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THE DETERMINATION AND DISTRIBUTION OF ORGANIC PHOSPHORUS
IN SEA WATER

PART I.

THE DETERMINATION OF ORGANIC PHOSPHORUS IN SEA WATER
WITH PERCHLORIC ACID OXIDATION

Technical Report No. 10



Office of Naval Research
Contract N8onr-520/III
Project NR 083 012
November 1952

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UNIVERSITY OF WASHINGTON DEPARTMENT OF OCEANOGRAPHY
(Formerly Oceanographic Laboratories)
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by

Andrew L. Hanson and Rex J. Robinson

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Richard H. Fleming
Executive Officer

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THE DETERMINATION OF ORGANIC PHOSPHORUS IN SEA WATER
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ABSTRACT

A method is proposed for the determination of organic phosphorus in sea water in which the organic material is oxidized with perchloric acid and the organic phosphorus converted to phosphate. Oxidation in a perchloric acid medium is superior to sulfuric acid: (a) The perchlorate salts formed on digestion of sea water are so readily water soluble in contrast to certain of the sulfates. (b) A small blank correction for impurities needs to be applied. Arsenic is prevented from interfering by volatilization of the arsenic chloride formed by heating the samples with concentrated hydrochloric acid. Total phosphorus is determined colorimetrically and the organic phosphorus calculated by deducting the inorganic phosphorus. Preliminary digestion with nitric acid is desirable before digesting samples of high organic content with perchloric acid.

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THE DETERMINATION OF ORGANIC PHOSPHORUS IN SEA WATER
WITH PERCHLORIC ACID OXIDATION*

INTRODUCTION

The occurrence and distribution of phosphorus in its various forms in the sea is of interest in connection with the productivity of the sea. Phosphorus occurs in the sea as inorganic phosphate and as organic phosphorus present in soluble organic forms and particulate matter. Inorganic phosphate is conveniently determined by a colorimetric method (Robinson and Thompson, 1948; Wooster and Rakestraw, 1951) and a considerable fund of information has been collected regarding its distribution. On the other hand little information is available on the occurrence and distribution of organic phosphorus because of the difficulty that has been experienced in its determination.

Organic phosphorus as particulate matter has been determined by separation of the particulate matter, oxidation in acid solution and estimation by the colorimetric method for inorganic phosphate (Redfield, Smith and Ketchum, 1937). Just what is retained as particulate matter depends upon the method of separation and of washing. Knowledge of the particulate organic phosphorus content gives incomplete information regarding the organic phosphorus content of the sea, unless the soluble organic phosphorus content is also known.

* This work was partly supported by the Office of Naval Research under Contract No. N8onr-520/III with the University of Washington.

Most frequently the total organic phosphorus content, which includes both soluble and particulate organic phosphorus, is obtained by determining total phosphorus and subtracting inorganic phosphate. Total phosphorus is determined by colorimetric estimation after acid oxidation of the organic phosphorus to phosphate. A number of procedures have been reported in which oxidation of the organic phosphorus has been made in sulfuric acid solution. Kneip and Scudler (1933) oxidized with 3 % hydrogen peroxide, Kalle (1933) with potassium persulfate, and Cooper (1934) with 30 % hydrogen peroxide. These methods failed to account for the oxidation of arsenite to arsenate and for subsequent estimation along with phosphate by the colorimetric method. Failure to correct for arsenate introduces considerable error since arsenic occurs in the sea to the extent of 0.2 to 0.5 μg atom per liter, mostly as arsenite (Gorgy, Rekestian and Lutz, 1948) and the organic phosphorus content is only about 0.5 to 0.6 μg atom per liter. Kalle (1935) attempted to prevent the interference of arsenate by reducing it to arsenite with thiourea. Cooper (1937), however, was unable to reduce arsenate in sea water using Kalle's method. Redfield, Smith and Ketchum (1937) digested sea water samples with hydrogen peroxide in sulfuric acid solution and reduced the arsenate by heating with sodium bisulfite for a period of eight hours. Harvey (1948) described another modification in which the samples were heated in the autoclave at 130°C. in sulfuric acid solution with sodium sulfite to reduce arsenate.

