

Method: ACRN-3 Revision: 5 Final Revision Date: 03/19/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 04/01/08	Acrolein	Page 1 of 6
Next Review: 04/01/12		Reviewed by: Jennifer Young

METHOD SUMMARY

The acrolein in the sample is reacted with 4-hexyl resorcinol in the presence of mercuric chloride and trichloroacetic acid under controlled conditions to form a blue color whose intensity is proportional to the concentration of acrolein. The intensity of the blue color is measured spectrophotometrically at 605 nm and is converted to ppm acrolein by means of a calibration curve prepared from standards of known concentrations of acrolein. The limit of quantitation is 0.5 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 C6-75, "Acrolein in Acrylonitrile," SOHIO Test Method, 1975.

"Determination of acrolein in alcoholic beverages", Devittori, M. Lab. Eidg. Alkoholverwalt., Italy. Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene (1970), 61(3-4), 185-206.

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Method: ACRN-3 Revision: 5 Final Revision Date: 03/19/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 04/01/08 Next Review: 04/01/12	Acrolein	Page 2 of 6 Reviewed by: Jennifer Young

INTERFERENCES

Acetaldehyde in 300-fold excess will cause a slight (10%) reduction in response of the method to acrolein. Acetaldehyde alone is not a positive interference.

APPARATUS AND REAGENTS

1. **Spectrophotometer**, Hitachi U-2000 or equivalent (CAL-1).
2. **Absorption cells**, 1 cm pathlength.
3. **Water bath**, capable of maintaining 60 ± 2 °C.
4. **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.
5. **Methanol**, ACS certified, absolute grade.
6. **Volumetric flasks**, 100 mL with stopper, Class A
7. **Amber volumetric flask**, 50 mL.
8. **Beaker**, 600 mL.
9. **Flasks or test tubes**, 25 mL.
10. **4-Hexylresorcinol solution**: (500 g/L) The solution may be prepared in the following manner: Weigh 25 ± 0.5 g of 4-hexyl resorcinol ([136-77-6] Aldrich, 20,946-5 or equivalent) into a 50 mL amber volumetric flask. Then pipette 25 mL of methanol into the flask, stopper and mix. Dilute to mark with methanol and mix.
11. **Trichloroacetic acid solution**: (Saturated) The solution may be prepared in the following manner: Weigh 450 ± 5 grams trichloroacetic acid ([76-03-9] Aldrich, ACS reagent 25,139-9 or equivalent) into a 600 mL beaker and add

Method: ACRN-3 Revision: 5 Final Revision Date: 03/19/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 04/01/08 Next Review: 04/01/12	Acrolein	Page 3 of 6 Reviewed by: Jennifer Young

45 mL water. Stir to dissolve. **Caution:** The solid acid and the solution are both corrosive and toxic.

12. **Mercuric chloride solution:** (30 g/L) The solution may be prepared in the following manner: Weigh 3g of mercuric chloride ([7487-9-7] Aldrich, ACS reagent 20,377-7, or equivalent) into a 100 mL volumetric flask. Dilute to volume with methanol, stopper and mix. **Caution:** Mercuric chloride (HgCl₂) is highly toxic and direct contact should be avoided.
13. **Color reagent:** To a 50 mL stoppered flask, add the following reagents, with repipets, in the following order: 10 mL of methanol, 0.25 mL 4-hexylresorcinol solution, 0.5 mL mercuric chloride solution and 13 mL of trichloroacetic acid solution. Mix well. The solution is stable at room temperature for 24 hours. Larger amounts of the reagent may be prepared when required.
14. **Acrolein** (Aldrich 11,022-1 or equivalent, inhibited with hydroquinone), **distill prior to use.** Distill 5 mL of acrolein in the micro-distillation apparatus. Retain 1-1.5 mL heart-cut and use in standard preparation that same day. Keep sealed vial in an ice bath until standards have been prepared and analyzed.
15. **Pipettes**, 1, 10 mL.
16. **Syringe**, 100 µL.

CALIBRATION PROCEDURE

1. For Stock I, weigh 95 ml of methanol into a tared stoppered 100 ml volumetric flask and record the weight as W_1 . Re-zero the balance and add $60 \pm 10 \mu\text{L}$ (W_2) of freshly distilled acrolein. Re-zero the balance and dilute to

Method: ACRN-3 Revision: 5 Final Revision Date: 03/19/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 04/01/08 Next Review: 04/01/12	Acrolein	Page 4 of 6 Reviewed by: Jennifer Young

the mark with methanol (W_3). Calculate the concentration of acrolein with the formula below (~500 ppmw).

- For Stock II, prepare as Stock I in a separate 100 mL volumetric flask, but use $80 \pm 10 \mu\text{l}$ of acrolein (~700 ppmw).

$$\frac{W_2}{(W_1 + W_2 + W_3)} \times 10^6 = \text{ppm (w/w) Acrolein}$$

where: W_1 = initial weight methanol, g
 W_2 = weight acrolein, g
 W_3 = Weight of methanol added to volume, g

- Using 100 ml volumetric flasks, make dilutions of Stock I and II in methanol.

<u>Stock</u>	<u>(ml)</u>	<u>~ppm</u>
I	0.1	0.5
I	0.2	1.0
I	0.6	3.0
II	0.7	5.0
II	1.0	7.0

- For each standard and a blank, pipette 10 ml of color reagent into a 25 ml test tube or flask, and pipette 1.0 ml of standard (or methanol for a blank).
- Seal and mix well.
- Place in a water bath at $60^\circ \pm 2^\circ \text{C}$ ($140^\circ \pm 4^\circ \text{F}$) for 40 ± 5 min.
- Immediately cool in running water.
- Within 15 min. after the standards are removed from the water bath, scan from 550 to 650 nm to find the maximum absorbance, typically at about 605

Method: ACRN-3 Revision: 5 Final Revision Date: 03/19/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 04/01/08 Next Review: 04/01/12	Acrolein	Page 5 of 6 Reviewed by: Jennifer Young

nm. Measure the absorbance of each standard at the maximum using 1 cm cells against the reagent blank.

- Determine the slope of the calibration points by calculating the linear regression with the absorbance as the ordinate and ppm as the abscissa.

SAMPLE ANALYSIS PROCEDURE

- For each sample and a blank, pipette 10 mL of color reagent into a 25 mL flask or test tube.
- Add 1.0 mL of sample or 1.0 mL of methanol for a blank.
- Seal and mix well.
- Place in a water bath at 60±2 °C (140±4 °F) for 40±1 min.
- Immediately cool in running water.
- Determine the absorbance of the sample in the same manner as the standard at the same wavelength used for calibration.
- If the absorbance of the sample is higher than the calibration curve maximum, dilute the sample with methanol to bring the absorbance within the calibration range.

CALCULATIONS

If the spectrophotometer does not calculate the acrolein directly, calculate the ppm acrolein present:

$$\text{ppmw} = \frac{\text{sample absorbance}}{\text{Slope}}$$

REPORT

Report the value obtained to the nearest 0.1 ppm. The limit of quantitation is 0.5 ppm. For example:

Method: ACRN-3 Revision: 5 Final Revision Date: 03/19/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 04/01/08	Acrolein	Page 6 of 6
Next Review: 04/01/12		Reviewed by: Jennifer Young

acrolein, ppmw = 0.6