DIONEX

Application Note

AN 56 July 1988

Determination of Trace Anions and Key Organic Acids in High Purity, Ammoniated, and Borated Waters Found in Steam Cycle Power Plants

INTRODUCTION

Ionic contamination has long been recognized as a primary cause of corrosion in steam cycle power plants. Accordingly, monitoring and controlling such contaminants are of great importance in power plant operations. Dionex's chemically suppressed Ion Chromatography (IC) technology is used worldwide to provide the required sub parts-per-billion (ppb) level measurement sensitivity for inorganic anions in high purity water. As described below, organic acid anions are now known to be a source of corrosion-causing contamination. This Application Note describes a method which uses gradient IC in combination with automated sample preconcentration to determine both organic and inorganic anions from a single sample injection. These include the anions of major significance: chloride, sulfate, acetate and formate; as well as additional ions such as fluoride, nitrite, bromide, nitrate and phosphate. Without gradient elution, an eluant strong enough to elute sulfate would cause the weakly retained organic acid anions and fluoride to coelute in the void volume. Using gradient elution, all of these anions can be determined at low ppb levels.

The anions are determined in the following sample types:

- High purity deionized water such as make-up demineralizer and condensate polisher effluent
- Deionized water containing up to 1 ppm ammonia
- Deionized water containing up to 1.2% boric acid (2000 ppm boron) as used in PWR primary reactors.

Power Plant Operating Limits In 1982 (Revised 1984),[1] the Electric Power Research Institute (EPRI) published pressurized water reactor (PWR) water chemistry guidelines for nuclear power plants which called for a limit of 20 ppb of chloride and sulfate in the boiler blowdown from recirculating boilers. Since recirculating boilers concentrate nonvolatile impurities by a factor of as much as 100X to 200X, feedwater contaminants should be held to significantly less than 1 ppb. EPRI published the *Interim Consenus Guidelines of Fossil Plant Cycle Chemistry* in 1986.[2] These guidelines call for maintaining chloride and sulfate to less than three ppb at many steam cycle locations. Cation conductivity is typically limited to less than 0.2 μS/cm^2 at these and other locations. The method presented in this Application Note supplies the sensitivity required to check these contaminant levels.

Organic Acid Contaminants In 1986, EPRI also published an Industrywide Survey of PWR Organics.[3] Two major conclusions that can be drawn from this report are that:

- Acetic and formic acids were the majority (> 90%) ionic organics found in PWR secondary cycles
- These organic acids were responsible for more than 50% of the cation conductivity in both feedwater and boiler blowdown, surveyed in more than 50% of the 13 plants.

Since fossil fuel water chemistry is similar to PWR secondary systems, the presence of acetate and formate is also likely in the feedwater and boiler blowdown of fossil fuel plants.

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LPN 034074 7/88

DISCUSSION OF METHOD

The method described in this Application Note uses sample concentration to increase sensitivity. (Sample concentration techniques are discussed in Part I of the Dionex *Ion Chromatography Cookbook.*) A volume of sample (usually 5 to 50 mL) is pumped through a short anion exchange concentrator column to trap the anion analytes. The concentrator column is connected to a 4-way valve in the same position as the sample loop in an inject valve. An IonPac• AG4A column is used as the concentrator in this application. The concentrator column is then switched by the 4-way valve into the eluant stream. The anions are eluted from the concentrator onto the IonPac AS4A separator column, where they are separated using gradient elution with a borate eluant. The eluant concentration is increased from 5 mM to 28 mM sodium tetraborate in 8 minutes. Detection is by conductivity with chemical eluant suppression. The total run time including column equilibration is 25 minutes. Example chromatograms of trace anions and organic acids are shown in Figures 1 and 2. (A more extensive discussion of gradient elution in Ion Chromatography can be found in Technical Note 19, included in the Anions section of the *IC Cookbook*).

