

MERCAPTAN SULFUR - COPPER NUMBER

UOP Method 197-89

SCOPE

This is a rapid procedure for estimating mercaptan sulfur in naphtha or other low-boiling petroleum distillates. Copper number is defined as the number of milligrams of copper required to titrate 100 mL of sample. Mercaptan sulfur is calculated from the copper number. Hydrogen sulfide, if present, will interfere and be included with the mercaptan. To determine the mercaptan content more precisely and distinguish mercaptans from hydrogen sulfide, use UOP Method 163. Mercaptan sulfur can be determined over a range of 15 mass-ppm to several percent.

OUTLINE OF METHOD

In a separatory funnel, a 100-mL hydrogen sulfide-free sample is repeatedly reacted with one-milliliter increments of a standardized blue tetra-ammonium copper sulfate solution until the lower aqueous phase remains colored. The first blue color to persist indicates an excess of the copper complex and, thereby, the endpoint of the titration. The copper number is calculated from the number of milliliters of copper reagent required to titrate the sample. The concentration of mercaptan in the sample, expressed as mass-ppm sulfur, is calculated from the copper number.

APPARATUS

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

Balance, readability 0.1-mg

Beaker, Griffin type, borosilicate glass, 400-mL, Fisher Scientific, Cat. No. 02-540L

Buret, Shellbach type, borosilicate glass, 50-mL, with PTFE-plug stopcock, Fisher Scientific, Cat. No. 03-740-5B

Cylinders, graduated, borosilicate glass, 10-, 100- and 250-mL, Fisher Scientific, Cat. Nos. 08-552B, -552E and -552F, respectively

Flasks, volumetric, Class A, borosilicate glass, with polyethylene stoppers, 100- and 1000-mL, Fisher Scientific, Cat. Nos. 10-210-5G and -5C, respectively

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, separatory, borosilicate glass, 125-mL, with PTFE-plug stopcock and polyethylene stoppers, Fisher Scientific, Cat. No. 10-437-5B

Hot Plate, magnetic stirring, Fisher Thermix, Model 310T, Fisher Scientific, Cat. No. 11-493-310T

Pipets, volumetric, Class A, 25-, 50- and 100-mL, borosilicate glass, Fisher Scientific, Cat. Nos. 13-650-2P, -2S and -2U, respectively

Stir bar, magnetic, Teflon coated, 25-mm, Fisher Scientific, Cat. No. 14-511-63

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 or distilled water, except where noted.

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

Ammonium hydroxide, concentrated, 28-30%, Fisher Scientific, Cat. No. A669

Cupric sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 98% minimum purity, fine crystal, Fisher Scientific, Cat. No. C493

Hydrochloric acid, concentrated, 36.5-38%, Fisher Scientific, Cat. No. A144

Hydrochloric acid, 10 vol-%. In a 100-mL volumetric flask dilute 10 mL of concentrated hydrochloric acid to 100 mL with water and mix.

Ice

Isooctane, 99.5% minimum purity, 500 ng/L maximum sulfur compounds, Fisher Scientific, Cat. No. 0301

Lead acetate test paper, Fisher Scientific, Cat. No. 14-862

Methanol, 99.9% minimum purity, 500 ng/L maximum sulfur compounds, Fisher Scientific, Cat. No. A454

Potassium hydrogen phthalate, primary standard, 99.95% minimum purity, Fisher Scientific, Cat. No. P243

Potassium iodide, granular, 99.5% minimum purity, Fisher Scientific, Cat. No. P410

Sodium hydroxide, pellets, 97% minimum purity, Fisher Scientific, Cat. No. S318

Sodium hydroxide, 4 mass-/vol-%. In a 400-mL beaker, dissolve 40 ± 0.1 g of sodium hydroxide pellets with water, allow to cool and transfer to a 1000-mL volumetric flask. Dilute to volume and mix.

Sodium thiosulfate solution, 0.1-M, Fisher Certified, Fisher Scientific, Cat. No. SS368. This solution, used as a reference titrant, is not a primary standard and may deteriorate. Store in an amber bottle protected from light and discard the solution if the slightest haze, due to sulfur, develops. Do not store for more than 6 months.

Starch indicator solution, stabilized, Fisher Scientific, Cat. No. SS408

Weighing dishes, polystyrene, 67/46 mm, Fisher Scientific, Cat. No. 02-202B

PREPARATION AND STANDARDIZATION OF REAGENT

Preparation

Prepare a 0.0157-*M* (1 mg/mL) copper reagent solution as follows: Weigh 3.93 g $\pm$ 0.1 mg of cupric sulfate pentahydrate into a weighing dish. Quantitatively transfer into a 1000-mL volumetric flask and dissolve in 300-400 mL of water. Cool in ice. Simultaneously cool 100 mL of the 4 mass-/vol-% sodium hydroxide solution in ice. The ice cooling is necessary to prevent the formation of copper oxide during the exothermic reaction. When both solutions are thoroughly chilled, very slowly add the sodium hydroxide solution to the cupric sulfate solution while vigorously stirring on the magnetic stirrer. From a graduated cylinder, slowly add 200 mL of ice-cooled concentrated ammonium hydroxide to the solution to dissolve the precipitated copper hydroxide. When clear, allow the deep blue solution to come to ambient temperature, remove and rinse the stir bar, catching the rinsings in the flask. Dilute to 1000 mL with water and mix well.

