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Journal of Chromatography A, 956 (2002) 65–70

JOURNAL OF
CHROMATOGRAPHY A

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Effects of common metal ions on the determination of anions by suppressed ion chromatography

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Abstract

The effects of common metal ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Al^{3+} and Fe^{3+}) on the determination of nitrate, phosphate and sulfate by suppressed ion chromatography were investigated. The responses of nitrate within 1–10 mg/l were not affected in the presence of six metal ions at 10 mg/l. The peak areas of 1.0 mg/l sulfate increased significantly at 10 mg/l Fe^{3+} or Al^{3+} up to 51.34 and 48.37%, respectively. In the presence of 10 mg/l Fe^{3+} , the peak area of 1 mg/l and 10 mg/l phosphates decreased by 91.44 and 33.71%, respectively. At 10 mg/l Al^{3+} the peak areas of phosphate also increased slightly. The adverse effect of Fe^{3+} on the determination of phosphate could be overcome effectively by reducing the pH of the samples. The method to overcome the adverse effect was studied. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metal cations; Inorganic anions

1. Introduction

Since its introduction in 1975 by Small et al. [1], ion chromatography (IC) has emerged as a powerful tool for the analysis of trace ions, especially for anions. Although suppressed IC has become well established for the determination of common anions in many fields, the determination of a small concentration of anions in the presence of a large concentration of other ions often produces inaccurate results.

Bynum et al. [2] reported that the determination of 0–100 mg/l sulfate was influenced by the presence of 8000 mg/l or higher of chloride. Smith [3]

described the effect of a large amount of hydroxide or sulfate on the behavior of chloride. The chloride peak heights and retention times were found to depend upon their concentrations. Singh et al. [4] addressed that the determination of sulfate in the sample with a very high concentration of metal chlorides was affected by the large amount of metal ions in the medium. They presumed that when the cation concentration in the influent suddenly increased due to the presence of large amounts of cations such as Na^+ , Ca^{2+} , or Mg^{2+} during the ion-exchange process, a significant accumulation of H^+ ions on the surface of the suppressor might have occurred. The accumulation of H^+ ions at the surface of the suppressor can cause the formation of the HSO_4^- ion pair after reacting with SO_4^{2-} . The formation of the HSO_4^- ion pair causes a decrease in the conductivity of sulfate ions due to the reduction in total ionic charge.

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Owing to various interferences in real samples, the analysis of phosphate has not been satisfactory for a long time [5]. Many methods have been used to eliminate these adverse effects of high levels of interfering anions on the determination of phosphate and improve the recovery of phosphate. First, the concentration of the matrix ions in the sample could be reduced prior to the analysis by using a suitable pre-column filled with an ion-exchange resin (in the form of Ag^+ or Ba^{2+}) [6–8], hollow-fibre ion-exchange membranes [9] or dialysis through membranes [10]. Other approaches to eliminate matrix contaminants used on-line heart-cutting or recycling methods [11,12]. However, all these methods generally had low recoveries of phosphate and were time consuming.

To our knowledge, little information is available about the influence of metal ions on the analysis of anions by IC, especially phosphate. In this paper, the influences of metal ions on phosphate, sulfate and nitrate were described and the elimination of the adverse effect of Fe^{3+} on the analysis of phosphate was investigated. These results may be beneficial to the users of suppressed ion chromatography involved in similar analysis.

2. Experimental

2.1. Instrumentation

The ion chromatograph used for this work was a Dionex (Sunnyvale, CA, USA) DX-300 IC system consisting of a gradient pump and conductivity detector. Separations were carried out using a Dionex IonPac AS14 analytical column with an IonPac AG14 guard column. The experimental conditions were as follows: sample loop, 50 μl ; eluent, 3.5 mM sodium carbonate–1.0 mM sodium hydrogencarbonate; flow-rate, 1.2 ml/min. Anions were detected by suppressed conductivity detection. Suppression was achieved by using a Dionex ASRS-ULTRA. A Dionex PeakNet chromatography workstation was utilized to control the instrument and for data processing.

2.2. Reagents and procedures

All reagents used were of analytical reagent grade

or better (obtained from different suppliers). Three analyte anions were prepared from NaNO_3 , KH_2PO_4 and Na_2SO_4 , respectively. All the metal ions were prepared from their chlorides. A 1000 mg/l stock solution of each ion was prepared in 18 M Ω water and used for further dilutions. All of the sample solutions were filtered through a membrane filter (0.45 μm) prior to injection. Stock solutions were stored at 4 °C.

