

Collection and Field Analysis of
Unsaturated Zone Ground Water Samples

Technical Detailed Procedure HP-13

NNWSI Project Quality Assurance Program
U. S. Geological Survey

Effective Date 8-29-83

UNCONTROLLED

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Collection and Field Analysis of Unsaturated Zone Ground Water Samples

1.0 Purpose

The purpose of this detailed procedure is to establish methods for the collection, preservation and analysis of ground water samples from unsaturated zone ground water, and to provide for the modification of those methods when necessary.

This procedure is intended to assure the continuing applicability, validity, and accuracy of this aspect of the activity performed for nuclear -waste repository studies of the U.S. Geological Survey (USGS).

2.0 Scope

These procedures shall be followed by all USGS personnel assigned to nuclear-waste repository studies who make such tests and by any contractor performing such tests for the USGS.

3.0 Procedure Modifications

Because the volume of available water found during sampling of the unsaturated zone is highly uncertain, two methods have been provided for several of the sample preservation and field analysis procedures. In sections which present two methods (ie. 4.2.1, 4.2.7, and 4.2.8), the method requiring a limited, small sample volume is presented first and a larger volume procedure follows. The USGS personnel responsible for sampling the unsaturated zone will determine at the time of sampling the procedure to be used based on the volume of sample water available.

If during the course of testing it is deemed necessary by the USGS geochemist to deviate from the approved procedure, the USGS site hydrologist shall be informed and the procedure modification shall be documented. The documentation shall describe the modification, the affected section or sections of the procedure, and be dated and signed by the hydrologist or a USGS designated responsible person.

4.0 Procedure

4.1 Principle

Some properties or constituents in ground water may change dramatically within a few minutes or hours after sample collection. Immediate analysis for certain of these constituents in the field is required if dependable results are to be obtained. Other constituents may be stabilized by preservative treatment. These treatments include refrigeration, the addition of metals such as mercury to minimize chemical changes due to biologic activity, or the addition of acid to prevent the precipitation of metal ions. The development of sophisticated portable field equipment allows for accurate and precise analysis of water for many unstable constituents or properties at the collection site.

4.2 Sample collection and preservation

4.2.1 Filtration

4.2.2 Acidification

4.2.3 Biocide

4.2.4 Stable isotopes of hydrogen and oxygen - D/H and $^{18}\text{O}/^{16}\text{O}$

4.2.5 Stable carbon isotopes $^{13}\text{C}/^{12}\text{C}$

4.2.6 Tritium- ^3H

4.2.7 Carbon-14

4.2.8 Chlorine-36

4.3 Field analyses

4.3.1 Temperature

4.3.2 Specific conductance

4.3.3 pH

4.3.4 Alkalinity

4.3.5 Dissolved oxygen

4.3.6 Eh (oxidation-reduction potential)

4.3.7 Bromide

4.4 Quality control

In order to evaluate the precision of sampling and analytical procedures, both sample replicates and standard samples must be prepared. Replicate samples for lab analysis should be collected by repeating from the beginning of the pertinent procedures. In addition, field determinations should be repeated, also from the beginning, on the same samples selected for lab replicates. Samples to be replicated may be selected on the basis of sample availability, but replicate collection and analysis should be performed on at least 10-20% of the samples collected. Replicates should be assigned unique sample numbers in sequence with actual sample numbers to avoid their recognition by participating labs.

At least ten 'standard samples' of the same water should also be prepared for lab analysis. These 'standards' should bear sample numbers which are interspersed with actual samples and sample replicates in order to minimize the probability that all the 'standards' will be analyzed consecutively. Data from these 'standard' samples will provide information on the reproducibility of analytical determinations on a large number of similar samples over time.

4.5 Reference

- 4.5.1 Wood, W.W., 1976. Techniques of Water-Resources Investigations of the U.S. Geological Survey Book 1, Chapter 02, Guidelines for Collection and Field Analysis of Ground-Water Samples for Selected Unstable Constituents.
- 4.5.2 Brown, E., Skougstad, M. W. Fishman, M. J., 1970. Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A1, Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases.

4.6 Revisions and Modifications

Revision of this procedures is to be expected as significant changes are made.

The use of equipment other than that specified may require minor modifications of the relevant procedures. Refer to manufacturer's instructions when using alternate equipment.

4.7 Sample Field Notes

The following pages have been provided as an example of the type or data to be recorded in the field. In addition, sample calculations are presented. With the possible exception of alkalinity, these calculations are simple enough to be performed in the field. A rough estimate of the alkalinity end point (ie, ml titrant added to reach pH 4.5) will allow for a preliminary determination of alkalinity in the field.

Example Data Sheet for Field
Preservation and Analysis of Unsaturated Zone Waters

Nevada Test Site

10 July 1983

Yucca Mtn. Well UZ-1

Depth interval 500-520'

<u>Time</u>	<u>Temp (°C)</u>	<u>SpC (umhos/cm)</u>	<u>pH</u>
19:04	15.2	850	
19:07	15.5	840	
19:11	15.7	810	
19:14	15.7	810	
19:19	15.8	810	
19:42	15.8	810	7.87
19:45	15.7	810	7.86
19:49	15.7	810	7.87

pH Buffers

Theoretical: 7.44, 9.26, @ 16°C

After measurements: 7.44, 9.26

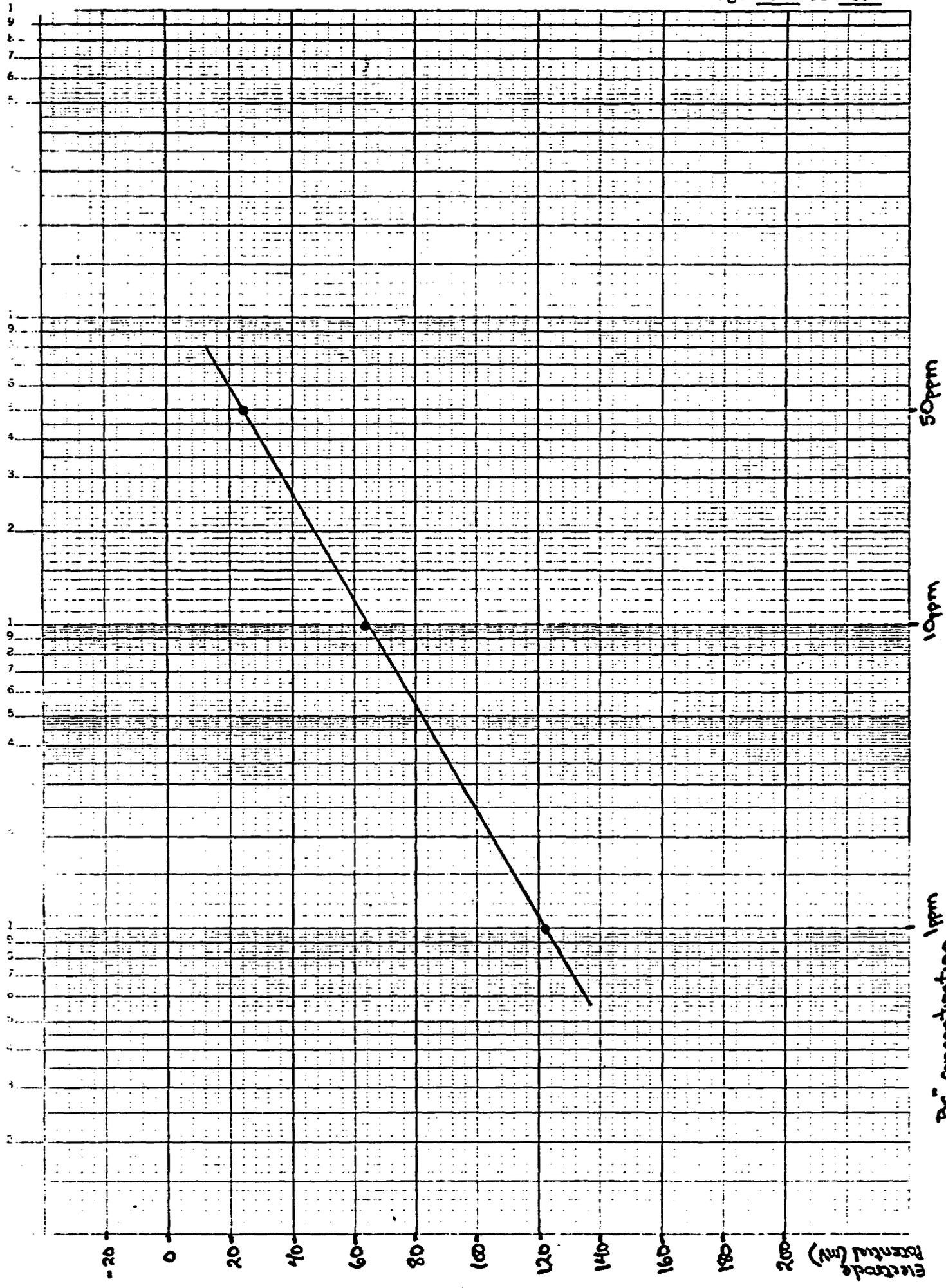
Bromide

1 ppm Br⁻ std: 122 mV

10 ppm Br⁻ std: 64 mV ΔmV = 58 mV

50 ppm Br⁻ std: 25 mV

Sample: 143 mV ie., < 1 ppm Br⁻



50ppm

10ppm

Br⁻ concentration ppm

Electrode Potential (mV)

NO. 11112 SAMPLES TO BE ANALYZED

BY (NAME) (TITLE) (OFFICE)

Samples

0.45 um 500 ml FA

500 ml FU

250 ml FC

50 ml D/H, ¹⁸O/¹⁶O

0.10 um 50 ml FA

Raw 500 ml RU

1000 ml ¹³C/¹²C

2000 ml ³H

(2) 55 gal ¹⁴C

55 gal ³⁶Cl

Water clear, prefilter not needed.

Trace metals filtered thru

0.10 um

500 ml filtered 0.45 um

250 ml filtered 0.10 um

Dissolved Oxygen

DO solubility @ 16°C: 10 mg/l

Correction Factor @4520': 0.84

DO solubility @16°C, 4520': 8.4 mg/l

DO w/Na₂SO₃: 0.1 mg/l

DO measurement: 0.1 mg/l

eg., 0.0 mg/l O₂

Alkalinity

50 ml aliquot

0.01639 N H₂S₄ titrant

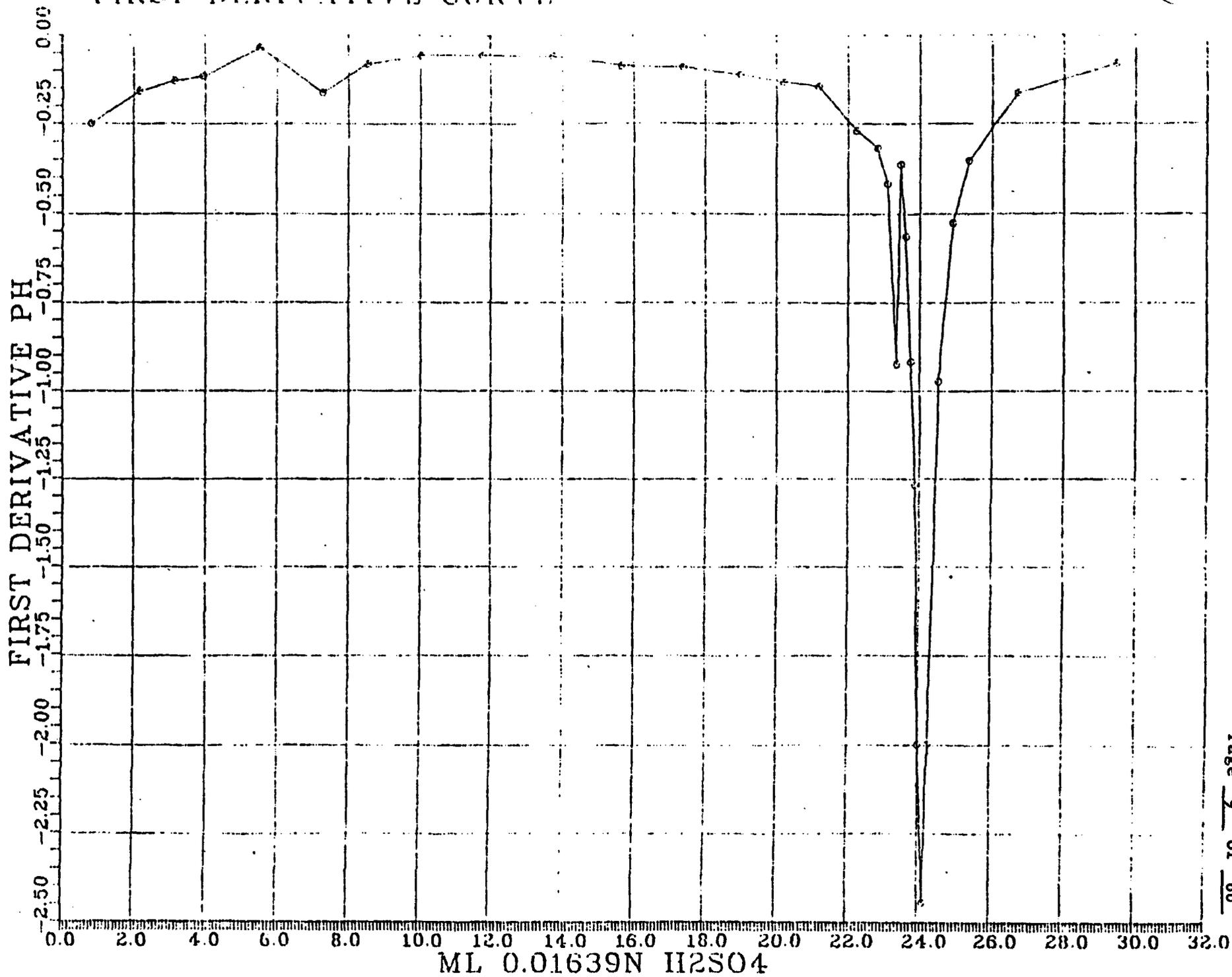
Buret level	pH	ml titrant	pH ml titrant
0.18	7.87	0.00	
1.83	7.46	1.65	-0.25
6.95	7.00	6.77	-0.09
18.41	6.08	18.23	-0.08
20.81	5.79	20.65	-0.12
21.97	5.62	21.79	-0.15
22.90	5.37	22.72	-0.27
23.12	5.30	22.94	-0.32
23.61	5.03	23.43	-0.55
23.72	4.99	23.54	-0.36
23.88	4.90	23.70	-0.56
24.00	4.79	23.82	-1.67
24.15	4.60	23.97	-1.27
24.20	4.50	24.02	-2.00
24.29	4.31	24.11	-2.11
24.38	4.09	24.20	-2.44
24.53	3.79	24.35	-2.00
24.90	3.43	24.72	-0.97
24.90	3.43	24.72	-0.97

