Determination of total phosphorus in sediments by means of high-pressure bombs and ion chromatography

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Abstract

The traditional standard method for the determination of total phosphorus is performed by oxidizing of phosphorus to phosphate in a strong acidic media. The determination of total phosphorus in natural waters using potassium persulphate provides an alkaline environment optimum for breaking the phosphorus bonds under high pressure and temperature. This work describes a methodology for the determination of total phosphorus in sediments using a mixture of potassium persulphate and NaOH. A Dionex Model 2000i/SP ion chromatograph, with an anion pre-column (Dionex AG4A), an anion separator column (Dionex AS4A), a suppressor column (Dionex AMMS-II) and a conductivity detector was used. The mobile phase (2 ml min^{-1}) was 1.7 mM NaHCO$_3$–1.8 mM Na$_2$CO$_3$. Results were compared with the traditional HCl method showing a relative standard deviation of 5%. Precision of the proposed methodology between 5 samples analyzed by triplicate was 4.61%. The method is of low cost and has an easy procedure.

Keywords: Sediments; Phosphorus; Phosphate; Sulfate; Inorganic anions

1. Introduction

Traditionally, aquatic nutrient studies have focused on the concentrations of nitrate (NO$_3^-$) and of soluble reactive phosphorus (PO$_4^{3-}$) in natural waters [1].

The ecological importance of the phosphates is due to their role in the metabolism of living organisms. Since it is scarce in the sphere, phosphate represents a limiting reagent for biological productivity. Therefore, when phosphorus is added to lakes, tanks, lagoons etc. the normal response of the ecosystem to the eutrophication, is a fast increase in algae productivity.

The largest part of phosphorus in sediments is found as particulate matter being generally immobile which makes it more soluble in the interstitial water. Diffusion, mixture and bioturbation can transport phosphorus from the sediments to the surface water greatly affecting the amount in water.

Determination of total phosphorus by the standard method uses potassium persulphate as the oxidizing reagent, however, it requires a strong acidic environment. Phosphorus analysis involves two general procedural steps: (a) conversion of the phosphorus form of interest to dissolved orthophosphate and (b) colorimetric determination of dissolved orthophosphate. Three standard digestion methods are generally used: the perchloric acid method (the most drastic and time consuming method); the nitric sulphuric acid method and the simplest persulphate oxidation method. After digestion, the liberated orthophosphate is determined colorimetrically, this being the acid ascorbic method more widely used [2].

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The digestion chromatographic methodology proposed herein uses the persulpahte digestion solution of Johnes and Heathwaite [1] and a modified technique for the digestion and determination of total phosphorus is reported. The method utilizes a high-pressure bomb for the persulphate digestion step. This technique converts all phosphorus forms in the sample into orthophosphate which is determined using ion chromatography, representing a convenient and more accurate and rapid method of phosphorus analysis. This digestion step, is the same for total phosphorus and nitrogen determination in sediment and water samples previously reported [3,4]. A comparison was made between the proposed digestion-chromatographic method and the standard method [2].

2. Experimental

Samples of sediments were taken from Sinamaica Lagoon, Venezuela. A standard from the NIST (1646 Estuarine Sediment) was used to confirm the validity of the method.

2.1. Standard method for total phosphorus

A 2.5-g mass of wet sediment sample or standard was ignited for 2 h at 550°C. After cooling to room temperature, 10 ml of HCl was added and solution was boiled for 1 h. The solution was made up to 10 ml with deionized water. Orthophosphate was determined by the acid ascorbic colorimetric method.

The water content of the sample was determined by drying for 24 h at 110°C to reach constant weight, and converting concentrations to g^{-1} of dry sediment.

2.2. Orthophosphate ascorbic acid standard method.

2.2.1. Reagents

Sulphuric acid, H_2SO_4, 2.5 M

A 70-ml volume of conc. H_2SO_4 was diluted to 500 ml with deionized water.

Potassium antimonyl tartrate solution

A 1.3715 g mass of $K(SbO)C_4H_4O_6 \cdot 0.5\ H_2O$ was dissolved in 400 ml water in a 500-ml volumetric flask and diluted to volume.

Ammonium molybdate solution

A 20-g mass of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was dissolved in 500 ml deionized water.

Ascorbic acid, 0.1 M

A 1.76-g mass of ascorbic acid was dissolved in 100 ml deionized water.

