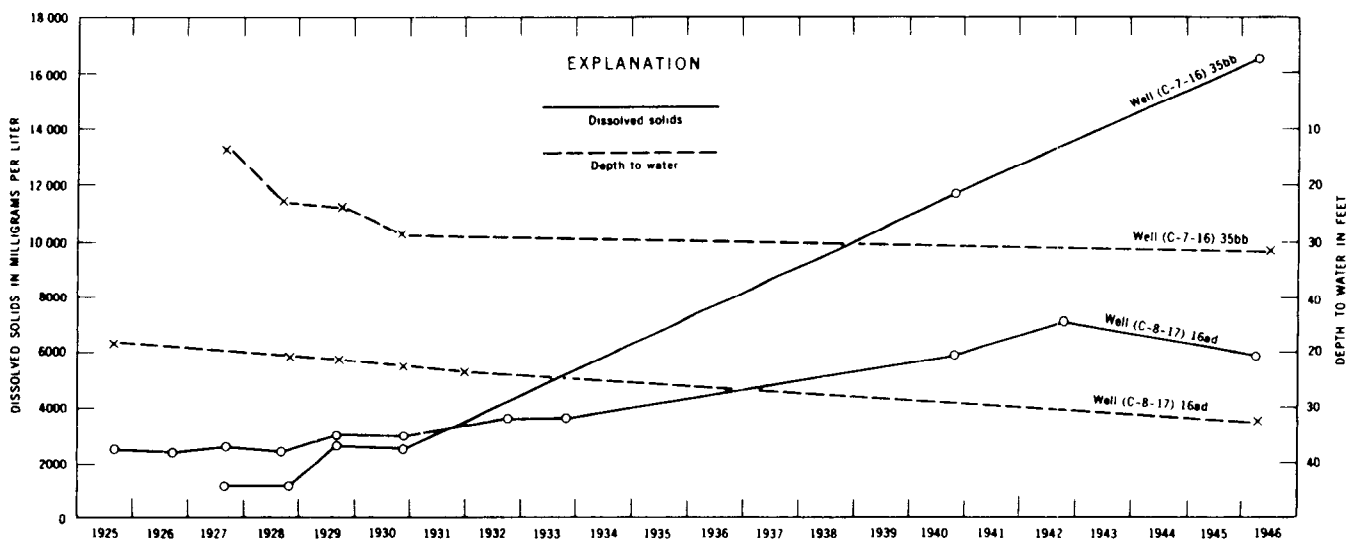

Figure 7. Dissolved solids and depth to water in two irrigation wells, Welton-Mohawk area, Yuma County, Ariz

and the length of the current path. The resistance is expressed as resistivity (the reciprocal of conductivity), usually in ohms per meter per square meter. Values for resistivity of aquifers obtained through electric logging thus are closely related to conductivity of the water and porosity of the rocks. The principal use of electric logs in the water-well industry has been as an aid in determining the physical properties of water-bearing formations and in correlating formations from well to well. Applications of logging equipment in hydrology were described by Patten and Bennett (1963) and by Keys and MacCary (1971).

If the conductivity of the water is considered the unknown, and if the other features of the aquifer that influence the observed resistivity can be evaluated on the basis of laboratory tests of drill cuttings from the formation or on the basis of previous experience with the same aquifer, the resistivity log provides an indication of water quality in place underground.

To determine water conductivity reliably from a resistivity log, the aquifer properties must be well known. Some investigators have used resistivity logs to compute approximate chemical analyses for water; however, this may be done satisfactorily only when water from the formation in question is known to display a well-defined relationship between conductivity and each of the constituents for which the computation is made. Jones and Buford (1951) described such computations for ground waters in Louisiana.

Another property generally determined in electric logging is the spontaneous potential that can be observed between an electrode and the land surface when no current is introduced. This potential is partly related to electrochemical effects such as selective movement of ions and water through clays acting as semipermeable membranes, and to electrical potentials that occur at interfaces between solutions of dissimilar composition.

