ELSEVIER

Journal of Chromatography A, 705 (1995) 390–395

JOURNAL OF CHROMATOGRAPHY A

Short communication

Phosphorus speciation in nickel plating baths by ion chromatography

Magdalena Biesaga, Marek Trojanowicz*

Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

First received 1 December 1994; revised manuscript received 28 February 1995; accepted 3 March 1995

Abstract

A non-supressed ion chromatographic method with conductivity detection for the simultaneous determination of hypophosphite, phosphite and orthophosphate was developed. Separation of phosphorus oxyanions from lactate present in the plating bath samples was achieved by modification of the succinate eluent with acetonitrile.

1. Introduction

Despite significant progress in recent years in the instrumentation and applications of high-performance ion chromatography, especially in environmental analysis, relatively few applications have been reported to the speciation of phosphorus. Because of the wide use of simple and condensed oxyanions of phosphorus in various industrial process, in various detergent preparations and fertilizers, there is a demand for this determination and high-performance liquid chromatography seems to be especially suitable for this purpose.

Several examples of such an application in single- and dual-column ion chromatographic systems have been reported. In a single-column system a mixture of monovalent oxyanions (hypophosphite, phosphite and orthophosphate) was analysed with succinic acid as eluent and conductivity detection [1] and with 4-amino-2-hydroxybenzoic acid as eluent and indirect UV absorptive detection [2]. These studies were carried out only with standard mixtures of anions. In the determination of pyrophosphate and tripolyphosphate, also in a single-column system, a better sensitivity with indirect UV than conductivity detection was found [3]. Series of carboxylic acids of various structures were recently tested as eluents in the single-column ion chromatography of phosphorus oxyanions with refractive index detection [4]. The best eluents for the determination of non-condensed anions were *p*-hydroxybenzoic acid and *p*-aminobenzoic acid, although complete baseline resolution of oxyanions was not achieved. The determination of the same anions was carried out also in a more complex system, where single-column chromatography was combined with a flow-injection postcolumn reaction detection system [5]. The separated hypophosphite and phosphite anions were oxidized to orthophosphate and then reacted with a chromogenic molybdenum reagent. Postcolumn reaction with Fe(III) with UV

* Corresponding author.

0021-9673/95/$09.50
SSDI 0021-9673(95)00303-7

absorption detection was also developed for the determination of phosphorus anions in a dual-column system with a sodium carbonate–sodium hydroxide eluent [6].

A technological process in which control of the speciation of phosphorus anions is needed for optimization of the process run is electroless nickel plating from hypophosphite baths. This process is based on the reaction [7]

$$Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni + 2H^- + H_2PO_3^-$$

However, the details of how this reaction occurs have not been finalised [8]. An important feature of this reaction is that nickel provides the necessary catalytic effect for this electroless process. The nickel plating process is improved by additions of small amounts of organic compounds, which results in increased stability of the bath, speed of deposition and brightness of the deposit.

Nickel coatings formed in the electroless process have high hardness and good mechanical resistivity. They are primarily employed as a corrosion-protective coatings on functional articles of complex shape. They are formed at 85–95°C in acidic solutions of pH 3.9 (fresh bath) containing 30 g/l nickel sulphate or chloride, lactic acid, 20 g/l sodium hypophosphite and some brightening components. Nickel salt is added to the bath during its use as long as the phosphite ($H_2PO_3^-$) concentration is lower than 1 *M*.

The aim of this study was to develop a method for the determination of hypophosphite, phosphite and orthophosphate in such a bath using a single-column ion chromatographic system with conductivity detection. The application of this technique for this purpose has not previously been reported.

2. Experimental

2.1. Apparatus

Ion chromatographic measurements were carried out using a Model 6200 ion chromatograph with a conductivity detector from Tecator (Hoganas, Sweden) and an HPLC system from Perkin-Elmer consisting of a Series 100 pump and a Bacharach Type 3D conductivity detector. As analytical columns, a 302 IC column from Vydac (Hesperia, CA, USA) and an OmniPac PAX 500 column from Dionex (Sunnyvale, CA, USA) were used.

2.2. Reagents

Sodium hypophosphite was purchased from Aldrich, sodium phosphite from BDH and succinic acid from Merck. Acetonitrile of HPLC grade was obtained from Baker. All other reagents were of analytical-reagent grade from POCh (Gliwice, Poland).

