

DETERMINATION OF TOTAL SOLUBLE PHOSPHORUS IN SEAWATER*

M. D. BORKAR

Health Physics Division, Bhabha Atomic Research Centre, Bombay-85 (AS)

ABSTRACT

In the determination of phosphorus in seawater, removal of arsenic was not considered as significant in some of the earlier methods. Strickland and Parsons recommended in their method for total phosphorus the use of potassium iodide to remove arsenic by volatilisation with perchloric acid. In the present method, sodium sulphite is used for the same purpose. Further, stannous chloride which is still widely used as a reducing agent for developing final phosphomolybdate blue colour, suffers from a number of disadvantages. The present method makes use of mixed reagent used by Portmann and Riley. The mixed reagent contains ascorbic acid as reducing agent. Confirmation of complete removal of arsenic and non-interference by silica under the conditions of the experiment was obtained. Values of phosphorus content of seawater samples collected from Bombay Harbour Bay are also presented.

INTRODUCTION

PHOSPHORUS occurs in seawater in the form of dissolved and particulate inorganic phosphate and as dissolved and particulate organic phosphate of biological origin. It also plays significant role in controlling fertility of seawater (Riley and Skirrow, 1965).

A number of methods are available for determining phosphorus in seawater (Martin, 1968 ; Hansen and Robinson, 1953 ; Murphy and Riley, 1962). Strickland and Parsons describe individual methods for determining reactive phosphorus, organic bound phosphorous and total phosphorus in seawater (Strickland and Parsons, 1965). Depending upon the method adopted and the form of phosphorus investigated the observed values show variations. The value for $PO_4\text{-P}$ content in seawater is 70 $\mu\text{g/l}$ (Polikorpov, 1966) and 88 $\mu\text{g/l}$ (Wedepohl, 1969).

Sharma *et al.* found the average value to be 61 $\mu\text{gm/l}$ for seawater off Tarapur Coast (Portmann and Riley, 1964). The present method is based on the one described by Strickland and Parsons for total phosphorus (Strickland and Parsons, 1965). Strickland and Parsons use KI to reduce arsenate to arsenite before volatilising arsenic with $HClO_4$, by evaporation. The solution is then cooled, treated with dilute ammonia, and evaporated to dryness. The phosphomolybdate blue colour is developed after dissolving the dried residue in water.

* Presented at the 'Symposium on Indian Ocean and Adjacent Seas—Their Origin, Science and Resources' held by the Marine Biological Association of India at Cochin from January 12 to 18, 1971.

The present method makes use of Na_2SO_3 for the reduction of arsenate to arsenite before volatilising arsenic with HClO_4 and eliminates treatment with ammonia. The phosphomolybdate blue colour is developed with mixed reagent used by Portmann and Riley (Harvey, 1948). The phosphorus is determined by internal addition method, using Beckman DU spectrophotometer, at 900 m μ wavelength.

Thanks are due to Dr. A. K. Ganguly, Head, Health Physics Division, BARC, for his keen interest and to Shri P. R. Kamath and Shri K. C. Pillai for helpful suggestions.

REAGENTS

- (1) Standard phosphate solution. 5 $\mu\text{gm/ml}$ prepared from Na_2HPO_4 (Analar-BDH).
- (2) 5% Na_2SO_3 (May and Baker).
- (3) 70% HClO_4 (Baker Analysed).
- (4) Mixed reagent prepared by adding the following reagents in order in 25 ml std. flask :
 - (i) 10 ml 5 N H_2SO_4 (Analar BDH)
 - (ii) 3 ml 4.8% Ammonium molybdate (G. R. E. Merck)
 - (iii) 1 ml 0.276% K-Sb-tartarate
 - (iv) 6 ml 1.76% Ascorbic acid

Make up to mark with distilled water. Mix thoroughly. The mixed reagent is stable for few hours and should be prepared fresh.

