

1-3001

Preliminary Report

SCOR CHEMISTRY INTERCALIBRATION SESSION

Honolulu, Hawaii, September 4-9, 1961

The SCOR oceanographic chemistry intercalibration working session was held in the Department of Chemistry at the University of Hawaii on 4-9 September 1961, under the general direction of Dr. Bostwick H. Ketchum of the Woods Hole Oceanographic Institution, Chairman of the SCOR Chemistry Committee. Part of the work was conducted aboard the Australian Research Vessel, H.M.A.S. Gascoyne. The working group offers its most sincere appreciation to the personnel aboard the Gascoyne, to Professor Harry Zeitlin of the University of Hawaii who was most cooperative in providing facilities and supplies at the University, and to Mr. Thomas Austin and Mr. Richard Barkley of the Bureau of Commercial Fisheries who arranged to provide us with the necessary sea water samples for analysis, with a photometer, and with some required glassware. Without their cooperation our investigation would have been impossible and they deserve full credit for making every possible effort to make our meeting a success.

Prior to and during the first two days of our working group session, chemical intercomparisons were conducted aboard the Soviet Oceanographic Research Vessel Vitiaz. The results of these intercomparisons are not included here since a separate report is being prepared by D. J. Rochford of Australia, who was one of the two visiting chemists on this cruise. Dr. T. J. Chow of Scripps Institution of Oceanography participated both in the work on the Vitiaz and in the analyses in the laboratory of the University of Hawaii.

The list of chemists who participated in the meetings is included in Table 1. The results of the analyses in the tables to follow are reported by number for each laboratory as in Table 1. Representatives of six countries (seven laboratories) all conducted intercomparisons of the inorganic phosphorus and the oxygen methods; three laboratories are intercomparing analyses for total phosphorus but the results of these analyses are not yet complete, and four laboratories have intercompared methods on nitrates. It should be emphasized that each of these analysts worked very hard for long hours during the week of the working session. Thus while it would have been desirable to intercompare other methods, such as nitrite and silicate, it would have been impossible to do so with the limited personnel and time that was available.

Others who were in attendance part of the time, but did not actively participate in the chemical analyses, were welcome for the contributions that they made to the discussions of the results. These included Dr. Ken Sugawara of Japan, Dr. D. J. Rochford of Australia, and Dr. J. D. H. Strickland of Canada.

INORGANIC PHOSPHATE

The intercomparison of phosphates included comparison of standard solutions, analysis of low phosphorus content sea water to which various additions of inorganic phosphate had been made, and analysis of unknowns obtained at various depths in the Pacific Ocean from 50 to 600 meters. The results are given in Tables 2-4. In every case five separate analyses were made on each solution and the results reported are the average values. Statistical analysis, as yet uncompleted, will permit us to evaluate the standard deviation for each analyst based upon this replication of samples.

The only variation which appeared to produce a significant difference in the results was the use of distilled water for the calibration of the method. The Australians calibrated in distilled water and used a salt effect correction of 1.1 but, even so, their values were consistently low in comparison to results obtained by analysts who calibrated using sea water. The salt effect correction computed from the data provided by this meeting would suggest that the proper salt effect correction is nearer 1.2 than 1.1. Jayaraman, the Indian analyst, was the only one to use a visual comparison for the phosphate determination. He also made up his standards in distilled water. His values were low by 20 to 40 per cent up to a concentration of about 2 $\mu\text{g A}$ of added phosphate per liter. Above this concentration his values were close to the mean. The agreement at the high concentrations may be related to the faster fading of the color in distilled water when compared to sea water, a difference in rate which is not so significant at the lower concentrations.

Comparison of standards

The comparison of standards was made by adding the appropriate amount of each analyst's standard solution to sea water so as to give a final concentration of 1.5 $\mu\text{g A/liter}$ plus the sea water blank. The data in Table 2 present the ratio of results (other standard/own standard). This, of course, eliminates the differences due to salt effect correction mentioned above since the analyst's own standard and those of others are measured in the same way.

Accepting Strickland's (1960)¹ estimate of precision at 3 $\mu\text{g A/liter}$ as applicable to the precision at 1.5 $\mu\text{g A/liter}$ ($\pm 0.11/n^{1/2}$, where n is the number of determinations), a range of the ratio for 5 analyses for each standard between 0.94-1.07 would indicate a complete agreement between the two compared standards. There is not a single comparison in the table that falls outside of this range, indicating that all of the standards are statistically identical. The fact that the ratios are so much closer to unity than this for every analyst may indicate that for the specially trained and highly competent group that cooperated in this meeting the precision which can be achieved by the method is greater than that given by Strickland for routine analyses. Our further study of these results will give a statistical estimate of the standard deviation for each analyst and will allow us to determine individual ranges of precision which will make this comparison somewhat more meaningful.

