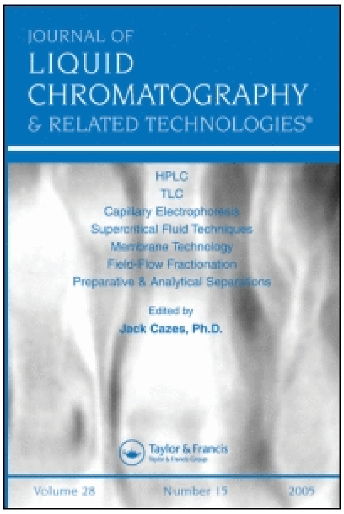

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

CHITOSAN--IRON(III)--CROSSLINKING (CH-Fe^{III}-CL) FOR PRE-CONCENTRATION OF PHOSPHATE IN SIMULATED SEAWATER

Tathyane Fagundes[a]; Edineli Crocetta Coelho[a]; Kelly Ferreira dos Santos[a]; Clóvis Antonio Rodrigues[a]
[a] NIQFAR—Núcleo de Investigações Químico-Farmacêuticas CCS, Universidade do Vale do Itajaí (UNIVALI), Itajaí, SC, U.S.A.

To cite this Article Fagundes, Tathyane , Coelho, Edineli Crocetta , Santos, Kelly Ferreira dos and Rodrigues, Clóvis Antonio(2002) 'CHITOSAN--IRON(III)--CROSSLINKING (CH-Fe^{III}-CL) FOR PRE-CONCENTRATION OF PHOSPHATE IN SIMULATED SEAWATER', Journal of Liquid Chromatography & Related Technologies, 25: 7, 1085 — 1092

To link to this Article: DOI: 10.1081/JLC-120003426

URL: http://dx.doi.org/10.1081/JLC-120003426

J. LIQ. CHROM. & REL. TECHNOL., 25(7), 1085–1092 (2002)

CHITOSAN–IRON(III)–CROSSLINKING ($CH–FE^{III}–CL$) FOR PRE-CONCENTRATION OF PHOSPHATE IN SIMULATED SEAWATER

Tathyane Fagundes, Edineli Crocetta Coelho,
Kelly Ferreira dos Santos, and
Clóvis Antonio Rodrigues*

NIQFAR—Núcleo de Investigações Químico-
Farmacêuticas CCS, Universidade do Vale do Itajaí
(UNIVALI), CEP 88.302-202, Itajaí, SC, Brasil

ABSTRACT

In this work, the pre-concentration of phosphate on chitosan–iron(III)–crosslinked ($CH–Fe^{III}–CL$) was investigated in simulated seawater. The results from the sorption experiments demonstrate the possibility of using $CH–Fe^{III}–CL$ to remove phosphate from seawater. Improved analytical performance for phosphate pre-concentration using the $CH–Fe^{III}–CL$ method was obtained compared to the conventional method. Based on the results, the methods will be applied to analyze river water, seawater, groundwater, and industrial water.

---

*Corresponding author. E-mail: clovis@ccs.unival.br

INTRODUCTION

Phosphate occurs naturally in a variety of chemical forms, and is widely distributed in soil, rocks, and ocean. Phosphate is a major factor in the environmental problem of eutrophication, which results in the excessive growth of algae in natural waters (1–3).

Many analytical methods have been developed for determining phosphate. The standard method for the determination of phosphate in natural waters is the spectrophotometric method, which involves the formation of an antimony phosphate molybdate complex followed by the reduction of molybdenum blue and vanadomolybdophosphoric heteropoly acid (HPAs) (4–6).

Determining trace amounts of ions in water requires a concentration step for analysis. Considerable attention is now being paid to the solid-phase extraction (SPE) as a way to concentrate the desired components from a matrix. An important application of SPE columns is pre-concentrating ions. Large volumes of samples are passed through the column that is then eluted with a small volume of solution at different compositions to recover the ion sorbed on the adsorbent. Column or batch procedures can be used for extraction (7).

Recently we have used chitosan–iron(III)–crosslinking (CH–Fe–CL) for pre-concentration of phosphate from aqueous solution in batch and column systems (8). In the present paper, SPE has been developed to analyze trace amounts of the phosphate in simulated seawater. A comparison between the proposed SPE method and the conventional method was made.

