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Pleasant Bayou Well Test
1988-Present

Sampling and Analysis Procedures for Gas, Condensate, Brine, and Solids

DISCLAIMER

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These sampling and analytical procedures are not written in stone. It is expected that changes will be incorporated over time to better define the composition of the produced fluids. All procedural changes, however, MUST be recorded in this book. Data to be recorded are 1) the new procedure, 2) the date of change, and 3) the reason for the change. We examine chemical data primarily by looking for changes, and don't wish to look for red herrings caused by changes in basic analytical procedures.

IGT has adopted the position that we should analyse major components on a regular basis and look for changes. As such, budgetary restraints are such that we use efficient analytical techniques such as ICP, gas chromatography, and Hach analyses to make analyses less expensive. While other techniques may provide more accuracy, reproducability, or a lower detection limit, there is a trade off between frequency of analyse versus analytical costs. IGT will provide samples to interested parties as requested.

The laboratories chosen to provide outside analyses are among the best we have found in over 8 years of Gulf Coast geopressured water well testing. All laboratories are staffed with competent experienced personnel. We have purposely included research oriented laboratories such as the Mineral Studies Lab at BEG and commercial laboratories such as Core Laboratories to provide a mix of state-of-the-art techniques and oil field experience.

The manual is devided into small written sections containing sample collection procedures, a list of on-site analytical procedures, and the shipping instructions to outside laboratories. Then the more massive analytical procedures follow in each section.

Chris Hayden, Supervisor, Well Testing, IGT

IGT

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Gas Sampling and Analysis - Pleasant Bayou Flow Test, 1988 - present

This section covers analyses performed on gas. Chemical analyses can only be related to well performance if the quantity of the various fluids are known. The IGT on-line data computer system measures the flowrate, the pressures, and the temperatures every 10 seconds. These values are automatically recorded over operator selected intervals both on magnetic media and on paper. This allows review of samples versus operating conditions.

This paper covers analyses performed on gas, including:

- An approximate sampling schedule during flow tests
- On-site sample handling and storage of gas samples
- Addresses of laboratories that perform off site analyses
- Sample shipping instructions
- Data archiving
- Quality Control/Quality Assurance

It is expected that the above procedures will change as the flow test progresses, but deviations from the written procedures should be approved by C. Hayden of IGT and noted on the results of the analysis.

Gas Sample Schedule: Gas samples for routine analysis should be collected monthly for the initial period of flow. After the gas composition has been stable over several analyses, and enough analyses are obtained to define baseline values, sampling frequency can decline to once per 2 to 3 months. Gas samples should also be collected during periods where flow characteristics are not "normal", such as at reduced rates.

Samples collected for special studies, such as the suite of samples collected to define total carbon dioxide, should be collected between one and two times per year when flow conditions are "normal". Other samples may occasionally be collected on an as-needed basis to assist in operating decisions.

Routine Gas Sample Collection and Analysis

Routine gas sample collection involves collecting a total of 3 samples in teflon lined 304 or 316 grade stainless steel cylinders with a working pressure of 1800 psi. Know your gases. Pleasant bayou gas contains at least 20 ppm of hydrogen sulfide, 8% of carbon dioxide, and over 500 ppm of benzene and derivatives. All exceed threshold limits for long term exposure. Read the physical and toxicological data in Appendix Gas-A and avoid breathing gas. Specific instructions are as follows:

1) Gather three clean 316 grade stainless steel cylinders, the vacuum pump, two adjustable wrenches, the draeger purge chamber, and the Draeger pump apparatus. Gather appropriate Draeger tubes needed for the analysis. As of June 1989, these will include hydrogen sulfide tubes, acetic acid tubes, and a water vapor tube. Tubes for measuring ammonia and mercury should be used once or twice a year, though to date neither of these components have been detected in the gas.

2) Remove the Swagelok cap and take the cylinder outdoors. Carefully open a valve. Always assume there is gas in the cylinder at 700 psi or so, so aim the cylinder toward the ground in a safe direction before opening. The cylinder should be under vacuum, and you should here a faint hiss as air is sucked in. If so, hook the cylinder up to the vacuum pump and draw a vacuum for at least two full minutes. If the cylinder did indeed have gas in it, it must be evacuated for 5 or more minutes.

   Never connect a cylinder that may contain pressure to the vacuum pump. This will certainly cause a massive oily mess, will destroy the vacuum pump, and may cause injury. Note that care should also be taken to not let the vacuum pump run without being connected to a cylinder, or oil will leak out and make a mess.

3) The first sample collection point is the sales/flare meter run. There are two 1/2 inch needle valves on top of the pipe with a Swagelok fitting. Crack the valve and blow gas for a few seconds, removing debris from the valves and flushing the sampling system. It will be loud, and eye and ear protection is advised. Connect the evacuated sample cylinder to the Swagelok fitting. Open the 1/2 inch valve first, before opening the cylinder valve. Only a few seconds are needed to collect a sample. Close both the cylinder valve and the 1/2 inch valve and remove the cylinder. Cap both ends with Swagelok caps.

4) Crack open the valve and establish a slow, barely audible, leak rate. Attach the Draeger flow through apparatus, which in a modified plastic squirt bottle, using the small rubber tubing provided.

5) Follow instructions given in the Gas Processors Association "Tentative Method of Test for Hydrogen Sulfide in Natural Gas Using Length of Stain Tubes" and the referenced Draeger literature reproduced in Appendix Gas-B, with the following changes.

   • Pump the hydrogen sulfide tube only 5 times, not 10. Multiply the resulting concentration by 2 and report to the nearest ppm.
   • Pump the mercury tube at least 25 times. Pump the water tube 100 times. Each will take a long time. The water concentration should be 0.1 mg/l or less.

6) Collect samples at the separator meter runs following the same procedures. It is not necessary to do the entire suite of Draeger analyses again. However, if ammonia is to be measured it should be determined on separator gas. The sales gas is too dry. Also, do not measure water content of separator gas. It is not representative. Likewise, there is too much water in the separator gas to use the mercury detector tubes.

7) Record the Draeger values, with date, time, and sample location, on the sheet in the Gas Analyses folder. Also remark the concentrations in the on-line data computer.

On-site Analyses: The routine gas analyses are to be performed on-site are Draeger "length of stain" tubes as described in the previous section.

More extensive gas chromatography tests can be performed on-site, especially during tests requiring quick turn around time and special data handling procedures such as the total carbon dioxide test. The on-site instrument is a Carle Model 111-H gas chromatograph with a Perkin Elmer Minigrator automatic integrator. The instrument is calibrated using an IGT manufactured chromatographic standard which is NBS traceable G. The composition of the standard, along with pertinent integrator information, is presented in Appendix Gas-C.

The chromatograph analyses C1 to C5 hydrocarbons, carbon dioxide, nitrogen, and oxygen. A C6+ peak is also eluted but a water vapor peak eluted right before the c6+ peak makes quantification difficult. The machine is capable of measuring hydrogen, but not at the low concentrations observed in this gas. The on-site chromatograph is an old instrument (it has been used at 7 different geopressured geothermal wells over the last 9 years) and several small leaks degrade the accuracy of the instrument. Maximum uncertainty for reported components is:

% Component	% Uncertainty
0.01 to 0.09%	50%
0.1 to 0.9%	10%
1.0 to 90%	5%

On Site Sample Storage and Handling: Gas samples should be shipped out for analysis as soon as possible. The addresses of the two laboratories that provide analyses are given below. Samples going to Litton Core Lab Chromaspec should be hand delivered by project personnel. The laboratory is located near Hobby Airport.

Samples shipped to IGT are classified as hazardous and CAN NOT BE SHIPPED BY MAIL. Use Federal Express located adjacent to Hobby Airport, and fill out the shippers certification as indicated in Appendix Gas-D. The box must have the address written on one side as well as having the air bill attached to another side. The box must also have "DANGER - Do Not Load in Passenger Aircraft" and "Flammable Gas" stickers attached. You must write "Inside Containers Comply With Prescribed Regulations" on the box side that has the stickers. Bring everything with you - the quality of help available at the Fed. Express office is variable at best.

Larry Scott
Litton Core Lab
8210 Mosley Road
Houston TX 77075

713-943-9776

Al Janos
Institute of Gas Technology
3424 South State Street
Chicago IL 60616

312-567-3679

Include a letter defining the number of samples, the charge number if appropriate, and analytical instructions. Chromaspec instructions are a gas analysis to C10. IGT instructions should specify following procedures followed on IGT Sample 89-05-038, Major Components in gas.

Off Site Gas Analyses: Litton Core Lab Chromaspec performs routine gas sample analyses for the petroleum industry. They follow accepted industry techniques for sample analysis. We have noted several minor problems with these analyses on this and other wells. These are discussed below after outlining Chromaspec's analytical procedure.

Chromaspec Procedure

1) Heat sample to temperature equal to the temperature of the gas in the system.
2) Release a small quantity of the sample into a heated sample loop, keeping the pressure below one atmosphere.
3) Analysing the sample by gas chromatography.

We have noted occasional problems with Chromaspec's carbon dioxide/ethane resolution. These peaks are eluted by the chromatograph at about the same time. There system is set up for regular natural gas, containing 0.5 to 4% carbon dioxide. These large carbon dioxide peaks associated with design well gas can cause problems. If an analysis is suspect, have the sample re run.

Chromaspec does not differentiate between aromatics such as benzene and aliphatics such as hexane. The quirks of standard gas chromatographic analyses are such that benzene gets reported with heptanes, the toluene gets reported with octanes, and so forth.

Chromaspec's lower limit of detection of hydrogen is about 0.1 mole percent.

Finally, Chromaspec terminates its analysis at C10 plus, a back flushed composite peak of all hydrocarbons heavier than C9.

IGT's analyses are defined both by the letter of instructions accompanying the samples and by the list of procedures defined in Appendix Gas-E.

Data Handling and Reporting: All gas analyses are to be reported in the Weekly reports to Eaton Operating Company. The original report sheets are filed in the IGT-Gas or the Chromaspec-Gas folder as appropriate. All gas analysis reports should contain the date, sample location, gas temperature and pressure, and the flowing brine temperature. Use the brine orifice meter temperature for brine temperature, and the orifice meter run pressure and temperature for the other data.

	1 Gases and vapours to be measured	Acetic acid	[illegible]	Benzene	Mercury vapour
2	Chemical formula	CH_3COOH	NH_3	C_6H_6	Hg
3	DRÄGER Tube(s) to be used	Acetic acid	Ammonia	Benzene	Mercury
4	Threshold limit value (1975 position)	10 ppm (25 mg/m³)	25 ppm (17.5 mg/m³	10 ppm (s) (30 mg/m³)	0.05 mg/m³
5	Threshold of smell (app.)	1 ppm	5 ppm	5 ppm	Odourless
6	1 ppm ≙ .... (20°C, 1013 mbar)	2.49 mg/m³	0.71 mg/m³	3.26 mg/m³	8.35 mg/m³
7	1 mg/m³ ≙ .... (20°C, 1013 mbar)	0.40 ppm	1.41 ppm	0.31 ppm	0.12 ppm
8	Molecular weight	60.05	17.03	78.11	200.61
9	Vapour pressure (at 20°C)	—	—	76 mm Hg (101 mbar)	0.00122 mm Hg (0.00163 mbar)
10	Volatility (at 20°C)	—	—	325 mg/l	0.013 mg/l
11	Lower ignition limit (20°C, 1013 mbar)	4.0 vol.%	15.0 vol.%	1.2 vol.%	—
12	Upper ignition limit (20°C, 1013 mbar)	17 vol.%	28 vol.%	8.0 vol.%	—
13	Flash point	40°C	—	−11°C	—
14	Group and hazard class (VbF)	—	—	A I	—
15	Ignition temperature	485°C	630°C	555°C	—
16	Evaporation factor (ether = 1)	—	—	3	—
17	Boiling point (at 1013 mbar)	118.5°C	−33.5°C	80.1°C	357°C
18	Specific gravity (liquid, 20°C)	1.049 g/cm³	—	0.8788 g/cm³	13.54 g/cm³
19	Respirator filter, code letter and colour	A, brown	K, green	A, brown	A, brown/red

Note: A dash (−) does not signify zero

– 147 –

	1 Gases and vapours to be measured	Hydrogen sulphide	Carbon dioxide (carbonic acid)	n-Butane
2	Chemical formula	H_2S	CO_2	C_4H_{10}
3	DRÄGER Tube(s) to be used	Hydrogen sulphide	Carbon dioxide	Hydrocarbon 0.1%/b
4	Threshold limit value (1975 position)	10 ppm (15 mg/m³)	5,000 ppm (9,000 mg/m³)	600 ppm (1,450 mg/m³)
5	Threshold of smell (app.)	< 0.1 ppm	odourless	—
6	1 ppm ≙ ....(20°C, 1013 mbar)	1.42 mg/m³	1.83 mg/m³	2.42 mg/m³
7	1 mg/m3 ≙ ....(20°C, 1013 mbar)	0.71 ppm	0.55 ppm	0.41 ppm
8	Molecular weight	34.08	44.01	58.12
9	Vapour pressure (at 20°C)	—	—	—
10	Volatility (at 20°C)	—	—	—
11	Lower ignition limit (20°C, 1013 mbar)	4.3 vol.%	—	1.5 vol.%
12	Upper ignition limit (20°C, 1013 mbar)	45.5 vol.%	—	8.5 vol.%
13	Flash point	—	—	—
14	Group and hazard class (VbF)	—	—	—
15	Ignition temperature	270°C	—	365°C
16	Evaporation factor (ether = 1)	—	—	—
17	Boiling point (at 1013 mbar)	−60.4°C	−78.52°C	−1°C
18	Specific gravity (liquid, 20°C)	—	—	—
19	Respirator filter, code letter and colou	B, grey	—	A, brown

Note: [illegible] signify zero

– 148 –

A dash does not signify zero

Taken From Drager Detector Tube Handbook

GPA

Tentative Method of Test for Hydrogen Sulfide in Natural Gas Using Length of Stain Tubes

Adopted as Tentative Standard, 1977

Gas Processors Association

1812 First Place

Tulsa, Oklahoma 74103

Tentative Method of Test for Hydrogen Sulfide in Natural Gas Using Length of Stain Tubes

1. SCOPE

1.1 This method covers the determination of hydrogen sulfide in natural gas in the range of 3 ppmv to 120 ppmv.

Note 1—Available apparatus extends the range up to 7 percent by volume. Cooperative testing by GPA has been completed only up to 120 ppmv.

1.2 The method as written is applicable to the determination of hydrogen sulfide in hydrocarbon vapors and in air.

2. SUMMARY OF METHOD

The sample is passed through the detector tube filled with a specially prepared chemical. Any hydrogen sulfide present in the sample reacts with the chemical to produce a color change. The length of stain (or color change) produced in the detector tube when exposed to a measured volume of sample is directly proportional to the amount of hydrogen sulfide present in the sample being tested. A bellows or piston type pump is used to suck a measured volume of sample through the tube at a controlled rate of flow. The length of stain produced is converted to ppm of H_2S by comparison with a calibration scale supplied by the manufacturer with each box of detector tubes. The apparatus is easily portable, is completely suited to making spot checks for hydrogen sulfide under field conditions.

3. APPARATUS

3.1 *Piston or bellows pump*—The pump is hand-operated and must be capable of sucking a minimum of 100 ml per stroke of sample through the detector tube with an accuracy of ± 2 ml.

3.2 *Detector Tube*—Tubes must be made of glass with break-off tips sized to fit the orifice of the pump. The chemical sealed in the tube must be specific for hydrogen sulfide and produce a distinct color change when exposed to a sample of gas containing hydrogen sulfide. Any substances known to interfere must be listed in instructions accompanying the tubes. The tube should have the calibration scale etched directly on the tube or other markings which provide for easy interpretation of hydrogen sulfide content from a separate calibration scale supplied with the tubes. Shelf life of the detector tubes must be a minimum of 2 years when stored according to manufacturer's recommendations.

3.3 *Gas Sampling Container*—Any container which provides for access of the detector tube into a uniform flow of sample gas at atmospheric pressure and isolated from the surrounding atmosphere.

3.3.1 A suitable container may be devised from a one pint polyethylene bottle. A ¼-inch O.D. polyethylene tubing sealed into the bottle and discharging near the bottom provides for flow of sample gas into the bottle. A ½-inch hole cut into the cap of the bottle provides both access for the detector tube and vent for gas flow. See Figure 1.

Note 2—A one pint polyethylene wash bottle is easily adapted to a suitable sample container.

3.3.2 Mylar gas collection bags are useful as gas sample containers when the supply of sample gas is limited. Mylar bags with a minimum capacity of two liters are an acceptable substitute for bottle described in 3.3.1.

3.4 *Barometer*—Any barometer equipped with a scale graduated in 1 mm of mercury subdivision and a range including the expected atmospheric pressure condition at the sampling site.

3.5 *Thermometer*—Standard laboratory thermometer graduated in 1°C subdivisions and including the range of sample temperatures expected during the test.

3.6 *Needle Valve and Tubing*—Any stainless steel needle valve which can be adjusted to control the flow of gas from source pressure into the gas sampling container. Polyethylene or gum rubber tubing may be used to connect the gas sampling container to the needle valve outlet.

Note 3—A pressure regulator may be used to control flow of the sample gas, in lieu of a needle valve.

4. SAMPLING

4.1 Select a sampling point which affords access to a representative sample of the gas to be tested (i.e.—a point on the main flow line). Flow line connections should have a centerline tap.

4.1.1 Open source valve, Figure 1, and blow down vigorously to clear foreign materials from source valve and connecting nipple. Close source valve.

4.1.2 Install needle valve (or pressure regulator) on outlet of source valve. Connect outlet of needle valve to gas sampling container using shortest length practicable of polyethylene or other suitable tubing.

4.1.3 Open source valve A and crack control valve B to obtain positive flow of gas through gas sample container venting to atmosphere through tube access and vent C.

4.1.4 Purge gas sample container until all air is displaced. A minimum purge time of 3 minutes is recommended.

Note 4—When using collection bags the same procedure is followed except that the deflated bag is attached directly to control valve B. The bag is filled once, disconnected and deflated. The bag is filled a second time and is then ready for the analysis.

5. PROCEDURE

5.1 Immediately before each series of measurements, test the pump for tightness by inserting an unopened tube and operating the pump. A loss in vacuum on the pump after 30 sec. indicates a leak.

5.1.1 Select the tube range that includes the expected amount of hydrogen sulfide present in the sample. Reading

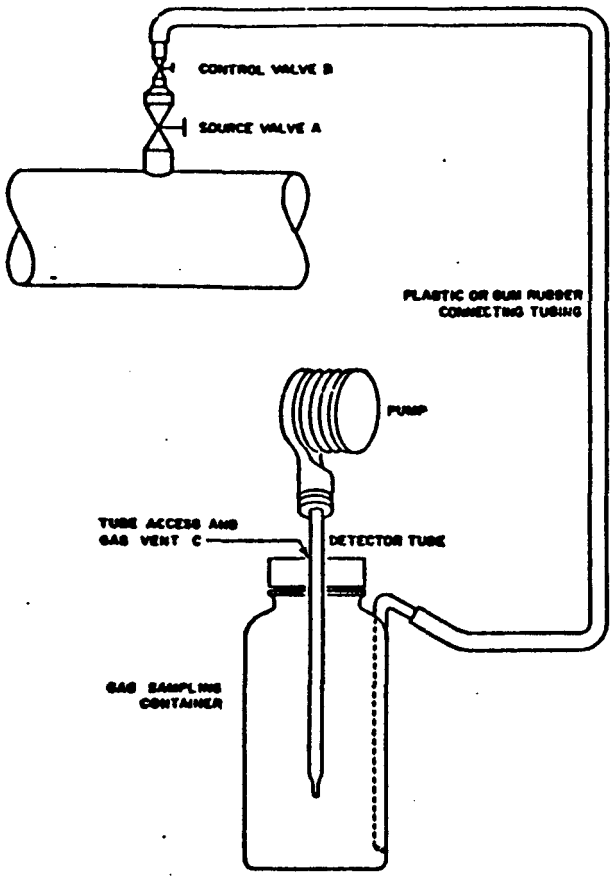


FIG. 1—Sampling manifold to be used with H_2S detector.

accuracy is improved when the stain extends at least 50 percent of the tube length. Consider multiple strokes and/or a lower range tube to achieve this length of stain.

5.1.2 Break off tips and insert outlet end of tube snugly into the pump head. Temperature of the tube must remain in the 0° to 40°C range throughout the test period.

5.1.3 Place detector tube well into gas sampling container through the tube access and vent C.

Note 5—Gas sample container must be completely purged of air and with control valve B adjusted to maintain a positive flow of gas leaving the tube access and vent C for the duration of the test.

5.1.4 Operate the pump to suck a measured volume of gas through the detector tube. Within limits set by manufacturer's instructions, use multiple strokes to maximize length of stain.

5.1.5 Remove the tube from the pump and immediately read the concentration of hydrogen sulfide from graduations on the tube or charts supplied with the tubes. The number opposite the end of the stain is the approximate hydrogen sulfide concentration. If the number of strokes used is different from the number specified by the manufacturer for a particular concentration, a correction must be made as follows:

$$\text{Corrected } H_2S \text{ Conc.} = \text{Scale reading} \times \frac{\text{Specified Strokes}}{\text{Actual Strokes}}$$

5.7 Record temperature of gas flowing through gas sample container and barometric pressure to provide data for gas volume corrections if required.

6. CALCULATIONS

6.1 Gas volume corrections may be desirable to improve precision of results. The effect of temperature is usually negligible; however, the barometric pressure becomes significant at altitudes above 2,000 feet. Correction for barometric pressure is done as follows:

$$\text{Corr. PPMV} = \text{ppmv (read from tube)} \times \frac{760 \text{ mm } H_g}{\text{Baro. Press. mm } H_g}$$

6.2 Check with manufacturer if it becomes necessary to test at gas temperatures outside the 0 to 40°C range.

7. PRECISION

7.1 The following criteria should be used for judging the acceptability of hydrogen sulfide concentration when determined using a "length of stain" detector tube. (95% confidence limit)

7.1.1 *Repeatability*—Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

Range of Sample Conc.	Repeatability
3–120	10% of amount found

7.1.2 *Reproducibility*—The results submitted by each of two laboratories should be considered suspect if the two results differ by more than the following amounts:

Range of Sample Conc.	Reproducibility
3–120	12% of amount present

Note 6—Precision limits shown above were obtained from raw data generated by 10–13 laboratories involved in cooperative testing of eight separate samples. Computations on the raw data were made using ASTM bulletin RR D-2-1007 "Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants." The cooperative tests were completed prior to finalizing the method write-up.

Note 7—Cooperative test results indicate a major source of error to be in the variance in response from lot number to lot number of tubes as supplied by the manufacturer. The fidelity of a given lot number of tubes can be verified by calibrating one or more tubes using a gas with a known concentration of hydrogen sulfide.

TABLE I
Length of Stain Method for Determination of H_2S in Natural Gas

Reproducibility of Labs

	Samples Mean/Lab						
	Lab Fld Gas 9 ppm	Lab Fld Gas 98 ppm	Lab Permeation Tube—44 ppm	Ecospan 88 ppm	Ecospan 18 ppm	Fld Gas 35 ppm	Fld Gas 93 ppm
Lab A	—	100	54	91	15	29	95
Lab B	—	101	42	89	13	28	—
Lab C	11	118	53	—	—	31	93
Lab E	9	—	47	84	14	—	—
Lab F	9	98	48	—	14	—	—
Lab G	—	—	43	79	21	29	93
Lab I	10	110	45	—	—	28	—
Lab J	9	91	43	86	10	29	100
Lab K	9	95	39	80	12	—	—
Lab P	7	98	—	86	9	38	101
Lab S	—	—	—	—	—	30	93
No. of Labs Participating	7	8	9	7	8	8	6
ppm H_2S Mean	9	101	46	85	13.5	30	96
% Error	0	3.1	4.5	3.4	25	14	3.2
Std. Deviation	1.2	8.7	5	4.4	3.6	3	3.7
Probable Error of Mean	.31	2.06	1.13	1.12	.87	.78	1.02
Probable Error	.81	5.83	3.38	2.96	2.5	2.2	2.50
Std. Deviation from Mean	.46	3.05	1.7	1.66	1.2	1.2	1.51
Std. Deviation for 95% Confidence Level	1.1	7.2	3.8	4.07	3.0	2.5	3.9

TABLE II
GPA Sulfur Analysis Work Group H_2S Data, May 11-June 7, 1976

			Experimental Data—Detector Tubes		
Gas Source	PPM H_2S	% Error	No. Determinations	PPM H_2S (Ave.)	
Ecospan	18	22%	38	14 ± 5	$\sigma = 1.4$
Ecospan	88	6%	36	83 ± 8	$\sigma = 2.2$
Permeation Tubes	44	5%	73	46 ± 8	$\sigma = 1.6$
Field Gas	9 ± 1*	11%	83	10 ± 3	$\sigma = 0.55$
Field Gas	98 ± 8*	5%	73	103 ± 13	$\sigma = 2.53$
Shamburger Lake Plant Inlet	35 ± 3*	11%	124	31 ± 4	$\sigma = 0.79$
Sun-Lateral #2	221 ± 15	2%	36	226 ± 13	$\sigma = 4.75$
Sun M. T. Cole #21	93 ± 7	9%	39	101 ± 6	$\sigma = 2.2$

σ (Standard Deviation for 95% Confidence Unit)

* Precision reflects repeatability of $CdSO_4$ method according to GPA Bulletin B-14

+ H_2S concentration was apparently continuously increasing during 4-5 hour period of $CdSO_4$ gas sampling. Determinations by detector tubes occurred near end of $CdSO_4$ method sampling and instrumental determinations even later.

TABLE III
Detector Tube H_2S Measurements by Tube Lot Numbers—June 7-8, 1976

	Drager 5/b Ch29801 5-60 ppm Range								Average
Lot No.	157091	1050184	1050185	1050126	1056371	1052101	255761		
No. Measurements	5	8	4	12	3	4	3		33
PPM H_2S	32 ± 1	30 ± 1	29 ± 1	29 ± 2	28 ± 0	29 ± 1	31 ± 1		30 ± 1
% Error	9%	14%	17%	17%	20%	17%	13%		17%
	Gastec 4LL 0-60 ppm Range								**Average**
Lot No.	51215	30710	30912	40113	40809	60116	50217	50913	
No. Measurements	19	13	6	9	6	4	4	4	65
PPM H_2S	30 ± 2	28 ± 2	38 ± 1	35 ± 1	35 ± 1	28 ± 1	27 ± 1	30 ± 1	32 ± 1
% Error	14%	20%	9%	3%	3%	20%	25%	14%	9%

Field Gas Source
Shamburger Lake Plant Inlet—35 PPM

Bei Rückfragen bitte die außen auf die Packung aufgestempelte Chargennummer angeben.
In all inquiries please state the batch number stamped on the outside of the box.
En cas de demandes, prière d'indiquer le No de série imprimé sur la boîte.

GEBRAUCHSANWEISUNG

DRÄGER-Röhrchen Quecksilberdampf 0,1/b

1. Allgemeines und Anwendungsbereich

Bestimmung von Quecksilberdampf (Hg-Dampf) am Arbeitsplatz.

Zur Handhabung der DRÄGER-Röhrchen und der Gasspürpumpe vgl. Abschnitt 4. dieser Gebrauchsanweisung und Gebrauchsanweisung 2341.

2. Beschreibung

Vgl. Abbildung.

Öffnungszeit (Dauer eines Pumpenhubes bis zur vollen Spannung der Sperrkette): 10 bis 20 Sekunden.

OPERATING INSTRUCTIONS

DRÄGER Tube Mercury Vapour 0.1/b

1. General and Application

Determination of mercury vapour (Hg vapour) at worksites.

For the use of DRÄGER Tubes and Gas Detector Pump refer to section 4. of these instructions and operating instructions 2341 e.

2. Description

Refer to illustration.

"Opening period" (time needed for the release of the compressed bellows, ending when the arrestor chain is fully tensioned): 10 to 20 seconds.

MODE D'EMPLOI

Tube réactif DRÄGER Vapeurs de mercure 0,1/b

1. Généralités et domaine d'utilisation

Détermination des vapeurs de mercure (vapeurs de Hg) sur le lieu de travail.

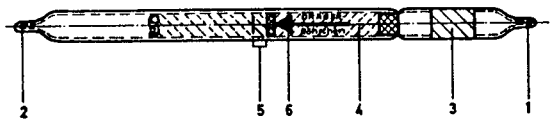
En ce qui concerne la manipulation des tubes réactifs DRÄGER et de la pompe détectrice de gaz, se référer au § 4 ci-après et au mode d'emploi 2341 f.

2. Description

Voir figure.

Durée d'ouverture (durée d'un coup de pompe jusqu'à tension totale de la chainette): 10 à 20 secondes.

1 und 2 zugeschmolzene Spitzen
3 Schreibfläche
4 Vorschicht (weiß)
5 Anzeigeschicht (schwach gelblichgrau) mit 1 Markierungsring
6 Pfeil (soll bei der Prüfung zur Pumpe weisen)



1 and 2 fused tips
3 writing surface
4 pre-layer (white)
5 indicating layer (pale yellowish grey) with 1 marking
6 arrow (must point towards the pump during the test)

1 et 2 pointes scellées
3 plage pour notices
4 couche préliminaire (blanche)
5 couche indicatrice (gris-jaunâtre pâle) avec 1 anneau de marquage
6 flèche (doit être dirigée vers la pompe lors de l'analyse)

3. Meßbereich (20° C, 1013 mbar)

0,1 bis 2 mg Hg pro m³.

Zur Erweiterung des Meßbereiches nach kleineren Konzentrationen vgl. Abschnitt 4.5.

4. Prüfung und Beurteilung des Ergebnisses

4.1. Pumpe vor jeder Meßreihe mit ungeöffnetem Röhrchen auf Dichtheit prüfen.

4.2. Spitzen des DRÄGER-Röhrchens abbrechen.

4.3. DRÄGER-Röhrchen dicht in den Pumpenkopf einsetzen (Pfeil weist zur Pumpe).

4.4. Die zu untersuchende Luft ist mit so vielen Hüben durch das Röhrchen zu saugen, bis sich die Anzeigeschicht bis zum aufgedruckten .Markierungsring gelborange verfärbt hat. Die Quecksilberdampf-Konzentration ergibt sich dann aus folgender Tabelle:

Hubzahl n	mg Hg pro m³
20	0,1
18	0,11
16	0,12
14	0,14
12	0,17
10	0,2
8	0,25
6	0,33
4	0,5
3	0,7
2	1
1	2

4.5. Durch Erhöhung der Hubzahl bis auf n = 40 lassen sich noch 0,05 mg Hg pro m³ bestimmen.

5. Bemerkungen

Die Hg-Röhrchen können nur einmal benutzt werden. Das gilt auch dann, wenn sich die Anzeigeschicht nicht verfärbt hat. Nach positivem Ergebnis sind die Verfärbungen längere Zeit haltbar (Röhrchen jedoch mit Gummikappen verschließen).

Röhrchen vor Licht schützen, da Anzeigeschicht lichtempfindlich ist.

3. Measuring Range (20° C, 1013 mbar)

0.1 to 2 mg Hg per m³.

Refer to section 4.5., regarding the extension of the measuring range to cover smaller concentrations.

4. Test and Evaluation of the Result

4.1. Before each test check the pump for tightness with the sealed DRÄGER Tube.

4.2. Break off the fused tips of the DRÄGER Tube.

4.3. Insert the DRÄGER Tube tightly into the pump head (arrow must point towards the pump).

4.4. Draw the air sample through the DRÄGER Tube using so many strokes until the indicating layer is discoloured yellow-orange up to the printed marking. The mercury vapour concentration follows then from the table underneath.

Number of strokes n	mg Hg per m³
20	0.1
18	0.11
16	0.12
14	0.14
12	0.17
10	0.2
8	0.25
6	0.33
4	0.5
3	0.7
2	1
1	2

4.5. When extending the number of strokes to n = 40, 0.05 mg Hg per m³ can be determined.

5. Remarks

The DRÄGER Tubes Hg can be used once only. This applies even if the indicating layer has not been discoloured. After positive result the discolourations last for some time (providing the tubes are sealed with rubber caps).

Protect tubes against light since indicating layer is sensitive to light.

3. Domaine de mesure (20° C, 1013 mbar)

0,1 à 2 mg de Hg par m³.

Concernant l'étendue du domaine de mesure vers des concentrations plus petites, voir § 4.5.

4. Analyse et évaluation du résultat

4.1. Avant chaque série de mesures, contrôler l'étanchéité de la pompe avec un tube réactif obturé.

4.2. Briser les pointes du tube réactif DRÄGER.

4.3. Insérer de manière étanche le tube réactif DRÄGER dans la tête de pompe (flèche vers la pompe).

4.4. Aspirer l'air à analyser à travers le tube réactif DRÄGER en effectuant le nombre de coups de pompe qui sera nécessaire pour que la couche indicatrice se soit colorée en jaune-orange jusqu'à l'anneau de marquage imprimé. On déterminera la concentration de vapeurs de mercure, selon le tableau suivant:

Nombre de coups de pompe n	mg de Hg par m³
20	0,1
18	0,11
16	0,12
14	0,14
12	0,17
10	0,2
8	0,25
6	0,33
4	0,5
3	0,7
2	1
1	2

4.5. En augmentant le nombre de coups de pompe jusqu'à n = 40, il est possible de déterminer encore 0,05 mg de Hg par m³.

5. Remarques

Les tubes réactifs de Hg ne peuvent être utilisés qu'une seule fois. Ceci est également valable dans le cas où la couche indicatrice ne s'est pas colorée. Après résultat positif, les colorations subsistent pendant un certain temps (à condition d'obturer les tubes réactifs au moyen des bouchons en caoutchouc).

Préserver de la lumière le tube réactif, la couche indicatrice étant sensible à la lumière.

6. Einfluß der Temperatur auf das Meßergebnis

Die Röhrchen können in einem Temperaturbereich von —10° C bis +40° C verwendet werden.

7. Spezifität

Die Anzeige beruht auf der Reaktion des Hg mit Kupfer(I)-jodid.

8. Vorgesehene Verbrauchszeit

2 Jahre bei Lagertemperaturen unter 30° C. Je kühler die DRÄGER-Röhrchen gelagert werden, desto besser bleiben ihre chemischen Eigenschaften erhalten.

9. Toxische Daten

MAK-Wert (BRD 1976): 0,1 mg/m³.

10. Flüchtigkeit von Quecksilber

Temperatur °C	Flüchtigkeit mg Hg/m³ Luft
0	2,2
9	5,0
12	6,6
18	11,1
20	13,2
25	19,5
30	29,7

6. Influence of the Temperature on the Measurement

The tubes can be used within —10° C and +40° C.

7. Specificity

The indication is based on the reaction of Hg with copper(I) iodide.

8. Predetermined Period of Use

2 years at storage temperatures below 30° C. The lower the temperature at which the DRÄGER Tubes are stored the smaller the change in their chemical properties.

9. Toxicity Data

Threshold limit value (U.S.A. 1976): 0,01 mg/m³.

10. Volatility of Mercury

Temperature °C	Volatility mg Hg/m³ air
0	2.2
9	5.0
12	6.6
18	11.1
20	13.2
25	19.5
30	29.7

6. Influence de la température sur le résultat de mesure

Les tubes réactifs peuvent être utilisés par températures comprises entre —10° C et +40° C.

7. Spécificité

L'indication repose sur la réaction du Hg avec l'iodure de cuivre (I).

8. Durée d'utilisation prévue

2 ans par températures de stockage inférieures à 30° C. Les propriétés chimiques des tubes réactifs DRÄGER se modifieront d'autant moins que la température de stockage sera peu élevée.

9. Données toxicologiques

Valeur MAC (RFA 1976): 0,1 mg/m³.

10. Volatilité de mercure

Température °C	Volatilité mg de Hg/m³ d'air
0	2,2
9	5,0
12	6,6
18	11,1
20	13,2
25	19,5
30	29,7

Unsere **Tabelle 2340** enthält alphabetisch geordnet die mit DRÄGER-Röhrchen meßbaren **Gase und Dämpfe,** wichtige **physikalische und toxikologische Daten** der Gase und Dämpfe sowie Literaturhinweise.

Bitte, fordern Sie diese Tabelle bei uns an!

Our **table 2340 e** contains in alphabetical order the **gases and vapours** measurable with DRÄGER Tubes, important **physical and toxicological data** of the gases and vapours as well as many references to literature.

This table will be sent to you on request.

Notre **tableau 2340 f** contient par ordre alphabétique les **gaz et vapeurs** pouvant être déterminés à l'aide des tubes réactifs DRÄGER, des données importantes **physiques et toxicologiques** ainsi que beaucoup de renvois à la littérature.

Ces tableaux vous parviendront sur demande!

Achtung!

Verbrauchte DRÄGER-Röhrchen nicht achtlos fortwerfen, damit sie nicht in Kinderhände gelangen!

Inhalt ätzt!

Zur Vernichtung von DRÄGER-Röhrchen vgl. auch 88. Folge der »Mitteilungen zum DRÄGER-Gasspürgerät«:

Caution

Do not allow the DRÄGER Tubes to fall into the hands of children.

Contents are corrosive.

For destroying the DRÄGER Tubes refer to Information Sheet No. 88.

Attention:

Ne pas jeter inattentivement les tubes réactifs DRÄGER épuisés afin qu'ils ne parviennent pas dans les mains des enfants.

Contenu corrosif.

En ce qui concerne la mise au rebut des tubes réactifs DRÄGER, voir également la communication No 88.

DRÄGERWERK · AG · LÜBECK

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DETERMINATION of the MAJOR COMPONENTS in a GAS

PRINCIPLE:

Determination and quantitation of gaseous fuels is accomplished by gas/solid and gas/liquid chromatographic separation.

SCOPE:

This gas chromatographic method is for the quantitative determination of the major components in a gas sample. The compounds that are analyzed include the fixed gases and the saturated and unsaturated hydrocarbons between methane and hexane with a hexane and heavier (C_6 plus) backflush. The typical limit of detection is 0.01 Vol%.

APPARATUS:

HACH-CARLE Series 500 multi-oven, multi-valve, multiple column by-pass microprocessor controlled gas chromatograph with thermal conductivity detector (TCD) and flame ionization detector (FID).

Digital Manometer (0 - 1000 torr absolute)

Vacuum Manifold attached to Sample Inlet

PE-Nelson "Turbochrom" P.C. based Data System

INSTRUMENT PARAMETERS:

INSTRUMENT: Hach-Carle Series 500 Gas Chromatograph

COLUMNS:

#	Length	Mesh		Description
1	20"	45/60	28%	DC 200/500 on Chromosorb P-AW
2	6'	60/80	3%	Sabaconatrille on Carbopack B
3A	8"	60/80	0.4%	Carbowax 1500 on Carbopack B
3B	16'	80/100	0.1%	Carbowax 1540 on Sperosil XOB-015
4A	17'	45/60	27.5%	Bis-2-(EE)A on Chromosorb P-AW
4B	12'	80/100	2.7%	Carbowax 1540 on Porasil C
5	9'	50/80	80%	Porapak N + 20% Porapak Q
6A	4'	80/100		Molecular Sieve 13X
6B	9'	45/60		Molecular Sieve 13X
7	3'	80/100		Molecular Sieve 5A
8	4"	45/60		Molecular Sieve 13X

COLUMN TEMPERATURES:	Oven 1	Oven 2
INITIAL COL TEMP (deg C):	70	68
INITIAL HOLD (min):	23	8.0
PROGRAM RATE #1 (deg C/min):	N/A	2.0
PROGRAM RATE #2 (deg C/min):	N/A	N/A
FINAL TEMP (deg C):	70	100

HOLD TIME (min):	N/A	12.5
INJECTION TEMP (deg C):	180	180
FLOWRATE - GAS:	30-He; 30-N_2	30-He
COLUMN PRESSURE (psig):	100-He 60-N_2	100-He
SPLIT RATIO (ml/min):	N/A	N/A
DETECTOR TYPE:	TCD	FID-
DETECTOR TEMP (deg C):	180	150

VALVE TIMING:

VALVE DESCRIPTION:		TIME(min)
Sample Isolation	(V3)	0.01
TCD Injection	(V4)	0.10
Mol Sieve Isolation	(V5)	3.70
(Propane +) Backflush	(V4)	10.50
Mol Sieve Return	(V5)	10.75
FID Injection	(V1)	23.10
(Hexane +) Backflush	(V1)	25.75
C4 and C5 Separation	(V2)	28.50
V2 Return	(V2)	58.50

QUANTITATION:

The quantitation method uses relative response factors with normalization of the sample to 100 percent. All response factors are calculated with reference to methane determined by the TCD. Methane is assigned the RRF value of 10.000.

SUMMARY OF METHOD:

SAMPLE PREPARATION:

Stainless steel gas cylinders are heated to ~60°C before sampling to ensure vaporization of any condensed hydrocarbons.

PREPARATION OF INSTRUMENT:

The temperature setpoints of the instrument are checked and the flame is ignited before the first standard is analyzed. No other instrument preparation is necessary.

SAMPLE ANALYSIS:

The gas sample is introduced into the GC via a vacuum manifold sampling system consisting of a fine needle valve and a digital manometer. The vacuum manifold is used for sub-ambient pressure samples and linearity checks. Two chromatographic methods are used in this analysis. The first is a column isolation method that analyses for the non-hydrocarbon gases, CH_4, and the C_2's using a thermal conductivity detector. Hydrogen is detected using the hydrogen transfer tube (HTT) with an auxilary N_2 carrier gas. The second method is a column by-pass method that analyses only for hydrocarbons with the flame

ionization detector. This method will resolve the unsaturated C_4 isomers and is used for a refinery gas type analysis. The C_6 plus backflush peak also includes any pentadienes.

The two chromatographic methods are run in series, therefore two seperate injections are made at different times. This is accomplished through the use of the sample loop isolation valve (V3) in the instrument. The first injection is for the TCD analysis, which requires approximately 20 minutes, followed by the second injection for the FID analysis. The total running time is 60 minutes.

Standards are run daily depending on the types of samples to be analysed that day. Several standards are used for calibration. These include synthesis gases, IGT certified natural gas standards, refinery gas standards and other various gas standards. In addition to these standard mixtures, air is injected routinely to calculate the oxygen/argon RRF. All response factors are recorded in a lab notebook to monitor operation of the instrument.

LIST OF COMPONENTS:

TCD	Expected Retention Time (min)	FID	Expected Retention Time (min)
Hydrogen	3.22	C_6 Plus (Backflush)	27.19
Carbon Dioxide	4.93	Methane	27.90
Ethene	6.70	Ethane + Ethene	28.46
Ethane	8.20	Acetylene	29.15
Acetylene	9.70	Propane	30.35
Oxygen/Argon	11.07	Propene	31.10
Nitrogen	12.00	Propadiene	31.70
Methane	14.40	Methyl Acetylene	35.50
Carbon Monoxide	15.80	i-Butane	38.38
		n-Butane	40.60
		1-Butene	40.87
		i-Butene	41.40
		t-2-Butene	42.87
		c-2-Butene	43.35
		1,3-Butadiene	44.80
		Pentene	46.70
		i-Pentane	50.70
		n-Pentane	54.63
		1-Pentene	54.83
		t-2-Pentene	56.04
		c-2-Pentene	58.00
		Pentene	58.60

DATA PROCESSING

All components are calculated as volume percent of the original sample. A computerized report format calculates the Heating Value and Relative Density from the volume percent and all components are also reported as weight percent.The Heating Value and Relative Density calculations are based on ASTM Method D-3588.

QUALITY ASSURANCE/QUALITY CONTROL

All standard runs are recorded in a laboratory notebook with their Relative Response Factors (RRF) for that day. Day to day reproducibility and trends are checked for each entry.

TIME:

Instrument Time: 1 hr.
Analyst Time: 45 min.

DETERMINATION of HEXANE and HEAVIER COMPONENTS in a GAS

PRINCIPLE:

Quantitation of hydrocarbons is accomplished by a gas/liquid chromatographic separation.

SCOPE:

This analysis is for the quantitation and identification of trace components that have boiling points between pentane (C_5) and approximately dodecane (C_{12}) in a gas by High Resolution Capillary Gas Chromatography/Flame Ionization Detection (HRCC-GC/FID). The analytical report includes the volume percent of benzene, toluene, xylenes and the remainder of the sample by carbon number. The typical range of analysis is between 0.5 ppmv to 1000 ppmv.

APPARATUS:

Sigma 1 or any Capillary GC

Heated gas sampling valve

PE-Nelson "Turbochrom" P.C. based Data System

INSTRUMENT PARAMETERS:

INSTRUMENT:	Sigma 1 or any Capillary GC
COLUMN:	60 meter DB-5; RSL-200; or equiv.
COLUMN TEMP. PROGRAM:	
INITIAL COL TEMP (deg C):	0
INITIAL HOLD (min):	1
PROGRAM RATE #1 (deg C/min):	5.0
PROGRAM RATE #2 (deg C/min):	N/A
FINAL TEMP (deg C):	275
HOLD TIME (min):	19
INJECTION TYPE:	1ml GAS LOOP (Heated)
INJECTION TEMP (deg C):	325
FLOWRATE - GAS:	N/A
COLUMN PRESSURE (psig):	30
SPLIT FLOW (ml/min):	300
DETECTOR TYPE:	FID
DETECTOR TEMP (deg C):	300

QUANTITATION:

Quantitation is performed by an internal standard calculation relative to the butanes and/or pentanes determined from the procedure for the Major Components in a Gas Analysis.

The specified aromatic compounds are tabulated separately and their contribution to the chromatogram areas are subtracted from the appropriate carbon number range. The remaining compounds are tabulated by carbon number ending at each n-alkane.

SUMMARY OF METHOD:

SAMPLE PREPARATION:

The gas cylinders are heated to ~60°C before sampling to ensure vaporization of any condensed hydrocarbons.

PREPARATION OF INSTRUMENT:

The capillary column is heated to 275 °C for approximately one half hour to bake off contaminants that have accumulated overnight before the first standard injection. The appropriate sensitivity range is selected for the standard that is selected. A gas standard of 1000 ppmv n-alkanes (CH_4 - C_6) is run in duplicate and checked for reproducibility of the peak areas and retention times. The second injection is allowed to run to the end of the column temperature program to clean the column and serve as a blank for the sample.

SAMPLE ANALYSIS:

The gas standard and samples are injected using a 1 ml heated gas sampling loop connected to the split/splitless injection port of the gas chromatograph. The injection is split at a flow rate of 300 ml/min.

LIST OF COMPONENTS:

Compound	Expected Retention Time (min)
i-Butane	2.95
n-Butane	3.50
neo-Pentane	3.75
i-Pentane	5.40
n-Pentane	6.30
n-Hexane	10.50
Benzene	12.65
n-Heptane	15.15
Toluene	17.60
n-Octane	19.50

Ethyl-Benzene	21.80
m,p-Xylene	22.20
o-Xylene	23.15
n-Nonane	24.05
n-Decane	28.00
n-Undecane	31.50
Naphthalene	34.45
n-Dodecane	34.70

DATA PROCESSING:

The quantitation method uses an internal standard that was obtained from the procedure for Major Components in a Gas Analysis. This is typically one of the butanes or pentanes. The specified aromatic compounds are tabulated separately and their areas are subtracted from the appropriate carbon number range. The remaining compounds are tabulated by carbon number ending at each n-alkane.

All components are calculated by volume percent from the internal standard compound that was used.

SAMPLE CALCULATION:

$$Conc_i\ (ppmv) = (Area_i) * (Conc_s\ (ppmv)) / (Area_s) * (MW_s) / (MW_i)$$

$Conc_i$ (ppmv) - Concentration of Analyte (i)
$Area_i$ - Area of Analyte (i)
MW_i - Molecular Weight of Analyte (i)
$Conc_s$ (ppmv) - Concentration of Internal Standard
$Area_s$ - Area of Internal Standard
MW_s - Molecular Weight of Internal Standard

QUALITY ASSURANCE/QUALITY CONTROL

The standard is checked for the correct retention time and peak areas of the components present.

TIME:

Instrument Time: 3 hrs.
Analyst Time: 1 hr.

Bei Rückfragen bitte die außen auf die Packung aufgestempelte Chargennummer angeben.
In all inquiries please state the batch number stamped on the outside of the box.
En cas de demandes, prière d'indiquer le No de série imprimé sur la boîte.

GEBRAUCHSANWEISUNG

DRÄGER-Röhrchen Quecksilberdampf 0,1/b

1. Allgemeines und Anwendungsbereich

Bestimmung von Quecksilber**dampf** (Hg-Dampf) am Arbeitsplatz.

Zur Handhabung der DRÄGER-Röhrchen und der Gasspürpumpe vgl. Abschnitt 4. dieser Gebrauchsanweisung und Gebrauchsanweisung 2341.

2. Beschreibung

Vgl. Abbildung.

Öffnungszeit (Dauer eines Pumpenhubes bis zur vollen Spannung der Sperrkette): 10 bis 20 Sekunden.

OPERATING INSTRUCTIONS

DRÄGER Tube Mercury Vapour 0.1/b

1. General and Application

Determination of mercury **vapour** (Hg vapour) at worksites.

For the use of DRÄGER Tubes and Gas Detector Pump refer to section 4. of these instructions and operating instructions 2341 e.

2. Description

Refer to illustration.

"Opening period" (time needed for the release of the compressed bellows, ending when the arrestor chain is fully tensioned): 10 to 20 seconds.

MODE D'EMPLOI

Tube réactif DRÄGER Vapeurs de mercure 0,1/b

1. Généralités et domaine d'utilisation

Détermination des **vapeurs** de mercure (vapeurs de Hg) sur le lieu de travail.

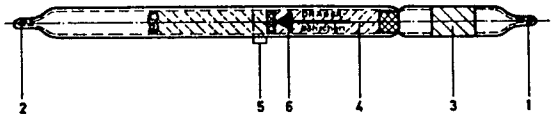
En ce qui concerne la manipulation des tubes réactifs DRÄGER et de la pompe détectrice de gaz, se référer au § 4 ci-après et au mode d'emploi 2341 f.

2. Description

Voir figure.

Durée d'ouverture (durée d'un coup de pompe jusqu'à tension totale de la chaînette): 10 à 20 secondes.

1 und 2 zugeschmolzene Spitzen
3 Schreibfläche
4 Vorschicht (weiß)
5 Anzeigeschicht (schwach gelblichgrau) mit 1 Markierungsring
6 Pfeil (soll bei der Prüfung zur Pumpe weisen)



1 and 2 fused tips
3 writing surface
4 pre-layer (white)
5 indicating layer (pale yellowish grey) with 1 marking
6 arrow (must point towards the pump during the test)

1 et 2 pointes scellées
3 plage pour notices
4 couche préliminaire (blanche)
5 couche indicatrice (gris-jaunâtre pâle) avec 1 anneau de marquage
6 flèche (doit être dirigée vers la pompe lors de l'analyse)

3. Meßbereich (20° C, 1013 mbar)

0,1 bis 2 mg Hg pro m³.

Zur Erweiterung des Meßbereiches nach kleineren Konzentrationen vgl. Abschnitt 4.5.

4. Prüfung und Beurteilung des Ergebnisses

4.1. Pumpe vor jeder Meßreihe mit ungeöffnetem Röhrchen auf Dichtheit prüfen.

4.2. Spitzen des DRÄGER-Röhrchens abbrechen.

4.3. DRÄGER-Röhrchen dicht in den Pumpenkopf einsetzen (Pfeil weist zur Pumpe).

4.4. Die zu untersuchende Luft ist mit so vielen Hüben durch das Röhrchen zu saugen, bis sich die Anzeigeschicht bis zum aufgedruckten Markierungsring gelborange verfärbt hat. Die Quecksilberdampf-Konzentration ergibt sich dann aus folgender Tabelle:

Hubzahl n	mg Hg pro m³
20	0,1
18	0,11
16	0,12
14	0,14
12	0,17
10	0,2
8	0,25
6	0,33
4	0,5
3	0,7
2	1
1	2

4.5. Durch Erhöhung der Hubzahl bis auf n = 40 lassen sich noch 0,05 mg Hg pro m³ bestimmen.

5. Bemerkungen

Die Hg-Röhrchen können nur einmal benutzt werden. Das gilt auch dann, wenn sich die Anzeigeschicht nicht verfärbt hat. Nach positivem Ergebnis sind die Verfärbungen längere Zeit haltbar (Röhrchen jedoch mit Gummikappen verschließen).

Röhrchen vor Licht schützen, da Anzeigeschicht lichtempfindlich ist.

3. Measuring Range (20° C, 1013 mbar)

0.1 to 2 mg Hg per m³.

Refer to section 4.5., regarding the extension of the measuring range to cover smaller concentrations.

4. Test and Evaluation of the Result

4.1. Before each test check the pump for tightness with the sealed DRÄGER Tube.

4.2. Break off the fused tips of the DRÄGER Tube.

4.3. Insert the DRÄGER Tube tightly into the pump head (arrow must point towards the pump).

4.4. Draw the air sample through the DRÄGER Tube using so many strokes until the indicating layer is discoloured yellow-orange up to the printed marking. The mercury vapour concentration follows then from the table underneath.

Number of strokes n	mg Hg per m³
20	0.1
18	0.11
16	0.12
14	0.14
12	0.17
10	0.2
8	0.25
6	0.33
4	0.5
3	0.7
2	1
1	2

4.5. When extending the number of strokes to n = 40, 0.05 mg Hg per m³ can be determined.

5. Remarks

The DRÄGER Tubes Hg can be used once only. This applies even if the indicating layer has not been discoloured. After positive result the discolourations last for some time (providing the tubes are sealed with rubber caps).

Protect tubes against light since indicating layer is sensitive to light.

3. Domaine de mesure (20° C, 1013 mbar)

0,1 à 2 mg de Hg par m³.

Concernant l'étendue du domaine de mesure vers des concentrations plus petites, voir § 4.5.

4. Analyse et évaluation du résultat

4.1. Avant chaque série de mesures, contrôler l'étanchéité de la pompe avec un tube réactif obturé.

4.2. Briser les pointes du tube réactif DRÄGER.

4.3. Insérer de manière étanche le tube réactif DRÄGER dans la tête de pompe (flèche vers la pompe).

4.4. Aspirer l'air à analyser à travers le tube réactif DRÄGER en effectuant le nombre de coups de pompe qui sera nécessaire pour que la couche indicatrice se soit colorée en jaune-orange jusqu'à l'anneau de marquage imprimé. On déterminera la concentration de vapeurs de mercure, selon le tableau suivant:

Nombre de coups de pompe n	mg de Hg par m³
20	0,1
18	0,11
16	0,12
14	0,14
12	0,17
10	0,2
8	0,25
6	0,33
4	0,5
3	0,7
2	1
1	2

4.5. En augmentant le nombre de coups de pompe jusqu'à n = 40, il est possible de déterminer encore 0,05 mg de Hg par m³.

5. Remarques

Les tubes réactifs de Hg ne peuvent être utilisés qu'une seule fois. Ceci est également valable dans le cas où la couche indicatrice ne s'est pas colorée. Après résultat positif, les colorations subsistent pendant un certain temps (à condition d'obturer les tubes réactifs au moyen des bouchons en caoutchouc).

Préserver de la lumière le tube réactif, la couche indicatrice étant sensible à la lumière.

6. Einfluß der Temperatur auf das Meßergebnis

Die Röhrchen können in einem Temperaturbereich von —10° C bis +40° C verwendet werden.

7. Spezifität

Die Anzeige beruht auf der Reaktion des Hg mit Kupfer(I)-jodid.

8. Vorgesehene Verbrauchszeit

2 Jahre bei Lagertemperaturen unter 30° C. Je kühler die DRÄGER-Röhrchen gelagert werden, desto besser bleiben ihre chemischen Eigenschaften erhalten.

9. Toxische Daten

MAK-Wert (BRD 1976): 0,1 mg/m³.

10. Flüchtigkeit von Quecksilber

Temperatur °C	Flüchtigkeit mg Hg/m³ Luft
0	2,2
9	5,0
12	6,6
18	11,1
20	13,2
25	19,5
30	29,7

6. Influence of the Temperature on the Measurement

The tubes can be used within —10° C and +40° C.

7. Specificity

The indication is based on the reaction of Hg with copper(I) iodide.

8. Predetermined Period of Use

2 years at storage temperatures below 30° C. The lower the temperature at which the DRÄGER Tubes are stored the smaller the change in their chemical properties.

9. Toxicity Data

Threshold limit value (U.S.A. 1976): 0,01 mg/m³.

10. Volatility of Mercury

Temperature °C	Volatility mg Hg/m³ air
0	2.2
9	5.0
12	6.6
18	11.1
20	13.2
25	19.5
30	29.7

6. Influence de la température sur le résultat de mesure

Les tubes réactifs peuvent être utilisés par températures comprises entre —10° C et +40° C.

7. Spécificité

L'indication repose sur la réaction du Hg avec l'iodure de cuivre (I).

8. Durée d'utilisation prévue

2 ans par températures de stockage inférieures à 30° C. Les propriétés chimiques des tubes réactifs DRÄGER se modifieront d'autant moins que la température de stockage sera peu élevée.

9. Données toxicologiques

Valeur MAC (RFA 1976): 0,1 mg/m³.

10. Volatilité de mercure

Température °C	Volatilité mg de Hg/m³ d'air
0	2,2
9	5,0
12	6,6
18	11,1
20	13,2
25	19,5
30	29,7

Unsere **Tabelle 2340** enthält alphabetisch geordnet die mit DRÄGER-Röhrchen meßbaren **Gase und Dämpfe**, wichtige **physikalische und toxikologische Daten** der Gase und Dämpfe sowie Literaturhinweise.

Bitte, fordern Sie diese Tabelle bei uns an!

Our **table 2340 e** contains in alphabetical order the **gases and vapours** measurable with DRÄGER Tubes, important **physical and toxicological data** of the gases and vapours as well as many references to literature.

This table will be sent to you on request.

Notre **tableau 2340 f** contient par ordre alphabétique les **gaz et vapeurs** pouvant être déterminés à l'aide des tubes réactifs DRÄGER, des données importantes **physiques et toxicologiques** ainsi que beaucoup de renvois à la littérature.

Ces tableaux vous parviendront sur demande!

Achtung!

Verbrauchte DRÄGER-Röhrchen nicht achtlos fortwerfen, damit sie nicht in Kinderhände gelangen!

Inhalt ätzt!

Zur Vernichtung von DRÄGER-Röhrchen vgl. auch 88. Folge der »Mitteilungen zum DRÄGER-Gasspürgerät«:

Caution

Do not allow the DRÄGER Tubes to fall into the hands of children.

Contents are corrosive.

For destroying the DRÄGER Tubes refer to Information Sheet No. 88.

Attention:

Ne pas jeter inattentivement les tubes réactifs DRÄGER épuisés afin qu'ils ne parviennent pas dans les mains des enfants.

Contenu corrosif.

En ce qui concerne la mise au rebut des tubes réactifs DRÄGER, voir également la communication No 88.

DRÄGERWERK · AG · LUBECK

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DRÄGERWERK · AG · LUBECK

Telephone: 8 10 21 Telex: 02 6807

3rd Edition **234—231 e** September 1977

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Tél. 8 10 21 Télescr. 02 6807

3ième Edition **234—231 f** Septembre 1977

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Printed in the Federal Republic of Germany

Bei Rückfragen bitte die außen auf die Packung aufgestempelte Chargennummer angeben.

In all inquiries please state the batch number stamped on the outside of the box.

En cas de demandes, prière d'indiquer le No de série imprimé sur la boîte.

1 DRÄGER Tube Ammonia 5/a

2 Standard range of measurement (20°C, 1013 mbar)	5 to 70 ppm ammonia
3 Number of strokes of the DRÄGER gas detector pump	$n = 10$
4 Relative standard deviation	15 to 10%
5 TLV	25 ppm ammonia

6 Description

Scale tube – orange indicating layer, reagent: bromophenol blue and acid – colour change to dark blue

7 Reaction principle

$$NH_3 + \text{acid} \xrightarrow{\text{Bromophenol blue as indicator}} \text{Ammonium salt}$$

8 Cross-sensitivity

Hydrazine and 1,1-dimethyl hydrazine react with the same sensitivity as ammonia (related to ppm). Organic bases (e.g. amines) are also indicated, but usually with a different sensitivity.

9 Extension of the range of measurement

9.1 Determination of NH_3 concentrations up to 700 ppm.

The number of strokes can be arbitrarily varied between $n = 2$ and $n = 10$. With $n = 2$, the range of measurement extends from 25 to 350 ppm. With $n = 1$, the range of measurement is about 50 to 700 ppm.

9.2 Determination of NH_3 concentrations below 5 ppm

Here the air (or gas) sample should be sucked through the DRÄGER Tube with more than 10 strokes (maximum 50 strokes). Evaluation results from the length of the discoloration using the following formula:

$$\frac{\text{Scale value read-off} \times 10}{\text{Number of strokes of the gas detector pump}} = \text{ppm } NH_3$$

Suction devices other than the DRÄGER gas detector pump can be used to suck-in the air sample. The rate of flow during measurement should be about 1 litre per minute. Evaluation is in accordance with the following formula:

$$\frac{\text{Scale value read-off}}{\text{Volume sucked through in litres}} = \text{ppm } NH_3$$

However, it must be ensured that the moisture content of the air sample is at least 5 mg per litre; with lower moisture contents the blue discoloration is not sharply delimited, but diffuse. More NH_3 than is actually present can then be indicated.

1 DRÄGER Tube Carbon Dioxide 1%

2 Standard range of measurement (20°C, 1013 mbar)	1 to 20 vol.% carbon dioxide
3 Number of strokes of the DRÄGER gas detector pump	$n = 1$
4 Relative standard deviation	10 to 5%
5 TLV	See Carbon Dioxide 0.1%/a Tube

6 Description

Scale tube – white indicating layer, reagent: crystal violet and hydrazine – colour change to bluish-violet.

7 Reaction principle

According to Beilstein (17):

$$CO_2 \text{ (Carbon dioxide)} + N_2H_4 \text{ (Hydrazine)} \xrightarrow{\text{Crystal violet as redox indicator}} NH_2 \cdot NH \cdot COOH \text{ (Carbonic acid monohydrazide)}$$

8 Cross-sensitivity

Other gases and vapours do not affect the indication.

1 DRÄGER Tube Water Vapour 0.1

2 Standard range of measurement (20°C, 1013 mbar)	0.1 to 40 mg water vapour per litre (The first division of the printed scale corresponds to 1 mg/litre, lower concentrations can only be estimated in the 10-stroke test)
3 Number of strokes of the DRÄGER gas detector pump	$n = 10$
4 Relative standard deviation	15 to 10%
5 TLV	—

6 Description

Scale tube – yellow indicating layer, reagent: activated selenium dioxide and sulphuric acid – colour change to reddish-brown.

7 Reaction principle

$$H_2O \text{ (Water vapour)} + SeO_2 \text{ (Selenium dioxide)} + H_2SO_4 \text{ (Sulphuric acid)} \rightarrow \text{Redddish-brown reaction product}$$

8 Cross-sensitivity

Unsaturated hydrocarbons, present in fairly high concentrations, change the colour of the entire indicating layer to a diffuse brown.

9 Extension of the range of measurement

The water vapour tubes are also suitable for the determination of lower moisture concentrations (below 1 mg H_2O per litre). The following test procedure has proved suitable for such measurements (see also IS 27): At least 10 litres of the gas to be investigated (e.g. compressed air, carbon dioxide, inert gases) are passed through the tube. The volume can be increased up to 1,000 litres. The rate of flow should be at least 40 litres per hour.

The discoloration of the indicating layer is brownish-red with a green border preceding it. Here also the total length of the discoloration is evaluated.

Since the calibration curve under these test conditions is different from that in the 10-stroke test (≙ 1 litre), evaluation should be carried out using the following formula:

$$\text{mg } H_2O \text{ per m}^3 \text{ (related to 760 mm Hg ≙ 1013 mbar)} = \frac{\text{Indication (tube) in mg per litre} \times 600}{\text{Gas sample volume in litres}}$$

Important: pressure reducers, connecting lines, flowmeters, etc. must be completely dry before starting measurement.

1 **DRÄGER Tube Hydrogen Sulphide 1/c**

2 **Standard range of measurement** (20°C, 1013 mbar)	1 to 20 ppm hydrogen sulphide 10 to 200 ppm hydrogen sulphide
3 **Number of strokes of the DRÄGER gas detector pump**	n = 10 n = 1
4 **Relative standard deviation**	10 to 5%
5 **TLV**	10 ppm hydrogen sulphide

6 **Description**

Scale tube – white indicating layer, reagent: lead compound – colour change to pale brown.

7 **Reaction principle**

H_2S (Hydrogen sulphide) + Pb^{2+} (Lead compound) → PbS (Pale brown lead sulphide) + $2H^+$

8 **Cross-sensitivity**

In the presence of fairly high SO_2 concentrations, the H_2S indication is somewhat too high (e.g. a mixture of 5 ppm H_2S and 40 ppm SO_2 gives an indication of about 8 ppm H_2S; a mixture of 10 ppm H_2S and 100 ppm SO_2 gives an indication of about 15 ppm H_2S).

SO_2 alone does not discolour the indicating layer.

9 **Extension of the range of measurement**

The number of strokes can be increased directly to n = 100, whereby the range of measurement is 0.1 to 2 ppm H_2S.

Concentrations below 0.1 ppm H_2S can also be determined by increasing the number of strokes above n = 100. Up to 500 strokes are possible, but it must be ensured that the indicating layer does not dry out during the test, since this would lead to diffuse discolorations which are difficult to evaluate.

1 **DRÄGER Tube Mercury Vapour 0.1/b**

2 **Standard range of measurement** (20°C, 1013 mbar)	0.1 to 2 mg mercury vapour per m³
3 **Number of strokes of the DRÄGER gas detector pump**	n = 20 to 1
4 **Relative standard deviation**	30 to 20%
5 **TLV**	0.05 mg/m³ mercury vapour

6 **Description**

Tube with a marking ring – white precleanse layer – pale yellowish-grey indicating layer, reagent: copper (I) iodide – colour change to a weak yellowish.

7 **Reaction principle**

Hg (Mercury) + CuI (Copper(I) iodide) → Cu-Hg complex (colour: weak yellowish-orange)

8 **Cross-sensitivity**

Chlorine leads to minus indications in Hg measurements (e.g. 1 ppm Cl_2 + 0.5 mg Hg/m³ gives an indication of 0.2 mg Hg/m³).

As yet, no interference with the Hg indication by other gases and vapours has been observed. This statement is based on investigations with the following substances:

0.25 ppm AsH_3; 1 ppm PH_3; 10 ppm H_2S; 50 ppm NH_3; 5 ppm NO_2; 5 ppm SO_2; 1 ppm N_2H_4.

9 **Extension of the range of measurement**

0.05 mg Hg/m³ can be determined with increase in the number of strokes to n = 40.

Further increase in the number of strokes is only admissible if a suitable drying agent is incorporated in front of the tube for absorption of atmospheric humidity. For this purpose, we used a U-tube filled with magnesium perchlorate and were able to measure 0.02 mg Hg/m³ with 100 strokes.

1 **DRÄGER Tube Acetic Acid 5/a**

2 **Standard range of measurement** (20°C, 1013 mbar)	5 to 80 ppm acetic acid
3 **Number of strokes of the DRÄGER gas detector pump**	n = 3
4 **Relative standard deviation**	15 to 10%
5 **TLV**	10 ppm acetic acid

6 **Description**

Scale tube – bluish-violet indicating layer, reagent: acid indicator – colour change to yellow

7 **Reaction principle**

CH_3COOH (Acetic acid) + Acid indicator → Yellow reaction product

8 **Cross-sensitivity**

Acetic acid anhydride is indicated with lower sensitivity: indication on the acetic acid scale multiplied by a factor of 4 gives approximately ppm acetic acid anhydride. Other acids are also indicated (e.g. formic acid, hydrochloric acid), but with different sensitivity.

1 **DRÄGER Tube Hydrogen Sulphide 0.5/a**

2 **Standard range of measurement** (20°C, 1013 mbar)	0.5 to 15 ppm hydrogen sulphide
3 **Number of strokes of the DRÄGER gas detector pump**	n = 10
4 **Relative standard deviation**	10 to 5%
5 **TLV**	10 ppm hydrogen sulphide

6 **Description**

Scale tube – white indicating layer, reagent: mercury complex – colour change to pale brown.

7 **Reaction principle**

H_2S (Hydrogen sulphide) + Hg complex → pale brown sulphide

8 **Cross-sensitivity**

As yet, no interference by other gases and vapours has been observed, but investigations are still in progress.

IGT

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P.O. Box 1775, Alvin, TX 77512

Condensate Sampling and Analysis - Pleasant Bayou Flow Test, 1988 - present

This section covers analyses performed on condensate. Chemical analyses can only be related to well performance if the quantity of the various fluids are known. The operator measures daily accumulations of condensate from both the gunbarrel and the glycol dehydrator. These values are recorded in the log book and the sum of the two condensate volumes is reported in the Morning Report. This allows review of samples versus operating conditions. This section includes:

- An approximate sampling schedule during flow tests
- On-site sample handling and storage of gas samples
- Adresses of laboratories that perform off site analyses
- Sample shipping instructions
- Data achiving

It is expected that the above procedures will change as the flow test progresses, but deviations from the written procedures should be approved by C. Hayden of IGT and noted on the results of the analysis.

Condensate Sample Schedule

Condensate production is measured daily by operators on duty. The condensate is the placed into the round brine tank through the tank hatch, and then the tank hatch should be securely closed. Note - The condensate samples are FLAMMABLE LIQUIDS with a flash point at or below normal ambient temperatures. Keep away from sparks or flame. Components of the condensate, especially benzene, may also be CARCINOGENIC. Wear appropriate protective gear. Do not inhale vapors or get condensate on skin. Wash immediately with soap and water if you come in contact with condensate.

Condensate samples should be analysed every two months for the initial period of flow. The date of collection should coincide with a gas sample analysis date. After the condensate composition has been stable over several analyses, and enough analyses are obtained to define baseline values, sampling frequency can decline to once per 3 or 4 months.

Generally, only gunbarrel condensate samples are analysed. The gunbarrel condensate condenses from the gas phase as the gas temperature drops from the brine temperature (near 290 °F) to sales gas temperature (near 80°F). The dehydrator condensate is an accumulation of hydrocarbons that are dissolved in glycol at dehyrator pressures and temperatures, but is then distilled out of the glycol in the reboiler.

Routine Condensate Sample Collection and Analysis

Routine condensate sample collection involves filling one 8 ml (1/4 fluid ounce) H. D. Polyethylene bottle between half way to three quarters full. The preferred fill point is the 1/2 inch ball valve on the top side of the gunbarrel. If water comes out the valve, the sample must be collected at the siphon outlet or from the five gallon accumulator. Sample date, "PB well", and "cond" shouuld be scratched into the plastic with a pen or paper clip. Permanent markers wipe off if the ink comes in contact with the condensate.

On-Site Analyses: The only on-site analysis performed on condensate is an occasional specific gravity measurement. A 16 ounce sample is caught in a plastic jar and sealed. The sample is brought in doors to cool. The condensate is poured into the large glass cylinder and the appropriate hydrometer is floated in the sample. Expect a specific gravity between 0.9 and 1.0, and choose your hydrometer accordingly. Record the sample temperature and the specific gravity. Dump the sample back into the 5 gallon accumulator so that the coorect daily production volume will be measured and recorded.

On Site Sample Storage and Handling: Condensate samples should be shipped out for analysis as soon as possible. Wrap the 1/4 ounce bottle in paper towels and place it in a 100 or 200 ml widemouthed H. D. polyethylene bottle and seal. This ensures no oil will leak out and cause an odor problem. The sample is then placed in a bob with packing material and is sent to IGT at the address given below.

Samples shipped to IGT are classified as a flammable liquid for mailing purposes. Use Federal Express located adjacent to Hobby Airport, and fill out the shippers certification as indicated in Appendix Condensate-A. The box must have the address written on one side as well as having the airbill attached to another side. The box must also have a "Flammable Liquid" sticker attached. You must write "Inside Containers Comply With Prescribed Regulations" on the box side that has the sticker. The sample can also be classified as "Crude Oil, Petroleum", with a ID No. of UN 1267. The rest of the sheet is not changed.

The sample can also be mailed. The flash point of the condensate is estimated to be about 60°F. Regulations specified in Issue 30, 3-19-89, Section 124.331 must be followed. This document is also included in Appendix Condensate-A. Flammable liquids are not acceptable for air transportation via mail, but are acceptable with Federal Express.

Al Janos
Institute of Gas Technology
3424 South State Street
Chicago IL 60616

312-567-3679

Include a letter defining the number of samples, the charge number if appropriate, and analytical instructions. IGT instructions should specify following procedures for "Aromatic Constituents and Carbon Number Distribution".

Off Site Gas Analyses: IGT's analyses are defined both by the letter of instructions accompanying the samples and by the list of procedures defined in Appendix Condensate-B.

Data Handling and Reporting: All condensate analyses are to be reported in the Weekly reports to Eaton Operating Company, in a table with previous analyses for easy comparison. The origional report sheets are filed in the IGT-Condensate folder. All condensate analysis reports should contain the date and sample location.

Special Condensate Sample Collection and Analysis

Special condensate sample collection involves either collecting a sample for specific gravity determination or collecting a sample of the gunbarrel water to determine the hydrocarbon content. These samples are collected infrequently, with one or two samples per year usually being sufficient. The preferred condensate fill point is the 1/2 inch ball valve on the top side of the gunbarrel. The preferred water fill point is the water outlet pipe leaving the gunbarrel separator.

On-Site Analyses: The only on-site analysis performed on condensate is an occasional specific gravity measurement. A 16 ounce sample is caught in a plastic jar and sealed. The sample is brought in doors to cool. The condensate is poured into the large glass cylinder and the appropriate hydrometer is floated in the sample. Expect a specific gravity between 0.9 and 1.0, and choose your hydrometer accordingly. Record the sample temperature and the specific gravity. Dump the sample back into the 5 gallon accumulator so that the coorect daily production volume will be measured and recorded.

Off-Site Analyses: Brine samples can be sent to IGT for analysis. At least 200 ml of brine should be sent. Ask for a quantitative extraction followed by a condensate analysis.

Quality Control/Quality Assurance

Various standard mixtures are prepared in the laboratory to test the relative response factors for the chromatograph. The accuracy of the chromatograph is only a small part of the uncertainty of the analysis.

The composition of the condensate sample is expected to change with ambient temperature, with the retention time in the gunbarrel, and with the gas flow rate. There is no way to prevent vapors from leaving the gunbarrel. There is no way to control the sales gas temperature within a range of less than ±15° F. It will be difficult to differentiate a change in the produced well effluents from the effects of changing ambient temperatures. Barring a large compositional shift, a baseline must be defined for these samples over at least a one year period before we can definately say whether anything is changing.

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Company: Institute of Gas Technology

Department/Floor No.:

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PRIORITY 1 - Delivery is scheduled early next business morning in most locations. It may take two or more business days if the destination is outside our primary service areas.
STANDARD AIR - Delivery is generally next business day or not later than second business day. It may take three or more business days if the destination is outside our primary service areas.

DELIVERY AND SPECIAL HANDLING CHECK SERVICES REQUIRED

1 ☐ HOLD FOR PICK-UP (Fill in Section H at right)
2 ☒ DELIVER WEEKDAY
3 ☐ DELIVER SATURDAY (Extra charge)
4 ☒ DANGEROUS GOODS (P-1 and Standard Air Packages only. Extra charge)
5 ☐ CONSTANT SURVEILLANCE SERVICE (CSS) (Extra charge) (Do Not Complete Section 5)
6 ☐ DRY ICE ____ Lbs
7 ☐ OTHER SPECIAL SERVICE ____
8 ☐
9 ☐ SATURDAY PICK-UP (Extra charge)
10 ☐

PACKAGES	WEIGHT	YOUR DECLARED VALUE (See right)	OVER SIZE
Total	Total	Total	

Received At
1 ☐ Regular Stop
2 ☐ On Call Stop
3 ☐ Drop Box 4 ☐ B.S.C. 5 ☐ Station

Federal Express Corp. Employee No.

Date/Time For Federal Express Use

YOUR DECLARED VALUE

DAMAGE OR LOSS
We are liable for no more than $100 per package in the event of physical loss or damage, unless you fill in a higher Declared Value to the left and document higher actual loss in the event of a claim. We charge 30¢ for each additional $100 of declared value up to the maximum shown in our Service Guide. Declared value restrictions are shown on the back of the Sender's Copy of this airbill. We make no expressed or implied warranties.

DELAY
There is always a risk of late delivery or non-delivery. In the event of a late delivery Federal Express will, at your request and with some limitations, refund all transportation charges paid. See back of Sender's Copy of this airbill for further information.

CONSEQUENTIAL DAMAGES
We will not be responsible or liable for any loss or damage resulting from delay, non-delivery or damage to a package, except as noted above. This includes loss of sales, income, interest, profits, attorney fees and other costs but is not limited to these items. Such damages are called consequential damages.

