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# Determination of anions at trace levels in power plant water samples by ion chromatography with electrolytic eluent generation and suppression

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## Abstract

An ion chromatographic method was developed for the determination of nine inorganic and organic acid anions at sub- to low- $\mu\text{g}/\text{l}$  levels in power plant water samples. In this method, samples were injected using a large-volume direct injection technique, the analyte anions were separated on a hydroxide-selective anion-exchange column using high-purity hydroxide eluents generated by an on-line electrolytic eluent generator and detected using the suppressed conductivity detection method. The method performance was evaluated by analyzing synthetic water samples containing additives encountered in the power plant water samples and four water samples from a fossil fuel power plant. The relative standard deviations of retention times of analyte ions separated on the hydroxide-selective anion-exchange column were less than 0.4%. The recoveries of analyte ions spiked into the synthetic water samples at concentrations of 0.13–1.0  $\mu\text{g}/\text{l}$  were in the range of 70–120%. The method detection limits for analyte ions in deionized water were 0.0099, 0.0056, 0.019, 0.057, 0.0084, 0.023, 0.067, 0.037, and 0.079  $\mu\text{g}/\text{l}$  for fluoride, acetate, formate, chloride, nitrite, sulfate, bromide, nitrate, and phosphate, respectively. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Water analysis; Inorganic anions; Organic acids

## 1. Introduction

It is essential for power plants to monitor the presence and movement of ionic impurities in various water streams used in the power generation process including feed water, boiler water, steam, and cooling water [1–3]. The presence of corrosive anionic species such as chloride and sulfate in the process water streams even at low- $\mu\text{g}/\text{l}$  levels can make the stainless steel components of a power plant, such as steam generators, boiler tubes, and

turbine blades, susceptible to stress corrosion cracking. The minimization of the concentrations of corrosive ions in the boiler feed water and in the effluent from the condensate polisher reduces the corrosion damage to various system components. The measurement of ionic impurities throughout the power generation process can provide valuable information regarding the source of contamination, the likely rates of contaminant build-up, and probable rates of corrosion, as well as extremely useful and timely data during the start-up and shut-down of power plants. The reliable and accurate determination of anions in power plant water samples at sub- to low- $\mu\text{g}/\text{l}$  levels is a challenging analytical problem. Over the past 20 years, ion chromatography

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(IC) has become an indispensable technique for addressing this problem because IC offers the unique capability to separate and identify individual ionic species at sub- to low- $\mu\text{g}/\text{l}$  levels [4–10].

There have been several recent advances in IC that have improved the determination of anions at trace levels. First, new and improved hydroxide-selective anion-exchange separation columns offer unique selectivity to separate inorganic and organic anions of interest for target applications [11–15]. Dilute solutions of alkali hydroxides are used as eluents for hydroxide-selective separation columns. Hydroxide eluents are ideal for both isocratic and gradient elution in IC because they are converted to water in the suppressor and the hydroxide concentration has little effect on background conductance. Thus, IC using hydroxide-selective columns can offer significant advantages in the determination of anions of interest at trace levels. Secondly, an electrolytic device capable of on-line electrolytic generation of high-purity carbonate-free potassium hydroxide eluents was introduced [10,16]. The preparation of carbonate-free alkali hydroxide eluents by conventional means is difficult because carbonate may be introduced as an impurity from the source chemical or by adsorption of carbon dioxide from the air. The presence of carbonate in hydroxide eluents often compromises the performance of an IC method. The carbonate contamination can cause undesirable chromatographic baseline drift during the hydroxide gradient, and possibly irreproducible retention times of target analytes. The on-line electrolytic potassium hydroxide eluent generator eliminates these problems and provides an ideal source of eluents for use with hydroxide-selective anion-exchange columns. The third recent advance in IC was the development of new and improved electrolytic suppressors [17,18]. These new electrolytic suppressors improve the determination of anions at trace levels because they offer several advantages such as ease of use, low baseline noise, and fast equilibration.

In this paper, we report a new IC method that utilizes the recent advances in IC for the determination of target anions at sub- to low- $\mu\text{g}/\text{l}$  levels in power plant water samples. In this method, the water sample is injected using the large-loop direct injection technique, the analyte anions are separated on a new hydroxide-selective anion-exchange column

using high-purity potassium hydroxide eluents generated by an on-line electrolytic eluent generator and detected using the suppressed conductivity detection method. The performance of the new method was evaluated by analyzing synthetic water samples containing additives encountered in the power plant water samples as well as water samples from a fossil fuel power plant.