EXPERIMENTAL

Reagents

The chitosan–iron(III)–crosslinking (CH–Fe–CL) was prepared according to literature (8). The chitosan was dissolved in a $Fe(NO_3)_3$ 0.1 M aqueous solution for 4 hours. An orange precipitate was obtained after addition of acetone. The solid was filtered and washed with acetone, to remove excess $Fe(NO_3)_3$, and finally dried in a vacuum. After that, the solid was put in contact with glutaraldehyde 15% (in acetone) solution for 2 hours.

Salts of common anions, of analytical reagent grade or better, were obtained from different suppliers. Phosphate standards for pre-concentration were prepared using potassium dihydrogenophosphate that had been dried in an oven at 105°C for 1 h (6). Simulated seawater was prepared by dissolving 31 g of NaCl, 10 g $MgSO_4$, and 0.05 g of $NaHCO_3$ in 1000 mL of bidistilled water (9).

Procedure

SPE was prepared by using a (50×4 mm i.d.) polypropylene column containing 100 mg of air-dried CH–Fe^{III}–CL. The polymer was placed in the column in suspension with distilled water and allowed to settle. The column was connected to water suction via a safety flask, and the sample was aspired through it. A pressure gradient was created across the column by applying vacuum. The flow rate was controlled by adjusting a valve on the safety flask.

100 mL of simulated seawater containing phosphate or seawater was aspired through the column, at 2.0 mL min^{-1}. The column was dried briefly under vacuum, and phosphate adsorbed was slowly eluted with HCl solution.

The efficiency of the HCl as a solution remover was determined by digestion of CH–Fe^{III}–CL (100 mg) with a mixture of concentrate nitric and hydrochloride acid, and the phosphate concentration was determined as described above. The recovery of phosphate under various conditions of elution was calculated by comparing the sample absorbance with the standard solution.

The adsorbed phosphate was determined spectrophotometrically as a phosphomolybdenium blue complex (6). A 50 mL of standard or sample was pipetted into a clean flask and then 10 mL of the combined reagent was added and mixed thoroughly. After at least 10 min, but no more than 30 min, the absorbance was measured at 880 nm (6). Calibration standard was prepared by diluting mixed stock solution 1000 mg^{-1} of KH_2PO_4 using a series of dilutions. The analyses were carried out in the spectrophotometer, UV/Vis Shimadzu UV 1601.

The results of the effect on the recovery are based on triplicate determinations.

The possibility of reuse of the CH–Fe^{III}–CL was determined. For this purpose, a loaded adsorbent was washed with distilled water, allowed to dry in air, and then loaded again with phosphate solution. Four determinations were made for this study.

Seawater

Seawater from Balneário de Camboriu beach was filtered through a 0.45 μm membrane filter and collected in a polyethylene container carefully cleaned with nitric acid. The samples were stored at −20°C until analysis, and before analysis, they were equilibrated to room temperature.

RESULTS AND DISCUSSION

Orthophosphate is the oxidized state of phosphorus ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) and its form is pH dependent. Orthophosphate is also the form in which phosphorus is most readily available for biological utilization (10).

Preliminary experiments showed that the HPO_4^{2-} is the predominant species in adsorption of phosphate onto CH–Fe^{III}–CL and $[FeHPO_4]^+$ complex in the polymer surface (8,11).

The percent recovery of phosphate of the CH–Fe^{III}–CL using HCl as eluent was of 97.8 ± 1.6% for eight determinations.

The results of the effect of HCl concentration on the recovery are presented in Table 1. The results show that the most suitable concentration of HCl is 6.0 M. Therefore, this concentration was chosen as the optimal concentration for the study of removal of phosphate for that adsorbent.

The results of the effect of the HCl volume on the phosphate recovery are presented in Table 1. The results show that the minimal volume of 6.0 M HCl employed in this study is 10 mL. Hence, 10 mL of HCl is chosen as the optimal volume for removal of phosphate.

