ADVANCES IN INSTRUMENTATION
Vol. 23: Part II

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New York — October 28-31, 1968

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INSTRUMENT SOCIETY OF AMERICA
Pittsburgh, Pennsylvania

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INTRODUCTION

The presentations given at the general sessions of the 1968 ISA Annual Conference are contained in two parts of Advances in Instrumentation, Volume 23. Papers of the Metrology and Test Measurement Symposia, although programmed concurrently with the Annual Conference, are published as two separate volumes.

The sessions, developed by fifteen Divisions representing four Departments, include papers that reflect the 1968 highlight "New Technologies in Instrumentation." Papers on topics ranging from Automation in Oceanography and Marine Engineering through Process and Control Problems of the Future, to Balloonborne Instrumentation for the Atmospheric Sciences emphasize instrumentation as the catalyst that brings together all fields of Science and Technology. The application of instrumentation to industry is evident from the sessions programmed by the Aerospace, Food, Power, and Pulp and Paper Divisions. Papers on areas such as the application of fluidics, and the application of both analog and direct digital control, underscore the importance of instrumentation in the development of new technological areas. The "systems approach" is applied to ocean sciences, laboratory research, electrical safety, waste water treatment and medicine.

ISA's role in the extremely important area of Standards is described in the papers on New and Future Instrument Standards. Several papers programmed by the Education and Research Department indicate ISA's continued cognizance and increasing involvement in covering trends in those fields.

The Data Handling and Computation Sessions include papers that discuss the methods of using computers to rapidly collect and process data yielding a useable output. The computer is shown as the tool that enables industry and science to make the optimum usage of instrumentation systems.

It should be evident from the above, that instrumentation is vital to the advancement of science and technology and that Volume 23 exemplifies instrumentation's state-of-the-art in 1968.

Owen W. Williams*
Program Coordinator

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SIMULTANEOUS NEAR REAL-TIME EVALUATION OF AUTOMATIC EQUIPMENT AND MANUAL METHODS FOR DETERMINING SEVERAL NUTRIENT CONCENTRATIONS OF SEAWATER

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ABSTRACT

An evaluation of automatic and simultaneous near real-time determinations of several nutrient concentrations in seawater has been completed by the Naval Oceanographic Office. A comparison between automatic and manual methods used to determine the concentration of nitrates, phosphates, and silicates in seawater has been made. It is shown that the rate of analysis is increased at least threefold by use of the automatic system with the precision (±0.1 to ±0.5%) being better than the manual methods by an order of magnitude under shipboard conditions. Engineering considerations and environmental testing are also reported.

INTRODUCTION

Among the many variables which are measured to describe ocean and oceanic processes, certain chemical constituents classified as nutrients play no small role. Analysis of phosphorous, nitrate, and silicate concentrations is usually an integral part of any survey effort attempting to describe an oceanic area. Historically, these analyses have been conducted manually by wet chemical methods combined with a colorimetric measurement. These analyses are accomplished on shipboard if possible, although accuracy and precision are difficult to maintain at sea. The chemical manipulations necessary dictate the use of a trained technician who is required to work under the restrictions and rigors of shipboard conditions.[1,2,3] As a consequence, the precision and accuracy of these measurements do not always fall within those values which could be obtained in a shore-based laboratory using identical techniques. Often samples are preserved, stored, and transported shoreward for analysis at a later date. However, this procedure is not scientifically the proper method. Unless undue precautions are taken, there is a distinct possibility that the composition of the sample alters while in storage prior to analysis. In fact, recent reports in the scientific literature indicate that unless specific attention is paid to the storage of seawater for later analysis, there occurs a measurable change in the nutrient (i.e. phosphate) concentration of such samples.[4,5]

This paper reports the results of tests conducted jointly by the Instrumentation, Research and Development, and Ocean Survey Departments of the Naval Oceanographic Office. The test work concerned the comparison of automatic and manual methods of analysis of seawater for nitrate, phosphate, and silicate concentration. In all, 263 samples and 22 standard solutions were analyzed either at the shore-based laboratory or at sea aboard research vessels. In addition, the effect of using different artificial sea waters in obtaining calibration curves was considered. The purpose of the test work was to determine if automatic techniques could be used to conduct nutrient analyses extensively on a continual basis at sea, both practically and economically. The instrument selected for investigating automation of the clerical procedures utilized was a commercially developed automatic instrument which has found wide

[1]Superior numbers refer to similarly numbered references at the end of this paper.