DO NOT SHIP CASH OR CURRENCY

PART #105591
REV. 10/88
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008

ORIGIN COPY

1813338424 AIRBILL NUMBER

SHIPPER'S CERTIFICATION FOR RESTRICTED ARTICLES/DANGEROUS GOODS
CHECK ONE ➡ ☐ 49 CFR ☐ ICAO (TYPE OR PRINT)

NO. OF PKGS	DANGEROUS GOODS IDENTIFICATION: PROPER SHIPPING NAME	CLASS OR DIVISION	UN OR ID NO.	SUBSIDIARY RISK	TOTAL NET QUANTITY	PACKING INSTRUCTIONS	AUTHORIZATION
1	Gasoline	Flammable Liquid	UN1203		Less than one ounce		

ADDITIONAL DESCRIPTION REQUIREMENTS FOR RADIOACTIVE MATERIALS (SEE BACK)

RADIONUCLIDE	FORM	ACTIVITY	CATEGORY OF LABELS	TRANS. INDEX	PACKAGE IDENTIFICATION
			☐ WHITE I ☐ YELLOW II ☐ YELLOW III ☐ NONE		

TRANSPORT DETAILS: THIS SHIPMENT IS WITHIN THE LIMITATIONS PRESCRIBED FOR ▶ PASSENGER AIRCRAFT ~~CARGO AIRCRAFT ONLY~~ (DELETE-NONAPPLICABLE)

AIRPORT OF DEPARTURE | AIRPORT OF DESTINATION | SHIPMENT TYPE ▶ NON-RADIOACTIVE ~~RADIOACTIVE~~ (DELETE-NONAPPLICABLE)

IF ACCEPTABLE FOR PASSENGER AIRCRAFT, THIS SHIPMENT CONTAINS RADIOACTIVE MATERIAL INTENDED FOR USE IN, OR INCIDENT TO, RESEARCH, MEDICAL DIAGNOSIS OR TREATMENT.

I HEREBY DECLARE THAT THE CONTENTS OF THIS CONSIGNMENT ARE FULLY AND ACCURATELY DESCRIBED ABOVE BY PROPER SHIPPING NAME AND ARE CLASSIFIED, PACKED, MARKED, AND LABELED, AND ARE IN ALL RESPECTS IN PROPER CONDITION FOR TRANSPORT BY AIR ACCORDING TO THE APPLICABLE INTERNATIONAL AND NATIONAL GOVERNMENT REGULATIONS.

NAME AND TITLE OF SHIPPER: Chris Hayden Supervisor

PLACE AND DATE:

EMERGENCY TELEPHONE NUMBER: 713 482 6634

SIGNATURE OF SHIPPER: Chris Hayden

SEE WARNING ON BACK

100 to 177, may be obtained from the Superintendent of Documents, Government Printing Office, Washington, DC 20402-9371.

124.22 Address Marking. The name and address of both the mailer and the addressee must be affixed to the outside of any package, the mailing of which is covered by 124, using a material or method which is not water-soluble and which cannot be easily rubbed off or smeared.

124.23 Labels. Except for controlled substances mailed under 124.384, labels or other markings required by Federal law or regulation of any Federal agency must be securely affixed to the outside of the package. Because of the limited quantities and preparation of hazardous materials acceptable by the Postal Service, there is no general requirement for hazardous materials warning labels. Most hazardous matter acceptable by the Postal Service, except etiologic agents, magnetized material, and matches under certain conditions, falls within the Other Regulated Materials (ORM) regulations of CFR 49, Subpart J, which does not require these labels.

124.24 Shipment by Aircraft Certification. Parcels of hazardous articles mailable under 124, which will be transported by aircraft, must be accompanied by a shipper's declaration for dangerous goods prepared in accordance with Department of Transportation Regulations (49 CFR, 172.204), completed and signed in triplicate by the mailer.

124.3 Hazardous Matter

124.31 Chemicals. The great variety of chemical compositions precludes the listing of each such item which may or may not be mailed. The acceptability of chemicals for mailing generally depends upon container fluid/vapor capacities, the ability of the complete package to contain the product, and the method of absorbing and containing the product in case of accidental leakage of the primary container. To permit mailability determinations on specific products, the following information is required:

a. Name of material.

b. Chemical composition by percentage of ingredient.

c. Flash point.

d. Toxic properties.

e. Irritant action to eyes and skin.

f. Special precautions necessary to permit handling to avoid harm to postal personnel or property or other mail matter.

g. Explanation of warning labels required by state or Federal regulations.

h. Proposed method of packaging.

124.32 Explosives. All explosives are nonmailable, except for toy propellant devices and some safety fuses in the domestic surface mail, upon specific approval of the appropriate Rates and Classification Center.

124.33 Flammable Materials

124.331 Flammable Liquids.

a. Flammable liquids and semiliquids with a flash point of 20 degrees F (-6.7 degrees C) (closed-cup) or below are nonmailable. If the flash point is above 20 degrees F and (-6.7 degrees C) up to 73 degrees F (23 degrees C) (closed cup), the item may be accepted in the domestic surface mail.

b. Flammable liquids must be in metal containers not over 1-quart capacity or in other containers not over 1-pint capacity, each packed in a strong outside container. Packages must be plainly and durably marked on at least one side with the proper shipping name of the flammable liquid. Flammable liquids are not acceptable for air transportation or international mail.

c. Flammable liquids with a flashpoint at or above 73 degrees F (23 degrees C), but less than 100 degrees F (37.8 degrees C) are acceptable for domestic surface transportation only, subject to the 1 gallon restriction described in 124.332c.

124.332 Combustible Liquids.

a. Combustible liquids with a flash point at or above 100 degrees F (37.8 degrees C) but no higher than 141 degrees F (60.5 degrees C) (closed-cup), may also be accepted for domestic surface transportation, subject to the 1 gallon quantity restrictions described in b and c below.

b. Combustible liquids with a flash point above 141 degrees F (60.5 degrees C) up to and including 200 degrees F (93.3 degrees C) (closed-cup) may be accepted for domestic surface or air transportation, subject to the quantity restrictions described below. There are no restrictions for liquids with a flash point above 200 degrees F (93.3 degrees C) (closed-cup).

c. Containers of combustible, or flammable, liquids described in this section must not exceed 1 gallon, and each must be packed in a strong outside container. For domestic air transportation, each outside container must have sufficient absorbent cushioning within to absorb all leakage. The cushioning material and primary container must be enclosed within another sealed container within the outside container, and the flash point must be listed on the outside of the parcel. Combustible liquids are not acceptable in international mail.

124.333 Flammable Solids. A flammable solid is any solid material, other than one classed as an explosive, which, under conditions normally incident to transportation is liable to cause fires through friction, retained heat from manufacturing or processing, or which can be ignited readily and, when ignited, burns so vigorously and persistently as to create a serious transportation hazard. To be acceptable in the domestic

AROMATIC CONSTITUENTS AND CARBON NUMBER DISTRIBUTION

PRINCIPLE:

Quantitation of hydrocarbons is accomplished by gas/liquid chromatographic separation.

SCOPE:

This method covers the analysis of a liquid hydrocarbon for specified aromatic compounds and for the breakdown of the sample by carbon number distribution from C_1 to approximately C_{25}. The analytical report typically includes the weight percentages of benzene, toluene, ethylbenzene, m- & p-xylenes, o-xylene, C_3-benzenes, naphthalene, C_1-naphthalenes, C_2-naphthalenes, C_3-naphthalenes, and the breakdown of the remainder of the sample by carbon number. The range of analysis for a typical individual component is from 10 ppmw to 100%.

INSTRUMENT PARAMETERS:

INSTRUMENT: Perkin-Elmer Sigma-1 Gas Chromatograph
COLUMN: 60 meter DB-5; RSL-200; or equiv.
COLUMN TEMP. PROGRAM:

INITIAL COL. TEMP. (deg. C):	20
INITIAL HOLD TIME (min.):	1
PROGRAM RATE #1 (deg. C/min.):	10
FINAL TEMP. (deg. C):	300
HOLD TIME (min.):	46
INJECTION TYPE:	manual syringe
INJECTION TEMP. (deg. C):	325
FLOWRATE - GAS:	N/A - Helium
COLUMN PRESSURE (psig):	30
SPLIT FLOW (ml/min.):	300
DETECTOR TYPE:	FID
DETECTOR TEMP. (deg. C):	340

DATA SYSTEM: PE-Nelson "Turbochrom" P.C.-based data system

SUMMARY OF METHOD:

PREPARATION OF INSTRUMENT:

The capillary column is heated to 300° C for approximately one half hour before the first injection to bake off contaminants that have accumulated overnight. The appropriate sensitivity range is selected for the samples to be analyzed. A column blank is run immediately preceding the sample to insure that the column is clean and to provide "background" data for later reprocessing of the sample data.

SAMPLE ANALYSIS:

-The sample is typically injected with a 1 ul syringe into the split/splitless injection port of the gas chromatograph. In the case of heavier, less-volatile samples, a solvent flush technique is used with 1 ul of sample in a 10 ul syringe. The injection is split at a flow rate of 300 ml/min.

LIST OF COMPONENTS:

Compound	Expected Retention Time (min.)	
Methane	1.95	
Ethane	2.05	
Propane	2.25	
n-Butane	2.85	
n-Pentane	4.25	
n-Hexane	6.00	
Benzene	7.60	
n-Heptane	8.55	
Toluene	10.20	
n-Octane	10.90	
Ethyl-Benzene	12.40	
m,p-Xylene	12.60	
o-Xylene	13.15	
n-Nonane	13.25	
C3 Benzenes	13.80 - 15.90	Eight individual peaks are identified
n-Decane	15.30	
n-Undecane	17.30	
Naphthalene	19.00	
n-Dodecane	19.10	
n-Tridecane	20.80	
C1 Naphthalenes	21.00 - 21.30	
n-Tetradecane	22.35	
C2 Naphthalenes	22.60 - 23.80	
n-Pentadecane	23.85	
C3 Naphthalenes	24.50 - 25.20	
n-Hexadecane	25.30	
n-Heptadecane	26.70	

LIST OF COMPONENTS: (continued)

n-Octadecane	27.85
n-Nonadecane	28.95
n-Eicosane	30.20
n-Heneicosane	31.25
n-Docosane	32.30
n-Tricosane	33.40
n-Tetracosane	34.55
n-Pentacosane	35.70

DATA PROCESSING:

The sample data are corrected for column bleed due to the temperature program by subtracting the column blank run data point-by-point from the sample run data. All subsequent data processing is performed on this "background subtracted" data. The specified aromatic compound peaks are identified and their areas are measured and tabulated. The carbon number distribution is then obtained by projecting a horizontal baseline under the chromatogram from a point just before the earliest peaks elute and integrating the entire data set above this baseline as one large peak. This large peak is then divided into "slices" by placing a vertical dropline from the data signal level to the horizontal baseline immediately after each n-alkane peak. The areas of these slices, corrected for the area contributions of any of the specified aromatics occurring within each slice, are used to determine the carbon number distribution. All components are calculated and reported in weight percent.

TIME FOR ANALYSIS:

The elapsed time for one analysis is 1.5 hours. The hands-on time required is approximately one hour.

REFERENCE:

UOP Method 690-87

QA/QC:

Various standard mixtures of n-alkanes are used to determine relative recoveries of the higher-boiling components of a sample compared to those of the lower-boiling components. Relative response factors based on these standard recoveries are used to correct the instrument response where appropriate. As indicated above under "DATA PROCESSING," a column blank run is used to determine the cleanliness and condition of the capillary column before a sample is analyzed and is also used for background correction.

IGT

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Brine Sampling and Analysis - Pleasant Bayou Flow Test, 1988 - present

This section covers analyses performed on brine. Chemical analyses can only be related to well performance if the quantity of the various fluids are known. The IGT on-line data computer system measures the flowrate, the pressures, and the temperatures every 10 seconds. These values are automatically recorded over operator selected intervals both on magnetic media and on paper. This allows review of samples versus operating conditions.

This paper covers all analyses performed on brine, including:

- An approximate sampling schedule during flow tests
- On-site sample handling and storage of brine samples
- Addresses of laboratories that perform off site analyses
- Sample shipping instructions
- Data archiving
- Quality Control/Quality Assurance

It is expected that the above procedures will change as the flow test progresses, but deviations from the written procedures should be approved by the project chemist and noted on the results of the analysis.

Brine Sample Schedule

Brine samples for routine analysis should be collected twice per month for the initial period of flow. After the brine composition has become relatively stable and enough analyses are obtained to define baseline values, sampling frequency can decline to once per month to once per two months. Brine samples should be collected with greater frequency during transients, during periods where flow characteristics are not "normal" such as at reduced rates, and during special events such as inhibitor pills.

Samples collected for special studies, such as the suite of samples collected to define total carbon dioxide and the suite collected for radioactivity tests, should be collected between one and two times per year when flow conditions are "normal". Other samples may occasionally be collected on an as-needed basis to assist in operating decisions, such as monitoring the oxygen content of injected brine.

Routine Brine Sample Collection and Analysis

Routine brine sample collection involves collecting a total of 5 bottles of brine in plastic jars. Special care is taken to cool the sample prior to flashing the sample to atmospheric pressure, and to exclude air contact. See Appendices Brine-A for reasons behind these precautions.

Specific instructions for routine samples are as follows:

1) Rinse a total of 5 small mouthed H.D. polyethylene jars with store bought distilled quality water. Do not use tap water, especially site tap water. At least one, but preferably 2, of the bottles should be one liter capacity. The remainder should be 0.5 liter capacity bottles. Leave caps off, invert jars, and allow to dry at least overnight.

2) You will need a 5 gallon bucket, the water hose, the 1/4 inch stainless steel looped tubing with a valve on one end, the welding quality carbon dioxide cylinder with the flexible plastic tube attached, two adjustable wrenches, and three clean, dry plastic bottles. Include a one liter plastic bottle in this group.

3) The first sample collection point is roughly 15 feet downstream of the primary choke. There are two 1/2 inch needle valves on top of the pipe with a gauge and two needle valves facing down with a Swagelok fitting. Samples are collected from the bottom of the pipe only. Make sure the bottom needle valve is closed and fully open the needle valve closest to the pipe. This valve is not to be used for controlling rates. This is your emergency shut off valve and you want it in pristine condition.

   Open the bottom valve and blow brine out the valve for a few seconds, then close this valve. Be careful - the brine is at 800 to 1200 psi pressure and is at 300° F. This superheated brine will violently flash when exposed to atmospheric pressure. This cleans debris that may have settled out.

4) Attach the 1/4 inch line to the needle valve. If you are not completely familiar with Swagelok fittings get the operator to help. They can be over tightened or under-tightened. Make sure the valve at the end of the tubing is closed. If it is open the tubing will whip around when the needle valve is opened, possibly causing injury or death. Place the loops into the bucket, insert the hose, and start running tap water into the bucket. Let the water flow during sample collection. This is cooling the brine.

5) Open the bottom needle valve slowly. The tubing should now be hot and under pressure. Look for leaks and shut both needle valves if a leak is found. Open the carbon dioxide cylinder, establishing a bleed rate that forms small bubbles. You do not want a blower.

   Grip the end of the tubing firmly and slowly crack open the valve on the end of the tubing. Brine should flow out. Adjust the rate so that the brine at the outlet is cool to the touch - a flow rate of about 1/2 liter per minute is good. Bleed at least 1/2 liter of brine through the system.

6) Insert the carbon dioxide tube into the first bottle, and the insert the plastic insert on the outlet of the valve into the bottle. You are now collecting a sample. Adjust flow rates by feel, making sure the end of the tube does not get warm to the touch. As the bottle fills, slowly withdraw both tubes simultaneously and cap the jar tightly.

7) Do the remaining two bottles the same way. Label bottles with well name, date, and sample location (in this case "after the choke" or "between chokes"). Place the samples in the refrigerator. Close both needle valves, bleed off pressure, and remove the tubing assembly. Close the carbon dioxide cylinder. Bring equipment to the disposal well.

8) Collect two disposal well samples from the pipe between the filter skid and the disposal wells following the same procedures. The pressure is less at this point, so globe valves are in place rather than needle valves. These valves are notoriously hard to turn. Bring along a small valve wrench.

9) Once though, run tap water through the tubing to flush out brine. Label the samples with well name, date, and "disp well". Store equipment in the lab trailer.

10) One sample is archived at BEG and another is archived on-site. These samples are stored in plastic bottles. Oxygen diffusion through the plastic eventually causes heavy metals, especially iron, to precipitate. These samples will not remain free of precipitates for an extended period of time.

On-site Analyses: Certain analyses of routine brine samples are to be performed on-site. Iron and alkalinity quantities have been found to vary during sample storage. Do not use the one liter sample for on-site analyses, and use only one bottle each from the after the chokes and from the disposal well samples. Alkalinity should always be run on one sample each from the after the chokes and the disposal well samples. Iron should also occasionally be checked. Analyse the sample the same day it is collected.

Alkalinity - Follow the procedures outlined in Hach Procedures For Water and Wastewater Analyses, pages 2-6 to 2.7. These are included in Appendix Brine-B. The following exceptions and options to the Hach procedures are to be followed.

- Use a 50 ml sample, not a 100 ml sample, and multiply the reading by 2 to get alkalinity in mg $CaCO_3$/l. The sample should be measured and transferred from the sample bottle to a 100 ml beaker using a 50 ml volumetric pipet. Use the rubber bladder assembly to fill and empty the pipet. Never use your mouth. If any spills, clean up and start again.

- Use the pH meter option of the Hach procedures. Proceed in increments of 5 after injecting the first 100 units of acid. Alkalinity is determined by calculating to delta pH between the incremental acid injections. Stop the test when the pH falls below 2.9.

- Store the original data sheets in the file marked alkalinity in C. Haydens file. Make sure the sample location and date are legible.

Iron - Iron analyses are to be performed occasionally on both after the choke and on disposal well brine samples. Follow the procedures outlined in Hach Procedures For Water and Wastewater Analyses, pages 2-52 to 2.54, for total iron. These are included in Appendix Brine-C. The following exceptions and options to the Hach procedures are to be followed.

- The samples must be diluted by a factor of between 50:1 to 200:1 to be read on the Spectronic-21. Perform serial dilutions using volumetric flasks, volumetric pipets, and store bought distilled quality water. Record the dilutions and adjust the iron concentrations accordingly. Analyse the solutions immediately.

- Do not perform the digestion procedure.

On-site Sample Storage and Handling: Brine samples should be stored in the refrigerator in the chemistry trailer. Samples to be sent out for further analyses should not be opened. Brine samples should be stored until a batch of between three to seven brine samples is available before sending out for analysis. This reduces the analytical costs at the outside laboratories.

The batch of One liter sized after the choke samples, with disposal well brine samples included based on the judgement of the project chemist, should be sent to BEG at the University of Texas for analysis. Another after the choke sample should be sent to IGT. There are no provisions for keeping samples refrigerated during shipment and no other preservation techniques.

All samples can be shipped either by first class mail or express air. The addresses of BEG and IGT follow:

Mineral Studies Laboratory
Bureau of Economic Geology
The University of Texas at Austin
University Station, Box X
Austin TX 78713

Sherman Chao
Institute of Gas Technology
3424 South State Street
Chicago IL 60616

Include a letter defining the number of samples, the charge number if appropriate, and analytical instructions. BEG instructions are defined by contract as either a BASIC or a DETAILED analysis. At least one sample per month should be a detailed analysis.

IGT's laboratory normally analyses for trace levels of phosphonate. At the discretion of the project chemist, IGT can analyse for other constituents as defined in the instructions. Several times per year IGT should analyse for major constituents that are also covered by BEG analyses. The BEG analysis is the "official analysis" put out in Weekly reports.

Off Site Brine Analyses: BEG's analyses are defined in [redacted] the list of procedures provided to IGT as shown in Appendix Brine-E. BEG has been temporarily not performing organic acids analyses and has been reporting results later than was contractually defined. Such deviations must be approved by the project chemist.

IGT's analyses are defined both by the letter of instructions accompanying the samples and by the list of procedures defined in Appendix Brine-F. This list of procedures attached in Appendix Brine-F may be incomplete if a new analysis is requested. If so, please ask for copy of the analytical methods and add them to the Appendix.

Data Handling and Reporting: Original BEG analyses are to be reported in the Weekly reports to Eaton Operating Company. The data sheets from BEG are filed in the BEG -Brine analyses folder. Duplicate analyses, QA/QC analyses, and standard analyses should not be included in the Weekly reports. That forum is reserved for the "official" brine analyses.

Backup IGT chemical analyses, which generally involve only between one and four chemical species, should be compared to BEG analyses. Results should be filed in the IGT-Brine analyses folder. Statistically significant discrepancies between IGT and BEG analyses should be mentioned in the Weekly reports and should be conveyed to BEG. BEG should perform follow-up analyses to resolve the problem.

Alkalinity titration data sheets should be dated and placed in the Alkalinity folder. Alkalinity values should be reported in a timely manner in the Weekly Report, and a determination as to whether there is a scale precipitation problem should be made. BEG also analyses the brine for alkalinity, but the sample precipitates calcite prior to analysis, so BEG results are NOT indicative of reservoir brine. These values are reported with other BEG analyses but are not used to detect scale precipitation.

Iron analyses data sheets are placed in the Iron folder. This data is archived but is generally not reported unless a significant change is noted. The amount of iron naturally in the brine is so high as to require a 50 to 1 or more dilution prior to analyses. This results in an analytical uncertainty too high to monitor corrosion. BEG also analyses the brine for iron in the routine analyses. These values are reported with the other BEG analyses, but, like the alkalinity analyses, the results are not believed to be representative of the brine in the pipe.

Special Brine Sample Collection and Analyses

Occasionally samples are collected and analysed to directly impact day by day operating procedures. These types of analyses would include determining the oxygen content of brine prior to injecting it down the disposal well with a pump, or determining the chlorides concentration or specific gravity of tank brine. The tests are performed on-site and are characterized by simplicity. For instance, the dissolved oxygen test kit used, a Chemetrics Model 0-1 and Model 0-100, involves breaking an ampule in the brine and comparing the resulting color against a series of standard. The chlorides procedure for field analyses is included in Appendix Brine-F with other IGT procedures.

The results of these analyses are expected to help make on the spot operating decisions, not to define the fluid produced from the well. As such, the degree of quality control is often not as high as with samples analysed in the laboratories. The results of these analyses are not reported unless they affect well operations.

Other samples, classified as special in contrast to the routine analyses described in the first section, are also performed. These samples are collected to study a particular topic, such as determining the total amount of carbon dioxide produced per barrel of brine or determining the radioactive elements in the brine. Sampling frequency is generally once per year or so. These samples involve collecting brine under specified conditions and analysing them with a well defined procedure.

Total Carbon Dioxide: The first set of special samples discussed are the total carbon dioxide samples. These samples are collected under pressure, and involve carefully measuring and analysing effluents that flash off the brine as the pressure is lowered as well as analysing the brine.

The procedures for collecting and analysing these samples have been outlined in "Parametric Study of Separator Performance" included in Appendix Brine-G. These consist of Flashing the sample to one atmosphere and measuring the amounts of gas and brine. The gas is analysed for major components using the onsite gas chromatograph. The carbon dioxide in a portion of the brine is stabilized with sodium hydroxide, and a measured quantity of the stabilized brine is transferred to a acid liberation/nitrogen purge carbonate train.

Nitrogen is bubbled through the sample, sweeping the carbon dioxide from the brine. The gas passes through a fuming sulfuric acid bubbler, which removes water vapor, and then to a pre-weighed Ascarite bulb. The amount of carbon dioxide remaining in the brine at one atmosphere is determined gravimetrically.

Though not explicitly documented in the procedures, the sample vessel to be used is a 1.0 liter, teflon lined, 304 or 316 grade stainless steel cylinder with a working pressure of 1800 psi or more. The cylinder should be flashed and analysed as soon as possible after collection.

Radioactivity: Radioactivity measurements are performed free of charge by Tom Kraemer of USGS. Dr. Kraemer has analysed the gas and brines of numerous DOE geopressured geothermal wells, including:

Fairfax Foster Sutter #1	Amoco Fee (Zone 5) #1
Pleasant Bayou #2 (1981)	Gladys McCall #1 (Sand 9)
L. R. Sweezy #1	HO&M Prairie Canal #1
Martin Crown Zellerbach #2	Wainoco P. R. Girouard #1
Riddle Saldana #2	Lear Koelemay #1
Edna Delcambre #1 (Zones 1 and 3)	

Dr. Kraemer was in the process of moving his laboratory facilities at the start of flow in 1988. To date he is only measuring the radium content of the brine. Past analyses also included uranium concentrations in the brine and radon concentrations in the gas. He expects to be able to resume these analyses late in 1989.

Brine samples for radium analyses are cooled and filtered through a 0.45 micron filter. The samples are sent via regular mail to Dr. Kraemer at the following address:

Dr. Thomas Kraemer
U. S. Geological Survey
431 National Center
12201 Sunrise Valley Drive
Reston, VA 22092

The Radium Analytical procedure, as described by Dr. Kraemer, is determined by the radon ingrowth technique. A measured volume of sample (usually 250 ml) is added to a bubbler flask which is then degassed and sealed, the time and date recorded. Radon from the decay of ^{226}Ra then accumulates in the flask. After 3 to 10 days the flask is connected to an extraction board and helium bubbled through the flask at 500 ml/min. The radon purged from the sample by the helium is removed in a liquid nitrogen cold trap, and the heliumk is returned continuously to the sample for further purging. Cycle time for purging is 20 minutes. The cold trap is then removed and the collected radon is transferred to a Lucas cell with helium. Date and time of transfer is recorded. The Lucas cell is then placed against a photomultiplier tube for counting.

Activity in the sample is calculated from sample volume, activity of radon in the Lucas cell and length of ingrowth from one degassing to another. The sample can be re-run as many times as necessary.

Quality Control/Quality Assurance: The accuracy and reproducability of analytical analyses is checked using one or more of the following safegaurds.

1) Duplicate analyses of samples. BEG routinely analyses one sample per batch as many as three times. The results of these analyses are on file in the BEG-Brine folder.

IGT also occasionally analyses the brine for a few of the components reported by BEG. These are usually major components, such as calcium, magnesium, or chloride. The results of these analyses, on file in the IGT-Brine folder, are compared to BEG results.

2) Standards are routinely run by both IGT and BEG. BEG analyses of the standards are reported. Both IGT and BEG also routinely use standard addition to check accuracy.

3) Sample integrity is difficult to assess. Certain elements and compounds are known to be lost during sample storage. The major components lost are iron and alkalinity. Such losses were readily apparent in the batch affects noted on BEG reports, where the concentration of a particular species would decline with the age of the sample. Iron and alkalinity are now measured onsite.

The possible loss of trace components such as mercury during sample storage have not been addressed. BEG reported in 1989 that they were also having difficulty recovering mercury spikes in samples, and have therefore raised the reported detection threshold from 0.005 to 0.05 mg/l. There has not been a detectable level of mercury reported by BEG to date.

There is evidence that silica values may be too low, which is the result of precipitation in the sample bottles (private communication, Dr. Capuano, BEG). The silica may be precipitating out of solution to reach a lower concentration that is stable at lower temperatures. Sample dilution for the silica analyses is being investigated.

4) See memos on sample batching problems in Appendix Brine-H.

IGT

3424 South State St., Chicago, IL 60616
P.O. Box 632, Hitchcock, TX 77563

Memorandum

To: File
From: C.Hayden
Subject: Reasons to cool oil field brines and to keep them under a carbon dioxide blanket during sample collection.

Brines sampled by IGT always have three characteristics that can cause problems with sample analyses. These are that the brines contain carbonate species, contain iron species, and they are collected from vessels that are hot and under pressure. Cooling a sample prior to releasing the pressure, and keeping the sample under a carbon dioxide blanket during collection, stabilizes the brine at least temporarily.

The ferrous iron in the produced brine will be oxidized to ferric iron in the presence of oxygen. The oxidation reaction is essentially complete and irreversable. This causes a problem because ferric iron forms gel-like oxide and hydroxide precipitates, and probably results in the co-precipitation of other heavy metals. This iron is very difficult to get back into solution for chemical analyses. A gas containing no oxygen, in this case carbon dioxide, is kept over the sample to physically exclude air from the sampling system.

The inert gas chosen is carbon dioxide because this gas also stabilizes the carbonate species in the brine. As a sample degasses after the pressure is reduced, the brine becomes deficient in carbon dioxide. This provides the driving force whereby two bicarbonate molecules can undergo a transformation to a carbonate ion and a molecule of carbon dioxide. The carbonate ions then form a precipitate with the available calcium, and probably result in co-precipitation of other compounds.

This can be short circuited, at least temporarily, by bubbling carbon dioxide through the sample. This keeps the partial pressure of carbon dioxide up at 15 psia, which, combined with the cooler temperature, is high enough to delay if not prevent calcium carbonate precipitation.

Removing hot brine from the pipes can be spectacular. The vapor pressure of water is dependent on brine temperature. When the pressure on the brine is lowered, as when a sample is collected, a portion of the brine vaporizes. The portion vaporized can be substantial as brine temperatures exceed 212° F. Dissolved gas in the brine also flashed, ensuring that the water vapor will be-swept from the sample container and not re-condense. This concentrates the sample as described below

RT

Calculation of Water Loss Due to Vaporization as Geopressured Geothermal Brines are Sampled Without Previous Cooling

It is known that if geothermal brines are collected without prior cooling the brine flashes upon exposure to atmospheric pressure. The quantity of brine lost due to vaporization has been estimated below. I used several assumptions in this work, listed in decreasing order of importance.

1 The person taking the sample realizes that problems exist and closes the sample jar as soon as possible. In this work I assumed the jar was closed, and therefore vaporization ceased, while the brine was still a hefty 203F.

2 There is no heat lost to conduction. This is obviously not true, as anyone who has burned thier hands on hot sample bottles knows, but the amount of heat lost to conduction is small relative to the heat capacity of water. In adition, most people sampling brine purge the lines and valves with large quantities of brine to remove impurities from the line and insure a fresh sample, thereby preheating the system.

3 Sodium chloride brines have lower thermal capacity than water. Specifically, a 10% NaCl brine has roughly 8% less thermal capacity than an equal volume of water. This is a risky extrapolation of data measured at 25F.

4 There is no recondensation in the sample jar.

5 Excaping steam is at the same temperature as the brine.

Heat of vaporization of water is taken as 540 cal/gram. Thermal capacity of water at varios temperatures are obtained from the CRC Handbook of Chemistry and Physics, 38th Edition.

Temperature at Sample Point	% Water Vaporized
284	7.2
266	5.6
248	4.1
230	2.5
212	.8

Brine A

Sulfuric Acid Standard Solution, 0.020*N*, Cat. No. 203-14	118 mL (4 oz)*
Sodium Thiosulfate Standard Solution, 0.1*N*, Cat. No. 323-37	118 mL (4 oz) MDB
Clamp Holder, Cat. No. 326-00	each
Support Stand, Cat. No. 563-00	each
Potassium Acid Phthalate Standard Solution, 400 mg/L as CO_2, Cat. No. 1885-11	473 mL (pt)
Voluette Ampule Standards for Acidity 0.500N, Cat. No. 14330-10	16
Stirrer, magnetic, Cat. No. 8415-10	each
Stirring Bar, Teflon-coated, Cat. No. 10764-16	each
TenSette Pipet Kit, 0.1-1.0 mL, Cat. No. 19700-01	each
Sodium Hydroxide Titration Cartridge, 0.1600*N*, Cat. No. 14377-01	each
pH Meter, portable, Cat. No. 19000-00	each
TitraStir Titration Stand, 115 V, Cat. No. 19400-00	each
TitraStir Titration Stand, 230 V, Cat. No. 19400-10	each
Pipet Tips, TenSette, 1 mL, Cat. No. 21856-96	50

*Larger sizes available.
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ALKALINITY

Titration Method

Adapted from *Standard Methods for the Examination of Water and Wastewater*

Introduction

Alkalinity refers to the capability of water to neutralize acids. The presence of carbonates, bicarbonates and hydroxides is the most common cause of alkalinity in natural waters.

Alkalinity is expressed as P (phenolphthalein) alkalinity or as T (total) alkalinity. Both types are determined by titration with Sulfuric Acid Standard Solution, 0.020*N*, to an end point evidenced by the color change of a standard indicator solution or determined with a pH meter. The P alkalinity is determined by titration to a pH of 8.3 (the phenolphthalein end point) and registers total hydroxide and one half of the carbonate present. The T alkalinity is determined by titration to a pH of 5.1, 4.8, 4.5, or 3.7, depending in the type of sample *as described in Note B*. The total alkalinity includes all carbonate, bicarbonate and hydroxide alkalinity.

This method is applicable for determining alkalinity in water, wastewater and sea water samples.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Samples should be analyzed as soon as possible after collection but can be stored at least 24 hours by cooling to 4°C (39°F) or below. Warm to room temperature before running the test.

Procedure for Buret Method

1. Take a water sample by filling a clean 50-mL graduated cylinder to the 50-mL mark. Pour the sample into a clean 250-mL erlenmeyer flask.
2. Add six drops of Phenolphthalein Indicator Solution and swirl to mix. Omit this step if a pH meter is used.
3. Titrate the sample with Sulfuric Acid Standard Solution, 0.020*N*, while swirling the flask until the solution changes from pink to colorless or the pH meter reads 8.3 *See Note A*.
4. Multiply the number of milliliters of sulfuric acid used by 20 to obtain the mg/L phenolphthalein alkalinity (as $CaCO_3$).*
5. Add six drops of *Bromcresol Green-Methyl Red Indicator Solution* or six drops of *Bromphenol Blue Solution* to the titrated sample and swirl to mix. Choice of indicator *is discussed in Note B*. Omit this step of a pH meter is used.
6. Continue the titration with Sulfuric Acid Standard Solution, 0.020*N*, to a light green blue-gray (pH 5.1), a light blue pink-gray (pH 4.8), or a light pink (pH 4.5) color if *Bromcresol Green-Methyl Red* is the indicator used. Titrate to a pure green (pH 3.7) if *Bromphenol Blue Solution* is used. Titrate directly to the desired pH value if a pH meter is used. *See Note B*.
7. Multiply the total number of milliliters of sulfuric acid used in both titrations by 20 to obtain the mg/L total alkalinity (as $CaCO_3$).* *See Note C*.

Procedure for Digital Titrator Method

1. Take a water sample by filling a clean 100-mL graduated cylinder to the 100-mL mark. Pour the sample into a clean 250-mL erlenmeyer flask.
2. Add six drops of Phenolphthalein Indicator Solution and swirl to mix. Omit this step if a pH meter is used.
3. Twist a Sulfuric Acid Titration Cartridge, 1.600*N*, onto a Digital Titrator. For samples that typically measure less than 100 mg/L alkalinity, use a 0.1600*N* Sulfuric Acid Titration Cartridge and divide the final reading by 10.
4. Attach a clean straight-stem delivery tube to the cartridge if a hand-held titration is to be made. Use a clean 90° delivery tube if the Digital Titrator is to be attached to a laboratory stand or a TitraStir™ Titration Stand.
5. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.
6. Titrate the sample while swirling until the solution changes from pink to colorless or, if a pH meter is used, titrate to a pH of 8.3. Read the concentration of phenolphthalein alkalinity in mg/L* from the Digital Titrator counter. *See Note A*.
7. Add six drops of *Bromcresol Green-Methyl Red Indicator Solution* to the titration flask and swirl to mix. Omit this step if a pH meter is used.
8. Continue the titration to a light greenish blue-gray (pH 5.1), a light bluish pink-gray (pH 4.8) or a light pink (pH 4.5) color. *See Note B*.
9. Read the concentration of total alkalinity from the Digital Titrator.* *See Note C*.

Notes

A. A demineralized water solution of the indicator and a buffer can be used to more accurately determine the end point of titration. Mix the contents of one *pH 8.3 Buffer Powder Pillow* with 50 mL of demineralized water in a 250-mL erlenmeyer flask and add six drops of Phenolphthalein In-

*mg/L value ÷ 17.12 = gr/gal equivalent

dicator Solution. The color produced indicates the exact point at which to end the titration for phenolphthalein alkalinity. The buffer solution without the indicator can be used to standardize the pH meter.

B. The following end points are recommended for determining total alkalinity in water samples of various compositions and alkalinity concentrations:

Sample Trait	End Point
Alkalinity approx. 30 mg/L	pH 5.1
Alkalinity approx. 150 mg/L	pH 4.8
Alkalinity approx. 500 mg/L	pH 4.5
Silicates or phosphates known present or suspected	pH 4.5
Industrial waste or complex system	pH 3.7

A demineralized water solution of the indicator and the correct buffer is recommended for determining the end point of the total alkalinity titration. Mix the contents of one pH 5.1 Buffer Powder Pillow with 50 mL of demineralized water in a 250-mL erlenmeyer flask and add six drops of *Bromcresol Green-Methyl Red Indicator Solution.* Repeat this preparation using pH 4.8 and ph 4.5 Buffer Powder Pillows. Titrate the prepared sample to the pH 5.1 end point for alkalinities of about 30 mg/L (as $CaCO_3$), to pH 4.8 for alkalinities around 150 mg/L and to pH 4.5 for alkalinities around 500 mg/L. For titration to pH 3.7, add one pH 3.7 Buffer Powder Pillow to 50 mL of demineralized water in a 250-mL erlenmeyer flask but use six drops of *Bromphenol Blue Solution* in place of *Bromcresol Green-Methyl Red Indicator.* The end point is a color change from purple, through blue, to pure green. The prepared buffer solutions without the indicators can be used to standardize the pH meter.

C. Carbonate, bicarbonate and hydroxide concentrations may be expressed individually using the relationships *shown in the Alkalinity Relationship Table.*

ALKALINITY RELATIONSHIP TABLE

Result of Titration	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Alkalinity
"P" Alkalinity equals zero	0	0	Equal to "T" Alkalinity
"P" Alkalinity less than one half of "T" Alkalinity	0	2 times "P" Alkalinity	"T" Alkalinity minus two times "P" Alkalinity
"P" Alkalinity equal to one half of "T" Alkalinity	0	2 times "P" Alkalinity	0
"P" Alkalinity greater then one half of "T" Alkalinity	Product of 2 times "P" minus "T" Alkalinity	2 times difference between "T" and "P" Alkalinity	0
"P" Alkalinity equal to "T" Alkalinity	Equal to "T" Alkalinity	0	0

D. Low range alkalinity concentrations can be determined more accurately by using a 200-mL sample in Step 1 and multiplying by 5 (Buret Method) or dividing by 2 (Digital Titrator Method).

E. The standard additions method check can be performed as follows:

1. Snap the neck off a fresh *Voluette® Ampule Standard for Alkalinity.* Using the TenSette™ Pipet, add 0.10 mL of standard to the sample and titrate to the correct end point.
2. Swirl to mix and again titrate to the end point. Note the amount of additional titrant used.
3. Make 0.20-mL and 0.30-mL standard additions, titrating to the end point after each. In the Buret Method, the alkalinity should increase 50 mg/L for each 0.1-mL increment of standard added. In the Digital Titrator Method, each 0.1 mL of standard will cause a 25-mg/L increase in alkalinity.

Required Reagents and Apparatus for Alkalinity Test Using Buret Method

Phenolphthalein Indicator Solution, 5 g/L,
Cat. No. 162-37 — 118 mL (4 oz) MDB*
Sulfuric Acid Standard Solution, 0.020*N*,
Cat. No. 203-16 — 946 mL (qt)
Bromcresol Green-Methyl Red Indicator Solution,
Cat. No. 451-37 — 118 mL (4 oz) MDB*
Buret, 25 mL, Cat. No. 504-40 — each
Flask, erlenmeyer, 250 mL, Cat. No. 505-46 — each
Cylinder, graduated, 50 mL, Cat. No. 508-41 — each

Required Reagent and Apparatus for Alkalinity Test Using pH Meter with Alkalinities Above 20 mg/L

Sulfuric Acid Standard Solution, 0.020*N*,
Cat. No. 203-16 — 946 mL (qt)
Beaker, 100 mL, Cat. No. 500-42 — each
Cylinder, graduated, 50 mL, Cat. No. 508-41 — each

Reagent and Apparatus for Alkalinity Test Using pH Meter With Alkalinities Below 20 mg/L

Sulfuric Acid Standard Solution, 0.020*N*,
Cat. No. 203-16 — 946 mL (qt)
Beaker, 250 mL, Cat. No. 500-46 — each
Cylinder, graduated, 100 mL, Cat. No. 508-42 — each

Required Reagents and Apparatus for Alkalinity by Digital Titrator

Phenolphthalein Indicator Solution, 5 g/L,
Cat. No. 162-37 — 118 mL (4 oz) MDB*
Bromcresol Green-Methyl Red Indicator Solution,
Cat. No. 451-37 — 118 mL (4 oz) MDB*
Sulfuric Acid Titration Cartridge, 1.600*N*,
Cat. No. 14389-01 — each
Flask, erlenmeyer, 250 mL, Cat. No. 505-46 — each
Cylinder, graduated, 100 mL, Cat. No. 508-42 — each
Digital Titrator, Cat. No. 16900-01 — each

Optional Reagents and Apparatus

Sodium Hydroxide Standard Solution, 0.020*N*,
Cat. No. 193-16 — 946 mL (qt)
Sodium Thiosulfate Standard Solution, 0.1*N*,
Cat. No. 323-37 — 118 mL (4 oz) MDB*
Clamp Holder, Cat. No. 326-00 — each
Cylinder, graduated, 250 mL, Cat. No. 508-46 — each
Support Stand, Cat. No. 563-00 — each
Buffer Powder Pillows, pH 4.5, Cat. No. 895-98 — 25
Buffer Powder Pillows, pH 4.8, Cat. No. 896-98 — 25
Buffer Powder Pillows, pH 5.1, Cat. No. 897-98 — 25
Buffer Powder Pillows, pH 8.3, Cat. No. 898-98 — 25
Clippers for opening pillows, Cat. No. 968-00 — each
Stirrer, magnetic, Thermolyne S-18525, Cat. No. 8415-10 — each
Stirring Bar, magnetic, Cat. No. 10764-16 — each
Voluette Ampules for Alkalinity, 0.500N,
Cat. No. 14278-10 — 16
Sulfuric Acid Titration Cartridge, 0.1600*N*,
Cat. No. 14388-01 — each
Buffer Powder Pillows, pH 3.7, Cat. No. 14551-98 — 25

IRON, TOTAL

1,10-Phenanthroline Method
Using FerroVer® Iron Reagent
Adapted from *Standard Methods for the Examination of Water and Wastewater*

Introduction

The 1,10-Phenanthroline Method is the most well-known test for ferrous and total iron. The 1,10-Phenanthroline reagent gives an orange color with ferrous iron and is free from common interferences. The indicator is combined with a reducing agent for total iron analysis in a single powder formulation called FerroVer® Iron Reagent. The amount of ferric iron present can be determined as the difference between the amount of ferrous iron and the results of a total iron test. The FerroVer Iron Reagent converts all iron present in the sample to the ferrous state, including precipitated or suspended iron such as rust, where it reacts with the 1,10-phenanthroline to give the orange color necessary for the determination. This test has been approved by the EPA for NPDES reporting purposes based on comparability studies if the sample is first digested.** Testing done for nonreporting purposes generally does not require sample digestion.

Sampling and Storage

Collect samples in plastic or glass bottles that have been washed with a detergent and rinsed with tap water, *1:1 Nitric Acid Solution* and distilled or demineralized water. Using a glass serological pipet and pipet filler, add 5.0 mL *Nitric Acid* for each liter or quart of sample taken and mix. Check the sample pH to assure that the pH is 2 or less. Add more nitric acid if necessary; 5.0 mL of *Nitric Acid* per liter is usually sufficient for potable waters. Samples preserved in this manner can be stored at least six months at room temperature. If only dissolved iron is to be reported, filter the sample immediately after collection—before nitric acid addition.

Digestion

Digestion is required if total iron is to be determined. If *Nitric Acid* has not been added to the sample previously, add 5 mL of *concentrated Nitric Acid* to one liter of sample, using a glass serological pipet and pipet filler. Transfer a 100-mL portion of the acidified sample to a 250-mL erlenmeyer flask. Add 5 mL of *1:1 Hydrochloric Acid*. Heat sample on a hot plate for 15 minutes at 95°C. Filter through a membrane filter and adjust the volume to 100 mL with demineralized water.

pH Adjustment

Using a pH meter, adjust the acidifed sample to a pH of 4 to 5 with *Ammonium Hydroxide*. Do not exceed pH 5 as this may cause loss of some iron as a precipitate. The sample is now ready for analysis. Where significant amounts of preservatives are used, a volume correction should be made for the extra acid and base by dividing the total volume (sample + acid + base) by the sample volume and multiplying the result times the final test reading.

Sample Preparation

1. Take a water sample by filling a clean 25-mL mixing graduated cylinder to the 25-mL mark. *See Note A.*
2. Add the contents of one FerroVer Iron Reagent Powder Pillow, stopper and invert several times to mix. *See Note B.* An orange color will develop if iron is present. Allow at least 3 minutes for the color to fully develop but do not wait more than 30 minutes before taking the readings.
3. Select the procedure group below that applies to your instrument and proceed with the test. *See Note C.* If a procedure group is not included for your instrument, *refer to Part 1, Using Other Instruments.*

Procedure Group 1—Bausch and Lomb Spectronic 20 and 21 (1-inch test tube)

a. Adjust the Wavelength control to 510 nm.
b. With the sample compartment of the Spectronic 20 empty, or using an opaque rod in the Spectronic 21, cover the sample compartment and adjust the Zero control for a reading of zero %T.
c. Place 1-inch test tube containing some of the original water sample into the sample compartment and cover the compartment. Adjust the Full Scale control for a meter reading of exactly 100% T.
d. Place a 1-inch test tube containing the treated water sample to be tested into the sample compartment, cover the compartment and read the percent transmittance. Refer to the Procedure Group 1 tables of the Ferrous Iron test to determine the mg/L total iron (Fe).

Procedure Group 2—Bausch and Lomb MiniSpec 20 (25-mm cell)

a. Adjust the Wavelength control to 510 nm.
b. Using the 1/2-inch adapter and insert, place the opaque rod in the empty sample compartment, cover the compartment and check the zero adjustment. Adjust if necessary.
c. Place a 25-mm cell containing some of the original water sample into the sample compartment and cover the compartment. Adjust the Full Scale control for a meter reading of exactly 100% T.
d. Place a 25-mm cell containing the treated water sample to be tested into the sample compartment, cover the compartment and read the percent transmittance. Refer to the Procedure Group 2 table of the Ferrous Iron test to determine the mg/L total iron (Fe).

Notes

A. If the sample is turbid, add a 0.2-gram scoop of *Rover® Rust Remover* to 25 mL of the original sample and swirl to dissolve. Use this water to standardize the instrument at zero mg/L. This will ensure that any turbidity that would be dissolved by the FerroVer Iron Reagent will also be dissolved in the blank.

If the sample is still too turbid to obtain a zero mg/L reading after the above treatment, add three 0.2-g scoops of *RoVer Rust Remover* to about 75 mL of the original sample, mix, and allow to stand for about five minutes. Clarify the sample by centrifuge or glass filter before running the test. The clarified sample is then used in Step 1 and when standardizing the instrument.

B. FerroVer Iron Reagent Powder Pillows are stable indefinitely depending on storage and handling conditions. A cool, dry

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atmosphere is recommended for the longest shelf life. The FerroVer Iron Reagent powder can be checked by adding the contents of one pillow to about 25 mL of water containing visual rust. If the characteristic orange color does not develop, the reagent has deteriorated beyond use and should be discarded.

C. A large excess of iron will inhibit full color development. A diluted sample should be tested if there is any doubt about the validity of a result.

D. Copper can interfere by forming a yellow, blue or violet color. If copper interference is suspected, add a 0.1-gram scoop of *RoVer Rust Remover* before adding the FerroVer Iron Reagent Powder Pillow in Step 2. Chloride does not interfere in amounts up to 185,000 mg/L as Cl^-. Magnesium does not interfere in amounts up to 100,000 mg/L as $CaCO_3$. Calcium interferes in amounts over 10,000 mg/L as $CaCO_3$.

E. A 1.0-mg/L iron standard solution can be prepared by pipetting 1.00 mL of Iron Standard Solution, 100 mg/L as Fe, into a 100-mL volumetric flask and diluting to the mark with iron-free demineralized water. The solution should be prepared fresh daily.

F. The standard additions method check can be performed as follows:
1. Snap the neck off a fresh Voluette® Ampule Standard for Iron (1,10-Phenanthroline Method) (Cat. No. 14254-10). Using the TenSette™ Pipet, add 0.10 mL of standard to the prepared sample measured in Step d.
2. Swirl to mix and allow three minutes for full color development. Again measure the color.
3. Add two additional 0.10-mL standard increments, taking a color reading after each addition. Each additional 0.1 mL of standard should cause a 0.2-mg/L increase in the reading.

Required Reagents and Apparatus

FerroVer Iron Reagent Powder Pillows, Cat. No. 854-99	100
Clippers, for opening pillows, Cat. No. 968-00	each

Optional Reagents and Apparatus

Ammonium Hydroxide, ACS, Cat. No. 106-11	473 mL (pt)
Nitric Acid, ACS, Cat. No. 152-11	473 mL (pt)
Demineralized Water, Cat. No. 272-16	946 mL (qt)*
RoVer Rust Remover, Cat. No. 300-20	30 mL (1 oz)*
pH Indicator Paper, 1-11, Cat. No. 391-33	5-roll pack
Measuring Spoon, 0.1 gram, Cat. No. 511-00	each
Pipet, transfer, 1.00 mL, Cat. No. 515-35	each
Pipet, serological, 2 mL, Cat. No. 532-36	each
Flask, filtering, 500 mL, Cat. No. 546-49	each
Flask, volumetric, 100 mL, Cat. No. 547-42	each
Measuring Spoon, 0.2 gram, Cat. No. 638-00	each
Hydrochloric Acid Solution, 1:1, Cat. No. 884-49	500 mL
Rust Suspension, Cat. No. 1279-36	15 mL (1/2 oz) DB
Filter Pump, Cat. No. 2131-00	each
Filter Holder, membrane, Cat. No. 2340-00	each
Filter Discs, glass 47 mm, Cat. No. 2530-00	100
Nitric Acid Solution, 1:1, Cat. No. 2540-11	473 mL (pt)
Hot Plate, Cat. No. 12067-00	each
Pipet Filler, Cat. No. 12189-00	each
Iron Standard Solution, 100 mg/L as Fe, Cat. No. 14175-14	118 mL (4 oz)
Voluette Ampule Standards for Iron (50 mg/L) Cat. No. 14254-10	16
TenSette Pipet Kit, 0.1-1.0 mL, Cat. No. 19700-01	each
pH Meter, portable, Cat. No. 19000-00	each

*Larger size available. See Part 3, List of Reagents.

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IRON, TOTAL

Ferrozine Method
Using FerroZine® Iron Reagent
L.L. Stookey, *Anal. Chem.* 42(7), 779 (1970)

Introduction

The FerroZine® Method for total iron is more than twice as sensitive as the 1,10-phenanthroline method. FerroZine Iron Reagent forms a purple-colored complex with trace amounts of iron in samples that are buffered to a pH of 3-5. This method is applicable for determining trace levels of iron in drinking water and sea water. It can be used to determine iron contamination in chemical reagents and glycols and can be used to analyze samples containing magnetite (black iron oxide) or ferrites. *See Note D.*

Sampling and Storage

Collect samples in plastic or glass bottles that have been washed with a detergent and rinsed with tap water, *1:1 Nitric Acid Solution* and distilled or demineralized water. NOTE; The following instructions are necessary only when prompt analysis is impossible. Using a glass serological pipet and pipet filler, add 5.0 mL *Nitric Acid* for each liter or quart of sample taken and mix. Check the sample pH to assure that the pH is 2 or less. Add more nitric acid if necessary; 5.0 mL of *Nitric Acid* per liter is usually sufficient for potable waters. Samples preserved in this manner can be stored at least six months at room temperature. If only dissolved iron is to be reported, filter the sample immediately after collection—before nitric acid addition. Just prior to testing stored sample, neutralize the acidified sample to a pH of 3-5 with *Ammonium Hydroxide, ACS*. Do not exceed pH 5 as this may cause loss of some iron as a precipitate. The sample is now ready for analysis. Where significant amounts of preservatives are used, a volume correction should be made for the extra acid and base by dividing the total volume (sample + acid + base) by the sample volume and multiplying the test result by this factor.

Sample Preparation

1. Take water sample by filling a clean 25-mL mixing graduated cylinder to the 25-mL mark. *See Note A.*
2. Add the contents of one *FerroZine Iron Reagent Solution Pillow*, stopper and invert several times to mix. *See Note B.* A violet color will develop if iron is present. *See Note C.* Allow at least 5 minutes for the color to fully develop but do not wait more than 30 minutes before taking the reading.

Sample Preparation

1. Take a water sample by filling a clean 2.5-cm sample cell to the 10-mL mark. *See Note A.*
2. Add the contents of one Ferrous Iron Reagent Powder Pillow, cap and invert several times to mix. An orange color will develop if ferrous iron is present. Allow at least 4 minutes for the color to fully develop but do not wait more than 30 minutes before taking the reading.
3. Select the procedure group below that applies to your instrument and proceed with the test. If a procedure group is not included for your instrument, *refer to Part 1, Using Other Instruments.*

Procedure Group 1—Bausch and Lomb Spectronic 20 and 21 (1-inch test tube)

a. Adjust the Wavelength control to 510 nm.

b. With the sample compartment of the Spectronic 20 empty, or using an opaque rod in the Spectronic 21, cover the sample compartment and adjust the Zero control for a reading of zero %T.

c. Place a 1-inch test tube containing some of the original water sample into the sample compartment and cover the compartment. Adjust the Full Scale control for a meter reading of exactly 100% T.

d. Place a 1-inch test tube containing the treated sample to be tested into the sample compartment, cover the compartment and read the percent transmittance. Refer to the following tables to determine the mg/L ferrous iron (Fe). *See Notes B and C.*

Concentration vs. %Transmittance

%T	%T Units									
Tens	0	1	2	3	4	5	6	7	8	9
10	2.52	2.42	2.32	2.23	2.15	2.08	2.01	1.94	1.88	1.82
20	1.76	1.71	1.66	1.61	1.56	1.52	1.47	1.43	1.39	1.35
30	1.32	1.28	1.25	1.21	1.18	1.15	1.12	1.09	1.06	1.03
40	1.00	.98	.95	.92	.90	.87	.85	.83	.80	.78
50	.76	.74	.72	.69	.67	.65	.63	.62	.60	.58
60	.56	.54	.52	.51	.49	.47	.45	.44	.42	.41
70	.39	.37	.36	.34	.33	.31	.30	.29	.27	.26
80	.24	.23	.22	.20	.19	.18	.17	.15	.14	.13
90	.12	.10	.09	.08	.07	.06	.04	.03	.02	.01

Bausch and Lomb Spectronic 20

Concentration vs. %Transmittance

%T	%T Units									
Tens	0	1	2	3	4	5	6	7	8	9
10	2.29	2.20	2.11	2.03	1.96	1.89	1.83	1.77	1.71	1.66
20	1.60	1.56	1.51	1.46	1.42	1.38	1.34	1.31	1.27	1.23
30	1.20	1.17	1.14	1.11	1.08	1.05	1.02	.99	.96	.94
40	.91	.89	.86	.84	.82	.80	.77	.75	.73	.71
50	.69	.67	.65	.63	.61	.60	.58	.56	.54	.53
60	.51	.49	.48	.46	.44	.43	.41	.40	.38	.37
70	.36	.34	.33	.31	.30	.29	.27	.26	.25	.23
80	.22	.21	.20	.19	.17	.16	.15	.14	.13	.12
90	.11	.09	.08	.07	.06	.05	.04	.03	.02	.01

Bausch and Lomb Spectronic 21

Procedure Group 2—Bausch and Lomb MiniSpec 20 (25-mm cell)

a. Adjust the Wavelength control to 510 nm.

b. Using the 1/2-inch adapter and insert, place the opaque rod in the empty sample compartment, cover the compartment and check the zero adjustment. Adjust if necessary.

c. Place a 25-mm cell containing some of the original water sample into the sample compartment and cover the compartment. Adjust the Full Scale control for a meter reading of exactly 100% T.

d. Place a 25-mm cell containing the treated sample to be tested into the sample compartment, cover the compartment and read the percent transmittance. Refer to the following table to determine the mg/L ferrous iron (Fe). *See Notes B and C.*

Concentration vs. %Transmittance

%T	%T Units									
Tens	0	1	2	3	4	5	6	7	8	9
10	2.07	1.98	1.91	1.83	1.77	1.70	1.65	1.59	1.54	1.49
20	1.45	1.40	1.36	1.32	1.28	1.25	1.21	1.18	1.14	1.11
30	1.08	1.05	1.02	1.00	.97	.94	.92	.89	.87	.85
40	.82	.80	.78	.76	.74	.72	.70	.68	.66	.64
50	.62	.61	.59	.57	.55	.54	.52	.51	.49	.47
60	.46	.44	.43	.42	.40	.39	.37	.36	.35	.33
70	.32	.31	.30	.28	.27	.26	.25	.23	.22	.21
80	.20	.19	.18	.17	.16	.15	.14	.13	.11	.10
90	.09	.08	.07	.07	.06	.05	.04	.03	.02	.01

Bausch and Lomb MiniSpec 20

Notes

A. Samples should be analyzed as soon as possible after collection to prevent air oxidation of ferrous iron to ferric iron. Ferric iron is not measured in this test.

B. A ferrous iron stock solution can be prepared by dissolving 0.7022 grams of *Ferrous Ammonium Sulfate Hexahydrate* in demineralized water and diluting to one liter. The stock solution contains 100 mg/L ferrous iron and should be prepared immediately before use. Diluting 1.00 mL of the stock solution to 100 mL using demineralized water gives a 1.0-mg/L ferrous iron standard solution. This solution should be prepared immediately before running the test.

C. The mg/L ferric iron (Fe^{3+}) can be found by subtracting the amount of ferrous iron (Fe^{2+}) from the results of one of the total iron tests.

Required Reagents and Apparatus

Ferrous Iron Reagent Powder Pillows, Cat. No. 1037-69	100
Clippers, for opening pillows, Cat. No. 968-00	each
Demineralized Water, Cat. No. 272-16	946 mL (1 qt)*

Optional Reagents and Apparatus

Hydrochloric Acid, ACS, Cat. No. 134-11	473 mL (pt)
Potassium Hydroxide Standard Solution, 12N, Cat. No. 230-11	473 mL (pt)
pH Indicator Paper, 1-11, Cat. No. 391-33	5-roll pack
Pipet, transfer, 1.00 mL, Cat. No. 515-35	each
Flask, volumetric, 100 mL, Cat. No. 547-42	each
Flask, volumetric, 1000 mL, Cat. No. 547-42	each
Ferrous Ammonium Sulfate Hexahydrate, ACS, Cat. No. 11256-14	113 g

*Larger size available. See Part 3, List of Reagents.

BEG Analytical Procedures for Brine

Chloride (Mohr Method)
Bromide (Spectrophotometry)
Iodide (Spectrophotometry)
Sulfate (Turbidimetry)
Fluoride (Ion Selective Electrode Potentiometry)
Reference ASTM D 1179-80
Alkalinity (Electrometric Titration)
Mercury (Spectrphotometry)
Ammonium (Steam distillation/Titration)
Total Dissolved Solids (ASTM D 1888-78)
Specific Gravity (ASTM 1429-76)
Conductivity (ASTM D 1125-82)

Procedure for analysing the following elements by
Inductively Coupled Plasma/Optical Emission Spectroscopy

Sodium	Potassium
Magnesium	Calcium
Aluminium	Iron
Titanium	Manganese
Cobalt	Chromium
Copper	Nickel
Molybdenum	Zinc
Arsenic*	Cadmium
Vanadium	Lead
Tin	Selenium
Lithium	Strontium
Barium	Boron
Phosphorus	Silica

* Reference included

BUREAU OF ECONOMIC GEOLOGY
THE UNIVERSITY OF TEXAS AT AUSTIN

Mineral Studies Laboratory
University Station, Box X · Austin, Texas 78713-7508 · (512) 471-1534 or 471-7721

DATE: 5 June 1989

TO: Chris Hayden

FROM: Steven W. Tweedy
Mineral Studies Lab

SUBJECT: MSL Personnel and Procedures

The Mineral Studies Laboratory (MSL) is a part of the Bureau of Econonic Geology, The University of Texas at Austin. Personnel and personnel qualifications of the MSL staff involved in this project are given below:

Dr. David W. Koppenaal, Ph.D. Chemistry, Chief Chemist (until November 1988)
Mr. Steven W. Tweedy, B.S. Chemistry, Chief Chemist (April 1989 - present), prior Research Scientist Associate IV, prior acting Chief Chemist (Nov-Apr).
Mr. Thomas L. Pinkston, B.S. Chemistry, Research Scientist Associate II, (until January 1989).
Mr. Raul Herrera, M.S. Mathematics, Research Scientist Associate I (Jan. 1989 - present)
Mr. Peter D. Salgo, B.A. Biochemistry, Research Scientist Associate I (temporary Feb. 1989 - present).
Mr. Rodney I. Heathcott, B.A. Physics, Research Scientist Associate II. (Apr. 1989 - present).
Mr. Joey Dodgen, undergrad. Chemistry, Research Assistant.

Copies of the procedures involved in this subcontract are attached. If you need any further information, please call.

BUREAU OF ECONOMIC GEOLOGY
THE UNIVERSITY OF TEXAS AT AUSTIN

SPECIFIC WORK INSTRUCTION

TITLE	REVISION: 0
MINERAL STUDIES LABORATORY ANALYTICAL PROCEDURE CHLORIDE BY TITRATION (MOHR METHOD) **SWI 1.1**	DATE: 10-31-86 PAGE: 1 OF 5

APPLICABILITY	SUPERSEDES
BUREAU-WIDE	THIS IS THE ORIGINAL ISSUANCE

APPROVAL	CONCURRENCE
William J. Hamm 12/8/86 DIRECTOR DATE	Not applicable PROGRAM COORDINATOR DATE 12-8-86 QUALITY ASSURANCE OFFICER DATE

1. SCOPE

1.1 This method covers the determination of chloride ions in water, wastewater, brines, and extract media. The method is best applied to clear, colorless solutions, as the endpoint can be obscured in cloudy or colored samples. Chloride concentrations in solid samples can also be determined provided appropriate sample dissolution can be effected.

1.2 Solution chloride concentrations ranging from 5 ppm to saturation can be determined.

2. SUMMARY OF METHOD

2.1 Near-neutral solution is titrated with silver nitrate in the presence of a potassium chromate indicator. Chloride quantitatively precipitates as silver chloride until, at the equivalence point, all chloride in solution is consumed. Thereafter, silver will precipitate as the more soluble orange-colored silver chromate, the first occurrence of which is used to mark the endpoint of the titration.

2.2 Relevant reactions:

$Cl^- + Ag^+ \longrightarrow AgCl$ (white ppt.)
$2\ Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4$ (orange ppt.)

3. SIGNIFICANCE

3.1 The classical Mohr method provides a convenient, simple, yet accurate procedure for chloride analysis, utilizing readily available equipment and reagents.

4. INTERFERENCES

4.1 Bromide, iodide, and cyanide register as equivalent chloride concentrations but are normally present at low levels relative to chloride. If the orthophosphate concentration is greater than 25 mg/L, Ag_3PO_4 will precipitate, thus interfering.

4.2 Sulfide, thiosulfate, and sulfite interfere but can be removed by treatment with hydrogen peroxide or oxidizing acid.

4.3 The potentiometric mercuric nitrate or ion chromatographic method may be more suitable for colored or turbid samples in which the endpoint is difficult to observe and for samples whose constituents may form precipitates with the indicator, such as iron and other heavy metal ions.

4.4 It is the responsibility of the analyst to ensure the validity of the method for untested matrices. This can be ascertained by quantitative recovery of a known amount of chloride added to the sample.

5. APPARATUS

5.1 Erlenmeyer flask, 250 mL

5.2 Burette, 50 mL, class A, calibrated in 0.1 mL increments

6. REAGENTS/MATERIALS

6.1 Potassium chromate indicator --

6.1.1 (0.25 M), dissolve 50 grams potassium chromate (K_2CrO_4) in 100 mL of water and add silver nitrate ($AgNO_3$) until a slight red precipitate is produced. Let the solution stand in the dark overnight. Filter solution and dilute to 1 liter with water.

6.2 Silver nitrate solution --

6.2.1 (0.0141 N), for sample chloride concentrations <5000 ppm -- Dissolve 2.395 g $AgNO_3$ in distilled water and dilute to 1 liter. Prepare fresh, store in amber bottle, do not use without frequent restandardization.

6.2.2 (0.20 N), for sample chloride concentrations >5000 ppm --Dissolve 33.971 g $AgNO_3$ in distilled water and dilute to 1 liter. Prepare fresh, store in amber bottle, do not use without frequent restandardization.

6.3 Standard chloride solution, 2,000 ppm --

6.3.1 Dissolve 3.2969 g oven-dried reagent grade NaCl in distilled water and dilute to 1 liter.

6.4 pH adjusting solutions --

6.4.1 Basic solution -- Make about 1 liter of solution by adding NaOH to 1 liter of distilled water until pH is 8.5.

6.4.2 Acidic solution -- Prepare an acidic solution by adding HNO_3 to 1 liter of distilled water until the pH is 5.5 (distilled water [pH typically 6] is usually sufficient for slightly basic samples).

7. PREPARATION OF APPARATUS

7.1 Prepare and set up titration equipment in the conventional manner. Check burette tip and stopcock for accurate delivery of titrant.

8. CALIBRATION

8.1 This procedure does not require instrument or apparatus calibration. Reagent standardization is required and is described in Section 9.

9. PROCEDURE

9.1 Standardization of $AgNO_3$ -- Perform daily.

9.1.1 Take a 5 mL aliquot of the stock chloride (step 6.2.1 or 6.2.2) solution. Dilute with pH adjusting solution to a consistent volume (25 mL). The pH should be between 7 and 9. Add 1 mL K_2CrO_4 indicator solution and titrate with silver nitrate solution to a light orange endpoint. The endpoint can be better detected against a white background. Be consistent in endpoint recognition. Repeat using 10 mL stock chloride (step 6.2.1 or 6.2.2) solution.

9.1.2 Repeat the above procedure for a blank.

9.1.3 Calculate normality of $AgNO_3$ using the equation:

$$\underline{N}\ AgNO_3 = [(C * V) / (A-B)] / 35{,}450$$

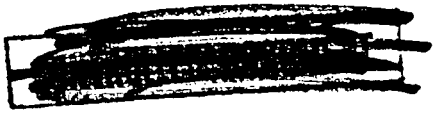
where:

C = Cl standard concentration, in ppm
V = volume, in mL, of chloride standard
A = $AgNO_3$ titrant volume for standard used
B = $AgNO_3$ titrant volume for blank

9.2 Sample Analysis --

9.2.1 Take an appropriate aliquot of sample, depending on suspected chloride concentration (see Note 1), dilute to approximately 100 mL with deionized water, and adjust pH with pH-adjusting solution to pH 7 to 9 and titrate as described in Section 9.1.1.

9.2.2 Titrant volumes should be greater than 5 mL and less than 40 mL; if not, use a different aliquot of sample or adjust titrant strength.



9.2.3 If the presence of sulfide, sulfite, or thiosulfate is suspected in the sample, add 1 mL H_2O_2 (30%) prior to titration.

Note 1. Guide to sample aliquots and titrant concentration:

Sample Type	Sample Volume, mL	Titrant Concentration
Brines	0.1 -- 1	0.2 N
Seawater, Brackish Water	1 -- 5	0.2 N
Fresh, Natural Water	10 -- 50	0.014 N

9.3 Blank Analysis:

9.3.1 Repeat titration as in step 9.2 with several reagent blanks.

9.3.2 Average the resultant blank titration volumes for use in equation given in section 10.2.

10. DATA HANDLING

10.1 Keep detailed records of the analysis and record the pertinent information in the procedure log book.

10.2 Chloride Concentration Calculation —

$$C = (A - B) * N * 35,450 / V$$

where:

C = chloride concentration, in solution, in ppm
A = volume, in mL, of $AgNO_3$ used for sample
B = volume, in mL, of $AgNO_3$ used for blank
N = normality of $AgNO_3$
V = sample volume, in mL

10.3 If the solution analyzed is a result of a solid sample dissolution or extraction procedure, appropriate calculations must be carried out to express the chloride concentration on the basis of the solid sample.

10.4 Salinity—
The dissolved salts in seawater may be expressed as salinity, S:

$$\% S = 1.80655 * C'$$ (see references 12.1 or 12.4)

where C' is the chloride concentration expressed in parts per thousand, by weight.

11. QUALITY ASSURANCE/CONTROL

11.1 Acceptable recoveries for reference standards must accompany any sample analysis. The determination of acceptable recovery criteria will depend on

the level of analysis required, amount of sample available, concentration, and so on.

11.2 A standard seawater sample is available from the Institute of Oceanographic Sciences for which a certified chloride concentration value of 1.937% Cl is given. Use this standard for procedure validation when titrating samples with high chloride content. The error should not exceed 1.0% relative.

11.3 Round-robin performance evaluation samples, distributed by the Environmental Protection Agency, are also available and may be useful for validation of this method at lower chloride concentrations. The error should not exceed 5.0% relative.

11.4 Precision and accuracy estimates on typical samples will be available in future revisions.

12. REFERENCES

12.1 American Public Health Association, Inc., 1980, Standard Methods for the Examination of Water and Wastewater, Method 407A, 15th ed.: New York, p. 270-271.

12.2 American Society for Testing and Materials: 1984, Annual Book of ASTM Standards, Vol. 11.01., Standard Test Method, D512-81, "Chloride Ion in Water," Philadelphia, Pennsylvania, p. 395-396.

12.3 American Petroleum Institute, 1968, API Recommended Practice for Analysis of Oil-Field Waters, 2nd ed.: Dallas, Texas, p. 16.

12.4 U.N.E.S.C.O., 1962, Technical Papers in Marine Science No. 1.

BUREAU OF ECONOMIC GEOLOGY
THE UNIVERSITY OF TEXAS AT AUSTIN

SPECIFIC WORK INSTRUCTION

TITLE	REVISION: 0
MINERAL STUDIES LABORATORY ANALYTICAL PROCEDURE BROMIDE BY SPECTROPHOTOMETRY **SWI 1.2**	DATE: 10-31-86 PAGE: 1 OF 5

APPLICABILITY	SUPERSEDES
BUREAU-WIDE	THIS IS THE ORIGINAL ISSUANCE

APPROVAL	CONCURRENCE
William Muehlberger 12/8/86 DIRECTOR DATE	Not applicable PROGRAM COORDINATOR DATE 12-8-86 QUALITY ASSURANCE OFFICER DATE

1. SCOPE

1.1 This method covers the determination of bromide in fresh water, brine water, and salt or silicate rock digests.

1.2 Bromide concentrations from 0.25 mg/L to approximately 1,000 mg/L can be determined.

2. SUMMARY OF METHOD

2.1 Bromide (Br^-) is oxidized to bromate (BrO_3^-) by hypochlorite (ClO^-) at a pH of 7.2. After elimination of excess hypochlorite with sodium formate the bromate is reacted with iodide to produce iodine (I_2), which is measured spectrophotometrically in solution.

2.2 Relevant reactions:

$$Br^- + 6ClO^- + 6H^+ \longrightarrow BrO_3^- + 3Cl_2 + 3H_2O$$
$$BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$$

3. SIGNIFICANCE

3.1 Chloride does not interfere with this bromide determination as it does with the bromide selective-ion electrode.

3.2 Bromide can be measured as low as 0.25 mg/L, which is comparable to instrumental methods such as ion chromatography.

4. INTERFERENCES

4.1 Iodide is also determined as equivalent bromide with this procedure. If iodide is present at significant levels, it must be determined independently and subtracted from the apparent concentration to get the actual bromide concentration.

4.2 Iron, manganese, nitrate, and organic matter can interfere with this procedure. Their effects can be eliminated by precipitation with CaO and filtration.

5. APPARATUS

5.1 Pye-Unicam SP8-100 UV spectrophotometer

5.2 Technicon BD40 digestion block

5.3 Timer

5.4 50 mL culture tubes calibrated to 25 mL

6. REAGENTS AND MATERIALS

6.1 Bromide standard stock solution (1,000 mg/L). Dissolve 1.4893 g KBr (oven-dry for 2 hours at 105°C, desiccate, then weigh) in 1,000 mL deionized water. Prepare fresh weekly.

6.2 Bromide standard solution (10 mg/L). Dilute 1 mL of the 1,000 mg/L bromide stock solution to 100 mL with deionized water. Prepare daily.

6.3 Calcium hypochlorite solution (0.25 M). Dissolve 35 g $Ca(ClO)_2$ in water and make up to 1,000 mL with water. Prepare this solution daily--the oxidizing power diminishes over time. Let precipitate settle; use clear solution only.

6.4 Hydrochloric acid solution (0.7 N). Dilute 11.6 mL 6 N HCl to 100 mL with water.

6.5 Calcium carbonate, American Chemical Society Reagent Grade

6.6 Corundum boiling stone

6.7 Sodium formate solution (7.35 M). Dissolve 250 g sodium formate (NaCHOO) in water and make up to 500 mL with water.

6.8 Sulfuric acid solution (25%). Dilute 25 mL concentrate H_2SO_4 (sp. gr. 1.84) to 100 mL with water. Cool before use.

6.9 Potassium iodide (KI) crystals, American Chemical Society Reagent Grade

7. PREPARATION OF APPARATUS

7.1 Calibration of culture tubes - deliver 25.00 mL, by pipet, into culture tubes and mark the meniscus level with an indelible, fine-point ink pen or permanently with a carbide-tipped pencil.

7.2 Heat the Technicon digestion block to approximately 150°C.

7.3 Turn on spectrophotometer, let warm up at least 30 minutes, and set wavelength to 400 nm.

8. CALIBRATION

8.1 Calibration of culture tubes is required (see 7.1).

8.2 Spectrophotometer zero calibration - using deionized water in the reference and sample cell positions, set to zero absorbance (100% transmittance).

8.3 Standardization with solutions of known bromide concentrations is required; the standardization procedure is included in section 9.

9. PROCEDURE

9.1 Prepare reagent blanks and working standards, using the 10 mg/L bromide standard, by delivery of 0, 12.5, 25.0, 50.0, and 100.0 micrograms of Br^- into culture tubes. (This corresponds to 0, 1.25, 2.50, 5.0, and 10 mL of the 10 mg/L bromide standard.) Dilute to 25 mL. Standard concentrations will then be 0, 0.5, 1.0, 2.0, and 4.0 mg/L.

9.2 Pipet 1 mL (brines) to 25 mL (fresh water) untreated filtered sample into a calibrated culture tube. For rock salt and/or rock digests, add enough sample solution to give approximately 50 to 100 micrograms Br^-. Add deionized water to each sample to 25 mL mark.

9.3 Add 2 mL of clear $Ca(ClO)_2$ to each tube.

9.4 Add 0.5 mL 0.7 N HCl and about 0.25 g $CaCO_3$ to maintain a pH of 7.0 to 7.2. The pH should be checked on a pH meter on several tubes; in freshly prepared $Ca(ClO)_2$, it should be about 7.0.

9.5 Add several pieces of corundum boiling stone to each tube to maintain even boiling. Mix thoroughly (with vortex).

Note 1. Do not analyze samples outside the 7.0 to 7.2 pH range.

9.6 Boil contents vigorously at 150°C on the digestion block for 10 minutes. Start timer when front row is boiling.

9.7 Remove tubes from block and carefully add 1 mL sodium formate solution to each tube. Mix thoroughly.

9.8 Return tubes to block. Boil 10 minutes to destroy residual hypochlorite. Remove tubes from block.

9.9 Cool contents of tube. When cool, add water to the 25 mL mark. Mix thoroughly. Let contents settle approximately 45 minutes.

9.10 Pipet 10.00 mL of standards and samples into 50 mL culture tubes (need not be calibrated).

9.11 Check zero setting of spectrophotometer. Re-zero if necessary.

9.12 For each standard or sample, perform the following steps:

9.12.1 Add 0.25 g KI to culture tube and mix.

9.12.2 Immediately add 1.0 mL 25% H_2SO_4 and mix (a yellow color should develop, indicating the formation of I_2).

9.12.3 Immediately transfer the treated standard or sample solution to a cuvette, place in spectrophotometer, and measure the absorbance of the solution at 400 nm.

Note 2. The timing of the KI and H_2SO_4 reagents addition and of the interval between reagent addition and measurement is critical to color development and should be kept consistent for all standards and samples. Add KI and H_2SO_4 reagents, mix, and measure the absorbance within 10 to 15 seconds.

Note 3. If sample absorbance is greater than that of the highest standard, dilute accordingly and redetermine absorbance on the diluted sample. Record the dilution factor. Alternatively, take a smaller sample aliquot than in step 9.10.

