METHOD SUMMARY

The sample is treated with potassium iodide which, in an acid medium, reacts with peroxides to form yellow I_3^- ions. The absorbance is measured at 360 nm by an ultraviolet spectrophotometer and is converted to concentration of peroxides by means of a calibration curve. Results are reported in the range of 0.1 to 0.5 ppm as total peroxides.

SAFETY

Acrylonitrile is hazardous to the health and dangerous to handle. Use acrylonitrile in a well ventilated hood. Review the MSDS for detailed information concerning toxicity, first aid procedures and safety precautions.

Acetic anhydride is a corrosive lachrymator and a flammable liquid. Keep refrigerated and use in a well ventilated hood.

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

REFERENCES

STM 16-76, "Peroxides in Acrylonitrile", SOHIO Test Method

INTERFERENCES

The color development is not specific for peroxides. Nitrite and oxidizing contaminants in both acrylonitrile and acetic anhydride can also react to give a high apparent peroxide concentration. High blanks may be caused by either of

two types of contributors. Ultraviolet absorbers in either sample or reagent may contribute to apparent I_3^- absorbance at 360 nm. Residual oxidants in sample and reagents can react with iodide to produce I_3^- absorbance. The factors contributing to high blanks cannot be isolated, since the reaction mixture is 83.5% acrylonitrile, itself a variable. However studies show that oxidant in acetic anhydride is a major contributor to a high blank. The calibration standard, hydrogen peroxide, could react chemically with one or more acrylonitrile contaminants which can be another source of variation.

APPARATUS AND REAGENTS

1. **Potassium Iodide**, Reagent Grade - Fisher #P256 or equivalent.
2. **Acetic Anhydride** - Eastman #4 or equivalent - keep refrigerated, ACS grade.
3. **Hydrogen Peroxide** - 30% wt. C.P. ACS grade. ([7722-84-1], Aldrich 21,676-3 or equivalent)
4. **Amberlyst 15 Ion Exchange Resin**- Rohm & Haas.
5. **Erlenmeyer flasks,** Amber or red glass-stoppered, 125 mL. Cleaned, DI water rinsed, and dried.
6. **Spectrophotometer** - Hitachi U2000 or equivalent.
7. **10 mm cells**, near-UV glass.
8. **Water**, ASTM, Type II , or equivalent. Minimum electrical resistivity 1.0 MΩ•cm at 298 K; maximum total organic carbon 50 µg/L; maximum sodium 5 µg/L; maximum chlorides 5 µg/L; maximum total silica 3 µg/L. Detailed specifications can be obtained from ASTM: www.astm.org.
9. **Glass column**, 2cm x 40cm
10. **Volumetric Flasks**, 100 mL, 500 mL, 1000 mL, glass-stoppered.
11. **Peroxide-free acrylonitrile**. Prepare by passing acrylonitrile through a 2 cm x 40 cm glass column packed with 50 cc of acid form ion exchange resin (Rohm and Haas Amberlyst 15 or equivalent resin may be used). Flow through the column should be approximately 8 to 10 bed volumes per hour as indicated by the level of peroxide to be removed. The absorbance obtained should be less than 0.01.
12. **Flask, Erlenmeyer**, 250 mL, stoppered.
13. **Sulfuric acid solution, 12N.** To ~ 400 mL of water, add 333 mL of concentrated sulfuric acid (sp gr = 1.84, strength 95.5-96.6%). Dilute to one liter with water.
14. **Neutral Ammonium Molybdate solution**, 3%. Dissolve 1.5 grams of ammonium molybdate (ammonium molybdate (IV) tetra hydrate, ACS reagent, Aldrich, 22,123-6 or equivalent).

15. **Sodium Thiosulfate solution**. 0.1000 N, volumetric standard, Aldrich 31,954-6.
16. **Starch indicator solution**.

CALIBRATION

Prepare standards according to the appropriate calibration document, or use the following procedure:

1. Pipette 0.5 mL of 30% H_2O_2 into a 100 mL volumetric flask, dilute to volume with water, and mix thoroughly. This stock peroxide solution contains approximately 0.15% H_2O_2.