The reuse of the CH–Fe^{III}–CL was determined to be efficient. The results, Table 2, show that no relevant differences were observed in absorbance between the new and the reused CH–Fe^{III}–CL.

The proposed method has been applied to pre-concentration of phosphate in simulated seawater. The determination of phosphate was performed using conventional and SPE methods. The results obtained in both cases are shown in Table 2. As can be observed in the standard method for low concentrations of phosphate, the reading of the absorbance was zero.

Table 1. Effect of Concentration and Volume of HCl Solution on the Recovery Phosphate. Phosphate Concentration 5 $\mu g\,L^{-1}$, Volume Solution 100 mL

Concentration Solution (M)	1	2	4	6
HCl	0.012[a]	0.016	0.027	0.042
Synthetic seawater[b]	0.001	0.005	0.000	0.000
Volume solution (mL)	5	10	15	20
HCl 6 M	0.012	0.014	0.016	0.014
Synthetic seawater[b]	0.003	0.006	0.000	0.004

[a] Units of the absorbance.

[b] After percolation for the column.

Table 2. Effect of the Number of Percolation of Samples of Synthetic Seawater on the Absorbance Intensity. Phosphate Concentration 5 μg L^{-1}, Volume Solution 100 mL

Solution	1	2	3	4
HCl	0.013[a]	0.011	0.009	0.011
Synthetic seawater[b]	0.002	0.000	0.002	0.003

[a] Units of the absorbance.

[b] After percolation for the column.

A working curve for pre-concentration of phosphate on CH–Fe^{III}–CL and standard methods is provided in Figure 1. The absorbance is seen to be linear with respect to phosphate concentration in the range 5.0–100 μg of PO_4^{3-} L^{-1}. Beyond 100 μg of PO_4^{3-} L^{-1}, the sensitivity is observed to decrease with increasing phosphate concentration.

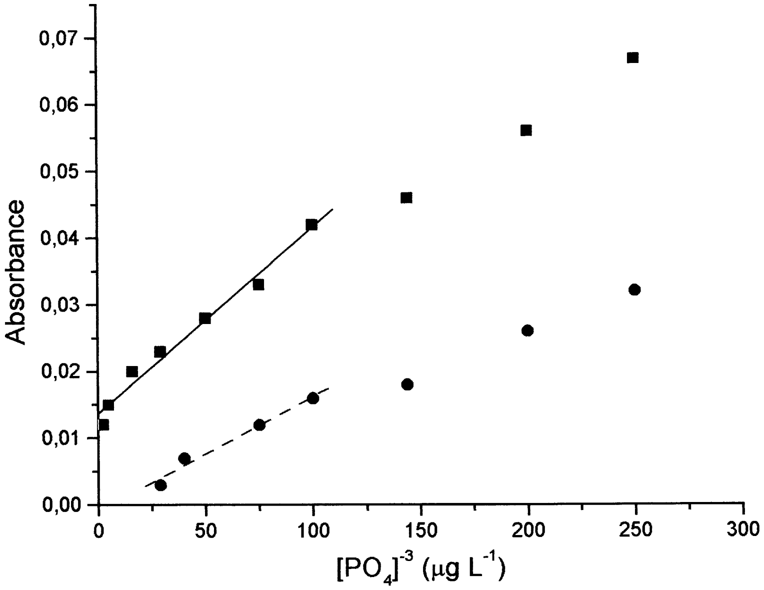

Figure 1. Dependence of pre-concentration methods on phosphate concentration. Absorbance intensity signals at 885 nm. ■ solid phase extraction; ● conventional methods.

Table 3. Comparison of Absorbance Intensity of the Synthetic Seawater Containing Phosphate by Solid Phase Extraction (SPE) and Conventional Method. (CM) Phosphate Concentration ($\mu g\,L^{-1}$)

PO_4^{3-}	2.5	5	16	29	50	75	100	144	200	250
SPE	0.012[a]	0.015	0.020	0.023	0.028	0.033	0.042	0.046	0.056	0.068
CM	0.000	0.000	0.000	0.003	0.008	0.012	0.016	0.018	0.026	0.032

[a] absorbance unit.