Note 4. If a sample of less than 10 mL is taken, reduce the KI and H_2SO_4 amounts proportionally.

10. DATA HANDLING

10.1 A linear relationship between bromide concentration and absorbance should be obtained for the standards. Calculate the linear regression coefficients (m,B) and correlation coefficient (r). The equation should be of the form:

$$C' = mA + B$$

where:

C' = bromide concentration of standard, in mg/L
m = slope of concentration vs. absorbance fit
A = solution absorbance, as measured
B = intercept of concentration axis

A correlation coefficient of at least 0.9990 should be obtained. If not, repeat standardization procedures or examine parameters responsible for poor fit.

10.2 Calculate the bromide concentrations in the samples according to the formula:

$$C = (mA + B) * F$$

where the previous definitions hold, and

C = concentration of bromide in sample, in mg/L
F = the dilution factor employed

10.3 Calculate the bromide concentration of the reagent blank according to the formula:

$$C'' = (mA + B) * F$$

where the previous definitions hold, and

C" = the concentration of bromide in the blank

10.4 Correct the sample bromide concentration for the blank contribution by subtraction of C" from C.

10.5 Record pertinent standardization and sample data in procedure log book.

11. QUALITY ASSURANCE/CONTROL

11.1 Standard Seawater (available from the Institute of Oceanographic Sciences) can be used for quality assurance purposes. The certified value for bromide is 69 mg/L, the error should not exceed +5% relative. In-house standard 82SAW06 can be used as a brine control with an accepted value of 485 + 16 mg/L bromide.

11.2 Precision and accuracy estimates on typical samples will be available in future revisions.

12. REFERENCES

12.1 American Society for Testing and Materials, 1984, Annual Book of ASTM Standards, Vol. 11.01 Water (I), D1246-"Iodide and Bromide in Water," Method C: Philadelphia, Pennsylvania, p. 480-482.

12.2 American Petroleum Institute, 1968, API Recommended Practice for Analysis of Oil-Field Waters, API RD 45, 2d ed.: Dallas, Texas, p. 36-37.

12.3 Environmental Protection Agency, Environmental Monitoring and Support Laboratory, 1979, Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, "Bromide, Methods 320.1": Cincinnati, Ohio, p. 320.1-1 through 320.1-5.

BUREAU OF ECONOMIC GEOLOGY
THE UNIVERSITY OF TEXAS AT AUSTIN

SPECIFIC WORK INSTRUCTION

TITLE	REVISION: 0
MINERAL STUDIES LABORATORY ANALYTICAL PROCEDURE IODIDE BY SPECTROPHOTOMETRY **SWI 1.4**	DATE: 10-31-86 PAGE: 1 OF 5

APPLICABILITY	SUPERSEDES
BUREAU-WIDE	THIS IS THE ORIGINAL ISSUANCE

APPROVAL	CONCURRENCE
	Not applicable
	PROGRAM COORDINATOR DATE
12/8/86	12-8-86
DIRECTOR DATE	QUALITY ASSURANCE OFFICER DATE

1. SCOPE

1.1 This method covers the determination of iodide in saline waters and brines.

1.2 Iodide concentrations from 1 mg/L to approximately 100 mg/L can be determined.

1.3 This procedure assumes a general knowledge of chemistry, chemical techniques, oxidation-reduction theory, and familiarity with UV-Visible spectrophotometry as prerequisites for its use.

2. SUMMARY OF METHOD

2.1 Iodide (I^-) contained in the sample is quantitatively oxidized to iodate (IO_3^-) by bromine water in a neutral to weakly acid medium (reaction 2.2.1). Excess bromine is then reacted with sodium formate, according to reaction 2.2.2. After removal of excess bromine, the iodate formed in reaction 2.2.1 is quantitatively reacted with excess added potassium iodide (KI) to form iodine (reaction 2.2.3), which is determined in solution spectrophotometrically. Three moles of iodine are thus formed for each mole of iodide in the sample.

2.2 Relevant reactions:

2.2.1 $I^- + 3Br_2 + 3H_2O \rightarrow IO_3^- + 6Br^- + 6H^+$

2.2.2 $Br_2 + NaHCOO^- \rightarrow H^+ + 2Br^- + Na^+ + CO_2$

2.2.3 $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

3. SIGNIFICANCE

3.1 Chloride and bromide do not interfere with this iodide determination.

4. INTERFERENCES

4.1 Iron, manganese, and organic matter can interfere. They can be removed by adding calcium hydroxide and filtering.

5. APPARATUS

5.1 Pye-Unicam SP8-100 UV spectrophotometer

5.2 Timer

5.3 50 mL culture tubes or test tubes, calibrated to 10 mL

5.4 1 cm pathlength quartz cuvettes

6. REAGENTS AND MATERIALS

6.1 Iodide standard stock solution (1,000 mg/L). Dissolve 1.308 g KI (oven-dry 2 hours at 105°C, desiccate, then weigh) in 1,000 mL deionized water. Prepare fresh weekly; store in the dark between use.

6.2 Iodide standard solution (10 mg/L). Dilute 1 mL of the 1,000 mg/L iodide stock solution to 100 mL with deionized water. Prepare fresh daily.

6.3 Buffer solution (pH 5.2). Shortly before use, mix the following: sodium acetate and acetic acid solutions in a 3:1 volume ratio.

6.3.1 Sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$): Dissolve 275 g of sodium acetate in water and make up to 1,000 mL with water.

6.3.2 Acetic acid: Mix 50 mL of glacial acetic acid with 400 mL of water.

6.4 Saturated bromine solution (0.26M). Add 4.4 g liquid bromine (approximately 1.4 mL) to 100 mL ASTM Type II water and stir until near complete dissolution. Prepare in fume hood and use caution when working with bromine or bromine water.

6.5 Sodium formate solution (HCOONa) (7.3M). Dissolve 50 g of sodium formate in water and make up to 100 mL with water.

6.6 Sulfuric acid solution (25%). Dilute 25 mL concentrated H_2SO_4 (sp. gr. 1.84) to 100 mL with water. Cool before use.

6.7 Potassium iodide (KI) crystals, American Chemical Society Reagent Grade.

7. PREPARATION OF APPARATUS

7.1 Calibration of culture tubes - deliver 10.00 mL, by pipet, into culture tubes and mark the meniscus level with an indelible, fine-point ink pen or permanently with carbide-tipped pencil.

7.2 Turn on spectrophotometer, let warm up at least 30 minutes, and set wavelength to 400 nm.

8. CALIBRATION

8.1 Calibration of culture tubes is required (see step 7.1).

8.2 Spectrophotometer zero calibration - using deionized water in the reference and sample cell positions, set to zero absorbance (100% transmittance).

8.3 Standardization with solutions of known iodide concentrations is required; the standardization procedure is included in section 9.

9. PROCEDURE

9.1 Prepare working standards, using the 10 mg/L iodide standard, by delivery of 0, 25.0, 50.0, 75.0, and 100.0 micrograms of I^- into culture tubes. Dilute to 10 mL.

9.2 For samples, pipet 2 ml (brines) or 10 mL (fresh water) untreated filtered sample into a calibrated culture tube. Dilute to 10 mL mark.

9.3 Add 2 mL of pH 5.2 buffer to each standard and sample. Follow steps 9.4 through 9.6 for each standard and sample.

9.4 Add 1 ml of saturated bromine water. Mix on Vortex mixer. Let oxidation reaction occur at room temperature for 5 minutes.

9.5 Add 1 ml of sodium formate solution to destroy residual bromine. Mix on vortex to completely remove bromine. The solution will be colorless at this juncture.

9.6 Pipet 5 mL of solution into a separate culture tube (need not be calibrated).

9.7 Check zero of spectrophotometer. Re-zero if necessary.

9.8 For each sample or standard, perform the following steps, in rapid succession:

9.8.1 Add 0.1 g KI to each culture tube, and mix (using vortexing).

9.8.2 Add 0.5 mL 25% H_2SO_4 and mix. A yellow color will develop, indicating the formation of I_2.

9.8.3 Transfer approximately 3 mL of the treated sample or standard to a cuvette, place in spectrophotometer, and measure the absorbance of the solution at 400 nm.

Note 1. The timing of the KI and H_2SO_4 reagents addition and of the interval between reagent addition and measurement is critical to color development and should be kept consistent for all standards and samples. A recommended procedure is to add the KI and H_2SO_4 reagents, mix, and measure the absorbance within 10 to 15 seconds.

10. DATA HANDLING

10.1 A linear relationship between iodide concentration and absorbance should be obtained for the standards. Calculate the linear regression coefficients (m, B) and correlation coefficient (r). The equation should be of the form:

$$C' = mA + B$$

where:

C' = iodide concentration of standard, in mg/L
m = slope of concentration vs. absorbance fit
A = solution absorbance, as measured
B = intercept of concentration axis

A correlation coefficient of at least 0.9990 should be obtained. If not, repeat standardization procedures or examine parameters responsible for poor fit.

10.2 Calculate the iodide concentrations in the samples according to the formula:

$$C = (mA + B) * F$$

where the previous definitions hold, and

C = concentration of iodide in sample, in mg/L
F = the dilution factor employed

10.3 Record pertinent standardization and sample data in procedure log book.

11. QUALITY ASSURANCE/CONTROL

11.1 Replicate samples should be co-analyzed with all samples to provide a precision estimate for this determination. No suitable water or brine reference samples exist with certified or recommended iodine concentrations. In the absence of such materials, analysis of samples spiked with known amounts of iodide should be performed to obtain an accuracy estimate (that is, by comparing recovered added iodide to known added iodide).

Maximum allowable accuracy for this procedure is ±15%, relative. Maximum allowable precision for this procedure is 10% relative standard deviation (rsd). Typical precision and accuracy estimates will be provided in the next revision of this procedure.

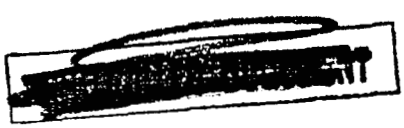
11.2 No water/brine samples exist with certified or recommended iodide concentration values. An in-house sample, analyzed numerous times over several years, is available with the following concentration:

Sample Designation	Sample Type	Accepted Value
83-200	Brine	33.5 ± 1.5 ppm

12. REFERENCES

12.1 Environmental Protection Agency, Environmental Monitoring and Support Laboratory, 1979, Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020, "Iodide, Method 345.1," Cinncinnati, Ohio, p. 345.1-1 through 345.1-4.

12.2 American Petroleum Institute, 1968, API Recommended Practice for Analysis of Oil-Field Waters, API RD 45, 2d ed.: Dallas, Texas, p. 36-37.



BUREAU OF ECONOMIC GEOLOGY
THE UNIVERSITY OF TEXAS AT AUSTIN

SPECIFIC WORK INSTRUCTION

TITLE	REVISION: 0
MINERAL STUDIES LABORATORY ANALYTICAL PROCEDURE SULFATE BY TURBIDIMETRY **SWI 1.3**	DATE: 10-31-86 PAGE: 1 OF 5

APPLICABILITY	SUPERSEDES
BUREAU-WIDE	THIS IS THE ORIGINAL ISSUANCE

APPROVAL	CONCURRENCE
DIRECTOR — DATE 12/8/86	Not applicable PROGRAM COORDINATOR — DATE QUALITY ASSURANCE OFFICER — DATE 12-8-86

1. SCOPE

1.1 This method covers the determination of sulfate ion in fresh water, brines, and extract media. Sulfate concentrations in solid samples can be determined provided appropriate sample dissolution can be effected.

1.2 Solution sulfate concentrations from 5 to 40 can be determined.

2. SUMMARY OF METHOD

2.1 Sulfate ion is precipitated as barium sulfate in an acidic medium. The resulting turbidity is measured on the secondary light path of a spectrophotometer and compared to a curve prepared from standard sulfate solutions.

2.2 Relevant reaction:

$SO_4^{2-} + Ba^{2+} \rightarrow BaSO_4$ (white, suspended ppt)

3. SIGNIFICANCE

3.1 This method is simple, expedient, and accurate and uses readily available equipment.

4. INTERFERENCES

4.1 Colored or suspended matter in the sample will interfere with the turbidity measurement. Suspended matter can be removed by filtration (through a 0.45 -mμ filter membrane). Color can be compensated for by using a sample as a blank.

4.2 Silica in excess of 500 ppm will interfere. In waters containing large quantities of organic material it may be impossible to precipitate barium sulfate satisfactorily.

4.3 Varying acid concentration--It is vital that all solutions contain the same acid concentration. When working with acidic samples, adjust standards and blanks to the same acid concentration.

5. APPARATUS

5.1 Spectrophotometer equipped with secondary light path

5.2 Vortex mixer

5.3 50 ml culture tubes calibrated to 10 mL

5.4 Stopwatch

6. REAGENTS/MATERIALS

6.1 Sulfate standard solution, 1,000 ppm SO_4^{2-} - dissolve 1.8141 g oven-dried potassium sulfate (K_2SO_4) in H_2O and dilute to 1 liter.

6.2 Barium chloride, $BaCl_2 \cdot 2H_2O$, crystals

6.3 Arabic gum solution - dissolve 0.5 g gum acacia in 50 mL distilled water, heat to dissolve. Add 50 mL acetic acid, let cool, and dilute to 100 mL with water.

6.4 Hydrochloric acid, HCl, 6N

7. PREPARATION OF APPARATUS

7.1 Calibration of culture tubes - pipet 10.00 mL of distilled water into culture tubes and mark the meniscus level with a carbide-tipped pen.

7.2 Let the spectrophotometer warm up for at least 30 minutes and set wavelength to 420 nm.

8. CALIBRATION

8.1 Calibration of culture tubes is required (see step 7.1).

8.2 Spectrophotometer zero calibration - using distilled, deionized H_2O in the reference and sample cell at the secondary light path positions, set to zero absorbance (100% transmittance).

8.3 Standardization with solutions of known sulfate concentrations is required; the standardization procedure is included in section 9.

9. PROCEDURE

9.1 When analyzing water samples, use the untreated, filtered fraction.

9.2 Prepare a series of standard SO_4^{2-} solutions containing 0, 200, 300, and 400 micrograms SO_4^{2-} (0, 0.1, 0.2, 0.3, and 0.4 mL, respectively, of the 1000 ppm standard) in 10 mL water. When working with acidic samples, adjust acid strength of standards and samples to a common concentration, then dilute to 10 mL. These standards will correspond to 0, 10, 20, 30, and 40 ppm.

9.3 A preliminary test should be made to determine the appropriate aliquot of sample, thereby saving time. Pipet 2 mL of a few representative samples into a 50 mL culture tube, dilute to 10 mL, and add 0.5 g $BaCl_2$ crystals. Visually compare with 2 mL of the 40 ppm standard SO_4^{2-} solution diluted to 10 mL. Determine aliquot of sample such that the solution will be less than 40 ppm.

9.4 Pipet appropriate aliquot of sample ($\leq$ 10 mL) into a calibrated culture tube and dilute to 10 mL.

9.5 Prepare sample blanks in the same manner. The sample blank should contain the same sample volume, total volume, and all reagents except $BaCl_2$. Measure the turbidity and record.

9.6 Add 1 mL 6N HCl and 1 mL gum arabic solution (to stabilize the $BaSO_4$ suspension) to all standards and samples. Omit addition of HCl if samples already contain greater than 5% acid.

9.7 Mix on vortex.

9.8 Add 0.5 g $BaCl_2$ $2H_2O$ crystals and mix on vortex to dissolve all crystals.

9.9 Wait at least 8 minutes, then measure turbidity at 420 nm using the secondary light path on the spectrophotometer. Use stopwatch and be consistent in timing the turbidity reading as $BaSO_4$ may settle out, causing a decrease in the observed turbidity.

9.10 If sample turbidity is greater than that of the highest standard, reanalyze with a smaller sample aliquot.

10. DATA HANDLING

10.1 Keep detailed records of the analysis and record the pertinent information in the procedure log book.

10.2 A linear relationship between sulfur concentration and turbidity should be obtained for the standards. Calculate the linear regression coefficients (m, B) and correlation coefficient (r). The equation should be of the form:

$$C' = mA + B$$

where

C' = sulfate concentration of standard, in mg/L
m = slope of concentration vs. absorbance fit
A = solution absorbance (turbidity), as measured
B = intercept of concentration axis

A correlation coefficient of at least 0.998 should be obtained. If not, repeat standardization procedures or examine parameters responsible for poor fit.

10.3 Calculate the sulfate concentrations in the samples using the equation:

$$C = [m (A - A') + B] * F$$

where previous definitions hold, and

C = concentration of sulfate in sample, in mg/L
A' = solution turbidity of untreated sample (blank)
F = the dilution factor (10/sample volume in mL)

11. QUALITY ASSURANCE/CONTROL

11.1 Acceptable recoveries for reference standards or control samples must accompany any sample analysis. Acceptability criteria must be determined in consideration of sample type, analyte concentration, analysis requirements, and so on.

11.2 A standard seawater sample is available from the Institute of Oceanographic Sciences for which a sulfate concentration value of 2776 ppm is accepted. Use this standard for procedure validation when analyzing samples with high sulfate content. The error should not exceed 3% relative.

11.3 Round-robin performance evaluation samples distributed by the Environmental Protection Agency are also available and should be used for validation of this method at lower sulfate concentrations. The error should not exceed 5% relative.

11.4 Precision and accuracy estimates on typical samples will be available in future revisions.

12. REFERENCES

12.1 American Society for Testing and Materials: 1984, Annual Book of ASTM Standards, Vol. 11.01., Standards Test Method, D516-82, "Sulfate Ion in Water": Philadelphia, Pennsylvania, p. 658-666.

12.2 American Public Health Association, Inc., 1980, Standard Methods for the Examination of Water and Wastewater, Method 426C, 15th ed.: New York, p. 439-440.

BUREAU OF ECONOMIC GEOLOGY
THE UNIVERSITY OF TEXAS AT AUSTIN

SPECIFIC WORK INSTRUCTION

TITLE	REVISION: 0
DETERMINATION OF FLUORIDE BY ION SELECTIVE ELECTRODE POTENTIOMETRY **SWI 1.11**	DATE: 06-17-87 PAGE: 1 OF 5
APPLICABILITY BUREAU-WIDE	**SUPERSEDES** THIS IS THE ORIGINAL ISSUANCE
APPROVAL William L. Fisher 6/11/87 DIRECTOR DATE	**CONCURRENCE** Not applicable PROGRAM DIRECTOR DATE Carolyn Condon 6/11/87 QUALITY ASSURANCE MANAGER DATE

1. SCOPE

   1.1 This method covers the determination of fluoride ion in solution. Fresh water, brines, and extract media are easily determined with minimal sample preparation.

   1.2 Solution fluoride concentrations greater than 0.1 ppm can be determined.

2. SUMMARY OF METHOD

   2.1 Fluoride is determined potentiometrically using a fluoride ion selective electrode in conjunction with a standard calomel reference electrode and a potentiometer (pH meter) having an expanded millivolt scale.

   2.2 Fluoride ions cause a potential to be developed across the lanthanum fluoride crystal of the electrode. The crystal contacts the sample solution at one face and an internal reference solution at the other. The cell is represented by: Ag/AgCl, Cl [0.3], F [0.001] LaF_3/test solution/SCE.

   2.3 The standard addition method is employed for quantitation.

3. SIGNIFICANCE

   3.1 This method is characterized by high sensitivity, fast response, simplicity, and a high degree of selectivity for fluoride ions against a background of other ions.

4. INTERFERENCES

4.1 Polyvalent cations such as Al^{3+}, Fe^{3+}, and Si^{4+} interfere by complexing with fluoride. The extent to which complexation occurs depends on solution pH and the relative amounts of Al^{3+}, Fe^{3+}, Si^{4+}, and fluoride present in the solution. The addition of a total ionic strength adjustment buffer (TISAB), pH 5.0-5.5, complexes these cations and eliminates the problem of fluoride complexation.

5. APPARATUS

5.1 Fluoride ion selective electrode (commercially available from several manufacturers).

5.2 Calomel reference electrode.

5.3 High Impedance Potentiometer, common pH meter with expanded millivolt scale.

5.4 Mixer, magnetic, with teflon-coated stirring bar.

5.5 Plastic beakers, 20 mL.

5.6 Volumetric pipettes, Class A or equivalent.

6. REAGENTS/MATERIALS

6.1 Stock fluoride solution, 1000 µg/mL. Dissolve 2.210 g anhydrous sodium fluoride (NaF) in distilled water and dilute to 1 L in volumetric flask.

6.2 Total ionic strength adjustment buffer (TISAB). Place approximately 500 mL distilled water in a 1-L beaker and add 57 mL glacial acetic acid, 58 g NaCl, and 0.3 g sodium citrate. Stir to dissolve. Slowly add 6N NaOH (~125 mL) while stirring, until pH is between 5.0 and 5.5. Transfer to a 1-L volumetric flask and dilute to mark.

7. PREPARATION OF APPARATUS

7.1 Turn on the potentiometer and let it warm up for 15 minutes. Inspect electrodes for proper levels of filling solutions; fill according to manufacturers instructions. Connect electrodes to proper input terminals.

8. CALIBRATION

8.1 The slope of the electrode response over the range of sample fluoride concentrations should be checked prior to any sample analysis to ensure Nernstian behavior. The slope is the change in electrode potential per ten-fold change in concentration and can be determined using the following procedure:

8.1.2 Make standard solutions containing 0.1, 0.5, 1.0, 2.0 µg/mL fluoride. Pipette 5 mL of each solution into plastic beakers and add by pipette 5 mL TISAB. Add stirring bar and wait for a stable

reading (<Δ1 mV/5 min.); record the millivolt reading for each solution. If sample solution concentrations are outside this concentration range (0.1-2.0 ppm), either dilute samples or increase concentration of these linearity check solutions.

8.1.3 A linear relationship between the log of the concentration of fluoride and the corresponding millivolt reading should be obtained. Calculate the linear regression coefficients (S, b) and correlation coefficient (r). The equation should be of the form:

$$E = b + S \log C$$

where:

E = millivolt reading
b = y intercept
S = slope
C = concentration of fluoride

A correlation coefficient of at least 0.998 should be obtained. If not, repeat calibration procedure or examine parameters causing poor fit. The slope of this curve for the fluoride electrode at normal room temperatures should be -59 ±4 for Nernstian behavior.

9. PROCEDURE

9.1 Pipette 5.0 mL of sample solution into small plastic beaker and add by pipette 5.0 mL TISAB.

9.2 Add magnetic stir bar and adjust stirring to a slow, constant speed.

9.3 Immerse electrodes in solution and wait for a stable millivolt reading (<Δ1 mV/5 min.). Record.

9.4 Add by pipette fluoride standard such that the concentration is increased by a factor of 2 to 5 times. Wait for a stable millivolt reading and record.

9.5 The concentration is calculated using a variation of the Nernst equation. (See section 10.2)

10. DATA HANDLING

10.1 Keep detailed records of the analysis and record the pertinent information on the Data Log and Worksheet in the Fluoride Procedure Log Book.

10.2 Calculate the fluoride concentrations in the samples using the equation:

$$C = \Delta C / ([10 \exp (E2 - E1/S)] - 1)$$

where:

C = concentration of fluoride ion in µg/mL
$\Delta C = (C_{std})\ (V_{std})/(V_{sample} + V_{std})$

where:
C_{std} = concentration (µg/mL) of fluoride in standard
V_{std} = volume, mL, of standard added
V_{sample} = volume, mL, of sample

E2 = millivolt reading after standard addition
E1 = initial millivolt reading
S = slope of fluoride electrode response versus concentration (See section 8.1.3).

10.3 If the solution analyzed is a result of an extraction procedure or a liquid dilution, appropriate calculations must be carried out to express the fluoride concentration on the basis of the original sample.

11. QUALITY ASSURANCE/CONTROL

11.1 A standard seawater sample is available from the Institute of Oceanographic Sciences for which a fluoride concentration value of 1.4 µg/mL is accepted. Use this standard for procedure validation when analyzing brines and seawater. The error should not exceed 10 percent relative.

11.2 Round-robin performance evaluation samples, distributed by the Environmental Protection Agency, are also available and may be useful when analyzing fresh or ground water. The error should not exceed 10 percent relative.

11.3 The following precision and accuracy data are illustrative for this procedure.

Sample No.	Replicate Data, F, µg/mL	RSD (%)	Mean	Accepted Value	Bias (%)
Seawater	1.5, 1.3, 1.5 1.5, 1.4, 1.4	5.8	1.43	1.4	2.1
EPA 478#3	0.61, 0.67, 0.68 0.62, 0.65, 0.60	5.3	0.64	0.63	1.6

12. BIBLIOGRAPHY

12.1 Annual Book of ASTM Standards, Vol. 11.01, Standard Test Method, D1179-80B, "Fluoride Ion in Water," American Society for Testing and Materials, Philadelphia, Penn., 1984, p. 461-463.

12.2 Standard Methods for the Examination of Water and Wastewater, Method 413B, American Public Health Association, Inc., New York, 1980, 15th ed., p. 335-337.

12.3 Radiometer Manuals, "Introduction to Radiometer Selectrodes", #ST56, and "Instructions for F1052F Fluoride Selectrode," #982-581.

12.4 Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, "Fluoride, Method 340.2." Environmental Protection Agency, EMSL, Cincinnati, Ohio, 1983, p. 340.21-340.23.

Designation: D 1179 – 80

Standard Test Methods for FLUORIDE ION IN WATER[1]

This standard is issued under the fixed designation D 1179; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

These methods have been approved for use by agencies of the Department of Defense and for listing in the DoD Index of Specifications and Standards.

1. Scope

1.1 These methods[2] cover the determination of fluoride ion in water. Two methods are given as follows:

	Sections
Method A (SPADNS Procedure, Photometric)	7 to 15
Method B (Ion Selective Probe)	16 to 23

1.2 Method A covers the accurate measurement of total fluoride in water through isolation of the fluoride by distillation and subsequent measurement in the distillate by use of the indicator sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate, also called 4,5-dihydroxy-3-(parasulfophenylazo)-2,7-naphthalene disulfonic acid, trisodium salt.[3] (This reagent is generally referred to as SPADNS reagent.) The procedure covers the range from 0.00 to 1.40 mg/L of fluoride.

1.3 Method B covers the accurate measurement of simple fluoride ion in water by means of an ion selective probe. With this method the necessity for distillation is eliminated because the probe is not affected by the interferences common to the colorimetric procedure. Concentrations of fluoride from 0.1 to 1000 mg/L may be measured.

2. Applicable Documents

2.1 *ASTM Standards:*

D 1066 Sampling Steam[4]

D 1129 Definitions of Terms Relating to Water[4]

D 1192 Specification for Equipment for Sampling Water and Steam[4]

D 1193 Specification for Reagent Water[4]

D 3370 Practices for Sampling Water[4]

E 60 Recommended Practice for Photometric Methods for Chemical Analysis of Metals[5]

E 275 Recommended Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near-1 Infrared Spectrophotometers[6]

3. Significance

3.1 Simple and complex fluoride ions are found in natural waters. Fluoride complexes with silicon, aluminum, and boron. These complexes may originate from the use of fluorine compounds by industry.

3.2 Fluoridation of drinking water to prevent dental caries is practiced by a large number of communities in this country. Fluoride is monitored to assure that an optimum treatment level of 1.4 to 2.4 mg/L, depending on the corresponding range of ambient temperatures of 32 to 10° C, is maintained.

4. Definitions

4.1 For definitions of terms used in these methods refer to Definitions D 1129.

[1] These methods are under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

Current edition approved July 3, 1980. Published August 1980. Originally published as D 1179 – 51. Last previous edition D 1179 – 72 (1978).

[2] Bellack, E., "Simplified Fluoride Distillation Method," *Journal of the American Water Works Association*, JAWWA, Vol 50, 1958, p. 530.

Bellack, E., and Schouboe, P. J., "Rapid Photometric Determination of Fluoride with SPADNS Zirconium Lake," *Analytical Chemistry*, ANCHA, Vol 30, 1958, p. 2032.

Both Methods A and B are similar to, but not identical with, those appearing in *Standard Methods for the Examination of Water and Wastewater*, 13th Ed., American Public Health Assn., Inc., New York, N. Y., pp. 168–178.

[3] Eastman No. 7309, Baker J189; Matheson, Coleman, and Bell DX 1475; Fisher 7309; or equivalent.

[4] *Annual Book of ASTM Standards*, Vol 11.01.

[5] *Annual Book of ASTM Standards*, Vol 03.05.

[6] *Annual Book of ASTM Standards*, Vol 14.01.

5. Purity of Reagents

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[7] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Unless otherwise indicated, references to water shall be understood to mean Type I reagent water conforming to D 1193.

6. Sampling

6.1 Collect the sample in accordance with D 1066, D 1192, or D 3370.

METHOD A—SPADNS PHOTOMETRIC METHOD

7. Scope

7.1 This method is applicable to the accurate determination of fluoride ion in water including most waste waters. Certain exceptions, such as concentrated brines and oily wastes, may occur.

8. Summary of Method

8.1 The fluoride is distilled from the same as hydrofluosilicic acid and is determined photometrically by its bleaching effect upon the SPADNS dye. Distillation may be omitted without loss of precision only if it is known that the concentration of certain interfering substances are below the values given in Table 1.

9. Interferences

9.1 In sample distillation, interference may be experienced as follows:

9.1.1 Aluminum in excess of 300 mg/L, silicon dioxide as colloidal silica in excess of 400 mg/L, and silicon dioxide as silicate in excess of 300 mg/L will retard fluoride recovery.

9.1.2 Fluoride in excess of 3.0 mg/L will hold up in the condenser to a certain extent causing low results and act as a positive interference for subsequent samples of lower fluoride content. In such cases the condenser should be flushed with 300 to 400 mL of water and added to the distillate. The distillate may then be diluted to 1.0 L. If the analyst prefers, a smaller sample aliquot diluted to 300 mL may be selected for distillation.

9.1.3 Chloride at high concentrations such as are encountered in brines or sea water (>2500 mg/L) may distill over and act as an interference in the subsequent color reaction. The chloride interference is easily corrected with the use of silver sulfate.

9.1.4 Sea water, brines, and generally samples of dissolved solids in excess of 2500 mg/L will cause bumping in the distillation flask. Dilution of the sample with fluoride-free water to a lesser dissolved solids concentration is effective.

9.1.5 Samples containing oily matter which may result in a two-phase distillate, an emulsion, or anything other than a clear distillate will prevent the accurate measurement of the fluoride. Such samples should be extracted initially with a suitable solvent (ether, chloroform, benzene, etc.) to remove the oily material and then warmed on a steam bath to remove traces of the solvent.

9.2 Table 1 lists the interferences, and the apparent effect of each, on the SPADNS procedure. Distillation is mandatory unless the concentration of these water constituents is below the indicated level.

10. Apparatus

10.1 *Distillation Assembly*—Glassware consisting of a 1-L, round bottom, borosilicate boiling flask, an adapter with a thermometer opening, a connecting tube, a condenser, and a thermometer reading to 200°C, assembled as shown in Fig. 1. Standard-taper or spherical ground glass joints shall be used throughout.

10.2 *Photometer*—Spectrophotometer suitable for use at 570 nm and providing a light path of at least 1.0 cm, or a filter photometer equipped with a green-yellow filter having maximum transmittance between 550 and 580 nm and providing a light path of at least 1.0 cm. Photometers and photometric practice described in this method shall conform to Recommended Practice E 60; spectrophotometers shall conform to Recommended Practice E 275.

[7] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N. Y., and the "United States Pharmacopeia."

11. Reagents[7]

11.1 *Acid Zirconyl-SPADNS Reagent*—Mix equal volumes of acid zirconyl reagent and SPADNS solution together to produce a single reagent. This reagent is stable for 2 years.

11.2 *Reference Solution*—Add 10 mL of SPADNS solution (11.6) to 100 mL of water. Dilute 7 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 10 mL and add to the diluted SPADNS solution. This solution is stable indefinitely and may be reused. The use of this solution permits the analyst to adjust the instrument so that the meter reading of the blank and standards may be used on the optimum portion of the meter scale, 0.0 to 0.8 absorbance units.

11.2.1 As an alternative, the reference solution may be omitted and the instrument adjusted to some convenient, but fixed point on the meter scale using the 0.00-mg F standard. (The fixed reading of 0.80 absorbance is suggested.) In this case, the zero standard serves as the reference solution and later adjustments of the instrument must be made to the same fixed point using the same solution.

11.3 *Silver Sulfate* (Ag_2SO_4), powder.

11.4 *Sodium Arsenite Solution* (2 g/L)—Dissolve 2 g of sodium arsenite ($NaAsO_2$) in water and dilute to 1 L.

11.5 *Sodium Fluoride, Standard Solution* (1.0 mL = 0.01 mg F)—Dissolve 0.2210 g of sodium fluoride (NaF) in water and dilute to 1.0 L. Dilute 100 mL of this solution to 1.0 L with water. Store in borosilicate glass or polyethylene.

11.6 *SPADNS Solution* (1.916 g/L)—Dissolve 0.958 g of SPADNS reagent (sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate), also called 4,5-dihydroxy-3-(parasulfophenylazo)-2,7-naphthalene disulfonic acid, trisodium salt, in water and dilute to 500 mL. This solution is stable indefinitely if stored in a well-sealed bottle, protected from sunlight.

11.7 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

11.8 *Zirconyl-Acid Reagent* (0.266 g $ZrOCl_2 \cdot 8H_2O$/L)—Dissolve 0.133 g of zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) in about 25 mL of water. Add 350 mL of concentrated HCl and dilute to 5000 mL.

12. Calibration

12.1 Prepare a series of standards using the fluoride standard solution (1 mL = 0.01 mg F) in the range from 0 to 1.40 mg/L by diluting appropriate volumes to 50 mL. The following series may be used:

Millilitres of Standard (1.0 mL = 0.01 mg F)	Concentration when Diluted to 50 mL, mg F/L
0.00	0.00
1.00	0.20
2.00	0.40
3.00	0.60
4.00	0.80
5.00	1.00
6.00	1.20
7.00	1.40

12.2 If the samples to be analyzed contain free chlorine, add 2 drops of $NaAsO_2$ solution to each standard. Add 10.0 mL of the mixed acid zirconyl-SPADNS reagent to each standard and mix well, using extreme care to ensure that all of the dye reagent is incorporated into the sample. The addition of the reagent must be made with all possible accuracy to ensure that exactly the same amount of dye is added to each standard. Set the photometer (see 10.2) to zero absorbance with the reference solution and obtain the absorbance readings of the standards; plot the curve of the absorbance readings versus the fluoride concentrations. A new standard curve should be prepared whenever a new batch of SPADNS reagent is prepared.

13. Procedure

13.1 *Distillation*:

13.1.1 Place 400 mL of water in the distilling flask and add 200 mL of concentrated H_2SO_4 (sp gr 1.84). Observe the usual precautions while mixing the H_2SO_4 by slow addition of the acid accompanied by constant swirling. Add sufficient boiling stones and assemble the apparatus as shown in the illustration.[8] Heat the solution in the flask, preferably with an electric heating mantle, until the temperature of contents reaches exactly 180°C. A quartz heating mantle is preferred in order to reach the re-

[8] Boiling stones prepared from 6- to 10-mm pieces of fritted, sintered borosilicate glass are effective and fluorine-free. Glass beads, solid or perforated, are ineffective. Boiling stones manufactured from alumina may contain fluorine.

quired 180°C in a minimum time. The tip of the thermometer must extend below the level of the liquid in the flask at this point. Discard the distillate. The procedure, to this point, serves to adjust the acid-water ratio for subsequent distillations.

13.1.2 **Caution**—Cool the acid-water mixture to below 100°C, add slowly 300 mL of sample, and mix thoroughly before application of heat. Distill as before until the temperature reaches 180°C. Positively do not allow the temperature to exceed 180°C, since, at this temperature and above, carry-over of sulfate becomes excessive and acts as an interference in the subsequent fluoride measurement.

13.1.3 Collect the distillate in any suitably calibrated vessel. If, however, the distillate is collected in a 300-mL volumetric flask as shown in the drawing, it is possible to ignore the thermometer and stop the distillation when the volume of distillate reaches 300 mL.

13.1.4 In the case of samples containing chlorides in concentrations which may interfere in the subsequent reaction, add Ag_2SO_4 to the distillation mixture at a rate of 5 mg/mg of chloride.

13.1.5 The acid-water distilling solution may be used repeatedly until the buildup of interference materials equal the concentration given in Section 9.

13.2 *Analysis*:

13.2.1 If the sample contains free chlorine, as might be expected in drinking water, remove it by adding 1 drop of $NaAsO_2$ solution for each 0.1 mg of chlorine present, to 50 mL of the distillate (or sample if distillation is not required). Add 2 drops of $NaAsO_2$ solution in excess. (In cases where the use of $NaAsO_2$ is required, also add 2 drops of $NaAsO_2$ solution to the blank and standards.)

13.2.2 Transfer a 50-mL aliquot, treated if necessary (see 13.2.1) and containing less than 0.028 mg of fluoride, or a lesser aliquot diluted to 50 mL, to a 50-mL Nessler tube or other suitable container. Add 10.0 mL of acid zirconyl-SPADNS reagent and mix, using the same precautions as observed for the standards (see 12.2). Read the absorbance at any subsequent time, first setting the absorbance reading of the photometer (see 10.2) to zero with the reference solution. If the absorbance reading of the sample falls beyond the highest reading of the standard curve, the procedure should be repeated using a smaller aliquot. The temperature of the sample must be the same as that used for the standards.

13.2.3 If an interference from aluminum is suspected, a correction may be made by simply delaying the absorbance reading. A delay of 2 h will provide for self correction of as much as 3 mg/L of aluminum.

14. Calculation

14.1 Calculate the concentration of fluoride ion, in milligrams per litre, as follows:

$$\text{Fluoride, mg/L} = 50A/V$$

where:

A = milligrams per litre of fluoride measured photometrically, and

V = millilitres of sample.

15. Precision[9]

15.1 The precision of this method was tested by 53 laboratories and found to be 0.089 at a concentration of 0.81 mg/L of F.

METHOD B—ION SELECTIVE ELECTRODE METHOD

16. Scope

16.1 This method is applicable to the measurement of fluoride ion in finished waters, natural waters, and most industrial waste waters. The necessity for distillation is eliminated and concentrations of fluoride from 0.1 up to 1000 mg/L may be measured.

16.2 The method is not applicable to samples containing more than 10 000 mg/L of dissolved solids.

17. Summary of Method

17.1 The fluoride is determined potentiometrically using an ion selective fluoride electrode in conjunction with a standard single junction, sleeve-type reference electrode, and a pH meter having an expanded millivolt scale, or a specific ion meter having a direct concentration scale for fluoride.

17.2 The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions.[10] The cell

[9] Precision statements are based on data supplied by Analytical Reference Service. Taft Engineering Center. Copies have been filed at ASTM Headquarters as RR:D-19-150.

[10] U. S. Patent No. 3.431.182 (March 4, 1969), assigned to Orion Research Co.

may be represented by Ag/Ag Cl, Cl^- (0.3), F^- (0.001) LaF_3/test solution/reference electrode.

18. Interferences

18.1 Extremes of pH interfere. Sample pH should be between 5 and 9.

18.2 Polyvalent cations of Si^{+4}, Fe^{+3}, and Al^{+3} interfere by forming complexes with fluoride. The degree of interference depends upon the concentration of the complexing cations, the concentration of fluoride, and the pH of the sample (see Table 2). Although the addition of a pH 5.0 buffer (see 20.1) containing citrate ion preferentially complexes aluminum (the most common interference), silicon, and iron, and eliminates the pH problem, the use of either one of two buffers (20.2 and 20.3) is recommended when aluminum is present, because it is more effective than the citrate buffers over a greater range of aluminum concentrations.

18.3 Interferences usually encountered in other methods, such as sulfate or phosphate, do not cause any problem.

19. Apparatus

19.1 *pH Meter*, with expanded mV scale or a specific ion meter.

19.2 *Fluoride Ion Selective Electrode.*[11]

19.3 *Reference Electrode*, single-junction; sleeve-type.

19.4 *Mixer*, magnetic, with a TFE-fluorocarbon-coated stirring bar.

20. Reagents

20.1 *Buffer Solution* (pH from 5.0 to 5.5)—To approximately 500 mL of distilled water in a 1000-mL beaker, add 57 mL of glacial acetic acid, 58 g of sodium chloride (NaCl), and 0.30 g of sodium citrate dihydrate. Stir the solution to dissolve and cool it to room temperature. Adjust the pH of the solution to between 5.0 and 5.5 with 5 *N* sodium hydroxide (NaOH) (about 150 mL will be required). Transfer the solution to a 1000-mL volumetric flask and dilute it to the mark with water.

20.2 *Buffer Solution for Aluminum* (THAM)—To approximately 500 mL of water, add 84 mL of reagent grade hydrochloric acid (36 to 38 %), 242 g of tris-(hydroxymethyl)-aminomethane (also known as 2-amino-2-(hydroxymethyl)-1,3-propanediol) and 230 g of sodium tartrate ($Na_2C_4H_4O_6 \cdot 2H_2O$). Stir to dissolve and cool to room temperature. Transfer to a 1000-mL volumetric flask and dilute to the mark with water.

20.3 *Buffer Solution for Aluminum* (ALCOA)—Prepare the buffer as follows: dissolve 60 g of citric acid monohydrate, 210 g of sodium citrate hydrate, and 53.5 g of ammonium chloride in 500 mL of water. Add 67 mL of ammonium hydroxide solution, normal laboratory strength (28 to 30 % NH_3 by weight), and dilute with water to 1 L.

20.4 *Sodium Fluoride, Standard Solution* (1.0 mL = 0.01 mg of F)—See 11.5.

21. Calibration

21.1 Prepare a series of three standards, 0.5, 1.0, and 2.0 mg/L, using the fluoride standard solution (1.0 mL = 0.01 mg of fluoride). Dilute the following volumes to 100 mL:

Millilitres of Standard (1.0 ml = 0.01 mg F)	Concentration when Diluted to 100 mL, mg F/L
5.00	0.50
10.00	1.00
20.00	2.00

21.1.1 For unusual waters containing high concentrations of fluorides the standards range may be expanded up to 1000 mg/L, if necessary.

21.2 Pipet 50 mL of each standard into a 150-mL beaker. Then pipet 50 mL of buffer. Mix it well on a magnetic stirrer.

21.3 *Calibration of a pH Meter*—Immerse the electrodes in each standard solution, starting with the lowest concentration, and measure the developed potential while mixing. The electrodes must remain in the solution for at least 3 min, or until the reading has stabilized. Using semilogarithmic graph paper, plot the concentration of fluoride in milligrams per litre on the log axis versus the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

21.4 *Calibration of a Specific Ion Meter*—Follow the directions of the manufacturer for the operation of the instrument. See 21.1 and 21.1.1 for selection of standards.

22. Procedure

22.1 Place 50.0 mL of the sample and 50.0 mL of buffer in a 150-mL beaker. Place the solution on a magnetic stirrer and mix it at

[11] Fluoride ion selective electrodes are available from most laboratory supply houses.

medium speed. Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution for at least 3 min or until the reading has stabilized. At concentrations under 0.5 mg/L of fluoride, it may require as long as 5 min to reach a stable meter reading; higher concentrations stabilize more quickly. If a pH meter is used, record the potential measurement for each unknown sample and convert the potential reading to the fluoride ion concentration of the unknown using the standard curve. If a specific ion meter is used, read the fluoride level in the unknown sample directly in milligrams per litre on the fluoride scale.

23. Precision[12]

23.1 The precision of this method, using the buffer solution in 20.1, was tested by 111 laboratories and found to be 0.030 at a concentration of 0.85 mg/L of fluoride.

23.2 The precision of the method using the buffer solution in 20.2 was tested by six operators in four laboratories in the presence of 20 mg/L of Al obtained from 247 mg/L of aluminum sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$]. The overall precision of the method within its designated range varies with the concentration being tested in accordance with Figs. 2 and 3, applying respectively to the low- and high-concentration ranges. The determination of the bias is shown in Table 3.

23.3 The precision of the method using the buffer solution in 20.3 was tested by seven operators in five laboratories using the same quantity of aluminum as in 23.2. The overall precision of the method within its designated range varies with the concentration being tested in accordance with Figs. 4 and 5, applying respectively to the low and the high concentration ranges. The determination of the bias is shown in Table 4.

[12] Study Number 33, Analytical Reference Service, U. S. Dept. of Health, Education and Welfare, 1969, p. 3, filed at ASTM Headquarters as RR:D-19-151.

SWI 1.13

ALKALINITY DETERMINATION BY ELECTROMETRIC TITRATION

1. SCOPE

1.1 This method covers the determination of alkalinity in all types of aqueous solutions.

1.2 Alkalinity concentrations from 10 mg/L (as bicarbonate-equivalent titration alkalinity) and up can be determined.

1.3 Titration endpoints of pH 8.3 (phenolphthalein), 4.5 (metacresol purple), or 2.5 are provided for in this procedure, allowing estimation of hydroxide, carbonate + bicarbonate, and organic acid anion equivalent titration alkalinities.

1.4 This method is a laboratory procedure. Alkalinity measurements should be made, whenever possible, in the field using an appropriate field analysis procedure. Many of the principles in this procedure also apply to field analyses, however.

2. SUMMARY OF METHOD

2.1 Basic ions present in the sample are titrated with standardized HCl to a pH endpoint of 8.3, 4.5 or 2.5, depending on sample and/or suspected acid neutralizing constituents. The amount of HCl consumed in the neutralization is proportional to the basic ion concentration. Concentrations are generally expressed as bicarbonate equivalent concentration in this procedure. Other concentration units, such as mg/L ppm $CaCO_3$, etc. can also be used, but may assume or require a knowledge of specific chemical composition of the sample.

2.2 The relevant reaction can be expressed as:

$$B^- + H^+ \text{---} > BH$$

where: B represents various basic ions, which may include contributions from borates, silicates, sulphides, phosphates [and organic acid anions] if they are present in the sample, as well as bicarbonates and carbonates found in most natural aqueous samples.

3. SIGNIFICANCE

3.1 Naturally colored waters and solutions that form colored precipitates upon HCl addition will interfere with the classical bromocresol green colorimetric method of endpoint detection. This interference is overcome by using the described electrometric method for detecting the endpoint.

4. INTERFERENCES

4.1 Alkalinity and pH may be unstable solution properties and can change between times of sampling and laboratory analysis. Field analysis of alkalinity concentrations, followed by laboratory confirmation, is encouraged.

4.2 Soaps, oily matter, and suspended solids may coat the electrode and cause a sluggish or erratic response. Allow additional time between samples for equillibrium to be reached and/or remove the interferents. Notify sample submittor if such behavior is exhibited.

5. APPARATUS

5.1 Metrohm Titroprocessor, Model 672.

5.2 Metrohm Dosimat. Model 655.

5.3 Titration vessel, 10 mL burette, amber, Metrohm type 6.1518.220; equipped with an antidiffusion tip.

5.4 Combination glass electrode. Metrohm type 6.02.

5.5 Disposable plastic beakers. 20-50 mL.

5.6 Magnetic stirring plate with teflon coated stirring bars.

5.7 Thermometer, capable of reading to within $\pm$ 0.1C.

6. REAGENTS AND MATERIALS

6.1 Hydrochloric acid (approximately 0.018N). Pipet approximately 3 mL of distilled 6N HCl into a 1 liter volumetric flask which is half filled with deionized water, then dilute to 1 liter. This solution must be standardized with THAM prior to daily use (section 9.1).

6.2 THAM [Tris-(hydroxymethyl)aminomethane] (approximately 0.100N). Dissolve 12.1 g $\pm$ 1 mg grams dry (1 hour @ 105oC) THAM deionized CO_2-free water and dilute to 1 L using a volumetric flask. Calculate exact normality. [Store solution in an airtight container to minimize CO_2 absorption.]

6.3 Reference buffer solutions, pH 4.00($\pm$.01), 7.00($\pm$.01), 10.00($\pm$.02), NBS traceable. Check the expiration date

on each buffer solution, discard any solution whose expiration date has elapsed.

6.4 Deionized water (DI-H_2O). ASTM type III (<1 uS) water or better. (ASTM Standard Specification D1193-77).

7. PREPARATION OF APPARATUS

7.1 Preparation of Dosimat

7.1.1 Fill the titration vessel with the 0.018N HCl and attach to the Dosimat. Refer to the Metrohm instruction manual for rinsing the delivery system and for removing trapped air bubbles.

7.1.2 The dosing speed is controlled by the (dv/dt) knob located on the Dosimat. The dial should be set to 3, but may be optimized for various sample types. Refer to the instruction manual for optimization methods.

7.2 Preparation of pH standardization.

7.2.1 Check the combination glass electrode for proper level of saturated KCl solution, and fill if necessary. Connect the electrode to the high impedance Input I, socket 4 terminal located on the back of the Titroprocessor.

7.2.2 Allow the instrument to warm up (30 minutes) and solutions to thermally equilibrate.

7.2.3 Take an accurate temperature reading in °C of a thermally stable solution that will be analyzed. Enter this value into the Titroprocessor as follows:

*Note: Throughout these instructions the keyboard entries on the Titroprocessor are noted within brackets and bolded, values that are displayed on the instrument screen will be in quotations.

7.2.3.1 Press the **[measure]** key until "meas pH" appears. Press the **[parameters]** key, "temp" now appears on the display, key in the correct temperature and then press **[enter]**.

7.2.4 Before use and between sample pH and alkalinity measurements, rinse the electrode with a continuous stream of deionized water and blot dry with a solt tissue. This will prevent any cross-contamination between samples.

7.2.5 Add a small magnetic stir bar to all solutions and adjust to a slow uniform stirring rate. If the potential reading is unstable then discontinue stirring.

7.2.6 Proceed with the pH standardization as described in section 8.

7.3 Preparation of HCl standardization.

7.3.1 Load the standardization method into memory as follows:

7.3.1.1 Press [user methods], the display shows "recall", key in 1-1 and [enter]. Display shows "set pH 1-1". The standardization method is now recalled and in a ready state.

*Note: User defined methods can accidentally be deleted from memory due to a power loss or by mistaken keystrokes; or newly optimized parameter values may supersede previous values. Refer to the Titroprocessor manual for entering the specific analysis parameters.

7.3.2 Check all parameters, formulas, constants and preparation steps before beginning the analysis. Typical values are listed below with each parameter. Some of the titration control parameters such as the pulse range. drift, (t)delay, and dv/dt are sample dependent variables and may be optimized by the analyst. The goal in optimization is to achieve a reasonably fast yet accurate titration. Whatever values are derived for these parameters, they should remain the same throughout the entire analysis.

*Note: Each parameter will appear in turn by pressing [enter].

7.3.2.1 Press [prep. steps]. The prep. steps contain any commands that precede the titration.

"add v	.001 mL"	reagent dump
"pause	10 sec."	titration'delay
"electr. input	1"	measuring input

7.3.2.2 Press [parameters]. The parameters control the various aspects of the titration:

"EP1 pH	ppp"	'ppp' is the stop endpoint. Enter desired end point. (pH 8.30,4.50,2.50)
"dyn. pH1	8.00"	Pulse range

		(reagent feed)
"drift 1	.3 mV/s"	Drift criteria
"t(delay)	1 sec"	time delayed end-point stop
"temp.	(xxx C)"	key in temp. of solutions.

*Note: refer to the user manual for a more detailed explanation of the pulse range, drift and the associated optimization techniques.

7.3.2.3 The normality and alkalinity calculation will be done by the microprocessor. Verify the formula for calculating the normality of HCl as follows:

Press [2nd] [fmla], display shows "F?"; enter [1]; the formula now appears:

F1=C00 x C01/EP1;5;mole/L

where:

C00 = mL of THAM EP1 = mL HCl used
C01 = N of THAM 5 = decimal places

7.3.2.4 The data output contained in the printed report is governed by the def records code. Report 2 is an excellent detailed printout of the analysis data. Key [def records], "report 2" is displayed. [When a graph of the titration is required: key [def records], enter 25, press [enter]. The printout will now include a detailed report and a plot of the titration.]

7.3.3 Proceed with the HCl standardization method as described in section 9.1.

7.4 Preparation for sample analysis.

7.4.1 Load the sample analysis method into memory as follows:

7.4.1.1 Press [user method], "recall" is displayed. Key in 1-2 and press [enter]. Display shows "set pH 1-2".

7.4.2 The same preparation steps and parameters as used in the HCl standardization will be used with the sample analysis. Verify the values (see section 7.3.2.1, and 7.3.2.2).

7.4.3 Check the HCO3 formula and the formula constants as follows:

Press [2nd][fmla], "F?" appears; enter [1]; the formula is displayed:

F1 = EP1*C01*C02*C03/C00;2;ppm

where:

F1=RS1=HCO3 ppm
C02 = 61.01(m.w. of HCO_3)
EP1 = mL of HCl required

C01 = normality of HCl
C03 = 1000

Press [fmla const].

"C01 =" appears; enter the new value calculated in standardization (see section 9.1.4); store this value by pressing [user methods] until "store 1-2" appears, press [enter] twice. Continue verifying the formula constants by pressing fmla const], each constant will appear in turn by pressing [enter].

7.4.4 Proceed with the sample analysis as detailed in section 9.2.

8. STANDARDIZATION

8.1 Press [measure] key until "measure pH" appears on display.

8.2 Press [prep steps] key and answer inquiries as follows:

8.3 In response to "t(print)", key in 60, then press [enter]. The pH of the solutions will be printed out every 60 seconds.

8.4 In response to "el.cal 0/1?", key in 1, then press [enter] . The electrical calibration sequence is now on and will proceed automatically.

8.5 In response to "T.cal.", key in the measured temperature in °C, then press [enter]. (See section 7.3.)

8.6 In response to "pH(S) 1", key in 4.00. Insert electrode in buffer solution of pH 4. Let the electrode equilibrate (typically 1-2 min.) and then press [enter]. The instrument is now reading the mV's which is displayed temporarily on the screen as "U cal.1 xxx mmV". When the system default drift criteria is met (<1mV/min.), the display will prompt for the second buffer.

8.7 In response to "pH(S) 2", key in 10.00. Insert electrode in the buffer solution of pH 10. Let the system equilibrate and then press [enter]. The

instrument now reads the mV created by this buffer and is displayed on the screen as "U cal.2 xxx mV", when the drift criteria is met the calibration report is automatically printed out.

8.8 The printed calibration data includes the relative slope and the measured isopotential point (IP). Theoretically the value for the slope is 1 and the IP is 0 mV. The slope will normally vary by ±.02 units and is an indication of the relative response of the electrode to the theoretical Nernstian response of 59.16 mV (@ 25°C). A deviation of greater than ±.02 units indicates a problem with the glass electrode or with the buffer solutions.

8.9 Check the calibration with the pH 7 buffer solution as follows:

[8.9.1] Insert electrode in buffer solution and press the [enter] key; when 2 consecutive printed pH measurements agree to within ± units, then the last measurement is the pH of [the solution.] The pH should be 7.00 ±.05 pH units, if not then the calibration procedure must be repeated.

8.10 Proceed with the instrument preparation required for HCl standardization as described in section 7.3.

9. PROCEDURE

9.1 Standardization of HCl.

9.1.1 Titrate 3 separate 1 mL aliquots of THAM with the 0.018N HCl to a pH endpoint of 4.5 as follows:

9.1.2 Pipette each standard into a plastic beaker, add a magnetic stir bar and insert electrode into the solution. Enter the sample specific data as outlined below and then press [enter].

9.1.2.1 Sample specific data entry:
Press [sample data] key: "Id #1" appears; key in an appropriate identifying number; then press [enter]; "COO =" now appears enter the aliquot of solution used; press [enter].

9.1.3 Start the titration by pressing [Go]. [When the stop endpoint is reached (pH 4.5), the titroprocessor will printout the report with the calculated normality of acid (the RS1 value).] Check that the stop endpoint is 4.5 ±.05 before proceeding with the next titration.

9.1.4 The normality of the acid can be figured by averaging the three RS1 values obtained. This is the CO1 constant used in calculating the sample HCO_3 values, see section 7.4.3.

9.1.5 Proceed with the instrument preparation for sample analysis as outlined in section 7.4.

9.2 Sample Analysis

Set up the apparatus for sample analysis according to section 7.4.

9.2.2 Pipet 5-25 mL of sample solution into a plastic beaker. Enter the sample specific data as detailed in section 9.1.2, then press [enter]. Start the titration by pressing [GO].

9.2.3 A printout of the report will automatically follow when the titration stops. The titration alkalinity, expressed as equivalent HCO_3 concentration, is printed as the 'RS1" value. Take notice of the stop endpoint. Occasionally the titration stops prematurely or over shoots the desired endpoint because of sample idiosyncrasies. If it deviates from 4.50 by $\pm$.05 pH units, the results may be in error. Repeat the sample analysis for verification.

10. DATA HANDLING

10.1 All pertinent information regarding this analysis can be recorded by instrument printout. The pH calibration data, the standardization results and the sample analysis data will be recorded automatically. When the analysis is complete, record all other analysis information on the same printout by using the following keystrokes:

[report] [parameters] [enter]
[report] [prep steps] [enter]
[report] [2nd] [fmla] [enter]
[report] [fmla const] [enter]

An example of the analysis information is given in Table 1 below.

10.2 Store the printout containing all the analysis data in an envelope in the Metrohm Titroprocessor Procedure Log Book.

10.3 Label the outside envelope with the analysis date, the MSL report numbers and the MSL ID numbers of the samples analyzed.

10.4 Report all alkalinity data obtained using this procedure as "titration alkalinity, expressed as equivalent bicarbonate concentration.

TABLE 1

FOR HCL STANDARDIZATION

Prep steps report

SET pH	1-1
prep.steps	
pause	60s
electr.input	1

Parameters report

Set pH	1-1
parameters	
EP1 pH	4.50
dyn. pH	8.00
drift1	.3 mV/s
t(delay) 1	1 s
temp.	25.0 C

Formula report

SET pH	1-1
formulae	
F1=C00*C01/EP1;5;mol/l	

Formula constants

SET ph	1-1
fmla const	
C01=	0.1

For Sample Analysis

Formula report

SET pH	1-2
formulae	
F1=EP1*C01*C02*C03/	
C00;2;ppm	

Formula constants

SET pH	1.2
fmla const	
C01=	.0163
C02=	61.01
C03=	1000

11. QUALITY ASSURANCE CONTROL

11.1 Replicate samples should be co-analyzed with all samples to provide a precision estimate for this determination.

11.2 Standard samples with certified bicarbonate values do not exist; round-robin performance valuation samples distributed by the Environmental Protection Agency are available however, and should be used to validate the procedure. The error should not exceed 5%. EPA WP18 concentrates 1 and 2 exist with reported bicarbonate values of 134 and 18.3 mg/L, respectively.

11.3 The following precision and accuracy data are illustrative for this procedure:

Sample#	Replicate Data HCO_3, mg/L	RSD,%	Mean	Accepted Value	Bias,%
EPA WP17 C#1	12.4, 12.2 12.0, 12.2	1.2	12.2	12.2	0.2
EPA WP17 C#2	90.5, 90.7 91.2	0.5	90.8	91.4	-0.7

12. REFERENCE

12.1 American Society of Testing and Materials: 1984, Annual Book of ASTM Standards, Vol. 11.01., Standards Test Method, D1067-82 Method B, "Acidity or Alkalinity of Water": Philadelphia, Pennsylvania, p. 125-129.

12.2 American Petroleum Institute. 1968, API Recommended Practice for Analysis of Oil-Field Waters, API RP 45, 2nd ed.: Dallas, Texas, p. 7-8.

12.3 Metrohm Titroprocessor User Manual Model 672.

12.4 Metrohm Dosimat User Manual, Model 655.

Designation: D 3223 – 80

Standard Test Method for TOTAL MERCURY IN WATER[1,2]

This standard is issued under the fixed designation D 3223; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This method has been approved for use by agencies of the Department of Defense and for listing in the DoD Index of Specifications and Standards.

1. Scope

1.1 This method covers the determination of total mercury in water in the range from 0.2 to 10.0 μg Hg/L (**1**).[3] The method is applicable to fresh waters, saline waters, and industrial and sewage effluents.

The analyst should recognize that the precision and accuracy of this standard may be affected by the other constituents in all waters, as tap, industrial, river, and waste waters. The cold vapor atomic absorption measurement portion of this method is applicable to the analysis of materials other than water (sediments, biological materials, tissues, etc.) if, and only if, an initial procedure for digesting and oxidizing the sample is carried out, ensuring that the mercury in the sample is converted to the mercuric ion, and is dissolved in aqueous media (**2,3**).

1.2 Both organic and inorganic mercury compounds may be analyzed by this procedure if they are first converted to mercuric ions. Using potassium persulfate and potassium permanganate as oxidants, and a digestion temperature of 95°C, approximately 100 % recovery of organomercury compounds can be obtained (**2,4**).

1.3 The range of the method may be changed by instrument or recorder expansion or both, and by using a larger volume of sample.

1.4 A method for the disposal of mercury-containing wastes is also presented (Appendix X1) (**5**).

2. Applicable Documents

2.1 *ASTM Standards:*

D 512 Test Methods for Chloride Ion in Water[4]

D 1129 Definitions of Terms Relating to Water[4]

D 1193 Specification for Reagent Water[4]

D 1245 Practice for Examination of Water-Formed Deposits by Chemical Microscopy[4]

D 1252 Test Method for Chemical Oxygen Demand (Dichromate Oxygen Demand) of Waste Water[4]

D 1426 Test Methods for Ammonia Nitrogen in Water[4]

D 3370 Practices for Sampling Water[4]

3. Summary of Method

3.1 The method consists of a wet chemical oxidation which converts all mercury to the mercuric ion; reduction of mercuric ions to metallic mercury, followed by a cold vapor atomic absorption analysis (**1,2**).

3.2 Cold vapor atomic absorption analysis is a physical method based on the absorption of ultraviolet radiation at a wavelength of 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in either a closed recirculating system or an open one-pass system. The mercury vapor passes through a cell positioned in the light

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[1] This method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

Current edition approved Oct. 31, 1980. Published January 1981. Originally published as D 3223 – 79. Last previous edition D 3223 – 79.

[2] Adapted from research investigations by the U. S. Environmental Protection Agency's Analytical Quality Control Laboratory, Cincinnati, Ohio, and Region IV Surveillance and Analysis Division, Chemical Services Branch, Athens, Ga.

[3] The boldface numbers in parentheses refer to the references at the end of this method.

[4] *Annual Book of ASTM Standards*, Vol 11.01.

path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration.

4. Significance and Use

4.1 The presence of mercury in industrial discharge, domestic discharge, and potable water is of concern to the public because of its toxicity. Regulations and standards have been established that require the monitoring of mercury in water. This method provides an analytical procedure to measure total mercury in water.

5. Definitions

5.1 For definitions of terms used in this method, refer to Definitions D 1129.

6. Interference

6.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water (2).

6.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on the recovery of mercury from spiked samples (2).

6.3 Sea waters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step chlorides are converted to free chlorine which will also absorb radiation at 253.7 nm. Care must be taken to assure that free chlorine is absent before mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). The dead air space in the reaction flask must also be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique (2).

6.4 Interference from certain volatile organic materials that will absorb at this wavelength is also possible. If this is expected, the sample should be analyzed by using the regular procedure and again under oxidizing conditions only, that is, without the stannous sulfate. The true mercury value can then be obtained by subtracting the latter value from the value obtained by the regular procedure.

7. Apparatus

NOTE 1—Take care to avoid contamination of the apparatus with mercury. Soak all glass apparatus, pipets, beakers, aeration tubes, and reaction flasks in chromic acid cleaning solution or 1 + 1 nitric acid, and rinse with mercury-free water before use.

7.1 The schematic arrangement of the closed recirculating system is shown in Fig. 1 and the schematic arrangement of the open one-pass system is shown in Fig. 2.

7.2 *Atomic Absorption Spectrophotometer*—A commercial atomic absorption instrument is suitable if it has an open-burner head area in which to mount an absorption cell, and if it provides the sensitivity and stability for the analyses. Also instruments designed specifically for the measurement of mercury using the cold vapor technique in the working range specified may be used.

7.2.1 *Mercury Hollow Cathode Lamp.*

7.3 *Recorder*—Any multirange variable speed recorder that is compatible with the UV detection system is suitable.

7.4 *Absorption Cell*—The cell (Fig. 3) is constructed from glass 25.4-mm outside diameter by 114 mm (Note 2). The ends are ground perpendicular to the longitudinal axis and quartz windows (25.4-mm diameter by 1.6 mm thickness) are cemented in place. Gas inlet and outlet ports (6.4-mm diameter) are attached approximately 12 mm from each end. The cell is strapped to a support and aligned in the light beam to give maximum transmittance.

NOTE 2—An all-glass absorption cell, 18 mm in outside diameter by 200 mm, with inlet 12 mm from the end, 18-mm outside diameter outlet in the center, and with quartz windows has been found suitable. Methyl methacrylate tubing may also be used.

7.5 *Air Pump*—A peristaltic pump, with electronic speed control, capable of delivering 1 L of air per minute may be used. Regulated compressed air can be used in the open one-pass system.

7.6 *Flowmeter*, capable of measuring an air flow of 1 L/min.

7.7 *Aeration Tubing*—A straight glass frit having a coarse porosity is used in the reaction flask. Clear flexible vinyl plastic tubing is used for passage of the mercury vapor from the reaction flask to the absorption cell.

7.8 *Lamp*—A small reading lamp containing a 60-W bulb is used to prevent condensation of moisture inside the cell. The lamp shall be

positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient. Alternatively, a drying tube, 150 by 18 mm in diameter, containing 20 g of magnesium perchlorate, may be placed in the line to prevent moisture in the absorption cell. **Caution**—If the presence of organic vapors is expected, the purity of the drying agent should be determined to establish the absence of traces of free perchloric acid in the salt. This is to prevent the formation of perchloric esters, some of which are known to be violently explosive compounds.

7.9 *Reaction Flask*—A 250 to 300-mL glass container fitted with a rubber stopper may be used.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type II, and shall be free of mercury.

8.3 *Mercury Standard Solutions*:

8.3.1 *Mercury, Stock Standard Solution (1 mL = 1 mg Hg)*—Dissolve 0.1354 g of mercuric chloride ($HgCl_2$) in a mixture of 75 mL of water and 10 mL of HNO_3 (sp gr 1.42) and dilute to 100 mL with water.

8.3.2 *Mercury, Intermediate Standard Solution (1 mL = 10 μg Hg)*—Pipet 10.0 mL of the stock mercury solution into a mixture of 500 mL of water and 2 mL of HNO_3 (sp gr 1.42) and dilute to 1 L with water. Prepare fresh daily.

8.3.3 *Mercury Working Standard Solution (1 mL = 0.1 μg Hg)*—Pipet 10.0 mL of the intermediate mercury standard into a mixture of 500 ml of water and 2 ml of HNO_3 (sp gr 1.42) and dilute to 1 L with water. Prepare fresh daily.

8.4 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

NOTE 3—If a high reagent blank is obtained, distill the HNO_3 or use a spectrograde acid.

8.5 *Potassium Permanganate Solution (50 g/L)*—Dissolve 50 g of potassium permanganate ($KMnO_4$) in water and dilute to 1 L.

8.6 *Potassium Persulfate Solution (50 g/L)*—Dissolve 50 g of potassium persulfate ($K_2S_2O_8$) in water and dilute to 1 L.

8.7 *Sodium Chloride-Hydroxylamine Sulfate Solution (120 g/L)*—Dissolve 120 g of sodium chloride (NaCl) and 120 g of hydroxylamine sulfate [$(NH_2OH)_2H_2SO_4$] in water and dilute to 1 L.

8.8 *Stannous Sulfate Solution (100 g/L)*—Dissolve 100 g of stannous sulfate ($SnSO_4$) in water containing 14 mL of concentrated sulfuric acid and dilute to 1 L. This mixture is a suspension and should be mixed continuously when being applied as a reagent.

8.9 *Sulfuric Acid (sp gr 1.84)*—Concentrated sulfur acid (H_2SO_4).

9. Precautions

9.1 This standard may involve the use of hazardous materials, operations and equipment. It is the responsibility of whoever uses this standard to establish appropriate safety practices and to determine the applicability of regulatory limitations prior to use.

10. Sampling

10.1 Collect the samples in accordance with Practices D 3370.

10.2 Collect samples in acid-washed glass or high density-hard polyethylene bottles. Samples shall be analyzed within 38 days if collected in glass bottles, and within 13 days if collected in polyethylene bottles **(6)**.

10.3 Samples shall be preserved with HNO_3 (sp gr 1.42) to a pH of 2 or less immediately at the time of collection, normally about 2 mL/L. If only dissolved mercury is to be determined, the sample, before acidification shall be filtered through a 0.45-μm membrane filter using an all-glass filtering apparatus.

[5] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N. Y., and the "United States Pharmacopeia."

11 Calibration

11.1 Transfer 0, 1.0, 2.0, 5.0, and 10.0 mL-aliquots of the working mercury solution containing 0 to 1.0 μg of mercury to a series of reaction flasks. Add enough water to each flask to make a total volume of 100 mL.

11.2 Mix thoroughly and add cautiously 5 mL of H_2SO_4 (sp gr 1.84) and 2.5 mL of HNO_3 (sp gr 1.42) to each flask.

NOTE 4—Loss of mercury may occur at elevated temperatures. However, with the stated amounts of acid the temperature rise is only about 13°C (25–38°C) and no losses of mercury will occur (2).

11.3 Add 15 mL of $KMnO_4$ solution to each bottle and allow to stand at least 15 min.

11.4 Add 8 mL of $K_2S_2O_8$ solution to each flask, heat for 2 h in a water bath at 95°C, and cool to room temperature.

11.5 Turn on the circulating pump and adjust its rate to 1 L/min. The pump may be allowed to run continuously throughout the entire series of samples.

11.6 Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate, as evident by loss of solution color.

11.7 After waiting 30 s treat each flask individually by adding 5 mL of the $SnSO_4$ solution and immediately attach the bottle to the aeration apparatus forming a closed system.

11.8 After the absorbance has reached a maximum and the recorder pen has leveled off, prepare the system for the next standard by one of the following procedures:

11.8.1 *Closed Recirculating System*—Open the by-pass valve and continue aeration until the absorbance returns to its minimum value. Close the by-pass valve, remove the stopper and frit from the reaction flask, and continue the aeration.

11.8.2 *Open One-Pass System*—Remove the stopper and frit from the reaction flask, open the valve, and evacuate the system with vacuum until the absorbance returns to its minimum value. Close the valve and continue aeration.

NOTE 5—Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a by-pass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media such as: (*a*) equal volumes of 0.1 *N* $KMnO_4$ solution and 10 % H_2SO_4, or (*b*) 0.25 % iodine in 3 % KI solution.

11.9 Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

12. Procedure

12.1 Transfer 100 mL or an aliquot diluted to 100 mL containing not more than 1.0 μg of mercury to a reaction flask.

12.2 Add cautiously 5 mL of H_2SO_4 (sp gr 1.84) and 2.5 mL of HNO_3 (sp sr 1.42) mixing after each addition (Note 4, 10.2).

12.3 Add 15 mL of $KMnO_4$ solution to each sample bottle. Shake and add additional portions of $KMnO_4$ solution until the purple color persists for at least 15 min.

12.4 Add 8 mL of $K_2S_2O_8$ solution to each flask and heat for 2 h in a water bath at 95°C and cool to room temperature.

12.5 Add 6 ml of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate as evident by loss of solution color.

12.6 Wait 30 s and add 5 mL of $SnSO_4$ solution to each flask individually and immediately attach it to the aeration apparatus.

12.7 Continue as described under 11.8.

13. Calculation

13.1 Determine the peak height of the unknown from the recorder chart and read the micrograms of mercury from the standard curve.

13.2 Calculate the mercury concentration in the sample as follows:

$$\text{Mercury (total), } \mu g/L = (W \times 1000)/S$$

where:

W = micrograms of mercury in aliquot determined from calibration curve, and

S = millilitres of aliquot used for analysis.

14. Precision and Accuracy (7, 8)[6]

14.1 The ASTM and the U. S. Environmental Protection Agency conducted a joint study of this method in October 1972. One hundred and one laboratories from the United States and Canada, including federal, state and local agencies, universities and private and industrial

[6] Data supporting the precision statement are available at ASTM Headquarters, 1916 Race St., Philadelphia, Pa. 19103, in Research Report File D 19-1019.

groups, participated in the interlaboratory study.

14.2 Eight water sample concentrates were prepared in sealed glass ampules by dissolving weighed amounts of reagent grade chemicals in reagent water, Type II, to produce accurately known concentrations of inorganic and organic mercury. All eight samples contained the same ratio of inorganic to organic mercury, 40 to 60, as mercuric chloride and methyl mercury chloride, respectively.

14.3 Each laboratory was instructed to dilute a separate 5.0-mL aliquot of each concentrate to 1 L with reagent water and to one litre with a natural water or waste of their choice. Then, the laboratory was instructed to perform a single analysis on each of the resulting sixteen samples. The natural water was also analyzed without a spike to determine the background level of mercury.

14.4 The precision of this method within the range from 0.2 to 10 μg mercury/L may be expressed as follows:

In Reagent Water, Type II:

$$S_t = 0.307X + 0.183$$
$$S_o = 0.076X + 0.293$$

In Natural Waters

$$S_t = 0.386X + 0.107$$
$$S_o = 0.145X + 0.023$$

where:

S_t = overall precision,
S_o = single-operator precision, and
X = determined concentration of mercury, μg/L.

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(3) Uthe, J. F., Armstrong, F. A. J., and Stainton, M. P., "Mercury Determination in Fish Samples by Wet Digestion and Flameless Atomic Absorption Spectrophotometry," Jour Fisheries Research Board of Canada, JFRBA, Vol 27, 1970, p. 805.

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(7) "ASTM-EPA Method Study of Total Mercury in Water," Environmental Protection Agency, Analytical Quality Control Laboratory, Cincinnati, Ohio, December 1972.

(8) *Water Quality Parameters, ASTM STP 573*, Am. Soc. Testing and Mats., 1975, pp. 566–580.

MSL-001

Determination of I^-

Iodide is measured by the oxidation-titration method described in the U.S. Environmental Protection Agency's Methods for Chemical Analysis of Water and Wastes, 1974, EPA 625-/6-74-003, p. 74-77.

Determination of NH_4^+-N, NO_3^--N, NO_2^--N, and Organic Forms of Nitrogen (Ho, in press)

General

Determination of NH_4^+, NO_3^-, NO_2^-, and organic forms of nitrogen in wastewaters is accomplished by steam distillation methods. Oil and grease derived from petroleum and coal processing must be removed by filtration through glass wool and then by successive extraction with benzene and cyclohexane before distillation begins. To prevent biological nitrogen transformation and assimilation, preservation of water samples with a suitable preservant such as chloroform and subsequent analysis of samples within 1 week are recommended. In our procedure, NH_4^+ is steam distilled in the presence of a specified amount of MgO, and $NH_4^+ + NO_3^- + NO_2^-$ are distilled in the presence of MgO plus Devarda's alloy (50 percent Cu, 45 percent Al, and 5 percent Zn) for 3 to 4 minutes. Nitrite was effectively destroyed with sulfamic acid ($HO{\cdot}SO_2{\cdot}NH_2$), thus allowing its quantitative measurement by subtracting the value of $(NH_4^+ + NO_3^-)$-N in sample treated with sulfamic acid from that of $(NO_2^- + NO_3^- + NH_4^+)$-N of the untreated sample. Organic forms of nitrogen in protein, oil brine, and coals were quantitatively converted to NH_4^+ by a micro-Kjeldahl method at 360°C on a temperature-controlled Technicon digester for 1 to 5 hours after clearing (that is, the complete oxidation of carbon as indicated by a white to greenish color of the digested material). Ammonium recovered by steam distillation is measured either by titration or by the spectrophotometric method. The latter is favored because of its high sensitivity and because only a small amount of sample is required. The methods are applicable to waters of various types. Interference by organic and inorganic substances in water has rarely been encountered.

Sample Preservation and Handling

To minimize biologic activities, water samples are taken in air-tight, screw-cap, polyethylene bottles of 1-L capacity. Five mL of chloroform is added to the sample; contents

should be shaken to dissolve some of the chloroform. If NO_2^- is to be analyzed, exposure of the sample to air must be eliminated, and the sample bottle must be filled with water to further minimize oxidation of NO_2^- to NO_3^-. Sample filtration should not be undertaken and is not necessary. Our experience showed that NH_4^+ in geothermal water samples preserved with chloroform and stored at 4°C for about 1 week in an unlighted refrigerator underwent little change. However, all analyses should be carried out immediately. The most unstable NO_2^- should be analyzed first, followed then by NH_4^+, NO_3^-, and Kjeldahl-N.

