Available online at www.sciencedirect.com

ScienceDirect

Chinese Chemical Letters 20 (2009) 1498–1501

CHINESE CHEMICAL LETTERS

www.elsevier.com/locate/cclet

Determination of inorganic anions in ethyl acetate by in-line hollow fiber membrane extraction with ion chromatography

Zhen Zhen Hu, Ying Ying Zhong, Yun Chang Fan, Yan Zhu [*]

Department of Chemistry, Xixi Campus, Zhejiang University, Hangzhou 310028, China

Received 15 May 2009

Abstract

In this work, a novel hollow fiber membrane extractor was set up to extract inorganic anions from ethyl acetate using deionized water. Inorganic anions in slightly soluble organic solvents can be determined by the in-line hollow fiber membrane extractor coupled with ion chromatography at first time. Different aspects of the extraction procedure such as magnetic stirring speed, extraction flow rate and extraction time were optimized to achieve high extraction efficiency and good separation results. Satisfactory linear range, limits of detection and good repeatability were obtained. The procedure was applied to analyze inorganic anions in two commercial ethyl acetate samples.

Keywords: Inorganic anions; Ethyl acetate; In-line hollow fiber membrane extraction; Ion chromatography

---

Ion chromatography is a common method to analyze inorganic anions. In the last years, with the rapid advances in ion chromatography, it is no longer a difficult problem to determine inorganic anions even in some water-miscible solvents such as methanol, iso-propanol, acetone and N-methylpyrrolidone [1–3]. However, it is still a conundrum to analyze inorganic anions in organic solvents which are slightly soluble in water even with traditional sample pretreatment methods such as evaporation-enrichment method, electrodialysis and column-switching technology [1,2].

Hollow fiber membrane extraction (HFME) is a new-developed sample pretreatment model based on liquid–liquid extraction. In traditional methods, organic solvents are often used as extraction solvents to extract organic compounds from aqueous solutions [4–13]. In the present work, a simple hollow fiber membrane extractor was set up to extract inorganic anions from ethyl acetate with deionized water. Inorganic anions in slightly soluble organic solvents can be determined by the in-line hollow fiber membrane extractor coupled with ion chromatography at first time. Different aspects of the extraction procedure such as magnetic stirring speed, extraction flow rate and extraction time were investigated. In addition, the proposed method was validated for quantitative purposes and applied to two commercial ethyl acetate samples.

1. Experimental

The analysis of inorganic anions in ethyl acetate consisted of three steps: (1) using the in-line hollow fiber membrane extractor to extract anions with deionized water from ethyl acetate meanwhile eliminate the matrix; (2)

---

[*] Corresponding author.
E-mail address: zhuyan@zju.edu.cn (Y. Zhu).

doi:10.1016/j.cclet.2009.07.016

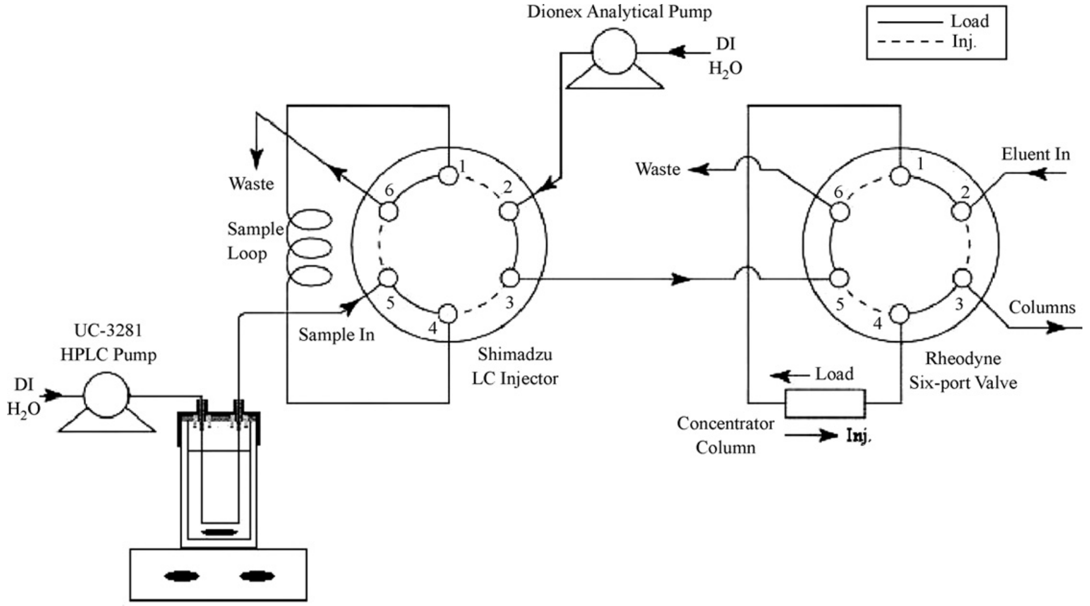

Fig. 1. Schematic diagram of in-line hollow fiber extractor coupled with ion chromatography.

concentrating the target analytes using a concentration column; (3) eluting out the concentrated anions for analysis by ion chromatography. Fig. 1 illustrates how these tasks were performed by the system. This initial configuration shows Shimadzu LC injector in the ‘‘Load’’ position and Rheodyne six-port valve in the ‘‘Inject’’ position.

