

## Factors affecting the ion chromatographic preconcentration behaviour of inorganic anions and organic acids

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### Abstract

An ion chromatograph employing an IonPac AC10 concentrator column and AS10 analytical column with an hydroxide eluent was used to investigate the preconcentration behaviour of inorganic anions and organic acids. Increased sample loading volumes resulted in decreased recoveries for weakly retained solutes, while the flow-rate at which the sample was loaded did not affect solute recovery, at least for flow-rates up to 5.0 ml/min. The recoveries obtained for weakly retained solutes were also influenced by the presence of sample matrix ions and the ion-exchange selectivity of the concentrator column. Formate and chloride were found to modestly decrease the recovery of fluoride, while the presence of sulfate had a more significant impact. Sample matrix effects were minimized by using a concentrator column with an ion-exchange selectivity that permits maximum retention of solutes, such as fluoride and formate, yet only moderate retention of anions, such as sulfate and oxalate. © 1997 Elsevier Science B.V.

*Keywords:* Sample handling; Inorganic anions; Organic acids

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### 1. Introduction

Ion chromatography (IC), with on-line sample preconcentration, is the most commonly utilized technique for the determination of low levels of ionic impurities found in power plant waters [1–7] and other high purity water samples [8–11]. Sample preconcentration is typically performed using a six-port switching valve, such as an injection valve, with the sample loop being replaced by an ion-exchange concentrator column. The sample is loaded onto the concentrator column in one direction using a sample loading pump, then back-flushed with eluent onto the analytical column, after which, separation and detection occur as normal [5]. The amount of sample

loaded onto the concentrator column is varied by keeping the loading time constant and changing the sample loading flow-rate; alternatively, the loading flow-rate can be kept constant and the sample loading time can be varied. Ideally, solute recovery is independent of the manner in which the sample was loaded. That is, the volume of sample used, or the loading flow-rate, has little or no effect on solute recovery, provided that the concentrator column has a reasonable ion-exchange capacity.

In reality, less than complete recoveries have been observed when preconcentrating anionic solutes, particularly for those anions with low ion-exchange affinities [5,12]. The issue of solute recovery is perhaps most important when preconcentrating analytes with a range of ion-exchange affinities, such as samples containing both inorganic and organic acid

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anions. As both groups of solutes are important in the analysis of high purity waters [7], sample pre-concentration methods applied to these samples should permit the quantitative recovery of both inorganic anions and organic acids during the sample loading step, then provide complete resolution of these ions during the separation step. In this work, we investigate factors affecting the preconcentration behaviour of inorganic anions and organic acids. The effect of parameters, such as sample loading flow-rate, sample volume, sample matrix ions and concentrator column selectivity, on solute recoveries will be discussed.

## 2. Experimental

### 2.1. Instrumentation

The ion chromatograph used in this work consisted of a Dionex Corporation (Sunnyvale, CA, USA) DX-300 system equipped with a CDM-II conductivity detector. An AMMS-II suppressor was used with a regenerant solution of 0.025 M sulfuric acid, operated at a flow-rate of 10 ml/min. A Dionex Auto-Regen Module was used in conjunction with the AMMS-II to allow continuous suppression over extended time periods. A Dionex IonPac AS10 (250×4 mm I.D.) analytical column was used for all separations, with an eluent of 100 mM sodium hydroxide, operated at a flow-rate of 1.0 ml/min. A Dionex DQP pump and an IonPac AC10 (50×4 mm I.D.) concentrator column were used for sample preconcentration. Dionex AI-450 chromatography software was used for system control and data collection.

### 2.2. Reagents and procedures

All solutions were prepared from analytical reagent grade chemicals in 18 MΩ water, obtained from a Milli-Q Plus water purification system (Millipore, Bedford, MA, USA). Commercially available (Dionex), 1000 μg/ml stock standards of fluoride, chloride, nitrite and sulfate were used, while 1000 μg/ml standard solutions of acetate, formate and oxalate were prepared from their analytical reagent grade sodium salts (Fluka, Ronkonkoma, NY, USA).

