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# Preconcentration determination of inorganic anions and organic acids in power plant waters

## Separation optimization through control of column capacity and selectivity

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### Abstract

An anion-exchange column has been developed for the separation of anions in power plant waters. The column has been 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. This new moderate capacity anion-exchange column was utilised for the preconcentration ion chromatography (IC) determination of key anions, at low  $\mu\text{g/l}$  levels, in a number of power plant waters. Correlation coefficients obtained for linearity plots of fluoride, acetate, formate, chloride, nitrite, sulfate and oxalate in pure water, ammoniated and morpholinated waters were in the range 0.996–0.999. The correlation coefficients obtained for the seven anions in borated water were in the range 0.995–0.999, except for fluoride and chloride, which were 0.993 and 0.991, respectively.

*Keywords:* Water analysis; Optimization; Sample preparation; Stationary phases, LC; Inorganic anions; Organic acids

### 1. Introduction

Monitoring the presence and movement of impurities in feed waters, boiler waters, steam condensate and cooling waters at power plants, both fossil-fired and nuclear, is of critical importance [1–3]. Water-borne impurities, present at sub- $\mu\text{g/l}$  levels, can build up through concentration mechanisms at significant quantities in the steam generators and turbines. These impurities initiate and propagate stress corrosion cracking in steam generator tubing, turbines and recirculation piping, resulting in decreased heat transfer efficiency; and eventually a loss

in generation capability [1]. Such damage can be minimized by maintaining impurity levels as low as possible and by taking an active role in identifying sources of the impurities.

Ion chromatography (IC) has become an increasingly important technique for the determination of extremely low levels of ionic impurities found in power plant waters [1–6], and other similar samples [7–10]. Typically, isocratic separations are used in conjunction with sample preconcentration to achieve the determination of  $\mu\text{g/l}$  levels of common inorganic anions, such as chloride, nitrate, phosphate and sulfate [5]. However, ionic strength gradients have been required in order to resolve weakly retained organic acid anions and still elute the strongly

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retained solutes, e.g. phosphate and sulfate, within a reasonable time [1]. Hydroxide or borate eluents are typically used for gradient elution, as they allow resolution of a wide range of anionic solutes; however, this approach generally suffers from the fact that peak response can be matrix dependent, and also the baseline shift during gradient elution limits sensitivity [11].

This paper discusses the strategy of using a moderate capacity, anion-exchange stationary phase with a unique selectivity that allows the isocratic separation of both weakly and strongly retained anions in approximately 20 min. This column eliminates the need for gradient separations, improving detection limits and method reliability for preconcentration IC analysis of power plant waters.

## 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 Dionex 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. After passing through the suppressor, the regenerant solution was directed to a Dionex Auto-Regen Module, in order to allow continuous suppression over extended time periods. A Dionex Ion-Pac AS10 (250×4 mm I.D.) analytical column and AC10 (50×4 mm I.D.) concentrator column were used with an eluent of 0.085 *M* sodium hydroxide, operated at a flow-rate of 1.0 ml/min. Dionex AI-450 chromatography software was used for system control and data collection.

### 2.2. Reagents and procedures

All solutions were prepared from reagent-grade chemicals in 18 M $\Omega$  water, obtained from a Milli-Q Plus water purification system (Millipore, Bedford, MA, USA). Commercially available (Dionex), 1000  $\mu$ g/ml inorganic anion standards were used, while 1000  $\mu$ g/ml solutions of acetate, formate and oxalate

were prepared from their reagent grade sodium salts (Fluka, Ronkonkoma, NY, USA).

On-line sample preconcentration was performed in the usual manner, i.e. the injection loop was replaced with a short 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]. The samples were delivered using a sample loading pump, operated at flow-rates of 1.0 to 3.0 ml/min. After initial optimization of the system, a concentration volume of 10 ml was chosen for all samples. Mixed standards, containing fluoride, acetate, formate, chloride, nitrite, sulfate and oxalate were prepared daily over the concentration range of 0.5, 1, 3, 5, 10 and 20  $\mu$ g/l. All samples were prepared in 100 ml polypropylene containers which had been previously rinsed with 18 M $\Omega$  Milli-Q water. Sample blanks were treated exactly in the same manner as samples. All sample measurements were performed in triplicate.

