Application Bulletin

℧ Metrohm

Of interest for:
Metallurgical industries, Water-supply and
effluent analysis laboratories

No. 49/1 e

Colorimetric determination of copper

Summary

Application Bulletin No. 43 described the polarographic determination of copper. For copper concentrations of 10 mg/L and below, however, colorimetric methods are also used, particularly in water analysis.

The method using sodium diethyl-dithiocarbamate can be employed down to a minimum limit of 0.01 mg/L Cu, but suffers from the drawback that the determination can also be affected by other metal ions.

The method using neocuproin has a minimum concentration limit of 0.1 mg/L Cu, but has the advantage of being unaffected by ions of other metals.

1. Determination of copper with sodium diethyl-dithiocarbamate

Reagents

▶ 20% citric acid solution

▶ 25% sulphuric acid solution

▶ 20% ammonium chloride solution

▶ 1% sodium diethyl-dithiocarbamate solution (shelf life app. 1 month)

▶ chloroform (analytical grade)

▶ standard copper solution:
dissolve 0.393 g $CuSO_4 \cdot 5H_2O$ in 1 litre distilled water (concentration: 0.1 g/L Cu).

Apparatus

2.662.0010 Photometer with 6.1108.010 light guide
(ev. 6.1250.000 mirror 10 mm)

Method

▶ Place 100 mL of the sample in a 250 mL separating funnel, and add 1 mL citric acid, 0.5 mL sulphuric acid, and 0.5 mL ammonium chloride. Finally, shake the solution with 10 mL chloroform; the chloroform layer separating out at the bottom is run off and thrown away. Add 2 mL sodium diethyl-dithiocarbamate, and shake four times, with 5 mL chloroform each time. The combined chloroform extracts are then poured into a 25 mL graduated flask, and made up to volume with fresh chloroform.

▶ The extinction of the sample at 430 nm is then measured on the 662 Photometer against a blank sample.

▶ The blank sample and the standard sample are treated in the same way.

▶ Concentrations of 0.01 – 1.0 mg/L Cu are measured with a layer thickness of 20 mm, and higher concentrations with a layer thickness of 10 mm.

▶ Lambert and Beer's law is obeyed by concentrations ranging from 0.01 – 1.0 mg/L Cu.

Calculation

$$\text{mg/L Cu} = E_s \frac{a}{E_{st}}$$

E_s = extinction of sample

E_{st} = extinction of standard solution
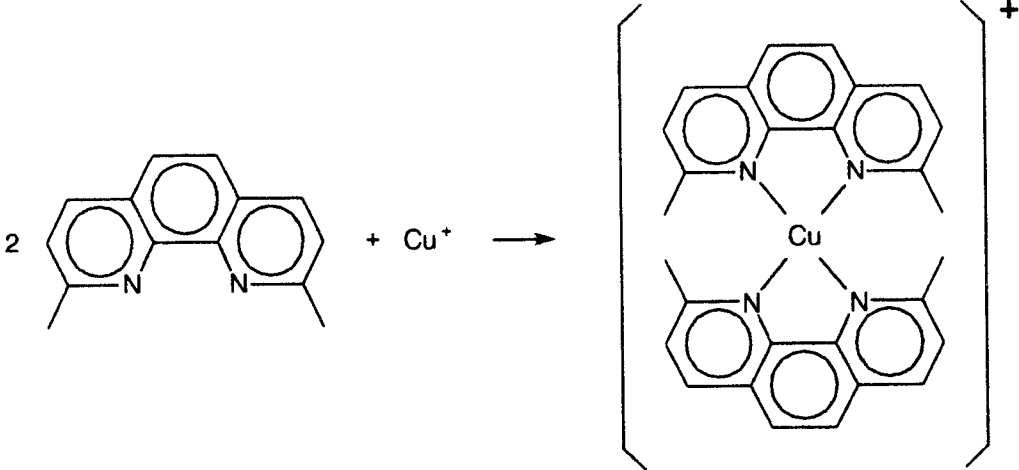
a = concentration of standard solution