One drop of chloroform was added to each 1000 ml of sample to protect acetate and formate from bacterial decomposition.

Sample preconcentration was performed in the usual manner, i.e. the injection loop was replaced with the AC10 concentrator column. The sample was loaded onto the concentrator column in one direction then back-flushed with eluent onto the analytical column, after which, separation and detection occur as normal [5]. During sample preconcentration, the sample concentration was kept constant, while the flow-rate was varied from 1.5 to 5 ml/min. Where required, the concentration (loading) time, which was automatically controlled by computer, was varied from 0.5 to 50 min. All samples were prepared daily in 1000 ml polypropylene containers that had been previously rinsed with 18 MΩ Milli-Q water. All sample measurements were performed in triplicate and the average peak area or peak height was used in these studies.

## 3. Results and discussion

### 3.1. Effect of sample volume and flow-rate

The IonPac AS10 analytical column and AC10 concentrator column used for this work were developed specifically for the preconcentration analysis of high purity waters. The packing materials were optimized, in terms of capacity and selectivity, to allow the isocratic separation of weakly retained organic and inorganic anions, in addition to more strongly retained anions, as discussed previously [7]. The AS10 analytical column consisted of a macroporous (2000 Å) ethylenevinylbenzene (EVB)-divinylbenzene (DVB) core particle, which was sulfonated and then coated with a monolayer of anion-exchange latex. The vinylbenzylchloride (VBC) latex particles were crosslinked with 5% DVB and partially functionalized with a (proprietary) tertiary amine to generate the appropriate anion-exchange selectivity [13]. The AC10 concentrator column utilized the same selectivity latex as the macroporous AS10 column, although a microporous core particle was used in order to minimize the interstitial volume of this column. In this work, we report on the

parameters affecting the preconcentration behaviour of both inorganic and organic acid anions when using the AS10 analytical and AC10 concentrator columns.

In order to investigate the effect of sample volume, two solutions with different concentrations of a weakly retained solute (fluoride) were preconcentrated upon the AC10 concentrator column, at a constant flow-rate, for varying time intervals. Ideally, the recovery for the fluoride peak should be equivalent at points where the total mass of fluoride passed through the concentrator column was the same in each case, provided that recovery is independent of sample volume. Fig. 1 shows the results obtained when increasing volumes of 100 (a) and 400 (b)  $\mu\text{g/l}$  fluoride solutions were preconcentrated using a sample loading flow-rate of 5.0 ml/min. All separations used an AS10 analytical column with a 100 mM NaOH eluent and suppressed conductivity detection. Quantitative recovery (95%) was obtained for the 100  $\mu\text{g/l}$  fluoride solution (a) up to a sample volume of 8.6 ml, which corresponds to 0.045  $\mu\text{equiv.}$  of fluoride loaded. A recovery of 75% was obtained after a sample volume of 32.7 ml (0.170

$\mu\text{equiv.}$ ) was loaded, while the recovery decreased to 50% after 68 ml (0.356  $\mu\text{equiv.}$ ) of the 100  $\mu\text{g/l}$  fluoride solution were loaded. The response for the 100  $\mu\text{g/l}$  fluoride peak reached a plateau after 100 ml of the solution had been loaded, indicating that the 'effective' capacity of the AC10 concentrator column was equal to 0.52  $\mu\text{equiv.}$  (for fluoride) under these conditions.

The recovery for the 400  $\mu\text{g/l}$  fluoride peak (b) was quantitative (95%) up to a sample volume of 6.8 ml, which corresponds to 0.141  $\mu\text{equiv.}$  of fluoride loaded. In this case, a recovery of 75% was obtained after a sample volume of 14.8 ml (0.308  $\mu\text{equiv.}$ ) was loaded, while the recovery decreased to 50% after 29.8 ml (0.620  $\mu\text{equiv.}$ ) of the 400  $\mu\text{g/l}$  fluoride solution was loaded. Clearly, the range over which quantitative solute recoveries were obtained decreased when fluoride was loaded in a larger sample volume. In addition, significantly higher amounts of fluoride could be loaded before the recovery decreased to 75 and 50% when the solute was loaded in a smaller total volume, indicating that sample volume has a significant effect on solute recovery. Similar behaviour has been observed previ-

