

Determination of Inorganic Anions in Ethyl Acetate by Ion Chromatography with an Electromembrane Extraction Method

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Abstract

In this work, the determination of inorganic anions in slightly water-soluble organic solvents (ethyl acetate) was realized by ion chromatography (IC) with a novel-efficient electromembrane extraction method. From an 8 mL ethyl acetate sample, three inorganic anions migrated through the pores of a polypropylene hollow fiber membrane, and into deionized water inside the lumen of the hollow fiber by the application of 600 V. The transport was forced by an electrical potential difference sustained over the liquid membrane, resulting in electrokinetic migration of inorganic anions from the donor compartment to the acceptor solution. After the electromembrane extraction, the acceptor solution was analyzed by IC with a sodium carbonate-sodium bicarbonate eluent. The applied voltage, stirring speed, and extraction time for controlling the extraction efficiency were optimized. Within 10 min of operation at 600 V, chloride, bromide, and sulfate were extracted with recoveries in the range 76–110%, which corresponded to a linear range of 0.01–1 mg/L. The procedure was applied to the analysis of inorganic anions in a real ethyl acetate sample and expands onto other slightly water-soluble organic solvents.

Introduction

During the last 15 years, hollow fiber membrane extraction (HFME) techniques have been widely used for sample preparation in important fields, such as environmental, pharmaceutical, peptides, and food and beverages chemistry (1–4). It has noteworthy advantages viz.; direct introduction of untreated samples, analyte preconcentration, elimination of interferences, low cost of chemical reagents and hollow fiber, convenience to couple with gas chromatography, high-performance liquid chromatography, ion chromatography (IC), etc. (5–7). Because the transport mechanism for the analytes across the liquid membrane of the HFME is based on passive diffusion, it often takes more than 30 min, sometimes even 60 min, for the extraction process to reach equilibrium.

In order to overcome this time-consuming disadvantage of conventional HFME, a newly-developed sample pretreatment model called electromembrane extraction (EME) was first demonstrated by Pedersen-Bjergaard and Rasmussen in 2005 (8). In this system, basic drug substances were transported across a thin artificial organic liquid membrane by the application of 300 V d.c. from a 300- μ L aqueous donor compartment. Compared with passive diffusion in traditional membrane extraction, electrokinetic migration appeared to be a much more efficient transport mechanism, providing high analyte recoveries in very short time. Later, Pedersen-Bjergaard et al. expanded this EME method to extract other targets, such as basic drugs, acidic drugs, peptides, and chlorophenols (9–17). They simulated the flux during the EME (18), and studied the parameters affecting it (15,19,20). A small, molecule-like metal ion (Pb^{2+}) was extracted using EME from amniotic fluid, blood serum, lipstick, and urine samples by Lee (21).

IC is the common method to analyze inorganic anions. In the last few years, with the rapid advances in IC, it is no longer a difficult problem to determine inorganic anions even in some water-miscible organic solvents such as methanol, isopropanol, acetone, N-methylpyrrolidone, p-toluenesulfonic acid, sodium caprylate, and ethylene glycolphenylether (22–25). However, the determination of inorganic anions in slightly water-soluble organic solvents is something that analytical chemists tend to avoid because the available methods, such as titrimetry, gravimetry, colorimetry, etc., are inadequate, and many of them are not very sensitive nor selective (26). Analysis of inorganic anions in slightly water-soluble organic solvents has been seemingly unreported, with exception to an in-line hollow fiber membrane extractor coupled with IC discussed in a previous work (7). Thirty min was needed for the entire extraction process, and the system was complicated with the column-switching method, resulting in an expensive consumption of accessories. In the present work, an electromembrane extractor was set up to extract inorganic anions from ethyl acetate using deionized water. The duration of the extraction process was shortened to 10 min, and the resulting system was simpler with similar sensitivities. The proposed method was validated for quantitative purposes and applied to a commercial ethyl acetate sample.

