

Regulated methods for ion analysis

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ABSTRACT

Ion chromatography is one of the analytical techniques that has been approved by the United States Environmental Protection Agency (EPA) for the determination of inorganic ions such as nitrite and nitrate in drinking water. Advantages of ion chromatography methodology include separation before detection, increased sensitivity, simple sample preparation, and faster analysis time compared to non-chromatography techniques.

This paper offers a discussion of approved ion chromatography methods 300.0 and B-1011 as well as other methods that are being currently reviewed and also new methodologies for the future.

INTRODUCTION

Concern for our environment has grown significantly throughout the world. Everywhere, the fear of polluting our globe is a continuing problem. There is a need for strict control of toxic substances and close monitoring of their presence in the environment in order to prevent contamination and protect our natural resources.

The United States Environmental Protection Agency (EPA) has established regulations and methodology for inorganic contaminants under the Safe Drinking Water Act. Fluoride, nitrite and nitrate are listed as primary pollutants since they can cause adverse health effects. Ion chromatography (IC) has become a well established technique for the determination of nitrite and nitrate in drinking water [1]. The EPA has approved IC methods 300.0 and B-1011 for the analysis of nitrite and nitrate in drinking water [2].

Chloride and sulfate are listed as secondary contaminants because they are organoleptic (affect the smell, taste, or appearance of water). They are not monitored by the EPA, hence, a laboratory can use any method (IC, ion selective electrode, flow injection analysis, etc.) to analyze for these analytes.

The ability of IC to separate the analytes of interest from interferences provides a distinct advantage over other analytical techniques in terms of

detection, sensitivity and is capable of multi-elemental analysis. This paper reviews methods 300.0 and B-1011 and describes other ion chromatographic methods under current evaluation by the EPA. It also proposes new a method for the future.

EXPERIMENTAL

Instrumentation

The liquid chromatograph consisted of a Waters (Waters Chromatography Division of Millipore, Milford, MA, USA) 500 or 600 Series pump, a Model 431 conductivity detector, a Model 441, 484, 486 or 490 UV detector, a pneumatic reagent delivery module (RDM), WISP auto sampler or a Rheodyne 710 manual injector, and either a Waters 840 or 860 data station. The analytical columns used were a Waters IC-Pak Anion (50 × 4.6 mm I.D.), Waters IC Pak Anion HR (75 × 4.6 mm I.D.), or Waters IC Pak Anion HC (150 × 4.6 mm I.D.), methacrylate-based anion exchanger.

The capillary electrophoresis system employed was the Waters Quanta 4000 with a negative power supply and an Hg lamp for 254-nm detection. The separation was carried out on a Waters AccuSep polyimide-coated fused-silica capillary (60 cm × 75 μm I.D.). While the Quanta 4000 is capable of both hydrostatic and electromigration injections, the hydrostatic sample introduction mode (10 cm for 30 s)

was used in this work. Data acquisition was performed with a Waters 860 data station. Detector time constant was set at 0.1 s and data acquisition rate was 20 points/s.

Reagents

Water (18 M Ω) (Millipore, Bedford, MA, USA) was used to prepare all solutions. Analytical-grade chemicals, sodium gluconate, boric acid, gluconic acid, lithium hydroxide monohydrate, ammonium sulfate and diphenylcarbohydrazide were obtained from Aldrich, Milwaukee, WI, USA and sodium tetraborate decahydrate and sodium chromate tetrahydrate were obtained from Mallinckrodt, Paris, KY, USA. Glycerin, ammonium hydroxide, and sulfuric acid were obtained from J. T. Baker, Phillipsburg, NJ, USA. HPLC-grade solvents were obtained as follows: acetonitrile and methanol from J. T. Baker and *n*-butanol from Aldrich. CIA-Pak OFM anion BT, is propriety chemical obtainable from Waters.

All standard mixtures were prepared by diluting 1000 ppm stock solutions containing a single anion. Eluents and carrier electrolytes were prepared fresh daily, filtered and degassed using a Millipore solvent carification kit prior to use.

RESULTS AND DISCUSSION

EPA Method 300.0

The original version of method 300.0 was approved for nationwide use as an alternate test procedure for the measurement of nitrate by ion chromatography for National Interim Primary Drinking Water Regulation (NIPDWR) compliance monitoring in 1984 [3]. Since IC can detect several anions simultaneously, chloride and sulfate were also included in the method, however only as secondary contaminants. Since levels of secondary contaminants are not legally enforceable. IC was recommended for chloride and sulfate measurements. The method was updated in 1989 to incorporate new column and hardware advances (300.0 Method A) [4].