Oil and grease samples derived from crude petroleum and coal products present a problem for steam distillation and subsequent analysis of the distillate for two reasons: (1) coating of MgO and Devarda's alloy by oil and grease occurs, thus inactivating the alloy as reducing agent; and (2) some of the oil is distilled and interferes with analysis of the latter. Therefore, removal of the oil and grease from such samples must be made before the analysis. The procedure for complete removal of crude oil and grease from wastewater for the determination of inorganic forms of nitrogen by steam distillation is outlined as follows:

1. Remove a large portion of the crude oil by passing the oily water through a layer of glass wool in a glass funnel.
2. Transfer the water into an appropriate separatory funnel and allow the oil, if any, and aqueous layers to separate. Collect the aqueous layer and place it into another separatory funnel.
3. Extract the aqueous layer with a one-third volume of benzene under a fume hood. After the layers are separated, collect the aqueous layer.
4. Extract the aqueous layer with a one-third volume of cyclohexane. The aqueous layer should be free of oil and grease emulsion. If not, repeat the benzene-cyclohexane extraction until a clear water can be obtained.

Apparatus

1. A slightly modified semimicro distillation apparatus designed by Bremner (1965a) is recommended. The schematic diagram is given in figure 5. The apparatus can be made from parts by a glassblower.

2. The distillation flasks of 50- to 200-mL capacity, ₹19/38 ground joint, and 15 cm in height are commercially available (ACE Glass, Inc., catalog number 6903). Side ears on necks of the flasks can be attached by a glassblower.

3. Use a 5- or 10-mL microburet with a 0.01- or 0.02-mL graduated scale and a detachable capillary tip (Kimax 17105-F or equivalent).

4. Technicon BD-40 heating unit with an automatic temperature control or equivalent, and 25 x 150 mm culture tubes with Teflon-lined screwcaps (Kimax 45066-A) are recommended for Kjeldahl digestion.

Reagents

1. Purity of water: All water used must be distilled and de-ionized using a Barnstead ultrapure cartridge (catalog number D0809 or equivalent) and should show negative reaction with Nessler's reagent.

2. Boric acid (2 percent): Dissolve 20 g of boric acid (H_3BO_3) in 1 L of water.

3. Magnesium oxide: Ignite reagent-grade light MgO at 800°C for 3 hours. Cool it to room temperature and store in a screw-cap jar.

4. Devarda's alloy (50 percent Cu + 45 percent Al + 5 percent Zn): Grind to pass through 60-mesh sieve.

5. Kjeldahl catalyst: Grind a mixture of K_2SO_4, $CuSO_4$, and Se at a weight ratio of 10:1:0.1 (Bremner, 1965b) with a mortar and pestle to a homogenous powder (that is, until free of visible granules of the mixture).

6. Nessler's reagent (Vogel, 1960b): Dissolve 35 g KI in 100 mL of water and add 4 percent mercuric chloride solution by shaking until a slightly red precipitate remains. This will consume about 325 mL of the mercuric chloride. Introduce NaOH solution (120 g NaOH in 250 mL of water) by shaking, and make up to 1 L by adding water. Add a little more mercuric chloride to assure a permanent turbidity. Store the solution in an amber glass bottle. Allow the precipitate to settle before a clear solution can be used.

7. Sulfamic acid (2 percent): Dissolve 2 g of sulfamic acid in 100 mL of water.

8. Mixed indicator solution: Dissolve 0.066 g of methyl red and 0.099 g of bromocresol green in 100 mL ethanol.

Standard Solutions

1. Hydrochloric acid (0.01N): Prepare a stock solution of approximately 0.1N by diluting 8.4 mL of concentrated HCl (37.2 percent) to 1 L of water. Dilute 100 mL of the stock solution to 1 L by adding water. Standardize the latter periodically with a primary standard base (0.1N THAM) using 6 drops of the mixed indicator. The end point will change sharply from green to pink.
2. THAM (Tris- [hydroxy methyl] amino methane), Fisher Scientific Co., solution (0.1N): Dissolve 12.114 g of THAM in 1 L of water.
3. Ammonium-N (1 mg/mL): Dissolve 4.7170 g of $(NH_4)_2SO_4$ (dried at 105°C) in water; add 5 mL of concentrated HCl, and make up to 1 L by adding water.
4. Nitrate-N (1 mg/mL): Dissolve 7.2187 g of KNO_3 (dried at 105°C) in water; add 5 mL of concentrated HCl, and make up to 1 L by adding water.
5. NO_2^--N (1 mg/mL): Dissolve 4.929 g of $NaNO_2$ (dried in desiccator under vacuum) in 1 L of water. A fresh standard must be prepared when necessary.
6. Organic-N (0.05 mg/mL): Dissolve 0.4825 g of acetanilide ($C_6H_5{\cdot}NH{\cdot}COCH_3$) in 1 L of water.

Determination of Various Forms of Nitrogen as NH_4^+-N by Steam Distillation-Titration

Procedure for NH_4^+-N.--Place a 50-mL Erlenmeyer flask containing 5 mL boric acid under the condenser tip to absorb the ammonia in distillate. It is not necessary to submerge the tip in the boric acid, provided the distillate is cooled to a temperature below 25°C. Pipet 1 to 50 mL of water sample into a 150-mL distillation flask to yield 0.10 to 1.0 mg of nitrogen. The volume of water should not exceed 50 percent of the flask capacity to avoid having the water boil over. Add about 0.05 g of MgO to the flask immediately before distillation to maintain a permanent turbidity of saturated MgO (pH 10.2). Excessive amounts of MgO should be avoided lest decomposition of labile nitrogenous organic substances should occur. Distill the sample for

3 minutes, beginning at the appearance of the first drop of distillate at the condenser tip at a distillation rate of 6 to 6.5 mL distillate per minute. Complete recovery of NH_4^+-N requires only 2 minutes. Prolonged distillation, especially in the presence of excessive amounts of MgO, results in substantial decomposition of amino sugars and possibly other unstable nitrogenous compounds. At the end of distillation, open the steam vent and wash the condenser tip with water. Add 6 drops of mixed indicator to distillate and titrate with 0.01N HCl to the pink end point.

Blanks and standards: Two blanks and two standards should be run at the same time with each batch of samples to ascertain reliability of results. Steam-wash the distillation apparatus for 10 minutes and follow with distillation of the blanks, which consist of only the same amount of MgO added to the sample. Distill two NH_4^+-N standards (0.10 to 1.0 mg) using a diluted stock NH_4^+-N standard of 0.1 mg/mL.

Calculation:

$$NH_4^+\text{-N (mg/L)} = \frac{(A-B) \times N \times 14.0067 \times 1000}{V}$$

where

A: volume in mL of standard HCl used for titrating sample distillate

B: volume in mL of HCl used for titrating blank distillate

N: concentration in normal of HCl used for titration

V: volume in mL of sample used in distillation

14.0067: atomic weight of nitrogen

Procedure for NO_3^--N.--Place a 50-mL Erlenmeyer flask containing 5 mL of boric acid under the condenser tip.

Pipet 1 to 50 mL of water sample into a 150-mL distillation flask to yield a nitrogen concentration of 0.10 to 1.0 mg. Add about 0.3 g MgO and 0.4 g Devarda's alloy to the flask. Distill the sample for 4 minutes, beginning at the first appearance of distillate at the condenser tip at a distillation rate of 6 to 6.5 mL per minute. Titrate the distillate with 0.01 HCl using 6 drops of mixed indicator. The end point changes from green to pink.

Blanks and standards: Steam-wash the apparatus for 10 minutes; then distill the blanks, which should consist of only the same amounts of MgO and Devarda's alloy as were added to the sample. Then distill two standard mixtures of $(NH_4^+ + NO_3^-)$-N containing NH_4^+-N and NO_3^--N at equal concentrations (0.05 mg/mL) and at a total nitrogen concentration of 0.10 to 1.0 mg, in the same manner and at the same time as the samples.

Calculation:

$$(NO_3^- + NH_4^+)\text{-N (mg/L)} = \frac{(A-B) \times \underline{N} \times 14.0067 \times 1000}{V}$$

where A, B, $\underline{N}$, and V are the same as that described for NH_4^+-N above. NO_3^--N is obtained by subtracting NH_4^+-N from the sum of $(NO_3^- + NH_4^+)$-N.

Procedure for NO_2^--N.—If NO_2^- is suspected, then distillation of an aliquot of the sample (25 to 50 mL) with MgO and Devarda's alloy will yield the sum of $(NH_4^+ + NO_3^- + NO_2^-)$-N. Place another aliquot of the sample (25 to 50 mL) into a 150-mL distillation flask. Add 1 mL of 2 percent sulfamic acid to water and swirl the contents for a few seconds (Bremner, 1965a). Proceed with the distillation with Devarda's alloy (0.4 g) and MgO (0.3 g). This distillation yields the sum of $(NH_4^+ + NO_3^-)$-N; then NO_2^--N is obtained by subtracting $(NH_4^+ + NO_3^-)$-N from $(NH_4^+ + NO_3^- + NO_2^-)$-N.

Blanks and standards: The blanks will include one with additions of 1 mL sulfamic acid, 0.4 g Devarda's alloy, and 0.3 g MgO, and another with Devarda's alloy and MgO only. The standard mixture will consist of equal concentrations of NH_4^+-N, NO_3^--N, and NO_2^--N (0.05 mg/mL each). Distill two standard mixtures of a total nitrogen concentration of 0.15 mg with sulfamic acid treatment; distill another two without the sulfamic acid in the same manner described above.

Calculation: The appropriate blank must be subtracted from the corresponding sample and standard so that background contamination in reagents (for example, sulfamic acid, Devarda's alloy, and MgO) can be corrected.

Procedure for Organic-N by Micro-Kjeldahl Method.--Pipet 1 to 25 mL of water (which has not been extracted with organic solvents) into a 50-mL culture tube to yield 0.10 to 1.0 mg organic-N. Add 1.0 g catalyst and 3 mL concentrated H_2SO_4. Place all culture tubes (including the blank and standard organic-N tubes) into the Technicon DB-40 holders. Evaporate all the water at 130°C; a temperature higher than 130°C will result in bumping and loss of sample.

Raise the temperature to 360°C and digest the sample until content turns a greenish-white color as a result of complete oxidation of organic carbon. Continue the digestion at 360°C for an additional 1 to 5 hours, depending on the nature of organic constituents present. Generally, for fresh biologic soluble materials (plant and animal tissues), 1 hour of digestion is sufficient. Three hours are required to digest soil leachate or soil organic matter, and 4 to 5 hours are needed for more refractory organic materials derived from peats, lignites, coals, and petroleum products. Cool digested sample to room temperature and dilute contents with a small amount of water. Wash the contents quantitatively into a 150-mL distillation flask with about 25 mL of water. Chill the flask in an ice bath.

Place a 50-mL Erlenmeyer flask containing 5 mL of boric acid under the condenser tip. Attach the chilled distillation flask onto the apparatus. Introduce 12 mL of 10N NaOH slowly through the funnel to the flask. If violent neutralization reaction occurs, submerge the distillation flask into an iced-water bath while delivering the NaOH. Distill content for about 4 minutes (or collect 25 mL of distillate).

Titrate distillate with 0.01N HCl in the presence of 6 drops of mixed indicator solution, which will change from a green to a pink end point.

Blanks and standards: The blank will consist of 1.0 g catalyst and 3 mL concentrated H_2SO_4. The standards will consist of 10 mL and 25 mL of acetanilide standard solution (0.05 mg organic-N/mL), 3 mL concentrated H_2SO_4, and 1.0 g catalyst in each tube. Digest and steam-distill the blank and standards in the same manner along with each group of samples.

Calculation:

$$\text{Kjeldahl-N (organic-N + } NH_4^+\text{-N)(mg/L)} = \frac{(A-B) \times N \times 14.0067 \times 1000}{V}$$

where all symbols are the same as those described for NH_4^+-N. Organic-N is obtained by subtracting NH_4^+-N from Kjeldahl-N.

Determination of various forms of Nitrogen as NH_4^+-N by Steam Distillation Spectrophotometry

General.--The chief drawback of the titration method described above is the lack of sensitivity and accuracy for nitrogen of all forms at concentrations below 2 ppm. To obtain sufficient amounts of nitrogen for titration, a large volume of the water sample (more than 50 mL) must be used. This may not always be possible. Because steam distillation effectively separates nitrogen of all forms from potential interfering matrix substances, subsequent determination of NH_4^+-N in distillate can readily be made by instrumental methods of the analyst's choice. For example, one of the rapid methods involves the use of Nessler's reaction-spectrophotometry as follows:

Procedure.--Place a 50-mL volumetric flask containing 1 mL of 0.1N HCl under the condenser tip to absorb the NH_3 in distillate. Distill a water sample containing up to 0.15 mg of total nitrogen according to the procedures given in section on determination of various forms of nitrogen as NH_4^+-N by steam distillation. Make a volume of 50 mL by adding water. Pipet 25 mL of distillate into a 50-mL culture tube and follow with the addition of 2 mL of Nessler's reagent. Mix the contents well. If NH_4^+ is present, a yellow color caused by formation of the complex $NH_2 \cdot Hg_2 \cdot I_3$ should appear.

Measure absorbance of the yellow color at 402 nm on a spectrophotometer after 15 minutes of color development.

Blanks and standards: Distill two blanks and two standards (0.05 to 0.15 mg of total nitrogen) in the same manner as the samples.

Calculation: Plot absorbance readings of blanks and standards against standard concentration (μg/mL); a straight line will be obtained.

$$\text{Nitrogen (mg/L)} = \frac{R \times 50}{V}$$

where

R: concentration of nitrogen from standard curve as µg/mL

V: sample volume (in mL) used in distillation

Comments.--Appropriate dilution of the distillate must be made before addition of Nessler's reagent if a preliminary test reveals a colloidal appearance. The latter phenomenon will result from the formation of an irreversible precipitate of $NH_2Hg_2I_3$ in the presence of NH_4^+-N concentration greater than 3 µg/mL. Thus, to prevent the risk of destroying the sample, withdraw a small part of the distillate for the test before dilution and analysis are made.

A second more sensitive method is recommended for the determination of NH_4^+-N in distillate at a concentration below 0.2 ppm. This method requires oxidation of NH_4^+ to NO_2^- with NaOCl followed by complexing the NO_2^- with sulfanilamide and subsequent formation of a sharp pink color with N-(1-Naphthyl)-ethylenediamine dihydrochloride. It has been shown that the oxidation method is about 10 times more sensitive than Nessler's method (Ho and Barrett, 1977).

Designation: D 1888 - 78

Standard Test Methods for PARTICULATE AND DISSOLVED MATTER, SOLIDS, OR RESIDUE IN WATER[1]

This standard is issued under the fixed designation D 1888; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

These methods have been approved for use by agencies of the Department of Defense and for listing in the DOD Index of Specifications and Standards.

1. Scope

1.1 These methods cover the determination of particulate, dissolved, and total matter, sometimes referred to as the suspended, dissolved, and total solids, in water. Two procedures, consistent with the total matter content, are provided as follows:

	Sections
Method A—Particulate and Dissolved Matter in Water with More Than 25 ppm of Total Matter	6 to 12
Method B—Particulate and Dissolved Matter in Water with 25 ppm or Less of Total Matter (Automatic Evaporation)	13 to 19

1.2 The methods actually cover the determination of (*1*) the constituents of water that can be removed by filtration, and (*2*) the residue on evaporation to dryness of either filtered or unfiltered samples; as a result, they do not always measure water components as defined. Separation of particulate matter by filtration requires precise definition of the filtering medium since some materials that are in no sense dissolved, for example, certain colloids, may not be removed by the filter used. Secondly, an evaporation residue will usually differ in composition from the particulate and dissolved matter present in the water.

1.3 When particulate matter is determined separately (the sample is filtered and the residue quantitatively assessed), provision is made for the use of either a membrane filter that will remove all particles over 0.45 μm in size or an asbestos fiber medium in a Gooch crucible. However, unless otherwise specified when results are reported, use of the membrane filter shall be assumed. It is further provided that all buoyant floating particles or large particulate agglomerations that cannot be dispersed throughout the sample by vigorous shaking need not be considered as fundamental constituents of the water under examination and may be excluded, therefore, from the test portion.

1.4 The methods include steps for the determination of volatile matter in the dry residue from either filtration or evaporation. They do not, however, cover water constituents that are (*1*) volatile at the boiling temperature, or (*2*) normally classified as "oily matter", which is extractable with organic solvents or volatile at the drying temperature of filtration residues. For the determination of the latter, refer to ASTM Method D 2778, Test for Solvent Extraction of Organic Matter from Water.[2]

2. Definitions

2.1 The terms *particulate matter*, *dissolve matter*, *total matter*, and others related to water constituents determined in these methods, are defined in accordance with ASTM Definitions D 1129, Terms Relating to Water,[2] as follows:

2.1.1 *particulate matter*—that matter, exclusive of gases, existing in the nonliquid state which is dispersed in water to give a heterogeneous mixture.

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[1] These methods are under the jurisdiction of ASTM Committee D-19 on Water.

Current edition approved April 28, 1978. Published August 1978. Originally published as D 1888 - 61 T. Last previous edition D 1888 - 67 (1974).

[2] *Annual Book of ASTM Standards*, Vol 11.02.

2.1.2 *dissolved matter*—that matter, exclusive of gases, which is dispersed in water to give a single phase of homogeneous liquid.

2.1.3 *total matter*—the sum of the particulate and dissolved matter.

2.1.4 *volatile matter*—that matter that is changed under conditions of the test from a solid or a liquid state to the gaseous state.

2.1.5 *fixed matter*—residues remaining after ignition of particulate or dissolved matter, or both.

2.2 For definitions of other terms used in these methods, refer to Definitions D 1129.

3. Interferences

3.1 Some evaporation residues readily absorb moisture; rapid weighing is essential to this method. Some residues contain materials, such as ammonium carbonate, that decompose below 103°C (217°F); others contain liquids, such as glycerol and sulfuric acid, that will remain as a liquid residue at 103°C (217°F) with or without solution of salts that might also be present.

3.2 Rapid weighing of ignited residues, also, is important because of possible moisture absorption. Furthermore, there is likelihood of interference from carbonates, organic matter, nitrite and nitrate nitrogen, water of hydration, chlorides, and sulfates which may be decomposed either completely or in part when ignited at 600°C (1112°F). No single temperature is known that will eliminate all these interferences. Reasonably reproducible results should be obtained, however, at the prescribed 600°C (1112°F).

3.3 Because the water being sampled is of necessity in contact with the sample container and tubing, it is important, especially in the case of glass, that the possible precipitation of cations or the absorption of substances originally present in the water, on these surfaces, be recognized.

4. Purity of Reagents

4.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to ASTM Specification D 1193, for Reagent Water.[2] Referee grade reagent water shall be used for Method A and the nonreferee grade for Method B.

4.3 Except for concentrated hydrochloric acid (HCl, sp gr 1.19), reagents including reagent water should be membrane-filtered prior to use.

5. Sampling

5.1 Collect the sample in accordance with the applicable ASTM method, as follows:

D 1066—Sampling Steam,[2]
D 1192—Specification for Equipment for Sampling Water, and Steam and[2]
D 3370—Practices for Sampling Water[2]

5.2 Because of the low concentration of total matter in some waters and the possible effects of aeration on others, sampling shall be carried out in a manner which reduces atmospheric exposure to a minimum. The type and size of the container shall be consistent with the nature of the water being sampled (see 15.1 and 18.1).

5.3 Samples containing 25 ppm or less of total matter on which only the total matter content is to be determined shall be immediately acidified with 0.2 ml of concentrated HCl (sp gr 1.19)/litre of water to prevent iron deposition on the walls of the container. If particulate matter is to be separately determined, the sample, regardless of total matter content, shall be filtered as soon as possible (see 17.3) and then acidified.

METHOD A—PARTICULATE AND DISSOLVED MATTER IN INDUSTRIAL WATER WITH MORE THAN 25 PPM OF TOTAL MATTER

6. Application

6.1 This method is primarily applicable to water that will yield a residue on evaporation at 103°C of at least 25 mg/litre.

[3] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N. Y., and the "United States Pharmacopeia."

Summary of Method

7.1 Total matter is determined by evaporation of an appropriate aliquot, or the particulate and dissolved matter are separated by filtration and individually assessed. The particulate matter is dried and weighed. The dissolved matter is determined by weighing the residue obtained after evaporating the filtered sample. Volatile matter and fixed matter under any of the above classifications are determined by weighing the residues remaining after ignition at a temperature of 600°C.

8. Apparatus

8.1 *Sample Reservoir*—A chemical-resistant container of 1 to 4-litre capacity.

8.2 *Membrane Filter Assembly*—See 15.4.

8.3 *Glass Petri Dish*, 150-mm diameter.

8.4 *Filter Crucible*—See 15.6.

8.5 *Evaporating Dish*—A straight-wall or round-bottom platinum dish of 80 to 100-mm diameter and approximately 200-ml capacity. A porcelain dish may be substituted for the platinum dish if the residue is not to be analyzed.

8.6 *Heater*—A controlled electric hot plate, infrared lamp, or steam bath for maintaining the temperature of the evaporating sample near the boiling point.

9. Reagents

9.1 *Chloroform or Benzene*, purified or USP grade.

9.2 *Ethyl Alcohol (95 %)*.

NOTE 1—Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for ethyl alcohol (95 %).

9.3 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

10. Procedure

10.1 Weigh a quantity of sample sufficient to yield on evaporation approximately 25 mg of residue if only the amount is to be determined, or at least 100 mg if this residue is to be analyzed. The sample shall be well shaken before removing the aliquot and inclusion of floating material or agglomerates that cannot be dispersed shall be avoided. If only total matter is to be determined, without classification, proceed in accordance with 10.3. If both particulate and dissolved matter are to be determined, proceed in accordance with 10.2.

10.2 *Particulate Matter*—This determination shall preferably be made using a membrane filter following the procedure given in 17.3.1, except that a 0.2-mg residue from the solvent washings shall be permissible. The less desirable alternative use of an asbestos fiber medium is described in 17.3.2. In either case the filtrate shall be immediately acidified with 0.2 ml of HCl (sp gr 1.19)/litre of water unless the sample contains significant amounts of alkaline chemicals, for example, sodium hydroxide (NaOH), whose composition would be affected by the acid; acidification will prevent deposition of iron on the sample container.

10.3 *Total Matter and Dissolved Matter*—Transfer the sample aliquot provided for total matter determination (10.1) or the filtrate obtained from the particulate matter separation (10.2) to a sample reservoir having a valve-controlled outlet. Fill an evaporating dish that previously has been ignited at 600 ± 25°C for 1 h, cooled in a desiccator, and weighed, to within approximately ¼ in. (6.3 mm) of the top with the sample from the reservoir. Heat the dish to evaporate the sample, but do not allow the sample to boil. Periodically add sample from the reservoir to the dish to prevent drying until the reservoir is empty. Rinse the reservoir several times with water, adding the rinsings to the contents of the evaporating dish. Then evaporate the remainder of the material in the dish to near dryness. Transfer to a 103°C oven and complete the evaporation. Dry the dish and its contents for 1 h (see 3.1), cool in a desiccator, and weigh. Repeat the cycle of drying (1-h periods), cooling and weighing until loss in weight is no more than 4 % of the previous weight. Record the weight of residue as "weight of total matter" (or, if the sample had been filtered, "dissolved matter"). Ignite the dish contents for 30 min at 600 ± 25°C, cool in a desiccator, and reweigh (see 3.2). Record the loss in weight as "weight of volatile matter" (or "volatile dissolved matter") and the weight of the ignited residue as "weight of fixed matter" (or "fixed dissolved matter").

11. Calculation

11.1 Calculate the result of each specific determination in parts per million, as follows:

$$\text{Matter, ppm} = (W_x/V) \times 1000$$

where:

W_x = W_1 = grams of total matter found,
W_2 = grams of particulate matter found,
W_3 = grams of dissolved matter found,
W_4 = grams of volatile matter found,
W_5 = grams of volatile particulate matter found,
W_6 = grams of volatile dissolved matter found,
W_7 = grams of fixed matter found,
W_8 = grams of fixed particulate matter found, or
W_9 = grams of fixed dissolved found, and
V = litres of sample used.

11.2 When particulate and dissolved matter have been separately determined, total matter, volatile matter, and fixed matter can be calculated by adding the two appropriate values.

11.3 If asbestos fiber filtration was used for the removal of particulate matter, it is mandatory that this be stated when reporting either particulate or dissolved matter. Otherwise, use of a membrane medium shall be assumed.

12. Precision

12.1 No statement can be made concerning the precision of this method. The precision is influenced by both the nature and the amount of entrained matter and by the effects of drying and ignition on its actual composition.

METHOD B—PARTICULATE AND DISSOLVED MATTER IN INDUSTRIAL WATER WITH 25 PPM OR LESS OF TOTAL MATTER (AUTOMATIC EVAPORATION)

13. Application

13.1 This method is intended primarily for steam condensate and distilled or demineralized water that contains 5 ppm or less of total matter. Because of the automatic evaporation feature, the method is desirable for use, however, on all waters containing up to 25 ppm of total matter, particularly if a large residue is desired for chemical analysis.

14. Summary of Method

14.1 Total matter is determined by evaporation, or the particulate and dissolved matter are separated by filtration and individually evaluated. The particulate matter is dried, freed of oily matter by extraction, dried again, and weighed. The solution of dissolved matter is evaporated to dryness using a dish provided with a constant-level control. Sufficient sample is evaporated to give the desired accuracy for the measurement and provide ample material for other analytical requirements. The residue is dried and weighed. Volatile matter in any of the three classifications is subsequently removed by ignition. The total, particulate, dissolved, volatile, or fixed matter are then calculated from the various weights obtained.

15. Apparatus

15.1 *Sample Reservoir*—A covered, 20-litre (5-gal) container of corrosion-resistant metal, suitable plastic, or chemical-resistant glass with necessary tubular connections. Most waters with very low total matter exhibit a pH in the range from 6 to 9. For samples of such waters, containers of TFE-fluorocarbon, block tin, polyethylene, or chemical-resistant glass shall be selected with that order of preference, depending upon the purity.

15.2 *Automatic Evaporation Assembly*—A dust shield, constant-level device, heater, and evaporation dish. Typical assemblies are described in 15.2.1 and 15.2.2.

15.2.1 *Evaporation Assembly A (Fig. 1):*

15.2.1.1 *Dust Shield*—A heat-resistant cover glass enclosing the Monel-sheathed ring heater, platinum evaporating dish, antenna, and electrical terminal posts, with provision for introducing the water sample through the base. Minimum practicable enclosed space is necessary to prevent condensation on the cover. The top of the dust shield is covered with a "dunce cap" to prevent foreign material from dropping into the dish while permitting free passage for the moisture-laden air. An open-bottom aluminum platform supporting two filter cylinders and having an opening under the glass cover is provided to supply filtered inlet air. Either a seal must be provided or filter material used between glass cover and the platform as well as between chassis and platform.

15.2.1.2 *Evaporator Assembly*, as shown under the glass cover—The Monel-sheathed ring heater is suspended over the platinum evaporating dish by two stainless steel arms

which are connected through the electronic control system to a power circuit containing a relay. The platinum dish is supported by an aluminum plate provided with leveling screws so that the distance from the dish to the heater can be adjusted. A stainless steel inlet tube is used for addition of sample at the pouring spout of the platinum vessel.

15.2.1.3 *Electronic Control Circuit*—Control of the water level in the platinum dish is effected by a capacitance-type electrode or antenna which can be made conveniently of a flat coil of platinum wire (16 to 20-gage). The antenna is suspended from a stainless steel arm which makes contact with the electronic control circuit[4] through a terminal post. A change of the water level activates the shut-off valve[5]; if the water level in the platinum dish does not return to the upper level control within 45 s after reaching this lower level of capacitance control, the current to the ring heater is broken by means of a time interlock. The purpose of this interlock is to prevent the drying of the dish at a temperature above the specified 103°C (217°F) level, should additional sample fail to reach the dish. Since the 45-s timer automatically turns off the heater when sample flow is interrupted, an additional timer is incorporated which may be used upon completion of evaporation to keep the heater on for a specified time period to lower the water level in the dish and thus facilitate its removal from the test assembly. An overflow device is incorporated in the assembly, also. A platinum wire electrode is positioned so that its tip is suspended slightly above the normal water level in the platinum dish. This electrode serves as an additional upper-water level control should a failure occur in the capacitance system.

15.2.2 *Evaporation Assembly B* (*Figs. 2, 3 and 4*).

15.2.2.1 *Dust Shield*—The dust shield compartment consists of a heat-resistant glass bell jar equivalent to that used on assembly "A" and is contained in an enclosed dust-shielded compartment. Air is provided through an external filter source into this shielded sample compartment.

15.2.2.2 *Evaporator Assemble*—The evaporator assembly as shown schematically in Fig. 4 consists of a balance,[6] one arm of which extends into the dust shield compartment. The balance arm extending into the dust shield holds a platinum sample dish. Also extending into this compartment from the balance base and mounted in the dust shield compartment is a heater connection consisting of the necessary wiring connections and a Monel-sheathed ring heater similar to that used in evaporator assembly A. In addition, a solenoid water sample valve[5] is provided with a ⅛-in. (3.2-mm) outside diameter stainless steel tubing connection feeding into the shielded sample compartment and then to the platinum sample dish. Automatic sample addition is accomplished by a level switch on the counter balance arm and this actuates the water sample valve. Control is effected by counter balance arm can be dampened by a dash pot. If desired, a timer mechanism can be installed to record the volume of water evaporated. Calibration of this assembly is accomplished by using a calibrated sample reservoir and timing the addition and evaporation rate. This calibration will have to be carried out under atmospheric conditions similar to those pertaining at the actual sampling location.

15.2.2.3 *Wiring Diagram*—The wiring diagram for this assembly is also shown in Fig. 3.

15.3 *Sampling Device* (*see Fig. 5*)—A cooling coil with overflow pipe and solenoid valve suitable for sampling from a water source to a continuous sample evaporator. (The cooling coil is, of course, necessary only when sample is above room temperature.)

15.4 *Membrane Filter Assembly*—A borosilicate glass or stainless steel funnel with a flat, fritted base of the same material, and mem-

[4] The RCA Thermocap Relay Unit manufactured by the Niagara Electron Laboratories, Niagara Falls, N. Y., or equivalent, has been found satisfactory for this purpose.

[5] The electrically-operated valve (No. 5004141312) sold by Diamond Power Specialty Corp., Lancaster, Ohio, or an air-operated valve (No. 1000A 2-way Demi G 303 with No. 5049 stainless diaphragm) manufactured by the G. W. Dahl Co., Inc., Bristol, R. I., have been found satisfactory for this purpose. The Dahl valve must be coupled with a solenoid air valve such as the Skinner Electric Valve, 3-way, vented, No. V5D4200 manufactured by Skinner Electric Valve Div., The Skinner Chuck Co., 100 Edgewood Ave., New Britain, Conn., or its equivalent. It is imperative that new valves be tested to determine that contamination does not occur from mechanical wear on materials of construction.

[6] The balance manufactured by the Fisher Scientific Co., Catalog No. 2-035, or its equivalent, has been found satisfactory for this purpose.

brane filters (0.45-μm pore size) to fit.[7]

15.5 *Glass Petri Dish*—150-mm diameter.

15.6 *Filter Crucible*—A Gooch crucible containing an evenly distributed filter mat, approximately 5-mm thick and composed of finely divided asbestos fiber, produced by pouring a slurry of acid-washed asbestos into the crucible under slight suction.

15.7 *Evaporating Dish*—A straight-walled or round-bottom platinum dish of 80 to 100-mm diameter and approximately 200-ml capacity.

16. Reagents

16.1 See Section 9.

17. Procedure

17.1 Select a volume of sample sufficient to yield an evaporation residue of approximately 25 mg if only the matter content is to be determined, or approximately 100 mg if the evaporation residue is to be analyzed.

17.2 If both particulate and dissolved matter are to be determined, proceed in accordance with 17.3; if only total matter is desired, follow the procedure starting with 17.4.

17.3 *Particulate Matter*—This water component is preferably separated by filtration using a membrane having a pore size of 0.45 μm (see 17.3.1); an alternative procedure using an asbestos fiber medium, generally considered to have a 5-μm pore size, is described in 17.3.2.

17.3.1 *Membrane Filtration*—Place $n + 1$ plain, white filter disk of the prescribed pore size in a 150-mm petri dish, where n equals the number of tests to be run. Place the dish and filters in a drying oven at 103°C for 15 min or in a vacuum desiccator for 30 min. If oven-dried, allow the filters to cool to room temperature while exposed to the air. Weigh each filter to the nearest 0.1 mg. With most balances it is desirable to have a polonium alpha emitter source to dispel effects of static electricity. Label filters with ball point pen and mark the extra filter *C* for "control." Proceed with the filtration in accordance with 17.3.1.1 through 17.3.1.5.

17.3.1.1 Place a weighed filter on the fritted base of the filter holder, and clamp the funnel portion of the apparatus in place on top of the filter. Place the filtration assembly on a filter flask of appropriate size and with the aid of a vacuum from a vacuum-pressure pump or water aspirator, pour the sample into the funnel and draw through the filter into the filter flask. Where sample bottles are employed for collection of the sample, the entire contents of a sample bottle should be filtered. Wash the bottle with an appropriate quantity of filtered water (may be obtained from the filter flask) and pour this also into the filter funnel. Transfer sample and washings to sample reservoir. Dry the membrane by drawing air through the filter and wash with chloroform or benzene until 10 ml of the washings leave not more than 0.1 mg of residue on evaporation at 103°C. Air-dry the sediment for several minutes. Discard the washings. Release the vacuum and with flat-bladed forceps, remove the filter from the fritted base and place in the petri dish.

17.3.1.2 Wet the control filter (*C*) with the sample water from the filter flask, and place it also in the petri dish.

17.3.1.3 Place the petri dish in the drying oven at 103°C for 30 min; allow the filters to cool to room temperature and equilibrate to ambient humidity after removing from the oven, and reweigh.

17.3.1.4 Record the weight of particulate matter adjusted for the difference between final and initial weight of the test filter as "weight of particulate matter." Make a positive or negative adjustment in the event of any weight change occurring in the "control" filter.

17.3.1.5 Place the filter used in the particulate matter determination in a clean, ignited, small, porcelain crucible, which has been weighed, after ignition and cooling, to the nearest 0.1 mg. Add approximately 1 ml of ethyl alcohol and ignite with a match when the filter is fully wetted. After the alcohol has burned off, place the lid on the crucible and ignite it in the furnace at 600 ± 25°C for at least 30 min. Remove the crucible from the furnace and allow it to cool to room temperature in a desiccator. Remove the crucible cover and weigh the crucible to the nearest 0.1 mg (see 3.2). Record the loss in weight as "weight of volatile particulate matter" and the weight of the ignited residue as "weight of fixed particulate matter."

[7] Suitable membrane filter holder and filters. HAWP04700, are available from Millipore Co., Bedford, Mass.

17.3.2 *Asbestos Fiber Filtration* (*Note* 2)—Filter the selected volume of sample through a filter crucible (see 15.6) that previously has been dried for 1 h at 103°C, cooled in a desiccator, and weighed. After filtration, wash the filter crucible contents twice with water, transferring the filtrate and washings to the sample reservoir for subsequent determination of dissolved matter as described in 17.4. Dry the crucible contents by drawing air through the crucible for several minutes; then wash the crucible contents with chloroform or benzene until 10 ml of the washings leave not more than 1 mg of residue on evaporation at 103°C. Discard the washings. Air-dry the sediment for several minutes; then place the crucible in an oven at 103°C for 1 h, cool in a desiccator, and weigh. Record the weight of the residue as "weight of particulate matter." Ignite the crucible contents for 30 min at 600 ± 25°C, cool in a desiccator, and reweigh (see 3.2). Record the loss in weight as "weight of volatile particulate matter" and the weight of the ignited residue as "weight of fixed particulate matter."

NOTE 2—Since asbestos fiber filters are generally considered to have a pore size of 5 μm, no process of coagulation shall be employed that will alter the content of either dissolved or particulate matter.

17.3.3 Immediately acidify the filtrate and washings with 0.2 ml of HCl (sp gr 1.19)/litre of water.

17.4 *Total Matter and Dissolved Matter*—Weigh a platinum dish that has been dried for 1 h at 103°C and cooled in a desiccator. Using Evaporation Assembly A or B, start the evaporation of the selected volume of sample for total matter only or the filtrate and washings from the particulate matter removal (see 17.3), as follows:

17.4.1 *Evaporation Assembly A*—With the current off, insert the clean, weighed platinum dish (previously ignited at 600 ± 25°C) in the evaporator assembly and adjust the dish height by use of the leveling screws in the aluminum base. Antenna adjustments, if necessary, may also be made at this time, using the set screw provided at the end of the antenna arm. Turn on the circuit and heater switches and set the control knob on the relay to allow water to rise to the proper level with respect to the antenna and the desired water level in the dish. It is advisable to operate the relay with the water level as close to the antenna as possible. Observe the evaporator for a period of time to ascertain the satisfactory operation of the relay and assure the absence of boiling in the dish.

17.4.2 *Evaporation Assembly B*—Adjust the apparatus to the most rapid rate feasible without boiling. The adjustment is accomplished by the addition of 7 to 10-g weights to the tare weight of the evaporating dish on the counter weight arm of the balance. With the top of the shielded compartment removed, manually trip the level switch on the counter balance arm several times to actuate the water sample valve and flush out the sampling line. Then place a carefully cleaned and weighed platinum dish on the balance pan in the shielded compartment. Place a clean bell jar carefully on the seal mounted on the support plate in the dust shielded compartment (Fig. 4). Close the shield compartment leaving the vent open. Turn on the heater current and observe the operation long enough to assure satisfactory performance.

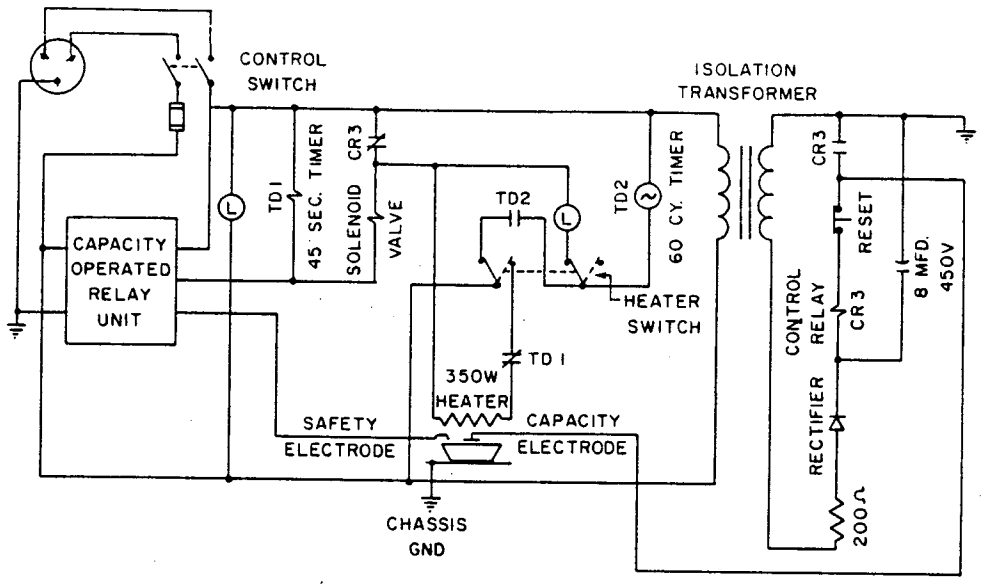
17.4.3 When evaporation is almost complete, remove the dish from the assembly, transfer to a 103°C oven, and heat to dryness. Continue heating for 1 h, cool in a desiccator, and weigh (see 3.1). Record the weight of the residue as "weight of total matter" (or, if sample had been filtered, "dissolved matter"). Ignite the dish and contents for 1 h at 600 ± 25°C, cool in a desiccator, and rewiegh (see 3.2). Record the loss in weight as "weight of volatile matter" (or "volatile dissolved matter"), and the weight of the ignited residue as "weight of fixed matter" (or "fixed dissolved matter").

18. Calculation

18.1 See Section 11.

19. Precision

19.1 See Section 12.



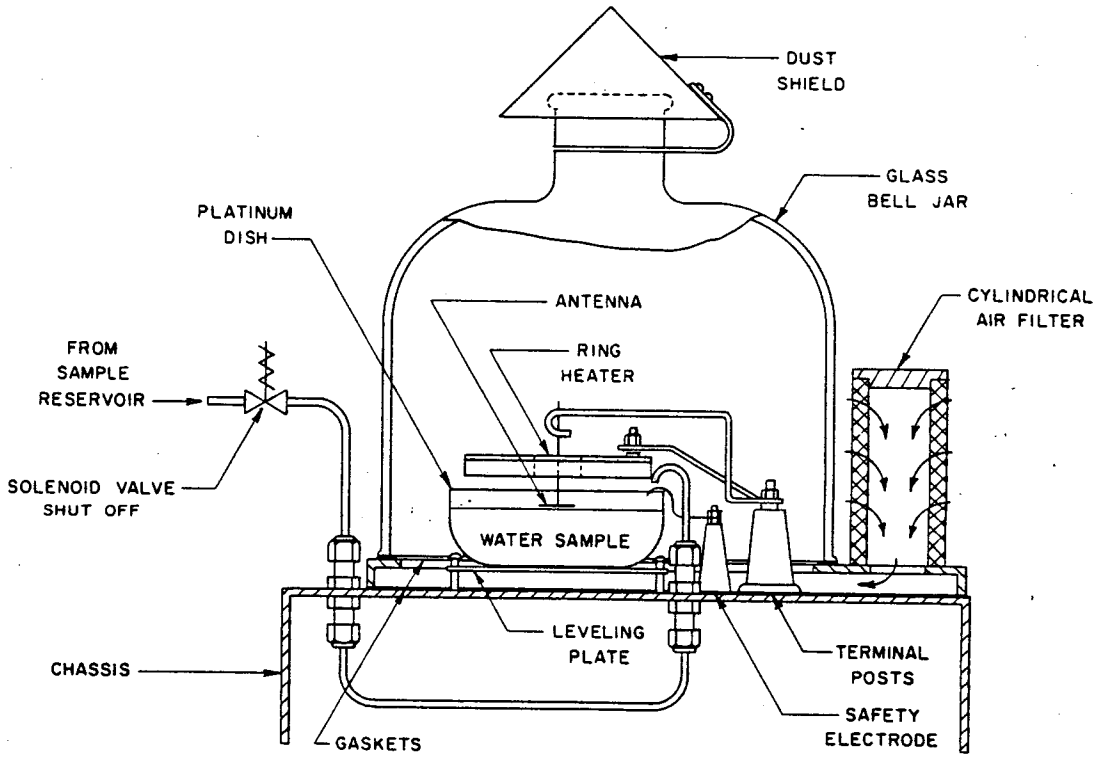


FIG. 1 Evaporation Assembly A.

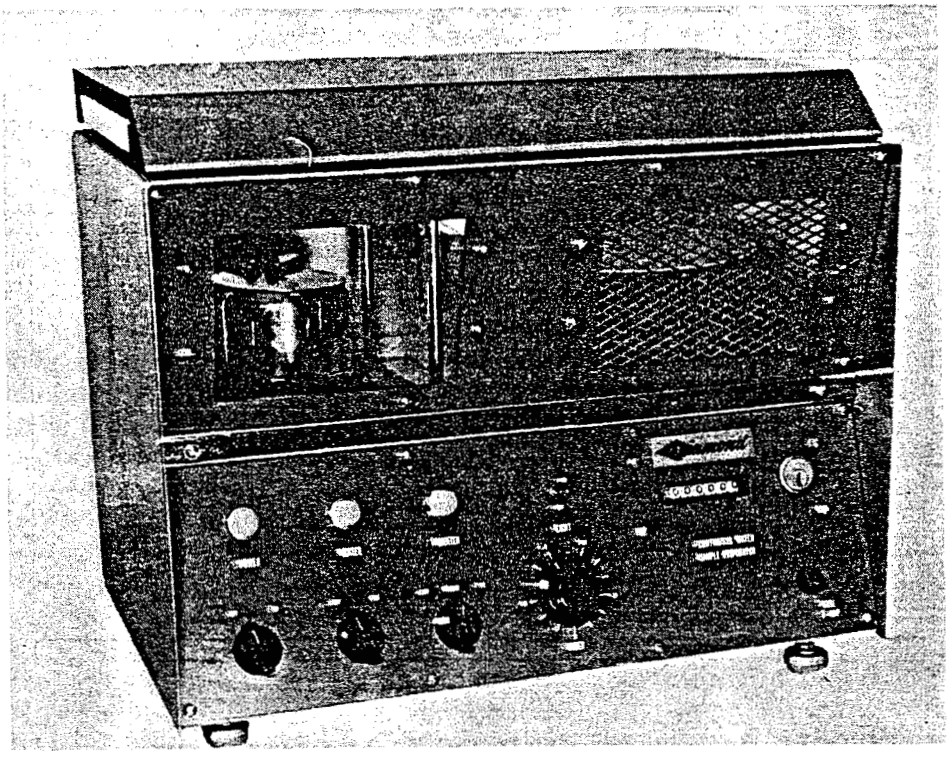


FIG. 2 Evaporation Assembly B.

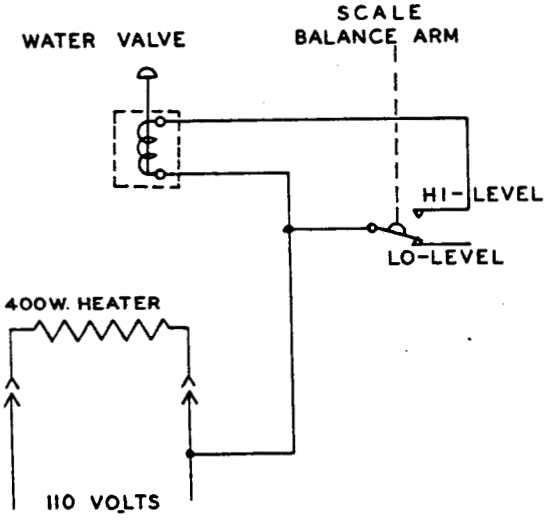


FIG. 3 Automatic Evaporation Circuit.

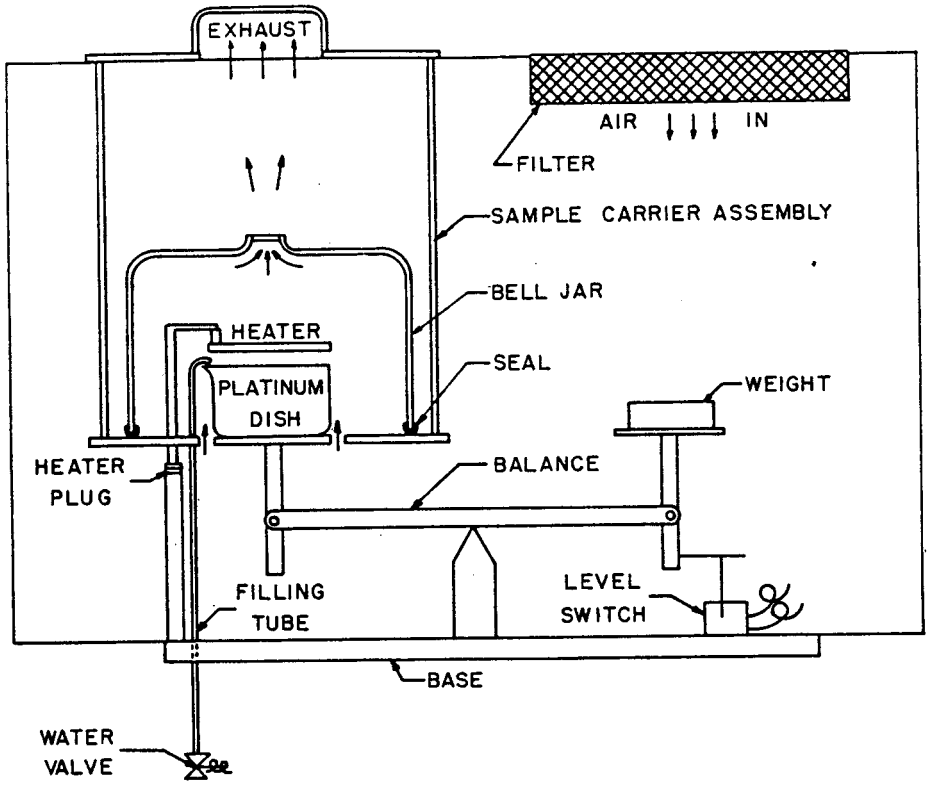


FIG. 4 Automatic Evaporation Assembly.

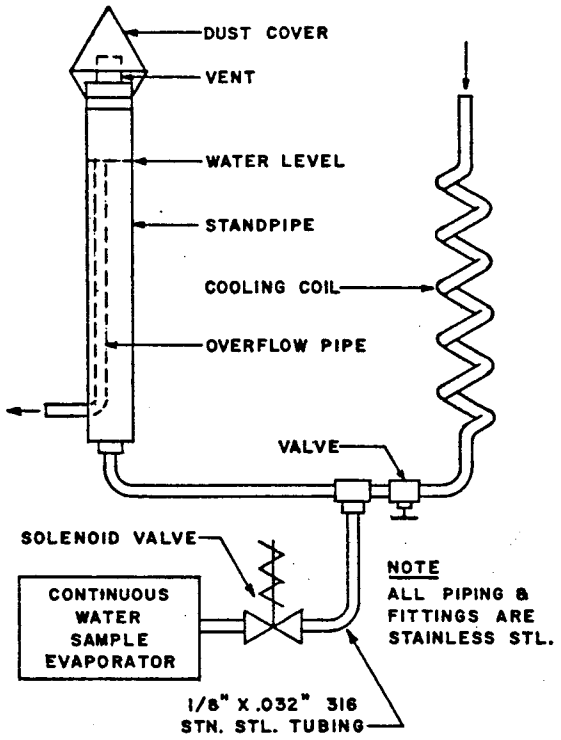


FIG. 5 Automatic Evaporator Sampling Equipment.

Designation: D 1429 – 76 (Reapproved 1981)

Standard Test Methods for SPECIFIC GRAVITY OF WATER AND BRINE[1]

This standard is issued under the fixed designation D 1429; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope and Application

1.1 These methods cover the determination of the specific gravity of water and brine free of separable oil, as follows:

	Sections
Method A – Pycnometer Method	6 to 10
Method B – Balance Method	11 to 15
Method C – Erlenmeyer Flask Method	16 to 19
Method D – Hydrometer Method	20 to 24

1.2 Methods A and B are applicable to clear waters or those containing only a moderate amount of particulate matter. Method B is preferred for samples of sea water or brines and is more sensitive than Method D which has the same general application. Method C is intended for samples of water containing mud or sludge.

2. Applicable Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam[2]

D 1129 Definitions of Terms Relating to Water[2]

D 1192 Specification for Equipment for Sampling Water and Stream[2]

D 1193 Specification for Reagent Water[2]

D 2777 Practice for Determination of Precision and Bias of Methods of Committee D-19 on Water[2]

D 3370 Practices for Sampling Water[2]

E 1 Specification for ASTM Thermometers[3]

E 380 Standard for Metric Practice[4]

3. Definitions

3.1 *brine* – water having more than 30 000 mg/litre of dissolved matter.

3.2 For definitions of terms used in this method refer to Definitions D 1129. For an explanation of SI units and symbols refer to Standard E 380.

4. Reagents

4.1 *Purity of Water* – Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type II.

5. Sampling

5.1 Collect the samples in accordance with Practices D 3370 and D Method 1066.

5.2 In view of the lack of a standard method for sampling mud or sludge, no instructions are given for sampling this type of material.

METHOD A – PYCNOMETER METHOD

6. Summary of Method

6.1 The sample is introduced into a pycnometer, stabilized at the desired temperature, and weighed. The specific gravity is calculated from this weight and the previously determined weight of reagent water that is required to fill the pycnometer at the same temperature.

7. Apparatus

7.1 *Bath* – Constant-temperature bath designed to maintain a temperature of 15.6 ±

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[1] These methods are under the jurisdiction of ASTM Committee D-19 on Water, and are the direct responsibility of Subcommittee D 19.09 on Saline and Brackish Water.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 14.01.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

1°C (60 ± 1.8°F). If any other temperature must be used due to local conditions, appropriate corrections shall be made.

7.2 *Pycnometer*—Cylindrical or conical glass vessel carefully ground to receive an accurately fitting 24/12 standard taper glass stopper provided with a hole approximately 1.0 to 2.0 mm in diameter, centrally located in reference to the vertical axis. The top surface of the stopper shall be smooth and substantially plane, and the lower surface shall be concave in order to allow all air to escape through the bore. The height of the concave section shall be approximately 5 mm at the center. The stoppered pycnometer shall have a capacity of about 24 to 30 ml, and shall weigh not more than 40 g. Suitable pycnometers are shown in Fig. 1.

7.3 *Thermometer*—An ASTM Gravity Thermometer having a range from −20 to + 102°C or −5 to + 215°F, as specified, and conforming to the requirements for Thermometer 12C or 12F, respectively, as prescribed in Specification E 1.

8. Procedure

8.1 Weigh a clean, dry, calibrated pycnometer, complete with stopper, on an analytical balance, and record this weight to the nearest 0.1 mg, as P.

8.2 Remove the stopper and fill the pycnometer with recently boiled reagent water that has been cooled to room temperature, to within several millimetres of the top. Remove the air bubbles. Immerse the unstoppered pycnometer up to the neck in a constant-temperature bath maintained at 15.6 ± 1°C (60 ± 1.8°F). Allow the pycnometer to remain in the bath for a period of time sufficient to establish temperature equilibrium. Twenty minutes is usually sufficient.

8.3 After temperature equilibrium has been established, and before removing from the bath, firmly insert the stopper and remove the excess water from the top of the stopper, taking care to leave the capillary filled. Remove the stoppered pycnometer from the bath and wipe it dry. Immediately weigh the pycnometer, and record this weight to the nearest 0.1 mg, as W.

8.4 Empty the reagent water from the pycnometer and dry, or rinse with the sample to be tested.

8.5 Using the sample to be tested, repeat the procedure in accordance with 8.2 and 8.3, recording the weight of the pycnometer containing the sample under test as S.

9. Calculations

9.1 Calculate the specific gravity of the sample as follows:

$$\text{Specific gravity} = (S-P)/(W-P)$$

where:

P = weight of the empty pycnometer,
S = weight of the pycnometer and contained sample, and
W = weight of the pycnometer and contained reagent water.

10. Precision

10.1 *Precision*—Results should not differ from the arithmetical mean by more than the following amounts:

Different operators and apparatus	0.002

METHOD B—BALANCE METHOD

11. Summary of Method

11.1 The specific gravity balance is essentially an analytical balance which uses a plummet to determine the weight of a liquid by displacement. The plummet is calibrated in a standard liquid, usually reagent water, before the determination is made. Any oil present in the sample will interfer with this determination; therefore, only freshly filtered samples should be used.

12. Apparatus

12.1 *Specific Gravity Balance*—A Westphal-type balance or any of several accurate specific gravity balances may be used.

13. Procedure

13.1 Locate the specific gravity balance in a draft-free enclosure. Clean the plummet by immersion in distilled water followed by acetone. Dry with air or a lint-free tissue. Calibrate the plummet by determining its difference in weight in air and in reagent water at 15.6 ± 1°C (60 ± 1.8°F); record this displacement as d_1.

13.2 Immerse the plummet in the sample, which has a stabilized temperature of 15.6 ± 1°C (60 ± 1.8°F). Make certain that the

plummet does not touch the bottom or the sides of the container. The liquid displacement, d_2, is the difference between the weight necessary to counterpoise the dry plummet in air and that necessary when the plummet is immersed in the liquid samples.

14. Calculations

14.1 Calculate the specific gravity of the sample as follows:

$$\text{Specific gravity} = \frac{d_2}{d_1}$$

where:

d_1 = difference in weight in air and in reagent water, and

d_2 = difference in weight in air and in the sample.

15. Precision

15.1 Precision—Results should not differ from the arithmetical mean by more than the following amounts:

Different operators and apparatus	0.003

METHOD C—ERLENMEYER FLASK METHOD

Summary of Method

16.1 The sample of mud or sludge is thoroughly stirred and poured into a wide-mouth Erlenmeyer flask until it is somewhat more than level full, the excess being struck off with a spatula blade. The specific gravity is calculated from this weight and the previously determined weight of water required to fill the flask completely.

16.2 If the sample is of a plastic solid consistency, the flask is partly filled with the sample and weighed. Water is then added to fill the flask completely, and the total weight is taken. The specific gravity is calculated from the weight of the volume of water displaced by the sample.

17. Procedure

17.1 Clean, dry, and weigh the Erlenmeyer flask to the nearest 0.1 g, and record this weight as F.

17.2 Fill the flask with reagent water or tap water. Both flask and water shall be at temperature equilibrium. Weigh the filled flask and record this weight as W. Empty and dry the flask.

17.3 If the sample flows readily, fill the flask completely with the sample, leveling the upper surface with a flat-bladed spatula held at an angle of 45 deg with the rim of the flask. Weigh, and record this weight as S.

17.4 Mix the sample thoroughly by stirring, but do not shake. If the sample does not flow readily, add sufficient sample to approximately half fill the flask, without exerting pressure, and weigh. Record the weight of the flask and sample as R. Fill the flask containing the sample completely with reagent water or tap water, whichever was used in accordance with 17.2, taking care to remove all entrained air bubbles, and weigh again. Record this weight at T.

18. Calculations

18.1 In the case of free-flowing samples, calculate the specific gravity of the sample as follows:

$$\text{Specific gravity} = (S - F)/(W - F)$$

where:

F = weight of the empty flask,

S = weight of the flask completely filled with sample, and

W = weight of the flask and contained water.

18.2 In the case of samples that do not flow readily, calculate the specific gravity of the sample as follows:

$$\text{Specific gravity} = (R - F)/[(W - F) - (T - R)]$$

where:

F = weight of the empty flask,

R = weight of the flask partly filled with sample,

T = weight of the flask partly filled with sample, plus water added to fill remaining volume, and

W = weight of the flask and contained water.

19. Precision

19.1 Results with a precision of 0.005 can be obtained.

METHOD D—HYDROMETER METHOD

20. Summary of Method

20.1 The hydrometer is a weighted bulb with a graduated stem. The depth to which the hydrometer sinks in a fluid is determined by

the density of the fluid. The specific gravity is read directly from the graduated stem. Any oil present in the sample will interfere with the determination; therefore, only freshly filtered samples should be used.

21. Apparatus

21.1 *Hydrometer*—A set of glass hydrometers (equipped with built-in thermometers) covering the range of specific gravities encountered in water and brine analyses. Graduations should not be greater than 0.002.

21.2 *Hydrometer Cylinder* of clear glass, or plastic. For convenience in pouring, the cylinder may have a lip on the rim. The inside diameter of the cylinder shall be at least 25 mm greater than the outside diameter of the hydrometer used. The height of the cylinder shall be such that the hydrometer floats in the sample with at least 25-mm clearance between the bottom of the hydrometer and the bottom of the cylinder.

22. Procedure

22.1 Fill the cylinder with the sample and carefully immerse the hydrometer. The hydrometer must float freely and not touch the sides of the cylinder. Allow the hydrometer to remain in the sample 5 min or until the thermometer establishes equilibrium. Read and record the specific gravity and temperature directly from the hydrometer.

23. Calculation for Correction to 60°F

23.1 The specific gravity may be corrected to 60/60°F by adding 0.0002 for each degree above 60°F. An example is as follows:

Specific gravity at 79°F	1.1225
Correction = (79 - 60) 0.0002 =	+ 0.0038
Specific gravity at 60°F	1.1263

24. Precision

24.1 Results with a precision of ± 0.004 can be obtained.

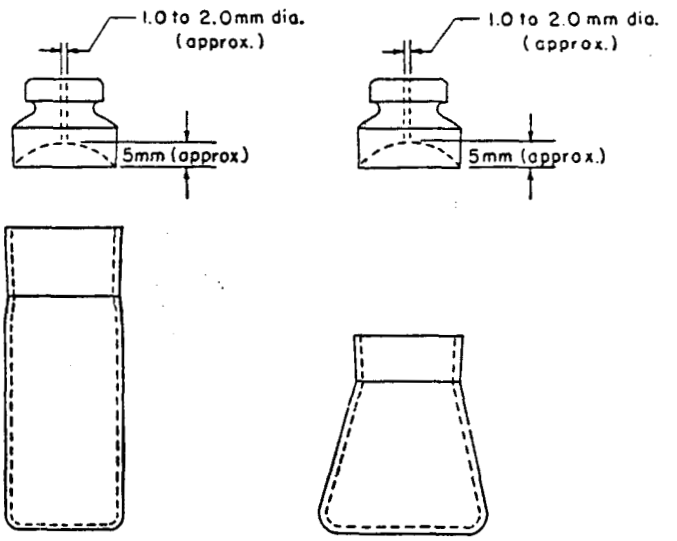

FIG. 1 Suitable Pycnometers

Designation: D 1125 – 82

Standard Test Methods for ELECTRICAL CONDUCTIVITY AND RESISTIVITY OF WATER[1]

This standard is issued under the fixed designation D 1125; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These methods cover the determination of the electrical conductivity and the electrical resistivity of water. These methods are applicable for such purposes as the detection of ionized impurities dissolved in condensed steam,[2,3] the approximate determination of dissolved electrolytes in natural and treated waters, such as boiler feedwater, boiler water, evaporator salines, and cooling water as well as saline waters including brackish water, sea water, and brines. The following methods are included:

2. Applicable Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam[4]

D 1129 Definitions of Terms Relating to Water[4]

D 1192 Specification for Equipment for Sampling Industrial Water and Steam[4]

D 2186 Test Method for Deposit-Forming Impurities in Steam[5]

D 3370 Practices for Sampling Water[4]

E 1 Specification for ASTM Thermometers[6]

3. Definitions

3.1 The term *electrical conductivity* in this method shall be defined in accordance with Definitions D 1129 as follows:

3.1.1 *electrical conductivity*—the reciprocal of the resistance in ohms measured between opposite faces of a centimetre cube of an aqueous solution at a specified temperature.

NOTE 1—The unit of electrical conductivity is siemens per centimetre. The actual resistance of the cell, R_x, is measured in ohms. The conductance, $1/R_x$, is directly proportional to the cross-sectional area, A (cm^2), and inversely proportional to the length of the path, L (cm).

$$1/R_x = K \cdot A/L$$

The conductance measured between opposite faces of a centimetre cube, K, is called conductivity. Conductivity values are usually expressed in microsiemens/centimetre (see 14.1 and 21.1), or in millisiemens/centimetre (see 28.1) at a specified temperature, normally 25°C.

3.2 The term *electrical resistivity* in this method shall be defined in accordance with Definition D 1129 as follows:

3.2.1 *electrical resistivity*—The resistance in ohms measured between opposite faces of a centimetre cube of an aqueous solution at a specified temperature.

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[1] These methods are under the jurisdiction of ASTM Committee D-19 on Water, and are the direct responsibilities of Subcommittee D19.11 on Water for Power Generation and Process Use.

Current edition Oct. 29, 1982. Published March 1983. Originally published as D 1125 – 50T. Last previous edition D 1125 – 77.

[2] See ASTM Methods D 2186, Test for Deposit-Forming Impurities in Steam, *1983 Annual Book of ASTM Standards*, Vol 11.02.

[3] Where the principal interest in the use of conductivity methods is to determine steam purity, reference may be made to the "Methods for Determination of Quality and Purity of Steam," ASME Power Test Code, Supplement on Instruments and Apparatus, Part 19.11. These methods may also be used for checking the correctness of water analyses. See Rossum, J. R. "Conductance Method for Checking Accuracy of Water Analyses," *Analytical Chemistry*, Vol 21, 1949, p. 631.

[4] *Annual Book of ASTM Standards*, Vol 11.01.

[5] *Annual Book of ASTM Standards*, Vol 11.02.

[6] *Annual Book of ASTM Standards*, Vol 14.02.

NOTE 2—The unit of electrical resistivity is ohm centimetre. The actual resistance of the cell, R_x, is measured in ohms, and is directly proportional to the length of the path, L (cm), and inversely proportional to the cross-section area, A (cm^2).

$$R_x = R \cdot L/A$$

The resistance measured between opposite faces of a centimetre cube, R, is called resistivity. Resistivity values are usually expressed in ohm·centimetre, or in megohm-centimetre, at a specified temperature, normally 25°C.

3.3 For definitions of other terms used in these methods, refer to Definitions D 1129.

4. Interferences

4.1 Exposure of a sample to the atmosphere may cause changes in conductivity/resistivity, due to loss or gain of dissolved gases. This is extremely important in the case of waters with low concentrations of dissolved ionized materials. The carbon dioxide, normally present in the air, can drastically change the conductivity/resistivity of pure waters. Contact with air should be avoided by using flow-through or in-line cells.

5. Apparatus

5.1 *Measuring Circuit:*

5.1.1 Instruments used for Methods A and B shall energize the conductivity cell with alternating current at an approximately constant frequency within the range from 25 to 3000 Hz. The instrument may be a manually operated Wheatstone bridge, a deflection meter, or a self-balancing recorder or indicator. If manually operated, the null balance may be a galvanometer, headphone, or electron ray tube of sensitivity commensurate with the required precision of measurement. Calibration may be in conductance or resistance units.

5.1.2 Instruments used for Method C operate by inducing an alternating current in a closed loop of water. By measuring the magnitude of this current under controlled conditions the conductivity of the water may be determined without the use of electrodes. Toroidally wound cells are used to induce currents with frequencies from several thousand to several tens of thousands of Hertz. The instrument may be a manually balanced bridge or a self-balancing recorder or indicator. Calibration may be in conductivity or conductivity ratio. For high-precision measurements, sample temperatures are critical, and special electrical thermometers are provided as part of the instrument where they are used to compensate for temperature changes.

5.2 *Cells*

5.2.1 Flow-through or in-line cells shall be used for measuring conductivities lower than 10 μS/cm, resistivities higher than 100 000 ohm·cm, to avoid contamination from the atmosphere. In all other cases, pipet type or dip cells can also be used.

5.2.2 A cell shall be chosen which will preferably give a cell resistance in the range 500 to 10 000 ohm (see Table 1).

5.2.3 Flow-through and in-line cells shall be mounted so that continuous flow of the sample through or past it is possible. Recommended flow through the cell is 0.3 m/s (see Practices D 3370, Table 2). The flow chamber and cell mounting shall retain calibration under conditions of pressure, flow and temperature change, and shall be resistant to corrosion. The chamber shall be equipped with means for accurate measurement of the temperature.

5.2.4 Platinized electrodes may be used for all measurements, except for conductivities below 0.1 μS/cm, resistivities over 10 mMohm·cm.

5.2.5 Cells of the design specified by the manufacturer of the instrument shall be used in Method C.

5.3 *Thermometers:*

5.3.1 *For Method A*—An ASTM Precision Thermometer, number 63C, as defined in Specification E 1 having a range from −8 to 32°C and a graduation of 0.1°C.

5.3.2 *For Method B*—A thermometer accurate to 0.5°C, when the instrument is not provided with manual or automatic temperature compensation.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[7] Other grades may be

[7] "Reagent Chemicals, American Chemical Society Specifications", Am. Chemical Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards" by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N. Y. and the "United States Pharmacopeia."

used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type I. In making up the potassium chloride solutions for Methods A and C, use water stabilized to the laboratory atmosphere by aspirating air through the water from a fritted-glass or stainless steel gas dispersion tube. The equilibrium point is reached when the conductivity remains constant. The equilibrium conductivity must be added to Table 2.

6.3 *Alcohol*, 95 % ethyl alcohol, isopropyl alcohol, or methyl alcohol.

6.4 *Aqua Regia*—Mix 3 volumes of concentrated hydrochloric acid (HCl, sp gr 1.19) with 1 volume of concentrated nitric acid (HNO_3 sp gr 1.42).

6.5 *Ethyl Ether.*

6.6 *Hydrochloric Acid* (sp gr 1.19)—Concentrated HCl.

6.7 *Hydrochloric Acid (1+1)*—Mix 1 volume of concentrated HCl (sp gr 1.19) with 1 volume of water.

6.8 *Platinizing Solution*—Dissolve 1.5 g of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) in 50 mL of water containing 0.0125 g of lead acetate ($Pb(C_2H_3O_2)_2$).

6.9 *Potassium Chloride* (KCl), dried at 105°C for 2 h.

6.10 *Potassium Chloride Reference Solution A*—Dissolve 74.2460 g of KCl (weighed in air) in water and dilute to 1 L at 20 ± 2°C.

6.11 *Potassium Chloride Reference Solution B*—Dissolve 7.4365 g of KCl (weighed in air) in water and dilute to 1 L at 20 ± 2°C.

6.12 *Potassium Chloride Reference Solution C*—Dissolve 0.7440 g of KCl (weighed in air) in water and dilute to 1 L at 20 ± 2°C.

6.13 *Potassium Chloride Reference Solution D*—Dilute 100 mL of reference solution C to 1 L with water at 20 ± 2°C shortly before using. Store the solution in a glass-stoppered bottle of chemical-resistant glass.

6.14 *Standard Sea Water.*[8]

NOTE 4—The electrical conductivity of each of the referenced solutions is given in Table 2. The values for electrical conductivities for the solutions are those of G. Jones and B. C. Bradshaw[9], the data of T. Shedlovsky[10] are used for Solution D. Solutions A, B, and C were prepared by Jones and Bradshaw by dissolving 71.1352, 7.4191, and 0.7453 g respectively of KCl (in vacuum) per 1000 g of solution (in vacuum). The method preparation given in Table 2 includes the corrections to weights of KCl (in air against brass weights) per litre of solution at 20°C and assumes the density of KCl – 1.98, density of brass = 8.4, and the density of air = 0.00118. The densities of 0.1 *N*, 0.10 *N* and 0.010 *N* KCl at 20°C, 1.04420, 1.00280, and 0.99871 g/mL, respectively, were interpolated from the data in the International Critical Tables.[11] Solution D may be prepared with sufficient accuracy by a tenfold dilution of Solution C.

7. Sampling

7.1 Samples shall be collected in accordance with the applicable ASTM method as follows: Practice 1066, Specification D 1192, and Practices D 3370.

7.2 Avoid exposure of the sample to atmosphere containing ammonia or acidic gases. Protect the sample to avoid gain or loss of dissolved gases, particularly if there is some delay before the conductivity measurements are made. Use a flow-type cell for sampling and measuring condensed steam or water having a conductivity of less than 10 μmhos/cm.

8. Preparation of Electrodes

8.1 A "broad" null position in the case of a manually operated instrument and sluggishness in rebalancing or stepwise action of an automatic recorder or an indicator may be an indication of deteriorated electrode surfaces. If such conditions are noted or if the cell constant as checked does not fall within reasonable limits of its nominal value, it is necessary to clean and replatinize the electrodes. In general, no mechanical cleaning should be attempted. In service where the presence of finely divided platinum is undesirable, platinization of electrodes may be omitted but only for field and routine testing of water having a conductivity below 0.1 μmho. On the other hand, clean and well-platinized electrodes are increasingly important in testing water of higher conductivities, particularly above 200 μmhos.

8.2 The cell manufacturer's instructions

[8] Two-hundred millilitres ampoules provided by the Standard Sea Water Service of I.A.P.S.O. at Charlottenlund Slot, Denmark, and available throughout the world through distributors, has been found satisfactory for this purpose.

[9] *Journal of Am. Chemical Society*, Vol 55, 1933, p. 1780

[10] *Journal of Am. Chemical Society*, Vol 54, 1932, p. 1411

[11] *International Critical Tables*, Vol 3, 1928, p. 87.

should be followed for cleaning the electrodes as well as other parts of the cell. A suitable cleaning solution consists of a mixture of 1 part by volume of isopropyl alcohol, 1 part of ethyl ether, and 1 part of HCl (1+1). After cleaning, thoroughly flush the cell with water. If the old platinum black coating is to be removed, judicious application of aqua regia to the electrodes, or electrolysis in HCl (sp gr 1.19) is frequently successful.

8.3 Platinize the electrodes of the cell with H_2PtCl_6 solution. A suitable plating apparatus consists of a 6-V d-c supply, a variable resistor, a milliammeter, and an electrode. The deposit should present a black, velvety appearance and should adhere well to the electrode surface. The procedure for platinizing is not critical. Good platinized coatings are obtained using from 1.5 to 3 C/cm^2 of electrode area. For example, for an electrode having a total area (both sides) of 10 cm^2, the plating time at a current of 20 mA would be from 12½ to 25 min. The current density may be from 1 to 4 mA/cm^2 of electrode area. Plate the electrodes one at a time with the aid of an extra electrode. During the plating, agitate the solution gently. When not in use, fill the cells with water to prevent the drying out of the electrodes while in storage.

9. Calibration

9.1 *Measuring Instrument*—A calibrating resistor is usually furnished with conductivity recorders and indicators by the manufacturer, together with information as to the correct scale reading the instrument shall assume when this resistor is connected to the recorder or indicator in place of the conductivity cell. Follow the manufacturer's instructions and periodically check the instrument. When lead wires between the instrument and the cell are long, check the installation at least once by connecting the calibrating resistor at the far end of the lead wire and noting the difference, if any, in reading with the long lead wire in the circuit. Check portable or manually operated instruments in a similar manner with one or several calibrating resistors. Note errors of significant magnitude and correct subsequent conductivity readings.

9.2 *Conductivity Cells*—For field and routine laboratory testing, check conductivity cells for cell constant by comparing instrument readings taken with the cell in question against readings on the same sample or series of samples taken with a conductivity cell of known or certified cell constant. Exercise care to ensure that both working and reference cells are at the same temperature or, alternatively, at different but known temperatures so that a correction as later described can be applied. Resistance-reading instruments will indicate in direct proportion to the cell constant, while conductance-reading instruments will indicate in inverse proportion to cell constant. Conductivity cells provided with platinized electrodes may be calibrated with reference solutions in accordance with Section 13.

10. Abbreviations and Symbols

10.1 Symbols used in the equations in Sections 14, 16, and 23 are defined as follows:

J = cell constant, cm^{-1},
K = conductivity, μmho/cm, at 25°C,
K_x = measured conductance, in S,
K_1 = conductivity, μmho/cm of the KCl in the reference solution at the temperature of measurement (Table 2),
K_2 = conductivity, in μmho/cm of the water used to prepare the reference solution, at the same temperature of measurement
R = resistivity, ohm·cm, at 25°C,
R_x = measured resistance, ohm.

METHOD A—PRECISION MEASUREMENT

11. Scope

11.1 This method is applicable to the measurement of the electrical conductivity of water when a higher degree of precision and accuracy is required than can be obtained by use of field and routine laboratory methods.

12. Summary of Method

12.1 The conductivity is measured at 25°C, avoiding the use of a temperature correction and thus eliminating a major source of error in the measurement.

13. Determination of Cell Constant

13.1 For the purposes of this method, the cell constant of the conductivity cell used shall be known within ±1 %. The manufacturer's certification of the cell constant within this accuracy shall be considered satisfactory. If the conductivity cell has been in service subsequent to this certification, it shall be rechecked by the manufacturer, or in the laboratory.

13.2 Rinse the conductivity cell several times with water, then at least twice with the reference solution that has a conductivity nearest to that of the sample under test (Table 2). Control the solution temperature to 25 ± 0.1°C. Measure the resistance of the cell. Repeat the measurement on additional portions of the reference solution until the value obtained remains constant to within the limit of the precision in accordance with Section 15.

13.3 For instruments reading measured resistance in ohms, calculate the cell constant from:

$$J = 10^{-6} \cdot R_x(K_1 + K_2)$$

13.4 For instruments reading measured conductance, mhos, from:

$$J = 10^{-6} \cdot (K_1 + K_2)/K_x$$

14. Procedure

14.1 *Conductivity Below 10 μmhos/cm—Resistivity Under 100 000 ohm·cm*—Use a flow-type conductivity cell. Adjust the sample stream, known to be free of corrosion products and extraneous contamination, to a proper flow rate and bring the temperature to 25 ± 0.1°C. Allow sufficient time to reach equalization of temperatures. Read the conductance or resistance.

14.2 *Conductivity Above 10 μmhos/cm—Resistivity Under 100 000 ohm·cm*—Either a flow-type, dip-type, or pipet-type cell may be used. If a flow-type cell is used, proceed in accordance with 12.1. If another type is used, rinse the cell thoroughly several times with water and then two or more times with the sample. Adjust the temperature to 25 ± 0.1°C. Read the conductance or resistance. Allow sufficient time for equalization of temperatures.

15. Calculation

15.1 For instruments reading measured resistance, in ohms, calculate the conductivity of the sample from:

$$K = 10^6 \cdot J/R_x$$

15.2 For instruments reading measured resistance, in ohms, calculate the resistivity of the sample from:

$$R = 10^{-6} \cdot R_x/J$$

15.3 For instruments reading measured conductance, in mhos, calculate the conductivity of the sample from:

$$K = 10^6 \cdot J \cdot K_x$$

15.4 For instruments reading measured conductance, in mhos, calculate the resistivity of the sample from:

$$R = 10^{-6} \cdot 1/J \cdot K_x$$

16. Report

16.1 Report the conductivity at 25°C in terms of micromhos per centimetre to the nearest 1 % of the determined conductivity.

