

COPPER IN GASOLINE AND NAPHTHA BY FLAME-AAS OR ICP-AES

UOP Method 962-98

SCOPE

This method is for determining trace concentrations of non-volatile, hydrocarbon soluble forms of copper present in gasoline, naphtha, kerosene and similar distillates by either Flame-Atomic Absorption Spectrometry (Flame-AAS) or Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). It is particularly useful on products that have been copper sweetened. The lower limit of quantitation is 5µg/kg (mass-ppb) copper. The method can be extended to other organic materials and concentration ranges. This method can be used in place of UOP Method 144.

OUTLINE OF METHOD

The sample is weighed into a beaker, evaporated to dryness and the residue is ashed in a muffle furnace. The ash is dissolved in hydrochloric and nitric acids and analyzed by either Flame-AAS or ICP-AES, using a freshly prepared standard and blank.

APPARATUS

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

Atomic absorption spectrophotometer (Flame-AAS), Perkin-Elmer, Model 3110

Balance, top-loading, readability 0.01-g

Beaker, Vycor™, 250-mL, Fisher Scientific, Cat. No. 02-541A

Cylinders, borosilicate glass, Class B, 10- and 25-mL, Fisher Scientific, Cat. Nos. 08-550B and 08-550C, respectively

Flasks, volumetric, Pyrex™, Class A, 100- and 1000-mL, Fisher Scientific, Cat. Nos. 10-210-5C and 10-210-5G, respectively

Flask, hexagonal base, 25-mL, Pyrex, Fisher Scientific, Cat. No. 20-814G

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.

Funnels, plastic, disposable, 55-mm diameter, Fisher Scientific, Cat. No. 10-320A

Furnace, muffle, capable of 500°C

Hollow cathode lamp, copper, Perkin-Elmer, Cat. No. N066-1296

Hot plate, capable of 400°C

Infrared heater, consisting of an infrared (IR) lamp and mount

Pipets, volumetric transfer, Class A, 10-mL, Fisher Scientific, Cat. No. 13-651-1K

Spectrometer, ICP-AES, Perkin-Elmer, Optima 3000

Tongs, beaker, Fisher Scientific, Cat. No. 02-620

Watch glass, Teflon™, 80-mm diameter, Fisher Scientific, Cat. No. 02-617-1G

Water purification system, Barnstead NANOpure II, three module, equipped with Pretreatment (D0835), Ultrapure (D0809) and Organic Free (D0820) replacement cartridges, for preparing ASTM D 1193 type I reagent grade water, 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 ASTM D 1193 type I reagent grade water.

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

Copper standard solution, 1000-µg/mL, SPEX CertiPrep, Cat. No. PLCU2-2X

Copper standard solution, 10-µg/mL. Pipette 10 mL of 1000-µg/mL copper standard solution into a 1000-mL volumetric flask containing approximately 250 mL of water. Using a graduated cylinder, carefully add 20 mL of nitric acid and swirl to mix. Fill to volume with water, cap and mix. This standard has a lifetime of one month.

Gloves, Silver Shield™ laminate (HF resistant), available in small (S), medium (M) and large (L) sizes, Fisher Scientific, Cat. Nos. 11-393-65A, -65B and -65C, respectively

Gloves, Zetex™ (temperature-resistant), Fisher Scientific, Cat. No. 11-392-50

Hydrochloric acid, Ultrex II™ ultrapure reagent, J. T. Baker, Cat. No. 6900-05

Hydrofluoric acid, Ultrex II™ ultrapure reagent, J. T. Baker, Cat. No. 6904-05

Nitric acid, Ultrex II™ ultrapure reagent, J. T. Baker, Cat. No. 6901-05

PROCEDURE

All labware is to be pre-cleaned by boiling in reagent grade 1:1 nitric acid (mix one part Ultrex II ultrapure reagent grade nitric acid with one part water). Extreme care must be taken to control contamination. All acids used are to be Ultrex II ultrapure reagent grade or equivalent.

Preparation of Calibration Standards

Prepare a fresh blank and 1- μ g/mL copper standard each time the analysis is performed.

1. Pipette 10 mL of 10- μ g/mL copper standard solution into 100-mL volumetric flask. Add none to a second 100-mL flask to be used as the blank.
2. Add 15 mL of hydrochloric acid, 1 mL of nitric acid and 30 mL of water to each flask. Swirl to mix the contents thoroughly.
3. Allow to cool, dilute to the mark, cap and mix well.

Sample Preparation

1. Using a top loading balance, weigh approximately 100 g (record mass to nearest 0.01 g) of sample into a 250-mL Vycor beaker.
2. Place the beaker on a cold hot plate in a fume hood and heat slowly to evaporate contents without boiling.
 - An infrared (IR) heater may be used to aid in evaporation.
3. Turn the hot plate to high (or about 400°C) after the volatile components have evaporated, and allow to heat until smoke evolution ceases.
4. Place the uncovered beaker in a 500°C muffle furnace for a minimum of two hours or until all carbon present has burned off.
5. Remove the beaker from the muffle furnace and, after the beaker has cooled sufficiently, cover it with a Teflon watch glass.
 - **CAUTION:** Beaker tongs and temperature-resistant gloves must be used to remove the hot beakers from the muffle furnace.
6. Using a 10-mL graduated cylinder, add approximately 7 mL of water, 3.8 mL of hydrochloric acid and 1.2 mL of nitric acid to the beaker. Add two drops of hydrofluoric acid to the beaker. Then cover the beaker with a Teflon watch glass and place on a hot plate. Heat gently for approximately 10 minutes, and then to a slow boil. Remove the beaker from the hot plate and allow it to cool.
 - Hydrofluoric acid is used to aid in the dissolution of the ash that may be embedded into the glass walls of the beaker. **CAUTION:** Use appropriate gloves and other personal protective equipment (see MSDS) when working with hydrofluoric acid.

