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## Determination of phosphate and sulphite in natural waters in the presence of high sulphate concentrations by ion chromatography under isocratic conditions

Hilda Ledo de Medina<sup>a,\*</sup>, Elizabeth Gutiérrez<sup>a</sup>, Marinela Colina de Vargas<sup>a</sup>,  
Graciela González<sup>b</sup>, Julio Marín<sup>a</sup>, Eduardo Andueza<sup>c</sup>

<sup>a</sup>Laboratorio de Química Ambiental, Facultad Experimental de Ciencias, Universidad del Zulia, Maracaibo 4011, Estado Zulia, Venezuela

<sup>b</sup>Laboratorio de Electroquímica, Ciclo Básico, Facultad de Ingeniería, Universidad del Zulia, Maracaibo 4011, Estado Zulia, Venezuela

<sup>c</sup>INPELUZ, Maracaibo, Estado Zulia, Venezuela

### Abstract

Phosphorus in aquatic systems is generally considered the limiting nutrient in most of cases. Its concentration may be below 0.01 mg/l. The sensitivity of the standard method for phosphate with ascorbic acid does not allow its determination in these kind of samples. Ion chromatography (IC) provides a suitable way for phosphate quantification. However, when the sulphate concentrations are significantly high, interference of the phosphate signal does occur. This can be avoided by precipitating sulphate as lead sulphate with lead perchlorate solution performing a potentiometric titration using a lead ion selective electrode (ISE). The samples are then filtered through a 0.45- $\mu$ m membrane filter and analyzed by IC.

A Dionex Model 2000i/SP IC, 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) was 1.7 mM NaHCO<sub>3</sub>-1.8 mM Na<sub>2</sub>CO<sub>3</sub>. An automatic Titroprocessor Metrohm with Dosimat E678 and a lead ISE Orion 94-82 coupled to a double junction reference electrode Orion 90-02 was used for the potentiometric titration of the samples.

In samples (e.g. interstitial waters) in the presence of sulphite, it is not possible to quantify this ion using IC with isocratic conditions, since it co-elutes with sulphate ion. In this case, sulphate may be determined potentiometrically, using a reduction solution to obtain hydrogen sulphide, then sulphite concentration is determined by the difference between IC and potentiometric results.

Water samples of estuary and lagoon with sulphate concentrations between 10.000 and 200 mg/l and phosphate concentrations between 0.020 and 0.090 mg/l were analyzed. The detection limit for phosphate was 1  $\mu$ g/l, and the relative standard deviation (R.S.D.) was less than 5 percent. The detection limit for sulphate was 3  $\mu$ g/l and the R.S.D. was less than 5 percent too.

The objective of this paper is to present an economical, sensitive and accurate way to avoid sulphate as interference with phosphate and sulphite in isocratic conditions by IC.

**Keywords:** Water analysis; Environmental analysis; Phosphate; Sulfite; Sulfate; Inorganic anions; Phosphorus

\*Corresponding author.

## 1. Introduction

Years of industrial and municipal waste discharge to riverine, estuarine and coastal waters have deteriorated the quality of these waters and of their corresponding habitats. Nutrient concentrations in water near large urban centers have increased as the result of discharge from wastewater treatment facilities. Higher nutrient concentrations enhance biomass productivity, that can lead to hypoxia and eutrophication [1].

Eutrophication is one of the most serious environmental problems involving water sources in all industrialized countries. As is well known, phosphorus is considered the main limiting factor for algal growth in most internal and coastal waters [2]. Its concentration may be below 0.01 mg/l.

Nutrients inputs to many aquatic systems from anthropogenic activities have greatly exceeded the inputs from natural sources for many decades. One important difference between marine and other water systems is the nutrient concentration in the water. Nutrient concentrations present in heavily eutrophicated seawater are normally lower than the natural background levels observed in river water [3].