16.2 Alternatively report the resistivity at 25°C in terms of ohm-centimetres to the nearest 1 % of the determined resistivity.

17. Precision

17.1 In addition to data available in the literature, a collaborative test program for the determination of precision and bias is in the planning stage.

METHOD B—FIELD AND ROUTINE LABORATORY MEASUREMENT

18. Scope

18.1 This method is applicable to field and routine measurements of the electrical conductivity of water.

19. Summary of Method

19.1 This method utilizes a flow-type conductivity cell to sample a continuous stream of the water under test, or, in the case of samples having conductivities greater than 10 μmhos/cm, any other convenient type of conductivity cell for testing a static sample. Temperature correction methods are also provided.

20. Procedure

20.1 *Conductivity Below 10 μmhos/cm*—Use a flow-type conductivity cell. Adjust the sample stream, known to be free of corrosion products and extraneous contamination, to a proper flow rate and bring the temperature to a steady value as near 25°C as possible. Read the temperature to the nearest 0.5°C. If the measuring instrument is provided with a manual temperature compensator, adjust this to the sample temperature valve. If an automatic temperature compensator is provided, no adjustment is necessary but sufficient time must be allowed to permit equalization of temperatures. Read the conductivity. If the instrument has no means of temperature compensation, determine a tem-

perature correction in accordance with the instructions in Section 21 to convert readings to 25°C.

20.2 *Conductivity Above 10 μmhos/cm*—Either a flow-type, dip-type, or pipet-type cell may be used. If a flow-type cell is used, proceed in accordance with 20.1. If another type is used, rinse the conductivity cell thoroughly several times with water and then two or more times with the sample. Measure the resistance or the conductance, and the temperature (to the nearest 0.5°C), on successive portions of the sample until a constant value is obtained. If the measuring instrument is provided with a manual temperature compensator, adjust this to the sample temperature value before reading the instrument. If an automatic temperature compensator is provided, no adjustment is necessary, but sufficient time must be allowed to permit equalization of temperature. If the instrument has no means of temperature compensation, determine a temperature correction in accordance with the instructions in Section 21 to convert readings to 25°C.

21. Temperature Coefficient of Conductivity/Resistivity

21.1 The conductivity/resistivity of water and aqueous solutions depends strongly upon the temperature. The coefficient varies depending upon the nature and composition of the dissolved electrolytes, and upon the concentration. The lower the concentration, the higher the coefficient, due to the effect of temperature upon the dissociation of water: $H_2O = H^+ + OH^-$. To avoid making a correction, it is necessary to hold the temperature of the sample to 25 ± 0.5°C. If this cannot be done, the temperature coefficient must be determined and a correction applied. This requires a series of conductivity and temperature measurements on the sample over the required temperature range.

21.2 In static systems, exercise care to avoid change of composition caused by loss of volatile constituents or by pick-up of contaminants from the air to the containing vessel during the series of measurements.

21.3 In flowing systems, split the sample into two or more streams, running each through a suitable heat exchangers and flow-type conductivity cell. Provide means for variable heating or cooling so that the desired range of temperature will be covered. Regulate the rate of flow through each cell so that each cell is measuring the same time fraction of the sample to eliminate the effect of a variable sample.

21.4 From the data obtained, plot conductivity against temperature. From this curve a table of temperature correction factors may be prepared, or the ratio of conductivity at temperature, T, to conductivity at 25°C may be plotted against temperature T, and this ratio or correction factor, Q, taken from the smoothed curve.

21.5 When using an instrument provided with a manual or automatic temperature compensator, follow the manufacturer's instructions to calibrate the compensator or check its accuracy and applicability to the sample being tested.

22. Calculations

22.1 For instruments reading measured resistance in ohms, calculate the conductivity of the sample from:

$$K = 10^6 \cdot J/R_xQ$$

22.2 For instruments reading measured resistance in ohms, calculate the resistivity of the sample from:

$$R = 10^{-6} \cdot R_xQ/J$$

22.3 For instruments reading measured conductance in siemens, calculate the conductivity of the sample from

$$K = 10^6 \cdot JK_x/Q$$

22.4 For instruments reading measured conductance, in siemens, calculate the resistivity of the sample from:

$$R = 10^{-6} \cdot Q/JK_x$$

22.5 Automatic recorders and indicators provided with temperature compensators, when used with conductivity cells of the required cell constant, usually read directly in terms of Siemens per centimetre referred to 25°C. No calculations are necessary if the compensator is corrected for the solution in the cell.

23. Report

23.1 Report the value of the conductivity at 25°C in terms of siemens per centimetre to the nearest 3 % of the determined conductivity.

23.2 Alternatively report value of the resis-

'ivity at 25°C in terms of ohm-centimetres to the nearest 3 % of the determined resistivity.

24. Precision

24.1 See 17.1.

METHOD C—CONDUCTIVITY OF SALINE WATERS BY ELECTRODELESS METHOD

25. Scope

25.1 This method is applicable to the measurement of the electrical conductivity of saline waters including sea water, brines, and brackish water as well as waste waters.

26. Summary of Method

26.1 The conductivity is measured with electrodeless cells by an inductive method. Errors caused by electrode polarization in concentrated electrolytes or electrode fouling caused by marine growth in sea water or such materials as waxes, tars, oils, paints in natural oil well brines, or waste water are thus avoided.

27. Calibration

27.1 Calibrate the electrodeless cells with the solutions listed in Table 2 by filling or immersing the cells. In either case, rinse the cells with several portions of the KCl solutions before measurement or calibration and then discard the solutions.

27.2 Follow the manufacturer's instructions on calibration, particularly in respect to setting controls so proper results are obtained and so proper adjustments are made according to the temperature of the solution.

27.2.1 It is especially important that electrodeless dip cells be calibrated in containers large enough to provide ample room about the dip cells for the solution current path.

27.3 If it is desired to test sea water, calibrate the instrument against standard sea water (see 6.14).

28. Procedure

28.1 As described in the Section 25, follow the manufacturer's instructions.

28.2 Rinse all cells with portions of the sample before making measurements in order to avoid sample contamination from electrolytes or salts which may have been left in the cell. This particularly is necessary in the case of fill-type cells.

28.3 Use a large enough container to prevent errors due to current path obstruction, or insufficient immersion of dip cells. All cells should be completely filled or immersed during the time measurements are made. Dip cells should contain no bubbles and should be inclined to prevent air entrapment.

28.4 Since most electrodeless systems employ automatic temperature compensation, locate these sensors in the sample stream as close as possible to the electrodeless cells.

28.4.1 Fill and dip cells generally contain integral temperature compensators.

28.5 Allow sufficient time for instruments to achieve equilibrium before a reading is taken.

29. Calculations

29.1 Consult the manufacturer's instructions to learn if the instrument provides direct reading results.

29.1.1 Precision "salinometers" may read out in a conductivity ratio which is generally converted to salinity, chlorinity, or density by use of tables available from UNESCO (Place de Fontenoy, Paris 7e) or the manufacturers.

30. Report

30.1 Report the results in siemens per centimetre for these more conductive materials, and include the temperature of measurement and the compensation temperature. Information should also be included as to manufacturer and the instrument model number.

30.1.1 The manufacturer's literature should be consulted, since a few instruments read directly in conductivity at the temperature of measurement without compensation.

30.1.2 Results are generally reported in millimhos per centimetre in place of siemens per centimetre to avoid the use of so many zeros to the right of the significant figures. Ten millimhos per centimetre equals 10 000 μmhos/cm.

31. Precision

31.1 This depends entirely on the instrument used and can best be obtained from the manufacturer.

TABLE 1 Recommended Cell Constants for Various Conductivity Ranges

Range of Conductivity, S cm	Cell Constant, cm^{-1}
0.05 to 20	0.01
1 to 200	0.1
10 to 2000	1
100 to 20 000	10
1000 to 200 000	50

TABLE 2 Electrical Conductivity Values Assigned to the Potassium Chloride in the Reference Solution[A]

Reference Solution	Approximate Normality of Solution	Method of Preparation	Temperature, °C	Electrical Conductivity μS/cm
A	1	74.2460 g of KCl weighed in air per 1 L of solution at 20°C	0	65 176
			18	97 838
			25	111 342
B	0.1	7.4365 g of KCl weighed in air per 1 L of solution at 20°C	0	7 138
			18	11 167
			25	12 856
C	0.01	0.7440 g of KCl weighed in air per 1 L of solution at 20°C	0	773.6
			18	1 220.5
			25	1 408.8
D	0.001	Dilute 100 mL of Solution C to 1 L at 20°C	25	146.93

[A] Excluding the conductivity of the water used to prepare the solutions. These tabulated conductivity values are in international units. When using measuring instruments calibrated in absolute units, multiply the tabular values by 0.999505.

BUREAU OF ECONOMIC GEOLOGY
THE UNIVERSITY OF TEXAS AT AUSTIN

SPECIFIC WORK INSTRUCTION

TITLE	REVISION: 0
DETERMINATION OF MAJOR, MINOR AND TRACE ELEMENTS BY ICP-OES: GENERAL SETUP AND ANALYSIS **SWI 1.5**	DATE: 04-13-87
	PAGE: 1 OF 13

APPLICABILITY	SUPERSEDES
BUREAU-WIDE	THIS IS THE ORIGINAL ISSUANCE

APPROVAL	CONCURRENCE
	Not applicable
	PROGRAM DIRECTOR DATE
DIRECTOR 4/14/87 DATE	Carolyn Condrow 4/15/87
	QUALITY ASSURANCE MANAGER DATE

1.0 SCOPE

1.1 This method covers the analysis of solution samples for up to 34 elements simultaneously with a direct reading inductively coupled plasma-optical emission spectrometer (ICP-OES). Elements comprising the array are listed in Table 1.

1.2 Sensitivity and analytical range will be defined per element in later sections on specific applications. Detection limits for each element at the most sensitive settings are listed in Table 1.

2.0 SUMMARY OF METHOD

2.1 Samples (natural water, brine water, extract media, or rock digests) are treated to obtain an appropriate solution matrix (i.e. acid strength, total dissolved solids, etc.).

Sample solutions are then introduced to the argon plasma, and the analyte elements within these solutions are thermally excited and emit photons. These photons, being characteristic of the element from which they were produced, are detected and quantitated through the utilization of a computerized, 34-element, direct reading, emission spectrograph.

TABLE 1. ICP-AES (MSL-BEG) detection limits.

Element	Wavelength (angstroms)	Absolute detection limit	Lowest quantitative concentration
Na	(5895.9)	0.084	0.42
K	(7664.7)	0.27	1.39
Mg	(2790.8)	0.063	0.32
Ca	(3158.9)	0.013	0.07
Al	(3082.2)	0.04	0.24
Fe	(2599.4)	0.004	0.02
Ti	(3685)	0.01	0.08
Mn	(2576.1)	0.001	0.005
Co	(2388.9)	0.006	0.03
Cr	(2677.2)	0.006	0.03
Cu	(3247.5)	0.006	0.03
Ni	(2316)	0.014	0.07
Mo	(2020.3)	0.010	0.05
Zn	(2025.5)	0.002	0.01
As	(1937.7)	0.060	0.30
Cd	(2265)	0.002	0.01
V	(3102.3)	0.008	0.04
Pb	(2203.5)	0.021	0.11
Sb	(2068.4)	0.160	0.80
Se	(1960.9)	0.137	0.69
Sn	(1899.9)	0.017	0.09
Li	(6707.8)	0.008	0.04
Be	(2348.6)	0.001	0.005
Sr	(4077.7)	0.001	0.005
Ba	(4554)	0.002	0.01
Zr	(3438.2)	0.013	0.07
U	(3859.6)	1.220	6.1
Th	(4019.1)	0.075	0.38
B	(2497.7)	0.007	0.04
P	(2136.2)	0.123	0.62
Ce	(4186.6)	0.110	0.55
La	(3794.8)	0.010	0.05
Si	(2516.2)	0.033	0.17
Rb	(7800.2)	1.421	7.11

Notes: 1. These detection limits are micrograms per milliliter of solution. Any process to dissolve a solid sample would generate a dilution factor and would therefore increase the limit of detection.

2. Most rocks require at least a 50 to 200 times dilution.

3. All solutions for this data were 10% hydrochloric acid.

4. The "lowest quantitative concentration" is generally considered to be five times the absolute detection limit. Other considerations, such as the degree and abundance of interfering elements, will also have a bearing on the validity of low concentration results.

Following the instrument's standardization process, the samples are analyzed sequentially. Each result is computed from three ten-second intensity measurements at specific wavelengths characteristic of each analyte element.

3.0 SIGNIFICANCE

3.1 Some advantages of ICP-OES analyses include:

3.1.1 Freedom from chemical interferences normally associated with atomic absorption spectroscopy (AAS).

3.1.2 Very wide dynamic quantitatable range (compared to AAS).

3.1.3 Simultaneous analysis of 34 elements (AAS is capable of only one element per analysis).

3.1.4 Computer data reduction in real time enabling the application of predetermined inter-element interference correction factors to be applied prior to data viewing. (Routinely, greater than 60 factors are applied to each analysis.)

3.1.5 Computer assisted operation enabling high sample throughput.

3.1.6 Equal or greater sensitivity for most elements compared to AAS. Elements having greater sensitivity by AAS include: lithium, sodium, potassium, rubidium, cesium, rhodium, lead and cadmium.

3.1.7 Very efficient excitation medium (argon plasma with peak temperatures of approximately 10,000 degrees Kelvin utilized).

4.0 INTERFERENCES

4.1 Spectral interferences (the result of unwanted spectral light emitted by concomitant elements being registered on the analyte channels of the spectrometer) occur as:

4.1.1 Direct overlap: spectral line of an interfering concomitant element falls directly on an analyte channel of the instrument.

4.1.2 Wing overlap: the interfering spectral line is resolved but registers an effect on an analytical channel due to line broadening.

4.1.3 Recombination continuum: broadband background spectral shifts.

4.1.4 Stray light: unwanted light reaching the detectors from sources such as ghosts from the grating (this is inherent to spectrometer components and design and is assumed to be negligible for a properly designed unit).

4.2 Procedure for automatic correction of spectral interferences:

NOTE: Only interferences from elements in our spectrometer array can be corrected by this procedure. However, all commonly occurring geologically significant elements are represented. For samples of unusual geological

composition, interferent elements in abundance must be considered and interpreted for correction via methods outlined in section 4.3

4.2.1 Obtain a pure element stock solution (1000 ppm) for each element to be tested as an 'interferent.' Initially, all elements in the spectrometer array are suspected. (See also section 4.3.)

4.2.2 Analyze each stock solution for spectral interferences by measuring all channels of the spectrometer while step scanning across the optimum profile position of the primary slit. (This effectively shifts the entire spectrum so as to record any feature in the surrounding spectral region of each detector.)

4.2.3 Plot out the data and interpret any interference as to its source (refer to section 4.1). Beware of contamination in the 'pure element' solutions which could be interpreted as an interference appropriate for correction.

4.2.4 Prepare a system calibration which is composed of:

a. Elements that are 'affected' by the spectrum produced by all 'interfering' elements. Each element should be calibrated for a range that is appropriate for the magnitude of the interfering signals encountered.

b. All solutions should contain the same matrix (i.e. acid).

4.2.5 Calibrate ICPQ system (see section 8).

4.2.6 Measure the apparent concentrations of the 'affected' elements by analyzing various levels of the 'interfering' elements (in single elements solutions). The relationship of 'interfering' element concentration versus apparent 'affected' element concentration should be linear.

4.2.7 Tabulate these relationships and enter the slopes into program CORR of command file ICP. If two elements interfere with each other, the most abundant is to be listed first in the 'CORR' file in order to prioritize the calculations. This file currently has 63 factors that are applied to all measurements. (See Table 2.)

4.2.8 During routine analyses these factors are applied thus:

a. Three intensity measurements are made and averaged.

b. The 'interfering' element is then quantitated and its effect on the 'affected' elements is calculated from the relationships established above.

c. The effect (in concentration units) is then subtracted from the total measured concentration of the 'affected' element prior to display of the results.

4.3 Spectral interferences that require manual correction:

Table 2. Correction factors for interelement interferences.

Correction no.	Interfering element	Affected element	Correction factor (µg/µg)
1	Al	Sb	0.00235
2	Al	Pb	0.0012
3	Al	Se	0.002
4	Al	P	0.002
5	Al	Cd	0.00002
6	Al	Sn	0.00025
7	Al	As	0.007
8	Al	Mo	0.000223
9	Fe	Mg	0.00047
10	Fe	Cr	0.00003
11	Fe	U	0.0016
12	Fe	Cd	0.00006
13	Fe	Se	0.00044
14	Fe	P	0.00027
15	Fe	B	0.0052
16	Fe	Co	0.0014
17	Fe	Sn	0.0001
18	Fe	As	0.00011
19	Fe	Be	0.00004
20	Fe	Pb	0.00017
21	Fe	Zr	0.00003
22	Fe	Mo	0.000025
23	Fe	Sb	0.00018
24	Fe	Ce	0.0009
25	Fe	Si	0.00034
26	Fe	La	0.00007
27	Mn	Mg	0.001
28	Mn	Se	0.0013
29	Mn	Co	0.00011
30	Mn	Sl	0.00188
31	Mn	Cr	0.00035
32	Mn	Th	0.00026
33	Mn	Si	0.00051
34	Mg	Zn	0.00007
35	Mg	Sn	0.00021
36	Mg	Co	0.00001
37	Ca	Zr	0.000038
38	Ca	Th	0.00042
39	Ti	Cu	0.00045
40	Ti	Ce	0.0027
41	Ti	Sn	0.00018
42	Ca	U	0.0006
43	Zr	Ce	0.1436
44	U	Ce	0.0245
45	U	Si	0.0021

Table 2. (cont.)

Correction no.	Interfering element	Affected element	Correction factor (μg/μg)
46	U	Cu	0.0016
47	U	Zn	0.00027
48	U	Ni	0.00067
49	U	Se	0.0019
50	U	Th	0.0075
51	U	P	0.00149
52	U	Co	0.00062
53	U	Cd	0.00011
54	U	Sb	0.0013
55	U	Sn	0.00127
56	U	Zr	0.00024
57	Zn	Mo	0.000268
58	Zn	As	0.0002
59	Zn	Sb	0.0015
60	Zn	Si	0.00059
61	Mo	Si	0.0119
62	Ce	Al	0.0115
63	Ce	Th	0.0386

4.3.1 Elements not in our spectrometer array:

The effect of spectral lines of interferent elements can be predicted, observed, and their magnitude defined relative to their concentration. Another analytical method would be required to provide the necessary quantitative data to correct the data manually.

4.3.2 References are available at MSL that document spectral lines of interferent elements coincident with analytical lines used for quantitative measurements. (References 12.5, 12.6.) A compilation of potential interfering elements for the analyte lines used in our spectrometer is given in Table 3.

4.4 Other corrections available:

4.4.1 Off-line background measurement with subsequent correction performed automatically is an alternative for interferences of the type described in Sections 4.1.2 and 4.1.3. This requires extensive investigation into sample type, total dissolved solids of the solutions, acid strength, etc. to properly apply. This procedure, to date, has not been used in routine analyses.

5.0 APPARATUS

5.1 Applied Research Laboratories ICPQ #137000 Quantometric Analyzer consisting of: (refer to ICPQ system schematic: Figure 1)

a. Thirty-four element direct reading polychromator
b. Rf generator (3 kW maximum)
c. Digital PDP-11/04 computer with dual floppy disks for instrument operation, data reduction and data storage.

5.2 Operating parameters for the ICPQ #137000

a.	incident power	-	1.6 kW
b.	plasma gas	-	argon
c.	plasma gas flow rate	-	1.5 L/min.
d.	coolant gas flow rate	-	10.5 L/min.
e.	carrier gas flow rate	-	1.1 L/min.
f.	solution uptake rate	-	2.8 mL/min.
g.	observation height	-	18 mm above coil
h.	diffraction grating	-	1080 grooves per mm

5.3 Torch and association hardware

a. Meinhard nebulizer
b. Fassel design torch
c. Scott spray chamber

6.0 REAGENTS/MATERIALS

6.1 Argon gas (commercial welding grade or better).

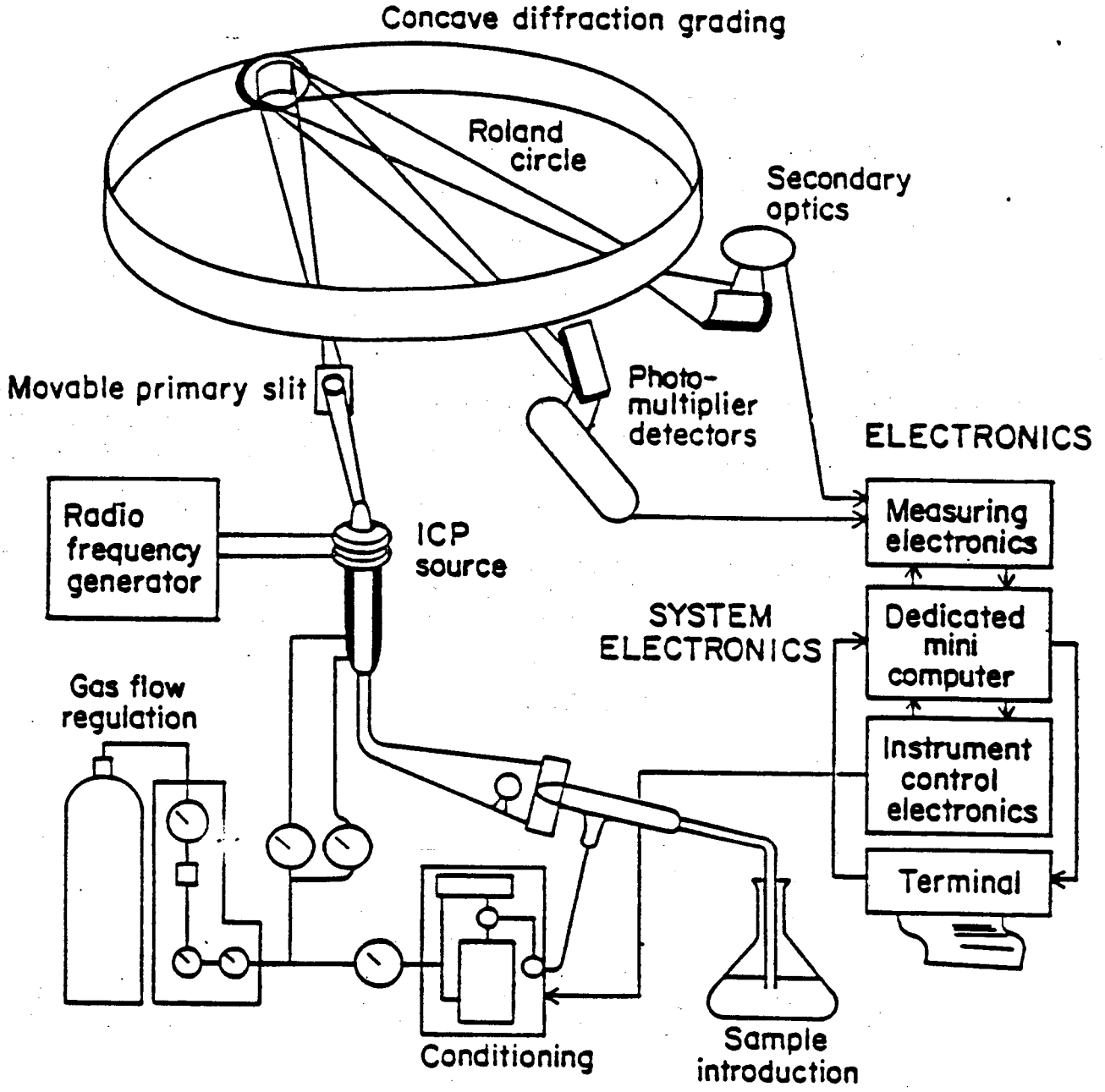
Table 3. Potential interferences requiring manual correction.

Analyte element	Spectral line (nm)	Potentially interfering elements (within 0.08 nm)	Reference table*
Al	308.215	Er,Lu,Tb,Ta,Gd,Pr,Ho,Re,Dy	14
As	193.696	none	20
B	249.678	Re,Ta,Ir,Gd, Os,Ru,W,Hf	46
Ba	455.403	Yb,Ta,Nb,Sm,Ru	49
Be	234.861	none	60
Ca	315.887	Re,Ho,Gd,Pr,Tb,Ru,Ta,Ir,W	87
Cd	226.502	Re,Os,Ir,Te	93
Ce	418.660	Pr,W,Nd,Nb,Tb,Sc,Dy	105
Co	238.892	Nb,Ta,Re,Tm,W,Pt	116
Cr	267.716	Ta,Hf,Ir,Dy,Re,Tm,Te,Pt,Lu,W, Nb	132
Cu	324.754	Tm,Tb,Ho,Eu,Nb,Hf,Os	150
Fe	259.940	W,Ir,Os,Hf,Re,Dy	207
La	379.478	W,Nb,Os,Ho,Ru,Pr,Tm,Gd,Nd	329
Li	670.784	Sm,Ru	346
Mg	279.079	Ta,Os,Re,Ho,Rh,Y,Tm,Dy	371
Mn	257.610	Rh,Re,Nb,Hf	376
Mo	202.030	Os	390
Na	589.592	Tm	406
Ni	231.604	Ir,Ta,Pt,Tl	446
P	213.618	none	473
Pb	220.353	none	484
Sb	206.833	Ge	588
Se	196.026	Bi	628
Si	251.611	Re,Hf,Pt,Bi,Rh,Yb,W	633
Sn	189.980	none	660
Sr	407.771	Yb,Y,Rh,Nd,Hg,Er,Dy,Eu,Gd	674
Th	401.913	Re,Tb,Nd,W,Gd,Sm	728
Ti	368.520	W,Tb,Dy,Ho,Pr,Nd	754
U	385.958	Nb,Pr,W,Ho,Nd,Ta	782
V	310.230	Os,Ta,Tm,Gd,Dy,Yb,Sm,Tb,Er,Ho,Re	799
Zn	202.548	W	860
Zr	343.823	Er,Tm,Re,Ho,Sm,Hf,Ru,Ta,Tb,Yb,Dy	872

*Line coincidence tables for inductively coupled plasma atomic emission spectrometry, Boumans, Pergamon Press, 1984.

Note: Potassium and rubidium were not included in this compilation.

Figure 1



NOTE: Consumption rate is approximately 25 cu. ft. per hour.

6.2 Distilled-deionized water of high quality.

6.3 Glassware or plasticware appropriate for sample dilutions (to include pipets, volumetric flasks, etc.).

6.4 Acids (reagent grade or better) to include nitric, sulfuric, perchloric, and hydrochloric.

6.5 Supplies necessary to support the computer system.

6.6 Single element stock solutions prepared from ultrapure materials for each element to be analyzed (to be used to prepare multi-element solutions required for routine calibration of the instrument).

7.0 PREPARATION OF APPARATUS

7.1 Begin operation of the ICPQ system by following the step-by-step procedure in the operator's manual (this manual written by MSL from literature and training provided by the manufacturer and includes necessary safety information).

7.2 Let system warm up in full operation for at least 30 minutes.

7.3 Profile the primary slit for peak signal while aspirating a low concentration of manganese (see instrument operation manual).
NOTE: This process will optimize all channels of the spectrometer simultaneously.

8.0 CALIBRATION/STANDARDIZATION

8.1 Requirements of a calibration scheme for ICP applications:

8.1.1 All elemental concentrations expected in the unknown sample solutions should be within the calibrated range. (Preferably in the linear response region of the instrument.)

8.1.2 Matrix composition in all of the calibrating solutions should match (acid strength, etc.).

8.1.3 Interfering elements must be measured and therefore must be included in the calibration scheme so the appropriate corrections will automatically be applied.

8.1.4 Adequately define analytical range by preparing a series of solutions containing varying concentrations of the elements of interest with reasonable intervals for non-linear situations.

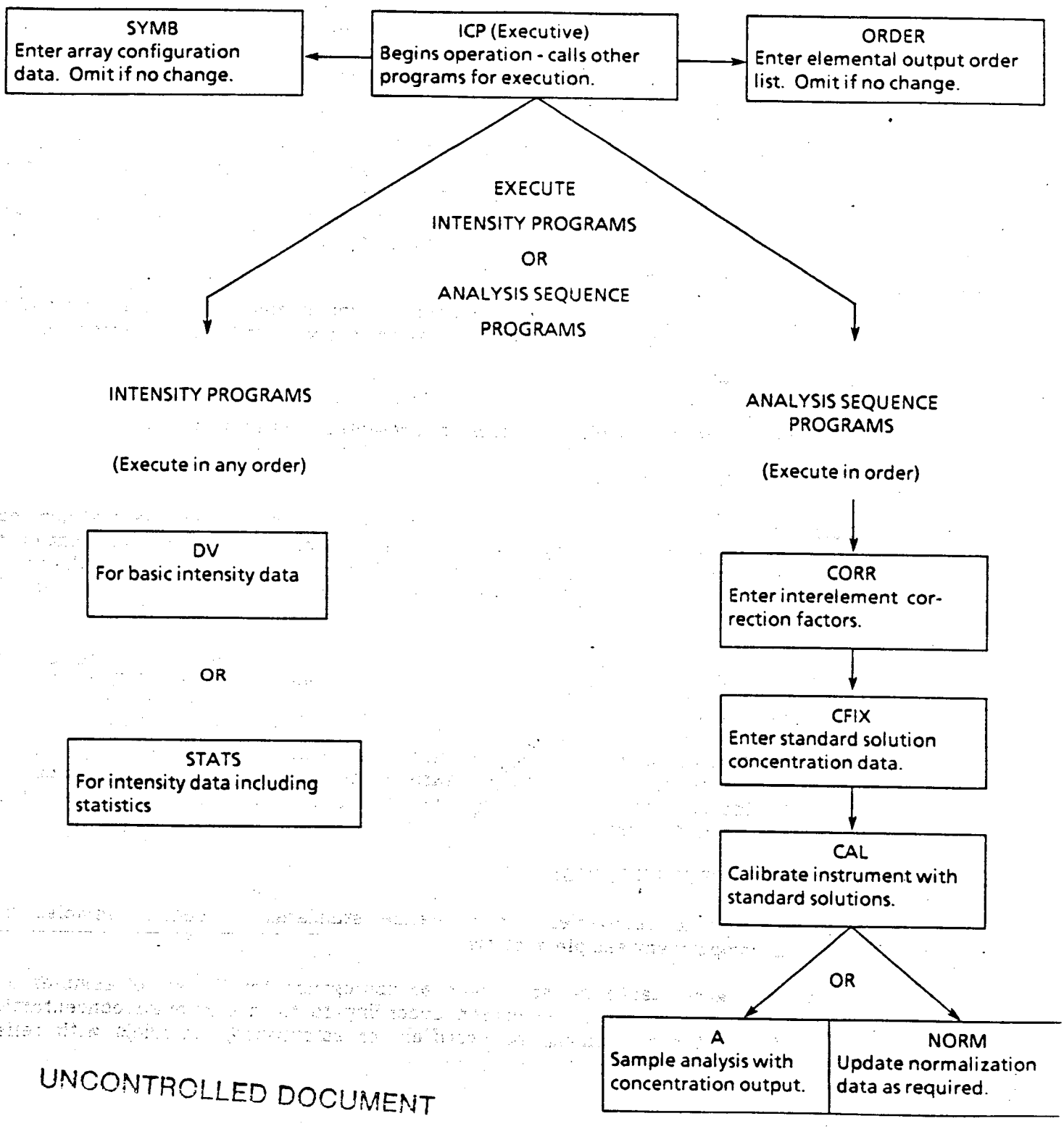
8.1.5 Specific calibration schemes will be presented in later sections in detail.

8.2 Once a calibration scheme has been prepared and tested for applicability and performance, the system is calibrated by following these steps: (Refer t Figure 2.)

Figure 2

ICPQ BLISS OPERATION

Program Execution Order



8.2.1 Prepare the computer for collection and storage of the instrument measurements by running commands: CORR, SYMB, ORDER, and CFIX from command file ICP.

8.2.2 Complete section 7.

8.2.3 Enter instrument measurements for calibrating solutions by running command CAL and introducing these solutions sequentially to the plasma. The CAL program ends with the output of the 'calibration table' which is used to quantitate the elements in the subsequent measurements.

8.2.4 After viewing the resultant 'calibration table' to verify that there are no problems (i.e. a poor calibration solution, an unsatisfactory measurement, etc. as indicated by the measurement and curve fit statistic) the analysis of solutions to determine unknown concentrations of elements resumes by sequentially running command A and introducing sample solutions to the plasma.

8.2.5 The calibration can be updated by running command NORM. Normalization is necessary to compensate for analyzer drift due to various factors.

9.0 PROCEDURE

9.1 Procedures for specific analyses are presented in later sections.

10.0 DATA HANDLING

10.1 Analytical results are stored permanently on floppy disk with several hard copy outputs available at any time. Detailed records of pertinent information are recorded in the appropriate procedure log book. Recorded data will include: 1) sample ID, 2) dilution factor, 3) calibration file name, 4) data storage file name, 5) date, 6) operator, 7) project, and 8) operator comments.

10.2 All calculations of results are performed automatically by the provided software of the system. Basically, the measurements are made, the equivalent concentration is determined from the calibration table, the effect of interfering elements is subtracted from the total concentration, and then the results are printed out prior to the analysis of the next sample. The results routinely include repeated measurement statistics that enable the experienced operator to identify data that are not reliable due to system performance below accepted standards.

11.0 QUALITY ASSURANCE/CONTROL

11.1 Acceptable recoveries for reference standards or control samples must accompany any sample analysis.

11.2 Reference standards used should be appropriate for the set of samples to be analyzed and should be chosen according to their elemental concentrations. These standards should be certified, or established, materials with reliable elemental values.

11.3 Optimum, reproducible day-to-day performance is of concern. Analysis of reference materials can be a vehicle for realizing long-term performance and is currently used. Another method to monitor this performance is under investigation at the Mineral Studies Laboratory and involves monitoring of both an atom and ion generated spectral line and adjusting the ICP parameters to establish and maintain a stable relative performance on an extended time basis. (Refer to 12.4.)

12.0 BIBLIOGRAPHY AND REFERENCES

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BUREAU OF ECONOMIC GEOLOGY
THE UNIVERSITY OF TEXAS AT AUSTIN

SPECIFIC WORK INSTRUCTION

TITLE	REVISION: 0
DETERMINATION OF MAJOR, MINOR, AND TRACE ELEMENTS BY ICP-OES: BRINE WATERS **SWI 1.6**	DATE: 04-13-87 PAGE: 1 OF 9

APPLICABILITY	SUPERSEDES
BUREAU-WIDE	THIS IS THE ORIGINAL ISSUANCE

APPROVAL	CONCURRENCE
DIRECTOR 4/14/87 DATE	Not applicable PROGRAM DIRECTOR DATE Carolyn Condon 4/15/87 QUALITY ASSURANCE MANAGER DATE

1. SCOPE

1.1 This method covers the analysis of brine samples for up to thirty-four elements simultaneously with a direct reading inductively coupled plasma-optical emission spectrometer (ICP-OES).

1.2 This method augments SWI 1.5 "Determination of Major, Minor, and Trace Elements by ICP-OES: General Setup and Analysis."

1.3 This procedure assumes that the analyst has a fundamental understanding of ICP-OES and a basic familiarity with the Applied Research Laboratories ICPQ #137000 Quantometric Analyzer. The procedure does not purport to review the fundamentals underlying the technique or to substitute for the instrument operating manuals. Rather, it is intended to document the actions required for normal, accurate, and reliable use of the technique.

2. SUMMARY OF METHOD

2.1 Brine water samples are treated to obtain an appropriate solution matrix (i.e., acid strength, total dissolved solids, etc.).

2.1.1 Determination of chloride concentration in the brine precedes analysis by ICP-OES. This enables the analyst to estimate the appropriate dilution required to result in sodium concentrations near 1000 milligrams per liter. This solution is analyzed for

sodium, potassium, magnesium, and calcium. A dilution factor of 50 to 100 is typical for medium to highly concentrated brines.

2.1.2 A more concentrated solution of the brine is analyzed for any minor or trace cations for which our spectrometer is capable. A dilution factor of 2.5 is used for highly concentrated brines and a factor of 1.25 is used for others.

2.2 Following instrument standardization, the sample solutions are analyzed sequentially.

3. SIGNIFICANCE

3.1 General advantages of ICP-OES include:

3.1.1 Freedom from chemical interferences normally associated with atomic absorption spectroscopy (AAS).

3.1.2 Very wide dynamic quantitatable range (compared to AAS).

3.1.3 Simultaneous analysis of 34 elements (AAS is capable of only one element per analysis).

3.1.4 Computer data reduction in real time enabling the application of predetermined inter-element interference correction factors to be applied prior to data viewing. (Routinely, greater than sixty factors are applied to each analysis.)

3.1.5 Computer assisted operation enabling high sample throughput.

3.1.6 Equal or greater sensitivity for most elements compared to AAS. Elements having greater sensitivity by AAS include: lithium, sodium, potassium, rubidium, cesium, rhodium, lead, and cadmium.

3.1.7 Very efficient excitation medium (argon plasma with peak temperatures of approximately 10,000 degrees Kelvin utilized).

3.2 ICP-OES demonstrates quality, high throughput, simultaneous elemental analysis of diluted brine water samples.

3.3 Elements in the spectrometer array are not significantly affected by the emission spectrum from high concentrations of sodium.

4. INTERFERENCES

4.1 Spectral interferences (refer to SWI 1.5 section 4 and SWI 1.5 Table 2 for a discussion of spectral interference identification and correction).

5. APPARATUS

5.1 Applied Research Laboratories ICPQ #137000 Quantometric Analyzer (refer to ICPQ system schematic: SWI 1.5 Figure 1).

6. REAGENTS/MATERIALS

6.1 Argon gas (commercial welding grade or better).
Note: consumption rate is approximately 25 cu. ft. per hour

6.2 Distilled or deionized water of high purity (ASTM Type II or equivalent)

6.3 Glassware and plasticware appropriate for sample dilutions (to include pipettes, volumetric flasks, etc.).

6.4 Hydrochloric acid solution (HCl); 6N (distilled).

6.5 Supplies necessary to support the computer system.

6.6 Single element stock solutions prepared from ultrapure materials for each element to be analyzed (to be used to prepare multi-element solutions required for routine standardization of the instrument).

6.7 Electric hot plates and steam bath.

7. PREPARATION OF APPARATUS

7.1 Set attenuator for each detector (refer to Table 1).

7.2 Begin operation of the ICPQ system by following the step-by-step procedure in the operators' manual.

7.3 Let system warm up in full operation for at least 30 minutes.

7.4 Profile the primary slit for peak signal while aspirating a low concentration of manganese (see instruction manual).
Note: this process will optimize all channels of the spectrometer simultaneously.

8. STANDARDIZATION

8.1 Standardization of the ICP-OES system for analyzing brine waters is accomplished with a set of standard solutions (refer to Table 1) prepared from single element stock solutions. These solutions contain 34 elements in various concentrations in order to adequately standardize each channel of the spectrometer. All standards are prepared to contain 10% hydrochloric acid (HCl).

8.2 Prepare the computer for collection and storage of the instrument measurements by running commands: CORR, SYMB, ORDER, and CFIX from command file ICP.

8.3 Complete section 7 above.

8.4 Enter instrument measurements for standard solutions by running command CAL and introducing these solutions sequentially to the plasma. The CAL program ends with the output of the "calibration table," which is used to quantitate the elements in the subsequent measurements.

TABLE 1

CALIBRATION SCHEME FOR WATERS (CWAT9)

Sol#: / Element:	#1	#2	#3	#4	#5	#6	#7	#8	#9	ATTEN. SET (CF)*
Na	0			50	100	200	500	1000	2000	10-5
K	0			50	100	500	200		20	11-3
Mg	0			50	100	500	200		20	10-4
Ca	0			1000	500	200	100		5	8-2
Al	0	10	20							9-2
Fe	0	10	20							9-11
Ti	0	10	20							9-8
Co	0	10	20							11-1
Cr	0	10	20							10-9
Cu	0	10	20							10-2
Mn	0	10	20							10-3
Ni	0	10	20							11-1
V	0	10	20							8-11
Zn	0	10	20							11-11
As	0	10	20							10-8
Cd	0	10	20							11-4
Mo	0	10	20							11-4
Pb	0	10	20							10-4
Sb	0	10	20							11-8
Se	0	10	20							11-11
Sn	0	10	20							10-7
Li	0	10	20							10-1
Be	0	5	10							10-4
Sr	0	100	20	50						9-2
Ba	0					20		50		8-8
Zr	0	10	20							10-6
U	0	10	20							8-5
Th	0	10	20							9-4
B	0	10	20							10-5
P	0					20				10-8
Ce	0	10	20							8-1
La	0	10	20							9-6
Rb	0	10	20							11-11
Si	0	10	20							10-6

All values are milligrams per liter (mg/L)
All solutions are ten percent hydrochloric acid by volume
*(C-F)= coarse-fine...sets the operating voltage for each detector

8.5 After viewing the resultant "calibration table" to verify that there are no problems (i.e., a poor standard point, a poor curve fit indicated by high RMS error), the analysis of solutions to determine unknown concentrations of elements resumes by running command A and measuring, in proper order, the sample and associated solutions.

8.6 The standardization can be updated by running command NORM. Normalization is necessary to compensate for analyzer drift due to various factors. The frequency of this operation is normally determined by analyzing a control solution after each 10 to 15 samples. The results of this measurement will indicate when analysis performance is outside of accepted limits, and therefore when normalization is required. The analyst should critically view any results obtained prior to the realization of unacceptable analyzer performance, and should reanalyze all samples suspected to be in error.

8.6.1 Normalization involves rerunning standardizing solutions that were designated during execution of CAL (one low concentration--blank--and one high concentration--depending on elemental concentrations in the samples--for each element). This program calculates factors to update the "calibration table" and applies them automatically to the subsequent measurements.

9. PROCEDURE

9.1 Prepare samples for ICP-OES measurements: (use field filtered-acidified split if available)

9.1.1 SOLUTION A: Review chloride results to determine the appropriate dilution required to obtain a solution whose sodium concentration is near 1000 milligrams per liter. Pipette accurately the determined aliquot into a clean 50 or 100 mL volumetric flask. Add 20% (x mL) 6N hydrochloric acid, dilute to three-fourths volume with double deionized water (DI-H_2O). Heat on hot plate or steam bath at approximately 90 degrees C for at least 30 minutes. Cool, dilute to volume with DI-H_2O, and mix well.
Note: In many cases, both strontium and barium can also be quantitated using this solution since these elements have low detection limits and may be abundant in brines.

9.1.2 SOLUTION B: For minor and trace cations in highly concentrated brines (>100,000 mg/L Cl), pipette accurately 10 mL of the sample into a 25 mL volumetric flask. Add 5 mL of 6N HCl, heat as in 9.1.1, cool, dilute with DI-H_2O. For less concentrated brines, use a 20 mL sample plus 5 mL 6N HCl in a 25 mL volumetric flask.
Note: Silicon is normally analyzed from solution B if requested, and should be prepared in plastic volumetric flasks.

9.2 Analyze SOLUTION A

9.2.1 Analyze this solution for sodium, potassium, magnesium, and calcium. (Include strontium and barium if appropriate.)

9.2.2 Use standard sea water as a reference sample. (For reference values see Table 2.)

9.2.3 Verify that the accuracy for the determined elements is within five percent of the "reference" values for standard sea water.

9.2.4 Monitor extended time performance by reanalyzing the sea water frequently (i.e., every 10 to 15 samples). If the results are not within acceptable limits (usually within five percent of the reference value or as specified by the requestor), discontinue analyses and update the calibration table by running command NORM and measuring the appropriate solutions.

9.2.5 Resume analyses by first analyzing the sea water reference standard, then samples as above.

9.2.6 Accept data for samples only after, and concurrent with, satisfactory match between measured and reference concentrations of the elements in standard sea water.

9.3 Analyze SOLUTION B

9.3.1 Analyze this solution for other elements in the brine water that are among the elements of the spectrometer array. Trace elements require a minimum amount of dilution to avoid falling below the elemental detection limits of the system.

9.3.2 Elemental abundances that are near detection are prone to high percentage errors and should be viewed accordingly. Data close to the detection limit of each element are routinely "flagged" by the the system and ultimately indicated on the final report.

9.3.3 Verify that the accuracy for the determined trace elements is within 15 percent (relative) of the reference values.

9.3.4 Perform system normalization when substandard conditions exist, as per 8.6 and 9.2.4.

10. DATA HANDLING

10.1 Analytical results are stored permanently on floppy disk with several printout options available at any time. Detailed records of pertinent information is recorded in the appropriate procedure log book, and is to include:

1) dilution factor for each sample
2) acid concentration
3) calibration file name used
4) data storage file name used
5) date of analysis and
6) any comments.

10.2 All calculations of results are performed automatically by the software provided by the system.

TABLE 2

STANDARD SOLUTIONS FOR WATER ANALYSIS

STD: Element	ICAP-23 EPA	ICAP-3 EPA	476#2 EPA	478#4 EPA	std. sea water
Na	1.0		40.0		11,040
K	10.0		7.2		409
Mg	1.0		7.1		1,320
Ca	1.0		32.0		422
Al	1.0			0.852	
Fe	1.0			0.796	
Ti	1.0				
Co	1.0			0.348	
Cr	1.0			0.304	
Cu	1.0			0.374	
Mn	1.0			0.478	
Ni	1.0			0.165	
V	1.0			0.848	
Zn	1.0			0.478	
As	1.0			0.182	
Cd	1.0			0.059	
Mo	1.2				
Pb	1.0			0.383	
Sb	1.0				
Se	1.0			0.048	
Sn					
Li					
Be	1.0			0.261	
Sr	8.1				8.1
Ba	1.0				
Zr					
U					
Th					
B		1.00			
P					
Ce					
La					
Rb					
Si		0.47			

EPA values listed are "true values"
Values for standard sea water are "reference values"
All data given in mg/L

10.3 Interpretation of the data produced by the computer should include:

10.3.1 Correlation of analyzed values for reference solutions with either "reference" or "certified" values and recognition of any discrepancies in the data set.

10.3.2 Recognition of data that is outside acceptable limits.

10.3.3 Rounding off of each data point to indicate the proper "significance." Do not report data with more than four significant figures.

11. QUALITY ASSURANCE/CONTROL

11.1 Replicate samples and reference standards (similar in composition to the samples analyzed) should be analyzed with all samples to provide precision and accuracy estimates for the analysis. In the absence of suitable reference standards, analysis of samples spiked with known amounts of analyte will suffice for the accuracy estimate. Maximum allowable accuracy for this procedure is +5% and +25% relative for major (Na, K, Mg, Ca) and trace elements, respectively. Maximum allowable precision for this procedure is 15% relative standard deviation (rsd).

11.2 Standard reference materials simulating a brine matrix are not available for these determinations. Dilute solution round-robin samples are available from the Environmental Protection Agency (EPA). These solutions are used to verify the applicability of the ICP-OES standardization scheme and as reference samples for these analyses (although some elements are not included - refer to Table 2).

11.3 Standard solutions used should be appropriate for the set of samples to be analyzed and should be chosen according to their elemental concentrations. These standards should be certified (see Table 2), or traceable to established reference solutions such as those available from the National Bureau of Standards (SRM Numbers 2121, 2122, 2123, 2124, 2125, 2126, and 2127, certified for Cd, Pb, Zn, Ba, Ca, Mg, Sr, Li, K, Na, Rb, B, Cr, Mn, Mo, Sb, As, Se, Sn, Co, Cu, Fe, Ni, Al, Be, P, and Si).

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Determination of Arsenic in Geologic, Biologic, and Water Samples by Flameless Atomic Absorption Spectrophotometry and Inductively Coupled Plasma Atomic Emisson Spectrometry Following Distillation

REFERENCE: Ho. C. L., Tweedy, S., and Mahan. C., **"Determination of Arsenic in Geologic, Biologic, and Water Samples by Flameless Atomic Absorption Spectrophotometry and Inductively Coupled Plasma Atomic Emission Spectrometry Following Distillation,"** *Journal of Testing and Evaluation*. JTEVA. Vol. 12, No. 2, March 1984. pp. 107-113.

ABSTRACT: A distillation method was used to separate arsenic trichloride from interfering substances in the presence of hydrochloric acid, hydrobromic acid, and hydrazine sulfate. Arsenic in distillate was determined by flameless graphite furnace atomic absorption spectrophotometry (GFAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). Liberation of arsenic trichloride by distillation was not inhibited by NO_3^-, Ni^{+2}, or other substances encountered in geological, biological, and water samples. Free nitric acid must be neutralized with potassium carbonate or removed by evaporation in the presence of sulfuric acid at 160°C (320°F) before arsenic trichloride distillation. Geochemical reference samples, U.S. Environmental Protection Agency (EPA) water standards, geological samples, and water samples were analyzed. Results of distilled arsenic trichloride in all reference samples agreed with the reported values. Without distillation, agreement with reported values was obtained only in water samples containing low matrix substances.

KEYWORDS: arsenic, distillation, water, graphite furnace, atomic absorption spectrophotometry, inductively coupled plasma atomic emission spectrometry

Arsenic deposits often occur near uranium mineralization zones [*1-4*]. Arsenic in coals shows more affinity for the inorganic fraction than for the organic part [*5*]. Gluskoter [*6*] showed that arsenic was probably associated with sulfide minerals in coal. Because of the widespread association of arsenic with uranium, noble metals, and many other ore deposits, arsenic levels in rocks, soils, sediments, and plants are used in mineral exploration [*7*].

The background level of arsenic was reported to be 0.4 μg/L in fresh water and 3 μg/L in seawater [*8*]. In oxidizing waters, arsenic exists as arsenate ions whereas in the presence of sulfide, the soluble arsenate is immobilized as arsenic sulfide [*9*].

Arsenic in coal may be in trace amounts, but use of large quantities of coals may release arsenic to the environment if the arsenic emission as vapor [*10*] is not effectively controlled. Leaching arsenic-containing sulfide minerals in mining areas by oxygenated meteoric water could also liberate arsenic as soluble arsenate to water systems.

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According to Thurston [*9*] the toxic level of arsenic in drinking water has not been properly defined.

The most commonly used method for arsenic determination involves reduction of As^{+5} and As^{-3} to arsine gas (AsH_3) and subsequent measurement of AsH_3 by a colorimetric method [*11*] or by flameless atomic absorption spectrophotometry [*12,13*]. The colorimetric method lacks the sensitivity needed to detect low arsenic concentration in water samples. The shortcoming of arsine generation has been the potential interference by substances in the sample matrix such as NO_3^- and certain metal ions, especially nickel (Ni^{+2}) [*12,14,15*]. Recent improvement in arsine generation has been reported by using aluminum as a reducing agent [*16*] for water containing up to 200-mg NO_3^-/L and by using a new reductant, BH_3CN^-, instead of the commonly used sodium borohydride in the presence of high Ni^{+2} concentration [*17*]. Aslin [*12*] showed that addition of ethylenediamine tetraacetic acid (EDTA) to the sample solution to complex Ni^{+2} could mitigate the suppressive effect of Ni^{+2} for arsine generation using sodium borohydride as a reductant. Nevertheless, Aslin's results on arsenic for the three U.S. Geological Survey (USGS) reference materials (GXR-1, GXR-2, and GXR-6) were significantly lower than those reported by Gladney et al [*18*].

Flameless atomic absorption spectrophotometry using a graphite furnace atomizer is a simple and ultrasensitive method for arsenic measurement. In practice, we have experienced serious difficulties in our laboratory in obtaining the desired accuracy and reproducibility in analyzing water samples that contain a high level of salts and in analyzing geological samples of varying metals content. These difficulties resulted, in part at least, from the following causes: (1) vaporization of residual salts and their redeposition on optical windows during atomization, thus accounting for the gradual reduction in absorbance signal; (2) corrosion of the graphite furnace tube surface by salts in the matrix; and (3) formation of arsenic complexes with unknown elements in the matrix, resulting in enhancement or suppression of the analyte to be measured. An extensive investigation by Chakraborti et al [*19*] has indicated that matrix effects play an important role in the determination of arsenic with graphite furnace atomic absorption spectrophotometry (GFAAS). The alkali metals sodium or potassium, sulfate, and aluminum all strongly interfere with the determination. Matrix modification with nickel salts does not prevent these interferences. Chakraborti et al concluded that accurate arsenic determination by GFAAS requires prior separation of the analyte from the matrix [*19*]. To mitigate the matrix effect, stan-

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dard addition has been adapted as a routine procedure for GFAAS analysis of trace elements including arsenic [*20*]. This procedure is time-consuming, and the chief drawback still remains, that is, systematic errors of various magnitudes as a result of matrix interferences cannot be eliminated.

Distillation of arsenic as arsenic chloride ($AsCl_3$) has not been as widely used for separation of arsenic as for arsine generation because arsenic chloride requires a 108°C (226°F) temperature and a strong hydrochloric acid medium for its vaporization [*11*]. However, separation of arsenic as arsenic chloride from complex matrix by distillation does have some advantage as compared to that by arsine generation. Unlike arsine generation, metal ions such as Ni^{+2} dissolved from geological samples; high salts content in brine and NO_3^- in wastewater do not interfere with the reduction of As^{+5} to As^{+3} nor inhibit the subsequent release of arsenic chloride during distillation.

The objectives of our investigation are (1) to develop a rapid distillation procedure for separation of arsenic chloride from various types of solution matrixes and (2) to analyze the arsenic in the distillate by GFAAS and inductively coupled plasma atomic emission spectrometry (ICP-AES).

Experimental Section

Distillation Apparatus

The distillation apparatus shown in Fig. 1 was assembled from parts (ACE Glass, Inc.).

Sample Dissolution for Determination of Arsenic by Distillation GFAAS

Geologic Samples (Soils, Sediments, Rocks, Ores)—Weigh 0.05- to 0.1-g samples (< 200 mesh) containing up to 5-μg arsenic and mix with 0.5-g flux [*11*] (potassium carbonate plus magnesium oxide at a weight ratio of three to one) on a piece of glassy weighing paper. Pour mixture into a 10-mL graphite crucible (Spex Industries). Fuse sample at 900°C (1652°F) in a muffle furnace for 20 min. After cooling, transfer the sample into a 100-mL distillation flask using a small spatula.

Biological Samples—Weigh 0.5- to 1.0-g finely ground plant material (< 200 mesh; 2.5- to 5.0-g wet homogenous animal tissue) into a 50-mL culture tube. Add 10-mL distilled, concentrated nitric acid. Let the contents sit at room temperature until the foam subsides. Heat contents at 100°C (212°F) followed by digestion at 140°C (284°F) on a Technicon BD-40 digestion block until contents turn white and dry. Transfer and wash contents into the distillation flask using a 2-mL aliquot of distilled 6*N* hydrochloric acid until a total volume of about 6 mL but less than 10 mL is obtained.

Water Samples—Evaporate 50- to 100-mL water with 2-mL concentrated nitric acid in a beaker on a hot plate until dry. If the sample contains organic matter, then digest the residue with concentrated nitric acid until the residue becomes white. Transfer contents into a 100-mL distillation flask using 6*N* hydrochloric acid, as described for biological samples.

Distillation Procedure—Attach a 50-mL beaker containing 5 mL of 5% nitric acid to a condenser tip and submerge into the nitric acid for arsenic chloride absorption. Add about 0.5-g hydrazine sulfate and 2-mL concentrated hydrobromic acid to a distillation flask and a few pieces of Carborundum® as boiling chips. Secure flask onto distillation apparatus using metal springs. For geologic samples introduce 5-mL 6*N* hydrochloric acid into a flask slowly through a separatory funnel followed by 2-mL concentrated hydrobromic acid (for biological and water samples, only hydrazine sulfate, boiling chips, and hydrobromic acid are needed). Heat the distillation flask with a small Bunsen burner until the residue in the flask becomes brownish and oily. Complete distillation takes for about 3 to 4 min. Arsenic chloride in aqueous hydrochloric acid is distilled at a temperature not exceeding 108°C (226°F) [*11*]. A standard arsenic solution of 5 μg and a blank must also be distilled under the same conditions as the samples. Excess hydrochloric acid is removed by evaporation on a hot plate until nearly dry. Add 5-mL nickel nitrate in 1% nitric acid into a beaker to dissolve arsenic for graphite furnace analysis. Our tests showed that arsenic remained as stable arsenate and thus was not lost as arsenic chloride during evaporation as long as nitric acid was present in the medium.

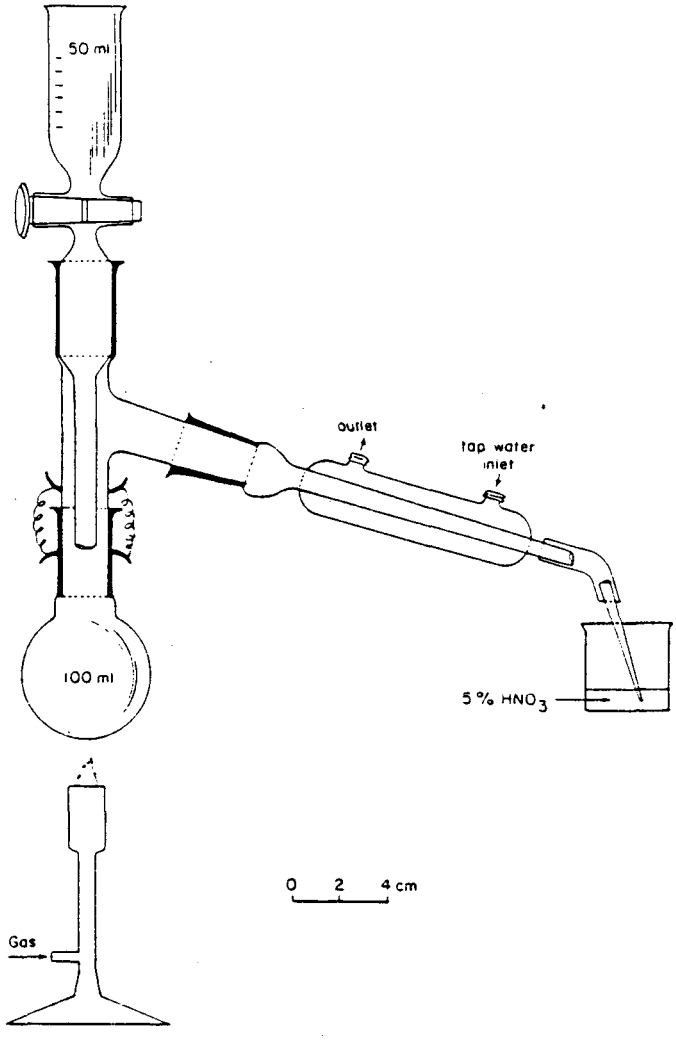

Fig. 1—*Distillation apparatus for arsenic chloride.*

Sample Dissolution for Determination of Arsenic by ICP-AES

Since the detection limit of arsenic by ICP is 0.043 ppm, the arsenic concentration in sample solution must be five times above its detection limit for quantitative measurement (that is, 0.22 ppm). The minimum amount of solution required for aspiration to the plasma torch is 10 mL. Thus, the arsenic content in a sample to be

analyzed by ICP must be greater than 2.5 μg for the following procedure to be applicable. Weigh a 0.5-g sample (< 100 mesh) and mix it with 1-g potassium carbonate plus magnesium oxide flux (or 1-g sample plus 2-g flux; the flux to sample weight ratio should not be less than two, lest incomplete recovery of arsenic occur). Fuse the mixture in a graphite crucible at 900°C (1652°F) for 20 min, as previously described. Distill arsenic chloride with 6-mL of 6*N* hydrochloric acid, 0.5-g hydrazine sulfate, and 2-mL hydrobromic acid until residue becomes oily and brown. Arsenic chloride in distillate is absorbed with 5 mL of 5% nitric acid in a small beaker. Arsenic standards ranging from 2.5 to 50 μg (or higher depending on the highest expected arsenic concentration in samples) and a blank must be distilled in the same manner as samples. Evaporate the excess hydrochloric acid in distillate on a hot plate to near dryness and take up the arsenic to a final volume of 10 mL with 5% nitric acid for ICP analysis.

Instrumentation Parameters

1. The following parameters were used on the atomic absorption spectrophotometer (Instrumentation Laboratories Model 651 equipped with a Model 555 flameless atomizer and a Model 254 autosampler).

wavelength, 193.7 nm;
background correction, deuterium hollow cathode lamp;
deuterium lamp current, 11 mA;
high voltage setting, 620 V;
band width, 1.0, nm;
arsenic cathode lamp current, 8 mA;
mode pressure, 317 kPa (45 psi); and
zero grade N_2 gas flow pressure, 138 kPa (20 psi).

The temperature program used is shown in Table 1. If an Eppendorf® micro-pipet is used, then a sample solution of 10 μL is injected to the graphite tube followed by drying at 75°C for 25 s and at 100°C for an additional 35 s.

2. The following are the parameters used on the inductively coupled plasma atomic emission spectrometer (Applied Research Laboratory QA-137 equipped with a minicomputer for data processing).

spectrometer: 1080 grooves/nm;
radio frequency (RF) generator: 27 mHz operated at 1600 W;
torch: concentric silica tubes;
nebulizer: coaxial, pneumatic; tip desalter, Scott spray chamber;
argon flow: 10.5 L/min for cooling the torch, 1.5 L/min for plasma, and 1.1 L/min for aerosol; and
solution aspiration rate: 2.8 mL/min.

Reagents

1. Magnesium oxide plus potassium carbonate flux mixture—weigh one part magnesium oxide and three parts of potassium carbonate into a large mortar and grind components to a homogeneous powder. Store mix in an airtight jar.

TABLE 1—*Temperature program used.*

Program Cycle	Temperature, °C	Time, s
Drying	125 to 150	4
Char	750, 1100	20 each
Atomization	2200	6

2. Nickel nitrate in 1% nitric acid solution containing 500-μg nickel/mL—dissolve 2.476-g $Ni(NO_3)_2 \cdot 6H_2O$ in 1 L of 1% distilled nitric acid.

3. Five percent nitric acid for arsenic chloride absorption—mix 50-mL distilled, concentrated nitric acid with 950-mL distilled-deionized water.

4. Arsenic standard solution (1-mg arsenic/mL)—dissolve 1.5361-g arsenic pentoxide in 100-mL distilled, concentrated nitric acid and make up to 1000 mL with distilled deionized water. Dilute the arsenic standard stock solution to appropriate concentrations as needed.

Results and Discussion

Reproducibility of Distillation

A typical example is shown by distilling six 5-mL aliquots of arsenic standards of 0.1-μg/mL concentration. Arsenic in distillate was made to a final 5-mL volume with nickel nitrate in 1% nitric acid. Each solution was injected onto the graphite furnace with an automatic sampler. Results are shown in Table 2. A relative standard deviation (RSD) of 5.6% on the six distilled standards was obtained. Nevertheless, this variation was not entirely attributed to the distillation procedure since a variation of a similar magnitude in instrument performance (about 3 to 6%) using a single standard solution was also encountered. This indicates that a precision of about 5% or better can be expected by the distillation procedure.

A calibration curve of distilled standards is shown in Fig. 2. Each point represents a single determination. A linear relationship at an arsenic concentration range of 0.01 to 0.1 μg/mL was readily obtained. All subsequent analyses reported in this investigation were accomplished using a final arsenic solution concentration below 0.1 μg/mL.

Effect of NO_3^-, Free HNO_3, and Ni^{+2}

Since NO_3^-, free nitric acid, and Ni^{+2} are potential interfering substances in arsine generation, it is essential that the degree of inhibition by these components on distillation of arsenic chloride be known before the procedure can be adapted for analysis of arsenic in wastewaters containing NO_3^-, geologic samples containing high nickel, and samples prepared with nitric acid. The recovery of 5-μg arsenic in the presence of these components is shown in Table 3. Clearly, none of these components interfered with the recovery of arsenic as a result of their presence during distillation of arsenic chloride. However, free nitric acid must be neutralized with potas-

TABLE 2—*Precision of six distilled arsenic standards at 0.1 μg/mL each.*

Standard	Absorbance at 193.7 nm
1	0.242
2	0.216
3	0.237
4	0.256
5	0.231
6	0.232
Mean	0.236
SD[a]	0.013
RSD[b]	5.6%

[a] SD is the standard deviation.
[b] RSD is the relative standard deviation.

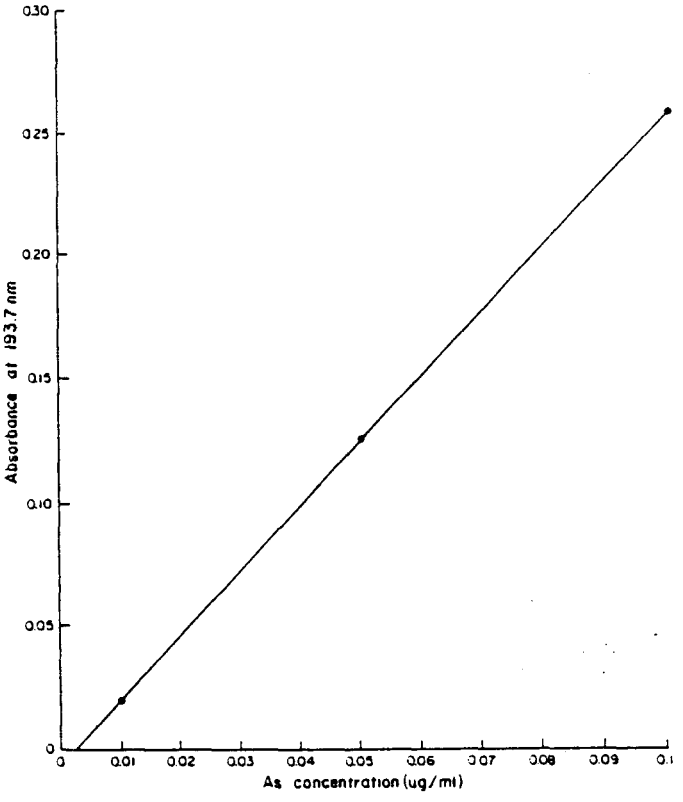

Fig. 2—*Calibration curve for arsenic by GFAAS.*

TABLE 3—*Effect of NO_3^-, free nitric acid, and Ni^{+2} on distillation of 5-μg arsenic as arsenic chloride.*

Interfering Substance	Arsenic Recovered, %[a]
0.4-mg NO_3^- (as KNO_3)	114
0.8-mg NO_3^- (as KNO_3)	104
2.0-mg NO_3^- (as KNO_3)	101
4.0-mg NO_3^- (as KNO_3)	105
5-mg $Ni(NO_3)_2 \cdot 6H_2O$ + 0.5 mL of 1.6*N* HNO_3	106
5-mg $Ni(NO_3)_2 \cdot 6H_2O$ + 0.5 mL of 1.6*N* HNO_3	105
10-mg $Ni(NO_3)_2 \cdot 6H_2O$ + 1.0 mL of 1.6*N* HNO_3	98
10-mg $Ni(NO_3)_2 \cdot 6H_2O$ + 1.0 mL of 1.6*N* HNO_3	104
Control	100
Standard deviation	4.7

[a]Each value represents a single determination. Free nitric acid added was neutralized with potassium carbonate before distillation.

sium carbonate or be removed by evaporation in presence of 2 mL of concentrated sulfuric acid at 160°C (320°F) before distillation. If not, the oxidizing acid will prevent As^{+5} from being reduced to As^{+3}. Free nitric acid also oxidizes hydrobromic acid to bromine. The latter, an oxidizing agent, will further prohibit reduction of As^{+5} to As^{+3}, thus, leading to low recovery for arsenic.

Application of the Distillation GFAAS Technique

The applicability of the distillation GFAAS technique to samples containing low concentrations of arsenic is shown by the results obtained by various laboratory operators analyzing U.S. Environmental Protection Agency (EPA) standard waters (Table 4).

The use of an Eppendorf micro-pipet for sample injection by inexperienced operators contributed to some of the errors in Samples 1 and 2. In spite of the analyst's lack of practical experience, a recovery of 96% of the arsenic at a concentration of 26 ppb can still be achieved without any difficulty.

TABLE 4—*Arsenic in EPA standard waters determined by the distillation GFAAS technique.*

EPA Standard	Reported Value, ppb	Found Value, ppb	Recovery, %
1	26.0	25.2 ± 1.4	97
2	109.0	104.9 ± 8.1	96
3	154.0	156.4 ± 2.3	102

[a]An average of three independent determinations by two operators.

The advantage of the distillation separation of arsenic chloride can be illustrated by the presence of matrix substances. Table 5 shows results obtained for the determination of arsenic in EPA water standards with and without distillation before GFAAS analysis. It can be seen that values for arsenic determined in the distilled EPA water standards agree reasonably well with the reported values, regardless of the concentration and variation in matrix substances present in samples as shown in Table 6. This evidence indicates that the presence of other substances in EPA 378_{10}, $476E_1$, and $476E_2$ did not inhibit the separation of arsenic chloride by distillation. On the contrary, without distillation the reported values on EPA 378_{10}, the diluted EPA $476E_2$, and EPA 378_{10} could not be readily reproduced to the acceptable degree of accuracy under the condition described above. However, when water standards contained no or low matrix substances (for example, laboratory-prepared standards and EPA $476E_1$, respectively, Table 6), arsenic values measured by GFAAS with and without prior distillation were in good agreement. These data suggest that the presence of matrix substances below a certain level can be tolerated in the determination of arsenic by direct injection of sample to the graphite furnace without a serious reduction in accuracy. Nevertheless, when matrix substances exceed a critical level, reliability of results could not be achieved without prior separation of arsenic by distillation. Dilution of such samples to lower the concentration of matrix substances also reduced the arsenic concentration below its detection limit. For example, our experience showed that high salt content in seawater and geothermal brine severely suppressed the arsenic absorbance signal so that

TABLE 5—*Arsenic in standard water samples with and without distillation before graphite furnace atomic absorption analysis.*

Standard Water	Reported Value	Found	
		Distilled	Not Distilled
EPA 378_{10} (no dilution)	40.0	45.1	54.2
378_{10} (1:5)[a]	8.0	8.1	5.8
$476E_1$ (1:2)	12.0	11.9	11.6
$476E_1$ (1:2)	12.0	11.3	...
$476E_1$ (no dilution)	24.0	24.0	...
$476E_2$ (1:5)	36.4	35.9	46.8
Lab prepared			
Standard 1	50	48.5	51.6
Standard 2	20	21.2	19.4

[a]Numbers in parentheses indicate that the sample was diluted two or five times with water.

TABLE 6—*Values for trace metals, μg/L.*

Metal	EPA 476E$_1$	EPA 476E$_2$	EPA 378$_{10}$
Silver	...	...	24
Aluminum	61	852	...
Arsenic	24	182	40
Barium	...	...	335
Beryllium	24	261	...
Cadmium	6.5	59	4.3
Chromium	4.4	304	42
Cobalt	30	348	...
Copper	8.7	374	...
Iron	16	796	...
Lead	30	383	38
Manganese	7.9	478	...
Mercury	0.4	7.6	4.0
Nickel	8.7	165	...
Selenium	8.7	48	7.3
Vanadium	78	848	...
Zinc	6.1	478	...
Strontium	...	...	...

negative absorbance values were invariably obtained. Thus, direct analysis of water samples for arsenic containing high salts has never been successful. Separation of arsenic chloride by distillation effectively eliminated the salt interference. Results are given in Table 7.

Using the distillation GFAAS technique, various types of waters have been routinely analyzed; some typical results are shown in Table 8. High arsenic content was invariably found in oxidizing waters that contained various amounts of NO_3^-. Low levels of arsenic usually occurred in highly reducing waters containing dissolved sulfides.

Determination of Arsenic in Geologic Samples

The number and level of potential interfering substances in geological samples, especially ores, are greater than those in waters. For example, high selenium (Se) often appears in zones of uranium mineralization in south Texas [*4*]. Selenium is known to severely interfere with arsenic measurement by the colorimetric method [*21*]. The present distillation procedure also allows simultaneous liberation of selenium tetrachloride with arsenic chloride in distillate. But the spectral line for selenium at 196.3 nm does not interfere with the arsenic line at 193.7 nm. Table 9 shows the results on arsenic in distilled samples analyzed by both GFAAS and ICP. Results on arsenic determined by ICP using samples prepared by multiple acids treatment (nitric acid plus sulfuric acid plus hydrofluoric acid) without prior distillation are also presented for comparison. It must be stressed that the final sample solution concentrations for ICP analysis were made the same with and without prior distillation so that

TABLE 7—*Arsenic in geothermal water by distillation GFAAS.*

Sample	Salinity, ‰	Arsenic, μg/L
80-1472	6.8	0.8 (0.5)[a]
80-1690	2.0	2.6 (2.3)[a]
80-1925	7.4	3.0
80-2343	0.12	2.4
80-2344	12.5	0.04
80-2345	11.6	1.8
80-2358	140.9	2.3

[a]Values by standard addition following distillation GFAAS analysis.

TABLE 8—*Arsenic content in ground water from south Texas.*

Sample	Arsenic, μg/L
79-193	23.3
79-194	21.8
79-195	<1.0
79-196	4.1
79-197	1.2
79-198	1.4
79-199	<1.0
79-301	38.6
79-640	67.6
79-768	97.5
79-644	118.2

dilution would not constitute a contributing factor to the error. The same distillates were used for the GFAAS and ICP analyses. After distillation, the arsenic measured by GFAAS and ICP showed that the relative standard deviation from the mean values of the two methods ranged from 0.2 to 7.0%. These deviations were significantly lower than those of the reported values obtained using the same method (7 to 25%, Table 9). The presence of matrix substances in the acid digested nondistilled samples led to significantly lower results for arsenic by ICP for GXR-2 and GXR-5 even though chemical interferences were practically absent because of the extremely high temperature of the argon plasma [*22*]. Nevertheless, when the arsenic level is sufficiently high to give a final arsenic solution concentration of greater than 2 μg/mL and a 0.5-g sample is dissolved with acids to make a final solution volume of 25 mL, then a reasonable accuracy on arsenic determination by ICP without prior distillation can still be achieved (for example, GXR-1, GXR-4, and GXR-6 in Table 9).

The accuracy and reproducibility of analyses of arsenic at low concentrations by ICP are shown in Table 10. Without the presence of matrix substances, recoveries of 102 and 99% of arsenic at concentration levels of 0.109 and 0.159 μg/mL, respectively, were readily achieved without prior distillation of the samples. This finding further demonstrates the necessity for separating arsenic from complex matrix substances before ICP measurements will show the expected reliability for arsenic content below a certain level. Inter-element correction is not necessary for distilled arsenic samples to be analyzed by ICP. On the contrary, without distillation, application of inter-element correction factors on arsenic determination by ICP was not sufficiently accurate for low arsenic concentrations relative to the presence of a large amount of matrix substances.

The distillation GFAAS has been routinely used for determination of arsenic in numerous geological samples from south Texas. Some typical results are shown in Table 11.

Again, the chief drawback of the ICP method was that the minimum amount of arsenic required for quantitative determination must be at least 2.5 times above its detection limit of 0.043 μg/mL and ten times higher than that needed for GFAAS (0.01 μg/mL). Thus, it may be expected that samples containing low arsenic (78-1523, and 78-1534) analyzed by ICP would more likely be in error as compared to samples analyzed by GFAAS, even though the same distillates were used in both methods. Nevertheless, when arsenic concentration exceeded its detection limit by more than three times, the precision by ICP was comparable and superior to GFAAS because dilution of samples was not needed, and the high stability of instrument performance (about 2% variability) ac-

TABLE 9-*Analysis of arsenic in reference materials using distillation GFAAS and ICP techniques, μg/g.*[a]

Sample	Reported Value [18]	Fused-Distilled			Acid-Digestion (No Distillation) ICP
		GFAAS	ICP	Mean	
GXR-1	460 ± 30 (7)	454	485	470 ± 22 (5)	501
GXR-2	31 ± 5 (16)	33	31	32 ± 1 (3)	17
GXR-3	4000 ± 450 (11)	4540	4550	4550 ± 7 (0.2)	4550
GXR-4	98 ± 10 (10)	89	84	87 ± 4 (4.0)	105
GXR-5	12 ± 3 (25)	14	14	14 ± 0.4 (3)	10
GXR-6	340 ± 30 (9)	356	381	369 ± 18 (5)	325
SGR-1[b] [23]	74.5	78	71	75 ± 5 (7)	...
Orchard leaves (NBS) 1571	12 ± 3 (25)	13	...	...	...

[a]Numbers in parentheses are relative standard deviation expressed as percent of mean values.
[b]SGR-1 is Green River shale.

TABLE 10—*Analysis of low arsenic by ICP, ppm.*[a]

Sample	Accepted Value	Found Value	Recovery, %
EPA 2	0.109	0.108, 0.116 (0.112)	103
EPA 3	0.154	0.154, 0.152 (0.153)	99

[a]Samples were not distilled because of low concentrations of matrix substances present.

