Rapid analysis of ultra trace amounts of anions in water by solid phase extraction and ion chromatography

H Salar Amoli*, M Rabbani† & P Simpson‡

Department of Chemistry, Iranian Organization for Science and Technology, No 71, Forsat St. Englab St., Tehran, Iran

Received 12 October 1999; revised 21 February 2000

The use of solid phase extraction (SPE) technique prior to ion chromatography (IC), for relative enrichment of inorganic anions is reported. The SPE is directly coupled with the IC and comparison has been made between the detection limits of IC, both on its own, and in combination with SPE. It has been shown that detection limits can be reduced 100 fold using this combined technique. A number of parameters such as eluent strength, pH and flow rate have been studied. The suppressed and non-suppressed SPE/IC have been examined for the analysis of aqueous samples. The suppressed SPE/IC is found to have lower detection limits than the non-suppressed method. Recovery data and matrix dependencies have been studied at concentration levels ranging from 1 to 10 μg/l. Comparing to off line SPE method, on line SPE/IC reduces the analysis time by at least factor of two.

Ion chromatography has quickly evolved since its initial introduction1. Nowadays its most significant application is in the routine determination of common inorganic anions in fresh and waste water2. The speed, sensitivity and selectivity of IC, combined with the facility to separate and simultaneously determine several ions of varying concentrations, makes this a unique instrument for ion analysis. Nevertheless there is still room for improvement, so as to increase the sensitivity for ultra trace analysis. There are industrial applications, such as in nuclear power station3 where extremely low concentrations (part per billion) of ions such as sulphate, sodium and chloride can cause corrosive damage. In the light of these requirements recent developments in IC have focused on lowering the detection limits, and increasing the speed of separation4-6. Off line SPE has been used in chromatographic investigations to improve the detection limits7,9. The SPE method is based on an equilibration of the analyses between the aqueous and an immobilized liquid phase coated onto a silica fiber as a stationary phase, i.e., polydimethylsiloxane.

In continuation of our studies on the direct links between SPE and IC10, we have been constantly trying to determine low level ions in aqueous phase. The aim of this research was to establish a method to make possible the separation of weak and moderately retained ions simultaneously by isocratic elution within a short period of time at very low concentration levels.

Experimental

A Dionex ion chromatograph consisting of a model 4500 equipped with a six valve injector (125 μl sample loop) and a conductivity detector was used. The analytical column was a strong anion exchange (Dionex AS4A SC, 250x4.0 mm) and a high capacity cation exchange column (Waters, IC pack C Cation Guard) was also used as a suppressor device. A connection tube with a 25 cm length and 5 mm o.d with a needle in the end, made of glass, was constructed by us for the on line SPE/IC. This tube was then mounted onto the injection port as shown schematically in Fig. 1. A 100 mg SPE cartridge (Varian Standard Bond Elut SAX packed with irregular acid washed silica base, 60 Å porosity, 0.85 µm particle size) was used to perform the SPE, followed by online injection into the IC system.

Fig. 1—Schematic diagram of SPE/IC

---

1Dept. of Chemistry, Islamic Azad University, Tehran, Iran
2Dept. of Chemistry, Birkbeck College, University of London, London, WC1E, UK
neq/g mean capacity, trimethylaminopropyl as functional group) was inserted into the top of the tube.

The determination of anions utilizing this method is a two step process as illustrated in Fig. 1. Position (A)-The sample is introduced into SPE cartridge, and the unwanted matrix pass through the connecting tube and then through a six port injection valve to waste. Position (B)-A solution of 2 ml NaOH (0.1 mM) is used to flush the anions from SPE through the connection tube and onto the injection valves. After loading, the valves are switched back to original injection position, and the sample is swept on to the analytical column, using carbonate/hydrogencarbonate as eluent.

Purified water (18 MΩ) using a Millipore milli-Q water purification system (Bedford, MA, USA) was used throughout. All chemicals were of analytical reagent grade. Stock standard solution of chloride, fluoride, nitrate, phosphate, sulphate and thiosulphate were prepared from their salts (Merck) at a concentration of 10 µg/ml and diluted when required. The eluent was prepared by dissolving appropriate amounts of sodium carbonate/hydrogencarbonate in purified water. Whenever required, ammonia solution (25% w/w) (Merck) was added dropwise to the eluent solutions until the desired pH was achieved. Benzoic acid (2 mM) was used as an eluent in non-suppressed mode.

To carry out the experiments, the SPE column were conditioned with methanol (1 mM) and the aqueous sample was run through the conditioned SPE column at a flow rate of approximately 5 ml min⁻¹. Subsequent to this enrichment procedure, 2 ml NaOH (0.1 mM) was used to flush the solutes directly toward the injection port. The identification and quantitative determination of the ions under examination, were accomplished by a comparison of retention times, peak heights and areas.

