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# Statistical Evaluation of Gas Chromatography for the Determination of Dissolved Gases in Sea Water

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A gas chromatographic method developed by the authors for the determination of dissolved gases in sea water has been evaluated with respect to precision and accuracy by comparison with other methods. Both laboratory and shipboard measurements were employed in the evaluation. Dissolved oxygen analyses made at sea under routine conditions of operation over a period of two weeks indicate statistically significant differences in precision for the three methods tested: gas chromatography ( $\pm 1.8\%$ ), standard Winkler method ( $\pm 1.0\%$ ), and a modification of the Winkler method ( $\pm 0.51\%$ ). No significant bias was found between gas chromatography and the improved Winkler method; a small but statistically significant bias ( $-1\%$ ) was found for the standard Winkler method relative to the other two. From a practical point of view, these differences are not considered important for routine survey operations. The dissolved  $N_2$  data obtained by gas chromatography are grouped about a mean value of 100% saturation, with approximately 95% of the values falling within  $(100 \pm 5)\%$  saturation. The advantages of gas chromatography (routine analyses by relatively nonskilled personnel to obtain simultaneous measurements of more than one gas on a small volume of liquid) are felt to be sufficient to warrant its further use in oceanography.

## INTRODUCTION

The application of gas chromatography to the determination of dissolved gases in sea water offers a number of advantages over methods presently in use. The technique is less time consuming, it is better suited for routine analytical work by relatively inexperienced personnel, sample size can be kept small, the instrumentation is relatively simple, and no significant loss is experienced in either precision or accuracy. Its greatest advantage, however, is that it makes possible the simultaneous determination of several gases on the same small sample of liquid ( $\sim 2$  ml). Furthermore, shipboard evaluation tests have shown that the equipment operates satisfactorily at sea with no adverse effects because of rolling or pitching, engine vibrations, etc.

In the evaluation of any new method in which emphasis is placed on fast routine analyses by nonprofessional personnel, an assessment of the precision and accuracy of the results is of paramount importance. The estimate of precision which is of interest in this case is that obtained in the field, for the same conditions under which the method is intended to be used. Laboratory

measurements under near ideal conditions, where a research analyst performs carefully replicated analyses on a single homogeneous sample, will always show much less scatter; estimates of precision in this case are of comparative interest only and should not be applied to more heterogeneous field data. The accuracy of the method depends on the presence or absence of systematic errors, or bias. At the time an analytical method is developed in the laboratory it is necessary to determine whether a bias exists. However, since biases may vary from time to time under conditions of field use, it is also necessary to make frequent checks of the method in the field by running a standard sample with a known value, or by comparison with a standard reference method. The close relationship between precision and accuracy should be noted; only when the precision is known, for example, can a statement be made as to whether a measured bias is statistically significant or not.

The use of gas chromatography at sea on several occasions by the authors has resulted in the accumulation of sufficient data from which an evaluation of the method under field conditions may be made. Although it is possible to include dissolved gases such as  $CO_2$  and  $H_2S$  in the separation scheme, in our work to test the feasibility of the

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method only oxygen and nitrogen were determined. In the following discussion, the applicability of gas chromatography for the analysis of dissolved oxygen in sea water is examined by comparing results with those obtained by the Winkler method, both in the laboratory and aboard ship. Data obtained on the dissolved nitrogen content of sea water are next presented and discussed. Finally, some conclusions are set forth as to the possible further usefulness of gas chromatography in oceanography.

### EXPERIMENTAL EQUIPMENT AND PROCEDURE

The basic essentials of the gas chromatographic method have been described previously by the authors (1,2). To summarize briefly, three operations are involved: (a) introduction of a measured volume of sea water into a special sample chamber, where the dissolved gases are stripped from the liquid; (b) separation of the gas mixture into its components by means of gas-solid chromatography; (c) determination of the amount of each component by means of thermal conductivity measurements. The essential feature of our method is step (a), in which a special sample chamber designed at NRL is employed (see Fig. 1). The equipment consists of the all-glass sample chamber divided into two sections by a coarse fritted glass disc, a six-way sampling valve, a gas chromatograph, and a standard 1-millivolt recorder. For large numbers of analyses, a recorder-integrator is desirable. Steps (b) and (c) are completely automatic and can be carried out with any good commercially available equipment. In our work we used a Fisher gas partitioner Model 25 and a Texas Instrument recorder-integrator. When the sample size is not limited,\* sea water from the sample is allowed to flow through the sampling loop of the six-way valve and discarded (position 1, Fig. 1). At the same time, the inert carrier gas (helium) is being bypassed by the valve through the sample chamber. When the sample loop has been sufficiently flushed, the valve is turned (position 2) and the carrier gas forces the sea water out of the loop up through the glass

\*When the amount of sample is limited, a measured volume (1 to 3 cc) can be taken with a Hamilton gas-tight Teflon-tipped syringe and transferred to the upper part of the sample chamber through a self-sealing rubber serum cap, as described in Ref. 1.

frit until all the liquid has been transferred to the upper part of the chamber. As the carrier gas comes up through the fritted disc in a stream of fine bubbles, it strips the solution of its dissolved gases quickly and effectively (Henry's law). The unknown gas mixture in the carrier gas stream passes through a drying column containing Drierite to remove water vapor, then into the gas partitioner, where separation of the gases is effected in the usual manner (Fig. 2). In our work, we used Linde Molecular Sieve 13X in the separation column.\* As each gas component passes through the thermal conductivity cell, the change in thermal conductivity of the helium due to the presence of the foreign gas affects the temperature of an electrically heated thermistor element, which is part of a Wheatstone bridge circuit. The change in temperature causes a corresponding change in resistance of the thermistor, and a resulting voltage signal is amplified and fed into the recorder, where it is recorded in the form of a symmetrical peak. The area under the peak, which is proportional to the quantity of foreign gas in the helium stream, is simultaneously integrated by the integration unit of the recorder-integrator and recorded as a separate trace.

Calibration is accomplished by carrying out the same sequence of analysis on samples of water containing known amounts of the gas in question. In our work, this was done most simply by saturating distilled water with air at a measured temperature and pressure. A stream of air is bubbled through approximately 100 ml of water for about 15 minutes to insure saturation. The sample of air-saturated water is then introduced into the sample chamber in the same manner as for the sea water samples.† The concentrations of dissolved oxygen and nitrogen in the distilled water, as determined from the values given in the literature (3,4) at the temperature and pressure of saturation, are divided by the measured peak areas, respectively, to give the calibration factors for each gas.

\*Since the separation of oxygen and nitrogen is relatively simple, only one separation column was needed. For more complex separation schemes it is sometimes necessary to employ more than one column (see Ref. 1).