Extensive investigation of various procedures for the determination of total phosphorus by Robinson and co-workers (Jesseph, 1932; Selbo, 1940) have indicated several inherent disadvantages in methods using sulfuric acid for the digestion of the samples. It is difficult to obtain sulfuric acid that is sufficiently free of interfering impurities. Anhydrous sulfate salts of

sodium, calcium, etc. separate on digestion and redissolve in distilled water with difficulty. Small undissolved salt nuclei often remain and cause excessive color development of the colloidal phosphomolybdate blue reduction complex.

Preliminary work of Selbo and Robinson (Selbo, 1940) indicated that oxidation of organic matter in sea water could be effected by perchloric acid. Use of perchloric acid results in a number of advantages: (a) The interfering impurities present in perchloric acid are of small magnitude. (b) The organic matter is quickly oxidized by the perchloric acid. (c) Salts, very soluble in water, are obtained upon digestion of the sample. A more complete examination of the method has been made by Hansen and Robinson (Hansen, 1950) and is reported in this paper. Recently, application of the perchloric acid method for lake waters (Robinson, 1941) has been made to sea water analysis by Rochford (1951).

THE PROPOSED METHOD

Reagents and Standard Solutions

All chemicals used in this investigation were of analytical grade.

Sulfuric Acid: 36 Normal, arsenic-free acid.

Perchloric Acid: 60 % or 72 % acid.

Hydrochloric Acid: 12 Normal acid.

Sodium Hydroxide: 1 Normal sodium hydroxide solution.

Ammonium Hydroxide: 15 Normal ammonium hydroxide.

Ammonium Molybdate-Sulfuric Acid Reagent: Ten g. of ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, were dissolved in 100 ml. of distilled water. This solution was added to 300 ml. of 18 N sulfuric acid. The reagent was kept in an amber glass-stoppered bottle and protected from light to prevent photochemical reactions from occurring.

Stannous Chloride Solution I. 2.15 g. of stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, were dissolved in 20 ml. of 12 N hydrochloric acid and diluted to 100 ml. with freshly boiled distilled water. The solution was stored in an amber glass-stoppered bottle and a piece of mossy tin added to counteract air oxidation. The solution was stable for about a month.

Stannous Chloride Solution II. Five ml. of Solution I were diluted to 25 ml. with freshly boiled distilled water. A small piece of mossy tin was added to stabilize the solution. The solution was prepared fresh each day.

Standard Phosphate Solution I. 0.840 g. of anhydrous potassium dihydrogen phosphate, KH_2PO_4 , was dissolved in distilled water and made up to 1 liter. The addition of 0.2 ml. of chloroform retarded possible bacterial action. One ml. of this solution contained 2.50 μg atoms of phosphate-phosphorus.

Standard Phosphate Solution IIa for Inorganic Phosphate. Ten ml. of Standard Solution I were diluted to 1 liter with a sodium chloride solution having a chlorinity similar to that of the sea water being tested. The addition of 0.2 ml. of chloroform retarded bacterial action. One ml. of this solution contained 0.0250 μg atom phosphate-phosphorus.

Standard Phosphate Solution IIb for Inorganic Phosphate. Forty ml. of Standard Solution I were diluted to 1 liter by means of the sodium chloride solution and 0.2 ml. of chloroform was added. One ml. of this solution contained 0.100 μg atom of phosphate-phosphorus.

Standard Phosphate Solutions IIa and IIb for Organic Phosphorus. Because no salt-effect correction is necessary for samples digested with perchloric acid, these standards were prepared in the same way as Standard Phosphate Solutions IIa and IIb for inorganic phosphate, except that they were diluted with distilled water rather than with sodium chloride. The phosphate-phosphorus concentrations of the standards remained the same in both cases.