Stock standard solutions (1000 mg/l) of sodium hypophosphite, sodium phosphite and sodium orthophosphate were prepared once a week by dissolving the appropriate amount of solid reagent in deionized water and kept in a refrigerator. Working standard solutions were prepared daily by appropriate dilution of the stock standard solutions with deionized water.

A 0.1 *M* eluent solution was prepared by dissolving succinic acid in deionized water and was stored in refrigerator. More dilute solutions for measurements were prepared daily by appropriate dilution with water and pH adjustment prior to the addition of organic modifier. Then, after filtration with a 0.45-μm nylon 66 membrane filter (Supelco), it was ultrasonicated for 15 min. All solutions were prepared using deionized water obtained from a Waters Milli-Q water-purification system.

Samples of nickel plating baths were kindly provided by Ms. Danuta Przybylska of the Institute of Precision Mechanics, Warsaw, Poland.

2.3. Procedure

Natural bath samples were diluted 10^4-fold with deionized water prior to injection. Injected samples and standard solutions were filtered through 0.22-μm nylon single-use syringe filters of 25 mm diameter (Supelco). Chromatography was performed using a 100-μl injection volume

and an eluent flow-rate of 1.0 ml/min. An optimized eluent solution of pH 3.6 contained 0.2 m*M* succinic acid and 5% acetonitrile. Measurements were carried out in room temperature without thermostating. An overnight constant flow of 0.3 ml/min was maintained.

3. Results and discussion

3.1. Optimization of separation of hypophosphite, phosphite and orthophosphate

Owing to the better detectability obtained for simple phosphorus oxyanions with conductivity detection in comparison with indirect UV measurements, the former was employed. The optimization of the ion chromatographic separation of hypophosphite, phosphite and orthophosphate with a Vydac 302 column and succinic acid solution as eluent confirmed the results obtained earlier by Ryder [1]. The best results were obtained with 20 m*M* succinic acid of pH 3.0, but a serious drawback to separation under such conditions was partial overlapping of the hypophosphite peak with the broad peak of chloride (Fig. 1); the resolution of the peaks for chloride (t_R = 12.3 min) and hypophosphite (t_R = 13.6 min) was only 0.7. Hence, in spite of the satisfactory separation of oxyanions of phosphorus, this method cannot be applied to real samples containing an excess of chloride as matrix component.

The application of a Dionex OmniPac PAX 500 anion column in the chromatography of oxyanions of phosphorus has not been reported previously. For this column succinic acid was also examined as the eluent in the concentration range 0.2– to 20 m*M* (Fig. 2). In this case the separation of simple phosphorus oxyanions together with lactate was carried out, as lactic acid is usually present in nickel plating baths. At a very low concentration of the eluent, when satisfactory separation for all the oxyanions considered was obtained, lactate exhibits the same retention time as hypophosphite. An increase in succinic acid concentration improves the separation of lactate and hypophosphite, but significantly deteriorates the separation of phosphite and orthophosphate.

An increase in pH above 4.0 for 0.2 m*M* succinic acid solution also results in the simultaneous elution of phosphite and orthophosphate and a worse separation of hypophosphite from the solvent peak than at pH 3.6.

For a given column and a particular eluting anion, a certain differentiation of the retention of separated anions can be expected from the change in dielectric properties of eluent. In high-performance ion chromatography, the addition of a non-aqueous solvent to the eluent has been employed, for instance, to change the extent of the hydrophobic adsorption of the eluent on the