← end point: 24.20 ml

$$\frac{1000}{50 \text{ ml}} \times 24.20 = \text{HCO}_3^-$$

$$\text{HCO}_3^- = 484 \text{ mg/l}$$

FIRST DERIVATIVE CURVE



Eh measurement:

$$E_{\text{ZoBell}} + \text{ref} = 450 \text{ mv}$$

$$E_{\text{ZoBell}} (\text{theor}) = 240 \text{ mv}$$

$$E_{\text{ZoBell}} (\text{obs}) = 232 \text{ mv}$$

$$E_{\text{ZoBell}} (\text{theor}) - E_{\text{ZoBell}} (\text{obs}) = 8 \text{ mv}$$

Time	E obs
20:25	260 mv
20:28	80 mv
20:32	-110 mv
20:35	-170 mv
20:38	-170 mv
20:42	-170 mv

$$E_{\text{h sys}} = E_{\text{obs}} + E_{\text{ZoBell}} + \text{ref} - E_{\text{ZoBell}} (\text{obs})$$

$$E_{\text{h sys}} = -170 \text{ mv} + 450 \text{ mv} - 232 \text{ mv}$$

$$E_{\text{h sys}} = 48 \text{ mv}$$

4.2.1 Filtration

1. Principle

Water that appears to be clear may contain considerable amounts of particulate matter in suspension. This is particularly true of water from new wells. The quantity of sediment discharge 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. In samples collected for the analysis of dissolved constituents, particulates must be removed prior to preservation and analysis. Samples collected for analysis of the following constituents need to be filtered in the field:

Ca, Mg, Na, and K
Sr, Li, Si, Fe, Mn, and Al
SO₄, Cl, Br, and I
NO₃, NO₂ and NH₄
D/H, ¹⁸O/ ¹⁶O.

Samples collected for determination of temperature, specific conductance, dissolved oxygen, Eh, pH, ¹³C/ ¹²C or ¹⁴C, should not be filtered.

The 0.45-micrometer porosity membrane 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 less than 0.45 micrometer 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 aluminum, iron and manganese, for example.

The use of 0.1-0.02 micrometer filter membrane may reduce variance of trace metal values between aliquots. The use of these sizes of filter membranes, however, requires considerably more filtration time because of rapid plugging from suspended solids in the sample, and so should be used primarily for filtering trace metal samples (Al, Fe, Mn).

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. A glass prefilter may be used to prevent premature clogging when filtering samples containing large amounts of suspended material. Careful notation of the filters used, volume of water filtered, and the amount and color of suspended material in the sample should be practiced.

2. Equipment needed for small volume sample
 - 2.1 Gelman (# 4280) 200 ml stainless steel pressure filtration funnel, or equivalent.
 - 2.2 Support for filtration funnel.
 - 2.3 Nitrogen (or inert gas) tank with pressure regulator
 - 2.4 Tygon B-44-4X. Clear food and beverage tubing 6.4 mm (1/4") ID, or equivalent.
 - 2.5 Small tubing clamps.
 - 2.6 Millipore membrane filters, or equivalent:
 - 47 mm 0.45 μ m
 - 47 mm 0.1 μ m
 - 2.7 Four polyethelene 50 ml sample bottles with polyseal or polypropylene caps. Bottles and caps should be washed twice inside with double-distilled, reagent grade nitric acid and rinsed with deionized water before use.
 - 2.8 Wash bottle, 500 ml, filled with deionized water.
 - 2.9 Deionized water.
 - 2.10 Ice chest filled with ice.
 - 2.11 Label tape.
 - 2.12 Permanent marker.
3. Summary of Method for small volume sample
 - 3.1 Apply label tape to sample bottles, overlapping ends to ensure adhesion. Write sample identifier, sample type designation and filter pore size on label and in field notes, as summarized in Table 1a.
 - 3.2 Disassemble filtration funnel by unscrewing end caps.

- 3.3 Place selected membrane filter on filter support screen and screw on bottom end cap.
- 3.4 View through filtration funnel to insure that filter is undamaged and properly in place. Secure filtration funnel in support.
- 3.5 Attach pressure tubing to top end cap and secure with small tubing clamp. Attach other end of tubing to pressure regulator and secure with a small hose clamp.
- 3.6 Connect pressure regulator to nitrogen tank.
- 3.7 Pour approximately 50 ml sample water into filtration funnel.
- 3.8 Screw on top end cap.
- 3.9 Open nitrogen tank valve. Slowly engage pressure regulator screw until secondary gage indicates 15-20psig. Check system for leaks and correct if necessary.
- 3.10 Discard first 50 ml of filtrate.
- 3.11 Close nitrogen tank valve and pressure regulator screw. Allow pressurized nitrogen to escape through filter or through side port.
- 3.12 Remove top end cap on filtration funnel and pour in approximately 200 ml sample water. Replace top end cap and place sample bottle under filtration exhaust port.
- 3.13 Open nitrogen tank valve. Slowly engage pressure regulator screw until filtrate begins to flow out of filtration funnel. Do not allow secondary gage to exceed 15-20psig.
- 3.14 Rinse sample bottle and cap three times with filtrate and collect filtered sample. Acidify (4.2.2) or chill samples as required (table 1a).
- 3.15 Repeat 3.12 through 3.14 until sufficient filtered sample has been collected.
- 3.16 Record total volume of water filtered, color of precipitate retained, and porosity of filter used.
- 3.17 After filtration is complete, close nitrogen tank valve and pressure regulator screw. Allow pressurized nitrogen to escape through filter or side port.

- 3.18 Disassemble filtration funnel and remove filter, taking care not to contaminate filter support with sediment caught on the membrane. Rinse filtration funnel with deionized water and allow to dry before reassembly.
4. Equipment needed for large volume sample
 - 4.1 Geotech (#0800) 142 mm backflush filter, or equivalent.
 - 4.2 Geotech Series I (#0740) or Series II (#0760) 115 V AC C-12V DC peristaltic pump, or equivalent.
 - 4.3 Power supply - 12 V DC storage battery or 112 V AC outlet.
 - 4.4 Schleidner & Schuell membrane filters (or equivalent):
 - 142 mm 0.45 nitrocellulose (#BA85)
 - 142 mm 0.10 nitrocellulose (#PH79)
 - 142 mm glass fiber prefilter (#25)
 - 4.5 Small tubing clamps
 - 4.6 Four polyethelene 500 ml sample bottles and one 250 ml sample bottles with polyseal or polypropylene caps. Bottles and caps should be washed twice inside with double distilled, reagent grade nitric acid and rinsed with deionized water before use.
 - 4.7 Deionized water.
 - 4.8 Label tape.
 - 4.9 Permanent marker.
 - 4.10 Ice chest filled with ice.
 - 4.11 500 ml wash bottle filled with deionized water.
5. Summary of method for large volume sample
 - 5.1 Apply label tape to sample bottles, overlapping ends to insure adhesion. Write sample identifier, sample type designation and filter pore size on label and in field notes.
 - 5.2 Disassemble backflush filter by loosening swing-away nuts.
 - 5.3 Place selected membrane filter between the two support screens resting on the bottom plate.
 - 5.4 Re-install top plate and hand tighten swing-away nuts.

- 5.5 Attach intake tubing to intake fitting on top plate using small tubing clamp. (Unit may be stored after use by unscrewing intake fitting rather than disconnecting intake tubing).
- 5.6 Attach approximately 30 cm pump tubing (medical grade silicon) to exhaust fitting on bottom plate using small tubing clamp.
- 5.7 Attach tripod legs to backflush filter.
- 5.8 Insert intake tubing in pump head and connect the pump head to the pump as directed in manufacturers instructions.
- 5.9 Connect pump to power supply.
- 5.10 Connect intake tubing to sample source or insert tubing in unfiltered sample if direct connection is unavailable.
- 5.11 Turn on pump and discard the initial several hundred milliliters of filtrate.
- 5.12 Rinse sample bottle and cap three times with filter effluent and collect filtered sample from exhaust tube. Acidify (4.2.2 or chill samples as required (table 1b)).
- 5.13 Record total volume of water filtered, color of precipitate retained, and porosity of filter used.
- 5.14 After filtering is complete unit should be disassembled and the filter removed, taking care that the lower screen is not contaminated by sediment caught on the membrane filter or upper screen. A clean membrane should be stored between the screens to prevent contact of the soiled upper and clean lower screens. Accidental interchange of upper and lower filter screens should be avoided.
- 5.15 Thorough cleaning of the filter plate with deionized water is required before storage.

Table 1a.--Summary of Small Volume Sample Requirements

Determinations	Sample size [*] / Container	Filter pore size	Preservation procedure	Designation
Ca, Mg, Na, K Li, Sr	50ml/ polyethelene, polyseal cap	0.45 μm	Acid rinse sample bottle and cap; acidify	FA
Si, Al, Fe, Mn	50ml/ polyethelene, polyseal cap	0.10-0.02 μm	Acid rinse sample bottle and cap; acidify	FA
SO ₄ , Cl, Br, I	50ml/ polyethelene, polyseal cap	0.45 μm	Acid rinse sample bottle and cap	FU
NO ₃ , NO ₂ , NH ₄	50ml/ polyethelene, polyseal cap	0.45 μm	HgCl ₂ tablet; chill and dark	FU
Alkalinity, pH (lab)	50ml/ polyethelene, polyseal cap	Unfiltered	Chill and dark	RO
D/H, ¹⁸ O/ ¹⁶ O	50ml/ glass, polyseal cap	0.45 μm	HgCl ₂ tablet	D/H, ¹⁸ O/ ¹⁶ O
¹³ C/ ¹² C, ¹⁴ C	1000ml/ glass, polyseal cap	Unfiltered	HgCl ₂ tablet; seal with paraffin	¹³ C/ ¹² C, ¹⁴ C
³ H	2000ml/ glass, foil- lined metal screw cap	Unfiltered	Secure cap with electrical tape	LC 0460
³⁶ Cl	2000ml/ polyethelene, polyseal cap	Unfiltered	None	³⁶ Cl

*Absolute minimum volumes required for analysis are as follows:
 Ca, Mg, Na, K, Li, Sr: 20ml
 Si, Al, Fe, Mn: 20ml
 SO₄, Cl, Br, I: 15ml
 Alkalinity, Ph: 20ml
 NO₃, NO₂, NH₄: 10ml
¹³C/¹²C, ¹⁴C: 500 ml
 D/H, ¹⁸O/¹⁶O: 15 ml

Table 1b.--Summary of Large Volume Sample Requirements

Determinations	Sample size/ container	Filter pore size	Preservation procedure	Designation
Ca, Mg, Na, K, Li, Sr	500ml/ polyethelene, polyseal cap	0.45 μ m	Acid rinse sample bottle and cap; acidify	FA
Si, Al, Fe, Mn	500ml/ polyethelene, polyseal cap	0.10-0.02 μ m	Acid rinse sample bottle and cap; acidify	FA
SO ₄ , Cl, Br, I	500ml/ polyethelene, polyseal cap	0.45 μ m	Acid rinse sample bottle and cap;	FU
NO ₃ , NO ₂ , NH ₄	250ml/ polyethelene, polyseal cap	0.45 μ m	HgCl ₂ tablet; chill and dark	FC
Alkalinity, pH	500ml/ polyethelene, polyseal cap	Unfiltered	Chill and dark	RU
D/H, ¹⁸ O/ ¹⁶ O	50ml/ glass, polyseal cap	0.45 μ m	HgCl ₂ tablet	DH, ¹⁸ O/ ¹⁶ O
¹³ C/ ¹² C	1000 ml/ glass, polyseal cap	Unfiltered	Ammoniacal strontium chloride reagent	¹³ C/ ¹² C
³ H	2000ml/ glass, foil-lined metal screw cap	Unfiltered	Secure cap with electrical tape	LC 0460
¹⁴ C	55 gal/ plastic-lined steel drum	Unfiltered	Precipitate inorganic carbon; collect precipitate	¹⁴ C
³⁶ Cl	55gal/ plastic-lined steel drum	Unfiltered	None	³⁶ Cl

4.2.2 Acidification

1. Principle

Ultra pure nitric acid is added to freshly collected samples in order to lower the pH to a value of 2.0 or less and thereby minimize oxidation, precipitation and sorption of dissolved constituents. Acidification is required for samples to be analyzed for major cations and trace metals only (i.e. Ca, Mg, Na, K, Sr, Li, Fe, Mn, Al).

2. Equipment needed

2.1 Double-distilled, reagent grade nitric acid.

2.2 50ml polyethylene or Teflon dropping bottle.

3. Summary of method

The acid may be conveniently transported in 50ml dropping bottles which have been acid washed prior to filling. The high purity nitric acid should be added to the sample bottles to be acidified after several milliliters of the filtered sample water have been collected. Usually 2 ml acid for each liter of sample is sufficient. Care must be taken to avoid contaminating the acid dropping bottle.

If contamination is suspected, the acid and the dropping bottle should be replaced.