Firstly, 8 mL ethyl acetate was placed into a sample vial. Deionized water was delivered by a UC-3281 HPLC pump (Union Opto-Electronic Technology Co., Ltd., Beijing, China) as acceptor phase through hollow fiber membrane to extract inorganic anions from ethyl acetate. The extract solution was loaded into 1.5 mL sample loop of Shimadzu LC injector. After the extraction was completed, Shimadzu LC injector was turned into the ‘‘Inject’’ position and Rheodyne six-port valve was turned into the ‘‘Load’’ position. The extract solution was transited from the sample loop to the concentration column with the deionized water by a Dionex analytical pump. Anions were retained on the concentration column and a little ethyl acetate which permeated into deionized water through hollow fiber membrane because of its slightly soluble in water was eliminated by washing the concentration column with deionized water at 2.0 mL/min. This step required 5 min. Meanwhile, the hollow fiber membrane was flushed by deionized water at 0.50 mL/min for 10 min to clean up anion residues before a new extraction cycle. Finally, by switching Rheodyne six-port valve into the ‘‘Inject’’ position, the anions were eluted out from the concentration column into the analytical column for separation.

All columns used in this work were purchased from Dionex (Sunnyvale, CA, USA). The separations were performed on an IonPac AS12A analytical column (250 mm × 4 mm I.D.) and an IonPac AG12A guard column (50 mm × 4 mm I.D.). An IonPac AG12A concentration column (50 mm × 4 mm) was used to concentrate the anions and eliminate the sample matrix. An eluent of 2.7 mmol/L sodium carbonate–0.3 mmol/L sodium bicarbonate was used to elute the four anions from the AS12A column at a constant flow rate of 1.00 mL/min. An anions self-regenerating suppressor (ASRS) with a 50 mA suppressor current from Dionex (Sunnyvale, CA, USA) was used to reduce the conductivity of the eluent.

2. Results and discussion

HFME is based on liquid–liquid extraction. Polypropylene hollow fiber membrane used in this work is a kind of hydrophobic microporous membrane. Ethyl acetate filled the pores of hollow fiber membrane because of its hydrophobic characteristic and contacted with deionized water in the inner wall of the hollow fiber membrane. Owing to the low solubility of the inorganic anions in the ethyl acetate and because of the correspondingly high solubility of

Table 1
Performance of the HFME with ion chromatography.

Anion	RSD (%)[a] ($n = 6$)	Linear range (mg/L)	Correlation coefficiency (r)	LOD (mg/L)
Chloride	7.63	0.01–2	0.9987	0.005
Nitrite	0.35	0.01–5	0.9992	0.001
Bromide	2.05	0.01–1	0.9955	0.002
Nitrate	0.98	0.01–5	0.9988	0.001

[a] Spiked at 1.00 mg/L.

the inorganic anions in the deionized water, anions were extracted from ethyl acetate through pores of the hollow fiber membrane into the deionized water.

In this work, parameters that might affect the extraction efficiency including magnetic stirring speed, extraction flow rate and extraction time were examined. The optimal parameters were as follows: stirring speed 450 rpm, extraction flow rate 30 μL/min, extraction time 30 min.

Limits of detection (LOD), linearity and reproducibility (RSD, %) of the proposed method were investigated under the optimal conditions. The analytical performance of the in-line HFME with ion chromatography is shown in Table 1.

Two ethyl acetate samples were analyzed to evaluate this HFME technique with the optimized method. As illustrated in Fig. 2a, chloride, nitrite and nitrate were found in sample 1, but bromide was not detected. Fig. 2b shows the chromatogram of sample 1 spiked at 0.05 mg/L chloride, nitrite, bromide and nitrate. Similar conditions were found in sample 2. Summary of analysis results for the two ethyl acetate samples are listed in Table 2. It is clear that this method is applicable to determine the inorganic anions in real organic samples.