Sea water with added phosphate

A large sample of surface, low phosphate sea water was provided by Mr. Barkley of the Bureau of Commercial Fisheries. Five-liter samples of this sea water were dispensed into each of seven carboys and a standard solution of inorganic phosphate (W.H.O.I. sample) was added to give a graded series of concentrations. No effort was made to do this with precision and the enrichments were made on Saturday night and the first analyses performed on Monday morning. Some biological changes could, of course, have occurred in the interim. Thus the recovery is not necessarily equal to the nominal amount which was added. The results of these analyses are reported in Tables 3, 3a and 3b. Each number reported is the mean of five analyses. The means and standard deviation for each sample are computed for all seven analysts and also for the five analysts who used sea water standards in calibrating their method.

¹Strickland, J. D. H. 1960. A manual of sea water analysis. Bull. 125. Fisheries Research Board of Canada vi + 185 pp. Ottawa, Canada.

This table makes it clear that those using distilled water for standardization are obtaining low results and that even the Australians' use of a salt error correction of 1.1 leaves their results generally lower than the average of the group using sea water for the standardization. Including these results in the averages introduces a constant bias in the results and produces a large standard deviation for the group as a whole. The standard deviations of the five analysts who use sea water for calibration appear reasonable up to about $2.5 \mu\text{g A/liter}$, ranging from .02 to .09 $\mu\text{g A/liter}$. At values of 3 $\mu\text{g A/liter}$ it is clear that the Woods Hole results are low. Concentrations such as these are never found in the Atlantic Ocean and the photometer used is not satisfactory for this concentration.

The determination of the amount of phosphate in the unenriched sea water is most uncertain, since the standard deviation is numerically similar to that observed at higher concentrations and thus constitutes a large percentage of the amount of phosphate present. In Table 3a are listed the amounts of phosphate corrected for the blank, i.e. for the amount each analyst determined in the unenriched sea water, in order to compare the recovery with the nominal amount added to the sample. As mentioned above, perfect recovery cannot be expected because of the way in which the samples were made up and because of the time lapse between the addition of the standard and the analysis. The one who came closest to the nominal addition in every case was Shah of Pakistan (4) and the one who came closest to the mean of the five who used sea water for their calibration was Armstrong of the United Kingdom (5). The deviations from the mean of the five analysts who used sea water calibrations are presented in Table 3b. For the two analysts who used distilled water calibrations the ratio of the mean value to their own is also presented. The Australians, who use a ratio of 1.1 in their calculation are still roughly 8 per cent low in the higher concentrations. The combined factor for salt effect correction would thus be 1.19, identical with that recommended by Cooper (1938)² for use with a photometer. Jayaraman's data were uncorrected for salt error and for the lower values the correction should be between 1.22 and 1.40. Cooper (1938) gives a salt effect correction for visual comparisons of 1.3-1.35. Jayaraman's data at the high concentrations are comparable to the mean of those using sea water for their standardization. At such concentrations the color in distilled water fades much more rapidly than it does in sea water and it could be that this fading has brought the two colors much more closely similar in these cases.

For the analysts who used salt water as a means of standardization, all but four of the deviations from the mean are within two standard deviations as listed in Table 3. Taking .05 as the standard deviation, fourteen of the thirty values are this amount or less, twelve are between .05 and .10, two are between .11 and .15 and two are greater than this. Most of the deviations are randomly distributed as a function of concentration but the two extreme ones are at the highest concentration. As mentioned above, the Woods Hole photometer is clearly inadequate for these high concentrations and to balance the very low value obtained by McGill of Woods Hole, Shah of Pakistan obtained a nearly equally high value compared to the average of all.

²Cooper, L. H. N. 1938. Phosphate in the English Channel. Journal Mar. Biol. Assoc. U. K. 23: 171.

Analysis of Unknowns

Samples of sea water obtained from eight different depths in the Pacific Ocean were provided by Mr. Barkley of the Bureau of Commercial Fisheries Honolulu Biological Laboratory. Each of these samples was about 10 liters in volume and they were simply stored in clear glass bottles until their analysis in the laboratory. The results are not, therefore, to be taken as characterizing the distribution of phosphorus in the ocean since biological changes could have taken place between the time of collection and the analysis. The samples obtained by each analyst should, however, have been identical and thus achieve the purpose of comparing the analytical technique. Each analyst did five samples of each bottle and the data in Table 4 are again the average of these five analyses. The mean value and standard deviation for all of the analysts and the mean and standard deviation of the five analysts who used sea water for calibration are computed.