†Air-saturated distilled water is stripped less efficiently of its dissolved gas than sea water. This is apparently due to the reduced surface tension of the latter, which results in much smaller bubbles of stripping gas. A trace of wetting agent, or an equal volume of degassed sea water left in the chamber before introduction of the distilled water sample, eliminates this effect.

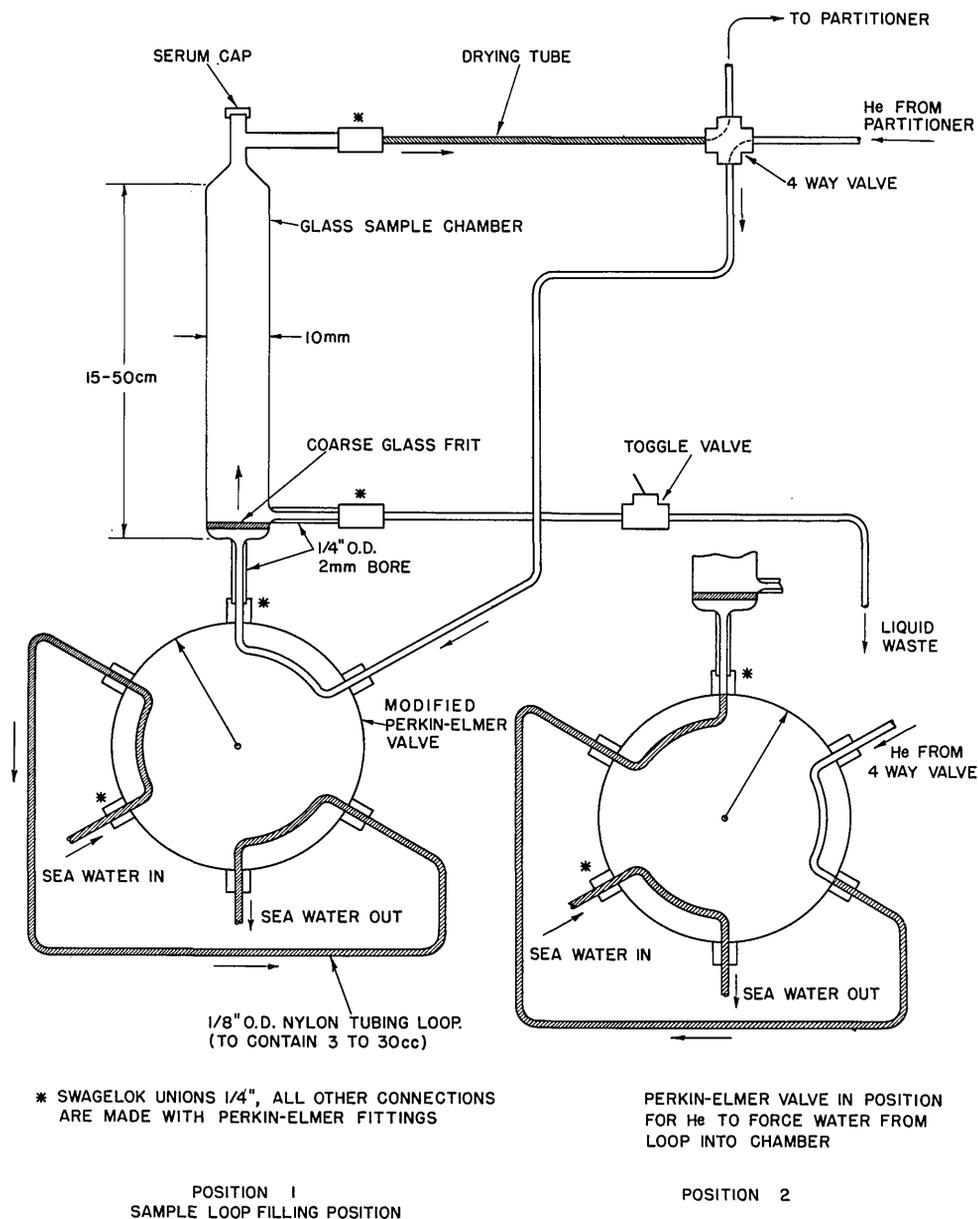


Fig. 1 - Sampling valve and stripping chamber

In the method described above, argon and oxygen are not separated by the Molecular Sieve column at room temperature. In air-saturated solutions about 5% of the total area under the oxygen peak is thus due to argon. Although a method has been developed for the separation and measurement of these two gases (5), in routine work the presence of argon can be corrected for without appreciable

error. It is assumed that the concentrations of nitrogen and argon dissolved in sea water are not affected by biological and chemical activity; therefore the ratio of their concentrations will be constant at a given temperature and salinity. Then

$$A_1 = C \frac{K_2}{K_1} A_2 \quad (1)$$

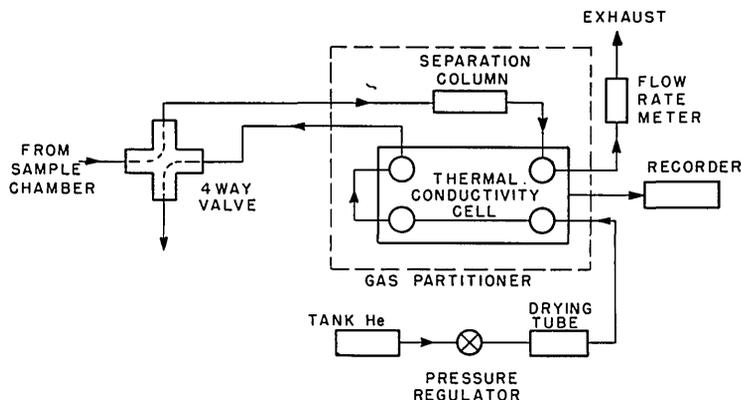


Fig. 2 - Gas partitioner schematic

where  $A_1$  is the calculated area due to argon,  $A_2$  is the measured area under the  $N_2$  peak,  $K_1$  is the calibration factor for argon (ml/l-cm<sup>2</sup>),  $K_2$  is the calibration factor for nitrogen (ml/l-cm<sup>2</sup>), and  $C$  is the ratio of dissolved argon to nitrogen in sea water at a given temperature. The correction is applied by subtracting  $A_1$  from the total area of the oxygen-argon peak to give the area due to oxygen. Further details on this correction, including experimental data to support its validity, are found in Ref. 6.

The two chemical methods used for determination of dissolved oxygen were both modifications of the classical Winkler procedure. One method, which we used throughout our work, is a semi-micromethod developed recently by Dr. J. H. Carpenter, of the Chesapeake Bay Institute (7). The other method, used in only part of our work, is a standard method typical of those methods in widespread use in chemical oceanography (8).