PROCEDURE

- (1) Filter 50 ml of freshly collected seawater through Whatman filter-paper No. 42 into four silica dishes, respectively.
- (2) Add 1, 2 and 3 ml of std. phosphate solution into three dishes, respectively.
- (3) Add 5 ml of 5% Na_2SO_3 in all the dishes followed by 5 ml of perchloric acid.
- (4) Place the dishes on hot plate and evaporate to dryness taking care to avoid spurting when the solids start separating. Continue heating till no more fumes are observed.
- (5) Allow to cool. Add about 30 ml distilled water to dissolve the solids. Transfer to 50 ml standard flask. Wash the dish and collect the washings in the std. flask until the volume is about 40 ml (Usually a turbidity is observed).
- (6) Add 5 ml mixed reagent and make up the volume to the mark by adding distilled water. Shake thoroughly and allow the colour to develop (The turbidity initially present disappears after half an hour).

[2]

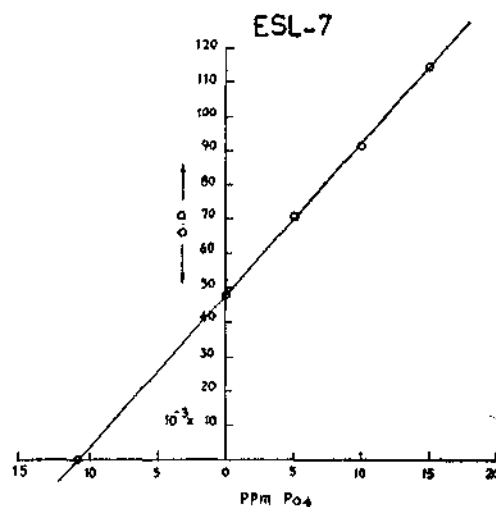
(7) Measure the Optical Density (O.D.) after one hour in 1 cm glass cell at 900μ wavelength.

(8) O.D. for chemical blank due to reagents used is also simultaneously determined as follows :

Add 5 ml of 5% Na_2SO_3 and 5 ml conc. HClO_4 in silica dish and evaporate to dryness. After the fumes have subsided, cool the residue and add about 30 ml distilled water. Transfer to 50 ml standard flask collecting the washing also. Add 5 ml mixed reagent and make up the volume to mark. Shake thoroughly and measure the O.D. after one hour.

DISCUSSION

In the determination of phosphorus, the main interference is from soluble arsenates and silicates in seawater. Portmann and Riley have stated that arsenic is present in seawater mainly as arsenate and the average content of arsenic is in the range of 2-4 $\mu\text{gm/l}$ (Harvey, 1948). Harvey used Na_2SO_3 to reduce arsenate to arsenite. However, it is not known, how much of this is arsenite and what is its interference in phosphate estimation. Strickland and Parsons in their method use KI to reduce arsenate to arsenite (Strickland and Parsons, 1965). Other reagents



used for the same purpose are ascorbic acid, hydroxylamine hydrochloride. In the present study, 5% Na_2SO_3 is used for the reduction and complete removal of arsenic is confirmed by spiking 5, 10, 15 μg of arsenic to sample of seawater respectively, and estimating the phosphate content. The results obtained are given below.

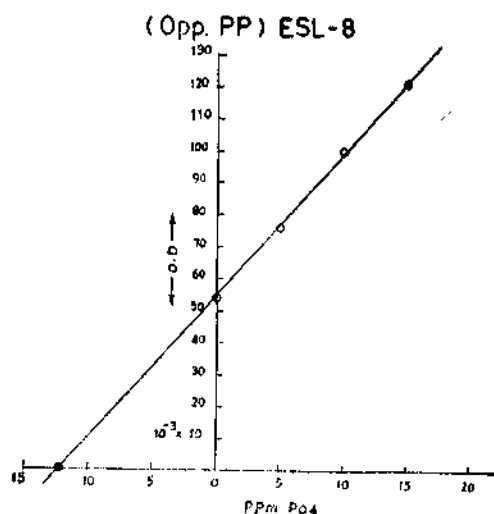
[3]

Vol. of seawater	Amount of Arsenic added	Absorbancy (O.D.)
50 ml	0 μg	0.0485
50 ml	4.83 μg	0.0500
50 ml	9.86 μg	0.0500
50 ml	14.49 μg	0.0050

Thus, the increase in O.D. observed after adding 14.49 μg of arsenic, is only 4%.

