

## INSTRUMENTS AND METHODS

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### Nitrogen/argon ratios by difference thermal conductivity\*

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**Abstract**—A method has been developed for the precise determination of dissolved nitrogen/argon ratios in sea water for the purpose of evaluating small changes in the dissolved nitrogen content. Nitrogen and argon are extracted from sea water (*in vacuo*) and separated from water vapor, carbon dioxide and oxygen. The residual nitrogen-argon mixture is swept over a thermal conductivity detector with a carrier gas of the same composition, except for having a slightly different argon mole fraction. Calibration is carried out by equilibrating sea water at various temperatures with air. The technique has been used successfully in the analysis of  $N_2/Ar$  ratios from the intermediate depths of the eastern tropical Pacific Ocean and the Cariaco Trench. Precision is estimated at  $\pm 0.2\%$  at the 95% confidence level; the accuracy depends on the solubility tables used and the method of equilibration.

#### INTRODUCTION

DURING our investigation of marine denitrification in the eastern tropical north Pacific Ocean (CLINE and RICHARDS, 1972), it became desirable to measure small amounts of biologically-produced nitrogen in the presence of a large dissolved air component. The amount of biological nitrogen expected was calculated from observed deficits in the nitrate distribution and found to be only 1% at a maximum of the quantity of nitrogen arising from the solution of air. Therefore, a method of high precision was required.

Previously, dissolved nitrogen in the oceans had been measured by mass spectroscopy (BENSON and PARKER, 1961a) and by gas chromatography (SWINNERTON, LINNENBOM and CHEEK, 1962). The former method was rejected by us because a mass spectrometer with sufficient precision was not available; the latter because it was felt that sufficient precision could not be attained. Similarly, volumetric analysis was also ruled out.

The procedure to be described here relies on the precise measurement of the dissolved nitrogen/argon ratio. If it is assumed that the parcel of water was originally at or near saturation with respect to argon (RICHARDS and BENSON, 1961), small changes in the nitrogen content can be estimated from the observed ratio. The use of the  $N_2/Ar$  ratio for studies of this type is particularly useful as the ratio is less sensitive to non-equilibrium solubility effects than the absolute measurement of either gas (BENSON, 1965).

Our principal concern was to estimate relative changes in the nitrogen/argon ratio, hence attention was focused on reproducibility rather than the absolute accuracy of the measurement. To date, we have used this technique successfully to monitor biologically-induced changes in molecular nitrogen in the eastern tropical Pacific Ocean and the Cariaco Trench. However, a precise analysis of this data requires a rather extensive discussion of oceanic mixing, non-equilibrium solution effects of dissolved nitrogen and argon (BENSON, 1965; CRAIG, WEISS and CLARKE, 1967), and the biological process of denitrification. The complete results of this study, including the dissolved nitrogen isotope distribution, will be given elsewhere in a more thorough treatment.

This procedure may also have application to the study of certain oceanic mixing problems, where dissolved nitrogen and argon are known to be conservative. Many of the oceanic water masses should fit this criterion.

#### THEORY

The application of difference thermal conductivity to the problem of detecting small quantities of excess nitrogen depends on reducing the sample to a binary mixture of nitrogen and argon and to the

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selection of a carrier gas of the same composition, but having a slightly different argon mole fraction. The mechanical configuration of the analyser (Fig. 1) is similar to that of a conventional gas chromatograph (NOGARE and JUVET, 1962), except that the sample column is not designed to separate the injected sample mixture. Hence, the output signal of difference thermal conductivity sensor (Fig. 1) is a function of the difference between the thermal conductivity of the carrier and that of the sample. The response can be translated into an equivalent nitrogen–argon ratio by calibrating the system against standard  $N_2/Ar$  mixtures. The advantage of this approach over gas chromatography is analogous to that of a null-type instrument, which is generally favored in high precision measurements.