4.2.3 Biocide

1. Principle

The percentage concentrations of the various components of the nitrogen cycle may change rapidly as a result of biologic activity. Mercuric chloride inactivates organisms present in the sample and thereby fixes nitrogen cycle components. It is also desirable to keep samples chilled (0-4°C) and dark until analyzed.

2. Equipment needed

2.1 HgCl₂ tablets - 10 mg Hg Cl₂ in a NaCl base (available from Central Lab).

2.2 Label tape.

2.3 Permanent marker.

3. Summary of Method

3.1 Apply label tape to sample bottle, overlapping ends to ensure adhesion. Write sample identifier, sample type designation and filter pore size on label and in field notes.

3.2 Collect filtered sample for nitrogen analysis.

3.3 Add 1 HgCl₂ tablet for each 250 ml sample water. Tablets may be divided for small samples if necessary.

3.4 Cap sample bottle.

3.5 Store sample in ice chest until analysis.

4.2.4 D/H and $^{18}\text{O}/^{16}\text{O}$

1. Principle

Different isotopic forms of water arising from the incorporation of naturally formed deuterium (^2H or D) and oxygen-18 into the H_2O molecule exhibit slightly different vapor pressures and freezing points. Because natural waters contain a mixture of isotopic forms ($^1\text{H}_2\ ^{16}\text{O}$, $^1\text{H}\ ^2\text{H}\ ^{16}\text{O}$, $^2\text{H}_2\ ^{16}\text{O}$, $^1\text{H}_2\ ^{18}\text{O}$, $^1\text{H}^2\text{H}^{18}\text{O}$, $^2\text{H}_2\ ^{18}\text{O}$, etc), the bulk isotopic composition will change as a result of evaporation, condensation, freezing, melting, or chemical and biological reactions in a process known as isotopic fractionation. The effects of isotopic fractionation are such that strong regional trends are observed in the isotopic composition of natural precipitation. These regional isotopic trends can be correlated to latitude, altitude, distance inland and season so that the stable oxygen and hydrogen isotopic composition of shallow ground waters may be used to infer conditions at the time of recharge. In ground water systems at higher temperatures, however, stable isotopic composition of water changes characteristically in response to exchange reactions with aquifer minerals, and no longer bears the isotopic ratio of the recharge water.

2. Equipment needed

- 2.1 50 ml glass sample bottle with polyseal cap.
- 2.2 HgCl_2 tablets - 10 mg HgCl_2 in a NaCl base (available from Central Lab).
- 2.3 Label tape.
- 2.4 Permanent marker.

3. Summary of Method

- 3.1 Apply label tape to sample bottle, overlapping ends to ensure adhesion. Write sample identifier, sample type designation and filter pore size on label and in field notes.
- 3.2 Rinse the sample bottle three times with filtered ($0.45\ \mu\text{m}$) water.

- 3.3 Fill the bottle to the shoulder with filtered (0.45 μm) sample, leaving a small air space.
- 3.4 Add one HgCl_2 tablet.
- 3.5 Cap tightly with Polyseal cap. If polyseal caps are unavailable, the cap may be sealed by wrapping with electrical tape and dipping the inverted bottle up to the shoulder in melted paraffin.

4.2.5 Stable carbon isotopes - $^{13}\text{C}/^{12}\text{C}$

1. Principle

Water may contain a number of dissolved inorganic carbon species including bicarbonate(HCO_3), carbonate(CO_3), carbonic acid(H_2CO_3), carbon dioxide (CO_2), and others. Addition of ammoniacal strontium chloride reagent causes precipitation of the carbonate species, allowing for storage of the sample prior to analysis of the stable carbon isotopic composition of the sum of these species.

2. Equipment needed

- 2.1 One liter glass sample bottle with polyseal cap.
- 2.2 50 ml capacity plastic syringe. Attach approximately 15cm of Tygon tubing to tip. A volumetric pipet and pipet bulb may also be used.
- 2.3 Ammoniacal strontium chloride hexahydrate solution: Dissolve 450g of reagent grade $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ in 1800g concentrated reagent grade NH_4OH . Allow the solution to remain undisturbed for 2 days. Decant the clear solution into glass field reagent bottles and seal tightly. Solution is stable for several years as long as it is kept tightly sealed thereby preventing contamination with atmospheric CO_2 .
- 2.4 Label tape.
- 2.5 Permanent marker.

3. Summary of Method

- 3.1 Apply label tape to sample bottle, overlapping ends to ensure adhesion. Write sample identifier and sample type designation on label and in field notes.
- 3.2 Rinse sample bottle and cap three times with sample water.
- 3.3 Fill sample bottle to about 90% of capacity with unfiltered sample water.
- 3.4 Rinse syringe and Tygon tubing with approximately 10 ml ammoniacal strontium chloride solution and discard rinse.

- 3.5 Add 50 ml ammoniacal strontium chloride solution to sample bottle.
- 3.6 Cap bottle tightly with polyseal cap. If polyseal caps are unavailable, the cap may be sealed by wrapping with electrical tape and dipping the inverted sample bottle up to the shoulder in melted paraffin.

4.2.6 Tritium - ^3H

1. Principle

Prior to the advent of atmospheric thermonuclear tests in 1953, tritium (^3H) was derived entirely from the natural process of nitrogen transmutation caused by the bombardment of cosmic rays, resulting in concentrations on the order of 10 tritium units (TU; 1TU = 1 ^3H atom in 10^{18} ^1H atoms). Because tritium is a radioactive isotope with a half life of only 12.3 years, water recharged before 1953 should now have tritium concentrations on the order of 2 to 4 TU. Waters recharged after 1953, however, can be expected to have tritium concentrations on the order of hundreds or thousands of TU. High tritium concentrations can therefore be used as an indicator of recently recharged modern water or as a tracer of mixing or leakage of such modern waters into older waters.

2. Equipment needed

- 2.1 Two 1 liter glass sample bottles with non-porous, metal screw caps. Caps should be lined with aluminum foil.
- 2.2 Black plastic electrical tape.
- 2.3 Tygon tubing - 30 cm.
- 2.4 Label tape.
- 2.5 Permanent marker.

3. Summary of Method

- 3.1 Apply label tape to sample bottles overlapping ends to ensure adhesion. Write sample identifier and sample type designation on label and in field notes.
- 3.2 Attach tygon tubing to sampling point in flow line.
- 3.3 Rinse sample bottle and screw cap three times with unfiltered sample water.
- 3.4 Insert tubing from which sample water is flowing to bottom of sample bottle. Allow bottle to fill and then overflow for 15 to 20 seconds.
- 3.5 Withdraw tubing from sample bottle slowly, then cap tightly.
- 3.6 Secure cap with electrical tape.

4.2.7 Carbon-14

1. Principle

Prior to the advent of large thermonuclear tests in 1953, ^{14}C in the global atmosphere was derived entirely from the natural process of nitrogen transmutation caused by bombardment of cosmic rays. Oxidation to CO_2 occurs quickly, followed by mixing with the atmosphere CO_2 reservoir and incorporation in natural water systems as dissolved inorganic carbon. Because the radioactivity of ^{14}C decreases characteristically with time, the apparent time that a ground water sample has been isolated from the atmosphere can be readily calculated if the ground-water has not received carbon from other sources.

Collection of samples for radiocarbon analysis involves either the collection of a sample and the isolation from atmospheric CO_2 , or the precipitation of the dissolved inorganic carbon present in a sample and subsequent collection of the precipitate with as little exposure to the atmosphere as possible.

2. Equipment needed for small volume sample

- 2.1 Glass sample bottle, 1 liter, with polyseal cap.
- 2.2 HgCl_2 - 10 mg HgCl_2 in a NaCl base.
- 2.3 Paraffin.
- 2.4 Small aluminum saucepan.
- 2.5 Electric hot plate.
- 2.6 Label tape.
- 2.7 Permanent marker.
- 2.8 Tygon tubing - 30 cm

3. Summary of method for small volume sample

- 3.1 Apply label tape to sample bottle, overlapping ends to ensure adhesion. Write sample identifier and sample type designation on label and in field notes.
- 3.2 Attach tygon tubing to sampling point in flow line.
- 3.3 Rinse sample bottle and cap three times with unfiltered sample water.

- 3.4 Fill sample bottle with unfiltered sample water by inserting tygon tube to the bottom of the bottle. Keep the end of the tube below the surface of the water to avoid aeration of the sample.
- 3.5 Allow water to overflow the sample bottle for 15 to 20 seconds.
- 3.6 Slowly withdraw tubing.
- 3.7 Add one HgCl_2 tablet and cap bottle.
- 3.8 Melt paraffin and dip inverted bottle up to the shoulder to seal.
4. Equipment needed for large volume sample
 - 4.1 3 plastic-lined 55 gallon drums.
 - 4.2 C-14 precipitator and connecting hoses.
 - 4.3 pH meter and combination electrode.
 - 4.4 pH 7 and pH 10 buffers.
 - 4.5 50 ml glass beakers
 - 4.6 2 small mouth, 2 qt. glass ball or Mason jars.
 - 4.7 8 liters 12N HCl
 - 4.8 Deionized water
 - 4.9 Garden hose with spray head; water supply.
 - 4.10 Nitrogen tank with two-stage regulator and connecting hoses.
 - 4.11 Barium chloride/lanthanum chloride reagent (two 2 liter aliquots required per sample): Boil for ten minutes enough deionized water to make the desired amount of solution. Add 580 g reagent grade BaCl_2 and 10 g reagent grade LaCl_3 to a polyethelene bottle for each 2 liter aliquot desired. Pour 2 liters boiling deionized water into each bottle and cap the container to provide an airtight seal. Shake to dissolve salts and add 5 ml clear NaOH reagent (4.12, below). Allow to stand covered overnight or longer until precipitate has settled. Decant supernatant and store in air-tight bottles. NOTE: Prepare only enough solution for use in several days.

- 4.12 Sodium hydroxide reagent (500 ml sufficient for approximately three samples): Boil for ten minutes enough deionized water to yield 500 ml. Pour boiling water into a pyrex container, seal and cool. Place a magnetic stir bar in the container, and add 200 g reagent grade NaOH pellets in 5 g increments, stirring until each 5 g addition has dissolved. Add 5 ml clear $\text{BaCl}_2/\text{LaCl}_3$ reagent (4.11, above). Allow to stand covered overnight or longer until precipitate has settled. Decant supernatant and store in an air tight bottle. NOTE: If NaOH pellets appear glossy and adhere firmly to each other, discard and use fresh pellets. Mix fresh solution monthly.
5. Summary of method for large volume sample.
- 5.1 Before sampling, rinse drums thoroughly with tap water. Add approximately 20 gallons tap water and 2 liters 12N HCl to each drum. Remember, ALWAYS ADD ACID to water. Cap the drums and roll for several minutes to allow cleaning solution to contact all sides of the liner. Drain and properly dispose of the acid solution. Rinse drums with tap water for 10 minutes by inserting garden hose and spray head into inverted drum. If water pressure is not available, fill drums with approximately 20 gallons tap water, roll and drain; repeat this rinse three times. Drain tap water from barrels. Add 5 gallons deionized water in each barrel, roll and drain.
- 5.2 Cap large hole in drum securely. Insert open N_2 line into small hole and allow to drop to bottom of drum. Open regulator to 20 psi and flush drum with approximately 30 cubic feet of N_2 (ie. 270 psi change in tank pressure). Close regulator, remove N_2 line and close drum securely.
- 5.3 After temperature, specific conductance and pH have stabilized at the sample site, connect garden hose to sampling line. Rinse the cover of the hose and insert

the hose into a clean barrel. Allow hose to drop to the bottom of the drum to minimize aeration. Note time required to fill drum and allow sample water to overflow the top of the drum for that time. Remove hose and tightly cap the drum. Repeat for remaining two drums if sufficient sample is available.

- 5.4 Store drums indoors until the samples can be precipitated. If possible begin precipitation by the day after collection.
- 5.5 Fill the precipitator with clean tap water. While stirring, add 12N HCl until the pH of the solution drops below 2 when measured 5 minutes after the last addition of acid. Stir ten minutes more and drain.
- 5.6 Rinse precipitator thoroughly with tap water and allow to drain for 5 minutes. Repeat tap water rinse.
- 5.7 If three barrels of sample water have been collected, use one barrel to rinse precipitator a third time. If excess sample water is unavailable, rinse a third time with 5 gallons deionized water. Allow to drain for 5 minutes.
- 5.8 Firmly screw an empty Mason jar into bottom of precipitator and fully open butterfly valve.
- 5.9 Close all top ports, leaving only lower sample spigot open slightly. Allow approximately 40 cubic feet of N₂ to enter the precipitator through the quick connect fitting (40 cu. ft. \approx 360 psi change in pressure). Close sample spigot and butterfly valve.
- 5.10 Remove bungs from one barrel of sample water and replace with garden hose and pressure line fittings. Connect pressure line to N₂ regulator and garden hose to top of precipitator. Set N₂ regulator to 10 psi to fill precipitator with sample. When sample has been removed from drum, disconnect hose at precipitator and plug hose fitting on precipitator. Close N₂ regulator.

- 5.11 Disconnect N₂ line from drum and connect to top of precipitator. Open regulator and adjust to minimum flow. Turn on stirrer.
- 5.12 Add 2 liters BaCl₂/LaCl₃ reagent.
- 5.13 Turn on heater.
- 5.14 Add NaOH reagent in 5 ml increments 10 minutes apart until the pH of the sample reaches 10. Measure pH using a pH meter calibrated with pH 7 and 10 buffers. Draw 100-200 ml sample from the spigot at the bottom of the precipitator and discard. Collect 50 ml sample water from spigot for pH measurement between additions of NaOH reagent.
- 5.15 Allow approximately four hours for the precipitator temperature to reach 70-80°C. The precipitator will automatically shut off when this temperature is reached.
- 5.16 Turn off valve, allowing precipitate to settle into the Mason jar for approximately one hour. Tap the sides of the precipitator with a mallet or one's hand to release any clinging precipitate.
- 5.17 Turn on stirrer for no more than 3 seconds and allow precipitate to settle for an additional half hour.
- 5.18 Close butterfly valve. Remove collection jar, cap tightly and label with sample identifier and sample type designation.
- 5.19 Drain precipitator and repeat steps 5.8 - 5.18 for second barrel of sample water.
- 5.20 Clean precipitator by repeating steps 5.5 - 5.6.