Nansen bottles were employed for sampling as in standard oceanographic work. As soon as the Nansen bottles were brought aboard the ship, aliquots of their contents were immediately transferred in the usual manner to glass sample bottles, which were then tightly stoppered. These were then analyzed for dissolved gas as soon as possible. In no case did more than 30 to 40 minutes elapse between the time the Nansen bottles were brought aboard and the time the last analysis was finished.

### STATISTICAL TREATMENT

Errors in analysis may be divided into two categories: random and systematic. Random errors

are estimated by the standard deviation  $s$ , which is defined as

$$s = \sqrt{\frac{\sum (X_i - \bar{X})^2}{n - 1}} \quad (2)$$

where  $\bar{X}$  is the mean of a group of  $n$  individual measurements  $X_i$ .

A more convenient equation for handling large numbers of data with a calculating machine is

$$s = \sqrt{\frac{\sum X_i^2 - (\sum X_i)^2 / n}{n - 1}} \quad (3)$$

The two equations are mathematically equivalent. Since the absolute magnitude of  $s$  will vary depending on whether large or small values are being measured, it is sometimes more convenient to express  $s$  as a percentage of the group mean; it is then called the relative standard deviation  $C$  (also known as the coefficient of variation):

$$C = \frac{s}{\bar{X}} \times 100. \quad (4)$$

The standard deviation is probably the most useful estimate of precision employed today. In addition to providing a measure of dispersion within a given group of measurements, it may also be used for comparison purposes. For example, as in this work, the precision of a new analytical method may be compared with the

precision of a standard method by calculating the ratio of the squares of the standard deviations of the two methods. This statistic is called  $F$ -ratio

$$F = s_1^2/s_2^2 \quad (5)$$

where  $s^2$  is the variance and the subscripts refer to the two different methods. Values of this ratio may be found in statistical tables which set the limits within which the  $F$ -value may fluctuate even though  $s_1 = s_2$ .

The standard deviation is useful in another way. When two different methods are used to analyze  $n$  samples, there are obtained  $n$  pairs of results, each pair consisting of one determination for a given sample by each method. On the assumption that two identical aliquots of a given sample behave alike if treated alike, the differences found between the members of each pair must then be due to (a) the methods, or, if the methods are identical, to (b) random variations. In the latter case the algebraic mean of the differences should in the long run approach zero. In either case, the individual differences  $d_i$  between the two measurements on each sample can be treated as a group of  $n$  items having a mean value  $\bar{d}$  and a standard deviation given by the relation

$$s_d^2 = s_1^2 + s_2^2 \quad (6)$$

In order to test whether the observed average difference  $\bar{d}$  is statistically different from the expected value of zero which should be obtained if the methods do not differ, the usual Student's  $t$ -test may be applied:

$$t = \frac{(d - 0) \sqrt{n}}{s_d} = \frac{\bar{d}}{s_{\bar{d}}} \quad (7)$$

where  $s_{\bar{d}} = s_d/\sqrt{n}$  is the standard error of the mean difference  $\bar{d}$ .

Values of  $t$  may be found in statistical tables which set the limits within which this ratio may fluctuate even though  $\bar{d}$  is not significantly different from 0; that is, within these allowed values of  $t$ , the value found for  $\bar{d}$  may be ascribed solely to random errors.

Obviously, it is impossible to say with certainty that the methods do or do not differ; one can say only that there is a certain probability that the

observed bias  $\bar{d}$  may or may not be real. It should be emphasized that while the magnitude of this probability will help in deciding whether  $\bar{d}$  is real or due solely to chance, it cannot help in determining whether  $\bar{d}$  has any practical significance. This decision must be based on the judgment and experience of the analyst. For example, the above ratio may be sufficiently large to say that there is a real bias of one method with respect to the other; yet if this is due to a very small value of  $s_{\bar{d}}$  (*i.e.*, both methods are highly precise), the actual magnitude of  $\bar{d}$  may still be negligible from a practical standpoint.

From Eq. (6) it is not possible to determine either  $s_1$  or  $s_2$  from the experimental value of  $s_d$ . However, if three methods are compared, one may consider the differences between the three pairs taken two at a time

$$s_{(1-2)}^2 = s_1^2 + s_2^2 \quad (8a)$$

$$s_{(1-3)}^2 = s_1^2 + s_3^2 \quad (8b)$$

$$s_{(2-3)}^2 = s_2^2 + s_3^2 \quad (8c)$$

and easily solve this system of three equations for the three unknown standard deviations  $s_1$ ,  $s_2$ , and  $s_3$ . It should be noted that these estimates of precision are obtained without the need for running replicates on any one sample, as is required if Eq. (2) or Eq. (3) is used to calculate  $s$ .

## RESULTS OF THE STATISTICAL EVALUATION OF MEASUREMENTS

### Precision of Laboratory Measurements

Carefully controlled laboratory measurements of the precisions of the gas chromatography method and the Carpenter modification of the Winkler method were first determined by analyzing replicate aliquots of a given sample of air-saturated distilled water for dissolved oxygen by each method. The analyses were carried out alternately, and careful checks were made on the constancy of barometric pressure and temperature during the course of the analyses to make sure that the dissolved gas content of the water did not change. The results are shown in Table 1.

The relative standard deviations of 0.11% and 0.48% are to be compared with a similar value of

TABLE I  
Replicate Measurements (Laboratory)  
for Dissolved Oxygen

	Oxygen Content (ml O <sub>2</sub> /liter)	
	Improved Winkler Method	Gas Chromatography
	5.185	5.19
	5.180	5.18
	5.183	5.22
	5.177	5.20
	5.175	5.14
	5.176	5.16
	5.167	5.19
	5.179	5.19
	5.170	5.15
mean	5.177	5.180
std. dev. s	±0.0058	±0.025
rel. std. dev. C	0.11%	0.48%
std. error of mean	±0.0019	±0.0083

0.43% for the standard Winkler method, estimated to be the highest precision likely for that method in a shore-based laboratory under near-ideal conditions (8).

#### Accuracy of Laboratory Measurements

As a check on the accuracy of the gas chromatography method relative to that of the Winkler method, a series of solutions of varying dissolved oxygen concentrations were prepared and run in duplicate by both methods. The results are shown in Table 2, and plotted in Fig. 3.