A special comment must be made concerning the two values presented for the Japanese analyst, Dr. Sugiura. The data listed opposite 3a are those originally handed in as the analyses for these samples. They were obviously out of line with all the others and it turned out that Sugiura had replaced the bulb in his photometer, apparently changing its position in the process. Unfortunately, the original sea water which had been used for his calibration had been exhausted by this time and he did not run a complete new calibration curve. On the basis of the optical density of one value, that for $1.5 \mu\text{g A/liter}$, he derived a new relationship between added phosphorus and optical density and the values listed under 3b are computed from this relationship. This experience emphasizes the necessity of recalibrating an instrument frequently and especially whenever any change is made. The shift might have been recognized at sea by comparison with previous stations but it would not necessarily be so if one were in a rapidly changing environment. In the calculation of the averages the values listed opposite 3a have been ignored and the values listed opposite 3b are used.

Again the inadequacy of the salt error correction is apparent in the Australian and Indian data and when these are included in the averages of all, the standard deviation becomes large at concentrations greater than $1 \mu\text{g A/liter}$. Below this concentration the standard deviation of all measurements is not significantly different from that derived for the analysts using sea water for their standardization. The Woods Hole data are the lowest at the two high values (greater than $2.2 \mu\text{g A/liter}$) emphasizing again the inadequacy of the Woods Hole photometer for high concentrations. On the whole the standard deviations for all analysts using sea water in their calibration are about what would be expected from previous knowledge of the method.

CONCLUSIONS

The following conclusions may be drawn from the intercomparison of the method for the determination of inorganic phosphate in sea water:

- 1) The only substantial error in the determination of phosphorus by the seven analysts present was in the failure to correct adequately for the salt error when distilled water was used for the standardization of the photometer, or for direct visual comparison. Where low phosphorus sea water is not available for the preparation of standards it may be desirable to use the synthetic sea water such as described by Strickland (1960, page 46) though no test of the validity of this artificial sea water was made at this meeting.

2) It was also discovered that the photoelectric eye photometer as used by the Woods Hole group is inadequate for the high concentrations of phosphate which may be expected in the Pacific or Indian Oceans.

3) The intercomparison of standards shows no variation among analysts.

4) With the exceptions noted in 1) and 2) above the method seems to be reproducible with a standard error of approximately $\pm .05 \mu\text{g A/liter}$ throughout most of the concentration range tested. At a later date this report will be expanded by determinations of the standard deviation for individual analysts, which is available by reason of the replication of samples.

OXYGEN COMPARISONS

In order to compare the methods for the determination of oxygen, the titration of standardizing solutions by various groups and the actual determination of oxygen in samples of sea water obtained aboard the Gascoyne were made. If this intercomparison were to be planned again, some definite changes and improvements in the system would be introduced. These will be discussed below.

Intercomparison of standards

Each analyst, in so far as was possible, compared by his own titration and method the standards of others with his own. The results are presented in Table 5, in which the ratio of the volume of thiosulfate for the "other" standard is divided by the volume of thiosulfate for the analyst's "own" standard. Had the stated normality of the standards differed from .01 it would have been necessary to divide these volumes by the normality as given by the analyst who supplied the standard. However, all the standards titrated and intercompared had an expressed normality of .01, making this correction unnecessary.

It was not possible to intercompare one standard. Jayaraman of India used a 0.1 N dichromate standard and titrated this with his 0.1 N thiosulfate. His thiosulfate was then volumetrically diluted to give a solution of 0.01 N. All others used the 0.01 N standard solution of potassium iodate or potassium biniodate. The titration of a dichromate standard diluted to give 0.01 N solution gives an unsatisfactory endpoint and consequently the few results that were obtained in this way are not included in Table 5.

Taking an accuracy of titration of 1 per cent, all of the standards, with two exceptions, were found to be identical. It was impossible for every analyst to analyze every other analyst's standard, because few realized the volume that would be needed for this intercomparison and before the end of the session all standards were exhausted. Enough was completed to permit the conclusion that the standards are satisfactory, with the two exceptions noted above. The two exceptions both gave a ratio of 1.02, indicating that these standards were somewhat stronger than those of the other analysts. Mantyla of Scripps, U. S. A., had two standards available. One of these had been sent on the Vitiaz for the work prior to the session and the other was borrowed from the Scripps ship Horizon when she was in Honolulu. The latter of these was used first and is called standard I for this group and was the one found to be high.