The sensitivity of the standard method for phosphate with ascorbic acid does not allow its determination in these kind of samples. Ion chromatography (IC) provides a suitable method for phosphate quantification in these cases. However, when the sulphate concentrations are significantly high, interference of the phosphate signal does occur. Diluting the sample with deionized water does not solve this problem, because of a significant decrease in the phosphate peak height.

The determination of phosphates in natural waters with the presence of high sulphate concentrations, may be achieved by precipitating sulphate as lead sulphate with lead perchlorate solution performing a potentiometric titration with a lead ion selective electrode (ISE) and chloride ISE. The samples are then filtered through a 0.45- $\mu$ m membrane filter and analyzed by IC.

Another problem, especially in environmental samples (e.g. interstitial waters) is the presence of sulphite which is not separated from the sulphate peak under isocratic conditions since sulphite co-

elutes with sulphate. In this case, sulphate may be determined potentiometrically, using a reduction solution to obtain hydrogen sulphide, and sulphate is determined as sulphide using a sulphide ISE [4]. Then sulphite can be determined by the difference between sulphite plus sulphate obtained by IC minus sulphate obtained by the potentiometric reduction method.

Water samples of estuary and lagoon with sulphate concentration between 10.000 and 200 mg/l and phosphate concentrations between 0.002 and 0.060 mg/l were analyzed. The detection limit for phosphate was 1  $\mu$ g/l, and the R.S.D. was less than 5 percent. The detection limit for sulphate was 3  $\mu$ g/l and the R.S.D. was less than 5% too.

The objective of this paper is to present a low cost, sensitive and accurate way to avoid sulphate as interference with phosphate and sulphite in isocratic conditions by IC.

## 2. Experimental

Samples of natural waters were taken from Lake Maracaibo and surficial sediments samples were collected using an Ekman dredge in Sinamaica Lagoon, both located in Zulia state, Venezuela. Interstitial waters was extracted from sediment samples by centrifugation and it was then filtered using a 0.45  $\mu$ m membrane filter. An USEPA NUTRIENTS WP284 certified standard was used to check the exactitude of the determination of phosphate concentrations using the chromatographic method.

### 2.1. Determination of phosphate by means of sulphate precipitation

#### 2.1.1. Lead ion selective electrode

#### Instrumentation

Orion Model 94-82 lead ISE; Orion Model 90-02 double junction reference electrode; Metrohm titroprocessor with dosimat E678.

A Perkin Elmer Model 3030B atomic absorption spectrometer was used to check lead concentration from lead perchlorate solution, under the following

conditions: 0.7 nm spectral bandpass and 283.3 nm resonance wavelength (air–acetylene flame).

#### Reagents

All reagents were of analytical reagent grade including methanol which was used to obtain 50% v/v, methanol–water mixed solvent system. Methanol was first purified by distillation.

Orion Research lead perchlorate solution, 0.1 M, was used as titrant.

#### 2.1.2. Chloride ion selective electrode

##### Instrumentation

Orion Model 94-17 chloride ISE; Orion Model 90-02 double junction reference electrode.

#### Reagents

0.1 M chloride standard solution (Orion Research).

#### 2.1.3. Sulphide ion selective electrode

##### Instrumentation

Orion Model 94-16 sulphide ISE; Analytical Balance METTLER AT 261 (Delta Range).

#### Reagents

0.1 M sulphate standard solution (Orion Research).

**Reduction solution:** An aliquot of 322 ml of hydriodic acid (57%), was added to 50 ml of hypophosphorous acid (50%) followed by 200 ml of concentrated hydrochloric acid. The mixture was boiled under reflux for 1.5 h while a stream of nitrogen was passed through the solution. The hydrogen sulphide was sparged from the reaction mixture with nitrogen. The final solution, which should be colorless or very pale straw, was cooled and stored in a dark glass bottle at about 25°C.