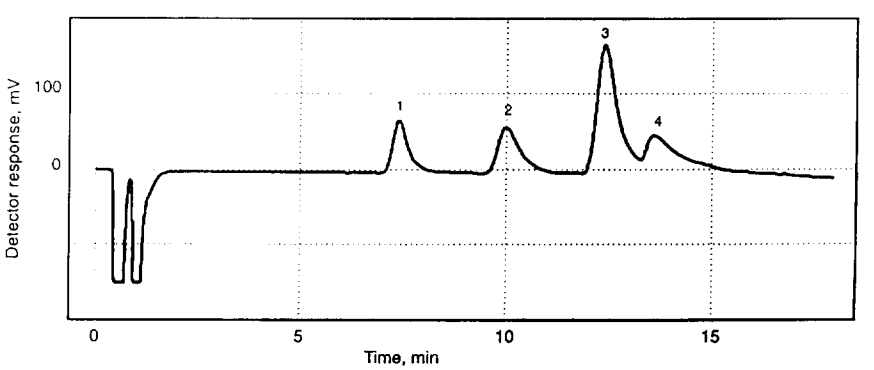

Fig. 1. Chromatogram obtained for a mixture of (1) 5 mg/l orthophosphate, (2) 5 mg/l phosphite and (4) 5 mg/l hypophosphite using 20 m*M* succinic acid (pH 3.0) as eluent with a Vydac 302 IC column. Sample volume, 500 μl; eluent flow-rate, 3.9 ml/min. Peak 3 corresponds to 5 mg/l chloride.

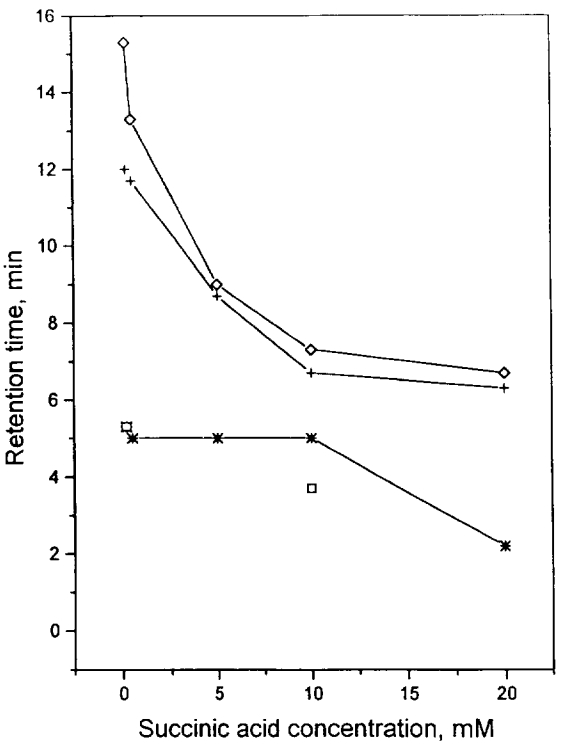

Fig. 2. Effect of concentration of succinic acid solution of pH 3.6 used as eluent on retention times of (*) hypophosphite, (◇) phosphite, (+) orthophosphate and (□) lactate at a flow-rate of 1 ml/min. Injection of 100 μl of solutions containing 0.1 m*M* lactate and 10 mg/l hypophosphite, orthophosphate and phosphite. Column, OmniPac PAX-500.

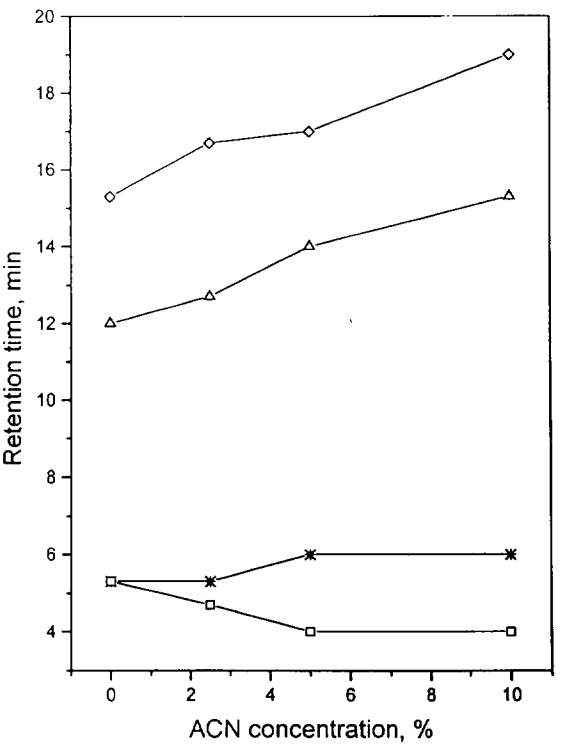

Fig. 3. Effect of addition of acetonitrile to 0.2 m*M* succinic acid (pH 3.6) used as eluent on retention times of (*) hypophosphite, (◇) phosphite, (△) orthophosphate and (□) lactate at a flow-rate of 1 ml/min. Injection of 100 μl of solutions containing 0.1 m*M* lactate and 10 mg/l hypophosphite, orthophosphate and phosphite. Column, OmniPac PAX-500.

