

Method: ACEN-14A Revision: 6 Final Revision Date: 08/15/07	Acetonitrile Specification Tests	INEOS Nitriles
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METHOD SUMMARY

This method is an older reference method made available for labs without either flameless atomic absorption or inductively coupled plasma spectrophotometers. The sample is evaporated to remove the organic material and digested with concentrated acids to convert iron to a water-soluble sulfate. The iron is reduced to the ferrous ion with hydroxylamine hydrochloride and reacted with ortho-phenanthroline to form an orange red complex. The absorbance of the color is measured spectrophotometrically at about 500 nm and is converted to concentration of iron by means of a calibration curve. Detection limit is 0.02 ppm.

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.

Perchloric acid is a corrosive liquid and also an acute irritant to eyes and skin. It is highly toxic by inhalation or ingestion. Perchloric acid reacts violently with organics. It may explode if shocked or heated. Store it away from organics in 250 mL quantities or less. Wear rubber gloves when handling.

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

REFERENCES

ACEN-14, "Iron by Graphite Furnace Atomic Absorption".

STM C15-76, "Iron in Acrylonitrile and Acetonitrile," SOHIO Test Method, 1976.

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INTERFERENCES

There are no known interferences to this method.

APPARATUS AND REAGENTS

1. **Spectrophotometer**, suitable for measurement in the visible range, e.g. P&E Model 552A.
2. **Cells**, absorption, 5 cm. Pyrex.
3. **Filter funnel**.
4. **Filter paper**, Whatman #42.
5. **Beaker**, 250 mL, low form.
6. **Hot plate**, explosion proof, for evaporating flammable materials.
7. **Flasks**, volumetric, 50, 250, 500 and 1000 mL, Class A
8. **Pipettes**, assorted sizes, Class A
9. **Water**, ASTM Type I, (≥ 16.6 megohm/cm)
10. **Acid mixture**: Combine 500 mL of concentrated sulfuric acid with 200 mL of concentrated nitric acid.
11. **Ammonium hydroxide**, [CAS 1336-21-6], concentrated.
12. **Congo red paper**.
13. **Hydrochloric acid** (1:1): Cautiously add 250 mL of concentrated hydrochloric acid (HCl) [CAS 7647-01-0] to an equal volume of water.
14. **Hydroxylamine hydrochloride** solution (100 g/Titer): Dissolve 25g of hydroxylamine hydrochloride [CAS 5470-11-1] in water in a 250mL volumetric flask. Dilute to the mark with water. This solution should be stored in a refrigerator where it should remain stable for several months.
15. **Iron solution** (standard, 1 ug/mL):

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(a) Stock solution (100 ug/mL): Dissolve 0.1000g of iron wire in 10 mL of 1:1 hydrochloric acid in a one liter volumetric flask. Dilute to the mark with water. The stock solution is stable indefinitely if stored in a tightly sealed glass stoppered bottle. Alternately, use purchased 1000 ppm aqueous atomic absorption standard and dilute accordingly.

(b) Standard solution (1 ug/mL): Pipet 10 mL of iron stock solution into a 1 liter volumetric flask. Dilute to the mark with water. A standard iron solution (1 mg/mL) can be purchased and the standard solution (1 ug/mL) prepared by diluting 1 mL to 1 liter with water in a volumetric flask. Fisher Scientific Co. Catalog No. SI124 is satisfactory for this purpose. Prepare the standard solution fresh from the stock solution whenever it is needed.

16. **Nitric acid**, concentrated [CAS 7697-37-2].
17. **Perchloric acid**, 70% [CAS 7601-90-3].
18. **1, 10-phenanthroline solution** (1 g/liter): Dissolve 0.50g of 1, 10-phenanthroline [CAS 66-71-7] in water in a 500 mL volumetric flask. Dilute to the mark with water. It may be necessary to heat the water to 76 ± 2 deg C to dissolve the 1, 10-phenanthroline.
19. **Sulfuric acid**, [CAS 7664-93-9] concentrated (sp gr 1.84).

PROCEDURE

1. Wash all glassware before using with (1:1) hydrochloric acid and rinse with distilled water to remove all traces of iron.
2. Filter the sample through Whatman #42 filter paper if it appears to be cloudy or if suspended matter is present. If the sample appears to be clear, no filtration is necessary.

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3. **CALIBRATION CURVE:**

- (a) Standard samples: Prepare standards containing 3, 5, 8, 10, 15 and 20 ug of iron in the following manner:

Pipet 3, 5, 8, 10, 15 and 20 aliquots of the standard iron solution into separate 50 mL volumetric flasks. Dilute to approximately 25 mL with ASTM water. Measure about 25 mL of ASTM water into an additional 50 mL volumetric flask for the zero standard. Add 1 mL of concentrated sulfuric acid to each of the standard samples and the zero standard.