Some work has been done in relating the observed potentials more specifically to the water-bearing materials and the composition of the water, but more would seem to be justified, because this technique, when carefully refined, might give considerable insight into electrochemical relationships in ground-water systems that may influence both water quality and movement. Resistivity measurements can also be made at the land surface and may indicate something about the composition of ground water near the surface. Techniques of surface geophysical exploration for water resources studies were described by Zohdy and others (1974).

Laboratory Procedures

The procedures considered to be sufficiently accurate and most acceptable for general use in water analysis in the United States have been described in several publications. The most widely known of these is "Standard Methods for the Examination of Water and Wastewater" (American Public Health Association and others, 1980, 1985). It is revised every few years by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation; and the 1980 volume is the 15th edition. A 16th edition was published in 1985. Other compilations widely used are those of the American Society for Testing and Materials (1978), the Association of Official Analytical Chemists (1980), and the U.S. Salinity Laboratory staff (1954). The U.S. Geological Survey compilation by Skougstad and others (1979) is also well known. A review of perodical literature on water analysis is published every 2 years in the journal *Analytical Chemistry*. The large volume of current literature in this field is indicated by the 665 articles referenced for the 2-year period October 1980 through September 1982 (Fishman and others, 1983). Automation and new instrumental methods have strongly influenced laboratory practice in the analysis of natural water in recent years.

Expression of Water Analyses

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

Hypothetical Combinations

Water analyses published before 1900 generally were expressed in terms of concentrations of combined salts, such as sodium chloride or calcium sulfate. This kind of terminology probably was used in part as an attempt to describe the residue obtained when the water was evaporated, but it also predated the concept of dissociated ions in solution introduced in the late 19th century by Arrhenius.

Although water chemists often use terms such as "calcium bicarbonate water" to describe a solution in which Ca^{2+} and HCO_3^- are the principal ionic species, they recognize this as a form of shorthand or abbreviation for the much more clumsy expression "a water in which calcium and bicarbonate are the predominant cation and anion, respectively."

Ionic Statement

Many organic compounds and some inorganic compounds exist in solution in water as uncharged molecules, but most inorganic solids dissociate when they go into solution in water. The closely knit structure of the solid is broken into positively charged cations and negatively charged anions that are separated by solvent molecules. On a macro scale, the positive and negative charges must be in balance.

Because the water analysis is intended to reflect the true composition of the solution, most of the reported concentrations are in terms of actual cations and anions that are present. There are some important exceptions, however. Elements such as nitrogen or boron that may occur in several different forms, or whose actual form in solution is unknown, may be reported in terms of the total concentration of the element. The very abundant element silicon is generally present in water as undissociated silicic acid but is conventionally reported in terms of the oxide, SiO_2. For some purposes, a considerably more detailed breakdown of constituents than is usually furnished is necessary to show which solute species are actually present.

Determinations Included in Analyses

With the sophisticated equipment and analytical methods now available, the analysis of a water sample could include most of the elements in the periodic table, as well as a considerable suite of naturally or artificially produced isotopes of these elements and a great many specific organic compounds. The principal interest of the analyst and the great preponderance of data, however, traditionally have been directed at major constituents that make up nearly all the dissolved inorganic material. Concern with minor constituents has increased greatly in recent times owing to their possible effects on human health and on animal and plant nutrition and toxicity, or effects related to other kinds of water use.

For the purposes of this discussion, major constituents are defined as those commonly present in concentrations exceeding 1.0 mg/L. The dissolved cations that constitute a major part of the dissolved-solids content generally are calcium, magnesium, sodium, and potassium; the major anions are sulfate, chloride, fluoride, nitrate, and those contributing to alkalinity, most generally assumed to be bicarbonate and carbonate. The silicon present usually is nonionic and is reported in terms of an equivalent concentration of the oxide, silica (SiO_2).

