A SYSTEM FOR THE ANALYSIS OF DISSOLVED OXYGEN, NITROGEN AND ARGON IN NATURAL WATERS

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Abstract

A complete system has been developed for the shipboard analysis of dissolved oxygen, argon and nitrogen. The system includes an <u>in</u> <u>situ</u> sampler, chromatographic analysis for oxygen, argon and nitrogen and three modes of calibration. The system has been tested in the laboratory and at sea. Estimations of the composition of argon, oxygen and nitrogen in dry air and in air-saturated water are reported. Sea trials indicated that thermistor detectors should be used in the chromatograph instead of hot-filament detectors.

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A more complete knowledge of the distribution of dissolved nitrogen, ygen and argon would provide useful information for further unraveling e processes which influence the ocean. The physical oceanographer has de use of the distribution of dissolved oxygen to aid in the identifica-К on of water types. Dissolved oxygen was used by Richards and Redfield 954) to discriminate Gulf Stream from Sargasso Sea waters. In his core thod Wüst (1964) used dissolved oxygen along with salinity and temperare to characterize water masses and traced the movement and spreading Antarctic water into the Caribbean. Because oxygen is extremely biogically active, these methods have been applied only to those parts of e ocean where biological activity is very low. Nitrogen and argon, rticularly the latter, would be much more suited for tracing application t the lack of sufficient knowledge on the distribution of these elements nders this.

The recent investigations of chemical oceanographers on the disibution of dissolved nitrogen, argon and neon, krypton, xenon have phasized that the usually accepted definition of saturation is a rough proximation which can veil the processes which govern the solution of ses. However, there is little agreement beyond that. Craig, Weiss and arke (1967) reviewed the more recent work in dissolved gases distribution d underlined the disagreement existing on the extent of deviation from turation. There has also been more thought on the processes which result these deviations. Benson (1965) has reviewed processes influencing dislved gas concentrations and suggests measurements which might be made to vestigate these processes.

The trend of studies of dissolved gas concentrations clearly indicates 6 the need for more accurate analyses of dissolved gases to improve knowledge of gas distributions in the oceans and to aid evaluation of suggested techniques for investigating the processes governing gas solution.

The difficulty involved in analyzing samples for dissolved gas concentrations has been the major obstacle to improving our knowledge of the distribution of the dissolved gases. Of the three gases, nitrogen is very unreactive and argon is inert. Only dissolved oxygen has been thoroughly surveyed because it can be determined by the Winkler method, a fairly complex titrimetric analysis. Carritt and Carpenter (1966) have reviewed the Winkler method and discussed its limitations. Nitrogen analysis has received much less attention. Rakestraw and Emmel (1937) developed an analysis for nitrogen using liquid sodium, but it was too time consuming to allow rapid analyses. Nitrogen has also been determined gasometrically, usually without any attempt to correct for the presence of inert gases.

In a series of papers Swinnerton, Linnenbom, and Cheek (1962a, 1962b) developed a technique for liquid-phase injection for analyzing dissolved gases. The sample is injected into a vertical glass tube, blocked at the lower end with a porous glass frit and through which flows the chromatograph carrier. Driven by the gas tension between the helium carrier and the sample, the dissolved gases are swept into the carrier. Because of the difficulty involved in separation, oxygen and argon emerged as one peak, nitrogen as another. The apparatus was used at sea along with the standard and modified Winkler method. The results were evaluated by Linnenbaum <u>et al</u> (1965). Swinnerton (1964) also described a method for separating argon and oxygen wherein oxygen was reacted with the hydrogen carrier over a palladium catalyst to form water. Two passes were required to determine argon, oxygen and nitrogen. Craig, Weiss, and Clarke (1967) used a molecular sieve column cooled to -78°C to separate oxygen and argon. The column was then warmed to drive off nitrogen. Samples taken at sea were treated by Toepler, pumping dissolved gases into sample tubes which were sealed then analyzed in a land-based laboratory.

This present system for the analysis of dissolved argon, oxygen and nitrogen in natural waters was designed specifically for use aboard ship. To avoid possibility of contamination arising from transferring the aliquot, a new sampler was designed, the sample bottle of which fits directly onto The sample aliquots were injected using the the analytic apparatus. principle developed by Swinnerton, et al (1962a, 1962b). Argon, oxygen and nitrogen was completely separated on a 30-foot column of molecular sieve 5A at -25°C, a temperature easily maintained by a commercial refrigeration unit. Electrolytic generation of oxygen and nitrogen and argon gas-injection were used for calibrating chromatograph response. Hot-filament thermal-conductivity detectors, sensitive to ship accelerations, hindered the chromatographic system from being used on its first sea trial. Thermistor detectors, insensitive to accelerations, could easily be substituted. Estimations of atmospheric composition, dissolved gases in distilled water and dissolved gases in Walden Pond water were used to evaluate the system on land.

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AN IN SITU SAMPLER

To minimize the possibility of air contamination which arises in drawing an aliquot from a water sampler and transferring the aliquot to the analytic apparatus, an in situ sampler was designed, the bottle of which fits directly onto the analytic apparatus. Figure (1) is a photograph of the sampler and Figure (2) is a schematic representation of it. An 8ounce rubber battery-acid bulb was used to draw the water through the glass sampling apparatus. The sample bottle was fashioned from a four-way stopcock and a piece of 10 mm glass tubing (Figure 3). This stopcock has 2 mm capillary arms, and a key with two 90° unconnected bore holes. To construct the sample bottle, two adjacent arms of the stopcock were joined to a length of 10 mm O.D. pyrex tube of approximately 5 ml volume while the other two arms were fitted with male 12/5 ground-glass ball joints. The rubber bulb was connected to a female ground-glass joint through a convenient length of rubber tubing. One arm of the sample bottle was connected to the rubber bulb. The other leads to the "trigger" of the sampler, which was borrowed from the Cobet sterile sampler. The trigger was 10 cm of 2 mm glass tube sealed at one end; its other end was connected to the sample bottle through a short length of Tygon tubing, and a female groundglass joint. The trigger was laid across the hinge which attached the sampler to the hydrowire. When broken by a messenger, the sampling system was opened and the rubber bulb drew water through the sample bottle. A repeating messenger would be released at the time of triggering if it had

[&]quot;These stopcocks (JA-4490 stopcock, 2 mm bore but with capillary side-arms, as in JS-3895) are available on special order from Scientific Glass Apparatus Co., Inc., 735 Broad Street, Bloomfield, N. J. 07003.