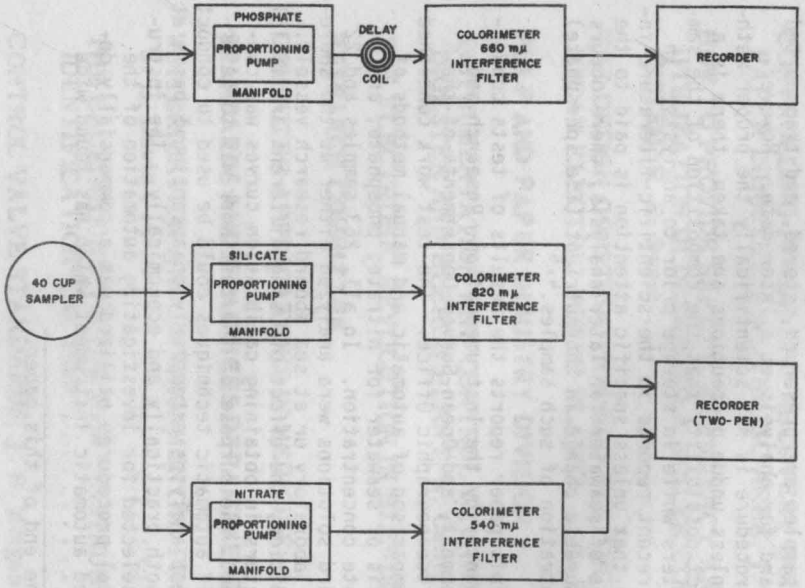

FIGURE 1. BLOCK DIAGRAM, AUTOMATIC-ANALYZER SYSTEM FOR PHOSPHATE, SILICATE AND NITRATE ANALYSES

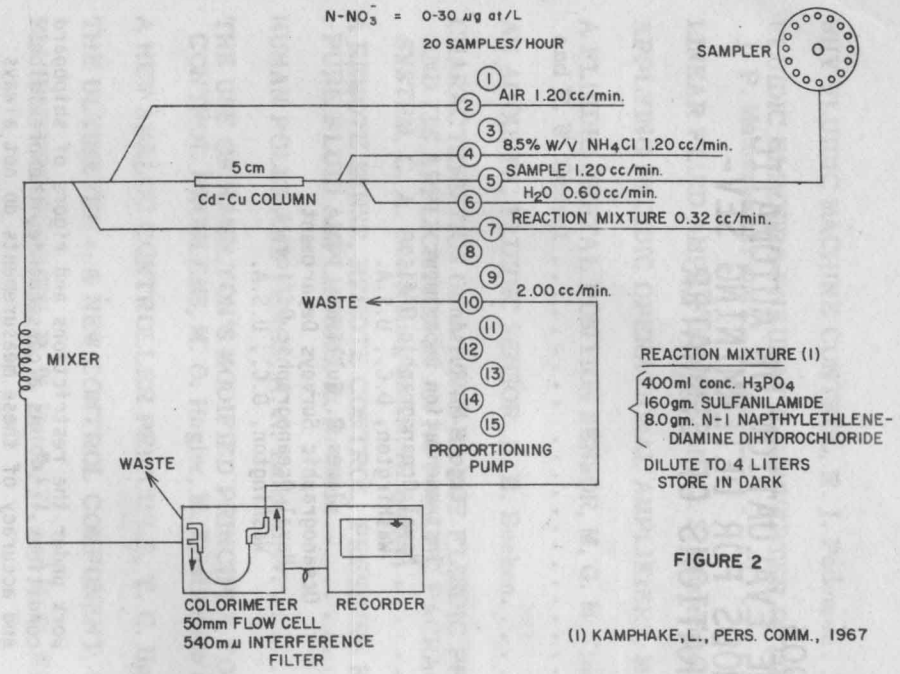

FIGURE 2

(1) KAMPHAKE, L., PERS. COMM., 1967

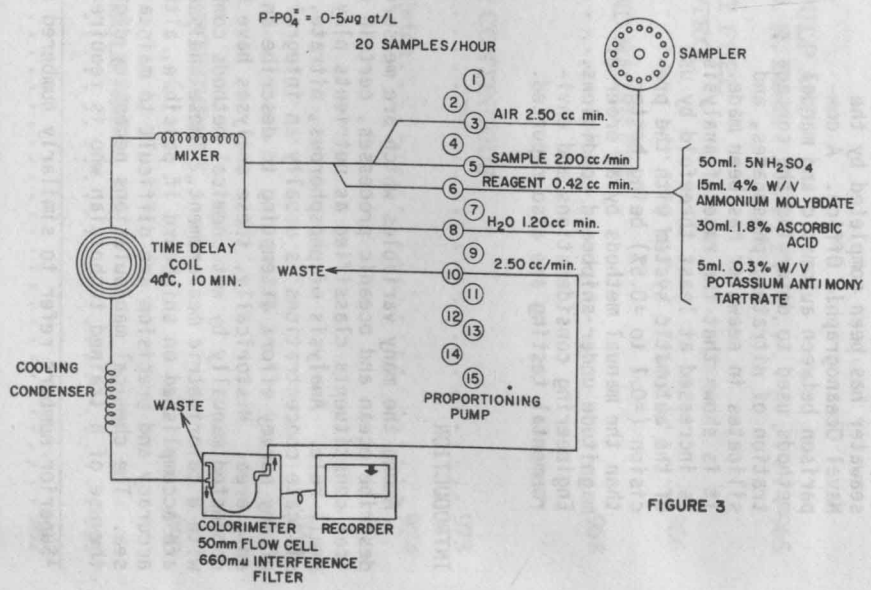

FIGURE 3

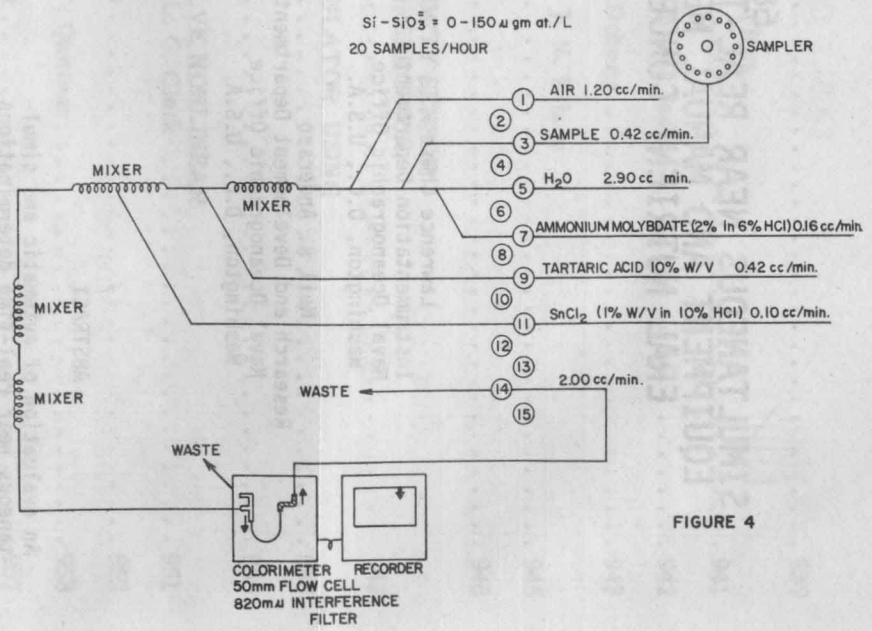

FIGURE 4

use for conducting chemical analyses in such institutions as hospitals.*

EXPERIMENTAL PROCEDURE

The automatic analyzer test work was done on two separate sea cruises using the laboratory and research facilities aboard the USNS SANDS and USNS LYNCH. Testing of the proportioning pump and the ancillary tubing was accomplished in the environmental test laboratory of the Instrumentation Department of the Naval Oceanographic Office. (The results of these tests will be reported later.) A block diagram of the overall analyzer system is presented in Figure 1.