Mantyla also found it to be high using Scripps standard II. The other standard in error was a very similar case. Armstrong of the United Kingdom had brought with him several vials containing standards. The one opened and used first gave a ratio of 1.02 when compared to the standards of those titrating it. Another, when opened, proved to be identical with the standards used by others. The reason for these two erroneous standards is completely unknown. It does emphasize the necessity for intercomparing the standards more frequently than has been done in the past. Each laboratory, when a new standard is prepared, should compare its titer with that of the standard previously used and some sort of international interchange of standards for the oxygen method should be arranged. It would be possible to have a single source of standard solutions, much as the Copenhagen water is used for salinity, which would ensure that the standards, at least, of all analysts are identical.

One deficiency of this method of intercomparing standards was not recognized until it was too late to do anything about it. Each analyst compared his own method using his own thiosulfate and the fact that identical results were obtained merely proved that all analysts are able to make up a satisfactory standard (with the two exceptions noted above). It does not prove that the different methods would give the same results. This experiment should have been planned with all analysts using a single source of thiosulfate and the comparison should be between the computed normalities of thiosulfate for the various analysts and the various standard solutions. Such a modification of the plan of this experiment would have evaluated the differences in the analytical techniques as well as the differences in the standard solutions.

Analysis of unknowns

On Wednesday, 6 September, the analysts boarded the Gascoyne which then proceeded south and east of the island of Oahu until the depth of water was 1000 fathoms. Three separate casts with Nansen bottles were made between about 10:00 a.m. and 2:00 p.m. Five depths were sampled, selected so as to give the maximum range in oxygen concentration, namely 50 meters, 200 meters, 400 meters, 600 meters, 900 meters. At each of these depths three Nansen bottles were placed on the wire about 2 meters apart and three oxygen samples were drawn by different analysts from each of these three Nansen bottles. Thus nine oxygen samples were obtained from each depth on each cast.

The ideal system for selecting the analyst to draw any one of these nine samples would have been completely random. Our time for this sampling procedure aboard the ship was limited, however, and a completely randomized sampling technique would have led to complete chaos. The system described in Table 6 for the sampling of this water was designed to offer the maximum number of inter-comparisons among the various analysts, and, after the first cast when some confusion occurred, the sampling system worked very smoothly and well.

These data will need to be analyzed for differences among casts, for differences among the first, second and third oxygen sample from each Nansen bottle, and for the differences introduced by the two-meter spacing of bottles at each depth. These have not yet been studied but the differences between each analyst and the average for all analysts at that depth on that cast have been derived and are presented here.

The analytical results for oxygen are presented in Table 7 in the same order and arrangement as the identification of analysts is presented in Table 6. The range of oxygen observed in these samples was from roughly 0.8 to 4.6 ml oxygen per liter, thus achieving the broad range of concentrations that was planned.

In Table 8 are presented the mean oxygen values for each depth and cast and the appropriate standard deviation. The means are generally the average of nine numbers with the exception of those cases, shown in Table 6, where no samples were obtained. This loss of samples occurred only in the first cast and probably resulted because some people were more liberal in rinsing and flooding over their bottles than others. Because of the limitation of volume, those who would ordinarily overflow a large volume of sample were unable to do so and the results may be prejudiced to the extent that this introduces an error. Also in Table 8 are shown the differences between a given analyst's value and the mean for all. Reference to Table 6 will indicate that these differences are sometimes the difference between one analysis and the mean, sometimes between two analyses and sometimes between three analyses and the mean. Thus they are statistically not uniformly weighted.

Most analysts had relatively small variations which fluctuated between plus and minus values from the mean value. The only exception to this was the group from Woods Hole whose oxygen values are consistently high, averaging high by + .14 ml/liter. The explanation for this is unknown but it will be discussed below.

The shortcoming of this type of experiment is that there is no absolute knowledge of what the true value for any cast and depth should be. The proper way to run this experiment would be to set up several equilibrating flasks of sea water using known gas mixtures for the equilibration. An absolute value for the oxygen content of the water would then be known and it would be possible to compare the value obtained by each analyst with the true value. This type of experiment has been conducted at Woods Hole, and if Dr. Dayton Carritt had been able to attend these meetings the oxygen evaluations would have been set up in this way. Setting up the experiment in this way would also have permitted each analyst to do a number of replicates on every sample rather than having the analyst vary from one to three samples on each cast and depth. The experiment as performed shows the relative difference between various analysts but does not indicate in any way whether the Woods Hole values are high or whether the values of all others are low. The democratic conclusion would favor the latter, but it is not necessarily correct.