FIGURE 1 <u>In Situ</u> Sampler

SCHEMATIC OF WATER SAMPLER



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FIGURE 2





Glass Sample Bottle, turned to Position I

been attached to the hydrowire below the sampler and tethered with a wire looped around the trigger. Care was taken so that the incoming messenger did not pin the tethering wire to the hinge. The bulb, sample bottle, and trigger were placed into a brass frame which was designed to hold the bottle, attach it to the hydrowire and provide some physical protection. The sampling bottle was held in place by small Castalloy clamps.

To prepare the sampler for lowering, the first step was to fill half of the rubber bulb with water, then the ground-glass joints were made up and secured with clamps. A glass trigger filled with water was kept handy. With the stopcock turned to Position I (Figure 3), which allows flow throughout the apparatus, all of the air and as much of the water as possible was forced from the apparatus by squeezing the bulb. The bulb was emptied as completely as possible, and the glass-sample bottle and tubing to the capillary trigger were free of air bubbles. Then the open end of the glass capillary was inserted into the rubber tube leading to the sample bottle. The trigger was then placed in the brackets on the hinge, and the sampler was prepared for attachment to the hydrowire. The sampler was easily secured to the wire by first guiding the wire through the split washer at the bottom of the frame then resting the wire against the stop in the hinge and securing the clamp with a dog bolt. A repeating messenger could have been added at this time.

After the sample has been drawn and before the sampler was taken from the wire, the stopcock was turned to Position II (Figure 4). Then the

[&]quot;If bubbles adhere to the interior of the sample bottle or in the tubing between the bottle and the capillary trigger, they can be eliminated by drawing air back into the volume so that the meniscus is near the bubble. If the meniscus worked past the bubble a few times, the bubble will break.





Glass Sample Volume, turned to Position II

sampler was removed from the wire, and the sample bottle set aside for analysis. When the stopcock was in Position II, the aliquot was isolated in a closed loop so that when the sample bottle was removed from the frame, the outer arms of the sample bottle were emptied and exposed to air without fear of contaminating the sample.

Precautions Against Contamination

With a sampler such as the one that has been designed here, there are opportunities for contamination. The possibility of most of these occurring has been minimized through design. A first possibility is that water, used to cock the sampler, will remain in the sample bottle and contaminate the <u>in situ</u> sample drawn into the volume. Flushing 250 ml of <u>in</u> <u>situ</u> water through the 5 ml volume of the bottle provides adequate dilution so that the concentration of contaminating water is reduced to less than one part per thousand. The efficiency of the flushing action was demonstrated by observing a better than 1,000 attenuation of a rhodamine dye concentration used to cock the sampler before it drew a sample of water.

A second possibility is that after the sample has been drawn <u>in situ</u>, the aliquot in the sample bottle could be contaminated by water in the bulb, or water from other depths, as the sampler is raised. To protect the aliquot in the sample bottle from these, 10 cm of capillary tubing have been added on either side of the sample bottle to present a diffusion barrier.

A third possibility is that great pressures acting on the compressibility of the materials involved will lead to errors. The volume of the glass-sample bottle could be affected. The volume of the rubber bulb could become a function of depth and act as a pump as the sampler is drawn from great depths. The compressibility of water itself could also become important. If the sampler is to be used much below 1,500 meters, these pressure effects should be investigated.

An Evaluation of the Sampler

The water sampler was used during a cruise in March, 1968, aboard the RV/CHAIN to the Sargasso Sea. It worked quite well but for one exception: the rubber of the squeeze bulbs became turgid and "lifeless" at temperatures below 8°C. If another type of rubber does not overcome this obstacle, a mechanically driven pump should be used.

THE CHROMATOGRAPHIC SYSTEM

The analytic system is built around a highly modified Varian Aerograph Model 90P-3 Gas Chromatograph with a four-filament thermal conductivity detector (Figure 5). Tungsten-3% rhenium filaments were used for added sensitivity and stability. The major modifications included liquid-phase injection and a refrigerated column. The column connected to the chromatograph in the usual manner, was placed alongside the chromatograph in a six-liter stainless steel Dewar. The output from the detectors was recorded and integrated on a Speedomax Wlmv., lsec. recorder equipped with a Disc Integrator.

The Column

Perhaps most crucial to the concept of a gas chromatographic analysis for major air components is the chromatographic separation of argon and oxygen. Swinnerton <u>et al</u> (1962a) separated combined oxygen and argon from nitrogen on Poropak Q and then estimated argon contamination in the combined peak from the concentration of N₂. N₂ was assumed to be saturated



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COLUMN -25°C



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with respect to temperature and salinity and unaltered by physical, chemical or biochemical processes. The concentration of Ar was then computed from atmospheric composition and gas solubility data.

Literature in chromatographic journals indicated that Linde molecular sieve 5\AA can be used as a column packing for the separation of argon, oxygen and nitrogen in quality control for gas process plants. However, since very similar physical adsorption characteristics of argon and oxygen give them almost identical retention time at room temperature, special column conditions must be used to encourage separation. Lard and Horn (1960) reported the first separations of argon and oxygen on a six-foot long 1/2" 0.D. column of molecular sieve 5\AA cooled to -79 °C. Later Gunter and Musgrave (1966) separated oxygen and argon on a sixteen-foot column (1/4") cooled to -9 °C in a brine slush; this unit was designed for field gas analyses. A column temperature of -9 °C produced good separations of argon and oxygen at 6.5 and 7.5 minutes with the drawback that nitrogen was eluted at 29 minutes, about five times as long as oxygen and argon.

The column used in this system was thirty feet, 1/4" O.D. copper refrigerator tubing 1 packed with molecular sieve 5Å 30/60 mesh. This longer length assures separation of argon and oxygen when a liquid-phase injection is used, which tends to produce a longer injection time that the gas injection. The column was evenly filled and thoroughly settled to obtain even-flow characteristics throughout the column. It was packed by drawing the molecular sieve into the column with both vacuum and gravity. The tubing was hung in a stairwell with a vacuum pump at the lower end

Refrigerator tubing is stressed because it is the cleanest available. Commercial tubing is apt to be contaminated with organics used in the extrusion process, these will poison the column.

while molecular sieve was added at the other. Settling was encouraged by passing a vibrator up and down the column.

To drive excess water from the sieve structure and thus activate the molecular sieve, it was heated to 300°C and purged with dry-ice-trapped δ helium at 100 cc/min for 24 hours.