Although the proportioning pump aspirates seawater samples, reagents, water, and air simultaneously, the sequence subsequently followed in the combining process differs for the three nutrient determinations to be made. In all cases, however, dilution by water occurs and air is bubbled into the system in order to clearly separate the samples and to enhance free flow. Following combination in the required sequence, thorough mixing takes place as the sample is pumped through a coil where color reaction occurs. The bath in turn feeds a continuous-flow colorimeter. The electrical output of the colorimeter varies with changes in concentration of the oceanic samples. These changes are read out on a strip-chart recorder as distinct peaks, the height of each being a function of the sample concentration. Details of each of the three procedures are discussed below.

Nitrate-Nitrogen. The procedure for the determination of the nitrate-nitrogen content of seawater was that of Morris and Riley.[6] A modification by Kamphake was included which added the combined reagents in phosphoric acid, rather than separately.[7] The procedure basically is the reduction of nitrate to nitrite by elemental cadmium (in the form of filings) containing catalytic quantities of copper, formation of the diazonium salt with sulphanilamide and coupling with napthylethylenediamine to form the azo compound which is then photometrically measured at 540 mμ. This procedure, of course, also yields the amounts of nitrite-nitrogen present in the sample. However, the nitrite-nitrogen content of seawater is often small relative to the nitrate-nitrogen concentration and the results of total nitrogen from nitrate and nitrite would serve equally well for the purpose herein intended. Therefore, differentiation between the nitrate and nitrite content of seawater was not considered in this study. (Removal of the reducing column will effect this differentiation if desired.) The manual method of analysis was identical to that of the automated procedure with two minor exceptions: The reagents were added separately and amalgamated cadmium filings were used as the reductor. A schematic flow-diagram of the automatic determination of nitrate in seawater is shown in Figure 2.

Phosphate-Phosphorous. The procedure employed for the phosphate determinations of seawater samples was that of Chan and Riley which is essentially an automated version of the earlier developed manual method by Murphy and Riley.[8,9] The method basically consists of the formation of a phosphomolybdate complex, reduction of the complex to a strongly colored heteropoly acid, molybdenum blue, with an ascorbic acid-potassium antimony tartrate solution and photometric measurement at 660 mμ. Unlike the procedure used in automatic analysis, the manual method differed in that the sample and added reagents were allowed to stand for at least 4 hours before photometric measurements were made at 885 mμ. In the automated method, the mixture of sample and reagents was passed through a heated (40° C) delay coil for 10 minutes prior to photometric measurement. The schematic flow-diagram of the automatic determination of phosphate in seawater is shown in Figure 3.

Silicate-Silicon. The procedure utilized for the determination of silicate in seawater is essentially that developed by Mullin and Riley.[10] The method consists of forming silicomolyblic acid, reduction to molybdenum with stannous chloride, and photometric measurement at 820 mμ. The manual method was similar with the exception that paramethylamenophenol sulphate (metol) was used as the reducing agent. The schematic flow-diagram of the automatic determination of silicate in seawater is shown in Figure 4.

TEST RESULTS

The results of standard analyses of seawater by the automated and manual methods are presented in Table 1 which provides a measure of the precision and accuracy of each procedure for nitrates, phosphates, and silicates. Only for the automated system is a complete nitrate analysis given due to experimental difficulties encountered with the use of the amalgamated cadmium reductor columns in the manual procedure, a situation previously experienced by Brewer and Riley.[5] The data for the nitrate, phosphate, and silicate content of all samples were obtained simultaneously with the automated system. The results of standard analyses of seawater at sea on the USNS LYNCH using the automated system are presented in Tables 2, 3, and 4. Comparable analyses by the manual method could not be carried out on this cruise due to the additionally large amount of work associated with such a technique. The results of the standard analyses by the automated and manual methods conducted on board the USNS SANDS are given in Table 5. A comparison of the standard deviations and coefficients of variation of the two methods obtained in the shore-based laboratory and at sea is offered in Table 6.

Standard Deviations. For automatic procedures, the standard deviations noted in the laboratory during analyses of nitrates, phosphates, and silicates were ±0.1, ±0.02, and ±0.1 μgm-at. per liter, respectively as shown in Table 1, where $\sigma = \left[\frac{(X_i - X)^2}{N - 1}\right]^{\frac{1}{2}}$. These correspond to coefficients of a variation of 0.6%, 2.3% and 0.6% in the respective replications.

*The instrument employed is marketed by the Technicon Corporation of Chauncey, New York.

The standard deviations for the corresponding manual methods, replicating the same seawater samples, for their phosphate and silicate content are ±0.01 and ±0.5 µgm-at. per liter, respectively. The coefficients of variations are 0.8% and 2.9%. The precision of the silicate analyses by the automated system is better by a factor of five over the corresponding manual method. The lower precision of the phosphate analyses of these standard samples by the automated method with respect to the manual analysis was related to the effect of temperature in the delay coil upon the development of the colored complex.

To each of the replicated seawater samples, 1.6, 0.6 and 5.8 µgm-at. of nitrate, phosphate and silicate, respectively, were added and the resulting solutions were then analyzed for these components. (An exception was the manual method for nitrate for the reason stated above.) The results of the automated procedures gave 1.7±0.1, 0.62±0.03 and 6.0±0.1 µgm-at. per liter for the nitrate, phosphate, and silicate contents of the standards corresponding to absolute differences from the added amounts of +0.1, +0.02 and +0.2 µgm-at., respectively. The comparable results for the manual methods for phosphate and silicate are 0.59±0.01 and 6.3±0.7 µgm-at. per liter, corresponding to absolute differences from the added amounts of -0.01 and +0.5 µgm-at., respectively. These results (Table 1) indicate that the accuracy for the phosphate determinations for the two methods are comparable but that the automated method is more than twice as accurate for silicate analyses. Additionally, standard deviations obtained by the automated methods are all less than the computed values for five replicates obtained by using the widely employed formula for the precision of these determinations, as given by Strickland and Parsons.[11] The precision obtained by the manual method for the silicate analyses is higher than the computed precision; for phosphate analyses, the precision is less.