Apparatus

The colorimetric estimations were made for the most part with Model AC Fisher Electrophotometer using filter A, of 685 m μ average wavelength and glass cells with optical paths of 5 cm. Some of the estimations were made with the Electric Eye Photometer developed by Ford (1950).

Analytical Procedures

Inorganic Phosphate. One-half ml. of ammonium molybdate reagent and 0.20 ml. of Stannous Solution II were thoroughly mixed with a 50 ml. sea water sample as soon after collection as possible. After seven minutes time for color development, the resulting color was measured in the Electrophotometer using distilled water as the reference solution. The phosphate value was obtained from a calibration curve prepared with standard phosphate solutions.

Total Phosphorus. Fifty ml. samples of sea water were treated with 3 ml. of 60 % perchloric acid in a 125 ml. Erlenmeyer flask. This volume of perchloric acid was equivalent to the salts of a typical sea water sample with a salinity of 30 ‰ plus an excess of 0.2 ml. for oxidation purposes. After evaporation on a hot plate to fumes of perchloric acid, a cover glass was placed on the flask and the sample was heated for about 5 minutes just below the fuming temperature of perchloric acid. In order to drive off the arsenic present, 3 ml. of 12 N hydrochloric acid were added and rapidly fumed off. After cooling, 30 ml. of distilled water were added to dissolve the salts. The excess acid was neutralized with a normal sodium hydroxide solution using phenolphthalein as the indicator. Dilute perchloric acid was added drop by drop until the solution was slightly acidic. The solution was diluted to 50 ml. and mixed thoroughly with 0.50 ml. of ammonium molybdate solution and 0.20 ml. of Stannous Chloride Solution II. After maximum color development,

the color was estimated in the Electrophotometer using distilled water as the reference solution. The phosphate value was obtained from a calibration curve prepared with standard phosphate solutions.

Blank solutions were prepared by treating a sodium chloride solution of the same chlorinity as sea water, with perchloric acid in the manner just described.

Notes on the Procedures. It has been frequently noted (Lundell and Hoffman, 1945) that under certain conditions perchloric acid reacts violently with organic material. Initial oxidation by nitric acid before the addition of perchloric acid eliminates this hazard by oxidizing the more easily oxidizable material. The amount of organic material in a typical sea water sample is relatively small and presents no hazard when being oxidized by perchloric acid; but if samples of abnormally high organic content such as plankton or mud are being analyzed, it is advisable to digest with a small amount of nitric acid previous to the perchloric acid oxidation. Water samples from East Sound, San Juan Islands, containing as high as 2 μg atoms of organic phosphorus per liter were digested directly with perchloric acid with no trouble. However, plankton samples obtained by filtration were treated first with small portions of nitric acid as a precaution and the oxidation with perchloric acid always proceeded without violence. It should be emphasized that, before using perchloric acid, one should be familiar with its hazards and the precautions to be followed to insure its safe use (Kuney, 1947).

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INVESTIGATION OF THE METHOD OF ANALYSIS

Testing the Method of Analysis

The method, just described, was tried on known amounts of sodium glycerophosphate in a sodium chloride solution, Cl = 17 ‰. A satisfactory recovery of the phosphorus was obtained.

The organic phosphorus content of a sea water sample was determined by the perchloric and the sulfuric acid-hydrogen peroxide procedures. The excess perchloric acid was neutralized with sodium hydroxide and the excess sulfuric acid with ammonium hydroxide as in the procedure of Redfield et al. (1937). The results are recorded in Table I. The total phosphorus concentrations in each case were corrected for a blank.

The blank for the sulfuric acid procedure was considerably greater than for the perchloric acid procedure. Thus the more than 3 ml. of concentrated sulfuric acid and 8 ml. of ammonium hydroxide, used in the above procedure, gave a blank of 1.09 µg atom of phosphorus per liter, and the 3 ml. of perchloric acid and several drops of sodium hydroxide solution, a blank of 0.36 µg atom per liter. Various attempts to purify the sulfuric acid and ammonium hydroxide did not reduce the magnitude of the blank.