In this connection a brief discussion of the possible sources of error in the standardization analysis for oxygen may be pertinent. In the first place, in the standardization of the thiosulfate, any error in the method would tend to produce a high titer and thus a low value for the normality of thiosulfate, ergo a low oxygen determination. The sources of error include the photo-oxidation of potassium iodide to free iodine, excess acidity which likewise produces free iodine from potassium iodide, or an unduly long titration time which also increases the free iodine. Likewise the errors for the titration of oxygen in sea water all tend to produce high values in the same sense as those quoted above. If the methods and reagents for both standardization and for titration are identical, it can be presumed that these errors may cancel out,

giving still a correct value for the oxygen content of sea water. If, however, the methods or reagents for the standardization are different from the methods or reagents for the titration, it is conceivable that analysts will get a high value for the titer on the thiosulfate which could then produce a low value for the calculated amount of oxygen in sea water. For these reasons it is essential that methods be developed to provide a standard solution which is a known amount of oxygen in sea water rather than the indirect standardization which was used by all analysts present. This unfortunately was not done and the only conclusion that can be reached from the above data is that the Woods Hole values are high compared to all of the other analysts who participated in this investigation.

NITRATE-N

Three analysts intercompared their methods for the determination of inorganic nitrate-N in sea water. These were the Australians (1), and the analysts from Scripps Institution (6) and from Woods Hole (7) in the United States. Both the Australians and Woods Hole analysts used the Mullin and Riley type of determination which depends upon reduction by hydrazine and determination of the nitrite in the final solution. The Australians filtered their samples before analysis but this was not done by Woods Hole. Dr. Chow of Scripps used the method that he has recently developed which involves a zinc reduction at 0°C and determination of the nitrite produced.

The nitrate calibrations were not entirely satisfactory because of the high value of nitrate present in the distilled water available at Hawaii. Also, we had selected as the low-N sea water sample "O" which had the lowest phosphate content of the series of samples collected at various depths (see Table 4). It developed that this sample of sea water did not have the lowest nitrate content so the analysts were left with considerable uncertainty concerning their reagent blank correction and concerning the correction which should be applied to their standards which were prepared in sea water sample "O".

The results of the determination of nitrate by these three analysts are presented in Table 9. The Woods Hole and Australian results correspond fairly closely throughout most of the range, but above the minimum value the results obtained by Dr. Chow of Scripps appear to be low. Even the Australian and Woods Hole results do not agree with the precision given by Strickland (loc. cit.) who, at the 30 $\mu\text{g A}$ per liter level, gives a precision of $\pm 1.3/n^{1/2}$ $\mu\text{g A/liter}$, in which n is the number of determinations. At a value of 4.5 $\mu\text{g A/liter}$, Strickland gives a precision of $\pm 0.3/n^{1/2}$ $\mu\text{g A/liter}$, using 1 cm cell in the former case and 10 cm cells in the latter. The values for samples "O", "P", "R", and "T", differ by greater amounts than would be expected on Strickland's comparison. As yet no evaluation of the precision achieved by each analyst who presented replicate results has been made.

Respectfully submitted,

Bostwick H. Ketchum, Chairman
SCOR Chemistry Committee for the Indian Ocean

Table 1. List of Participants in the
SCOR Chemical Intercalibration Session in Hawaii, September 4-9, 1961

Analyses:--	PO_4^{3-}	ΣP	O_2	NO_3
1) Australia				
F. Davis	x	x	x	
B. S. Newell				x
2) India				
R. Jayaraman	x		x	
3) Japan				
Y. Sugiura	x		x	x
4) Pakistan				
Riaz Ali Shah	x		x	
5) United Kingdom				
F. A. J. Armstrong	x		x	
United States				
6) Scripps Institution				
A. Mantyla	x		x	
T. J. Chow		x		x
7) Woods Hole Oceanographic				
D. McGill	x		x	
N. Corwin		x		x

Table 2. Phosphate: Comparison of standards
at a concentration of 1.5 $\mu\text{g A/l}$ in low P sea water.

		ratio $\frac{\text{other}}{\text{own}}$							Mean by Analyst
Analyst	Standard	1	2	3	4	5	6	7	
1		X	0.99 ₃	0.99 ₃	0.99 ₃	0.99 ₃	0.99 ₃	0.98 ₅	0.99 ₁
2		1.0	X	1.0	1.0	1.0	1.0	1.0	1.0
3		---	1.04 ₆	X	1.00 ₇	---	0.96 ₇	---	1.00 ₇
4		0.99 ₃	---	1.05 ₃	X	1.00 ₅	---	---	1.01 ₇
5		0.98 ₈	0.98 ₈	0.99 ₃	1.03 ₇	X	1.01 ₈	0.99 ₈	1.00 ₃
6		1.02 ₁	1.04 ₆	1.02 ₀	1.01 ₂	0.96 ₆	X	1.04 ₀	1.01 ₇
7		1.02 ₀	1.03 ₁	1.00 ₆	1.02 ₃	1.01 ₃	1.00 ₈	X	1.01 ₇
Mean of standard		1.00 ₄	1.02 ₁	1.01 ₁	1.01 ₂	0.99 ₅	0.99 ₇	1.00 ₅	

Each number is the mean of five analyses.

