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Separation and detection of group I and II cations by ion chromatography

DANIEL L. CAMPBELL*, JOHN STILLIAN, STEVE CARSON, ROBERT JOYCE and SHAWN HEBERLING
Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086 (U.S.A.)

ABSTRACT

Lithium, sodium, magnesium and calcium are routinely monitored in environmental samples and in analysis of ultrapure water for semiconductor and power generation facilities. The use of graphite furnace, atomic absorption and ICP have long been recognized as the analytical instruments of science for the detection and quantization of these cations. These spectral detectors have been the detection method of choice because of their inherent speed, sensitivity, and lack of interferences.

This paper will present results of a recent advance using ion chromatography with chemical suppression and conductivity detection for group I and group II cations. The method allows the separation and detection of lithium, sodium, ammonium, potassium, magnesium, calcium and morpholine at the sub-μg/l levels in ultrapure water and common power plant waters.

INTRODUCTION

This paper discusses many new applications of cation-exchange ion chromatography to the analyses of power plant and semiconductor water chemistries. With the continued development of ion chromatography during the past few years, the full capabilities and potential of modern ion chromatographs are only now being exploited. With these improvements in the ability to analyze high purity water, it is expected that more power plants and semiconductor manufacturing facilities will employ ion chromatography for solving their water chemistry problems than ever before.

High-performance ion chromatography (HPIC) techniques have long been employed in power plant laboratories for recognition, qualitative identification, and quantitative analysis of ionic impurities and various additives, both inorganic and organic. In this paper, the most recent cation developments and applications to analysis of ultrapure water samples and steam generator water samples will be presented.

Monitoring the presence and movement of impurities in feed waters, boiler waters, steam, and cooling waters at all power plants, fossil-fired and nuclear, is increasingly important. This is because submicrogram/liter (ppb) concentrations of these impurities, through concentration mechanisms, can accumulate in kilogram quantities in steam generators and turbines. Buildup of deposits can result in decreased heat transfer efficiency and, more seriously, in initiation and propagation of stress

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corrosion cracking and in other corrosion mechanisms in steam generator tubing, turbines, recirculation piping and other "balance-of-plant", water cycle components. Corrosion problems of this type lead to component failures and power plant shutdowns, costing the affected utility up to a million dollars a day for replacement power [1] and millions more for repairs.

Considerable research has been conducted showing increased evidence that it is the low ppb levels of chloride, sulfate, and organic acids, amongst other ionic contaminants, that are harmful to steam generators over the expected plant life of 30 years [2]. By minimizing the concentration of corrosive ions in boiler feedwater and effluent from condensate polishers, corrosion damage to turbines and nuclear power plant steam generators can be minimized. Minimizing the concentrations of the trace counter ions, sodium and potassium, is equally important for controlling condensate polisher slippage and for controlling crevice build-up in steam generators. Measurements of ionic contamination throughout the system can provide corrosion engineers and water chemistry personnel with valuable information regarding the source of the contamination, the likely rates of contaminant build-up, and the probable rates of corrosion, as well as extremely useful and timely data during the start-up and shutdown of power plants. Continuous monitoring of these ions in condensate polishing systems also indicates when an ion exchange demineralizer requires regeneration.

Recent developments in ion chromatography instrumentation have resolved a number of practical difficulties in high purity samples, and ion chromatography is now finding increased application in the direct quantitative analysis of trace cation and neutralizing amines in many power plant matrices. In the remainder of this paper, we shall consider a number of these important cation analyses both qualitative and quantitative analyses, that have been recently developed.

EXPERIMENTAL

Equipment

All chromatography in these studies was performed on a Dionex Series 4500i ion chromatograph, as shown in Fig. 1.

The entire flow path of the chromatograph is constructed from polymeric and other non-metallic materials in order to eliminate corrosion from the acidic eluents used. All eluents were mixtures of dilute hydrochloric acid (HCl) and/or 2,3-diaminopropionic acid monohydrochloride (DAP), (Fluka, Ronkonkima, NY, U.S.A.). A cation trap column (CTC) filled with high-capacity, low-efficiency cation-exchange resin in the hydrogen form was placed between the pump and the injection valve. This column removed metals and other cation contaminants from the eluent, thus protecting the analytical column from unnecessary capacity losses and retention time shifts.

