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**EQUIPMENT AND PROCEDURES FOR THE
COLLECTION AND DETERMINATION OF
DISSOLVED GASES IN NATURAL WATERS**

W. DYCK
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EQUIPMENT AND PROCEDURES FOR THE COLLECTION AND DETERMINATION
OF DISSOLVED GASES IN NATURAL WATERS

Abstract

Using a 180° radius mass spectrometer with a 4500 gauss magnet and an inlet system that permits partial separation of gas constituents by trapping less volatile components, the following components were determined quantitatively in gases dissolved in natural waters: H₂, He, CH₄, Ne, N₂, O₂, H₂S, Ar, and CO₂. The total amount of dissolved gas was also determined in a calibrated inlet system using an absolute pressure gauge. The set-up permits the analysis of 8 unknown and one standard sample in a normal working day with a practical detection limit of 0.5 ppm He, 5 ppm Ne and H₂S, and about 200 ppm for the remaining gases based on total amount of dissolved gas. The average precision for all the components is ±16 per cent based on one standard deviation but varies between components depending on concentration levels and interferences. Although the mass spectrometer is capable of much greater precision, sampling errors and changes in composition during storage for some components did not warrant greater precision. The He loss from water stored in 300-cc glass bottles capped with plastic-lined metal caps for one month was about 10 per cent. H₂ and CH₄ were found to be most prone to change during storage due to bacterial action. The presence of up to 1 per cent O₂, even in samples from strongly reducing environments, suggests that it is introduced into the sample during handling in atmospheric air.

A stainless steel water sampler and a portable winch with a depth counter permitted the sampling of drillholes at any depth.

Résumé

Au moyen d'un spectromètre de masse à rayon de 180° équipé d'un aimant de 4500 gauss et d'un système d'introduction qui permet d'effectuer une séparation partielle des constituants gazeux en captant les gaz les moins volatils, on a déterminé les quantités des gaz suivants dissous dans des eaux naturelles: H₂, He, CH₄, Ne, N₂, O₂, H₂S, Ar et CO₂. On a également déterminé la quantité globale de gaz dissous dans un système d'introduction étalonné au moyen d'un manomètre indicateur de pression absolue. Cette assemblage permet d'analyser huit échantillons inconnus et un échantillon standardisé au cours d'une journée normale de travail et les limites pratiques de la détection sont de 0,5 ppm pour l'He, 5 ppm pour le Ne et le H₂S, et environ 200 ppm pour les autres gaz en se basant sur la quantité totale de gaz dissous. La précision moyenne pour toutes les substances composantes est de ±16 pour cent pour un écart-type, mais elle varie d'une substance composante à l'autre selon les niveaux de concentration et les interférences. Même si le spectromètre de masse permet une précision beaucoup plus grande, les erreurs d'échantillonnage et les changements de composition qui se produisent pendant l'entreposage dans le cas de certaines substances n'ont pas permis une précision plus grande. La perte d'He de l'eau gardée pendant un mois dans des bouteilles de verre de 300cc fermées avec des capsules de métal recouvertes de plastique a été d'environ 10 pour cent. On a constaté que le H₂ et le CH₄ étaient les substances les plus susceptibles de subir des changements pendant l'entreposage à cause des bactéries. La présence d'O₂, dont la teneur peut atteindre jusqu'à 1 pour cent même dans les échantillons prélevés dans des milieux fortement réducteurs laisse supposer que ce gaz s'infiltré dans l'échantillon au cours de sa manipulation dans l'air.

Une échantillonneuse d'eau d'acier inoxydable et un treuil portatif muni d'un compteur de profondeur ont permis de prélever des échantillons dans des trous de forage à n'importe quelle profondeur.

EQUIPMENT AND PROCEDURES FOR THE COLLECTION AND DETERMINATION
OF DISSOLVED GASES IN NATURAL WATERS

INTRODUCTION

In order to determine the usefulness of dissolved gases in ground waters for mineral exploration it was necessary to set up facilities which would permit the determination of the major and trace components of gases dissolved in ground waters. Since He was one of the desired trace elements because of its association with U, the use of a mass spectrometer became necessary, even though a number of the gases could be determined individually by other less expensive means. For oxygen and sulphide ions selective membrane electrodes have been developed and are available commercially. Carbon dioxide can be determined with a flue gas analyzer. There are also a number of chromatographic columns and techniques on the market which permit quantitative determinations of gas components of simple mixtures.

During the process of setting up the analytical facilities and working out procedures it became apparent that there was really no equipment on the market that permitted the sampling of drillholes at predetermined depth or to store samples of water without losing the dissolved gas in them. Apparatus and methods for analysis as well as for sampling were therefore worked out simultaneously.

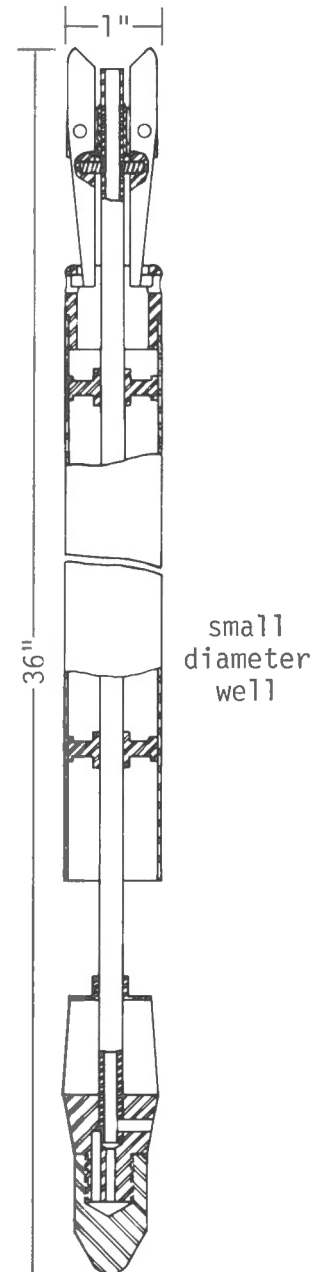
This report is a detailed account of equipment and procedures for the collection and determination of gases dissolved in natural waters.

