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Techniques of Water-Resources Investigations
of the United States Geological Survey

CHAPTER D2

GUIDELINES FOR COLLECTION AND FIELD ANALYSIS OF GROUND-WATER SAMPLES FOR SELECTED UNSTABLE CONSTITUENTS

By Warren W. Wood

Book 1
COLLECTION OF WATER-DATA BY DIRECT MEASUREMENT

PREFACE

The Department of the Interior has a basic responsibility for the appraisal, conservation, and efficient utilization of the Nation's natural resources, including water as a resource, as well as water involved in the use and development of other resources. As one of the several Interior agencies, the U.S. Geological Survey's primary function in relation to water is to assess its availability and utility as a national resource for all uses. The U.S. Geological Survey's responsibility for water appraisal includes not only assessments of the location, quantity, and availability of water but also determinations of water quality. Inherent in this responsibility is the need for extensive water-quality studies related to the physical, chemical, and biological adequacy of natural and developed surface- and ground-water supplies. Included, also, is the need for supporting research to increase the effectiveness of these studies.

As part of its mission the Geological Survey is responsible for a large part of water-quality data for rivers, lakes, and ground water that is used by planners, developers, water-quality managers, and pollution-control agencies. A high degree of reliability and standardization of these data is paramount.

The series of manuals on techniques describes procedures for planning and executing specialized work in water-resources investigations. The material is grouped under major subject headings called books and is further subdivided into sections and chapters. Book 1 is on the collection of water data by direct measurement. Section D is on water quality.

The unit of publication, the chapter, is limited to a narrow field of subject matter. This format permits flexibility in revision and publication as the need arises. "Guidelines for Collection and Field Analysis of Ground-water Samples for Selected Unstable Constituents" is the second chapter to be published under Section D of Book 1. The chapter number includes the letter of the section.

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GUIDELINES FOR COLLECTION AND FIELD ANALYSIS OF GROUND-WATER SAMPLES FOR SELECTED UNSTABLE CONSTITUENTS

By Warren W. Wood

Abstract

The unstable nature of many chemical and physical constituents in ground water requires special collection procedures and field analysis immediately after collection. This report describes the techniques and equipment commonly used in the collection and field analysis of samples for pH, temperature, carbonate, bicarbonate, specific conductance, Eh, and dissolved oxygen.

Introduction

Samples of ground water are obtained and analyzed to evaluate the chemical and physical quality of the water and to aid in understanding the geochemical and hydrologic relationships in an aquifer. These objectives require that the water sample represent the geochemical environment as accurately as possible.

Some properties or constituents in ground water may change dramatically within a few minutes or hours after sample collection. Immediate analysis in the field is required if dependable results for these parameters are to be obtained. Samples for other constituents may be stabilized by preservative treatment. Some examples of preservative treatment are refrigeration or the addition of toxic metals such as mercury to minimize chemical changes due to biologic activity and the addition of acid to prevent the precipitation of metal ions.

This manual is designed to provide guidelines for the collection and field analysis of common unstable constituents or properties of relatively shallow ground water and is intended to be a supplement to the manual on "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases" (Brown and others, 1970). Techniques for sampling and analyses for unusual or uncommon constituents as well as deep ground waters have been omitted from this report. The reader is referred to Presser and Barnes (1974) for techniques on collection and field analysis of ammonia and hydrogen sulfide gas.

The techniques and equipment described in this manual are derived from many workers including William Back, Ivan Barnes, H. C. Claasen, Bruce B. Hanshaw, Gerth E. Hendrickson, John D. Hem, Blair Jones, Donald Langmuir, F. J. Pearson, Jr., Jack Rawson, and Isaac Winograd. My sincere thanks goes to these and other workers from whom I have acquired information included in this manual.

The recent development of sophisticated portable field equipment has permitted a very accurate and precise analysis of water for some unstable constituents or properties at the collection site; however, all methods described in this manual are subject to revision as improved techniques and equipment are developed or become available.

The English units used in this report may be converted to metric units by the following factors:

From	Multiply by	To obtain
feet	0.3048	metres
gallons	3.785	litres
gallons per minute	.06309	litres per second
inches	25.4	millimetres
	2.54	centimetres
ounces	28.349	grams

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General criteria for sampling of ground water for geochemical studies

A working hypothesis on geochemical controls affecting the water in an aquifer is essential before collection of water samples is begun. All water analyses for the area of study, including those that are available from city, county, state, and Federal agencies, should be evaluated prior to the development of a sampling program, even though the accuracy of these analyses may be inadequate for the purposes of a particular study. Surface-water analyses, particularly of samples collected under base-flow conditions, should not be overlooked in evaluating existing chemical and physical data. Additional information on geochemical conditions can often be obtained by the extrapolation of data from known areas or regions of similar hydrologic, geologic, and climatic environments.

The working hypothesis on the chemical controls affecting the water quality of an aquifer, as developed from existing data, will aid in selecting the sites for the collection of samples; identifying the number and types of field or laboratory analyses required; and determining the methods for sample collection, treatment, and preservation. This information is required so that the applicable equipment, instruments, containers, and preservatives can be obtained and the sampling and analytical schedules can be organized.

Method of sample collection

Springs

Excellent samples for the determination of some water-quality constituents can be obtained from springs if suitable sampling precautions are taken. Small springs in unconsolidated deposits can be sampled by driving a well point or slotted pipe to a depth of 1 metre or less into the ground adjacent to the spring. The water will often flow from this type of installation. If it does not flow, a small "pitcher pump" can be used to collect the sample. Attempts to collect samples from small springs and seeps, without the use of pipes, result in almost certain contamination of the sample by soil bacteria, particulate matter, and atmospheric oxygen. It is often difficult, even when using a driven pipe, to collect a sample that does not contain dissolved oxygen. If the water contains easily oxidized metals such as iron and manganese, the dissolved-oxygen contamination may preclude the use of a small spring or seep as a satisfactory site for the collection of samples for the determination of these metals and other properties or constituents such as pH and oxidation-reduction potential. If the sample is to be used for the determination of trace metals, it is necessary to use plastic pipe and well screen that has been thoroughly cleaned, rather than iron pipe.

Large springs in consolidated rock usually are better sampling points than other types of springs. However, obtaining a representative sample of vigorously upswelling water at the orifice of a large spring may be difficult and may require a boat manned by several people. Even if the spring depression is narrow and can be waded, collection of a representative sample by forcing a bottle held by hand or attached to a rod down into the upswelling water is difficult. In either case, where the sample is collected directly in the bottle, the sample is always contaminated with oxygen.

Although thief-type samplers (fig. 1) can be used to collect unoxygenated samples, they are usually difficult to emplace in a "boiling spring." An additional problem with the use of thief samplers is that the closing messenger may not function properly in upswelling waters. Both nonmetallic and brass thief samplers are available. The nonmetallic type should be used for the collection of samples to be analyzed for trace metals.

A heavy metal pipe pushed into the mouth of a spring can be used to provide a steady flow from which the sample can be collected. Although this sampling system minimizes the potential for atmospheric contamination, experience has shown that dissolved oxygen is inevitably present in samples collected in this manner. The samples collected by use of the metal pipe may not be suitable for the analysis of trace metals or other properties affected by dissolved oxygen.

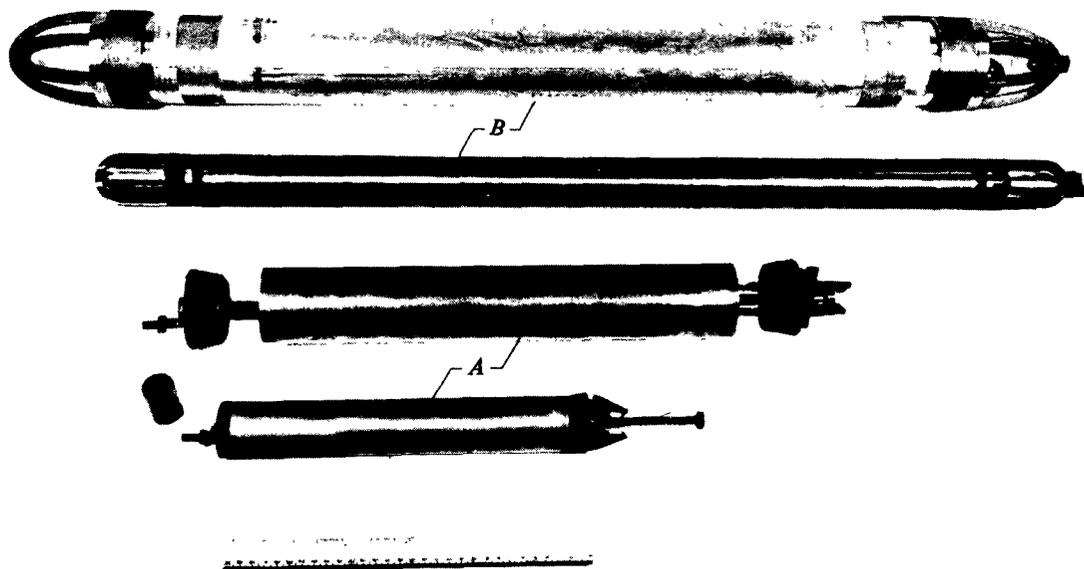An inexpensive ($20–$30) submersible-elec-

Figure 1 —Thief-type samplers. A, Foerst. B, Ball-valve

tric pump of the type sold at garden-supply stores and used for home water fountains can be a very effective sampler. These pumps, which have plastic housing, impellers, and tubing, can be used to collect samples for trace metals as well as major constituents. A suggested procedure is to secure the pump to a pole or pipe and push it into the mouth of a spring. With the delivery tube running to the shore, the pump is started and the sample collected. These pumps will deliver 10–20 litres per minute and greatly simplify the process of sampling from springs.

The main disadvantage of this pump system is that it requires an independent power supply. However, these pumps have a low power requirement, usually less than 2 amps, and can be used with a 12-volt automobile battery fitted with an inexpensive ($10–$20) inverter. The inverter, which converts 12-volt direct current to 110-volt alternating current, is connected to the battery, and the pump is plugged into the inverter. Because the cord supplied with these pumps usually is too short for most sampling, a waterproof connector and extension cord must be added. A portable gasoline-powered generator will also provide a satisfactory power supply, but it is usually more awkward to use than the automobile battery and inverter arrangement.

In spite of the limitations and sampling difficulties, sample collection from springs can be useful for many constituents if the limitations are recognized and considered prior to sampling.

Wells

The depth of the pump in a well and the water level during pumping should be known before samples are obtained. If the water level is at or near the pump intake, atmospheric oxygen may be entrained in the discharge and easily oxidized metals such as iron may precipitate prior to sampling. If water-level and pump depth information is not available, the discharge should be checked for dissolved oxygen before samples are collected. If ground water in the region being studied normally contains no oxygen, the presence of oxygen indicates contamination by the pumping process. However, in ground-water systems that contain little oxidizable material, dissolved oxygen may exist naturally. The presence of naturally dissolved oxygen may be verified by sampling other wells in the aquifer.

Multiple-screen or open-hole wells that receive water from several aquifers should be avoided in sampling for geochemical studies. Pumping from between well packers can sometimes be used to obtain samples from a particu-

lar aquifer in multiple-aquifer wells if the sample information justifies the cost involved. A driller's log that gives the construction details of the well as well as a lithologic description of the units penetrated is essential.