The separation of a seven-anion standard mixture shown in Fig. 1 was generated using a Dionex AS4A column, sodium hydrogencarbonate–sodium carbonate eluent, anion suppressor device and conductivity detector [5]. Although the chromatogram

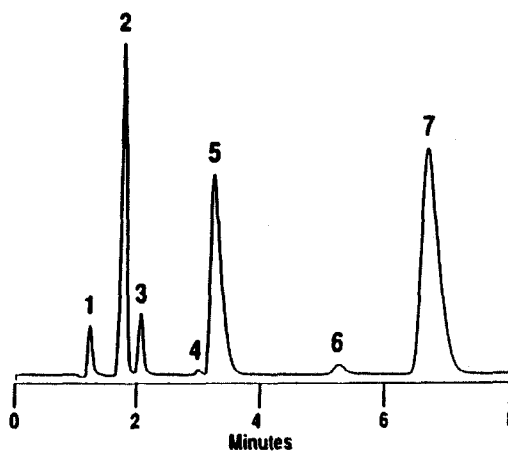


Fig. 1. Separation of a standard anion mixture using the Dionex AS4A column. Peaks: 1 = fluoride (2 ppm); 2 = chloride (20 ppm); 3 = nitrite (2 ppm); 4 = bromide (2 ppm); 5 = nitrate (10 ppm); 6 = phosphate (2 ppm); 7 = sulfate (60 ppm). Chromatogram was taken from EPA test method 300.0.

shows seven common anions, method 300.0 is only approved for nitrite and nitrate in chlorinated drinking water.

Recently there has been a joint EPA–ASTM collaborative study of an extension of EPA Method 300.0 [6] for expansion to both primary and secondary contaminants in drinking and waste water. The method is currently under committee review.

EPA Method B-1011

In 1987, method B-1011, *The determination of nitrite/nitrate in water using single column ion chromatography* [7] was recommended to the Office of Drinking Water (ODW) by the Environmental Monitoring Systems Laboratory (EMSL), Cincinnati, OH, USA as equivalent to EPA method 300.0 for nitrate. The method was published in the *Federal Register* as a proposed new method at the same time as the EPA published the *National Primary and Secondary Drinking Water Regulations, Proposed Rule*, in 1989. Formal EPA approval was accomplished when method B-1011 was published in the *National Primary and Secondary Drinking Water Regulations* on January 30, 1991.

There are conflicting opinions on whether to use single (EPA method B-1011) or dual (EPA method 300.0) column IC for nitrate analysis. The EPA evaluated data from a comparability study for both

of the methods and concluded that they both were successful in analyzing nitrate, *i.e.*, precision, accuracy and acceptance limits were met [2].

The upper chromatogram of Fig. 2 contains a separation of nitrite and nitrate in a chlorinated drinking water sample using method B-1011 which includes a Waters IC-Pak Anion column, lithium hydroxide eluent and UV detector. By changing the detection mode to ultraviolet absorbance, the effects of interferences are eliminated and both nitrite and nitrate are easily detected since they both absorb at 214 nm.

The real utility of UV detection is for drinking water samples that are not chlorinated. The EPA requires that non-chlorinated drinking water samples be preserved by an addition of sulfuric acid until the sample pH is less than 2 [1]. This could add greater than 1000 ppm sulfate to the sample. The lower chromatogram in Fig. 2 shows a ground water sample containing over 200 ppm calcium carbonate and preservation with sulfuric acid added 1500 ppm sulfate. The sample was diluted 1:100 to avoid col-