SAMPLE COLLECTION AND STORAGE

Near-surface waters are easily scooped up and bottled. Water samples from depth can be collected using one of a number of commercially available samplers. However, none of these were small enough to fit inside small diamond-drill holes. The instrument shop of the Geological Survey of Canada therefore undertook to construct a sampler and a portable winch which would take water samples from any desired depth. These two pieces of hardware are illustrated in Figures 1 and 2 and Figure 3 is a photograph illustrating the items assembled for use.

The water sampler used holds approximately 350 cc. It is made of stainless steel hence water samples can also be analyzed for ionic species without running the risk of contamination. The action of the sampler is as follows: a 1/16-inch wire cable is passed through the centre tube of the sampler and fastened at the bottom. By engaging the spring-loaded jaws in smooth holes at the top, the bottom and top are open and permit free flow of water through the tube during lowering of the sampler. When the desired depth has been reached a messenger or tripping weight is sent down on the cable which spreads the jaws releasing the tube so that it can drop onto the rubber stopper at the bottom of the sampler. Although the top of the sampler remains open to

the water in the hole at all times, very little mixing takes place during the upward movement of the sampler. This has been demonstrated many times during the sampling of drillholes with large amounts of H₂ near the



Final assembly of
Water Sampler.

Figure 1. Mechanical drawings of the small diameter drillhole water sampler.

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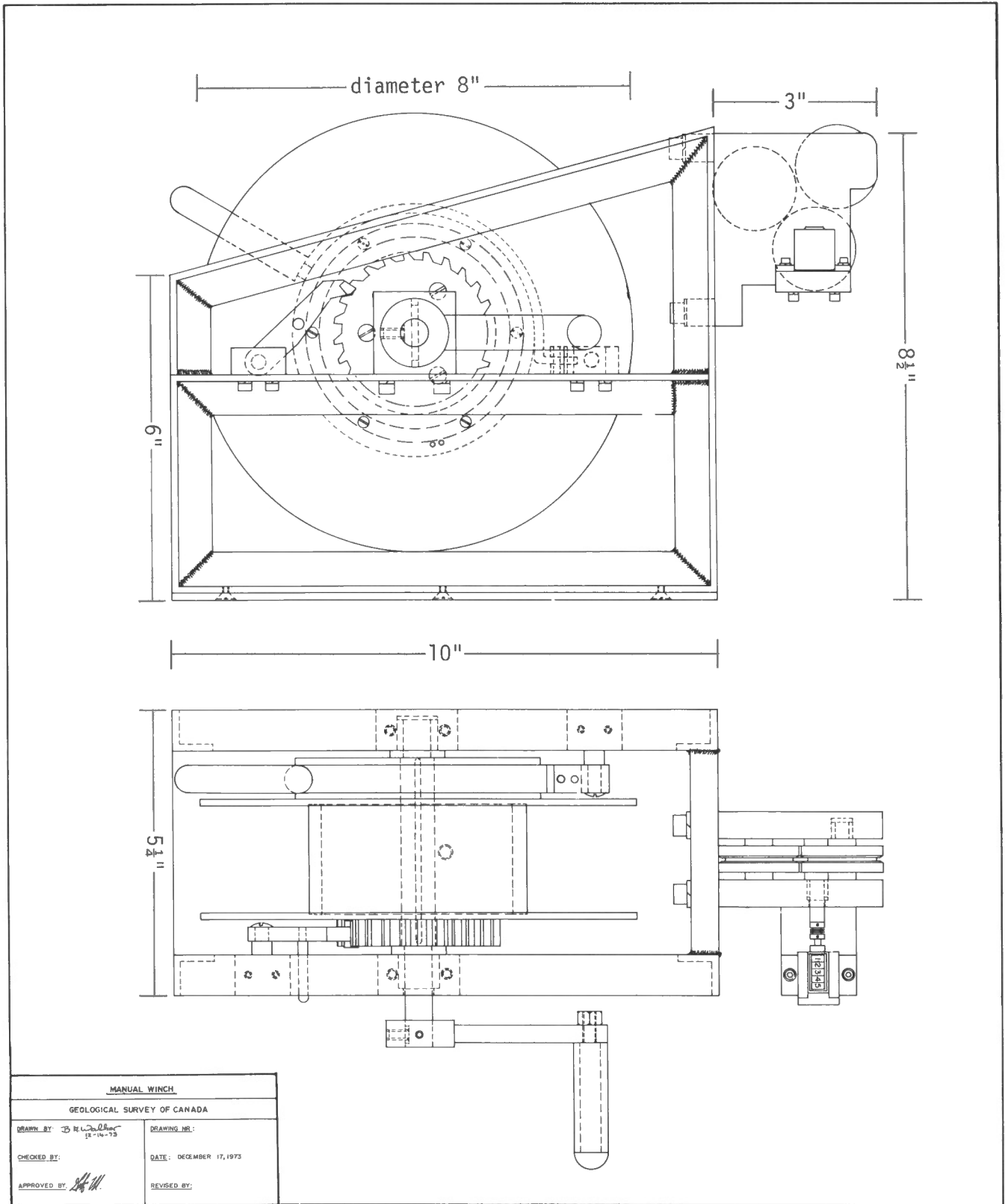


Figure 2. Mechanical drawings of portable winch with depth counter.



Figure 3. Small diameter drill hole water sampler and winch assembly.

top; samples from below this H₂-rich layer contained no H₂. Also, once the sampler emerges from the water in the hole the top inch spills, removing possibly mixed sample. With a well made tripping mechanism and tripping weight, holes with a slope of up to 45° can be sampled successfully with this equipment.

The mechanical drawings for the winch are shown in Figure 2. The frame is of aluminum and the shafts of brass. The sprocket, brake disc, and V-shaped cable guide pulleys are of bakelite. The V-shaped counter pulley is made of lucite and measures one decimetre per turn. For drillhole sampling the winch is fastened to a tripod. For lake sampling it is clamped to the seat of the boat. The three rather closely spaced pulleys are necessary to prevent slippage of the cable and hence erroneous depth readings.