If any uncertainty exists as to depth of the producing aquifer or depth of the well, the total depth of the well should be measured and a flowmeter survey conducted to determine the source of the water prior to sampling. Difference in temperature of water compared to other wells in the area may represent different production depths. A flowmeter survey can also be useful in determining if multiple-aquifer flow exists in the system and can offer an explanation for chemical quality anomalies that are often observed within an apparent single-aquifer system.

To obtain a representative sample from an aquifer at a given location, a well must be pumped until the temperature, pH, and specific conductance are constant. This is the minimum required precaution for insuring that a sample adequately represents the water in the aquifer. pH is usually the last parameter to obtain a reproducible reading and, consequently, is the most sensitive test for many wells. There is no specific volume of water that constitutes a minimum pumping time. Municipal, irrigation, and industrial wells that are in nearly constant use require only a few minutes of pumping before stable conditions are observed and samples can be collected with confidence.

Standby, observation, new, and little-used wells may require a day or more of pumping before the water is of constant quality. A log of specific conductance, pH, and temperature for water pumped from these seldom used wells should be kept until these parameters stabilize. Measurement of drawdown during this stabilization period is often helpful because changes in the proportions of discharge coming from different producing zones may be reflected by new pumping levels.

The most representative water samples usually can be obtained from municipal, industrial, or irrigation wells. Because of their constant pumping and high yield, these wells draw water from a large area of the aquifer and usually insure a representative sample. In ad-

dition, other hydrologic data are usually available at these sites. Available data on approximate discharge and duration of pumping prior to sampling should be recorded for any of these wells.

Potential contamination, precipitation of solutes, and loss of dissolved gases can be minimized by collecting the sample as close to the wellhead as possible. Many domestic and other types of wells are poorly designed for sampling. The plumbing is often inaccessible, and samples can be obtained only after water has gone through a pressure tank, water softener, or iron filter. Analysis of water from these wells are of little value in geochemical studies.

Wells that do not have a suitable sampling point often can be modified so that a representative sample can be collected. However, before any modifications are performed, permission of the well owner should be obtained. Any field kit used for such modifications should include a battery-powered electric drill and bits and taps for $\frac{1}{8}$-inch and $\frac{1}{4}$-inch pipe thread. In addition, plugs, petcocks, plastic tubing, and wrenches for these pipe sizes should be included in a field kit. (See table 1 for a suggested list.) Adaptors, reducers, couplings, and nipples of all standard sizes and material are essential for utilizing existing sampling taps. Many sampling taps on industrial and municipal wells have either a garden-hose fitting or a smooth-surface faucet that requires a special adaptor.

Often the only wells for which complete hydrologic data are available are small-diameter observation wells that are not equipped with a pump. If the diameter of the well is sufficiently large, a submersible pump can be used to obtain samples. If the water level is less than 7 metres below the surface, a pitcher pump may be used for sample collecting. In using this method, however, it is difficult to prevent oxygenation.

For small-diameter wells, a hand-operated thief sampler can be used to collect samples from any depth in the wells. The quality of the water standing in an unused well generally does not reflect the quality of the water in the aquifer. Before sampling with a thief sampler, the well should be bailed until the specific con-

Table 1 —Supplies and equipment included in a field kit suitable for water sampling from a well

Two each square-head male pipe-thread plugs, ⅛, ¼, ½, and ¾ inch.
Two each reducer bushings, ¾ to ½, ½ to ¼, and ¼ to ⅛ inch, male pipe thread to female pipe thread
Two each reducer couplings, 1 to ¾, ¾ to ½, ½ to ¼, and ¼ to ⅛-inch pipe thread
Two each long nipples, male pipe thread, 1, ¾, ½, ¼, and ⅛ inch.
One each tees, ¾ and ½ inch.
One each elbows, ¾ and ½ inch.
15–50 feet of ⅜-inch plastic tubing.
15–50 feet of ¼-inch plastic tubing.
15–50 feet of ½-inch plastic garden hose with fittings.
Two each male connectors garden hose to pipe filtering.
1–6 feet of soft rubber hose, ¼-inch ID, and ⅜-inch ID.
Three each male connectors, ¼-inch tube to ⅛-inch pipe thread
⅜-inch tube to ⅛-inch pipe thread
⅜-inch tube to ¼-inch pipe thread
¼-inch tube to ¼-inch pipe thread
Two each tubing union tees, ¼ and ½-inch tubing.
Two each tubing unions, ¼ and ⅜ inch.
Two each male branch tees, ¼ and ⅜ inch.
Two each low pressure needle valves, ¼ and ⅜-inch tubing.
A tool box containing two pipe wrenches and two crescent wrenches as well as screwdriver, pliers, hacksaw, and so forth.
Several shutoff and control valves of the common tube and pipe sizes are desirable.

ductance, pH, and temperature of the water are constant. Collection of a sample by bailing and filtering a sample from a thief sampler without introducing dissolved oxygen is nearly impossible.

For some wells, it may be advantageous to use a motor-operated small-diameter unit controlled by an uphole power source and switch. Motorized units are of course more expensive than hand operated ones, and the operation is more involved because a truck with a power winch must be used to raise and lower the unit. Again, the well should be bailed until the values of pH, temperature, and specific conductance are constant.

A small-diameter hand-operated bailer may also be used to collect samples from wells. Figure 2 shows such a homemade bailer that can be made in about an hour at a cost of a few dollars. Copper tubing, stainless steel, or PVC
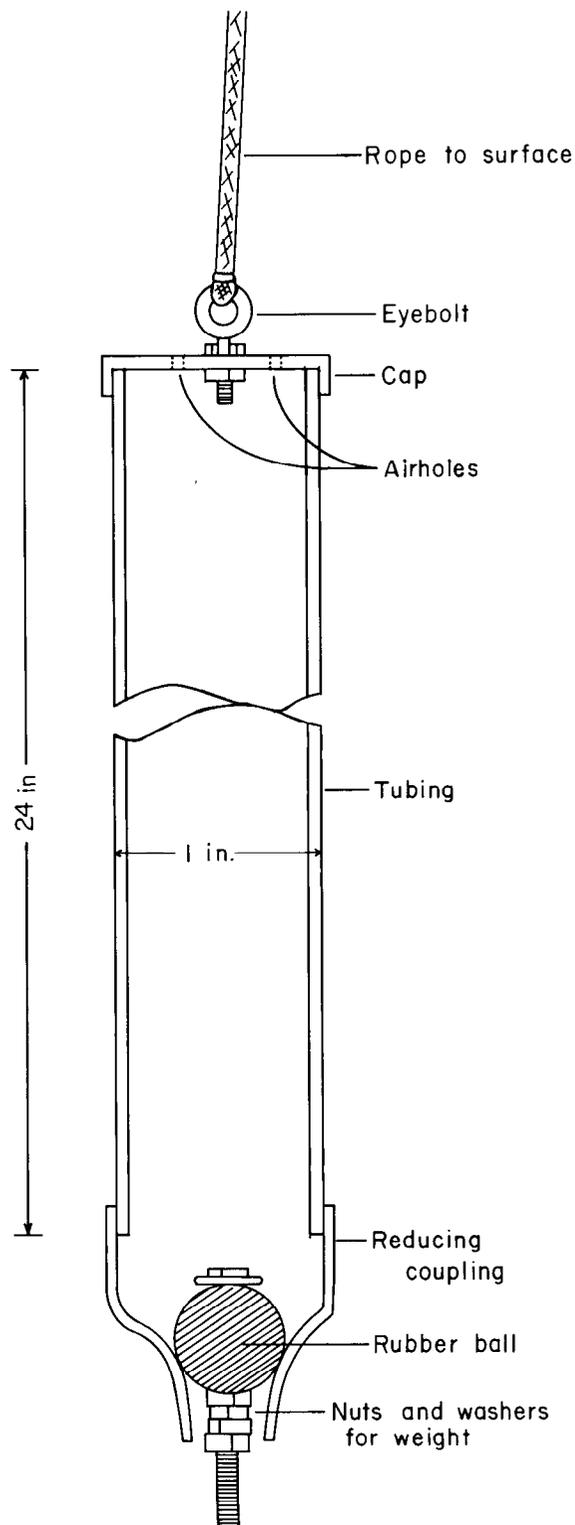

Figure 2 - "Homemade" bailer for collecting water samples from small-diameter wells

(polyvinyl chloride) plastic can be used; if plastic is used, a weight must be attached to the unit so that it will submerge. Plastic and stainless-steel construction is preferable if analyses are to be made for trace metals. The sample is contaminated with oxygen in this system, and particulate matter is often collected if the bailer strikes the bottom of the well. With any bailer or thief-type sampler, there is always the danger that the sample is a mixture of stagnant water in the well bore and water from the aquifer. Even the precaution of checking the sample for constancy of pH, temperature, and specific conductance may not give complete assurance of a representative sample.

A problem of fluid quantity exists with any of the bailer or thief-type methods of collection because an inordinate amount of time may be required to make 50 or 100 trips with a sampler to insure that the stagnant water in a well has been removed. Airlift pumping is an effective method of developing small-diameter wells but is generally a poor method of collecting a sample for chemical analysis. The air used for pumping obviously contaminates the sample, but perhaps more importantly, the turbulance with which the water is brought to the surface may have significant effects on pH, carbonate, bicarbonate, and temperature.

A useful combination of sampling techniques in small-diameter wells is to use the air pump to remove water until chemical conditions are stable and then to make several trips with a thief sampler or bailer to collect the sample. With all bailer or thief methods, it is extremely difficult to avoid oxidizing iron or manganese when filtering. For this reason, analyses for these elements should not be made if the bailer sample contains particulate matter that requires filtering.

Unfortunately, there are no well-defined criteria that apply to all methods of sampling for trace metals. The only general rule is to avoid contact with any metals in the collection system. Because this rule is often in conflict with the practical problems of collecting the sample, some compromise is usually necessary, and each sampling situation must be evaluated individually.

Unsaturated zone

Water sampling beneath a waste-disposal pond, feedlot, sanitary landfill, recharge pond, or any other system in which there is unsaturated flow requires special techniques. One method that has been used consists of a buried porous-ceramic cup (suction-lysimeter) with two lines to the surface, by which vacuum and pressure are applied, and from which the sample is collected. The construction details of this device are shown in figure 3. Additional details are given by Wood (1973).