Concentrator columns. The analysis of ultra-trace quantities of anions in the ppb range was first described by Wetzel *et al.* [3]. The injection loop was replaced with a short guard column containing ion-exchange material similar to that of the analytical column to strip, *i.e.* "concentrate," ions from measured volumes of relatively clean aqueous samples. This process concentrates the desired species leading to a lowering of detection limits by orders of magnitude. The unique advantage of their use to the

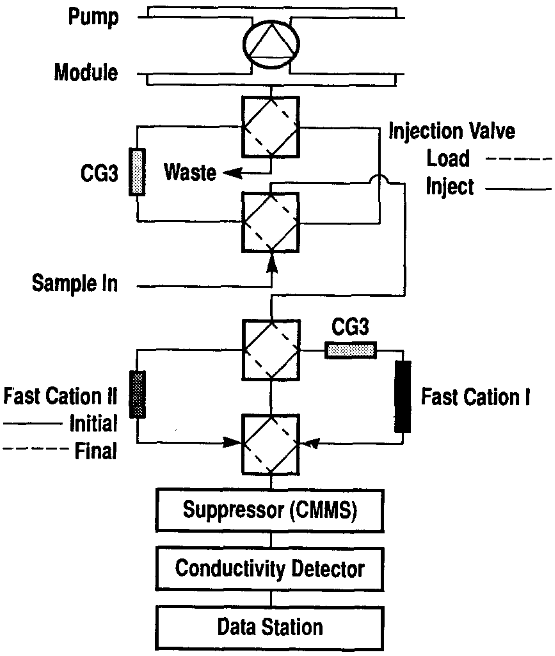


Fig. 1. Fast cation configuration for determining ppb levels of monovalent and divalent cations.

analyst is the capability of routine analysis of ions at sub-ppb (μg/l) levels, without extensive and laborious sample pretreatment.

The principal function of any concentrator is to strip ions from a sample matrix, without compromising the integrity of the analysis. For cation determinations, any cation-exchange column can function as a concentrator, assuming that it has adequate capacity and that the resin is compatible with the eluent. Short columns containing the same resin (guard columns) or columns with higher-capacity resins have both shown excellent performance characteristics for sample concentration. Commonly, to prevent overloading the concentrator column and/or loss of sample ions, a higher-capacity concentrator resin is used.

Sample loading is performed via a separate positive-displacement pump. Kinetics of mass transfer on pellicular ion-exchange resins is fast. This allows sample loading pump flow-rates of approximately 3–5 ml/min to be used, and sample concentration efficiencies high enough to assure good quantization [4]. Flow direction during concentration is also critical. The sample is loaded in one direction and then "backflushed" for injection with eluent flow in the opposite direction.

This configuration concentrates the cations in a compact band at the bottom of the column. When injected, all of the ions are rapidly eluted off the concentrator onto the guard, if present, and analytical columns, a desired effect. If instead, the sample is loaded in the same flow direction as the eluent flow, the cations are concentrated at the head of the column rather than at the bottom. When injected, the cations begin chromatographic separation in the concentrator before reaching the analytical columns. This is only useful when increased capacity is needed for better resolution of the ions. However, for the column switching techniques described in this paper and for ions with large differences in capacity factor (k'), sample loading in the same direction as the eluent flow can severely reduce analytical performance. Almost always the function of the concentrator is to strip the ions of interest and not act as an analytical column. In order to ensure this, it is recommended that concentration be performed in a backflush manner routinely. A CG3 column is used as the concentrator for all applications in this paper.

Analytical columns. The analytical columns used in this study are the Dionex Fast Cation I, the CG3 and the Fast Cation II columns. These columns are packed with a pellicular cation-exchange resin. The resin is made from 13-μm diameter substrate made of styrene–divinylbenzene polymer resin and coated with cation-exchange latex particles. The Fast Cation I is a 250 × 4 mm column with 4% cross-linked latex, and the Fast Cation II is a 50 × 3 mm column with 2% cross-linked latex. All columns were used for the column-switching method. Use of a CG3 column with the Fast Cation I column improves resolution of the monovalents, and this was found in this study to improve quantization of samples containing ppm (mg/l) levels of ammonium or morpholine.

Column switching. Traditionally mono- and divalent cations have been difficult to analyze in the same injection because of large k' differences on cation-exchange materials. Column-switching procedures have been applied widely in gas chromatography during the past 20 years to deal with similar problems. In general, switching allows diversion of different sample components to different columns for maximum resolution with minimum time [5].

In this application for trace level analysis of cations, column switching has the effect of eluting the two groups of cations (mono- and divalents) through separate columns optimized for the chromatography of the respective groups. The monovalent cations elute through the Fast Cation I/CG3 combination. The divalent cations elute through a shorter column, the Fast Cation II. (The monovalent cations elute through both column sets, but their retention on the short Fast Cation II column is negligible.) The columns are different in two characteristics. First, the Fast Cation I/CG3 has the much higher capacity necessary to retain the monovalent cations. Second, the lower crosslinked latex used in the short Fast Cation II is designed to decrease retention of divalent cations without decreasing efficiency [6].

At injection, the Fast Cation II is placed in front of the Fast Cation I/CG3. Following injection, all the cations begin eluting through the Fast Cation II. The position of the two columns is reversed 1.25 min after injection with the use of the column switching valve.