The ease with which gases escape from water once removed from its natural equilibrium environment became apparent in 1967 during tests with Rn in natural waters (Dyck, 1969). To keep the loss of gas from a water sample as low as possible during storage, i. e., the time between collection and analysis, it was found that completely filled glass bottles closed with a plastic-lined screw cap would retain Rn satisfactorily but not He. For He a better seal was required. This was found in the caps used by home-brewers for bottling beer. Although beer bottles are satisfactory, 10 oz. (310 ml)

soft drink bottles, being more slender, were found to be stronger when completely filled with water and subjected to large temperature changes. The rate of loss of total dissolved gas, He, H₂, and CH₄ from such bottles with different initial concentrations are shown in Figure 4. The samples were prepared by bubbling He and manufactured gas (a mixture of H₂, CH₄, and CO) simultaneously through tap water, filling a number of bottles with the water and capping them. The results of these tests together with He loss from 260-ml wide-mouth (30 mm) screw-cap glass bottles is also shown in Figure 4. The most striking feature of Figure 4 is the nearly complete disappearance of H₂ from the water samples even though the dissolved gas in one set of samples contained over 11 per cent H₂ initially. This, as well as the disappearance of CH₄ from one set of samples, can only be explained in terms of bacterial action. After an apparent incubation period of 7 to 10 days, rapid depletion of H₂ and CH₄ took place. Loss of most of this gas through the wall of the bottles can be ruled out because the He loss is, at most, 20 per cent and averages out at about 10 per cent at the end of the one-month test period. However, the small but evident drop in the total amount of dissolved gas can be attributed to the loss of H₂ and CH₄. The conclusion to be drawn from this test is rather obvious: if accurate H₂ and CH₄ determinations are required the samples have to be analyzed immediately or measures taken to preserve the initial gas composition. Cooling the samples to 2° or 3°C slows down bacterial action without affecting the ionic or gaseous composition in any way and hence appears to be the best solution of the problem if analyses can be carried out within a week or ten days.

For two reasons, bottle fullness is also of utmost importance in preserving the initial gas composition of a water sample. One rather obvious reason is the dilution or change caused by atmospheric air if it is bottled with the water. Our studies show that most waters contain between 20 and 50 std. cc of air/litre of water. Hence a few cc of air in the neck of a 300-cc bottle can cause severe distortion of the composition of the dissolved gas. A second, less obvious reason is the increased loss of gas through the cap of a bottle if there is an air space between the water and the cap. Note the reduced loss of He (Fig. 4) from the screw-cap bottles stored upside down, even though the initial He concentration in this set was much higher than in the set of bottles stored right side up (4.2% vs 0.7%).

SAMPLE ANALYSIS

The analytical facility consists of a sample inlet system and a mass spectrometer. The inlet system, presented schematically in Figure 5, was manufactured by Vacumetrics and modified for the needs of this work. Except for the cold traps, it is an all stainless steel system with Nupro bellows valves and Swagelok fittings. The cold traps are made of borosilicate type glass. The legend of Figure 5 explains briefly the functions of the various components of the inlet system. The particular combination of components was arrived at after

many tests made to determine the best possible combination of the number of gas components, detection limits, precision, and sample throughput. The system is evacuated to 10^{-6} mm Hg by a combination of liquid nitrogen trap, Hg diffusion pump, and rotary fore-pump.

The mass spectrometer is a standard model MS-20 manufactured by A. E. I. Scientific Apparatus Ltd. It is equipped with a 4500 Gauss permanent magnet, a variable 2KV accelerating voltage, and a small (20.7 mm) and a large (50.8 mm) radius collector. It gives satisfactory resolution of unit masses between mass 2 and 100 even with large differences in concentration of elements. The analyzer is evacuated to a pressure of 10^{-8} or 10^{-9} mm Hg using a liquid nitrogen trap, oil diffusion pump and rotary pump. It should be noted that an ion-vac pump was connected to the analyzer but was found to give large He back-pressures and therefore is used on weekends only to keep the system at low pressures and free from contamination.

When the inlet system and the analyzer are evacuated to 10^{-6} and 10^{-8} mm Hg, respectively, and cold traps 4 and 5 (Fig. 5) cooled down with a dry ice- $\text{CCl}_4\text{-CHCl}_3$ mixture, a 50-ml water sample is introduced into flask 2 through septum 1 using a hypodermic needle attached to a thin plastic tube from which all air has been expelled by drawing part of the sample through it before poking the needle through septum 1. When 50 ml of sample are drawn into the evacuated inlet system the needle is withdrawn from the septum. After 3 minutes of vigorous boiling aided by magnetic stirrer 3, the sample is thoroughly degassed and begins to freeze. After another 2 minutes no pressure change is observed on the absolute pressure gauge 8. With a volume of 1 litre, the total pressure in the inlet system, excluding trap 11, is between 1 and 3 mm Hg for most 50-ml samples. That this degassing procedure is nearly

linear in removing dissolved air from water is indicated by the degassing test results listed below:

ml of water degassed	10.0	20.0	40.0	80.0
standard cc of air recovered	0.28	0.53	1.06	2.03

That the degassing procedure is virtually 100 per cent efficient is evident from two tests in which 10.0 cc of water in equilibrium with air were degassed in the usual manner and then completely evaporated and recondensed in the dry ice traps.

	Pressure in inlet system, mm Hg	
	5' test	evaporation
Test 1	0.200	0.207
Test 2	0.204	0.198

Also, the International Critical Tables, Vol. 3, p. 258, give a volume of 18.0 std. cc of CO_2 free air per 1 of water at 22°C as the solubility of air. The results of this study show that Ottawa tap water in equilibrium with atmospheric air contains 19.4 std. cc of CO_2 free air (see Table 4). Allowing for errors this 8 per cent excess in Ottawa tap water lends support to the 100 per cent degassing efficiency claim. As the gas evolves from the water it expands into the whole of the inlet system, except charcoal trap 11. Water and other easily condensed volatiles such as SO_2 are trapped by traps 4 and 5. The total pressure of the liberated dissolved gas is indicated by the Baratron absolute pressure gauge 8, which operates on the principle of changes in capacitance between a fixed and a flexible diaphragm. The gauge is capable of reading pressure in the range of 0.002 to 100 mm Hg with an accuracy of

Table 1
Outline of analytical steps and gas components analyzed

Phase	Procedural step	Sample fraction analyzed	Components sought	Mass read	Interference
I	Admission, degassing, and drying of sample	-whole	H_2	2	H_2 (from CH_4 + water)
			CH_4	15	^{15}N
II	Condensation of sample in liquid N_2 (trap 10) and activated charcoal (trap 11)	-noncondensable	He Ne	4 20	^{40}Ar (doubly charged)
III	Evaporation of liquid N_2 condensable fraction (trap 10)	condensable in liquid N_2	H_2S	34	
			CO_2	44	
IV	Evaporation of fraction condensable in activated charcoal (trap 11)	condensable in activated charcoal at liquid N_2 temperature	N_2	28	CO , C_2H_4
			O_2	32	
			Ar	40	