In general, the system is operated by applying a vacuum greater than soil-moisture tension to a buried porous cup and thereby inducing the water to flow into the cup. To withdraw the sample, an increased vacuum is applied which causes water to flow past the check valve into the vacuum line. Gas pressure (inert gas) is then applied to one tube of the two-tube sys-
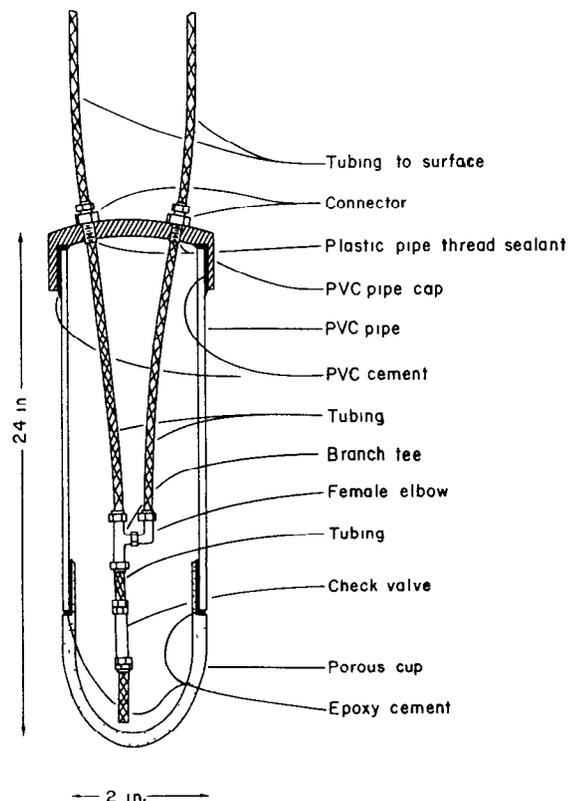

Figure 3.—Porous-cup assembly used for sampling in the unsaturated zone.

tem to force the sample to the surface. A check valve in the cup assembly prevents pressurization of the porous cup and backflow of the sample. This system has been used successfully in fine sand where there has been significant amount of flow; whether it will give satisfactory results in all unsaturated flow requirements has not yet been ascertained.

Sample filtration and acidification

Water that appears to be clear may contain considerable amounts of particulate matter in suspension. This is particularly true of water from new or little-used wells, such as those used for water-level observations or standby municipal and industrial supplies. The quantity of sediment discharged from a well is affected by the type of pump, construction of the well, screen size, type of screen, the pumping rate, and drawdown as well as the chemical stability of the system. The particulate matter in a water sample must be removed prior to most analyses, particularly if the sample is to be acidified, because the addition of acid will cause much of the particulate matter to dissolve. For example, the acid used for bicarbonate titration will dissolve particulate calcium carbonate, resulting in an analysis that shows an anomalously high bicarbonate content. The addition of acid prior to filtering may also result in exchange of hydrogen ions from the acid with cations from the particulate matter, thereby increasing the cation concentration of the water.

The wrong filtering technique will do as much damage to the accuracy of some analyses as will no filtering at all. Samples used for temperature measurements, dissolved oxygen, Eh, and pH should not be filtered. Vacuum filtering exposes the sample to the atmosphere and may also remove dissolved carbon dioxide from the water. The removal of carbon dioxide may significantly change the concentration of bicarbonate, carbonate, and influence the pH. Ground-water samples for the determination of these and other properties or constituents affected by the loss of carbon dioxide or contamination by oxygen should not be vacuum filtered.

A simple modification of the Skougstad-type plastic filter (Brown and others, 1970), commonly used by the U.S. Geological Survey, permits exclusion of the atmosphere during filtering. The top of the unit may be modified to include an inlet-delivery tube that extends to within a fraction of an inch of the bottom of the inside of the filter. The old pressure inlet is used as the new outlet, and control valves are placed on the inlet and the outlet tubes (fig. 4). This modification permits incoming water from a sampling line connected to the well discharge to fill the filter from the bottom, expelling air and overflow sample through the exit line. Discharge to the filter unit is controlled by the valve on the intake.

Before beginning filtration, the filter unit should be completely disassembled and thoroughly washed with the water to be sampled. Take special care to install a new styrofoam filter-support pad or insure that there are no stains or particulate matter on the old pad. A new membrane filter of the proper diameter (102 mm) and pore size (0.45 μm) is fitted to the filter unit, and the top and bottom are securely fastened.

Water introduced into the filter will immediately begin to drip from the discharge tube, and this water can be used to rinse pipets, sample bottles, and other equipment. Once the filter unit is full and all air is expelled, water is permitted to continue flowing through the
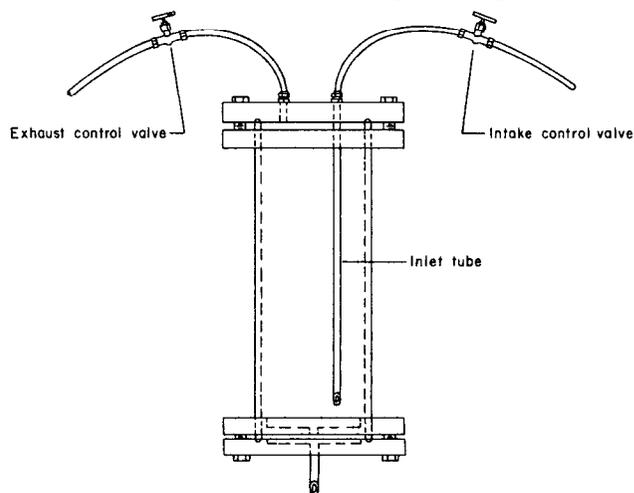

Figure 4.—Modified Skougstad-type water filter.

filter and out the exit tube until three or four filter volumes have flushed through the unit. This procedure makes certain that water that has been in contact with the atmosphere and any soluble impurities in the unit are removed.

The valve on the exit tube is closed, and the pressure from the well is used to filter the water. Pressure is controlled by the valve on the inlet tube and should be adjusted so that it is only sufficient to create a gentle flow from the discharge tube. A large pressure drop across the filter should be avoided to minimize the loss of dissolved gases from the sample. A sample bottle that has been thoroughly rinsed several times with the sample filtrate is placed under the filter for collection of the sample.

If water pressure is insufficient for filtering, an inert gas such as nitrogen or argon can be used to force the sample through the filter. To utilize gas pressure for filtration, the filter unit is filled with water as above, and the gas source is attached to the exit tube, the inlet tube is closed, the pressure is applied, and the sample collected from the discharge tube. Compressed air or carbon dioxide should not be used because these gases will influence the composition of the sample.

The 0.45-micrometre porosity filter has been widely adopted for separation of suspended matter from water samples. It represents a compromise between complete removal of the particulate material and speed with which filtration may be completed. Colloidal material with particles less than 0.45 micrometre in diameter is generally present in surface water and may occur in some ground water. Such material can pass through the filter and may strongly influence analytical values for iron and manganese (Kennedy and others, 1974). The problem may be partly alleviated by using 0.10-micrometre porosity filters (Kennedy and others, 1974).

The filtering process produces a "filter cake" of particulate material that decreases the particle size that can pass through the filter. Building of a filter cake may destroy the comparative uniformity of trace metals in successive aliquots. There is no apparent solution to this dilemma, but careful notation of the volume of water filtered and the amount of suspended material in the sample may be useful in evaluating analytical results.

The use of 0.1-micrometre filter membrane may reduce variance of trace metals between aliquots. The use of this filter membrane, however, requires considerably more filtration time because of rapid plugging from suspended solids in the sample. The 0.1-micrometre membrane filter should be used only in special situations that have been discussed with the district water-quality specialist or with personnel of the Central Laboratory System.

Porosity of the filter used should be recorded with the analytical data. Chemical analysis of particulate material retained by the filter may be important for some studies. To use this information the total volume of water filtered must be known.

If the filtered samples are to be acidified, double-distilled reagent-grade nitric acid should be added to the sample bottles after a few millilitres of the sample have been collected, to minimize oxidation, precipitation, and adsorption. Acid is more effective in preventing precipitation than in removing the precipitated minerals from the walls of the sample bottles. Sufficient acid must be added so that the resultant pH is 3.0 or less; usually 1 millilitre of acid to 1 litre of sample is sufficient. Convenient containers for transporting ultra high purity acid in the field are 2-ounce polyethylene or Teflon dropping bottles (fig. 5). Disposable glass ampoules of acid obtained from the Central Laboratory are even more convenient to use than the dropping bottles, and the chance of contamination is less with the ampoules. The ampoules can be carried in the field in their styrofoam shipping case with little danger of breakage.

Sampling for trace metals analysis

Some of the preceding sections have shown that the collection of water samples for trace metals analysis without contamination by atmosphereic oxygen is difficult. Contamination of samples with the trace metals themselves also may present a serious problem because of the widespread use of metallic casing, screen,
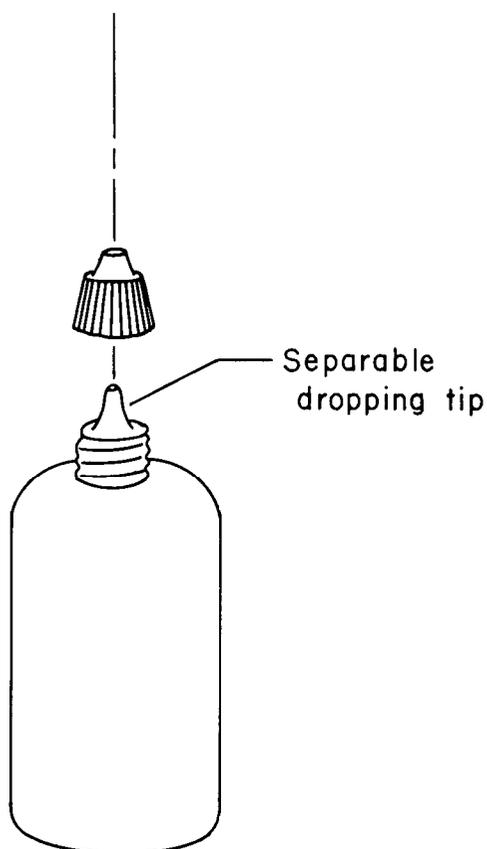
Figure 5 —Acid bottle used for field sampling

and pump columns for well construction. One solution to this potential contamination problem is the installation of a nonmetallic well and screen equipped with a nonmetallic pump or sampling device. This procedure is extremely expensive for an areal survey and is seldom practiced. Another solution to this problem is to confine the sampling to springs which are not in contact with metallic objects.

Because of the lack of definable springs in many aquifers and the near nonexistence of nonmetallic well construction, some compromise on the collection of samples for trace metals analysis is necessary. The usual compromise is to sample from a high capacity well which has been installed and operating for several years. The rationale of this choice is based upon the short time of contact of the water with the well structure (often less than 30 seconds). Except under unusual circumstances, the short contact should preclude contamination of the sample with trace metals. If samples from wells with metal construction are collected for trace metals analysis, this should be clearly stated with the published data.

Field-analysis procedures

Specific conductance

The specific conductance of a water sample is a measure of its ability to carry an electrical current under specific conditions. Specific conductance, which is a measure of the ionized salts, gives an indication of the concentration of dissolved solids in the water.

There are several reasons for determining the specific conductance of a sample in the field at the time of collection rather than waiting for a laboratory measurement. The field determination can be used as an aid in evaluating whether a sample is representative of water in the aquifer. For example, in new or little used wells, or in wells that have been recently drilled, grouted, or cemented, chemical changes in the pumped water may be rather large, and the well may require prolonged pumping to insure that the sample is representative of water in the aquifer. Specific-conductance determinations can be used to indicate that sufficient water has been pumped and that the quality of the water is stabilized.

A specific-conductance value that is markedly different from values obtained in nearby wells may indicate a different source of water, such as induced recharge, contamination from the surface, or leakage from a formation that contains water of different quality. Detection of an anomaly may indicate that more detailed sampling or reevaluation of the well is required. If so, the work can usually be done more economically at the time the original sample is collected rather than several weeks or months later.