A column temperature of -25°C was selected because this temperature can be held by commercially available refrigerators.¹ This system used a Varian Aerograph Refrigerated Bath (Catalog No. 02-248) to cool antifreeze in a stainless steel Dewar which contained helium traps, and the molecular sieve column. Temperature regulation was not critical as long as excursions were in the order of ± 2 °C. With these fluctuations the recorder base line remained steady and separation was not noticeably affected.

Liquid-Phase Injection Manifold

The greatest modification to the chromatograph was the manifold system and scrubbing apparatus to accommodate liquid-phase injection (Figure 6). The manifold controlled helium carrier and an independent helium supply to the scrubbers of the liquid-phase injection apparatus which plugged into AA. The manifold was set to several different modes which were used in the course of liquid-phase injection. With Valve 1 open, and 2 and 3 closed, carrier flow bypassed the scrubbers. This mode was used when a sample bottle was attached in preparation for injection. With 4 and 5 open helium from the independent supply was run through the liquid-phase injection unit to purge air from the lines (Figure 7). With Valves 1, 4, and 5 closed, and 2 and 3 open, liquid-phase injection was possible (Figure 8). The standby mode was 1 open, and the remaining valves closed.

Acceptable separations were obtained when the column was cooled to -10°C with brine slurry.











FIGURE 8

A tube filled with Anhydrone (MyClO₄) was placed in the carrier line before the column to dry the carrier moistened during injection. All plumbing within the manifold system was 1/4" copper refrigeration tubing joined with Swagelok brass fittings. The liquid injection unit was plugged into the manifold with Swagelok quick-disconnect plugs.

C Liquid-Phase Injection Apparatus

The principal component of the liquid-phase injection unit was the scrubber which was designed after that described by Swinnerton <u>et al</u> (1962a). It was constructed from a 10 mm glass sealing tube topped with a 10 cm length of 10 mm tube. The top of that tube was drawn down to 1/4" 0.D. to fit a Swagelok fitting. The sealing tube below the frit was joined to 7 mm capillary tubing and ended in a female 12/5 ground-glass ball joint. This joint accommodated one of the sides of the sample bottle. The other side of the sample bottle went to another female 12/5 ground-glass joint then to 1/4" 0.D. glass which went into a Swagelok fitting. The two 1/4" 0.D. glass ends were secured to Swagelok quick-disconnect fittings by using nylon ferrules. These disconnect fittings then plugged into the manifold of the chromatograph as schematized in Figures 7 and 8 and described in the previous section.

Chromatograph Operation

Helium carrier flow regulated out of a tank at 60 psig was trapped at -25°C in the refrigerated Dewar. The helium flow rate was maintained at 100 ml/min with the flow-control valve on the chromatograph. The independent helium supply to the manifold was regulated at 20 psig and trapped at -25°C. To promote maximum detector sensitivity, a filament

current of 250 ma was applied, and the detector temperature was adjusted to 38°C. The signal attenuator was adjusted to the proper setting as the peaks were anticipated: usually 1 for argon, 4 for oxygen, and 2 for nitrogen.

Liquid-Phase Injection Procedure

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To prepare to inject a liquid sample (see section on sampling for a description of the sample bottle and sampling procedure), the groundglass joints of the sample bottle were mated to the injection apparatus and secured with spring clamps (since the injector was subjected to 20 psig, it was necessary to use more than one clamp per joint to prevent leaking). With Valves 2 and 3 closed, and 1, 4, and 5 opened (Figure 6), the helium from the independent supply swept through the scrubber and capillary tubing to the sample bottle, diluting and removing all traces of air after 5 minutes (Figure 7). Valves 3 and 4 were then closed. To initiate liquid-phase injection, Valve 1 was closed and Valves 2 and 3 were opened. Then the key of the glass stopcock was turned 90° (in either direction), and the helium carrier forced the aliquot from the sample bottle into the scrubber where a fine stream of bubbles stripped the dissolved air from the liquid into the carrier helium (Figure 8). The stripping process was allowed to continue for 5 minutes. Then Valve 1 was opened, and 2 and 3 were closed. The sample bottle was then removed, and the next bottle prepared.

The Detector Circuit, Recorder and Integrator

The signal from the Wheatstone bridge of the chromatograph detector circuit was displayed on a Speedomax W 1 mv, 1 sec., strip chart recorder.

Integration was simultaneously performed by a ball and disc integrator from the Disc-Integrator Company. Signal attenuation was manually adjusted on the chromatograph. Attenuation was available in steps of 2ⁿ, where

$$n = 0, 1, 2....9$$

The accuracy of each of these units was stated to be 0.1% although, in later discussions on the response of the analytic system, it shall be shown that the combined response of the detector circuit, recorder and integrator to replicate gas injections was reproducible to 0.4% at best.

Monitoring the Response to a Sample Analysis and Programmed Injection

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The widely differing peak heights observed during the analysis of either gas- or liquid-phase injection of an air component and the desire to obtain maximum sensitivity possible for each gas required that the attenuation be manually adjusted. The attenuator was set to 1 while argon was eluted, then switched to 8 for oxygen. Nitrogen was recorded at 2.

Because nitrogen is eluted about 2.5 hours, compared to 0.5 hours for argon and oxygen, it was possible to program an analysis so that several proceeded simultaneously on the same column. A sample was injected. Then after the response to argon and oxygen has been recorded, another sample was injected. Four injections may be made until there is a danger of overlapping the nitrogen peaks with argon and oxygen peaks. Total time to analyze four samples for oxygen, nitrogen and argon was five hours.

An Evaluation of the Chromatographic System

The system has been used extensively in the laboratory and tested at sea aboard the RV/CHAIN during March, 1968, on a cruise to the Sargasso

Sea. The system was completely and easily operable on land. At sea a periodic variation in the base line, coinciding with ship accelerations, was noticed. The problem was finally assigned to the hot-wire filaments when it was noticed that the noise was least when the filaments were aligned parallel to the roll axis of the ship. This problem can be easily solved by replacing the hot-wire filaments with thermistor detectors supplied by Gow-Mac. Thermistors will give not only stability at sea, but an 8-fold increase in sensitivity.