As shown in Table I, the results for total phosphorus (and also for organic phosphorus) by the perchloric acid method were somewhat larger than by the sulfuric acid procedure. It is not known whether this is due to greater efficiency of oxidation by the perchloric acid, or due to error arising from the establishment and application of the quite large blank for the sulfuric acid method. However, in general, it may be said that the results by a method utilizing a large blank are apt to suffer in accuracy.

The organic phosphorus was calculated by deducting from the total phosphorus value the inorganic phosphate which amounted to 1.58 μg atom per liter. An organic phosphorus content of 0.63 μg atom per liter was obtained using the sulfuric acid method and 0.88 μg atom per liter using the perchloric acid procedure. Provision for reduction of arsenate was not included in either method so that the final concentrations found represented the sum of phosphate, arsenate and oxidized arsenite.

Time of Color Development and Stability of Color

It was determined that, after the addition of the reagents, maximum color intensity developed in 3 minutes in distilled water or in sea water digested with perchloric acid; this color was stable for about 8 minutes before fading began. On the other hand, in undigested sea water samples, full color developed in about 6 minutes and was stable for 27 minutes before fading began.

Effect of Perchlorate upon Color Intensity

For some time it has been known that, for a given amount of phosphate, less color is developed in the estimation of phosphate in an undigested sea water sample than in distilled water. This is known as the salt effect. When sea water is digested with sulfuric acid or perchloric acid, hydrogen chloride is evolved and salts of sulfate or perchlorate remain. No salt effect was noted. Table II, when phosphate was estimated in a sulfate or perchlorate medium and the color compared with that developed in distilled water medium. This is in accordance with the explanation of Cooper (1938) that the salt effect is due to the formation of certain yellow molybdenyl halides.

TABLE I

Determination of Organic Phosphorus in Sea Water

Phosphate Concentrations ($\mu\text{g atoms/L.}$)

Sulfuric Acid Procedure		Perchloric Acid Procedure	
Total P [*]	Organic P	Total P ^{**}	Organic P
2.11	0.53	2.36	0.78
1.89	0.31	2.49	0.91
2.08	0.50	2.47	0.88
2.48	0.90	2.54	0.96
2.36	0.78	2.36	0.78
—	<u>0.74</u>	<u>2.53</u>	<u>0.95</u>
2.21 ave.	0.63 ave.	2.46 ave.	0.88 ave.

Inorganic phosphate concentration 1.58 $\mu\text{g atom per liter.}$

* Corrected for a blank of 1.09 $\mu\text{g atom per liter.}$

** Corrected for a blank of 0.36 $\mu\text{g atom per liter.}$

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TABLE II
Effect of Various Salts on Color Development

Medium g/50 ml.	Phosphate Concentration ($\mu\text{g atom/L.}$)	
	Added	Found
2 g. NaCl	1.20	1.00
2 g. Na ₂ SO ₄	1.20	1.20
	2.20	2.20
2 g. NaNO ₃	1.60	1.50
2 g. NaClO ₄	1.60	1.60

Arsenite Interference

It is generally thought that arsenic in sea water is present mainly as arsenite with inappreciable amounts of arsenate. However, Armstrong and Harvey (1950), as a result of experiments which they have performed, suggested that arsenate may be the predominating form. According to Zinzadze (1935), arsenate but not arsenite forms a blue reduction product with the reagents for the phosphate determination and thus would be estimated along with phosphate. However, if arsenite is oxidized to arsenate in the oxidization of organic phosphorus, there would be interference in the estimation of total phosphorus. Experimentally, it was demonstrated by the authors that this is the case, Table III. Sea water samples with added arsenite were digested with perchloric acid and estimated colorimetrically. From these values was subtracted the total phosphorus of the sea water, containing no added arsenite. The total phosphorus value also included arsenic present in the sea water which had been oxidized to arsenate as well as phosphorus. The results indicated that the added arsenite had been oxidized though not quantitatively.