The specific conductance of a sample can change with time owing to the precipitation of minerals from the water once the sample is in the environment of the container. A sample that has been acidified or otherwise treated will not yield an accurate representation of the specific conductance of the water in the

aquifer; therefore, it is essential to obtain an accurate field determination.

Summary of the method

The ability of a solution to conduct an electrical current is a function of the concentration and charge of the ions in solution and of the rate at which the ions can move under the influence of an electrical potential. As the number of ions per unit volume of solution increases, the rate at which individual ions can move decreases because of interionic attraction and other effects. A graph of total ion concentration versus specific conductance, even for solutions of a single salt, is a straight line only for values below 1,000 micromhos/cm. As specific conductance increases to above 5,000 micromhos/cm, the regression line curves significantly; beyond 50,000 micromhos/cm, the specific conductance may be an unsatisfactory index of ion concentration.

The temperature of the electrolyte affects the ionic velocities and, consequently, the specific conductance. For example, the specific conductance of potassium chloride (KCl) solutions changes about 2 percent per degree Celsius near 25°C.

Specific-conductance meters used in the field should be battery operated, should be equipped with temperature compensator, and should read directly in micromhos/cm at 25°C. The direct reading meter is recommended to save time in converting resistance values to specific conductance and to insure that the value is read in the field.

The cell should be checked before initial use and should be checked daily during regular use. A 0.00702 N potassium chloride (KCl) solution (dissolve 0.5234 g KCl dried at 180°C for 1 hour in distilled water and dilute to exactly 1 litre) has a specific conductance of 1,000 micromhos/cm at 25°C. Routine checks are made by using the 0.00702 N standard solution at the ambient temperature. The temperature control on the instrument is set at 25°C, and the ambient temperature of the standard KCl solution is recorded. A value of specific conductance is obtained and compared with the values given in figure 6 for the ambient temperature. The value obtained should be within 5 percent of that in figure 6.

Next, the temperature-adjustment knob is moved to the ambient temperature, and the meter is read. The value obtained should be 1,000 micromhos/cm, regardless of the ambient temperature. This procedure checks the temperature compensator, the conductance cell, and the electrical circuit of the instrument.

If the value obtained for the standard solution is not within the specified precision, the cell must be reconditioned and replatinized according to the instructions given in Brown, Skougstad, and Fishman (1970) or in the literature supplied by the manufacturer of the instrument. The carbon-type electrode supplied with some conductance meters needs no platinizing and should be replaced if it fails to perform to the specified accuracy.

Application and interferences

Apparatus

1. Mark V Electronic Switchgear (Chemicon Co.)[1] with cell constants of 0.1 and 1.0 or equivalent direct-reading meter.
2. Thermometer, 0–50°C graduated in 0.1°C.

Procedure

The following general procedure is supplemental to the instructions supplied by the manufacturer:

1. Rinse measuring cell with several volumes of sample water.
2. Bring temperature of cell to that of water being measured by immersing measuring cell in well discharge for at least 5 minutes. Some plastic cells have a high heat capacity and will cause drifting of the reading if not in thermal equilibrium with the sample.
3. Record reading, temperature, time, date, cell constant, and any meter constants.
4. Remeasure, with fresh sample, until reproducible readings are obtained.

Temperature

The temperature of ground water is important for numerous applications. For example, temperature measurements are critical in

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[1] The use of brand names in this report is for identification purposes only and does not imply endorsement by the U S Geological Survey
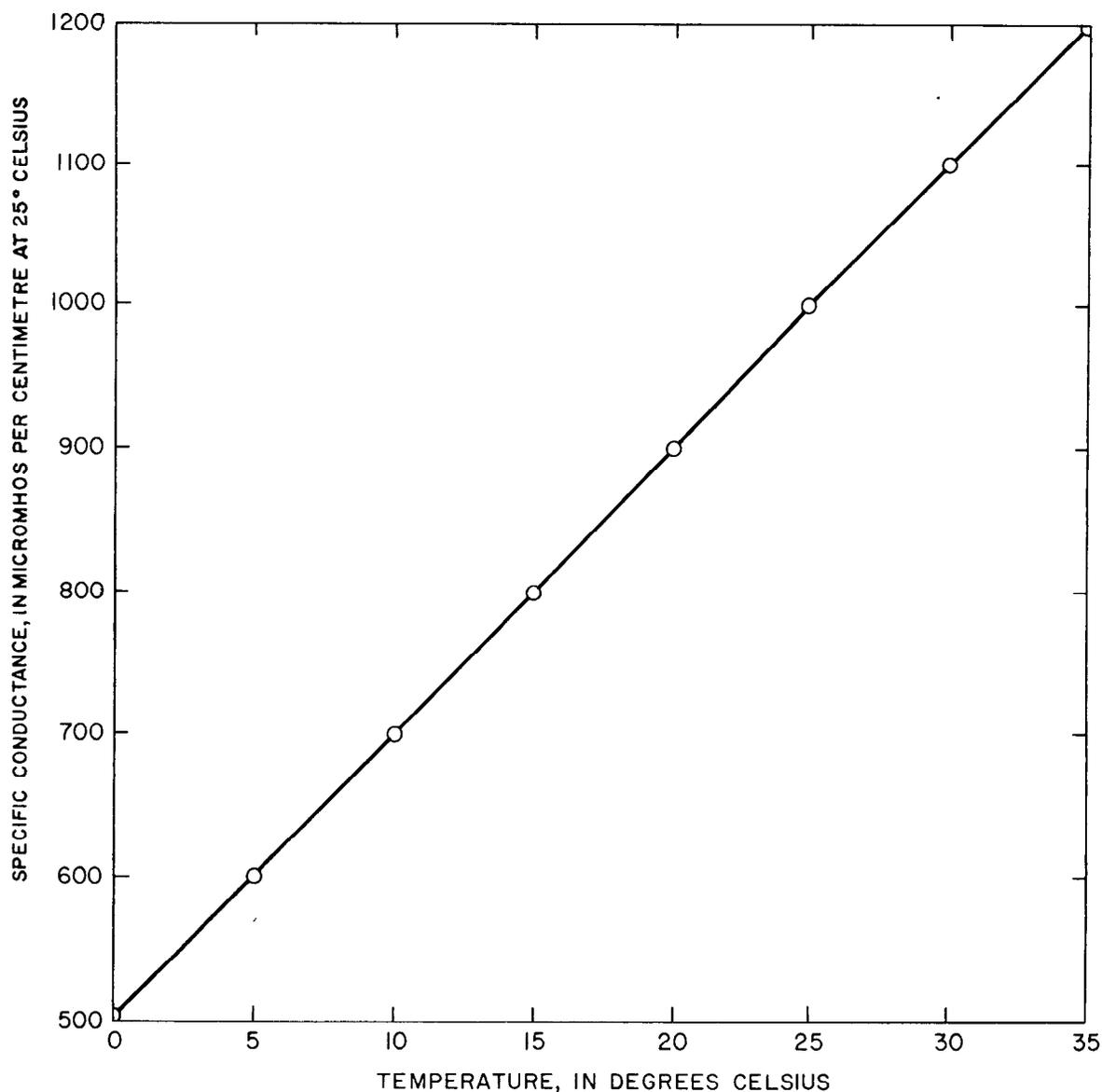
Figure 6 —Specific conductance of a 0 00702 N potassium chloride solution at various temperatures

identifying recharge from nearby surface-water sources. For accurate geochemical evaluation of equilibrium thermodynamics, it is desirable to know the temperature of the water in the aquifer within ±0.1°C.

Summary of the method

The temperature is recorded by a mercury-filled thermometer that is permitted to equilibrate in a sample that is continuously pumped into a dewar flask. The well should be pumped continuously until three identical consecutive readings of temperature are obtained.

Application and interference

The foregoing method may be used to measure the temperature of any ground-water sample but is most accurate when the ambient temperature is within 20°C of the ground-water temperature. New or little-used wells may develop new producing zones during pumping, thereby varying the proportion of

water entering the well from different depths and causing either an instantaneous change or continual drift in the temperature measurements. Drawdown may cause dewatering of certain beds and may cause a change in the temperature. Insufficient pumping time to allow equilibration of water temperature in the casing and pump column will also cause drifting of the temperature.

Apparatus

1. Dewar flask (a "thermos" bottle with a narrow mouth is adequate).

2. Partial immersion thermometer calibrated in 0.1°C or 0.2°F with the usual range of 5–25°C, or any range expected in the ground water in the study area. To minimize breaking the thermometer, steel or brass armor is suggested. The thermometer should be accurate to ±0.1°C as checked against the Bureau of Standards calibrated thermometer.

Procedure

Samples should be collected as close to the wellhead as possible. A continuous stream of water should be conducted through a short plastic tube into the bottom of the flask, allowing a continuous flow of water out of the flask. Readings should be taken after 5 minutes of flow at 1-minute intervals and recorded until no change is observed. If collection by continuous flow is impossible, the sample should be collected in the dewar flask and stoppered, with the thermometer inserted through the access hole. The first sample should be allowed to equilibrate 1 or 2 minutes and should then be discarded. The flask should be quickly refilled, and the temperature should be recorded immediately. This process should be continued until three identical consecutive readings are obtained. A box similar to that shown in figure 7 is useful for carrying equipment and preventing breakage.

pH of solutions

The pH of a solution is a measure of effective hydrogen-ion concentration or, more accurately, it is the negative logarithm of the hydrogen-ion activity in moles per litre:
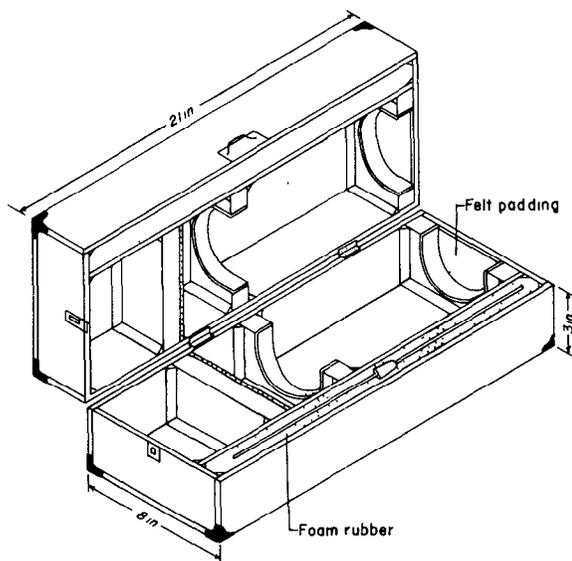

Figure 7 —Carrying box for thermometer, reading lens, and dewar flask

$$pH = -\log [H_+].$$

In aqueous solutions, pH is controlled by reactions that produce or consume H_+ including practically all dissociations of acids, bases, and hydrolysis. The primary control over pH in most potable ground water is the carbonate system including gaseous and dissolved carbon dioxide, bicarbonate, and carbonate ions. Other dissolved gases, such as hydrogen sulfide and ammonia, can also affect the pH of the solution.

