

Method: ACRN-28 Revision: 5 Final Revision Date: 03/18/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 08/15/07	Organic Impurities by Gas Chromatography	Page 1 of 9
Next Review: 08/15/11		Reviewed by: Karen Runge

METHOD SUMMARY

The trace impurities listed below are separated and detected using a gas chromatograph with an FID detector.

	Quantitation <u>Limit (ppm)</u>
Acetone	< 5
Acetonitrile	< 10
Benzene	< 5
Crotononitrile	< 5
Methylacrylonitrile	< 10
Propionitrile	< 5
Oxazole	< 5
Methyl Vinyl Ketone	not determined
Methanol	not determined

These limits are for the apparatus and procedure specified. They may be different for other instrument configurations and procedures.

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.

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Method: ACRN-28 Revision: 5 Final Revision Date: 03/18/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 08/15/07	Organic Impurities by Gas Chromatography	Page 2 of 9
Next Review: 08/15/11		Reviewed by: Karen Runge

REFERENCES

E1863-97(2002) "Standard Test Method for Analysis of Acrylonitrile by Gas Chromatography" <http://www.astm.org/>

INTERFERENCES

Applied properly to product grade acrylonitrile, this method has no known interferences.

APPARATUS AND REAGENTS

- Carrier Gas** - Helium minimum purity 99.995 Mol. %.
- Hydrogen** - high purity.
- Air** - Hydrogen free, high purity.
- Balance**, analytical, sensitive to ± 0.1 mg.
- Serum Bottles**: 50 mL capacity with crimp-top caps and TFE/silicone septa
- Syringe**, 10 μ l. For autosampler or manual injection.
- Disposable Syringes**: 1 cc capacity.
- Crimper and Decapper**: for serum vials.
- Vials**: 2 ml autosampler with snap-on septa/lids.
- Syringes**: gas tight glass, 100 and 500 μ l capacity (SGE Cat No. 005200 and 007200).
- Water**: ASTM type II or equivalent. Minimum electrical resistivity 1.0 M Ω •cm at 298 K; maximum total organic carbon 50 μ g/L; maximum sodium 5 μ g/L; maximum chlorides 5 μ g/L; maximum total silica 3 μ g/L. Detailed specifications can be obtained from ASTM: www.astm.org.
- Gas Chromatograph** - HP-5890 with an FID and split injection system or equivalent.
- Column**: 90 to 120m, 0.53 mm ID, 3.0 micron film of Rtx -1 Other columns may be used after it has been established that such columns are capable of separating all major impurities and the internal standard from the acrylonitrile under operating conditions appropriate for the column.
- Integrator** - HP-3396A or equivalent data acquisition system.
- Stock Reagents**: Known purity acetone, acetonitrile, acrylonitrile, benzene, crotonitrile, isobutanol, methyl vinyl ketone, methacrylonitrile, oxazole and propionitrile.

CALIBRATION

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Method: ACRN-28 Revision: 5 Final Revision Date: 03/18/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 08/15/07	Organic Impurities by Gas Chromatography	Page 3 of 9
Next Review: 08/15/11		Reviewed by: Karen Runge

Calibration standards are made by adding known amounts of methanol, acetonitrile, acetone, oxazole, propionitrile, methyl vinyl ketone, methacrylonitrile, cis-crotonitrile, trans-crotonitrile, and benzene to low impurity acrylonitrile. These standards are analyzed on the gas chromatograph to get component area counts. Calibration factors are generated for the components.

CALIBRATION PROCEDURE

NOTE:List all reagent lot numbers, concentrations, the balance used for weighing and the name or initials of calibrator on an appropriate calibration/response factor log document.

Stock Acrylonitrile

1. Collect 2 liters of high purity (stock) acrylonitrile from a suitable high quality source.
2. Inject the stock acrylonitrile 3 times using the gas chromatograph (GC) that you are calibrating.
3. Determine the average area count (AC) for each known impurity. These values will be needed below in step 13 of Calibration Standards to calculate the total concentrations of compounds in the standards made with this acrylonitrile.