3. Results and discussion

3.1. The basic data of anions

Three anions (NO_3^- , PO_4^{3-} and SO_4^{2-}) and six common metal ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Al^{3+} and Fe^{3+}) were selected for this study because: (i) three anion peaks could be well separated; and (ii) they were of interest and commonly found in environmental analysis. In order to avoid the effect of high levels of chloride on analyzed anions and the overload to the AS14 column (a medium capacity column), the concentrations of metal ions used were 10 mg/l in this experiment. Generally, the concentrations of 1–10 mg/l were calibrated for quantitative analysis of anions, so the concentration of 1 mg/l and 10 mg/l were selected for anion analysis in this test. The relative standard deviations (RSDs) of the peak areas were less than 2.7% (data from seven consecutive injections).

3.2. Effects of metal ions on the response of anions

The effect of six metal ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Al^{3+} and Fe^{3+}) on the peak area response of nitrate, phosphate and sulfate were summarized in Table 1. The peak areas of 1–10 mg/l nitrate were relatively stable in the presence of 10 mg/l metal ions, respectively. This indicates that the peak areas of 1–10 mg/l nitrate were slightly affected by the presence of 10 mg/l of metal ions.

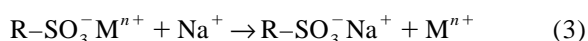
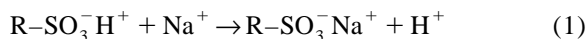
Although peak areas of sulfate were relatively stable in the presence of Na^+ , K^+ , Ca^{2+} or Mg^{2+} , the peak areas of 1.0 mg/l sulfate at 10 mg/l Al^{3+} or Fe^{3+} were affected with variations of +48.37 and +51.34%, respectively. This result could be ex-

Table 1
Effects of 10 mg/l metal ions on the response of anions

Metal ions	Nitrate, % variation		Phosphate, % variation		Sulfate, % variation	
	1.0 mg/l	10.0 mg/l	1.0 mg/l	10.0 mg/l	1.0 mg/l	10.0 mg/l
Na ⁺	+1.23	−1.28	+4.58	−2.22	+2.06	−2.49
K ⁺	−0.26	+1.37	−0.82	+1.22	+2.69	+0.71
Ca ²⁺	−0.83	−1.86	+7.99	+4.24	+2.56	+2.09
Mg ²⁺	+0.87	−1.80	+9.36	+3.49	+4.81	+3.00
Al ³⁺	−1.62	−1.03	+15.97	+4.41	+48.37	+6.76
Fe ³⁺	−1.06	−0.75	−91.44	−33.71	+51.34	+20.27

Percentage variations come from the peak area of anions in the presence of metal ions in samples against the peak areas of anions in the absence of the metal ions, all of the peak areas are averages of triplicate injections.

plained as follows: In a typical anion-exchange resin (e.g. IonPac AS14), beads of surface sulfonated styrene–divinyl benzene were contacted with a suspension of colloidal anion-exchange material. The cationic functionality of the small particles was attracted to the anionic sulfate groups on the larger bead by a strong electrostatic attachment [13]. The anionic sulfate groups on the large bead could not be covered completely by the cationic functionality of the small particles in the column. When the column was washed with the eluent containing a large amount of Na⁺, the uncovered sulfate groups were combined with sodium by electrostatic interaction. The polyvalent metal ions in the sample (such as Ca²⁺, Mg²⁺, Al³⁺ and Fe³⁺) were prone to be attracted to the uncovered sulfate groups in place of Na⁺. The reaction is reversible so that sufficient Na⁺ in the eluent could displace the polyvalent metal ions downwards in the column as they undergo further exchanges between the solution and resin phases. Finally, the polyvalent metal ions eluted with some analyte anions. This process may be represented simply as:



On the basis of the number of the metal ion charge, the trivalent metal ions were held more strongly than divalent and univalent metal ions, then accompanied by anions such as sulfate and phos-

phate, were eluted out. In suppressed IC, the suppressor exchanged all the influent cations for H⁺ and reduced the eluent (a mixture of sodium hydrogencarbonate and sodium carbonate, for anion analysis) background to that of weakly conducting H₂CO₃. At the same time, the suppressor converted the common anions Cl[−], Br[−], I[−] and SO₄^{2−} to strongly ionized acids HCl, HBr, HI and H₂SO₄, which were detectable with excellent sensitivity [1]. When Al³⁺ or Fe³⁺ was eluted with anions in the suppressor, the cations would exchange protons with the rate of 1:3 so that the concentration of protons in the suppressor was higher than that of protons in the presence of Na⁺ by exchanging protons with the rate of 1:1. A high concentration of proton in the suppressor could improve the formation of carbonic acid so that the eluent background was reduced more than before. Fig. 1. shows the chromatograms of 1 mg/l (A) and 10 mg/l (B) anions in the presence of 10 mg/l Al³⁺ and Fe³⁺. In Fig. 1, the retention times of anions were shorter in the presence of Al³⁺ or Fe³⁺ than when Al³⁺ or Fe³⁺ were absent. The shorter retention times might be due to the hydroxides from the hydrolysis of the trivalent ions. The compounds of hydroxide could bring the efficiency of the column down. However, it is necessary to state that this result is contrary to the result that Singh et al. have found. In their experiment, the salt concentrations were very high, up to several hundred milligrams per litre, but in our experiment, the concentration of metal ions in the sample solution was only 10 mg/l. In addition, they only discussed the effects of sodium chloride on sulfate and the effects of Ca²⁺ and Mn²⁺ on oxalate. The trivalent metal ions were not mentioned.