Standardization

Standardize the copper reagent solution in duplicate as follows: Into a 400-mL beaker, pipet 100 mL of the copper reagent. Add a magnetic stir bar and place the beaker on a magnetic stirring hot plate and stir slowly. Heat the solution at just below the boiling point while stirring, to drive off the ammonia, until approximately 20-25 mL remains. Using a graduated cylinder, slowly add approximately 10 mL of 10 vol-% hydrochloric acid to dissolve the black copper oxide precipitate which has formed. The solution should turn clear, light greenish blue. If it does not, add additional amounts of 10 vol-% hydrochloric acid.

Rinse the beaker walls with water, remove the beaker from the hot plate and allow the solution to cool to ambient temperature. Place the beaker on a magnetic stirrer (without heating), and neutralize the copper reagent by slowly adding 5 to 10 mL of 4 mass-/vol-% sodium hydroxide until a faint turbidity, resulting from the formation of copper hydroxide, appears. While stirring, add approximately 0.5 g of potassium hydrogen phthalate buffer to dissolve the copper hydroxide. Remove the beaker from the magnetic stirrer and cool the solution in an ice water bath. Return the beaker to the magnetic stirrer and, with stirring, dissolve approximately one gram of potassium iodide crystals in the solution. With continued stirring, immediately titrate the copper solution with 0.1-*M* sodium thiosulfate until the yellow brown color from the liberated iodine almost disappears. Add 3 to 5 mL of starch solution and continue the titration until the blue color disappears and creamy white cuprous iodide remains. Record the volume of sodium thiosulfate titrant used.

Calculate the titer of the copper reagent solution in mg/mL to 3 significant figures as follows:

$$T = 0.0635 G$$

where:

G = volume of 0.1-*M* sodium thiosulfate titrant, average of 2 determinations, mL

T = titer of copper reagent solution, mg/mL

0.0635 = conversion factor to convert mL of titrant to concentration of copper reagent, mg/mL, calculated from:

$$\frac{(63.546)(0.1)(1000)}{(1000)(100)}$$

where:

63.546 = molecular weight of copper, g/mole

0.1 = molarity of sodium thiosulfate, moles/L

1000 = (numerator) conversion factor for g to mg, mg/g

1000 = (denominator) conversion factor for L to mL, mL/L

100 = volume of copper reagent titrated, mL

If the copper reagent has been made as previously described, one milliliter of the copper reagent will be approximately equivalent to 1 mg of copper or 1 mg of mercaptan sulfur.

The copper reagent must be standardized periodically. If a black copper oxide precipitate forms in the solution, it must be discarded and a new solution prepared.

PROCEDURE

Prior to the sample titration, qualitatively determine if hydrogen sulfide is present using lead acetate paper. Moisten a piece of lead acetate paper with water and fasten one end of the paper to the stopper of a bottle containing 100 mL of sample. Do not allow the paper to contact the hydrocarbon sample. Allow it to stand for about one minute. If the paper turns silver-black, hydrogen sulfide is present.

If hydrogen sulfide is present, reacting the sample with copper reagent will give false, high results for mercaptan since hydrogen sulfide will be included. For quantitation and distinction of the two species use UOP Method 163.

If hydrogen sulfide is absent, determine mercaptan as follows: Since mercaptans oxidize easily, it is important that samples are handled quickly to minimize their exposure to air. Distillates containing high concentrations of mercaptan must be pre-diluted using sulfur-free naphtha or isooctane. Pipet a 100-mL sample, or 100 mL of a sample dilution containing no more than 40 mg of mercaptan sulfur, into a 125-mL separatory funnel. Add 1.0 mL of the standardized copper reagent from a buret, stopper and shake for 0.5 to 3 minutes. Observe whether the blue color of the lower aqueous phase disappears (see Note 1). Daylight is the preferred source of light for observing this color change. If the lower phase remains blue for 3 minutes, the test is complete. If the color disappears within the 3 minute period, draw off the lower aqueous layer and discard. Repeat the procedure with the addition of one-milliliter increments of fresh copper reagent until the blue color persists for 3 minutes (see Note 2). Record the total volume of standard copper reagent solution used in the determination.

Determine the relative density of the sample by ASTM Method D 4052 or other acceptable technique.

CALCULATIONS

Calculate the copper number to the nearest whole number as follows:

$$\text{Copper Number} = \frac{\text{VTD}}{\text{S}}$$

where:

- D** = final sample volume, if diluted, mL
S = original sample volume, if diluted, mL
T = titer of copper reagent, previously defined
V = volume of copper reagent titrant, mL

Calculate the mercaptan sulfur concentration to the nearest mass-ppm as follows:

$$\text{Mercaptan Sulfur, mass-ppm} = \frac{10C}{R}$$

where:

- C** = copper number, previously calculated
R = relative density of the sample, g/mL
10 = factor to convert 10^3 (mg/g to mass-ppm) divided by 100 (sample volume titrated, mL)

NOTES

1. If an emulsion problem occurs and the lower aqueous phase does not separate easily, the addition of 5-10 mL of sulfur-free methanol with each copper reagent addition may help to better separate the phases at the beginning of the titration. However, near the titration endpoint, methanol additions are to be avoided to better see the blue color of the copper reagent.

2. Do not confuse a bluish opalescence, which sometimes appears, with the blue color of the copper-ammonia complex. If the funnel is held against white paper, the blue color is easily distinguished.

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) for mercaptan sulfur in a light naphtha was calculated to be 7.5 mass-ppm at a mercaptan sulfur concentration of 400 mass-ppm. Two tests performed in one laboratory by different analysts on different days should not differ by more than 29 mass-ppm (95% probability), at the stated level.

Reproducibility

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

REFERENCES

ASTM Method D 4052, www.astm.org
 UOP Method 163

SUGGESTED SUPPLIER

Fisher Scientific, 1600 W. Glenlake Ave., Itasca, IL 60143