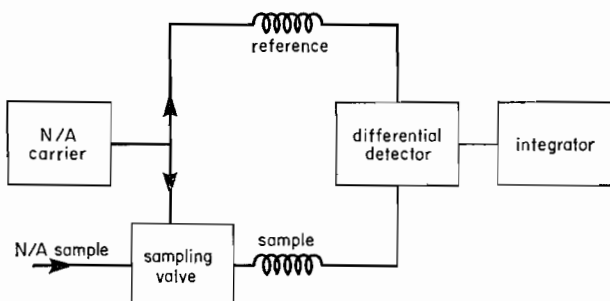


Fig. 1. Schematic drawing of the thermal conductivity analyzer system.

The thermal conductivity ( $G$ ) of a  $N_2/Ar$  mixture is related to the thermal conductivity of argon and nitrogen by:

$$G \simeq G_N(1 - X_A) + G_A X_A, \quad (1)$$

where ( $X$ ) is mole fraction and the subscripts  $A$  and  $N$  stand for argon and nitrogen, respectively. The integrated output signal ( $R$ ) of a linear differential thermal conductivity detector (Fig. 1) is linearly proportional to the volume of the injected sample ( $V$ ), and to the difference between the thermal conductivity of the carrier and the sample (NOGARE and JUVET, 1962), i.e.:

$$R = VK'(G - G^0), \quad (2)$$

where  $K'$  is a constant and the superscript 0 stand for the carrier.

By introducing the relation of equation (1) in the last equation, one obtains:

$$R = VK'(G_A - G_N)(X_A - X_A^0), \quad (3)$$

or

$$R = KV(X_A - X_A^0) = KV(X_N - X_N^0). \quad (3a)$$

Hence, the response of the analyser is linearly proportional to the mole fraction of argon (or nitrogen) in the sample, assuming constant detector sensitivity, constant flow rates, temperature, etc. The nitrogen-to-argon ratio ( $N_2/Ar$ ) is related to the mole fraction of the two gases by:

$$N_2/Ar = \frac{X_N}{X_A} = \frac{1}{X_A} - 1 = \frac{X_N}{1 - X_N}. \quad (4)$$

The precision of the present method—for  $N_2/Ar$  determinations—can be compared to that of a conventional gas chromatography (WEISS, 1970a) by assuming that the analytical errors of the two methods are limited by a relative error ( $E$ ) in measuring the response ( $R$ ) of the difference thermal conductivity detector. This imprecision would result in a relative error  $2E$  in the ratio if the gases are separated by gas chromatography and the ratio calculated by dividing the two responses. For the same instrumental error ( $E$ ), the estimated relative error in  $N_2/Ar$  when determined by the difference thermal conductivity analyser will be [calculated by differentiating equation (4) with respect to  $R$  and dividing the derivative by  $N_2/Ar$ ]:

$$\frac{d(N_2/Ar)}{(N_2/Ar)} = - \frac{(X_A - X_A^0)}{X_A X_N} E. \quad (5)$$

As the nitrogen to argon ratio in the oceans is approximately 37 (CRAIG, WEISS and CLARKE, 1967), the expected relative error in the ratio is:

$$\frac{d(N_2/Ar)}{(N_2/Ar)_{SW}} \approx -39 (X_A - X_A^0) E. \quad (5a)$$

In the present study,  $X_A^0$  was approximately 0.026 (as compared to 0.027 in sea water) and the inaccuracy in measuring ( $R$ ) was estimated to be 1%. Hence, the theoretically expected random error is calculated to be approximately 0.04%.

#### EXPERIMENTAL

The extraction of dissolved air gases was carried out in the vacuum system shown in Fig. 2. High vacuum gas sampling tubes (ca. 250–300 ml) were used to introduce the samples into the line and the extraction carried out in a manner similar to that described by BENSON and PARKER (1961b). Oxygen was removed from the mixture by passing it over hot copper (ca. 600°C) for approximately 15 minutes; carbon dioxide was trapped with liquid  $N_2$  (– 196°C). Volumes of gas extracted were measured before and after the removal of oxygen and compared to solubility tables (WEISS, 1970b) as an independent check of possible air contamination.