Some other dissolved constituents are included in many chemical analyses because they may be particularly significant in considering suitability of water for certain purposes. Sometimes these constituents attain concentrations comparable to those of major components. They include aluminum, boron, hydrogen ion or acidity, iron, manganese, phosphate, organic carbon, forms of nitrogen other than nitrate, and dissolved gases, especially carbon dioxide, oxygen, and hydrogen sulfide.

Minor constituents in addition to the ones listed above, whose occurrence in fresh natural water has been investigated to a significant extent, include the alkali metals lithium, rubidium, and cesium, the alkaline-earth metals beryllium, strontium, and barium, the metallic elements titanium, vanadium, chromium, molybdenum,

cobalt, nickel, copper, silver, zinc, cadmium, mercury, and lead, the nonmetals arsenic, antimony, selenium, bromine, and iodine, and the naturally radioactive elements uranium, radium, radon, and thorium. Each of these is separately discussed in a later section of this book.

Increasing concern over the presence of undesirable wastes or waste-alteration products and residues has produced a growing body of data on specific organic compounds, both natural and manmade, in water and on manmade radioactive elements and nuclides.

Certain properties of water solutions besides the contents of specific ions have commonly been included in water analyses. Hardness in water is commonly expressed in terms of an equivalent quantity of calcium carbonate. Other properties often included in a water analysis are color, specific conductance, dissolved solids, specific gravity, suspended matter, turbidity, biochemical or chemical oxygen demand, sodium-adsorption ratio, and various forms of radioactivity. These constituents and properties will be discussed in more detail as appropriate in following sections of this book

Units Used in Reporting Analyses

Over the years, a wide variety of units have been used in reporting water analyses. Considerable progress has been made toward standardization of these units, but using the data available in published literature often requires a general understanding of the units and systems used in the past and how they compare with more modern units. The two most common types of concentration units are those that report weights of solute per weight of solution and those that report weights of solute per unit volume of solution.

Weight-Per-Weight Units

A concentration reported in weight-per-weight is a dimensionless ratio and is independent of the system of weights and measures used in determining it. For many years, the water analyses made by U.S. Geological Survey and many other laboratories in the United States were reported in "parts per million." One part per million is equivalent to one milligram of solute per kilogram of solution. One percent, of course, is one part per hundred, or ten thousand parts per million.

"Parts per thousand" sometimes is used in reporting the composition of seawater. In this connection, "chlorinity" and "salinity" have been defined in terms of parts per thousand (grams per kilogram) for use in studies of seawater composition (Rankama and Sahama, 1950, p. 287).

At one time the unit "parts per hundred thousand" was in common use. "Parts per billion" or "parts per trillion" is sometimes used in reporting trace constituents.

Because water is a liquid, definite quantities for analysis are ordinarily measured in the laboratory by means of volumetric glassware. The laboratory results, therefore, are in terms of weights of solute per unit volume of water. These results must be converted to a weight basis to obtain parts-per-million values. The conversion usually is done by assuming that a liter of water weighs exactly 1 kilogram and, hence, that milligrams per liter and parts per million are equivalent. This assumption is strictly true only for pure water at 3.89°C. The presence of dissolved mineral matter tends to increase the density, and at higher temperatures the density decreases. For practical purposes, however, the error introduced by assuming unit density does not reach a magnitude comparable to other anticipated analytical errors until the concentration of dissolved solids exceeds about 7,000 milligrams per liter. For highly mineralized waters, a density correction should be used when computing parts per million from milligrams per liter. Volumetric glassware is calibrated for use at 20°C, and ordinary laboratory temperatures are usually close to this value. Concentrations expressed in milligrams per liter are strictly applicable only at the temperatures at which the determination was made, but for most purposes for which the concentration values might be used, the effect of volume change caused by temperature changes of the solution is not important.

The reporting of dissolved constituents in milligrams (or micrograms) per liter has become standard practice in water analysis throughout the world. This avoids calculated density corrections.