## 2. Experimental

### 2.1. Instrumentation

A Dionex DX 600 IC system (Dionex, Sunnyvale, CA, USA) consisting of a GS50 gradient pump, an EG40 eluent generator module, an LC25 chromatography module, and an ED40 conductivity detector was used in the experiments. A PeakNet 6.2 chromatography workstation was used for instrument control, data collection, and processing. An EGC-KOH cartridge was installed in the EG40 eluent generator and used to generate potassium hydroxide eluents on-line. To remove trace amounts of dissolved carbon dioxide and anionic contaminants in the deionized water, a Dionex ATC-1 column (24 mm  $\times$  9 mm) packed with a high-capacity anion-exchange resin in the hydroxide form was installed between the pump outlet and the inlet of the EGC-KOH cartridge. The LC25 chromatography module maintained the temperature of the guard and separator columns and the conductivity cell at 30 °C. A sample loop with a volume of 1000  $\mu\text{l}$  was made from a length of 0.030-in. I.D. polyether ether ketone (PEEK) tubing and its volume was verified by measuring the mass difference between the sample loop filled with deionized water and the empty loop (1 in. = 2.54 cm). The separations of target analyte anions were performed on IonPac AS15-5  $\mu\text{m}$  (150 mm  $\times$  3 mm I.D.) and AG15-5  $\mu\text{m}$  (30 mm  $\times$  3 mm I.D.) columns. An Anion Atlas Electrolytic Suppressor (AAESTM) operated in the recycle mode was used as the suppressor. Details of the IC system operating conditions are presented in Table 1.

### 2.2. Reagents, samples, and procedures

A stock standard solution containing 20 mg/l

Table 1  
IC system operating conditions

Columns:	IonPac AS15, 5 $\mu\text{m}$ (150 $\times$ 3 mm) IonPac AG15, 5 $\mu\text{m}$ (30 $\times$ 3 mm)				
Trap columns:	IonPac ATC-1 Trap, 4 mm				
Eluent:	KOH (source: EG40)				
Temperature:	30 $^{\circ}\text{C}$				
Pump program:	Time (min)	Flow (ml/min)	A (%)	Valve	EG40 Conc. (mM)
	0.0	0.50	100	Load	40
	0.01	0.50	100	Load	7.0
	3.0	0.50	100	Inject	7.0
	8.0	0.50	100	Inject	7.0
	15	0.50	100	Inject	40
	25	0.50	100	Load	40
	30	0.50	100	Load	40
Injection volume:	1000 $\mu\text{l}$				
Detection:	Suppressed conductivity				
Suppressor:	Anion Atlas electrolytic suppressor, recycle mode				
Suppressor current setting:	50 mA				

fluoride, 30 mg/l chloride, 100 mg/l nitrite, 100 mg/l bromide, 100 mg/l nitrate, 150 mg/l phosphate, and 150 mg/l sulfate, available from Dionex (P/N 56933), was used in this study. Sodium acetate (99.99%) and sodium formate (99.99%), obtained from Aldrich (Milwaukee, WI, USA), were used to prepare a stock standard solution containing 100 mg/l acetate and 100 mg/l formate. The two stock standard solutions were used to prepare a composite standard solution containing 0.40 mg/l fluoride, 3.0 mg/l acetate, 3.0 mg/l formate, 0.60 mg/l chloride, 2.0 mg/l nitrite, 3.0 mg/l sulfate, 2.0 mg/l bromide, 2.0 mg/l nitrate, and 3.0 mg/l phosphate. The calibration standard solutions were prepared daily by diluting the composite standard solution to the expected concentration range for the target anions using deionized water.

Deionized water with a specific resistance of 18.2 M $\Omega$  cm from a Milli-Q Plus deionized water system (Millipore, Bedford, MA, USA) was used to prepare all the solutions. Extreme caution was taken to prevent any possible contamination from the environment and the sample handling when preparing all trace-level calibration standard solutions. All calibration standards and spiked samples were stored

in polyethylene containers that had been thoroughly cleaned and presoaked in deionized water for at least 24 h.

Hydrazine (99.8%) and ethanolamine (>99.5%) were obtained from Aldrich; ammonium hydroxide (trace metal grade, 20–22%) was obtained from Fisher Scientific (Pittsburgh, PA, USA); boric acid (99.8%) was obtained from BDH (Poole, UK); and sodium carbonate (ACS grade) was obtained from EM Science (Gibbstown, NJ, USA). These chemicals were used as additives to prepare synthetic matrices without further purification. To simulate the water sample matrices encountered in the power plant operation, four synthetic water samples were prepared using deionized water and additives including hydrazine, ethanolamine, ammonium hydroxide, boric acid, and sodium carbonate. Table 2 summarizes the concentrations of additives in the four synthetic water samples. The synthetic water samples were spiked with 0.13  $\mu\text{g/l}$  fluoride, 1.0  $\mu\text{g/l}$  acetate, 1.0  $\mu\text{g/l}$  formate, 0.20  $\mu\text{g/l}$  chloride, 0.67  $\mu\text{g/l}$  nitrite, 1.0  $\mu\text{g/l}$  sulfate, 0.67  $\mu\text{g/l}$  bromide, 1.0  $\mu\text{g/l}$  nitrate, and 1.0  $\mu\text{g/l}$  phosphate.