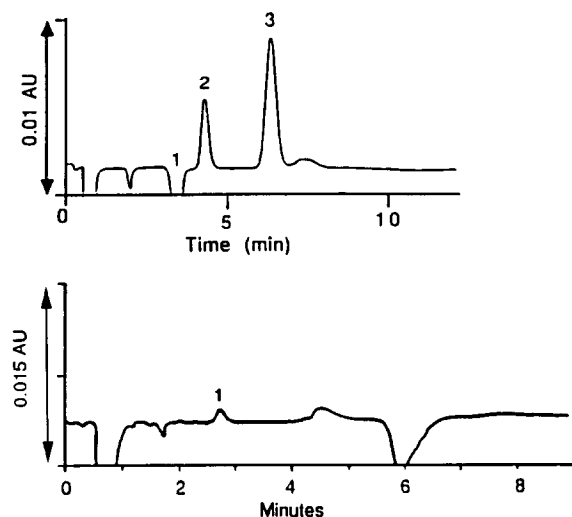


Fig. 2. Upper chromatogram: Analysis of nitrite and nitrate in chlorinated drinking water using EPA method B-1011. Conditions, column: Waters IC-Pak Anion, eluent: 2.5 mM lithium hydroxide, flow-rate: 1.2 ml/min, detection: UV at 214 nm. Peaks: 1 = chloride; 2 = nitrite-N (32 $\mu\text{g/l}$); 3 = nitrate-N (68 $\mu\text{g/l}$). Lower chromatogram: Use of EPA method B-1011 for the analysis of non-chlorinated drinking water (H_2SO_4 preserved). Same conditions except eluent: 5 mM lithium hydroxide. Peak 1 = Nitrate-N (3.75 $\mu\text{g/l}$).

umn overloading by such a high sulfate level and then chromatographed.

One would not have been able to use conductivity detection for this sample due to the vastly different anion concentrations and the significant conductivity response of sulfate. There was no problem analyzing it using UV detection. In fact, the EPA's Laboratory Certification Manual states that, due to the close elution times for nitrate and sulfate anions, conductivity detection methods may not be used to analyze for nitrate in samples preserved with sulfuric acid [1].

EPA Method A-1000

Also in 1987, method A-1000, *Conductivity Detection of Anions Using Single Column Ion Chromatography* [7] was forwarded to the EPA Environmental Monitoring Systems Laboratory, Cincinnati, OH, USA. Method A-1000 was cited in the Manual for the Certification of Laboratories Analyzing Drinking Water, as a recommended method for the determination of chloride and sulfate in 1989 [1]. A chromatogram of a standard mixture of seven anions in water using a Waters IC-Pack Anion column, borate-gluconate eluent, and conductivity detection is given in Fig. 3.

Waters test method B-1012 for nitrite/nitrate in wastewater

Waters submitted data collected by Enwright Environmental Laboratories [8] to the EPA Environmental Monitoring Systems Laboratory, Cincinnati,

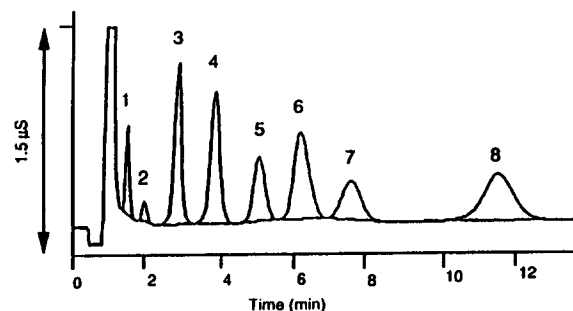


Fig. 3. Separation of a standard anion mixture using EPA method A-1000. Conditions, column: Waters IC-Pak Anion, eluent: borate-gluconate, flow-rate: 1.2 ml/min, detection: conductivity. Peaks: 1 = fluoride (1 ppm); 2 = hydrogencarbonate; 3 = chloride (2 ppm); 4 = nitrite (4 ppm); 5 = bromide (4 ppm); 6 = nitrate (4 ppm); 7 = phosphate (6 ppm); 8 = sulfate (4 ppm).

ti, OH, USA, in 1990. A Waters Chromatography single-column IC method for nitrite and nitrate was compared to the EPA approved cadmium reduction method 353.3, in order to obtain alternate test procedure (ATP) approval. The analysis of nitrite and nitrate in a sample obtained from a sewage treatment plant is shown in Fig. 4. Method B-1012 prescribes the use of a Waters IC-Pak Anion HC column, modified borate/gluconate eluent, and UV detection in series with conductivity detection. The sample was diluted 1:4. The reported results of the analysis were based on data from the UV detector, rather than the conductivity detector, due to better sensitivity and fewer interferences for nitrite and nitrate determination. However, simultaneous detection is advantageous because it offers more information per analysis. This test method is currently being reviewed by the EPA.

