

<b>Method:</b> <b>ACRN-5</b> Revision:         6 Final Revision Date: 08/15/07	<b>Acrylonitrile  Specification Tests</b>	<b>INEOS Nitriles</b>
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## METHOD SUMMARY

The aldehydes in the sample are reacted with 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH) and then with an oxidizer to form a blue color whose intensity is proportional to the concentration of aldehydes present. The intensity of the blue color is measured spectrophotometrically at about 620 nm and is converted to ppm aldehydes as acetaldehyde by means of a calibration curve prepared from standards of known concentrations of acetaldehyde. Detection range is 2-20 ppm. Repeatability for an individual analyst should be better than 2.5 ppm.

## 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.

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

## REFERENCES

STM C17-76 (SOHIO Test Method) "Aldehyde in Acrylonitrile"

## INTERFERENCES

The inhibitor, MEHQ, usually present in acrylonitrile, will react with the oxidizing reagent to produce a color that interferes with this procedure. The inhibitor is

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removed by washing the sample with dilute caustic or by distillation. About 65% of the acrolein present will also react.

## APPARATUS AND REAGENTS

1. **MBTH Color Reagent**, (0.08 g/L)  
The solution may be prepared in the following manner: Dissolve 0.08 gm of 3-methyl-2 benzothiazolinone hydrazone hydrochloride in water and dilute to 1000 mL. Store in a brown bottle.  
Note: Fresh color reagent should be used with each new calibration curve and replaced monthly. Using color agent longer will result in bias high results.
2. **Oxidizer Reagent**  
The solution may be prepared in the following manner: Add 8.33 gm ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) and 8.0 gm sulfamic acid to a 1000 mL volumetric flask. Dissolve in water and dilute to volume. Store in a brown bottle.
3. **Spectrophotometer** - Hitachi U2000 or equivalent (CAL-1).
4. **Quartz Cells**. 1 cm pathlength
5. **Acetaldehyde** - Eastman #468 or equivalent. This should be re-distilled prior to use as a standard at least every month. This may be done using helium as a carrier gas and an ice water solution as the coolant for the condenser.
6. **ASTM Type II water** , or equivalent. Minimum electrical resistivity 1.0  $\text{M}\Omega\cdot\text{cm}$  at 298 K; maximum total organic carbon 50  $\mu\text{g/L}$ ; maximum sodium 5  $\mu\text{g/L}$ ; maximum chlorides 5  $\mu\text{g/L}$ ; maximum total silica 3  $\mu\text{g/L}$ . Detailed specifications can be obtained from ASTM: [www.astm.org](http://www.astm.org).
7. **Syringes**, 50  $\mu\text{L}$ , 10  $\mu\text{L}$ .
8. **Balance**, analytical, readability to 0.1 mg.

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9.     **MEHQ**, (4-methoxyphenol), CP grade.
10.   **3-Methyl-2-benzothiazolinone hydrazone hydrochloride** [CAS 4338-98-1] Fisher EK119-8688 or equivalent.
11.   **Ferric chloride hexahydrate**, [CAS 10025-77-1] ACS reagent grade, Aldrich 23,648-9 or equivalent.
12.   **Sulfamic Acid**, [CAS 5329-14-6] 99%, Aldrich 24,277-2 or equivalent.
13.   **Acrylonitrile**, inhibitor free.
14.   **Sodium Hydroxide**, 5N. The solution may either be purchased (ACS Certified) or be prepared in the following manner: Add 200 g of reagent grade sodium hydroxide to ~ 600 mL of water. Dissolve and dilute to 1 liter.
15.   **Volumetric flasks**, 50 mL, Class A
16.   **Pipettes**, 1, 2, 25 mL, Class A
17.   **Separatory funnel**, 2L with stopper.
18.   **EPA Vials**: 40 mL plus teflon lined septum and screw cap.

## CALIBRATION

### Inhibitor Removal

Remove the inhibitor by one of the following procedures:

1.     Extraction - To a 2 liter separatory funnel, add 600 mL of acrylonitrile, 540 mL of water and 60 mL of 5N sodium hydroxide. Shake, allow solution to separate into layers, and discard the bottom layer. Add 600 mL of water, shake, allow solution to separate and discard the bottom layer. This procedure may also remove some aldehydes.
2.     Distillation - Distill at least 95% of the acrylonitrile. The distilled material from the distillation test may be used for MEHQ free acrylonitrile.  
Both procedures to remove the inhibitor may also remove some aldehyde.

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## Standard Preparation

### Stock Solutions

1. Weigh five 40 mL EPA vials with Teflon-lined septa and screw cap.
2. In a hood, add 40 mL of scrubbed acrylonitrile at room temperature to each vial.
3. Weigh each stock solution just prior to and just after the acetaldehyde addition. Using an ice cold 50 µL syringe, add about 0, 10, 20, 30 and 40 µL of the distilled, chilled acetaldehyde below the acrylonitrile surface.
4. From the weight added, calculate the ppm acetaldehyde added to each of the vials (Stock Solutions):

$$\text{Acetaldehyde, ppm} = [W1 \div (W1 + W2)] \times 10^6$$

Where:        W1 = weight acetaldehyde added, g.

                  W2 = weight acrylonitrile, g.

### Standard Solutions

1. Dilute each Stock Solution with acrylonitrile to give the desired acetaldehyde standards by pipetting 1.0 mL of each above stock solution into another 50 mL volumetric flask containing about 40 mL scrubbed acrylonitrile, then dilute to volume with the scrubbed acrylo, stopper tightly and mix thoroughly.
2. Calculate ppm acetaldehyde added in each standard.  
For Example: 250.3 ppm x 1 mL ÷ 50 mL = 5.01 ppm acetaldehyde added.
3. Pipette 25 mL of MBTH solution and 1.0 mL of the standard into a 50 mL volumetric flask. Let sit for 45 ± 5 minutes.
4. Pipette 2.0 mL of the oxidizer reagent into each flask. Dilute to volume with water and mix thoroughly. Let sit for 20 ± 1 minutes.

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5. Scan the 4<sup>th</sup> standard from 700 to 600 nm and measure the absorbance against the blank. Use the "Trace" option in the Hitachi to find the maximum absorbance (~ 620 nm).
6. Determine the absorbance of each standard against the 0 standard at the maximum absorbance wavelength.
7. After the determination of the last standard, a "1<sup>st</sup> order" linear curve will be generated by the program in the Hitachi. If the data points ("+"s) are in good agreement with the instrument generated line, then "store" the curve. If one or more points are in poor agreement, repeat those and replot.
8. Enter the date, worksheet(s), initials of calibrator and any comments in the appropriate log.

## PROCEDURE

1. Remove the inhibitor from the sample by extraction or distillation as outlined in the calibration procedure.
2. Pipette 1.0 mL of the sample into a 50 mL volumetric.
3. Pipette 25 mL of MBTH solution into each flask and let sit for 45±5 min.
4. Add 2 mL of the oxidizer reagent into each flask. Dilute to volume with water and mix thoroughly.
5. Let set for 20±1 min.
6. Measure the absorbance at the maximum near 620 nm in the same manner as the standards.

## CALCULATIONS

The sample ppmw will be calculated using the stored value from the slope and intercept in the Hitachi.

## REPORT

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Report aldehyde as acetaldehyde to the nearest ppm:

aldehydes, ppmw = 4