2. Standardization of the stock peroxide solution should be done in duplicate along with a reagent blank. Dissolve 2g of potassium iodide in 100 mL of water in each of three 250 mL Erlenmeyer flasks. Add 25 mL of 12N sulfuric acid and 3 drops of 3% ammonium molybdate solution to each and swirl to mix.

3. Pipette 25 mL of the stock peroxide solution into two of the flasks, pipette 25 mL of water into the third flask used as the blank. Stopper the flasks and swirl to mix.

4. Allow to stand for 5 minutes, then titrate the liberated iodine with 0.1N sodium thiosulfate until the color becomes pale yellow. Add 1-2 mL of starch indicator and continue the titration to the sharp disappearance of the blue color.

5. Correct the volume for the blank titration and calculate the exact H_2O_2 concentration of the stock peroxide solution. The solution should contain about 1500 mg/L H_2O_2.

$$H_2O_2, \text{ mg/L} = \frac{V \times N \times 17.01}{S} \times \frac{1000 \text{ mL}}{L}$$

$$= \frac{V \times N \times 17.01 \times 10^3}{S}$$

Where:

V = Average volume sodium thiosulfate required for standardization, mL,
N = Exact normality 0.1N sodium thiosulfate titrant.
S = Volume peroxide stock solution taken for standardization = 25 mL.
17.01 = mg H_2O_2 per meq

6. Pipette 1 mL of the assayed H_2O_2 stock solution into a 100 mL volumetric flask containing approximately 50 mL of AN. Dilute to volume with acetic anhydride and mix well. The solution contains approximately 15 mg/L H_2O_2. Calculate the exact concentration.

7. Pipette 0.5, 1.0, 2.0, 3.0 and 5.0 mL of the approximately 15 mg/L H_2O_2 solution into separate 100 mL volumetric flasks. Dilute each to volume with peroxide - free acrylonitrile and mix well. These standards contain approximately 0.07, 0.15, 0.30, and 0.45 mg/L H_2O_2. Calculate the concentration in ppm (w/w).

   ppm (w/w) = Concentration in mg/L / density of acrylonitrile.

   For a 0.30 mg/L H_2O_2 solution:

   0.30 mg/L / 0.807 g/mL = 0.37 ppmw

8. Pipette 5.0 mL of acetic anhydride into each of five 125mL glass-stoppered amber or red Erlenmeyer flasks. Add 0.5g of potassium iodide to each. Pipette 25 mL of each of the four standards into the flasks. Pipette 25 mL of peroxide free acrylonitrile into the fifth flask to serve as a blank. Stopper the flasks and swirl to dissolve the potassium iodide.

9. Allow the flasks to stand for 40 ± 2 minutes. Fill a 1 cm UV cell with the most concentrated standard solution and scan from 315nm to 415nm to find the maximum absorbance. Measure the absorbance of each solution at the maximum using 1 cm cells and the blank as a reference.

10. Prepare a calibration curve by plotting the absorbance of each standard vs ppm H_2O_2.

PROCEDURE

1. Pipette 25 mL of the acrylonitrile sample into one of the flasks. Pipette 25 mL of peroxide-free acrylonitrile into the second flask to serve as a blank.

2. Pipette 5 mL of acetic anhydride into each of two 125 mL glass stoppered amber or red Erlenmeyer flasks. Add 0.5g of potassium iodide. Stopper the flasks and swirl to mix.

3. Allow to stand for 40 minutes ±2, then measure the absorbance of the acrylonitrile sample solution at 365 nm using 1 cm cells and the blank as a reference.

4. Determine the peroxide concentration of the sample, as ppmw H_2O_2, by reference to the calibration curve.

CALCULATIONS

Concentrations are determined manually by applying the slope and intercept formula from the calibration curve determined in Step 10 of the Calibration Procedure. If the UV spectrometer data system has a calibration/analysis feature, apply according to the manufacturer's instructions.

REPORT

Report the peroxide content of the sample in parts per million (ppmw) H_2O_2 to the nearest 0.01 ppmw.