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CALIBRATING THE CHROMATOGRAPH

When a chromatograph is used as an instrument of quantitative analysis, one concern is the conversion of a measured response to an accurate estimate of the quantity of substance to pass the detector. In the present system, the time integral of a detector voltage, directly proportional to the concentration of the substance, is the measured response. A strip chart recorder replaces the voltage-time integral with an area by equating voltage and time to linear distances. Calibration then is measuring the linear factor necessary to convert area into an accurate estimate of the quantity of substance that passed the detector.

This system uses a thermal-conductivity detector; therefore, the calibration factor is a measure of a heat transfer coefficient for the detector. This calibration factor T_X is called the molar coefficient of heat conductance for X; its units are micro-moles per unit-area at Attenuation 1.

Since T_X is a measure of machine response, it is affected by several factors. It is a function of the carrier gas; the carrier gas in this

study was helium The following are machine variables which can affect T_X : carrier flow rate, filament current, filament block temperature, geometry of the detector, and the material used for filaments and the condition of the filaments. T_X varies from one chromatograph to another and drifts with time in the same machine.

Messner et al (1959) found that a relative measure of two T_v 's

 $R_{X:Y} = T_X:T_Y,$

where X and Y are two different substances, is constant among all machines providing the T_X 's, forming $R_{X:Y}$, have been measured on the one machine under identical conditions and that the same carrier gas and thermal-conductivity detection are used in all machines. The constancy of $R_{X:Y}$ should greatly ease the chore of machine calibration. By calculating $R_{N_2:02}$ and $R_{Ar:02}$, only calibration for oxygen T_{02} would be necessary to calculate T_{0_2} , T_{N_2} , and T_{Ar} . In this study the constancy of $R_{X \cdot Y}$ was used only in the calculation of T_{Ar} . There was not the time to prove the constancy of $R_{X,Y}$ to one part per thousand, particularly relative to variations in concentration of X and Y. However, even if there were a slight variation of R_{X:Y} with concentration, calibration work could be greatly $R_{Ar:0_2}$ and $R_{N_2:0_2}$ could be plotted for constant concentration of simplified. oxygen against varying argon and nitrogen concentrations expressed in peak height. Although the work involved in determining the R_{X:Y}'s for a number of concentrations might be tedious, it would only need to be done once.

It is intriguing that if $R_{Ar:0_2}$, as a function of argon peak area, and $R_{N_2:0_2}$, as a function of nitrogen peak area, were determined for a single amount of oxygen, then these functions would apply to all chromatographic

systems using helium carrier and hot-filament or thermistor heat-conductivity detectors.

Calibration Procedures

The major problem encountered in accurately determining T_X is a method of accurately injecting small amounts of substance into the chromatograph. The present analytical system offered three ways of solving this problem:

(1) A gas sample valve (a standard Aerograph Gas Sampling Valve, Model No. 57034) allowed the injection of gas samples whose volumes can be repeated to $\pm 0.1\%$ although the exact volume was unknown.

(2) Oxygen and nitrogen were electrolytically generated in the scrubber. Accurate measurement of the equivalents of electricity allowed a precise estimate of the gas produced.

(3) Injection of measured volumes of water saturated with gas at a known temperature and pressure can provide a third way if the solubility of the gas is well known. The solubility of oxygen, argon and nitrogen is well established (Green and Carritt (1967), Klots and Benson (1963), and Douglas (1965)).

A more detailed discussion of the equipment and procedure will follow.

Of the three methods available in the present analytical system, a combination of gas-phase injection through the gas-sample valve and injection of electrolytically produced gas was used to calculate T_{0_2} , T_{N_2} , T_{Ar} . T $_{0_2}$ and T_{N_2} were estimated by electrolytically generated gas calibration. Gas-phase injection was used to calculate $R_{Ar:0_2}$. Then each time T_{0_2} was calculated, T_{Ar} was found thus:

$$T_{Ar} = R_{Ar:0_2} \times T_{0_2}$$

Although the volume of the gas-sample valve was not known accurately, this is not important for a calculation of R. In forming the ratio, the volume cancels out. The injection of gas-saturated water samples was not used for calibration since it was decided to reserve this method as a means of testing the accuracy of the calibration technique, employing electrolytically generated gas and gas-phase injection through the sample valve.

Gas-Injection Calibration

A Varian Aerograph six-way gas-sample valve was installed in the chromatograph to greatly simplify gas-phase injection. According to the claims of Varian Aerograph, the gas-sample valve allows the replication of a volume to 0.1%. The exact volume injected is an unknown quantity. For example, the gas-sample valve installed had a 250 micro-liter sample loop; the delivered volume was later found to be closer to 720 micro-liters. In calculating T_X the quantity injected is calculated from the ideal gas law. Temperature was taken from a thermocouple taped to the sample loop of the gas-sample valve. The pressure was assumed to be ambient because of the injection procedure. Because of uncertainty in these measures of temperature, pressure, and volume, gas-phase injection was never used to calculate T_X . However, these uncertainties become less bothersome in calculating $R_{X:Y:}$

$$T_{X} = \frac{P_{X}V}{T_{X}RA_{X}}$$
$$T_{Y} = \frac{P_{Y}V}{T_{y}RA_{y}}$$

 $R_{X:Y} = \frac{P_X T_Y A_Y}{P_Y T_X A_X}$

The volume cancels out. Any absolute error in the determination of temperature or pressure is greatly reduced by forming the ratio.

System Response to Gas-Phase Injection

Replicate injections of oxygen, nitrogen and argon were made to study the response of the system to gas-phase injection. The gas-sample valve, column, detector, recorder and integrator were the units specifically involved. Without knowing the volume, it was impossible to know the quantity of gas injected. Instead a number proportionate to the moles injected was used since the constant of proportionality would be identical for all injections:

$$n = \frac{pv}{TR}$$
$$n = (p/T)k$$

where k = v/R = constant.

Then

$$T'_{x} = (p/T)k \div S_{x}$$

 $S_{x} = peak area at Attenuation 1.$

So although the numerical value of T_X could not be calculated, a number proportional to T_X was; and these numbers were used to study the distribution of responses.

The results for replicate injections of argon, oxygen and nitrogen are listed in Table (1). The system showed well-defined response for the three gases since the three measured means had standard deviations of less than 1%. Calculations of the 95% confidence limits for the real mean and standard deviation, as estimated from the sample sizes, measured mean and standard deviation, also support this conclusion because the intervals are in the order of 1% the measured means.