Where the English or U.S. customary system of units is used, analyses are sometimes expressed in grains per gallon. The particular gallon that is meant must be specified, as the U.S. gallon and the Imperial, or British, gallon are not the same. The unit is still seen fairly frequently in connection with hardness in water. Reports dealing with irrigation water commonly express concentrations in tons per acrefoot. The ton is 2,000 pounds, and an acre-foot is the amount of water needed to cover 1 acre to a depth of 1 foot.

Streamflow or discharge represents a rate quantity. Rate concepts may be significant in some studies of river-water composition, and the dissolved-solids load, a rate quantity, is generally expressed in tons per day.

Conversion factors that indicate the relationships of the various units to each other are given in table 8. Factors changing grains per gallon or tons per acre-foot to parts per million, or the reverse, would be the same as those shown for conversions to or from milligrams per liter, if it is valid to assume unit density of the water. For highly mineralized water, these factors must take into account the density of the water. Hardness values are

sometimes expressed in degrees. Conversion factors for these units, which differ in different countries, are given in the discussion of hardness in water elsewhere in this book.

Equivalent-Weight Units

For manipulations that involve the chemical behavior of dissolved material, the chemist must express analytical results in units that recognize that ions of different species have different weights and different electrical

Table 8. Conversion factors for quality-of-water data

[U.S. gallon is used for all units involving gallons]

To convert—	To—	Multiply by—
Calories	Joules	4.184
Grains per gallon	Milligrams per liter	17.12
Milligrams per liter	Grains per gallon	.05841
Milligrams per liter	Tons per acre-foot	.001360
Milligrams per liter	Tons per day	second-feet×
		0.002697
Tons (U.S. short)	Tons (metric)	.9072
Acres	Hectares	.4047
Miles	Kilometers	.6214
Tons per acre	Metric tons per	
	hectare	2.2417
Parts per hundred		
thousand	Parts per million	10
Grams	Ounces (avoirdupois)	.03527
Ounces (avoirdupois)	Grams	28.35
Gallons (Imperial)	Gallons (U.S.)	1.2009
Liters	Quarts (U.S.)	1.057
Quarts (U.S.)	Liters	.9463
Second-foot days[a]	Acre-feet	1.983471
Second-feet[b]	Gallons per minute	448.8
Second-foot days	Gallons per day	646,317
Gallons per minute	Liters per second	.06309
Acre-feet[c]	Gallons	325,851
Acre-feet	Cubic feet	43,560
Acre-feet	Cubic meters	1,233.5
Cubic feet	Cubic meters	.028317
Cubic feet	Gallons	7.481
Ca^{2+}	$CaCO_3$	2.497
$CaCl_2$	$CaCO_3$	.9018
HCO_3^-	$CaCO_3$	.8202
[d]HCO_3^-	CO_3^{2-}	.4917
Mg^{2+}	$CaCO_3$	4.116
Na_2CO_3	$CaCO_3$	.9442
NO_3^-	N	.2259
N	NO_3^-	4.4266

[a] 1 s-ft/d=1 cfs for 24 h.
[b] 1 s-ft=1 cfs.
[c] 1 acre-ft=an area of 1 acre 1 ft deep.
[d] In the reaction $2HCO_3^-=CO_3^{2-}+H_2O+CO_2(g)$ (for computing total dissolved solids).

charges. For example, in the mass-law calculations discussed earlier, concentrations of ions and other dissolved species are given in moles per liter. A mole of a substance is its atomic or molecular weight in grams. A solution having a concentration of 1 mole per liter is a molar solution; thus, the molarity of a solution is its concentration in a weight per volume unit. A molal solution is one that contains 1 mole of solute per 1,000 grams of solvent. For dilute solutions up to about 0.01 molar, these two units are equal, within ordinary experimental error.

Concentrations in milligrams per liter are readily converted to moles per liter by dividing by the atomic or formula weight of the constituent, in milligrams. When parts-per-million values are treated in this way, the concentration unit obtained is usually called "formality," the number of formula weights per 1,000 grams of solution.

