METHOD SUMMARY

Hydrogen cyanide is extracted from the sample as a water soluble salt by means of a solution containing sodium hydroxide, ammonium hydroxide, and potassium iodide. The aqueous extract is then titrated with standard silver nitrate and the following reactions take place:

$$2\ NaCN + Ag^{+} \rightarrow NaAg(CN)_2 \quad \text{(Soluble in excess CN-)}$$

$$NaAg(CN)_2 + Ag+ \rightarrow 2AgCN \xrightarrow{NH_4OH} Ag(NH_3)_2CN \text{ (soluble)}$$

$$Ag(NH_3)_2CN + KI \rightarrow AgI + KCN \xrightarrow[\text{Alkaline}]{\text{excess CN-}} NaAg(CN)_2 \text{ (soluble in excess CN-)}$$

When all the cyanide ion has been removed from the solution, the first excess drop of the silver nitrate solution will react with the potassium iodide to form an insoluble precipitate.

$$AgNO_3 + KI \longrightarrow AgI \downarrow$$

The hydrogen cyanide content is calculated from the quantity of silver nitrate required to titrate the sample to the first appearance of silver iodide precipitate.

Repeatability of this method in acetonitrile by the same operator has been measured at the 95% confidence level to be 1.98 ppm. Reproducibility of results between laboratories has not been determined.

SAFETY

Acetonitrile is hazardous to the health and dangerous to handle. Use acetonitrile in a well ventilated hood. Review the MSDS for detailed information concerning toxicity, first aid procedures and safety precautions. Care should be taken in the

preparation of the caustic iodide solution (item 14 below), that the solvent volumes and order of additions be followed exactly to prevent excessive heating of the solution.

Refer to the appropriate safety section or site manual for the necessary protective equipment to use when handling any reagents or samples.

REFERENCES

STMC-10, "Hydrogen Cyanide in Acrylonitrile and Acetonitrile," SOHIO Test Method, 1976.

ASTM E1178-97 "Standard Test Methods for Analysis of Acrylonitrile" http://www.astm.org/

ACS publication "Reagent Chemicals, Ninth Ed."

INTERFERENCES

There are no known interferences to this method.

APPARATUS AND REAGENTS

1. **Separatory funnel**, 250 mL.
2. **Buret**, micro, 10 mL.
3. **Flasks, Erlenmeyer**, 250 mL.
4. **Pipette**, 100 mL, Class A
5. **Flasks, volumetric**, 1000 mL. Class A
6. **Bottle**, plastic, 1000 mL.
7. **Graduated cylinder,** 100 mL, Class A
8. **Balance**, top loading.
9. **Water**, ASTM, Type II.
10. **Silver Nitrate, 0.01N** - The solution may be prepared in the following manner: Dilute 100 mL of 0.1N $AgNO_3$ [CAS 7761-88-8] (standardized, Fisher SS72 or equivalent) using the 100 mL pipette to one liter with water.
11. **Potassium Iodide**, [CAS 7681-11-0] reagent grade, Fisher P 410 or equivalent.
12. **Sodium Hydroxide**, [CAS 1310-73-2] reagent grade, Fisher S318 or equivalent.

13. **Ammonium Hydroxide**, [CAS 1336-21-6] ACS reagent, Fisher A669 or equivalent.
14. **Caustic - Iodide Solution** - The solution should be prepared in the following order: Dissolve 3.6g ± 1g of potassium iodide and 44.1g of sodium hydroxide in 700 mL of water. After these are dissolved and mixed, add 180 mL of concentrated ammonium hydroxide and dilute to one liter with water and mix. Solutions are stable for at least six months. When larger quantities are needed, it may be prepared in one of the following ways:
    a. To make 45 gallons of solution: Dissolve 612g ± 1.0g of potassium iodide and 7500g ± 5g of sodium hydroxide in 31.5 ± 0.5 gallons of water. After these are dissolved and mixed, add 8.1 ± 0.1 gallons of concentrated ammonium hydroxide. Dilute to 45 ± .5 gallons with water and mix.
    b. To make 40L of solution: Dissolve 144g of potassium iodide and 1764g of sodium hydroxide in 27L of water. After these are dissolved and mixed, add 7200 mL of concentrated ammonium hydroxide. Dilute to 40L with water and mix.

CALIBRATION

The silver nitrate titrant is prepared from a purchased volumetric standard, which is standardized against NIST reference material (See the ACS Reagent Chemicals reference for calibration procedure). Under normal circumstances it is not necessary to re-standardize this titrant.

PROCEDURE

1. Add 100 mL of caustic iodide to a 250 mL Erlenmeyer flask using the graduated cylinder.

2. Blank the caustic iodide by slowly titrating with 0.01N $AgNO_3$ to a slight opalescence that persists.

3. Transfer the contents of the Erlenmeyer flask to 250 mL separatory funnel. Add 100 mL of sample with a graduated cylinder. CAUTION: Avoid breathing acetonitrile vapors or ammonia vapors from the caustic iodide reagent. Use a well ventilated hood.

4. Stopper and shake the separatory funnel for 1 minute ± 10 seconds: Be sure to vent the funnel to relieve pressure. Then let the funnel stand in a holder until the layers separate.

5. Draw off the bottom (aqueous) layer into a 250 mL Erlenmeyer flask.

6. Slowly titrate contents of the Erlenmeyer flask with standard 0.01N $AgNO_3$ until an opalescence is obtained. Record this volume of $AgNO_3$.

CALCULATIONS

Calculate the ppm HCN in the sample as follows:

$$\text{HCN, ppm} = \frac{(\text{mL } AgNO_3)\,(\text{N } AgNO_3)\,(0.054) \times 10^6}{(\text{mL sample})\,(0.78)}$$

Where: 0.054 = milliequivalent wt of HCN

0.78 = specific gravity of acetonitrile

REPORT

Report ppm HCN to the nearest 0.1 ppm.

Example: HCN, ppm = 4.1