

AN ABSTRACT OF THE THESIS OF
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AN ANALYTICAL METHOD FOR THE DETERMINATION OF

MOLECULAR HYDROGEN IN SEAWATER

Abstract Approved: Redacted for privacy
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I have developed an analytical method for the determination of molecular hydrogen in seawater. It is based on the change of hydrogen concentration in a 30 cc. volume of air as it is equilibrated with a one-liter sample of seawater. The change in hydrogen concentration in the air is measured using a gas chromatograph with a helium ionization detector. The system has been utilized aboard ship on several occasions and has been proven to be both dependable and readily transportable. The accuracy of a single measurement is limited to about plus or minus fifteen per cent by the analytical precision of the method. The precision is limited by the random errors in the GC analysis. Shipboard and laboratory experiments have shown that contamination of near-surface and near-bottom samples can be a major problem unless special precautions are taken.

AN ANALYTICAL METHOD FOR THE DETERMINATION
OF MOLECULAR HYDROGEN IN SEAWATER

by
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I. INTRODUCTION

It is only in the last few years that the non-conservative trace gases in the oceans have been extensively studied. Other gases such as oxygen, inert gases and radioisotopes have captured the attention of oceanographers because they can more easily be used for the tracing of water masses and as tools for the study of gas exchange across the air-sea interface. Today, the non-conservative trace gases are receiving a great deal of attention. Chemically active dissolved gases such as hydrogen, methane and nitrous oxide (Hahn and Junge, 1977) are being very extensively studied. A primary reason for this increased interest is that these gases all have large anthropogenic sources. In addition, each of these gases is involved in many important biological cycles.

The first studies of dissolved hydrogen in the oceans were carried out in 1971 (Williams and Bainbridge, 1973). These authors noted that contamination of their water samples occurred when samples were drawn from the ship's fire main supply. However, they did not discuss the possibility that water samples taken anywhere in the vicinity of the ship might be contaminated by corrosion of the ship's hull. Thus their average surface value dissolved hydrogen of 22 nL/L must be regarded to be somewhat high.

At this time the most extensive reported studies of dissolved hydrogen are those of Seiler and Schmidt (1973, 1974). During cruises in the North and South Atlantic oceans, they observed dissolved hydrogen

concentrations between 8 and 57 nL/L. The average hydrogen concentration of 22 nL/L corresponds to supersaturation by a factor of 240% (Gordon, Cohen and Standley, 1977). In one vertical profile taken in the Gulf of Cadiz, a dissolved hydrogen concentration of 230 nL/L was reported at depth; a value an order of magnitude higher than the surface value.

Schmidt and Seiler (1970) reported a precision of about three per cent when analyzing air or calibration standards with their method, which is based on the conversion of hot mercuric oxide to mercury vapor by molecular hydrogen. The mercury vapor is then measured by atomic absorption spectrophotometry. When the analysis was extended to the measurement of surface water samples, the precision degraded to about fifteen per cent, indicating that they had not perfected a technique for quantitatively extracting molecular hydrogen from seawater.

Seiler and Schmidt do not describe any special precautions to be taken when collecting hydrogen samples, nor do they discuss the possibility of contamination of their surface samples by the ship. They do, however, discuss the possibility of biologically produced hydrogen increasing the measured concentration of the gas in their samples.

Seiler and Schmidt (1973) showed that the bacteria Alginomonas is capable of producing enough hydrogen in one hour to double the concentration in a water sample. This could be a particular problem with deep water samples since Jannasch and Wirsén (1973) have shown that many microbiological processes are greatly accelerated when deep water samples are brought to the surface.

One eventual goal of any series of analyses for dissolved hydrogen

in the oceans is to be able to categorize the oceans as either a source or a sink in the geochemical cycle of molecular hydrogen. The data available at this time is not extensive enough to allow us to describe the oceans as either a source or a sink for hydrogen. The estimates of the fluxes and reservoirs for a molecular hydrogen are still very rough.

The annual global production of hydrogen is estimated to be 21.6 to 26.2×10^{12} grams (Seiler and Schmidt, 1974). About fifty per cent of this production is from anthropogenic sources -- chiefly the incomplete combustion of hydrocarbon fuels. The oceanic production of hydrogen is estimated to be five to ten per cent of the total. This estimate is based on the average degree of supersaturation they found in surface waters and the calculated rates of transfer across the air-sea interface. Seiler and Schmidt (1973) have also reported that bacterial activity is probably the largest contributor to biologically produced hydrogen in the oceans. In the terrestrial environment, bacterial production of hydrogen is so great that if the gas were not converted to secondary products such as methane, hydrogen would be a major constituent of the atmosphere (Schlegel, 1974).

The possible sinks for hydrogen have not been well defined. At this time there is not enough data on global variations in atmospheric hydrogen to indicate either a strong oceanic or terrestrial sink for this gas. Contamination problems associated with seawater samples taken in the vicinity of oceanographic research vessels cast doubt on the reliability of existing surface hydrogen measurements. Thus the degree of surface saturation of the oceans and localized variations in the degree of saturation are not well documented. If the oceans should

turn out to be a sink for hydrogen in the atmosphere, then the eventual fate of the dissolved hydrogen in the oceans becomes a very interesting problem for further study.

The first step in any attempt to define the role of the oceans in the geochemical cycle of hydrogen must be the large-scale collection of data on the concentration of the element. Since the existing methods for the analysis of hydrogen in seawater are relatively new and are open to many sources of contamination, I have concentrated on the development of an improved analytical method and the definition of the random and systematic errors encountered in the analysis.

II. OBJECTIVES

The primary objective of this research was the development of a rapid and accurate method of analysis for dissolved hydrogen in seawater. Among the most important guidelines in this development were the precision and accuracy of the analysis, the time required to process a sample and the suitability of the equipment for use during extended periods at sea.

In any chemical analysis, the precision of the method is a primary concern. When analyzing a dissolved trace gas in seawater, it can be difficult to measure the analytical precision. The determination of a reactive gas is complicated by the fact that it may be difficult to carry out exact replicate measurements. Since hydrogen can be geologically produced in seawater, true replicate sampling would require that water samples be analyzed concurrently or that biologically produced hydrogen should not change the hydrogen content of the sample from one sample to the next. The analytical methods for many reactive gases specify that the water sample be "poisoned" to reduce biological activity. I have found that the commonly accepted methods of poisoning, the addition of sulfuric acid or Hg_2Cl_2 , may greatly increase the observed hydrogen content of the sample. In this system I have attempted to reduce the possibility of biological contamination by reducing the time required for a single analysis to about 25 minutes and by storing the water samples in glass containers which may be thoroughly cleaned to remove organic substrates for bacterial growth.

Another factor limiting the precision of the analytical method is the contamination inherent in the classical methods for obtaining water

samples in oceanographic studies. I have included an extensive treatment of this subject in the discussion of the results of this research. It is sufficient to note at this point that sampling methods must be very carefully designed to avoid systematic errors in the analysis for dissolved hydrogen.

In addition to its possible contribution to errors caused by sample alteration, the time required to process a sample is an important determinant in the scope of research objectives. A discussion of the geochemistry of any constituent of seawater must be based on a certain minimum number of samples. The goal for the system described here was the ability to analyze a sample in less than 30 minutes. This goal was met during a thorough test of the system on a 30-day shakedown cruise aboard the Texas A&M Research Vessel GYRE in the Gulf of Mexico and the Caribbean Sea in the summer of 1975.

The durability of the analytical system is a primary concern when the equipment is expected to perform for extended periods at sea. The system described in this work uses a minimum number of glass or metal parts and interconnects these with flexible Teflon¹ tubing. The durability of the system was confirmed during the shakedown cruise when system operating efficiency was limited only by the characteristics of the Beckman GC-55 gas chromatograph. This is in marked contrast to an earlier system using a glass vacuum extraction line. With this system breakage was a major problem.

A secondary objective in the design of the system was the reduction

¹ "Teflon" is a registered trademark of E.I. DuPont & Nemours Corp.

of the overall complexity of the equipment. Not only is simpler equipment generally more reliable, it is also less dependent on operator skill for successful operation. This system has only two manually operated valves and a motor speed control in addition to the four valves associated with the GC inlet system. This is a notable improvement over earlier extraction systems which required the operation of about 12 valves in addition to those in the GC inlet system.

During the shakedown cruise aboard the GYRE and on several subsequent cruises, experiments were carried out to measure the degree of saturation of surface and deep waters with respect to atmospheric hydrogen. The data collected on these cruises has resulted in a much better understanding of the problems involved in the determination of dissolved hydrogen. As understanding of the problems involved in the analysis increased, many changes in the analytical and sampling systems were made. Much of the knowledge gained in the course of these investigations can be applied to other trace gas analyses using different sample separation and detection systems.

III. METHODS

The determination of the hydrogen concentration in a water sample is carried out in several discrete steps. The major steps in the analytical procedure are: 1) collection of the water sample; 2) equilibration of the water sample with a known volume of air; 3) determination of the change in hydrogen concentration of the air after it is equilibrated with the water. The relationship between the change in hydrogen concentration in the air and the dissolved hydrogen concentration in the water are explored in detail in the discussion of the experimental results.

A. Water Sampling

Water samples to be analyzed for hydrogen are normally collected in OSU (Mesecar, 1976) or Niskin bottles of 2-liter or greater capacity. Each analysis requires about 1.5 liters of water and to avoid contact of the water with the atmosphere, a sampler of at least 2-liter capacity is normally used. The exception to this rule is that a few samples have been used which were drawn from paired 1.1 liter Niskin bottles mounted on a rosette sampler.

To minimize the opportunities for the seawater to change its dissolved gas content by exchange with the atmosphere, those portions of the water sample which have been in direct contact with the atmosphere should not be used. This means that the last 20% of the water in the sampling bottle should not be used for dissolved gas analyses. Since the first portion of the seawater which is drained into the glass analytical flask has been in contact with the air, it is discarded by al-

lowing the water to overflow from the top of the flask. The amount of overflow was generally about one-half liter. The analytical flasks are 1-liter round-bottom boiling flasks with 24/40 standard taper ground glass necks. The flasks are stoppered with matching ground glass stoppers in a manner which excludes trapped air bubbles. These flasks were chosen for several reasons: the flasks are inexpensive and widely available; the spherical shape of the container allows free circulation of the water during calibration, facilitates cleaning and reduces heat transfer through the walls. This last feature reduces the changes in temperature experienced by the sample during equilibration. The volume of water contained by each flask was measured with a graduated cylinder to about 2% accuracy. The accuracy of the determination of the water volume was found to have only a very small effect on the overall accuracy of the analysis.