Figure 1. Gradient Elution of Trace Inorganic Anions, Acetate and Formate

Columns: IonPac® AG4A, AS4A
Sample Volume: 20 mL
Eluant: 5–28 mM Sodium Tetraborate Gradient
Suppressor: AMMS

Peaks:	ppb
1. Fluoride	3
2. Acetate	30
3. Formate	7
4. Chloride	8
5. Nitrite	5
6. Carbonate	
7. Bromide	8
8. Nitrate	17
9. Phosphate	17
10. Sulfate	17

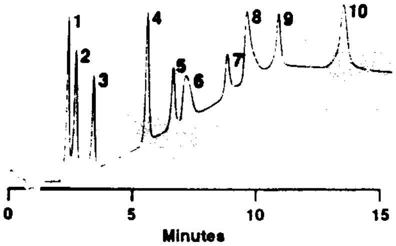
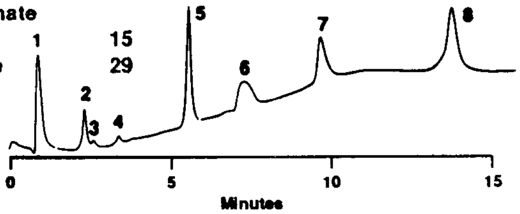


Figure 2. Trace Anions, Acetate and Formate in 1.2% Boric Acid

Peaks:	ppb
1. 1.2% Boric Acid	
2. Fluoride	1.4
3. Acetate	1.5
4. Formate	0.7
5. Chloride	12
6. Carbonate	
7. Nitrate	15
8. Sulfate	29

Columns: IonPac® AG4A, AS4A
Sample Volume: 20 mL
Eluant: 5–28 mM Sodium Tetraborate Gradient
Suppressor: AMMS



Trap Column An Anion Trap Column (ATC) is placed between the gradient pump and the injection valve to remove trace anions from the eluant. The trap column must be regenerated periodically by flushing with 100% of eluant 1 (70 mM sodium tetraborate). This should be done whenever the baseline shift from the gradient run increases significantly from its normal value of 2 to 6 µS.

Determination of Maximum Sample Volume Increasing the sample volume will increase the quantity of analyte which is delivered to the separator column, increasing the method sensitivity. If the sample volume is too large, anions from the sample matrix will elute the analyte anions from the concentrator column. Therefore, the maximum sample volume depends on the sample matrix. The maximum sample volumes for the three different sample matrices used in the power industry (DI water, 1 ppm ammonia and 1.2% boric acid) were determined by preparing plots of peak height versus volume concentrated for each anion. Deviation from linearity indicates that analyte ions are being eluted from the concentrator by the sample matrix. The most weakly retained analyte (fluoride) will be the first to be eluted. Plots for fluoride are shown in Figure 3. With deionized water (and 1 ppm ammonia samples), all anion plots are linear through the maximum volume concentrated, 45 mL. For the 1.2% boric acid sample, the fluoride plot deviates from linearity above 25 mL, indicating that some of the fluoride is being eluted from the concentrator by the boric acid in the sample. From these plots, it was determined that 20 mL of sample should be the recommended volume for boric acid solutions, and

Figure 3a. Peak Height versus Volume 30 ppb Fluoride in Deionized Water

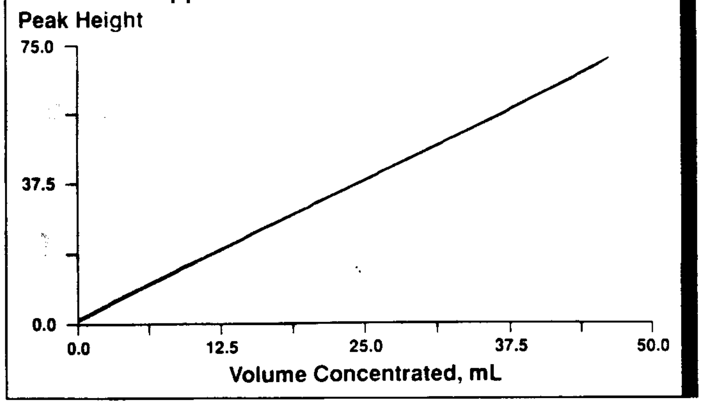
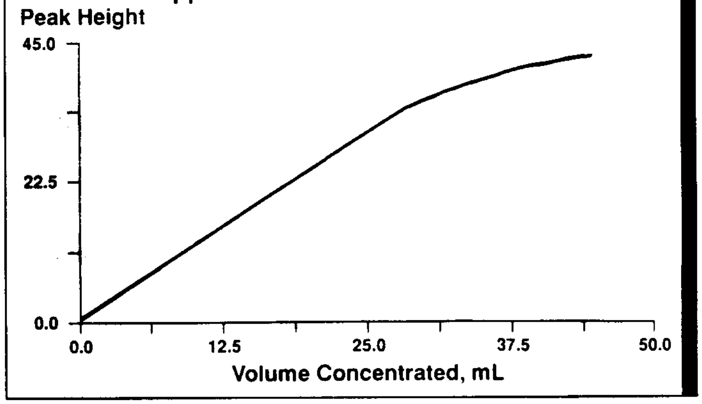


Figure 3b. Peak Height versus Volume 30 ppb Fluoride in 1.2% Boric Acid



that sample volumes of at least 45 mL can be used reliably for the DI water or 1 ppm ammonium samples.