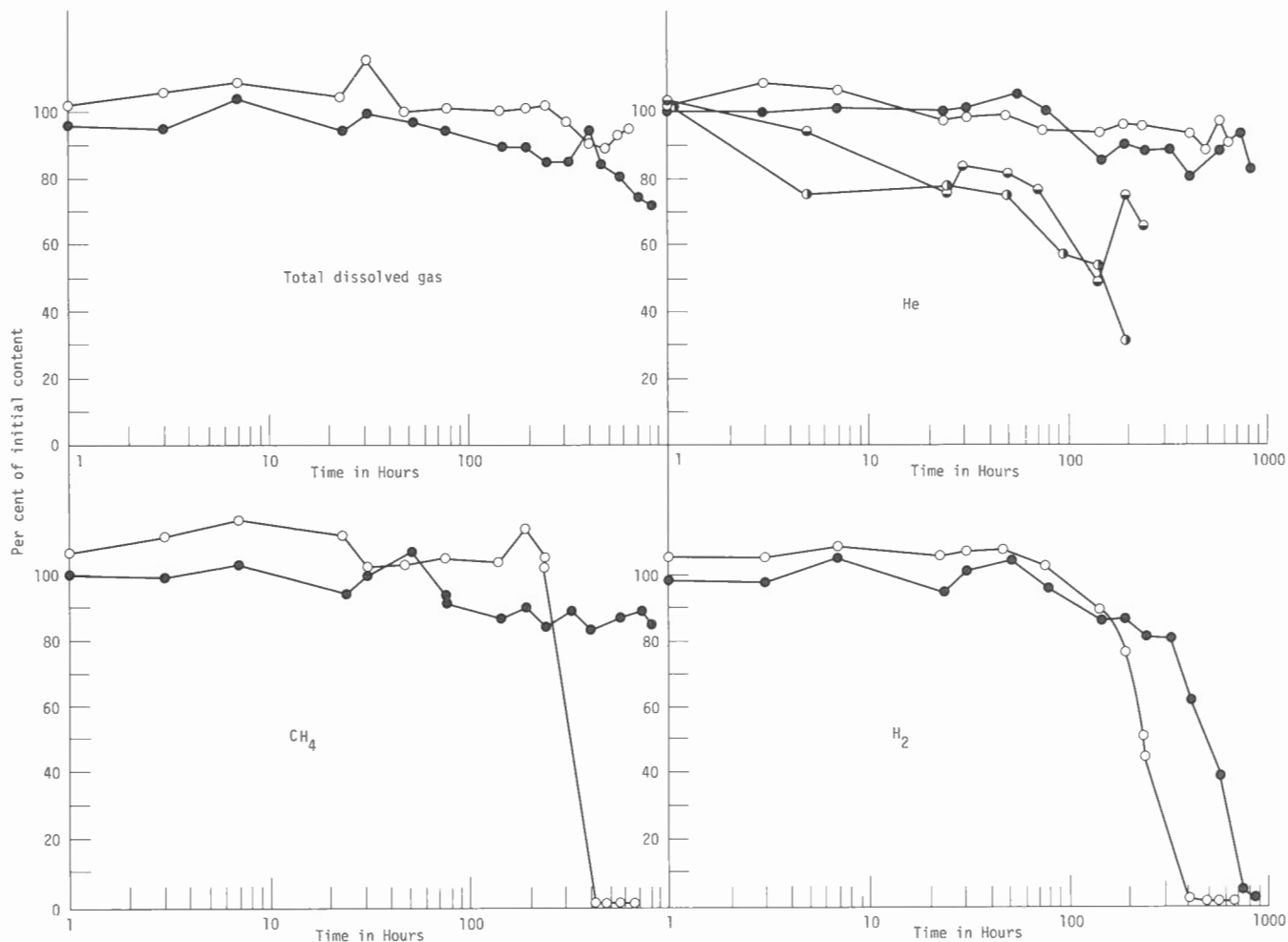


Figure 4. Loss of total dissolved gas, He, H₂, and CH₄ from tap water stored in two types of completely filled glass bottles.

better than ± 1 per cent at pressures above 0.1 mm. Filter 6 was introduced into the line to prevent particulate matter from soil gas samples from entering the inlet system and obstructing the leak to the mass spectrometer.

The actual mass analysis is carried out in four phases by admitting various sample fractions to the analyzer through leak 9. The leak, although variable, was set during calibration tests at about 10^{-4} cc/sec. and left at this setting for all analyses. Although lower leak rates would give better results with some components, they were not available on the particular inlet system purchased for this work.

The four phases or procedural steps are summarized in Table 1. This particular overall procedure was arrived at after many and varied tests to optimize the overall efficiency and accuracy of analysis. Because of the poor detection of He in air by the mass spectrometer, the interference of CO from CO₂ in the N₂ mass peak, and the interference of N₂O in the CO₂ mass peak, it was decided to separate the dissolved gas sample into three simpler fractions thereby removing interferences and hence permitting more accurate analyses. Also, to detect fractions of ppm of He it was necessary

to condense the bulk of the sample and operate the mass spectrometer in the static mode. Because H₂ and CH₄ condense only partially in activated charcoal at liquid nitrogen temperature these two compounds were read on the mass spectrometer before separating the sample into fractions. For CH₄ the mass 15 peak was chosen because O, usually present, interferes with the mass 16 peak of CH₄. By cooling the activated charcoal in trap 11 and the glass beads in trap 10, down to liquid nitrogen temperature and opening the stopcock to trap 11, the bulk of the sample condenses leaving only the noble gases He, Ne, and traces of Ar and small amounts of H₂ and CH₄ in the gas phase. CO₂ and H₂S are condensed in trap 10, O₂, N₂, Ar, H₂, CH₄ in trap 11. After this the valve between analyzer and pumps is closed and the noncondensable sample fraction admitted to the analyzer for 2.0 minutes. In this way fractions of ppm of He and Ne can be detected easily. However, because there is always a trace of Ar in this noncondensable fraction, the doubly charged ⁴⁰Ar signal causes an error in the singly charged ²⁰Ne signal. After the He and Ne are read and pumped away, the H₂S and CO₂ are evaporated and measured in the