4.2.8 Chlorine - 36

1. Principle

Chlorine - 36 is produced continually in the atmosphere by bombardment of ^{40}Ar by cosmic rays and by activation of chlorine at the soil surface by secondary neutrons of cosmic ray genesis. In addition, ^{36}Cl is also produced in the atmosphere during thermonuclear explosions. ^{36}Cl is quickly reduced to chloride and incorporated in natural water systems. Because chloride behaves as a conservative constituent in many ground water systems, and because of negligible production of the isotope in most sub-surface environments, measurement of ^{36}Cl in ground water samples may provide a useful tool in the attempt to age date ground waters.

2. Equipment needed for small volume sample

2.1 Two 1 liter polyethelene or glass sample bottles with polyseal caps.

2.2 Label tape.

2.3 Permanent marker.

3. Summary of method for small volume sample

3.1 Apply label tape to sample bottles, overlapping ends to ensure adhesion. Write sample identifier and sample type designation on label and in field notes.

3.2 Rinse the sample bottles and caps three times each with unfiltered sample water.

3.3 Fill the bottles to the shoulder with unfiltered sample, leaving a small air space.

3.4 Cap tightly with polyseal cap.

4. Equipment needed for large volume sample

4.1 Plastic-lined 55 gallon steel drum.

4.2 Label tape.

4.3 Permanent marker.

5. Summary of method for large volume sample

5.1 Apply label tape to steel drum. Write sample identifier and sample type designation on label and in field notes.

- 5.2 Thoroughly rinse drum and screw plug with unfiltered sample water.
- 5.3 Fill drum with unfiltered sample water.
- 5.4 Cap tightly with screw plug.

4.3.1 Temperature

1. Principle

Temperature is recorded by a mercury-filled thermometer that is permitted to equilibrate in a sample that is continuously pumped into a Dewar flask or other suitable, large volume container. In order to ensure a representative sample the well should be pumped continuously until three identical consecutive readings of temperature are obtained. The most accurate readings are obtained when ambient temperature is within 20°C of the ground water temperature. New 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 equilibrium of water temperature in the casing and pump column will also cause drifting of the temperature.

2. Equipment needed

2.1 Calibrated partial immersion thermometer graduated in 0.1 C or 0.2 F with the range of 0-50°C, or any range expected in the ground water in the study area. Partial immersion thermometer should have etched line indicating depth of immersion to be used. The thermometer should be accurate to $\pm 0.1^\circ\text{C}$ as checked against a NBS calibrated thermometer.

2.2 1 liter Dewar flask

3. Summary of Method

Measure temperature as close to the well head as possible by immersing thermometer in the flow line to immersion depth mark and reading directly after bulb has time to equilibrate. At high discharge this may not be possible, so temperature is measured in a large (approximately 1 liter) sample collected in a Dewar flask. Record time and temperature in field notes after each reading. Continue measurements until 3 consecutive readings are identical ($\pm 0.03^\circ\text{C}$).

4.3.2 Specific Conductance

1. Principle

The specific conductance of a water sample is a measure of its ability to carry an electrical current, and is an indication of the concentration of dissolved solids in the water.

The field determination of specific conductance can be used as an aid in evaluating whether a sample is representative of water in the aquifer. Specific conductance determinations can also 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 drilling fluid, or leakage from the formation that contains water of different quality. Detection of an anomaly may indicate that more detailed sampling or reevaluation of the well is required. The specific conductance of a sample may change with time as a result of exposure to atmospheric conditions once it has been removed from the aquifer. It, therefore, is essential to obtain an accurate field determination.

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 1000 micromhos/cm. As specific conductance increases to above 5000 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.

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 ensure that the value is read in the field. This procedure is meant to supplement any manufacturers instructions.

2. Equipment needed

- 2.1 Lab-line Lectro Mho-Meter with the cell constants of 0.1 and 1.0, or an equivalent direct-reading meter.
- 2.2 Calibrated thermometer, 0-50° graduated in 0.1°C.
- 2.3 0.00702 N potassium chloride standard solution, prepared by dissolving 0.5234 g of reagent grade KCl (dried at 180° for 1 hour) in distilled water and diluted to exactly 1 liter. This solution has a specific conductance of 1000 micromhos/cm at 25°C, or equivalent.

3. Summary of Method

- 3.1 To check the calibration and operation of this instrument, turn the range selector to "test". Note that a balance occurs precisely at the central scale division 1.0 when the "Press" button is depressed.

With the cell disconnected and range selector on any measuring scale, check to see that the balance indicator shows full scale deflection when the "Press" button is depressed. Partial deflection and indecisive balance indicates that the battery should be replaced. Only use an "EverReady" type 266, 9 volt Battery, or an approved equivalent.

Set temperature control on the instrument at 25°C, and record the ambient temperature of the standard KCl solution. Check cell before initial use and check daily during regular use. Clean the measuring cell thoroughly and rinse with distilled water

or KCl solution. Fill the measuring cell with KCl solution and plug the connecting cable into the "measuring cell" socket. Hold the "Press" button down and slowly rotate the measuring dial until the balance indicator moves to center scale. Read the dial scale at which this occurs and multiply by the range factor. Compare this value with the values given in figure 1. The value obtained should be within 5% of that in figure 1. Move the temperature adjust knob to the ambient temperature and read meter (only the 10^3 scale is temperature compensated!). The value obtained should be 1000 micromhos/cm, regardless of the ambient temperature. This step 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. Carbon-type electrodes need no platinizing and should be replaced if they fail to perform to the specified accuracy.

- 3.2 To measure the specific conductance of the sample, begin with several volumes of sample water. Immerse measuring cell in large container filled with water from well discharge for at least 5 minutes to bring the cell temperature to that of the water to be measured.
- 3.3 Fill the measuring cell with fresh sample and plug cable into the "measuring cell" socket. Set temperature the temperature dial to the temperature of the sample and turn the selector switch to the anticipated range of measurement. Remember only the 10^3 scale is temperature compensated. Hold the "Press" button down and slowly rotate the measuring dial until the balance indicator moves to center scale. Read the dial setting at which this occurs and multiply by the range factor. The result is the specific conductance of the sample in micromhos/cm at 25°C.

- 3.4 Record reading temperature, time, date, cell constant, and meter constants.
- 3.5 Repeat step 3.3 with fresh sample until reproducible reading are obtained.

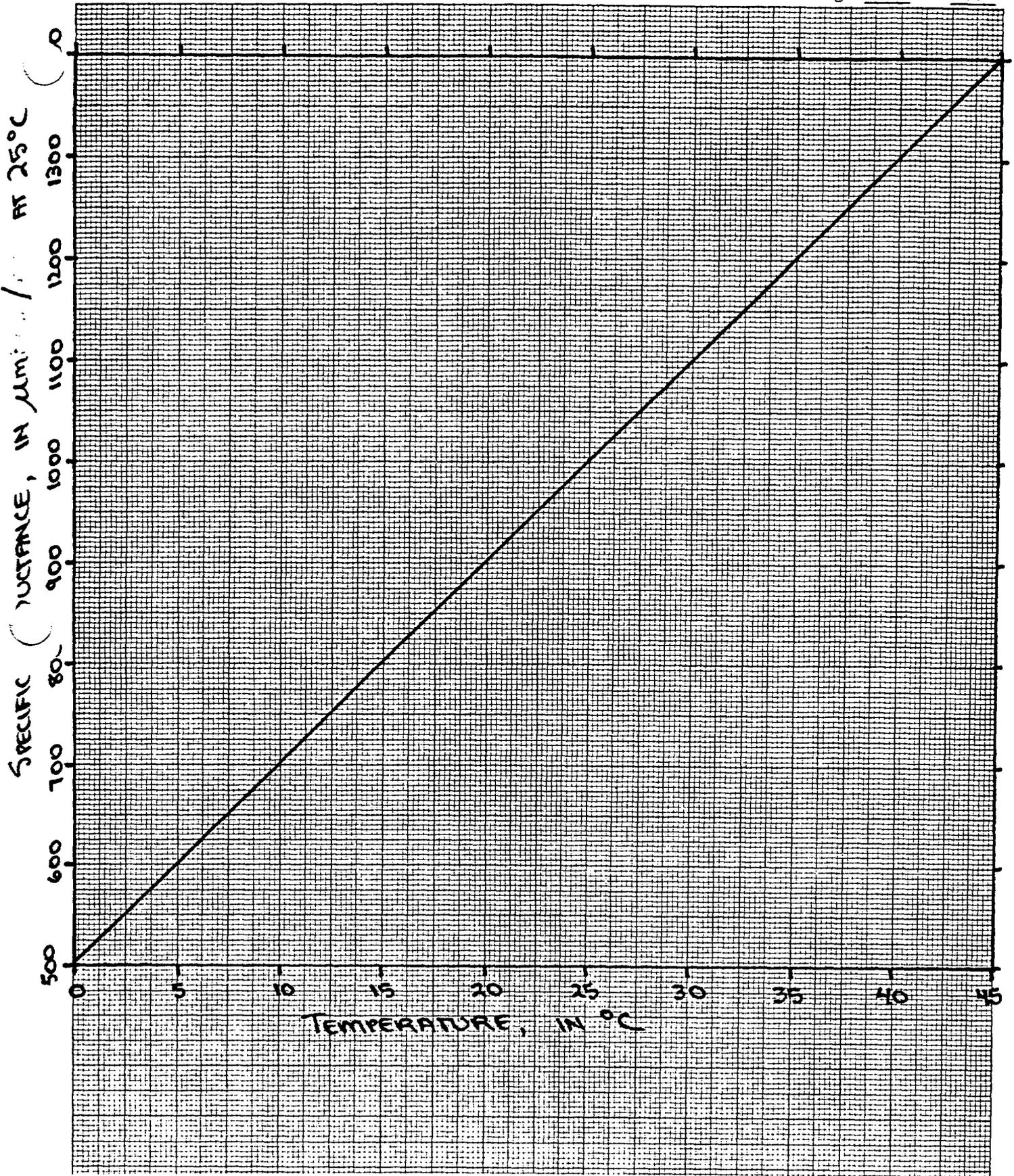


Figure 1. Specific conductance of a 0.00702 N KCl solution as a function of temperature.

4.3.3 pH

1. Principle

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

$$\text{pH} = - \log [a^{\text{H}^+}]$$

In aqueous solutions, pH is controlled by reactions that produce or consume H⁺, including practically all dissolution and hydrolysis reactions. The primary control over pH in most potable ground water is the carbonate system, although other dissolved species, such as hydrogen sulfide and ammonia, can also affect the pH of the solution.

The pH is determined with a glass hydrogen ion membrane 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. Because pH is exponentially related to concentration, great care must be exercised in making a measurement.

A high sodium content will give an anomalous pH reading, which must be corrected according to the recommendation of the manufacturer of the pH electrode. Measurement of pH is temperature sensitive, so the standard buffers should be within ±1°C of the sample solution for precise determinations.

2. Equipment required

- 2.1 Orion 399 A/F pH meter or equivalent. An expandable scale is necessary for detailed work of ±0.005 pH units.
- 2.2 Orion-Ross combination pH electrode or equivalent. Spare electrodes desirable.
- 2.3 pH buffer solutions 4.01, 6.86, 7.41, 9.18 and 10.4 in 100 ml containers. (Buffers should be prepared fresh regularly by dissolving Fisher Scientific Dry Buffer Salts in deionized water and diluting to 1 liter in a volumetric flask.)
- 2.4 Filling solution for reference electrode.
- 2.5 Plastic pail.

- 2.6 Calibrated thermometer.
- 2.7 Deionized water.
- 2.8 500 ml plastic squeeze wash bottle for distilled water.
- 2.9 Small box of Kimwipes or equivalent.
- 2.10 Three small beakers.
- 2.11 One small glass Erlenmeyer flask.

3. Method

- 3.1 Check and fill the combination electrode with internal filling solution recommended by the manufacturer.
- 3.2 Select two buffer solutions bracketing the expected pH of the water sample. Generally the 6.86 and 7.41, or the 7.41 and 9.18 buffers will be appropriate. Adjust the buffer solutions to near the sample temperature by immersing the bottles in a pail of sample water. To prevent floating the partially-filled buffer bottles, heavy steel washers may be epoxied to the bottom of the bottles.
- 3.3 Record the water temperature after both temperature and specific conductance have stabilized.
- 3.4 Set up and level the pH meter in the shade and check to insure that the needle is properly adjusted.
- 3.5 Rinse electrode with deionized water.
- 3.6 Place the lower pH buffer in a beaker and place the electrode into the buffer. Set the temperature dial to the temperature on the buffer and set the slope bezel to 100%.
- 3.7 Turn on the meter and adjust the calibration knob to the correct pH value. The pH of the buffer solution varies with temperature, so it is necessary to refer to the temperature pH curve supplied with the buffer (figures 2-5) in order to determine the actual pH at the operating temperature. Record the theoretical pH of the buffers used in field notes. If the electrode has not been used recently, or has been allowed to dry for several days, it may take 10-20 minutes or

longer for it to stabilize. (Electrodes should be hydrated for at least 24 hours before use. If the electrode will not stabilize, try a new pH electrode. To keep the electrode from drying out and ready for use, the electrode tip should be immersed in a rubber or plastic sack in which has been placed a few milliliters of deionized water with a few drops of filling solution and pH 6.86 buffer added.)