This 1.25-min time period allows for all the cations to be removed from the concentrator and for the monovalent cations to have been eluted onto the Fast Cation I/CG3, but before the divalent cations have been eluted off of the Fast Cation II. This technique keeps the more strongly-retained divalent cations from reaching the higher-capacity Fast Cation I/CG3 columns. After the monovalent cations elute through the Fast Cation I/CG3, they then pass through the Fast Cation II again, actually passing through the divalent cations. All the cations then elute from the Fast Cation II to the suppressor and detector, with the monovalent cations eluting first, followed by the divalent cations.

Conductivity detection. A Dionex cation micromembrane suppressor (CMMS) is used as part of the conductivity detector. It minimizes background conductivity from the eluent and enhances detector response. Regenerant is 100 m*M* tetrabutylammonium hydroxide (TBAOH). The hydroxide ions in the regenerant migrate across the anion-exchange membrane in the suppressor and react with hydronium ions in the eluent, producing water. At the same time, the anions (chloride) in the eluent cross into the regenerant and are replaced by the hydroxide ion. The suppression reaction has two effects: one, it decreases the conductivity of the acidic eluent by converting it to water, and two, it pairs the analytes with hydroxide counter ions. The combination of the two effects is a significant increase in the signal-to-noise ratio, which lowers the detection limit and widens the operating range.

The regenerant solution is continuously recycled by a Dionex AutoRegen Accessory. This device recirculates the regenerant solution through a high-capacity anion-exchange column in the hydroxide form. In this manner, anions in the suppressor regenerant effluent are removed and replaced by the hydroxide ions necessary for continuous eluent suppression.

Regenerant flow-rate in the AutoRegen Accessory was 5 ml/min. Higher and lower regenerant flow-rates produced minor changes in background conductivity without affecting performance. As the separate cation groups in the stream pass through the conductivity cell, they produce a peak-shaped trace on a recording chart. The heights or areas of the peaks are proportional to the specific cation concentrations, and quantization is achieved by comparing peak heights or areas to the same peak heights or areas for a calibration standard with known concentration.

Data station. Ion identity, analysis time, peak retention time, ion concentration, number of injections per standard, total number of standards, and type of calibration methods (area, height, linear, quadratic, etc.) were collected using a Dionex AI-450 computer data station. In these studies, multilevel calibration was used with linear least-squares best fit regression analysis, and peak heights were found, in general, to have better linearities and better reproducibilities. Unless otherwise noted, all calculations are based on comparison of peak height measurements and not peak areas.

Reagents

One cannot emphasize the need for high-quality deionized water too strongly. Blanks are as important for accurate trace level analysis as properly prepared standards and, in some ways, more important. Blanks establish the baseline reference for analysis. If a working detection limit of 50 parts-per-trillion (ppt, ng/l) is to be achieved, then the blank must be at least 10–20 ppt lower.

Water used in the preparation of the standards should be 18 $M\Omega \cdot cm$ deionized water. The quality of the dilution water for standards must be determined by ion chromatography, since even 18 $M\Omega \cdot cm$ water may contain several ppb of the ions of interest. To do this, analyze your dilution water in exactly the same manner as you would your sample.

At ppb levels, changes of contamination during collection or storage are high. Every container and every procedural step constitute a potential source of contamination. Polystyrene containers with leak-tight caps can be used to store 1 to 5 ppb levels of inorganic cations for up to 8 days [7]. Reagent-grade or better chemicals should be used in all tests. Unless otherwise indicated, all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Other grades may be used, provided it is ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

RESULTS AND DISCUSSION

Methods

The goal of this project was to identify and develop as few analytical methods as possible for the broadest range of cationic chemical species found in power plant waters. The Fast Cation column-switching method proved very promising. One method was optimized for: (1) samples of ultrapure water, (2) water containing up to 1 ppm ammonium, (3) water containing up to 20 ppm morpholine and (4) water containing up to 1.2% boric acid. In each of the different power plant waters, both linearity and reproducibility studies were conducted.

Power plant water containing 1.2% boric acid and 1 ppm lithium hydroxide required alternate methods to achieve acceptable resolution of the lithium from other cations in the samples. Two existing isocratic, non-column-switching methods, were used: one for the determination of monovalent cations only, and one for the determination of divalent cations only.

Each sample was concentrated at different volumes ranging from 3.3 to 50 ml. Overloading effects, linearity, sensitivity and reproducibility were evaluated to determine a single concentrator volume useful for all water samples. This volume was experimentally found to be approximately 10 ml. All the data presented here is based on a 10-ml volume concentration. By modification of eluent and sample volumes, individual sample matrices can be optimized for increased sensitivity and reproducibility.

Trace cations in ultra-pure water

The method employed for trace cations in ultrapure water uses the column-switching method with the Fast Cation I/CG3 columns and the Fast Cation II column (see Table I). Fig. 2 represents a standard chromatogram for cations in ultra-pure

TABLE I

FAST CATION COLUMN-SWITCHING METHOD

Optimized for all Matrices except 1.2% boric acid and 1 ppm lithium.