## 3. Results and discussion

### 3.1. Separator column development

The object of this work was to develop a method based on an anion-exchange stationary phase for use with preconcentration ion chromatography that allowed the isocratic separation of fluoride, acetate, formate, chloride and sulfate in less than 20 min. A further goal was to characterize a concentrator column which allowed quantitative retention of these ions from deionized water and other matrices, including borated and morpholinated waters. The requirement to achieve quantitative preconcentration in the last two matrices is an important one, as both additives are routinely used in the power industry. In a nuclear reactor, boric acid is usually added (~1%) to the primary cooling water to control the rate of fusion by absorbing neutrons; while ammonia or morpholine are added to the secondary loop of power plants to control pH and oxygen [1].

The isocratic separation of the important anions fluoride, acetate, formate, chloride and sulfate is difficult to achieve (within a reasonable run time) using conventional ion-exchange columns. One pos-

sible solution which allows resolution of weakly retained anions, such as fluoride and acetate, yet gives reasonable run times for the strongly retained sulfate ion, is to use a moderate to high capacity column in conjunction with a monovalent eluent, e.g. hydroxide. The high column capacity should permit suitable retention of fluoride and acetate, while a monovalent eluent best exploits the differences in ion-exchange selectivity between divalent and monovalent analytes. In IC, a plot of the log of analyte capacity factor ( $K'_A$ ) vs. log eluent concentration [E], results in a straight line with a negative slope equal to the ratio of the valency of the analyte ion to that of the eluent ion [12,13]. Therefore, an increase in the concentration of a monovalent eluent decreases the retention of a divalent analyte twice as rapidly as that of a monovalent analyte.

Furthermore, the use of a high capacity column should provide the degree of matrix independence necessary for dealing with high ionic strength samples, such as borated or morpholinated water, and also for the large water dip typically associated with sample preconcentration [4,5]. In addition to an appropriate capacity and selectivity, it was also desirable that the column provide good chromatographic efficiency. Consequently, the primary goal of this work was to characterize a stationary phase which has a moderate to high ion-exchange capacity, an appropriate selectivity for this application, which allows the isocratic separation of fluoride, acetate, formate, chloride and sulfate within a reasonable period of time, and good chromatographic efficiency.

The stationary phase material developed utilised a high porosity substrate, consisting of ethylene vinylbenzene–divinylbenzene (50:50, w/w) polymer, which was sulfonated and then coated with a layer of anion-exchange latex. The vinylbenzyl-chloride latex particles were cross-linked with 5% divinylbenzene and fully functionalized with an appropriate tertiary amine to generate the desired selectivity [14]. The highly porous nature of the substrate increased the surface area of resin, providing more active sulfonated sites for attraction of the oppositely-charged latex particles. The pores in the substrate were approximately 2000 Å, while the latex was approximately 60 Å in diameter. Therefore, the latex could penetrate the pores, creating an anion-exchange monolayer on both the internal and external surfaces

of the substrate. As a result, virtually all of the high surface area of the macroporous substrate was bonded with latex particles.

The columns initially produced using the material described above resulted in excessive retention times for sulfate. To further reduce sulfate retention, without significantly affecting monovalent retention, the ion-exchange site density in the latex was decreased by adding a “monomer spacer” to the latex polymerization system. This prevented a certain proportion of the total number of possible sites from being functionalized, creating a packing material with the desired ion-exchange site density. In turn, the reduced site density allowed divalent ions to be retained more often by a single ion-exchange site, rather than two, resulting in lower retention times for divalent anions, such as sulfate. Hence, the resulting ion exchanger was a compromise between increased capacity and lower ion-exchange site density. Pursuing this column strategy, along with the use of a hydroxide eluent, allows for good resolution between the weakly retained monovalent solutes while still providing a reasonable analysis time for the divalent sulfate anion.

One negative consequence of using a latex with 5% cross-linking is that moderately retained hydrophobic anions, such as nitrate, exhibit long retention times on this column. Weakly retained monovalent ions tend to be hydrophobic and a somewhat high level of cross-linking was used as an alternative (to higher capacity) to gain increased retention for these solutes [14]. This resulted in reasonable retention of solutes, such as formate and acetate, without excessive retention of sulfate. This approach seemed a reasonable compromise, considering that the primary goal of this development was to allow the isocratic determination of acetate, formate, fluoride, chloride and sulfate in power plants waters, a matrix where nitrate is not routinely found.