A least squares analysis of this data gives a value for the straight line intercept of 0.0096, which when subjected to the *t*-test proves to be not significantly different from zero. A least squares value for the slope, with the added restriction that the straight line must pass through the origin, gives a value of 0.9988; application of the *t*-test shows this to be indistinguishable from unity, as judged by the precision of the data. A comparison of variability of the gas chromatography data based on (a) replication and (b) deviations of the ordinate points from the straight line shows no significant difference; there appears to be no other contribution to the scatter of the values about the line than the random fluctuations

normally observed in repeated determinations on the same sample.

#### Comparison of Laboratory Measurements Between Analysts

Gas chromatography analyses for dissolved oxygen were performed in sextuplicate on air-saturated distilled water by four analysts: one skilled professional, two laboratory technicians, and a summer student employee with no previous experience in this type of analysis. The analyses were performed in a random order by the analysts, and no significant changes in the dissolved gas content of the water due to barometric pressure or temperature changes took place during the course of the analyses. The data are given in Table 3.

The *F*-test applied to the ratio of the largest and smallest of the four variances showed no significant difference.\* This absence of a significant difference was confirmed by applying Bartlett's test for homogeneity of variance to all four values of *s*<sup>2</sup>. When the variances are homogeneous, they can then be combined by pooling

\*Since the larger number is arbitrarily placed in the numerator, ratio values less than unity are eliminated, and the tabulated 5% probability level for *F* (designated *F*<sub>0.05</sub>) becomes doubled to 10%.

TABLE 2

Laboratory Comparison of the Gas Chromatography and the Improved Winkler Methods for Dissolved Gases

Sample	Oxygen Content (ml O <sub>2</sub> /liter)	
	Improved Winkler Method	Gas Chromatography
1	6.50	6.49
	6.49	6.48
2	5.62	5.57
	5.58	5.57
3	4.05	4.12
	4.04	4.02
4	2.72	2.67
	2.73	2.66
5	2.67	2.66
	2.64	2.72
6	1.36	1.34
	1.35	1.36
7	0.56	0.55
	0.56	0.56
		std. dev. (s)
(a) replication		±0.032
(b) scatter of G values about straight line		±0.031

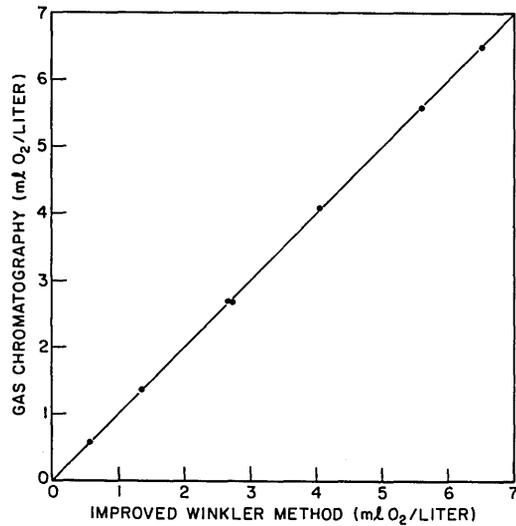


Fig. 3 - Comparison of results obtained for dissolved O<sub>2</sub> by gas chromatography and by the Winkler method

TABLE 3  
Comparison Between Analysts Performing Gas Chromatography

	Oxygen Content (arbitrary units)*			
	Skilled Professional	Laboratory Technician	Laboratory Technician	Student Employee
	4527	4648	4574	4546
	4547	4608	4616	4510
	4579	4676	4545	4610
	4615	4590	4495	4530
	4561	4558	4555	4576
	4571	4550	4590	4660
mean	4566.7	4605.0	4562.5	4572.0
std. dev. s	±30.0	±49.7	±41.7	±55.7
rel. std. dev. C	0.66%	1.1%	0.91%	1.2%
variance s <sup>2</sup>	900	2472	1734	3098
ratio of variances $F = 3098/900$				= 3.44
critical value $F_{0.05}$ (10% level)				= 5.05

\*Arbitrary units as measured by an integrator (proportional to peak area).

sums of squares to give an estimate of  $s_b^2 = 2051$ , the within-analyst variance. The variance between analysts is calculated from their averages to be  $s_b^2 = 2981$ ; this should not differ significantly from the within-analyst variance if the analysts agree within the random error of the experiments. The ratio of variances  $s_b^2/s_w^2$  is calculated to be 1.45; the critical value of  $F$  at the 10% level is 3.10 (*i.e.*, a ratio as high as 3.10 can be obtained by chance 1 out of 10 times), and the differences between averages are therefore not significant.

### Shipboard Measurements

Analyses in quintuplicate were carried out on each of nine water samples, collected over a period of five days at different locations. These samples were drawn from the surface in a plastic bucket and were intended solely for establishing whether replication at sea involves more scatter of data than similar replication in a shore-based laboratory. Two analysts were involved, alternating between the gas chromatography and the improved Winkler methods on successive samples. The data are shown in Table 4. The within-sample variance for each method was obtained by pooling sums of squares for all nine samples. The difference in method variance, as judged by the  $F$ -test applied to within-sample variability, is seen to be highly significant. However, there is no significant bias between the methods, as judged by the  $t$ -test applied to the observed differences between the averages obtained by the two methods on a given sample. If the data for each method are arranged separately according to analyst and subjected to statistical analysis, no significant difference between analysts is observed on the basis of within-sample variance.

It must be recognized that the estimates of precision obtained from the data in Table 4 are somewhat unrealistic in that they are based entirely on replication of a given sample. This usually tends to underestimate what is found in actual practice. An attempt was made to obtain a more realistic comparison of operations involving the two methods by including possible variations due to sampling with different Nansen bottles. A special rack which was designed to hold several Nansen bottles was lowered to a predetermined depth. After the usual 10 minutes allowed in standard hydrographic work to reach equilibrium with the

surroundings, the bottles were tripped in rapid succession by an electrical signal from the ship. Each cast in a given set of data therefore represents a homogeneous volume of sea water from which replicate samples were simultaneously obtained in different Nansen bottles. Aliquots from each Nansen bottle were taken immediately after surfacing for analysis by the two methods. The data are shown in Table 5. The  $F$ -test indicates that there is about an 8% chance that the ratio of method variances actually found could be accidental; it cannot be maintained, therefore, that the methods differ significantly in precision from this data. The paired-difference technique applied to the distribution of differences between the results obtained by the two methods on each bottle indicates no significant bias between the methods. With the further assumption of no significant difference between the precision of the methods, the entire body of data in Table 5 can be subjected to analysis of variance; no significant effect of using different Nansen bottles is found.

