

COPPER IN GASOLINE AND NAPHTHA

UOP Method 144-88

SCOPE

This method is for determining low concentrations of copper present as a hydrocarbon-soluble form in gasoline, kerosine and similar distillates. It is particularly useful on products that have been copper sweetened. The lower limit of detection is 5 μg of copper per liter of sample (approximately 6 parts per billion). Silver and bismuth may interfere. However, the presence of these metals in a sample of hydrocarbon is unlikely. The complexation with ethylene-diaminetetraacetate (EDTA) and citrate prevents interference from all other metals.

OUTLINE OF METHOD

An aqueous extract containing the copper is prepared. To this is added a solution of sodium diethyldithiocarbamate which forms a yellow-colored complex with copper. The colored complex is extracted quantitatively with butyl acetate.

Determination of the copper present is made by comparing the intensity of the yellow color, spectrophotometrically or visually, to standards.

APPARATUS

Balance, readability 0.1-mg

Beakers, 30- and 100-mL, Fisher Scientific, Cat. No. 02-540-F and H, respectively, or equivalent

Bottle, polyethylene, 1000-mL

Cells, spectrophotometer, glass, cylindrical, 20-mm light path, matched set of 2 cells, Fisher Scientific, Cat. No. 14-385-932D, or equivalent

Cuvettes, round, for visual color comparison only, 105-mm high x 19-mm diameter, Fisher Scientific, Cat. No. 14-385-900D, or equivalent

Cylinders, graduated, 25-, 500- and 1000-mL, Fisher Scientific, Cat. Nos. 08-550-C, -G, -H, respectively, or equivalent

Flasks, volumetric, 250-, 500- and 1000-mL, Class A

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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Funnel, powder, polypropylene, 65-mm diameter, Fisher Scientific, Cat. No. 10-348A, or equivalent

Funnels, separatory, 125- and 1000-mL with Teflon stopcocks and polyethylene stoppers, Fisher Scientific Cat. Nos. 10-437-11C and -F, respectively, or equivalent

pH indicator strips, papers, ColorpHast, pH 0 to 14, EM Science, Sargent-Welch Scientific. Cat. No. S-65271, or equivalent

Pipets, Mohr, long-tip, 2- and 5-mL, Fisher Scientific, Cat. Nos. 13-664-8J and -K, or equivalent

Pipets, volumetric, Class A, 10-, 15-, 20- and 25-mL, Fisher Scientific, Cat. Nos. 13-650-2L, -M, -N and -P, respectively, or equivalent

Scoop-spatula-spoon, porcelain, Fisher Scientific, Cat. No. 14-430A, or equivalent

Spectrophotometer, 5-mm band pass, photometric stability of ± 0.003 absorbance units near zero absorbance, Milton Roy Co., Model 601, available from Fisher Scientific, Cat. No. 14-385-267, or equivalent

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 by polystyrene amberlite type resins. The water must meet Type II requirements described in ASTM D 1193. Unqualified references to solutions mean aqueous solutions.

Ammonium hydroxide, concentrated, 28-30%, J. T. Baker, Cat. No. 9721, or equivalent

n-Butyl acetate, 99% minimum purity, Fisher Scientific, Cat. No. B-396, or equivalent

Carbamate solution, 250 mg/250 mL. Weigh 250 ± 0.1 mg of sodium diethyldithiocarbamate, "carbamate," into a 250-mL volumetric flask and dilute to the mark with water.

Citric acid, anhydrous, 99.5% minimum purity, Aldrich Chemical Co., Cat. No. 25,127-5, or equivalent

Citric acid solution, 25 mass/vol-%. Dissolve 62.5 ± 0.01 g citric acid in water in a 250-mL volumetric flask. Dilute to the mark with water and mix.