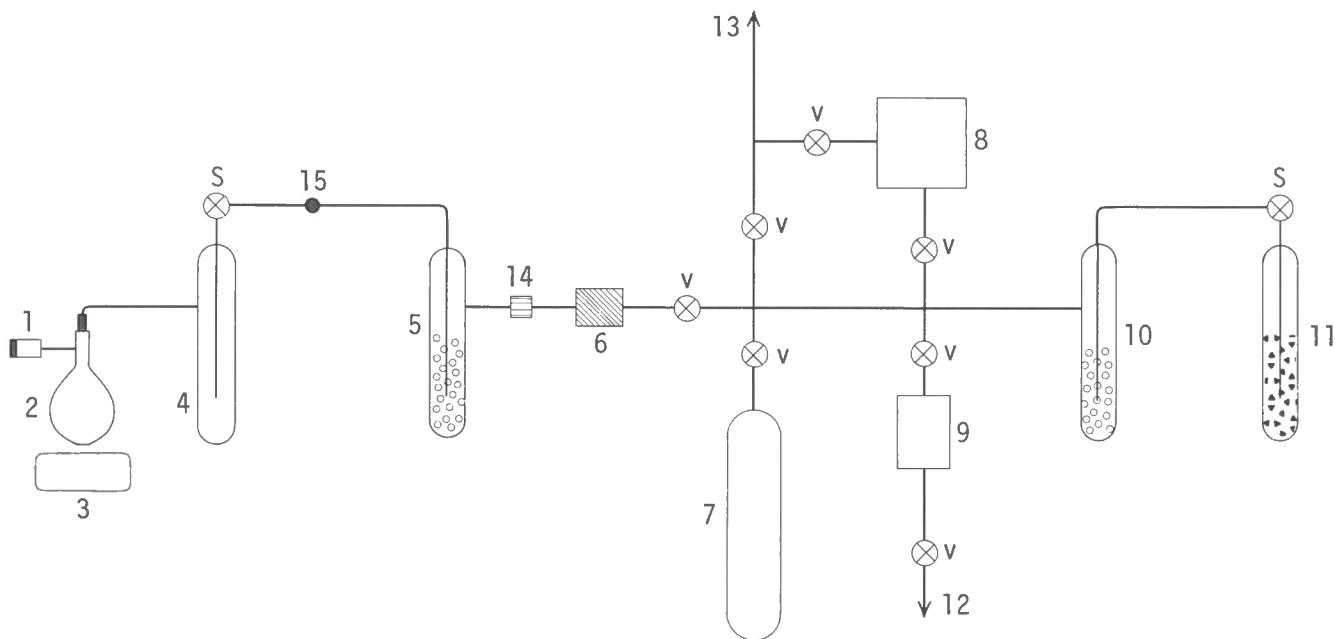


Figure 5. Inlet system for gas analyses.

dynamic mode. Similarly N_2 , O_2 , and Ar are measured dynamically after they are released from the charcoal by warming up the traps with hot water. It should be noted that several compounds, e. g., C_2H_6 and Cl_2 , could also be measured with minor modifications in the procedure but were omitted from the list of compounds because several hundred such measurements gave negative results. SO_2 , also of interest in mineral exploration because it is released from sulphide deposits under oxidizing conditions, could not be detected in this setup. Its great affinity for water and relatively high freezing point and low concentrations in natural waters (ppb levels) make it a difficult compound to detect.

All current signals generated by the various components of a sample in the analyzer of the mass spectrometer are amplified by vibrating reed electrometers and recorded on a chart recorder. Net currents are obtained by subtracting background currents obtained by simulating a run without an actual sample in the system.

CALIBRATIONS AND CALCULATIONS

For quantitative work the system is calibrated using atmospheric air, pure gases, and mixtures of pure gases with known composition. Aging, small shifts in position, and failure of filaments are the main reasons for calibration at intervals of 6 to 8 weeks. Standard samples for calibration are treated in the same manner as unknowns in order to eliminate internal errors such as changes in effective volume of traps due to cooling, reading of dials, small leaks in the system, etc. Typical calibration curves obtained in November, 1973 are shown in Figure 6. In this figure analyzer currents

are expressed in mpA (millipicoamperes; $1 \text{ mpA} = 10^{-15} \text{ A}$). It can be rather time consuming to calibrate the mass spectrometer for all 9 components over the wide range of concentrations encountered in natural samples. For example; the concentration of He in the dissolved gas in natural surface waters is 2 ppm. Some ground waters, on the other hand, contain several per cent He in the dissolved gas. Similarly, atmospheric air contains 320 ppm CO_2 whereas the dissolved gas in some ground waters is virtually pure CO_2 . Although the mass spectrometer exhibits excellent linearity over a concentration range of about 10^3 , extrapolation over a concentration range of 10^5 can result in large errors. To keep these errors to a minimum, sample pressure is lowered for major components so that current readings are within the calibrated range of the analyzer. For He and Ne both static and dynamic calibration runs are shown in Figure 5. The pressures for He (static) and Ne (static), N_2 , O_2 , and Ar were calculated from the total pressure of dry atmospheric air as measured by the Baratron pressure gauge and the composition of air given in the Handbook of Chemistry and Physics. The other curves were obtained by admitting pure gases in turn to the inlet system, measuring their pressure with the Baratron pressure gauge, and measuring the analyzer current in the dynamic mode. For accurate work at ppm levels gas mixtures of pure gases and air are used for calibration. The two curves for H_2S were included to show shifts that may occur over a large concentration range. The CH_4 also exhibits some nonlinearity when extended into higher pressure. Because these shifts appear around 10^5 mpA two sets of curves are used for calculation of unknowns — one set for concentrations below 10^5 mpA and one for concentrations above. This shift appears to be related to