Four power plant water samples, including main steam, condensate pump discharge, economizer inlet

Table 2  
Composition of synthetic water sample matrices studied

Component	Added concentration (mg/l)			
	Matrix I	Matrix II	Matrix III	Matrix IV
Hydrazine	0	0.1	0.1	0.1
Ethanolamine	0	3.0	3.0	3.0
Boric acid	0	10.0	10.0	10.0
Ammonium	0	0.04	0.04	0.04
Carbonate	0	0	1.0	2.0

water, and boiler drum water, were obtained from Four Corners Fossil Fuel Power Plant (Fruitland, NM, USA) operated by Arizona Public Services. The samples were analyzed directly without any pretreatment. For the boiler drum water sample, 1000-fold dilution was also performed prior to analysis in order to quantify the concentrations of sulfate and phosphate due to the high concentrations of sulfate and phosphate present in the original sample.

To perform analysis of standards and sample solutions, the standard or sample was loaded into the sample loop with a 5-ml syringe. The six-port injection valve in the LC25 chromatography module was set up such that the syringe was used to pull the sample slowly into the 1000- $\mu$ l sample loop to avoid any possible contamination. To ensure that the system was free of contamination, the system was equilibrated with 40 mM KOH generated by the EG40 eluent generator at 0.5 ml/min for at least 30 min upon system start-up. The system cleanliness was verified by analyzing a deionized water blank prior to analyzing calibration standards and samples.

### 3. Results and discussion

#### 3.1. Optimization of chromatographic conditions

Various water streams used in the power plant operation contain inorganic anions such as chloride and sulfate as well as low-molecular-mass organic anions such as acetate and formate. In this study, the IonPac AS15-5  $\mu$ m column was chosen as the separation column because this newly-developed column is a hydroxide-selective anion-exchange column designed specifically for rapid and efficient separation of target analyte anions including fluoride,

acetate, formate, chloride, nitrite, sulfate, bromide, nitrate, and phosphate [19]. For accurate determination of target analyte ions at sub- to low- $\mu$ g/l levels, it is critical to maximize the analyte response while minimizing the chromatographic baseline noise. To increase the analyte response, the large-volume direct inject technique was used to inject 1000  $\mu$ l of sample in this method. Since the IonPac AS15-5  $\mu$ m column has sufficient ion-exchange capacity, no noticeable band broadening of analyte peaks was observed due to the loading of such large sample volume. The use of the large-volume direct injection technique eliminates the need for the sample pre-concentration step that typically involves the use of a concentrator column and is more cumbersome and time-consuming.

To minimize the chromatographic baseline noise, the use of anion Atlas electrolytic suppressors was investigated. The recently developed anion Atlas electrolytic suppressors are continuous electrolytically-regenerated suppressors designed mainly for the suppression of carbonate–hydrogen carbonate-based eluents in IC [17,18]. One of the key advantages of the anion Atlas electrolytic suppressor is that it provides very low chromatographic baseline noise (typically 1–2 nS/cm) even when it is operated in the recycle mode. The suppression capacity of the anion Atlas suppressor is 25-mN eluent at 1.0 ml/min. This study determined the maximum concentration of KOH eluents at 0.5 ml/min that could be suppressed effectively using the anion Atlas suppressors. Three anion Atlas suppressors were tested. The results showed that the anion Atlas suppressors were able to suppress up to 45 mM KOH at 0.5 ml/min. Table 3 summarizes the typical baseline noise values

Table 3  
Typical baseline noise values obtained using KOH eluents and anion Atlas electrolytic suppressors

Suppressor unit	Average baseline noise <sup>a</sup> (nS/cm)		
	30 mM KOH	40 mM KOH	45 mM KOH
1	0.3	0.5	0.6
2	0.9	0.8	0.6
3	0.6	1.0	0.8

The flow rate was 0.50 ml/min. The suppressors were operated in recycle mode with an operating current of 50 mA.

<sup>a</sup> Average peak-to-peak noise measured in 1-min segments over 20 min.

obtained using the anion Atlas electrolytic suppressors and KOH eluents of 30, 40, and 45 mM at 0.5 ml/min. When the suppressors were supplied with 50 mA of current and operated in the recycle mode, the average peak-to-peak noise measured in 1-min segments over 20 min ranged from 0.3 to 1.0 nS/cm.

Several factors were considered when optimizing the hydroxide gradient conditions for the separation of target analyte ions on the IonPac AS15-5  $\mu\text{m}$  column. First, the maximum concentration of the KOH eluent used in the gradient was limited to 45 mM during the hydroxide gradient so that the anion Atlas electrolytic suppressor could be operated within its effective suppression capacity. Second, the gradient condition was optimized to ensure good resolution of target analyte ions from borate since the power plant water samples might contain boric acid as an additive. In the optimized gradient separation, the concentration of the KOH eluent was maintained at 7 mM for 8 min to allow resolution of weakly retained ions such as fluoride, acetate, and formate. A hydroxide gradient from 7.0 to 40 mM KOH was then performed using the EG40 eluent generator to separate more strongly retained anions including chloride, nitrite, sulfate, bromide, nitrate, and phosphate. The separation was performed at 30 °C to ensure consistent retention times for the target analytes.