The concept of chemical equivalence can be introduced by taking into account the ionic charge. If the formula weight of the ion is divided by the charge, the result is termed the "combining weight" or "equivalent weight." When a concentration value in milligrams per liter is divided by the combining weight of that species, the result is an equivalent concentration that is useful for many purposes. Table 9 contains reciprocals of combining weights of cations and anions generally reported in water analyses. Milligrams-per-liter values may be converted to milliequivalents per liter by multiplying the milligrams per liter by the reciprocals of the combining weights of the appropriate ions.

The term "equivalents per million," which is used for the value obtained when parts per million is used instead of milligrams per liter as a starting point, is a contraction that has been generally adopted for the sake of convenience. In more exact language, the unit is "milligram-equivalents per kilogram" if derived from parts per million and "milligram-equivalents per liter" if derived from milligrams per liter. The term "milligram equivalents" is shortened by chemists to "milliequivalents," abbreviated "meq."

In an analysis expressed in milliequivalents per liter, unit concentrations of all ions are chemically equivalent. This means that if all ions have been correctly determined, the total milliequivalents per liter of cations is equal to the total milliequivalents per liter of anions. The relation of water composition to solid-mineral composition is made more clearly evident when the analysis is expressed in milliequivalents per liter. There are disadvantages to using these units, however, in that they require knowledge or assumptions about the exact form and charge of dissolved species. Laboratory determinations do not always provide this kind of information. For a species whose charge is zero, as for silica, an equivalent weight cannot be computed. A concentration of such species in moles or millimoles per liter is generally equally useful, however.

Table 9. Conversion factors: milligrams per liter$\times F_1$=milliequivalents per liter; milligrams per liter$\times F_2$=millimoles per liter (based on 1975 atomic weights, referred to carbon-12)

Element and reported species	F_1	F_2
Aluminum (Al^{3+})	0.11119	0.03715
Ammonium (NH_4^+)	.05544	.05544
Antimony (Sb)		.00821
Arsenic (As)		.01334
Barium (Ba^{2+})	.01456	.00728
Beryllium (Be^{2+})	.22192	.11096
Bicarbonate (HCO_3^-)	.01639	.01639
Boron (B)		.09250
Bromide (Br^-)	.01252	.01252
Cadmium (Cd^{2+})	.01779	.00890
Calcium (Ca^{2+})	.04990	.02495
Carbonate (CO_3^{2-})	.03333	.01666
Cesium (Cs^+)	.00752	.00752
Chloride (Cl^-)	.02821	.02821
Chromium (Cr)		.01923
Cobalt (Co^{2+})	.03394	.01697
Copper (Cu^{2+})	.03147	.01574
Fluoride (F^-)	.05264	.05264
Hydrogen (H^+)	.99216	.99216
Hydroxide (OH^-)	.05880	.05880
Iodide (I^-)	.00788	.00788
Iron (Fe^{2+})	.03581	.01791
Iron (Fe^{3+})	.05372	.01791
Lead (Pb^{2+})	.00965	.00483
Lithium (Li^+)	.14407	.14407
Magnesium (Mg^{2+})	.08229	.04114
Manganese (Mn^{2+})	.03640	.01820
Mercury (Hg)		.00499
Molybdenum (Mo)		.01042
Nickel (Ni)		.01704
Nitrate (NO_3^-)	.01613	.01613
Nitrite (NO_2^-)	.02174	.02174
Phosphate (PO_4^{3-})	.03159	.01053
Phosphate (HPO_4^{2-})	.02084	.01042
Phosphate ($H_2PO_4^-$)	.01031	.01031
Potassium (K^+)	.02558	.02558
Rubidium (Rb^+)	.01170	.01170
Selenium (Se)		.01266
Silica (SiO_2)		.01664
Silver (Ag^+)	.00927	.00927
Sodium (Na^+)	.04350	.04350
Strontium (Sr^{2+})	.02283	.01141
Sulfate (SO_4^{2-})	.02082	.01041
Sulfide (S^{2-})	.06238	.03119
Thorium (Th)		.00431
Titanium (Ti)		.02088
Uranium (U)		.00420
Vanadium (V)		.01963
Zinc (Zn^{2+})	.03059	.01530