Analytical columns	Dionex Fast Cation I, CG3 and Fast Cation II
Concentrator	CG3
Eluent	13.5 m*M* HCl, 0.23 m*M* DAP
Backpressure	1500–2000 p.s.i.
Flow-rate	2 ml/min
Column switch	1.25 min
Suppressor	Dionex CMMS
Regenerant	100 m*M* TBAOH, 5 ml/min with AutoRegen
Background conductivity	2–10 μS
By-pass loop	20 μl

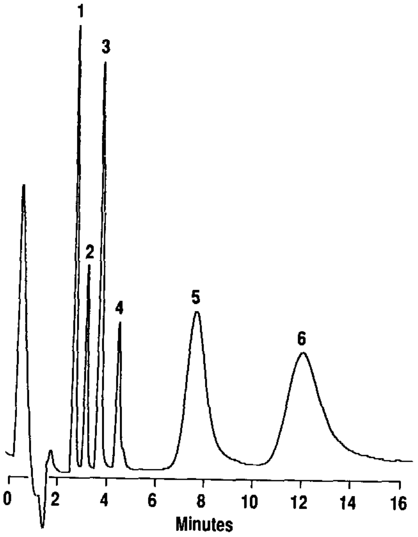


Fig. 2. Trace cations in ultrapure water. Column: Fast Cation I/CG3, Fast Cation II. Concentrator: CG3. Eluent: 13.5 m*M* HCl, 0.23 m*M* DAP. Flow-rate: 2 ml/min. Column switch: 1.25 min. Detector: conductivity, 3 μS. Suppressor: CMMS. Regenerant: 100 m*M* TBAOH. Volume concentrated: 10 ml. Peaks 1 = Li^+ (1 ppb); 2 = Na^+ (1 ppb); 3 = NH_4^+ (3 ppb); 4 = K^+ (3 ppb); 5 = Mg^{2+} (5 ppb); 6 = Ca^{2+} (10 ppb).

water. Six mixed multi-element standards ranging from 0.5, 1, 3, 5, 10 and 15 ppb of lithium, sodium, ammonium, potassium, magnesium and calcium were prepared. Sample volumes of 3.3, 9.9, 19.9, 39.9 and 49.9 ml were used. Three to five replicate measurements were made for each sample. Linearities of the cations for all volumes concentrated were found to have correlation coefficients (*r*) greater than 0.9960. No overloading of the concentrator or the analytical columns was observed over this analytical range.

The correlation coefficient for sodium over the range of 0.5 to 10 ppb using 10 ml concentrated was determined to be 0.9992. The relative standard deviation (R.S.D.) for 26 replicated analyses of a sodium standard at the 0.5-ppb level was 1.6%. Magnesium also showed a high degree of linearity over the range of 1 to 15 ppb with a correlation coefficient of 0.9989 using 10 ml concentrated. The R.S.D. for 24 replicate analyses of a magnesium standard at the 5-ppb level was 4.8%. All other monovalent and divalent cations showed similar performance capabilities as shown in Table II.

Power plant waters containing ammonium

The method employed for trace cations in water containing ammonium uses the column-switching method with the Fast Cation I/CG3 columns and the Fast Cation II column (see Table I). Fig. 3 represents a standard chromatogram for cations in 1 ppm ammonium. Six mixed multi-element standards ranging from 0.5, 1, 3, 5, 10 and 15 ppb of lithium, sodium, potassium, magnesium and calcium were prepared. Ammonium was varied from 200–1000 ppb in each of the mixed standards. Sample volumes of 3.3,

TABLE II

ANALYTICAL PERFORMANCE CAPABILITY

	Cations (ppb)						
	Li^+	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Morpholine
In ultra pure water							
Level	0.5	0.5	1.0	1.0	5.0	5.0	
n	26	26	24	26	24	23	
R.S.D. (%)	2.8	1.6	5.9	2.6	4.8	5.8	
In 5 ppm morpholine							
Level	0.5	0.5	1.0	1.0	5.0	5.0	5000
n	20	20	20	20	20	21	20
R.S.D. (%)	4.5	5.0	4.2	6.1	6.5	11.7	2.7
In 1 ppm ammonium							
Level	0.5	0.5	1000	1.0	5.0	5.0	
n	24	23	24	24	23	22	
R.S.D. (%)	3.5	3.6	0.36	6.4	3.8	15	
In 1.2% boric acid							
Range	0.5–10	0.5–10	1–15	1–15			
Recovery (%)	97.4	98.3	98.2	106			

5.0, 9.9 and 19.9 ml were used. Three to five replicate measurements were made for each sample. Linearities of the cations for all volumes concentrated were found to have correlation coefficients (*r*) greater than 0.9900. Volumes greater than 10 ml with 1-ppm

