Determination of Trace Cations in Power Plant Waters Containing Morpholine

**INTRODUCTION**
Morpholine and ammonium are used as additives in power plant waters. Morpholine acts as a corrosion inhibitor, whereas ammonium is used to control pH. In this matrix, it is critical to determine the presence of inorganic cation contaminants. This method uses the IonPac CS14 column to quantify trace concentrations of lithium, sodium, potassium, magnesium, and calcium in the presence of high levels of ammonium and morpholine. Acetonitrile can be added to the eluent to improve peak shape and optimize resolution for some of the cations of interest.

**EQUIPMENT**
Dionex Chromatography system comprising:
- Advanced Gradient Pump (AGP)
- Liquid Chromatography Module (LCM-3), equipped with Model 9126-038 Rheodyne Injector or equivalent
- Sample Preparation Module (SPM) [ for 8200 Process Analyzer ]
- Conductivity Detector Module (CDM-3)
- Sample Loading Pump, RP-1

**REAGENTS AND STANDARDS**
- Deionized water (DI H2O), Type I reagent grade, 17.8MW / cm resistance or better. Methanesulfonic Acid (MSA) (+99% pure) Acetonitrile (ACN) HPLC grade

**CONDITIONS**

<table>
<thead>
<tr>
<th>Time</th>
<th>E1</th>
<th>V5</th>
<th>V6</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>100</td>
<td>1</td>
<td>0</td>
<td>Prime RP-1 with sample</td>
</tr>
<tr>
<td>5.0</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>Load sample to CG-14</td>
</tr>
<tr>
<td>6.0</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>Inject</td>
</tr>
</tbody>
</table>

- Columns: (2) IonPac CG14 (2-mm) guard columns, one used as a guard column, the other as a concentrator column
- (1) IonPac CS14 (2-mm) analytical column
- Eluent: 8 mM Methanesulfonic acid or 8 mM Methanesulfonic acid in 5% acetonitrile (v/v)
- Eluent Flow Rate: 0.25 mL/min
- Rinsing Flow Rate: 1.0 mL/min
- Sample Volume: 1.0 mL
- Detection: Suppressed Conductivity
- Suppressor: CSRS-I (2-mm), AutoSuppression, Recycle Mode (without acetonitrile); External Water Mode (with acetonitrile)
- Pump programs:

1) 8 mM methanesulfonic acid
2.) 8 mM methanesulfonic acid with 5% acetonitrile

<table>
<thead>
<tr>
<th>Time</th>
<th>E1</th>
<th>V5</th>
<th>V6</th>
<th>Remarks (rinse)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>100</td>
<td>1</td>
<td>0</td>
<td>Prime RP-1 with sample</td>
</tr>
<tr>
<td>5.0</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>Load sample to CG-14</td>
</tr>
<tr>
<td>6.0</td>
<td>100</td>
<td>0</td>
<td>1</td>
<td>Rinse CG-14 with w/ 5% ACN</td>
</tr>
<tr>
<td>8.0</td>
<td>100</td>
<td>1</td>
<td>1</td>
<td>Inject</td>
</tr>
</tbody>
</table>

Timed Events Programs (for operation of 8200 Process Analyzer):

1.) 8 mM methanesulfonic acid

<table>
<thead>
<tr>
<th>Step</th>
<th>Time</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>ACI SPM valve 3 OFF</td>
</tr>
<tr>
<td>Initial</td>
<td>-</td>
<td>ACI RP-1 OFF</td>
</tr>
<tr>
<td>1</td>
<td>0.3</td>
<td>ACI RP-1 ON</td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
<td>AGP Run Gradient Clock</td>
</tr>
<tr>
<td>3</td>
<td>9.9</td>
<td>CDM-3 AutoOffset ON</td>
</tr>
<tr>
<td>4</td>
<td>10.0</td>
<td>ACI SPM valve 3 OFF</td>
</tr>
<tr>
<td>4</td>
<td>10.0</td>
<td>ACI RP-1 OFF</td>
</tr>
<tr>
<td>4</td>
<td>10.0</td>
<td>Start Sampling</td>
</tr>
</tbody>
</table>