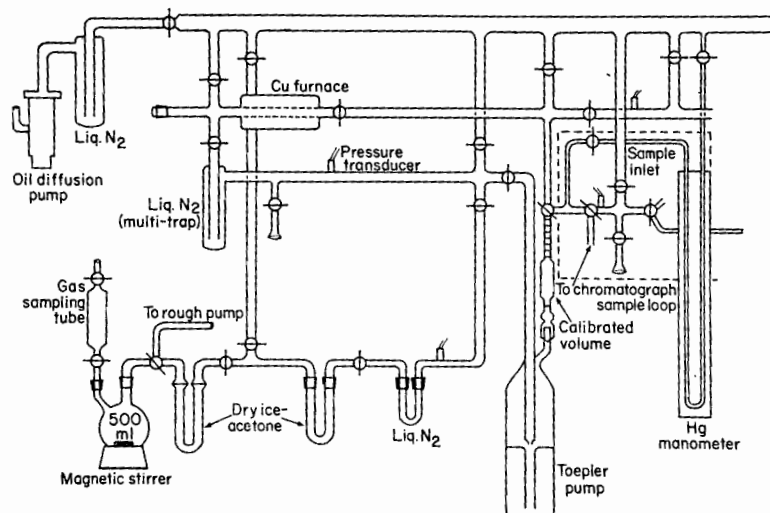


Fig. 2. Vacuum extraction and purification system.

Although our purpose was to measure  $N_2/Ar$  ratios directly, actual concentrations of nitrogen and argon can be obtained from a knowledge of sample volumes and the volume of the extracted nitrogen plus argon.

The resulting nitrogen/argon mixture was transferred to the sample inlet system (Fig. 2) with the aid of the toepler pump, where a portion of it was loaded into the sampling valve loop; the remainder was transferred to a breakseal for isotopic analysis of nitrogen.

The columns (sample and reference sides) consisted of 1/8 in.  $\times$  6 ft. stainless steel tubing packed with 60/80 mesh chromosorb W (Johns-Manville Corporation), an inert solid support, which was used to provide flow resistance and sample delay. Nitrogen is not separated from argon on this support, but the mixture is analysed as a single component. Carrier flow rate was maintained at 6 ml/min. The sample loop was constructed from 1/8 in. o.d. stainless steel tubing; its volume was approximately 0.7 cm<sup>3</sup>. Columns, detector and sampling valve were inserted in an insulated box for thermal stability.

The carrier gas was a nitrogen/argon mixture ( $X_A = 0.026$ ) prepared for us by Matheson Gas Products of Cucamonga, California, to have a ratio similar to that found in normal ocean water ( $N_2/Ar = 37.4$ ).

The detector system used in this investigation consisted of a Carle® micro-thermistors detector, bridge amplifier and micro-sampling valve (No. 2014) (Fig. 1). Detector output was optimized at a bridge current of 15 mA, which provided the greatest signal-to-noise ratio.

The output signal of the thermistor bridge was amplified by a factor of 1000, using a chopper-type operational amplifier (Analog Devices type 260K), and fed to an electronic integrator. The integrator is a modified version of an analog-to-frequency converter described elsewhere (BEN-YAAKOV, 1968). The output signal of the integrator, which is in the form of a repetitive sawtooth, was fed to a 1 mV FS strip chart recorder and the peak area was read manually by summing up the total length of sawtooth ramps generated by the signal.

All samples injected into the chromatograph were introduced at a somewhat variable pressure, usually in the pressure range of 250–300 mm Hg. This situation was due to design characteristics of the vacuum line, and variable sample size. It was determined, however, that detector response was linear with pressure down to approximately 150 mm Hg, below which value the peak shape and baseline characteristics deteriorated significantly. Sample loop pressure was monitored with a mercury manometer mounted on the inlet system (Fig. 2), and regulated by means of a hand-operated air pump located on the toeppler pump.