**Sulphide antioxidation buffer (SAOB):** A 80.00 g weight of analytical grade sodium hydroxide was dissolved and 320.00 g of reagent grade sodium salicylate in about 500 ml of deionized water in a 1000-ml volumetric flask, then 72.00 g of ascorbic acid was added and filled to the mark. A 25% SAOB

solution was prepared as required. This solution had an important constant high pH for maintaining the level of sulphide ions.

#### 2.1.4. Ion chromatography

##### Reagents and instrumentation

Samples were analyzed using a Dionex Model 2000 i/SP IC with an anion pre-column (Dionex AG4A), an anion separator column (Dionex AS4A), a suppressor membrane (Dionex AMMS-II) and a conductivity detector. The mobile phase (flow-rate 2 ml/min) was 1.7 mmol/l  $\text{NaHCO}_3$ –1.8 mmol/l  $\text{Na}_2\text{CO}_3$  and the suppressor solution was 12.5 mmol/l  $\text{H}_2\text{SO}_4$ . The injection loop volume was 100  $\mu\text{l}$ .

### 3. Procedure

Performance of the ISEs was first evaluated by direct potentiometry. Standard solutions of the elements in the range of  $10^{-1}$  to  $10^{-5}$  M were used and calibration graphs were drawn. Ion solution concentration was checked by an average slope.

#### 3.1. Lead ion selective electrode

A 5-ml standard or sample were taken and pH was adjusted between 4.0 and 4.5 (optimal range obtained). A 5-ml volume of methanol was added to get a 50% methanol solution. The potentiometric titration using 0.1 M lead perchlorate solution was made to avoid the sulphate interference precipitating as lead sulphate, the end-point is obtained by a jump in potential. The rate of addition of lead perchlorate solution must not be faster than 0.33 ml/min near the end-point.

#### 3.2. Chloride ion selective electrode

The chloride ISE was used as indicator in the potentiometric titration of sulphate with  $\text{BaCl}_2$  solution, 0.1 M, for a 5-ml standard or sample in an acidic medium.

### 3.3. Determination of total phosphorus by digestion procedure and IC methods

#### 3.3.1. Reagents

Sodium hydroxide solution (3.75 mol/l) 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 NaOH solution to 500 ml of deionized water. A 50-g amount of  $K_2S_2O_8$  was dissolved in the solution and diluted to 1 l. This oxidizing reagent was prepared fresh, as needed [5].

#### 3.4. Digestion procedure to determine total phosphorous in water

The oxidizing reagent (2 ml) was added to 4 ml to water sample, placed in the PTFE vessel and capped. The crucible was put into the stainless-steel body of the Parr bomb (Parr No. 4745, Parr Instrument Company, Illinois, 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 IC [5].

#### 3.5. Reduction distillation method for detection of sulphate

The reduction mixture was continuously refluxed and purged with nitrogen for one hour to maintain an inert atmosphere. The calibration graph and sulphate concentrations in liquid samples were obtained using 1.00 ml of standard solution or sample. Readings were taken after stable potential values were reached and the cell was rinsed carefully between measurements. A new volume of antioxidant solution before each measurement was used.

#### 3.6. Ion chromatography

After sulphate precipitation with potentiometric method, samples were filtered through 0.45- $\mu$ m membrane filter, and injected onto the chromatographic system. A blank of the lead perchlorate

solution was injected into the chromatograph to produce a base line. Calibration standards were prepared by diluting mixed stock solutions containing 1000 mg/l of  $PO_4^{3-}$  using a series of dilutions.

Standards and samples were injected into an IC 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 was plotted and the least squares method with a regression linear was used to quantify unknown concentrations.

## 4. Results and discussion

Performance of the ISEs was first evaluated by direct potentiometry. Standard solutions of lead perchlorate in the range of  $10^{-1}$  to  $10^{-5}$  M were used and calibration graphs were drawn. An average slope of 28.0 mV per decade change in lead concentration was found. This result shows agreement with theoretical values. Least squares analysis of these data gave the relation:  $y = -28.0 \log x - 753$ . The correlation coefficient was 0.9998. The detection limit was  $1.20 \cdot 10^{-5}$  M. At this point, the ISE was ready to be used as the sensor in the titration procedure.