Automated Analyses At Sea. In Tables 2, 3, and 4, for analyses conducted at sea, the data presented are comparable to those of Table 1 for the automatic analyzer only. Replication of seawater samples for their nitrate content resulted in an average standard deviation of ±0.03 µgm-at. N per liter. Upon analysis of the same seawater after known amounts of nitrogen were added, absolute differences were observed which had a range of from -0.08 to +0.01 µgm-at. N per liter with the average being -0.06 µgm-at. liter. These results represent an improvement of an order of magnitude in the standard deviations (i.e. from ±0.1 to ±0.03 µgm-at. N per liter) and comparable accuracy of the automated nitrate analyses at sea versus operation in the shore-based laboratory. The phosphate analyses at sea gave an average standard deviation of ±0.05 µgm-at. P per liter, or approximately twice the value of that obtained in the shore-based laboratory analyses. The absolute errors ranged from +0.01 to +0.09 µgm-at. P per liter resulting in an average error of +0.05 µgm-at. P liter. This represents a twofold degradation in the accuracy of the phosphate determination when conducted at sea. The silicate analyses on board ship gave an average standard deviation of ±0.14 µgm-at. Si per liter, comparable to that obtained on shore. The range of absolute errors was from -1.13 to +0.64 µgm-at. Si per liter with an average error of -0.1 µgm-at. Si per liter, a twofold improvement in magnitude compared to the shore-based analyses. It should be noted further that the variations of the results of the three analyses for the different added constituents are not significant at the 95% confidence level.

A measurement program was conducted on the USNS SANDS in January 1968 which was analogous to that carried out previously on the USNS LYNCH, but at this time included a comparison of the two analytical methods. The results are given in Table 5. The standard deviations obtained by the automated methods for the nitrate, phosphate and silicate analyses were ±0.01, ±0.01 and ±0.00 µgm-at. element per liter, respectively. The absolute differences observed using the analyzer were -0.02, +0.01 and +3.83 µgm-at. nitrate, phosphate and silicate per liter, respectively. The analogous manual analyses for the nitrate, phosphate and silicate content gave standard deviations of ±0.41, ±0.02 and ±0.31 µgm-at. element per liter with corresponding absolute differences of +2.30, -0.04 and +1.30 µgm-at. element per liter, respectively.

The accuracy of the automated methods, with the exception of the silicate analyses on the USNS SANDS cruise, was comparable when the instrument was taken to sea. In the case of silicate results, the lower accuracies obtained were probably due to an electronic malfunction of the recorder used for this analysis as a consequence of voltage fluctuations in the ship's power system. The basis for the comparable accuracies of the nitrate and phosphate results are undoubtedly a result of the operator becoming more experienced in the operation of the instrument. The accuracy of the manual analyses deteriorated considerably when carried out at sea, not surprising when one considers the rigors of shipboard life which the analyst must endure.

The results of the automated and manual methods obtained in the laboratory and at sea are presented in Table 6. As can be seen, the precision of the automated nitrate analyses performed at sea increased in precision by an order of magnitude on the analyses performed in the laboratory; those of the phosphate and silicate analyses did not change appreciably. The decreased precision of the phosphate analyses on the USNS LYNCH cruise was the result of poor temperature control in the delay coil. This was corrected prior to the USNS SANDS cruise by encasing the delay coil in a sand bath with the noted increase in precision obtained. Standard deviations of the manual methods for phosphate and silicate determinations remained approximately constant when the analyses were moved onto the research vessel, attesting to the extreme care put forth by the analyst. However, with the exception of the phosphate analyses on the USNS LYNCH, the precision of the automated methods is at least as good as the analogous manual methods and in most instances better.

Analysis Rate. The rate of analysis is also a factor to consider when comparing the methods herein described. As indicated in Figures 1, 2, and 3, the rate of analysis was 20 duplicate samples per hour,

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actually 120 analyses per hour or two per minute. The highest rate which the analyst achieved manually was 6 samples per hour with no duplication (i.e., 18 analyses per hour). Thus, the automated system used in these analyses is approximately 7 times faster than can be achieved by an experienced analyst working manually, with the accuracy and precision of the data obtained from the instrument being at least as good and in some instances significantly superior.

The results of seawater analyses for the nitrate, phosphate, and silicate content are plotted in Figures 5, 6, and 7 as a function of depth for four stations on the USNS LYNCH cruise in September 1967. Of the three distributions considered, the best agreement occurs in the nitrate analyses, although a significant variation exists in the profiles obtained with the manual methods compared to the results of the automated system.. Since all samples were obtained from the same water sampler, nonsystematic operator error is considered the cause of this descrepency. The phosphate and silicate profiles shown in Figures 6 and 7 reflect considerably larger differences between the analyses than what is observed in the nitrate determinations. Moreover, aside from the profile at 14°56'N, 53°26'W, the automated analyses seems to result in data which are consistently lower in quality than those from the manual analyses. The minimum observed in each phosphate profile (Figure 6) obtained by manual techniques is not presently understood. In each case, however, this minimum is the eighth sample analyzed, pointing to the possibility of a systematic error being present in the manual method.