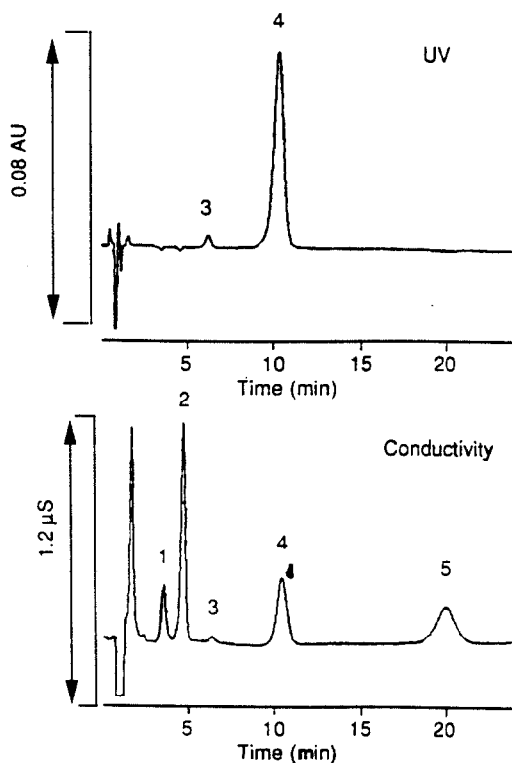


Fig. 4. Analysis of nitrite and nitrate in wastewater by Wates test method B-1012. Conditions, column: Waters IC-Pak Anion HC, eluent: modified borate-gluconate, flow-rate: 2.0 ml/min, detection: upper chromatogram; UV at 214 nm, lower chromatogram; conductivity. Peaks: 1 = hydrogencarbonate; 2 = chloride; 3 = nitrite (0.27 ppm); 4 = nitrate (8.95 ppm); 5 = sulfate.

EPA Method 218.6

The EPA has established regulations and methodology for hexavalent chromium Cr(VI) due to its adverse health effects even at trace levels. Atomic absorption; furnace technique and inductively coupled plasma are EPA approved methods for the determination of chromium in drinking water [2]. However, these methods are only marginally sensitive and selective when used for the analysis of complex matrices such as industrial waste water.

A joint EPA-ASTM collaborative study of EPA method 218.6 [9], the analysis of hexavalent chromium in reagent, drinking, and waste water using IC with post-column derivatization and UV-VIS detection at 530 nm, was completed in December, 1990. The ASTM subcommittee D19.05 on inorganics in water approved the data in June, 1991. Fig. 5 is an example of a 10- $\mu\text{g/l}$ hexavalent chromate standard under the test method conditions: a Waters IC-Pak Anion HC column, ammonium sulfate-ammonium hydroxide eluent, post-column reagent diphenylcarbohydrazide-methanol-sulfuric acid, and a UV-VIS detector. The advantages of

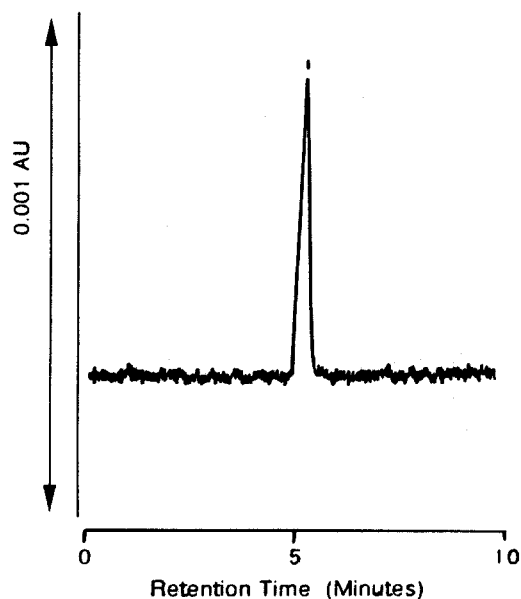


Fig. 5. Separation of a chromate standard using EPA method 218.6. Conditions, column: Waters IC-Pak Anion HC, eluent: 25 mM ammonium sulfate-10 mM ammonium hydroxide, flow-rate: 1.5 ml/min, post-column reagent: diphenylcarbohydrazide-methanol-sulfuric acid, detection: UV at 530 nm. Peak: 1 = hexavalent chromate (10 $\mu\text{g/l}$).