Of the statistics for the three gases, notice that those of nitrogen appear to be the best with a standard deviation of .25% the measured mean. (Table 1.) The 95% confidence limits for the real mean and standard deviation are correspondingly low. The nitrogen numbers are more precise compared to oxygen and argon as a result of the behavior of the column and the recorder. The gas-sample valve always injected about the same quantity; fluctuations of 5% may occur because of changes in temperature and pressure. And because the $\mathrm{T}_{\mathrm{x}}\,'\mathrm{s}$ for oxygen, argon and nitrogen are within 10%, areas adjusted to Attenuation 1 are within 10%. However, due to the characteristics of the column, argon and oxygen emerged about 20 minutes after injection as high, narrow peaks while nitrogen emerged at 2.5 hours as a low and broad peak. Since all peaks must be read by a 1 mv recorder, the oxygen and argon peaks were highly attenuated, and the nitrogen peak was not. As read from the strip chart, oxygen and argon had areas of approximately 2,000 (arbitrary units) at Attenuation 64X while the much broader, less attenuated nitrogen peak integrated to 20,000 at Attenuation 8X. Nitrogen was measured with about ten times the resolution as oxygen and argon, and a comparison of the standard deviations bears this out. Although the inherent advantages of integrating with high resolution can be

TABLE 1

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Gas ·	Number of Samples	T x 10 ⁴	95% Confidence Interval_for µ _T in % of T	Measured Std. Dev. <u>s</u> in % of T	95% Confidence Interval_for σ _T in % of T
Ar	12	1.3986	$1.3986 \times 10^{-4} \pm .47\%$.74%	$.52\% \stackrel{<}{=} \sigma_{\rm Ar} < 1.20\%$
N2	10	3.6601	$3.6601 \times 10^{-4} + .17\%$.24%	.17% ≤ σ _{N2} < .45%
0 ₂	9	2.8022	$2.8022 \times 10^{-4} \pm .26\%$.96%	.69% <u>-</u> σ ₀₂ < 1.69%

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Statistical Analysis of Gas-Phase Injection Data

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demonstrated only now statistically in gas-phase injection, it is recommended that the resolution of integration be equal for all peaks so that the accuracy of detection is not sacrificed by attenuating. Compared to the present method of integration, an electronic integrator would be advantageous because in electronic integration, area is measured by counting a frequency proportional to the chromatograph signal. Since the electronic integrator can work with an unattenuated signal, resolution is not sacrificed through attenuation.

Electrolytic Calibration

The liquid-phase injection of oxygen and nitrogen electrolytically generated in the scrubber was used to calculate T_{0_2} and T_{N_2} . This method offers several inherent advantages. First, the electrolytic calibration technique required a liquid-phase injection. Thus the calibration procedure and analysis of liquid samples were performed in the same apparatus and in a similar manner. Secondly, the limiting accuracy of the technique was the precise measurement of a small electric current, time, and the efficiency of the electrochemical reactions at the electrodes. Lastly, since the quantity of gas generated depended upon the time a current is passed through the electrolyte, it was possible to investigate T_{0_2} and T_{N_2} with varied quantities of injected gas. The present system could investigate quantities of oxygen and nitrogen varying from 1 to 100 micro-moles. With little adaptation, quantities lower by a factor of 100 could be generated.

The techniques of electrolytic generation of oxygen and nitrogen are taken from Lingane (1958). Bright platinum electrodes each of total area less than 1 cm² were sealed into the scrubbing chamber. (In this work

the response calibrations of oxygen and nitrogen was carried out in the same scrubbing chamber used for the analysis of water samples.)

<u>Oxygen calibration by electrolysis</u>. Lingane (1958) states that two general conditions must be met to assure accuracy in electrolytic gas \Leftrightarrow generation. It is most important that the 0.5 M potassium sulfate electrolyte be scrupulously pure. In particular it must be free of Fe^{II} and Fe^{III} which can undergo an oxidation reduction cycle leading to large negative results. To insure the purity of the electrolyte, the solution was stored in an anodic mercury stripping cell. Spot checks for iron were made with a colorimetric thiocyanate test described by Sandell (1950).

The second condition stressed by Lingane is that the current density on the electrodes exceed 50 ma/cm². In this system the area of the electrodes was a little under 1 cm² and the applied current was 64.3 ma. A Leeds and Northrup coulometric analyzer, Catalog No. 7960, was the constant current source.

To initiate an oxygen response calibration, about 5 ml of 0.5 M potassium sulfate was injected into the scrubbing chamber and purged with helium for ten minutes to remove all traces of air. Then with the helium carrier scrubbing the electrolyte, the current was applied to the electrodes for the approximate time required to produce the desired amount of oxygen. The micro-coulombs passed through the cell were read directly from the coulometric analyzer. The theoretical conversion yield of the reaction

$$H_2^0 \rightarrow 1/2 \ 0_2^{} + H_2^{}$$

is 0.2500 micro-moles of oxygen per micro-equivalent of electrons. However, due to inescapable side-reactions, the experimental yield is somewhat

smaller. Using the potassium sulfate electrolyte, Lingane (1958) has found the experimental value to be 0.2496 micro-moles oxygen/micro-equivalent of electrons, reproducible to 0.1%. It must be emphasized that the yield reported by Lingane was obtained in a system extremely free of contamination, a claim that was difficult to make for the conditions for electrolysis in the present system since electrolysis took place in the same chamber where samples were scrubbed. It would be advisable in any future system to install a separate scrubbing chamber which is used solely for the purpose of electrolytic calibration. This still would allow calibration under conditions almost parallel to analysis and keep the electrolysis cell free from unnecessary contamination.

<u>Results of electrolytic oxygen calibration</u>. The reproducibility of this calibration technique represents the combined reproducibilities of several parts of the analytic system: electrolytic generation of oxygen, the gas-scrubbing technique, column, detector, recorder and integrator. Since there were indications of nonlinearity of response with variation of sample size, only values for T_{0_2} calculated from similar amounts of oxygen were used in determining the statistics. This practice seems reasonable since the calibration technique was to calculate T_{0_2} by generating a quantity of oxygen approximately equal the quantity to be analyzed. For twelve determinations of T_{0_2} , the measured values of the mean \overline{T}_{0_2} and standard deviation σ_{0_2} were, respectively, 1.7708 x 10^{-4} micro-moles/unit area, and 3.09 x 10^{-6} micro-moles/unit area; the standard deviation was 1.23% of \overline{T}_{0_2} . With 95% confidence the real mean is within the interval

 $1.7708 \times 10^{-4} \pm 1.11\%$

and the real standard deviation within the interval

$$(2.19 \leq \sigma_{02} < 0-5.25) \times 10^{-6},$$

or expressed in percentages of the measured mean

$$(1.24\% \leq \sigma_{0_2} < 2.96\%).$$

By accepting the measured mean and standard deviation to be the real mean and standard deviation, the power of the liquid-phase injection apparatus to measure \overline{T}_{0_2} and differences from \overline{T}_{0_2} have been plotted as a function of the number of analyses (Figure 9). The lower curve on the plot is the minimum deviation from \overline{T}_{0_2} that can be detected with 95% confidence; the units of the ordinate is percent of \overline{T}_{0_2} . On the upper section of the plot are the intervals within which \overline{T}_{0_2} can be accepted as verified with 95% confidence.