**Results and discussion**

**Optimization of IC**

A series of experiments with differing strengths of the eluent at various pH levels were carried out. These experiments suggest that the best eluent concentrations for rapid analysis are in the range 1.7 to 2.1 mM and 1.5 to 1.8 mM for carbonate and hydrogencarbonate respectively. In these circumstances, the pH of the eluent has important effects. Slight ionization of the eluent occurs at pH 9, so only the monovalent ions can be eluted and there is insufficient power for the elution of SO₄²⁻ and PO₄³⁻. At pH 9.5, the CO₃²⁻ partially exists and contributes to the divalent anions. A rapid analysis is possible at pH 9.7 when the actual proportion of CO₃²⁻ is increased.

The background conductivity of 1.7 mM hydrogencarbonate and 2 mM carbonate as eluent in suppressed mode at pH 9.5 was 16 µS cm⁻¹. By increasing the pH of the eluent to 9.7, the background increased to 21 µS cm⁻¹.

The flow rate also effects the separation efficiency and running time. High flow rates, shortens the chromatographic run which adversely affects the separation efficiency, which in turn reduces the column life. In this study, a flow rates of 0.5 to 3 ml min⁻¹ were examined, and it was found that a flow rate of 2 ml min⁻¹ to be the best condition for rapid analysis with lesser damage to other factors.

**Recovery results for the sample enrichment by SPE**

Systematic investigation were carried out in order to optimize the preconcentration of anions from the aqueous sample. To have a satisfactory preconcentration, followed by quantitative IC analysis, the recovery of the analytes should be close to 100%. The resulting data for four replicates analysis were obtained, and the recovery (R), which is defined as the peak area after preconcentration divided by the peak area after a direct injection onto IC was calculated. When the eluent volume is less than 800 µl, a quantitative recovery could not be obtained. By increasing the volume of the eluent to 1000 µl, the recovery increased to about 90% for most ions. In this work, 2 ml eluent was used to achieve highest recovery for all ions. Also, it was found that efficient recovery could be achieved only when the concentration of samples are more than 10 µg/l for all concerned anions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>suppresed IC</th>
<th>non-suppressed IC</th>
<th>SPE/IC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>250</td>
<td>350</td>
<td>2</td>
</tr>
<tr>
<td>Chloride</td>
<td>250</td>
<td>350</td>
<td>2</td>
</tr>
<tr>
<td>Bromide</td>
<td>250</td>
<td>350</td>
<td>2</td>
</tr>
<tr>
<td>Nitrate</td>
<td>350</td>
<td>470</td>
<td>4</td>
</tr>
<tr>
<td>Sulphate</td>
<td>500</td>
<td>700</td>
<td>5</td>
</tr>
<tr>
<td>Phosphate</td>
<td>500</td>
<td>700</td>
<td>5</td>
</tr>
</tbody>
</table>
In order to evaluate the reproducibility of chloride and nitrate at very low concentrations in combined technique, replicate analysis was carried out and the peak heights were measured. Statistical evaluation show relative standard deviations below 3% for both ions. Long hour stability was examined within a day during routine operation, showing the relative standard deviations to have increased to 4%. Day to day variations over a period of a working week was also investigated. While the mobile phase and sample solutes were freshly prepared everyday, a small variation which caused an increase in relative standard deviations to below 5% were observed. With respect to the sensitivity of SPE/IC, the changes are not significant.

Suppressed SPE/IC

IC has long been used for the determination of inorganic anions and there are numerous papers discussing the column and suppresser technology and the range of solutes which can be analyzed by improving in chromatographic hardware\(^\text{11-14}\).

Although technologies and techniques such as column switching have been introduced for reducing the detection limits of the major anions in IC analysis\(^2\), these are not favorable, since they are time consuming and result in peak broadening. Hence, in this study, SPE has been used for preconcentration of ions present in liquid solutions. Using SPE prior to the IC, significantly increases the ability of the instrument for analysis of a sample at very low concentrations (µg/l). Table 1 lists detection limits for major anions in water with IC and SPE/IC methods. In direct injection to IC, 125 µl of the prepared sample at various concentrations were introduced into the column. For a combined method 50 ml of appropriate ion concentration was introduced into the micro extraction column, washed with 2 ml NaOH (0.1 mM), and then the appropriate volume (125 µl) was directed toward the IC. The limit of detection was taken as twice the standard deviation of the noise. The results in Table 1 show that extremely low detection limits can be obtained using the combined technique. Figure 2, shows a chromatogram of major anions in water by suppressed SPE/IC. The separation is achieved in a short time at very low level concentrations. In this experiment, the fluoride peak appears sufficiently resolved from the void volume peak, thus allowing a quantitative determination. The time taken for separation of seven major anions (Fig. 2) is much less than chromatograms obtained by off line method\(^1,9\).

### References