TABLE I

CHROMATE ANALYSIS USING POST-COLUMN DERIVATIZATION AND UV

All data expressed as $\mu\text{g/l Cr}^{6+}$. TV = true value, PCD = post-column derivatization.

Sample	TV	PCD at 530 nm	UV at 365 nm
<i>Reagent water</i>			
1	8.0	10.4	10.1
2	20.0	21.5	22.5
3	40.0	41.8	40.7
4	100	104	100
5	800	782	787
<i>Wastewater</i>			
6	20.0	21.8	18.6
7	100	99.9	107
8	140	148	151
9	800	798	800
10	960	906	960

this method include better sensitivity and no interferences. Although post column derivatization with UV-VIS detection at 530 nm is stipulated in the method, direct UV detection at 365 nm can also be employed. Table I shows data taken from Waters contribution to the collaborative study of the EPA method 218.6 for chromate. A comparison of the true values of chromate for ten samples to values obtained from both detection techniques shows a good correlation of the results. This suggests that direct UV detection at 365 nm can be simpler alternative to post-column derivatization for non-compliance monitoring of hexavalent chromium.

Test methods for disinfection by-products

The EPA is developing regulations for various disinfection by-products (DBPs) in drinking water. Because of its sensitivity and precision, IC is a good choice for analyzing the by-products of chlorine dioxide and ozone oxidation (*i.e.*, chlorite, chlorate and bromate) [10].

EPA method 300.0 contains a "Method B" for oxyhalides [4]. However, since these analytes are not regulated by the EPA any method can be used. Waters test method for Oxyhalides, A-119 [11] is described in Fig. 6 as an extension of EPA Method A-1000. This method incorporates a Waters IC-Pak

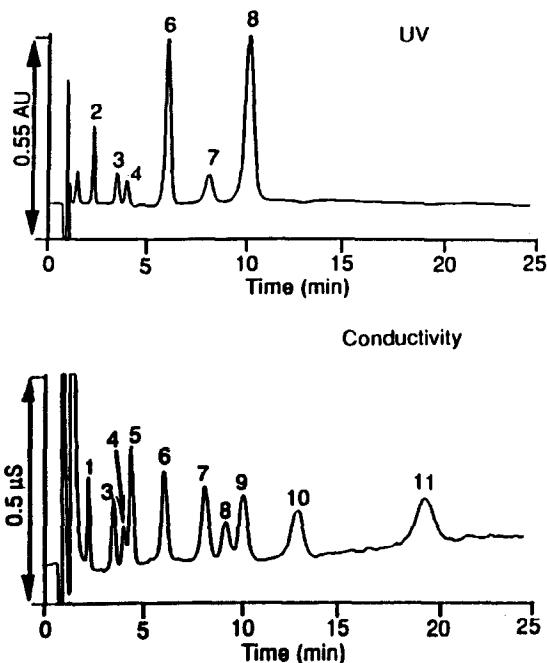


Fig. 6. Separation of a standard anion mixture using Waters test method for oxyhalides. Conditions, column: Waters IC-Pak Anion HC, eluent: borate-gluconate, flow-rate: 2.0 ml/min, detection: upper chromatogram; UV at 214 nm, lower chromatogram; conductivity. Peaks: 1 = fluoride (1 ppm); 2 = iodate (4 ppm); 3 = chlorite (4 ppm); 4 = bromate (4 ppm); 5 = chloride (1 ppm); 6 = nitrite (2 ppm); 7 = bromide (4 ppm); 8 = chlorate (4 ppm); 9 = nitrate (4 ppm); 10 = phosphate (6 ppm); 11 = sulfate (4 ppm).

Anion HC column, borate-gluconate eluent, and a UV detector followed by a conductivity detector. The two chromatograms are the result of a simultaneous detection of an eleven-anion standard mixture in water. UV detection allows one to take advantage of UV absorption properties of iodate, chlorite, bromate, nitrite, bromide, and nitrate. In the chromatogram obtained with conductivity detection, iodate coelutes with fluoride, bromate and chloride are partially separated, and it is difficult to resolve nitrate from chlorate. Thus iodate, bromate, nitrite, and nitrate are best quantitated by UV, while the other anions could best be quantitated by conductivity.