One would expect the distribution of machine errors in the analyses of natural water samples to be the same as the distribution of errors obtained in measuring \overline{T}_X . Thus for a one-sample analysis, a value for dissolved oxygen that is within the interval 100 $\pm 3.4\%$ of saturation as calculated from solubility tables is accepted as being saturated with 95% confidence. That a 1% variation from saturation can be detected by analyzing about 50 samples indicates much to be gained by improving the accuracy of calibration. This can be helped by improving the conditions for the electrolysis reaction. Another factor influencing the large value of σ_{02} is that the T_{02} represents numbers taken over the span of two weeks, long enough for noticeable machine drift to occur. A fairer estimate of σ_{02} would be made if only values of T_{02} were used which had been estimated within two days. Figure 10 plots the size of the standard deviation in





FIGURE 10

percent of the mean against the sample size required to detect a 1% variation from the mean at 95% confidence level. The plot indicates that a value for the standard deviation of 0.5% would give much more powerful results with many fewer samples. This value is probably attainable with the modifications previously mentioned.

<u>Nitrogen calibration by electrolysis</u>. Lingane (1958) also discussed the nitrogen-hydrogen coulometer. The electrolytic cell for the present system was the same as that described for electrolytic generation of oxygen. The electrolyte was very pure 0.1 M hydrazine sulfate. One restriction for the generation of oxygen, eased for nitrogen, is the value of the minimum allowable current density. For the generation of nitrogen, it may be as low as 7 ma/cm². The overall reaction is

$$N_2H_2^+ = N_2 + 2H_2 + H^+$$

As for oxygen the theoretical yield is .2500 micro-mole N_2 /micro-equivalent electrons. Lingane reports an actual yield of .2494 micro-moles N_2 /microequivalent of electrons with a reproducibility of $\pm 3\%$. Again it must be stressed that Lingane observed this conversion with very clean apparatus and pure electrolyte. In this work all measures of T_{N_2} were made using the same scrubber for generating nitrogen that was used for analysis of natural water samples. There is the possibility that measured T_{N_2} values were biased because of contaminated electrolyte. Again it is recommended that a separate cell be used only for measuring T_{N_2} .

<u>Results of electrolytic nitrogen calibration</u>. Measures of T_{N_2} were made in the same manner as for T_{0_2} . For eight estimates of T_{N_2} , the

measured mean \overline{T}_{N_2} and standard deviation σ_{N_2} were, respectively, 1.5722 x 10^{-4} and 2.969 x 10^{-6} or 1.89% \overline{T}_{N} . With 95% confidence the real mean falls within the interval

$$(1.5722 \pm 1.64\%) \times 10^{-4}$$

The real standard deviation is within

$$(3.853 \le \sigma < 36.50) \times 10^{-8}$$

or in terms of percent of $\overline{T}_{N_{O}}$

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1.25% \leq \sigma < 3.84\%.
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The power of analysis for dissolved nitrogen has been calculated in Figure 11. Two curves are plotted against the number of analysis. The plot on the upper portion of the figure shows the 95% confidence interval for accepting a hypothesized value, such as saturation. The lower curve is the difference from the hypothesized value which can be accepted with 95% confidence. These numbers indicate that the reproducibility of the electrolytic calibration technique for nitrogen should be improved. As it was indicated in Figure (10) (previous section), the standard deviation should be 0.5% the mean so that one sample can detect variations from a hypothesized mean of 1%. This could best be done by using a separate scrubbing cell for nitrogen calibrations.

Another factor causing a large value of σ_{N_2} is that values of T_{N_2} used in forming the mean and standard deviation were taken from calibrations that were separated by weeks. Any long-term drift in the real value



of T_{N_2} would be manifest by enlarging the value of the measured standard deviation. Perhaps better estimates of the mean and standard deviation could be calculated if many values of T_{N_2} were calculated over the period of two days.

A DETERMINATION OF THE COMPOSITION OF

THE ATMOSPHERE

As a test of the ability to separate and analyze oxygen, nitrogen and argon, two gas injections of atmospheric air were made and the results analyzed. The injections were made through the gas-sample valve by pumping air through an Anhydrone trap to collect water vapor, to the gas-sample valve. The injections were made as described before. To convert integrated area to moles of gas, T_{N_2} and T_0 were determined electrolytically while T_{Ar} was determined from

$$T_{Ar} = R_{Ar:0_2} \times T_{0_2}$$
.

Thus the values determined depend only upon the measurement of a current, time, and an $R_{X:Y}$ which was determined by the chromatograph. The mole percents were then calculated on the basis that oxygen, nitrogen and argon make up 99.95% the atmosphere. The results for two such runs are listed in Table (2). The mole percents calculated for oxygen, argon and nitrogen have been compared to the composition of air as determined by Glueckauf (1951). Notice that the differences measured for nitrogen and oxygen come closer than .5 percent to measuring the relative amounts of these gases. This is better than one would guess could be done by the estimate N of the number of trials necessary to detect 1 percent difference with a 95%

	Esti	mated Mc	ole %	Dev Val	iation ues of (in % from Gleukauf (1951)
Sample No.	0 ₂	N2	Ar	۵ ⁰ 2	^{∆N} 2	ΔAr
1	21.03	78.02	.90	. 40	 08	-3.2
2	20.72	78.32	.90	-1.05	. 30	-3.2
Average	20.88	78.17	.90	32	.11	-3.2

Two Estimates of the Composition of Dry Air

TABLE 2

confidence. The argon values are off much more compared to the other gases. This is reasonable because argon is present in the atmosphere in very small quantities compared to oxygen and nitrogen, and the peaks are correspondingly smaller.