- 3.8 Turn meter to the standby position and remove the electrode from the lower pH buffer. Remember to always have the meter on standby when the probe is out of fluid, otherwise the electrode can be easily polarized.
- 3.9 Rinse the electrode thoroughly with deionized water and then with a small amount of the next buffer.
- 3.10 Place the electrode into the higher pH buffer, bracketing the expected pH of the sample.
- 3.11 Switch on the meter and allow several minutes for stabilization to occur before making final adjustments.
- 3.12 Make any final adjustments necessary by turning the temperature (slope) knob then turn slope bezel so that the temperature knob indicates the actual temperature of the buffer.
- 3.13 Turn the meter to the standby position.
- 3.14 Check the adherence of the response of the electrode to the theoretical Nernst slope. On the Orion meter this is simply the percent slope value read off the slope bezel. To check the response on other meters you must measure the potential of each buffer and calculate the actual slope using the Nernst equation.
- 3.15 If the observed percentage is less than 92% on the slope bezel, the electrode would be replaced and the slope rechecked by repeating steps 3.5 - 3.14. Comparison of electrode response to the theoretical response is a check of the efficiency of the electrode system. The lack of agreement between the observed

electrode system and the Nerst equation does not indicate that the observed pH values are incorrect.

All that is indicated is a potential source of trouble and that some part of the system is not operating as efficiently as it should.

- 3.16 Rinse the electrode with distilled water and then with the lower pH buffer solution. Recheck the value of the lower pH buffer by placing the electrode in the buffer solution and switching the meter on. If drift from the original setting has occurred, repeat steps 3.5 - 3.16.
- 3.17 Special care is in order when using the expanded scale on Orion meters. These scales, covering only 2.8 pH units, are designed to be calibrated, at any pH value, on the middle pH unit mark and then sloped up or down, a maximum of 1.4 pH units. Since it may be difficult to closely anticipate in advance the pH of a sample in the field, it is common practice to calibrate on one of the scale's end pH marks and slope up to 2.4 units across the entire scale. This procedure very often results in a Nernst slope of less than 92% of the theoretical slope after standardizing on the second buffer. This is because the circuits are designed to fix the calibration voltage in the middle of the scale and to slope (i.e. adjust the temperature potentiometer) the second voltage at either end of the scale. When this is the case, it is necessary to standardize a second time but instead of calibrating with the slope scale initially on 100%, calibrate the first buffer with the slope scale equal to its value at the end of the first standardization plus one-half the deviation from 100%. In other words, split the difference between 100% and the final slope at the end of the first standardization attempt, and begin

the second standardization with that value proceeding as in 3.5 - 3.15. This has the effect of having the error caused by calibrating with your first buffer at an end pH value instead of at the middle value. Calibrate on the first buffer with this half-the-difference slope reading, and when sloping to the second buffer, very little correction on the temperature knob is usually required.

If the final percentage on the slope bezel is still less than 92% at the end of the second standardization attempt, it is time to look to other parts of the system (i.e. change electrodes) for causes of error, and to start over.

- 3.18 Thoroughly rinse the electrode with sample water and place it in a fresh sample aliquot that has been collected in a glass beaker. Be sure the nylon junction tip or the ground glass junction port is just below the water level in the flask. This beaker may be placed in a container of sample water to reduce temperature change during the measurement.
- 3.19 Turn on meter. Do not swirl or stir sample.
- 3.20 Allow one minute for equilibration. Record the time and pH value to the nearest 0.01 unit.
- 3.21 Turn meter to standby position.
- 3.22 Repeat steps 3.18 - 3.21, using newly collected samples, if available, until three consecutive readings differ by no more than ± 0.02 pH unit. If equilibrium is not attained in several minutes, outgassing of CO_2 may be occurring. Out gassing may be reduced if the electrode system is placed through a tightly fitting stopper into a sample-filled flask. In such cases the initial reading from step 3.22 may be the best.
- 3.23 Thoroughly rinse electrode with deionized water.
- 3.24 Immediately after completing the measurement, rinse electrode with lower pH buffer, insert electrode into temperature equilibrated buffer, and wait for equilibration as described in 3.20 and record the value.

Thoroughly rinse the electrode with deionized water, then with a small amount of the second buffer.

- 3.25 Place the electrode in the second buffer, turn on the meter, wait for equilibration, and record the value.
- 3.26 If the buffers are reading more than ± 0.02 pH units different from the value the manufacturer's temperature curve, drift has occurred during the measurement. If the cause of the drift can be identified in the system, it should be rectified (for example, replace the electrode if it will not yield a stable buffer reading), and the measurement repeated. If the cause can not be pinpointed (for example, external temperature fluxuations causing different electronic response) the measurement can be corrected for the amount of drift that has occurred. The corrected reading is simply the measurement reading changed proportionally to reflect the drift of the two buffers readings, and weighted to reflect the nearness of the measurement reading to both of the standardization points.

If during readings a static charge builds on the plastic pH meter face causing erratic meter movement, antistatic spray may be sprayed on the meter face to minimize interference. Keep the meter protected from extreme temperature changes during measurements, as this will affect the stability of the electronic system and consequently the precision of the measurement.

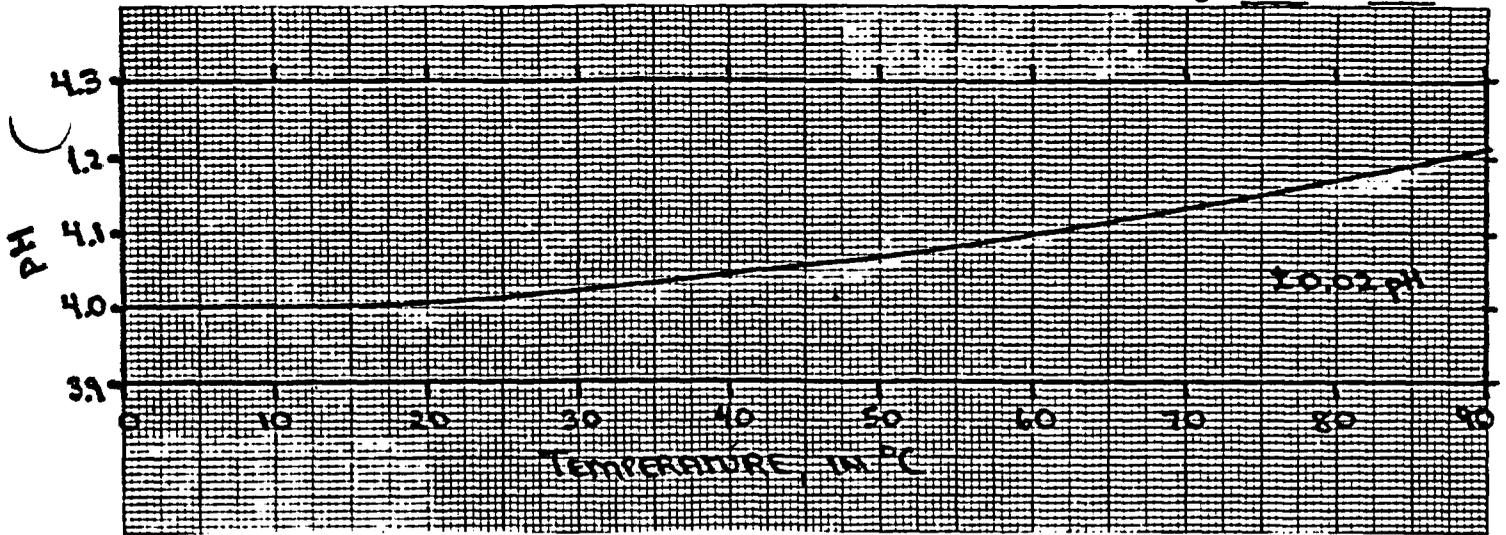


Figure 2. pH as a function of temperature for Fisher pH 4.01 Dry Buffer Salt solution.

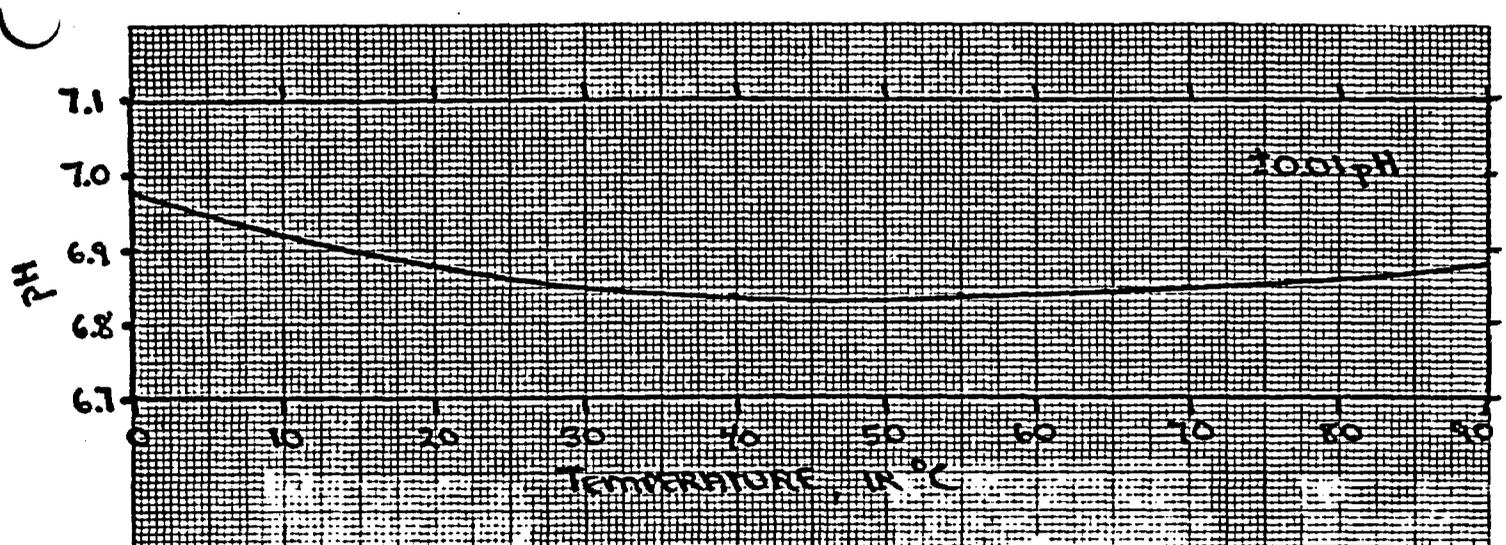


Figure 3. pH as a function of temperature for Fisher pH 6.86 Dry Buffer Salt solution.

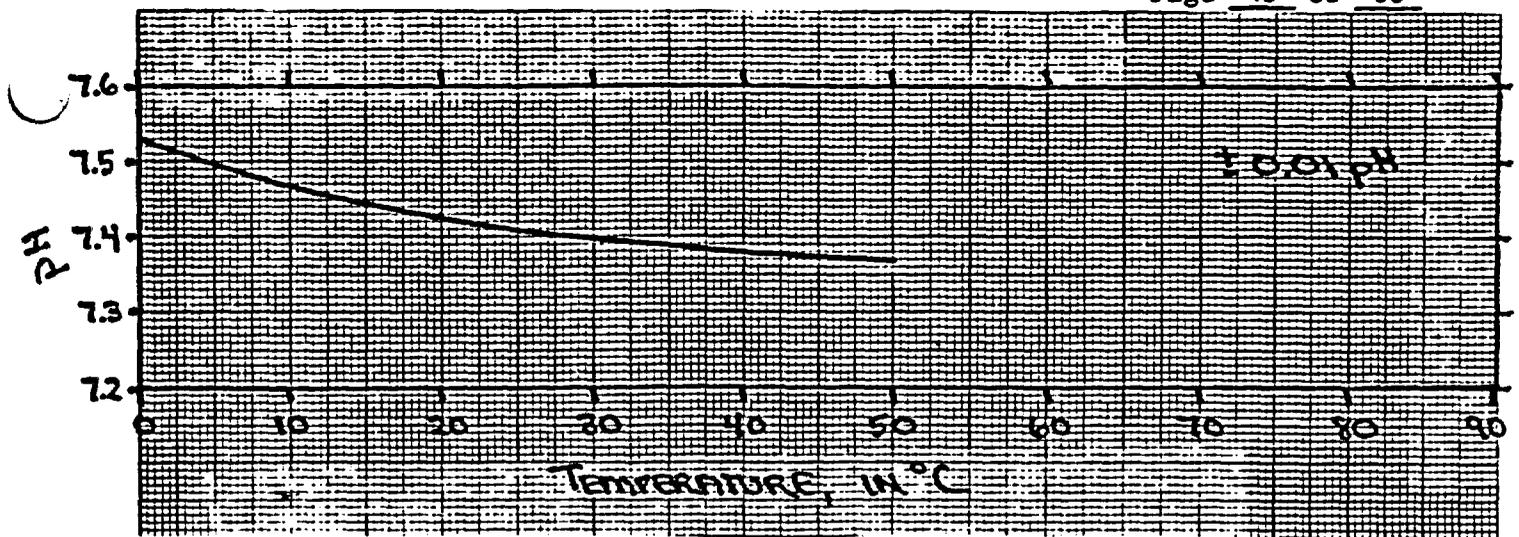


Figure 4. pH as a function of temperature for Fisher pH 7.41 Dry Buffer Salt solution.