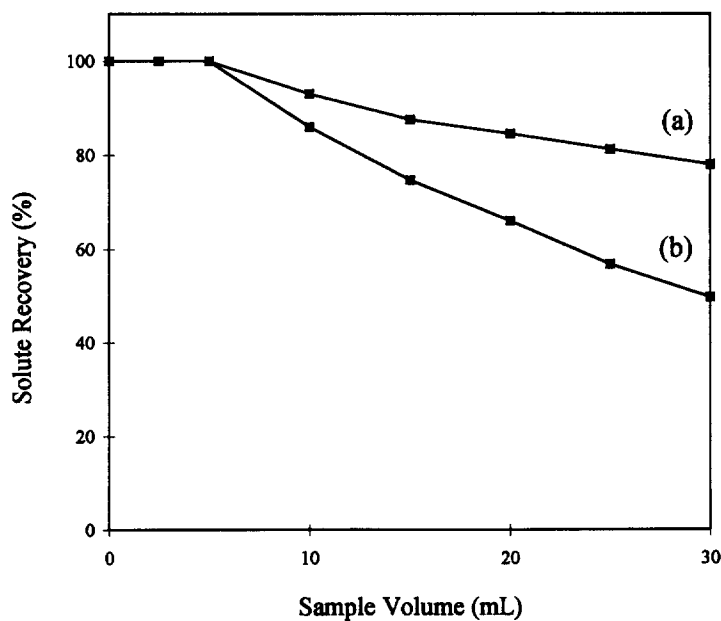


Fig. 1. Effect of sample volume on fluoride peak recovery. Conditions: analytical column, Dionex IonPac AS10; concentrator column, Dionex IonPac AC10; eluent, 100 M sodium hydroxide; flow-rate, 1.0 ml/min; detection, suppressed conductivity; regenerant, 0.05 M sulfuric acid at 10 ml/min; sample, 100 (a) and 400 (b)  $\mu\text{g/l}$  fluoride solutions preconcentrated at a flow-rate of 5.0 ml/min.

ously for weakly retained solutes preconcentrated upon surface-aminated ion-exchange resins [5,12].

Having established the effect of sample volume on the AC10 concentrator column, the influence of flow-rate on the preconcentration process was then investigated. To minimize any volume effects, relatively low sample volumes were used for the flow-rate studies. Fig. 2 shows peak recoveries obtained after preconcentrating 400  $\mu\text{g/l}$  fluoride for different time intervals, at flow-rates of 5.0 (a) and 2.5 (b) ml/min. At points where equal sample volumes (amounts) had been loaded, the peak recoveries were essentially equivalent, regardless of the sample loading flow-rate. For instance, the recovery for 400  $\mu\text{g/l}$  fluoride loaded for 3.0 min at 5.0 ml/min (0.312  $\mu\text{equiv. total}$ ) was 76.0%, compared to a recovery of 75.3% when the same solution was loaded for 6.0 min at 2.5 ml/min. When 400  $\mu\text{g/l}$  fluoride was loaded for 6.0 min at 5.0 ml/min, a recovery of 49.7% was obtained, compared to a recovery of 49.3% when the same solution was loaded for 12 min at 2.5 ml/min. Comparable results were also obtained for fluoride solutions preconcentrated at other flow-rates, indicating that this parameter has no

significant effect on solute recovery, at least up to flow-rates of 5.0 ml/min. Again, this behaviour is similar to that previously observed for solutes preconcentrated upon surface-aminated ion-exchange resins [12].