7. Transfer the contents, quantitatively, into a 25-mL flask. Fill to volume with water, cap and mix.

- Note: If an internal standard is required for ICP analysis, add it now. Check with the specific instrument manufacturer for recommendations concerning elements, concentrations and wavelengths to be used as internal standards on their instruments.

Copper Determination

Use either Flame-AAS or ICP-AES to perform the copper determination. See the specific manufacturer's instrument manual for setup instructions. This method assumes the analyst is familiar with the operation of the equipment.

Flame-AAS Analysis

Use the following operating parameters for the AAS instrument:

Copper wavelength, nm	324.754
Slit setting, nm	1.3
Flame type	Air-acetylene (100-mm burner head)

Light the flame of the AAS and allow it to stabilize for 5 minutes. Adjust the burner position while aspirating a copper standard to achieve maximum response. Read solutions in the following order: blank, standard, samples and then reread the standard as a sample. The final read of the standard should compare to the known concentration to within 3% relative. If not, reread the series.

Note: After reading the standard, it is best to rinse for about a minute. This will reduce the chance of copper memory effects. Aspirating a 1% nitric acid rinse between samples will also help reduce copper memory.

ICP-AES Analysis

Start the ICP-AES and ignite the plasma according to the manufacturer's recommendations. Allow 15 minutes warm up after the plasma is ignited before starting the analysis. Use the copper 324.754 nm line for the analysis. If an internal standard is being used, use the element, wavelength and concentration level recommended by the instrument manufacturer. Aspirate the blank and standard to establish the calibration curve prior to the aspiration of the samples. Allow sufficient wash-out time between standards, blanks and samples to minimize memory effects. Read solutions in the following order: blank, standard, samples and then reread the standard as a sample. The final read of the standard should compare to the known concentration to within 3% relative. If not, reread the series.

CALCULATIONS

Calculate the concentration of copper in the sample, to one significant figure below 10 µg/kg, to two significant figures between 10 and 990 µg/kg and to three significant figures at or above 1000 µg/kg, as follows:

$$\text{Copper, } \mu\text{g/kg} = 1000 \frac{\text{CV}}{\text{M}}$$

where:

C = concentration of copper in solution as determined by the instrument, $\mu\text{g/mL}$

M = sample mass, g

V = volume of aspirating solution flask, mL

1000 = factor to convert $\mu\text{g/g}$ (mass-ppm) to $\mu\text{g/kg}$ (mass-ppb)

PRECISION

ASTM Repeatability

A nested design was carried out for copper analysis using two analysts. Each analyst carried out tests at two copper concentrations on two separate days, performing two tests each day, using both the AAS and ICP. The total number of tests was 16 each using both AAS and ICP. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated for copper and are listed in the Table. Two analyses performed in one laboratory by the same analysts on the same day should not differ by more than the ASTM allowable differences shown in the Table at the concentrations listed with 95% confidence.

UOP Repeatability

A nested design was carried out for copper analysis by two analysts, with each analyst carrying out tests at two concentrations on two separate days and performing two tests each day, using both the AAS and ICP. The total number of tests performed was 16 each using both AAS and ICP. Using a stepwise analysis of variance procedure, the within-lab estimated standard deviations (esd) were calculated for copper and are listed in the Table. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the UOP allowable differences shown in the Table at the concentrations listed with 95% confidence.

Table
ASTM and UOP Repeatability, $\mu\text{g/kg}$ (mass-ppb)

Instrument	Copper Concentration	ASTM Repeatability		UOP Repeatability	
		Within-Day esd	Allowable Difference	Within-Lab esd	Allowable Difference
AAS	186	6.6	26	7.9	36
ICP	178	2.9	11	5.9	26
AAS	15	1.1	4	2.3	14
ICP	13	1.1	4	0.9	4

The data in the Table represent a short-term estimate 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 long-term repeatability if a suitable, stable control standard can be maintained.

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time for one analysis is four hours. The labor requirement is 0.7 hours for each sample.

REFERENCES

ASTM Method D 1193, www.astm.org
UOP Method 144, "Copper in Gasoline and Naphtha"

SUGGESTED SUPPLIERS

J. T. Baker, 222 Red School Ln., Phillipsburg, NJ 08865 (908-859-2151)
Fisher Scientific, 585 Alpha Dr., Pittsburgh, PA 15238 (412-490-8300)
Perkin-Elmer Corp., 761 Main Ave., Norwalk, CT 06859-0270 (203-834-6281)
SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840-1253 (908-549-7144)