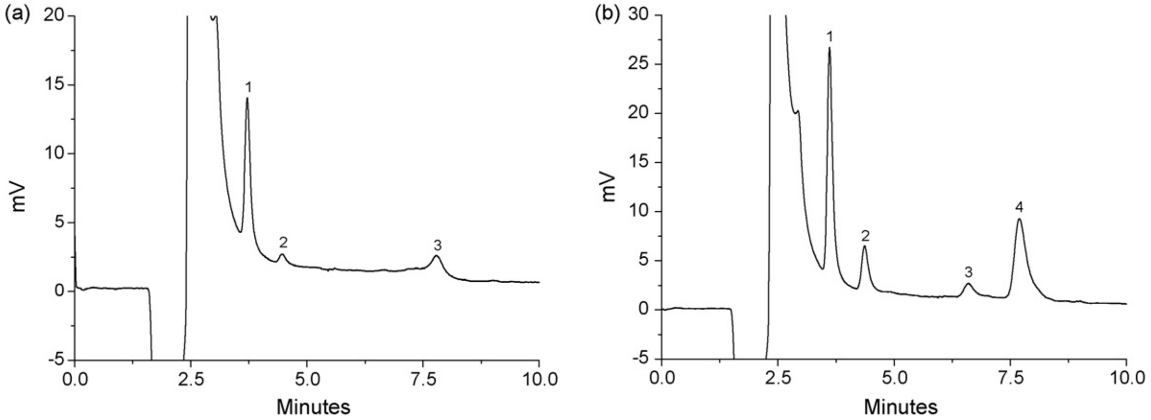

Fig. 2. Chromatogram of samples. (a) Sample 1. Peak identities: (1) chloride, (2) nitrite, (3) nitrate; (b) sample 1 spiked at 0.05 mg/L. Peak identities: (1) chloride, (2) nitrite, (3) bromide (4) nitrate.

Table 2
Analysis results of two ethyl acetate samples.

Anion	Sample 1[a]			Sample 2[b]		
	Found (mg/L)	Spiked (mg/L)	Recovery (%, mean ± RSD, $n = 3$)	Found (mg/L)	Spiked (mg/L)	Recovery (%, mean ± RSD, $n = 3$)
Chloride	0.45 ± 0.03	1.00	108 ± 4	0.18 ± 0.02	0.50	77 ± 8
Nitrite	0.065	0.05	70	0.069 ± 0.001	0.05	72
Bromide	ND[c]	0.10	110	ND[c]	0.10	109 ± 9
Nitrate	0.067 ± 0.001	0.05	86	0.029 ± 0.002	0.05	99 ± 6

[a] Hangzhou Shuanglin Chemical Reagent Factory.
[b] Shanghai Shengxiang Chemical Reagent Co., Ltd.
[c] Not detectable.

Acknowledgments

This work was supported by National Natural Science Foundation of China (No. 20775070), by Zhejiang Provincial Natural Science Foundation of China (No. R4080124), and Zhejiang Qianjiang Project of Science and Technology for Competent People (No. 2008R10028).

References

[1] E. Kaiser, M.J. Wojtusik, J. Chromatogr. A 671 (2) (1994) 253.

[2] E. Kaiser, J. Rohrer, J. Chromatogr. A 858 (2) (1999) 55.

[3] L.E. Vanatta, J. Chromatogr. A 1213 (1) (2008) 70.

[4] S. Pedersen-Bjergaard, K.E. Rasmussen, Anal. Chem. 71 (14) (1999) 2650.

[5] J. Norberg, E. Thordarson, Analyst 125 (4) (2000) 673.

[6] S. Muller, M. Moder, S. Schrader, P. Popp, 25th International Symposium on Capillary Chromatography, Elsevier Science Bv, Riva Del Garda, Italy, 2002, p. 99.

[7] L.M. Zhao, M.K. Lee, Anal. Chem. 74 (12) (2002) 2486.

[8] O.B. Jonsson, U.L. Nilsson, Anal. Bioanal. Chem. 377 (1) (2003) 182.

[9] K. Kuosmanen, T. Hyotylainen, K. Hartonen, M.L. Riekkola, Analyst 128 (5) (2003) 434.

[10] C. Basheer, A. Parthiban, A. Jayaraman, H.K. Lee, S. Valiyaveettil, 25th International Symposium on Chromatography, Elsevier Science Bv, Paris, France, 2004, p. 274.

[11] C.H. Yan, H.F. Wu, Rapid Commun. Mass Spectrom. 18 (24) (2004) 3015.

[12] N. Fontanals, T. Barri, S. Bergstrom, J.A. Jonsson, J. Chromatogr. A 1133 (1/2) (2006) 41.

[13] J.M. Wu, H.K. Lee, J. Chromatogr. A 1133 (1/2) (2006) 13.