B. Equilibration

The water sample is equilibrated with a known amount of air without transferring it from the flask. This is done with a specially designed gas circulating system. The equilibrator and the other elements of the analytical system are shown in Figure 1. Equilibration is carried out in the sample flask by inserting the glass equilibrator head, which has a male 24/40 standard taper joint, into the flask. The equilibrator head is designed to place a coarse fritted cylinder near the bottom of the flask. The equilibrator head is inserted into the flask inside a plastic hood which is flushed with outside air. This results in a more uniform hydrogen concentration in ambient

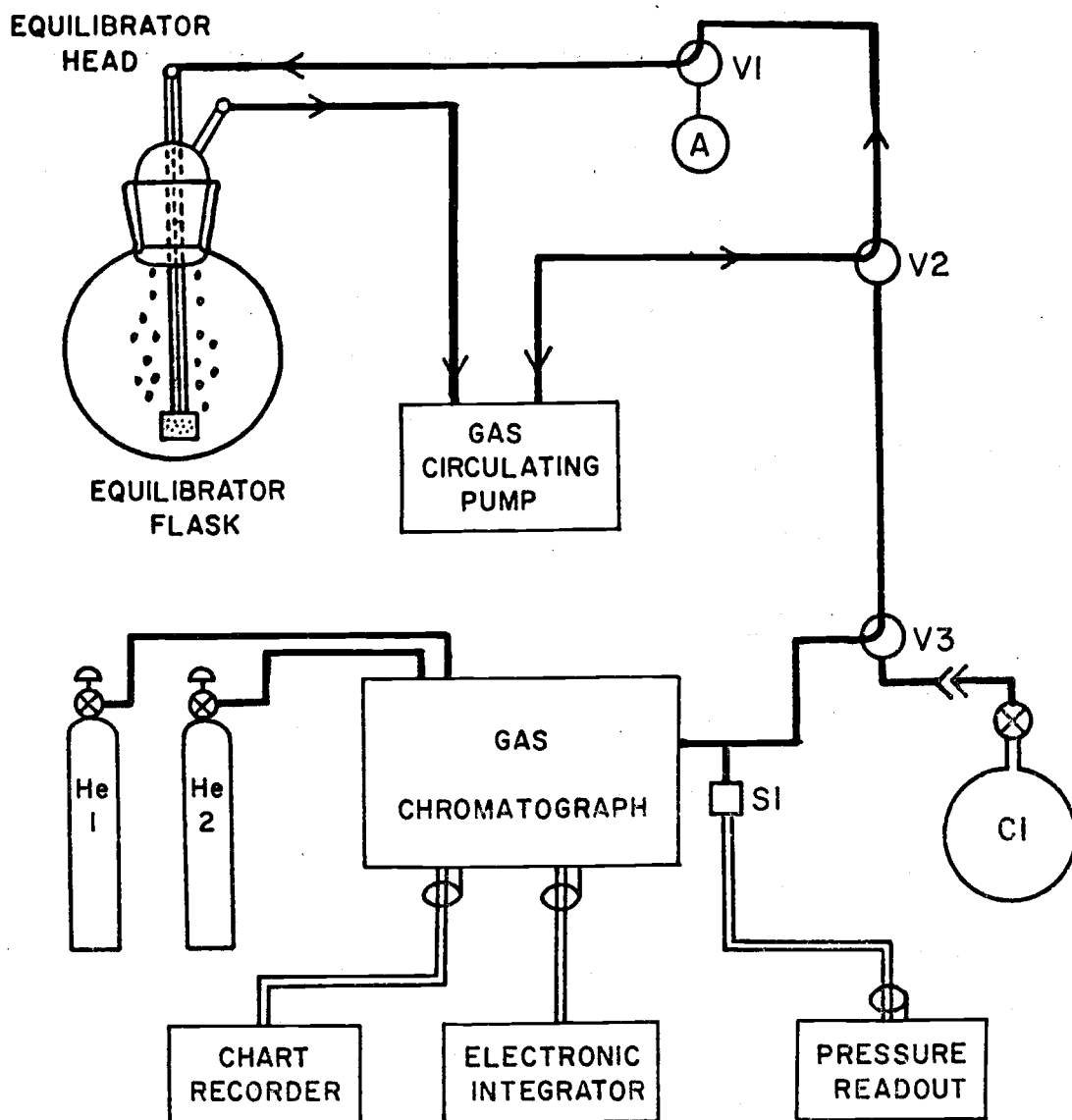


Figure 1. Block Diagram of Equilibrator System.

Seawater of known H_2 content is admitted at point A for backfilling when pumping equilibrated air into the GC. Flask CI contains a calibration mixture used to determine the HID response factor.

air trapped in the equilibrators than would be the case if lab air was used. The air trapped inside the closed equilibrator system is recirculated through the fritted cylinder and the water sample by a variable speed peristaltic pump. The pump is normally run at about 250 ml/min. Laboratory experiments have shown that the equilibration is essentially complete in eight minutes. The equilibration time is extended to 15 minutes to allow time to analyze an air sample which is drawn from the equilibrator just before the system is closed. The change in hydrogen concentration is computed relative to this air sample. During the 15-minute equilibration, the air in the system is circulated through the water sample more than 80 times.

To prevent extensive amounts of water being carried into the gas circulating path and into the GC, 20 ml. of water are removed from the sample flask before inserting the equilibrator head. The water volume used in the calculations is corrected for this removal. At the end of the equilibration a sample of the air inside the equilibrator is removed and analyzed with the GC. Two different methods were used to remove this sample. The first was to simply switch valve V2 and pump the air in the equilibrator into the GC. This method results in a partial vacuum in the equilibrator and may cause leakage of air into the system. A second and more satisfactory method is to switch both valves V1 and V2. The sample flask is then backfilled with seawater of known hydrogen content from a flask connected at point A. This method prevents the formation of a partial vacuum above the water sample. In addition, a much greater fraction of the air can be transferred to the GC.

To calculate the concentration of dissolved hydrogen in the water

sample, the volume of air equilibrated with the water must be known. Two methods have been used to measure this volume. During our first cruise with the system, the volume was determined by expanding the air in the system into the known volume of the GC inlet system. The volume of air was calculated from the change in pressure as the air expanded into the larger volume. After the first cruise, the volume was determined by measuring the volume of water required at point A to completely fill the air volume inside the equilibrator. The gas volume for each flask is determined by the shape and dimensions of the flask and equilibrator head. The gas volumes for the flasks used in this work ranged from 28 to 31 cc.

An important design feature of the equilibrator is that neither the water nor the air in the system come in contact with any metals until the equilibration is complete. This eliminates the possibility of producing molecular hydrogen through the corrosion of metals during equilibration. The flask and the equilibrator head are constructed from Pyrex¹ glass and the tubing connecting the equilibrator head to the pump is 3.2 mm heavy wall Teflon. Valves V1 and V3 are constructed with only Teflon in contact with the gas stream. The tubing in the peristaltic pump is 8-mm heavy wall Tygon².

The equilibrator system, including the flask, valves, pump and pump speed control is mounted in a wooden base approximately 61 cm wide, 25 cm deep and 46 cm high. The hood which shrouds the top of the

¹ Pyrex is a registered trademark of the Corning Glass Company

² Tygon is a registered trademark of the Norton Plastics and Synthetics Division

flask is constructed of clear acrylic plastic and has a volume of about four liters. Since the air pump used to flush this hood with outside air has a flow rate of about 250 cc/min., the hood has a flushing time of about 20 minutes.

C. Gas Chromatographic Analysis of Hydrogen

Both the equilibrated air and the reference air sample are analyzed for their hydrogen content with a Beckman model GC-55 gas chromatograph with a helium ionization detector. The gases in the sample are separated on two columns of Molecular Sieve 5A. The first column has a length of 1.4 meters and the second a length of 2 meters. A backflushing system allows the bulk gases in the sample (N_2 , O_2 and CO_2) to be trapped on the first column, then flushed from the system without passing through the detector. The chromatograph contains separate ovens for the detector and columns and provides outputs for a chart recorder and an electronic integrator. The operating parameters of the GC system are tabulated in Appendix I.

To determine the concentration of hydrogen in a gas mixture several variables must be accurately measured. The first step in the determination is to deliver a fixed amount of gas to the separatory column. In our system a stainless steel sample loop of fixed volume is switched into the carrier gas flow path. The amount of gas injected may be calculated from the volume and pressure of the gas in the sample loop. The volume of the loop was determined by weighing the amount of distilled water needed to fill the loop. Since the same loop is used for both the samples and calibration gas mixtures, the volume of the loop can-

cels out of the equations.

The pressure of the gas in the sample loop is measured with a solid-state electronic pressure sensor. The accuracy of this sensor has been measured by comparison of readings with those of a capacitance manometer held at the same pressure. The capacitance manometer was in turn checked against a mercury manometer throughout its range from zero to 1000 mm-Hg. The differences between the readings from the solid-state sensor and the capacitance manometer are plotted vs the sensor reading as the sensor error in Figure 2. The sensor used with the GC has an accuracy of plus or minus 0.5% of its reading throughout the range of GC inlet pressures used in the analysis. While the sensor is designed with a full-scale range of 1550 mm-Hg, the pressure in the sample loop is normally less than 1200 mm-Hg. Since some drift in sensor output results from changes in the temperature of the supporting electronics, the sensor is generally calibrated against an aneroid barometer at least once a day.

The solid-state sensor has two distinct advantages over the Bourdon-tube pressure gauge we had previously used. The first advantage is the ease with which the sensor's digital output can be read. This is particularly important at sea where vibration and acceleration can make it very difficult to read a gauge with the usual needle and scale. The second advantage of this sensor is in its small internal volume -- about one cc compared to the 12 cc of the Bourdon-tube gauge. As a result of this smaller volume, the proportion of the gas sample which if available for analysis in the GC sample loop is increased.