Summary

The pH is determined with a glass hydrogen ion electrode compared against a reference electrode of known potential by means of a pH meter or other potential measuring device with a very high input impedance. A detailed description of pH and reference electrodes and their operations are given in Langmuir (1971), Durst (1969), and Garrels and Christ (1965). Because pH is exponentially related to concentration, great care must be exercised in making a measurement. Details of measurement are given by Barnes (1964).

Interference

A high sodium concentration will give an anomalous pH reading, which must be cor-

rected according to the recommendation of the manufacturer of the pH electrode. This correction is usually necessary only if pH is greater than 11, and sodium concentration is more than 10 moles per litre. Measurement of pH is temperature sensitive, so the standard buffers should be within ±1°C of the sample solution for precise determinations.

Apparatus, reagents, and checklist

1. Orion 401 pH meter or equivalent (a meter with a scale, at least 15 cm long, is necessary for detailed work of ±0.02 pH units).
2. pH buffer solutions 4.00, 7.00, and 10.00; 500 ml each.
3. Corning triple-purpose pH electrode 476021, or equivalent.
4. Orion single-junction reference electrode 90–01, or equivalent.
5. Filling solution for reference electrode.
6. Holder for electrodes, Multiflex or equivalent.
7. Plastic pail.
8. Thermometer.
9. Distilled water.
10. 500-ml plastic squeeze wash bottle for distilled water (color coded so as not to be confused with other reagents in wash bottles).
11. Box of small Kimwipes or equivalent.
12. Mixed bed deionizer in a delivery tube, 16-ounce size Deeminac or equivalent (useful for final treatment if commercial distilled water must be purchased).
13. Three 100-ml plastic beakers.
14. One 250-ml plastic beakers.
15. Card table or other portable table on which to work.

Procedure

The following procedure has been found useful in supplementing the pH meter manufacturer's instructions:

1. Check and fill reference electrode with internal filling solution recommended by the manufacturer. On Orion reference electrode, press cap and permit some of the filling solution to drain from the electrode to insure complete electrolite contact before inserting electrode in sample.
2. Adjust buffer solution and electrodes to ±1°C of the sample temperature by letting sample water run over submerged bottles and electrodes. (Be careful not to let sample water enter the filling hole of the reference electrode.) To prevent floating of partially filled buffer bottles, epoxy heavy steel washers to the bottom of the bottles. Alternatively, a small water bath can be constructed that holds two buffer bottles and sample beaker firmly in place during determination (fig. 8).
3. Record temperature of water.
4. Level meter and check to insure that the needle is properly adjusted.
5. Place 7.00 buffer in color-coded insulated beaker and place electrodes in the buffer. The pH of the buffer is equal to 7.00 only at 25°C; therefore, it is necessary to use the temperature-correction curve supplied by the manufacturer. Figure 9 is an example of a typical curve of temperature versus pH for a commercial buffer of pH 7.00. Turn on meter and adjust to correct pH value. If the electrodes have not been used recently, or have been allowed to dry for several days, it may take 10–20 minutes for them to stabilize. If electrodes will not stabilize, try either a new reference or pH electrode. To keep electrode from drying out and ready for use, the electrode tip should be immersed in a rubber or plastic sack (such as the finger cut from a plastic glove) in which has been placed a few millilitres of buffer solution.
6. Turn meter off or to standby position and remove electrodes from 7.00 buffer. Rinse thoroughly with distilled water and blot dry. Place electrodes in either pH 4.00 or pH 10.00 buffer, bracketing the expected pH of the sample. Switch on meter and allow several minutes for stabilization to occur before making final adjustment. Turn meter to off or standby position.
7. Check adherence of the response of the electrodes to the theoretical Nernst slope. According to manufacturer's instructions, and before adjusting meter with pH 7.00 buffer, the slope indicator is set to 100 percent, and the temperature compensator is set to the correct temperature (of water and buffer). After the electrode is placed in the second buffer, the temperature compensator is adjusted until the correct value of the second buffer is obtained.
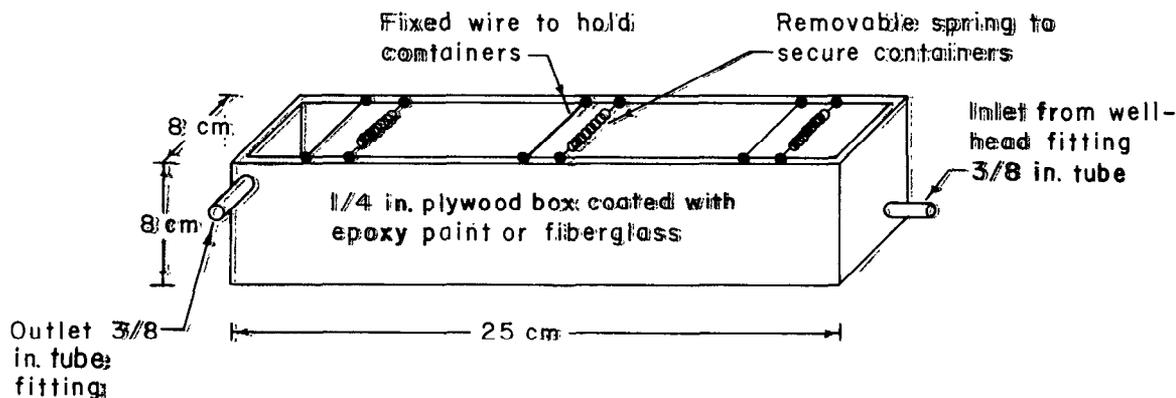
Figure 8.—Portable water bath for maintaining buffers and sample at wellhead temperature.

Then the slope indicator is adjusted until the temperature compensator points to the temperature of the solution. The percentage of theoretical slope can now be read on the slope scale.

Experience has shown that if the observed percentage differs from the theoretical value by ±10 percent, the reference electrode should be replaced and the slope rechecked by repeating steps 5–8. The theoretical Nernst slope for temperatures commonly encountered in ground water is shown in figure 10. Comparison of electrode response to the theoretical response (Nernst equation) is a check on the efficiency of the electrode system. The lack of agreement between the observed electrode system and the Nernst equation does not indicate that the observed pH values are inaccurate. All that is indicated is a potential source of trouble and some part of the system is not operating as efficiently as it should. Generally, combination pH-reference electrodes do not conform to the theoretical curve as closely as do the individual electrodes.

8. Rinse electrode with distilled water and blot dry. Recheck value of pH 7.00 buffer. If value is within ±0.02 pH of the correct value, proceed with next step. If drift from original setting has occurred, repeat steps 5–8.

9. Thoroughly rinse electrode with sample water and then place electrodes in a sample collected in a 250-ml plastic beaker. Turn on meter. Do not swirl or stir sample. Allow at least 2 minutes for equilibration. Record value. Turn meter to off or standby position. Repeat
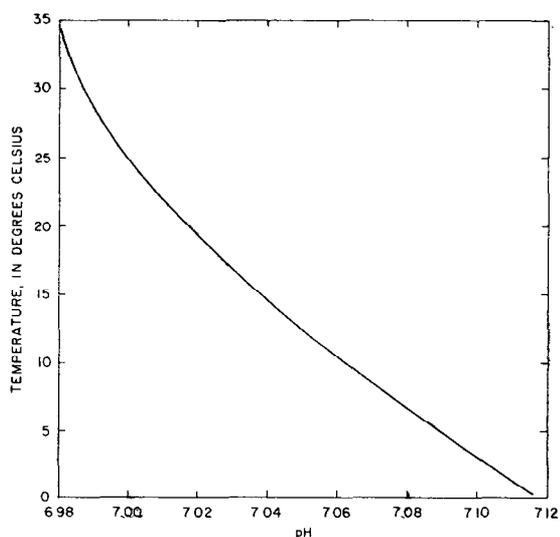
Figure 9—Relationship between temperature and pH for a typical commercial buffer solution

step 9, using newly collected samples until three consecutive readings differ by no more than ±0.02 pH unit. If equilibrium is not attained in several minutes, out gassing of CO_2 may be occurring. In such cases the initial reading may be the best. Out gassing may be reduced if the electrode system is placed through a tightly fitting stopper into the water-filled beaker.

10. Place electrodes in temperature equilibrated buffer 7.00. Turn on meter. If reading is within ±0.02 of original buffer reading, then analysis is complete. Turn meter off or to standby position. If reading has changed from original value, repeat steps 5–10. NOTE: In

Figure 10.—Relationship between temperature and the Nernst slope.

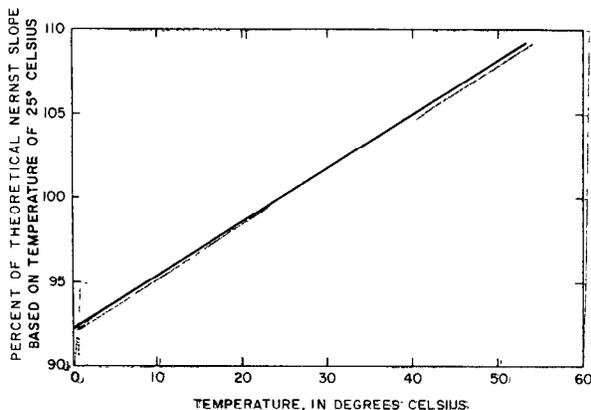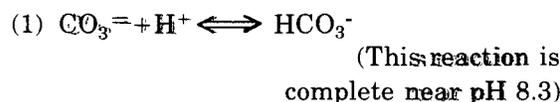dry, windy climates, such as in the southwestern United States, a static charge tends to build on the plastic face of a pH meter, which causes erratic movement of the indicator needle. Antistatic spray, of the type used for phonograph records, sprayed on the meter face will minimize this interference. It is also desirable to keep the meter protected from extreme temperature changes during measurement, as this will affect the stability of the electronic system and consequently the precision of the measurement. In cold waters, slow electrode response may occur from the precipitation of the saturated filling solution in the reference electrode, thereby reducing the fluid contact. This can be remedied by allowing the filling solution to reach ambient temperature before filling the reference electrode.
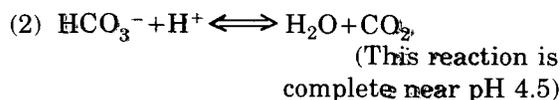
Carbonate and bicarbonate

For chemical equilibrium calculations related to carbonate minerals, it is essential to have an accurate value for pH, carbonate, and bicarbonate concentrations. Carbonate and bicarbonate determinations for ground water must be made in the field at the time of sampling if the concentrations are to accurately represent those originally present in the water. These parameters are particularly subject to change if the sample is collected and stored in certain types of plastic bottles that are permeable to carbon dioxide.

Summary of the method

Detailed descriptions of the theory and practice of potentiometric titration of carbonate and bicarbonate is given in Barnes (1964), Weber and Stumm (1963), and Brown, Skougstad, and Fishman (1970). In general, the carbonate (CO_3^{-2}) and bicarbonate (HCO_3^-) concentrations are determined by titration of the water sample with a standard solution of strong acid. The following equations govern the reactions involved:

(1) $CO_3^= + H^+ \rightleftharpoons HCO_3^-$

(This reaction is complete near pH 8.3)

and

(2) $HCO_3^- + H^+ \rightleftharpoons H_2O + CO_2$,

(This reaction is complete near pH 4.5)

The end point of the carbonate or bicarbonate titration process is determined from (A) a plot of pH versus titrant volume, where the end point corresponds to an inflection point of the curve (fig. 11) or (B) a plot of

$$\frac{\Delta pH}{\Delta ml \ of \ titrant}$$

the rate of change in pH per unit volume of titrant versus the average titrant volume between two successive values. The end point is the value at which occurs the maximum rate of change of pH per volume of titrant added (fig. 11).