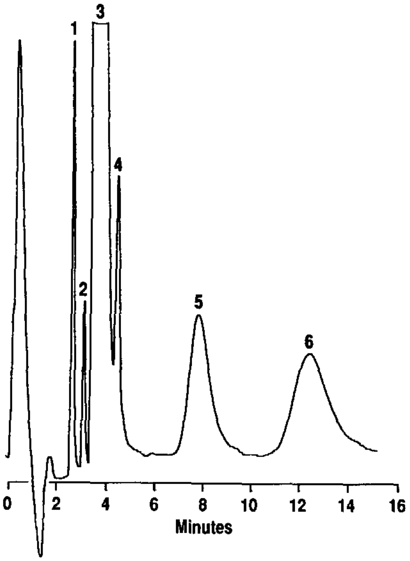


Fig. 3. Trace level cations in power plant waters containing 1 ppm ammonium. Conditions as in Fig. 2. Peaks: 1 = Li^+ (1 ppb); 2 = Na^+ (1 ppb); 3 = NH_4^+ (1 ppm); 4 = K^+ (3 ppb); 5 = Mg^{2+} (5 ppb); 6 = Ca^{2+} (10 ppb).

levels of ammonium began to compromise the reproducibility and linearity of sodium and potassium. The reproducibilities of calcium and magnesium were also affected by sample volumes greater than 10 ml with 1 ppm ammonium.

The correlation coefficient for sodium over the range of 0.5 to 10 ppb using 10 ml concentrated in water containing 200 to 1000 ppb ammonium remained greater than 0.9990. The R.S.D. for 23 replicate analyses of a sodium standard at the 0.5-ppb level was 3.6%. Magnesium's linearity over the range of 1 to 15 ppb in 200 to 1000 ppb ammonium exhibited a correlation coefficient of 0.9910 using 10 ml concentrated. The R.S.D. for a magnesium standard at the 5-ppb level was 3.8%. Calcium was the only cation which had a R.S.D. greater than 10%. All other cations showed similar performance capabilities over the analytical range as shown in Table II.

The reproducibility of ammonium from the concentrator was 0.36% R.S.D. at the 1-ppm concentration and 10 ml concentrated for 24 replicate analyses, as shown in Table II. Linearity of ammonium from the concentrator column over the range of 200–500 ppb revealed a correlation coefficient of 0.9990. Concentrations higher than 500 ppb were non-linear for both peak height and peak areas. Current development work is being conducted on improving quantization and the linear working range of ammonium.

A recently invented technique has shown promising results for quantitating ppm levels of ammonium and trace level cations in the same injection. A standard slider valve for concentrator work is comprised of a concentrator side and a by-pass loop side. In the inject position, the by-pass loop is flushed with the next sample to be concentrated. This purges the previous sample from the system tubing. When the valve is switched to load, the small volume in the by-pass loop (10 to 100 μl) is injected into the ion chromatograph. This volume behaves as a normal-loop sample injected through the column and the conductivity detector. For ultrapure water no peaks are detectable from the ions in the loop injection because of their low level. When samples of water containing ppm levels of cation additives are flushed through this loop and injected, measurable peaks for the additives can be detected and are capable of being quantified. This procedure can often be optimized for monitoring a major additive and for measuring trace level components in the same run.

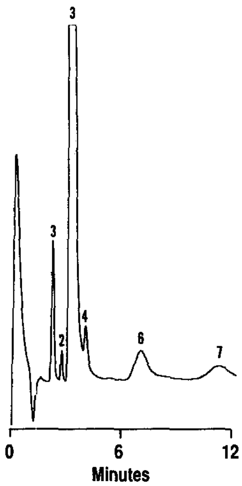
By adjusting when the concentrator is injected and when data sampling begins, the peak due to the by-pass loop can be accurately detected or eliminated from a chromatographic run. This technique shows strong promise for waters containing ammonium or lithium. An example of this effect is shown in Fig. 4 where the ammonium (peak 3) appears twice.

The first peak labeled 3 is caused by the by-pass loop and the second, larger peak labeled 3 is due to the ammonium from the concentrator column. Linearity of the ammonium from the by-pass loop measured from 250 ppb to 2500 ppb showed a correlation coefficient of 0.9980.

Power plant waters containing morpholine

Diethylenimide oxide or tetrahydro-1,4-isoxazine, commonly known as morpholine, is becoming popular as a corrosion inhibitor. Morpholine, with a pK_a of 8.3 [8], exists as a weak base in normal power waters.