### 3.2. Effect of competing matrix ions

The results above indicated that the latex agglomerated AC10 concentrator column gave similar performance, in terms of sample loading volume and flow-rate, to that expected for a conventional, anion-exchange material. The main purpose of this work was to then investigate the influence of competing matrix anions on the preconcentration process. The effects of matrix anions were initially studied by preconcentrating a mixture containing 100  $\mu\text{g/l}$  of fluoride, acetate, formate, chloride, nitrite, sulfate and oxalate for increasing time intervals. Fig. 3 shows examples of plots of sample volume versus peak area for two of the weakly retained anions, fluoride (a) and formate (b), for a moderately retained anion, chloride (c) and for a strongly retained anion, sulfate (d).

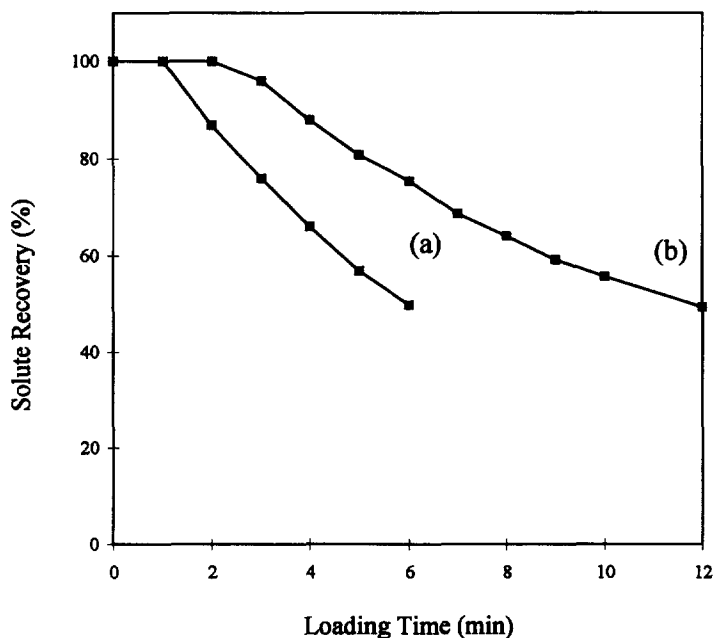


Fig. 2. Effect of flow-rate on fluoride peak recovery. Conditions: as for Fig. 1, except for sample, 400  $\mu\text{g/l}$  fluoride solutions preconcentrated at flow-rates of 5.0 (a) and 2.5 (b) ml/min.

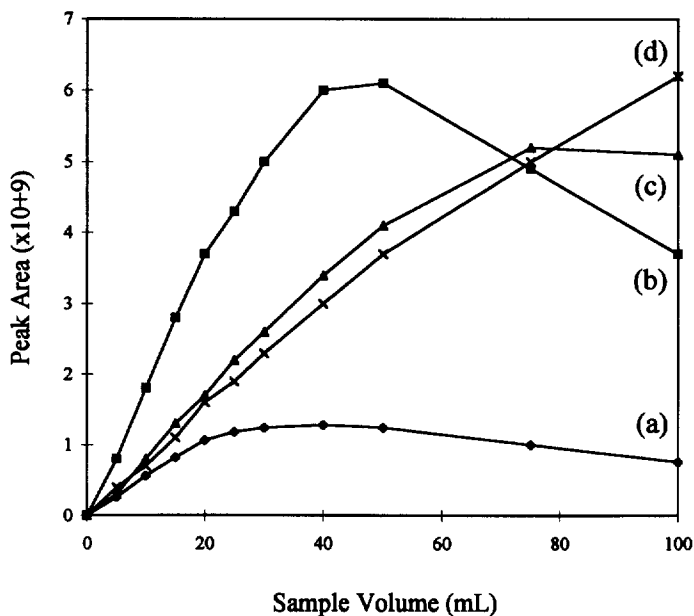


Fig. 3. Influence of sample matrix ions on peak response. Conditions: as for Fig. 1, except for sample, 100  $\mu\text{g/l}$  mixture of fluoride (a), formate (b), chloride (c), and sulfate (d) pre-concentrated at a flow-rate of 5.0 ml/min.