Fig. 1 shows a representative chromatogram obtained for a standard solution of nine target anions; the analyte concentrations in this standard ranged from 0.13  $\mu\text{g/l}$  for fluoride to 1.0  $\mu\text{g/l}$  for phosphate. The baseline shift during the hydroxide gradient was typically less than 60 nS/cm over a run time of 30 min. The minimal baseline shift during the gradient was due to the use of high purity carbonate-free hydroxide eluents generated by the EG40 KOH eluent generator. Because of low baseline noise, chromatographic peaks of target anions could be easily quantified. It is very important to establish a system blank in the determination of anions at trace levels. Fig. 2 shows a representative system blank chromatogram obtained for a sample of 18 M $\Omega$  cm laboratory-deionized water. Trace amounts of acetate (0.049  $\mu\text{g/l}$ ), formate (0.081  $\mu\text{g/l}$ ), and chloride (0.25  $\mu\text{g/l}$ ) in the sample originated from the point-of-use deionized water system were detected.

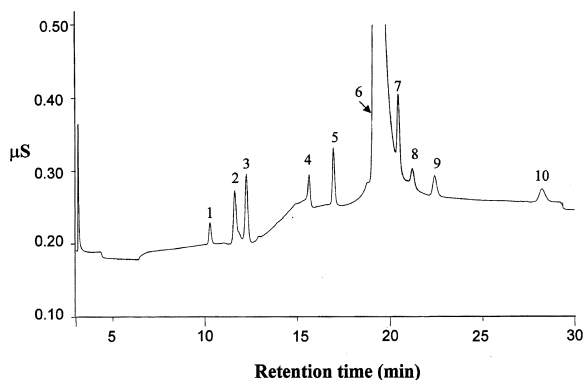


Fig. 1. A representative chromatogram obtained for the sample of 18 M $\Omega$  cm deionized water spiked with nine target anions. Peak identification and spike concentration: 1=fluoride (0.13  $\mu\text{g/l}$ ), 2=acetate (1.0  $\mu\text{g/l}$ ), 3=formate (1.0  $\mu\text{g/l}$ ), 4=chloride (0.2  $\mu\text{g/l}$ ), 5=nitrite (0.67  $\mu\text{g/l}$ ), 6=carbonate, 7=sulfate (1.0  $\mu\text{g/l}$ ), 8=bromide (0.67  $\mu\text{g/l}$ ), 9=nitrate (0.67  $\mu\text{g/l}$ ), and 10=phosphate (1.0  $\mu\text{g/l}$ ).

### 3.2. Evaluation of method performance

The method performance was evaluated by analyzing samples prepared from four synthetic water sample matrices that were designed to simulate those encountered in the power plant operation. The composition of the four synthetic water sample matrices is given in Table 2. Calibration curves for target anions were obtained using standards prepared in deionized water. The calibration standards and the linearity of calibration curve for each target anion are listed in Table 4. The results show that calibration

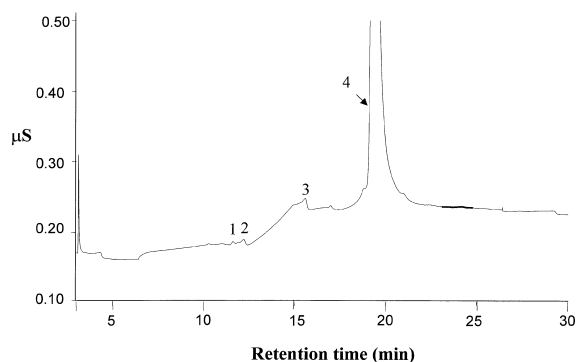


Fig. 2. A representative chromatogram obtained for the sample of 18 M $\Omega$  cm deionized water. Peak identification and concentration: 1=acetate (0.049  $\mu\text{g/l}$ ), 2=formate (0.081  $\mu\text{g/l}$ ), 3=chloride (0.25  $\mu\text{g/l}$ ), and 4=carbonate.

Table 4  
Calibration curve data for target anions in deionized water

Analyte	Concentration of calibration standards ( $\mu\text{g/l}$ )	Correlation coefficient ( $r^2$ )
Fluoride	0.013, 0.040, 0.13, 0.40, 1.3	0.9971
Acetate	0.10, 0.30, 1.0, 3.0, 10	0.9982
Formate	0.10, 0.30, 1.0, 3.0, 10	0.9988
Chloride	0.020, 0.060, 0.20, 0.60, 2.0	0.9993
Nitrite	0.067, 0.20, 0.67, 2.0, 6.7	0.9997
Sulfate	0.10, 0.30, 1.0, 3.0, 10	0.9990
Bromide	0.067, 0.20, 0.67, 2.0, 6.7	0.9971
Nitrate	0.067, 0.20, 0.67, 2.0, 6.7	0.9999
Phosphate	0.10, 0.30, 1.0, 3.0, 10	0.9999

curves for target anions had good linearity; the correlation coefficients ( $r^2$ ) of the calibration curves were 0.997 or greater.