The method employed for trace cations in water containing morpholine uses the column-switching method with the Fast Cation I/CG3 columns and the Fast Cation II



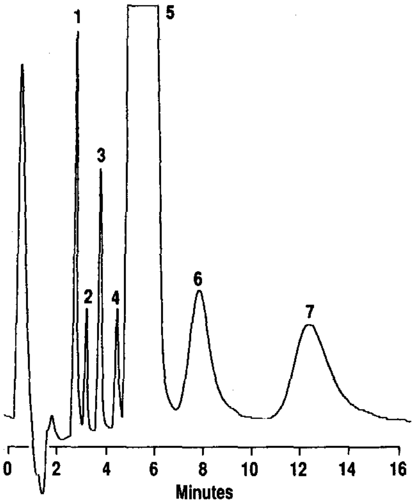


Fig. 4. Trace level cations in power plant waters containig 1 ppm ammonium. Column: Fast Cation I and II. Concentrator: CG3. Volume concentrated: 10 ml. Eluent: 13.5 m*M* HCl, 0.229 m*M* DAP. Flow-rate: 2 ml/min. Range: 3 μS. Column switch: 1.25 min. Suppressor: CMMS. Regenerant: 100 m*M* TBAOH, 3–5 ml with AutoRegen. Peaks: 2 = Na^+ (1 ppb); 3 = NH_4^+ (1 ppm); 4 = K^+ (3 ppb); 6 = Mg^{2+} (5 ppb); 7 = Ca^{2+} (5 ppb).

Fig. 5. Trace level cations in power plant waters containing morpholine. Conditions as in Fig. 2. Peaks: 1 = Li^+ (1 ppb); 2 = Na^+ (1 ppb); 3 = NH_4^+ (3 ppb); 4 = K^+ (3 ppb); 5 = morpholine$^+$ (5 ppm); 6 = Mg^{2+} (5 ppb); 7 = Ca^{2+} (10 ppb).

column (see Table I). Fig. 5 represents a standard chromatogram for cations in 5 ppm morpholine. Six mixed multi-element standards ranging from 0.5, 1, 3, 5, 10 and 15 ppb of lithium, sodium, ammonium, potassium, magnesium and calcium were prepared. Morpholine was varied from 1 to 20 ppm in each of the different samples. Sample volumes of 3.3, 5.0, 9.9 and 19.9 ml were used. Three to five replicate measurements were made for each sample. Linearities of the cations for all volumes concentrated were found to have correlation coefficients (*r*) greater than 0.9900. Volumes greater than 10 ml with ppm levels of morpholine exhibited overloading of the analytical columns and shifting retention times of the cations.

The correlation coefficient for sodium over the range of 0.5 to 5 ppb using 10 ml concentrated in water containing 1 to 20 ppm morpholine was 0.9989. The R.S.D. for 20 replicate analyses of a sodium standard at the 0.5-ppb level was 5.0%. Magnesium linearity over the range of 1 to 15 ppb in 1 to 20 ppm morpholine exhibited a correlation coefficient of 0.9993 using 10 ml concentrated. The R.S.D. for 20 replicate analyses of a magnesium standard at the 5-ppb level was 6.5%. Calcium was the only cation which had a R.S.D. greater than 10%. All other cations performance capabilities were similar over the analytical range as shown in Table II.

The reproducibility of the morpholine from the concentrator demonstrated a R.S.D. of 2.7% at the 5-ppm concentration and 10 ml concentrated for 20 replicate analyses, as shown in Table II. Linearity of morpholine from the concentrator column over the range of 1 to 20 ppm morpholine by peak area was 0.9970, as shown in Fig. 6.

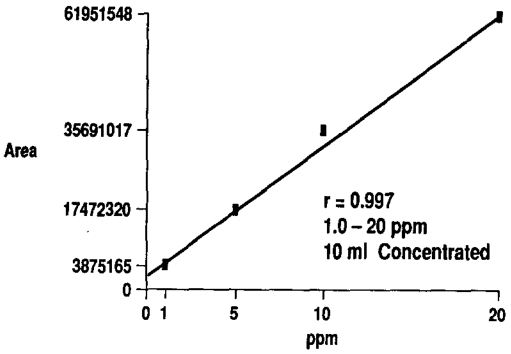


Fig. 6. Linearity of morpholine in power plant waters by area. Range: 10 μS. Other conditions as in Fig. 4.

Trace cations in the presence of 1.2% boric acid

The method employed for trace cations in water containing boric acid also uses the column-switching method with the Fast Cation I/CG3 columns and the Fast Cation II column (see Table I).

In dealing with this matrix the most noticeable problem is the difficulty in preparing sample standards. After adding sufficient quantity of boric acid for a 1.2% solution, blanks of the cations can be as high as 20 ppb!

In this study, the solution of 1.2% boric acid was pumped through a cation trap column (CTC) in the hydrogen form to reduce the cation contamination. This procedure produced ultrapure boric acid solutions, but the procedure was time consuming and tedious. Because of the limited volume of boric acid solution produced, limited experiments were performed.