For the weakly retained anions, fluoride, acetate and formate, the peak response increased with sample volume in a linear fashion up to a maximum point, beyond which the response rapidly decreased, as shown for fluoride (a) and formate (b) in Fig. 3. The 'breakthrough' point, i.e. the point at which the peak response started to decrease, was related to the molar concentration of each anion and its selectivity towards the ion-exchange resin. Less fluoride could be quantitatively loaded on the resin than acetate than formate, as would be expected from the relative ion-exchange affinities of the three solutes. The moderately retained anions, chloride and nitrite, displayed similar behaviours, although a greater volume of sample could be loaded before the peak response started to decrease, as shown for chloride in Fig. 3c. The peak response for the strongly retained anions, sulfate and oxalate, continued to increase with increasing sample volume over the time period investigated, as shown for sulfate in Fig. 3d.

During the initial stages of loading the mixture containing seven anions, the recoveries obtained for fluoride were similar to that observed for a solution containing fluoride only. A recovery of 92% was obtained after loading 10 ml of a 100  $\mu\text{g/l}$  fluoride

solution, compared to a recovery of 89% for fluoride loaded in the presence of 100  $\mu\text{g/l}$  of the other anions. Similarly, a recovery of 84% was obtained after loading 20 ml of the 100  $\mu\text{g/l}$  fluoride solution, compared to a recovery of 83% for fluoride loaded in the presence of the other anions. However, the peak response (hence recovery) for fluoride started to decrease rapidly beyond this point, as shown in Fig. 3a, indicating that the sample matrix anions were now reducing the ability of fluoride to bind to the concentrator column. The recoveries of the other weakly retained anions were also affected by the presence of the sample matrix anions, although to a lesser extent than the most weakly retained (fluoride) ion.

In order to further investigate the effect of competing matrix anions, solutions of fluoride, in the presence of other anions, were then pre-concentrated on the AC10 concentrator column. Fig. 4 shows the fluoride peak response obtained when increasing volumes of 100  $\mu\text{g/l}$  fluoride were pre-concentrated in the absence of other ions (a) and in the presence of 100  $\mu\text{g/l}$  of formate (b), chloride (c) and sulfate (d). Initially, similar recoveries were obtained for fluoride pre-concentrated in the absence of other ions and

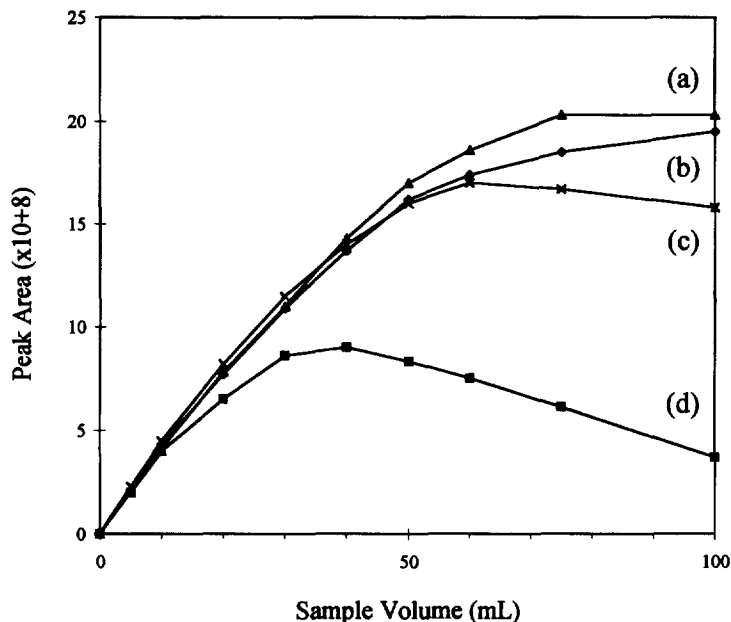


Fig. 4. Effect of formate, chloride or sulfate on fluoride peak response. Conditions: as for Fig. 1, except for sample, 100  $\mu\text{g/l}$  of fluoride (a), 100  $\mu\text{g/l}$  of fluoride and formate (b), 100  $\mu\text{g/l}$  of fluoride and chloride (c) and 100  $\mu\text{g/l}$  of fluoride and sulfate (d) preconcentrated at a flow-rate of 5.0 ml/min.

in the presence of either formate or chloride. For instance, a recovery of 80% was obtained after loading 50 ml of a 100  $\mu\text{g/l}$  fluoride solution, compared to a recovery of 83% for fluoride loaded in the presence of formate and 78% for fluoride loaded in the presence of chloride. Beyond this point, the peak response for fluoride was somewhat lower in the presence of either formate or chloride than if loaded in the absence of these anions, hence, these anions only had a modest effect on fluoride recovery.

