

AMMONIA IN HYDROCARBONS

UOP Method 958-98

SCOPE

This method is an extraction procedure that, when used in conjunction with UOP Method 959, allows the determination of ammonia in liquid hydrocarbon streams. Other nitrogen species, if present, are not detected by this method. This procedure yields quantitative results and has been tested in the range of approximately 0.5 to 10 mass-ppm ammonia. Higher concentrations can be determined by dilution of the aqueous extract as noted in UOP Method 959, or by performing the extraction using a larger volume of water and/or a smaller sample size (preferred if the ammonia level can be estimated).

OUTLINE OF METHOD

Ammonia is extracted from the hydrocarbon sample using water (see *Note 1*). The amount of ammonium ion present in the extract is determined using UOP Method 959, an ion chromatographic method. The result from that determination is used to calculate the ammonia in the original sample. Hydrocarbon solutions containing ammonia are unstable and have a tendency to lose ammonia with time (see *Note 2*). Therefore, it is necessary to perform the hydrocarbon extraction and run the UOP Method 959 analysis within the same working day. If the ion chromatographic analysis can not be run immediately, the sample extracts must be refrigerated (see UOP Method 959).

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Funnel, separatory, 125-mL, Fisher Scientific, Cat. No. 10-436A

Pipets, volumetric transfer, Class A, 20- and 50-mL, Fisher Scientific, Cat. Nos. 13-650-2N and 13-650-2S, respectively

Refrigerator, laboratory, explosion proof, Fisher Scientific, Cat. No. 97-950-1

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).
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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Water purification system, Barnstead NANOpure II, three module, equipped with Pretreatment (D0835), Ultrapure (D0809) and Organic Free (D0820) replacement cartridges, Fisher Scientific, Cat. Nos. 09-050-254, 09-034-104, 09-034-3 and 09-034-175K, respectively

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized and distilled water that is subsequently treated with a Barnstead NANOpure II water purification system to produce ionically pure, 18 megohm-cm, organic-free, water.

Vials and caps, for sample water extract, Fisher Scientific, Cat No. 03-339-10H. Rinse the vials and caps five times with water, allow to air dry and store with the caps on.

PROCEDURE

Sample Extraction

If the ammonia concentration can be estimated, the sample volume can be decreased and/or the extract water volume increased (from that called for below) to minimize dilution of the extract required for the ion chromatographic (UOP Method 959) determination. The volumes used must be recorded for later use in *CALCULATIONS*.

1. Obtain the density of the hydrocarbon sample by ASTM Method D 4052.
2. Pipet 50 mL of the hydrocarbon sample into a 125-mL separatory funnel.
3. Pipet 20 mL of water into the separatory funnel. Stopper and shake the separatory funnel for five minutes, venting frequently by opening the stopcock with the funnel inverted (into a fume hood). Then allow 10 minutes for the two phases to separate.
4. Drain a portion of the aqueous extract into a 15-mL sample vial, and cap the vial. Discard the hydrocarbon layer.
5. Analyze the aqueous extract by ion chromatography as directed in UOP Method 959 (see *Note 2*).

CALCULATIONS

Calculate the ammonia concentration in the aqueous extract using the equation below. Report results to one significant figure below one mass-ppm, to two significant figures at or above one mass-ppm.

$$A = 0.944 \frac{BE}{CD}$$

where:

- A** = concentration of ammonia in the hydrocarbon sample, mass-ppm
- B** = mass of water used to extract the sample, g
- C** = volume of the hydrocarbon sample, mL
- D** = density of the hydrocarbon sample (from ASTM D 4052), g/mL
- E** = concentration of ammonium in extract (from UOP Method 959), mass-ppm
- 0.944** = factor to convert ammonium to ammonia (molecular weight of ammonia divided by the molecular weight of ammonium, 17/18)

NOTES

1. Experiments have shown 98 to 107% recovery of ammonia from hydrocarbon samples using water to extract the hydrocarbon, which is considered adequate for the intended use of this method.
2. Hydrocarbon samples containing ammonia are unstable and will lose ammonia with time. This is especially true at ambient and elevated temperatures, but will also happen slowly under refrigeration. Therefore, samples must be extracted as quickly as possible after they are sampled, and the extracts analyzed within the same working day. If there is to be some delay (but not longer than a few hours) between sampling and extraction or between extraction and analysis, refrigerate the samples or extracts. For the same reasons, it is difficult, if not impossible, to maintain a control standard for monitoring this analysis.

PRECISION

ASTM Repeatability

A nested design was carried out by two analysts at two different concentration levels on one day. Each analyst performed four analyses at each concentration level for a total of 16 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the mean concentrations shown in the Table. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the ASTM allowable differences shown in the concentration range listed in the Table with 95% confidence.

UOP Repeatability

A nested design was carried out by two analysts at two different concentration levels on one day. Each analyst performed four analyses at each concentration level for a total of 16 analyses. Using a stepwise analysis of variance procedure, the within-lab estimated standard deviations (esd) were calculated at the mean concentrations shown in the Table. Two analyses performed in one laboratory by different analysts on the same day should not differ by more than the UOP allowable differences shown in the concentration range listed in the Table with 95% confidence. The data were all collected on one day due to sample instability problems.

Table
ASTM and UOP Repeatability, mass-ppm

<u>Component</u>	<u>Concentration Range</u>	<u>ASTM Repeatability</u>		<u>UOP Repeatability</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Ammonia	1 to 2	0.06	0.2	0.08	0.3

The data in the Table are short-term estimates of repeatability. When the test is run routinely in the field, a control standard and chart should be used to develop a better estimate of the long-term repeatability (if a stable control standard can be obtained).

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

TIME FOR ANALYSIS

The labor required for this procedure, without the UOP Method 959 determination, is 0.33 hours and the elapsed time is 0.5 hours. Including the UOP Method 959 determination, the total labor and elapsed times are 1.33 hours and 2.5 hours, respectively.

REFERENCES

ASTM Method D 4052, www.astm.org

UOP Method 959, "Ammonium Determination in Aqueous Solutions by Ion Chromatography"

SUGGESTED SUPPLIER

Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-562-8300)