The integrated output signal ( $R$ ) from the detector was normalized for sample pressure ( $P$ ) and daily variations in the instrument sensitivity ( $m$ ). Normalized response is given as:

$$R' = \frac{R}{(P)(m)} \quad (6)$$

Because the measurement of standards and samples extended over a time interval of several weeks, it became necessary to monitor changes in the sensitivity, which arose from daily variations in carrier flow rate, fluctuations in ambient temperature, or changes in the response characteristics of the electrical components. Correction for variations in the response characteristics of the system was carried out by running a prepared nitrogen/argon mixture ( $X_A = 0.0271$ ) against the carrier gas ( $X_A = 0.026$ ) as a function of sample pressure before each analysis. This curve was always linear with a near-zero intercept. The equation of the line was determined by least squares regression analysis; its slope was set equal to the sensitivity parameter ( $m$ ). The same carrier gas and sensitivity monitor were used throughout the study.

Standard nitrogen/argon mixtures were prepared by equilibrating distilled and artificial sea water at various temperatures in a 4-liter aspirator bottle. Air saturated with water vapor was pumped gently over the surface of the water, which was stirred magnetically to produce a smooth vortex without the injection of air bubbles. The air was also thermostated to the desired equilibrium temperature. Temperature control was maintained at approximately  $\pm 0.2^\circ\text{C}$  with a Lauda® model IC-6 refrigeration unit. To insure that equilibrium had been attained, all standard solutions were allowed to equilibrate for a period of time in excess of 60 hours. Barometric pressure was measured routinely during the equilibration, but any variations in barometric pressure would presumably affect argon and nitrogen solubility equally. The equilibrium nitrogen/argon ratio was calculated from the solubility equations given by WEISS (1970b).

#### RESULTS

The results of the calibration are shown in Table 1. The argon mole fraction scale has been expanded arbitrarily by setting  $\Delta = (X_A \times 1000) - 25.00$ . The best fit of the calibration data was found by linear regression analyses and is represented by the equation:

$$R' = -2.908 \Delta + 6.315, \quad (7)$$

where  $R'$  is the normalized response [equation (6)].

In order to estimate the error in  $\Delta$  that would arise from a single measurement of  $R'$ , the 95% confidence interval for the entire calibration line was calculated using the F-test with  $(2, n - 2)$  degrees of freedom (NUTRELLA, 1963). As the error band diverges only slightly at the extremities of the line, the uncertainty in  $X_A$  that would arise from a single observation of  $R'$  is approximately  $\pm 4 \times 10^{-5}$ . From this value, the associated error in the nitrogen/argon ratio within the constraints of the calibration was calculated to be  $\pm 0.07$  at the 95% confidence interval or about  $\pm 0.21\%$ .

The argon mole fraction of the carrier gas can be estimated from equation (7). By setting  $R' = 0$ , the argon concentration was found to be 0.02712, which is well within the preparation tolerance of  $\pm 10\%$  as quoted by the Matheson Company.

The method described above has been used in the eastern tropical north Pacific Ocean to evaluate small changes in dissolved nitrogen content that has arisen from denitrification, although in principal it also could be used effectively to study mixing processes where nitrogen and argon are known to be conservative. To demonstrate its application to the study of marine denitrification, we present one of two profiles taken during the cruise of the R. V. T. G. Thompson (TGT-066) (Univ. of Washington, 1972) to the eastern tropical north Pacific Ocean. The observed nitrogen/argon ratio (Fig. 3) is plotted versus potential temperature.

Table 1. Calibration data for equilibrated sea water and distilled water.

Salinity (%)	Temperature (°C)	$\Delta_{\text{std}}^*$	$R'\dagger$	$\partial R'\ddagger$
0.0	26.0	0.251	5.69	0.15
0.0	26.6	0.229	5.49	0.15
0.0	25.5	0.272	5.57	0.15
34.91	29.0	0.533	4.80	0.12
34.91	29.0	0.533	4.66	0.12
34.91	29.0	0.533	4.72	0.12
34.91	18.5	0.982	3.26	0.10
35.20	18.5	0.986	3.40	0.10
34.91	14.0	1.180	2.81	0.12
34.91	10.0	1.358	2.24	0.15
34.91	10.0	1.358	2.06	0.15
34.91	10.0	1.358	2.37	0.15
34.91	10.0	1.358	2.46	0.15

\*Equilibrium argon mole fraction calculated from solubility equations of WEISS (1970b).