Profiles of the nitrate, phosphate and silicate distributions obtained in the Caribbean Sea in the USNS SANDS in January 1968 are presented in Figures 8, 9, and 10. As in the vertical profiles in Figures 5, 6, and 7 which were taken on the USNS LYNCH, a constant displacement of the automated data to lower values occurs relative to that obtained using manual methods. Plotted in these profiles are also data from an earlier cruise on the R.V. Atlantis II in December 1964. These analyses were done manually and, interestingly, the profiles are evenly distributed between those obtained on the USNS SANDS cruise by the automated and manual methods. One is tempted to postulate that the historical data are quite variable when considering the relatively constant relationship of the profiles obtained by the USNS SANDS cruise. The extremely low value for nitrate obtained by the manual analysis of a sample of seawater from approximately 800 meters at 14°25'N, 65°25'W is obviously in error. The values at approximately 2200 meters for both the automated and manual methods indicate what can happen when a distilled water sample is inadvertently analyzed in place of a seawater sample.

Mutual Interference Effects. In Table 7 are data obtained from an experiment to investigate possible mutual interference of the nitrate, phosphate, and silicate analyses. When 1.70 µgm-at. N as nitrate were added to a sample of seawater whose nitrate, phosphate and silicate content had been determined by replications, there was a response in the phosphate and silicate content in both the automated and manual methods of the same order of magnitude. The phosphate response increased by 2-5% whereas the silicate response increased 11-14%. When 0.44 µgm-at. P as phosphate was added, the corresponding increases in responses for the nitrate and silicate analyses were 1% and 13% respectively for the automated system and 4% and 11% respectively for the manual methods. The results when ±11.17 µgm-at. Si as silicate were added show the nitrate and phosphate responses increase 2% and 22% respectively in the automated system with the comparable values for the mutual methods being 1% and 24%.

These results clearly show that mutual interferences are present in these analyses as well as indicating a possibility that high results may occur in the determinations under consideration from mutual interference effects and that, in some instances, these effects may be significant. The minimal effect is shown to be in phosphate and silicate interference on the nitrate determination. There is also a relatively small effect on the phosphate determination by the presence of nitrate. An appreciable effect (approximately 11-13%), however, occurs on the results of the silicate analysis when nitrate is present. The largest interference is seen to be associated with the mutual effects of phosphate and silicate on each other with the mutual effects of silicate on the phosphate analyses being the larger of the two. We are unable to completely explain these results but feel at the present that the causes lie in the chemistries which are involved in the determinations rather than instrumental or calibration errors, as has been indicated previously for silicate analyses. Results obtained relating to observed differences in the phosphate determination of seawater by the automated and manual methods have recently been duplicated by other investigators with the results shown in Figure 11. Comparable manual determinations for phosphate give higher values than is obtained by the analogous automated analyses with the variation possibly becoming larger with increasing phosphate concentration. Additionally, on several occasions, nitrate responses from the polystyrene cups used in the sampler were observed and great care was required to eliminate this possible source of error.

To investigate the mutual interference effects of the phosphate and silicate analyses, calibration curves of each were run using different formulae for the matrix of each standard solution as well as adding a constant amount of phosphate or silicate to the other corresponding calibration solution. The results are shown in Figures 12 and 13. As can be seen, the expected absolute instrument response of the particular nutrient measured is dependent on the matrix (blank addition) of the solution employed. Completely unexpected, however, were the results showing variations in the slopes of the calibration curves indicated in Figures 12 and 13 for phosphates and silicates. Although the results are unexplainable at the present time, these observations appear to substantiate our contention that the particular phenomenon causing these peculiar results and the approximate constant difference between the automated and manual methods of analyses, particularly with respect to the phosphate and silicate analyses, is of a fundamental nature associated with the chemical reactions involved in the determinations.