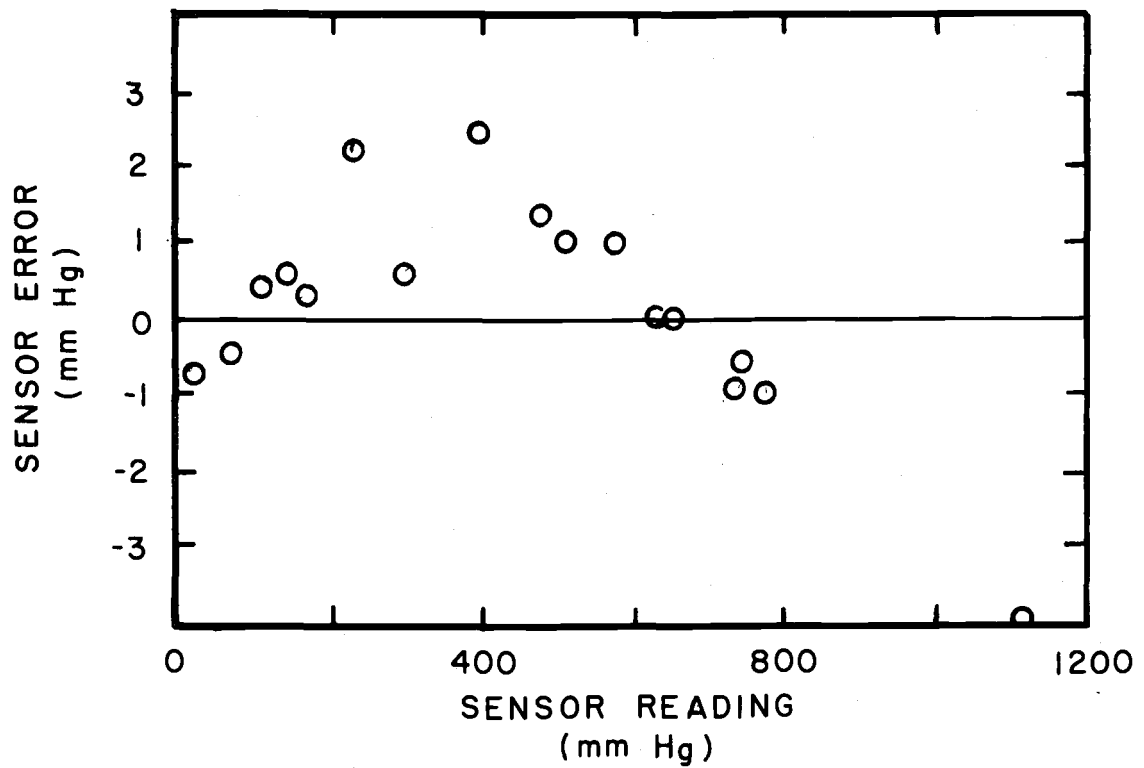


Figure 2. Sensor Error vs Sensor Reading.

D. Calibration of Gas Chromatograph

The concentration of hydrogen in a gas sample is determined by measuring the area of the hydrogen peak at the output of the helium ionization detector (HID). The peak area is normally determined with a Hewlett-Packard model 3373 electronic integrator. The stripchart records of the analysis offer an alternative method of recovering peak area information should the integrator fail to operate satisfactorily. The hydrogen concentration is determined by correcting the peak area to a sample loop pressure of 760 mm-Hg¹ and comparing the area with that of a gas mixture of known composition. This is done by calculating a mean response factor from several injections of the calibration mixture. In this work the response factor will be defined as:

$$C_r = \frac{A \times 760}{C \times P_{inj}}$$

where the A is the peak area for hydrogen produced by the injection of a mixture with C parts per million by volume of hydrogen at a pressure of P_{inj} . From this equation it can be seen that the response factor is the peak area that would result from the injection of a mixture of 1.0 ppmV H₂ at a pressure of one atmosphere.

For accurate determination of the concentration of hydrogen in a gas mixture, the detector should produce an output signal which is related only to the amount of hydrogen in the sample loop. In other words, the response factor should be independent of the injection pres-

¹ 1 mm-Hg = 133.3 Pascals

sure and the concentration of hydrogen in the gas mixture. This has been demonstrated with two gas mixtures of different hydrogen composition as shown in Figure 3. The scatter in the values of the response factor is typical of analyses carried out at sea with our GC. A relative error about 12% is normal under these conditions. In careful laboratory work the error can be reduced to less than five per cent with gas mixtures of 1-2 ppmV H_2 .

The response factor is critically related to the rate of gas flow through the detector. Since the gas flow rates are normally reduced at the end of an operating period to conserve expensive helium, it is very difficult to obtain the same response factor in consecutive working periods. This is because it is impossible to exactly reset the gas flow rates and GC column conditions from day to day. The variations in response factor over a period of several days are shown in Figure 4. The paired sets of analyses labeled A and B in this figure are the result of samples taken at the beginning and end of a 12-hour operating period without changing the operating parameters. These paired sample sets indicate that the response factor remains constant throughout an operating period.

E. Calculation of H_2 Concentration in Air and Water Samples

After the response factor has been determined, the hydrogen concentration in an air sample can be measured. The concentration (in ppmV) of hydrogen in a sample is given by:

$$C_s = \frac{A \times 760}{C_r \times P_{inj}}$$

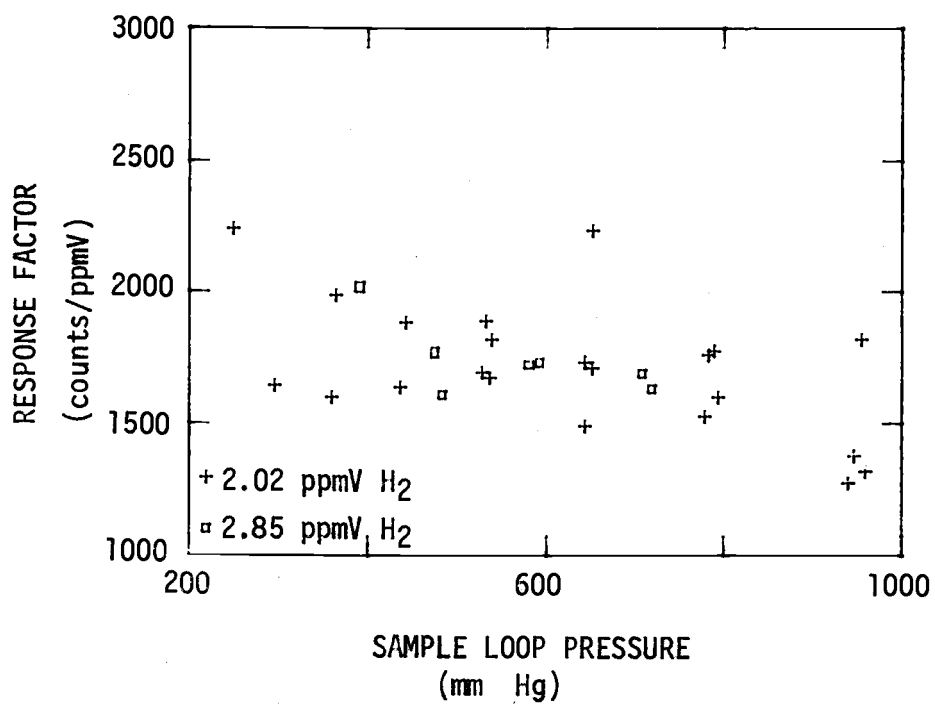


Figure 3. HID Response vs Sample Loop Pressure.

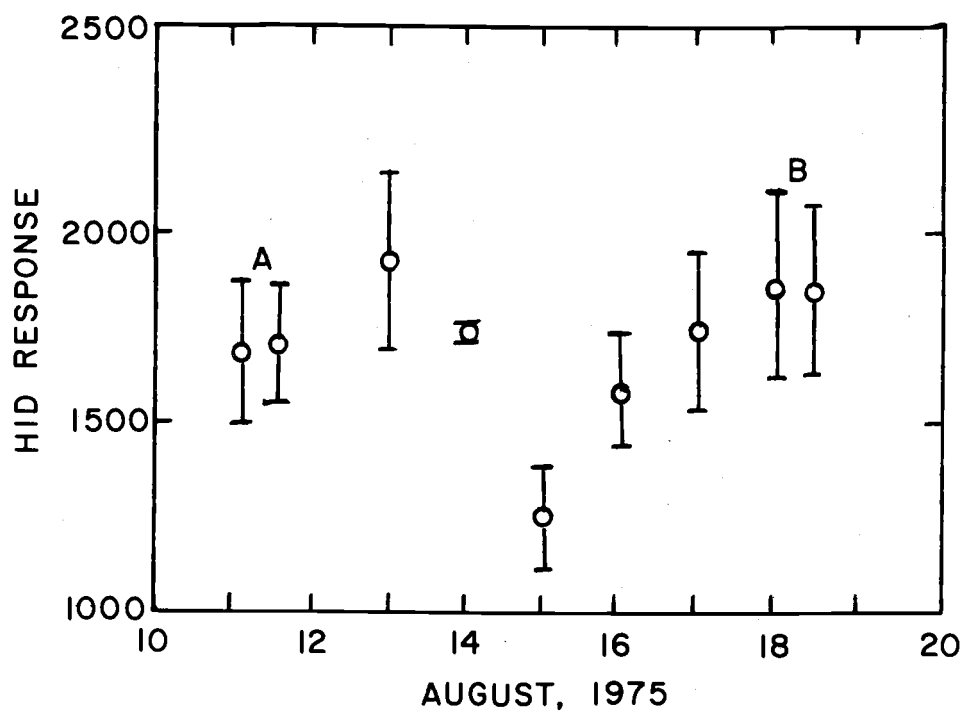


Figure 4. Variations in HID Response over a 7-day Period.

Sample Pairs A and B were taken at the beginning and end of 12-hour operating periods. Error bars extend one standard deviation from the sample mean.

where C_r is the measured response factor for the operating period and P_{inj} is the pressure of the air sample in the GC sampling loop.

When the concentrations of hydrogen in the air before and after equilibration with a water sample have been determined, the concentration of the dissolved hydrogen in the water sample before equilibration is calculated using an equation derived from the mass balance for molecular hydrogen in the closed equilibrator system. The total amount of molecular hydrogen in the system before equilibration (in nL-STP) is:

$$H_2 = C_w \times V_w + C_{air} \times V_{air} \quad (1)$$

where C_w is the measured concentration of molecular hydrogen in the water sample in nanno-liters per liter, V_w is the volume of the sample in liters, C_{air} is the measured concentration of H_2 in the air in ppmV and V_{air} is the volume of air in the equilibrator in cubic centimeters. After the air is equilibrated with the water the amount of hydrogen is unchanged, but the amount of hydrogen dissolved in the water sample will be determined by the solubility of hydrogen in the water and the concentration of hydrogen in the air. If the measured concentration of hydrogen in the equilibrated air is C_{eq} then the concentration in the water will be $\beta \times C_{eq} \times 10^{-6}$ cc H_2 /cc water where β is the solubility in cc- H_2 per cc-water at one atmosphere of hydrogen partial pressure. The total amount of hydrogen in the water is then $\beta \times C_{eq} \times V_w \times 1000$ nL. The total amount of hydrogen present inside the equilibrator is then:

$$H = \beta \times C_{eq} \times V_w \times 1000 + C_{eq} \times V_g \quad (2)$$

Since the system is closed, the amount of hydrogen in the system is the same after equilibration as it was before and we may equate the right-hand sides of Equations 1 and 2. Upon solving for C_w we have:

$$C_w = (\beta \times C_{eq} \times V_w \times 1000 + C_{eq} \times V_g - C_{air} \times V_g) / V_w \quad (3)$$

This is the equation which is used to compute the concentration of hydrogen in a water sample.