Chloride ISE exhibited a near Nernstian response for the range of  $1.0 \cdot 10^{-1}$  to  $1.0 \cdot 10^{-5}$  M  $Cl^-$  ( $r = 0.9999$ ). To test the precision, five replicates of standard at different concentrations of chloride ion were analyzed. Concentration on logarithmic scale versus potential on linear scale were plotted. This resulted in a straight line with a slope of 55.00 mV. Least squares analysis of these data gave the relation:  $y = -55 \log x - 8.33$ . The correlation coefficient was 0.9999 and the detection limit was  $5.8 \cdot 10^{-5}$  M.

Calibration curves for sulphate (as sulphide) in the range of  $10^{-1}$  to  $10^{-5}$  M of  $SO_4^{2-}$  solution were carried out using the reduction distillation method. The Nernstian slope of  $28.1 \pm 0.1$  mV is in agreement with the theoretical value. The treatment of the data for this graph by the least squares method provided the following straight line equation:  $y = -28.1 \log x - 799.0$ . The line had a correlation coefficient of

0.9999 and the detection limit of  $1.3 \cdot 10^{-5}$  M sulphate solution.

#### 4.1. Titration of sulphate

With the digested procedure described earlier to convert total phosphorus to orthophosphate, a digested standard sample (USEPA Nutrients WP284) was titrated with lead perchlorate in the present method, and the results were compared with those obtained using barium chloride as titrant. Table 1 shows that accuracy and reproducibility using lead perchlorate were better than when using barium chloride. The applied procedure demonstrated that phosphate concentrations were not affected by the sulphate precipitation. The difference between results using chloride and lead ISEs may be due to several interferences frequently present when using the chloride ion electrode. The interfering effects of halide, thiocompounds, complexing and reducing compounds are well recognized.

The additional advantage of using lead perchlorate solution is the partial precipitation of lead as lead chloride which is of special importance in waters with high chloride concentrations (e.g. sea waters) Fig. 1.

Slightly high solubility product ( $1.8 \cdot 10^{-8}$ ) of lead sulphate in water will lead to an indistinct end-point and it may be necessary to add a polar solvent to decrease the solubility of the precipitate. Solvents of low dielectric constant such as methanol can decrease the solubility of lead sulphate [4,6]. The

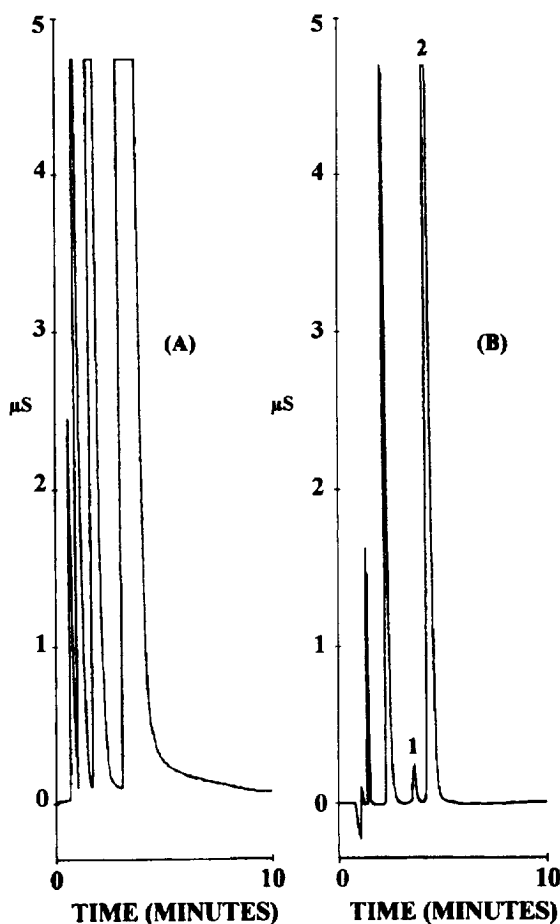


Fig. 1. Elimination of sulphate interference in the detection of phosphate by ion chromatography. (A) Before precipitation; (B) after precipitation. Peaks: 1=phosphate (0.764 mg/l); 2=sulphate.