$\Delta_{\text{std}} = [(X_A)_{\text{std}} \times 1000] - 25.00$ , where  $X_A$  is defined above.

†Normalized response given by equation (6).

‡ $\partial R' = (2F)^{\ddagger} (SR)^{\ddagger} \left[ \frac{1}{n} + \frac{(A - \Delta)^{\ddagger}}{S_{AA}} \right]^{\ddagger}$  for  $F_{0.95}(2, n - 2)$ .

A linear  $N_2/Ar$  relationship should obtain between the depths 150 and 800 meters (Fig. 3), as suggested from a linear  $T-S$  plot over the same depth interval. For comparison, the normal equilibrium ratio has been calculated for this depth interval, assuming that each parcel of water was in equilibrium with a standard atmosphere at the observed potential temperature and salinity. A mixing equilibrium ratio was also calculated, assuming that the core properties were at equilibrium and

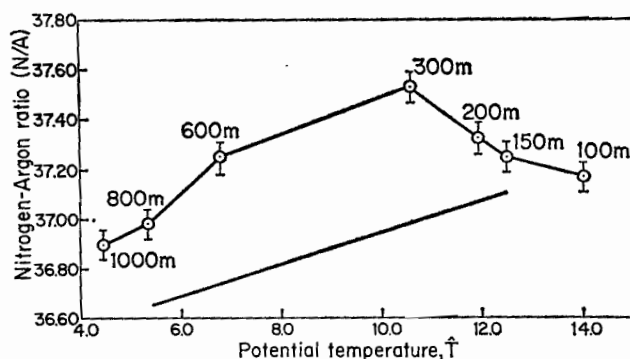


Fig. 3. A plot of the observed  $N_2/Ar$  ratio versus potential temperature for Sta. 20 ( $19^\circ 46.4'N$ ,  $107^\circ 06.6'W$ ). Depths are given in meters; the estimated error in the ratio is approximately  $\pm 0.07$ . The solid line indicates the normal equilibrium ratio.

that linear mixing between the two boundaries prevailed. These two equilibrium distributions do not differ significantly from each other. However, as discussed by BENSON (1965), and CRAIG, WEISS and CLARKE (1967), non-equilibrium effects such as air injection, surface pressure anomalies, and lateral mixing may obscure the true equilibrium state. For this reason, the normal ratio in the cores of the respective water masses must be determined before an accurate accounting can be made of the excess nitrogen. Positive departures in the observed  $N_2/Ar$  from the equilibrium solubility line suggests that excess nitrogen has been produced in the mixing interval. This is in agreement with the view that this region is a site of active denitrification (CLINE and RICHARDS, 1972).

## DISCUSSION

The results of this investigation demonstrate the applicability of 'difference thermal conductivity' to the estimation of small quantities of excess nitrogen. With improvements in the chromatographic hardware, such as better flow and temperature control, there is reason to believe that the precision could be further increased. Improvement in the absolute accuracy will depend on significant refinements in gas solubility data or upon an independent, accurate analysis of nitrogen/argon mixtures.

The estimated random error of this method is approximately  $\pm 0.2\%$  (95% confidence level) of the ratio, and depends on the range of calibration. Errors can be minimized by choosing a carrier gas similar in concentration to the samples under study. The precision of the mass spectrometric method (BENSON and PARKER, 1961a; RICHARDS and BENSON, 1961) was reported to be  $\pm 0.3\%$  in the ratio, but the confidence interval was not given.

Currently, the major disadvantage of this procedure is the slow sample processing time for routine analysis (as sample capture was necessary for  $^{15}\text{N}/^{14}\text{N}$  analysis), but it may be possible to adapt this method to an on-line aqueous stripping analysis such as that used by SWINNERTON, LINNENBOM and CHEEK (1962), and WEISS (1970a), which would greatly accelerate the analysis time.

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