F. Analysis of Sediments

Analysis of sediment samples requires only a few simple modifications to the system. The one liter sample flask is replaced with 50-ml graduated cylinder with a female standard taper joint. A sediment sample of about 10 ml volume is taken from a box core with an open-ended plastic syringe. This sample is then transferred to the graduated cylinder and the cylinder filled with seawater of known hydrogen concentration. The cylinder is stoppered and shaken to break up the sediment sample. If the sediment appears difficult to disperse, a Teflon-coated stirring bar may be inserted to act as an agitator.

After the sediment has been dispersed, the sample is treated exactly as is a water sample: 10 cc of liquid is removed, a reference air sample is taken and equilibration is begun. The calculation of the concentration of hydrogen in the sediment sample must be corrected for the amount of hydrogen added with the diluting seawater and the diluting effect of the water. Since the ratio of gas to air volumes in the equilibrator has been changed by an order of magnitude, there is a signifi-

cant increase in the expected error of the analysis.

IV. RESULTS OF FIELD TESTS

A. Water Column

During the shakedown cruise in August of 1975 and on subsequent cruises many problems affecting the analytical system were solved and data collection begun. In the course of these cruises we collected dissolved hydrogen data for the upper 200 meters of the water column at approximately 30 stations in the Gulf of Mexico, the Caribbean Sea, off the Oregon coast and over the Galapagos rift zone off the coast of South America. Each of these cruises provided an opportunity to improve various elements of the analytical system while providing useful data on dissolved hydrogen concentrations in seawater. In this work I will concentrate on the dissolved hydrogen data collected from water samples taken in the upper 200 meters of the water column as it best demonstrates the problems involved in the analysis.

Data on the concentration of dissolved hydrogen in the upper 200 meters of the water column in the Caribbean Sea and the Gulf of Mexico was collected between 14 and 23 August, 1975 aboard R/V GYRE. Vertical profiles of hydrogen concentration for these stations (stations 10-17) are shown in Figure 5. Stations 10 and 11 are located in the Caribbean Sea to the south of Cuba, while stations 15-17 are located in the Gulf of Mexico. The latter stations were occupied on a transit between St. Petersburg, Florida and Galveston, Texas.

A distinct feature of the profiles in Figure 5 is the apparent minimum in hydrogen concentration which lies between 50 and 100 meters in depth. This minimum is probably a sampling artifact caused by con-

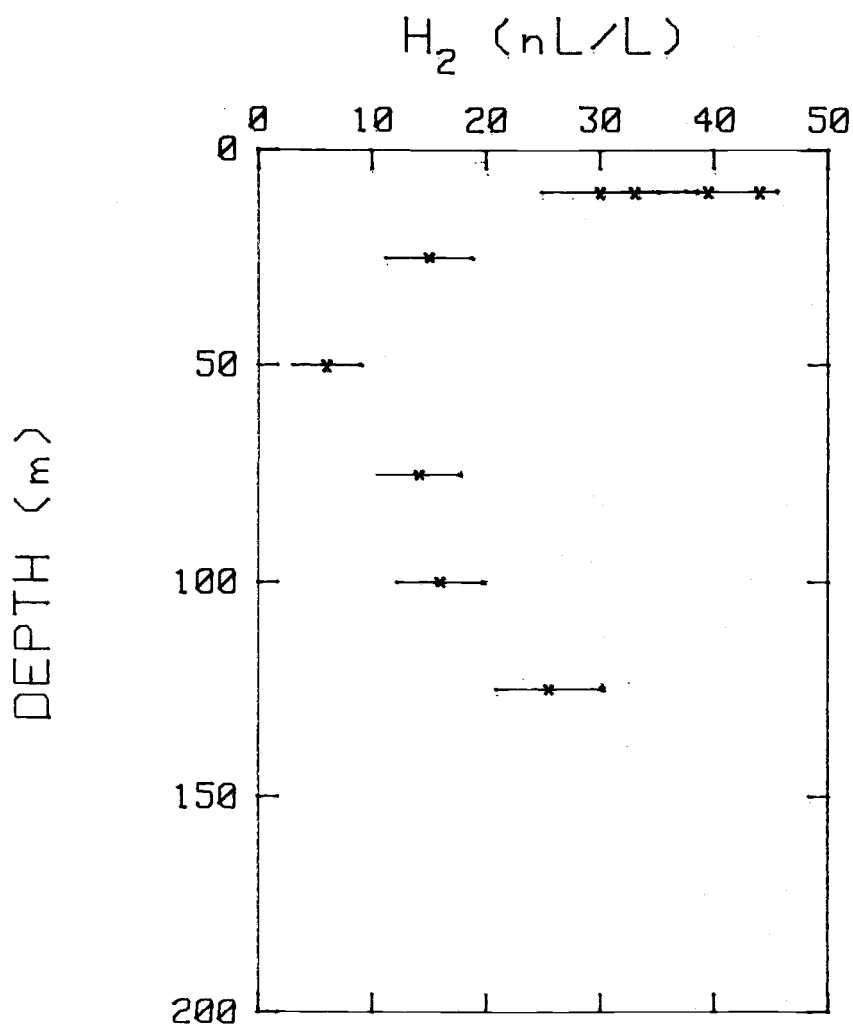


Figure 5. Profiles of Dissolved Hydrogen in the Caribbean and Gulf of Mexico*

This station lies to the south of Cuba. Error bars in this and subsequent profiles extend to the estimated error at one standard deviation.

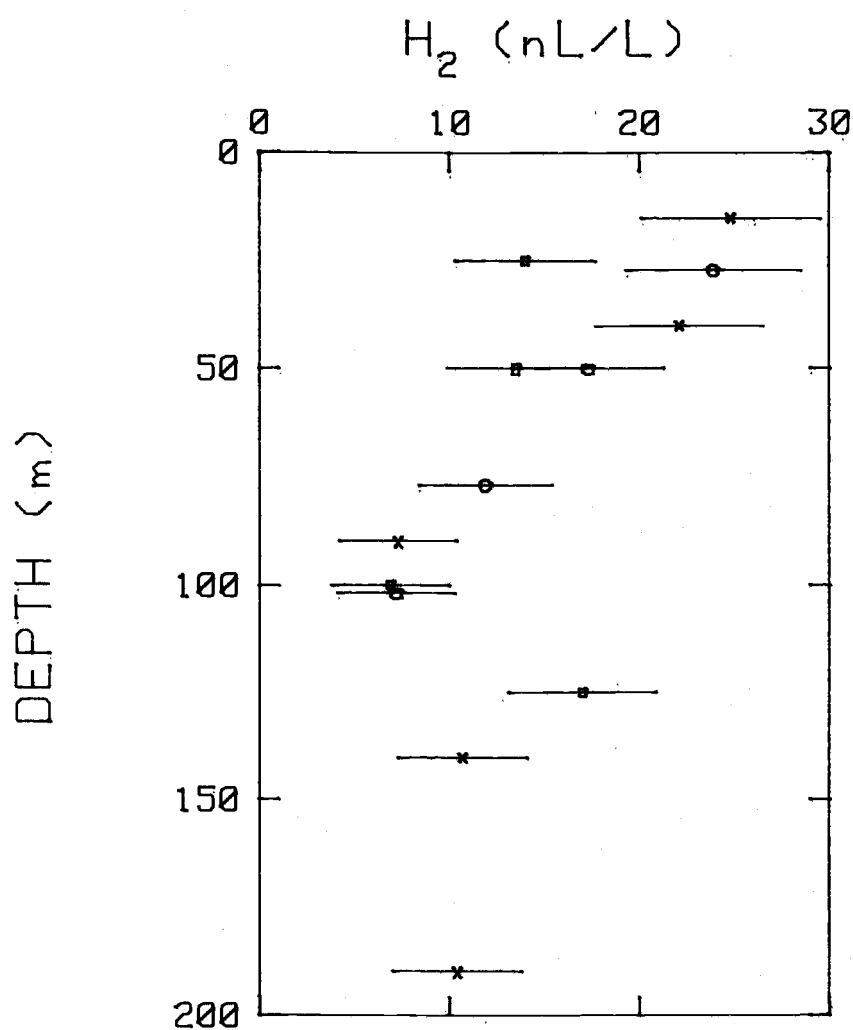


Figure 5B. Profile of H_2 vs Depth in the Caribbean Sea South of Cuba.

Station 11, 16 Aug. cast--x; Sta. 11, 17 Aug. cast--□;
Sta. 11, 17 Aug. cast--o.

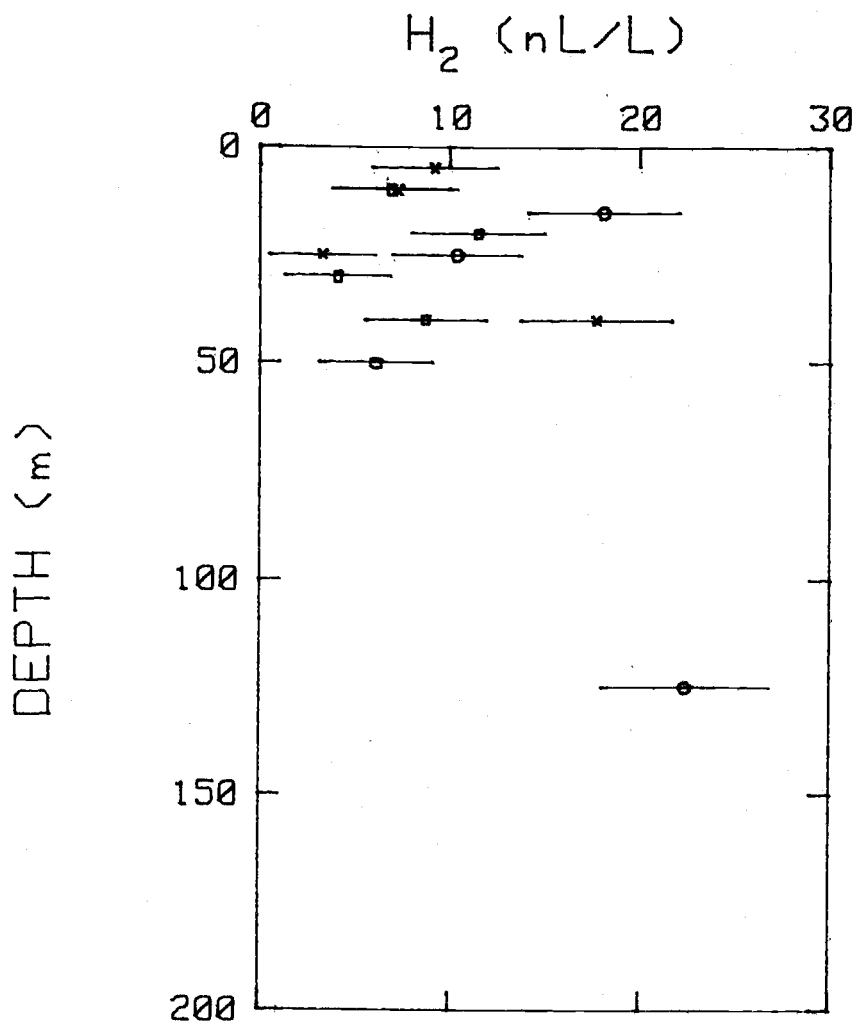


Figure 5C. Profiles of H_2 vs Depth at three stations in the Gulf of Mexico.