The approach in (B) is less subjective and permits consistent choice of the end point, but requires exacting analytical procedures and the assurance of complete equilibration of pH after each increment of acid added.

Salts of weak organic and inorganic acids, such as silica, which cannot be corrected for, may yield erroneous results when present in large amounts. In addition, oils, greases, and colloidal material, if present, may tend to foul the pH electrode and prevent its proper operation.

Apparatus and reagents

1. All equipment and reagents used for pH determinations. (See section on pH determination.)
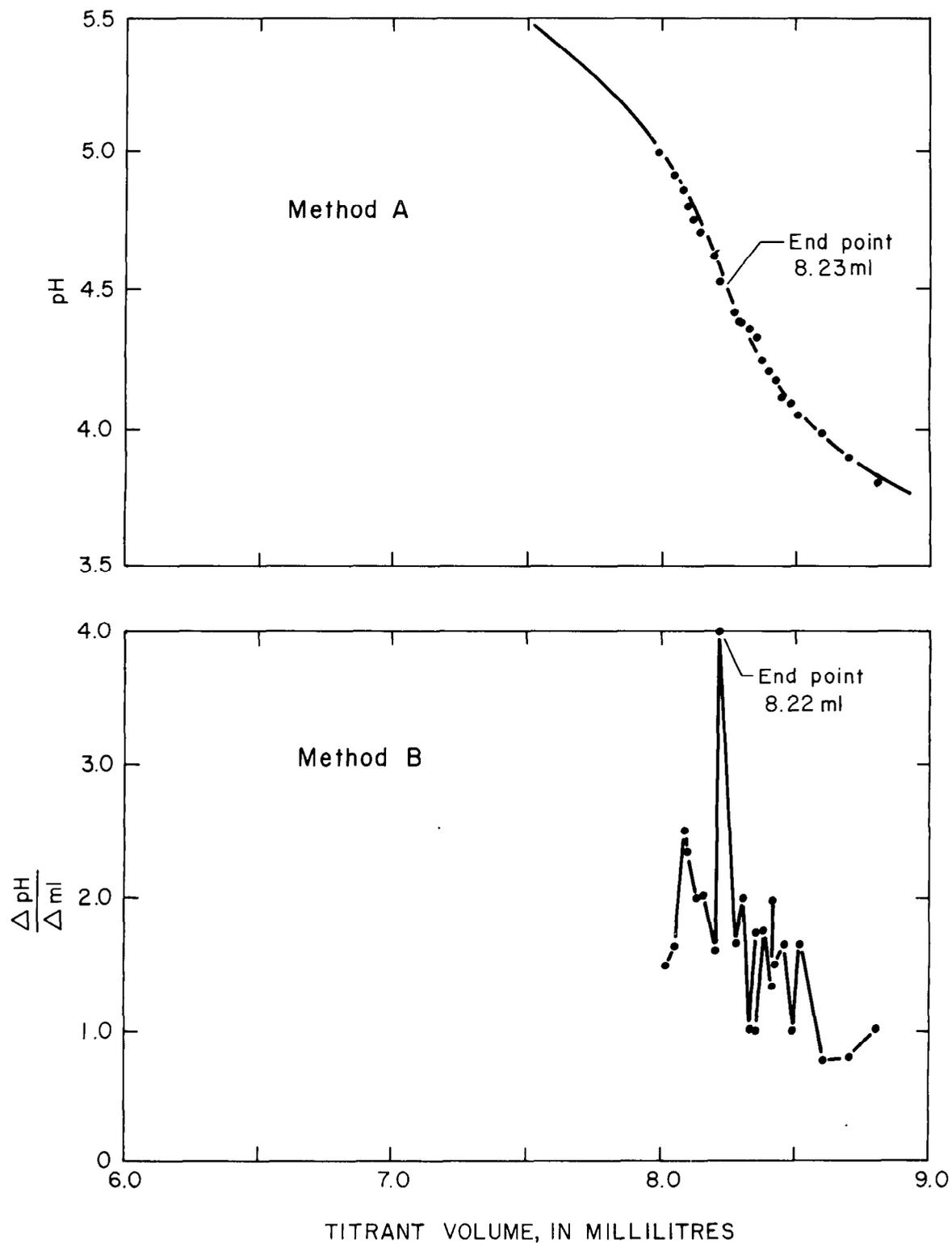
Figure 11 —Two methods of determining the end point for bicarbonate determinations.

2. Buret, 25-ml capacity with 0.1-ml graduation and Teflon stopcock.

3. Portable battery-powered magnetic stirrer, Lapine or equivalent with extra batteries.

4. Teflon coated stirring bar, small size.

5. Ring stand, clamp holder, and universal V-jawed clamp.

6. 25- and 50-ml class A volumetric pipets.

7. 250-ml plastic-squeeze acid bottle with nozzle for filling buret (color-coded bottle to prevent confusion with distilled water bottle).

8. 1 litre of $0.01639 N$ sulfuric acid packaged in two 500-ml plastic bottles to prevent breakage. (Prepared according to Brown and others, 1970).

9. Wire pen cleaner for dislodging foreign debris in buret tip.

10. Cap to prevent dust from entering buret.

11. Buret meniscus reader (useful for poor light conditions often encountered in the field).

A padded wooden box (fig. 12) is useful for carrying volumetric glassware and small accessories such as meniscus reader, stirring bar, wire pen cleaner, and so forth.

Procedure

1. Adjust temperature of titrant to $\pm 2°C$ of the sample by immersion of securely stoppered acid-storage bottles in a water bath of the sample fluid; set up and fill buret to 0.00 ml; cap buret with dust cover.

2. From a pressure-filtered sample (see section on filtration) pipet 50 ml into a clean dry 100-ml beaker. Under no circumstances should the sample be diluted or concentrated in any way. The pipet is rinsed three times with the sample water before final sample is placed in the beaker. If titration cannot be completed

with one filling of the buret, discard sample and use a smaller sample size. There is a great chance for error in refilling a buret during a titration.

3. Insert pH and reference electrodes into the sample. The electrodes should be calibrated in 7.00 and 4.00 buffer solutions at the temperature of the sample, then washed in sample or distilled water and blotted, not wiped, dry. (See section on pH determinations.) Insert the clean dry stirring bar and adjust stirrer to slow speed.

4. If pH is greater than 8.3, add sulfuric acid by drops, recording volume accurately with 0.05-ml increments and pH values to 0.02 pH units until pH is below 8.00 (See table 2 for useful recording format.)

When the pH of sample during titration declines below 8.00, or the initial value is less than 8.3, add acid in increments of 1 ml and record pH value at each increment. Continue this procedure until pH declines to approximately 5.5. From pH 5.5 to pH 4.0, add acid by

Figure 12 —Carrying box for volumetric glassware electrodes and other small fragile items.

Table 2 —Results of a typical bicarbonate titration showing method of recording the data

pH	millilitres of acid	$\dfrac{\Delta \text{pH}}{\Delta \text{vol}}$
7.94	0.00	----
7.57	1.20	0.31
7.11	2.00	.57
6.79	3 00	.32
6 67	4.00	12
6 40	5 00	.27
6.14	6.00	.26
5.78	7.00	.36
4.98	8.00	80
4.95	8.02	1.50
4.90	8.05	1.67
4.85	8 07	2.50
4.78	8.10	2.33
4.74	8.12	2 00
4.68	8.15	2.00
4.60	8.20	1.60
4.52	8.22	4.00
4.42	8 28	1.67
4.38	8.30	2.00
4.35	8.33	1.00
4.30	8.35	1 67
4.25	8.39	1 67
4.21	8.41	2 00
4 18	8.43	1.50
4.13	8.46	1.67
4.10	8.48	1.50
4.05	8 51	1.67
3 98	8.60	78
3 90	8.70	.80
3 80	8.80	1.00

drops, recording pH at each volume increment. The most sensitive part of the titration is usually between 4.8 and 4.3. Adding acid in fractions of a drop is desirable in this range. (Carefully touch ¼ or ½ drop to sample surface and pull away from buret tip.) Allow 15–20 seconds for equilibration.

Calculations

Calculations for the carbonate content are made by using the equation

$$CO_3^= \text{ in mg/l} = \frac{1,000}{ml_{(s)}} \times (ml_{(a)} \text{ to end point near pH 8.3}) \times (0.9835).$$

Calculations for bicarbonate are made by using the equation

$$HCO_3^- \text{ in mg/l} = \frac{1,000}{ml_{(s)}} \times (ml_{(a)} \text{ between end points near 8.3 and 4.5} - (ml_{(a)} \text{ to end point near 8.3}),$$

where $ml_{(a)}$ and $ml_{(s)}$ = volumes of standard 0.01639 N sulfuric acid and samples, respectively, and end points are determined as in figure 11. Because of the relatively small amount of time required for this analysis, it is best to repeat titration to insure precision.

Eh (Oxidation-reduction potential)

A chemical reaction in which an element undergoes a loss or gain of orbital electrons is referred to as oxidation or reduction and may be represented by the following general expression:

$$\text{reduced species} \rightarrow \text{oxidized species} + ne^-,$$
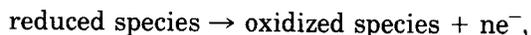
where $ne-$ is the number of electrons involved per atom. The standard oxidation potential, $E°$, for a half-cell reaction of this type is the potential that would occur if the two species are both present at unit activity at 25°C and one atmosphere pressure. When the activities of participating species differ from unity, the potential observed at equilibrium is termed the redox potential (oxidation-reduction potential). The redox potential, represented by the symbol Eh, is related to the standard potential and the activities of participating substances by the Nernst equation:

$$Eh = E° + \frac{RT}{nF} \ln \frac{\text{oxidized state}}{\text{reduced state}},$$

where $E°$ is the standard potential of the reaction, R is the universal gas constant, T is the absolute temperature in degrees Kelvin, F is the Faraday constant, n is the number of electrons involved in a half-cell reaction, and $\ln \frac{\text{oxidized state}}{\text{reduced state}}$ is the natural logarithm of the ratio of the products of the activities of oxidized species to that of the reduced species. The potential is reported as volts or millivolts, relative to the potential of the hydrogen electrode, taken as zero, and may be positive or negative (the greater the negative value, the more the reducing tendency of the system). An excellent review article on Eh-pH determination has been presented by Langmuir (1971).

Some writers have preferred the notation "pE," defined as the negative logarithm of the molar activity of the electrons, which avoids some of the unit conversion calculations required by the Nernst equation (Stumm, 1966).

Eh is generally a qualitative tool for the ground-water geochemist. However, it has been used very effectively in explaining the concentration of many minerals that exhibit more than one oxidation state under natural conditions. See, for example, the relation of iron in natural water to Eh as shown by Back and Barnes (1965).