Combined reagent

The above reagents were dissolved in the following proportions for 100 ml of the combined reagent: 50 ml 2.5 M H_2SO_4, 5 ml potassium antimonyl tartrate solution, 15 ml ammonium molybdate solution and 30 ml ascorbic acid solution. After addition of each reagent the solution was mixed.

Stock phosphate solution

A 219.5-mg mass of anhydrous KH_2PO_4 was dissolved in deionized water and diluted to 1000 ml.

2.2.2. Procedure

A 10-ml volume of standard or sample was pipetted into a clean dry tube and then neutralized up to pH 7. Then 1.6 ml combined reagent was added and mixed thoroughly. After at least 10 min, but no more than 30 min, absorbance was measured at 880 nm in a spectronic 21.

2.3. Determination of total phosphorus by proposed digestion and ion chromatography methods

2.3.1. Reagents

Sodium hydroxide solution (3.75 mol l^{-1}) was made by dissolving 75 g of NaOH in 500 ml of deionized water. The oxidizing reagent was made by adding 15 ml of the 3.75 mol l^{-1} NaOH solution to 500 ml of deionized water. An amount (50 g) of $K_2S_2O_8$ was dissolved in the solution and diluted to 1 l. This oxidizing reagent was prepared fresh as needed.

2.3.2. Digestion procedure

Sediments were centrifuged for 10 min at 15 000 rpm, lyophilized for 4 h at −50°C and at 330 Pa in a Labconco lyophilizer (Labconco Corporation, Kansas City, KS, USA). The oxidizing reagent (4 ml) was added to 0.20 g of sediment sample, placed in the PTFE vessel and capped. The crucible was put into the stainless-steel body of the Parr bomb (Parr trademark No. 4745, Parr Instrument Company, IL, USA) and closed by tightening the stainless-steel screw cap. The system was placed into a pre-heated oven at 110°C and kept at this temperature for 4 h. The bombs were opened after cooling to room temperature and samples were diluted up to 25 ml. During the digestion procedure, phosphorus compounds were converted into orthophosphate. The orthophosphate formed was measured by ion chromatography.

2.3.3. Determination of phosphate by ion chromatography

Samples were diluted tenfold before injection onto the chromatographic system, because the sulphate peak, derived from potassium peroxidisulphate after the digestion procedure, interferes in the detection of phosphate. After dilution, sulphate was precipitated as lead sulphate using lead perchlorate and a lead ion selective electrode as sensor [5]. Then samples were filtered using a 0.45-μm membrane and injected onto the chromatographic system. A blank of the oxidizing reagent was injected onto the chromatographic system to produce a base line. All reagents were of analytical reagent grade and deionized water was used. Calibration standards were prepared by diluting

mixed stock solutions containing 1000 mg l^{-1} of P-PO$_4^{3-}$ using a series of dilutions.

2.4. Apparatus

Samples were analysed using a Model 2000i/SP ion chromatograph (Dionex, CA, USA) using an anion pre-column (Dionex AG4A), an anion separator column (Dionex AS4A), a suppressor column (Dionex AMMS-II) and a conductivity detector Dionex CDM-2). The mobile phase (flow-rate 2 ml min^{-1}) was 1.7 mmol l^{-1} NaHCO$_3$–1.8 mmol l^{-1} Na$_2$CO$_3$ and the suppressor solution was 12.5 mmol l^{-1} H$_2$SO$_4$. The injection volume, conductivity, sensitivity and chart speed were 100 μl, 30 μS and 0.5 cm s^{-1} respectively.

2.5. Procedure

Standards and samples were injected into an ion chromatograph with a retention time of 10 min, which enabled the sulphate peak to be the last to elute. During a run, external standardization was used with recalibrations after every 10 samples. A standard graph was developed and the peak area versus concentration regression was used to quantify unknown concentrations. A filter (0.45 μm) was needed to eliminate any particulate matter from the digested sample.