**Table 3. Phosphate: Analysis of sea water containing
graduated amounts of phosphate standards**

Notation:--	<u>0</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	
approx. spike μg A/l :--	none	0.5	1.0	1.5	2.0	2.5	3.0	
<u>Analyst</u>								
1	0.11	0.57	1.19	1.47	1.88	2.34	2.80	DW std. Salt ef- fect corr. = 1.1
2	0.21 ₂	0.53 ₄	1.09 ₈	1.32 ₄	1.78	2.56	3.06 ₈	DW std. No salt effect corr.
3	0.29	0.67 ₆	1.36 ₀	1.70 ₈	2.18 ₈	2.76	3.18	
4	0.18 ₂	0.68 ₉	1.24 ₄	1.69 ₄	2.20 ₆	2.75 ₀	3.25 ₀	
5	0.19	0.64 ₂	1.35 ₄	1.64 ₆	2.06 ₀	2.54 ₆	3.00 ₄	
6	0.15 ₄	0.65 ₄	1.42 ₈	1.65 ₆	2.16 ₆	2.65 ₂	3.01 ₂	
7	0.24 ₈	0.65 ₈	1.32 ₆	1.70 ₂	2.11	2.64	2.96	
Mean of all	0.19 ₈	0.63 ₂	1.28 ₆	1.60 ₀	2.05 ₆	2.60 ₇	3.03 ₅	
Standard deviation	0.05 ₉	0.05 ₈	0.11 ₄	0.14 ₆	0.16 ₄	0.14 ₄	0.14 ₇	
Mean of five (3-7)	0.21 ₄	0.66 ₄	1.34 ₂	1.68 ₁	2.14 ₆	2.66 ₉	3.08 ₁	
Standard deviation	0.05 ₅	0.01 ₉	0.06 ₇	0.02 ₈	0.06	0.08 ₈	0.12 ₆	

Each number in the table is the mean of five analyses.

Table 3a. Phosphate: Analysis of sea water
containing graduated amounts of phosphate standards, corrected for blank

<u>Analyst</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	
1	0.46	1.08	1.36	1.77	2.23	2.69	
2	0.32	0.89	1.11	1.57	2.35	2.86	DW Std. No salt corr.
3	0.39	1.06	1.41	1.84	2.47	2.91	
4	0.51	1.06	1.51	2.02	2.57	3.07	
5	0.45	1.16	1.46	1.87	2.36	2.81	
6	0.50	1.28	1.50	2.01	2.50	2.85	
7	0.41	1.08	1.45	1.86	2.40	2.61	
Mean of All	0.43 ₄	1.08 ₇	1.40	1.85	2.37 ₉	2.83	
Mean of those using SW std.	0.45	1.13	1.47	1.92	2.46	2.85	

Each number in the table is the mean of five analyses.

Table 3b. Phosphate: Deviations from means of
five comparable analyses (see text) of the spiked sea water series
(blank corrected)

<u>Analyst</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
1	+ .01	- .05	- .11	- .15	- .23	- .16
ratio	.996	1.05	1.08	1.08	1.10	1.06
2	- .13	- .24	- .36	- .35	- .11	+ .01
ratio	1.40	1.27	1.32	1.22	1.05	.995
3	- .06	- .07	- .06	- .08	+ .01	+ .06
4	+ .06	- .07	+ .04	+ .10	+ .11	+ .22
5	00	+ .03	- .01	- .05	- .10	- .04
6	+ .05	+ .15	+ .03	+ .09	+ .04	00
7	- .04	- .05	- .02	- .06	- .06	(- .24)?

Each number in the table is the mean of five analyses.