2.) 8 mM methanesulfonic acid with 5% acetonitrile

<table>
<thead>
<tr>
<th>Step</th>
<th>Time</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>ACI SPM valve 3 OFF</td>
</tr>
<tr>
<td>Initial</td>
<td>-</td>
<td>ACI RP-1 OFF</td>
</tr>
<tr>
<td>1</td>
<td>0.3</td>
<td>ACI RP-1 ON</td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
<td>AGP Run Gradient Clock</td>
</tr>
<tr>
<td>3</td>
<td>11.9</td>
<td>CDM-3 AutoOffset ON</td>
</tr>
<tr>
<td>4</td>
<td>12.0</td>
<td>ACI SPM valve 3 OFF</td>
</tr>
<tr>
<td>4</td>
<td>12.0</td>
<td>ACI RP-1 OFF</td>
</tr>
<tr>
<td>4</td>
<td>12.0</td>
<td>Start Sampling</td>
</tr>
</tbody>
</table>

note: ACI = Advanced Computer

**PREPARATION OF SOLUTIONS AND REAGENTS**

1 M Methanesulfonic acid (MSA) Eluent Concentrate

Weigh 96.10 g of methanesulfonic acid (MSA). Carefully add this amount to a 1-L volumetric flask containing about 500 mL of deionized water. Dilute to the mark and mix thoroughly.

8 mM Methanesulfonic acid (MSA)

Pipette 8.0 mL of the 1.0 M MSA eluent concentrate into a 1-L volumetric flask. Dilute to 1 L using deionized water. Degas the eluent.

8 mM Methanesulfonic acid (MSA) / 5% Acetonitrile

Pipette 8.0 mL of the 1.0 M MSA eluent concentrate into a 1-L volumetric flask. Dilute to approximately 800 mL using deionized water. Degas the eluent. Add 50 mL of acetonitrile and mix until all components are in solution. Dilute to a final volume of 1.0 L using deionized water.

5% Acetonitrile for Rinsing

Add 50 mL of acetonitrile to approximately 800 mL using deionized water in a 1-L volumetric flask and mix until all components are in solution. Dilute to a final volume of 1.0 L using deionized water.

Stock standard solution (1000 mg/L)

Lithium (Li+) 1000 mg/L: Dissolve 6.108 g of lithium chloride (LiCl) in deionized water and dilute to 1.000 liter.

Sodium (Na+) 1000 mg/L: Dissolve 2.542 g of sodium chloride (NaCl) in deionized water and dilute to 1.000 liter.

Ammonium (NH4+) 1000 mg/L: Dissolve 2.965 g of ammonium chloride (NH4Cl), in deionized water and dilute to 1.000 liter.

Potassium (K+) 1000 mg/L: Dissolve 1.907 g of potassium chloride (KCl) in deionized water and dilute to 1.000 liter.

Morpholine (tetrahydro-1,4-oxazine [C4H9NO])

1000 mg/L: Pipet 1.00 mL of morpholine into 800 mL of deionized water and dilute to 1.000 liter.

Magnesium (Mg2+) 1000 mg/L: Dissolve 8.365 g of magnesium chloride, hexahydrate MgCl2.6H2O in deionized water and dilute to 1.000 liter.

Calcium (Ca2+) 1000 mg/L: Dissolve 3.668 g of calcium chloride, dihydrate CaCl2.2H2O in deionized water and dilute to 1.000 liter.

Calibration
Intermediate standards (low mg/L) are prepared by appropriate dilutions of the stock solutions. Calibration standards (mg/L) are prepared by further diluting the intermediate standards. Prepare a minimum of three concentration levels to bracket the expected concentrations of the sample of interest.

**DISCUSSION AND RESULTS**

Trace cations in a power plant morpholine matrix are determined by concentrating 1 mL of sample on a 2-mm CG14 concentrator column. No sample pretreatment is necessary. The 2-mm column and suppressor system used in this application has advantages over a 4-mm system: lower eluent flow rates, higher suppression capacity, and less waste generation.