Table 4. Comparison of Absorbance Intensity of the Seawater by SPE, Conventional Method (CM), and Inner Standard Method (IS). Phosphate Concentration (62.5 μg L^{-1})

Method	Absorbance Unit[a]	[Phosphate ± SD] μg L^{-1}
SPE (seawater)	0.068 ± 0.004	265.6 ± 15.6
IS (seawater + phosphate)[b]	0.025 ± 0.005	31.2 ± 19.5
CM (seawater)	0.006 ± 0.002	23.4 ± 7.8
Phosphate standard	0.016 ± 0.006	62.5 ± 23.4

[a] n = 4.
[b] 25 mL of KH_2PO_4.

The correlation between the absorbance measurement and corresponding phosphate concentration was evaluated by means of least square regression methods; we obtained the following equation:

$$\text{For CH}-\text{Fe}^{III}-\text{CL } y = 0.015(\pm 0.004) + 0.265c(\pm 0.007)r = 0.9939$$

$$\text{For standard methods } y = -0.0018(\pm 0.0008) + 0.174c(\pm 0.016)r = 0.9822$$

The limit of detection (LD) for pre-concentration on CH–Fe^{III}–CL methods was found to be 0.7 μg L^{-1}, which was determined using the 3 σ method (12,13).

The proposed procedure was applied to phosphate determinations in seawater samples collected on Balneário de Camboriu beach. The analytical performance was evaluated by the standard addition method as a reference method. Some preliminary results are presented in Table 4.

These results show that the concentration of phosphate, in the water of the sea, determined by the method of standard addition and the conventional method is smaller when compared with the method of SPE.

The complete evaluation of the use of the CH–Fe(III)–CL for analysis of phosphate in a variety of sample matrices is currently underway, and the results will be the subject of a future publication.

CONCLUSION

Considering the low phosphate concentration in seawater and groundwater samples, two different procedures were compared for pre-concentration in simulated seawater. The results from the sorption experiments demonstrate the possibility of using CH–Fe^{III}–CL to adsorb phosphate in seawater. Improved analytical performance was obtained for phosphate pre-concentration using the CH–Fe^{III}–CL method compared to the conventional method. Based on the results, the methods will be applied to analyze river water, seawater, groundwater, and industrial water.

ACKNOWLEDGMENT

This work was supported by grants from PIBIC/CNPq, ProBIC/ProPPEx/UNIVALI.

REFERENCES

1. De Marco, R.; Pejcic, B.; Chen, Z. Analyst **1998**, *123*, 1635–1640.
2. Shotyk, W.; Immenhauser-Potthast, I.; Vogel, H.A. J. Chromatogr. A. **1995**, *706*, 209–213.
3. Wu, R.S. Mar. Poll. Bull. **1999**, *39*, 11–22.
4. Williams, W.J. *Handbook of Anion Determination*; Butterworth: London, 1994.
5. Zui, O.V.; Birks, J.W. Anal. Chem. **2000**, *72*, 1699–1703.
6. Colina, M.; Lebo, H.; Gutiérrez, E.; Villalobos, E.; J. Marin. J. Chromatogr. A. **1996**, *739*, 223–227.
7. Fritz, J.S.; Dumont, P.J.; Schmidt, S.W. J. Chromatogr. A. **1995**, *691*, 133–140.
8. Fagundes, T.; Bernardi, E.L.; Rodrigues, C.A. J. Liq. Chromatogr. & Rel. Technol. **2001**, *24*, 1189–1198.
9. Parsons, T.R.; Maita, Y.; Lalli, C.M. *A Manual of Chemical and Biological Methods*; Pergamon Press: New York, 1984; 6.
10. Maher, W.; Woo, L. Anal. Chim. Acta **1998**, *375*, 5–47.
11. Smith, R.M.; Martell, A.E. *Critical Stability Constants*; Plenum Press: New York, 1975; Vol 2, 215.
12. Vanatta, L.E.; Coleman, D.E. J. Chromatogr. A. **1997**, *770*, 105–114.
13. Santoyo, E.; Santoyo-Gutiérrez, S.; Verma, S.P. J. Chromatogr. A. **2000**, *884*, 229.

Received September 8, 2001
Accepted December 11, 2001
Manuscript 5649