It was also noted that arsenite causes a blue color with the phosphate reagents even though it is not thought to form a complex. Figure 1 shows the extent of the color development by arsenite in different media. Almost as much color is developed by arsenite in distilled water or in a medium containing the digested sea water salts as by an equivalent amount of phosphate, while in a chloride medium considerably less color is formed. Thus arsenite in sea water would cause an error of comparatively small magnitude.

TABLE III

Oxidation of Arsenite with Perchloric Acid in a Sea Water Medium

Added	Arsenite Concentration ($\mu\text{g atoms/L.}$)	
	Found as Arsenate	
	Fumed 5 min.	Fumed 1 hr.
2.00	0.22	0.96
	0.10	1.08
	0.10	2.03
	0.19	2.00
	0.17	1.62

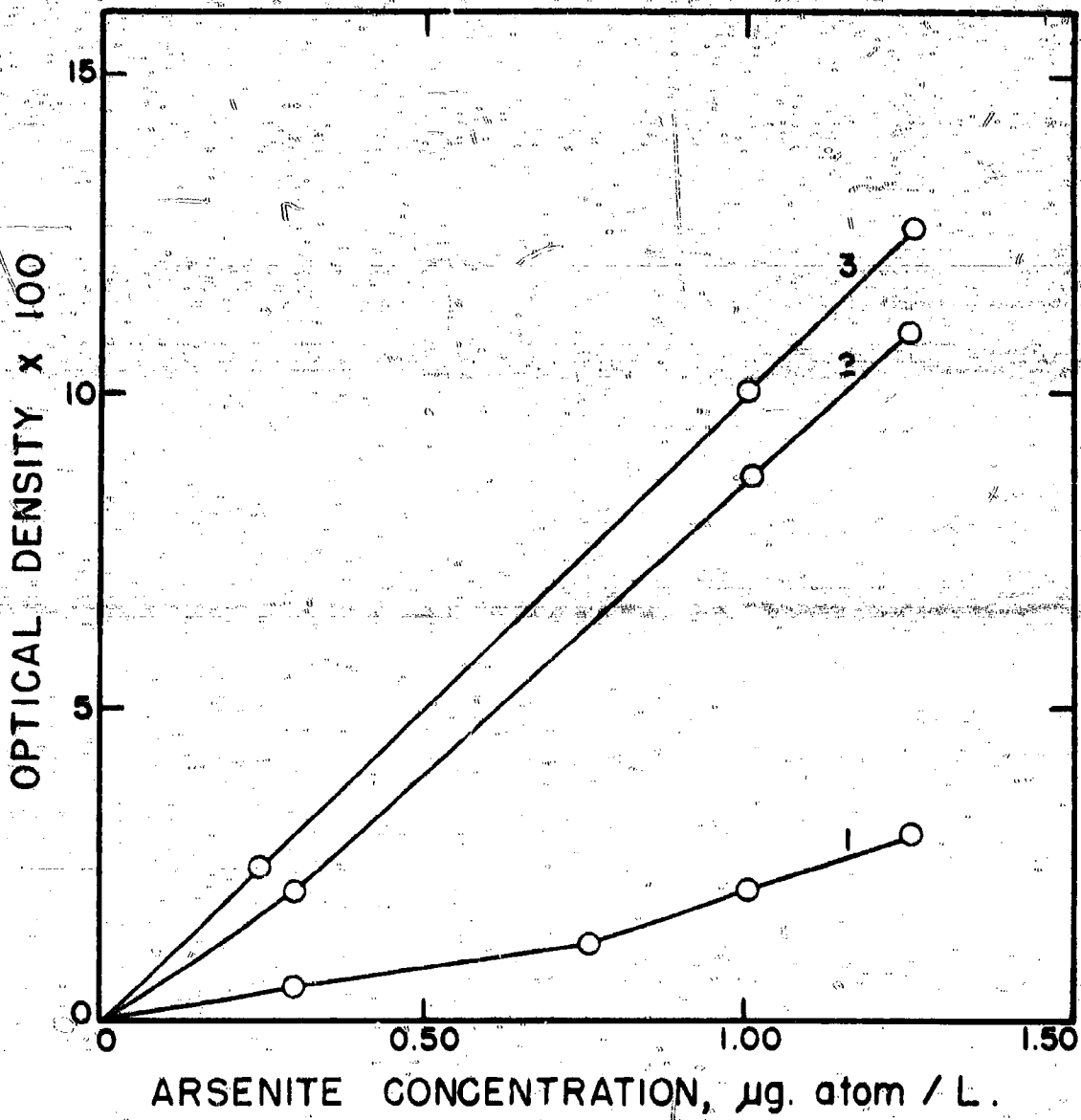


Figure 1. ARSENITE INTERFERENCE IN VARIOUS MEDIA

1. Arsenite in sodium chloride solution, Cl = 17 ‰.
2. Arsenite in distilled water or in digested sea water, Cl = 17 ‰.
3. Calibration curve for phosphate in sodium chloride solution, Cl = 17 ‰.