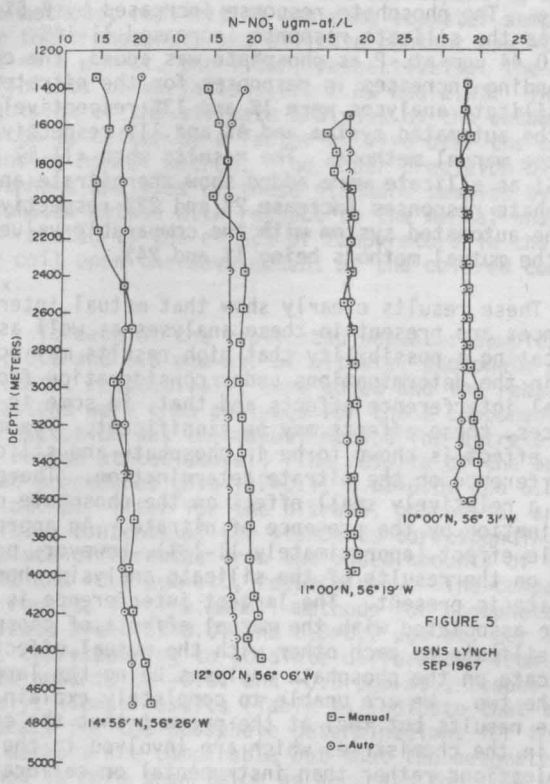


FIGURE 5

USNS LYNCH
SEP 1967

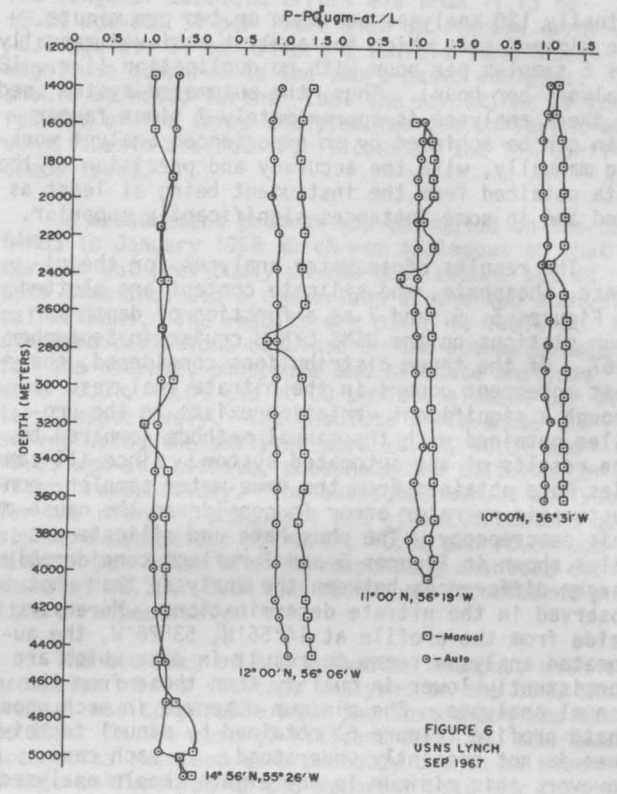


FIGURE 6

USNS LYNCH
SEP 1967

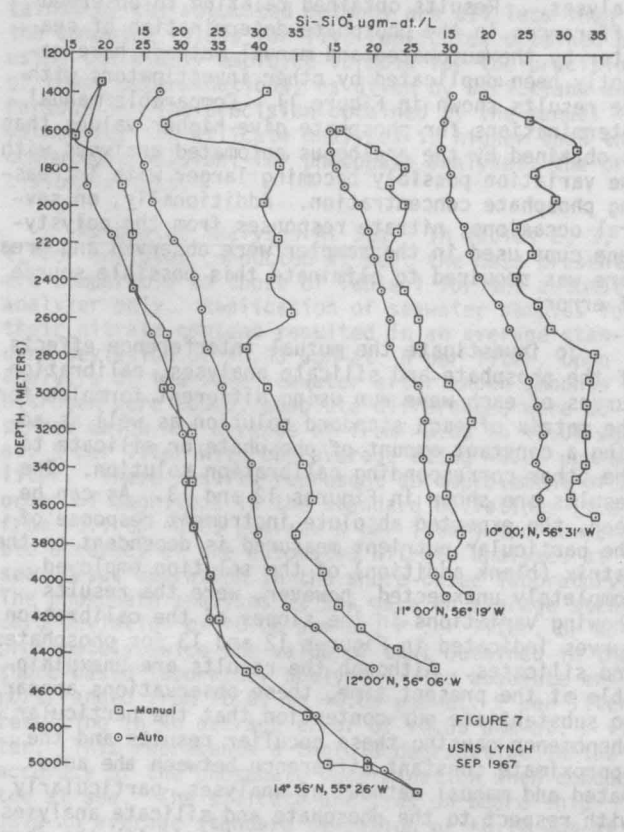


FIGURE 7

USNS LYNCH
SEP 1967

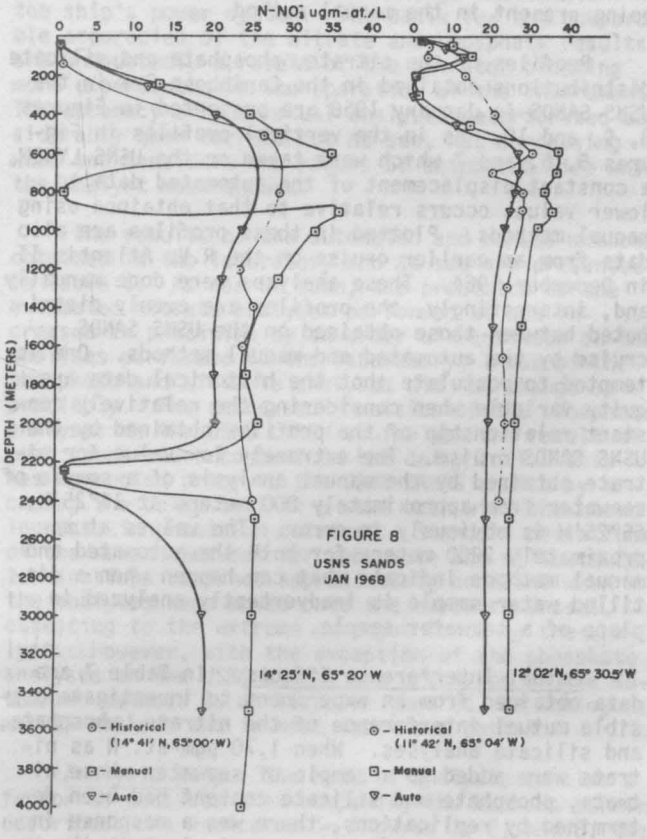


FIGURE 8

USNS SANDS
JAN 1968

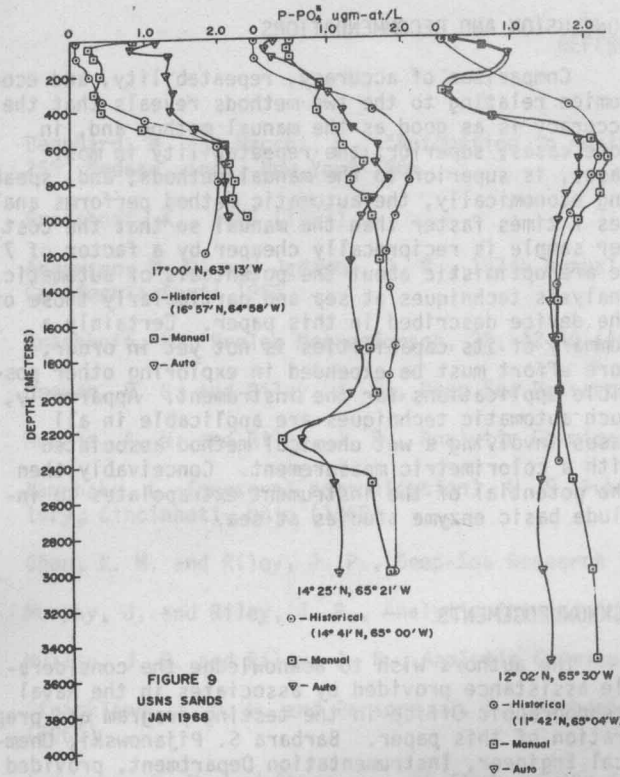


FIGURE 9
USNS SANDS
JAN 1968

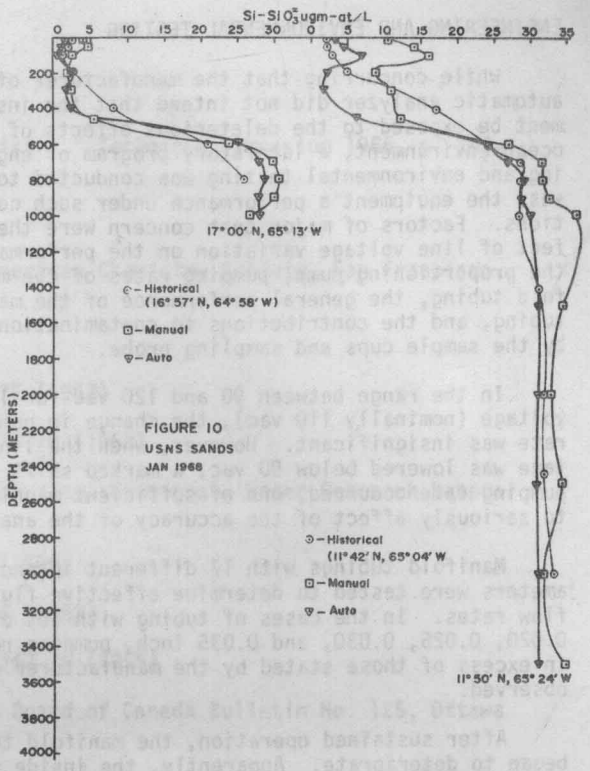


FIGURE 10
USNS SANDS
JAN 1968

$P\text{-}PO_4^{\equiv}$
COMPARISON OF MANUAL AND AUTOMATIC ANALYZER
SAMPLES ON CRUISE RV YAQUINA JAN. 1968

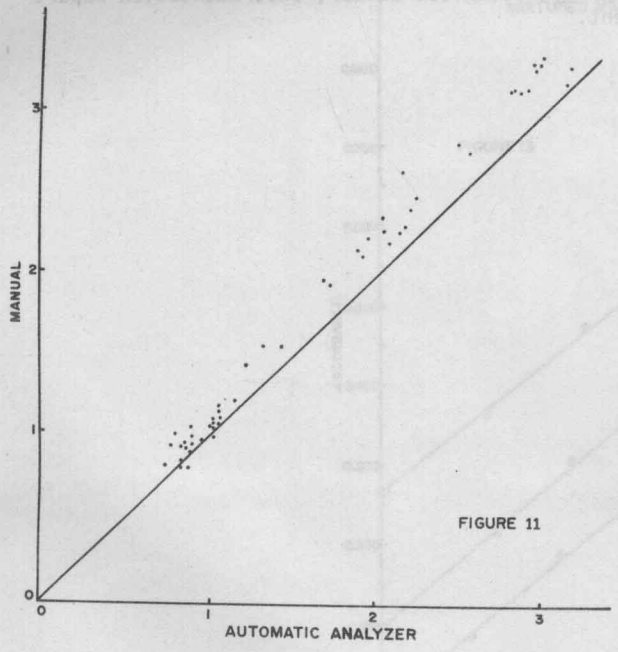
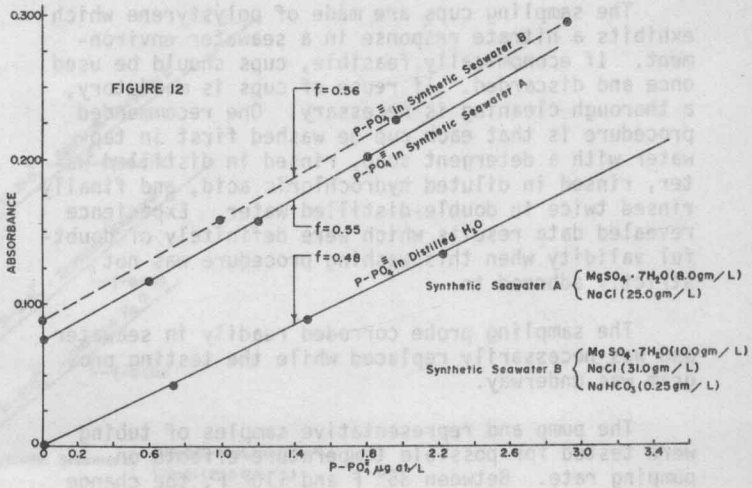


FIGURE 11

$P\text{-}PO_4^{\equiv}$ CALIBRATION CURVES IN SYNTHETIC SEAWATER MIXTURES VS. DISTILLED H_2O 660mμ



ENGINEERING AND ENVIRONMENTAL TESTING

While concurring that the manufacturer of the automatic analyzer did not intend that the instrument be exposed to the deleterious effects of the ocean environment, a laboratory program of engineering and environmental testing was conducted to assess the equipment's performance under such conditions. Factors of major test concern were the effect of line voltage variation on the performance of the proportioning pump, pumping rates of the manifold tubing, the general performance of the manifold tubing, and the contributions to contamination made by the sample cups and sampling probe.

In the range between 90 and 120 vac for line voltage (nominally 110 vac), the change in pumping rate was insignificant. However, when the line voltage was lowered below 90 vac, a marked shift in pumping rate occurred, one of sufficient magnitude to seriously affect of the accuracy of the analysis.

Manifold tubings with 17 different internal diameters were tested to determine effective fluid flow rates. In the cases of tubing with IDs of 0.020, 0.025, 0.030, and 0.035 inch, pumping rates in excess of those stated by the manufacturer were observed.

After sustained operation, the manifold tubing began to deteriorate. Apparently, the inside surface became altered by sedimentary accretion, leading to cell-like partings of samples while pumping was underway. In addition, after prolonged use, the tubing began to lose mechanical integrity and required piecemeal replacement as necessary. It is worthy of note that changing the manifold tubing at sea is an awkward task, complicated by the design of the connecting nipples and the proximity of other glass components of the instrument, all compounded by the motion of the ship.