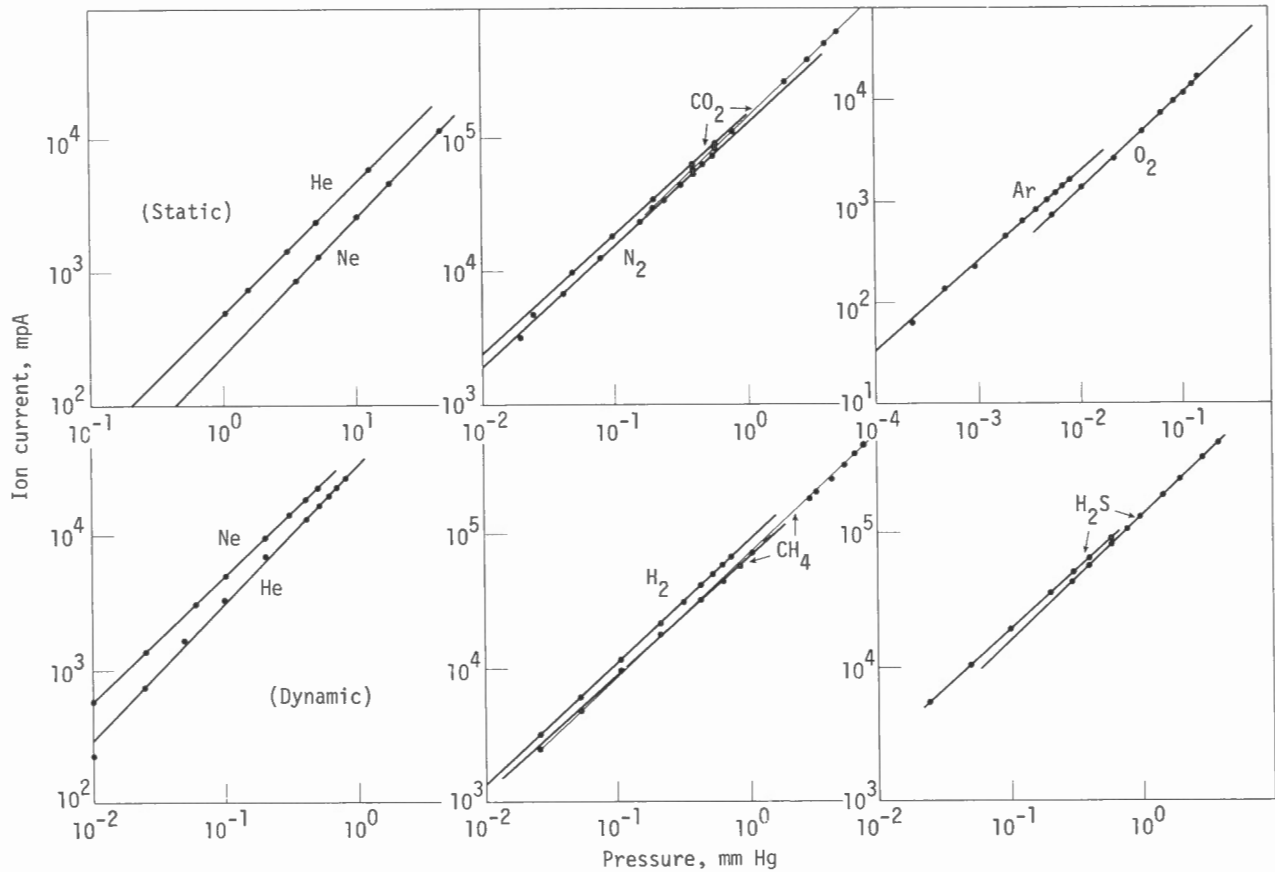


Figure 6. Typical calibration curves.

Table 2

Performance parameters of the analytical facility.

Component	Background, mpA		Sensitivity, mpA/mm Hg P x 10 ³ at 10 ⁴ mpA	Detection Limit Pressure		Precision %**
	Drift	± Mean		mm Hg x 10 ⁵	ppm* 10 ⁵	
H ₂	10	130	114	10	100	40
He	2	0	33	3	30	-
He(st)	2	0	45 100	0.002	0.02	15
CH ₄	2	0	91	1	10	30
Ne	2	0	50	2	20	-
Ne(st)	2	0	25 600	0.004	0.04	50
N ₂	5	75	164	3	30	18
O ₂	2	8	115	2	20	32
H ₂ S	2	0	116	1	10	30
Ar	2	8	167	1	10	26
CO ₂	30	60	200	15	150	56

* Calculated for a 1.0 mm Hg P sample (1.2 standard cc), the average gas content of a 50-ml water sample.

** Average values from Table 4 modified for H₂ and CH₄ by including duplicate analyses of 4 standard gas samples. For H₂S estimated value only.

st =static all others are dynamic.

Table 3

Variables and their values responsible for the sensitivity and detection limit of the gas analysis system

Variable	Value
Sample size (Inlet system pressure)	50ml H ₂ O (1mm Hg)
Sample leak rate into analyzer	10 ⁻⁴ std. cc/sec
Analyzer pump pumping speed	10 l/sec
Electron current	100μ A
Electron energy	70 eV
Ion repeller voltage	+8 V
Slit width	10μ
Sample enrichment	
Mode of operation; static vs dynamic	
Electrometer stability and sensitivity	
Interferences, e. g., ⁴⁰ Ar ⁺⁺ in ²⁰ Ne ⁺	

nonlinearity in the electronics associated with the mass spectrometer. The main instrument performance parameters for each gas component are listed in Table 2. He and Ne data are in both the dynamic and the static mode of operation of the mass spectrometer. For the other components only the dynamic parameters are listed. High background levels in some mass positions are due mainly to cracked hydrocarbons from the diffusion pump. A little H₂ and O₂ is also present as a result of residual H₂O in the system. The minimum drift of 2 mpA is due to noise in the electronics. The sensitivity is calculated from the curves shown in Figure 6. It is fairly constant over the useful pressure range, increasing slightly with a decrease in pressure. By pressure is meant the pressure in the inlet system. The sensitivity and detection limit are a function of a number of variables. These are listed in Table 3 for reference. The various values listed in Table 3 were selected after many tests for the best possible combination for all components, even though for any one component other settings would be more effective. The ion repeller voltage was chosen so as to favour the detection of He. The detection limits in mm Hg are calculated from the background drift and the sensitivity as given in Table 2 and in ppm by assuming a sample pressure of 1.0 mm Hg. This value is close to the average sample pressure obtained from a 50-ml water sample in the 1000 cc inlet system. In actual practice the detection limit will vary from day to day depending on such factors as variations in room temperature and pumping rates of pumps and other factors which affect drift or electronic stability and analyzer pressure. Also interferences such as H₂ from CH₄ reduce the effective detection limit when present in samples. For example: A sample containing 1 per cent CH₄ would also appear to contain between 150 and 200 ppm H₂ if no allowance

were made for the cracking of CH₄. For a more detailed discussion on interferences the reader is referred to the section on errors. Similarly, the precision quoted in Table 2 is amplified in more detail in the section on errors.