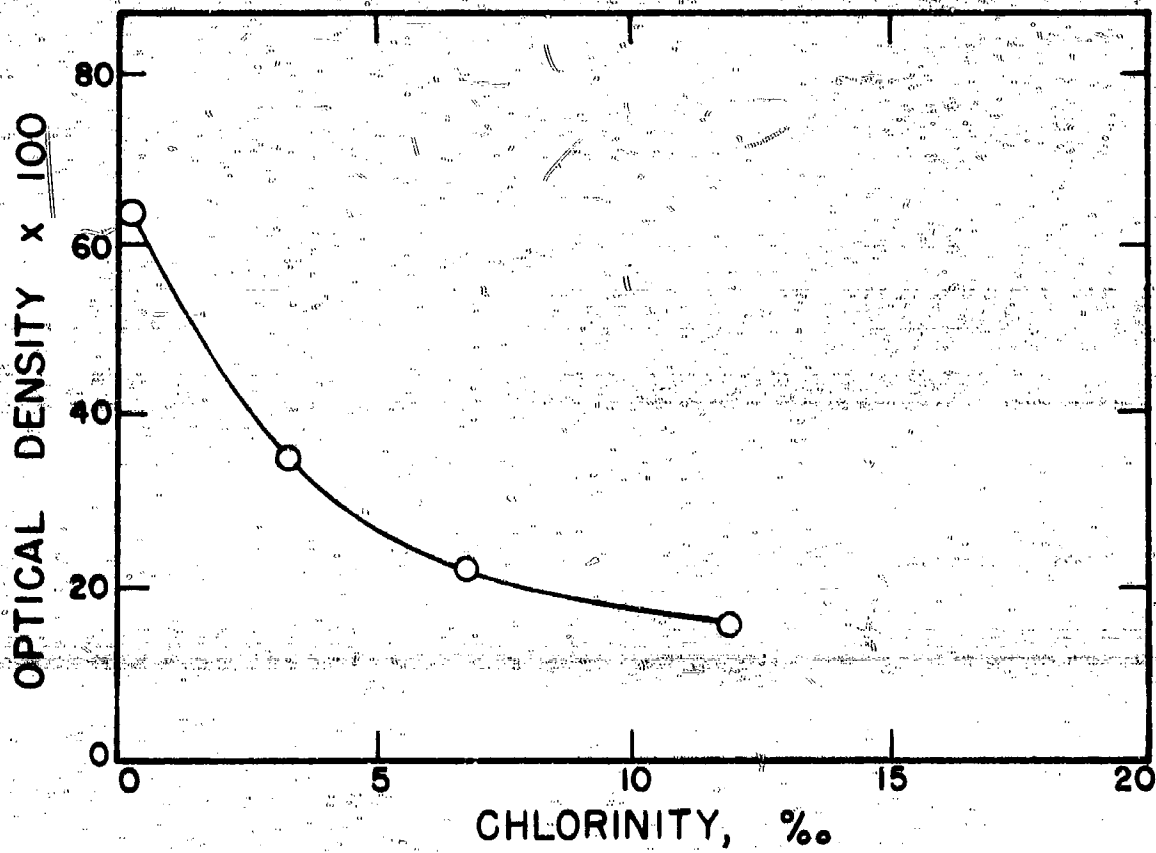


Figure 2. ARSENITE COLOR DEVELOPMENT WITH VARIATION IN CHLORIDE CONCENTRATION.

The color developed by arsenite was found to depend upon the chloride concentration. This is demonstrated by the results shown in Figure 2. An arsenite concentration of 12 μg atom per liter, which is twenty to fifty times its probable concentration in sea water, was used to accentuate the effect at various chloride concentrations. Considerably less color was developed by arsenite at the higher chlorinities. Thus in undigested sea water, arsenite interference can ordinarily be neglected but should be considered when samples containing no chloride are being analyzed.

Elimination of Arsenic

In an attempt to eliminate interference by arsenic, a reduction procedure using sulfite was tried. It was found that, in a sea water sample digested with perchloric acid, arsenate was apparently reduced to arsenite after heating for 1 hour at 90°C . in the presence of 0.4 g. of sodium bisulfite. The method was not satisfactory, however, as the results were erratic.

In order to completely eliminate all forms of arsenic, a volatilization procedure was developed. After digestion for 5 minutes with perchloric acid, 3 ml. of concentrated hydrochloric acid were added to the digested sea water samples and rapidly fumed off. This procedure was found to be effective when tried with samples to which known amounts of arsenite had been added. The arsenic was probably driven off in the form of arsenic trichloride.

Analysis of Sea Water Samples

The values given in Table IV were obtained when sea water samples collected in Dabob Bay were analyzed by the recommended procedure. The inorganic phosphate concentration increased with depth as is usually the case with stratified waters. The organic phosphorus values showed no definite correlation with depth. The results in Table IV are given to illustrate the applicability of the method, and not the occurrence and distribution of organic phosphorus in sea water which will be discussed more fully in a later paper.