Interference of silicate in the phosphate estimation was also studied. 150 μg of Si as sodium silicate with 5 ml mixed reagent and diluted to 50 ml, gives O.D. of the same order as that for chemical blank after 2 hours.

Amount of Si added	O.D.
150 μg	0.0120
150 μg	0.0125
150 μg	0.0120

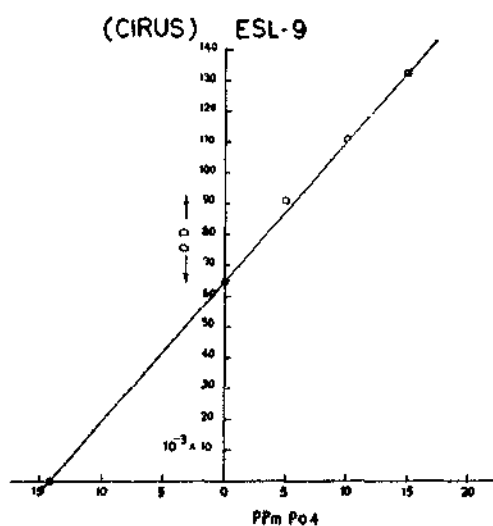


Therefore, it can be concluded that silicates do not interfere in this method at the concentration present in seawater. However, silicate develops colour after several hours.

Stannous chloride is still very widely used for developing the phosphomolybdate blue colour. However, it suffers from a number of disadvantages (Riley and Skirrow, 1965). Among the other reducing agents, used are metol sulphate, hydroquinone, phenyl hydrazine and mixed reagent. In this method the mixed reagent is used for

developing the blue colour as described above. The mixed reagent reacts rapidly with the phosphate to give the blue complex containing Sb and which has an Sb : P atomic ratio of 1 : 1 (Riley and Skirrow, 1965). Optical density given by the mixed reagent is negligible and that due to chemical blank is 0.015. The following values were obtained for the $\text{PO}_4\text{-P}$ content of sea-water samples collected between Apollo Pier and Trombay in the Bombay Harbour Bay. The samples were collected before monsoon.

Station	Vol.	Absorbancy after deducting BKG(O.D.)	$\text{PO}_4\text{-P}$ $\mu\text{g/l}$
ESL 1	50 ml	0.0287	43.73
ESL 3	"	0.0380	57.92
ESL 5	"	0.0357	54.46
ESL 6	"	0.0365	55.62
ESL 7	"	0.0480	70.11
ESL 8	"	0.0540	79.9
ESL 9	"	0.0650	92.94



Complete recovery for organic bound phosphate was not studied.

REFERENCES

- HANSEN, A. L. AND R. J. ROBINSON 1953. *J. Mar. Res.*, **12** : 31.
- HARVEY, H. W. 1948. *J. Mar. Biol. Ass. U.K.*, **27** : 337-359.
- MARTIN, D. F. 1968. *Marine Chemistry*. Marcel Dekker Inc., New York, **1** : 1-123.
- MURPHY, J. AND P. RILEY 1962. *Analytica Chimica Acta*, **27** : 31-36.
- POLIKORPOV, G. G. 1966. *Radio-ecology of aquatic organisms*. Reinhold New York.
- PORTMANN, J. E. AND J. P. RILEY 1964. *Analytica Chimica Acta*, **31** : 1-509.
- RILEY, J. P. AND G. SKIRROW 1965. *Chemical oceanography*. Academic Press, London and New York, **2** : 1-362.
- SHARMA, T. P. AND OTHERS 1968. *Major and minor elements distribution in marine Biosphere off Tarapore Coast*. BARC/HP/BS/4.
- STRICKLAND, J. D. H AND T. R. PARSONS 1965. A manual of seawater analysis. *Fisheries Research Board of Canada, Bulletin*, **125**.
- WEDEFOHL, K. H. 1969. *Handbook of Geo-Chemistry*. Springer-verlag Berlin, Heidelberg, New York, pp. 1-310.