The calibration data for each component are used to calculate the intercept and slope by the least squares method of log transformed data. The calculation of the composition of soil gas samples or gases dissolved in waters is performed by the computer using the measured ion currents of the unknown samples and the slopes and intercept obtained from the calibration curves. The program for these computations was written in Fortran 4 by D. J. Hobbs (Geochemistry Section, Geological Survey of Canada) and is given in the Appendix. This program also includes calculations of Rn but the Rn determinations are carried out on a separate sample fraction using an alpha scintillometer technique described elsewhere by Dyck (1969).

ERRORS

The error inherent in an analytical value can be broken down into two types – analytical and sampling error. The analytical error includes such factors as instrumental and procedural variations; e. g., faulty or noisy electronics, errors in reading meters and gauges and recording of data, calculation errors, etc. In a complex procedure such as the one described in this report, involving a number of steps and several electronic reading devices, it becomes time consuming to determine the errors involved in each step and in each instrument. No attempt has therefore been made to identify and evaluate each error in each step of the procedure and/or instrument. But rather, only the main sources of error are identified qualitatively and an overall sampling and analytical error quoted as determined by replicate or multiple analyses of several types of samples. The types of samples and the error associated with the analyses of these samples are listed in Table 4. The atmospheric air samples were collected out of the window on the 7th floor of the Geological Survey of Canada building in Ottawa over a period of six months during 1973. In a similar way tap water samples came from the Ottawa Municipal water supply, except that only one large sample (40 l) was collected at one time, stored in the laboratory until equilibrated with the air in the laboratory, and analyzed routinely with other samples during 1973. The Carlsbad Springs spring-water samples were collected all at once from one spring and analyzed the same day.

The per cent precision is calculated from the expression:

$$\text{Precision} = \frac{2 (\text{standard deviation})}{\text{mean}} \times 100$$

The larger the % precision the poorer the reproducibility of the data. Although some spread in the data in Table 4 is due to sampling error, it is clear that for low values of O₂ and for Ne and CO₂ generally, the analytical error dominates. For Ne it is easy to see and test the effect doubly charged ⁴⁰Ar has on the

Table 4

Arithmetic means, standard deviations, and precisions of three types of samples collected in 1973.

Variable	Units	No. Analyses	Mean	St. Dev.	Minimum	Maximum	Precision* %
A. <u>Ottawa atmospheric air</u>							
He	ppm	18.	5.11	.32	5.0	6.0	13
Ne	ppm	18.	18.55	1.72	16.0	21.0	19
CO ₂	%	17.	.094	.04	.04	.18	85
N ₂	%	18.	79.74	2.75	76.35	86.32	7
O ₂	%	18.	21.31	.58	20.35	22.52	6
Ar	%	18.	.98	.08	.84	1.17	18
B. <u>Ottawa tap water</u>							
Dissolved							
Gas**	cc/l	17.	21.88	1.05	19.99	23.86	5
He	ppm	17.	2.88	.33	2.00	3.00	23
Ne	ppm	17.	9.88	4.029	4.00	17.00	82
CO ₂	%	17.	3.29	.72	2.02	4.28	44
N ₂	%	17.	62.81	2.71	58.47	69.49	9
O ₂	%	17.	35.41	1.04	33.45	37.40	6
Ar	%	17.	1.81	.16	1.57	2.05	19
C. <u>Carlsbad Springs spring water</u>							
Dissolved							
Gas**	cc/l	10.	82.44	1.40	80.65	83.98	3
H ₂	%	10.	.09	.01	.08	.12	29
CH ₄	%	10.	82.34	.50	81.67	83.14	1
He	ppm	10.	34.20	1.61	32.00	38.00	10
Ne	ppm	10.	1.00	0.00	1.00	1.00	-
CO ₂	%	10.	4.24	.79	2.60	5.73	38
N ₂	%	10.	9.45	1.82	7.96	14.00	39
O ₂	%	10.	.80	.33	.55	1.69	83
Ar	%	10.	.43	.08	.38	.65	41

$$* \text{ Precision} = \frac{2 (\text{Standard Deviation})}{\text{mean}} \times 100$$

** At room temperature and pressure (23°C and 750 mm Hg approximately)

singly charged ²⁰Ne signal. As there is always much more Ar in a sample than Ne and not all of it condenses in the charcoal trap in a reasonable time, the Ne signal is masked by a variable Ar signal. It is not quite clear however, why CO₂ has such poor precision. It is believed that at low concentrations a varying hydrocarbon peak from the oil in the diffusion pump gives

poor reproducibility and at higher concentrations difficulties are encountered in freezing quantitatively the CO₂ as the gas sample is condensed. The mean of 940 ppm CO₂ instead of the accepted 320 ppm for atmospheric air suggests a bias at low concentrations as a result of extrapolation of calibration curves into low regions of concentration where direct pressure readings cannot be made accurately. O₂ exhibits poorer

precision at concentrations less than 1 per cent because it is being picked up to a varying degree by the water sample during handling, i. e. , bottling and introduction into the inlet system. This source of error applies to all gas components; in other words during the brief intervals when the water sample is exposed to atmospheric air, exchange of components between the water phase and air will take place. This exchange will be small for components that are at or near their equilibrium with air but can be significant when concentrations differ greatly. Similarly, some dissolved gas will be lost from the sample during handling. This is the main reason for expressing concentrations in terms of the amount of dissolved gas rather than on unit volume of water. Loss of gas by degassing during pouring is not going to change the composition of the dissolved gas as much as it will change the concentration of the gaseous components in the water sample. In any case, the amount of dissolved gas is also measured so that the reader can convert from dissolved gas composition to concentration in the water phase. The magnitude of the analytical error for H_2 , CH_4 , He, and total dissolved gas at moderate concentrations can also be deduced from results plotted in Figure 4. Although these results portray the loss of gas from bottles in

storage, the day-to-day fluctuations give an indication of the magnitude of the overall error. These curves also point out the most significant error for H_2 and CH_4 -namely bacterial consumption of these two components. Even if the technique were capable of very high precision, the consumption of these gases by bacteria can completely remove them from the water sample unless extensive precautions are taken. No measure of precision was obtained for H_2S . Its pungent odour and biogenic activity make it unpleasant and difficult to work with.