Cupric sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 98% minimum purity, Fisher Scientific, Cat. No. C-493, or equivalent

Copper stock standard, 400 μg Cu/mL. Weigh $1.571 \text{ g} \pm 0.1 \text{ mg}$ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and transfer to a 1000-mL volumetric flask. Dissolve in water, dilute to the mark and mix. Prepare fresh monthly and store in a polyethylene bottle.

Copper working standard, 10 μg Cu/mL. Pipet 25 mL of the copper stock standard into a 1000-mL volumetric flask, dilute to the mark with water and mix. Prepare on a daily basis as needed and store in a polyethylene bottle.

EDTA, disodium salt, dihydrate, J. T. Baker, Cat. No. 1-8993, or equivalent

EDTA solution, 4 mass/vol-%. Dissolve 20 ± 0.01 g of EDTA disodium salt in about 400 mL of water contained in a 500-mL volumetric flask. Dilute to the mark with water and mix.

Hydrochloric acid, concentrated, 37%

Hydrochloric acid, approximately 4-*M*. Dilute 333 mL of concentrated hydrochloric acid to 1000 mL and mix.

Hydrochloric acid, approximately 1-*M*. Dilute 83 mL of concentrated hydrochloric acid to 1000 mL and mix.

Sodium hypochlorite, approximately 5% solution. “Clorox”, or any equivalent household bleach is suitable.

Sodium diethyldithiocarbamate, “carbamate”, 99% minimum purity, Fisher Scientific, Cat. No. S-287, or equivalent

Sodium sulfate, granular, 12-60 mesh, 99% minimum purity, J. T. Baker, Cat. No. 3375, or equivalent

STANDARDIZATION

Spectrophotometric Analysis

Into each of seven 125 mL separatory funnels, place 20 mL of 4-*M* hydrochloric acid. Using 2- and 5-mL long-tip Mohr pipets, add 0.2, 0.5, 1, 2, 3 and 4 mL of the copper working standard (10 μg Cu/mL) to the first six funnels, respectively. Mix well by swirling after addition. Add no copper standard to the seventh flask which will serve as a blank. Next add 10 mL of citric acid solution followed by 20 mL of concentrated ammonium-hydroxide to each flask. Swirl and allow to cool. Add 15 mL of EDTA solution followed by 10 mL of carbamate solution. Again swirl to mix and wait approximately 15 minutes for the copper-carbamate complex to form. Add by pipet 20 mL of *n*-butyl acetate, stopper the separatory funnels and shake for 2 minutes. Allow the layers to separate for 2 minutes. Using a pH indicator strip, test a drop of the aqueous layer to verify that the pH is greater than 9. If not, repeat the above procedure but add approximately 25 mL of ammonium hydroxide. Drain and discard the lower aqueous layer. To the yellow butyl acetate layer containing the copper complex, add 25 mL of 1-*M* hydrochloric acid. Stopper and shake for 30 seconds. Allow the layers to separate for 1 minute, drain the lower acidic-aqueous layer and discard.

Using the plastic powder funnel and a scoop-spatula-spoon, add to each funnel approximately 5 g of sodium sulfate. Stopper and shake for one minute to absorb all moisture from the organic phase. Briefly clean the neck of each flask using a paper towel and, sequentially, decant each extract through the neck of the separatory funnel directly into a 20-mm spectrophotometric cell. Measure the absorbance at 430 nm, using *n*-butyl acetate as the reference solution for the standards and the reagent blank.

From the absorbance readings, calculate the net absorbance and plot the net absorbance values versus 0, 2, 5, 10, 20, 30 and 40 μg of copper per 20 mL of *n*-butyl acetate. The resulting calibration curve should be similar to the accompanying Figure.

Preparation of Color Standards for Visual Comparison

If visual color comparison of extracts is to be made, prepare the standards as described under *Spectrophotometric Analysis* and decant the yellow extracts into matched round cuvettes. Prepare samples for analysis at the same time to avoid possible color changes.

PROCEDURE

The procedure for making a determination is essentially the same whether the colored solution is measured spectrophotometrically or visually.