Table 4. Phosphate: Analysis of unknowns

Notation:--	N	O	P	Q	R	S	T	U
Depth:--	<u>50 m</u>	<u>150 m</u>	<u>200 m</u>	<u>250 m</u>	<u>300 m</u>	<u>400 m</u>	<u>500 m</u>	<u>600 m</u>
<u>Analyst</u>								
1	0.40	0.26	0.44	0.68	0.88	1.24	2.03	2.57
2	0.35	0.32	0.42	0.60	0.72	0.99	1.72	2.41
3 a	0.90	0.75	0.99	1.15	1.67	1.70	2.90	3.51
3 b	0.42	0.27	0.50	0.67	0.89	1.24	2.28	2.78
4	---	0.23 ₀	0.42 ₀	0.64 ₈	0.91 ₄	1.38 ₆	2.27 ₀	2.85 ₂
5	0.42 ₂	0.27 ₄	0.45 ₈	0.73 ₀	0.94 ₄	1.32 ₂	2.19 ₀	2.75 ₂
6	0.37 ₀	0.25 ₂	0.42 ₄	0.74 ₀	0.93 ₀	1.36 ₈	2.24 ₆	2.77 ₂
7	0.46 ₈	0.33 ₆	0.50	0.81 ₂	0.92 ₂	1.29 ₀	2.12 ₀	2.65 ₂
Mean of all	0.40 ₅	0.27 ₉	0.45 ₂	0.69 ₇	0.88 ₆	1.26 ₂	2.12 ₂	2.68 ₄
Standard deviation	0.04 ₂	0.03 ₆	0.03 ₆	0.07 ₀	0.07 ₆	0.13 ₃	0.19 ₉	0.15 ₂
-----	-----	-----	-----	-----	-----	-----	-----	-----
Mean of 3b-7	0.42 ₀	0.27 ₄	0.46 ₀	0.72 ₀	0.92 ₀	1.32 ₁	2.22 ₁	2.76 ₁
Standard deviation	0.04 ₀	0.03 ₇	0.03 ₉	0.06 ₅	0.02 ₀	0.05 ₉	0.06 ₅	0.07 ₂

^a Original data as presented after inserting new bulb in photometer; not used in computing averages.

^b Data corrected on basis of partial recalibration of photometer (see text).

Each number in the table is the mean of five analyses.

Table 5. Oxygen: Comparison of standards on titration
against individual thiosulfate solutions

		ratio $\frac{\text{other}}{\text{own}}$						
Analyst	Standard	1	3	4	5		6	7
					I	II	I only	
1		X	1.00 ₀	---	1.02 ₀	---	1.02 ₀	0.99 ₈
3		---	X	---	---	---	---	---
4		0.99 ₇	1.00 ₂	X	---	---	---	---
5	II	1.00 ₃	0.99 ₉	1.00 ₅	X	X	1.02 ₉	1.00 ₀
6	I	0.97 ₂	0.96 ₀	0.97 ₂	---	---	X	---
	II	0.99 ₉	0.98 ₇	1.00 ₀	---	---	1.02 ₈	---
7		1.00 ₄	1.01 ₀	1.00 ₅	1.02 ₀	0.99 ₆	1.01 ₃	X

Table 6. Plan of oxygen sampling aboard the Gascoyne on 6 September 1961.

The numbers in the table correspond to the analysts listed in Table 1.

(X = no sample obtained)

Depth:--	Cast	50 m			200 m			400 m			600 m			900 m		
		a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
I	1	1	7	5	3	X	2	6	1	7	5	3	4	2	6	1
	2	7	5	3	4	2	6	1	7	5	3	4	X	6	1	7
	3	X	3	4	2	X	1	7	5	3	4	2	X	1	7	X
II	1	3	4	2	6	1	7	5	3	4	2	6	1	7	5	3
	2	4	2	6	1	7	5	3	4	2	6	1	7	5	3	4
	3	2	6	1	7	5	3	4	2	6	1	7	5	3	4	2
III	1	6	1	7	5	3	4	2	6	1	7	5	3	4	2	6
	2	1	7	5	3	4	2	6	1	7	5	3	4	2	6	1
	3	7	5	3	4	2	6	1	7	5	3	4	2	6	1	7

Table 7. Oxygen concentrations (ml/l) determined by the various analysts (see Table 5) for the samples obtained on the Gascoyne on 6 September 1961.