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Experimental

Reagents

Sodium carbonate anhydrous from Beijing Reagents Institute (Beijing, China) and sodium bicarbonate from Shanghai Hongguang Chemical Factory (Shanghai, China) were used to prepare the eluents. All eluents were prepared daily. Ethyl acetate was purchased from Chengdu Kelong Chemical Reagent Factory (Chengdu, China). Deionized water from a Millipore Mill-Q water system (Millipore Co., Milford, MA) was used to prepare all eluents, standard solutions, and samples. A polypropylene (PP) hollow fiber membrane (420- μm inner diameter, 50- μm wall thickness and 0.1–0.2- μm wall pore size) was bought from Zhejiang University Hongquan Environmental Engineering Co., Ltd (Hangzhou, China). An Accurel Q3/2 PP hollow fiber membrane (600- μm internal diameter, 200- μm wall thickness, and 0.2- μm pore size) was purchased from Membrana (Wuppertal, Germany).

A mixed standard solution (1000 mg/L) containing chloride, bromide, and sulfate was prepared from the sodium salts obtained from Shanghai Zhenxin Chemical Factory (Shanghai, China) and kept in a refrigerator at 4°C. Working standards were prepared daily by spiking a known amount of 1000 mg/L mixed anions standard solution into ethyl acetate. All chemicals used were of analytical-reagent grade.

The equipment of electromembrane extractor

The equipment used is illustrated in Figure 1. One end of a 15-cm PP hollow fiber membrane was connected with a syringe tip, and another end was inserted into a Teflon tube. The positive electrode was inserted into the lumen of the hollow fiber membrane through a small hole of the Teflon tube. Acrylate adhesive was used to seal the interspaces between the positive electrode and the Teflon tube so that the acceptor solution would not leak into the sample solution, and the positive electrode was fixed on the Teflon tube. The syringe tip, the negative electrode, and the Teflon tube were all fixed on the cap of the sample vial.

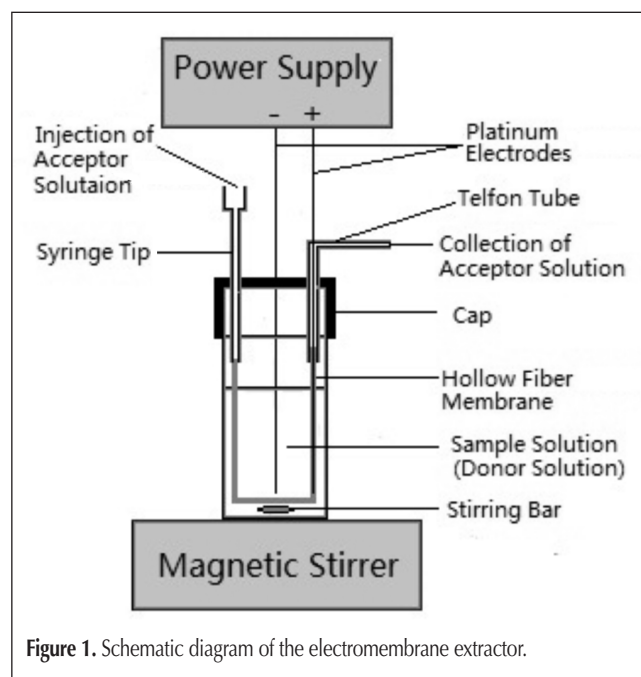


Figure 1. Schematic diagram of the electromembrane extractor.

The high voltage DC power supply used was a model DW-P303-0.1ACD8 from Dongwen High Voltage Power Supply Plant (Tianjin, China) with the voltage in the range 0–10 kV, and with a current output in the range 0–10 μA . Platinum wires from Hushi Laboratory Equipment Co. Ltd. (Shanghai, China) were placed in the sample and acceptor solutions and used as electrodes. During the experiments, the extraction unit was agitated on a 99-2 magnetic stirrer from Shanghai Shen Sheng Biotech Co. Ltd. (Shanghai, China).

Procedure for EME

The experiments were performed according to the following procedure: 8 mL ethyl acetate was filled into a glass sample vial, and lumen from the hollow fiber membrane was filled with deionized water by a syringe. The hollow fiber membrane was then placed in the sample together with the negative electrode. The two electrodes were connected with the power supply, and the voltage (typically 600 V) was applied for 10 min. After the extraction was completed, the voltage was turned off; 100 μL of the acceptor solution was collected by depressing the syringe through the syringe tip, and transferred into IC for further analysis.

IC conditions

The analysis of inorganic anions was performed by a Dionex (Sunnyvale, CA) DX-120 ion chromatograph equipped with a 25- μL sample loop. An IonPac AG12A guard column (50 mm \times 4 mm, i.d.) and an IonPac AS12A analytical column (250 mm \times 4 mm, i.d.) with an eluent of 2.5 mmol/L sodium carbonate–0.3 mmol/L sodium bicarbonate was used at a constant flow rate of 1.00 mL/min. An anions self-regenerating suppressor (ASRS) with a 50 mA suppressor current was used to reduce the conductivity of the eluent. Data acquisition was achieved with a N2000 workstation (Hangzhou, China).