A final test of the methods as they are actually employed during routine operations aboard an oceanographic vessel was made during a cruise off Puerto Rico. The three methods previously mentioned were used: gas chromatography as described above, the Carpenter modification of the Winkler method, and the standard Winkler method. Sampling operations were carried out over a period of about two weeks by means of standard Nansen casts. As soon as the Nansen bottles were brought aboard, three aliquots were taken from each bottle for analysis by the three methods. As before, two analysts alternated on successive casts in performing the gas chromatography and Winkler analyses. A total of 94 different samples were thus analyzed for dissolved oxygen, each by three different methods; the data were then analyzed by the paired difference technique (Eqs. (8)), utilizing the differences between the methods taken two at a time. The data (only partially listed to save space) are shown in Table 6. Two points should be noted. The variances of the three methods are significantly different, and the relative bias of the standard Winkler method with respect to the other two methods is highly significant (there is less than 1 chance in 1000 that  $t$  values as high as 9.46 and 3.74 could occur by accident). However, the bias of the gas chromatography method with respect

TABLE 4  
Reproducibility of Replicate Analyses Aboard Ship for Dissolved O<sub>2</sub>

Sample	Analyst	Oxygen Content by Improved Winkler Method (ml O <sub>2</sub> /liter)					Analyst	Oxygen Content by Gas Chromatography (ml O <sub>2</sub> /liter)					
		1	A	4.56	4.57	4.57		4.57	4.57	B	4.54	4.49	4.56
2	B	4.58	4.56	4.58	4.56	4.59	A	4.58	4.58	4.58	4.52	4.59	
3	A	4.54	4.53	4.54	4.54	4.55	B	4.46	4.64	4.54	4.48	4.51	
4	B	4.54	4.54	4.55	4.54	4.56	A	4.50	4.55	4.52	4.53	4.62	
5	A	4.51	4.50	4.51	4.52	4.50	B	4.57	4.45	4.48	4.53	4.54	
6	B	4.50	4.50	4.51	4.51	4.50	A	4.55	4.50	4.48	4.55	4.52	
7	A	4.51	4.51	4.51	4.50	4.51	B	4.50	4.46	4.55	4.52	4.49	
8	B	4.55	4.54	4.54	4.56	4.56	A	4.62	4.60	4.64	4.64	4.60	
9	A	4.56	4.55	4.57	4.55	4.57	B	4.59	4.48	4.58	4.51	4.60	
variance $s^2$ (within samples)						0.000072	(within samples)						0.00195
std. dev. $s$						$\pm 0.0085$ ml/liter							$\pm 0.044$ ml/liter
rel. std. dev. $C$						0.20%							1.0%
Ratio of method variances $F = 0.00195/0.000072 = 27$								– highly significant					
Relative bias of methods ( $t$ -test applied to difference between averages) – not significant													
Differences between analysts – not significant													

TABLE 5  
Reproducibility of Replicate Sampling of Sea Water As Measured by Dissolved O<sub>2</sub> Content in Samples From Five Nansen Bottles Cast Together

Cast	Analyst	Oxygen Content by Improved Winkler Method (ml O <sub>2</sub> /liter)					Analyst	Oxygen Content by Gas Chromatographic Method (ml O <sub>2</sub> /liter)					
		1	2	3	4	5		1	2	3	4	5	
1	A	4.53	4.52	4.48	4.52	4.43	B	4.43	4.47	4.44	4.49	4.37	
2	B	4.52	4.52	4.55	4.51	4.54	A	4.56	4.44	4.58	4.46	4.49	
3	A	4.10	4.07	4.04	4.04	4.10	B	4.10	4.17	4.05	4.07	4.16	
variance $s^2$ (within cast)						0.00097	(within cast)						0.0028
std. dev. $s$						$\pm 0.031$ ml/liter							$\pm 0.053$ ml/liter
rel. std. dev. $C$						0.70%							1.2%
Ratio of method variances $F = 0.0028/0.00097 = 2.89$													
Critical $F_{0.05}$ value, (10% level) = 2.69													
$F_{0.025}$ (5% level) = 3.28													
Relative bias of methods													
( $t$ -test applied to differences between methods on a given bottle) – not significant													
Differences between bottles – not significant													

TABLE 6  
Dissolved O<sub>2</sub> Analyses by Three Methods

Sample	Analyst	Oxygen Content by Winkler Method (ml O <sub>2</sub> /liter)		Analyst	Oxygen Content (ml O <sub>2</sub> /liter) by Gas Chromatography (G)	Difference		
		Carpenter Modification ( <i>W<sub>c</sub></i> )	Standard ( <i>W<sub>0</sub></i> )			<i>W<sub>c</sub>-W<sub>0</sub></i>	<i>W<sub>c</sub>-G</i>	<i>W<sub>0</sub>-G</i>
1	A	4.61	4.57	C	4.60	0.04	0.01	-0.03
2	C	4.59	4.56	A	4.62	0.03	-0.03	-0.06
3	A	4.13	4.07	C	4.10	0.06	0.03	-0.03
·	·	·	·	·	·	·	·	·
·	·	·	·	·	·	·	·	·
92	C	4.08	4.01	A	4.10	0.06	-0.02	-0.09
93	A	4.64	4.56	C	4.71	0.08	-0.07	-0.15
94	C	4.69	4.62	A	4.70	0.07	-0.01	0.08
mean $\bar{d}$		—	—		—	0.0497	0.0135	-0.0367
std. dev. <i>s</i>		0.023	0.046		0.084	0.0509	0.0876	0.0962
rel. std. dev. <i>C</i>		0.51%	1.0%		1.8%	—	—	—
<i>F</i> ( $s^2/s_{w_c}^2$ )		—	4.05		14.0	—	—	—
<i>t</i>		—	—		—	9.46	1.50	3.74
significant		—	yes		yes	yes	no	yes
Difference between analysts—not significant.								

to the Carpenter modification of the Winkler method is not statistically significant; in the long run, any bias between results for these two methods will be negligible.

During routine operation of the gas chromatography method, daily calibration runs are made in duplicate (before and after a given series of analyses) on air-saturated water to check the performance of the equipment. The calibration data obtained during the two-week testing period just described are listed in Table 7; each value in the table is the mean of the two calibrations made that day. When the data are grouped according to analyst, and the ratio of their variances is calculated, the *F*-test indicates no significant difference between analysts. (It must be remembered in calculating the standard deviation that each item in this set of data is an average of two duplicate determinations.)