Stock Standard

1. Purchase the following known purity reagents: acetone, acetonitrile, benzene, crotonitrile, isobutanol, methacrylonitrile, oxazole, propionitrile, methanol and methyl vinyl ketone.
2. Determine the cis- and trans-crotonitrile percentages by injecting small amount of the mixture (a needle full of a 10 ul syringe may work (about 0.6 ul)), then measure the peak areas and calculate the relative percentage of each.
3. Tare a 50 mL serum bottle with septum.
4. Add 47 mL of stock acrylonitrile to the bottle. Weigh to the nearest 0.1 mg and record as the initial weight.
5. Use the glass syringes to add the following amount of each component to the bottle.

Component

_____ μ l _____

Method: ACRN-28 Revision: 5 Final Revision Date: 03/18/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 08/15/07	Organic Impurities by Gas Chromatography	Page 4 of 9
Next Review: 08/15/11		Reviewed by: Karen Runge

Acetone	50
Acetonitrile	150
Benzene	50
Crotononitrile	250
Methacrylonitrile	250
Oxazole	50
Propionitrile	50
Methanol	50
Methyl Vinyl Ketone	50

6. Weigh the bottle after each addition and record the weight to the nearest 0.1 mg.
7. Cap the bottle and shake to mix.
8. Label the serum bottle with a title, preparation date, expiration date and preparer's initials.
9. Determine the individual component weight by subtracting the previous weight from the weight after a component is added.
10. Calculate the added concentration (mg/kg) of each component (comp.) as follows:

$$\text{Component Concentration (mg/kg)} = \frac{\text{Comp. Wt. (mg)}}{\text{Total Wt. (kg)}} \times \frac{\text{Comp. Purity (\%)}}{100}$$

Stock Internal Standard Preparation

1. Tare a 50 mL serum bottle with septum.
2. Add 50 mL of water to the bottle and record the weight to the nearest 0.1 mg (initial wt.).
3. With a 1 cc disposable syringe, add 0.25 mL of isobutanol to the bottle and record the weight to the nearest 0.1 mg (final wt.).
4. Cap the bottle and shake to mix.
5. Label the bottle with a title, preparation date, expiration date, and preparer's initials.
6. Calculate the isobutanol concentration (mg/kg) using the following formula:

Isobutanol Concentration =

$$\frac{\text{Final Wt. (gm)} - \text{Initial Wt. (gm)}}{\text{Final Wt. (gm)}} \times \frac{\text{Isobutanol purity (\%)} \times 10^6}{100}$$

Calibration Standards

1. Prepare three standards by diluting the stock standard with stock acrylonitrile.

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Method: ACRN-28 Revision: 5 Final Revision Date: 03/18/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 08/15/07	Organic Impurities by Gas Chromatography	Page 5 of 9
Next Review: 08/15/11		Reviewed by: Karen Runge

2. Tare a 50 mL serum bottle with septum.
3. Add about 48ml of stock acrylonitrile to the bottle and weigh (all weights to the nearest 0.1 mg). This will be your Initial Wt.(A) for the internal standard calculation.
4. Use a 1 cc syringe to add 0.2 ml of the internal standard (prepared in the previous section) to the bottle. Record the weight (Final Wt.(A) for the internal standard calculation, Initial Wt.(B) for the component calculation).
5. Use a 1 cc syringe to transfer 0.25 cc of stock standard to the bottle and record the weight (Final Wt.(B) for the component calculation).
6. Cap the bottle and shake to mix.
7. Label each bottle with a title, preparation date, expiration date and preparer's initials.
8. Repeat steps 2 to 7 and make two more calibration standards by adding 0.5 and 1.0 cc of stock standard to stock acrylonitrile.
9. Calculate the concentration (mg/kg) of each component added (including isobutanol) to each standard using the following formulas:

Internal Standard concentration =

$$\frac{\text{Final Wt.(A)(gm)} - \text{Initial Wt.(A)(gm)}}{\text{Final Wt.(B)(gm)}} \times \text{Isobutanol Concentration in Internal Std, mg/kg}$$

Component concentration =

$$\frac{\text{Final Wt.(B)(gm)} - \text{Initial Wt.(B)(gm)}}{\text{Final Wt.(B)(gm)}} \times \text{Component Concentration in Stock Std, mg/kg}$$

10. Analyze each calibration standard in triplicate (three injections of each standard).
11. Obtain area counts for the components and internal standard from integrator or chromatography data system.
12. Average the area counts (AC) for each component in the three injections of a standard.
13. To compensate for the amount of each component in the stock acrylonitrile used to dilute the standard, calculate the total component concentrations (mg/kg) by standard as follows:

Total Comp. Conc. (mg/kg) =

$$\frac{\text{Added Comp. Conc. mg/kg} \times \text{Avg AC Cal. Std}}{\text{Added Comp. Conc. mg/kg}}$$

Method: ACRN-28 Revision: 5 Final Revision Date: 03/18/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 08/15/07	Organic Impurities by Gas Chromatography	Page 6 of 9
Next Review: 08/15/11		Reviewed by: Karen Runge

Avg AC Cal Std - Avg AC Stock Acrylo

14. Enter the area counts and calculated total component concentrations into the data acquisition system calibration table. The data system will generate a calibration factor and curve for each component. To perform a manual calculation, refer to the Calculation section below.