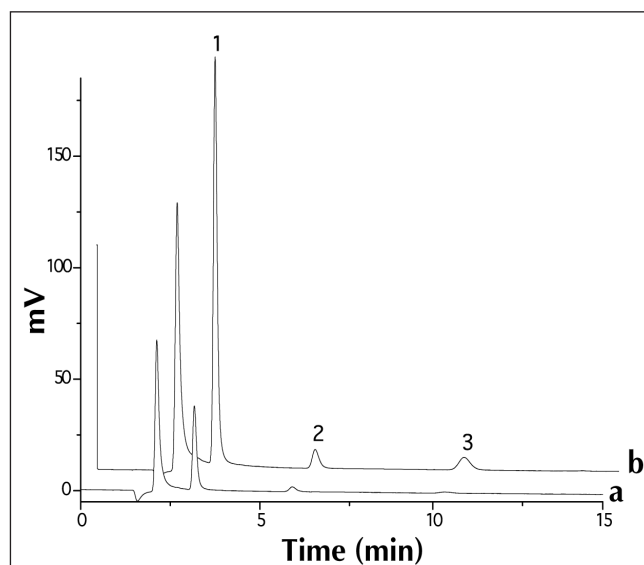


Figure 2. Chromatograms demonstrating the strong effect of voltage on cross membrane transport: (A) extraction performed without application of voltage for 10 min. Stirring speed: 600 rpm. (B) acceptor phase after 10 min of EME at 600 V. Stirring speed: 600 rpm. Peak identities: 1, chloride; 2, bromide; 3, sulfate. Spiked concentration: 1 mg/L chloride, bromide, and sulfate in ethyl acetate.

Results and Discussion

Comparison between EME and conventional HFME

To demonstrate the efficiency of the proposed EME method, a comparison was made between the EME and conventional HFME by extracting the analytes from the same sample. A PP hollow fiber membrane with a smaller inner diameter was used; the sample stirring speed was 600 rpm. Figure 2A shows a typical chromatogram of inorganic anions after 10 min of HFME, while Figure 2B shows a chromatogram of the same analytes after 10 min of EME at 600 V. In the former case, only two small peaks were detected as the only driving force of HFME was passive diffusion. Evidently, the voltage enabled a more efficient extraction.

The choice of hollow fiber membrane

In this study, two kinds of PP hollow fiber membrane were used with different inner diameters and wall thickness. Figure 3 illustrates the effect of the membrane used in EME. Peak areas of all anions were larger when the Hongquan membrane was used. With the thinner wall thickness, anions reached the inner wall of the Hongquan membrane easier. Based on this result, the Hongquan membrane was used for the rest of the study.

EME applied voltage

A series of experiments with various extraction voltages between 100–600 V were conducted. The results are summarized in Figure 4. The highest peak areas were obtained at 600 V. Beyond that, a decrease was observed. It may have been due to the oxidation of the inorganic anions and the heat generated at the relative high voltage. As a result, 600 V was chosen as the optimal applied voltage.

Magnetic stirring speed

Magnetic stirring was applied to facilitate the mass transfer process and the extraction efficiency. The stirring speed was optimized for an efficient extraction. Figure 5 illustrates the variation in chromatographic peak areas of inorganic anions as a function of the stirring speed. Peak areas of three anions reached their maximum values at 600 rpm because of the better approach

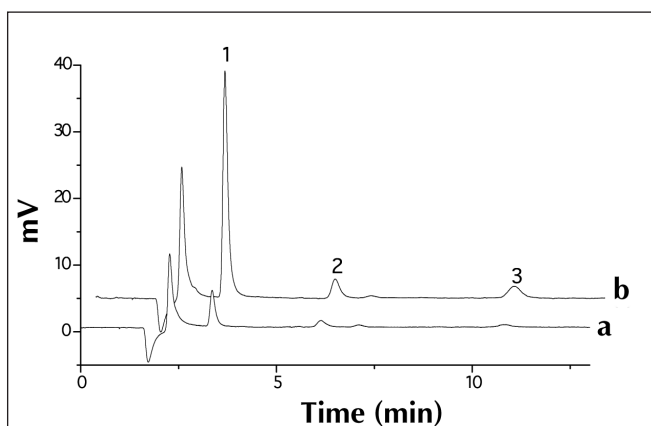


Figure 3. Effect on the membrane used in EME. (A) Membrana membrane. (B) Hongquan membrane. Peak identities: 1, chloride; 2, bromide; 3, sulfate. Applied voltage: 200 V. Stirring speed: 450 rpm. Extraction time: 10 min. Spiked concentration: 1 mg/L chloride, bromide, and sulfate in ethyl acetate.