Station 15--x; Station 16--□; Station 17--o.

tamination of some of the water samples. The samples close to the ship and those near the hydrographic weight probably reflect increased hydrogen levels caused by the reaction of zinc metal with seawater. This problem is examined in more detail in the section V.

Those samples taken more than 25 meters below the ship or above the hydro-weight generally have hydrogen concentrations near the atmospheric saturation value (~ 9 nL/L). Due to the large effect of sampling problems and the marginal quality of supporting oceanographic data at these stations no attempt has been made to correlate the observed hydrogen profiles with either temperature or salinity profiles. A listing of the available data is included in Appendix II.

In October of 1975 the analytical system was employed on R/V YAQUINA cruise Y7510D off the Oregon coast. The data from two stations occupied at this time are presented in Figure 6. The profiles again show an increase in dissolved hydrogen concentrations near the surface. This increase is again probably due to contamination of the samples with water altered by the presence of the ship. Very low hydrogen concentrations appear in the 50-100 meter depth range where samples are probably uncontaminated. These concentrations are often less than 15% of atmospheric saturation values. Below 100 meters the hydrogen concentrations increase to values at or above the atmospheric saturation level. At these stations little contamination from the hydrographic weight is expected since the weight was encased in stainless steel and all galvanized fittings were coated with silicone rubber. More extensive data will be required to confirm these values and explain the variations in the dissolved hydrogen content of the samples taken at these

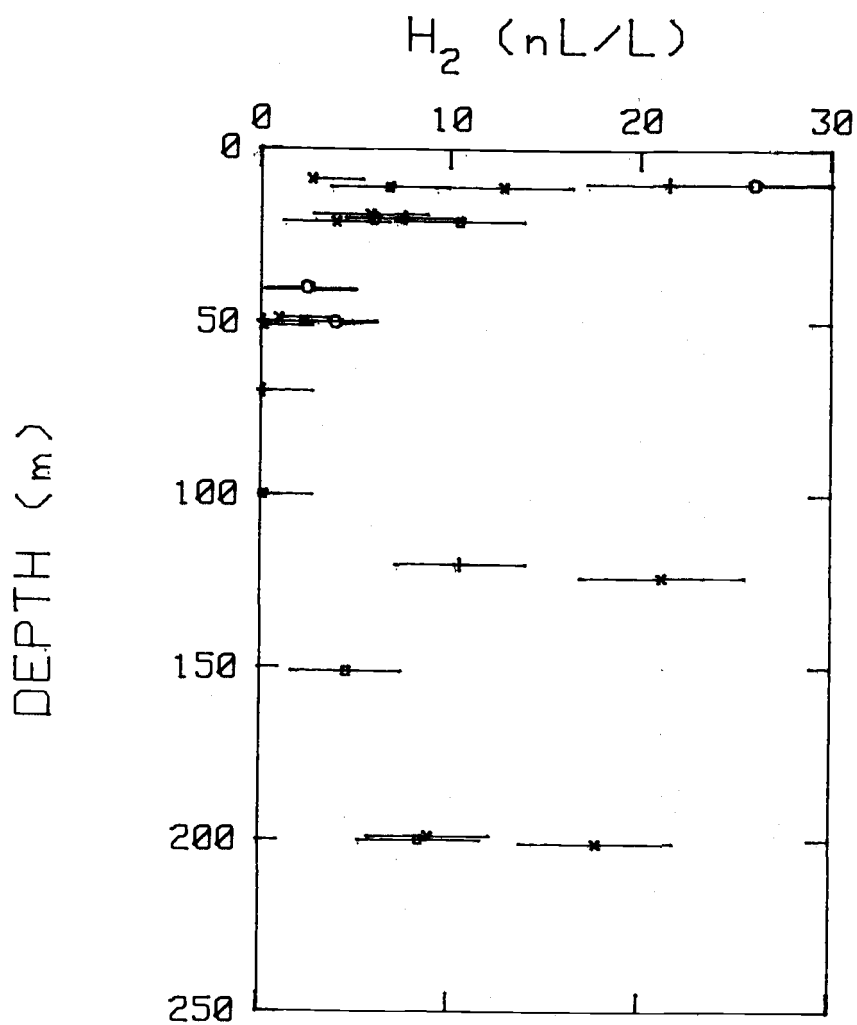


Figure 6. Dissolved Hydrogen at Three stations off the Oregon Coast.

Station 1, cast 1--+; Sta. 1, cast 2--x; Sta. 2--□ (Oct., 1975). Station NH-10--o (Oct., 1976).

stations.

Figure 6 also contains data collected in October of 1976 in the same geographic area as the stations occupied in 1975. The data collected in 1976 definitely fits the pattern established in 1975.

During July and August of 1976 analyses for dissolved hydrogen were conducted on the Pleiades cruise of R/V MELVILLE along the Galapagos Spreading Center off the coast of South America (Lat. $0^{\circ}36'N$, Long. $86^{\circ}09'W$). These vertical profiles show much the same pattern as we have seen at the other geographic locations. The primary difference evident in the data shown in Figure 7 is that the minimum if present is located much lower in the water column. The surface samples again show an increase in dissolved hydrogen concentration to a level which corresponds to 120 to 180% of the saturation level.

A large set of near-bottom water samples was taken during the cruise to explore the possibility of alteration of the water characteristics by mixing with hydrothermal waters. The mean hydrogen concentration of these samples was not significantly different from samples taken much higher in the water column.

The F-test for equality of variances at the 90% confidence level showed that the variance in the near-bottom samples was no greater than might be expected from replicate analyses of a uniform water sample. Thus the presence of localized sources or sinks for molecular hydrogen at the sea bottom cannot be demonstrated from this data set.

The lack of a sharp increase in the hydrogen concentration at the bottom of all casts using the stainless steel hydrographic weight and fittings contamination by the hydrographic weight has been largely

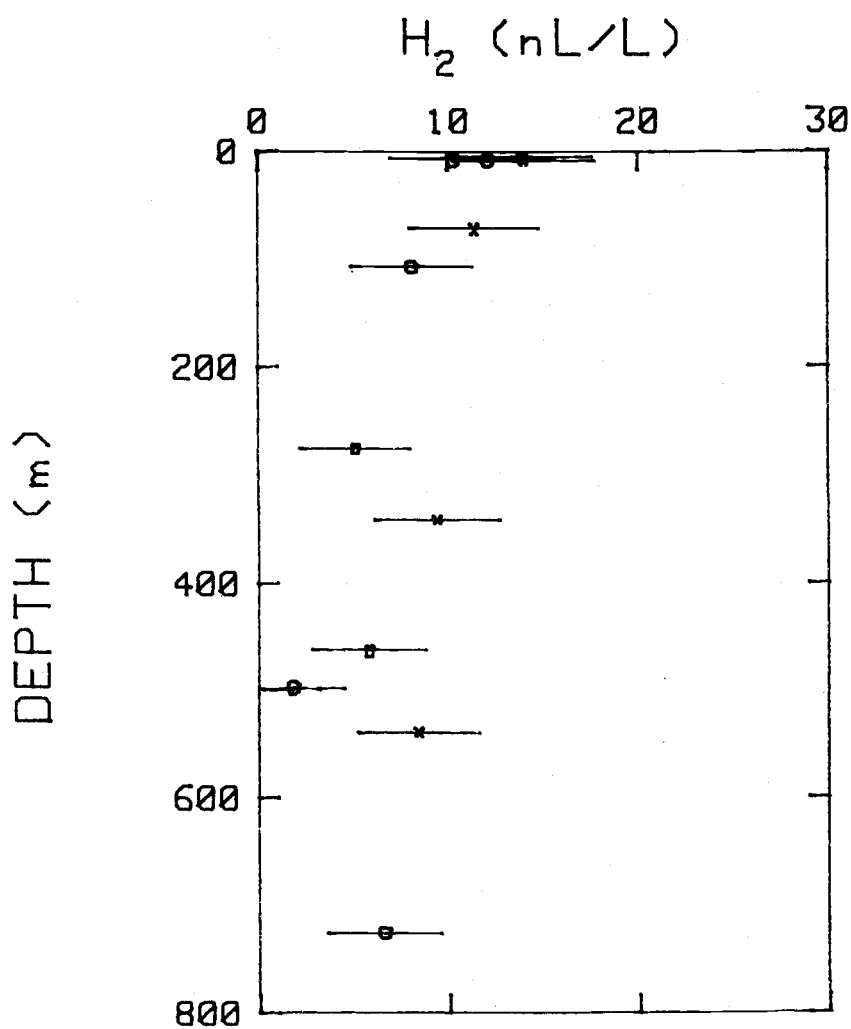


Figure 7. Profile of Dissolved Hydrogen in the Area of the Galapagos Spreading Center.

Station 47--x; Sta. 58--□; Sta. 91--o.

eliminated.

B. Sediments

Sediment samples were collected and analyzed at stations 11 and 12 on the GYRE cruise. The results of these analyses are summarized in Table 1.

Table 1. Molecular Hydrogen in Sediments

Station	Sample Depth (cm below surface)	H ₂ (nL per L sediment)	Comments
11	4	5.9×10^2	Box Core #1
11	6	1.0×10^3	
11	10	2.4×10^3	
11	13	1.3×10^4	
11	10	2.8×10^2	Box Core #2
11	20	1.8×10^2	
11	30	7.4×10^1	
11	35	7.1×10^3	
12	3	7.7×10^1	
12	10	1.3×10^2	
12	20	3.0×10^2	
12	30	1.3×10^3	

The sediment samples show a generally increasing concentration of molecular hydrogen with depth. The molecular hydrogen values are far above the values measured in the water column. Due to sampling errors and contamination problems, no reliable data was collected in the lower 30 meters of the water column on the GYRE cruise. As a result we have no indications of a near-bottom gradient to show that the bottom sediments are a source of molecular hydrogen to the oceans.