True capacity factor ( $k'$ ) values cannot be obtained in a simple manner for pellicular columns, since this requires an accurate knowledge of the volume of the active stationary phase in the column [15]. Consequently, pellicular columns are perhaps best compared to conventional columns using the adjusted retention ( $t'_r$ ) values for each column. This value is defined as:

$$t'_r = t_r - t_m \quad (1)$$

Table 1  
Comparison of retention data for the AS10 and AS4A columns

Anion	$t_r$ (AS10) <sup>a</sup>	$t_r$ (AS4A) <sup>a</sup>	$t'_r$ (AS10) <sup>b</sup>	$t'_r$ (AS4A) <sup>b</sup>	$k'$ (AS10)	$k'$ (AS4A)
Fluoride	3.02	0.88	0.57	0.32	0.2326	0.2222
Chloride	9.18	1.43	6.73	1.42	2.7469	0.9861
Nitrite	12.26	1.75	9.81	2.06	4.0042	1.4306
Sulfate	13.40	6.86	10.95	12.28	4.4694	8.5278

<sup>a</sup> The flow-rates used for AS10 and AS4A columns were 1.0 and 2.0 ml/min, respectively.

<sup>b</sup> The adjusted retention values were normalized for flow-rate differences;  $t_m$  (AS10)=2.45 min and  $t_m$  (AS4A)=0.72 min.

where  $t_r$  is the total retention time for a solute and  $t_m$  is the retention time of the column void peak. Table 1 compares the retention times, adjusted retention and capacity factor values for several anions on the macroporous AS10 column and a Dionex AS4A, which is a conventional microporous, latex agglomerated column. This data clearly demonstrates the increased retention achieved for the monovalent anions, relative to that of the divalent anion (sulfate), when using the macroporous AS10 column.

### 3.2. Sample preconcentration

The principle function of any concentrator column is to quantitatively strip ions from a sample matrix without compromising the integrity of the analysis. For the determination of anions, the concentrator column must have adequate anion-exchange capacity to quantitatively trap solute ions from the sample solution; however, the capacity should be sufficiently low to permit the subsequent removal of the bound solute ions as a compact band. In addition, the concentrator column should have an appropriate selectivity which allows efficient removal of the bound solute ions with the eluent used for the separation step. Finally, it should have a low interstitial volume, in order to minimize the size of the water dip [16]. The concentrator column developed for this work used the same selectivity latex as the macroporous AS10 column but the substrate was microporous, hence the latex only covered the exterior surface of the resin. This modification minimized the interstitial liquid present in the concentrator column, thus reducing the size of the water dip.

Sample loading on the concentrator column was performed using a separate, positive displacement

pump. Because the kinetics of mass transfer on pellicular ion-exchange resins is very rapid, the sample could be quantitatively loaded onto the concentrator column at flow-rates of 2–3 ml/min. A more detailed study on the effects of sample loading times and flow-rates will be discussed in detail in a subsequent paper. Fig. 1 shows the chromatogram obtained from preconcentrating 5.0 ml of a standard containing fluoride, acetate, formate, chloride, nitrite, sulfate and oxalate (0.5–1.0 µg/l) upon the Ion-Pac AC10 concentrator column, followed by separation with 0.085 M NaOH upon the Ion-Pac AS10 analytical column. During the preconcentration of more complex samples matrices, such as borated water, it was found to be necessary to wash the concentrator column with as much as 3 ml of deionized water prior to the sample “strip” step, in order to minimize any interferences caused by borate during the analysis [6]. The incorporation of this “wash” step into the preconcentration procedure resulted in good peak shapes for the trace level anions, even in samples containing as much as 1.2% boric acid, as shown in

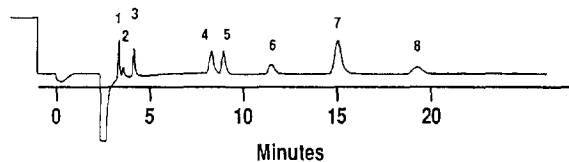


Fig. 1. Trace level anions in ultra-pure water. Conditions: analytical column, Dionex Ion-Pac AS10; concentrator column, Dionex Ion-Pac AC10; eluent, 0.085 M sodium hydroxide; flow-rate, 1.0 ml/min; detection, suppressed conductivity; regenerant, 0.05 M sulfuric acid at 10 ml/min; sample, 5.0 ml deionized water preconcentrated at a flow-rate of 2.0 ml/min; Solutes: (1) fluoride (0.5 µg/l), (2) acetate (1 µg/l), (3) formate (1 µg/l), (4) carbonate, (5) chloride (1 µg/l), (6) nitrite (1 µg/l), (7) sulfate (1 µg/l) and (8) oxalate (1 µg/l).