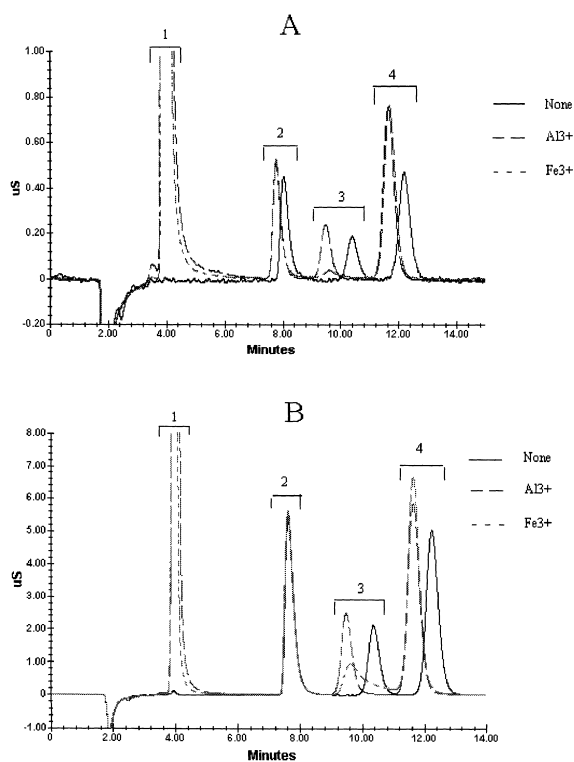


Fig. 1. Chromatograms of 1 mg/l (A) and 10 mg/l (B) anions in the presence of 10 mg/l Al^{3+} and Fe^{3+} . (1) Chloride, (2) nitrate, (3) phosphate, (4) sulfate.

It was obvious from the results in Table 1 that phosphate analysis was unreliable in the presence of Fe^{3+} , Al^{3+} , Mg^{2+} and Ca^{2+} . The effect of Fe^{3+} on the response of phosphate was most serious in six metal ions. In the presence of 10 mg/l Fe^{3+} , the peak areas of 1 and 10 mg/l of phosphate decreased by 91.44 and 33.71%, respectively, against that in the absence of Fe^{3+} . This was mainly due to the fact that phosphate was a complexing agent and could form complexes with Fe^{3+} in basic solution. The stability constant ($\log \beta$) of $\text{Fe}^{3+}\text{-HPO}_4^{2-}$ was very high (9.75). Although Ca^{2+} and Mg^{2+} also could form complexes with phosphate in basic solution, the complexing was much lower than that of Fe^{3+} . In the presence of 10 mg/l Ca^{2+} , Mg^{2+} or Al^{3+} , the responses of 1 mg/l phosphate increased greater than that of 10 mg/l phosphate, respectively. The retention time of phosphate in the presence of Al^{3+}

and Fe^{3+} also decreased greatly. The effects of Al^{3+} on phosphate were similar to the effects of trivalent metal ions on sulfate described above.

3.3. Effect of pH on the peak areas of phosphate in the presence of Fe^{3+}

Complexation between Fe^{3+} and phosphate resulted in a decreased response of phosphate and the peak shape of phosphate tailed severely. Phosphate acid had three grades of dissociation equilibrium with the dissociation constants $\text{p}K_1(2.17)$, $\text{p}K_2(7.65)$ and $\text{p}K_3(10.20)$. The concentration of HPO_4^{2-} could

Table 2
Effects of pH on the peak area of 1 mg/l phosphate in the presence of 10 mg/l Fe^{3+}

pH	Peak area	Reduction (%)
5.4	5520	(without Fe^{3+})
3.8	476	-91.36
2.5	4172	-24.41
2.0	4968	-10.00
1.5	4352	-21.16
1.0	3983	-27.84

Percentage reduction, as compared to the peak area of pure phosphate, all of the peak areas are averages of triplicate injections.

