Flow Solution™ FS 3700 Automated Chemistry Analyzer

Post-distillation Cyanide by Flow Injection Analysis and Photometric Detection USEPA 335.4
Cartridge Part Number 330352CT

Scope and Application

This method is used for the determination of cyanide in distilled samples, including water, wastewater, soil, and sludge, in accordance with USEPA method 335.4. This method also applies to the determination of total cyanide in samples distilled by other methods, such as Standard Methods 4500-CN and ASTM D2036, with the assumption that calibration standards are prepared with the same sodium hydroxide concentration used for samples.

Method Performance

<table>
<thead>
<tr>
<th>Range</th>
<th>5.0–500 µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate</td>
<td>30 samples/hour</td>
</tr>
<tr>
<td>Precision</td>
<td>1% RSD at mid-point of range</td>
</tr>
<tr>
<td>Method Detection Limit (MDL)</td>
<td>0.5 µg/L</td>
</tr>
</tbody>
</table>

The range may be extended to analyze other concentrations by changing the size of the sample loop.

Figure 1. General flow diagram for Post-distillation Cyanide by USEPA 335.4
Reagents and Calibrants

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>CAS #</th>
<th>Chemical Formula</th>
<th>Part Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barbituric acid</td>
<td>67-52-7</td>
<td>C₄H₄N₂O₃</td>
<td></td>
</tr>
<tr>
<td>Brij®-35</td>
<td>9002-92-0</td>
<td>(C₄H₄O)nC₁₂H₂₆O</td>
<td>326126</td>
</tr>
<tr>
<td>Challenge Matrix, ASTM D7365</td>
<td></td>
<td></td>
<td>327788</td>
</tr>
<tr>
<td>Chloramine-T trihydrate</td>
<td>7080-50-4</td>
<td>CH₃C₆H₄SO₂NNaCl • 3H₂O</td>
<td></td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>7647-01-0</td>
<td>HCl</td>
<td></td>
</tr>
<tr>
<td>Potassium cyanide</td>
<td>151-50-8</td>
<td>KCN</td>
<td></td>
</tr>
<tr>
<td>Potassium hydroxide</td>
<td>1310-58-3</td>
<td>KOH</td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>110-86-1</td>
<td>C₅H₅N</td>
<td></td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>1310-73-2</td>
<td>NaOH</td>
<td></td>
</tr>
<tr>
<td>Sodium phosphate, monobasic</td>
<td>7558-80-7</td>
<td>NaH₂PO₄</td>
<td></td>
</tr>
<tr>
<td>Water, deionized</td>
<td></td>
<td>H₂O</td>
<td></td>
</tr>
</tbody>
</table>

Additionally, the following chemicals may be needed for sample preservation or treatment

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>CAS #</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid, glacial</td>
<td>64-19-7</td>
<td>C₂H₄O₂</td>
</tr>
<tr>
<td>Acetone</td>
<td>67-64-1</td>
<td>C₃H₆O</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>50-81-7</td>
<td>C₆H₆O₆</td>
</tr>
<tr>
<td>5-[4-Dimethylaminobenzylidene]rhodanine</td>
<td>536-17-4</td>
<td>C₁₂H₁₄N₂OS₂</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>107-15-3</td>
<td>C₇H₈N₂</td>
</tr>
<tr>
<td>Silver nitrate</td>
<td>7761-88-8</td>
<td>AgNO₃</td>
</tr>
<tr>
<td>Sodium arsenite</td>
<td>7784-46-5</td>
<td>NaAsO₂</td>
</tr>
</tbody>
</table>

Summary of USEPA Method 335.4

Method

1. Prior to analysis, off-line manual distillation releases cyanide from cyanide complexes. Sodium cyanide is converted to cyanogen chloride by reaction with chloramine-T at a pH less than 8. The cyanogen chloride then reacts with pyridine-barbituric acid to form a red-colored complex. The absorbance is measured at 570 nm.

Interferences

1. Several interferences are encountered with this method. Some of the known interferences to this method include aldehydes; nitrate/nitrite; and oxidizing agents, such as chlorine, thiocyanate, thiosulfate and sulfide. Multiple interferences may require the analysis of a series of laboratory-fortified sample matrices (LFM) to verify the suitability of the chosen treatment. Some interferences are eliminated or reduced by the distillation.

2. Sulfides adversely affect the procedure by producing hydrogen sulfide during distillation. Sample treatment is described in Sample Handling and Preservation.
3. High results may be obtained for samples that contain nitrate or nitrite. During distillation, nitrate and nitrite form nitrous acid that reacts with some organic compounds to form oximes. These oximes decompose under test conditions to generate HCN. Pretreatment with sulfamic acid eliminates nitrate and nitrite interferences. Sample treatment is described in *Sample Handling and Preservation*.

4. Oxidizing agents such as chlorine decompose most cyanides. Remove oxidizing agents that decompose cyanides by adding ascorbic acid if analysis is to be performed within 24 hours; otherwise, use sodium arsenite. Sample treatment is described in *Sample Handling and Preservation*.

5. Other compatible procedures for removing or suppressing interferences may be used, provided they do not adversely affect overall method performance.

6. Method interferences can be caused by contaminants in the reagents, reagent water, and glassware, which may bias the results. Take care to keep all such items free of contaminants.

![Figure 2. Post-distillation Cyanide Calibration Series](insert image link)
### Figure 3. Calibration curve and statistics

<table>
<thead>
<tr>
<th>Name</th>
<th>Type</th>
<th>Std. Conc (ppt)</th>
<th>Avg Height</th>
<th>Calc. Avg Conc (ppt)</th>
<th>%RSD</th>
<th>Regs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal Std 1</td>
<td>1pM</td>
<td>10.00000</td>
<td>794.1</td>
<td>21.6038</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Cal Std 20</td>
<td>1pM</td>
<td>20.00000</td>
<td>2795.5</td>
<td>21.6038</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Cal Std 50</td>
<td>1pM</td>
<td>50.00000</td>
<td>677.5</td>
<td>44.5997</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Cal Std 100</td>
<td>1pM</td>
<td>100.00000</td>
<td>1472.7</td>
<td>98.9931</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Cal Std 250</td>
<td>1pM</td>
<td>250.00000</td>
<td>3947.1</td>
<td>258.2623</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Cal Std 500</td>
<td>1pM</td>
<td>500.00000</td>
<td>6965.3</td>
<td>494.9425</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>