Figs. 3 and 4 show the chromatograms obtained for a sample of Matrix III and a sample of Matrix III spiked with target anions at concentrations ranging from 0.13  $\mu\text{g/l}$  for fluoride to 1.0  $\mu\text{g/l}$  for phosphate. Matrix III was comprised of deionized water spiked with 0.1 mg/l hydrazine, 3.0 mg/l ethanolamine, 10 mg/l boric acid, 40  $\mu\text{g/l}$  ammonium and 1.0 mg/l carbonate. As shown in Fig. 3, an unknown anionic species eluted between fluoride and acetate, and borate originating from the boric acid added to the sample matrix eluted between formate and chloride. Since borate and the unknown anionic species in Matrix III were well separated from the target anions, they did not interfere with the de-

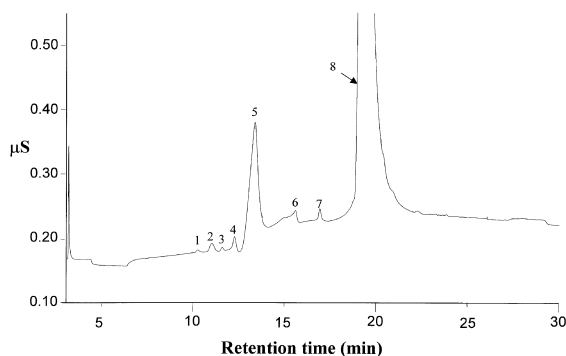


Fig. 3. A representative chromatogram obtained for the sample of Matrix III. Peak identification and concentration: 1=fluoride (0.023  $\mu\text{g/l}$ ), 2=unknown, 3=acetate (0.074  $\mu\text{g/l}$ ), 4=formate (0.30  $\mu\text{g/l}$ ), 5=borate, 6=chloride (0.22  $\mu\text{g/l}$ ), 7=nitrite (0.18  $\mu\text{g/l}$ ), and 8=carbonate.

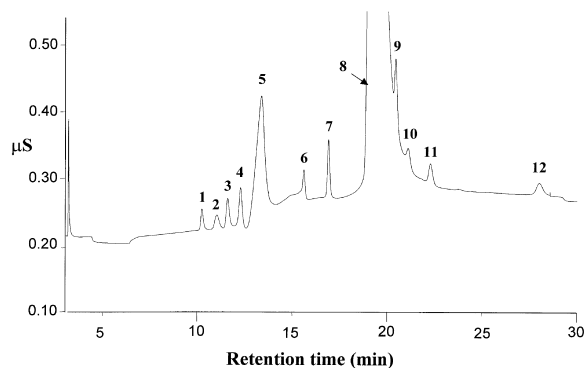


Fig. 4. A representative chromatogram obtained for the sample of Matrix III spiked with nine target anions. Peak identification and spike concentration: 1=fluoride (0.13  $\mu\text{g/l}$ ), 2=unknown, 3=acetate (1.0  $\mu\text{g/l}$ ), 4=formate (1.0  $\mu\text{g/l}$ ), 5=borate (unknown), 6=chloride (0.20  $\mu\text{g/l}$ ), 7=nitrite (0.67  $\mu\text{g/l}$ ), 8=carbonate (1.0 mg/l), 9=sulfate (1.0  $\mu\text{g/l}$ ), 10=bromide (0.67  $\mu\text{g/l}$ ), 11=nitrate (0.67  $\mu\text{g/l}$ ), 12=phosphate (1.0  $\mu\text{g/l}$ ).

termination of these target anions. The sample matrix was also designed to determine whether the method could be applied to the analysis of water samples containing increased amounts of carbonate. The concentration of carbonate in Matrix III was  $\sim 1000$  times of the concentration of sulfate. Although sulfate eluted on the shoulder of the carbonate peak, the sulfate peak could be quantified easily using this method because of low chromatographic baseline noise yielded by the anion Atlas electrolytic suppressor.

Table 5 summarizes the retention time reproducibility data for nine target anions separated on the IonPac AS15-5  $\mu\text{m}$  column obtained through the replicate analysis of samples prepared from the four synthetic water matrices. The results indicate that the retention times of target anions were essentially independent of the sample matrices and the relative standard deviations of retention times for nine consecutive measurements were less than 0.4%. The retention time reproducibility data obtained for target anions compare well with the results obtained in a previous study under similar conditions [10]. Experiments were also performed to determine the recoveries of nine target analyte ions spiked into the four synthetic water sample matrices at concentrations ranging from 0.13  $\mu\text{g/l}$  for fluoride to 1.0  $\mu\text{g/l}$  for sulfate and phosphate. The recoveries of target anions were calculated after the subtraction of the