With a graduated cylinder place 500 mL of the hydrocarbon sample in a 1000-mL separatory funnel. Pipet 10 mL of the sodium hypochlorite solution into the funnel and shake vigorously for 5 minutes. Add by pipet 15 mL of 4-*M* hydrochloric acid and shake for another 5 minutes. Allow the layers to separate and drain the sodium hypochlorite-acid layer into a clean, dry, 30-mL beaker.

Pipet a 20-mL aliquot of the sodium hypochlorite-acid mixture into a 125 mL separatory funnel. Add 20 mL of concentrated ammonium hydroxide, swirl and let cool. Add 25 mL of *n*-butyl acetate, stopper and shake for 2 minutes to remove any yellow organic color bodies which might later interfere with the yellow copper-carbamate complex. Allow the layers to separate for 2 minutes and quantitatively collect the lower aqueous layer into a 100-mL beaker. Discard the upper butyl acetate layer, pour the aqueous layer back into the separatory funnel and repeat the extraction two more times or until the butyl acetate layer is water-white. Return the ammoniacal, aqueous layer to the separatory funnel. Add 10 mL of citric acid solution, 15 mL of EDTA-solution followed by 10 mL of carbamate solution. Swirl to mix and allow 15 minutes for the copper-carbamate complex to form.

Add by pipet 20 mL of *n*-butyl acetate, stopper the separatory funnel and shake for 2 minutes. Allow the layers to separate for 2 minutes. Using a pH indicator strip, test a drop of the aqueous layer to verify that the pH is greater than 9. If not, repeat the analysis but add approximately 25 mL of ammonium hydroxide. Drain and discard the lower aqueous layer. To the yellow butyl acetate layer containing the copper complex, add 25 mL of 1-*M* hydrochloric acid, stopper and shake for 30 seconds. Allow the layers to separate for approximately 1 minute, drain the lower acidic-aqueous layer and discard.

Using the plastic powder funnel and a scoop-spatula-spoon, add approximately 5 g of sodium sulfate to the sample extract. Stopper and shake for one minute to absorb all moisture from the organic phase. Briefly clean the neck of each flask using a paper towel and decant the extract through the neck of the separatory funnel directly into a 20-mm spectrophotometric cell. Determine the net absorbance at 430 nm, using *n*-butyl acetate as the reference solution for the extracts and reagent blank. Determine the absorbance within 30 minutes of the *n*-butyl acetate addition and avoid undue exposure to light. If the color is too intense, take a smaller sample volume and repeat the analysis. If a visual comparison is to be made, decant the extract into a round cuvette.

Determine the micrograms of copper per 20 mL from the spectrophotometric calibration curve or by visual comparison to the previously prepared standards.

CALCULATIONS

$$\text{Copper, } \mu\text{g/L} = \frac{1000 AB}{CV}$$

where:

A = mass of Cu/20 mL from calibration curve or from color standards, μg

B = volume of sodium hypochlorite plus volume of hydrochloric acid used for extraction, 25 mL

C = volume of aliquot of sodium hypochlorite-acid extract used for analysis, 20 mL

V = volume of sample, typically, 500 mL

1000 = conversion factor, $\mu\text{g/mL}$ to $\mu\text{g/L}$

When 500 mL of sample is used and there are no deviations from the other specified volumes, the expression becomes:

$$\text{Copper, } \mu\text{g/L} = 2.5 A$$

where A is as previously defined.

PRECAUTIONS

Keep all glassware scrupulously clean in order to avoid contamination from copper. The best results are obtained when the glassware is reserved only for these analyses.

When extracting the hydrocarbon with the hypochlorite-acid mixture, vent the funnel frequently. Do this also when scrubbing the ammoniacal solution with *n*-butyl acetate.