TABLE 11—*Arsenic in geologic samples from south Texas determined by GFAAS and ICP after distillation, μg/g.*

Sample	Same Distillate	
	ICP	GFAAS
78-1504	14.9	15.9
78-1510	8.5	8.5
78-1523	6.2	7.4
78-1534	5.3	8.5
	Different Distillate	
78-1487	24.4	21.8
78-1491	94.9	107.0
78-1500	18.8	15.8
78-1518	43.4	45.0
78-1526	59.5	55.8
78-1529	22.5	18.4
78-1540	14.4	18.5

counted for the reliability of results. Furthermore, the high analytical efficiency of the ICP (about 4 min/sample) is especially suitable for routine analysis of a large number of geological samples. The chief advantage of the GFAAS method was its ultra-sensitivity; thus, the GFAAS method is ideally suited for measuring arsenic in wastewaters and other samples with low arsenic content. After distillation, matrix interferences are eliminated, thus making the time-consuming standard addition method unnecessary.

Summary and Conclusions

Distillation in the presence of hydrochloric acid, hydrobromic acid, and hydrazine sulfate effectively separates arsenic as arsenic chloride from matrix interferences. The distillation process requires about 4 to 5 min for completion. Tests on prepared standards, standard water from EPA, USGS geologic exploration samples, Green River shale (SGR-7) and National Bureau of Standard (NBS) orchard leaves showed that results obtained by distillation GFAAS and distillation ICP were all in reasonable agreement with the reported values. High salt content in seawater and geothermal brine severely suppressed the arsenic absorbance signal invariably to negative values. Thus, without separation of arsenic chloride by distillation, we found that it was impossible to determine arsenic in water containing high salts by GFAAS. Dilution of such samples to lower salt concentration also reduced the arsenic concentration to below its detection limit. Results of laboratory-prepared arsenic standards and some of the EPA water standards containing low levels of salts appeared to be unaffected by distillation. This indicates that certain levels of matrix substances can be tolerated by the GFAAS analysis of arsenic without serious error. Separation of arsenic trichloride from high level of matrix substances was also beneficial for ICP analysis of low arsenic concentrations. Nevertheless, for high arsenic concentrations, results by ICP were comparable with and without prior distillation. Our findings suggest that interference by high levels of matrix substances on arsenic determination by GFAAS and ICP becomes critical particularly at low arsenic concentrations.

The distillation of arsenic chloride was not affected by the presence of NO_3^-, Ni^{+2}, or other metal ions dissolved from geological samples or salts in seawater and brine. Free nitric acid severely inhibited the recovery of arsenic as arsenic chloride since the oxidizing acid yields arsenic in the As^{+5} form, thus preventing reduction to As^{+3} by the mild reducing agent hydrazine sulfate. Free nitric acid oxidizes hydrobromic acid to bromine, which also converts As^{+3} to As^{+5}. Therefore, free nitric acid must be neutralized with potassium carbonate or removed by evaporation in the presence of sulfuric acid at 160°C (320°F) before arsenic chloride distillation.

The methods, distillation GFAAS and distillation ICP, are applicable to samples ranging from salt-saturated brines to ores. The GFAAS method is ultra-sensitive and only a small amount of sample is required (3 to 5 mL of arsenic at a concentration of 0.01 up to 0.1 μg/mL); standard addition is not needed for accurate measurement. The ICP method is less sensitive. The optimum arsenic concentration required for quantitative measurement ranges from 2.5 to 10^4 times the detection limit (0.043 μg/mL). But the latter is noted for its stability (about 2% variability in instrument performance) and high efficiency (4 min per sample, including data processing). Inter-element correction is not needed for distilled samples

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IGT, From M. Tomson, Rice U.

PHOSPHONATES IN BRINES

Principle

Phosphonates are organic phosphorus compounds used to control scale formation. These compounds are UV-catalytically oxidized to orthophosphate by persulfate. The orthophosphate reacts with sodium molybdate in an acidic medium to form molybdophosphoric acid which upon reduction with stannous chloride yields a blue colored complex. This complex has a maximum absorbance at 725 nm and is measured spectrophotometrically.

Interferences

Silicates and arsenates react quantitatively with sodium molybdate to form blue heteropoly acids. The isobutyl alcohol extraction step is designed to eliminate these interferences, and those from other molybdo-metal complexes. Inorganic phosphates or phosphites present may also be included in the phosphonates determination, but their additive effects should be accounted for by the use of the sample blank solution. The following ions which occur in the brine waters may potentially interfere: Al, Fe(III), Mg, Ca, Ba, Sr, Li, Na, K, NH4+, carbonate, nitrate, sulfate.

Apparatus

1. 2 oz. square glass bottles, reaction bottles
2. UV lamp, Hach catalog # 20823-00
3. Pipets, 10 ml, Class A; various Eppendorf pipets
4. Separatory funnels, 125 ml
5. UV-VIS absorption cells, 2, matched, 5 cm path length
6. UV-VIS spectrophotometer, Hitachi Model 100-60

Reagents

1. Perchloric acid, 70% AR grade
2. Molybdate solution: Dissolve 25 g. sodium molybdate in 250 ml deionized water (DDIW).
3. Stannous chloride solution: Dissolve 0.30 g. AR grade stannous chloride in 20 ml concentrated HCl and dilute to 250 ml with DDIW.
4. Isobutyl alcohol, AR grade
5. Methyl alcohol, AR grade
6. Potassium persulfate crystals

7. 1.00 ppm Phosphorus solution: Prepared by diluting 1.0 ml of a commercially bought 1000 ppm stock standard to 1000 ml with DDIW.

Procedure

1. Pipet an aliquot of 10 ml of sample into 5 reaction bottles. Pipet 1, 2 and 3 ml of the 1 ppm standard into 3 of the bottles respectively. This results in spikes of 1, 2 and 3 ug P. Add 1 ml perchloric acid to each. Take appropriate care when dispensing perchloric acid. Allow the solutions to react until all solids are dissolved (approximately 5 minutes).

2. Add 0.1 g potassium persulfate crystals to each of the three spiked bottles and one of the unspiked bottles and immerse the UV lamp in each for 15 minutes.

3. Transfer the contents of each bottle to five separate 125 ml separatory funnels with DDIW washings. Make up to a constant volume with DDIW. To this add 4 ml perchloric acid and mix well. Then add 5 ml of the sodium molybdate reagent. Mix well again and wait exactly 10 minutes.

4. Add 40 ml isobutyl alcohol, stopper the funnel and shake the contents vigorously for 60 seconds. Let the 2 layers separate and discard the aqueous phase (the bottom layer).

5. Add 25 ml DDIW, stopper and shake for 30 seconds. Let the 2 layers separate again and discard the aqueous. Repeat this washing twice.

6. Add 25 ml of the stannous chloride reagent and shake vigorously for 45 seconds. Let the layers separate.

7. Pipet 10 ml off from the top of the organic phase into a clean, dry screw top test tube. Add 0.5 ml methyl alcohol to remove turbidity. Stopper and shake.

8. Measure the absorbance of this solution at 725 nm in the 5 cm path cells. The sample that did not go through the UV digestion step is used to zero the instrument and to fill the reference cell.

Calculation

A graph is made of ug P spike added (x-axis) versus absorbance (y-axis). The method of standard additions is used to extrapolate and calculate the ug of P present in the original sample.

$$\text{phosphonates, mg/l P} = \frac{\text{ug P from graph}}{\text{ml sample used}}$$

IGT

QA/QC

The multiple point standard addition technique provides its own internal standard QC check. The curve should be a straight line and the correlation should not be less than 0.95. A replicate sample is run for every 10 samples.

Limits of Detection

With a 10 ml sample, the detection limit in typical brines will be 0.005 mg/l P.

Time of Analysis

The analyst should allow a minimum of 2 hours per sample, including clean-up time.

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IGT

ELEMENTAL ANALYSIS OF BRINE BY ICP

Principle

Brine samples are acidified with HCl and generally diluted 1:100 in 0.5% HNO3 to bring the elemental concentrations within the instrumental linear range. The elements are quantified by an inductively coupled argon plasma emission spectrometer.

Interferences

The high solids content of brines may present interferences which can be remedied by dilution. Analytical wavelengths and background points are selected to avoid any spectral interferences from concomitant elements.

Apparatus

1. Sequential scanning atomic emission spectrometer system, Thermo-Jarrell Ash Atomscan 25 (ICP) (Note 1)

Reagents

1. Hydrochloric acid, concentrated, Ultrex (or similar) grade

2. Nitric acid, concentrated, Ultrex (or similar) grade

3. Elemental standards, appropriate to element being analyzed, prepared by serial dilution of Spex ICP grade stock standards. The analytical standard currently used for these analyses is called BRINE-STD and contains the following elemental concentrations: 10.0 ppm Ba, Mn, Si; 50.0 ppm Ca, Fe, Mg, Na, Sr; 40.0 ppm K; 8.0 ppm Li in 0.5% nitric acid. The blank is called BRINE-BLK and contains only 0.5% nitric acid. (These names are for reference only and are included with the method stored in the computer.)

Procedure

1. When the sample is received for analysis, a subsample is removed and acidified with the minimum amount of concentrated HCl to effect dissolution of any solids present. An initial 1:100 dilution is made with double deionized water (DDIW) and acidified with concentrated nitric acid to a final concentration of 0.5%.

2. The ICP is set up according to the manufacturer's specifications. DDIW is aspirated to condition the instrument.

3. The method named BRINE is loaded and the samples analyzed.

4. The following analytical lines are utilized for the emission readings:

Element	Wavelength, nm	BKG Wavelength Offset
Ba	233.527	-0.056
Ca	315.887	-0.152
Fe	239.562	-0.056
K	766.490	-0.292
Li	670.784	-0.350
Mg	279.080	-0.050
Mn	257.610	-0.038
Na	589.592	-0.173
Si	288.158	-0.168 & +0.088
Sr	346.447	-0.137

Calculations

The sample concentrations are calculated from a 2-point standardization curve which is set up and stored in the computer. The concentrations in mg/l are read directly from the computer printout if the dilution was initially entered as a correction factor. If not entered, multiply the results printed by the inverse of the dilution (e.g. if the dilution was 1:100, multiply by 100).

Notes

1. Alternatively, the samples may be analyzed by flame atomic absorption spectrometry using a Perkin-Elmer Model 603 instrument.

QA/QC

Spiked samples are run on each sample type to determine any interference effects and to check recovery. The recovery should be better than 95%. A QC standard is run at the beginning and end of each analytical run to check the performance and calibration the instrument. This standard should also have 95% or better recovery. Duplicate samples are analyzed every 5 samples and the instrument is recalibrated every 8 samples.

Limits of Detection

For a brine sample, the detection limit for these metals is approximately 0.1 mg/l.

Time of Analysis

The analyst should allow 2 hours for instrument setup, calibration and analysis of up to 10 samples.

References

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HACH

ANALYTICAL PROCEDURE

CHLORIDE PROCEDURES

Introduction

This analysis includes procedures for the Buret Method and the Digital Titrator Method.

Chlorides are present in all potable water supplies and in sewage, usually as a metallic salt. When sodium is present in drinking water, chloride concentrations in excess of 250 mg/L give a salty taste. If the chloride is present as a calcium or magnesium salt, the taste detection level may be as high as 1000 mg/L chloride.

Chloride is essential in the diet and passes through the digestive system unchanged to become one of the major components of raw sewage. The wide use of zeolite in water softeners also contributes a large amount of chloride to sewage and wastewaters.

High chloride concentrations in water are not known to have toxic effects on man, although large amounts may act corrosively on metal pipes and be harmful to plant life. The maximum allowable chloride concentration of 250 mg/L in drinking water has been established for reasons of taste rather than as a safeguard against physical hazard.

The Mohr Argentometric Method, the most widely known test for chloride, uses a chromate indicator. The sample is titrated with a silver nitrate standard solution to selectively precipitate first the chloride present, then the chromate. The end point of the titration is indicated by the first appearance of the red silver chromate precipitate.

The newer Mercuric Nitrate Method has become popular due to the sharp yellow to pinkish-purple end point of diphenylcarbazone and the absence of a precipitate during the titration. A single, stable powder has been developed combining the color indicator with an appropriate buffer to establish the correct sample pH. Interferences are discussed in the procedural notes for each test method.

A Sodium Chloride Standard Solution, 1000 mg/L as Cl, is available from Hach for checking the accuracy of the test. A procedure detailing the use of the Voluette® Analytical Standards System of standard additions *is given in the final note of each titration method.*

> ***WARNING***
>
> *Some of the chemicals used in this procedure may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings on the reagent labels. If you have questions, please contact Hach. In the procedure, hazardous substances appear in italic typeface wherever they are used in the test and deserve extra care in handling. It is always good practice to wear safety glasses when handling chemicals. Wash thoroughly if contact occurs. Follow instructions carefully.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Samples can be stored at room temperature for a least seven days.

pH Adjustment

Highly alkaline samples should be adjusted to a pH of approximately 2.5 with *5.25N Sulfuric Acid Standard Solution* before testing. Highly acidic samples should be adjusted to approximately pH 2.5 with *5.0 N Sodium Hydroxide Standard Solution.* Where a significant amount of acid or base has been used, a volume correction should be made by dividing the total volume (sample + acid or base) by the sample volume and multiplying the result times the final test reading.

CHLORIDE
Mercuric Nitrate Method†
For Water, Wastewater and Sea Water

Procedure for Buret Method

1. Take a water sample by filling a clean 100-mL graduated cylinder to the 100-mL mark. Pour the sample into a clean 250-mL Erlenmeyer flask.
2. Add the contents of one *Diphenylcarbazone Reagent Powder Pillow* and swirl to mix. *See Note A.*
3. Titrate the sample with *Mercuric Nitrate Standard Solution* while swirling the flask until the color changes from yellow to a light pink. *See Note B.*
4. Multiply the number of mL of *Mercuric Nitrate Standard Solution* used by 5 to obtain the mg/L chloride (Cl).* *See Note C.*

Procedure for Digital Titrator Method

1. If performing a hand-held titration, attach a clean, straight-stem delivery tube to a *2.256N Mercuric Nitrate Titration Cartridge. See Note D.* Twist cartridge onto titrator body. If Digital Titrator is to be attached to a laboratory stand, use a clean, 90°-delivery tube.
2. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.
3. Take a water sample by filling a clean 100-mL graduated cylinder to the 100-mL mark. Pour the sample into a clean 250-mL Erlenmeyer flask.
4. Add the contents of one *Diphenylcarbazone Reagent Powder Pillow* and swirl to mix. *See Note A.*
5. Titrate the sample while swirling the flask until the color changes from yellow to light pink.
6. Read the concentration of chloride in mg/L from the digital counter.* *See Note C.*

Notes

A. The results will not be affected if a small portion of the *Diphenylcarbazone Reagent Powder* does not dissolve.

B. When the total amount of *Mercuric Nitrate Standard Solution* required exceeds 25 mL per titration, a sample dilution is recommended to minimize errors from multiple buret readings. The final results are then multiplied by the dilution factor.

More concentrated titrating solutions are available for samples which consistently require more than 25 mL of *Mercuric Nitrate Standard Solution, 0.0141N,* per test. When using *Mercuric Nitrate Standard Solution, 0.141N,* multiply the number of mL used by 50 to obtain the mg/L chloride.

C. The results may be expressed as mg/L sodium chloride by multiplying the mg/L chloride by 1.65.

D. For chloride concentrations below 100 mg/L, use a *0.2256N Mercuric Nitrate Titration Cartridge* and divide the counter reading by 10.

E. Chromate, ferric iron and sulfite in excess of 10 mg/L interfere with this method. Sulfite interference can be eliminated by adding three drops of *30% hydrogen peroxide* per 100 mL of water sample before running the test. Sulfide interference can be removed by adding the contents of one *Sulfide Inhibitor Reagent Powder Pillow* to about 125 mL of the sample, mixing for one minute and filtering through a folded filter paper. Iodide and bromide interfere directly and are titrated as chloride.

†Adapted from *Standard Methods for the Examination of Water and Wastewater*

*mg/L value ÷ 17.12 = gr/gal equivalent

Appendix Brine - F: 8

F. The standard additions method check can be performed as follows:

1. Snap the neck off a fresh *Voluette Ampule Standard for Chloride* (Cat. No. 14250-10). Using the TenSette™ Pipet, add 0.10 mL of standard to the sample titrated in Step 3 or 5 of the procedure.
2. Swirl to mix and titrate again to the end point. Note the amount of additional titrant used.
3. Make 0.20-mL and 0.30-mL standard additions, titrating to the end point after each. The volume of titrant required should increase 2.5 mL for each 0.1 mL of standard added in the Buret Method. In the Digital Titrator Method, the reading should increase 12.5 digits for each additional 0.1 mL of standard.

Required Reagents and Apparatus for Buret Method

Cat. No.	Description	Unit
285-16	*Mercuric Nitrate Standard Solution, 0.0141N* (May be harmful if swallowed or cause irritation)	946 mL (qt)
836-96	*Diphenylcarbazone Reagent Powder Pillows* (May cause skin, eye and respiratory tract irritation)	50
504-40	Buret, automatic, 25 mL	each
505-46	Flask, Erlenmeyer, 250 mL	each
508-42	Cylinder, graduated, 100 mL	each
968-00	Clippers, for opening pillows	each

Required Reagents and Apparatus for Digital Titrator Method

836-96	*Diphenylcarbazone Reagent Powder Pillows*	50
921-01	*Mercuric Nitrate Titration Cartridge, 2.256N* (Poison. May cause irritation)	each
505-46	Erlenmeyer Flask, 250 mL	each
508-42	Cylinder, graduated, 100 mL	each
968-00	Clippers, large	each
16900-01	Digital Titrator	each

Optional Reagents and Apparatus

144-11	*Hydrogen Peroxide Solution, 30%* (Strong oxidant. Causes irritation)	473 mL (pt)
183-11	Sodium Chloride Standard Solution, 1000 mg/L as Cl	473 mL (pt)
326-00	Clamp Holder	each
563-00	Support Stand	each
1083-67	Funnel, poly, 65 mm	each
20663-37	Dropper, plastic, unmarked	each
1894-57	Filter Paper, folded, 12.5 cm	100
1920-31	*Mercuric Nitrate Standard Solution, 0.141N* (Poison)	236 mL (8 oz)
2418-99	*Sulfide Inhibitor Reagent Powder Pillows* (Harmful dust)	100
2449-37	*Sulfuric Acid Standard Solution, 5.25N* (Poison. Causes irritation)	118 mL (4 oz) MDB
2450-37	*Sodium Hydroxide Standard Solution, 5.0N* (Poison. Causes irritation)	118 mL (4 oz) MDB
14250-10	*Voluette Ampule Standards for Chloride* (May be harmful if ingested)	16
19700-01	TenSette Pipet	each
14393-01	*Mercuric Nitrate Titration Cartridge, 0.2256* (Poison)	each
19000-00	pH Meter, portable	each

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Appendix Brine-F:9

1079

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(Procedures - page 183)

Short-chain aliphatic acid anions in deep subsurface brines: A review of their origin, occurrence, properties, and importance and new data on their distribution and geochemical implications in the Palo Duro Basin, Texas

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Abstract—Short-chain aliphatic acid anions, which are produced during the thermal maturation of sedimentary organic matter, are common in oil-field brines and other deep formation fluids. Their abundance and distribution are controlled primarily by their rates of formation, thermal and bacterial destruction, and reservoir flushing. This first part of this manuscript reviews literature on their abundance and distribution in deep basin brines, their geochemical and biogeochemical properties, and their geochemical importance, which far outweighs the number of analytical measurements that have been published. The second part reports new data from the Palo Duro Basin in the Texas Panhandle.

Deep brines from the Palo Basin contain short-chain aliphatic acid anions in concentrations ranging up to 440 mg/l. The observed order of abundance is acetate » propionate > butyrate > valerate. Aliphatic acid anion contents vary randomly with subsurface temperature, depth, and geologic age, but correlate well with groundwater residence time, as inferred from $\delta^{18}O$ measurements. Groundwaters having the longest residence times contain the highest organic acid anion contents. Organic content, I^-, and Br^- in these deep brines appear to have a common source, and all of the aliphatic acid anions, most of the I^- and some portion of the Br^- are interpreted to have been derived from lipid-rich sedimentary organic matter. This observation complicates the use of Br^- as a conservative marker constituent when inferring groundwater origin and evolution using Cl^-/Br^- relationships. Also, simplified calculations indicate that these organic acid anions are not important in complexing metals. Their presence in relatively high concentrations in this basin with its low petroleum potential indicates that they cannot be used alone as petroleum proximity indicators.

Key words: short-chain aliphatic acids and acid anions, volatile fatty acids and acid anions, acetate, propionate, butyrate, valerate, iodide, bromide, alkalinity, biodegradation, thermal decarboxylation, oil-field brines, Palo Duro Basin, Texas, radioactive waste disposal, groundwater origin and evolution, radionuclide and metal complexation, petroleum proximity indicators.

INTRODUCTION

Short-chain aliphatic acids, sometimes referred to as volatile fatty acids (VFAs), are a group of water-soluble, monofunctional organic compounds of the general formula:

R—COOH

where R is a straight or branched-chain alkyl group containing 1–4 carbon atoms. Interestingly, the single-carbon species, formic acid, is not generally found in natural, unpolluted waters. Because their acid dissociation constants fall in the range of $10^{-4.6}$–$10^{-4.8}$ (Martell and Smith, 1977), short-chain aliphatic acids occur predominantly as their anions in natural waters of pH 5.0 and greater, and are henceforth referred to as short-chain aliphatic acid anions (SCA^3s) in this two-part manuscript.

The abundance and importance of SCA^3s in geochemical systems far out-weighs the number of analytical measurements that have been published. SCA^3s occur almost ubiquitously in oil-field brines (cf. Carothers and Kharaka, 1978), but have been also reported in non-petroliferous brines, marine pore waters, spring, lake, and creek waters, rain water, hot and cold springs, and even meteoritic materials (Hatton and Hanor, 1984). In oil-fields brines, SCA^3s have well defined roles: (a) in subsurface mineral dissolution leading to porosity enhancement; (b) as precursors to natural gas: and (c) as possibly proximity indicators of hydrocarbon accumulations, and thus are of great interest to the petroleum industry. Other geochemical properties of general interest include their: (i) contribution to titratable alkalinity, pH, and Eh; (ii) metal complexation and transport characteristics; and (iii) possible role as tracers of subsurface flow.

The first part of this manuscript summarize available literature on the origin and occurence of SCA^3s in deep subsurface brines, their geochemical and biogeochemical properties, and their geochemical significance in such systems. The second reports new data, which for the most part are summarized in Means and Hubbard (1985), on the occurrence and

distribution of SCA^3s in deep groundwaters from the Palo Duro Basin in Texas and interprets these data, to the extent possible, in the context of previous reported measurements and interpretations.

REVIEW

Origin and occurrence

An exact mechanism for the formation of SCA^3s in subsurface brines has not been formulated, but it is likely that several different processes are involved. SCA^3s are well known by-products of acid-forming bacteria such as sulfate-reducers and methanogens (Hatton and Hanor, 1984). These bacteria also consume aliphatic acid anions. Under aerobic conditions they are readily metabolized to CO_2 and H_2O. Hence, their presence in natural waters would tend to indicate chemically-reduced conditions, or, likely, the apparent absence of aerobic microorganisms.

SCA^3s may also be produced abiotically during the thermal maturation of sedimentary organic material (Surdam *et al.*, 1984), and in turn can be thermally degraded (via decarboxylation) into methane, ethane, propane, and butane. The preferred origin, according to Hatton and Hanor (1984), is the thermocatalytic degradation of the polycondensate precursors to petroleum. Kerogen that has been subjected to experimental stepwise oxidation yields both mono- and dicarboxylic acids, in addition to phenols (Surdam and Crossey, 1985). The acids and phenols appear to be bonded to the periphery of the kerogen molecules, and are readily released during the early stages of thermal cracking. The fact that elevated concentrations (up to thousands of milligrams per liter) of SCA^3s have been measured in very old groundwaters suggests a high degree of thermochemical and biochemical stability in such systems relative to their higher molecular weight analogues (Hatton and Hanor, 1984).

Observations of SCA^3s in groundwater from petroleum-producing regions date back to 1882 in the Russian literature, summarized by Hatton and Hanor (1984), but few investigations were recorded during the interval from then until the late 1960's and early 1970's. Willey *et al.* (1975) identified SCA^3s information fluids from Miocene and Eocene sediments in the Kettleman North Dome oil field in California. Acetate concentrations ranged from 106 to 4071 mg/l, and acetate/propionate ratios averaged approximately 10:1. Normal-butyrate and iso-butyrate concentrations ranged from below detection limit to 174 and 157 mg/l, respectively; n-valerate and iso-valerate concentrations ranged from below detection limit to 32 and 85 mg/l, respectively.

Carothers and Kharaka (1978) measured SCA^3s in 95 formation water samples from 15 oil and gas fields in Tertiary-aged sediments from the San Joaquin Valley of California and Houston and Corpus Christi areas of Texas. Three different temperature regimes corresponding to significantly different concentrations and species of SCA^3s were defined. Zone 1 was characterized by subsurface temperatures lower than 80°C and SCA^3s in concentrations of less than 60 mg/l, consisting principally of propionate. The concentrations of SCA^3s in Zone 2 (80–200°C) were much higher (up to 4900 mg/l) and decreased with increasing temperature. Acetate generally composed 90% or more of the total organic anions. No SCA^3s were believed to be present in Zone 3 (temperatures > 200°C), based on the extrapolation of data from Zone 2. The trends of Zone 2 and the absence of SCA^3s in Zone 3 were explained by thermal decarboxylation as in the reaction:

$$CH_3COO^- + H_2O \rightleftharpoons CH_4 + HCO_3^- \qquad (1)$$

The degree of decarboxylation was also interpreted to be a function of the time elapsed from first introduction of the SCA^3 into the reservoir, which was approximated by the age of the sedimentary formation. Accordingly, the average concentration of aliphatic acid anions in Zone 2 generally decreased with increasing age of the reservoir rocks. Because the temperature boundaries between Zones 1, 2, and 3 were based on data from Tertiary-aged sediments, Carothers and Kharaka (1978) indicated that the boundaries most likely occur at lower or higher temperatures for older or younger rocks. The microbiological degradation of acetate by methanogenic bacteria and dilution by mixing with meteoric waters were postulated to explain the composition and concentration of SCA^3s in Zone 1.

The first observation of SCA^3s in Louisiana pore waters appears to have been reported by Dickey *et al.* (1972), who measured total SCA^3 concentrations, including acetate up to 142 mg/l, in some 40 brines from southwest Louisiana. More recently, Workman and Hanor (1985) have reported total SCA^3 levels in excess of 150 mg/l in deep brines from the Iberia oil field in the Tertiary section of south-central Louisiana. In the deeper brines, SCA^3 concentrations are dominated by acetate and propionate, which appear to be undergoing preferential decarboxylation relative to the butyrates and valerates, yielding by-products of methane, ethane, and bicarbonate. By the time the deeper brines have migrated to shallower regions, the predominance of acetate and propionate has given way to that of n-butyrate, the most abundant SCA^3 in the shallowmost part of the section. The data of Workman and Hanor (1985) also suggest that butyrates and valerates are considerably more recalcitrant to degradation than either acetate or propionate.

Similar SCA^3 abundances and distributions were recently reported for the Port Barre and Fordoche oil fields, also in the Tertiary section of south Louisiana (Hanor and Workman, 1986). In all three settings, the SCA^3s appear to have been generated at greater depths and transported upward through the sedimentary section, where they have undergone preferential degradation. Hanor and Workman (1986) conclude

that the spatial distribution of the SCA^3's in each of three oil fields is unique and complex, but, ultimately controlled by local variations in the rates of production, degradation, and transport.

Only recently have dicarboxylic acids been identified in deep formation fluids. Surdam *et al.* (1984) analyzed 13 oil-field waters, largely from Cretaceous fields in the Rocky Mountains, and found acetic acid in concentrations ranging up to 10,000 mg/l and difunctional acids (C_3 and C_4) in concentrations up to 25 mg/l. Kharaka *et al.* (1985) studied the organic geochemistry of deep groundwaters from the High Island Field, offshore, Texas, which occurs in middle- and lower-Pleistocene sandstones with subsurface temperatures ranging from 50 to 100°C. Acetate concentrations ranged from 2.4 to 1525 mg/l, however most samples contained less than 200 mg/l acetate. Propionate and iso-valerate were the second and third most abundant organic species, with concentrations ranging up to 226.2 mg/l for propionate and 19.1 mg/l for iso-valerate. SCA^3 concentrations generally increased with increasing subsurface temperature and accounted for from 10 to 80% of the dissolved organic carbon (DOC) content of the various formation fluids. Other species identified included, in approximate order of decreasing abundance, C_4 and C_5 dicarboxylic acids, C_6–C_{10} dicarboxylic acids, C_6–C_9 monocarboxylic acids, methyldicarboxylic acids, and phenols. C_4 (butanedioic acid) and C_5 (pentanedioic acid) dicarboxylic acid concentrations ranged up to 63 and 36 mg/l, respectively. C_2 and C_3 dicarboxylic acids were not detected, presumably because of the low solubility of calcium oxalates (C_2) and malonates (C_3) in high-Ca waters. The observations of Surdam *et al.* (1984) and Kharaka *et al.* (1985) suggest that dicarboxylic acids may frequently occur with SCA^3's in oil-field brines, but that the dicarboxylic species are quantitatively much less important.

Contribution to alkalinity, pH, and Eh

SCA^3's may account for a significant portion of the total aqueous alkalinity of natural groundwaters, particularly deep basin brines. As discussed above, the acid dissociation constants for short-chain aliphatic acids fall in the range of $10^{-4.6}$–$10^{-4.8}$, while that of carbonic acid (H_2CO_3) is approximately $10^{-6.3}$ (Smith and Martell, 1976). Because of these similarities it is difficult to accurately differentiate between organic and inorganic alkaline species using standard potentiometric titration procedurs. Preanalytical sample treatment intended to isolate organic from inorganic alkaline species (e.g. removing carbonate species by acidification and purging) may help but must be conducted with care, as SCA^3's may also be volatilized during the process. Neglecting to account for the SCA^3 contribution to titrated alkalinity can yield incorrect and misleading data for carbonate ions and other inorganic hydrogen acceptors. The study of formation fluids in Miocene sediments from the Kettleman North Dome in California is an example. Kharaka and Berry (1974) evaluated brine evolution and amino acid chemistry in this setting. Merino (1975) emphasized chemical equilibria in the interstitial solutions and diagenetic mineralogy. Both studies interpreted high measured alkalinities as bicarbonate and other inorganic species, leading Merino (1975) to report apparent brine supersaturation by 1000 times with respect to calcite. Kinetic inhibition of calcite crystallization by magnesium and sulfate ions in the brine was offered as an explanation for the apparent supersaturation. Willey *et al.* (1975) resolved the difficulties with respect to the apparent $CaCO_3$ supersaturation problem in these brines by showing that the high measured alkalinity values were chiefly caused by acetate and propionate with lesser contributions from higher molecular weight (butyrate and valerate) ions. After accounting for the contribution of the SCA^3's to the measured alkalinities, some of the samples were found to contain no detectable bicarbonate (Willey *et al.*, 1975).

Similar studies for other geographic regions show that SCA^3's account for 50–100% of total alkalinity in groundwater from the San Joaquin Valley of California and the Houston and Corpus Christi area of Texas (Carothers and Kharaka, 1978), 5–100% of total alkalinity in deep pore waters from southwest Louisiana (Dickey *et al.*, 1972), 5–35% of titration alkalinity in the Iberia, Port Barre, and Fordoche Oil Fields of south Louisiana (Workman and Hanor, 1985; Hanor and Workman, 1986), 10–90% of total alkalinity in groundwaters from the High Island Field, offshore Texas (Kharaka *et al.*, 1985), and most of the titration alkalinity in oil-field brines from the North Coles Levee Field of the southern San Joaquin Valley, California (Surdam and Crossey, 1985). In formation fluids where the most of the titration alkalinity is associated with organic anions, it is likely that pH is buffered by SCA^3's rather than inorganic carbon species.

Furthermore, Carothers and Kharaka (1980) postulated from $\delta^{13}C$ values of dissolved HCO_3^- that the carbon in carbonate cements of the sandstone reservoir rocks is mainly organic in origin. The $\delta^{13}C$ values of HCO_3^- ranged from -20 to $+28$ per mil relative to PDB. Microbiological degradation of organic matter appeared to be the dominant process controlling the low and high values in shallow production zones where subsurface temperatures were less than 80°C. The low values were obtained in groundwater where SO_4^{2-} concentrations exceeded 25 mg/l and probably resulted from the degradation of organic acid anions by sulfate-reducting bacteria, as in:

$$CH_3COO^- + SO_4^{2-} \rightleftarrows 2HCO_3^- + HS^- \quad (2)$$

High $\delta^{13}C$ values probably resulted from degradation of acetate by methanogenic bacteria, as in reaction (5) below. In the deeper zones where temperatures exceed 85°C and bacteria cannot thrive, the thermal

decarboxylation of SCA's (primarily acetate) was concluded to be the major source of CO_2 in dissolved carbonate cements.

With regards to Eh, subsurface waters in sedimentary basins are typically highly reducing (Eh < -200 mV), and dissolved organic species appear to be the principal reducing agents (Kharaka *et al.*, 1980). The reducing effects of SCA's may be indirect, such as providing the energy source for bacterially-mediated production of HS^- or CH_4, as in equations (2) and (5), or SCA's may be directly involved in the chemical reduction of ferric iron, yielding ferrous iron, CO_2, and hydrogen ions, as suggested by Surdam *et al.* (1984). The presence of SCA's in formation fluids having subsurface temperatures less than 80°C is almost a sure indicator of chemically-reducing conditions, as SCA's, particularly acetate, are readily metabolized by aerobic bacteria, as discussed in the following section.

Biogeochemistry

The biodegradation of the SCA's is pertinent in that it may affect their concentration and speciation in oil-field waters. Levorsen (1967) and Davis (1967) report that both aerobic and anaerobic bacteria may be present in different petroliferous environments to temperatures of about 80°C; however, aerobic and anaerobic bacteria do not generally coexist (Carothers and Kharaka, 1978). Aerobic bacteria readily degrade short-chain aliphatic acids (Verschueren, 1983). In fact acetate is as or more biodegradable than glucose, linear alkyl sulfonate, and diethylene glycol, and all four compounds have been suggested for use as reference carbon sources in biodegradation test systems that measure oxygen consumption (Stainken *et al.*, 1983). The ready biodegradability of acetate and other SCA's in aerobic environment stresses the need for immediate sample preservation in the field.

The anaerobic biodegradation of SCA's is much complex, and the literature is not entirely consistent on mechanistic pathways. Novak and Ramesh (1975) describe anaerobic degradation as a multi-step process in which complex compounds are degraded to SCA's by facultative bacteria and then to CH_4 and CO_2 by methanogenic bacteria, which are capable of degrading only a few of the SCA's. High concentrations of aliphatic acid anions (2000–3000 mg/l) can inhibit biodegradation (Schulze and Raju, 1958). However, Kaspar and Wuhrmann (1978) conclude that "acetate-splitting" rather than "methanogenesis from fatty acids" is the rate-limiting step in the anaerobic degradation of organic matter to methane. Likewise, Mechalas (1974) and Claypool and Kaplan (1974) report that methanogenic bacteria are unable to utilize any aliphatic acid anions that are larger than acetate. The four primary catabolic reactions of anaerobic degradation may be summarized as follows (Kasper and Wuhrmann, 1978). Organic matter is degraded to an aliphatic acid anion, represented here by n-nonane and propionate:

$$C_9H_{20} + 6H_2O \rightleftharpoons 3C_3H_5O_2^- + 7H_2 + 3H^+ \quad (3)$$

The fatty acid anion is then degraded further by another group of bacteria to acetate, carbonate, and hydrogen, via:

$$C_3H_5O_2^- + 3H_2O \rightleftharpoons C_2H_3O_2^- + HCO_3^- + 3H_2 + H^+ \quad (4)$$

Methanogenesis by acetate-splitting produces CO_2 and CH_4 as follows:

$$C_2H_3O_2^- + H_2O \rightleftharpoons HCO_3^- + CH_4 \quad (5)$$

Another mechanism for methane production involves the recombination of CO_2 and H_2:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad (6)$$

According to this sequence of reactions, the anaerobic decomposition of organic matter to methane proceeds via an acetate intermediate, and different groups of bacteria are involved in reactions (3), (4), and (5). Hence, the relative abundances of the various SCA's in a bacterially-altered shallow zone (< 85°C) of a sedimentary section depends on the type of bacteria present. Acetate will predominate if the system lacks methanogenic bacteria, and the higher molecular weight organic anions will be favored if the bacteria necessary for the reaction (4) are absent.

Precursors to natural gas

Decarboxylation of these acid anions to the components of natural gas via reactions (1) and (5) above and similar reactions for the higher molecular weight acid anions is believed to occur in the reservoir rocks, and is postulated to be a significant mechanism for the formation and migration of natural gas. This hypothesis is supported by ^{13}C values of dissolved HCO_3^- (Carothers and Kharaka, 1980) as well as a strong correlation between the relative abundances of the various SCA's (94% acetate, 5% propionate, 2% butyrate) and their decarboxylated gas counterparts (90% methane, 5% ethane, 2% propane) in the San Joaquin Valley of California and the Corpus Christi and Houston areas of Texas. The volume of gas that can be generated by this mechanism was calculated to be adequate to produce the amounts of gas present in the fields examined by Carothers and Kharaka (1978). Subsequent laboratory experiments on the thermal decarboxylation of solutions of acetate at 200 and 300°C show that the concentration of acetic acid, not acetate, controls the reaction rates, which follow a first-order equation (Kharaka *et al.*, 1983). The catalysis of the thermal decarboxylation reaction by titanium, silica, stainless steel, gold, and magnetite is discussed by Palmer and Drummond (1986). Extrapolation to 100°C suggests that a solution containing 10,000 mg/l acetic acid (as the acid form) can be reduced to 10 mg/l in as short a time as 130 years (Kharaka *et al.*, 1983). However, the applicability of

this phenomenon to the formation of significant natural gas deposits in other regions remains to be shown.

Petroleum proximity indicators

It has been suggested that elevated concentrations of SCA^3s, which frequently occur in oil-fields waters, may serve as indicators for the proximity of petroleum. This theory appears to have been originated in the Russian literature (e.g. Zinger and Kravchik, 1972; Bykova *et al.*, 1971; Kartsev *et al.*, 1971; Shvets and Bykova, 1971), where consistently higher concentrations of SCA^3s were reported in groundwater from petroliferous areas than in waters from non-producing zones. More recently, as described above, Carothers and Kharaka (1978) developed a relationship between the decarboxylation of SCA^3s and the formation and migration of natural gas in the San Joaquin Valley of California and the Houston and Corpus Christi areas of Texas. Extremely high SCA^3s concentrations (thousands of mg/l) such as those measured by Carothers and Kharaka (1978) would appear to suggest the proximity of petroleum. However, the complex interactions that may diminish SCA^3 concentrations in oil-field waters must be appreciated. Thermal decarboxylation, chemical oxidation, biodegradation, and groundwater mixing may greatly reduce SCA^3 contents, and hydrologic flow may transport them far from their sedimentary organic source.

Hence, their occurrence must be viewed in conjunction with other indicators for petroleum proximity, including geophysical data along with other geochemical evidence. Organic geochemical evidence clearly cannot stand alone.

Porosity enhancement

According to Surdam *et al.* (1984), the discovery of secondary porosity in sandstone has been the most significant advance in the study of clastic diagenesis in the past decade. It was initially thought that most secondary porosity in sandstone resulted from carbonate dissolution, but is is now recognized that silicate dissolution can also be an important mechanism.

Recent experimental data (Surdam *et al.*, 1984; Surdam and Crossey, 1985) indicate that it is possible to dissolve and transport aluminium and calcium as organic complexes acid solutions. Acetic acid increased the solubility of aluminum by one order of magnitude; oxalic acid (a dicarboxylic species) increased the solubility of aluminum by three orders of magnitude. Thermal maturation experiments showed that oxalic acid was one of the species formed during the heating of kerogen.

The degree to which porosity enahancement develops depends upon the ratio of organic to inorganic matter, initial composition of the organics, the sequence, rates, and magnitude of diagenetic reactions, fluid flux, and sand/shale geometry. Depending on variations of these parameters and probably others, a wide range of porosity effects can likely be attributed to carboxylic acids. The thermal regime corresponding to maximum porosity enhancement likely corresponds to the temperature at which SCA^3s and other organic acids are most abundant, which according to Carothers and Kharaka (1978) is approximately 80–135°C.

Tracers of subsurface flow

Recent studies of the Iberia, Port Barre, and Fordoche Oil Fields of Louisiana suggest a new application for SCA^3s in deep basin brines, that is, tracers of subsurface flow (Workman and Honar, 1985; Hanor and Workman, 1986). Here, total SCA^3 concentrations vary spatially from over 150 mg/l in deeper portions of the basin to generally less than 10 mg/l in the central portions. Acetate appears to have preferentially degraded relative to propionate in some areas and propionate appears to have preferentially degraded relative to the butyrates and valerates in others, suggesting relatively selective decarboxylation of the lower molecular weight SCA^3s, yielding methane, ethane, and bicarbonate as by-products. The inferred decarboxylation reactions, which may be either thermally- or bacterially-mediated, appear to control the abundance of individual SCA^3s, and biodegradation and/or mixing with low-SCA^3 waters cause the progressive decrease in total SCA^3 concentration along the groundwater flow path, which is up the flanks of nearby salt domes. The spatial distribution of SCA^3s is complex, but systematic, and must ultimately be related to rates of advective transport, dispersive mixing, and chemical (or biochemical) reaction. The new proposed application of these organic compounds thus lies in helping to unravel the dynamics of certain types of subsurface flow systems.

NEW DATA FROM THE PALO DURO BASIN, TEXAS

Interest in the organic geochemistry of deep brines from the Palo Duro Basin stems from the fact that a sequence of Permian bedded salts within the lower San Andres Formation underlying Deaf Smith County, in the northwest portion of the basin, is currently being considered for location of a repository for the disposal of high-level nuclear wastes (U.S. Department of Energy, 1984). The U.S. Nuclear Regulatory Commission (1982, Section 6.2) states that organic compounds in groundwater must be identified as part of the characterization of sites for high-level radioactive waste repositories. This manuscript describes the significance of SCA^3s in deep brines in terms of radioactive waste disposal issues, including ground water origin, petroleum proximity indicators, and generalized geochemical controls on the occurrence and distribution of SCA^3s in deep subsurface formation fluids.

The Palo Duro Basin is one of several shallow intracratonic basins which together constitute the larger Permian Basin. It is bounded on the north and south by faulted Precambrian basement highs and to the west and east, by low, positive relief regions that separate the Palo Duro Basin from the Tucumcari and Hardeman Basins, respectively (Fisher and Kreitler, 1985).

The basin, which initially formed during the early Pennsylvanian, is asymmetric and tilted to the east, with the thickest sediments near the southern margin. Underlying the basin are six complexly faulted basement terranes, which range in composition from granitic to diabasic. Three distinct styles of sedimentation were experienced during the basin's history: (a) normal marine and basic margin sedimentation from Cambrian to early Permian: (b) evaporite deposition throughout most of the Permian: and (c) dominantly fluvial, lacustrine, or eolian from Triassic to the present (Fisher and Kreitler, 1985).

Three major hydrostratigraphic units roughly correspond to these three phases of sedimentary deposition. The Upper Aquifer consists of Triassic and younger sediments that were deposited primarily in fluvial, fluvial–deltaic, and lacustrine and environments. The Middle and Upper Permian evaporitic strata comprise the Evaporite Aquitard. The lower Hydrostratigraphic Unit consists of: (i) pre-Pennsylvanian sandstone, dolomite, and limestone: (ii) early-Pennsylvanian arkosic sandstone ("granite wash"), shelf-margin limestone, and thick sequences of shale: and (iii) early-Permian (Wolfcampian) clastic, limestone, and dolomitic facies (Fisher and Krietler, 1985).

Sample collection

A total of 15 groundwater samples from 7 different wells in the Palo Duro Basin were collected at the wellhead in the period from May 7, 1982 through September 15, 1984. The wells include Mansfield No. 1, Mansfield No. 2, J. Friemel No. 1, and Detten No. 2 in the western part of the basin and Harman No. 1, Zeeck No. 1, and Sawyer No. 1 in the east. Well locations are shown in Fig. 1. Sample depths and geologic formations represented are listed in Table 1. An overview of the geochemical setting is provided in Fisher and Kreitler (1985).

Because of the volatility and aerobic biodegradability of SCA's, strict sample collection and preservation procedures must be followed. Samples were filtered in the field (0.45 or 0.4 μm polycarbonate membranes), collected in prewashed

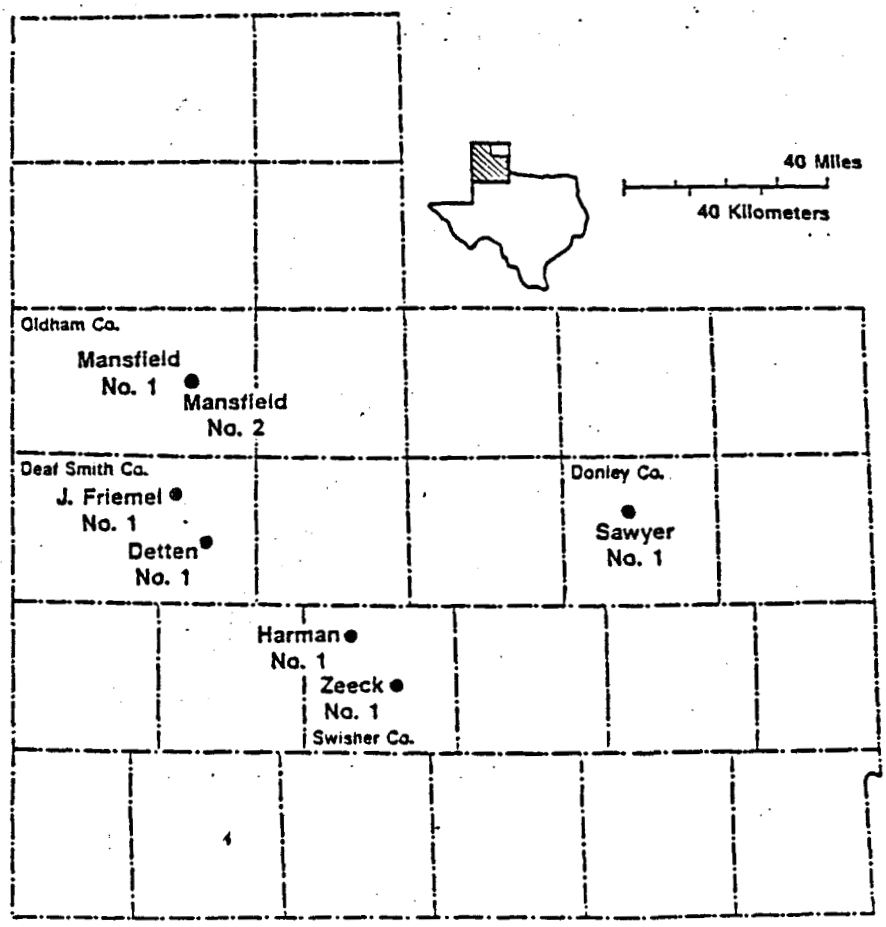

Fig. 1. Well locations in the Palo Duro Basin, Texas.

Table 1. Total organic carbon (TOC), I^-, Br^-, and $\delta^{18}O$ content and subsurface temperature of Palo Duro Basin brines.

Well and Production Zone	Aquifer Depth and Age	Subsurface Temperature (°C)	TOC (mg/l)	I^- (mg/l)	Br^- (mg/l)	$\delta^{18}O^{(d)}$ (SMOW)
J. Friemel No. 1 8th Production Zone	2,754 - 2,798 ft. Permian San Andres	27(a)	223	25(a)	1180(a)	+6.8
J. Friemel No. 1 7th Production Zone	5,825 - 5,926 ft. Lower Permian Wolfcamp	38(b)	5.8	1.8(b)	147(b)	-3.5
J. Friemel No. 1 6th Production Zone	7,300 - 7,326 ft. Pennsylvanian Carbonate	52(b)	8.6	5.0(b)	155(b)	-2.4
J. Friemel No. 1 4th Production Zone	7,890 - 7,904 ft. Pennsylvanian Granite Wash	55(b)	15.8	11.7(b)	270(b)	-2.1
J. Friemel No. 1 1st Production Zone	8,168 - 8,200 ft. Pennsylvanian Granite Wash	55(b)	16.1	8.8(b)	161(b)	-2.5
Mansfield No. 2 Shallow Well Sample	728 - 758 ft. Upper Permian Seven Rivers	23(c)	0.7	<0.5(c)	6.2(c)	-9.2
Zeeck No. 1 4th Production Zone	2,930 - 2,970 ft. Permian San Andres	32(a)	177	15(a)	800(a)	+4.1
Zeeck No. 1 3rd Production Zone	5,470 - 5,550 ft. Lower Permian Wolfcamp	41(b)	109	35(b)	512(b)	+1.9
Zeeck No. 1 1st Production Zone	7,140 - 7,230 ft. Pennsylvanian Carbonate	56(b)	52.0	56(b)	805(b)	+2.5
Mansfield No. 1 2nd Production Zone	4,514 - 4,638 ft. Lower Permian Wolfcamp	41(b)	61.0	4.3(b)	118(b)	-4.9
Mansfield No. 1 1st Production Zone	4,818 - 4,890 ft. Lower Permian Wolfcamp	38(b)	7.0	2.3(b)	107(b)	-5.1
Sawyer No. 1 5th Production Zone	3,172 - 3,189 ft. Lower Permian Wolfcamp	35(b)	101	17(b)	330(b)	+0.8
Sawyer No. 1 4th Production Zone	4,258 - 4,342 ft. Pennsylvanian Granite Wash	39(b)	34.0	34(b)	460(b)	0
Warman No. 1 Dissolution Zone	1,157 - 1,187 ft. Upper Permian Salado-Tansill and Yates	22(c)	121	4.9(c)	47(c)	-7.1
Batten No. 2 Dissolution Zone	1,310 - 1,323 ft. Upper Permian Seven Rivers	20(c)	22.0	0.4(c)	2.4(c)	-8.3

(a) Dutton and Orr (1985)
(b) Fisher and Kreitler (1985)
(c) Dutton (1985)
(d) L. P. Knauth (1986)

narrow-mouth flint glass bottles after discarding the first several hundred milliliters of filtrate, and then preserved with $HgCl_2$ (0.05 weight percent total sample volume).

Analytical methods

Total organic carbon (TOC) content was measured using potassium persulfate wet oxidation in a sealed ampule followed by infrared spectroscopic determination of CO_2 using the O.I. Corporation Model 524C Organic Carbon Analyzer. The method has a detection limit of approximately 0.1 mg/l.

High Cl^- concentrations were found to interfere with the TOC analyses by consumption of the persulfate oxidizing agent accompanying oxidation of Cl^- to Cl_2 and chlorates. Chloride interference was eliminated by sample dilution and increased oxidant concentrations. Sample dilution, in turn, decreases the sensitivity of the analysis in direct relation to the dilution factor, though this was not a problem in this particular set of samples because of the relatively high TOC concentrations observed.

Acetic, propionic, iso-butyric, n-butyric, and n-valeric acid anions were analyzed using direct-injection packed column gas chromatography (GC) (60/80 mesh Carbopack C/0.3% Carbowax 20M/0.1% H_3PO_4) with FID detection. The method, which is described in greater detail in Means and Hubbard (1985), has a detection limit of approximately 1 mg/l and accuracy of $\pm 10\%$ in the optimal concentration range of > 10 mg/l for each aliphatic acid anion.

The addition of NaCl was found to significantly enhance the chromatographability and reduce the absorption of SCA^3s by the column packing. Consequently SCA^3 standards were made up to NaCl concentrations of approximately 200,000 mg/l. The Palo Duro groundwater samples are brines with Cl^- concentrations generally on the order of 100,000 to 200,000 mg/l (Dutton, 1985; Dutton and Orr, 1985; Fisher and Kreitler, 1985; Kosanke *et al.*, 1985). Hence no further addition of NaCl was necessary.

The development of more sophisticated analytical techniques, such as derivatization (esterification) followed by capillary GC or gas chromatography/mass spectrometry (GC/MS) analysis was attempted without satisfactory results. Pre-analytical solvent extraction clean-up is not readily applicable because of the hydrophilic nature of SCA^3s. The packed column GC procedure described above is sensitive and reproducible. Other applicable GC and liquid chromatography procedures for SCA^3s are described by Hatton and Hanor (1984).

Results

TOC, I^-, Br^-, and $\delta^{18}O$ contents of the Palo Duro brines are reported in Table 1, along with the sample depth, subsurface temperature, and the geologic formation from which each sample was obtained. Short-chain aliphatic acid anion data are presented in Table 2. Each of the organic values reported in Tables 1 and 2 represents the average of six or more analyses.

Total SCA^3 content in Palo Duro brines range up to 440 mg/l and are comprised principally of acetate. Relative abundance of individual SCA^3's average 100:10:5:trace for acetate, proprionate, total butyrate,and valerate, respectively.

When normalized to carbon content and compared with the TOC data in Table 1, SCA^3's are shown to account for approximately $100 \pm 25\%$ of TOC in 10 of the 15 samples (Table 2). Agreement between TOC and SCA^3 data to within $\pm 25\%$ is considered to be quantitative because the accuracy of each analysis is approximately 10% in the optimal concentration ranges (> 5 mg/l for TOC and > 10 mg/l for each aliphatic acid anion). The apparent excess of SCA^3's relative to TOC in the Mansfield No. 2 dissolution zone sample (229%) and to a lesser extent in J. Friemel No. 1, Zone 7 (131%) can be explained in view of their very low SCA^3 and TOC contents, which are close to the detection limits, where analytical results are less accurate. The apparent deficiency of SCA^3's relative to TOC in Mansfield No. 1, Zone 1 and the Detten No. 2 dissolution zone sample may also be at least partially attributed to this effect. However, the deficiencies in normalized SCA^3 relative to TOC content in other samples (Mansfield No. 1, Zone 1; Sawyer No. 1, Zone 5; and Zeeck No. 1, Zone 4) appear to be significant and likely indicate the presence of organic species that have not yet been identified. GC/MS analysis preceded by extraction by methylene chloride and derivatization by diazomethane on selected Palo Duro Basin brines identified a number of other organic species, such as phenol, high molecular weight fatty acids, alcohols, and a few organo-sulfur compounds (Means and Hubbard, 1985). However, their concentrations are extremely low (μg/l range) and account for less than 1% of the TOC in the samples analyzed. The inferred unidentified organic constituents are likely polar, low molecular weight species, otherwise they would have been detected using the above GC/MS procedure. Low molecular weight dicarboxylic acids or hydroxy acids represent a distinct possibility (Kharaka *et al.*, 1985; Surdam *et al.*, 1984).

Controls on the occurrence and distribution of short-chain aliphatic acid anions

As described in the above Review, Carothers and Kharaka (1978) described a temperature-dependent relationship between the abundance and distribution of SCA^3's in formation fluids from the San Joaquin Valley of California and the Houston and Corpus Christi areas of Texas. Broad similarities in SCA^3 content and distribution were observed, corresponding to 3 different temperature regimes. Their Zone 1

Table 2. Short-chain aliphatic acid anion contents of Palo Duro Basin brines.

Well and Production Zone	Acetate (mg/l)	Propionate (mg/l)	Isobutyrate (mg/l)	n-Butyrate (mg/l)	n-Valerate (mg/l)	Total SCA^3 Content (mg/l)	Percent TOC of Sample
J. Friemel No. 1 8th Production Zone	359	51	11	19	<1	440	83
J. Friemel No. 1 7th Production Zone	18	1	<1	<1	<1	19	131
J. Friemel No. 1 6th Production Zone	23	2	<1	<1	<1	25	118
J. Friemel No. 1 4th Production Zone	42	2	<1	<1	<1	44	113
J. Friemel No. 1 1st Production Zone	36	3	<1	<1	<1	39	99
Mansfield No. 2 Shallow Well Sample	4	<1	<1	<1	<1	4	229
Zeeck No. 1 4th Production Zone	212	31	28	11	<1	282	69
Zeeck No. 1 3rd Production Zone	225	23	2	4	1	255	97
Zeeck No. 1 1st Production Zone	131	10	1	2	<1	144	113
Mansfield No. 1 2nd Production Zone	54	5	<1	2	<1	61	42
Mansfield No. 1 1st Production Zone	3	<1	<1	<1	<1	3	17
Sawyer No. 1 5th Production Zone	129	14	1	3	1	148	61
Sawyer No. 1 4th Production Zone	63	2	<1	<1	<1	65	77
Harman No. 1 Dissolution Zone	226	5	<1	<1	<1	231	77
Detten No. 2 Dissolution Zone	6	2	<1	<1	<1	8	15

was characterized by subsurface temperatures lower than 80°C and SCA^3s, predominantly propionate, in concentrations of less than 60 mg/l. Zone 2 corresponded to subsurface temperatures from 80 to 200°C and contained SCA^3s in concentrations up to 4900 mg/l. Acetate generally composed 90% or more of the total SCA^3 content, which peaked at 80°C and decreased with increasing temperature. Zone 3, which was not sampled directly, was inferred to contain no SCA^3s. The decrease in SCA^3 concentrations with increasing temperature in Zone 2 and their absence in Zone 3 were attributed to thermal decarboxylation.

The Palo Duro Basin brines are relatively cool (20–56°C in Table 1; Fisher and Kreitler, 1985; Dutton and Orr, 1985; and Dutton, 1985) and correspond thermally to the Carothers and Kharaka (1978) Zone 1. However, acetate predominates in the Palo Duro system (Table 2), whereas propionate predominates in Zone 1 in the Carothers and Kharaka (1978) study. Also, total SCA^3 concentrations range up to 440 mg/l in Palo Duro Basin brines, whereas concentrations in the Carothers and Kharaka (1978) Zone 1 are less than 60 mg/l. The higher concentrations of SCA^3s associated with relatively cool subsurface temperature may indicate lack or paucity of bacteria necessary for reaction (5) above.

Further dissimilarities in the abundance and distribution of SCA^3s relative to the 3 zones of Carothers and Kharaka (1978) are exhibited in data from the Iberia Oil Field in south-central Louisiana (Workman and Hanor, 1985). Here, the speciation of SCA^3s varies with depth, with acetate predominating in deeper regions and heavier SCA^3 dominating in shallow zones. Clearly, there are no general rules governing the abundance and distribution of SCA^3s in subsurface waters. The environmental controls on SCA^3 chemistry are complex, and various processes such as thermal decarboxylation, bacterial transformation, and groundwater mixing apparently play important but relatively different roles in different hydrogeochemical settings.

While the SCA^3 data from the Palo Duro Basin (Table 2) are not directly interpretable in terms of subsurface temperature, depth, spatial distribution, or geological age, there is a correlation with $\delta^{18}O$ measurements on the same samples, shown in Fig. 2. The samples with $\delta^{18}O$ less than -6 per mil are from above the salt-bearing part of the Permian section and are shown here only for completeness. The two samples with $\delta^{18}O$ above 2.0 and total aliphatic acid anion concentrations above 250 ppm are from the San Andres Formation, which is located midway in the salt-bearing section and presumably is isolated from the brines in the Wolfcamp, Pennsylvanian Carbonate and granite wash aquifers, all of which are located well below the salt-bearing section. The remaining samples are all from the deep basin brine aquifer system and show a general correlation between $\delta^{18}O$ and concentrations of SCA^3s. The $\delta^{18}O$

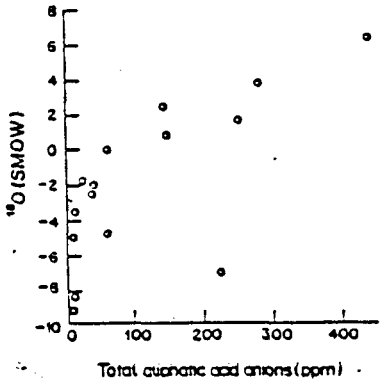

Fig. 2. Total short-chain aliphatic acid anion content plotted as a function of $\delta^{18}O$.

data have been interpreted to represent differing degrees to which the deep basin brines have come to oxygen isotope equilibrium with the bulk carbonates of the aquifer rocks (Knauth and Hubbard, 1984; Fisher and Krietler, 1985). Knauth and Hubbard (1984) consider the differences in $\delta^{18}O$ values to be related to total residence times in carbonate rocks (the more positive the value the longer the residence time for those samples not in isotopic equilibrium), whereas Fisher and Krietler (1985) consider the oxygen isotopic variation to represent mixtures between an older, oxygen isotope equilibrated brine and a much later, non-equilibrated groundwater. However, Zaikowski *et al.* (1984) and Hubbard *et al.* (1984) show from a combination of ^{20}Ne and ^{36}Ar data and the geological history of the Palo Duro Basin that some of the brines with low $\delta^{18}O$ values may have been in the subsurface since the Permian and that they were likely saturated, or near-saturated when they entered the subsurface. Thus the interpretations noted, which are based principally on oxygen isotope data, are highly simplified and do not provide a basis for definitive conclusions.

Furthermore, the noble gas data presented by Zaikowski *et al.* (1984) and Hubbard *et al.* (1984) suggest possible cross formational flow in the deep basin brine aquifers at areas not penetrated by the wells. From this perspective the $\delta^{18}O$ values and SCA^3 concentrations of the brines may be the integrated result of water-rock reactions in an unknown fraction of the deep basin brine aquifers, not just in the aquifer lithologies from which they were sampled.

In summary, the abundance and distribution of SCA^3s in groundwater reflect the rates of several major processes, including: (a) their genesis from sedimentary organic matter and expulsion into formation fluids; (b) thermal decarboxylation; (c) bacterial transformation and degradation; and (d) reservoir flushing. The rate of these various processes in turn depend upon parameters such as temperature, pressure, pH, redox potential, bacterial conditions, and groundwater flow rates. A previous study suggests that SCA^3 contents decrease with increasing

age of the geologic formation in which they reside (Carothers and Kharaka, 1978). However, in the Palo Duro Basin the concentrations of SCA's in the brines may depend on groundwater residence time in a given lithology, that is, longer groundwater residence times in carbonate lithologies appear to be associated with higher SCA concentrations.

Radionuclide complexation

One of the concerns in siting and assessing the performance of a geologic repository for the disposal of high-level radioactive wastes is the rate at which radionuclides will migrate in groundwater upon waste package failure. Radionuclide transport rates depend not only upon groundwater flow rate, but also upon radionuclide solubility and speciation. It has been shown previously that complexed radionuclides migrate faster because complexation increases radionuclide solubility and diminishes the extent of radionuclide adsorption by geologic substrates (Means *et al.*, 1978).

The discussion below presupposes that, at some point in time after waste disposal in a Palo Duro Basin site, a hypothetical waste package is breached and radionuclides are introduced by some mechanism in to a Wolfcampian, Pennsylvanian, or granite wash carbonate aquifer. The issue addressed here is the extent to which SCA's in Palo Duro Basin brines would be expected to complex chemically with radionuclides and affect their mobility in groundwater, relative to the inorganic ligands in the brines.

The effects of SCA's on radionuclide complexation in complex solutions such as the Palo Duro Basin brines are best investigated by using thermodynamic chemical equilibria calculations as described, for example, by Jenne (1979). Complex equilibria calculations for organo-actinide systems are constrained by the incompleteness of and inaccuracies in the thermodynamic data base (Cleveland, 1979) and are beyond the scope of this study. Consequently, radionuclide complexation by SCA's in Palo Duro Basin brines is qualitatively evaluated by examining simple stability constant relations.

Table 3 lists stability constant values for selected metals and actinides, four organic ligands, and three inorganic ligands. Humic acid, fulvic acid, and EDTA are included for comparative purposes because they have been shown to contribute to actinide solubility and mobility in field studies (Cleveland and Rees, 1981) and laboratory investigations (Boggs and Seitz, 1984). In addition, fulvic acid has been identified in deep groundwater from candidate repository sites in Sweden (Means, 1982) but has not been found in deep brines from the Palo Duro Basin. The three inorganic ligands were chosen because they are present in Palo Duro Basin brines (Molecke, 1983; Fisher and Kreitler, 1985).

Examination of the stability constant (K) data in

Table 3. Logarithmic stability constants (log K) for selected radionuclide- and metal–ligand complexes at 25°C ($M^{z+} + L^{y-} \rightleftharpoons ML^{z-y}$)

	Log K						
Metal	Acetate	Humic Acid	Fulvic Acid	EDTA	Cl^-	SO_4^{2-}	F^-
Na^+	-0.13(a)	—	—	1.7(k)	—	0.7(m)	—
Ca^{2+}	0.45(a)	3.2(c)	3.4(i)	10.71(k)	—	1.0(m)	0.6(m)
Fe^{2+}	1.0(a)	—	5.6(j)	14.3(k)	—	2.2(m)	0.8(m)
UO_2^{2+}	2.4(a)	5.1(d) 7.8(e) 4.7-6.7(f)	5.6-7.4(f)	7.4(k)	-0.1(m)	1.8(m)	4.5(m)
PuO_2^{2+}	2.1(a)	—	—	16.2(b)	0.1(m)	—	—
Al^{3+}	1.5(a)	—	3.7(i)	16.3(k)	—	—	6.1(m)
Am^{3+}	2.0(a)	7.3(g)	—	17.8(k)	-0.1(m)	1.6(m)	3.4(m)
Cm^{3+}	2.0(a)	—	—	18.1(k)	—	1.9(m)	3.3(m)
Pu^{3+}	2.0(b)	—	—	18.4(b)	-0.1(m)	1.3(m)	—
Th^{4+}	3.9(a)	13.2(h)	10.8(h)	23.2(k)	0.18(m)	3.2(m)	7.8(m)
U^{4+}	—	4.5-7.0(f)	4.9-6.6(f)	25.8(h)	—	3.4(m)	9.9(m)
Pu^{4+}	5.1(b)	—	—	25.8(b)	0.14(m)	3.7(m)	8.8(m)

(a)Martell and Smith (1977)
(b)Cleveland (1979)
(c)Choppin and Shanahag (1981)
(d)Shanahag and Choppin (1981)
(e)Kuribek and Podlaha (1980)
(f)Li et al. (1980)
(g)Bertha and Choppin (1978)
(h)Nash and Choppin (1980)
(i)Schnitzer and Khan (1972)
(j)Pagenkopf (1978)
(k)Martell and Smith (1974)
(m)Smith and Martell (1976)

Table 3 shows that acetate is a much weaker ligand than EDTA. K's for most of the EDTA complexes in Table 3 are 10–20 orders of magnitude higher than K's for the acetate complexes. Humic and fulvic acids are also stronger ligands than acetate but not as strong as EDTA. Stability constants for humate/fulvate-metal complexes are approximately 3–9 orders of magnitude higher than for the acetate complexes. Clearly, the presence of EDTA or, to a lesser extent, humic and fulvic acids in the waste disposal environment is undesirable because stability constant data suggest that they form much stronger complexes with radionuclides.

Relative to the inorganic ligands in Table 3, acetate and the other SCA's, all of which have very similar complexation characteristics (Hatton and Hanor, 1984), form stronger actinide complexes than chloride, slightly stronger complexes than sulfate, and weaker complexes than fluoride. Using the mass action equation:

$$M^{x+} + L^{y-} \rightleftharpoons ML^{x-y} \tag{7}$$

where:

$$K = \frac{[ML^{x-y}]}{[M^{x+}][L^{y-}]} \tag{8}$$

and assuming that $[L^{y-}]$ is approximated by the total ligand concentration $[L']$ in systems where $[L']$ is greater than the total actinide concentration $[M']$, then:

$$K[L'] = \frac{[ML^{x-y}]}{[M^{x+}]} \tag{9}$$

In other words, the molar ratio of complexed metal to uncomplexed metal is equal to the product of the stability constant and the total complexing agent concentration. Hence, high ligand concentrations can compensate for low stability constants, and vice versa.

Applied to the stability constant data in Table 3 and average SCA's (Table 2) and typical iorganic ligand concentrations (Molecke, 1983; Fisher and Kreitler, 1985) in Palo Duro Basin brines, the relative complexing capacities of SCA's and the inorganic ligands can be compared. Chloride is a much weaker ligand than acetate; however, chloride concentrations in Palo Duro Basin brines are much higher. Assuming an average stability constant of 10^0 for actinide–chloride complexes from Table 3 and an average total chloride concentration of 3.75 M:

$$\frac{[MCl^{x-1}]}{[M^{x+}]} = K \cdot [Cl'] = 10^0 \cdot 3.75 \tag{10}$$
$$= 3.75$$

Similar calculations may be done for sulfate and fluoride:

$$\frac{[MSO_4^{x-2}]}{[M^{x+}]} = K \cdot [SO_4'] = 10^{2.4} \cdot 10^{-1.96} \tag{11}$$
$$= 2.8$$

$$\frac{[MF^{x-1}]}{[M^{x+}]} = K \cdot [F'] = 10^{5.8} \cdot 10^{-4.3} \tag{12}$$
$$= 31.6$$

Average SCA's concentrations in the 15 Permian and upper Pennsylvanian groundwater samples average $10^{-2.7}$ M (Table 2), and actinide-acetate stability constants average $10^{2.3}$ (Table 3), therefore:

$$\frac{[MCH_3COO^{x-1}]}{[M^{x+}]} = K \cdot [CH_3COO'] \tag{13}$$
$$= 10^{2.3} \cdot 10^{-2.7}$$
$$= 1.3$$

Therefore the total amount of actinide associated with SCA's in Palo Duro Basin brines is expected to be significantly less than that associated with chloride, sulfate, or fluoride. According to these calculations SCA's concentrations would have to be much higher than those observed before complexation of actinides by SCA's will dominate the collective amount of actinide complexation by chloride, sulfate, and fluoride.

These simple calculations for 25°C are not intended to be a rigorous quantitative treatment of metal complexation by SCA's. Chemical equilibria in brines are very complex, with numerous competing reactions. Even state-of-the-art chemical speciation and reaction-pathway codes, such as EQ3/EQ6 (INTERA, 1983), suffer from data limitations and problems in handling high ionic strength solutions.

Note that Gardner (1974) evaluated organic versus inorganic trace metal complexes in sulfidic marine waters and concluded that various free amino acids and carboxylic acids (including acetate) were not as effective in metal complexation as the inorganic ligands, bisulfide and polysulfide.

Palmer and Drummond (1986) point out that acetate may be able to survive hydrothermal temperatures (< 300°C) long enough to promote the mobility of certain metals and that acetate–metal complexes are stronger than chloro–metal complexes. However, Kharaka *et al.* (1985) studied organic-inorganic interactions in various oil-field brines using the equilibria code, SOLMNEQ II, and predicted that complexation between Al, Zn, Pb, and U and mono- and dicarboxylic acid anions would be minor relative to the chloro-metallic complexes. Metal complexation with sterically-favorable organic ligands such as salicylic acid (o-HOC_6H_4COOH) was shown to be more significant, however species such as salicylic acid have not been reported in significant quantities in oil-field brines. Kharaka *et al.* (1985) conclude that SCA's may play an indirect role in promoting metal transport in deep formation fluids, i.e. by controlling the pH and Eh of the groundwaters. We conclude that very high concentrations of SCA's or their dicarboxylic analogues will be required before these weak organic ligands exhibit

significant metal transport characteristics. Further study is needed.

Groundwater origin and evolution

Attempts to reconstruct the chemical history of subsurface brines derived from seawater, such as Palo Duro Basin brines, require the use of one or more "marker" constituents. Such a constitutent must neither precipitate during the evaporation of seawater nor participate in diagenetic reactions with subsequent mineralogical environments. Bromide content has been considered a conservative parameter because it is relatively free from participation in diagenetic reactions. Both Rittenhouse (1967) and Carpenter (1978) have used Cl^-/Br^- ratios to infer the origin of some oil-field brines. While the assumption that Br^- is probably not significantly removed via precipitation or adsorption during diagenesis is probably correct, data presented below suggest that additional Br^- may be introduced by decomposing organic matter such as red and brown algae, which contain up to more than 3000 mg/kg Br^-.

The organic geochemistry of the Palo Duro Basin brines (Table 2) may appear to have no direct bearing on groundwater origin and evolution, but when examined in conjunction with iodide (I^-) and bromide (Br^-) concentrations (Table 1), some interesting trends appear. Short-chain aliphatic acid anions and iodine (whether present as I^- or IO_3^-, both of which may be thermodynamically stable under environmental conditions) have been shown to have a common origin in oil-field brines, namely, they are both water-soluble anions released from lipid-rich kerogen into groundwater (Wedepohl, 1978b). Hitchon and Horn (1974) correlated I^- and the presence of petroleum in formation waters in Paleozoic strata from Alberta, Canada. Carothers and Kharaka (1978) showed that I^- concentrations increase with increasing concentrations of SCA^3s and concluded that they are derived from the same marine sedimentary organic matter source.

Iodide in oil-field brines unquestionably has a strong contribution from sedimentary organic matter. Iodide concentrations in oil-field brines range from 10 to 70 mg/l (Carothers and Kharaka, 1978) or up to 56 mg/l in this study (Table 1), and typically exceed 10 mg/l (Hitchon and Horn, 1974). Iodide concentrations average only 0.002 mg/kg in fresh water (Bowen, 1979) and only 0.06 mg/l in seawater (Wedepohl, 1978b), and even 15-fold evaporation of seawater would give rise to total iodide concentrations not exceeding 1 mg/l. Iodide occurs in a minor constituent of various evaporite minerals, but only rarely forms separate minerals (Wedepohl, 1978b). Consequently the dissolution of evaporites is unlikely to contribute much I^- to groundwater. On the otherhand I^- is highly enriched in sedimentary organic matter, particularly that derived from marine brown and red algae and, to a lesser extent, marine flowering plants (Wedepohl, 1978b). Such organic matter is believed to be an important precursor to petroleum (Eisma and Jurg, 1969) and is postulated to be the primary source of I^- in Palo Duro Basin brines.

Sedimentary organic matter also appears to contribute significantly to Br^- concentrations in certain Palo Duro Basin brines. Seawater and fresh water possess average Br^- concentrations of 65 mg/l (Wedepohl, 1978a) and 0.014 mg/kg (Bowen, 1979), and Br^- is the thermodynamically stable species in both (Wedepohl, 1978a). Because of the relatively high concentrations of Br^- in seawater, evaporative concentration of seawater is capable of generating Br^- values in the upper hundred to low thousand mg/l range. Halite contains approximately 65 ppm Br^-; hence, dissolution of halite by seawater would result in a brine having a Br^- content less than 100 mg/l (Carpenter, 1978). Oil-field brines are sometimes enriched in Br^-, with concentrations ranging up to 1800 mg/l (Wedepohl, 1978a). Strong correlations have been observed between Br^- and organic matter in some petroliferous sediments and the enrichment of Br^- in oil-field brines has been linked in part with the breakdown of organic matter rich in bromine. Red and brown algae are particularly enriched in Br^-, with concentrations ranging up to 3300 mg/kg (Wedepohl, 1978a).

Permissive evidence for the organic contribution of Br^- in Palo Duro Basin brines is provided by the strong correlations between Br^- and I^- and SCA^3 contents (Figs 3 and 4). All of the SCA^3s, most of the I^-, and a portion of the Br^- concentrations are interpreted to have been derived from Paleozoic, lipid-rich sedimentary organic matter. This observation suggests that there are limitations regarding the use of Br^- as a conservative marker constitutent, paticularly in oil-field brines.

In conclusion SCA^3s in deep brines appear to be useful in unraveling brine origin, evolution, and migration. The interactive nature of organic, inorganic and isotopic geochemical evidence stresses the need for consideration of their relations in such systems.

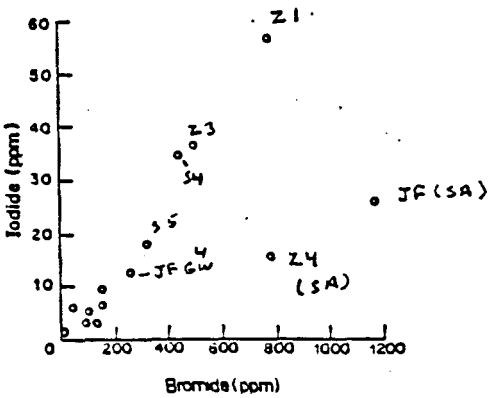

Fig. 3. Total bromide content plotted as a function of total iodide content.

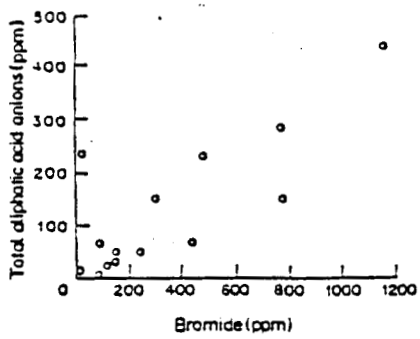

Fig. 4. Total bromide content plotted as a function of total short-chain aliphatic acid anion content.