effectiveness of the organic solvents decreased in the order methanol>dioxane [7]. In this work, the effect of the addition of two kinds of solvents was examined: dioxane in 50% concentration and methanol in 50 and 75% concentration on the titration curves. The optimum methanol volume in the titration solution was found to be 50% which is shown in Fig. 2.

In alkaline media, lead may get precipitated as lead hydroxide and in acidic media ( $\text{pH} < 3.5$ ), which affect the solubility of the electrode membrane.

Precipitation titration was carried out at various pH and different sulphate concentration values in order to determine the effect of pH on the titration

Table 1  
Accuracy of the proposed method

Sample	Phosphorus (mg/l)						
	Reported		Found by precipitation with				
	<i>x</i>	$\sigma$	Lead Perchlorate		Barium Chloride		
		<i>x</i>	$\sigma$	<i>x</i>	$\sigma$		
Standard* US EPA nutrients (WP284)	0.100	0.010	0.0885	0.0005	0.0545	0.0010	

*n*=3.

\* U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory, Cincinnati.

Confidence limit 95%: 0.08–0.12 mg/l.

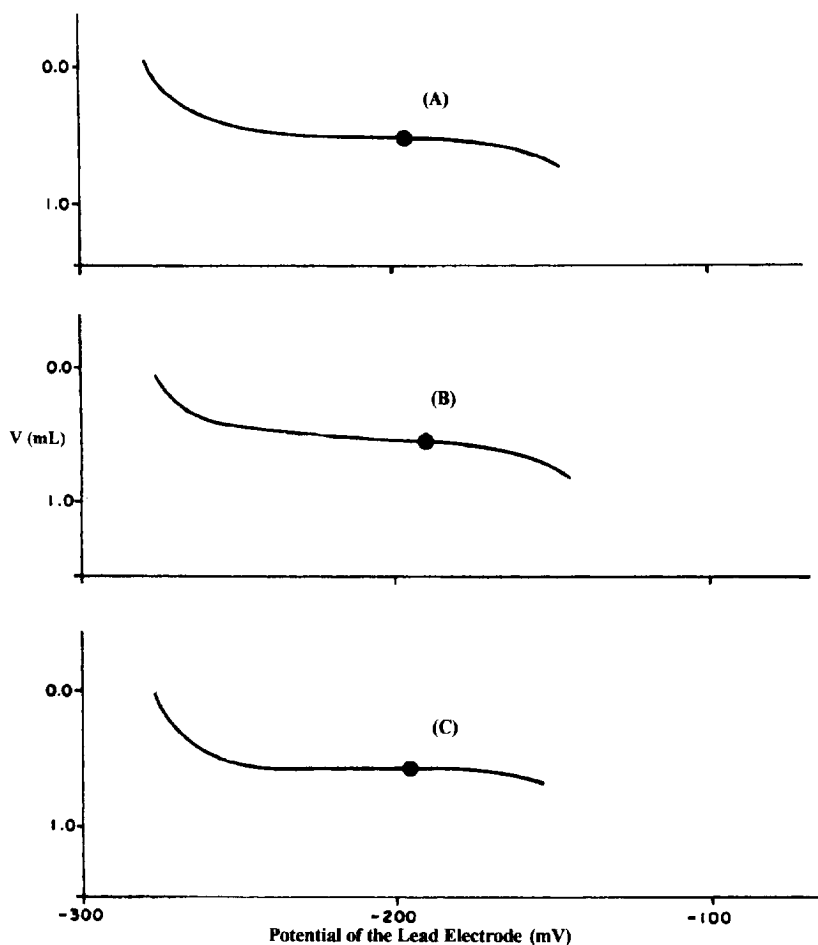


Fig. 2. Titration curves of sulphate in 50% methanol. (A):  $V_{Pb(ClO_4)_2}=0.611$  ml;  $V_{BLANK}=0.11$  ml;  $U=-194.8$  mv.;  $V_{SO_4^{2-}}=5$  ml;  $[SO_4^{2-}]=1 \cdot 10^{-3}$  M. (B):  $V_{Pb(ClO_4)_2}=0.607$  ml;  $V_{BLANK}=0.11$  ml;  $U=-190.9$  mv.;  $V_{SO_4^{2-}}=5$  ml;  $[SO_4^{2-}]=0.99 \cdot 10^{-3}$  M. (C):  $V_{Pb(ClO_4)_2}=0.602$  ml;  $V_{BLANK}=0.11$  ml;  $U=-199.7$  mv.;  $V_{SO_4^{2-}}=5$  ml;  $[SO_4^{2-}]=1 \cdot 10^{-3}$  M.

performance. Results without methanol are shown in Fig. 3. Results with methanol were also obtained. It was concluded that the pH has to be within the range of 4.0–5.0 for optimum results.

All concentrations reported in this paper only refer to the aqueous phase of the solution titrated. pH was measured before adding methanol since the Sorensen pH scale was defined for aqueous solutions only.

Due to the fact that for the Ion Pac AS4A used in our work, solvent levels may cause significant reductions in column capacity, organic solvents were not used in the precipitation step. However, using other columns (e.g. AS4A-SC, AS11, AS12) which are

compatible with those solvents, the method may be used completely as it was described.

#### 4.2. Ion chromatography

Standards were injected into the IC to obtain phosphate concentrations. The detection was achieved after elution from the column by means of a conductivity detector, recorded and quantified with an integrator. Response for  $PO_4^{3-}$  was linear in the working range 0.001–1.000 mg/l. The correlation coefficient ( $r$ ) for a linear least squares fit was 0.9980. The  $r$  coefficient showed gave a linear