Colorimetric determination of copper

Limit of determination	0.5 mg/L Cu
Remarks	▶ Iron is masked by the addition of citric acid. ▶ Larger quantities and lead cause a white turbidity. ▶ The following correction must be applied if nickel is present: 10 µg Ni corresponds to 1 µg Cu. ▶ Copper cyanide complexes must be destroyed with sulphuric acid and hydrogen peroxide.
Theorys	The method depends on the formation of a yellow compound by the reaction of cupric ions with sodium diethyl-dithiocarbamate, which is then extracted with an organic solvent (i.e. chloroform). $2\ (C_2H_5)_2 - N - CS - S - Na\ +\ Cu^{2+}\ \rightarrow\ Cu^{2+}[\ -S-CS-N-(C_2H_5)_2\ ]_2\ +\ 2\ Na^+$
Bibliography	▶ *Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung* 3. Auflage, Verlag Chemie GmbH, Weinheim ▶ Gubin, Hass, Hoffmann, Reichmuth Mitteilung der Vereinigung der Grosskesselbesitzer (1955)

2. Determination of copper with neocuproin

Reagents	▶ sodium citrate solution 0.6 g $Na_3C_6H_5O_7 \cdot 2H_2O$ in 100 mL distilled water. ▶ neocuproin (2,9-dimethyl-1,10-phenanthroline) analytical grade: 0.2 g in 100 mL iso-amyl alcohol. ▶ 10% hydroxylamine hydrochloride ▶ anhydrous sodium acetate (analytical grade) ▶ iso-amyl alcohol (analytical grade) ▶ anhydrous sodium sulphate (analytical grade) ▶ standard copper solution: dissolve 0.393 g $CuSO_4 \cdot 5H_2O$ in 1 litre distilled water (concentration 0.1 g/L Cu).
Apparatus	2.662.0010 Photometer with 6.1108.010 light guide (ev. 6.1250.000 mirror 10 mm)
Method	▶ Adjust the pH of the sample to pH 5 – 6 with dilute acetic acid or dilute ammonium hydroxide, as the case may be, and place 10 mL of it in a separating funnel with 1 mL sodium citrate solution, 1 mL hydroxylamine hydrochloride solution, 1 mL neocuproin solution, 1 gm sodium acetate and 20 mL iso-amyl alcohol, and shake for ½ minute. The yellow upper layer is dried with anhydrous sodium sulphate. ▶ The blank and standard samples are treated in the same way. ▶ The extinction of the sample is measured against the blank sample in the 662 Photometer. ▶ For concentrations of 0.1 ... 1.0 mg/L Cu use a layer thickness of 20 mm, and for higher concentrations use a layer thickness of 10 mm. ▶ Lambert and Bee's law is obeyed by concentrations ranging from 0.1 ... 10 mg/L Cu.

Colorimetric determination of copper

Calculation	$$\text{mg/L Cu} = E_s \, \frac{a}{E_{st}}$$ E_s = extinction of sample E_{st} = extinction of standard solution a = concentration of standard solution
Limit of determination	0.1 mg/L Cu
Remarks	▶ The determination is unaffected by the presence of other cations. ▶ An orange-yellow precipitate is produced by higher concentrations of nitrate, perchlorate and halide ions, but since only the copper complex is extracted, the determination remains unaffected. ▶ Instead of iso-amyl alcohol, n-amyl or n-hexal alcohols can be used as extraction solvents.
Theory	The method depends on the formation of an orange-yellow complex by the reaction of cuprous ions with neocuproin. For this reason, the cupric ion is first reduced to the cuprous state with hydroxylamine. The complex is then extracted for colorimetric measurement with iso-amyl alcohol.
Bibliography	▶ G.F. Smith, W.H. McCurdy Anal. Chem. 24, 371 (1952)