O·I·Analytical

Methodology

Post-Distillation Cyanide by Segmented Flow Analysis (SFA)

(Cartridge Part #A002692)

1.0 Scope and Application

1.1 This method is used for the determination of cyanide in distilled samples that includes water, wastewater, soil, and sludge.

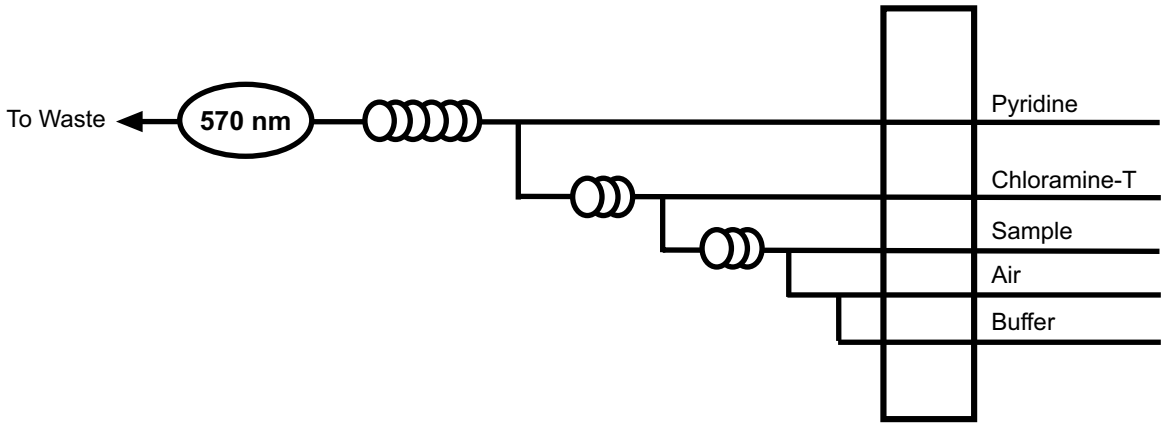
1.2 The Method Detection Limit (MDL) for this method is 2.6 µg/L. The applicable range of this method is 5.0–500 µg/L. The range may be extended to analyze higher concentrations by sample dilution.

2.0 Summary of Method

2.1 Cyanide is released from cyanide complexes by an off-line manual distillation and collected in a sodium hydroxide receiver solution. Sodium cyanide is converted to cyanogen chloride by reaction with chloramine-T at a pH less than 8. The cyanogen chloride then reacts with the pyridine-barbituric acid reagent to form a red colored complex. The complex is measured at 570 nm (References 15.2 and 15.5). For manual distillation procedures, see Reference 15.2.

2.2 The quality of the analysis is assured through reproducible calibration and testing of the SFA system.

2.3 A general flow diagram of the SFA system is shown below (see Section 17.0 for a detailed flow diagram).



3.0 Definitions

Definitions for terms used in this method are provided in Section 16.0, “Glossary of Definitions and Purposes.”

4.0 Contaminations and Interferences

4.1 Several interferences are encountered with this method. Some of the known interferences are 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.

4.2 Sulfides adversely affect the procedure by producing hydrogen sulfide during distillation. If a drop of the sample on lead acetate test paper indicates the presence of sulfide, treat 25 mL more of the stabilized sample (pH ≥ 12) than that required for the cyanide determination with lead carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for analysis. Avoid a large excess of lead and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.

4.3 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation nitrate and nitrite will form nitrous acid that will react with some organic compounds to form oximes. These oximes will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

4.4 Oxidizing agents, such as chlorine, decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch paper (KI-starch paper) at the time of collection; a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper; then add an additional 0.06 g of ascorbic acid for each liter of sample volume. Sodium arsenite has also been employed to remove oxidizing agents.

4.5 Other compatible procedures for the removal or suppression of interferences may be employed provided they do not adversely affect the overall performance of the method.

4.6 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that bias analyte response.

5.0 Safety

5.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been fully established. Each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level.

5.2 For reference purposes, a file of Material Safety Data Sheets (MSDS) for each chemical used in this method should be available to all personnel involved in this chemical analysis. The preparation of a formal safety plan is also advisable.

5.3 The following chemicals used in this method may be highly toxic or hazardous and should be handled with extreme caution at all times. Consult the appropriate MSDS before handling.

5.3.1 Barbituric Acid ($C_4H_4N_2O_3$)

5.3.2 Chloramine-T ($CH_3C_6H_4SO_2NNaCl \cdot 3H_2O$)

5.3.3 Hydrochloric Acid, concentrated (HCl)

5.3.4 Potassium Cyanide (KCN)

5.3.5 Potassium Hydroxide(KOH)

5.3.6 Pyridine (C_5H_5N)

5.3.7 Sodium Hydroxide (NaOH)

5.3.8 Sodium Phosphate, monobasic monohydrate ($NaH_2PO_4 \bullet H_2O$)

Warning: The cyanide ion, hydrocyanic acid, all cyanide salts, and most metal-cyanide complexes are extremely dangerous (Reference 15.4). As a contact poison, cyanide need not be ingested to produce toxicity. Also, cyanide solutions produce fatally toxic hydrogen cyanide gas when acidified. For these reasons, it is mandatory that work with cyanide be carried out in a well-ventilated hood by properly trained personnel wearing adequate protective equipment.

5.4 Unknown samples may be potentially hazardous and should be handled with extreme caution at all times.

5.5 Proper personal protective equipment (PPE) should be used when handling or working in the presence of chemicals.

5.6 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.

6.0 Apparatus, Equipment, and Supplies

6.1 Segmented Flow Analysis (SFA) System (OI Analytical Flow Solution IV) consisting of the following:

6.1.1 Model 502 Multichannel Peristaltic Pump

6.1.2 Random Access (RA) Autosampler

6.1.3 Expanded Range (ER) Photometric Detector with 5-mm path length flowcell and 570-nm optical filter

6.1.4 Data Acquisition System (PC or Notebook PC) with WinFLOW™ software

6.1.5 Post-Distillation Cyanide Cartridge (OI Analytical Part #A002692)

6.2 Sampling equipment — Sample bottle, amber glass, with polytetrafluoroethylene (PTFE)-lined cap. Clean by washing with detergent and water, rinsing with two aliquots of reagent water, and drying by baking at 110°–150°C for a minimum of one hour.

6.3 Standard laboratory equipment including volumetric flasks, pipettes, syringes, etc. should all be cleaned, rinsed and dried per bottle cleaning procedure in Section 6.2.

7.0 Reagents and Calibrants

7.1 Raw Materials

7.1.1 Barbituric Acid ($C_4H_4N_2O_3$)

7.1.2 Chloramine-T ($CH_3C_6H_4SO_2NNaCl \cdot 3H_2O$)

7.1.3 Hydrochloric Acid, concentrated (HCl)

7.1.4 Potassium Cyanide (KCN)

7.1.5 Potassium Hydroxide (KOH)

7.1.6 Pyridine (C_5H_5N)

7.1.7 Sodium Hydroxide (NaOH)

7.1.8 Sodium Phosphate, monobasic monohydrate ($NaH_2PO_4 \cdot H_2O$)

7.1.9 Brij®-35, 30% w/v (OI Analytical Part #A21-0110-33)