of anions to the hollow fiber membrane. However, the peak areas of the three anions decreased with further increasing of the stirring speed, due to the bubble formation in the ethyl acetate, which had a harmful influence on mass transfer process. As a compromise, 600 rpm was used in further optimization.

Extraction time

EME is an equilibrium distribution process. To achieve equilibrium, extractions were carried out for 5 to 30 min. As shown in from Figure 6, peak areas of three anions increased with increasing extraction time from 5 to 10 min, but declined thereafter. One possible reason for the decrease of extraction efficiency for the three anions above 10 min may be that the longer extraction time resulted in the oxidation of the anions at a relative high voltage. Therefore, 10 min was chosen as the optimum EME duration.

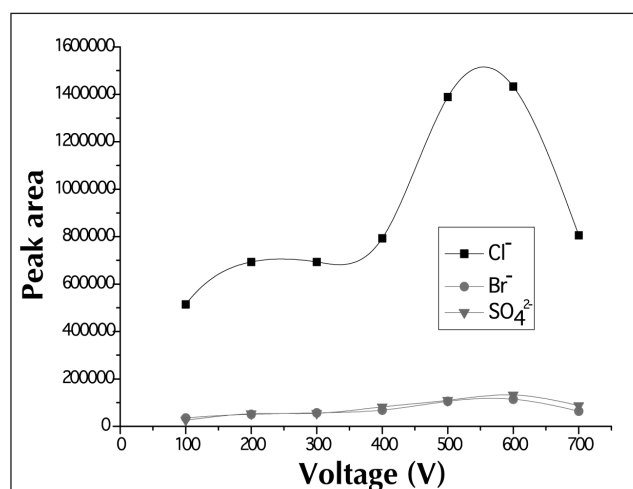


Figure 4. Effect of applied voltage on peak areas. Stirring speed: 450 rpm. Extraction time: 10 min. Spiked concentration: 1 mg/L chloride, bromide, and sulfate in ethyl acetate.

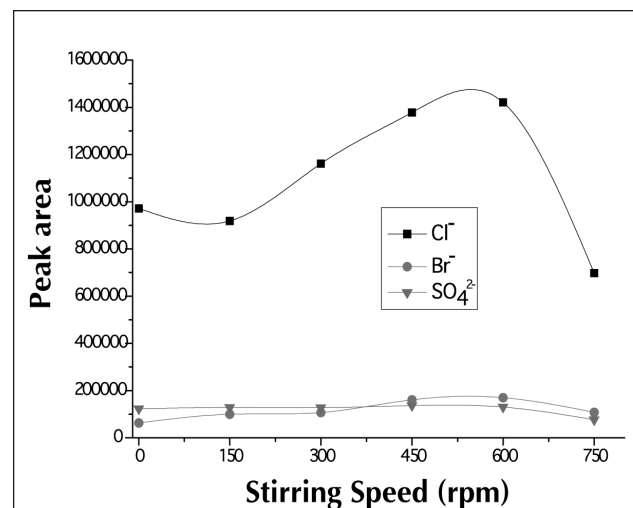


Figure 5. Effect of magnetic stirring speed on peak areas. Applied voltage: 600 V. Extraction time: 10 min. Spiked concentration: 1 mg/L chloride, bromide, and sulfate in ethyl acetate.