Composition of Anhydrous Residue

The means of expressing analytical results discussed to this point all use concentrations of solutes. These concentration values are generally the deciding factors in the evaluation of water quality. Some geochemists, however, have preferred to express analytical data for water in terms they believed were more directly comparable to rock-composition data. To this end, they expressed analyses in terms of the percentage of each element or ion in the anhydrous residue remaining after evaporating the water. Clarke (1924a, b) used this reporting procedure, usually with a value for dissolved-solids concentration and percentages of the components which he termed "percentage composition of anhydrous residue."

The supposed advantage of this method of expressing analyses is that it may demonstrate similarities among waters that have similar geochemical origins but whose analyses might appear dissimilar because of dilution effects. For example, the composition of water from a river usually will appear to change a great deal as a result of increases or decreases in flow rate when one examines water analyses expressed in concentrations. When the data are recalculated to percentage composition of dry residue, at least part of the fluctuation in composition disappears.

Although for some geochemical considerations the calculation of percentage composition of residue is useful, this is not a good way of expressing the chemical composition of a solution, and since Clarke's time it has gradually disappeared from the literature.

Instead of computing percentage composition from actual weights of constituents, some investigators have computed percentages based on total anions or cations, in equivalents per million. The first extensive use of this kind of computation was by Chase Palmer (1911), and a related procedure has been adapted extensively in more recent times in certain graphical methods of study of water quality. These methods will be considered later in this book.

Concentration in Terms of Calcium Carbonate

The hardness of water is conventionally expressed in water analyses made in the United States in terms of an equivalent quantity of calcium carbonate. Some such convention is needed for hardness because it is a property imparted by several different cations, which may be present in varying proportions. However, the actual presence of the indicated number of milligrams per liter of calcium and carbonate ions certainly should not be assumed.

Another convention that is followed by many water-analysis laboratories is to express the results of the

alkalinity titration in terms of an equivalent amount of calcium carbonate. Although the titrated alkalinity is sometimes not exactly assignable to one or more specific ionic species, the latter assignment gives a much clearer indication of the composition of the solution. In any event, alkalinity (to methyl-orange end point) expressed as milligrams per liter of $CaCO_3$ can be converted to an equivalent concentration of HCO_3^- in milligrams per liter by dividing the former by 0.8202. (See table 8.)

The formula weight of $CaCO_3$ is very near 100. Thus, hardness or alkalinity values in terms of milligrams per liter of $CaCO_3$ can be converted to milliequivalents per liter of cations or anions by dividing by 50. Analyses are occasionally seen in which other constituents are reported in terms of calcium carbonate. This form of expression is a way of expressing concentrations in terms of equivalent weights. The use of milliequivalents per liter for each specific ion gives at least equally useful results.

Comparison of Units of Expression

Table 10 shows a single water analysis expressed in milligrams per liter, milliequivalents per liter, millimoles per liter, percentage composition of dry residue, percentage of total cation and anion equivalents, and grains per U.S. gallon. It is assumed that the milligrams-per-liter values are equal to parts per million and that milliequivalents per liter are equal to equivalents per million for a water of this dissolved-solids concentration.

All the numbers in table 10 were derived from the same original analytical data. It is assumed that dissolved bicarbonate would be converted to carbonate in the dry residue, with loss of an equivalent amount of carbon dioxide and water. Computations of the type used in preparing the table use conversion factors given in table 8.