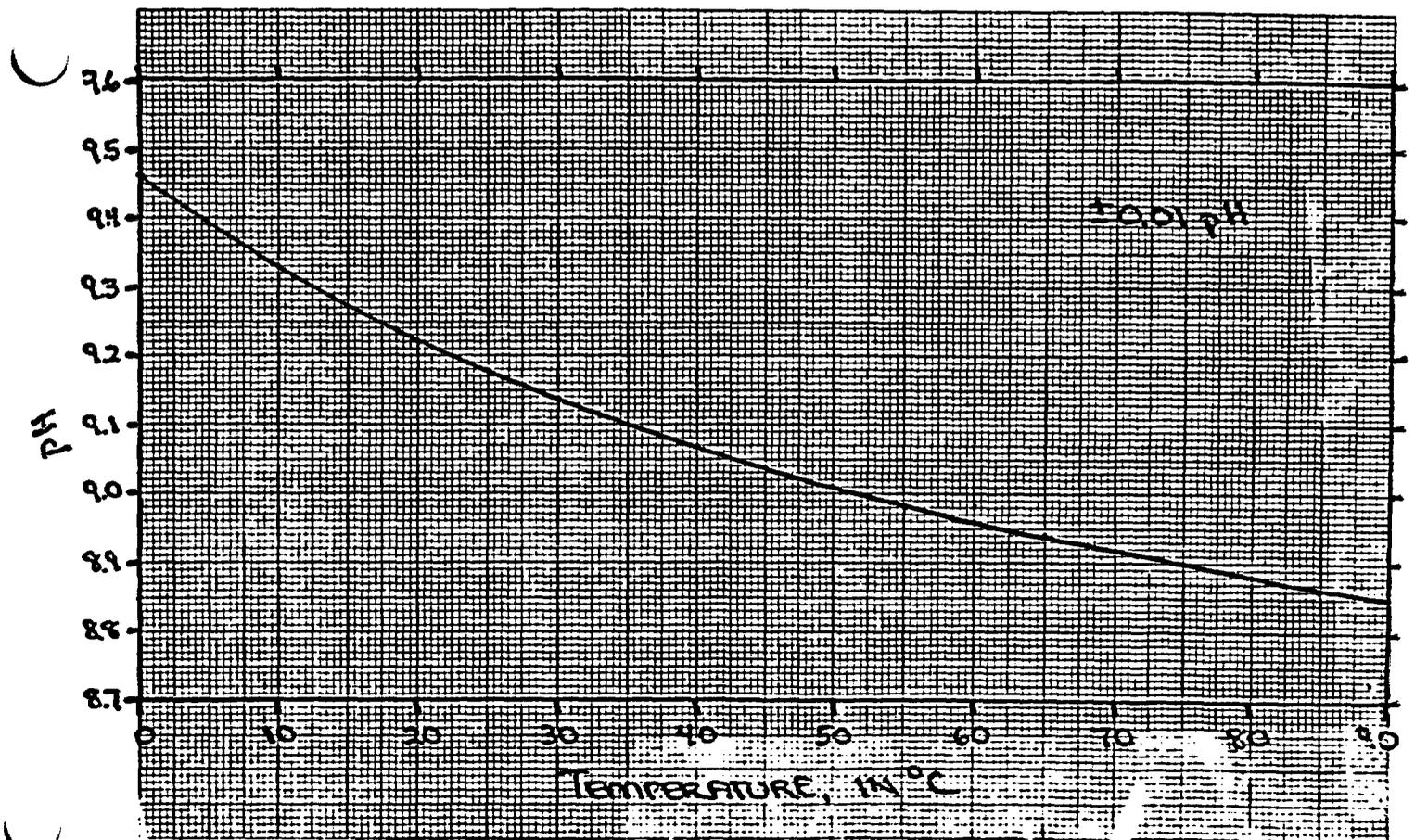


Figure 5. pH as a function of temperature for Fisher pH 9.18 Dry Buffer Salt solution.

4.3.4 Carbonate and bicarbonate alkalinity

1. Principle

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 from ground water should usually be made in the field at the time of sampling if the concentrations are to accurately represent those originally 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.

The carbonate (CO_3) and bicarbonate (HCO_3) concentrations are determined by potentiometric titration of the water sample with a standard solution of sulfuric acid.

The reactions involved are:

- 1) $\text{CO}_3^{2-} + \text{H}^+ = \text{HCO}_3^-$ (This reaction is complete near pH 8.3).
- 2) $\text{HCO}_3^- + \text{H}^+ = \text{H}_2\text{CO}_3^0$ (This reaction is complete near pH 4.5).

The end point of the bicarbonate titration process is graphically determined from either a plot of pH versus titrant volume, where the end point corresponds to an inflection point of the curve (figure 6a), or a plot of the rate of change in pH per unit volume between two successive values (i.e. $\Delta\text{pH}/\text{ml}$ of titrant, figure 6b). The end point is the value at which occurs the maximum rate of change of pH per volume of titrant added. The latter approach is less subjective and permits consistent choice of the end point, but requires exacting analytical procedures. The assurance of complete equilibrium of pH after each increment of acid added is required for both methods.

Salts of weak organic and inorganic acids, such as silica, 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.

2. Materials needed

- 2.1 All equipment and reagents used for pH determinations, section 4.3.3.
- 2.2 Buret, 25-ml or 50-ml capacity with 0.1-ml graduation and Teflon stop cock. Schellbach burets are helpful under field conditions.
- 2.3 Portable AC/battery-powered magnetic stirrer, with extra batteries.
- 2.4 Teflon coated stirring bar, small size.
- 2.5 Ring stand, clamp holder, and universal V-jawed clamp.
- 2.6 25 and 50-ml class A volumetric pipets.
- 2.7 100 or 150-ml glass beaker.
- 2.8 0.5 liter a 0.01639 N sulfuric acid packaged in a plastic bottle to prevent breakage. (Prepared according to Brown and others, 1970.

3. Summary of Method

- 3.1 Adjust temperature of titrant to $\pm 2^{\circ}\text{C}$ of the sample by immersion of the securely stoppered acid-storage bottles in a water bath of the sample fluid.
- 3.2 Fill buret and record level.
- 3.3 Filter a sample as per section 4.2.1.
- 3.4 Rinse the pipet three times with sample water into a clean, dry 100-ml beaker. Under no circumstances should the sample be diluted or concentrated in any way.
- 3.5 Calibrate pH electrode in 7.41 and 4.01 buffer solutions at the temperature of the sample as specified in section 4.3.3, pH determination.
- 3.6 Rinse electrodes in sample.
- 3.7 Insert the clean, dry stirring bar and adjust the stirrer to slow speed.
- 3.8 Insert the pH electrode into the sample in the 100 ml beaker as per section 4.3.3, pH determinations.

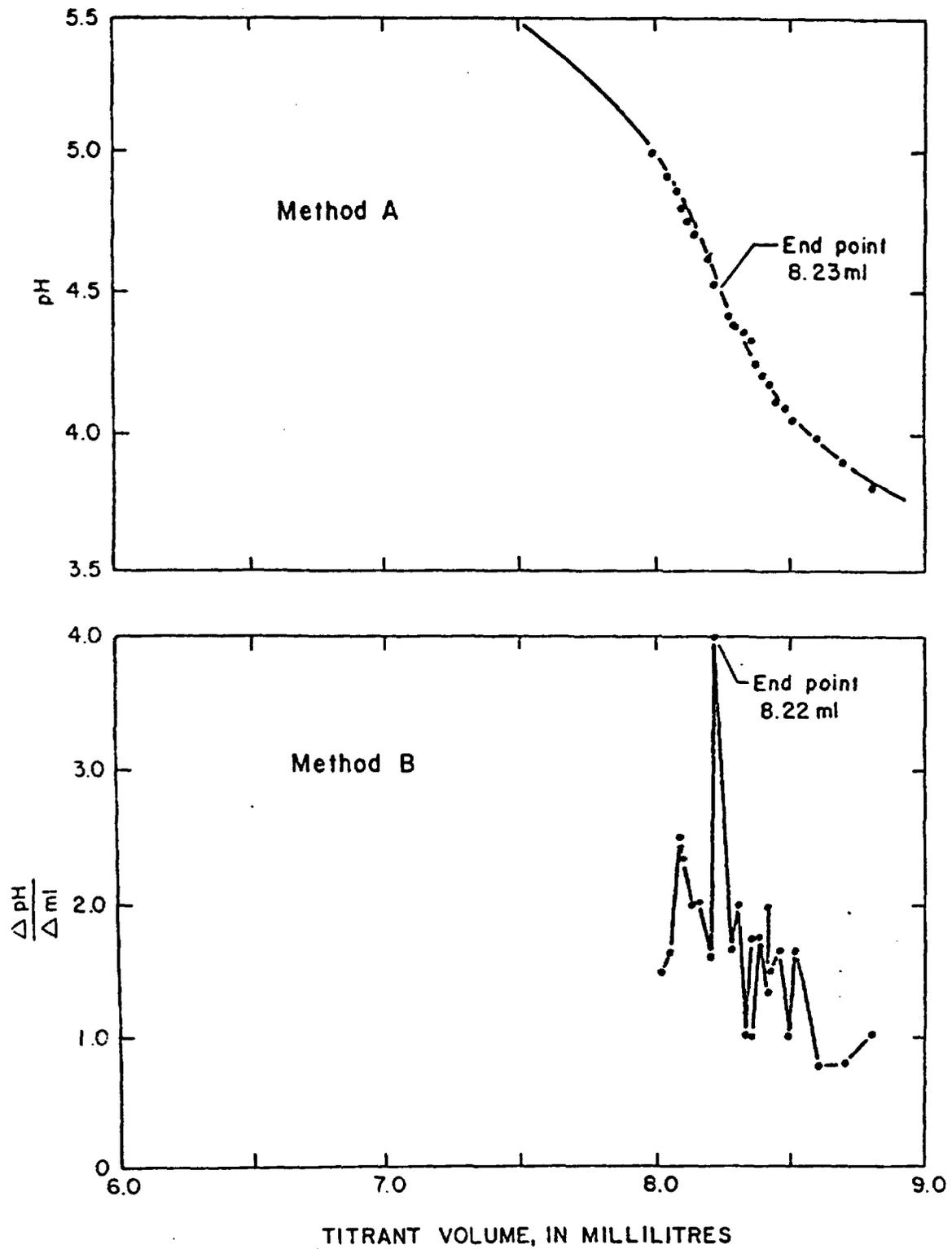


Figure 6. Methods of determining the end point for alkalinity titrations.

3.9 If pH is greater than 8.3, add sulfuric acid titrant by drops. Record titrant volume and pH value after turning off stirrer between each addition of acid.

Record data as follows:

pH	Buret level	milliliters of titrant	pH <u>vol titrant</u>
7.87	0.18	0.00	-
7.46	1.83	1.65	-0.25

3.9 When the pH of sample during titration declines below 8.00, slowly add acid until pH declines to approximately 5.5. Record pH and amount of acid added. Subsequent titrant addition might be as large as 0.1 ml but should be decreased to single drops as pH falls below 5.0 and the end point is approached. Be careful to get the last drops on the buret tip into the sample after each addition. Also, with each addition of titrant in this last part of the titration, stir the sample for a pre-set time after addition of titrant and turn off the stirrer. Take the pH reading after another pre-determined interval. This is to eliminate the streaming potential caused by protons (H+) moving past the electrode tip during stirring. Acid additions should continue until pH is below 4. If titration cannot be completed within one filling of the buret, discard sample and start again using a 25 ml sample size.

4. Calculations

Calculate the carbonate content (if initial pH is greater than 8.3):

$$\text{CO}_3^{2-} \text{ (in mg/l)} = \frac{983.5}{\text{ml(s)}} \times [\text{ml (a) to end point near pH 8.3}]$$

Calculate the bicarbonate content:

$$\text{HCO}_3^{2-} \text{ (in mg/l)} = \frac{1000}{\text{ml}(s)} \times [\text{ml}(a) \text{ between end points near}$$

pH 8.3 and pH 4.5)]

Where:

ml(s) = sample volume

ml(a) = volume of standard 0.01639 N sulfuric acid.

End point is determined as in figure 6.

4.3.5 Dissolved Oxygen

1. Principle

Oxygen dissolved in ground water is usually derived from contact with the atmosphere and the unsaturated zone before reaching the water table. The solubility of oxygen in water is dependent upon the partial pressure of oxygen in the atmosphere, the dissolved solids concentration, and the temperature. Dissolved oxygen can exist at great depths in aquifers which have little or no oxidizable material in the water flow path or where the water's residence time is short compared to the rate of oxygen consumption.

Great care must be taken to prevent aeration of the sample during collection and analysis. A flow chamber may be used in combination with a portable dissolved oxygen meter to prevent sample contact with the atmosphere, minimizing sample aeration and supplying a continuous record of dissolved oxygen during the pumping of a well. In the absence of a flow cell, dissolved oxygen may be measured in unaerated, rapidly flowing sample water.

For precise dissolved-oxygen determinations, the meter should be calibrated before each use. One sample of the water to be analyzed should be deoxygenated by adding an excess of sodium sulfite solution; a second sample should be aerated to saturation. The dissolved-oxygen concentration of the air-saturated sample can be determined from figures 7 and 8, provided the water temperature and the barometric pressure or altitude of the sampling site are known. Figure 7 shows the dissolved-oxygen concentration of air-saturated water at sea level as a function of temperature. Figure 8 shows correction factors that must be applied to the apparent oxygen concentration when the atmospheric pressure varies from 760 mm of mercury. By the use of these two figures, the correct value of dissolved oxygen in the air-saturated sample can be obtained and the meter calibrated.

Oxygen permeable membranes used for the electrode system are permeable to a variety of other gases, none of which are easily depolarized at the indicator electrode. The concentrations of most of these gases in ground water usually 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.

2. Materials needed

- 2.1 Yellow Springs model 54 ARC oxygen meter with sensor, or equivalent.
- 2.2 Flow chamber with flow control valve.
- 2.3 Bottle of electrolyte for the sensor.
- 2.4 Extra membranes for the sensor.
- 2.5 Calibrated thermometer.
- 2.6 Two 8-ounce plastic bottles
- 2.7 1-liter plastic bottle for aeration of the reference sample.
- 2.8 Battery operated aerator and glass frit.
- 2.9 Saturated solution of sodium sulfite.