Summary of the method

Eh is measured with a noble metal (usually platinum) and a reference electrode system using a pH meter that can be read in millivolts. Reference solutions with known Eh are used to obtain the potential and to check the accuracy of the electrode system. Unlike pH buffer solutions, the Eh reference solutions are not used to adjust the system to the correct range of values. The potassium ferric-ferro cyanide solution described by ZoBell (1946), which has been proved satisfactory as a standard reference solution by many geochemists, is the standard recommended in this manual.

At 25°C, the potential of the ZoBell solution relative to the standard hydrogen electrode is +0.428 volts. The potential varies with temperature according to the following equation:

$$Eh = 0.428 - 0.0022 \, (t-25) \text{ volt}$$
(Ivan Barnes, oral commun., 1972).

At 25°C, the saturated calomel (mercury-mercurous chloride) reference electrode, which is commonly used, has a reference voltage of +0.244 volts relative to the potential of the standard hydrogen electrode. The voltage varies with temperature according to the following equation:

$$Eh = 0.244 - 0.00066 \, (t-25) \text{ volt}$$
(Garrels and Christ, 1965, p. 127),

where t is the temperature in degrees Celsius.

By combining the half-cell potentials for the platinum-calomel electrode system and ZoBell solution and utilizing the equations for potential variation with temperature (emf = $Eh_{ZoBell} - Eh_{Calomel}$), the theoretical potentials for the system at different temperatures can be calculated. The relationship of theoretical potentials of this system to temperature is shown in figure 13. The relationship for a silver–silver chloride reference electrode and platinum electrode system to temperature is also plotted in figure 13.

The measurement of Eh of a system requires that the observed potential be adjusted to a potential relative to the standard hydrogen electrode.

In equation form,

$$Eh_{Sys} = E_{obs} + Eh_{ZoBell+ref} - E_{ZoBell \, (obs)},$$
where
Eh_{Sys} = The true Eh of the environment, relative to the standard hydrogen electrode,

E_{obs} = the observed potential of the environment, relative to the reference electrode,

$Eh_{ZoBell+ref}$ = the theoretical Eh of the reference electrode and ZoBell solution, relative to the standard hydrogen electrode, and

$E_{ZoBell(obs)}$ = the observed potential of ZoBell solution, relative to the reference electrode.

Application and interferences

Redox potential measurements in laboratory solutions where activities of oxidized and reduced species may approach unity can be expected to match theoretical calculated poten-
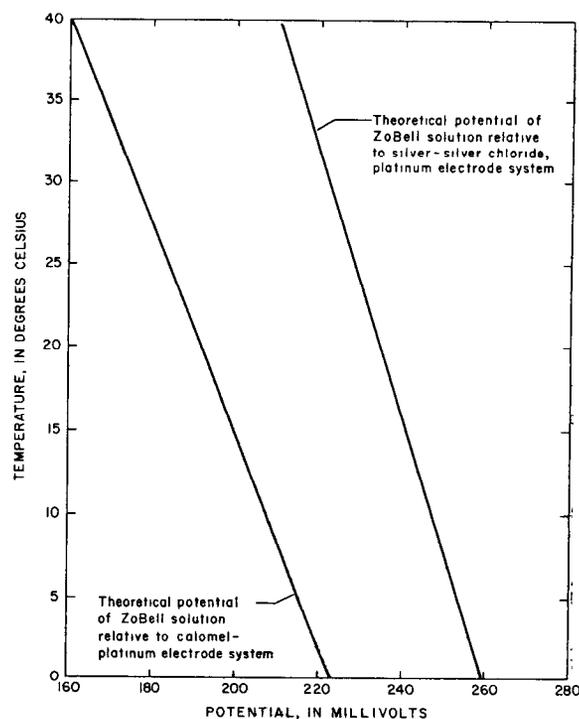

Figure 13.—The potential of ZoBell solution, relative to reference-electrode systems, at various temperatures

tials reasonably well. Experience has shown that many natural water systems do not give measured Eh values that can be quantitatively interpreted. Measurements made in water containing dissolved oxygen, for example, give values lower than might theoretically be expected. Garrels and Christ (1965) attribute this to a slow, rate-determining step in the reaction of aqueous oxygen with other ions. If dissolved oxygen (DO) is above 0.01 mg/l, the DO determination may be more useful than attempting to determine Eh. It is also generally useless to try to measure Eh in systems containing hydrogen sulfide.

Back and Barnes (1965) were able to correlate measured redox potentials with dissolved ferrous iron contents of ground water in moderately reducing systems. Most other experiences with Eh measurements that are described in the literature lead one to conclude that the measurement is primarily a qualitative tool. It may give useful information about systems whose solid and solute components are reasonably well known from other kinds of

measurements. Limitations and uncertainties inherent in Eh measurements were discussed by Stumm (1966) and Doyle (1968). Charged colloidal material and differences in composition and concentration of the unknown and reference solutions may create errors. Oil and grease may coat the noble-metal electrode, preventing contact with the sample.

Apparatus and reagents

1. Orion 401 specific-ion meter or equivalent.

2. Orion combination electrode 96-78-00 or equivalent and Orion electrode filling solution 90-00-01 or equivalent. (Thimble platinum and separate reference electrodes are also suitable.)

3. ZoBell reference solution:
Dissolve

　　1.4080 g of potassium ferrocyanide K_4Fe
　　　$(CN)_63H_2O$ $(0.00333M)$
　　1.0975 g of potassium ferricyanide K_3Fe
　　　$(CN)_6$ $(0.00333M)$

7.4555 g of potassium chloride KCl $(0.10M)$ in distilled water to make 1 litre. This solution is stable for several months but should be kept in a black plastic bottle and out of sunlight as much as possible. It has a standard potential of +428 millivolts at 25°C. This solution is poisonous and should be handled with care.

4. Ring stand, clamp holder, and universal V-jawed clamp.

5. Eh cell (fig. 14).

6. Plastic 100-ml beaker.

7. Water bath for ZoBell solution (plastic pail or bottom half of a 1-gallon plastic bottle).

8. Thermometer.

9. Equipment for measuring dissolved oxygen.

10. Small strips of crocus cloth for polishing platinum electrode.

Procedure

1. Fill combination electrode with proper filling solution (Orion 90-00-01 or equivalent). Depress body and let some of the fluid drain to waste. Bring ZoBell solution to the temperature of sample by allowing sample to flow over closed bottle. Record temperature. While the ZoBell solution is equilibrating to the sample
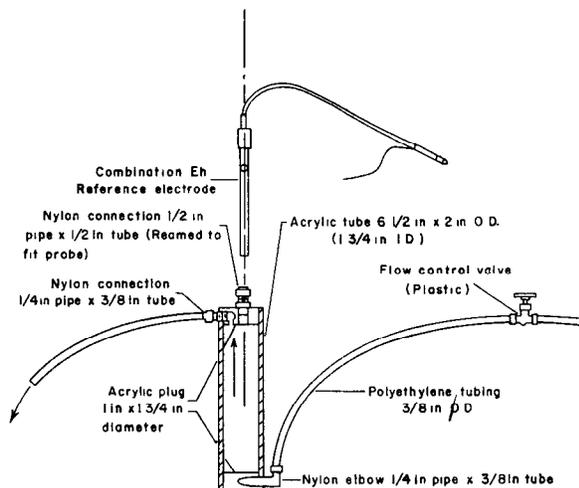

Figure 14 —Eh measuring cell

temperature, determine the presence of dissolved oxygen in the water sample. If dissolved oxygen is greater than 0.05 mg/l, do not proceed with the Eh measurement. If dissolved oxygen is absent, proceed with step 2.

2. Place combination electrode in the ZoBell solution that has been equilibrated to the sample temperature. Plug electrode leads into meter and turn function switch on meter to millivolt mode. Allow several minutes for electrode to equilibrate while maintaining the bottle of ZoBell solution in the water bath. Record reading. If reading differs by more than 10 millivolts from the theoretical value at that temperature (fig. 13), replace reference electrode fluid and repeat measurement. If that procedure will not bring the reading within 10 millivolts of the theoretical value, polish the platinum end of the electrode with a piece of crocus cloth and recheck reading. If this procedure fails, the electrode should be replaced. If reading is within ±10 millivolts of the theoretical value, rinse electrode with sample water and proceed with step 3.

3. Place electrode in the plastic Eh cell pointing up (fig. 13) and let the water flow through the cell. Filler hole in side of electrode should be above the top of Eh cell. Make sure all air bubbles are removed from the system. Use control valve on inlet to insure that the head of sample is below level of reference solution of the electrode or some of the sample will be forced into the reference electrode and

change the potential of the system. Clamp Eh cell onto the ring stand.

4. Turn function switch on meter to millivolt mode and allow the water to flow through the cell until the readings stabilize. Stabilization usually occurs within 20 minutes but may require as much as an hour or more. Turn off sample flow to prevent any streaming potential and immediately record meter reading. This is the observed Eh of the sample, or more specifically, the observed full-cell emf relative to the reference electrode.

5. Record the data and calculate the Eh relative to the standard hydrogen electrode as follows:

Data record

A. Temperature of sample _____ _____

B. Observed potential, in millivolts, of ZoBell solution, relative to reference electrode, at sample temperature ____ _____

C. Theoretical potential, in millivolts, of ZoBell solution, relative to reference electrode, of sample temperature (fig. 13) _____ _____

D. Theoretical potential, in millivolts, of reference electrode system and ZoBell solution, relative to the standard hydrogen electrode, at sample temperature (fig. 15) _____ _____

E. Observed potential of sample, in millivolts _____ _____

Calculations

I Checking the electrode

Calculate difference between observed potential and theoretical potential of ZoBell solution, relative to reference electrode,

$$B-C = \text{difference.}$$

If this difference is less than ±10 millivolts, proceed with next step. If difference is greater than ±10 millivolts, see step 2 of procedure for remedial measures.

II Calculate the Eh of the system

$E-B+D=Eh$ value of the system. Report Eh value [either positive (+) or negative (−)] to nearest 10 millivolts.
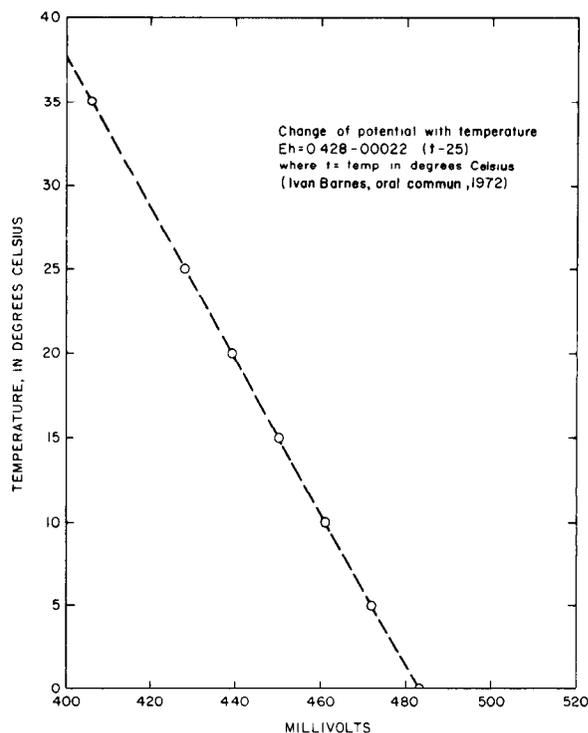
A field example may help to clarify the procedure:

Figure 15.—The potential of ZoBell solution, relative to the standard hydrogen electrode, at various temperatures.