stationary phase [9] and for selectivity mediation [10]. In this study it was found that an increase in the acetonitrile content in the succinic acid eluent up to 10% does not affect significantly the retention of phosphite and orthophosphate, but essentially improves separation of hypophosphite and lactate by lowering the retention time of lactate (Fig. 3). For a 0.2 m*M* succinate eluent of pH 3.6 with 5% acetonitrile added, the retention time for chloride was 20.6 min and no signal was observed for 20 mg/l nitrate and sulfate under such conditions. Under the optimized conditions it was also found that the presence of nickel(II) in the injected solutions at concentrations up to 2 mg/l, corresponding to the Ni content in fresh baths, does not influence of phosphorus species. The chromatogram of a synthetic mixture of phophorus oxyanions is shown in Fig. 4A and the calibration data are given in Table 1. The limit of detection under optimized conditions for a 100-μl sample volume was estimated to be 0.1 mg/l for hypophosphite and 0.5 mg/l for phosphite and orthophosphate.

An advantage of the use of an OmniPac PAX-500 column instead of a Vydac 302 IC is the use of a 100-fold less concentrated eluent at a four-fold lower flow-rate.

3.2. Determination of phosphorus oxyanions in plating baths

Owing to high concentration of species to be determined in samples of nickel plating baths, the analyte solutions were diluted 10^4-fold with