#### Dissolved N<sub>2</sub> Shipboard Data

The statistical distribution of dissolved N<sub>2</sub> data obtained by gas chromatography is of interest. On a several-week cruise in the Greenland Sea, data obtained during routine dissolved gas analyses with the chromatograph included 659 analyses for dissolved N<sub>2</sub>. This population sample is large enough to justify analysis according to the grouped frequency distribution technique (an arrangement of observations of the variable in ordered classes). Expressing the N<sub>2</sub> values found as percent saturation,\* the frequency histogram shown in Fig. 4 is obtained. The results are symmetrically grouped about a mean of 99.43%

\*Percent saturation is the ratio (N<sub>2</sub> found/N<sub>2</sub> at saturation) × 100. The saturation value for N<sub>2</sub> is the volume of N<sub>2</sub> (reduced to 0° C and 760 mm Hg) dissolved by 1 liter of sea water at a given temperature and salinity, when the sea water is in equilibrium with air at a pressure (dry) of 760 mm Hg. The saturation values for N<sub>2</sub> at various temperatures and salinities were obtained from Ref. 9.

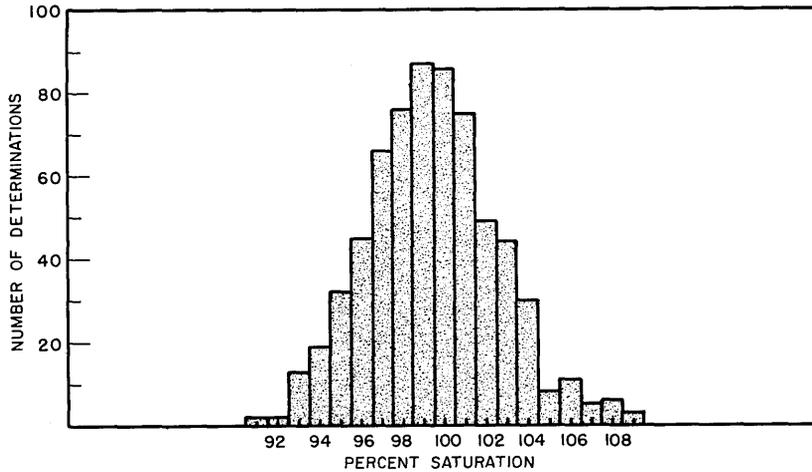


Fig. 4 - Frequency histogram of dissolved N<sub>2</sub> values

TABLE 7  
Gas Chromatography Calibration Data

Day	Analyst	Gas Content*	
		O <sub>2</sub>	N <sub>2</sub>
1	C	1.325	1.266
2	A	1.334	1.269
3	C	1.336	1.279
4	A	1.310	1.245
5	C	1.321	1.250
6	A	1.312	1.237
7	C	1.320	1.259
8	A	1.321	1.262
9	C	1.344	1.275
10	A	1.319	1.257
11	C	1.342	1.266
mean		1.3258	1.26045
std. dev. <i>s</i>		±0.0163	±0.0179
rel. std. dev. <i>C</i>		±1.23%	±1.42%
std. error of mean		±0.0036	±0.0039
difference between analysts - not significant			

\*Arbitrary units, proportional to peak area.

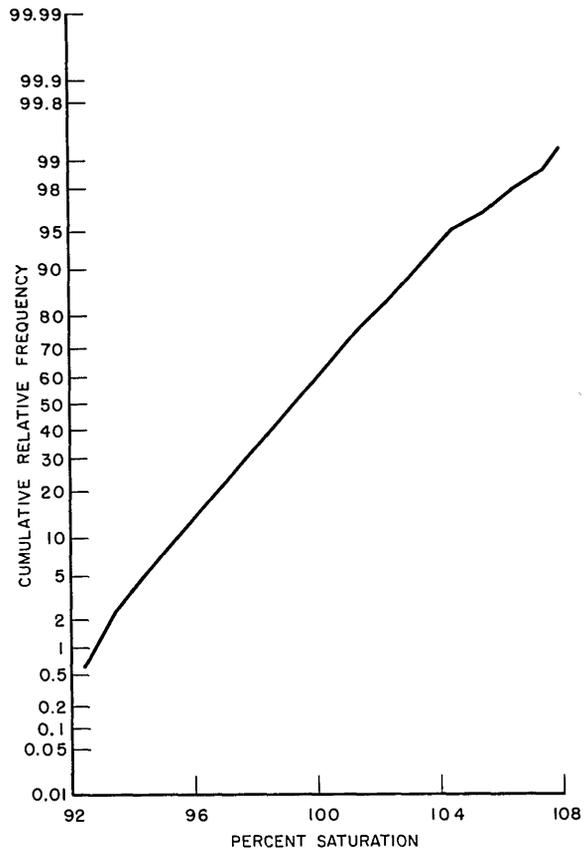


Fig. 5 - Cumulative frequency distribution of dissolved N<sub>2</sub> values, using a probability scale for relative frequency

saturation, with a standard deviation of  $\pm 3.14$ . Thus, 95% of the results fall within  $(99.43 \pm 6.15)\%$  saturation, and 99% between  $(99.43 \pm 8.09)\%$  saturation. The apparently normal distribution indicated by Fig. 4 is confirmed by the probability plot shown in Fig. 5; the straight line is evidence that the frequency distribution of results follows the normal distribution law

(i.e., independent variations of equal magnitude are occurring in a completely random fashion).

Other results obtained by the authors for dissolved  $N_2$  in sea water include a population sample of 270 determinations (obtained in the Andaman Sea), in which the results are symmetrically grouped about a mean of 100.08% saturation with a standard deviation of  $\pm 2.95$ , and a sample of 95 determinations (obtained in the Atlantic off Puerto Rico) having a mean of 99.45% saturation, with a standard deviation of  $\pm 1.75$ .

## DISCUSSION

It should be emphasized once again that the gas chromatography method used in the collection of data set forth in this report was developed for routine analyses to be performed by relatively unskilled personnel. Considerable improvement is of course possible but at the added expense of more elaborate equipment and increased requirements for personnel skill. Whether this is advisable from a practical point of view depends on the objectives of the oceanographer who is collecting data on dissolved gases. Thus, it is possible to obtain matched thermistors of much higher resistances for use in the thermal conductivity cell to give increased precision and sensitivity; on the other hand, these are much more sensitive to fluctuations in the external environment and would require a much tighter control of operating parameters such as cell temperature, carrier gas flow rate, and current input to the cell. Other sources producing variability in the results are the performance of the recorder-integrator, variations in the ship's power supply, and rf pickup by exposed cables and wiring. The latter two factors were particularly troublesome on the USNS GILLISS at the time the data in Table 6 were collected, even though voltage regulators and shielded wiring were used; it may in part explain the large standard deviation of  $\pm 1.8\%$  as compared to smaller values in other situations where this was not a source of trouble.