Petroleum proximity indicators

According to Dutton *et al.* (1982) the Palo Duro Basin possesses most of the geological and geochemical characteristics necessary for the generation and accumulation of hydrocarbons, namely reservoirs, traps, and source rocks. The thermal regime is the weakest link in the basin's petroleum production potential and borders between mature and immature. Actual discoveries in the interior of the Palo Duro Basin have been sparse, and little exploration activity is currently being conducted.

As noted above, SCA^3 concentration in Palo Duro Basin brines show no trend with depth nor the geologic formation in which they reside. The presence of SCA^3s in the Palo Duro system and the apparent lack of significant accumulations of petroleum suggest that SCA^3s cannot be viewed as direct indicators of petroleum proximity, at least in the Palo Duro Basin.

CONCLUSIONS

Short-chain aliphatic acid anions (SCA^3) are common in oil-field brines and other deep subsurface brines, particularly anaerobic brines that have not been flushed by recent meteoric water. They appear to be formed during the thermal and/or bacterial decomposition of sedimentary organic matter. Their abundance and distribution are controlled primarily by their rates of formation, *in-situ* thermal decarboxylation (which is related to temperature and pH), and biotransformation (which is related to redox potential). Reservoir flushing and groundwater circulation must also be considered. SCA^3 in subsurface waters are of geochemical interest because of their well-defined roles:

(1) in subsurface mineral dissolution leading to porosity enhancement (Surdam *et al.*, 1984); Surdam and Crossey, 1985);
(2) as precursors to natural gas (Carothers and Kharaka, 1978);
(3) as possible petroleum proximity indicators (Zinger and Kravchik, 1972);
(4) as tracers of subsurface groundwater flow (Workman and Hanor, 1985; Hanor and Workman, 1986); and
(5) as major contributors to titratable alkalinity (Willey *et al.*, 1975).

They may also provide valuable information regarding:

(6) metal complexation and transport characteristics in subsurface fluids;
(7) groundwater pH and redox characteristics; and
(8) groundwater evolution and origin.

Clearly the number of published measurements of SCA^3 in deep groundwaters is not commensurate with their potential importance and significance in such systems.

Short-chain aliphatic acid anion (SCA^3) content in 15 Palo Duro Basin, Texas brines ranges up to 440 mg/l. Relative abundances of individual SCA^3s average 100:10:5:trace for acetate, propionate, total butyrate, and valerate, respectively. The brines occur in Pennsylvanian through Upper Permian strata at depths ranging from 728 to 8200 ft with corresponding subsurface temperatures of from 17.5 to 55°C. SCA^3s account for $100 \pm 25\%$ of the measured total organic carbon (TOC) content of 10 of the 15 groundwaters. The presence of as yet unidentified organic species, perhaps hydroxy- or dicarboxylic acids, is inferred in the few samples where TOC content significantly exceeds total SCA^3 content normalized to carbon.

The distribution and abundance of SCA^3s in deep formation fluids from this and other well described geologic settings (e.g. Carothers and Kharaka, 1978; Workman and Hanor, 1985; Kharaka *et al.*, 1985; Hanor and Workman, 1985) show wide variations, even in samples from similar temperature regimes. We conclude that environmental controls or SCA^3 chemistry are complex, and that various processes, particularly thermal decarboxylation, bacterial transformation, and groundwater mixing play important but relatively different roles in different hydrogeochemical settings.

SCA^3 contents in Palo Duro Basin brines do not correlate well with either subsurface temperature, depth, or geologic age, but correlate roughly with $\delta^{18}O$ data. High SCA^3 values are found in samples having the highest $\delta^{18}O$ contents. Other principal causes of the observed variations remain unknown.

Simple stability constant relationships suggest that, at their average concentrations in Palo Duro Basin brines, SCA^3s would be expected to complex certain metals to a lesser extent than the inorganic ligands present in the brines. At higher SCA^3 concentrations or in low ionic strength solutions, the metal complexation characteristics of SCA^3s may be more significant.

Strong positive correlations between SCA^3, I^-, and

Br^- contents of Palo Duro Basin brines suggest spatial commonalities in origin. All of the SCA^3s, most of the I^-, and a portion of the Br^- concentrations are interpreted to have been derived from Paleozoic, lipid-rich sedimentary organic matter. The importance of this observation lies in the use of Br^- as a conservative "marker" constitutent in evaluating groundwater origin and evolution. The possible organic source of Br^- in certain formation fluids should be recognized when interpreting groundwater evolution through relationships between Br^- and other ions.

Finally, SCA^3s are commonly observed in oil-field brines, but they are also observed to occur in nonproducing regions, such as the central part of Palo Duro Basin. Hence, they may not be direct indicators of petroleum proximity.

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This procedure is not being used. Must be validated on P.B. Brine

Determination of Total Alkalinity in Brines

Abstract

The measurement of total alkalinity by determining the end-point of the titration of brine with strong acid was found to be dependent on the conditions of the titration procedure. Successive titrations performed in open beakers resulted in variable curve shapes and corresponding end-points (alkalinities). However, replicate titrations performed under a constant 100% CO_2 atmosphere in restricted beakers yielded nearly identical results. Therefore, the method employing a constant 100% CO_2 atmosphere is recommended as a more reliable standard procedure for the purposes of reporting comparative brine alkalinity through time.

Introduction

Alkalinity is the total mineral acid neutralizing capacity of a sample. Alkalinity is an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known. Total alkalinity is usually determined by adding a standard acid to water and recording the volume used to neutralize a sample to pH 4.5. This procedure is usually sufficient for relatively fresh water samples where the acid neutralizing capacity is due to the bicarbonate, carbonate, and hydroxide species. However, weak acids such as acetic, boric, phosphoric and silicic can also contribute titratable alkalinity species (for the brine's scaling tendency, we are interested only in the bicarbonate and carbonate). These additional species, when present in a brine, will effectively "flatten-out" the titration curve of pH vs. volume acid added. This interference usually results in a less well defined end-point (also known as the equivalence point where all alkalinity species have been neutralized). For this reason it is necessary to construct a potentiometric titration curve of pH vs. volume of acid added to determine the equivalents of alkalinity originally present in the sample which will be equal to the equivalents of acid added to reach the end-point. The end-point is recognized as an inflection point in the titration curve or the point where the curve changes concavity.

The usual titration procedure involves titrating samples in an Erlenmeyer flask at room temperature. However, as the dissolved CO_2 in the sample exsolves, the pH increases. This results in an extremely erratic titration curve during the early stages of titration and variable curve shapes in replicate samples. This variation in curve shape can be prevented by performing the titration under a controlled CO_2 partial pressure because CO_2 partial pressure has no affect on total alkalinity (as measured corresponding to an inflection point of the titration curve). This method yields nearly identical curve shapes on replicate samples and thus improves the reproducibility of alkalinity determinations.

Experimental Procedure and Results

Samples were collected by the Rice University brine research group at the well site on February 27, 1987 by slowly circulating the brine through a coil of tubing immersed in a ice bath and bubbling carbon dioxide through the sample as the bottle filled. These clear (precipitate-free) samples were tightly sealed and remained refrigerated until the time of analysis.

Two titrations of 100 ml samples of Gladys McCall brine were performed in open beakers without bubbling carbon dioxide through the samples. The resulting titration curves are shown in Figure 1. The x-axis also represents the addition of acid from left and right.

The first sample (represented by diamonds) was titrated immediately without letting the sample equilibrate with the atmosphere prior to titration. Note the highly erratic nature of pH during the early phase of titration where the pH of the sample was being controlled by the kinetic effects of CO_2 exchange with the atmosphere. The end-point of this titration occurred at a pH of 3.3 and an alkalinity of 427 mg/l HCO_3-.

The second sample (represented by circles) was allowed to de-gas for approximately 30 min prior to titration. The sample pH drifted from 5.8 to 7.2 during this equilibration period. As expected, the titration curve was smoother but the end-point was found to occur at a pH of 3.0 and a total alkalinity of 360 mg/l HCO_3-.

Thus, by waiting 30 min for gas exchange with the atmosphere, the measured alkalinity decreased by approximately 15%. (Recall that these samples had been collected under a CO_2 partial pressure of 1 atmosphere and therefore a considerable amount of degassing was taking place). Therefore it is apparent that the alkalinity measurements are extremely sensitive to the nature of CO_2 exchange which is not easily controlled in an open beaker.

Revised procedure:

Two more brine samples were titrated in a revised procedure where the partial pressure of carbon dioxide above the sample was kept constant at one atmosphere. This was accomplished by the use of a stoppered beaker which had two holes; one for the pH electrode and one samller hole for both the CO_2 and digital titrator delivery tubes. The sample was stirred with a magnetic stirrer while pure carbon dioxide was slowly bubbled through the sample. The resulting titration curves are shown in Figure 2. Note that the morning and afternoon titrations were essentially identical. The measured end point was at pH = 3.2 with total alkalinity of 475 mg/l as HCO_3- (bicarbonate). A re-titration after the addition of a known amount of $NaHCO_3$ was within 1% of the previous result.

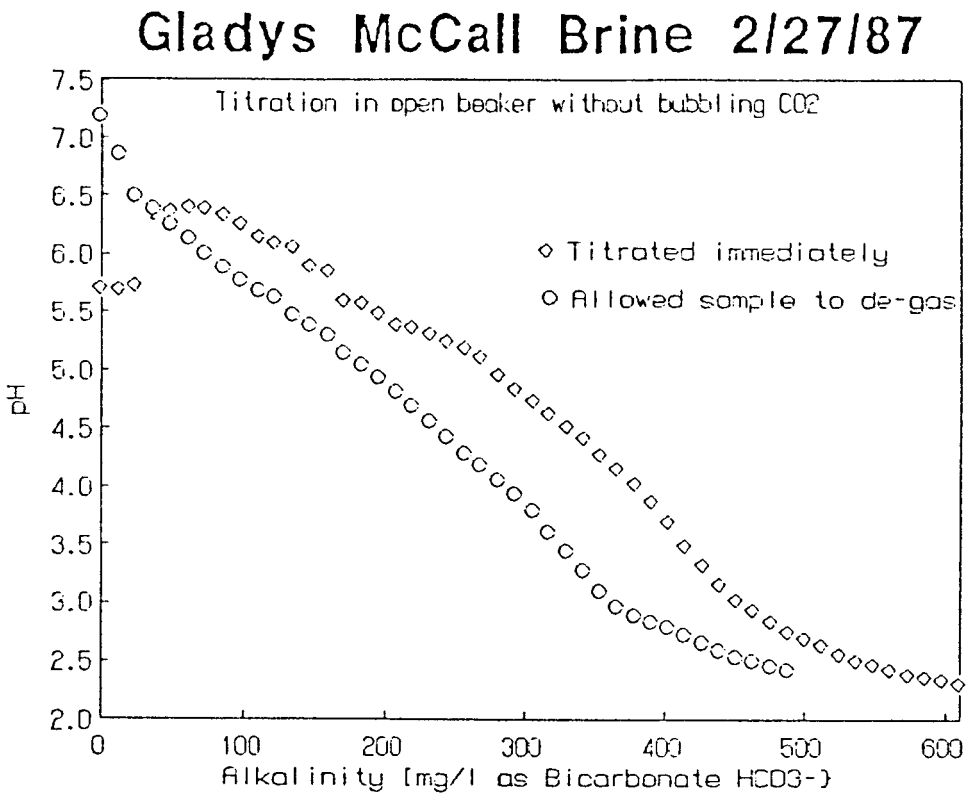

Figure 1. Titration of brine sample in open beaker without bubbling CO_2. Replicate analyses are shown to be dependent on titration conditions resulting in variable curve shapes and different end-points.

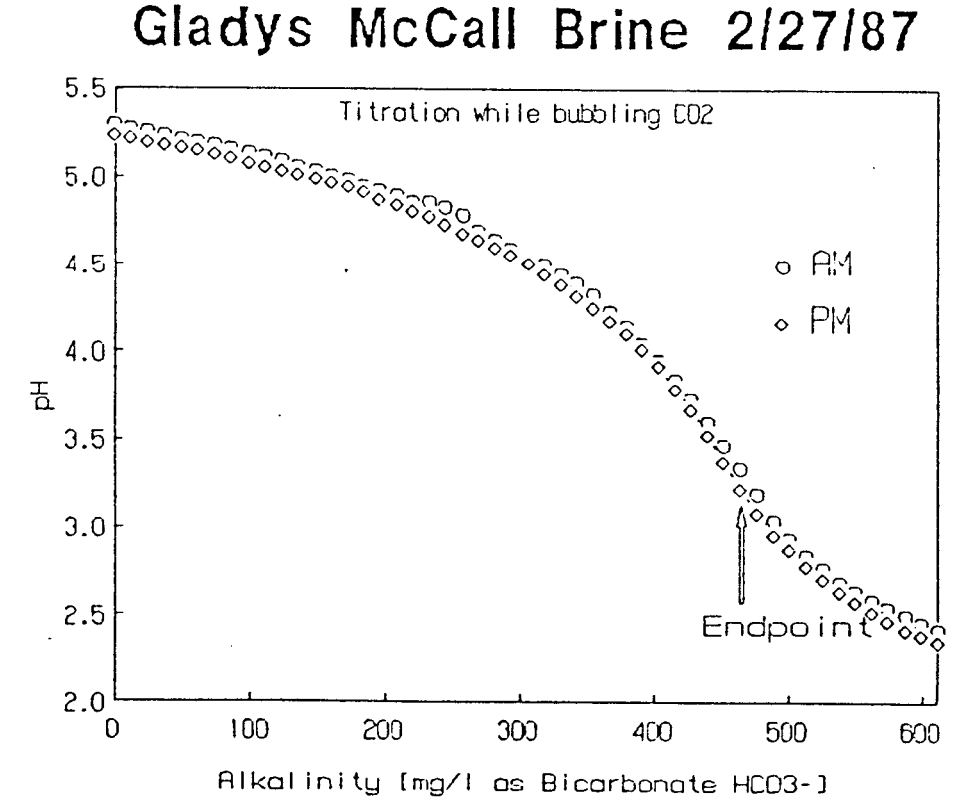

Figure 2. Titration of brine sample in restricted beaker under constant 100% CO_2 atmosphere. Morning and afternoon titrations yield virtually identical end-points at 475 ± 5 mg/l HCO_3^-.

Conclusions

In terms of reproducibility of results, the revised potentiometric titration method under a constant CO_2 atmosphere is superior for determining alkalinity. It is recommended that future reported values of alkalinity be measured by this procedure. This will provide a more rigorous basis for comparing changes in brine alkalinity in the future.

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Appendix

Calculations

Potentiometric titration to end-point pH:

$$\text{Alkalinity, mg } HCO_3^-/l = \frac{A \times N \times 61{,}000}{\text{ml sample}}$$

where

A = mL standard acid used*
N = Normality of standard acid used**

*Using the HACH digital titrator:

$$\text{ml} = \frac{\text{digits}}{800}$$

**Using the HACH procedure:

N = 1.600 ± 0.005 Sulfuric Acid

Conversion of reported alkalinity as calcium carbonate to alkalinity as bicarbonate:

Alkalinity (mg/l) as $CaCO_3$ x 1.22 = alkalinity (mg/l) as HCO_3-

Appendix Brine-G

"Parametric Study of Separator Performance"

containing procedures for "total carbon dioxide analysis"

INSTITUTE OF GAS TECHNOLOGY

PARAMETRIC STUDY OF SEPARATOR PERFORMANCE

by

Christopher G. Hayden
Philip L. Randolph

Paper Presented at

FIFTH GEOPRESSURED-GEOTHERMAL ENERGY CONFERENCE

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TABLE OF CONTENTS

ABSTRACT

After testing to determine reservoir characteristics of the HO&M Prairie Canal Co., Inc., Well No. 1, an additional flow test was performed to study operating characteristics of the separator used on tests of Wells of Opportunity. The separator study consisted of combining gas and brine flow-rate data with analyses of simultaneously collected gas and brine samples at each of six separator pressures in the range of 140 to 1029 psia. Brine temperatures at sample collection times varied between 187°F and 238°F. Temperatures, pressures, and brine chemistry were such that significant carbonate precipitation did not occur.

Total gas remaining in solution in brine leaving the separator varied between 0.6 and 7.0 SCF/bbl and was reasonably consistent with laboratory data on gas solubility. This dissolved gas contained 27 to 35 mole percent CO_2.

The partition of hydrocarbon species between the gas and brine was found to be a linear function of partial pressure of each species. At a methane partial pressure of 922 psia, 4.9 SCF of methane (11.6% of total produced) remained in solution in brine leaving the separator. For the gas compositions produced, separator efficiencies (percentage of component in the gas stream) varied between extremes as follows:

Gas Component	Separator Efficiency at 140 psia	Separator Efficiency at 1025 psia
Gaseous CO_2	83.4-86.0	36.0-39.6
CO_2+HCO_3^- + CO_3^{--} as CO_2	62.0-64.0	27.4-30.0
Methane	98.7-98.8	84.5-86.6
C2+	99.0-99.1	88.8-91.0

CO_2 content of flare line gas leaving the separator varied between extremes of 6.2 mole percent at 1029 psia and 11.6 mole percent at 140 psia. The sum of quantities of CO_2 in gas and brine from the separator also varied with operating conditions. However, total CO_2 content of produced brine including HCO_3^- and CO_3^{--} was found to be constant.

The partition of hydrocarbons and CO_2 between gas leaving the separator and brine leaving the separator was found to depend upon temperatures as well as pressure. This dependence is such that thermal energy recovery from brine before separation would improve the quality of gas recovered at any specific separator pressure.

INTRODUCTION

Conduct of the three flow tests to determine reservoir and fluid properties of the HO&M Prairie Canal Co., Inc., Well No. 1 required numerous increases in separator pressure because of increasing injection pressure on the disposal well. Field data interpretation during those tests revealed substantial variations in CO_2 content of gas from the separator plus variations in total produced gas/brine ratio that appeared to correlate with separator pressure rather than production well conditions.

During the first two flow tests, a Rice University team headed by Drs. John Oddo and Mason Thomson was on location performing inhibitor studies. Their evaluation of scaling potential required knowledge of separator efficiency for CO_2 removal (Oddo and Thomson, 1981). Field interactions between IGT and Rice University personnel developed mutual understanding of the importance of equilibria between $CO_2(g)$, $CO_2(aq)$, HCO_3^-, and CO_3^{--} (the $CO_2/HCO_3^-/CO_3^{--}$ system) in relation to both removal of CO_2 gas by the separator and the formation of carbonate scale. It was recognized that total inorganic carbon in this system should be constant but that the partition among species in the $CO_2/HCO_3^-/CO_3^{--}$ system may well depend upon operating conditions. This in turn led to definition of a practicable sample collection and analysis procedure to provide relevant quantitative data.

An additional flow test was performed so that the sample collection and analysis procedure could be implemented for a wide range of separator pressures. Details of that flow test, presentation of data obtained, and interpretation of that data are covered in this paper.

PROCEDURES

Operational Constraints and Sample Collection

The March 5, 1981, study of separator performance was preceded by about 8 days of production involving three flow tests between February 21, 1981, and March 2, 1981. This operating experience defined operational constraints upon conduct of the separator study. The most significant of these were as follows:

- Brine rates in excess of 4500 bpd were accompanied by substantial sand production and rapidly increasing injection pressure at the disposal well.
- Operation at separator pressures less than 250 psig would require brine flow to the reserve pit which had to be minimal because the remaining pit capacity was limited.
- Reasonably stable operation was only possible in the range of separator pressures and temperatures encompassed by the points shown in Figure 1. These points are the brine temperatures and separator pressures at the times of collection of 52 gas samples analyzed during the entire sequence of well tests.

The overall effect of these constraints was that operation at low separator pressure required low production rates and that high separator pressure required high rates. This in turn resulted in higher brine temperatures for the higher separator pressures.

Production for the separator study began at 1940 hours on March 4, 1981. Since the wellhead had been cooling during a prior 2-day shut-in period, an initial flow rate of about 4500 bpd was selected to provide the fastest heating possible without excessive sand production and buildup of disposal well injection pressure. By 0030 hours on March 5, 1981, surface brine temperature had increased to above 200°F and reasonably stable

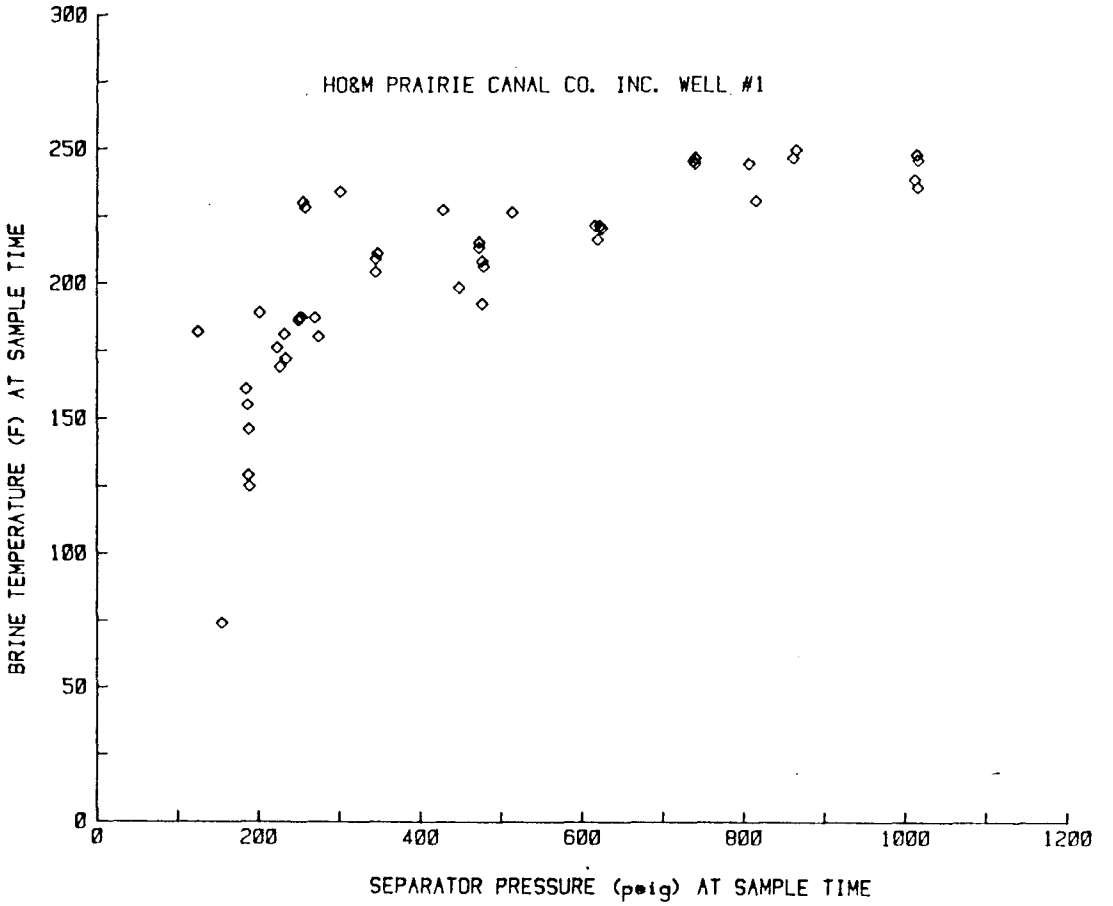

Figure 1. BRINE TEMPERATURES AND SEPARATOR PRESSURES AT GAS SAMPLE COLLECTION TIMES

operation had been achieved. Therefore, the first suite of gas samples were collected at that time.

Changes in operating conditions for the separator study during March 5, 1981, are portrayed graphically in Figure 2. Collection of suites of samples for analysis after changes in brine production rate was delayed until after "bottoms up" following each change. In addition, an hour of consistent production following each change in separator pressure was a prerequisite for sample collection. Two suites of samples were collected for each of six different separator pressures. However, one of the samples collected at 266 psia was lost due to a leaky valve on the sample vessel.

Produced Gas/Brine Ratio

One-half-hour average flare line gas and brine production rates, corrected to 14.73 psia and 60°F, were deduced from orifice meter and separator brine turbine data using the procedures described in the companion paper, "Gas/Brine Ratios from Tests of Five Wells of Opportunity" by P. L. Randolph. Aspects of those procedures particularly relevant to the separator study are as follows:

- Orifice meter gas flow was calculated using measured gas composition for each separator pressure and with correction for water vapor content at orifice meter temperature.
- Brine Rate for each 1/2-hour interval was reduced to standard conditions using average values of separator pressure and brine temperature for that time interval plus properties of water.
- An estimate of gas content of brine to the disposal well was calculated for each 1/2-hour time interval using the algorithm developed by S. K. Garg for methane solubility in distilled water. (Garg et al., 1978).

Resultant calculated gas/brine ratios are shown in Figure 3. The ratio of flare line gas to produced brine and the calculated total produced gas/brine ratios are shown in the upper two curves. The lower portion of the figure shows calculated gas content of disposal well brine as well as measured values for quantity of gas liberated by reducing pressure on cooled brine to ambient temperature and pressure. Sampling and analysis procedures to develop these data points are described in the next section of this paper.

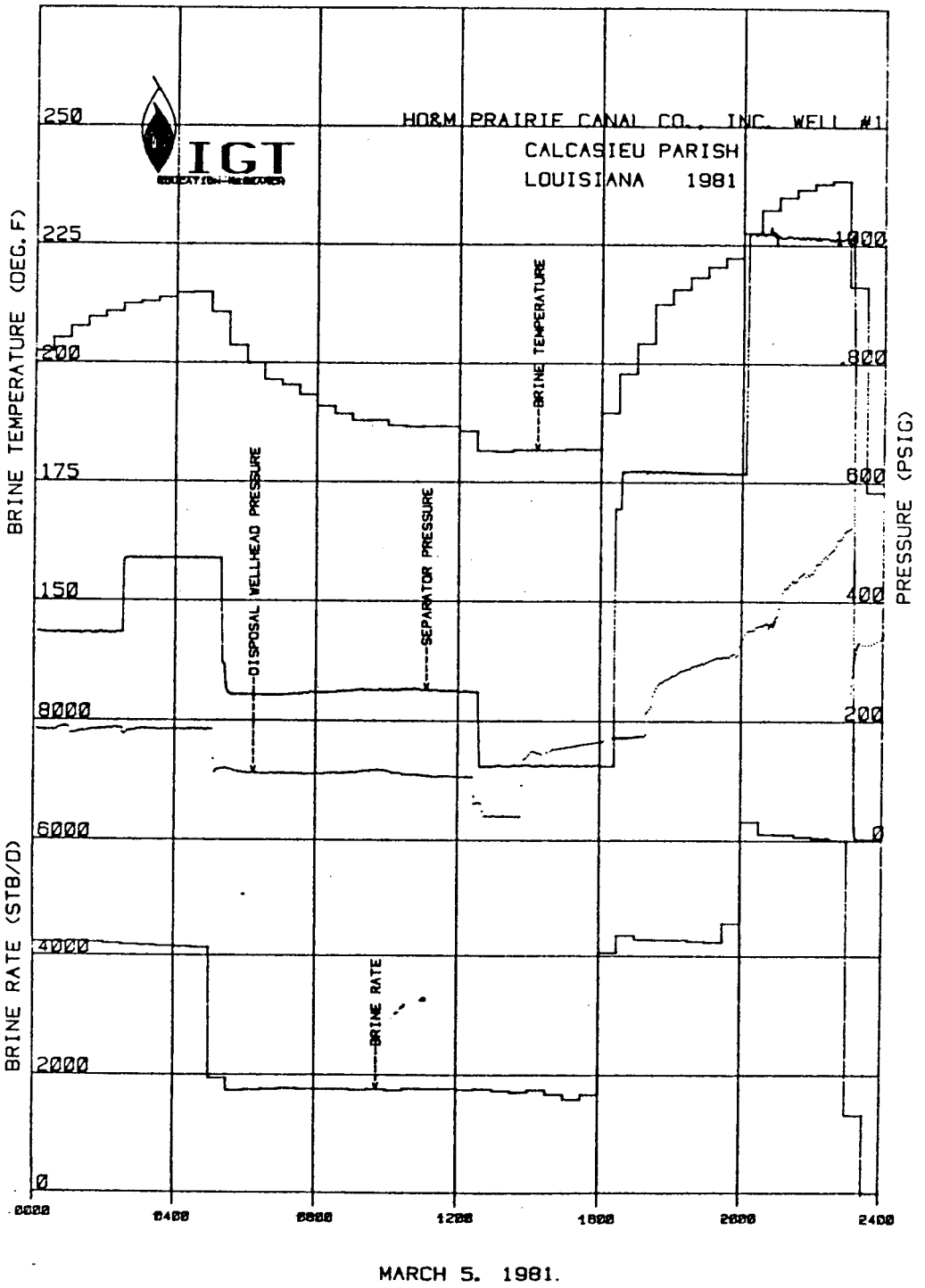

Figure 2. OPERATING CONDITIONS FOR SEPARATOR STUDY, March 5, 1981

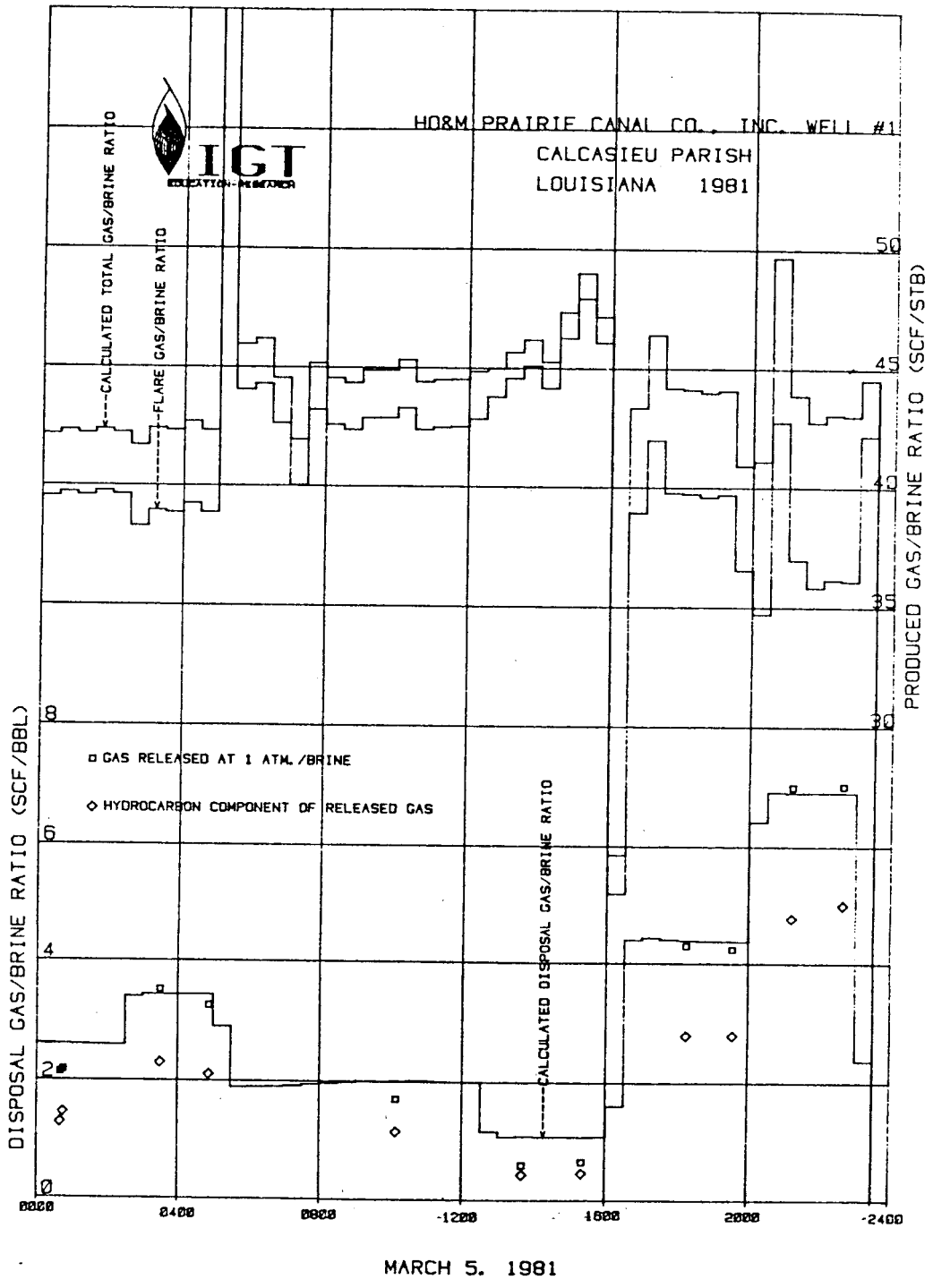

Figure 3. GAS/BRINE RATIOS DURING SEPARATOR PERFORMANCE STUDY

The largest excursions in flare line gas/brine ratio are due to changes in stored gas content of the separator during changes in pressure and flow rate. Gas/brine ratio was reasonably constant at the time of the collection of each suite of samples for analysis.

Gas/Brine ratios used for several calculations in this study are field data. Further data refinement at IGT showed minor differences between the actual produced gas/brine ratio shown in Figure 3 and gas/brine ratios used in the narrative of this paper. These minor differences do not affect trends and conclusions reached in this study.

Sampling and Analytical Procedures

To obtain definitive data on the partitioning of various gaseous species between the aqueous and gas phases in the separator, IGT collected and analyzed suites of samples in the following manner:

- Samples of flare line gas and brine after the separator were collected at separator pressure in preheated stainless steel pressure vessels.
- Gas chromatographic analyses were performed immediately on flare line gas samples.
- Brine samples were cooled to ambient temperature by immersion of the sample vessels in a cold water bath.
- After cooling, gas was liberated from the brine by reducing the pressure to 1 atmosphere using apparatus appropriate for quantitative determination of the released gas volume. The sample was agitated to promote equilibrium between the gas and the liquid phases.
- Gas chromatographic analysis was performed on the gas liberated during the pressure reduction.
- After reducing the pressure to 1 atmosphere, the brine volume was measured while simultaneously the carbon dioxide and carbonates were stabilized by addition of aqueous sodium hydroxide.
- A quantitative acid liberation/nitrogen purge was performed on an aliquot of the alkaline brine to measure the total inorganic carbon remaining in solution. This includes both dissolved carbon dioxide and carbonate species.
- An aliquot of untreated brine was titrated with 1N sulfuric acid to determine alkalinity, which was reported as bicarbonate. For total carbon dioxide calculations 1 mole of bicarbonate is equivalent to 1 mole of carbon dioxide, because the two species are indistinguishable using these analytical techniques.

The full procedure as described above was used only on samples collected on March 5, 1981. During earlier flow tests, many samples were analyzed that were not in suites of simultaneously collected gas and brine samples. The majority were flare line gas samples. These are useful in examining the effect of separator temperature on the quality of the gas recovered.

RESULTS

Gas Liberated by Pressure Reduction to 1 Atmosphere

Quantities of various gaseous species per stock tank barrel of brine determined from the flare line and from pressure reduction on brine to the disposal well are tabulated in Table 1. The right side of the table provides a tabulation of sums of these quantities. Means and standard deviations for these sums are also tabulated.

Examination of Table 1 reveals an overall increase in hydrocarbon gas/brine ratio during the experiment with possible perturbations associated with changes in brine production rate. The increase is most notable for the heavier hydrocarbons. We believe these variations are due to reservoir characteristics. They are substantially greater than those observed using the same field equipment and procedures on tests of aquifers whose gas content was below saturation.

In contrast, the CO_2 content of gas liberated by pressure reduction is greatest for the lowest separator pressure and does not vary in the same manner as hydrocarbon content of brine. This is due to the dependence of CO_2 liberated upon the pressure and temperature steps in the liberation process.

Total CO_2 Content of Produced Brine

After liberation of CO_2 by the separator and by pressure reduction to 1 atmosphere on cooled brine, a substantial quantity of CO_2 remains in the brine in the forms of

- Dissolved CO_2
- Bicarbonate (HCO_3^-) ions
- Carbonate (CO_3^{--}) ions.

All these species must be taken into account in relation to both gas production and formation of carbonate scale. Brine from the HO&M Prairie Canal Co., Inc., Well 1 had two characteristics that greatly facilitate understanding of gas production:

- Calcium and magnesium content of produced brine was too low for significant carbon loss due to carbonate scale formation at any of the pressure and temperature conditions of the experiment.
- The alkalinity titration did not reveal end points suggestive of interference from other chemical species.

Table 2 augments the previous sum of gases liberated by pressure reduction to 1 atmosphere. This augmentation consists of taking into account total CO_2 content, including $CO_2(aq)$, HCO_3^-, and CO_3^{--} remaining in the cooled brine at 1 atmosphere pressure. Total CO_2 content of the brine is that from analysis of gases liberated by pressure reduction plus the CO_2 liberated from the remaining brine by acid. It averages 7.53 SCF/STB with a standard deviation of only 1.9 percent of this average.

The column labeled Total CO_2 Plus Hydrocarbons reflects the total quantity of gas

Table 1. GAS LIBERATED BY PRESSURE REDUCTION

Date	Time	Flow Rate (STB/Day)	Separator Pressure (psia)	Brine Temperature °F	Flare Line (SCF/STB)					Disposal Well Brine (SCF/STB)					Sum (SCF/STB)				
					CO_2	CH_4	C_2H_6	C_3+	Total	CO_2	CH_4	C_2H_6	C_3+	Total	CO_2	CH_4	C_2H_6	C_3+	Total*
5 Mar 81	2238	6050	1025	238	2.24	31.80	0.96	0.166	35.17	1.99	4.91	0.111	0.011	7.02	4.23	36.71	1.07	0.18	42.19
5 Mar 81	2112	6110	1029	235	2.12	30.59	1.00	0.194	33.90	2.19	4.69	0.107	0.011	7.00	4.31	35.28	1.11	0.21	40.91
5 Mar 81	1933	4260	630	221	3.05	33.14	0.95	0.150	37.29	1.44	2.73	0.061	0.005	4.24	4.49	35.87	1.01	0.16	41.53
5 Mar 81	1815	4300	632	216	2.89	34.07	0.99	0.157	38.11	1.50	2.73	0.061	0.006	4.30	4.39	36.80	1.05	0.16	42.40
5 Mar 81	1520	1730	140	187	4.98	36.65	0.99	0.133	42.75	0.19	0.46	0.010	0.001	0.66	5.17	37.11	1.00	0.13	43.41
5 Mar 81	1340	1790	140	187	4.64	34.58	0.94	0.125	40.29	0.16	0.43	0.010	0.001	0.60	4.80	35.01	0.95	0.13	40.89
5 Mar 81	1008	1760	266	187	3.81	34.27	0.91	0.122	39.11	0.55	1.13	0.025	0.002	1.71	4.36	35.40	0.94	0.12	40.82
5 Mar 81	0453	4160	487	215	3.22	32.99	0.90	0.123	37.23	1.15	2.06	0.044	0.004	3.26	4.37	35.05	0.94	0.13	40.49
5 Mar 81	0330	4180	485	213	3.09	31.89	0.86	0.119	35.96	1.23	2.25	0.048	0.004	3.53	4.32	34.14	0.91	0.12	39.49
5 Mar 81	0045	4240	360	204	3.46	32.44	0.84	0.115	36.86	0.72	1.43	0.030	0.003	2.18	4.18	33.87	0.87	0.12	39.04
5 Mar 81	0040	4240	360	204	3.46	32.44	0.84	0.115	36.86	0.85	1.26	0.026	0.002	2.14	4.31	33.70	0.87	0.12	39.00
		Mean Value													4.45	35.36	0.98	0.14	40.93
		Standard Deviation													0.29	1.18	0.08	0.03	1.41
		Standard Deviations as Percent of Mean Value													6.5	3.3	8.2	19	3.4

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Table 2. GAS CONTENT OF BRINE, INCLUDING ALL CARBON DIOXIDE

Date	Time	Flow Rate (STB/Day)	Separator Pressure (psia)	Brine Temperature °F	Gas Liberated From Cooled Brine by Pressure Reduction to One Atmosphere (SCF/STB) CO_2	CH_4	C_2H_6	C_3^+	total	Acid Liberated CO_2 (SCF/STB)	"Total" CO_2 (SCF/STB)	Alkalinity Bicarbonate as CO_2 (SCF/STB)	Gaseous CO_2 (SCF/STB)	Total CO_2 Plus Hydrocarbons* (SCF/STB)	Total Gaseous Species† (SCF/STB)	Gaseous CO_2 in Total Gas (Mole %)
5 Mar 81	2238	6050	1025	238	4.23	36.71	1.07	0.18	42.19	3.24	7.47	1.81	5.66	45.43	43.62	13.0
5 Mar 81	2112	6110	1029	235	4.31	35.28	1.11	0.21	40.91	3.41	7.72	1.84	5.88	44.32	42.48	13.8
5 Mar 81	1933	4260	630	221	4.49	35.87	1.01	0.16	41.53	3.13	7.62	1.86	5.76	44.66	42.80	13.5
5 Mar 81	1815	4300	632	216	4.39	36.80	1.05	0.16	42.40	3.19	7.58	1.89	5.69	45.59	43.70	13.0
5 Mar 81	1520	1730	140	187	5.17	37.11	1.00	0.13	43.41	2.56	7.73	1.94	5.79	45.97	44.03	13.2
5 Mar 81	1340	1790	140	187	4.80	35.01	0.95	0.13	40.89	2.68	7.48	1.92	5.56	43.57	41.66	13.3
5 Mar 81	1008	1760	266	187	4.36	35.40	0.94	0.12	40.82	2.99	7.35	1.94	5.41	43.81	41.87	12.9
5 Mar 81	0453	4160	487	215	4.37	35.05	0.94	0.13	40.49	3.16	7.53	1.86	5.67	43.65	41.79	13.6
5 Mar 81	0330	4180	485	213	4.32	34.14	0.91	0.12	39.49	3.28	7.60	1.81	5.79	42.77	40.96	14.1
5 Mar 81	0045	4240	360	204	4.18	33.87	0.87	0.12	39.04	3.28	7.46	—	—	42.32	40.45	13.8
5 Mar 81	0040	4240	360	204	4.31	33.70	0.87	0.12	39.00	2.96	7.27	—	—	41.96	40.09	13.5
Mean Value					4.45	35.36	0.98	0.14	40.93		7.53	1.87	5.69	44.01	42.13	13.4
Standard Deviation					0.29	1.18	0.08	0.03	1.41		0.14	0.05	0.14	1.34	1.33	0.4
Standard Deviation as Percent of Mean Value					6.5	3.3	8.2	18.9	3.4		1.9	2.7	2.5	3.0	3.2	2.9

* Hydrocarbons, plus CO_2 gas, plus acid liberated CO_2.

† Hydrocarbons, plus CO_2 gas, plus acid liberated CO_2, minus alkalinity CO_2 (mean values used where none others were available.

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that could be recovered from produced brine by acid treatment. The column labeled Gaseous Species is total gas recoverable from the brine without breakdown of HCO_3^-. As revealed in the last column, this gas would contain about 13.4 percent CO_2. For the Prairie Canal well, these last two colums provide upper limits on gas recovery from a separator and CO_2 content of such recovered gas.

Effect of Separator Static Pressure on Gas Remaining in Post-Separator Brine

The relationship between the volume of gas remaining in the brine after the separator and the separator static pressure is given in Figure 4. The volume of gas increases approximately linearly with increasing pressure, but the y-intercept does not equal zero. Determining the quantity of each gaseous species resolves this apparent anomaly.

Figure 5 is a plot of the volume of methane liberated from the brine by a pressure reduction to 1 atmosphere versus the partial pressure of methane in the separator. The data form a straight line ($r^2 = 0.994$) with a y-intercept of -0.21 SCF/STB. This negative intercept is primarily due to the amount of methane remaining in the brine after the pressure reduction. The partial pressure of methane above the brine varies from 8.65 psia to 10.43 psia after the pressure reduction, which would leave about 0.10 to 0.13 SCF/STB still dissolved in the brine (Yamamoto et al., 1976), assuming Henry's law is valid in this range.

Another factor which lowers the y-intercept is the previously discussed coupling of separator pressure and brine temperature due to operational constraints on this experiment. Samples collected at the lower separator pressures had lower temperatures because of the low brine production rates. Similarly, high separator pressures required high flow rates and therefore involved higher brine temperature.

The temperature dependence of methane solubility in water would cause more methane to remain in the brine at higher temperature-pressure regimes than would pressure alone in an isothermal system.

Figure 6 is a plot of the volume of ethane liberated from brine after the separator by a pressure reduction to 1 atmosphere. The data form a straight line ($r^2 = 0.989$) with a y-intercept of 0.0002 SCF/STB. The same factors that affect the slope of the methane plot should also affect the ethane plot. The values are much smaller than

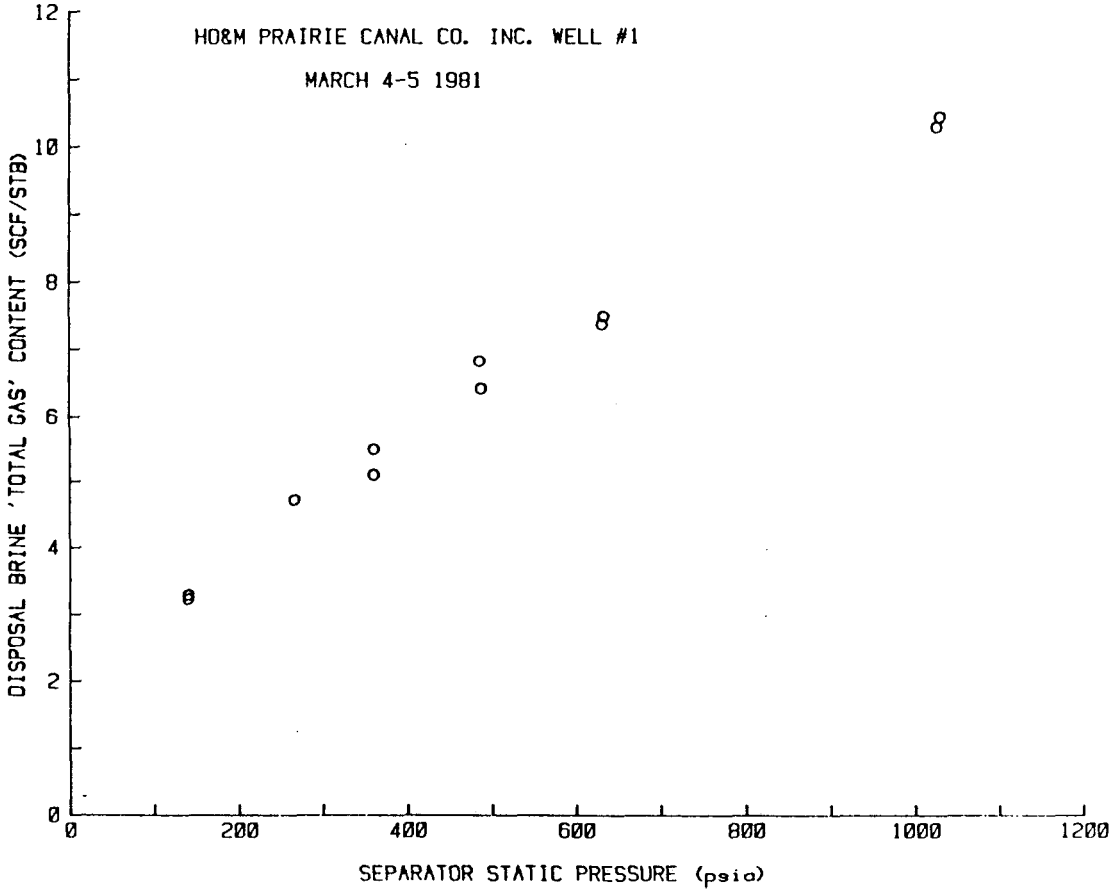

Figure 4. DISPOSAL BRINE "TOTAL GAS" CONTENT VS. SEPARATOR STATIC PRESSURE

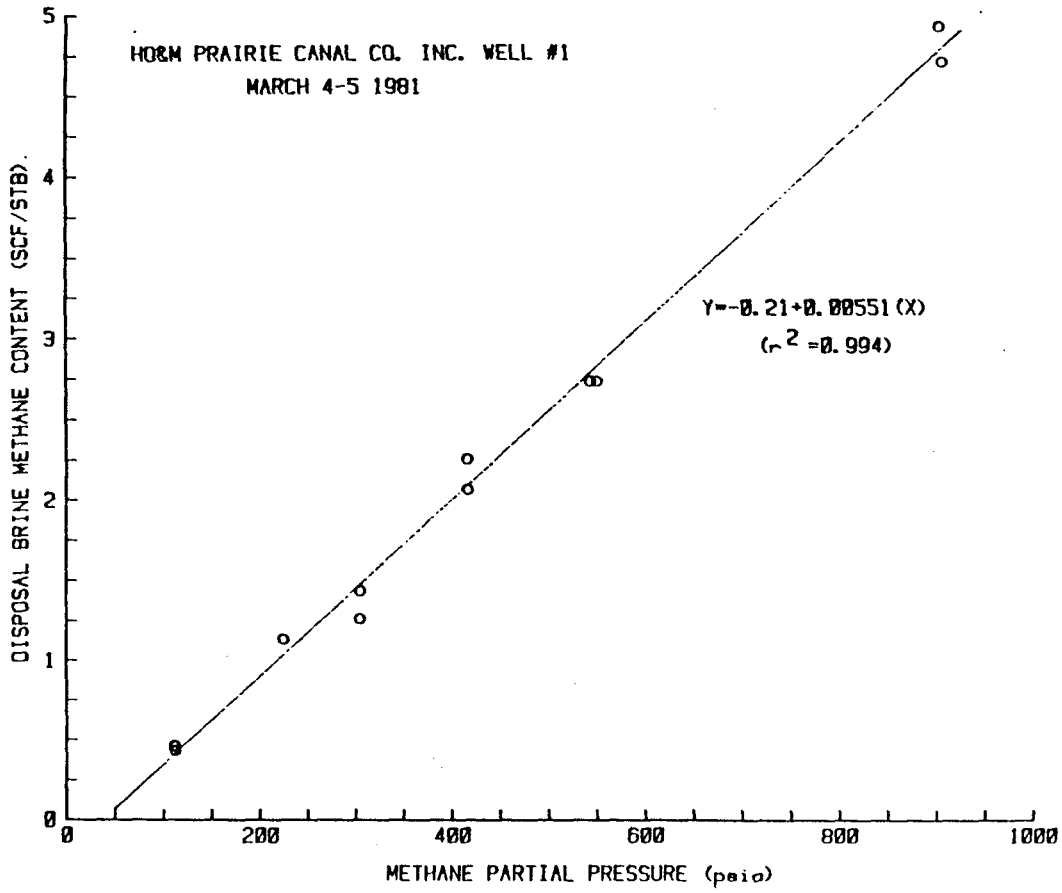

Figure 5. DISPOSAL BRINE METHANE CONTENT VS. METHANE PARTIAL PRESSURE

those of methane, and the scatter in the data prohibits a careful analysis of the plot. The scatter is even more pronounced in Figure 7, which is a plot of the sum of propane, butanes, and pentanes liberated from the disposal brine by reduction of pressure to 1 atmosphere. The plotted data form a straight line (r^2 = 0.974) with a y-intercept equal to 0.0004 SCF/STB.

These data clearly indicated that the quantities of hydrocarbons liberated from disposal brine are primarily dependent on the partial pressure of each hydrocarbon species in the gas phase of the separator. In addition, there is very little deviation from simple Henry's law plots that would consist of straight lines passing through the origin.

The behavior of carbon dioxide is very different from that of hydrocarbons. Figure 8 is a plot of the total inorganic carbon system versus the partial pressure of CO_2 in the separator. The total amount of CO_2 in the system remains relatively constant, as is indicated by the darkened circles forming a line across the top of the plot. The partitioning of this inorganic carbon helps explain why the total gas versus separator pressure plot does not have a zero-intercept.

The total amount of inorganic carbon left in the brine leaving the separator is shown by the open circles. The points are obtained by adding the amount of CO_2 liberated at 75°F and 1 atmosphere to the CO_2 in solution at 75°F and 1 atmosphere, which is represented by the diamonds in the plot. The data points form a relatively straight line (r^2 = 0.965) with a y-intercept of 2.1 SCF/STB.

There are two factors which would move the y-intercept from the origin. The overriding factor we have identified is the presence of bicarbonate. As noted earlier, a mole of bicarbonate is indistinguishable from a mole of dissolved carbon dioxide with the analytical techniques employed. Titrations of the brine solution indicate that there is an average of 1.87 SCF CO_2/STB of equivalent bicarbonate in solution. The bicarbonate, as determined by an acid titration, is expressed as SCF CO_2/STB in the plot by the triangles.

Apparently the bicarbonate does not appreciably add to the partial pressure of carbon dioxide in the solution. The pH of the solution and the high partial pressure of carbon dioxide in the solution favor bicarbonate as the stable form. This evidence supports the practice of subtracting bicarbonate from the sum of the inorganic carbon before determining separator efficiency for removing carbon dioxide from the brine.

The separator pressure-brine temperature

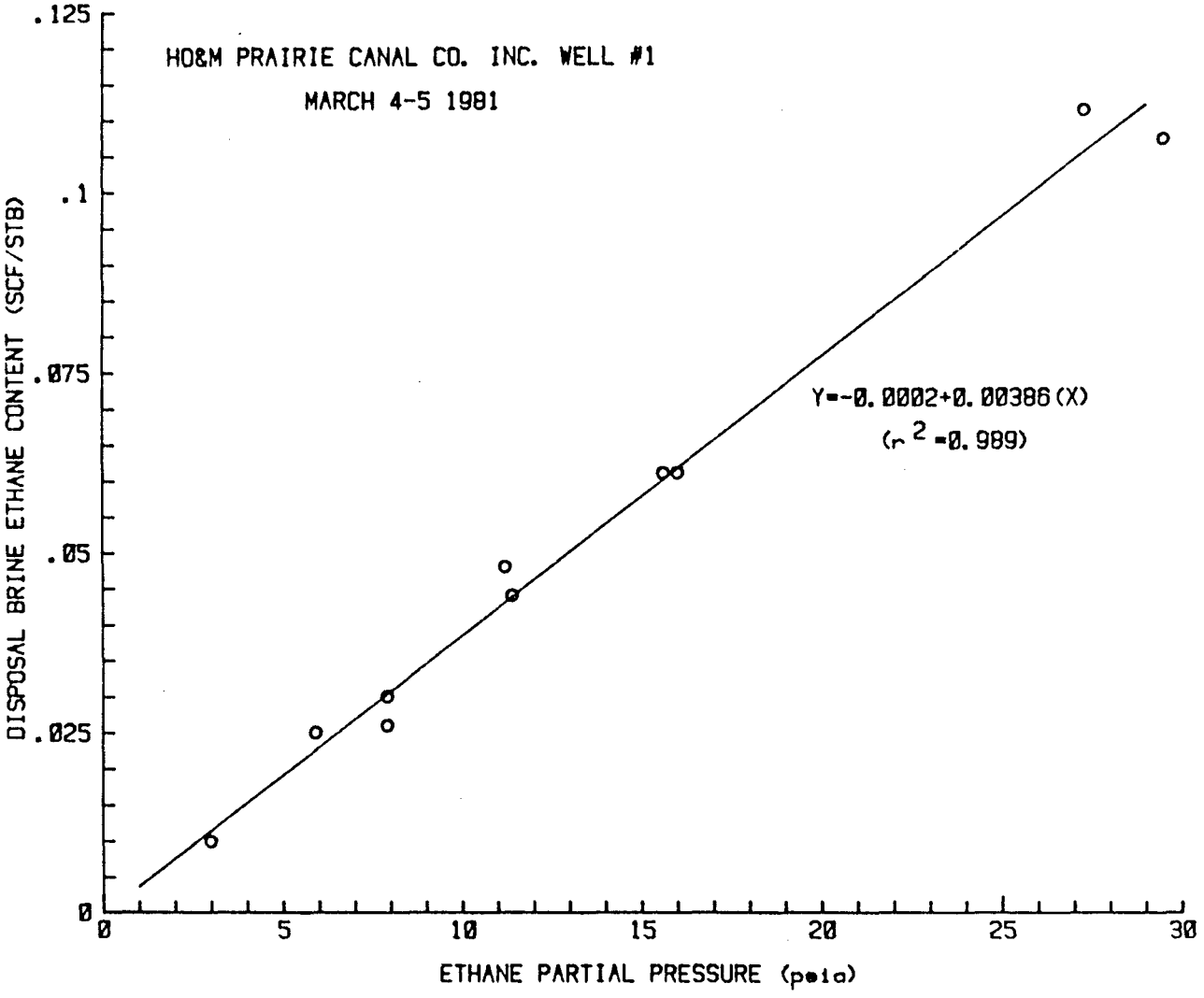

Figure 6. DISPOSAL BRINE ETHANE CONTENT VS. ETHANE PARTIAL PRESSURE IN SEPARATOR

coupling also affects the slope of the plot, but the effect is opposite to that of hydrocarbons. Hydrocarbon solubility in brine decreases with decreasing temperature to a minimum which occurs at about 160°F. Carbon dioxide solubility, however, increases with decreasing temperature in the temperature range discussed. The observed pressure-temperature coupling would tend to raise the y-intercept, and the effect would be more pronounced than in the hydrocarbon-brine systems. This may be the reason that the intercept of 2.1 SCF/STB is above the 1.87 SCF/STB CO_2 content of bicarbonate determined by titration.

Figure 9 summarizes the partial pressure dependence of all species reported. Hydrocarbon solubility characteristics appear remarkably consistent and markedly different from those of carbon dioxide. The behavior of each component deviates little from the linear dependence predicted by Henry's law.

Similar but less complete data have been obtained by IGT on tests of other wells. Figure 10 contains data on the volume of methane liberated from disposal brine by a pressure reduction to 1 atmosphere versus the partial pressure of methane in the separator for three wells (Eaton Operating Company, 1981; Randolph and Rockar, 1981). The volumes are within a fairly small range for a given separator pressure. Many factors other than pressure are known to affect methane solubility in brine; these include temperature, salinity, and volume of carbon dioxide. In the absence of consideration of such factors, data from the Prairie Canal well test cannot be considered predictive of other wells, but the close agreement shown is encouraging for development of a prediction procedure.

Comparisons to Previously Published Data at Separator Pressures and Temperatures

Interpretation of data from the test of the Wainoco P. R. Girouard Well No. 1 included testing of published algorithms for calculating methane solubility in brines against observed gas content of brine from the separator (Eaton Operating

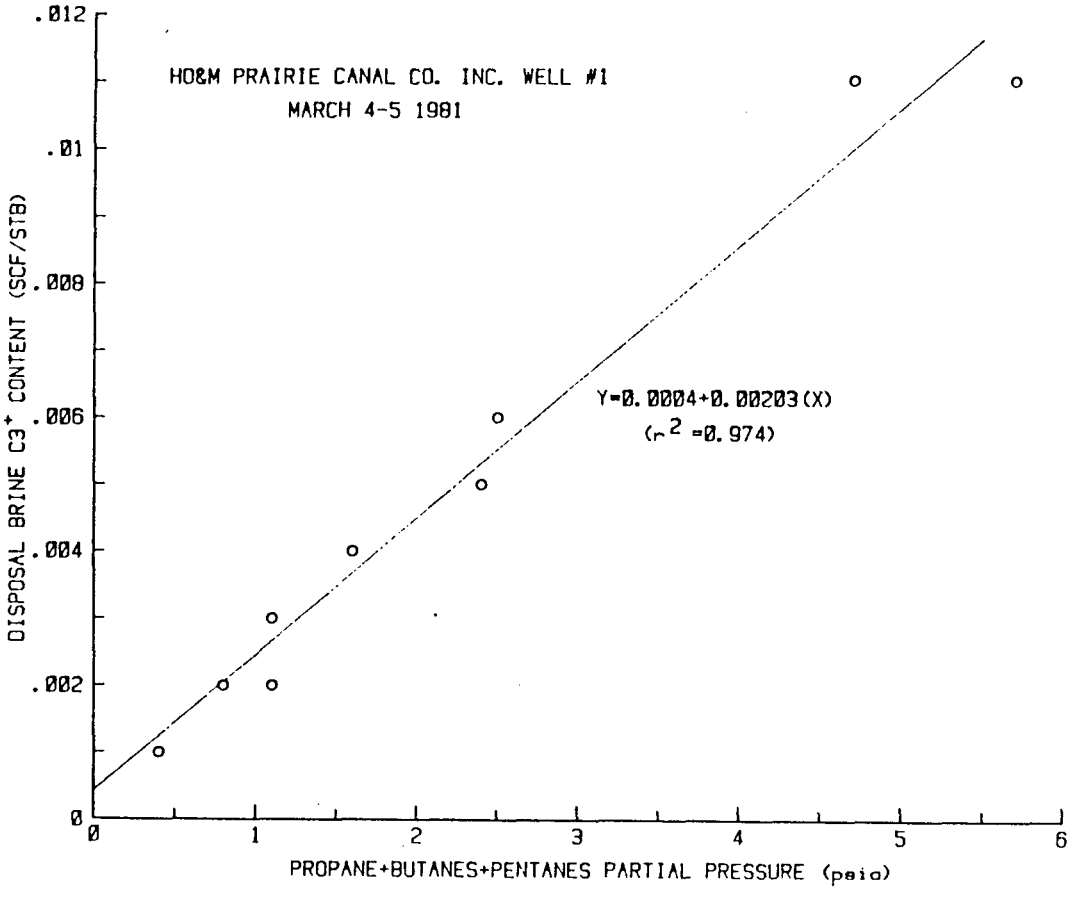

Figure 7. DISPOSAL BRINE C3+ CONTENT VS. C3+ PARTIAL PRESSURE

Company, 1981). It was concluded that the algorithm developed by S. K. Garg et al. (1978) for methane solubility in distilled water provided a reasonably accurate estimate of total gas liberated from separator brine by pressure reduction to 1 atmosphere. Comparisons were made between values calculated with this algorithm and measured values for the 25 analyses of gas from brine during tests of this well. Agreement was within 0.5 SCF/STB for all but three data points. Those three data points were all for samples collected when free gas was believed entrained in brine to the disposal well because of the combination of high brine rate and sand loading in the separator. The algorithm provided similarly excellent agreement with the small number of data points from the Riddle-Saldana Well No. 2 (Eaton Operating Company, forthcoming) and the Pleasant Bayou No. 2 Well (Randolph and Rockar, 1981).

Figure 11 provides comparisons between data from the controlled study of separator performance and reported laboratory data points on methane solubility in distilled water at 220°F. Actual laboratory data points from the papers by J. E. Davis and J. J. McKetta (1980) and by O. L. Culberson and J. J. McKetta (1951) are shown. Lines connecting these points were drawn only to illustrate data trends. The circles on this figure again illustrate the excellent agreement between total gas liberated from separator brine by pressure reduction to 1 atmosphere after cooling and the data published by Culberson and McKetta. (The Garg algorithm [Garg et al., 1978] was developed to fit the data of Culberson and McKetta.)

Total gas content of separator brine, including CO_2 liberated by acid, is greater than laboratory observed solubility of methane in distilled water. On the other hand, methane content of brine from the separator is only 50 to 80 percent of laboratory measured methane solubility in distilled water. This reflects a greater depression of methane solubility than could be caused by the modest amount of dissolved solids in brine from this well (43,000 mg/l).

Figure 12 provides a comparison between measured CO_2 content of brine from the separator and laboratory data points on CO_2 solubility in distilled water at 212°F published by G. Houghton, A. M. McLean, and P. O. Ritchie (1957). As previously shown in Figure 8, the y-axis intercept of field data is primarily due to HCO_3^- and CO_3^{--} species in the brine. The difference in slopes of the two lines exceeds reasonable expectation for solubility depression due to dissolved salts. Depression of CO_2 solubility by dissolved hydrocarbons is hypothesized to be a major factor.

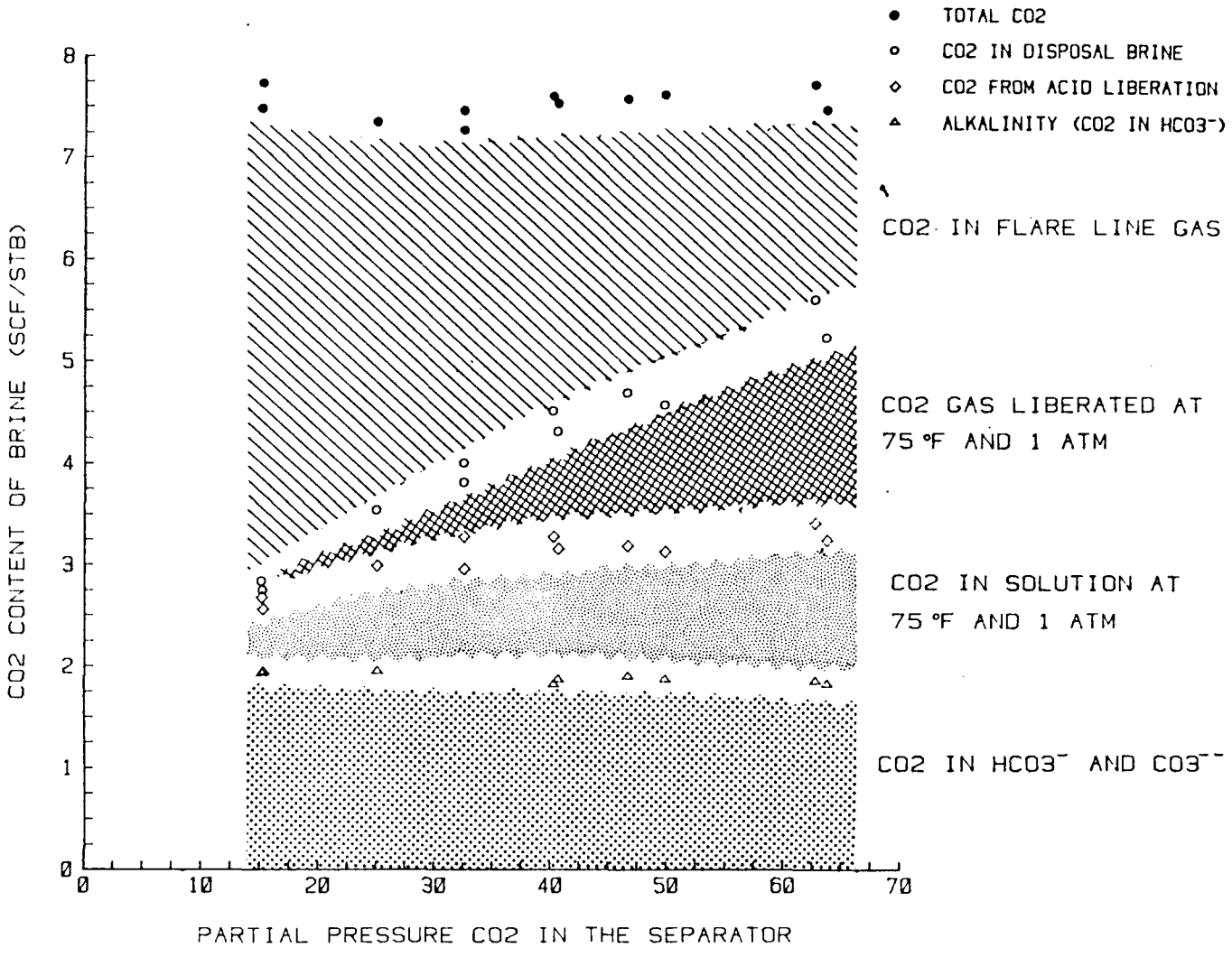

Figure 8. CARBON DIOXIDE PARTITIONING AMONG EXPERIMENTAL STEPS

Effect of Separator Pressure and Temperature Upon Quality of Gas

Figure 13 shows CO_2 content of flare line gas vs. separator pressure for 44 of the 52 flare line gas samples analyzed in the field during the test of the HO&M Prairie Canal Co., Inc., Well No. 1. The other 8 samples were collected during times of transient conditions that often cause anomalous gas compositions. A substantial portion of the scatter in the points shown is still due to long-term variations of both composition of produced gas and the produced gas/brine ratio.

The symbols for plotted points are coded for 25°F ranges in brine temperature. Lines on the graph have been drawn to roughly indicate areas characterized by these temperature ranges. These lines are not isotherms from data interpretation or from theory.

The CO_2 content of separator gas at the highest brine temperatures achieved varied between 11.6% at a separator pressure of 125 psig and 6.2% at a separator pressure of 1014 psig. For lower temperatures at any specific pressure, CO_2 content of gas is reduced.

Figure 14 shows the relationship between heating value of gas from the separator and separator pressure for several temperature ranges. Lines have again been drawn to provide an approximate separation of temperature ranges. The relationships are less clear than for CO_2 because of the long-term variations in natural gas liquids content of produced gas during the series of well tests. The range was between 0.75 and 1.0 gallons/MCF. Such range has a greater effect upon heating value of produced gas than upon volume.

Nevertheless, the observed range of heating values of about 920 to 975 Btu/SCF may well be significant in relation to gas sales. If separator pressure had to be as high as 1000 psig to meet CO_2 and heating value requirements of a gas sales contract from a well having the characteristics of Figures 11 and 12, the penalty would be about 5000 Btu of hydrocarbon energy left in each barrel of brine from the separator.

Although quantitative evaluation of various

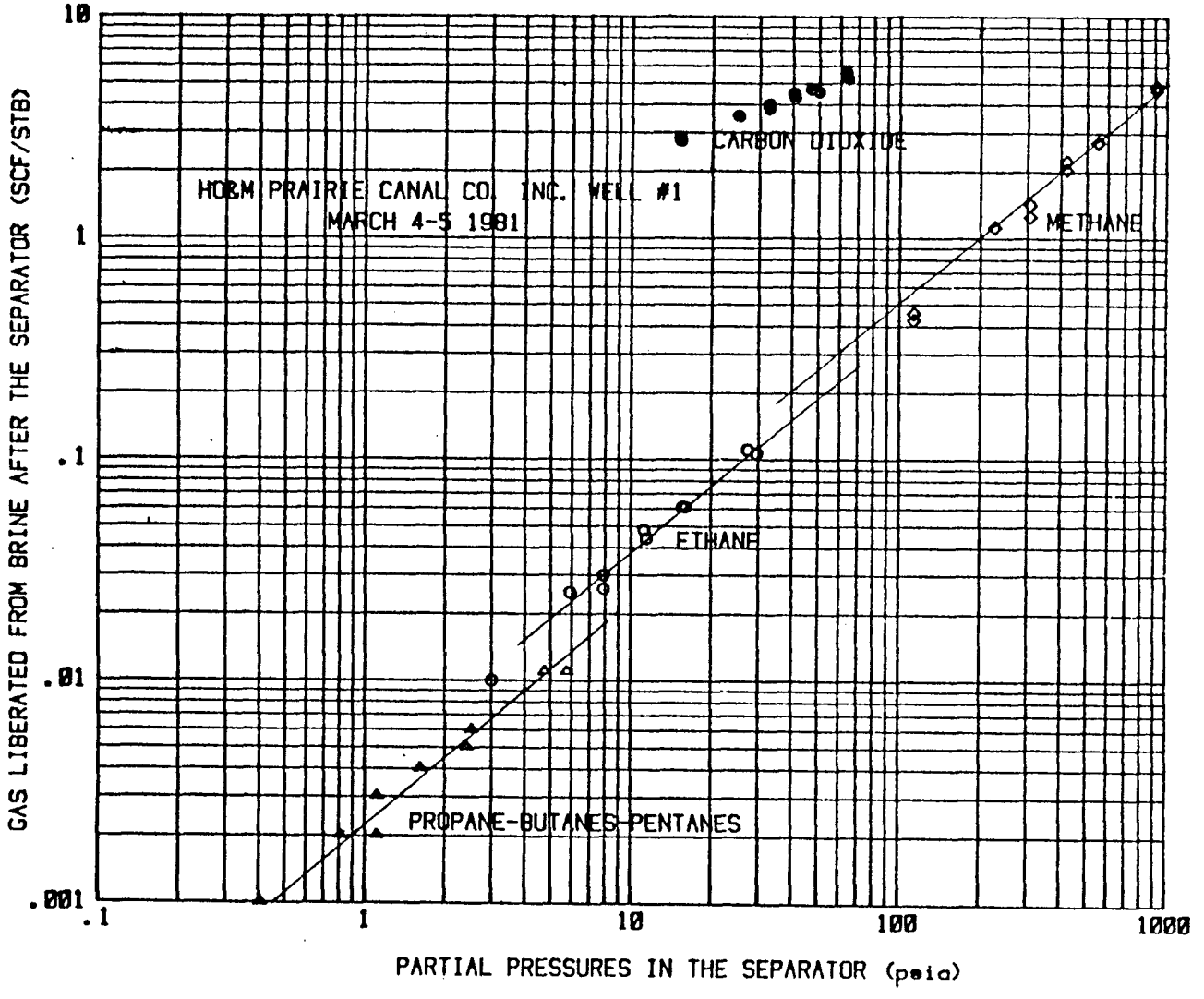

Figure 9. GAS LIBERATED FROM POST-SEPARATOR BRINE VS. SEPARATOR PARTIAL PRESSURES

conceivable surface facilities is beyond the scope of this paper, it is interesting to note that recovery of thermal energy before separation of gas and brine would improve the quality of gas recovered at any particular separator pressure. Or from a different perspective, prior thermal energy recovery may permit lower separator pressure for gas meeting the quality criteria of a sales contract. Thus, quantity of gas marketed per barrel of produced brine could increase.

Separator Efficiency

Separator efficiency is defined as the percentage of specific species present in produced brine that leaves the separator through the gas line. This percentage is useful in relation both to consideration of scaling potential and to examining the trade-off between gas quality and gas recovery.

However, separator efficiency determined on one test will not be valid for other tests. This is because the absolute amount of each chemical species remaining in separator output brine is dependent upon partial pressure in the separator for that species. This partial pressure is, in turn, dependent upon the gas composition and the separator pressure, not on the produced GWR.

Figure 15 shows separator efficiency as a function of separator pressure for CO_2, methane, and natural gas liquids (C2+). The points shown are those for all gas and brine samples that were simultaneously collected from the Prairie Canal well, including the separator study on March 5, 1981. Efficiencies for CO_2 are shown on two bases. The open circles are on the basis of total CO_2, including that liberated from HCO_3^- or CO_3^{--} species by acid. The basis for the closed circles is gaseous CO_2 as estimated by subtracting CO_2 in the form of HCO_3^-, determined by the alkalinity titration, from the total CO_2.

The scatter in points at any particular pressure is due both to variations in temperature and to changes in gas composition during the series of well tests. The effect of composition changes is particularly large for natural gas liquids (C2-C5 hydrocarbons).

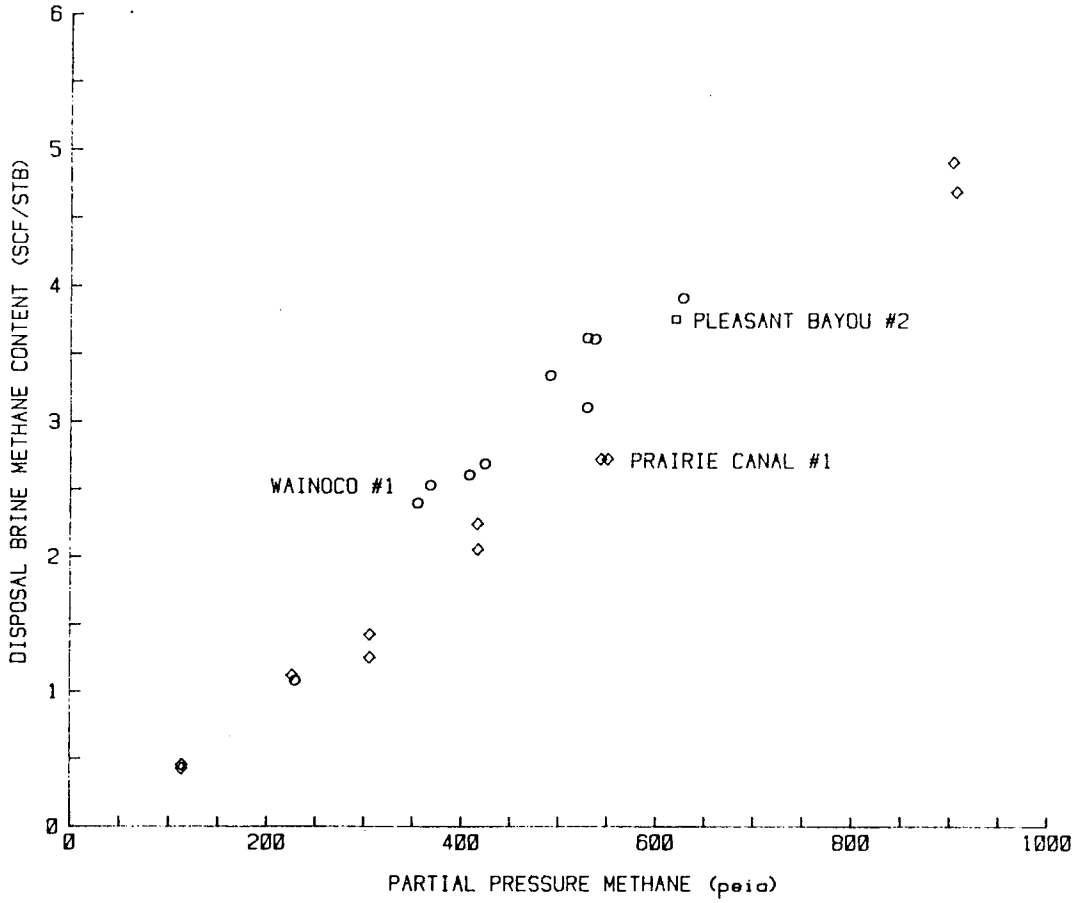

Figure 10. COMPARISON OF METHANE REMAINING IN DISPOSAL BRINE AFTER THE SEPARATOR FOR THREE WELLS

Effect of Brine Residence Time

IGT's work on Wells of Opportunity indicates that efficiency of the separator used is independent of brine residence time for residence times of 2 minutes or longer. The separator used consisted of a single 10-foot-long horizontal pressure vessel with an inside diameter of 38.5 inches. It had a minimum of internal baffles so that sand could be readily removed. The upper portion contained brine deflectors near the inlet. The lower half contained a weir so that three-phase separation was possible in the event of significant oil production. On the Prairie Canal well test the separator was operated with the brine level at mid-elevation and above the weir. Brine was removed from the "oil" outlet so that brine residence time was maximized. In the absence of sand, liquid volume was about 7.2 barrels so that a brine rate of 10,400 BPD would have given a 1-minute brine residence time.