TABLE IV

Determination of Organic Phosphorus in Sea Water

Depth meters	Temp. °C.	Salinity ‰	Phosphorus, Inorganic	µg atoms/L Organic
S	18.63	25.46	0.66	0.36
20	8.96	29.07	2.00	0.36
50	8.46	29.51	2.19	0.57
75	8.06	29.60	2.19	0.59
100		29.72	2.50	0.32
140	7.51	29.97	2.74	0.48
175	7.49	30.10	3.07	0.45

Location: Dabob Bay, Puget Sound, Lat. 48° 45.0'N, Long. 122° 49.7'N.

Time: 20 July 1950

Tide: Ebb

SUMMARY AND CONCLUSIONS

1. Organic phosphorus in sea water has been determined after oxidation of the organic material with perchloric acid. With samples of high organic content, preliminary digestion with nitric acid should precede the perchloric acid digestion.
2. Perchloric acid is superior to sulfuric acid as a digestion medium; its salts are more readily water soluble and its blank smaller.
3. Neither perchlorate nor sulfate give a salt effect in the colorimetric determination of phosphate.
4. In the colorimetric determination of phosphate, the speed of color development in a medium containing perchlorate is the same as in distilled water, both of which have faster rates of development than a medium containing chloride.
5. Arsenite in a chloride medium yields but a slight color intensity with the phosphate reagents; in a distilled water medium, its color intensity is almost equal that of an equivalent amount of phosphate.
6. Arsenic can be prevented from interfering in the determination of organic phosphorus by treatment of the samples with concentrated hydrochloric acid and volatilization of the arsenic.

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