V. DISCUSSION

A. Mathematical Analysis of Expected Random Errors

In addition to actual operations, the capabilities and limitations of the system were explored through a mathematical analysis of the expected random errors associated with a single dissolved hydrogen measurement. This analysis reveals the sensitivity of the final result to random errors in each of the measured variables used in the calculation of the dissolved hydrogen concentration. The results of this treatment are being used to evaluate the most important steps required to improve the precision of the analytical method. I have found the steps in the analysis which contribute the most random error are those involving the GC analysis of air samples.

Equation (3), used to compute C_w , the dissolved hydrogen in a water sample is:

$$C_w = (\beta \times V_w \times C_{eq} \times 1000 + C_{eq} \times V_g - C_{air} \times V_g) / V_w \quad (3)$$

In this equation the independent variables are defined as follows:

β	Bunsen Coefficient (cc/cc-atm)
C_{eq}	Measured concentration of H_2 in gas phase after equilibration (ppmV)
V_w	Volume of water sample (L)
V_g	Volume of gas phase in equilibrator (cc)
C_{air}	Measured concentration of H_2 in gas phase after equilibration (ppmV)

To compute the expected random error associated with a single measure-

ment of dissolved hydrogen, the partial derivative of C_w with respect to each of the independent variables is taken:

$$\frac{\partial C_w}{\partial V_g} = \frac{C_{eq} - C_{air}}{V_w} \quad (4A)$$

$$\frac{\partial C_w}{\partial V_w} = \frac{-V_g \times (C_{eq} - C_{air})}{V_w^2} \quad (4B)$$

$$\frac{\partial C_w}{\partial C_{eq}} = 1000 \times B + \frac{V_g}{V_w} \quad (4C)$$

$$\frac{\partial C_w}{\partial C_{air}} = \frac{-V_g}{V_w} \quad (4D)$$

$$\frac{\partial C_w}{\partial \beta} = C_{eq} \times V_w \times 1000 \quad (4E)$$

The expected variances and the typical values of the independent variables are then determined. The values in Table 2 have been determined from actual experimental data.

Table 2. Experimental Variances

Variable	Typical Value	Variance
V_g	30 cc.	1.0
V_w	1.00 L	.0001
C_{eq}	0.70 ppmV	.0049
C_{air}	0.60 ppmV	.0036
β	0.015 cc/cc-Atm	5.6×10^{-7}

The values of the variance in the determination of the concentration of hydrogen in an air sample have been set equal to the variance in the determination of hydrogen in a gas mixture of known composition. This value is available from the numerous analyses of calibration gas mixtures used to determine the HID response factor. The variance in V_w and V_g are set by the precision with which the volume of the equilibrator system was originally determined and by the accuracy with which the operator can withdraw 20 cc of water from the flask at the start of the equilibration. The uncertainty in the value of β which was taken from the data of Gordon, Cohen and Standley (1977) is determined by the range of actual values of β for the water samples at a station. For some of the data presented in this paper, the actual values of β range as much as five per cent above or below the value used to calculate C_w for the whole station. Thus the five per cent estimate for the uncertainty in β is set not by the accuracy with which the solubility can be determined,

but by the range of values of temperature and salinity over which a single estimate of β was used in the calculation. In each of these estimates, the variances of the variables were calculated by squaring the standard deviation from the true value or sample mean.

From the partial derivatives of equation (3) for C_w (shown in equations 4A-4E) and the estimates of the variances for each of the variables in the equation the expected random error in a single determination of C_w can be calculated. This error is given by:

$$E \approx \left[\left(\frac{\partial C_w}{\partial V_g} \right)^2 \times \sigma_{V_g}^2 + \left(\frac{\partial C_w}{\partial V_w} \right)^2 \times \sigma_{V_w}^2 + \left(\frac{\partial C_w}{\partial C_{eq}} \right)^2 \times \sigma_{C_{eq}}^2 + \left(\frac{\partial C_w}{\partial C_{air}} \right)^2 \times \sigma_{C_{air}}^2 + \left(\frac{\partial C_w}{\partial \beta} \right)^2 \times \sigma_{\beta}^2 \right]^{1/2}$$

To evaluate this expression, the expected values of each of the variables is substituted into equations 4A-4E for each of the partial derivative terms. The values of the product of the resulting terms are shown in Table 3.

It is apparent that the major contributors to the random error in a hydrogen determination are the uncertainties in the measurement of the concentration of hydrogen in the air before and after equilibration (Terms P3 and P4). For the typical values used in this treatment the value of C_w is 13.5 nL/L and the expected error is 3.7 nL/L, about 27 per cent.

In order to illustrate more clearly the effect of differing levels of GC error on the total expected error in a single analysis, I calculated the total expected error as a function of the GC error and the

Table 3. Error Terms of Partial Derivatives and Variances

Term	Value
$P1 = \left(\frac{\partial C_w}{\partial V_g}\right)^2 \times \sigma_{V_g}^2$	$(.01)^2 \times 1.0 = 0.0001$
$P2 = \left(\frac{\partial C_w}{\partial V_w}\right)^2 \times \sigma_{V_w}^2$	$(-3.0)^2 \times 1 \times 10^{-4} = 0.001$
$P3 = \left(\frac{\partial C_w}{\partial C_{eq}}\right)^2 \times \sigma_{C_{eq}}^2$	$(45)^2 \times 4.9 \times 10^{-3} = 9.9$
$P4 = \left(\frac{\partial C_w}{\partial C_{air}}\right)^2 \times \sigma_{C_{air}}^2$	$(-30)^2 \times 3.6 \times 10^{-3} = 3.2$
$P5 = \left(\frac{\partial C_w}{\partial \beta}\right)^2 \times \sigma^2$	$(700)^2 \times 5.6 \times 10^{-7} = 0.3$

concentration of hydrogen in the water sample. The results of these calculations are shown in Figure 8. The majority of the analyses carried out at sea fall near the curve for 10% GC error. The curve produced by an assumed GC error of 2% probably represents the best attainable performance with this analytical method and the HID gas chromatograph employed.

The validity of these estimates of the random error associated with the analysis was confirmed during the GYRE cruise in 1975. At this time four replicate samples were analyzed and found to have a mean dissolved hydrogen concentration 35.3 nL/L with a standard deviation of 3.6 nL/L. As is shown in Figure 8, this standard deviation is consistent with the estimated random errors in the analysis at a level of

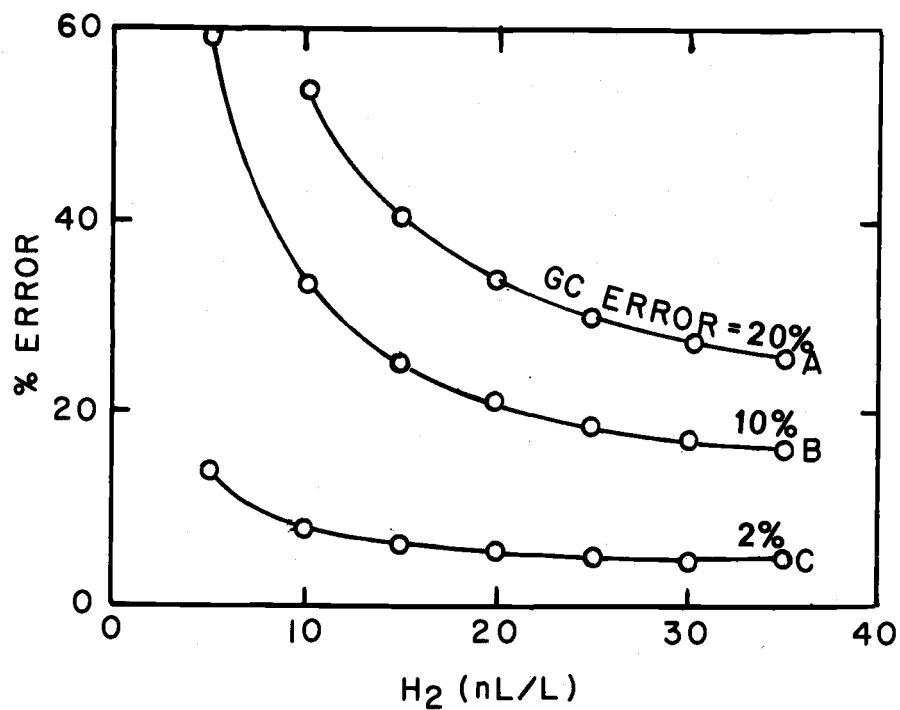


Figure 8. Total Analytical Error as a Function of Dissolved Hydrogen Concentration and GC Error.

10% GC error.

B. Test for Systematic Error from Multiple Gas Injections

For many of the water samples analyzed, more than one GC analysis was made on the equilibrated air. Each of these GC samples results in a separate figure for the H_2 concentration in the water. To reduce the number of data points for plots it is desirable to take the mean of these results for a given water sample. To use this mean value as representative of the true sample concentration, one must assume that the scatter of individual values about the mean is a product of random and not systematic errors. This was tested by taking the logarithms of the ratio of a given result to the hydrogen concentration from the immediately following GC injection. When the ratios are randomly distributed, the logarithms of these numbers should be evenly distributed about zero. Conversely, if there is a consistent decline in measured H_2 concentration from one GC injection to the next, the ratio will always be greater than one and the logarithm will always be positive. In this case it was easier to test an alternate hypothesis: the mean value of the logarithms is not zero. This hypothesis was tested on the data from the GYRE cruise where multiple GC injections were made. Student's T-test was used to determine whether the mean of the logarithms is significantly different from zero. The mean of the logarithms is -0.057 with a value of T of 0.72. This value of T indicates that there is more than a fifty per cent probability that the mean is different from zero by chance alone. Since the probability that the distribution of the logarithms is random is so high, I conclude that there

is no systematic trend in the H_2 concentrations determined from successive GC injections of the same equilibrated air. Therefore, it is possible to reduce the number of data points on the vertical profiles with confidence that the mean of the several measurements of a given water sample yield a value representative of the actual hydrogen concentration in the sample. This procedure was carried out on the data presented in the vertical profiles in this work.