From an operations standpoint the data in Table 6 probably represent the best (and most severe) test which could be given, since these data were collected under actual field conditions without parallel replication. At the same time, it represents the conditions under which the largest scatter in the results may be expected. Thus, from a statistical point of view, a set of measurements made over a long interval of time will generally show a

greater dispersion than replicate analyses on a given sample performed in a short time. It is therefore not surprising that the standard deviations obtained in Tables 4 and 5 for the gas chromatography method should be less than that obtained from the data in Table 6.\* And, of course, it is even less surprising that results obtained in a laboratory under carefully controlled conditions should be so much better from a precision standpoint than those obtained in the field. In making estimates of precision, we therefore need to distinguish carefully among the following cases:

1. The reproducibility obtained by a single analyst performing replicate analyses on a given sample in a short time under near-ideal conditions in a laboratory (Table 1). This merely measures the ability of an analyst to repeat himself in the most favorable of circumstances. The estimate of precision in this case is of use only if subsequent analytical work is to be carried out under the same conditions.

2. The reproducibility obtained by an analyst performing replicate analyses on a given sample in a short time under field conditions (Table 4). This again measures the ability of an analyst to repeat himself, albeit under more difficult circumstances.

3. The reproducibility obtained by an analyst performing replicate analyses on a series of different (but similar) samples over a long period of time under field conditions (Table 7). This represents a more realistic approach than case 2. The scatter between replicate results on a given sample will itself show a day-to-day variation for a number of reasons, such as small variations between samples, variations in day-to-day performance of the analyst, and the fact that a source of error which may cause a constant bias over a short period of time may itself tend to fluctuate, so that over a long period it becomes just another source of random variation.

4. The reproducibility obtained by different analysts performing analyses under field conditions on different (but similar) samples over a long period of time without replication (Table 6). This is the best test which can be given a method, since it removes the unconscious tendency which

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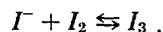
\*On the other hand the standard deviation for the improved Winkler method is actually greater in Table 5 than in Table 6.

most of us have to be influenced by our previous result when running replicates. Of course without replication one must plan the work according to some suitable statistical scheme (*e.g.*, where more than one method is used on each sample) which will allow an estimate of precision to be made.

From these considerations, one selects the estimates of precision calculated from the data in Table 6 as being the most realistic:  $\pm 1.8\%$  for gas chromatography,  $\pm 1.0\%$  for the standard Winkler method,  $\pm 0.51\%$  for the improved (Carpenter modification of the Winkler method), the differences between all three being significant from a statistical viewpoint. Some remarks are in order about these differences. It is possible, as pointed out above, to improve the gas chromatographic technique but at the expense of more elaborate equipment and possibly a need for more skilled personnel. The Winkler method, on the other hand, is a chemical method involving fairly complex reactions in solution and requiring manipulative techniques which call for a certain amount of skill on the part of the operator. In the hands of a skilled chemist the Winkler method becomes a highly precise and accurate method of analysis, but in the hands of a non-chemist it is quite possible that errors can arise from time to time which he may not recognize, even though he has been trained to go through the motions of making the analysis. For example, the Winkler method, being itself based on oxidation-reduction reactions, is subject to a number of interferences in sea water which do not affect gas chromatography—nitrite, sulfite, hydrogen sulfide, dissolved iron, some organics, waste pollutants, *etc.* All these considerations must be weighed in choosing a method for routine survey operations.

From the standpoint of accuracy, it seems quite evident that neither gas chromatography nor the Carpenter-modified Winkler method are affected by systematic errors. Strictly speaking, one should say only that their *relative* bias is zero, but it is extremely improbable that two such dissimilar methods should by coincidence be affected by systematic errors to the same extent. The existence of a small but statistically real negative bias of the standard Winkler method relative to the other two is of interest. A closer examination of the chemical basis of the Winkler technique reveals a possible reason. Near the end

of the series of chemical reactions which occur during the analysis, elemental iodine is formed in acid solution, the amount of iodine being proportional to the quantity of dissolved oxygen originally present. The elemental iodine is then titrated to a suitable endpoint with standardized thiosulfate. Unless adequate precautions are taken, varying losses of free iodine can occur, depending on the manipulative techniques employed by the analyst. Excess iodide ion is usually added at the beginning in order to tie up the elemental iodine as triiodide ion:



The formation of  $I_3^-$  does not interfere with the thiosulfate titration and prevents loss of the elemental iodine as  $I_2$ . However, if the concentration of excess  $I^-$  ion is too small, sufficient  $I_2$  may exist to allow losses. That is, if a large excess of  $I^-$  ion is not present, the  $I^-$  term in the expression for the above equilibrium cannot be considered constant, and the proportion of free  $I_2$  will vary, depending on the relative concentration levels. The concentration of excess  $I^-$  ion in the Carpenter-modified Winkler method is a factor of 10 times greater than in the standard Winkler method; loss of  $I_2$  is therefore much less likely. While the authors have not investigated this possibility, it is advanced as a reasonable explanation for the slight, but consistently lower results obtained by the standard Winkler method.

The zero bias of the gas chromatography method, as judged by its agreement with the Carpenter-modified Winkler method, emphasizes the point that the instrumental responses of the chromatograph must have been correctly calibrated by the simple calibration technique used by the authors. This involves bubbling a stream of air for about 15 minutes through 100 ml of distilled water to produce an air-saturated solution, which is then treated exactly the same as the unknown samples. The inlet point for the stream of air is about 3 inches below the surface of the water. Because of this extra hydrostatic head of 3 inches, one might argue that the water becomes supersaturated. That such is not the case is shown by the zero bias of the method, since a calibration solution which is supersaturated would give a low calibration factor and cause low results to be obtained. The considerable turbulence in the small

volume during the saturation process obviously prevents any supersaturation effect. To test this point further, the authors carried out several experiments involving saturation of water contained in long vertical tubes under such conditions that little or no turbulence resulted. A stream of finely divided bubbles of air was led in at the bottom of the column, and at the end of a sufficiently long period of time the flow of air was shut off and samples of water were withdrawn from the bottom of the tube for analysis. Varying degrees of supersaturation were found, depending on the height of the water column and the degree to which mixing was minimized. Deliberate agitation of these solutions always reduced the supersaturation, although not eliminating it entirely; the extent of water surface area through which the gas could escape was small compared to the total volume, so that the approach to equilibrium with the atmosphere became slower as the supersaturation decreased.