Recovery experiments were performed on the monovalent cations (see Table II). All cations were shown to have recoveries better than 97%. The recovery value was determined by the ratio of the peak height of a standard 50-μl loop injection of a known mass concentration to the peak height of a 10-ml concentrated sample with the same theoretical mass concentration. This data indicates that the boric acid solution should have an analytical performance similar to other power plant waters.

Trace cations in the presence of 1.2% boric acid and lithium hydroxide

The column-switching method with the Fast Cation I/CG3 column and Fast Cation II column did not have the resolution necessary to quantitate 1 ppb sodium in the presence of 1 ppm lithium, regardless of the boric acid concentration. Two isocratic methods were used to detect and quantitate the cations: a method for the determination of the monovalent cations and a separate method for the determination of the divalent cations.

The monovalent cations were separated using an isocratic eluent of 10 m*M* hydrochloric acid, the Fast Cation II column as a guard, and the Fast Cation I column as the analytical column. The flow-rate of the eluent is 2 ml/min. A solution of 100 m*M* TBAOH was used as the regenerant with the Dionex CMMS. This combination allows for the maximum resolution of 1 ppm lithium and 1 ppb sodium (Fig. 7).

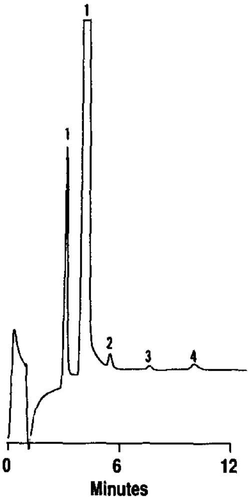


Fig. 7. Trace level monovalent cations in power plant waters containing 1.2% boric acid and 1 ppm lithium hydroxide. Column: Fast Cation II. Analytical column: Fast Cation I. Concentrator: CG3. Volume concentrated: 2 ml. Eluent: 10 m*M* HCl. Flow-rate: 2 ml/min. Range: 10 μS. Suppressor: CMMS. Regenerant: 100 m*M* TBAOH, 3–5 ml with AutoRegen. Peaks: 1 = Li^+ (1000 ppb); 2 = Na^+ (3 ppb); 3 = NH_4^+ (4 ppb); 5 = K^+ (6 ppb).

The divalent cation determination uses only the Fast Cation I column for the separation. The monovalent cations elute in the void volume. The divalent cations can be determined in under 6 minutes with an isocratic eluent of 34 m*M* hydrochloric acid, 9 m*M* 2,3-diaminopropionic acid monohydrochloride at a flow-rate of 2 ml/min. Again 100 m*M* TBAOH was used with the Dionex CMMS.

ADVANCED CATION SEPARATIONS

Dionex recently introduce a new column, the Ion Pac CS-10, specifically for the analysis of alkaline metals and alkaline earth metals. It is 250 mm × 4 mm cation-exchange column with an approximate capacity of 30 μequiv./column.

The pellicular particles used in the CS-10 column consist of a latex coating on a non-porous core. The non-porous core consists of an 8.5-μm diameter 50% cross-link ethylvinylaromatic polymer bead. The high cross-link of the core assures virtually no swelling of the core occurs if organic solvents are used. The core particles are synthesized so as to obtain directly a spherical particle with negative surface charge. While pellicular anion-exchange can be made via electrostatic attachment of the anion-exchange particles to this surface, the preparation of cation-exchange materials from this same core particle requires a double layer attachment process. The primary pellicle consists of an anion-exchange latex coating. The size and composition of this anion-exchange latex was chosen so that the magnitude of anion-exchange retention is relatively minor. The secondary pellicle is a 175-nm cation-exchange latex coating. This layer comprises the analytical ion-exchange layer with a nominal efficiency for magnesium using standard operating conditions of 24 000 plates/m [9].