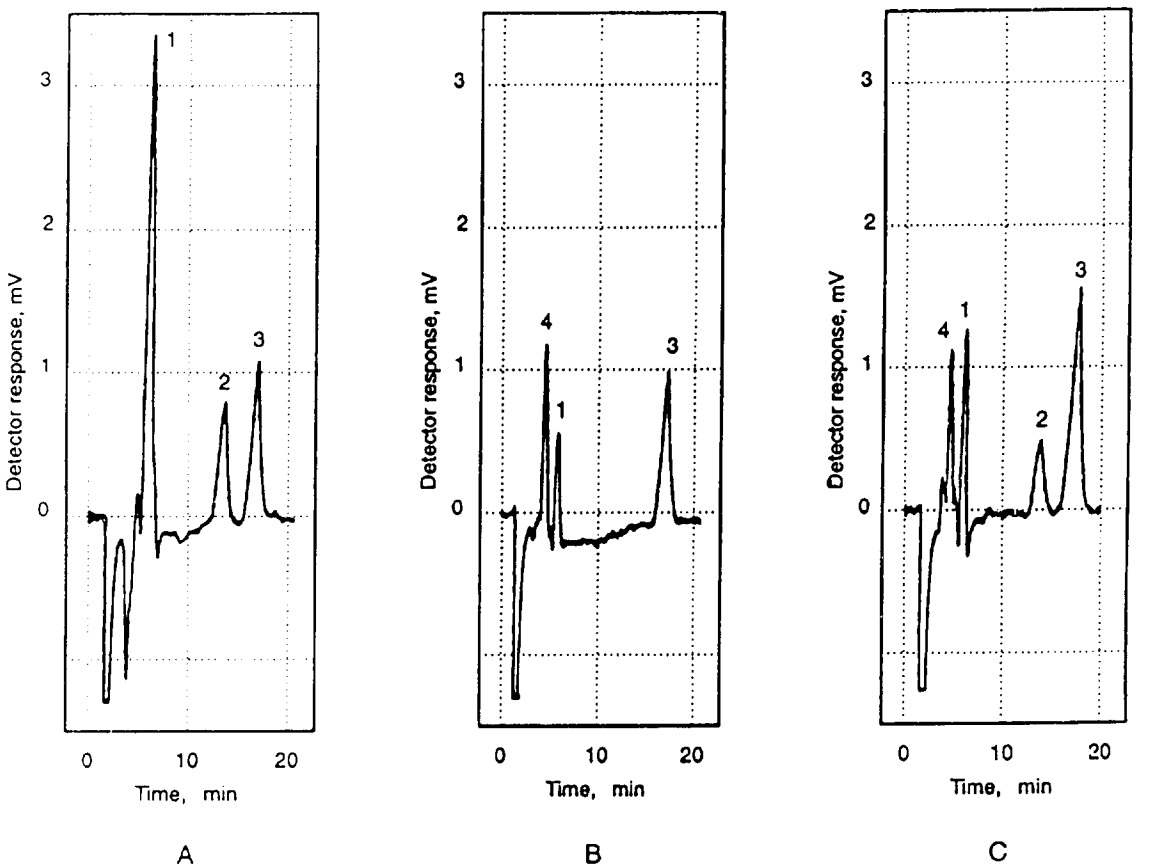

Fig. 4. Chromatograms obtained for (A) a standard mixture containing 5 mg/l each of (1) hypophosphite, (2) orthophosphate and (3) phosphite, (B) a 10^4-fold diluted plating bath sample and (C) a 10^4-fold diluted bath sample spiked with 2 mg/l of orthophosphate, phosphite and hypophosphite, using as eluent 0.2 m*M* succinic acid (pH 3.6) containing 5% acetonitrile with an OmniPac PAX-500 column. Flow-rate, 1 ml/min; sample injection volume, 100 μl. Peak 4 corresponds to lactate.

distilled water prior to chromatographic analysis. Examples of chromatograms obtained for fresh and spiked bath solutions are shown in Fig. 4B and C, respectively. The quantitative results are given in Table 2. The R.S.D. ($n = 9$) obtained for a 5 mg/l concentration of each analyte was

Table 1
Characteristics of calibration graphs (peak height vs. concentration) obtained for ion chromatography of phosphorus oxyanions with an OminPac PAX 500 column using as eluent 0.2 m*M* succinic acid (pH 3.6) with 5% acetonitrile at a flow-rate of 1 ml/min and an injection volume of 100 μl

Analyte	Retention time (min)	Parameters of calibration plot		
		Upper limit of linear response (m*M*)	Slope (mV/m*M*)	Intercept (mV)
Hypophosphite	5.3	0.08	43.5	0.13
Phosphite	12.0	0.13	13.3	0
Orthophosphate	15.3	0.10	13.2	0.02

Table 2
Determination of oxyanions of phosphorus in $1:10^4$ diluted solution of nickel plating bath samples under optimized conditions with an OmniPac PAX 500 column using as eluent 0.2 m*M* succinic acid (pH 3.6) with 5% acetonitrile at a flow-rate of 1 ml/min and an injection volume of 100 μl

Sample	Analyte	Concentration found (mg/l)	Recovery (%)	
			2 mg/l added	4 mg/l added
Fresh bath	Hypophosphite	1.0	110	94
	Phosphite	<0.5	104	101
	Orthophosphate	<0.5	104	99
Spent bath	Hypophosphite	1.3	91	84
	Phosphite	3.5	127	120
	Orthophosphate	0.5	104	99

3.4, 1.0 and 4.0% for hypophosphite, phosphite and orthophosphate, respectively.

Acknowledgement

This work was financed by the University of Warsaw, Grant No. BST-472/9/94.

References

[1] D.S. Ryder, J. Chromatogr., 354 (1986) 438.
[2] M.C. Mehra and C. Pelletier, Chromatographia, 30 (1990) 337.
[3] W.D. MacMillan, J. High Resolut. Chromatogr. Chromatogr. Commun., 7 (1984) 102.
[4] D. Hatton and W.F. Pickerin, Talanta, 3 (1993) 307.
[5] Y. Hirai, N. Yoza and S. Ohaski, J. Chromatogr., 206 (1981) 501.
[6] P. Hoffman, I. Schmidtke and I.H. Lieser, Fresenius Z. Anal. Chem., 335 (1989) 402.
[7] A. Brenner and G. Riddel, Proc. Am. Electroplaters Soc., 33 (1946) 23; 34 (1947) 156.
[8] J.K. Dennis and T.E. Such, Nickel and Chromium Plating, Newnes-Butterworths, London, 1972.
[9] Y.E. Pazukhina, O.A. Shpigun, I.N. Voloshchik and M.L. Litvina, Zh. Anal. Khim., 43 (1988) 117.
[10] S. Rabin and J. Stillian, J. Chromatogr. A, 671 (1994) 63.