Calibration For each analyte ion, calibration curves are linear in all three sample types over the range of 0 to 30 ppb using a 20 mL sample volume. Since the slopes are affected by the sample matrix, either the standard addition method should be used, or calibration standards should be prepared in the same matrix as the sample. (Calibration methods are discussed in Part I of the *IC Cookbook*, and in the *Handbook of Ion Chromatography*, P/N 32769.)

CONDITIONS

Trap Column:	Anion Trap Column (ATC)
Concentrator Column:	IonPac AG4A
Separator Column:	IonPac AS4A
Sample Pump Flow Rate:	4 mL/min.
Eluant 1:	70 mM Sodium Tetraborate ($Na_2B_4O_7 \cdot 10\ H_2O$)
Eluant 2:	18 MΩ Deionized Water
Eluant Flow Rate:	2 mL/min.
Suppressor:	Anion MicroMembrane (AMMS)
Regenerant:	25 mN Sulfuric Acid
Regenerant Flow Rate:	15 mL/min.
Initial Background Conductivity:	Approximately 3 µS
Final Background Conductivity:	Approximately 6 µS

GRADIENT PROGRAM

Time	%1	%2	Comments
0.0	0	100	Rinse concentrator column with DI water
2.0	0	100	End rinse
2.1	7	93	Start separator equilibration
12.1	7	93	Inject and start gradient
20.1	40	60	End gradient
25.0	40	60	End run

COMPUTER OR INTEGRATOR TIMED EVENTS PROGRAM

Time	Description	Comments
0.0	Inject Valve to INJECT	
0.0	GPM Run ON	Rinse concentrator column with DI water
2.1	Inject Valve to LOAD	
2.1	Sample Pump ON	Load sample on concentrator
7.1	Sample Pump OFF	20 mL of sample concentrated
12.1	Inject Valve to INJECT	Inject sample, begin gradient run
12.1	Start Sampling	Begin data acquisition

The programs begin with a two minute DI water rinse of the concentrator column to remove eluant solution. Without the rinse, the eluant remaining in the concentrator prevents analyte ions from being retained. The rinse is followed by a 10 minute separator column equilibration period. During this period, the concentrator is loaded with sample. The program is written for a sample volume of 20 mL with a sample pump flow rate of 4.0 mL/min. At this sample pump flow rate, up to 40 mL can be loaded in the 10 minute loading period. The actual chromatography run time is from the injection at 12.1 minutes to after sulfate has eluted at 25 min.

SOLUTIONS AND REAGENTS

Eluant 1: 70 mM sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$)

Dissolve 26.6 g sodium tetraborate decahydrate per liter of 18 MΩ deionized water.

Eluant 2: Deionized water

Regenerant: 25 mN sulfuric acid

Dilute 1 bottle of Dionex concentrated regenerate solution (P/N 39601) to 4 liters deionized water, or dilute 3 mL of concentrated sulfuric acid to 4 liters of deionized water.

RECOMMENDED EQUIPMENT

Dionex Series 4500i Chromatograph equipped with a Gradient Pump Module (GPM), a conductivity detector and a sample loading pump. This method is best performed in an automated mode with either an AutoIon® 450 or 400, or a 4270 or 4290 integrator with Timed Events Module and an AI-2 Automation Interface.

REFERENCES

1. *PWR Secondary Water Chemistry Guidelines, Revision 1,* (1984), Steam Generator Project Office, Nuclear Power Division, Electric Power Research Institute (EPRI), Palo Alto, CA.
2. *Interim Consensus Guidelines on Fossil Plant Cycle Chemistry Report,* No. EPRI CS-4629, (EPRI).
3. *Industrywide Survey of PWR Organics,* No. EPRI NP-4698, (EPRI).