Depth:--		50 m			200 m			400 m			600 m			900 m		
		a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
Cast I	1	4.55	4.74	4.69	4.31	X	4.09	3.44	3.46	3.63	1.29	1.20	1.35	0.87	0.80	0.78
	2	4.73	4.61	4.53	4.34	4.20	4.34	3.54	3.63	3.56	1.19	1.34	X	0.82	0.78	1.10
	3	X	4.59	4.54	4.23	X	4.35	3.65	3.53	3.47	1.34	1.20	X	0.84	0.98	X
II	1	4.47	4.65	4.33	4.20	4.36	4.60	3.59	3.52	3.62	1.18	1.10	1.15	1.10	0.92	0.83
	2	4.65	4.36	4.34	4.37	4.55	4.48	3.55	3.56	3.36	1.14	1.15	1.27	0.88	0.90	0.88
	3	4.37	4.44	4.59	4.55	4.43	4.38	3.64	3.46	3.45	1.17	1.26	1.27	0.85	0.88	0.84
III	1	4.38	4.59	4.78	4.43	4.36	4.45	3.83	3.74	3.85	1.50	1.17	1.21	0.82	0.84	0.75
	2	4.59	4.74	4.69	4.32	4.43	4.24	3.76	3.88	4.04	1.11	1.26	1.26	0.78	0.73	0.75
	3	4.68	4.45	4.57	4.40	4.20	4.22	3.93	4.04	3.83	1.36	1.32	1.19	0.77	0.76	0.92

Table 6. The mean oxygen, standard deviation, and the difference between each analyst's oxygen value and the mean of all for each depth and cast

Cast	Depth (m.)	Mean \pm σ	Difference by Analyst						
			1	2	3	4	5	6	7
I	50	4.62 ₅ \pm 0.08 ₆	- .07 ₃	---	- .06 ₃	- .08 ₃	+ .02 ₈	---	+ .11 ₃
	200	4.26 ₆ \pm 0.09 ₇	+ .08 ₄	- .09 ₂	+ .04 ₄	+ .07 ₄	---	+ .07 ₄	---
	400	3.54 ₆ \pm 0.07 ₉	- .04 ₆	---	- .07 ₆	---	- .00 ₁	- .10 ₆	+ .09 ₁
	600	1.27 ₃ \pm 0.07 ₄	---	- .07 ₃	- .07 ₈	+ .07 ₀	+ .07 ₇	---	---
	900	0.87 ₁ \pm 0.11 ₃	- .07 ₁	- .00 ₁	---	---	---	- .06 ₁	+ .16 ₉
II	50	4.46 ₇ \pm 0.13 ₂	+ .12 ₃	- .11 ₃	- .00 ₃	+ .18 ₃	---	- .07 ₇	---
	200	4.43 ₆ \pm 0.12 ₄	- .07 ₁	---	- .05 ₆	---	+ .01 ₉	+ .23 ₆	+ .13 ₁
	400	3.52 ₈ \pm 0.09 ₀	---	- .11 ₈	+ .00 ₇	+ .07 ₉	+ .06 ₂	- .07 ₈	---
	600	1.18 ₈ \pm 0.06 ₃	- .03 ₁	- .00 ₈	---	---	+ .08 ₂	- .06 ₈	+ .07 ₇
	900	0.89 ₈ \pm 0.08 ₁	---	- .05 ₈	- .03 ₈	- .01 ₈	+ .00 ₂	---	+ .20 ₂
III	50	4.60 ₈ \pm 0.13 ₁	- .01 ₈	---	- .03 ₈	---	- .03 ₈	- .22 ₈	+ .12 ₆
	200	4.33 ₉ \pm 0.09 ₈	---	- .11 ₉	+ .00 ₁	+ .08 ₈	+ .09 ₁	- .11 ₉	---
	400	3.878 \pm 0.10 ₈	+ .00 ₉	- .04 ₈	---	---	- .04 ₈	- .12 ₈	+ .16 ₃
	600	1.26 ₄ \pm 0.11 ₇	---	- .07 ₄	+ .01 ₂	+ .02 ₆	- .12 ₄	---	+ .23 ₆
	900	0.79 ₁ \pm 0.06 ₀	- .03 ₆	+ .01 ₉	---	+ .02 ₉	---	- .04 ₁	+ .12 ₉
Arithmetic mean			- .01 ₃	- .06 ₂	- .02 ₆	+ .05 ₀	+ .00 ₈	- .05 ₄	+ .14 ₄

Table 9. Nitrate: Analysis of unknowns

<u>Sample</u>	<u>Depth</u>	All in $\mu\text{g A/L}$		
		<u>(1)*</u>	<u>(6)**</u>	<u>(7)#</u>
N	50 m	0.5	0.6	0.5
O	150 m	2.5	1.0	1.7
P	200 m	5.0	1.4	4.4
Q	250 m	---	2.0	7.7
R	300 m	9.0	3.6	11.5
S	400 m	18.0	10.0	17.8
T	500 m	36.0	13.0	29.5
U	600 m	----	----	37.2

*Mean of 4 analyses.

**Single result presented

#Mean of 3 analyses.