3. Instrument Method

- 3.1 Add several milliliters of saturated sodium sulfite solution to an 8-ounce plastic bottle.
- 3.2 Pour unfiltered sample into the bottle. Replace the cap and shake.
- 3.3 Prepare the oxygen meter for calibration according to the manufacturer's instructions.
- 3.4 Switch the meter to the 0-10 position.
- 3.5 Remove the sensor guard and insert the sensor into the deaerated sample. If the dissolved oxygen in the sample is greater than 0.1 mg/l, add saturated sodium sulfite in small increments until a reading of 0.1 mg/l or less is obtained. Add an excess of several milliliters after a reading of 0.1 mg/l is obtained. If the deaerated sample remains above 0.0 mg/l O₂, subtract the value measured for the deaerated sample from that measured for the raw sample to obtain dissolved oxygen concentration.

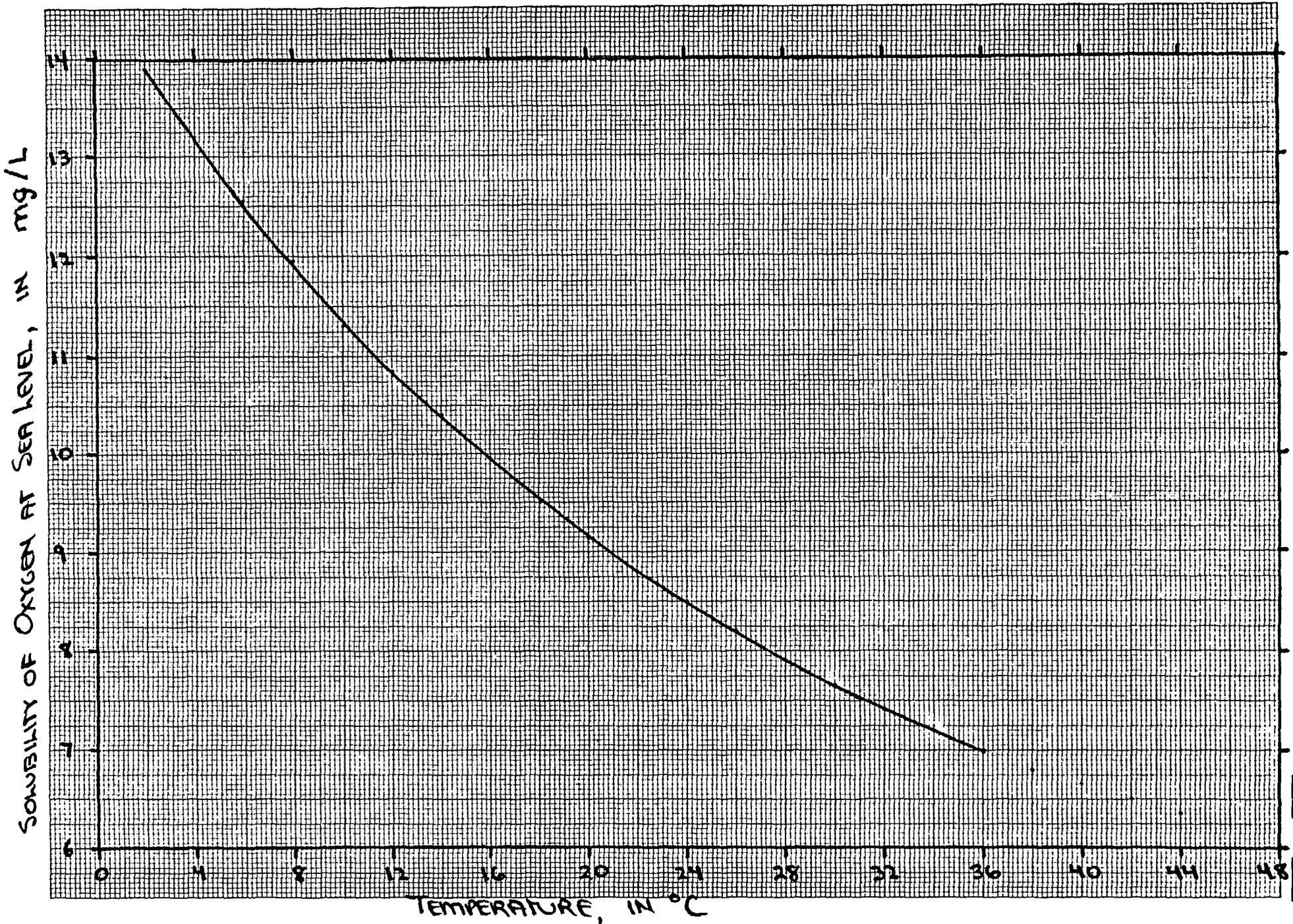


Figure 7. Solubility of oxygen in water at sea level as a function of temperature.

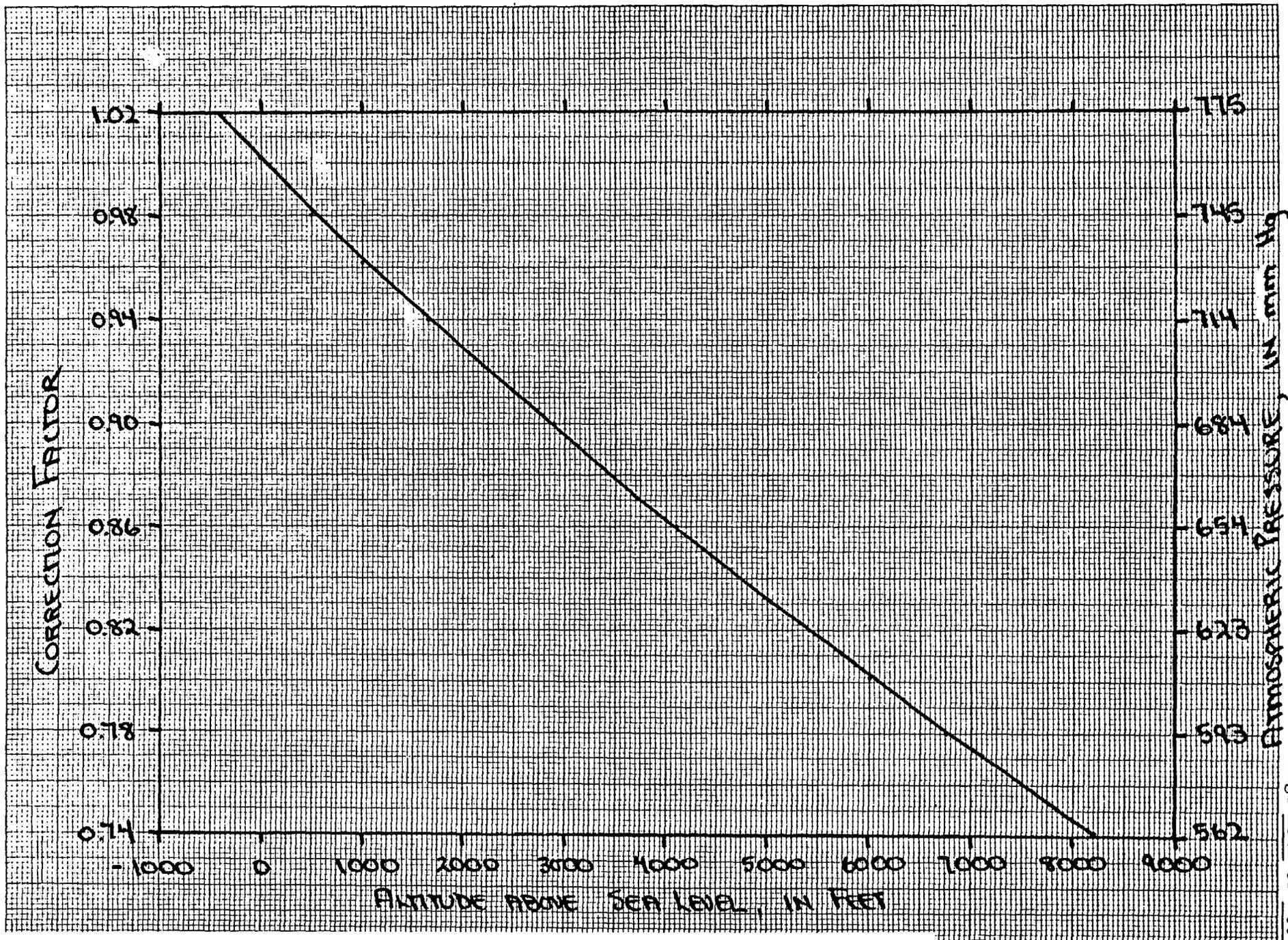


Figure 8. Correction factor for the solubility of oxygen as a function of altitude and atmospheric pressure.

- 3.6 Pour a second sample into a 1-liter plastic bottle and aerate for several minutes with the battery-operated aerator. Keep the bottle in a flowing sample water bath to maintain temperature.
- 3.7 Calculate the dissolved oxygen concentration of the air-saturated sample using figures 7 and 8.
- 3.8 Pour an aliquot of the aerated sample into a clean 8-ounce plastic bottle.
- 3.9 Switch meter to the 0-10 position and insert the sensor into the aerated sample. Agitate the sensor until the maximum reading is obtained.
- 3.10 With the calibration control, adjust the dissolved oxygen reading to the value obtained in step 3.7.
- 3.11 Place sensor in the flow chamber. Place the "O" ring over the sensor, being careful not to disturb the membrane. Replace the sensor guard and tighten until the "O" ring is compressed very slightly.
- 3.12 Replace the top of the flow chamber and gently open the flow control valve.
- 3.13 Measure the dissolved-oxygen concentration at about 5-10 minute intervals until a stable reading is obtained. Record the value to the nearest 0.1 mg/l.

4.3.6 Eh(Oxidation-reduction potential)

1. Principle

The redox potential, represented by the symbol Eh, is related to the standard potential and the activities of participating substances by the Nernst equation:

$$E_h = E^{\circ} + \frac{RT}{nF} \ln \frac{\text{oxidized state}}{\text{(reduced state)}}$$

Where E_0 = standard potential of the reaction.

R = the universal gas constant

T = the absolute temperature

F = the Faraday constant

n = the number of electrons involved in a half cell reaction.

$\ln \frac{\text{(oxidized state)}}{\text{(reduced state)}}$ = 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 standard hydrogen electrode, and may be positive or negative. The greater the negative value, the more the reducing of the system.

Eh is measured with a noble metal electrode, 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 check the accuracy of the electrode system. The Eh reference solutions are not used to adjust the system to the correct range of values. ZoBell solution, a potassium ferric - ferro cyanide solution, has proved satisfactory as a standard reference solution and is recommended. By combining the half

cell potentials for the platinum-silver-silver chloride electrode system and ZoBell solution and utilizing the equations for potential variation with temperature, the theoretical potentials for the system at different temperatures can be calculated. The relationship of the theoretical potentials of this system to temperature is shown in figure 9. The calculation of Eh of a system requires that the observed potential be adjusted to a potential relative to the standard hydrogen electrode:

$$E_{h_{sys}} = E_{obs} + E_{h_{ZoBell + ref}} - E_{ZoBell (obs)},$$

Where: $E_{h_{sys}}$ = the true Eh of the environment, relative to the stand hydrogen electrode.

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

$E_{h_{ZoBell + ref}}$ = the theoretical Eh of ZoBell solution, relative to the standard hydrogen electrode (fig. 10).

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

Redox potential measurements in laboratory solutions where activities of oxidized and reduced species may approach unity can be expected to match theoretical calculated potentials reasonably well. Many natural water systems do not give measured Eh values that can be quantitatively interpreted. Measurements made in water containing dissolved oxygen give values lower than might theoretically be expected. This is attributed to a slow, rate determining step in the reaction of aqueous oxygen with other ions. If dissolved oxygen is present in the sample, the dissolved oxygen determination will be more useful than attempting to measure Eh.

2. Materials needed

- 2.1 Orion 399 A/F specific-ion meter or equivalent.
- 2.2 Fisher platinum/Ag/AgCl combination electrode 13-639-82 and filling solution So-P-135 or equivalent. Separate platinum and reference electrodes are also suitable.
- 2.3 ZoBell reference solution:

Dissolve:

- 1.4080g of potassium ferrocyanide $K_4Fe(CN)_6 \cdot 3H_2O$ (0.00333 M)
- 1.0975g potassium ferricyanide $K_3Fe(CN)_6$ (0.00333 M)
- 7.4555g of potassium chloride KCl (0.10 M)

in distilled water to make 1 liter. This solution is stable for several months, but should be kept in an opaque bottle and out of sunlight as much as possible. It has a standard potential of + 428 millivolts at 25°C. The solution is poisonous and should be handled with care.

2.4 Eh cell:

U-shaped drying tube with side arms

- (2) Hoffman pinch cocks
- (2) Small tubing clamps
- (2) Solid rubber stoppers to fit drying tube, one bored to admit electrode (2.2, above).

Several feet of Tygon tubing to fit U-tube side arms.

- 2.5 Plastic 100-ml beaker.
- 2.6 Plastic pail for ZoBell solution water bath.
- 2.7 Calibrated thermometer
- 2.8 Equipment for measuring dissolved oxygen (refer to section 4.3.5)
- 2.9 Small strips of crocus cloth for polishing the platinum electrode.



Figure 9. The theoretical potential of ZoBell solution relative to silver-silver chloride, platinum electrode system as a function of temperature.