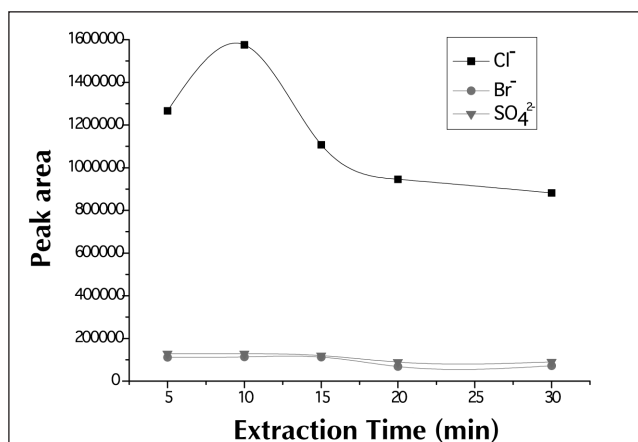


Figure 6. Effect of extraction time on peak areas. Applied voltage: 600 rpm. Stirring speed: 600 rpm. Spiked concentration: 1 mg/L chloride, bromide, and sulfate in ethyl acetate.

Anion	RSD (% , $n = 6$)	Linear range (mg/L)	Correlation coefficient (r)	LOD (mg/L)
Chloride	12.32	0.01–1	0.9976	0.001
Bromide	6.45	0.02–1	0.9970	0.020
Sulfate	4.08	0.01–1	0.9979	0.004

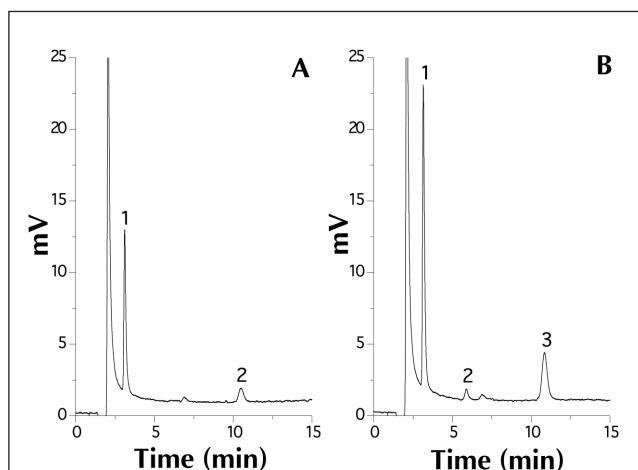


Figure 7. Chromatogram of the sample. (A) Sample peak identities: 1, chloride; 2, sulfate. (B) Sample spiked at 0.100 mg/L. Peak identities: 1, chloride; 2, bromide; 3, sulfate.

Anions	Found (mg/L)	Spiked (mg/L)	Total (mg/L)	Recovery (%) (mean \pm RSD, $n = 3$)
Chloride	0.118 \pm 0.010	0.100	0.205 \pm 0.010	87 \pm 9
Bromide	ND [†]	0.100	0.110 \pm 0.005	110 \pm 5
Sulfate	0.044 \pm 0.004	0.050	0.082 \pm 0.002	76 \pm 3

* Chengdu Kelong Chemical Reagent Factory
[†] ND, not detectable.

Analytical performance and analysis of real sample

Detection limits (LOD), linearity, and reproducibility of the proposed method were determined under the optimal conditions. The analytical performance of EME with IC is shown in Table I. It can be seen that the relative standard deviations of the four anions were smaller than 12.32% ($n = 6$). The calibration curve is based on linear regression for spiked concentrations of the anions of interest prior to blank correction. The linearity was evaluated within 0.01–1 mg/L. Each anions exhibited good linearity with the regression coefficient of $r > 0.9970$. LODs for the three anions were calculated at a signal-to-noise ratio of 3. The higher LOD of bromide may be caused by its relative stronger reduction at a higher voltage.

The ethyl acetate sample was analyzed to evaluate this technique with the optimized method. As illustrated in Figure 7A, chloride and sulfate were found in the sample, but bromide was not detected. Figure 7B shows the chromatogram of the sample spiked at 0.100 mg/L chloride, bromide, and sulfate. The summary of analysis results for the ethyl acetate sample are listed in Table II. It is clear that this method is applicable to determine the inorganic anions in a real organic sample.

Conclusion

In this work, the determination of inorganic anions in slightly water-soluble organic solvents (ethyl acetate) was realized by IC with a novel efficient EME. The extraction time was shortened and the equipment was easily available in most labs. The EME method transferred inorganic anions from ethyl acetate into an aqueous solution, which was then available for analysis with IC successfully. Extraction procedures were optimized to achieve high efficiency and preconcentration. The current method exhibits good linearity and repeatability over satisfactory linear range. This has been shown to be an effective approach for routine analysis of inorganic anions in real slightly water-soluble organic samples.

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