October 6, 1971 @ 0930, St. Paul, Minnesota; G. Ehrlich, H. Reeder, W. Wood
Well 2–N, artificial-recharge site 539 feet deep, 6-inch diameter, finished in the Prairie duChein
Pumping 10 gal/min for 22 hours
Temperature of water from well is 10.0°C

The observed potential of ZoBell solution, relative to the combination reference–platinum electrode, at 10°C was +215 millivolts. (Theoretical potential for ZoBell solution, relative to this electrode system, at 10.0°C is +207 millivolts (fig. 13). The 8-millivolt difference was considered small, and the decision was made to proceed with the measurements.) The observed potential of the water sample after system stabilized in 30 minutes was −120 millivolts.

Data record:

A. Temperature of sample _____ 10°C

B. Observed potential, in millivolts, of ZoBell solution, relative to reference

electrode, at sample temperature ____ +215

C. Theoretical potential, in milli-
volts, of ZoBell solution relative to
reference electrode, at sample tempera-
ture (from fig.13) _____ +207

D. Theoretical potential, in milli-
volts, of reference electrode system and
ZoBell solution, relative to standard
hydrogen electrode, at sample tem-
perature (fig. 15) _____ +461

E. Observed potential of sample, in
millivolts _____ −120

Calculations:
I. B−C=(+215)−(207)=+8 millivolts
II. $Eh_{sys}=E-B+D = (-120) - (215) + (461) =$
+126 millivolts
Report at +130 millivolts.

Dissolved oxygen

Oxygen dissolved in ground water usually is
derived from contact with the atmosphere be-
fore recharge to the aquifer. The solubility of
oxygen in water is dependent upon the partial
pressure of oxygen in the atmosphere, the dis-
solved solids, and the temperature. The experi-
ence of the author has indicated that the pres-
ence of dissolved oxygen in ground water is a
more common occurrence than is generally be-
lieved. This is particularly true in hydrologi-
cally stressed systems. Dissolved oxygen can
exist at great depths in aquifers which have
little or no oxidizable material in the water
flow path and can also be present in any
aquifer where the water's residence time is
short compared to the rate of oxygen consump-
tion.

Summary of the method

Methods commonly used for the determina-
tion of dissolved oxygen are described in
"Standard Methods for the Examination of
Water and Wastewater" (American Public
Health Association and others, 1971). Some of
these methods are subject to rather serious in-
terferences. Regardless of the method used,
great care must be taken to prevent atmos-
pheric aeration of the sample during collection
and analysis. Use of a flow chamber to prevent
contact of the sample with the atmosphere and
use of a portable dissolved-oxygen meter for
analysis eliminates or minimizes the effects of

most interferences and yields a continuous rec-
ord of dissolved oxygen during the pumping of
a well.

The sensing element of the dissolved-oxygen
meter is basically a polarographic system in
which two solid metal electrodes in contact
with an electrolyte are separated from the test
solution by an oxygen-permeable membrane.
The membrane serves as a diffusion barrier
against impurities. The rate that oxygen dif-
fuses through the membrane is proportional to
the pressure differential across the membrane.
When oxygen diffuses through the membrane,
it is rapidly consumed at the cathode. Thus, the
rate of diffusion is proportional to the absolute
pressure of oxygen outside the membrane.
When a suitable polarizing voltage is applied
across the cell, the consumption of oxygen at
the cathode causes a current to flow through
the cell. This current is directly proportional to
the quantity of oxygen consumed.

For precise dissolved-oxygen determina-
tions, the meter should be calibrated before
each use. Preferably, the calibration should be
accomplished on the water under test. One
sample of the water should be deoxygenated by
adding an excess of sodium sulfite; a second
sample should be aerated to saturation. The
dissolved-oxygen concentration of the air-
saturated sample can be determined from
figures 16 and 17, provided the water tempera-
ture, barometric pressure, and altitude of the
sampling site are known. In the absence of in-
terferences, a more precise dissolved-oxygen
value for the aerated sample can be deter-
mined by use of the Alsterberg azide modifica-
tion of the Winkler method (Brown and others,
1970, p. 126) or any approved modification of
this technique. Where interfering substances
are suspected, calibration should be ac-
complished on distilled water aerated to sat-
uration.

The meter must be precisely calibrated ac-
cording to the manufacturer's instructions
before each use. In general, satisfactory cali-
bration can be accomplished by using air-
saturated water. In this procedure, the water
sample is aerated by being shaken in the pres-
ence of air for 15–20 minutes (a 1-litre un-
capped narrow-mouthed bottle half full works
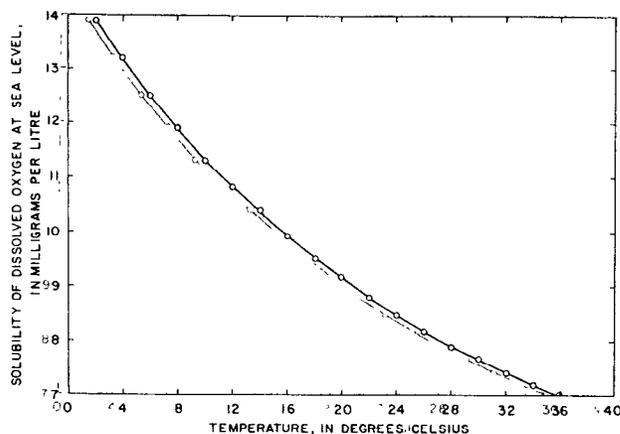well) or by using a battery-powered aerator for

Figure 16 —Solubility of oxygen in water at sea level as a function of temperature.
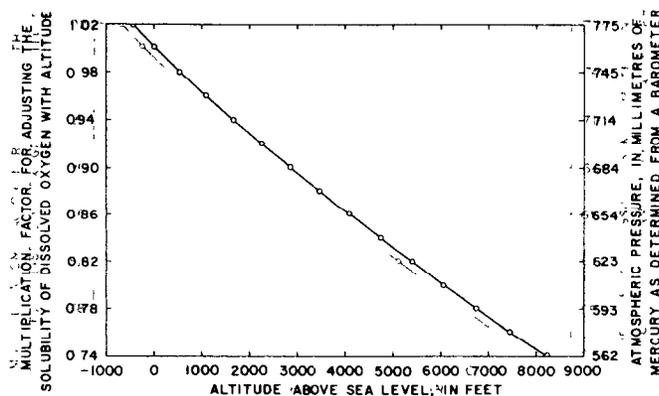

Figure 17.—Correction factor for the solubility of oxygen at different atmospheric pressures and altitudes.

5-10 minutes. Temperature of the water is then measured. Figure 16 shows the dissolved-oxygen concentration of air-saturated water at sea level as a function of temperature. Figure 17 shows correction factors that must be applied to the apparent oxygen concentration when the atmospheric pressure varies from 760 mm of mercury. By use of these figures, the correct value of oxygen dissolved in the air-saturated sample can be obtained and the meter calibrated.

Application and interferences

The membrane-electrode method is applicable for the measurement of dissolved oxygen in any well or spring from which a sample can be collected without aeration.

Oxygen-permeable membranes used for the electrode system are permeable to a variety of other gases, none of which is easily depolarized at the indicator electrode. In addition, the concentrations of most of these gases in ground water probably are too small to cause significant interference with dissolved-oxygen determinations. However, use of the membrane electrode in water containing such gases as hydrogen sulfide without loss of sensitivity requires frequent changing of the membrane, replacement of the electrolyte, and recalibration of the electrode.

Apparatus and reagents

11. Yellow Springs model 54 ARC oxygen meter with sensor, or equivalent.

2. Flow chamber with flow control valve (fig. 18).

3. Ring stand, clampholder and universal V-jawed clamp.

4. Bottle of electrolyte for the sensor.

5. Extra membranes for the sensor.

66. Thermometer.

7. Two 8-ounce plastic bottles.

8. 1-litre plastic bottle for aeration of the reference sample.
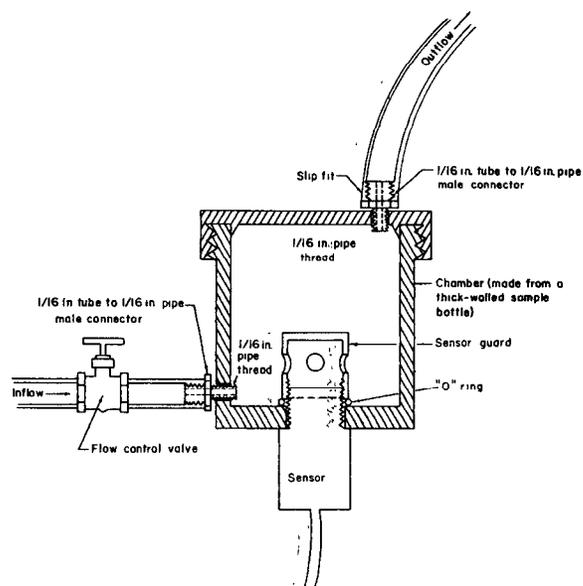
9. Battery-operated aerator.

Figure 18.—Flow chamber for determination of dissolved oxygen from a pumped well.

10. Battery-operated magnetic stirrer and stirring bars.

11. Saturated solution of sodium sulfite.

12. Cobaltous chloride solution.

13. Reagents and plasticware for Alsterberg azide modification of Winkler method for dissolved-oxygen determination (Brown and others, 1970, p. 126).

Procedure

1. Pour sample into an 8-ounce plastic bottle to which has been added several millilitres of saturated solution of sodium sulfite and a trace of cobaltous chloride. Replace cap and stir on magnetic stirrer for several minutes.

2. Prepare oxygen meter for calibration according to manufacturer's instructions.

3. Switch meter to the 0–10 position. Remove sensor guard and insert the sensor in deaerated sample. If dissolved oxygen in sample is greater than 0.0 mg/l, add saturated sodium sulfite in small increments until a reading of 0.0 mg/l is obtained. Add an excess of several millilitres after a reading of 0.0 mg/l is obtained.

4. Pour a second sample into a 1-litre plastic bottle and aerate for 5–10 minutes with battery-operated aerator.

5. Determine the dissolved-oxygen concentration on an aliquot of the aerated sample by the Alsterberg azide method (Brown and others, 1970, p. 126). If the barometric pressure is known, the dissolved-oxygen concentration of the air-saturated sample can be determined from figures 16 and 17.

6. Pour an aliquot of the aerated sample into a clean 8-ounce plastic bottle. Switch meter to the 0–10 position and insert the sensor in aerated sample. Adjust speed of magnetic stirrer until maximum reading is obtained.

7. With the calibration control, adjust the dissolved-oxygen reading to the value obtained by step 5.

8. Place sensor in the flow chamber (fig. 18). Place the "O" ring over the sensor, being careful not to disturb the membrane. Replace sensor guard and tighten until the "O" ring is depressed very slightly. Place the top on the flow

chamber and gently open the flow control valve. Measure the dissolved-oxygen concentration at about 5–10 minute intervals until a stable reading is obtained. Record the value to the nearest 0.1mg/l.

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