A DETERMINATION OF DISSOLVED 02, N2 and Ar IN AN AIR-SATURATED WATER SAMPLE

Several analyses were made of air-saturated distilled water to determine the analytic capability of the analytical system with liquidphase injection. Air-saturated water was prepared in a "Worthington" saturator (Sholander, 1955). The aliquots were drawn into the sample bottle in the same general way <u>in situ</u> samples were drawn, one end of the sample volume was emersed into the water, and the other end connected to a collapsed rubber bulb. Once the sampler was full of water and free of bubbles, the rubber bulb was allowed to draw a volume of 250 ml through the sample thoroughly flushing it with air-saturated water. The temperature of the water bath and the ambient pressure were noted at the time the sample was drawn. Injection of the sample into the chromatograph followed the technique outlined previously. T_{0_2} and T_{N_2} were measured by electrolytic calibration and $T_{\rm Ar}$ was computed from

$$T_{Ar} = R_{Ar:0_2} \times T_{0_2}$$

The results of four analyses are listed in Table (3). Compared with saturation values, the average deviation measured for oxygen, nitrogen and argon are, respectively, 0.65%, -2.4%, and 0.77%. This places the

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		Analy	<u>sis ot </u>	Alr-Sa	turated	water Sa	mpies				,
Sample No.	Temp. °C	Total Pres. Atm.	Estim O ₂	ated V m1/1 ^N 2	alues Ar	Calcu 02 ¹	lated Va ml/l N2	lues Ar ²	$\begin{array}{r} 0_2 \\ 0_2^{1} \\ \underline{}_2^{1} \\ \underline{}_2 \end{array}$	02 ¹ x	100, Ar
1	20.7	.9732	6.34	11.60	.298	6.25	11.90	. 306	1.5	-2.5	-2.7
2	20.7	.9739	6.31	11.64	.288	6.26	11.91	. 306	. 78	-2.3	-5.8
3	21.20	.9928	6.13	3	.290	6.18		.274	81		5.8
4	21.25	.9922	6.06	3	.275	6.17		.274	-1.73		.36

¹ Values of Green and Carritt, 1967.

² Values of Klots and Benson, 1963

³ Nitrogen peak lost on account of integrator pen failure.

values well within the 95% confidence interval for acceptance computed from measured means and deviations of T_{02} and T_{N2} .

ANALYSIS OF SAMPLES FROM WALDEN POND

Several samples from Walden Pond were taken to evaluate the complete response of the system: sampler, injection procedure, and analysis. The object of the expedition was to survey a point of Walden Pond where deep water afforded a variety of water temperatures and dissolved gas volumes. An Industrial Instruments STD was taken along to provide information on the thermal structure, but the lack of a means of accurately determining the depths hampered the operation severely. (The depth sensor on the STD was broken.) The inability to correlate temperature with depth and the samples with a depth and temperature rather limit the scope of discussion of this section. While not much can be said on a quantitative level describing natural processes responsible for the observation, a qualitative analysis is still possible.

Using the <u>in situ</u> samplers, four samples were taken--the bottle number and approximate depths are noted in Figure (12). No. 1 was taken 1.4 m from the surface; No. 10 taken at 4 m in the thermocline. Nos. 3 and 4 were replicates of water just off the bottom about 19 meters down.

The samples were taken back to the laboratory and analyzed as soon as possible. About four hours lapsed between the first sample was taken and the last injection. The results of the analyses are listed in Table (4) along with dissolved gas values for water in equilibrium with air saturated with water vapor at a total pressure of one atmosphere. The comparison of the measured numbers with "saturation" values is not meant to infer a



TABLE	4
-------	---

			<u>m10</u>	2 <u>/1</u>		min ₂	/1		mlA	r/1	
Bottle No.	Temp. °C	Depth M	Est. ¹	. Sat. ²	Δ ³	Est. ¹	Sat. ⁴	۵ ³	Est. ¹	Sat. ⁴	۵ ³
1 .	15	1.4	7.65	7.09	8.0%	13.39	13.23	1.2%	. 355	.344	3.2%
. 10	14	4	9.12	7.25	25.7%	15.46	13.51	14.4%	.404	. 352	14.8%
3	5.6	24	6.62	8.87	-25.4%	16.83	16.16	4.1%	.419	.428	-2.1%
4	5.6	24	6.46	8.87	-27.2%	5			. 42 3	. 428	-1.1%

Analyses of Walden Pond Samples

¹ Determined by chromatographic analysis.

 2 Saturation values (Green and Carritt 1967) at T for 1 atmosphere water vapor saturated air.

$$\frac{3}{\frac{\text{Est} - \text{Sat}}{\text{Sat}}} \times 100$$

⁴ Saturation values (Klots and Benson 1963) at T for 1 atmosphere water vapor saturated air.

⁵ Recorder pen failure.

statistical test, rather, differences from saturation are meant to point out the presence of dynamic processes which result in deviations from saturation values.

Except for Sample No. 4 from the thermocline, the nitrogen and argon values are very near saturation; the average deviation for argon and nitrogen are, respectively, 1.7% and 2.6%. The oxygen numbers show more deviation. This is understandable because oxygen is biologically active. The surface sample, taken in the late afternoon of a moderately sunny, spring day, shows an 8% oversaturation of oxygen. No doubt some of this oversaturation was produced by photosynthesis. The bottom samples show about 26% undersaturation. These negative values reflect the biochemical demand on oxygen at the bottom of the lake. Last fall, before turnover, samples from the lake bottom were analyzed for gas content. The oxygen concentration of these samples was 95% down from saturation. If the water sampled on the bottom this spring was renewed last fall in the turnover and not since then, it would not be unreasonable to estimate that oxygen would be reduced 25%.

All the estimates on No. 4 showed oversaturation compared to the temperature of the sample. Although it is impossible to draw conclusions about the physical processes or experimental errors which lead to these high values, it is interesting to speculate and demonstrate how these speculations could be investigated using solubility data for oxygen, nitrogen and argon.

Oversaturation Through Mixing

One process that could explain oversaturation is the mixing of two waters saturated with air at different temperatures. A graphical test can be used to determine whether or not it was possible that a water sample could have become oversaturated through the mixing of two such waters.