The sampling cups are made of polystyrene which exhibits a nitrate response in a seawater environment. If economically feasible, cups should be used once and discarded. If reuse of cups is mandatory, a thorough cleaning is necessary. One recommended procedure is that each cup be washed first in tap water with a detergent soap, rinsed in distilled water, rinsed in diluted hydrochloric acid, and finally rinsed twice in double-distilled water. Experience revealed data results which were definitely of doubtful validity when this washing procedure was not strictly adhered to.

The sampling probe corroded readily in seawater and was necessarily replaced while the testing program was underway.

The pump and representative samples of tubing were tested for possible temperature effects on pumping rate. Between 35° F and 110° F, the change in rate was insignificant in terms of results.

The results of the testing program are scheduled in the near future for publishing by the Testing Division of the Instrumentation Department, Naval Oceanographic Office, Washington, D.C.

CONCLUSION AND RECOMMENDATIONS

Comparison of accuracy, repeatability, and economics relating to the two methods reveals that the accuracy is as good as the manual method and, in some cases, superior; the repeatability in most cases, is superior to the manual methods; and, speaking economically, the automatic method performs analses 7 times faster than the manual so that the cost per sample is reciprocally cheaper by a factor of 7. We are optimistic about the potentials of automatic analysis techniques at sea and particularly those of the device described in this paper. Certainly a summary of its capabilities is not yet in order; more effort must be expended in exploring other possible applications for the instrument. Apparently, such automatic techniques are applicable in all cases involving a wet chemical method associated with a colorimetric measurement. Conceivably then the potential of the instrument extrapolates to include basic enzyme studies at sea.

ACKNOWLEDGEMENTS

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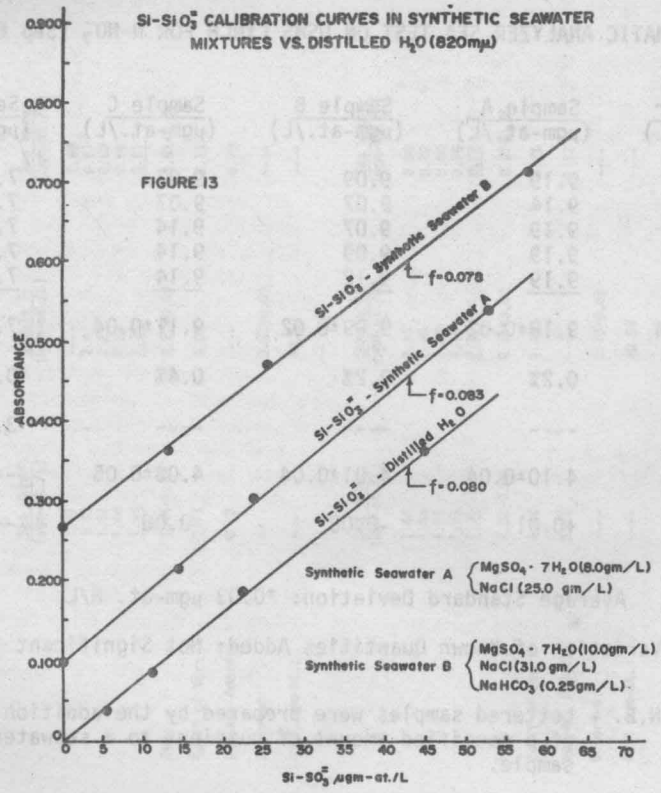

Table 1

LABORATORY COMPARISON OF AUTOMATIC VS MANUAL TECHNIQUE

	$N\text{-}NO_3^-$ (µgm-at./L)	$P\text{-}PO_4^{\equiv}$ (µgm-at./L)		$Si\text{-}SiO_3^{\equiv}$ (µgm-at./L)	
	Auto.	Auto.	Man.	Auto.	Man.
	15.4	0.84	1.22	17.7	16.8
	15.7	0.88	1.22	17.9	16.7
	15.6	0.87	1.22	17.8	17.0
	15.6	0.85	1.21	17.9	17.3
	15.5	0.89	1.21	17.8	17.8
Avg:	15.6±0.1	0.87±0.02	1.22±0.01	17.8±0.1	17.2±0.5
Coeff of Var:	0.6%	2.3%	0.8%	0.6%	2.9%
µgm-at. Added:	1.6	0.60	0.60	5.8	5.8
Observed: (5 replicates)	1.7±0.1	0.62±0.03	0.59±0.01	6.0±0.1	6.3±0.7
Diff µgm-at.:	+0.1	+0.02	-0.01	+0.2	+0.5

Standard Deviation, Nitrate, Phosphate, Silicate (µgm-at./L)

Automatic:	±0.1	±0.02	±0.1
Manual:	----	±0.01	±0.5

Table 2

AUTOMATIC ANALYZER SEA TEST ON USNS LYNCH FOR $N\text{-}NO_3^-$ (Sep 67)

	Sea Water (µgm-at./L)	Sample A (µgm-at./L)	Sample B (µgm-at./L)	Sample C (µgm-at./L)	Sea Water (µgm-at./L)	Sample D (µgm-at./L)
	5.14	9.19	9.09	9.07	7.08	10.48
	5.04	9.14	9.07	9.07	7.08	10.48
	5.07	9.19	9.07	9.14	7.12	10.48
	5.06	9.19	9.09	9.14	7.15	10.44
	5.07	9.19	9.12	9.14	7.13	10.44
Avg:	5.08±0.04	9.18±0.02	9.09±0.02	9.11±0.04	7.11±0.03	10.47±0.02
Coeff of Var:	0.8%	0.2%	0.2%	0.4%	0.4%	0.2%
µgm-at. Added:	4.09	----	----	----	3.41	----
Observed:	----	4.10±0.04	4.01±0.04	4.03±0.05	----	3.36±0.03
Diff µgm-at.:	----	+0.01	-0.08	-0.06	----	-0.05

Average Standard Deviation: ±0.03 µgm-at. N/L

Variation of Known Quantities Added: Not Significant

N.B. - Lettered samples were prepared by the addition of a specified amount of nutrient to a seawater sample.

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