- (b) Color development: Treat the standard samples and the zero standard as directed in Steps 12-14.
- (c) Absorbance measurement: Establish the wavelength of maximum absorbance for each instrument by scanning the region 50 nm above and below 500 nm using the 10 ug standard in the 5 cm sample cell and water in the reference cell. Use the wavelength **which gives maximum absorbance** if it falls within the specified limits. If it does not, recalibrate and readjust the wavelength. Measure the absorbance of each standard and the zero standard at the wavelength of maximum absorbance against water and record absorbance.
- (d) Using graph paper, plot the absorbance vs concentration (0-20 ug iron) and prepare a calibration curve by drawing the best straight line. Record the spectrophotometer settings on the graph paper.

4. Pour 125 mL of sample into an acid-washed 250 mL beaker. A 125 mL sample of acetonitrile weights approximately 100 grams. **CAUTION:** Hazardous sample. See SAFETY section.
5. Place on a hot plate. The hot plate must be used inside a fume hood.
6. Evaporate to complete dryness very slowly. Allow to cool until the beaker can be handled safely.
7. Add 3 mL of acid mixture to the 250 mL beaker. Also add 3 mL of acid mixture to a second beaker. This will become the reagent blank. From now on, add the same quantities of reagents to the blank as to the sample.

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8. Place on the hot plate and heat until the acid boils and the white fumes of sulfuric acid are observed. Then remove from the hot plate to cool.
9. If the residue is colored, repeat the digestion or perform the optional perchloric acid oxidation. If colorless, proceed to Step 10 for dissolution of the residue.
Optional Perchloric Acid Oxidation: If undigested organic matter is present, the following optional oxidation may be performed. After the beaker has cooled, cautiously add 0.2 mL of 70% perchloric acid. **CAUTION:** Hazardous reagent: See SAFETY section. Carry out this oxidation step in a specially constructed oxidation fume hood. Return the beaker to the hot plate, apply heat, and fume until 2 to 3 mL of solution remains. Repeat the perchloric digestion if the residue is colored.
10. After the beaker has cooled, add approximately 10 mL ASTM Type I water to dissolve the residue.
11. Transfer the solution quantitatively to a 50 mL volumetric flask.
12. Add 2 mL of hydroxylamine hydrochloride to the solution and swirl to mix; then add 10 mL of 1, 10-phenanthroline. The reagents must be added in this order so that the reduction reaction can take place.
13. Place a small piece of congo red paper in the flask and add concentrated ammonium hydroxide dropwise until the paper turns red. Dilute to the mark with ASTM water and mix well.
14. Allow the solution to stand for 20 minutes for maximum color development.
15. Zero the spectrophotometer with empty cells, at the wavelength of maximum absorbance.
16. Fill a 5 cm sample cell with the sample; fill the reference cell with the reagent blank.
17. Measure the net absorbance of the sample and record.

CALCULATIONS

1. Determine the iron content of the sample in micrograms from the net absorbance from the calibration curve.

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2. Calculate the iron contents in parts per million from the following equation:

$$\text{Iron, ppm} = \frac{a \div b}{c} = \frac{\mu\text{g}}{\text{g}}$$

where: a = net absorbance
b = slope from calibration curve
c = sample weight, g

REPORT

Report the iron concentration in parts per million to the nearest 0.01 ppm. Minimum report value is 0.02 ppm. Report value less as <0.02 ppm.

Example: Iron, ppm = 0.03.

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**WORKSHEET FOR
CALCULATION OF CALIBRATION CURVE**

C denotes Concentration

A denotes Net Absorbance

Standard#	C	C ²	A	CA
1	_____	_____	_____	_____
2	_____	_____	_____	_____
3	_____	_____	_____	_____
4	_____	_____	_____	_____
5	_____	_____	_____	_____
6	_____	_____	_____	_____

Sum: $\Sigma C =$ _____ $\Sigma C^2 =$ _____ $\Sigma A =$ _____ $\Sigma CA =$ _____

Average: $\bar{C} =$ _____ $\bar{A} =$ _____

Number of Points: n=_____

Step

(1) $\Sigma CA =$ _____

(2) $(\Sigma C) (\Sigma A) \div n =$ _____

(3) Step (1) - Step (2) = _____

(4) $\Sigma C^2 =$ _____

(5) $(\Sigma C)^2 \div n =$ _____

(6) Step (4) - Step (5) = _____

(7) Slope: $b = \text{Step (3)} \div \text{Step (6)} =$ _____

(8) $\bar{A} =$ _____

(9) $b\bar{C} =$ _____

(10) Intercept: $a = \text{Step (8)} - \text{Step (9)} =$ _____

(11) Net absorbance of sample: $A_s =$ _____

(12) $A_s - a = \text{step (11)} - \text{step (10)} =$ _____

(13) Concentration in Sample: $C_s = \text{Step (12)} \div \text{Step (7)} =$ _____