## Forms of Dissolved Material—Complexes, Ion Pairs, and Polymers

Organic compounds and some inorganic substances occur in aqueous solution as uncharged molecules. Most inorganic compounds, however, dissociate into charged ions when they dissolve in water. Positively charged units are cations and negatively charged units are anions. There must be an overall balance between cations and anions in solution to maintain electrical neutrality. However, there are some interactions among ionic species that result in association of oppositely charged ions to form complex ions. Some examples have already been cited, and many more will be considered later in this book.

Chemical analyses of water generally report the total quantity of a particular element or ion without indicating its actual form in solution. For use in chemical thermodynamic calculations, the concentrations of participating reactants or products must be identified as specific solute species.

Complex ions are solute species made up from two or more single ions of opposite charge. For example, ferric iron in solution may hydrolyze to form a hydroxide complex:

$$Fe^{3+}+H_2O \rightleftharpoons FeOH^{2+}+H^+.$$
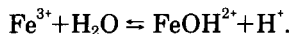
The Fe^{3+} and OH^- in this unit are chemically bound to each other. If the concentration of ferric iron is high enough, the formation of complex species may also involve association of monomeric units to give dimers

$$2FeOH^{2+} \rightarrow [Fe(OH)_2Fe]^{4+},$$
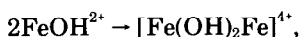
and hydrolysis and polymerization may continue, giving a final product approaching the composition $Fe(OH)_3^0$ that contains many individual Fe^{3+} and OH^- ions linked together.

A special type of complex, here called an ion-pair, is an association of equally charged units to form a neutral species:

$$Ca^{2+}+SO_4^{2-} \rightleftharpoons CaSO_4(aq).$$
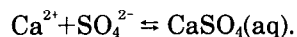
In this complex, the Ca^{2+} and SO_4^{2-} components are believed to be separated by one or more layers of intervening water molecules. Some authors have used the term "ion pair" in a less rigorous context.

"Polynuclear" complexes are defined by Baes and Mesmer (1976, p. 2) as complexes containing more than one cation. This is a broader definition than the one implied above for polymeric species. The term "polynuclear" will not be used in this book.

SIGNIFICANCE OF PROPERTIES AND CONSTITUENTS REPORTED IN WATER ANALYSES

The properties and constituents that are determined in water analyses are discussed individually in the following sections. For most constituents, the subjects considered are the form of dissolved species, solubility and

Table 10. Chemical analysis of a water sample expressed in six ways

[Sample from flowing well, 488 ft deep. Water from the Lance Formation. NW1/4 sec 30, T. 57 N., R. 85 W., Sheridan County, Wyo. Collected August 3, 1946]

Constituent	mg/L or ppm	meq/L or epm	mM/L	Gravimetric percent	Percentage of epm	Grains per U.S. gallon
Silica (SiO₂)	7.9		0.131	0.40		0.46
Iron (Fe)	.17		.003	.01		.01
Calcium (Ca)	37	1.85	.925	1.87	6.1	2.16
Magnesium (Mg)	24	1.97	.985	1.21	6.5	1.40
Sodium (Na) } Potassium (K) }	611	26.58	26.58	30.80	87.4	35.69
Bicarbonate (HCO₃)	429	7.03	7.03	[1]10.63	23.1	25.06
Sulfate (SO₄)	1,010	21.03	10.52	50.90	69.2	59.00
Chloride (Cl)	82	2.31	2.31	4.14	7.6	4.79
Fluoride (F)	.6	.03	.032	.03	.1	.04
Nitrate (NO₃)	.0	.00	.000	.00	.0	.00
Boron (B)	.2		.019	.01		.01
Dissolved solids: Calculated	1,980	60.80	48.535	100.00	200.00	115.65
Hardness as CaCO₃: Total	191		1.91			11.16
Noncarbonate	0		.00			0
Specific conductance (micromhos at 25°C).	2,880	2,880	2,880	2,880	2,880	2,880
pH	7.3	7.3	7.3	7.3	7.3	7.3

[1]As carbonate (CO₃).