The only data to date that suggest declining separator efficiency due to short residence time were obtained while producing brine at 6000 to 6500 STB/day after experiencing heavy sand production. That evidence consisted of the following:

- Calculated total produced gas/brine ratio was about 3 SCF/STB lower than those representative of both earlier and later test data.
- All five brine samples liberated excess gas upon pressure reduction to 1 atmosphere after cooling. For one of these, the excess was greater than 27 SCF/STB. The excess gas in this 300 ml brine sample would have occupied a bubble volume of about 1 ml at the separator pressure of 1014 psig at the time of sample collection.

Brine residence time when these data were collected was probably less than the 1.7 minute calculated from brine rate and separator volume. This is because sampling was preceeded by heavy sand production and both ends of the separator were found to contain about 14 inches of sand after the test. Also, at the times of possible degraded separator efficiency, gas from the separator was oscillating between extremes of zero and about one million cubic feet per day with a period of about 1 minute. Whether brine rate out of the separator, and therefore residence time, was also varying is not known.

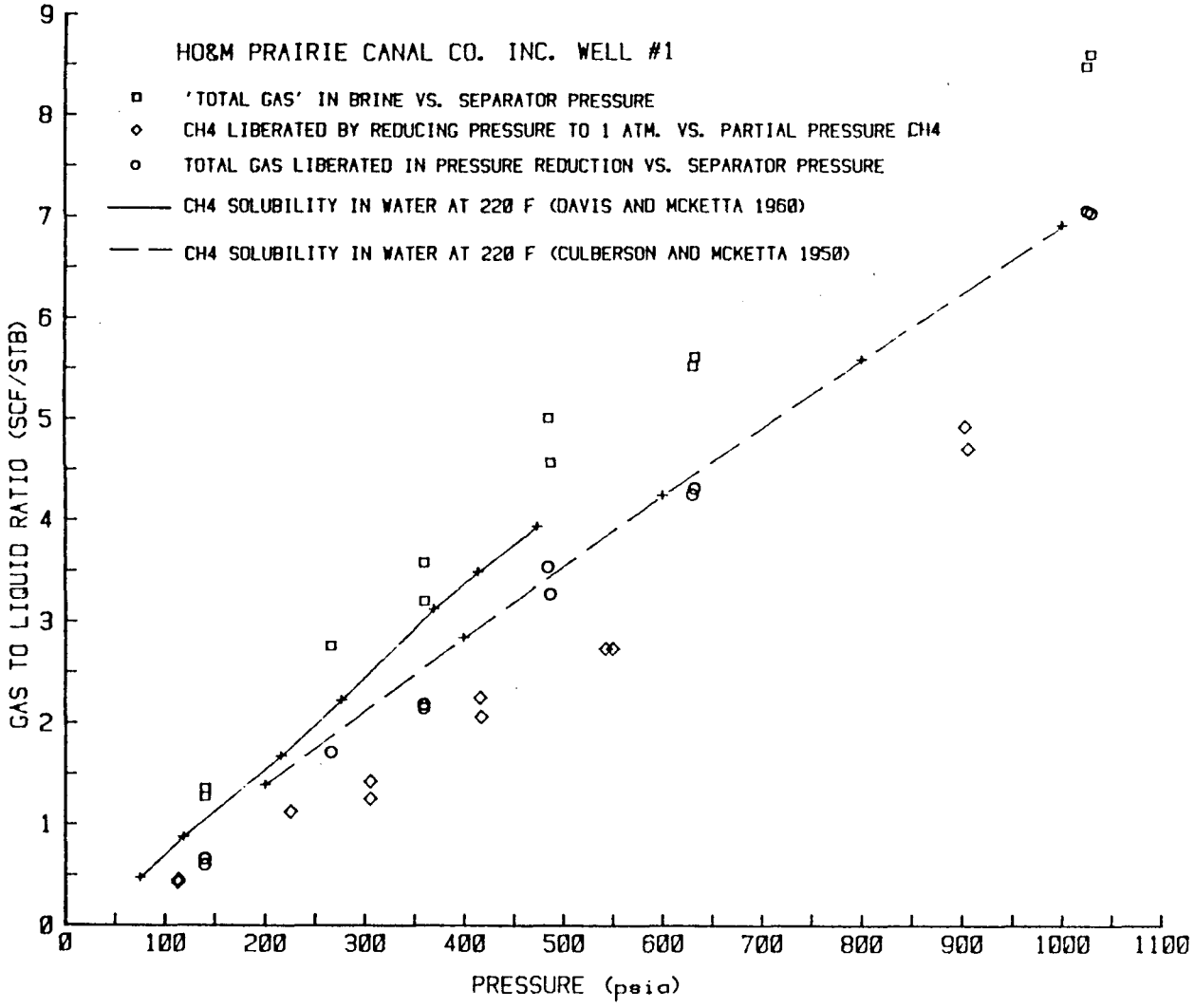

Figure 11. COMPARISON BETWEEN SEPARATOR PERFORMANCE STUDY AND LABORATORY DATA ON METHANE SOLUBILITY

CONCLUSIONS AND OBSERVATIONS

Data and analyses support several conclusions of substantial relevance to both conduct of well tests on aquifers and to economics of energy production from aquifers.

1. Quantity of each hydrocarbon component of a gas mixture in solution in brine leaving a conventional separator can be estimated at constant temperature using a linear relationship to partial pressure of that component in the separator gas.
2. Total gas in solution in brine leaving a separator is consistent with the limited laboratory data on solubility of gases in brine at separator pressure and temperature. Consistency includes the depression of hydrocarbon solubility by CO_2 that has been observed in the laboratory at much higher pressures.
3. Carbon dioxide gas in the separator is but one entity in several equilibria between $CO_2(g)$, $CO_2(aq)$, HCO_3^-, CO_3^{--}, and carbonate solids. Carbonate solids were absent from surface facilities on the Prairie Canal well test, and the total equivalent CO_2 in the species present per barrel of brine was found to be constant. However, the fraction observed as CO_2 gas, and also total produced gas, was found to be dependent upon separator operating conditions.
4. Quality of gas from the separator increases with increasing separator pressure because solubility of CO_2 increases more rapidly than solubility of methane and solubility of natural gas liquids does not increase as fast as that of methane.
5. Thermal energy recovery from brine before the separator would improve the quality of gas recovered at any specific separator pressure. Or, conversely, in the particular case of a gas having the composition observed at the Prairie Canal well, prior cooling of brine may well increase marketable gas from single-stage separation by 2 to 4 SCF per barrel of brine.
6. Separator efficiency for gas recovery from brine is <u>not</u> an inherent characteristic of the

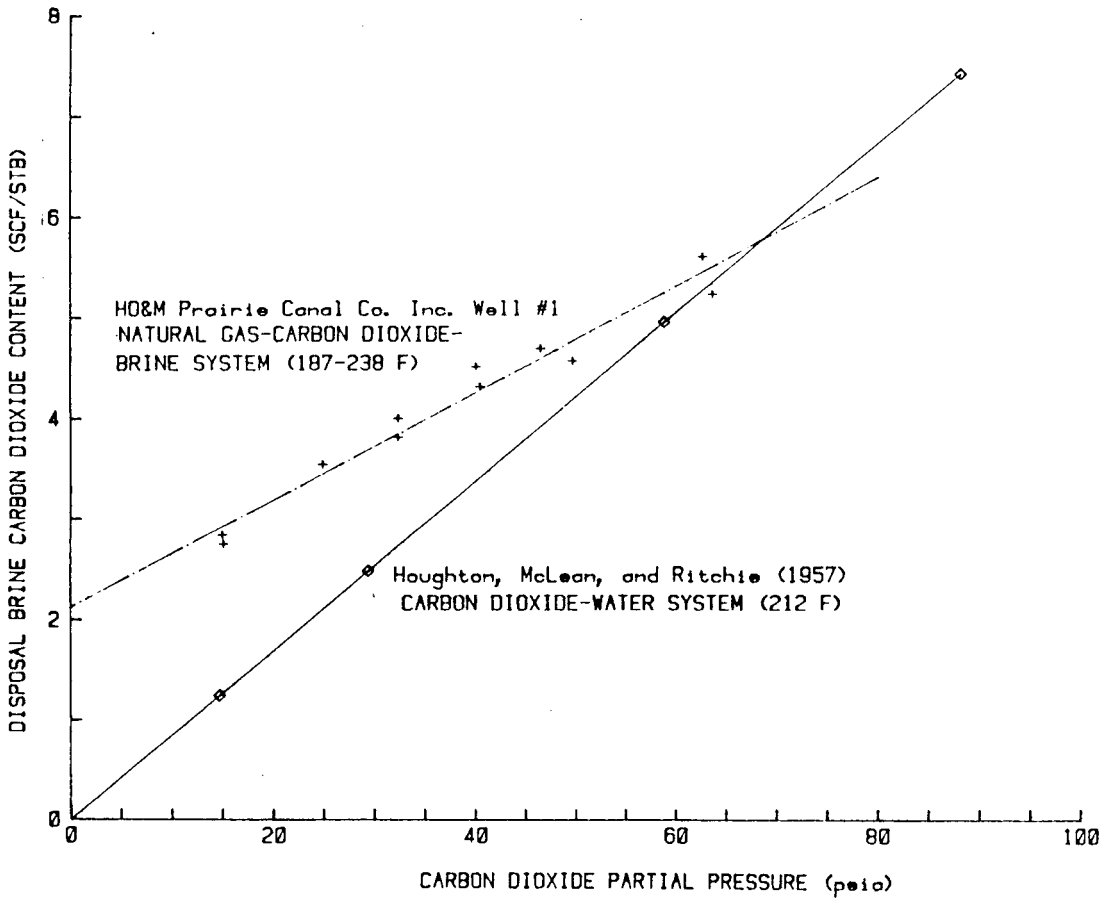

Figure 12. COMPARISON BETWEEN MEASURED CO_2 CONTENT OF POST-SEPARATOR BRINE AND LABORATORY DATA ON CO_2 SOLUBILITY IN WATER

separator hardware. In addition to operating pressure, this efficiency is a function of brine temperature, gas composition, and produced gas/brine ratio.

7. Secondary recovery of gas from disposal brine is possible by using a second separator in series operating at a lower pressure. The feasibility of this recovery is governed by disposal well pressure requirements, salable gas requirements, and other economic factors.

A corollary outcome of this separator performance study is the focusing of attention on the importance and complexity of the $CO_2/HCO_3^-/CO_3^{--}$ system with respect to evaluating production from aquifers. Observations resulting from consideration of this system are as follows:

1. Heating value of hydrocarbons produced with each barrel of brine is a more relevant measure of energy production than standard cubic feet of gas produced.
2. Quantitative definition of the CO_2 component of produced gas requires simultaneous sampling of gas and brine streams plus analyses to define CO_2 content as CO_2 gas, CO_2(aq), HCO_3^-, and CO_3^{--}. These data should be obtained and analyzed at multiple separator pressures to establish validity of results obtained.
3. It is questionable whether laboratory studies of the NaCl brine/CH_4/CO_2 system will provide an adequate basis for conclusions regarding saturation of real brines at reservoir pressure and temperature. This is due to the effect of HCO_3^- and CO_3^{--} observed on real well tests.
4. CO_2 content of recovered gas, and therefore total produced gas, may well differ between scaling and nonscaling surface conditions. Also, use of carbonate scale inhibitors that affect the equilibria between CO_2, HCO_3^-, and CO_3^{--} may well change CO_2 content of gas through the orifice meter.

ACKNOWLEDGMENTS

The authors are grateful for contributions by numerous members of the Department of Energy, Eaton Operating Company, Institute of Gas Technology, Weatherly Engineering team that made the study possible. Of particular importance were agreements to extend the test for this study by Mr. Fred Goldsberry (DOE) and Dr. Ben Eaton (EOC), discussions with Dr. John Oddo (Rice University), and the valuable contributions of Dr. Terry Osif (IGT) and Mr. Wayne Wilkiel (IGT).

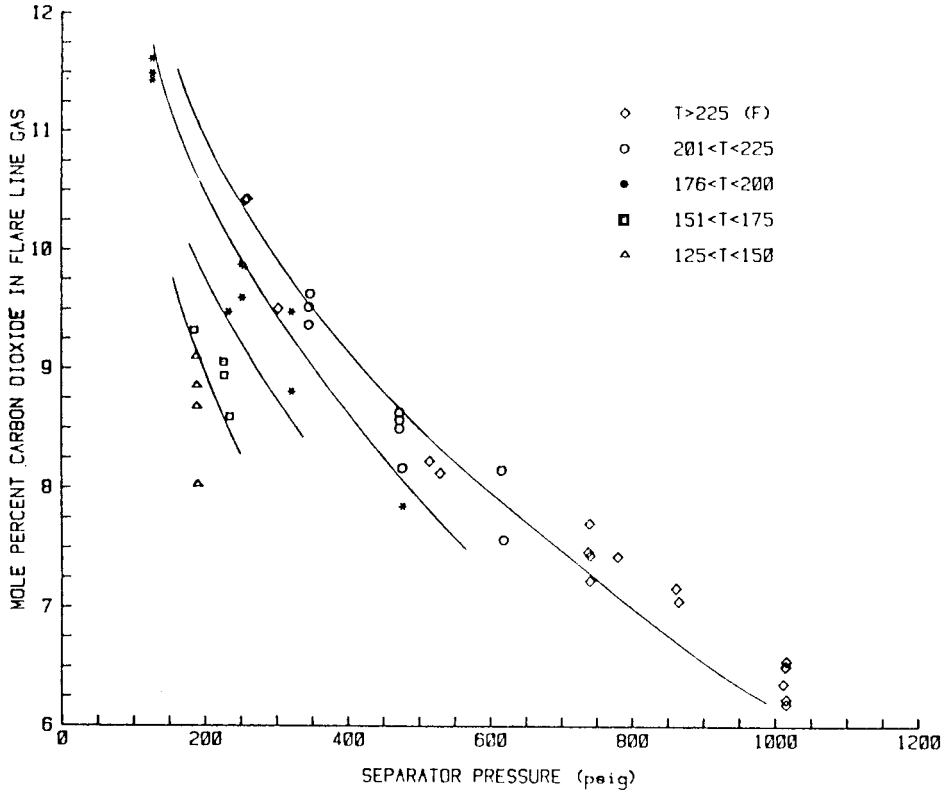

Figure 13. CARBON DIOXIDE CONTENT OF FLARE LINE GAS VS. SEPARATOR PRESSURE

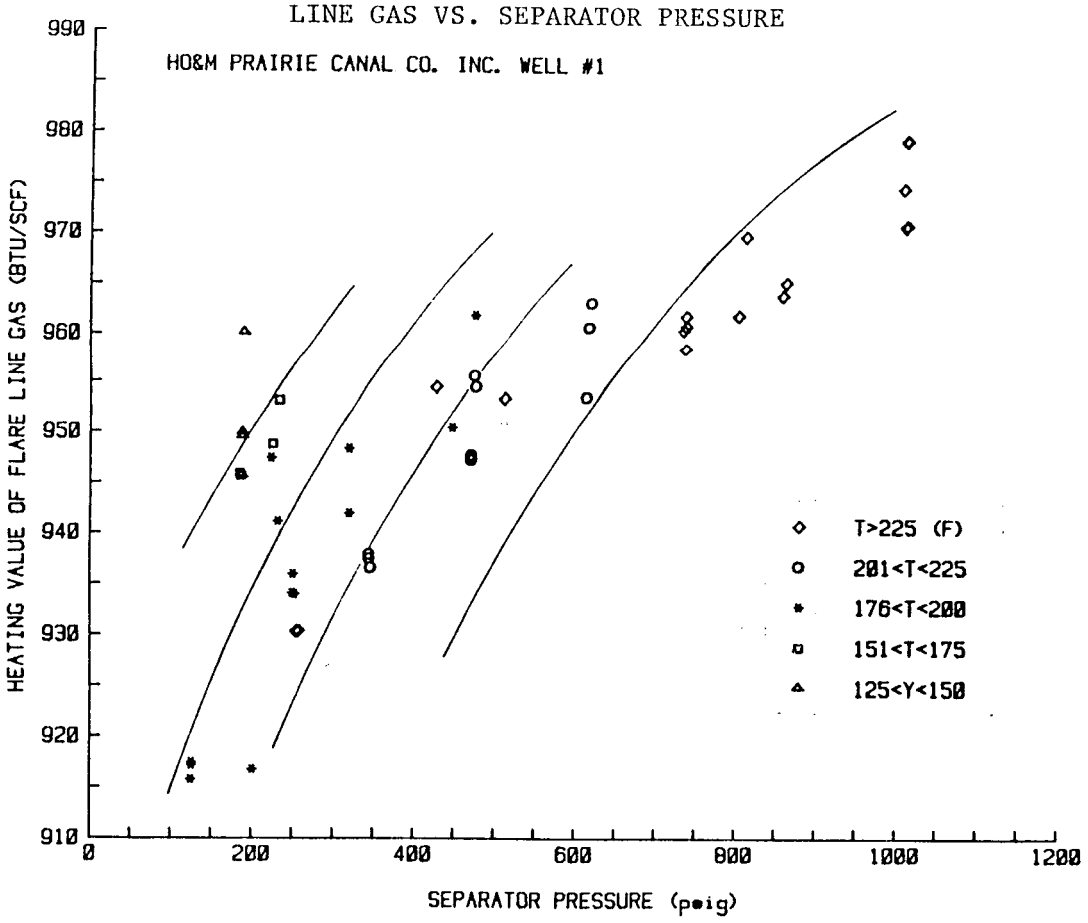

Figure 14. HEATING VALUE OF FLARE LINE GAS (Btu/SCF)

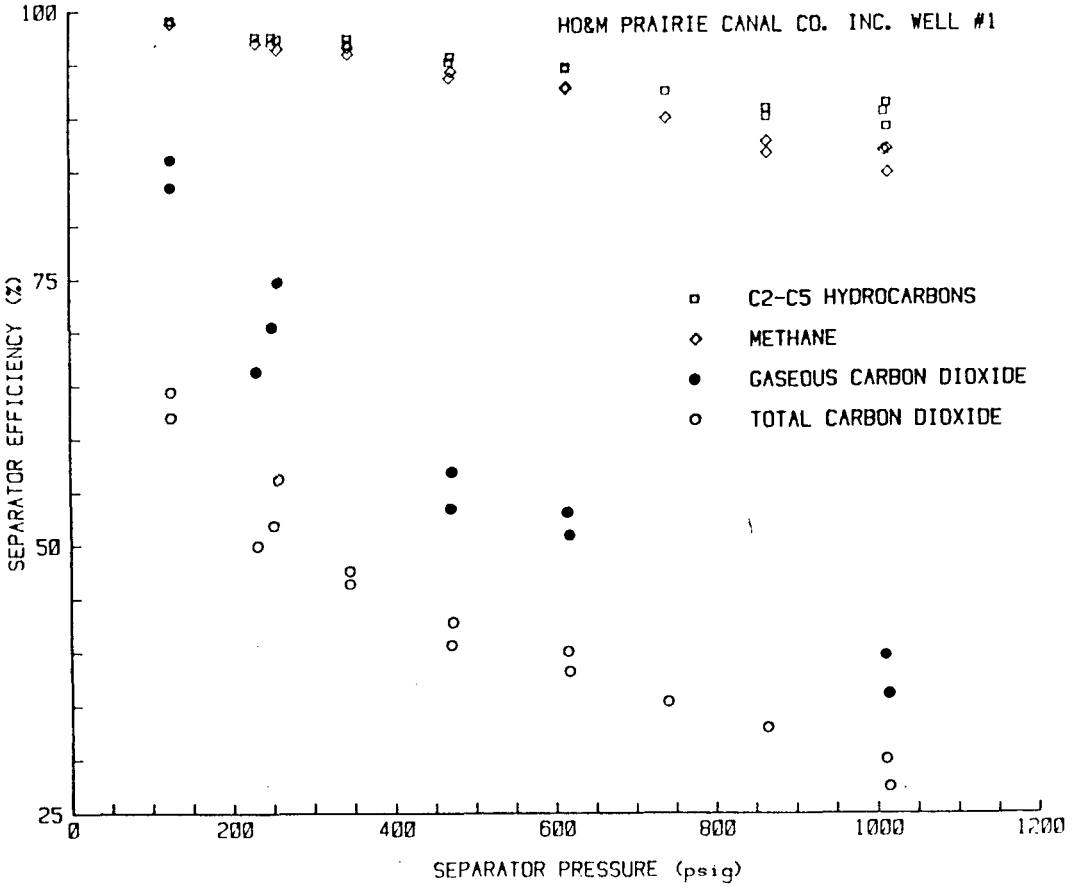

Figure 15. SEPARATOR EFFICIENCY VS. SEPARATOR PRESSURE FOR VARIOUS FRACTIONS

This work was funded by the U.S. Department of Energy under contract number DE-AC08-80ET27081, "Testing Geopressured-Geothermal Reservoirs in Existing Wells." Work by the Institute of Gas Technology was performed on a subcontract from Eaton Operating Co., Inc., under that contract.

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Correspondence regarding the accuracy and reproducability of P.B. brine analyses.

BUREAU OF ECONOMIC GEOLOGY
THE UNIVERSITY OF TEXAS AT AUSTIN

Mineral Studies Laboratory
University Station, Box X · Austin, Texas 78713-7508 · (512) 471-1534 or 471-7721

February 10, 1989

Mr. Chris Hayden
Institute of Gas Technology
1713 Crestwood Court
Texas City, Texas 77591

SUBJECT: Analytical Data for Pleasant Bayou, Subcontract #S1-14636

Dear Chris:

It has come to my attention upon review of our contract that the measurement of organic acid anions was included in the "standard brine" analysis and in fact have not been measured. Also, questions concerning the apparent trends in the reported data for some elements have been under debate and are discussed in the following:

1. ORGANIC ACID ANIONS:

The above-mentioned contract has been in effect since March 1, 1988 and to date the determination of the content of organic acid anions in the samples have not been measured. This capability will not be available at the Mineral Studies Laboratory (MSL) within the remaining time of our current agreement.

The decision not to analyze for these constituents was based on discussions between Dave Koppenaal and Chris Hayden during the first part of the contract for the following reasons:

1) the MSL did not have QA procedures set up to perform this analysis (routine capability for determining these constituents will be established at the MSL in the near future, possibly by 04/01/89), and

2) Chris said that these data are not currently needed by him for the current subcontract and, if these data become important before the MSL can deliver them, then IGT will send the appropriate samples to another analytical laboratory for the required measurements.

The charges for previously analyzed Pleasant Bayou brine samples were for "standard brine" or "detailed brine" analysis and therefore have inadvertently included charges for organic acid anion analysis that were not performed. This mistake will be corrected in future billing.

2. VARIATIONS IN THE ANALYTICAL DATA REPORTED TO DATE

I have been informed of concerns over a possible "batch effect" in the results of some of the minor and trace constituents reported by the MSL for the Pleasant Bayou brine samples. In other words, the data appears to show trends that are not real. This has prompted repeat analyses to determine if noticed trends are real. The constituents that were measured again include sodium, magnesium, calcium, potassium, strontium, barium, iron, manganese, lithium, boron, silica, zinc, and chloride. These constituents were measured for samples collected from May 30, 1988 to January 20, 1989.

Results/Conclusions:

A. All previously reported ICP-OES data is valid. Values are within the expected experimental uncertainty for the procedures used (refer to the attached procedure).

B. Three samples were found to have higher recoveries for chloride in the original analysis than in the repeat analysis. Following further analyses, the original data was proven to be in error and therefore, the most recent data is the most reliable. These samples and the new data are:

88-1152	(OCT 3,1988)	71700 mg/L chloride
88-1153	(OCT 17,1988)	72000 mg/L chloride
88-1154	(OCT 28,1988)	71600 mg/L chloride

Note: This and the rest of the data for the currently pending samples will be formally reported very soon.

C. The data from the repeat ICP-OES and chloride analyses are presented in Table 1 for your information. Please understand that the intent of this repeat analysis is to compare relative concentrations of each element through the sampling period. To do this, the samples were analyzed sequentially in a short period of time with little attention being paid to absolute accuracy. The data therefore should not be used in place of the previously reported data.

This new data has indicated that a "batch effect" does exist in the original analysis for some elements. This is not unusual for this type of ICP-OES analysis and thereby contributes to it's inaccuracy.

The reliability of the results for brine samples by ICP-OES is:

Major elements (Na,Mg,Ca,K) is +/- 5% relative

Minor/trace (Sr,Ba,Fe,Mn,Zn,Li,Si,B) is +/- 25% relative

Alternative analytical methods are recommended if trends of this magnitude for minor/trace elements are to be definitive.

Please call me if you have any questions or comments.

Sincerely,

Steven W. Tweedy
Acting Chief Chemist

cc: D. Ratcliff
R. Capuano

ANALYSIS REPORT

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MINERAL STUDIES LABORATORY
BUREAU OF ECONOMIC GEOLOGY
THE UNIVERSITY OF TEXAS AT AUSTIN

STEVEN W. TWEEDY
CHIEF CHEMIST

Table 1

BRINE FROM THE PLEASANT BAYOU TEST WELL
RESULTS OF RE-ANALYSIS

page 1

MSL ID #	DATE COLLECTED	Na (mg/L)	Mg	Ca	K	Sr	Ba	Fe	Mn
88-673	30MAY88	36400	560	7380	531	895	741	47.1	15.9
88-676	14JUN88	37500	577	7520	557	955	757	47.2	16.3
88-678	01JUL88	36200	571	7570	544	911	742	59.7	16.6
88-735	21JUL88	36900	578	7710	535	903	752	49.5	17.3
88-942	05AUG88	36900	579	7810	581	985	751	47.7	17.6
88-944	24AUG88	36700	572	7690	555	921	743	46.9	17.2
88-1152	03OCT88	36000	582	7760	563	877	746	46.7	17.5
88-1153	17OCT88	37400	584	7720	578	933	747	50.7	17.6
88-1154	28OCT88	37600	580	7740	582	955	749	49.9	17.8
88-1220	29NOV88	38700	589	8010	588	959	782	49.4	18.4
88-046	19DEC88	38100	590	7940	601	952	778	54.0	18.3
88-047	10JAN89	37700	588	7860	580	882	761	49.1	18.1
88-048	20JAN89	37600	587	7890	584	915	768	51.4	17.9
MEAN		37208	580	7738	568	926	755	49.9	17.4
STDEV		778	9	175	22	33	13	3.6	0.8
RELSTDEV		2	1	2	4	4	2	7.2	4.4
MAXIMUM		38700	590	8010	601	985	782	59.7	18.4
MINIMUM		36000	560	7380	531	877	741	46.7	15.9
RANGE		2700	30	630	70	108	41	13.0	2.5
COUNT		13	13	13	13	13	13	13.0	13.0

< less than indicated value
• reported value near detection limit
nd - not determined
ins - insufficient sample

ANALYSIS REPORT

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CHIEF CHEMIST

Table 1 (cont.)

PLEASANT BAYOU BRINE RESULTS

page 2

MSL ID #	Zn (mg/L)	Li	SiO2	B	Cl
88-673	0.41	29.6	87.9	25.9	70310
88-676	0.43	29.4	92.3	32.1	69590
88-678	0.40	28.6	94.6	29.6	71590
88-735	0.35	25.3	82.3	27.1	72340
88-942	0.43	24.4	81.7	27.2	71660
88-944	0.39	24.9	81.2	26.4	72230
88-1152	0.40	25.8	80.9	26.6	71700
88-1153	0.39	26.3	80.9	26.6	72030
88-1154	0.43	26.1	81.4	27.0	71560
88-1220	0.33	26.1	82.6	27.4	72640
88-046	0.21	23.9	79.7	26.8	71590
88-047	0.25	24.0	80.6	26.7	71650
88-048	0.25	23.3	78.0	27.1	72270
MEAN	0.36	26.0	83.4	27.4	71628
STDEV	0.08	2.1	5.0	1.7	835
RELSTDEV	21	8.0	6.0	6.0	1
MAXIMUM	0.43	29.6	94.6	32.1	72640
MINIMUM	0.21	23.3	78.0	25.9	69590
RANGE	0.22	6.3	16.6	6.2	3050
COUNT	13	13.0	13.0	13.0	13

< less than indicated value
* reported value near detection limit
nd - not determined
ins - insufficient sample

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Table 2

QA/QC REFERENCE SAMPLE ANALYSIS RESULTS

page 1

MSL ID #	Na (mg/L)	Mg	Ca	K	Sr	Fe	Mn	Zn
SEA/EPA TM	11330	1303	399	403	8.28	1.776	0.969	1.671
	10750	1287	401	394	8.06	1.719	0.925	1.643
	11350	1316	407	408	8.24	1.616	0.859	1.691
MEAN	11143	1302	402	402	8.19	1.704	0.918	1.668
STDEV	341	15	4	7	0.12	0.081	0.055	0.024
RELSTDEV	3	1	1	2	1.43	4.760	6.033	1.445
ACCEPTED:	11070	1320	422	409	8.10	1.850	0.990	1.660
BIAS:	73	-18	-20	-7	0.09	-0.146	-0.072	0.008
% BIAS:	0.7	-1	-5	-2	1.15	-7.910	-7.306	0.502

MSL ID #	Cl (mg/L)
SEA/EPA TM	19450
	19270
	19300
MEAN	19340
STDEV	96
RELSTDEV	0.5
ACCEPTED:	19373
BIAS:	-33
% BIAS:	-0.2

< less than indicated value
nd - not determined
* reported value near detection limit
ins - insufficient sample

ANALYSIS REPORT

UNIVERSITY STATION, BOX X
AUSTIN, TEXAS 78713-7508
(512) 471-7721 (ext. 426)

MINERAL STUDIES LABORATORY
BUREAU OF ECONOMIC GEOLOGY
THE UNIVERSITY OF TEXAS AT AUSTIN

STEVEN W. TWEEDY
CHIEF CHEMIST

INVESTIGATOR:	PROJECT/ACCOUNT:	DATE:	REPORT #:
Chris Hayden	IGT,0170488-00	30 May 1989	R-093-88 ,R-105-88, R-011-89, R-024-89 R-036-89

SAMPLE PREPARATION / TREATMENT

These samples were analyzed on an as received basis. For all analyses, the samples were shaken prior to removing an aliquot for analysis to include any precipitated solids. These samples were not filtered nor preserved prior to receipt by the MSL.

SAMPLE ANALYSIS METHODS

Constituents	Technique	MSL Procedure #
Na,K,Mg,Ca,Fe,Mn,	ICP-OES	SWI 1.6
Sr,Ba,Zn,Li,SiO2,Cr,		SWI 1.5
Cu,Ni,As,Cd,Pb,Sn,B		
Mercury	Cold-Vapor AA	-----
Ammonia (NH3)	Distillation-titration	MSL 001
Chloride	Titration	SWI 1.1
Sulfate	Turbidimetric	SWI 1.3
Bromide	Spectrophotometric	SWI 1.2
Iodide	Spectrophotometric	SWI 1.4
Fluoride	Ion Electrode	SWI 1.11
Alkalinity	pH Titration	------
Density, TDS	Gravimetric	------

RESULTS

Sample analysis results are presented in Table 1.

The associated QA/QC analysis results are presented in Tables 2 and 3.

COMMENTS

As we discussed on the phone, two items have been discovered which require some qualification; 1) The procedure for mercury in brines cannot measure values as low as previously reported, and 2) The measured values for alkalinity by the MSL are potentially low due to excessive time between collection and measurement.

< less than indicated value
nd - not determined
* reported value near detection limit
ins. - insufficient sample

ANALYSIS REPORT

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The problem with the sensitivity of the mercury determination became apparent when a modest spike of mercury could not be recovered at all when following the procedure as written. Before an acceptable recovery of added mercury could be obtained, the starting volume and the pre-treatment of the sample, were changed significantly. The result: the detection limit had to be increased to 0.050 mg/L from 0.005 mg/L. If this change makes the mercury determination inappropriate, it can be discontinued.

The problem of low results for alkalinity (when elapsed time between collection and analysis becomes excessive) became apparent when the HULIN sample was re-analyzed for this constituent. In a period of three months the determined alkalinity for this sample went from 12.12 meq/L to 0.63 meq/L. The sample changed significantly in appearance, turning orange and developing a heavy orange precipitate. This dramatic change casts shadows on all determined alkalinity values to date. It is conforting, however, to find out from you that in-situ measurements of alkalinity were made on the dates of collection.

THIS IS THE FINAL REPORT FOR THESE SAMPLES, PLEASE REPLACE PREVIOUSLY REPORTED DATA WITH THE ATTACHED TABLES

SAMPLE DISPOSITION:

The remains of these samples are being archived at the MSL.

ANALYSTS:

Tweedy
Herrera
Salgo
Dodgen

< less than indicated value
• reported value near detection limit

nd - not determined
ins - insufficient sample

IGT

3424 South State St., Chicago, IL 60616
P.O. Box 1775, Alvin, TX 77512

Solids Sampling and Analysis - Pleasant Bayou Flow Test, 1988 - present

This section covers analyses performed on solids. Chemical analyses can only be related to well performance if the quantity produced can be determined. The operator measures weekly accumulations of solids from both the separators at the sand check point. These values are recorded in the log book and the Weekly Report. The filters also catch solids, though the concentration is too small to measure. There is so little solids production that:

- There are no routine solid samples - all samples are special samples.
- We use IGT and Core Laboratories interchangably for most analyses.
- We use service and specialty companies, in particular Champion Chemical, Nutro, and Cormet Engineering if the type of analysis falls into thier specialties.

Types of Samples

Solids accumulation is measured weekly by operators on duty. The solids check point are sand traps on both separators. Generally a total of less than 1/4 cup of sand, scale, rust, and debris is collected during a two week period. These samples are not analysed.

We occasionally get solids samples. These include the following:

- Flakes or pieces of material caught in the chokes or turbines.
- Large accumulations of solids in the separator.
- Solids samples caught on the in-line filter elements.
- Bailer samples from the disposal well.

Types of Analyses

The types of analyses requested depends on the sample type. IGT and Core Labs provide sieve analyses and x-ray diffraction analyses for sand type samples. IGT also use an acid disolution, monitoring the carbon dioxide, calcium, strontium, and iron dissolved from the sample. The IGT procedure is presented in Appendix Solids-A. Core Lab procedures are provided in Appendix Solids-B.

Hydrocarbon type samples can be dissolved and analysed by gas chromatography at IGT or by infrared spectroscopy at Champion Chemical, if corrosion inhibitor buildup is suspected. Both Champion Chemical and Nutro provide, free of charge, wet chemical analysis of materials that may impact their corrosion and scale inhibitor chemicals.

For metal samples and salt like materials, Core Labs and IGT can perform energy dispersive x-ray spectrometry or x-ray fluorescence analyses. These are elemental analyses, in contrast to

x-ray diffraction which determines crystalline compounds.

X-ray analyses are great, but cost about $350 each, so use them with discretion.

Data Handling and Reporting: All solids analyses are to be reported in the Weekly reports to Eaton Operating Company. The origional report sheets are filed in the PB-Solids folder.

Analytical Laboratories: The addresses and contacts of laboratories used are provided below:

Sherman Chao/Karen Crippen
Institute of Gas Technology
3424 South State Street
Chicago IL 60616
312-567-5739

Mike Dixon/Bill Reese
Core Laboratories
5295 Hollister Road
Houston TX 77040
713-460-9600

N. Grahmann
Champion Chemical Inc
P. O. Box 45509
Houston TX 77045
713-431-2561

Larry Smith/Robert Mills
Nutro Products
P. O. Box 21187
Houston TX 77226
713-675-3421

Quality Control/Quality Assurance

There is so few solids samples obtained that it is difficult to perform any QA/QC checks, other than those performed in the lab of choice. The method employed in the fluids analyses - sendind duplicate or alternate samples to different labs - is not appropriate given the high cost of many of these analyses and the fact that 6 months or more may pass before a sample is obtained.

SEMI-QUANTITATIVE MINERALS AND CLAYS

Principle

Carbonate containing minerals are gravimetrically determined by mild acidification of a disaggregated sample. The silicate-like minerals are subsequently isolated by a float-sink separation on the acid insoluble portion and weighed. The float portion (containing the <2 micron sized particles) is by definition the clays. Heat and ethylene glycol treatment of the clay fraction followed by XRD analysis of the resulting lattice structures allow a mathematical determination of the relative amounts of kaolinite, illite and expandable clay present. A semiquantitative determination of the minerals present in the original sample (quartz, albite, microcline) is made by adding a known internal standard, taking the XRD pattern and comparing the peak intensities to a standard mixture.

Scope

This method is applicable to geological, coal and shale samples.

Interferences

If the sample has been too finely ground, the silicate-like minerals will be retained in the float fraction. In any event, there will always be a positive bias from the finely grained silicate-like minerals inevitably present which cannot be avoided. Some minerals also tend to be highly oriented when mounted for XRD study and care must be taken when mounting to either maximize or randomize this effect so as to achieve consistent patterns.

Apparatus

1. Hot plate
2. Vacuum filtering apparatus
3. 0.45 micron membrane filters with aluminum pans
4. 100 ml conical centrifuge tubes
5. Centrifuge
6. Pressure filtering device, capable of withstanding up to 90 psi
7. Muffle furnace
8. Ethylene glycol chamber, constructed from a sealed desiccator containing a small amount of ethylene glycol in the bottom.
9. Glass microscope slides, cut in half widthwise

10. Philips X-ray diffractometer, Norelco vertical goniometer

11. Aluminum XRD cells

12. Plastic mixing balls and vials, Spex 6133, Spex 3112

13. Spex Mixer/Mill, Model 8000

14. Agate mortar and pestle

15. Standard sieves, 100 mesh and 325 mesh

Reagents

1. 5% (v/v) acetic acid Dilute 50 ml glacial acetic acid to 1 liter with DDIW.

2. Sodium carbonate solution Add sodium carbonate to DDIW to a pH of 10.

3. Ethylene glycol

4. Corundum (Al2O3) Ground to -325 mesh.

Procedure A (Clay separation and determination)

1. Grind or disaggregate the sample to pass through a 100 mesh screen.

2. Accurately weigh out 2 to 5 grams of sample and place in a 100 ml beaker. Add 20 ml 5% acetic acid and digest on a hot plate for 2 hours.

3. Remove and cool. Filter through a tared 0.45 micron membrane filter. Save the filtrate for possible ICP analysis. Dry and reweigh the filter to obtain the weight of the acid insoluble solids.

4. Wet the filter with the sodium carbonate solution. Transfer the solids to a 100 ml centrifuge tube. Add more solution to make the volume around 85 ml. Note that the tubes must be mass balanced for the centrifuge to operate properly.

5. Agitate the tube to wet all the solids. Lay the tube flat for 15 minutes to equilibrate.

6. Spin the tube at 750 rpm for 4 minutes (Note 1). Decant the liquid from the tube into a beaker. Add more sodium carbonate solution and repeat the procedure until the top solution remains clear. (This usually requires a minimum of 3 spins.)

7. The material concentrated at the bottom of the centrifuge tube is the sink or silicate-like fraction. Quantitatively transfer it to a tared aluminum weighing dish, dry at 100 C and reweigh to obtain the weight of the silicate-like minerals.

8. The material suspended in the carbonate solution is the float or clay fraction. Assemble the pressure filtration vessel using another 0.45 micron membrane filter. Filter the suspended clay particles, discarding the filtrate.

9. Resuspend the clay fraction in a minimum amount of DDIW and transfer a few drops of the suspension to each of three halved glass slides. Allow the solids to air dry. (Note 2)

10. Place one slide in the ethylene glycol chamber and allow it to equilibrate for at least 48 hours.

11. Just prior to XRD analysis, place another slide in a muffle furnace preheated to 375 C. Ash for 1 hour. Keep in a desiccator until used.

12. Turn on the XRD spectrometer according to manufacturers recommendations. Set the x-ray energy to 35 KeV and 23 ma.

13. Scan the x-ray diffraction patterns of both the ethylene glycol treated and the heated glass slides from a 2-theta of 15.0 to 5.0 using steps of 0.01 degrees and counting for 1 second.

14. If necessary, scan the remaining slide from 70.0 to 5.0 2-theta to aid in the pattern identification.

15. Measure the intensity of the bands at d-spacings of 10 Angstrom (2-theta = 8.8 degrees) and 7 Angstroms (2-theta = 12.5 degrees) of the patterns obtained in step 13.

Calculations (Clay)

$$\% \text{ acetic acid soluble minerals} = 100 - \frac{100\ (\text{g. acetic acid insoluble material})}{\text{g. total sample}}$$

$$\% \text{ silicate-like minerals} = 100 \times \frac{\text{g. sink fraction}}{\text{g. total sample}}$$

$$\% \text{ clays} = 100 - \% \text{ acetic acid soluble minerals} - \% \text{ silicate-like minerals}$$

$$\% \text{ Kaolinites} = \frac{7,H/2.5}{7,H/2.5 + 10,H} \times 100$$

$$\% \text{ Illites} = \frac{7,H}{7,G} \times \frac{10,G}{10,H} \times (100 - \% \text{ Kaolinites})$$

$$\% \text{ Expandable clays} = 100 - \% \text{ Kaolinites} - \% \text{ Illites}$$

7,H = 7 Angstroms, heated
7,G = 7 Angstroms, glycol treated
10,H = 10 Angstroms, heated
10,G = 10 Angstroms, glycol treated

Procedure B (Mineral determination)

1. Grind the sample to pass through a 325 mesh screen.

2. Weigh out 1 g. of the sample into a mixing tube. Add enough Al2O3 standard to make the concentration of corundum in the sample plus standard equal to 35%. Shake in the Spex mixer for 15 seconds.

3. Mount the sample + standard into an aluminum XRD cell using the backloading technique (Note 3). Measure the x-ray diffraction pattern from 25.0 to 30.0 degrees 2-theta with steps of 0.01 degrees and counting of 1 second. This is usually done with 5 replicates.

4. Measure (with a ruler if desired) the peak intensities of the corundum at a 2-theta of 25.5, quartz at 26.6, microcline at 27.4 and albite at 27.9.

5. Measure the XRD pattern of the original (-325 mesh ground) sample from 70.0 to 5.0 2-theta to confirm the presence of these minerals and the absence of others. If any others are detected, they may be quantified using similar techniques.

Calculations (Mineral) (Note 4)

$$\% \text{ Quartz} = \% \text{ Al2O3} \times 0.182 \times I(q) / I(c)$$

$$\% \text{ Microcline} = \% \text{ Al2O3} \times 0.348 \times I(m) / I(c)$$

$$\% \text{ Albite} = \% \text{ Al2O3} \times 0.271 \times I(a) / I(c)$$

(These percentages are usually normalized to the percent of silicate-like minerals found in the sink fraction of the clay separation.)

% Calcite = % acetic acid soluble (from clay separation)

(This should be confirmed by the XRD pattern of the original sample.) If there are other acetic acid soluble compounds present, the calcite may be determined by measuring the calcite peak height at 2-theta of 29.3 as in step B-4 and calculated by:

$$\% \text{ Calcite} = \% \text{ Al2O3} \times 0.310 \times I(ca) / I(c)$$

The difference between this value and the acetic acid soluble value should be the % of other acid soluble minerals.

% Al2O3 is determined in step B-2.
I(c) = intensity of corundum peak
I(q) = intensity of quartz peak
I(m) = intensity of microcline peak
I(a) = intensity of albite peak
I(ca) = intensity of calcite peak

Notes

1. The time required for the centrifugation process is calculated from a modified formula derived from Stokes law. See Reference 1.

2. This procedure of mounting a sample maximizes the orientation of the major basal 001 plane, thus maximizing the peaks at 7 and 10 Angstroms.

3. Backloading the sample provides for the randomization of the oriented minerals. A glass slide is fastened to the front of the aluminum XRD cell with cellophane tape. The -325 mesh sample is sifted onto the glass, filling the cell opening. Another glass slide is then taped to the back of the cell so the sample is sandwiched between. Turn the cell over and remove the first glass slide. This gives a superior flat surface for the XRD analysis.

4. The constants in the mineral calculations were derived from a synthetic standard + Al2O3 made up to approximate the concentrations normally seen in the samples received.

Time of Analysis

The analyst should allow a minimum of four days to complete this analysis.

References

1. J.C. Hathaway, *Clay Mineral Bulletin*, 3, 1956, pp. 8-13.

2. C.R. Ward, *Illinois State Geological Survey Circular 498*, 1977.

3. H.L. Barwood, C.W. Curtis, J.A. Guin and A.R. Tarrer, *Fuel*, 61, 1982, pp. 463-469.

4. S.J. Russell and S.M. Rimmer, *Analytical Methods for Coal and Coal Products*, *Vol* III, C. Karr, Ed, pp. 146-159, Academic Press, New York, 1979.

5. G. Brown, Ed., *The X-ray Identification and Crystal Structures of Clay Minerals*, Jarrold and Sons Ltd., Norwich, Great Britain, 1961.

ANALYTICAL PROCEDURES

X-Ray Diffraction Analysis

The samples selected for quantitative X-ray Diffraction Analysis are disaggregated with a mortar and pestle, weighed and transferred to deionized water, where further disaggregation is performed with a sonic probe. The samples are then centrifugally size-fractionated into sand/silt (>4 microns) and clay-size (<4 microns) fractions. The suspended clay-size fractions are decanted and vacuum-deposited on silver metal membrane filters to produce oriented mounts. Each clay mount is analyzed dry (relative humidity = 50%) and after treatment with ethylene glycol. If necessary, samples are analyzed a third time following heat treatment (375^{o}C for one hour).

The sand/silt fractions of each sample are dried and weighed to determine weight loss due to the removal of clay-size material. The dried sand/silt fractions are then mixed with alumina (Al_2O_3) as an internal standard and ground in water to a fine powder using a micronizing mill. The resultant slurries are dried, disaggregated and packed into aluminum powder holders using a modified pellet press.

Quantitative XRD analyses are performed using an automated Philips 3620 powder diffractometer. The weight percentages of minerals present in the sand/silt fractions are determined using internal standard ratio techniques. The weight percentages of the various clay minerals (and other clay-size rock forming minerals) in the clay-size fractions are determined by Lorentzian profile fitting/empirical peak-area-ratio methods. The whole-rock compositions are then calculated by mathematically combining the XRD data from both size fractions.

Compositions and species of clay minerals detected in the clay-size fractions are determined according to procedures outlined by Weaver (1956), Jonas and Brown (1959), Carroll (1970), Reynolds (1980), and Srodon (1980). The detectability limit is 0.5% - 1.0% for crystalline phases present in the size fractions analyzed.

ANALYTICAL PROCEDURES

The samples selected for quantitative X-ray Diffraction Analysis are disaggregated with a mortar and pestle, weighed and transferred to deionized water, where further disaggregation is performed with a sonic probe. The samples are then centrifugally size-fractionated into sand/silt (>4 microns) and clay-size (<4 microns) fractions. The suspended clay-size fractions are decanted and vacuum-deposited on silver metal membrane filters to produce oriented mounts. Each clay mount is analyzed dry (relative humidity = 50%) and after treatment with ethylene glycol. If necessary, samples are analyzed a third time following heat treatment (375^{o}C for one hour).

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Compositions and species of clay minerals detected in the clay-size fractions are determined according to procedures outlined by Weaver (1956), Jonas and Brown (1959), Carroll (1970), Reynolds (1980), and Srodon (1980, 1984). The detectability limit is 0.5% - 1.0% for crystalline phases present in the size fractions analyzed.

MATERIAL SAFETY DATA SHEET

stitute of Gas Technology
3424 South State Street
Chicago, IL 60616
(312) 567-3650

IGT

METHANE

CAS # 000-074-828

Date: September 1987

SECTION I. MATERIAL IDENTIFICATION

MATERIAL NAME: METHANE
DESCRIPTION: Compressed gas (Max. 2000 psig) in cylinders
OTHER DESIGNATIONS: CH_4, Methyl Hydride, Marsh Gas, Natural Gas

SECTION II. INGREDIENTS AND HAZARDS	%	HAZARD DATA
METHANE	93 min*	Simple asphyxiant**
Typical Impurities: (See ASTM D1945 for method of analysis)		
Ethane	<4	Simple asphyxiant
Propane	<1	Simple asphyxiant
Butanes	<0.4	Simple asphyxiant
C_xH_{2x+2} (x=5 and above)	<0.1	
Carbon dioxide	<0.7	
Nitrogen	<0.6	
Oxygen	<0.1	

* "Commercial" methane or a high-methane natural gas (a trace of odorants, such as mercaptans, may be added as an odorizer). Purified methane is >99% CH_4 with very low impurity levels.

** The TLV (ACGIH, 1979) requires a minimal oxygen content of 18% by volume in workplace air at 1 atm.

SECTION III. PHYSICAL DATA

Boiling point at 1 atm, °C	-161.5	Density at -162°C, liquid, g/cc	0.43
Critical temperature, °C	-82.1	Freezing point at 1 atm, °C	-182.6
Critical pressure, atm	45.8	Molecular weight	16.04
Specific gravity, gas (Air = 1)	0.55		

Appearance & Odor: Colorless, odorless and tasteless gas (Unless odorants added to odorize). Also has been shipped and handled as cold liquid (LNG) in insulated containers.

SECTION IV. FIRE AND EXPLOSION DATA			Lower	Upper
Flash Point and Method	Autoignition Temp.	Flammability Limits in Air		
-306°F	1004°F	% by volume	5.0	15

Extinguishing Media: Flame can be extinguished with CO_2, dry chemical or halocarbon gas. A hazard of re-ignition or explosion exists if flame is extinguished without stopping flow of gas or cooling the surroundings! Use water spray to cool surroundings! Control and then shut off gas flow when feasible, but it may be necessary or desirable to allow flame at cylinder or storage tank to continue burning while cooling containers and surroundings with water from a safe distance or from unmanned hose stations. Danger of rocketing cylinders and explosion exists. (Methane cylinders have fusible metal (165°F or 212°F) safety devices for pressure relief.)

SECTION V. REACTIVITY DATA

When suitably contained and kept unmixed with air or other oxidizing agents, methane is stable under normal storage and handling conditions. It does not polymerize; it is non-corrosive. However, it readily forms flammable/explosive mixtures with air (see Sect. IV).

In the presence of catalysts or sources of ignition, violent or explosive reactions can occur between methane and oxidizing agents, such as chlorine, bromine pentafluoride, oxygen difluoride, and nitrogen trifluoride. It explodes spontaneously on mixing with chlorine dioxide.

A mixture of liquid methane and liquid oxygen is an explosive. Even at -190°C liquid fluorine explodes on contact with liquid methane.

SECTION VI. HEALTH HAZARD INFORMATION	TLV Simple Asphyxiant (See Sec. II)

Methane is non-toxic. However, it can act as an asphyxiant by displacing or partially displacing the air required to support life. Workers exposed to oxygen deficient atmospheres become cyanotic, experience diminished mental alertness and impaired muscular coordination, and dyspnea. Collapse and death can occur at very low oxygen levels. Contact with liquefied methane can produce freeze burns.

FIRST AID

Contact of liquid with skin: Remove victim from contact. Flush affect area with lots of tepid water. Do not apply direct heat to area. Loosely apply dry sterile, bulky dressings to protect area from infection/injury. Get medical help.

Inhalation: Remove to fresh air. Quickly restore and/or support breathing as required. Have trained person administer oxygen if available. (Mouth-to-mouth resuscitation should be used immediately for a victim of methane asphyxiation!) Get medical help.

SECTION VII. SPILL, LEAK, AND DISPOSAL PROCEDURES

Notify safety personnel. Evacuate area. Provide optimum, explosion-proof ventilation. Shut off methane source if possible. Remove sources of heat or ignition if feasible.

DISPOSAL: Remove leaking cylinder to isolated area outdoors or place into a hood with adequate forced ventilation. Keep concentration of gas below 25% of LEL by ventilation. Allow gas to discharge at controlled, slow to moderate rate. Defective cylinders tagged to indicate defect. Close valve and return to supplier.

SECTION VIII. SPECIAL PROTECTION INFORMATION

Provide adequate general and local exhaust ventilation (explosion proof) to prevent work place atmospheres from reaching 20% of LEL. Thoroughly test methane lines for leakage with nitrogen pressure before use, especially in enclosed areas. Give special attention to ventilation for enclosed areas.

Provide air supplied or self-contained breathing equipment for emergency or nonroutine situations where methane level is excessive. The use of cartridge or canister respirators may result in suffocation.)

Safety shield, gloves, glasses and safety shoes are recommended when handling cylinders.

SECTION IX. SPECIAL PRECAUTIONS AND COMMENTS

Store cylinders in a well-ventilated, low fire-risk area. Outdoor or detached storage preferred. Keep cylinders away from oxidizing agents and sources of heat or ignition. Protect cylinders against physical damage. Follow general safety procedures for handling and storing compressed gas cylinders. No part of a cylinder should be exposed to temperature above 125°F.

Ground all lines and equipment used with methane to prevent static sparks. Use non-sparking tools. No Smoking where methane is used or stored.

A 19% oxygen concentration in the air is the minimum recommended for working without special breathing equipment. (Air/methane at 19% oxygen is near the LEL.)

DOT CLASSIFICATION: FLAMMABLE LABEL: FLAMMABLE, Red Label

DATA SOURCE(S) code: 2,4-11,17-18,23,25

IGT

CERTIFICATE

of

ANALYSIS

This certifies that the composition of the natural gas contained in IGT Cylinder Number GC152, as reported below, has been measured by comparison with that of a primary standard methane certified by the National Bureau of Standards.

COMPONENT	MOLE %
Oxygen	NOT DETECTED ($\leq$ 0.003)
NITROGEN	2.52 $\pm$ 0.01
CARBON DIOXIDE	1.031 $\pm$ 0.007
METHANE	90.60 $\pm$ 0.07
ETHANE	3.99 $\pm$ 0.02
PROPANE	1.000 $\pm$ 0.007
I-BUTANE	0.298 $\pm$ 0.005
N-BUTANE	0.303 $\pm$ 0.005
I-PENTANE	0.101 $\pm$ 0.004
N-PENTANE	0.099 $\pm$ 0.004
N-HEXANE	0.053 $\pm$ 0.005
TOTAL	100.00

CERTIFICATE NO. GCR-223

CALCULATED PROPERTIES (ASTM D 3588-81):

GROSS CALORIFIC VALUE (TOTAL HEATING VALUE): 1028.0 ($\pm$ 0.9) Btu per cubic foot saturated with water vapor at 60°F and 14.735 psi (or 30.00 inches of 32°F mercury) absolute pressure.

RELATIVE DENSITY (SPECIFIC GRAVITY): **0.618** ($\pm$ 0.001), relative to Air = 1 at 60°F and 14.735 psi absolute pressure.

IMPORTANT NOTICE: All IGT cylinders require a pressure regulator with CGA-350 connector for methane service.

Consignee:

INSTITUTE OF GAS TECHNOLOGY
ATTENTION: CHRIS HAYDEN
902 RIGEL
FRIENDSWOOD, TX 77546

A. Attari
Associate Director,
Chemical Research Services

Purchase Order No.: 65071-03
Date of Shipment : 12/21/87

6719001

DRÄGER-Röhrchen
Schwefelwasserstoff 1/c

GEBRAUCHSANLEITUNG 234–19001 · 11. Ausgabe · April 1985

1 Allgemeines und Anwendungsbereich

Bestimmung von H_2S in Luft und in technischen Gasen.
Die Röhrchen sind zusammen mit der DRÄGER-Gasspürpumpe zu verwenden.
Zur Handhabung des Gasspürgerätes und der DRÄGER-Röhrchen vgl. Abschnitt 4 dieser Gebrauchsanleitung und Gebrauchsanleitung 4341.
Wichtig:
Es ist nicht zulässig, diese Röhrchen mit Pumpen anderer Hersteller zu kombinieren, da es dann zu erheblichen Anzeigefehlern kommen kann. Eine solche Kombination verstieße gegen bestehende Richtlinien.

2 Beschreibung

Vgl. Abbildung.
Öffnungszeit (Dauer eines Pumpenhubes bis zur vollen Spannung der Sperrkette): 15 bis 25 Sekunden.

DRÄGER Tube
Hydrogen Sulphide 1/c

OPERATING INSTRUCTIONS 234–19001e · 11th Edition · April 1985

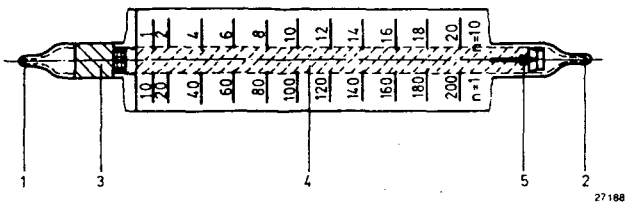
1 General and application

Determination of H_2S in air and in technical gases.
The tubes are to be used in conjunction with the DRÄGER Gas Detector Pump.
For use of the Gas Detector and the DRÄGER tubes, see Section 4 of these Operating Instructions and Instructions for Use 4341e
Important:
It is not permissible to combine the tubes with pumps made by other manufacturers, since this may cause considerable errors in indication. Such a combination would offend against relevant regulations.

2 Description

See illustration.
Opening time (duration of one pump stroke until the limit chain is completely taut): 15 to 25 seconds.

1 und 2 zugeschmolzene Spitzen
3 Schreibfläche
4 Anzeigeschicht (weiß) mit Skalen; Zahlenwerte = ppm H_2S
5 Pfeil (soll bei der Prüfung zur Pumpe weisen)



1 and 2 fused tips
3 writing surface
4 indicating layer (white) with calibrated scales. Numerical values = ppm H_2S
5 arrow (must point towards pump during measurement)

3 Meßbereich *(bei 20°C, 1013 mbar)*

Bei 1 Hub: 10 bis 200 ppm H_2S.
Bei 10 Hüben: 1 bis 20 ppm H_2S.

1 ppm H_2S = 1,42 mg/m³
1 mg H_2S/m³ = 0,71 ppm
} 20°C, 1013 mbar

4 Prüfung und Beurteilung des Ergebnisses

4.1 Pumpe vor jeder Meßreihe mit ungeöffnetem Röhrchen auf Dichtheit prüfen.
4.2 Spitzen des DRÄGER-Röhrchens abbrechen.
4.3 DRÄGER-Röhrchen dicht in den Pumpenkopf einsetzen. (Pfeil weist zur Pumpe.)
4.4 Prüfgas zunächst mit 1 Hub durch das DRÄGER-Röhrchen saugen. Liegt H_2S vor, so verfärbt sich die weiße Anzeigeschicht hellbraun. Länge der Verfärbung = Maß für die H_2S-Konzentration. *Auf der 1-Hub-Skala Konzentration in ppm ablesen.* Liegt der Wert über 20 ppm, so ist die Prüfung beendet. Werden weniger als 20 ppm abgelesen, so ist die Prüfung mit 9 weiteren (also insgesamt 10) Hüben fortzusetzen. H_2S-Konzentration in ppm jetzt auf der 10-Hub-Skala ablesen.

5 Bemerkungen

Nach negativem Prüfbefund kann das DRÄGER-Röhrchen H_2S 1/c *am selben Tag bis zu* zehnmal benutzt werden; nach positivem Befund nicht mehr verwendbar. Verfärbungen sind lange Zeit haltbar, wenn Spitzen mit Gummikappen verschlossen werden.

6 Einfluß der Umgebungsbedingungen auf das Meßergebnis

6.1 Temperatur
Die DRÄGER-Röhrchen können in einem Temperaturbereich von 0° bis 40°C verwendet werden.
6.2 Feuchtigkeit
Im Bereich von 3 bis 30 mg H_2O pro Liter hat die Feuchtigkeit keinen Einfluß auf die Anzeige.
6.3 Luftdruck
Zur Korrektur des Druckeinflusses ist die Anzeige mit dem folgenden Faktor zu multiplizieren:

$$\text{Korrekturfaktor} = \frac{1013}{\text{tatsächlicher Luftdruck (in mbar)}}$$

$$\text{Korrekturfaktor} = \frac{760}{\text{tatsächlicher Luftdruck (in Torr)}}$$

7 Spezifität (Querempfindlichkeit)

Anzeige beruht auf Farbreaktion mit Bleiverbindung; es entsteht hellbraunes Bleisulfid.
In Gegenwart größerer SO_2-Konzentrationen fällt die H_2S-Anzeige etwas zu hoch aus (z. B. Gemisch von 5 ppm H_2S und 40 ppm SO_2 ergibt Anzeige von etwa 8 ppm H_2S); SO_2 allein verfärbt die Anzeigeschicht nicht.
Andere Gase und Dämpfe beeinflussen die H_2S-Anzeige nicht.

8 Vorgesehene Verbrauchszeit

Verbrauchsdatum und Lagertemperatur vgl. Angaben auf der Banderole.

9 Toxische Daten

Maximale Arbeitsplatz-Konzentration (MAK): 10 ppm (Bundesrepublik Deutschland 1984).

10 Hinweis

Auf Wunsch des Benutzers liefern wir die folgenden Informationen:
a) Die für die Kalibrierung der Prüfröhrchen verwendete Methode.
b) Den Einfluß von Testbedingungen (einschließlich Reaktionsablauf) auf die Umsetzung und auf die Zuverlässigkeit der Anzeige, sofern uns diese Effekte bekannt sind.

11 Filteratemschutz

Falls Filteratemschutz erforderlich und zulässig, dann Filter mit dem Kennbuchstaben **B** verwenden.

Unsere **Tabelle 4340** enthält alphabetisch geordnet die mit DRÄGER-Röhrchen *meßbaren* **Gase und Dämpfe**, wichtige **physikalische und toxikologische Daten** der Gase und Dämpfe sowie Literaturhinweise
Bitte, fordern Sie diese Tabelle bei uns an.

Achtung!

Verbrauchte DRÄGER-Röhrchen nicht achtlos fortwerfen, damit sie nicht in Kinderhände gelangen!

Inhalt ätzt!

3 Range of Measurement (corresponding to 20°C, 1013 mbar)

With 1 stroke: 10 to 200 ppm H_2S
With 10 strokes: 1 to 20 ppm H_2S

1 ppm H_2S = 1.42 mg/m³
1 mg H_2S/m³ = 0.71 ppm
} *20°C, 1013 mbar*

4 Test and Evaluation of the Result

4.1 Before each series of measurements, test the pump for tightness using an unopened tube.
4.2 *Break-off the tips of the* DRÄGER tube.
4.3 Insert the DRÄGER tube tightly in the pump head (arrow points towards the pump).
4.4 First suck the air sample through the tube with 1 pump stroke. If H_2S is present, the white indicating layer turns pale brown. The length of the discoloration is a measure of the H_2S concentration. Read-off the concentration in ppm on the 1-stroke scale. If the value is above 20 ppm, the test is completed. If it is less than 20 ppm, the test should be continued with 9 further (a total of 10) strokes. Now read-off the H_2S concentration in ppm on the *10-stroke scale.*

5 Remarks

After a negative test result, the H_2S 1/c tube can be used up to ten times on the same day. *The* tube cannot be used again after a positive result. Discolorations can be kept for a long time i the tips are sealed with rubber caps.

6 Influence of Ambient Conditions on the Result of Measurement

6.1 Temperature
The DRÄGER tubes can be used in a temperature range of from 0° to 40°C.
6.2 Humidity
Between 3 and 30 mg H_2O per litre, humidity has no influence on the indication.
6.3 Atmospheric pressure
For pressure correction, multiply the tube reading by the following factor:

$$\text{Conversion factor} = \frac{1013}{\text{actual atmospheric pressure (in mbar)}}$$

$$\text{Conversion factor} = \frac{760}{\text{actual atmospheric pressure (in Torr)}}$$

7 Specificity (Cross-Sensitivity)

Indication is based on a colour reaction *with a lead compound – pale brown lead sulphide i* produced.
In the presence of fairly high SO_2 concentrations, the indication is somewhat too high (e. g. *mixture* of 5 ppm H_2S and 40 ppm SO_2 gives an indication of about 8 ppm H_2S); SO_2 alon does not change the colour of the indicating layer.
Other gases and vapours do not affect the H_2S indication.

8 Shelf Life

See expiration date and storage temperature on label of the box.

9 Toxicity Data

Threshold Limit Value: 10 ppm (U.S.A. 1984).

10 Information

At the request of the tube user, we will supply the following information:
a) The methods used for calibration of the detector tubes.
b) The effects (including reactions) on the operation and accuracy of the gas detector tub unit caused by specific environmental conditions described by the user, if the effects ar known to us.

11 Filter Protection

Should filter protection be necessary and acceptable, filters with the code letter B should b used.

Our table 4340e contains in alphabetical order the **gases and vapours** measurable wi DRÄGER tubes, important **physical and toxicological data** of the gases and vapours as w as many references to literature.
This table will be sent to you on request

Caution

Do not allow DRÄGER tubes to *fall into the hands of children.*

Contents are corrosive!

Bei Rückfragen bitte die außen auf die Packung aufgestempelte Chargennummer angeben.

In all inquiries please state the batch number stamped on the outside of the box.

6719001

Tube réactif DRAGER Hydrogène sulfuré 1/c

MODE D'EMPLOI 234–19001f · 11ième Edition · Avril 1985

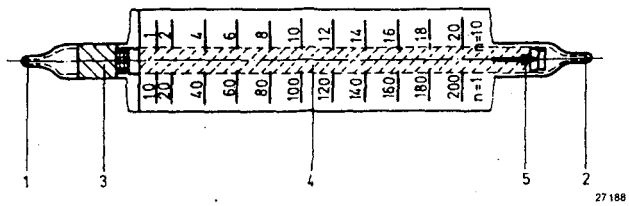
1 Généralités et domaine d'utilisation

Détermination de l'H_2S dans l'air et dans les gaz techniques.
Les tubes sont à utiliser avec la pompe détectrice de gaz DRÄGER.
En *ce qui concerne la manipulation* de l'appareil détecteur de gaz et des tubes réactifs DRÄGER, voir le paragraphe 4 ci-après et le mode d'emploi 4341f.
Important:
Il est strictement à déconseiller de les associer à une pompe qui serait de fabrication autre que Dräger; une combinaison de ce genre pourrait conduire à d'importantes erreurs d'indication, et serait de toutes façons contraire aux directives en vigueur.

2 Description

Voir figure.
Durée d'ouverture (durée d'un coup de pompe jusqu'à tension totale de la chaînette): 15 à 25 *secondes*

1 et 2 pointes scellées
3 plage pour notices
4 couche indicatrice (blanche) avec échelles; valeurs des chiffres = ppm H_2S
5 flèche (doit être dirigée vers la pompe lors de l'analyse)



3 *Domaine de mesure* (à 20°C, 1013 mbar)

Pour 1 coup de pompe: 10 à 200 ppm H_2S.
Pour 10 coups de pompe: 1 à 20 ppm H_2S.

1 ppm H_2S = 1,42 mg/m³
1 mg H_2S/m³ = 0,71 ppm
} 20° C, 1013 mbar

4 Analyse et évaluation du résultat

4.1 Avant chaque série de mesures, contrôler l'étanchéité de la pompe avec un tube réactif obturé.
4.2 Briser les pointes du tube réactif DRÄGER.
4.3 Insérer le tube réactif DRÄGER dans la tête de pompe (flèche vers la pompe).
4.4 Aspirer l'air à analyser à travers le tube réactif DRÄGER en effectuant 1 coup de pompe. En présence d'H_2S, la couche indicatrice blanche se colore en brun *clair*. La longueur de la coloration est la mesure de la concentration en H_2S. Lire la concentration en ppm sur l'échelle valable pour 1 coup de pompe. *Si la valeur lue est inférieure à 20 ppm*, continuer l'analyse en effectuant 9 coups de pompe supplémentaires (donc 10 au total). Lire ensuite la concentration de l'H_2S *en ppm sur* l'échelle valable pour 10 coups de pompe.

5 Remarques

Après résultat négatif, le tube réactif DRÄGER H_2S 1/c peut être réutilisé 10 fois au maximum le même jour; après résultat positif, il n'est plus utilisable. Les colorations *sont stables assez* longtemps à condition d'obturer les tubes réactifs à l'aide de bluchons en caoutchouc.

6 *Influence* des conditions ambiantes sur le résultat de mesure

6.1 Température
Les tubes réactifs DRÄGER peuvent être utilisés par températures comprises entre 0° et 40°C.
6.2 Humidité
Dans le domaine situé entre 3 et 30 mg d'H_2O par litre, l'humidité n'a *aucune influence* sur l'indication.
6.3 Pression atmosphérique
Pour la correction de l'influence de la pression atmosphérique, le résultat obtenu est à multiplier par le facteur suivant:

$$\text{Facteur de correction} = \frac{1013}{\text{Pression atmosphérique effective (en mbar)}}$$

$$\text{Facteur de correction} = \frac{760}{\text{Pression atmosphérique effective (en Torr)}}$$

7 Spécificité (sensibilité transversale)

L'indication repose sur la *réaction colorée avec une* combinaison de plomb; il se produit du sulfure de plomb brun clair.
En présence d'*importantes concentrations* de SO_2, les valeurs d'H_2S indiquées par le tube réactif sont légèrement trop élevées (par ex. d'un mélange de 5 ppm d'H_2S et de 40 ppm de SO_2 résulte une indication d'environ 8 ppm d'H_2S); le SO_2 seul ne colore pas la couche indicatrice.
D'autres gaz et vapeurs n'ont aucune influence sur l'indication d'H_2S.

8 Durée d'*utilisation prévue*

La date limite et la température de stockage sont imprimées sur la banderole de la boîte.

9 Données toxicologiques

Concentration maximum autorisée sur les lieux de travail (MAC): 10 ppm (R.F.A. 1984).

10 Information

Sur demande nous tenons à *la disposition des clients les communications* suivantes:
a) méthode utilisée pour le calibrage des tubes réactifs.
b) l'influence des *conditions de test (y compris* le cours de la réaction) sur la conversion et la fiabilité de l'indication, pour autant que ces effets nous soient connus.

11 Protection respiratoire par cartouches filtrantes

Au cas où une protection respiratoire par cartouche filtrante *est nécessaire et permise*, ce sont les cartouches filtrantes portant la lettre caractéristique B qui sont à utiliser.

Notre ***tableau 4340f*** *contient* par ordre alphabétique les **gaz et vapeurs** pouvant être déterminés à l'aide des tubes réactifs DRÄGER, des données importantes **physiques et *toxicologiques*** *ainsi* que beaucoup de renvois à la littérature.
Ces tableaux vous parviendront sur demande.

Attention:

Tubito de control DRÄGER Sulfuro de hidrógeno 1/c

INSTRUCCIONES DE USO 234–19001s · 11a Edición · Abril 1985

1 Generalidades y campo de *aplicación*

Determinación del H_2S en el aire y los gases industriales.
Los tubitos de control se usarán *conjuntamente con la* bomba detectora de gases DRÄGER.
Por lo que atañe a la manipulación del detector de gases y de los tubitos de control DRÄGER *ver el punto 4 de estas instrucciones* y las *instrucciones* de uso 4341s.
Importante:
No está autorizada la combinación de estos tubitos con bombas de otros fabricantes, ya que ello conduciría a errores de indicación considerables. Una combinación tal infringe las *normas existentes*.

2 Descripción

Ver ilustración
Tiempo de apertura (duración de una carrera de la bomba hasta la tensión total de la cadenilla de seguridad): 15 hasta 25 segundos.

1 y 2 puntas fundidas
3 superficie para anotaciones
4 capa indicadora (blanca) *con* escalas; valores numéricos = ppm de H_2S
5 *flecha (debe señalar en* el análisis hacia la bomba)

3 Campo de medición (a 20°C, 1013 mbar

Con 1 carrera: *10 hasta 200 ppm de* H_2S
Con 10 carreras: 1 hasta 20 ppm de H_2S

1 ppm de H_2S = 1,42 mg/m³
1 mg H_2S/m³ = 0,71 ppm
} 20°C, 1013 mbar

4 Análisis y evaluación del resultado

4.1 Antes de iniciar una serie de medidas verifique la estanqueidad con un tubito de control sin abrir.
4.2 Rompa las puntas del tubito de control DRÄGER.
4.3 Inserte firmemente el tubito de control DRÄGER en la cabeza de la bomba (la flecha señalando hacia la bomba).
4.4 Se aspira primero el gas a analizar a través del tubito de control DRÄGER con una carrera de la bomba. Si existe H_2S se colorea de pardo *claro la capa indicadora blanca*. Longitud de la coloración = medida de la concentración de H_2S. Sobre la escala de 1 carrera se lee la concentración en ppm. Si el valor es superior a 20 ppm, el análisis ha terminado. Si se leen menos de 20 ppm se proseguirá el análisis con 9 carreras más (en total 10 carreras), y la *concentración de* H_2S *se leerá ahora* en ppm en la escala de 10 carreras.

5 Observaciones

Después de un resultado negativo puede volver a utilizarse de nuevo el tubito de control DRÄGER Sulfuro de hidrógeno 1/c hasta 10 *veces en el mismo día; no* pudiendo emplearse, si el resultado es positivo. Las coloraciones se mantienen largo tiempo, cuando se cierran las puntas con caperuzas de goma.

6 Influencias de las condiciones del ambiente

6.1 Temperatura
Los tubitos de control DRÄGER pueden utilizarse dentro *de un campo de temperaturas* de 0° hasta 40°C.
6.2 Humedad
Dentro de un límite de 3 hasta 30 mg de H_2O por litro carece la humedad de influencia alguna sobre la *indicación*.
6.3 Presión del aire
Para corregir la influencia de la presión se multiplica la indicación por el siguiente factor:

$$\text{Factor de corrección} = \frac{1013}{\text{presión del aire real (en mbar)}}$$

$$\text{Factor de corrección} = \frac{760}{\text{presión del aire real (en Torr)}}$$

7 Especificidad (Sensibilidad transversal)

La indicación se basa en la reacción cromática con un compuesto plúmbico, *originándose* sulfuro de plomo de color pardo claro.
En presencia de altas concentraciones de SO_2 resulta ser un tanto elevada la *indicación* (*p.* ej., una mezcla de 5 ppm de H_2S y 40 ppm de SO_2 da una indicación de 8 ppm de H_2S aproximadamente). El SO_2 solo no colorea la capa *indicadora*.
Otros gases y vapores no influyen sobre la indicación del H_2S.

8 Tiempo de utilización previsto

Ver fecha de expiración y temperaturas de almacenaje en la banderola del estuche.

9 Datos toxicológicos

Concentración máxima *admisible en el lugar* de trabajo (MAK): 10 ppm (RFA 1984).

10 Nota

A solicitud del usuario suministramos las siguientes informaciones:
a) Método empleado en la calibración de los tubitos de control.
b) Influencia de las condiciones de ensayo sobre la reacción y su curso, así como sobre la exactitud de la indicación, en tanto nos sean *conocidos estos efectos*.

11 Protección respiratoria mediante filtro

De ser necesaria y estar autorizada la protección respiratoria mediante filtro, se usarán entonces los marcados con la letra distintiva B.

Nuestra **Tabla 4340s** contiene por orden alfabético los **gases y vapores** medibles con los tubitos de control DRÄGER, y **datos físicos y toxicológicos** importantes de los gases y vapores, así como referencias bibliográficas.
Esta tabla le será suministrada previa solicitud.

Cuidado!

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