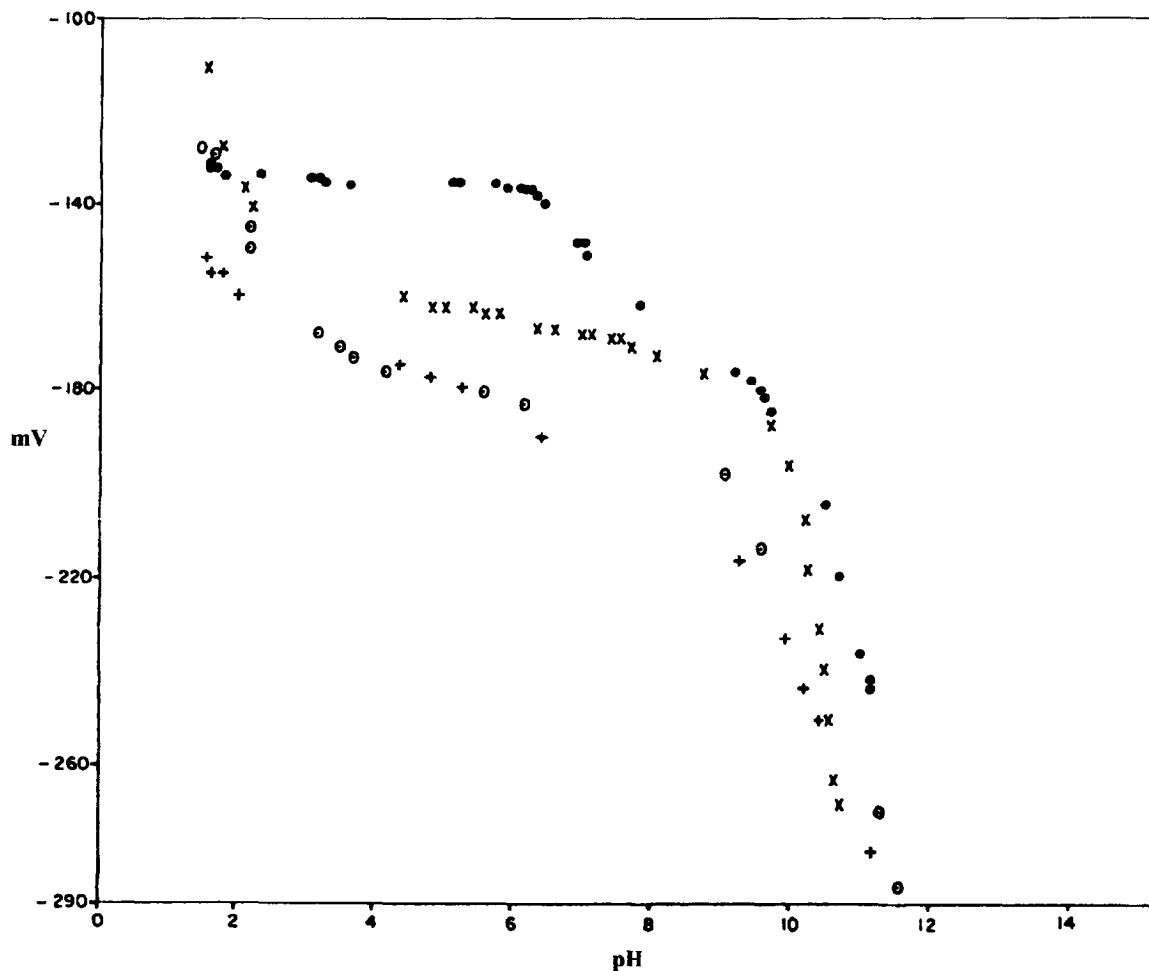


Fig. 3. Effect on pH on titration curves of sulphate: (●)  $10^{-2}$  M; (×)  $10^{-1}$  M; (○)  $10^{-4}$  M; (+)  $10^{-5}$  M.

response for the detector over the whole calibration range used in this work. The mean R.S.D. was <4.5%.

#### 4.3. Application to natural water samples

To ascertain the applicability of the proposed method, phosphate ions were determined in natural saline waters from Lake Maracaibo. As can be seen in Table 2, the results show good agreement within experimental error. Fig. 4 is a chromatogram of Lake Maracaibo water sample where the low phosphate concentration (0.006 mg/l) can be observed. This indicates that the proposed method is a useful

Table 2

Orthophosphate concentration in samples of water from Lake Maracaibo using IC after precipitation with lead perchlorate

Sample	mg P-PO <sub>4</sub> <sup>3-</sup> /l	
	<i>x</i>	<i>σ</i>
1	0.086	0.0047
2	0.043	0.0015
3	0.022	0.0006
4	0.006	0.0002
5	0.029	0.0011