Two different eluents can be used, 8 mM MSA with or without 5% acetonitrile. The benefit of having organic solvent in the eluent results in improved morpholine peak shape, better separation between morpholine and magnesium, and increased response for the divalent cations. The CSRS is operated in the external water mode with 5% acetonitrile in the eluent. When using the eluent containing acetonitrile, the sample is loaded onto the CG14 concentrator column and then rinsed with 2 mL of 5% acetonitrile. This process replaces the aqueous mobile phase in the concentrator with one more nearly matched to the eluent while still retaining the cations of interest. The concentrator column is then switched in line with the eluent stream and the analytical columns. The cations of interest are eluted from the concentrator and separated on the guard and analytical columns. Figures 1 - 4 illustrate how the system performs these tasks. When 8 mM MSA without acetonitrile is used as the eluent, the CSRS is operated in the recycle mode and the step represented by Figure 3 is omitted.

To validate this method, precision and linearity were determined for the case with 5% acetonitrile in the eluent. A multilevel calibration based on the values listed in Table 1 yielded good r² values over a wide range. A sample with analyte concentrations within the calibration range showed acceptable precision for both concentration and retention time. Figure 5 shows a representative chromatogram of the sample and Table 2 summarizes the precision results for 21 replicates. For comparison, Figure 6 shows the same sample run with 8 mM MSA and the CSRS in the recycle mode. The maximum sample volume that can be loaded for this method without significant deviation from linearity is 50 mg/L morpholine. A system blank is determined by running deionized water as a sample. Figure 7 illustrates a chromatogram of a blank for the 5% acetonitrile method.

This method using the IonPac CS14 is a useful analytical procedure to determine trace cations in power plant waters containing high morpholine and ammonium. Reproducibility and linearity are within acceptable limits. This method is applicable to on-line and grab sample analysis. The addition of acetonitrile to the eluent improves morpholine peak shape and resolution, permitting quantitative analysis of morpholine.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Conc (mg/L)</th>
<th>RSD, Conc (%)</th>
<th>Retention Time (min)</th>
<th>RSD Retention Time (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>0.125</td>
<td>0.375</td>
<td>1.25</td>
<td>3.75</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.3</td>
<td>1.5</td>
<td>5.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Ammonium</td>
<td>37.5</td>
<td>112.5</td>
<td>375.0</td>
<td>1125.0</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.5</td>
<td>1.5</td>
<td>5.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Morpholine</td>
<td>500.0</td>
<td>1500.0</td>
<td>5000.0</td>
<td>15000.0</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.5</td>
<td>1.5</td>
<td>5.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Calcium</td>
<td>2.5</td>
<td>7.5</td>
<td>25.0</td>
<td>75.0</td>
</tr>
</tbody>
</table>

Table 1. Multilevel Calibration for Trace Cations in Morpholine Mix for 8 mM MSA w/ 5% ACN

<table>
<thead>
<tr>
<th>Cation</th>
<th>Conc (mg/L)</th>
<th>RSD, Conc (%)</th>
<th>Retention Time (min)</th>
<th>RSD Retention Time (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>0.5</td>
<td>4.2</td>
<td>4.30</td>
<td>0.3</td>
</tr>
<tr>
<td>Sodium</td>
<td>2.0</td>
<td>3.8</td>
<td>4.72</td>
<td>0.3</td>
</tr>
<tr>
<td>Ammonium</td>
<td>150.0</td>
<td>3.9</td>
<td>5.55</td>
<td>0.3</td>
</tr>
<tr>
<td>Potassium</td>
<td>2.0</td>
<td>3.7</td>
<td>6.76</td>
<td>0.8</td>
</tr>
<tr>
<td>Morpholine</td>
<td>2000.0</td>
<td>3.0</td>
<td>8.15</td>
<td>0.6</td>
</tr>
<tr>
<td>Magnesium</td>
<td>2.0</td>
<td>2.0</td>
<td>11.16</td>
<td>0.3</td>
</tr>
<tr>
<td>Calcium</td>
<td>10.0</td>
<td>2.7</td>
<td>12.93</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 2. Reproducibility for Trace Cations in Morpholine Mix for 8 mM MSA w/ 5% ACN
Figure 1: Prime RP-1 with sample

Figure 2: Load sample to CG14

Figure 3: Rinse CG14 with 5% ACN

Figure 4: Schematic of IC system: chromatographing the retained ions
Several factors can affect the success of this method. Morpholine can decompose to a variety of compounds such as: formic acid, methylamine, ethylamine, and glycolic acid. The presence of amines could potentially interfere with the separation of the analytes of interest. In addition, it is important to minimize contamination by using the highest quality deionized water and using special care when handling chemicals and instrumentation.

REFERENCES
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