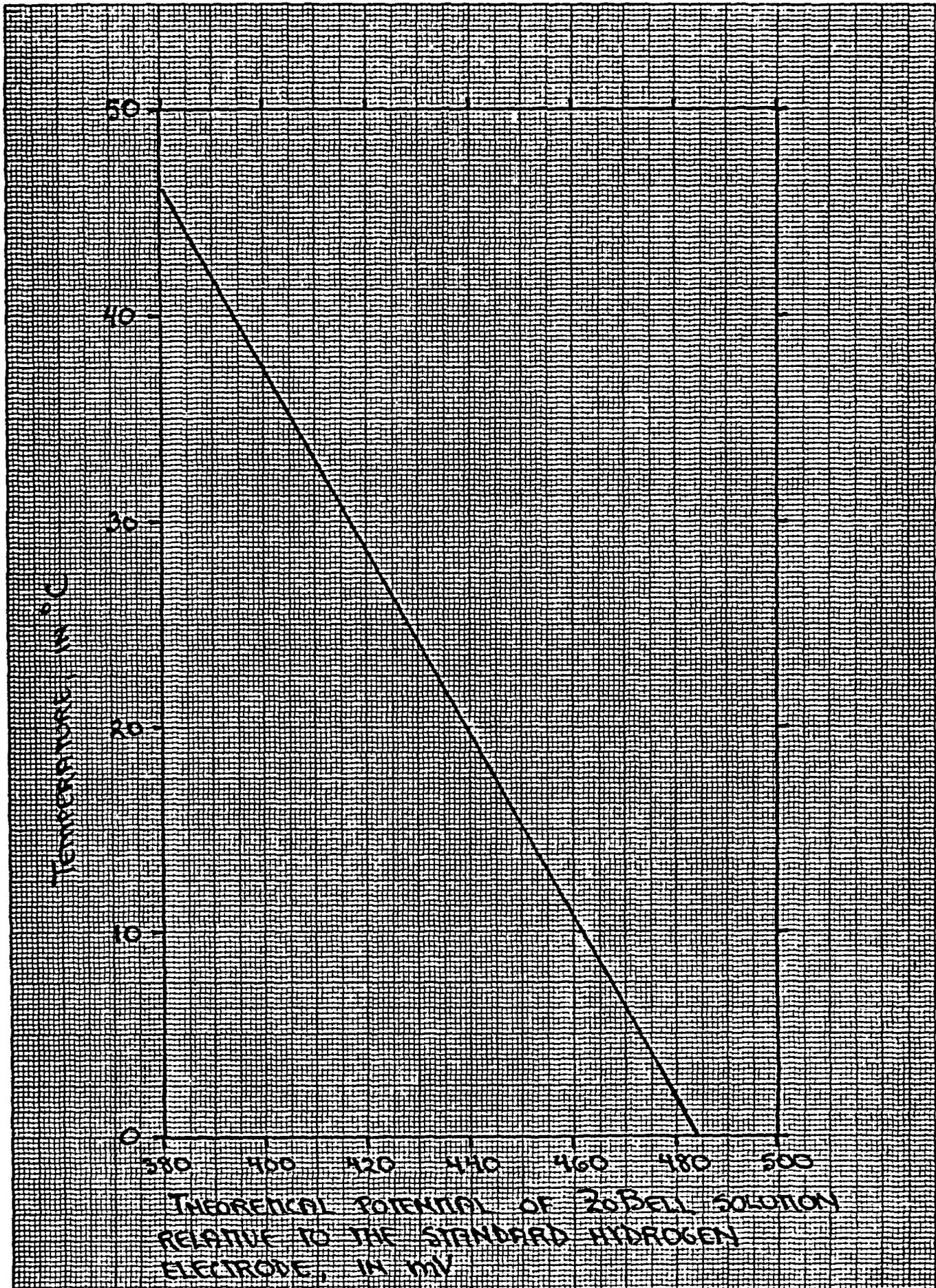


Figure 10. The potential of Zobell relative to the standard hydrogen electrode as a function of temperature.

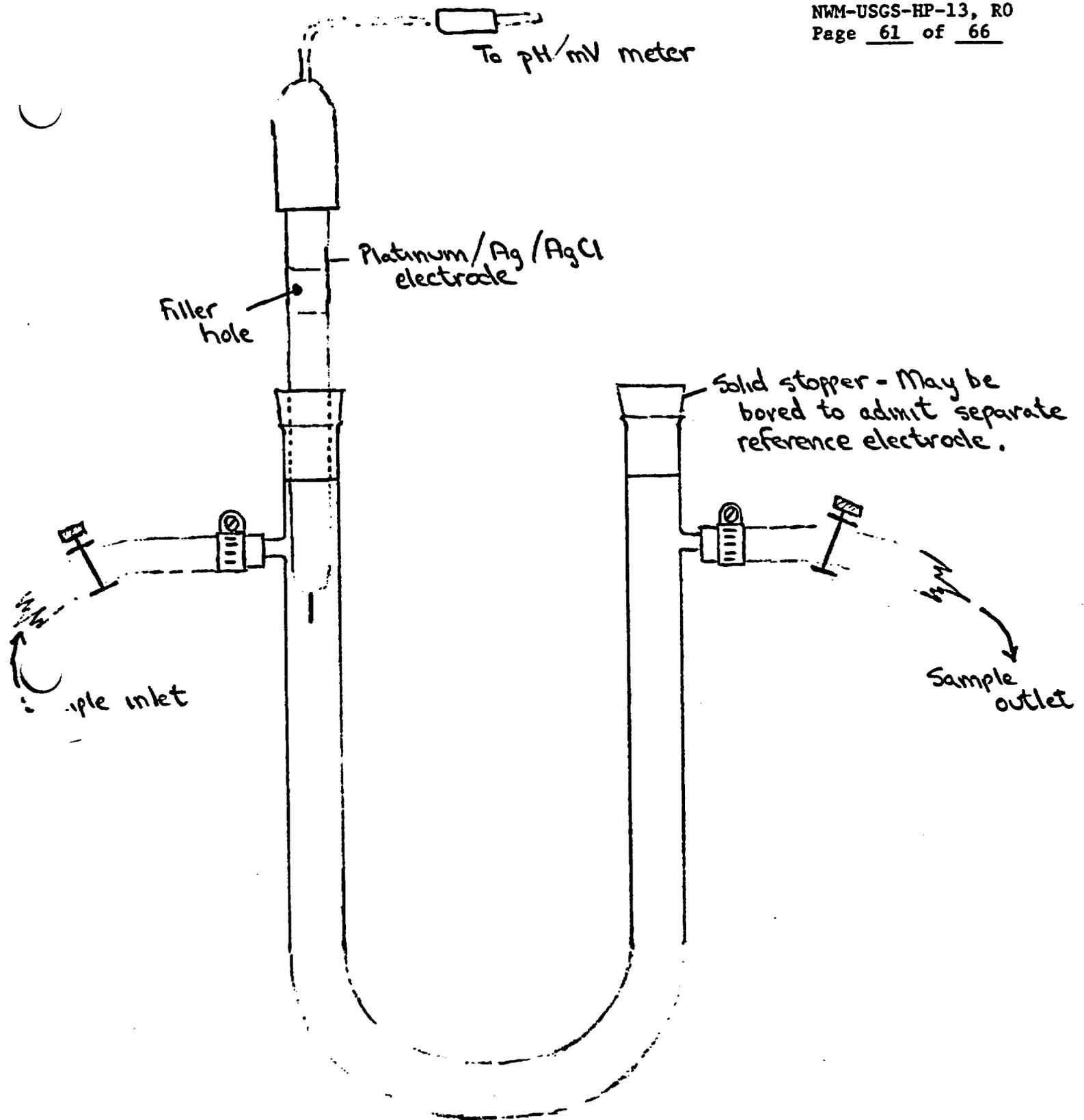


Figure 11. Eh measuring cell.

3. Method

- 3.1 Determine the presence of dissolved oxygen as per section 4.3.5. If dissolved oxygen is present, do not proceed with the Eh measurement. If dissolved oxygen is absent, proceed with step 3.6.
- 3.2 Fill the combination electrode with the proper filling solution.
- 3.3 Depress body and let some of the fluid drain to waste.
- 3.4 Bring ZoBell solution to the temperature of the sample by allowing the sample to flow over the closed bottle of solution.
- 3.5 Record temperature as per section 4.3.1 on data record. Also record the theoretical E of ZoBell solution ($E_{\text{ZoBell}}^{\text{E}}$ (theor)) at the sample temperature, as plotted in figure 9, and the theoretical Eh of ZoBell solution ($E_{\text{ZoBell}}^{\text{Eh}}$ + ref) at the sample temperature, as plotted in figure 10.
- 3.6 Place combination electrode in the ZoBell solution that has been equilibrated to the sample temperature.
- 3.7 Plug electrode leads into the meter and turn the function switch on the meter to millivolt mode. Allow several minutes for electrode to equilibrate while maintaining the bottle of ZoBell solution in the water bath.
- 3.8 Record the millivolt reading ($E_{\text{ZoBell}}^{\text{E}}(\text{obs})$) on the data record.
- 3.9 If the reading ($E_{\text{ZoBell}}^{\text{E}}(\text{obs})$) differs by more than 10 millivolts from the theoretical value at that temperature from figure 9 ($E_{\text{ZoBell}}^{\text{E}}$ (theor)) replace the reference electrode fluid and repeat the measurement.
- 3.10 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 the reading.
- 3.11 If this procedure fails, the electrode should be replaced.

- 3.12 If the reading is within ± 10 millivolts of the theoretical value, rinse the electrode with sample water and proceed with step 3.13.
- 3.13 Place electrode in the upright Eh cell and let the water flow through the cell as shown in figure 11. The filler hole in the side of the electrode should be above the top of the Eh cell.
- 3.14 Remove all air bubbles from the system.
- 3.15 Use the control valve on the inlet to ensure that the head of the sample is below the level of the reference solution of the electrode or some of the sample will be forced into the reference electrode and change the potential of the system.
- 3.16 Turn the function switch on the meter to millivolt mode and allow the water to flow through the cell until the readings taken every 3-5 minutes stabilize. Stabilization usually occurs within 20 minutes, but may require as much as an hour or more. If readings fail to stabilize, polish the electrode using crocus cloth and proceed to step 3.13.
- 3.17 Turn off the sample flow by closing both pinch cocks to prevent any streaming potential and immediately record the meter reading on the data sheet. This is the observed Eh of the sample (E_{obs}), or more specifically, the observed full-cell emf relative to the reference electrode.
- 3.18 Calculate the true Eh of the system ($E_{h_{sys}}$), relative to the standard hydrogen electrode as shown in 1, and record in field notes.

4.3.7 Bromide

1. Principle

Drilling principle fluid may be spiked with a bromide salt in order to provide a conservative tracer of that fluids presence. Monitoring of bromide concentrations may be useful as an on-site indication of contamination of sample waters by drilling fluids.

2. Equipment Required

- 2.1 Orion 407 A/F Specific ion meter or equivalent.
- 2.2 Orion 94-35 Bromide Sensing Electrode or equivalent.
- 2.3 Orion 90-01 reference electrode or equivalent.
- 2.4 Orion 90-00-01 electrode filling solution.
- 2.5 Volumetric flasks - 100 ml and 1 liter.
- 2.6 Volumetric pipetes - 1, 5, 10, 100 ml.
- 2.7 250 ml beakers.
- 2.8 Ionic Strength Adjustor (ISA) - 1M NaNO₃ solution:
Prepare by dissolving 8.5g reagent-grade sodium nitrate in 100 ml deionized water.
- 2.9 Bromide 1000ppm standard solution: Prepare by placing 1.29 g reagent grade NaBr in a 1 liter volumetric flask. Add about 500 ml deionized water. Swirl to dissolve, and dilute to the 1 liter mark with deionized water.
- 2.10 Bromide 50 ppm standard solution: Pipet 5 ml 100 ppm standard solution into 100 ml volumetric flask. Dilute to 100 ml mark with distilled water. Add 1 ml ISA.
- 2.11 Bromide 10 ppm standard solution: Pipet 1 ml 1000 ppm Bromide standard solution into 100 ml volumetric flask. Dilute to 100 ml mark with deionized water. Add 1 ml ISA.
- 2.12 Bromide 1 ppm standard solution: Pipet 1 ml 1000 ppm Bromide standard solution into 1 liter volumetric flask. Dilute to 1 liter mark with deionized water. Add 10 ml ISA.
- 2.13 Portable AC/battery-powered magnetic stirrer with spare batteries.

- 2.14 Small Teflon coated stirring bar
 - 2.15 Graph paper - 4 cycle, semi-log
 - 2.16 Polishing cloth
 - 2.17 Plastic bucket
 - 2.18 Deionized water
 - 2.19 500 ml wash bottle for deionized water.
3. Summary of Method
- 3.1 Fill Ag/AgCl reference electrode with internal filling solution.
 - 3.2 Plug reference and bromide electrode leads into meter and insert electrodes into holder, level the meter and check to ensure that the meter is properly adjusted.
 - 3.3 Prepare 1, 10, 50 ppm bromide standard solutions (2.10 - 2.12). Adjust standard solutions to sample temperature by immersing the bottles in a pail of sample water. To prevent floating, heavy steel washers may be epoxied to the bottoms of the bottles.
 - 3.4 Pour 100 ml 1 ppm bromide standard solution into beaker. Rinse electrodes with deionized water, blot dry and insert into 1 ppm standard. Switch meter to mV position. Stir thoroughly. Allow several minutes to stabilize and record potential. Return standard to its bottle.
 - 3.5 Repeat step 3.4 with 10 ppm and 50 ppm bromide standard solutions.
 - 3.6 Determine the difference between the first (1 ppm Br⁻; 3.4) and second (10 ppm Br⁻; 3.5) potential readings. Correct electrode operation is indicated by a difference of 53 to 59 millivolts in a solution temperature of 20° -25°C. If the change in potential is not within this range, refer to electrode instruction manual.
 - 3.7 Plot on semi-log paper the concentration (log axis) versus the potential (linear axis) for the three points measured. Insert the calibration curve in the field notebook.
 - 3.8 Store used standard solutions for checking calibration curve on the order of every hour. Prepare a new calibration curve with fresh standard daily.

- 3.9 Rinse electrodes with deionized water and blot dry. Also thoroughly rinse all glassware used for standardization with deionized water.
- 3.10 Rinse 100 ml volumetric pipet and beaker with sample water. Pipet 100 ml sample water into beaker. Add 1 ml ISA to beaker. Stir thoroughly.
- 3.11 Wait for potential to stabilize and record in field notes.
- 3.12 Determine bromide concentration from the calibration curve and record in field notes.
- 3.13 Store electrodes in excess 1 ppm Br^- standard between sample measurements.