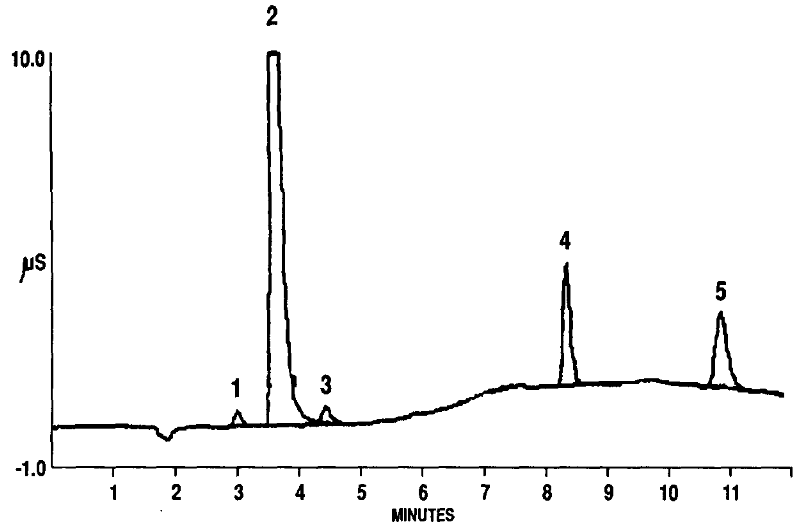


Fig. 8. Calibration standard for cations in high-purity water, Virginia Power Company, Surrey Power Station. Column: CG-10, CS-10. Concentrator: CG-10. Trap column: CTC. Eluents: (EI) 30 m*M* HCl, 0.5 m*M* DAP and (E2) 50 m*M* HCl, 12 m*M* DAP. Eluent switch: 2.0 min. Flow-rate: 1 ml/min. Volume concentrated: 30 ml. Suppressor: CMMS-II. Regenerant: 50 m*M* TBAOH. Peaks: 1 = Na^+ (0.2 ppb); 2 = NH_4^+ (2.0 ppb) ;3 = K^+ (0.5 ppb); 4 = Mg^{2+} (1.0 ppb); 5 = Ca^{2+} (2.0 ppb).

This column used with an eluent step change has shown high resolution and sensitivity for the monovalent cations, even with high ratios of ammonium to sodium, and improved efficiencies and sensitivities for the divalent cations. These improvements for the divalent cations have lowered their detection limits by at least an order of magnitude compared to the column switching technique presented in this paper. This CS-10 has developed the ability to monitor, for the first time, sub-ppb levels of divalent cations in ultrapure and power plant waters.

Fig. 8, developed by Dennis Bostics, Senior Chemist of Virginia Power Company, shows an example of the capability of the CS-10 column for the separation of cations at low and sub-ppb levels. Note the resolution of the monovalents and efficiency for the divalents using an eluent step change. The eluent for this separation begins with a weak 30 m*M* hydrochloric acid–0.5 m*M* 2,3-diaminopropionic acid monohydrochloride eluent; 2 min after injection the eluent is step changed to a stronger eluent, 50 m*M* hydrochloric acid–12 m*M* 2,3-diaminopropionic acid monohydrochloride, for eluting the divalent cations. After the calcium is eluted from the column, the eluent is switched back to the weak eluent for reequilibration of the column. During the reequilibration of 5 to 10 min, the next sample can be concentrated for analysis.

Fig. 9 is an actual sample of Virginia Power's unit one feedwater. For this chromatogram, 60 ml of sample were concentrated. Again, notice the resolution of the low sodium, sub-ppb, in the presence of the higher ppb levels of ammonium. Under these conditions it has been discovered that hydrazine is also retained on this column. The peak labeled potassium in this chromatogram is actually a coelution of potassium

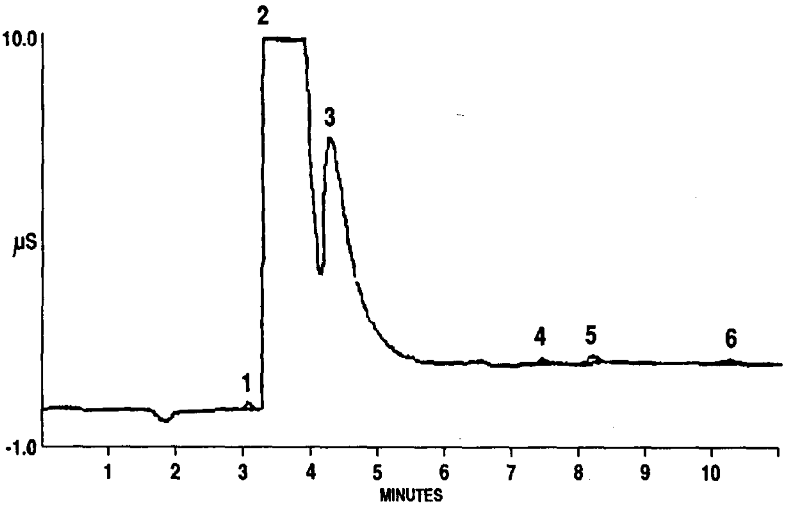


Fig. 9. Unit 1 feedwater, Virginia Power Company, Surrey Power Station. Volume concentrated: 60 ml. Other conditions as in Fig. 8. Peaks: 1 = Na^+ (0.017 ppb); 2 = NH_4^+ (36 ppb); 3 = K^+ (0.94 ppb); 4 = Mg^{2+} (0.008 ppb); 5 = Mn^{4+}; 6 = Ca^{2+} (0.018 ppb).

and the hydrazine present in the feedwater. Finally, it has been discovered that manganese is detected very well using this technique and can be accurately determined to low ppt levels. In conclusion, the use of the new CS-10 column holds strong promise for the rapid determination of both monovalent and divalent cations to low ppt levels in ultrapure and power plant waters.

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