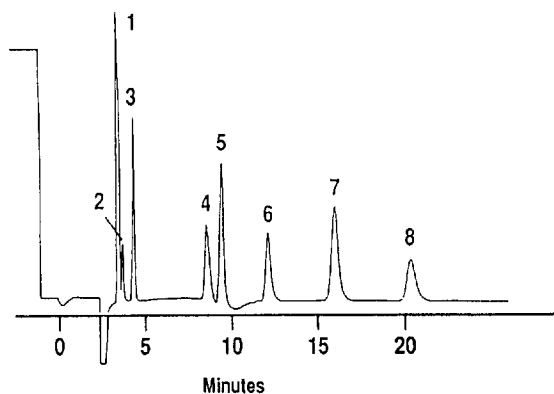


Fig. 2. Trace level anions in borated water. Conditions: as for Fig. 1, except sample, 10 ml water containing 1.2% boric acid preconcentrated at a flow-rate of 2.0 ml/min; Solutes: (1) fluoride (4  $\mu\text{g/l}$ ), (2) acetate (8  $\mu\text{g/l}$ ), (3) formate (8  $\mu\text{g/l}$ ), (4) carbonate, (5) chloride (8  $\mu\text{g/l}$ ), (6) nitrite (8  $\mu\text{g/l}$ ), (7) sulfate (8  $\mu\text{g/l}$ ) and (8) oxalate (8  $\mu\text{g/l}$ ).

Fig. 2. This same procedure could also be applied successfully to the preconcentration of anions in other complex samples, such as water containing ammonium hydroxide and morpholine, as shown in Figs. 3 and 4, respectively.

The correlation coefficients ( $R^2$ ) obtained for linearity plots of the seven important anions, fluoride, acetate, formate, chloride, nitrite, sulfate and oxalate, in pure water were all  $>0.999$ , except for acetate, which was 0.998. However, in the case of acetate, this result was most likely due to the instability of acetate ions in aqueous solutions and the resulting difficulty in making stable standards,

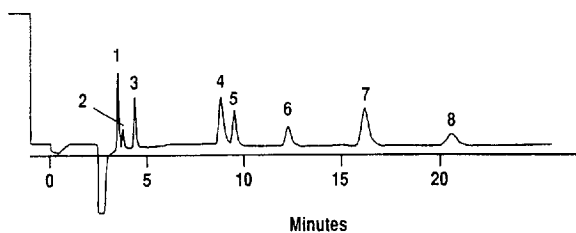


Fig. 3. Trace level anions in ammoniated water. Conditions: as for Fig. 1, except sample, 10 ml water containing 2  $\mu\text{g/ml}$  ammonium hydroxide preconcentrated at a flow-rate of 2.0 ml/min; Solutes: (1) fluoride (1  $\mu\text{g/l}$ ), (2) acetate (2  $\mu\text{g/l}$ ), (3) formate (2  $\mu\text{g/l}$ ), (4) carbonate, (5) chloride (2  $\mu\text{g/l}$ ), (6) nitrite (2  $\mu\text{g/l}$ ), (7) sulfate (2  $\mu\text{g/l}$ ) and (8) oxalate (2  $\mu\text{g/l}$ ).