Test method for inorganic and organic halides using capillary ion electrophoresis

Capillary ion electrophoresis (Waters' trade

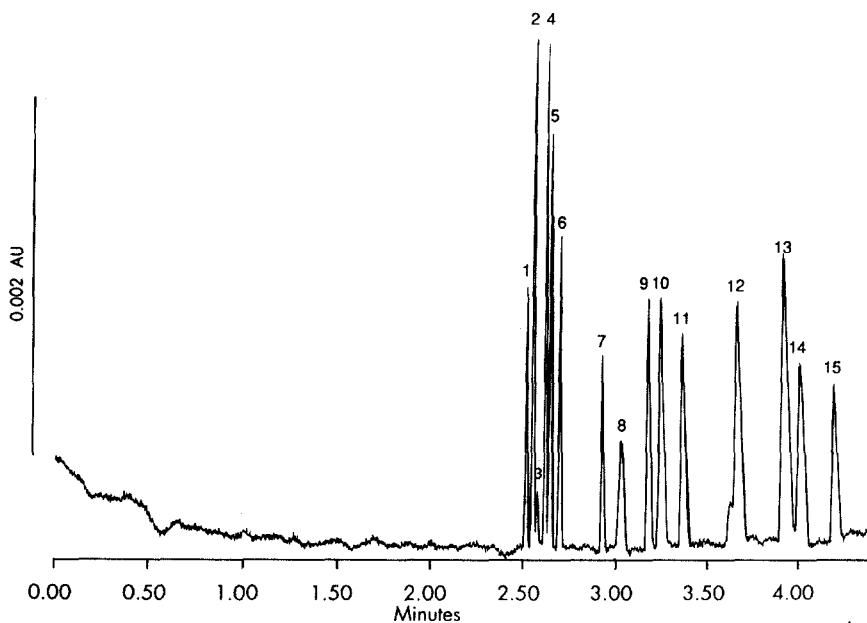


Fig. 7. Electropherogram of a standard anion mixture using a proposed Waters test method for the analysis of anions in water by capillary ion electrophoresis. Conditions, capillary: Waters AccuSep 60 cm \times 75 μ m I.D. fused silica. electrolyte: 5 mM chromate with 0.3 mM CIA-Pak OFM anion-BT (patent pending) at pH 8, potential: 20 kV at 18 μ A (negative), detection: 254 nm indirect, injection: hydrostatic (10 cm for 30 s). Peaks: 1 = bromide (4 ppm); 2 = chloride (2 ppm); 3 = iodide (4 ppm); 4 = sulfate (4 ppm); 5 = nitrite (4 ppm); 6 = nitrate (4 ppm); 7 = chlorate (4 ppm); 8 = perchlorate (4 ppm); 9 = fluoride (1 ppm); 10 = phosphate (4 ppm); 11 = chlorite (4 ppm); 12 = carbonate (4 ppm); 13 = acetate (5 ppm); 14 = monochloroacetate (5 ppm); 15 = dichloroacetate (5 ppm) (Courtesy of William R. Jones, Millipore Waters Chromatography).

name: Capillary Ion Analysis, CIA) is a branch of Capillary electrophoresis optimized for the rapid analysis of low-molecular-weight anions and cations that separates ions according to their mobility in electrolytic solutions [12,13]. Capillary ion electrophoresis is a powerful separation technique that offers rapid, highly efficient separations with different selectivities (compared to IC) obtained from nanoliters of sample volume [14]. Fig. 7 illustrates a proposed Waters Test Method for the analysis of anions in water by CIA. This method utilizes a Waters Quanta 4000, Waters AccuSep capillary, chromate/CIA-Pak OFM anion BT electrolyte, and indirect UV detection. The electropherogram demonstrates the ability of capillary ion electrophoresis to analyze primary and secondary contaminants as well as other anions of environmental concern, in less than 5 min. It would require four different methods to analyze these components by IC at considerably longer run times.

CONCLUSIONS

EPA methods for primary and secondary contaminants using ion chromatography offer several advantages. The ability to chromatographically separate various anion species from interferences before detection. Detector versatility enables one to mask interferences/coeluting peaks and increase sensitivity. Sample preparation typically involves just a dilution and filtration step prior to injection into the IC.

The capillary ion electrophoresis method will be submitted for ASTM-EPA consideration. Capillary ion electrophoresis offers a significant improvement over IC in efficiency and analysis time. The unique selectivity provides an alternative solution to coelution problems that occur with IC.

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