Table 5  
Retention times and reproducibility data for target analyte anions

Analyte	Spiked concentration ( $\mu\text{g/l}$ )	Average retention time (min) $\pm$ RSD (%) <sup>a</sup>			
		Matrix I	Matrix II	Matrix III	Matrix IV
Fluoride	0.13	10.24 $\pm$ 0.20	10.28 $\pm$ 0.14	10.26 $\pm$ 0.19	10.26 $\pm$ 0.15
Acetate	1.0	11.57 $\pm$ 0.18	11.64 $\pm$ 0.10	11.61 $\pm$ 0.21	11.61 $\pm$ 0.12
Formate	1.0	12.19 $\pm$ 0.15	112.31 $\pm$ 0.07	12.29 $\pm$ 0.21	12.29 $\pm$ 0.11
Chloride	0.20	15.58 $\pm$ 0.09	15.605 $\pm$ 0.04	15.60 $\pm$ 0.06	15.60 $\pm$ 0.08
Nitrite	0.67	16.88 $\pm$ 0.08	16.89 $\pm$ 0.03	16.88 $\pm$ 0.05	16.86 $\pm$ 0.08
Sulfate	1.0	20.40 $\pm$ 0.13	20.41 $\pm$ 0.06	20.36 $\pm$ 0.06	20.36 $\pm$ 0.07
Bromide	0.67	21.04 $\pm$ 0.13	21.00 $\pm$ 0.02	20.99 $\pm$ 0.14	20.96 $\pm$ 0.06
Nitrate	0.67	22.23 $\pm$ 0.15	22.18 $\pm$ 0.03	22.18 $\pm$ 0.11	22.12 $\pm$ 0.05
Phosphate	1.0	28.03 $\pm$ 0.39	28.05 $\pm$ 0.11	27.95 $\pm$ 0.20	27.92 $\pm$ 0.10

<sup>a</sup> The average retention time and relative standard deviation (RSD) data were calculated from nine replicate measurements ( $n=9$ ).

matrix blank. The results, presented in Table 6, show that the average recoveries were generally in the range of 70–120%. These results suggest that the method performed well for these samples considering that the target anions were added at concentrations of 1.0  $\mu\text{g/l}$  or lower.

The method performance was also evaluated by determining the method detection limits for nine target anions in four synthetic sample matrices. To determine the method detection limits, replicate measurements ( $n=7$ ) of sample matrices spiked with analyte ions at concentrations ranging from 0.04  $\mu\text{g/l}$  for fluoride to 0.3  $\mu\text{g/l}$  for sulfate and phosphate were made. The results are summarized in Table 7. For the four synthetic sample matrices, the method detection limits for target anions were generally lower than 0.1  $\mu\text{g/l}$ . For target analytes in samples of deionized water, the method detection

limits obtained using the Atlas electrolytic suppressor in this study are two to six times lower than those obtained in a previous study [20] under similar conditions. The low method detection limits obtained using this method can be attributed primarily to the low baseline noise afforded by the anion Atlas electrolytic suppressors.

### 3.3. Analysis of water samples from a fossil fuel power plant

The method was used to analyze four power plant water samples collected from Four Corners Fossil Fuel Power Plant. The water samples included main steam, condensate pump discharge, economizer inlet water, and boiler drum water. Fig. 5 shows the chromatogram obtained for the main steam water sample, which did not contain additives. The results

Table 6  
Spike recovery data obtained for target analyte anions in different matrices

Analyte	Spiked concentration ( $\mu\text{g/l}$ )	Average recovery (%) $\pm$ RSD (%)			
		Matrix I	Matrix II	Matrix III	Matrix IV
Fluoride	0.13	94 $\pm$ 3.3 <sup>a</sup>	98 $\pm$ 4.7	119 $\pm$ 11	95 $\pm$ 3.4
Acetate	1.0	51 $\pm$ 5.2	71 $\pm$ 10	84 $\pm$ 11	106 $\pm$ 14
Formate	1.0	69 $\pm$ 3.2	78 $\pm$ 2.4	88 $\pm$ 1.9	119 $\pm$ 5.4
Chloride	0.20	91 $\pm$ 10	99 $\pm$ 4.0	121 $\pm$ 5.6	106 $\pm$ 6.9
Nitrite	0.67	92 $\pm$ 2.9	91 $\pm$ 1.2	103 $\pm$ 4.7	91 $\pm$ 2.4
Sulfate	1.0	91 $\pm$ 3.2	78 $\pm$ 2.5	71 $\pm$ 3.9	93 $\pm$ 2.3
Bromide	0.67	93 $\pm$ 4.9	91 $\pm$ 5.7	83 $\pm$ 12	102 $\pm$ 4.0
Nitrate	0.67	103 $\pm$ 6.7	93 $\pm$ 4.7	95 $\pm$ 2.4	117 $\pm$ 5.8
Phosphate	1.0	97 $\pm$ 4.3	97 $\pm$ 7.8	95 $\pm$ 3.9	113 $\pm$ 9.1

<sup>a</sup> The average recovery and relative standard deviation (RSD) data were calculated from nine replicate measurements ( $n=9$ ).