C. Sample Contamination

A very important result of this research has been the discovery that the standard, accepted methods of obtaining seawater samples can cause large errors in the analysis of dissolved hydrogen. The galvanic protection of a ship's iron fittings with zinc cathodic protection electrodes can generate hydrogen concentrations near the vessel far above the natural levels. A sample calculation showed that an oceanographic vessel which uses (dissolves) 100 kg of zinc per year for cathodic protection produces about 1.0×10^6 nL of hydrogen per second. This is an approximate figure for a typical oceanographic vessel. Since the vessel may remain relatively stationary for several hours while conducting sampling operations, the degree of contamination of surface waters can be very large. Moreover, since some of the zinc blocks may be 3 to 4 meters below the sea surface, contamination is certain to extend immediately to this depth. The degree of contamination at greater depths is dependent upon the magnitude of the vertical eddy diffusion coefficient. This factor is in turn dependent on the stability and turbulence in the surface waters. Examination of CTD records from the GYRE cruise showed that the surface layer was well

mixed to about 40 meters depth. Some degree of contamination could be expected to this depth if the ship remained stationary with respect to the surface waters for several hours. Since the ship may also be moving through the water to maintain a vertical wire angle, the problem of determining the exact depth to which high surface hydrogen values may be mixed is beyond the scope of this work. The station profiles from both the GYRE and YAQUINA Cruises indicate that surface contamination extends to 20 meters in all cases.

For most hydrographic casts it is necessary to place a 75-100 kilogram weight at the bottom of the hydrographic (hydro) wire. This weight is necessary to maintain the wire in a nearly vertical line despite vertical and horizontal motions of the vessel. This weight is normally constructed of lead with steel and zinc-plated (galvanized) fittings. These fittings will react with seawater to produce molecular hydrogen. This source of hydrogen presents a potential source of contamination for water samples taken near the bottom of the hydrographic wire.

An experiment was carried out aboard the GYRE to measure the degree of sample contamination which might result from the evolution of hydrogen from the hydro weight. A large plastic container was filled with seawater from the ship's seawater pumping system. A sample was taken to measure the background dissolved hydrogen level, then a small submersible pump was immersed in the container to circulate the seawater. This pump was allowed to run for 25 minutes and a second water sample was taken to check for generation of hydrogen by the pump alone. The hydrographic weight was then immersed in the seawater and samples were taken 13 and 31 minutes later. The resulting values of the dis-

solved hydrogen concentration are plotted against time in Figure 9. The hydro weight was immersed at point A.

The high background hydrogen value indicated in Figure 9 is probably due to production of hydrogen by the reaction of metals in the ship's pumping system which is also cathodically protected. The sharp increase in the dissolved hydrogen concentration after the immersion of the hydro weight indicates a very high rate of hydrogen production. The slope of the curve corresponds to a hydrogen production rate of 566 nL/minute. During a standard hydrographic cast the sampling bottles are allowed to remain at rest at the sampling depths for at least 5 minutes to ensure that thermometers have come to thermal equilibrium and that the containers are thoroughly flushed. In the course of this 5-minute period more than 2500 nL of H_2 could be generated. The extent to which this hydrogen will contaminate sampling bottles above the weight will depend on a number of factors. Perhaps the most important of these is the surface sea state. If the seas are high enough to cause appreciable rolling or pitching of the ship, the hydrographic wire will be moving vertically in relation to the deep water being sampled. In this case the hydro weight and sample bottles will mechanically mix the water surrounding the wire. If the vessel is maintaining headway for control, much of the contaminated water may be left behind. Since these factors are difficult to quantitatively estimate, contamination from the hydroweight was reduced as much as possible by placing the lowest sampling bottle at least 50 m above the weight or, later, by using a stainless steel covered weight.

When minimal precautionary measures are taken it is possible to

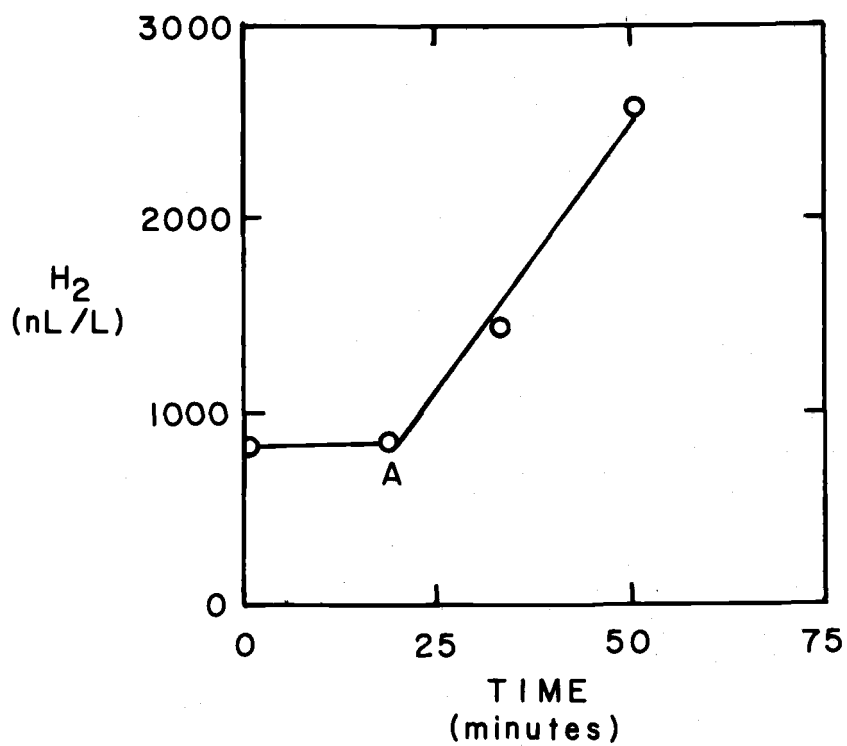


Figure 9. Plot of Hydrogen Production by the Hydrographic Weight vs Time.

The weight was immersed in the container at point A.

obtain uncontaminated water samples in the middle of the water column. This fact is evident in the lower H_2 values at the bottom of the third cast at Station 11 on the GYRE cruise where the weight was placed 50 m below the lowest sample bottle. The deeper samples in the third cast have hydrogen concentrations which are much smaller than were measured at Station 10 and on the first two casts at Station 11. After the GYRE cruise a stainless steel covered hydro weight was used for hydrographic work where dissolved hydrogen samples were to be taken. The lower samples in those casts should not be contaminated to any significant degree.

Since contamination of water samples with hydrogen produced through contact of seawater with metals in the sampling system is a major problem, we conducted an experiment to quantify this source of error. In this experiment samples of different metals with measured surface areas were exposed to known amounts of seawater for a known length of time and the amount of hydrogen produced was measured. The experiment was carried out by immersing the metal samples in seawater contained in 50-ml equilibration flasks. The salinity of the seawater was approximately 35 parts per thousand and the temperature was about 21 degrees (laboratory ambient). After an immersion time ranging from 15 to 55 minutes, the water sample was analyzed for dissolved hydrogen in the usual manner. From the calculated final concentration of hydrogen in the water and gas phases, the total amount of hydrogen generated was calculated. This figure was then divided by the immersion time and the area of the metal to yield the production rate in $nL-H_2$ per cm^2 per minute. In those cases where more than one metal was in contact

with the seawater, they were in electrical contact. The surface area of the more active metal was used in the calculation. The results of this experiment are shown in Table 3. It can be seen from this table that zinc and aluminum, when in contact with iron, present a severe problem in any attempt to collect uncontaminated water samples. Even a small galvanized fitting in the vicinity of a water sampler will generate enough hydrogen in a few minutes to alter the concentration of the gas in several hundred liters of seawater. An oceanographic vessel of moderate size may have as much 5000 square centimeters of zinc surface exposed to act as cathodic protection for the ship's hull and fittings. Using the data in Table 3, the resulting rate of hydrogen production is about 7.8×10^5 nL-H₂/minute. While this is almost a hundred times lower than the estimate based on the total consumption of zinc by the vessel in a year, both figures are high enough to indicate that it should be nearly impossible to collect uncontaminated water samples near a large vessel of any kind.

Table 3. Production of Hydrogen by Metals in Contact with Seawater

Metal(s)	H ₂ Production (nL/cm ² · min)	
Zn/Fe	156	
Al/Fe	54.0	
Al/SS*	6.90	(mean of 3 samples)
Al	7.56	
Pb/Fe	7.4	
Brass/Fe	1.85	

* SS sample is type 301 stainless steel.

D. Overall Precision and Accuracy of Method

The overall precision of the analytical method is limited by the ten per cent random errors in the GC analysis of the equilibrated air. These errors in the GC analysis account for about 97 per cent of the total random errors in a single measurement of hydrogen. The causes and some possible remedies for this problem are discussed in Section VI of this work. The precision levels of the other variables used in the calculation of the hydrogen concentration cannot be significantly improved without major changes in the equilibration system.

The overall accuracy of the method is limited by the analytical precision. I have not detected any systematic errors large enough to affect the results of the analysis at the current level of precision. There is other strong evidence that systematic errors are insignificant. Lilley (1977) has measured hydrogen concentrations in the vicinity of the Galapagos Spreading Center with an analytical system based on the stripping of hydrogen from seawater with helium, subsequent collection of the dissolved hydrogen in a cryogenic trap and GC-HID analysis of the trapped gases. His measured hydrogen concentrations for deep water samples of similar temperatures and salinities are not significantly different from those measured one year earlier with the equilibrator system. The close agreement between two methods using very different procedures for acquiring a representative gas sample is strong evidence that neither method is subject to large systematic errors.

VI. SUGGESTED SYSTEM IMPROVEMENTS

The analysis of the random errors in a single determination of dissolved hydrogen points out that random errors in the GC analysis of the air before and after equilibration are the major contributors to the total random error. For this reason, the most significant improvement in analytical precision will be gained by improving the GC system. The primary problem with the GC system is that the Beckman GC-55 is sensitive to the large-scale accelerations experienced aboard ship in heavy weather. This problem has been traced in part to the mechanical design of the GC. A particular problem is the flexing of 1.6 mm O.D. tubing in the gas flow system. The flexing of the tubing causes minute changes in the effective diameter of the tubing, thus altering the gas flow rates to the detector. These changes in flow can cause output signals which are impossible to distinguish from hydrogen peaks. The obvious solution to this problem is to rebuild the GC system to increase the mechanical integrity of the gas flow system.

A second, and related problem also occurs in the gas flow system of the GC. In operations at sea and in the laboratory we have found that the flow regulators in the HID discharge helium supply line must maintain a very high degree of regulation. In actual practice, the mechanical flow regulators now used often become noisy after several weeks of operation. The noise in the gas flow rates leads to a general degradation of the signal-to-noise ratio in the gas analysis. This problem could possibly be eliminated by installation of an electronically controlled mass-flow regulator in the HID helium supply line.

If the GC system can be improved to the point where it can consistently deliver the two percent precision it attains under optimum laboratory conditions, the overall precision should reach five per cent, a figure which should be adequate for the geochemical investigations for which the system is intended.