*n* = 3

Mean R.S.D. = 3.69%

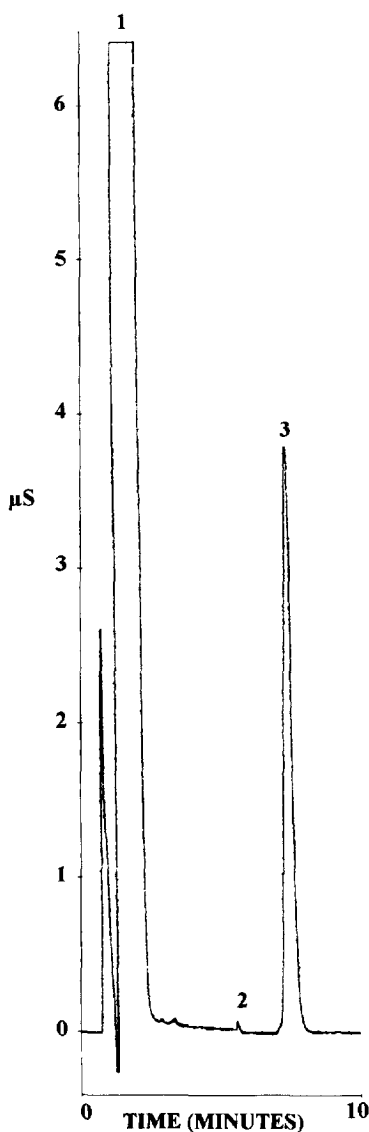


Fig. 4. Resolution of phosphate peak after precipitation of sulphate with lead perchlorate in Lake Maracaibo water sample. Peaks: 1 =  $\text{Cl}^-$ ; 2 =  $\text{PO}_4^{3-}$  (0.006 mg/l); 3 =  $\text{SO}_4^{2-}$ .

alternative for the determination of sulphate ions in natural waters, particularly saline waters.

#### 4.4. Sulphate and sulphite determination

Due to the fact that sulphite can not be determined separately by IC with an AS4 column and using isocratic conditions, a methodology was used to

Table 3  
Sulphate and sulphite data obtained on sediment interstitial water

Sample	Concentration (mM)				
	Sulphate by ISE (1)	$\sigma$	Sulphate plus sulphite by IC (2)	$\sigma$	Sulphite (2)–(1)
1	12.27	0.050	12.96	0.259	0.69
2	1.86	0.004	1.97	0.005	0.11
3	0.14	0.007	0.17	0.003	0.03
4	4.60	0.007	5.20	0.120	0.60
5	0.41	0.003	0.77	0.023	0.36
6	0.12	0.006	0.47	0.003	0.34

R.S.D. IC: 1.66% ( $n=3$ ).

R.S.D. ISE: 1.92% ( $n=3$ ).

solve this problem using a sulphide ISE. The reduction of sulphate to sulphide in an acid mixture with a nitrogen atmosphere is the base of the method as it was previously described.

Sediment interstitial waters from Sinamaica Lagoon were analyzed by IC and sulphide ISE after the reduction step. Results are shown in Table 3 where it can be noticed that the R.S.D. values are below 2% in both methods which demonstrates their good reproducibility.

Moreover, sulphite concentration will be the difference between sulphate plus sulphite value obtained by IC minus sulphate value by ISE.

In Table 4, results for standard addition using Orion sulphate solution are presented to show the recovery obtained with both methodologies. Mean recovery for both are higher 98%. Values of R.S.D. represent a very good reproducibility also. Both techniques really have different sensitivity which is shown in the R.S.D. values, however ISE and IC are complementary to each other in this work.

Sulphate and sulphite can be quantitated individually by the described procedure in an easy manner and using very simple low cost equipment which is found commonly in the most research laboratories.

## 5. Conclusion

The method described in this paper present an economical, sensitive and accurate way to avoid



Table 4  
Results of standard additions of Orion sulphate solution for the determination of sulphate by ISE and IC

Sample	Sulphate concentration (mM)		Found	
	Taken	Added	Sulphide ion selective electrode	Ion chromatography
1	0.073	0.022	0.093	0.094
2	2.610	1.500	4.020	4.110
3	0.096	0.050	0.145	0.145
4	0.120	0.100	0.219	0.217

Mean difference: 2.58%; mean recovery ISE: 98.64%; mean recovery ISE: 99.10%; mean R.S.D. ISE: 2.93%; mean R.S.D. IC: 1.13%;  $n=3$ .

sulphate as interference with phosphate and sulphite in isocratic conditions by IC and may be applied to determine total phosphorus.

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