3. Results and discussion

After digestion and dilution, the samples were injected into the ion chromatograph to obtain total

Table 1
Accuracy of the proposed method

Sample	Phosporus (% w/w)					
	Reported		Found			
			SM		IC	
	x	σ	x	σ	x	σ
*Estuarine standard sediment (SRM-1646)	0.054	0.005	0.0536	0.0005	0.0535	0.0005

$n = 3$.
SM: Standard method (ascorbic acid).
IC: Ion chromatography-proposed method.
* From National Bureau of Standard.

phosphorus concentrations as orthophosphate. The detection was achieved after the elution from the column by means of a conductivity detector, recorded and quantified with an integrator (Fig. 1). Response of PO_4^{3-} was linear in the working range $0.01–1.0$ mg l^{-1}. The correlation coefficient (r) for a linear least squares fit was 0.9991 and the equation was $y = 3.2912e{-}06x - 0.0934$, where y is the concentration and x is peak area. The r coefficient showed that the conductivity detector gave linear response over the whole calibration range used in this work. The relative standard deviation (R.S.D.)
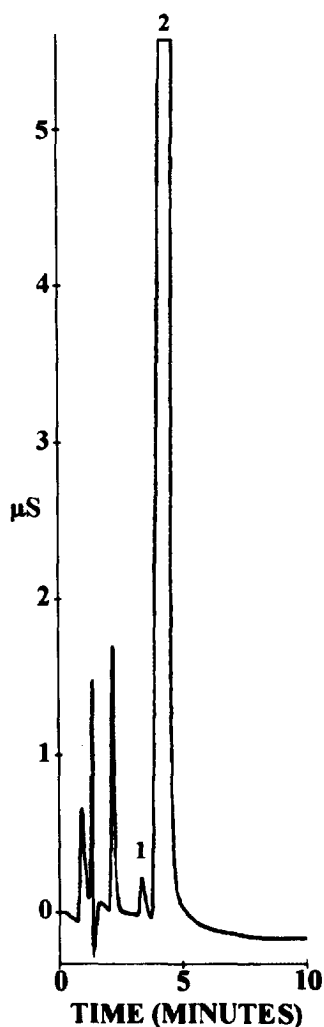
was 1.65%. The detection limit was 0.006 mg P g^{-1} sediment.

The accuracy was tested by analysing the reference material (NIST-1646) Estuarine Sediment which reports $0.05\pm0.005\%$ (w/w) of phosphorus, and freeze dried samples digested using the proposed method. The results are given in Table 1. The mean concentrations from the Parr-type digestion procedure did not differ significantly ($p<0.05$) from the values obtained by the standard method. The F test calculated using Table 1 values showed that the two methods have similar precision.

Calculated $F = 1.000$

Theoretical $F = 3.179$ ($p = 0.05$)

With the digested procedure described earlier to convert total phosphorus to orthophosphate, a digested standard sample was titrated with lead perchlorate. Phosphate concentrations were not affected by the sulphate precipitation, as is shown in Table 1 using phosphate standard sample. Perchlorate elutes at a high retention time and therefore does not interfere with phosphate concentration which elutes earlier [5].

In Table 2, the concentrations of phosphorus in sediments from Sinamaica Lagoon, after the digestion step of the proposed method by ion chromatography, are compared with those obtained by the digestion and colorimetric standard methods. The results obtained by the proposed method were in good agreement with those obtained using the standard methods, being the difference less than 5%. The R.S.D. using both methods was below 1%.

Table 3 shows the results obtained by the

Fig. 1. Separation of phoshate in digested sample. Peaks: $1 = PO_4^{3-}$ (0.055%, w/w); $2 = SO_4^{2-}$.

Table 2
Comparison of total phosphorus concentrations by the standard method and the proposed method using ion chromatography

Sample	Phosphorus (mg g^{-1} dry sediment)			
	Standard method		Proposed method	
	x	σ	x	σ
Sinamaica Lagoon sediment	0.041	0.0003	0.039	0.0002

$n = 5$.

Table 3
Total phosphorus concentration in samples of sediment from Sinamaica Lagoon using ion chromatography

Sample	mg P g^{-1} dry sediment	
	x	σ
1	0.1278	0.0015
2	0.1169	0.0040
3	0.1834	0.0010
4	0.1410	0.0010
5	0.0756	0.0055

$n = 3$.
Mean R.S.D. = 4.61%.

proposed method using 5 different samples of sediments from Sinamaica Lagoon analyzed by triplicate (R.S.D. = 4.61%). One of the advantages of this method is its applicability in the determination of low concentration samples (detection limit: 0.006 mg P g^{-1}) as those found in Sinamaica Lagoon.

4. Conclusion

The determination of phosphorus by ion chromatography gives reproducible and accurate results. The persulphate digestion-ion chromatographic method for the determination of total phosphorus has the advantage of achieving high precision utilizing only a small amount of sample.

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