VIII. CONCLUSIONS

I have developed an analytical system for the measurement of dissolved hydrogen which yields rapid and reasonably accurate results. The accuracy of a single measurement is probably limited by the analytical precision to about plus or minus fifteen per cent. The only known systematic error is the direct contamination of the water sample prior to the analysis.

The large errors which can result from production of hydrogen by elements of the sampling system is an effect which has not been noted in earlier reports on the analysis of hydrogen in seawater. Near-surface and near-bottom samples in particular, require special sampling precautions to preserve the validity of the samples. The requirement for the removal of chemically active metals from the sampling and analytical systems cannot be too strongly stressed. From this work I must conclude that it is impossible to collect uncontaminated water from the upper ten meters of the water column with a standard hydrographic cast.

The major contributor to the random errors in the analysis is the analysis of the gas samples with the gas chromatograph. The Beckman GC-55 used in this work is a much more versatile and complex instrument than is necessary for the hydrogen analysis. Unfortunately, some of this complexity has resulted in operating problems in a shipboard environment. Steps have been taken to correct many of these operating and sampling problems, but much work remains to be done.

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APPENDIX I. GC OPERATING PARAMETERS

INJECTION SYSTEM	1.97 cc sample loop connected to multiport valve.
SEPARATORY COLUMNS	Backflush -- 1.4 m molecular sieve 5A Main Column -- 2.0 m molecular sieve 5A
COLUMN TEMPERATURE	Operating -- 55°C Bakeout -- 250°C
CARRIER GAS	Ultra-pure Helium (less than 3 ppmV total impurities, U.S. Bureau of Mines, analyzed)
HID DISCHARGE GAS	Same as above
GAS FLOW RATES	Column -- 20 cc/min. Discharge supply -- 100 cc/min.
DETECTOR OVEN TEMP.	150°C

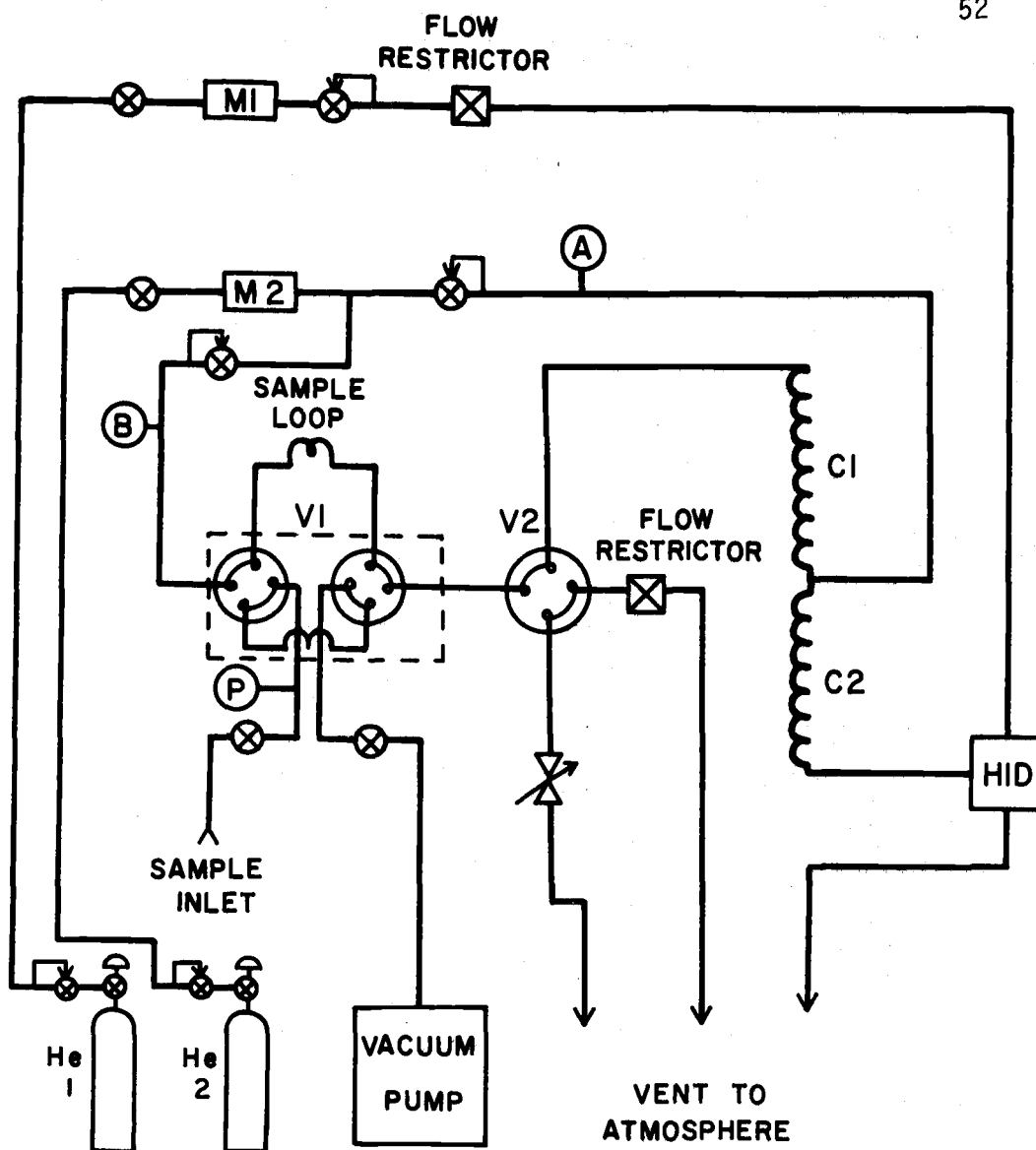


Figure 10. Gas Flow Diagram of Gas Chromatograph.

M1 and M2 are flow meters calibrated for Helium at 80 PSI. V1 is the sample inlet valve and V2 is the column backflush valve. C1 is the pre-column which is back-flushed and C2 is the main separatory column. A and B are column head pressure gauges and P is the inlet pressure sensor.

APPENDIX II. TABLES OF H_2 , O_2 AND HYDROGRAPHIC DATA

The tables are arranged in the order of the profiles appearing in the text.

CRUISE 75-G-10 R/V GYRE TEXAS A&M UNIVERSITY

Z	H_2	O_2	Salinity	Temperature
Station 10; 19-47N, 80-12W; 14 August 1975; 2200Z				
10	44.0	-----	-----	-----
10	39.5	-----	-----	-----
10	33.0	-----	-----	-----
10	30.0	-----	-----	-----
25	15.0	-----	36.078	-----
50	6.0	-----	36.073	-----
75	14.2	-----	36.090	-----
100	16.0	-----	36.171	-----
125	25.5	-----	36.250	-----
150	186.4	-----	36.516	-----

Station 11; 20-74N, 85-11W; 15 August 1975; 1600Z

15	24.8	-----	36.201	-----
40	22.1	-----	36.202	-----
90	7.3	-----	36.245	-----
140	10.7	-----	36.748	-----
190	10.4	-----	36.750	-----

Station 11; 20-29N, 82-19W; 16 August 1975; 1600Z

25	14.0	-----	36.078	-----
50	13.5	-----	36.073	-----
100	6.9	-----	36.176	-----
125	17.0	-----	36.250	-----

Station 11; 20-47N, 83-17W; 17 August 1975; 0200Z

27	23.9	-----	-----	-----
50	17.3	-----	-----	-----
77	11.9	-----	-----	-----
102	7.2	-----	-----	-----

CRUISE 75-G-10 R/V GYRE TEXAS A&M UNIVERSITY

Z	H ₂	O ₂	Salinity	Temperature
Station 15; 27-03N, 83-45W; 22 August 1975; 1130Z				
5	9.2	4.497	36.127	-----
10	7.3	4.470	36.130	-----
25	3.3	4.625	-----	-----
40	17.7	4.839	36.379	-----
Station 16; 26-38N, 84-24W; 22 August 1975; 1700Z				
10	6.9	4.752	36.266	-----
20	11.5	4.588	36.267	-----
30	4.1	4.841	36.291	-----
40	8.7	4.824	36.311	-----
Station 17; 26-05N, 85-17W; 23 August 1975; 1400Z				
15	13.1	-----	36.228	-----
25	10.4	-----	36.276	-----
50	6.1	-----	36.471	-----
125	22.4	-----	36.406	-----

CRUISE Y-7510D R/V YAQUINA OREGON STATE UNIVERSITY

Z	H ₂	O ₂	Salinity	Temperature
---	----------------	----------------	----------	-------------

Station 1; 45-00N, 125-07W; 30 October 1975; 1930Z; Cast 1

10	21.5	-----	32.309	-----
20	7.6	-----	-----	-----
50	0.2	-----	-----	-----
70	0.0	4.391	-----	-----
120	10.6	3.622	-----	-----

Station 1; 45-01N, 125-08W; 30 October 1975; 2230Z; Cast 2

9	2.7	-----	-----	-----
11	12.8	-----	-----	-----
19	5.8	-----	-----	-----
21	4.0	-----	-----	-----
49	1.0	-----	-----	-----
51	0.0	-----	-----	-----
124	21.2	-----	-----	-----
199	9.0	-----	-----	-----
201	17.8	-----	-----	-----

Station 2; 44-48N, 124-32W; 31 October 1975; 0500Z

11	6.8	6.030	-----	-----
21	10.5	6.031	-----	-----
50	2.3	5.433	-----	-----
100	0.0	3.619	-----	-----
151	4.6	3.067	-----	-----
200	8.5	2.390	-----	-----

CRUISE W-7610A R/V WECOMA OREGON STATE UNIVERSITY

Z	H ₂	O ₂	Salinity	Temperature
Station NH-10				
10	26.0	7.17	32.339	-----
20	6.0	7.14	32.513	-----
40	2.5	5.12	32.857	-----
50	4.0	-----	33.136	-----

CRUISE PLIEADES II R/V MELVILLE S.I.O.

Z	H ₂	O ₂	Salinity	Temperature
Station 47; 0-36N, 86-09W; 24 June 1976; 0700Z				
9	14.0	4.74	34.223	26.36
73	11.4	2.97	34.251	19.96
343	9.4	0.46	34.367	12.00
538	8.4	0.41	34.638	7.90
Station 58; 0-36N, 86-09W; 26 June 1976; 1100Z				
6	13.9	4.78	33.977	26.40
276	5.1	1.60	34.952	12.00
463	5.8	0.30	34.668	8.38
Station 91; 0-42N, 86-02W; 3 July 1976; 0700Z				
8	12.1	4.61	33.450	27.00
8	10.3	4.61	33.450	27.00
107	8.1	2.60	35.126	17.51
497	1.8	0.36	34.645	8.00
725	6.6	0.98	34.578	6.00