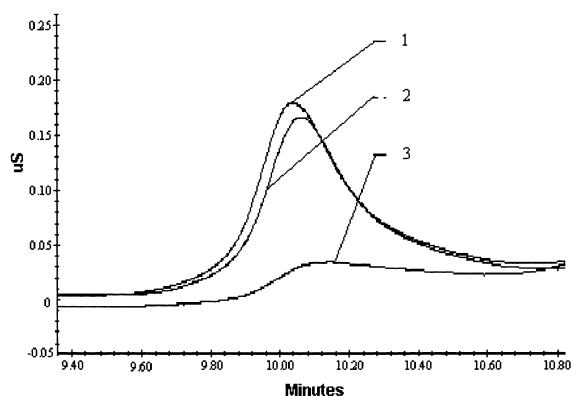


Fig. 2. Effect of the pH on 1.0 mg/l phosphate in the presence of 10 mg/l Fe^{3+} . (1) 1 mg/l phosphate standard pH 2.0; (2) 1 mg/l phosphate + 10 mg/l Fe^{3+} , pH 2.0; (3) 1 mg/l phosphate + 10 mg/l Fe^{3+} , pH 3.8.

Table 3
The recoveries of anions in the samples ($n=5$)

Sample	pH	Recovery (%)		
		Nitrate	Phosphate	Sulfate
Anions:Fe ³⁺ (1:10 mg/l)	3.8	101.2	11.42	153.6
	2.0	99.67	97.25	103.4
Anions:Fe ³⁺ (10:10 mg/l)	3.8	100.3	75.32	105.6
	2.0	100.5	98.45	102.4
Tap water 1	6.9	100.2	43.60	110.0
	2.0	101.1	82.47	97.55
Tap water 2	7.0	99.80	52.36	109.8
	2.0	100.1	89.64	102.9

be changed within the different pH's of the solutions. In the low pH range, the complexation between Fe³⁺ and HPO₄²⁻ will be restrained. Table 2 showed the effects of the pH on the response of phosphate in samples containing 1 mg/l phosphate and 10 mg/l Fe³⁺. The peak areas of phosphate in the presence of Fe³⁺ arrived at maximum values when the pH of samples was near to 2.0. At the same time, the peak shape of phosphate was improved (see Fig. 2). The peak area of 1.0 mg/l phosphate at 10 mg/l Fe³⁺ was about 90% of the peak area of pure phosphate. This indicated that reducing the pH value of the sample solution could help to settle the problem during the determination of phosphate in the presence of large concentrations of Fe³⁺.

When the pH of the sample was lower than 2.0, not only the sensitivity of phosphate reduced for the increase of H₃PO₄, but also the acid added could change the ratio of HCO₃⁻/CO₃²⁻. It was necessary to run a calibration standard under the same pH of solution for analysis of phosphate.

3.4. Recovery test

Under the chosen conditions, the recovery tests were shown in Table 3. It was found that good results could be achieved in the low pH range of samples. Although the obtained recoveries of phosphate in tap water with acid added was not sufficiently high, the results were better than without acid added. Reducing the pH of the sample solution could help to determine the phosphate as accurately as possible.

4. Conclusion

On the basis of the results presented in this paper, we could conclude that: the peak areas and retention times of 1–10 mg/l nitrate were slightly affected in the presence of 10 mg/l of six metal ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, Al³⁺ and Fe³⁺), respectively. However, the accurate analysis of phosphate and sulfate in the presence of Fe³⁺ and Al³⁺ by suppressed IC needed caution. In the case of 10 mg/l Al³⁺, the responses of sulfate and phosphate at 1–10 mg/l enlarged and the retention times were shortened. The effects of 10 mg/l Fe³⁺ on 1–10 mg/l phosphate and sulfate were most serious in the six metal ions. Not only did the peak area of phosphate decrease and the peak area of sulfate increase, but also the retention times of the two anions were greatly shortened. Generally, the effects of the trivalent metal ions on the analysis of anions were more serious than the effects of divalent and univalent metal ions. Moreover, the influences of 10 mg/l metal ions on anions at 1 mg/l were larger than on the anions at 10 mg/l. When the amount of metal ions (i.e. polyvalent metal ions) in the samples was higher than that of analyte anions (i.e. phosphate and sulfate), the adverse effects needed to be dealt with in the analysis of anions. Hydrochloric acid was used to adjust the pH of the sample solution to 2.0 in order to overcome the adverse effect of Fe³⁺ on the determination of phosphate. The precipitation of Al³⁺ and Fe³⁺ in the basic solution also could be used to remove a large amount of such metal ions in the sample. Briefly, the effects of the metal ions on

the response of anions should not be ignored in daily experiments.

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