While there are a number of steps that can be taken to improve precision if required, it is felt that at this stage of the project it is more important to analyze more samples with lower precision.

REFERENCE

- Dyck, W.
1969: Field and laboratory methods used by the Geological Survey of Canada in Geochemical Surveys, No. 10: Radon Determination Apparatus for Geochemical Prospecting for Uranium; Geol. Surv. Can., Paper 68-21, 30 p.

APPENDIX

Computer program for the calculation of dissolved gas composition.

```
PROGRAM WILLI(INPUT,OUTPUT,PUNCH)
COMMON TITLE(8),FORM(8),NAME(10),NC(20),IC(20),A(20),B(20),
* X(10),P(10),C(10),D(20,300),PR(11,300),UNITS(10)
```

```
1 FORMAT(I2,F8.0,I2)
2 FORMAT(8A10)
3 FORMAT(10A6)
4 FORMAT(A4,A1,2F10.0)
5 FORMAT(1H0,A4,A1,2F10.5)
6 FORMAT(1H ,A6,2XA6,F7.2,F7.3,F7.1,F6.1,F6.2,F7.1,10F8.0)
7 FORMAT(1H ,A6,2XA6,12F9.2)
8 FORMAT(1H ,A6,2XA6,F8.2,F10.2,F8.2,2F9.2,F9.1,2F9.0,4F9.2)
9 FORMAT(1H1,34HINPUT DATA (CURRENTS IN MPA) FOR 8A10/      1H0,56H
* MAP SAMPLE P.GAS RN RN P.DUM P.NOA P.MEAS 9A8,A6/1H0
* ,54H SHEET NUMBER MM.HG DEC.F. CPM. MM.HG MM.HG MM.HG /)
10 FORMAT(1H1,23HPRESSURES (MM.HG) FOR 8A10/
* 1H0,35HMAP SH. SAMPLE TOTAL P. P. CAL. 9A9,A6/)
11 FORMAT(1H1,31HDISSOLVED GAS COMPOSITION FOR 8A10/
* 43H0 MAP SAMPLE VG RN C.TOT. 9A9,A6/
* 41H SHEET NUMBER (CC/L) (PC/CC) PCT. 10(3XA6)/)
12 FORMAT(1H1,25HCURVE A B 8A10)
13 FORMAT(2A6,F7.2,F8.2,I5,I4,I5,I7,I4,I7,4I5)
PVAL(I)=10.0**(B(NV+I)*ALOG10(X(I))+A(NV+I))
```

C

```
100 READ 1,NV,VC,ISORT
IF(NV.EQ.0)STOP
READ 2,TITLE,FORM
READ 3,NAME,UNITS
PRINT 12,TITLE
M=NV+6
DO 105 I=1,M
READ 4,NC(I),IC(I),A(I),B(I)
105 PRINT 5,NC(I),IC(I),A(I),B(I)
M=NV+10
N=0
110 READ FORM,(D(I,N+1),I=1,M)
IF(D(1,N+1).EQ.6H )GO TO 112
N=N+1
IF(MOD(N,50).EQ.1)PRINT 9,TITLE,NAME
PRINT 6,D(1,N),D(2,N),D(5,N),(D(NV+5+I,N),I=1,5),(D(I+5,N),I=1,NV)
GO TO 110
112 DO 130 M=1,N
IF(D(6,M).GT.1.)D(6,M)=D(6,M)-0.015*D(7,M)
DO 115 I=1,NV
X(I)=D(I+5,M)
IF(X(I).LE.0.0)X(I)=1.E-6
115 P(I)=10.0**(B(I)*ALOG10(X(I))+A(I))
IF(D(3,M).NE.1HS)P(3)=PVAL(3)
IF(D(4,M).NE.1HS)P(4)=PVAL(4)
IF(X(6).GE.1.E5)P(6)=PVAL(6)
IF(X(1).GE.1.E4)P(1)=PVAL(1)
IF(X(2).GE.3.E3)P(2)=PVAL(2)
PG=D(5,M)
IF(D(NV+8,M).GT.0.)P(5)=P(5)*PG/D(NV+8,M)
IF(D(NV+8,M).GT.0.)P(6)=P(6)*PG/D(NV+8,M)
FAC=D(NV+9,M)
IF(FAC.EQ.0.)FAC=0.3
PREM=D(NV+10,M)
```

```

IF (PREM.EQ.0.) PREM=P(3)+P(5)+P(6)
FAC=(PG-PREM)/FAC
DO 120 I=1,3
120 P(I+6)=P(I+6)*FAC
PCAL=0
DO 125 I=1,NV
PR(I+1,M)=P(I)
125 PCAL=PCAL+P(I)
PR(1,M)=PCAL
IF (MOD(M,50).EQ.1) PRINT 10,TITLE,NAME
130 PRINT 7,D(1,M),D(2,M),PG,PCAL,(P(I),I=1,NV)
L=0
DO 140 M=1,N
IF (D(1,M).NE.D(1,M-1).AND.ISORT.EQ.1)L=0
L=L+1
PG=D(5,M)
DO 136 I=1,NV
C(I)=D(I+5,M)
IF (C(I).LE.0.) GO TO 136
C(I)=PR(I+1,M)/PG*1.E6
IF (I.GE.3.AND.I.LE.5) GO TO 136
C(I)=C(I)*1.E-4
136 CONTINUE
CCAL=PR(1,M)/PG*100.
ICCAL=CCAL*100.0+0.5
VG=PG*VC
RNG=-1.0
IF (D(NV+6,M).NE.0.) RNG=D(NV+7,M)/(D(NV+6,M)*VG*0.292)
IF (MOD(L,50).EQ.1) PRINT 11,TITLE,NAME,UNITS
PUNCH 13,D(1,M),D(2,M),VG,RNG,ICCAL,(C(I),I=1,NV)
140 PRINT 8,D(1,M),D(2,M),VG,RNG,CCAL,(C(I),I=1,NV)
GO TO 100
END

```