However, the presence of a strongly retained anion (sulfate) had a more significant effect on the recovery obtained for fluoride. A recovery of only 40% was obtained for fluoride after loading 50 ml of a 100  $\mu\text{g/l}$  fluoride solution in the presence of 100  $\mu\text{g/l}$  sulfate, compared to 80% for fluoride loaded in the absence of sulfate. The fluoride recovery decreased rapidly beyond this point, despite the fact that sulfate was present at a lower molar concentration; approximately 1:5 in this case. Therefore, the presence of sulfate significantly reduces the capacity of the concentrator column to quantitatively bind weakly retained solutes. The resin used for the AS10 and AC10 columns was specifically optimized, in terms

of capacity and selectivity, to give maximum retention of fluoride and acetate, yet permit only moderate retention of divalent hydrophilic anions, such as sulfate. For instance, the  $k'$  values for fluoride and sulfate are 0.23 and 4.5, respectively, upon the AS10 analytical column, compared to 0.22 and 8.5 upon a Dionex AS4A column, which has a conventional ion-exchange selectivity [7]. Consequently, the impact of sulfate on the recoveries of the weakly retained ions, fluoride, acetate and formate, is less than would be expected for the same solutes if a conventional ion-exchange concentrator column was used, due to the unique selectivity of the AC10 packing material.

Indeed, sulfate has been previously observed to have a very significant impact upon solute recoveries, even for moderately retained anions, such as chloride and nitrite, when performing sample preconcentration upon surface-aminated, polystyrene (PS)-DVB ion-exchange resins [13]. Therefore, both the ion-exchange selectivity and the capacity of the concentrator column are important when preconcentrating samples containing inorganic anions and organic acids. Obviously, the capacity of the concen-

trator column has to be sufficiently high to trap ions from a reasonable volume of sample; and the selectivity of the packing material should permit maximum retention of solutes such as fluoride and formate, yet allow only moderate retention of anions, such as sulfate and oxalate. The results shown in Figs. 3 and 4 indicate that the AC10 concentrator column has the appropriate selectivity and sufficient capacity to permit quantitative recoveries for all ions in 10–15 ml of a sample containing 100  $\mu\text{g/l}$  each of fluoride, acetate, formate, chloride, nitrite, sulfate and oxalate. This amount is certainly more than adequate for the concentration range required for ultrapure water analysis, although these results indicate that low recoveries will occur when preconcentrating large volume samples containing weakly retained solutes in the presence of modest (mid-to-low  $\mu\text{g/l}$ ) levels of strongly retained anions.

#### 4. Conclusions

Sample preconcentration is a complex process and the selection of appropriate sample loading parameters are critical to its success. The sample loading behaviour of the AC10 concentrator column was found to be similar to that previously observed for solutes preconcentrated upon surface-aminated ion-exchange resins. Increasing sample volumes reduced the recovery of weakly retained solutes that were preconcentrated upon the AC10 concentrator column, while the flow-rate at which the sample was loaded did not affect solute recovery, at least for flow-rates up to 5.0 ml/min. The presence of sample

matrix ions also affects the recoveries of weakly retained solutes. Formate and chloride were found to modestly decrease the recovery of fluoride, while the presence of sulfate had a more significant impact. The extent to which sample matrix ions influence solute recovery is dictated largely by the ion-exchange selectivity of the concentrator column. The most appropriate selectivity for the preconcentration of samples containing inorganic anions and organic acids is one that allows maximum retention of solutes such as fluoride and formate, yet only moderate retention of anions such as sulfate and oxalate.

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