Table 7  
Method detection limits obtained for analyte anions in different matrices<sup>a</sup>

Analyte	Spike concentration ( $\mu\text{g/l}$ )	Method detection limit ( $\mu\text{g/l}$ )			
		Matrix I	Matrix II	Matrix III	Matrix IV
Fluoride	0.04	0.0099	0.013	0.0038	0.0041
Acetate	0.3	0.0056	0.012	0.0098	0.010
Formate	0.3	0.019	0.024	0.011	0.016
Chloride	0.06	0.057	0.025	0.042	0.046
Nitrite	0.2	0.084	0.013	0.015	0.0081
Sulfate	0.3	0.023	0.021	0.033	0.010
Bromide	0.2	0.067	0.016	0.110	0.036
Nitrate	0.2	0.037	0.035	0.043	0.10
Phosphate	0.3	0.079	0.014	0.024	0.077

<sup>a</sup> The estimated method detection limits were calculated as the standard deviation of the mean measured concentration ( $n=7$ ) multiplied by 3.143 (Student's  $t$ -value at 99% confidence).

show that this sample contained 0.16  $\mu\text{g/l}$  fluoride, 1.2  $\mu\text{g/l}$  acetate, 3.2  $\mu\text{g/l}$  formate, 0.18  $\mu\text{g/l}$  chloride, 0.81  $\mu\text{g/l}$  nitrite, 0.30  $\mu\text{g/l}$  sulfate, and 0.27  $\mu\text{g/l}$  nitrate. No bromide or phosphate were detected in this sample. Fig. 6 shows the chromatogram obtained for the condensate discharge water sample that was comprised of the steam condensate from the turbine and did not contain additives. The condensate discharge water sample contained 0.16  $\mu\text{g/l}$  fluoride, 1.2  $\mu\text{g/l}$  acetate, 3.9  $\mu\text{g/l}$  formate, 1.3  $\mu\text{g/l}$  nitrite, and 0.15  $\mu\text{g/l}$  nitrate. These levels were similar to the concentrations of these ions in the

main steam water sample. The condensate discharge water sample also contained 0.44  $\mu\text{g/l}$  chloride, 3.6  $\mu\text{g/l}$  sulfate, and 0.86  $\mu\text{g/l}$  phosphate, which were significantly higher than the concentrations of these ions in the main steam water sample. Fig. 7 shows the chromatogram obtained for the economizer inlet water sample. This sample was the condensate water before it entered the boiler. Ammonia and hydrazine were added to the water as additives. The ionic composition of this sample was similar to the condensate discharge water sample, as expected. Fig.

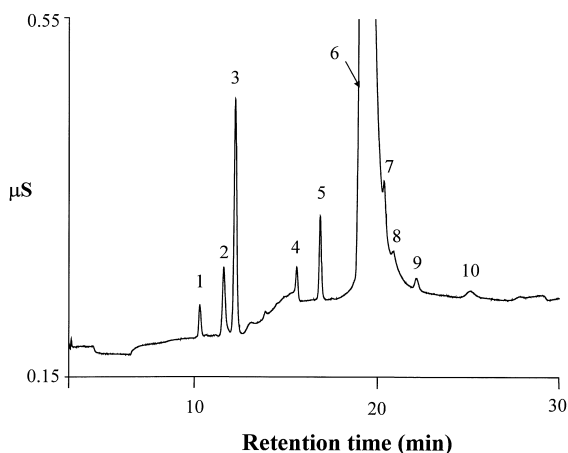


Fig. 5. The chromatogram obtained for the main steam water sample. Peak identification and concentration: 1=fluoride (0.16  $\mu\text{g/l}$ ), 2=acetate (1.2  $\mu\text{g/l}$ ), 3=formate (3.2  $\mu\text{g/l}$ ), 4=chloride (0.18  $\mu\text{g/l}$ ), 5=nitrite (0.81  $\mu\text{g/l}$ ), 6=carbonate, 7=sulfate (0.30  $\mu\text{g/l}$ ), 8=unknown, 9=nitrate (0.27  $\mu\text{g/l}$ ), 10=unknown.

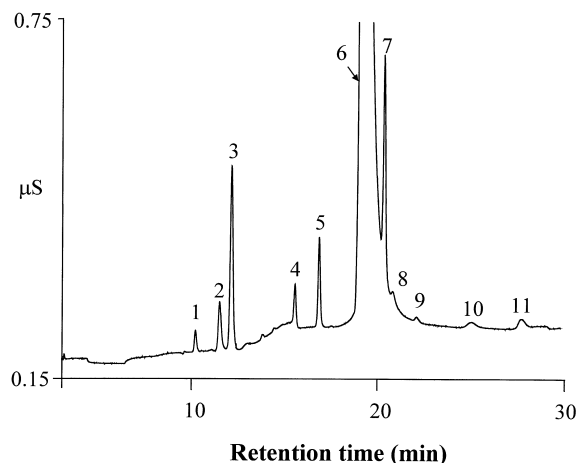


Fig. 6. The chromatogram obtained from the condensate discharge water sample. Peak identification and concentration: 1=fluoride (0.16  $\mu\text{g/l}$ ), 2=acetate (1.2  $\mu\text{g/l}$ ), 3=formate (3.9  $\mu\text{g/l}$ ), 4=chloride (0.44  $\mu\text{g/l}$ ), 5=nitrite (1.3  $\mu\text{g/l}$ ), 6=carbonate, 7=sulfate (3.6  $\mu\text{g/l}$ ), 8=unknown, 9=nitrate (0.15  $\mu\text{g/l}$ ), 10=unknown, and 11=phosphate (0.86  $\mu\text{g/l}$ ).