PRECISION

Repeatability

Based on two tests performed by each of two analysts, on each of two days (8 tests), the within-laboratory estimated standard deviation (esd) was calculated to be 3.27 at a copper concentration of 21 $\mu\text{g/L}$. Two tests performed in one laboratory by different analysts on different days should not differ by more than 12.8 (95% probability) at the stated level.

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time and labor requirement for calibration and one analysis are identical, 6 hours. In groups of 4 samples, the elapsed time and labor requirement are 8 hours.

REFERENCE

ASTM Method D 1193, www.astm.org

Furman, N. Howell, Editor, *Standard Methods of Chemical Analysis*, D. Van Nostrand Co., Inc., (1962), Vol. 1, 6th ed., 407

SUGGESTED SUPPLIERS

Aldrich Chemical Co., 940 W. St. Paul Ave., Milwaukee, WI 53233

J.T. Baker Chemical Co., 222 Red School Ln., Phillipsburg, NJ 08865

Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219

Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077

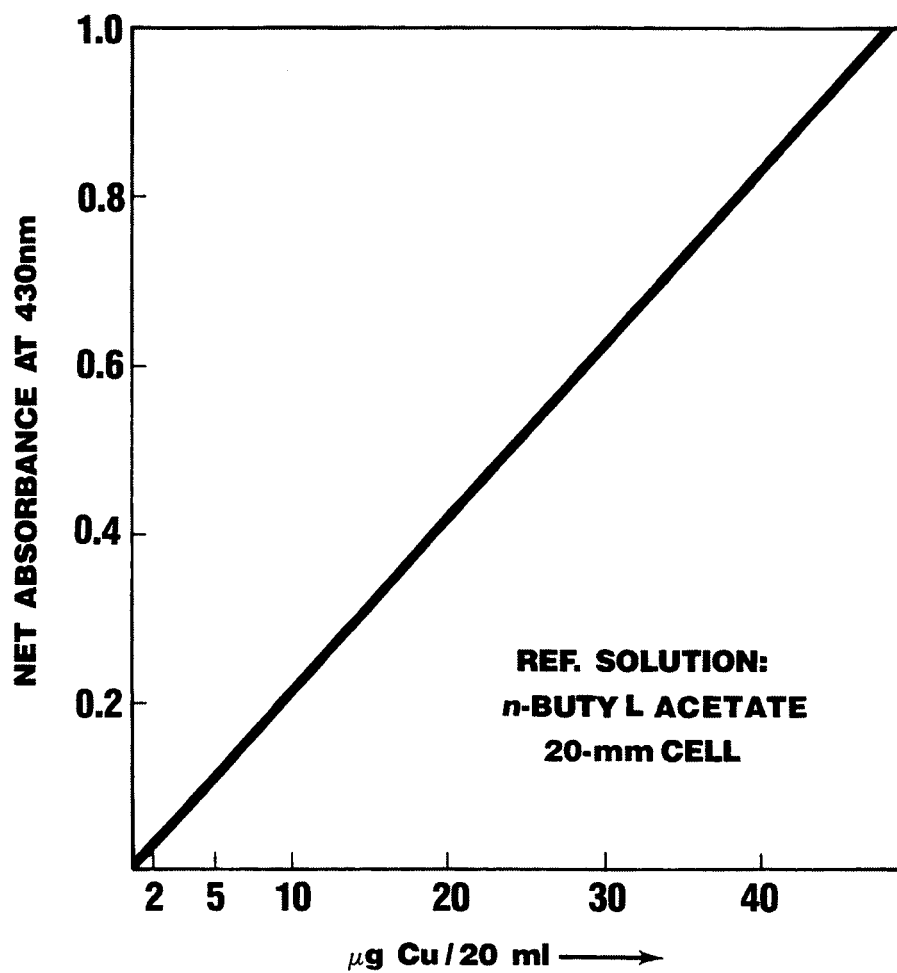


Figure
Typical Calibration Curve for Determination
of Copper in Gasoline and Naphtha