The authors have routinely determined dissolved nitrogen simultaneously with dissolved oxygen. The precision with which nitrogen is determined should not be significantly different than for oxygen, since both results are obtained from exactly the same sequence of operations on the same equipment. The data in Table 7 support this statement. For the same reason, one may advance the argument that systematic errors in the determination of nitrogen do not exist. Direct experimental support of this statement is lacking, since no other method of analysis for dissolved nitrogen was used.\* It may be instructive, however, to examine our results more closely. The dissolved nitrogen data reported in the preceding section in terms of percent saturation consists of three separate groups of data. Each group shows a spread in the data, the three means being 99.43, 100.08, and 99.45% saturation, with standard deviations of  $\pm 3.14$ ,  $\pm 2.95$ , and  $\pm 1.75\%$  saturation, respectively. Except for the last group, it is unlikely that such dispersion could be explained in terms of the precision of the method, since this would require a much larger standard deviation for the nitrogen analyses than for the oxygen

analyses. The explanation for this spread must be sought elsewhere (see below). Of more interest is the fact that the observations always center about a mean very close to 100% saturation. Since the existence of any systematic errors would result in a shifting of this mean (without affecting the scatter of the data about the mean), its constancy at 100% saturation argues strongly against the existence of any such errors.

This observed spread in the percent saturation values for nitrogen has been observed by others. Rakestraw and Emmel (10) on a sample consisting of 85 determinations, reported a spread of 95 to 108%, the data being grouped about a mean of 100.4%. Hamm and Thompson (11), from a sample of 47 determinations for combined "nitrogen plus inert gas" content of Pacific water, reported a range of 93.7 to 109.1%, the data being grouped about a mean of 100.9% saturation with a standard deviation of  $\pm 3.5$ . Various explanations have been advanced to explain this spread. Rakestraw and Emmel suggest that such a spread in apparent saturation values is a result of temperature and salinity variations. Carritt (12) pointed out the possibility that the spread in data could have been caused by atmospheric pressure variations at the sea surface at the time saturation occurred. It is quite likely that the spread in data is caused by a combination of these factors. It is also quite likely that while each of these factors over a short time period might be considered as reasonably constant and thus act as a source of systematic error, their combined effect over much longer periods becomes variable and a source of random error. Figures 4 and 5 show that our dissolved nitrogen data follow a normal distribution law, which implies that the observed departures from the mean are caused by factors which fluctuate in a random fashion.

The use of the gas chromatograph for the analysis of other dissolved gases simultaneously with dissolved oxygen is perhaps one of the strongest recommendations which can be made in its favor. Previous work on dissolved nitrogen, for example, was carried out on samples collected at sea and analyzed weeks and even months later at a shore-based laboratory by manometric methods which in some cases did not even separate nitrogen from the other inert gases. The one disadvantage cited thus far in the case of gas

\*Laboratory measurements for dissolved  $N_2$  by the Van Slyke method (based on manometry) show a dispersion approximately equal to that obtained by gas chromatography ( $\pm 0.5\%$ ). No shipboard comparison was attempted, since the Van Slyke method is normally not used in routine oceanographic survey work.

chromatography (a precision of  $\pm 1.8\%$  for dissolved oxygen work in the field, as compared to  $\pm 1.0\%$  for the standard Winkler method and  $\pm 0.5\%$  for the modified Winkler method) must be weighed against its many advantages: simultaneous measurement of more than one dissolved gas, its advantages over manometry for dissolved nitrogen determinations, its ready application for routine operations, its reduced requirements for personnel skill as compared to Winkler titrations, its lesser susceptibility to introduction of systematic errors because of the ease and simplicity of calibration, and its greater ease of operation aboard ship in a rough sea as compared to the difficulties of carrying out a chemical titration.

One further advantage of gas chromatography might be mentioned. In situations where many routine analyses must be made and the data interpreted from chart readings, gas chromatographs have already been successfully tied in with digital computer systems (*e.g.*, in the petroleum industry), where the computer not only performs calculations on large amounts of data rapidly and precisely but through its memory bank can carry out complicated data interpretation operations. The recent emphasis on the development of automated data handling and digital processing of data aboard ship suggests the ready adaptability of the gas chromatograph to such systems. For example, in place of the recorder-integrator used in our work, an electronic integrating component could be substituted which would print out results on punched tape for use directly in a computer. Programming instructions could be worked out very simply for the computer to perform all the calculations of calibration factors, correction for argon, solubilities of dissolved oxygen and nitrogen, and percent saturation. The punched tape would need only three other bits of information: temperature, salinity, and barometric pressure (the latter needed for calibration calculation). The first two are normally measured with most Nansen casts as a matter of routine. Several checks could be built into such a program, such as a running comparison of all corrected nitrogen and oxygen calibration factors. These values should remain constant if the day-to-day performance of the equipment remains unchanged. The ratio of the calibration factors for these two

gases before and after a given run would also serve as an internal check for performance of the equipment during the run. A third check which could be programmed into the computer instructions might be a comparison of percent saturation for nitrogen against some established limits (*e.g.*, 95 to 105%).

## CONCLUSIONS

The usefulness of the simple gas chromatographic technique described in this report for routine oceanographic survey work should by now be well established. From a practical standpoint, the disadvantage of a slightly greater spread in data when compared to the more precise Winkler technique is far outweighed by the advantages: accuracy, ease and simplicity of calibration, routine operation by relatively unskilled personnel, performance capability in a rough sea, and, above all, the capability of obtaining simultaneous measurements on more than one dissolved gas on a small volume sample. To these should be added the potential advantage of a capability for direct tie-in with data processing systems aboard ship. For nonroutine work connected with special research projects, the precision of the chromatograph can be improved to match any existing methods but at the expense of more elaborate equipment than is described in this article.

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13. ABSTRACT <p>A gas chromatographic method developed by the authors for the determination of dissolved gases in sea water has been evaluated with respect to precision and accuracy by comparison with other methods. Both laboratory and shipboard measurements were employed in the evaluation. Dissolved oxygen analyses made at sea under routine conditions of operation over a period of two weeks indicate statistically significant differences in precision for the three methods tested: gas chromatography (<math>\pm 1.8\%</math>), standard Winkler method (<math>\pm 1.0\%</math>), and a modification of the Winkler method (<math>\pm 0.51\%</math>). No significant bias was found between gas chromatography and the improved Winkler method; a small but statistically significant bias (<math>-1\%</math>) was found for the standard Winkler method relative to the other two. From a practical point of view, these differences are not considered important for routine survey operations. The dissolved <math>N_2</math> data obtained by gas chromatography are grouped about a mean value of 100% saturation, with approximately 95% of the values falling within <math>(100 \pm 5)\%</math> saturation. The advantages of gas chromatography (routine analyses by relatively non-skilled personnel to obtain simultaneous measurements of more than one gas on a small volume of liquid) are felt to be sufficient to warrant its further use in oceanography.</p>			

14. KEY WORDS	LINK A		LINK B		LINK C	
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Measurement Sea Water Dissolved Gases Gas Chromatography Statistical Analysis						

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