FIGURE 13

Notice the line joining the points (T_{min}, C_{max}) and (T_{max}, C_{min}) on a solubility temperature curve for oxygen (Figure 13). T_{max} and T_{min} are the maximum and minimum temperatures plausible in the situation being studied. For Walden Pond in spring, 20°C and 4°C are reasonable limits. In the case where two saturated waters at different temperatures are mixed, the point (C,T) representing the new, supersaturated water will fall somewhere on the line (T_1, C_1) (T_2, C_2) depending upon the concentrations mixed. It is then easily seen that any mixture that is supersaturated as a result of the mixing of two saturated water masses of different temperatures must have a point (C,T) which falls within the bow formed by line (T_1, C_1) (T_2, C_2) and arc (T_1, C_1) (T_2, C_2) . This condition can be stated analytically by requiring that

$$\frac{C_{\max} - C}{T - T_{\min}} \stackrel{2}{\stackrel{}{=}} \frac{C_{\max} - C_{\min}}{T_{\max} - T_{\min}}$$

Sample No. 4 cannot pass this test for oxygen, nitrogen and argon. By using only the temperature and one gas concentration, it is impossible to find the proportions of two saturated waters that mixed to give supersaturated water. Any line that can be drawn through (C,T) and intersect the saturation curve in two points would represent a solution. If values for argon and nitrogen gases and temperature of the sample is known, then it is possible to find a solution to give the original temperatures and relative amounts.

Three equations describe the temperature T and dissolved argon A and nitrogen N as functions of the original temperatures T_1 and T_2 and

fractions x and (1-x) of the mixing waters

$$A = xf_{A}(T_{1}) + (1-x)f_{A}(T_{2})$$
(1)

$$N = x f_N(T_1) + (1-x) f_N(T_2)$$
(2)

$$T = xT_{1} + (1-x)T_{2}$$
(3)

where $f_A(T)$ and $f_N(T)$ are the solubility functions of argon and nitrogen at one atmosphere of water-saturated air. Upon rearrangement and combination, (1) and (2) become

$$\frac{A - f_A(T_2)}{N - f_N(T_2)} = K = \frac{f_A(T_1) - f_A(T_2)}{f_N(T_1) - f_N(T_2)}$$

and (3) rearranges so that

$$x = \frac{T - T_2}{T_1 - T_2}$$
(4)

A general graphical solution requires two plots. On the first constant values of $\frac{A - f_A(T_2)}{N - f_N(T_2)}$ and T_2 are plotted on a rectangular grid of A and N. A second graph of constant values of T_1 on a rectangular grid of T_2 and K solves T_1 . Using (4) x is computed finishing the solutions.

Changes from Saturation through Bubble Entrapment and Heating and Cooling

After leaving the surface saturated with respect to a temperature and pressure, water can undergo other physical changes which will render dissolved gas values oversaturated with respect to the temperature of the sample. Two processes promoting such a change are the addition of a small bubble of gas to already saturated water or the heating of waters once equilibrated with air at a lower temperature. If it is assumed that nitrogen has not been diminished by any physical, chemical or biochemical means, then it is possible to write equations expressing the measured quantities of argon and nitrogen in terms of a solubility function and a small bubble of Volume Q, whose gas is at standard temperature and pressure.

Then

$$A = f_{Ar}(T) + .0093Q$$
$$N = f_{N_2}(T) + .7808Q$$

The solutions of T and Q are plotted as functions of A and N on Figure (14). Values of Q and T appear as a grid whose intersecting lines are constant values of constant T and Q; for each point in the A,N plane there corresponds one solution in the Q,T plane. The points (0.355, 13.39), (.404, 15.46), and (.419, 16.83) have been marked on Figure (14) as P_1 , P_2 , and P_3 . The coordinates of these points in the Q,T grid are, respectively, (off of the grid), (8.2, 0.25), and (8.3, 2.0). Equilibrium solubilities for the measured temperatures have been noted as P'_1 , P'_2 , and P'_3 .

The proximity of P_1 , and P'_1 indicate the measured solubilities are not far from the saturation solubilities calculated from the sample tempera-



FIGURE 14

ture. P_2 is very close to saturation but its temperature of saturation would have to have been 8.2°C instead of the 14°C; this shift indicates heating of saturated water. The discrepancies between P_3 and P'_3 are more anomalous since compared to the sample temperature, argon is undersaturated and nitrogen oversaturated. If this is taken as an example of bubble entrapment, the Q = 2 ml and T = 8.3°C. For placid Walden Pond, this seems rather unlikely. If the argon value is taken to be an accurate gauge of temperature when the water sank, then nitrogen must have become supersaturated.

Such are the type of arguments one is able to develop with a plot such as this. It must be kept in mind that this discussion was not intended as an explanation of the data from Walden Pond but rather an example of how such data may be used to examine physical, chemical and biochemical processes which can result in solubilities different from saturation.

CONCLUSIONS

A system for the analysis of dissolved oxygen, nitrogen and argon in natural waters has been described. A sampler has been constructed and "cruise" tested, the sample bottle of which fits directly onto the analytic apparatus to minimize the possibility of contamination. A chromatographic system has been built which would be suitable for seagoing use with a very minor modification; the hot-wire thermal-conductivity detector, sensitive to ship accelerations, should be replaced by a thermistor detector. The 30-foot column packed with molecular sieve 5Å provided good separation of

argon, oxygen and nitrogen with either gas- or liquid-phase injection. Four samples can be analyzed for oxygen, argon and nitrogen in 5 hours. Response to oxygen and nitrogen was calibrated only by an electrolyticinjection technique; argon response was calibrated only from the ratio of detector response of argon to oxygen. The response for all three gases could also be accomplished by injection with a gas-sample valve or liquid injection of air-saturated distilled water samples. A suggestion is made that the calibration of all chromatographs using thermal-conductivity detectors and helium carrier could be much simplified if the ratios of heat conductances of argon, oxygen and nitrogen were studied. Accurate tabulation of these values would allow any chromatograph using thermal-conductivity detectors and helium carrier to calibrate for response to all three gases by measuring the response to only one gas. In a determination of the composition of air, oxygen and nitrogen were estimated within 0.5% and argon was estimated to 3%. In the analyses of 5 air-saturated water samples, oxygen, argon and nitrogen varied from accepted saturation values by, respectively, -.65%, .77%, and -2.4%. Four analyses of water samples from Walden Pond were analyzed. The results were discussed from the standpoint of demonstrating the investigations of deviation from saturation possible when oxygen, argon and nitrogen are not available. Graphical solutions of two problems of gas solutions in fresh waters were offered: the problem of gas saturation resulting from mixing of two different saturated waters, and the problem of the heating and cooling of saturated water contaminated by an air bubble.

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