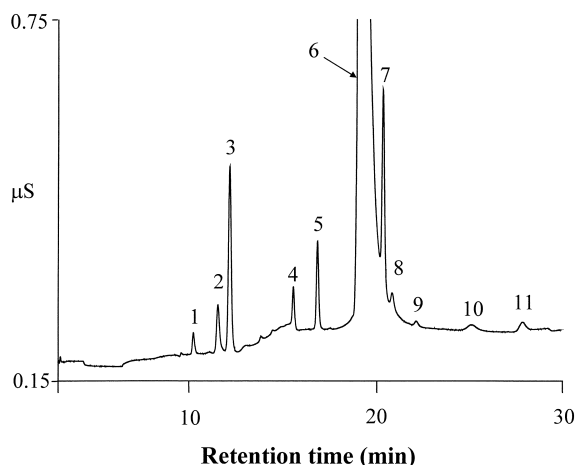


Fig. 7. The chromatogram obtained for the economizer inlet water sample. Peak identification and concentration: 1=fluoride (0.16  $\mu\text{g/l}$ ), 2=acetate (1.1  $\mu\text{g/l}$ ), 3=formate (3.8  $\mu\text{g/l}$ ), 4=chloride (0.42  $\mu\text{g/l}$ ), 5=nitrite (1.3  $\mu\text{g/l}$ ), 6=carbonate, 7=sulfate (3.2  $\mu\text{g/l}$ ), 8=unknown, 9=nitrate (0.17  $\mu\text{g/l}$ ), 10=unknown, and 11=phosphate (0.78  $\mu\text{g/l}$ ).

8 shows the chromatogram obtained for a boiler drum water sample. The boiler drum is where the water and steam are separated for the steam to go to the turbine. This sample contained trisodium phosphate and sodium hydroxide as additives. There were

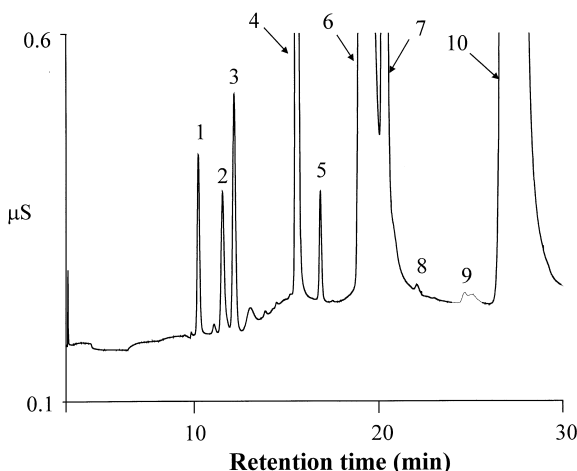


Fig. 8. The chromatogram obtained for the boiler drum water sample. Peak identification and concentration: 1=fluoride (1.2  $\mu\text{g/l}$ ), 2=acetate (3.1  $\mu\text{g/l}$ ), 3=formate (4.0  $\mu\text{g/l}$ ), 4=chloride (33  $\mu\text{g/l}$ ), 5=nitrite (1.3  $\mu\text{g/l}$ ), 6=carbonate, 7=sulfate (130  $\mu\text{g/l}$ ), 8=unknown, 9=nitrate (0.19  $\mu\text{g/l}$ ), and 10=phosphate (1600  $\mu\text{g/l}$ ).

significant amounts of phosphate (1600  $\mu\text{g/l}$ ), sulfate (130  $\mu\text{g/l}$ ), and chloride (33  $\mu\text{g/l}$ ) in this sample due to the addition of trisodium phosphate and sodium hydroxide and the associated ionic impurities.

#### 4. Conclusions

The results obtained from analyzing synthetic and real power plant water samples suggest that the new IC method developed in this study can be applied to determine target anions at trace levels in power plant water samples. The hydroxide-selective AS15-5  $\mu\text{m}$  column provides rapid and efficient separation of target analyte anions including fluoride, acetate, formate, chloride, nitrite, sulfate, bromide, nitrate, and phosphate. The use of the EG40 KOH eluent generator eliminates the problems associated with the preparation of alkali hydroxide eluents and provides an ideal source of eluents for use with hydroxide-selective anion-exchange columns such as the AS15-5  $\mu\text{m}$  column. Method detection limits at the ng/l level can be readily achieved using the large loop direct injection technique because of the lower baseline noise afforded by the anion Atlas electrolytic suppressor. The new method is potentially more amenable to on-line operations because the anion electrolytic suppressor is operated in the recycle mode.

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