Preparation and Storage of Stock Standard Solutions

1. Fresh stock acrylonitrile will be used every time stock or calibration standards are prepared. However, if a very clean and pure acrylonitrile sample is obtained from the unit, it will be stored and used to prepare standards for an indefinite period.
2. Reagents will be kept no more than one year.
3. Internal standard will not be kept for more than 6 months. After that time, the old standard will be discarded and new standard prepared.
4. Calibration standards will not be kept for more than 6 months. After that time, the old standard will be discarded and a new standard prepared.

Calibration Frequency

The calibration frequency of this method shall be determined by the results of the injection of an appropriate check standard or on a fixed schedule.

SAMPLE ANALYSIS PROCEDURE

Confirm that stable instrument conditions have been established as listed in Table 1. Add internal standard to the sample in the same manner as the Calibration Standards. Inject the sample and calculate the amount of each component.

CALCULATIONS

Component results are typically calculated by the chromatography data system. This data system calculation should be the equivalent of the following process:

1. Calculate a response factor for each component from the calibration:

$$RF = \frac{(\text{Peak area of component})}{(\text{Peak area ISTD})} \times \frac{(\text{Conc. ISTD})}{(\text{Conc. Component})}$$

Method: ACRN-28 Revision: 5 Final Revision Date: 03/18/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 08/15/07	Organic Impurities by Gas Chromatography	Page 7 of 9
Next Review: 08/15/11		Reviewed by: Karen Runge

where Conc. ISTD and Conc. Component are the concentrations of ISTD and component in the calibration standard solution.

2. Calculate the component concentration in the sample:

$$\text{Conc. Component} = \frac{(\text{Area component}) \times (\text{Conc. ISTD})}{(\text{Area ISTD}) \times \text{RF}}$$

REPORT

Impurities are report as ppmw, or as less than the quantitation limits listed in the Method Summary.

Acetone.....	<10 ppm
Methacrylonitrile.....	150 ppm
Acetonitrile	25 ppm
Propionitrile	15 ppm
Benzene	8 ppm
Oxazole	5 ppm
c-, t-crotononitrile	110 ppm

Method: ACRN-28 Revision: 5 Final Revision Date: 03/18/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 08/15/07		Page 8 of 9
Next Review: 08/15/11	Organic Impurities by Gas Chromatography	Reviewed by: Karen Runge

TABLE 1
Separation Conditions Using the Rtx-1 Capillary Column

Gas Chromatograph: HP-5890 with split injector, and flame ionization detector (FID), or equivalent.

Column: 90 to 120m X 0.53mm ID x 3.0 micron film of methyl silicone, preferred 105m column from Restek

Injection Flows:

Column: 5 mL/min.

Split: 20 mL/min.

Septum purge: 4.0 mL/min.

Temperatures: Oven Program: Initial = 50 °C (hold 20 min.)

Rate 1 = 5 °C/min.

Final 1 = 100 °C (hold 0 min.)

Rate 2 = 15 °C/min.

Final 2 = 250 °C (hold 5 min.)

Injector: 250 °C

Detector: 280 °C

Detector Flows: Fuel Air: 360 mL/min.

Fuel Hydrogen: 33 mL/min.

Injection Size: 1 to 2 µL.

Integrator: HP-3393A or equivalent chromatography data system

Any of the above parameters may be adjusted as necessary to obtain best separation and sensitivity.

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Method: ACRN-28 Revision: 5 Final Revision Date: 03/18/03	Acrylonitrile Specification Tests	INEOS Nitriles
Last Review: 08/15/07 Next Review: 08/15/11	Organic Impurities by Gas Chromatography	Page 9 of 9 Reviewed by: Karen Runge

Figure
Chromatogram of Acrylonitrile Calibration Standard