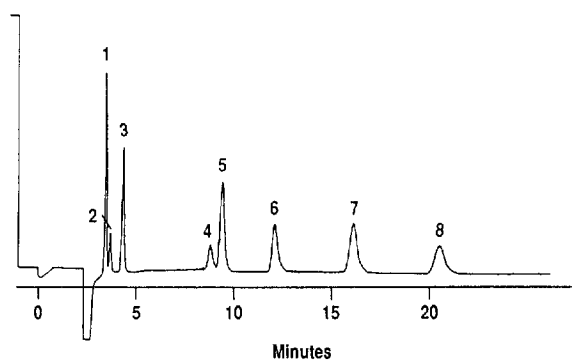


Fig. 4. Trace level anions in morpholinated water. Conditions: as for Fig. 1, except sample, 10 ml water containing 20  $\mu\text{g/ml}$  morpholine preconcentrated at a flow-rate of 2.0 ml/min; Solutes: (1) fluoride (2  $\mu\text{g/l}$ ), (2) acetate (4  $\mu\text{g/l}$ ), (3) formate (4  $\mu\text{g/l}$ ), (4) carbonate, (5) chloride (4  $\mu\text{g/l}$ ), (6) nitrite (4  $\mu\text{g/l}$ ), (7) sulfate (4  $\mu\text{g/l}$ ) and (8) oxalate (4  $\mu\text{g/l}$ ).

rather than any problems associated with the preconcentration process. The peak area precision for the seven anions was  $<10\%$  R.S.D. for 20 replicate injections at the 10  $\mu\text{g/l}$  level, when preconcentrating a 10-ml volume. The linearity results obtained for the preconcentration of a number of spiked power plant waters are summarized in Table 2. While the correlation coefficients obtained for the seven anions in ammoniated and morpholinated matrices were not as good as those for pure water, they still were in an acceptable range of 0.996–0.999.

The correlation coefficients obtained for the seven anions in 1.2% boric acid were in the range 0.995–0.999 for all the ions, except for fluoride and chloride which were 0.993 and 0.991, respectively. In the case of fluoride, the poor result may be due to the formation of  $\text{BF}_4^-$ , or other borate–fluoride complexes [i.e. hetero-ligand complexes, such as  $\text{B}(\text{OH})_3\text{F}^-$  or  $\text{B}(\text{OH})_2\text{F}_2^-$ ], in the sample or concentrator column. This, in turn, could lead to low recoveries under some conditions, particularly as the formation of these complexes is both pH and concentration dependent [17]. In the case of chloride, the low correlation coefficient was almost certainly due to the elution of boric acid, as a negative dip near chloride, which made peak integration difficult at low concentrations. Although the vast majority of borate was removed from the concentrator column during the wash step, there is still some possibility

Table 2  
Linearity results (correlation coefficients –  $R^2$ ) obtained for the preconcentration of spiked power plant waters

Anion	Range ( $\mu\text{g/l}$ )	Pure water <sup>a</sup> ( $R^2$ )	Ammonia <sup>b</sup> ( $R^2$ )	Morpholine <sup>c</sup> ( $R^2$ )	Boric acid <sup>d</sup> ( $R^2$ )
Fluoride	0.5–10	0.999	0.998	0.999	0.993
Acetate	1–20	0.998	0.999	0.996	0.999
Formate	1–20	0.999	0.997	0.999	0.998
Chloride	1–20	0.999	0.996	0.998	0.991
Nitrite	1–20	0.999	0.998	0.999	0.995
Sulfate	1–20	0.999	0.997	0.999	0.997
Oxalate	1–20	0.999	0.998	0.998	0.996

<sup>a</sup> A 10-ml volume was preconcentrated for all samples.

<sup>b</sup> Ammonia was present at 2  $\mu\text{g/ml}$ .

<sup>c</sup> Morpholine was present at 20  $\mu\text{g/ml}$ .

<sup>d</sup> Boric acid was present at 1.2%.

for borate to interfere in quantitative analysis of chloride.

#### 4. Conclusions

A method based on a moderate capacity, macroporous anion-exchange column has developed that is able to isocratically separate weakly retained organic acid anions, such as acetate, formate and fluoride, as well as strongly retained anions, such as sulfate, in less than 20 min. This method also allows good resolution of the weakly retained anions away from the water dip. A microporous concentrator column with the same selectivity was used, allowing the preconcentration determination of the seven important anions, fluoride, formate, chloride, nitrite, sulfate and oxalate, down to sub- $\mu\text{g/l}$  levels. Excellent linearity was obtained for the preconcentration of all solutes in pure water, ammoniated and morpholinated waters; while the correlation coefficients for the seven anions in borated water were in the range 0.995–0.999, except for fluoride and chloride, which were 0.993 and 0.991, respectively. A more detailed study on the effects of sample loading times and flow-rates will be discussed in a subsequent paper.

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