

NOTE

Selective Complexometric Determination of Copper in Alloys using L-Cysteine

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An accurate, selective and rapid complexo-titrimetric method is described for the determination of copper in alloys. The method is based on the selective complexing ability of L-cysteine with copper. Copper in the alloy solution, initially complexed by the addition of EDTA solution and the excess EDTA is titrated against lead nitrate solution (pH 5.0-6.0) using hexamine and xylenol orange. A known excess of L-cysteine in water is then added to release the EDTA from the Cu-EDTA complex. This is subsequently titrated against lead nitrate to the sharp end point as before. The amount of EDTA replaced from the complex is thus equivalent to the amount of copper in the alloy solution.

Complexometric methods of determination of copper have superseded the classical iodimetric method because they are less prone to interference from ions commonly encountered in the analysis of various materials containing copper. In these methods the sample is dissolved in a suitable medium, the Cu(II) is complexed with EDTA and the complex is decomposed by reducing Cu(II) to Cu(I) and stabilized as a Cu(I) species. The EDTA subsequently released from the complex is determined titrimetrically. Many methods are reported in literature for the determination of copper based on the technique of masking. Thus binary or ternary reagent mixtures such as ascorbic acid and thiocyanate^{1,2}, ascorbic acid and thiourea³, ascorbic acid, thiourea and 1,10-phenanthroline⁴ or a single reagent serving as a reductant as well as a complexing agent such as thiosulphate⁵, thiourea⁶, thioglycolic acid⁷, mercaptopropionic acid⁷ and mercaptosuccinic acid⁸ have been used for decomposing the Cu(II)-EDTA complex. The applicability of such a method for the analysis of numerous alloys and ores is also studied and reported^{2,7,8}. Thiols are known to react with Cu(II) to form a strong Cu(I) complex as follows



In this paper, the results of a study on the feasibility of using L-cysteine, which can form a strong complex with Cu(II) is reported. The reagent is found to be a better chelating agent than the ones earlier reported.

EDTA solution, (approx. 0.01 M) is prepared by dissolving the disodium salt of EDTA in distilled water. Lead nitrate solution (0.02 M)

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is prepared by dissolving lead nitrate in distilled water and standardised by the chromate method⁹. L-cysteine is 0.5% solution in water and xylene orange is 0.5% solution in water.

About 1.0–1.5 g copper base alloys are dissolved in conc. HNO₃ and the oxides of nitrogen expelled with the help of conc. H₂SO₄ till the brown fumes cease to evolve. The residue is extracted with distilled water and made up to 250 ml in a standard flask. 5 ml aliquots are used for the titration. The solution is diluted to about 100 ml and the pH is adjusted to 5.0–6.0 with hexamine. The excess of EDTA is titrated with 0.02 M lead nitrate solution using xylene orange as indicator. L-Cysteine solution in water is then added in excess over 1 : 3 (metal to reagent). The change of colour from green to yellow is observed during addition of cysteine solution. The solution is kept aside for about 5 minutes with intermittent shaking. The EDTA released is then titrated against the lead nitrate solution to the same end point as before. For comparison, the copper content in the alloys were also determined by thiocyanate method. The results of analysis are presented in Table 1.

TABLE 1
ANALYSIS OF COPPER ALLOYS

Alloy	% of copper found* by complexometric titration	% of copper found† by thiocyanate method—Gravimetric
Cu-Ni	71.21	71.26
Bronze	80.88	80.79
Brass	67.61	57.64
Aluminium-bronze	77.25	77.16
Gun-metal	85.11	84.94

*Average of four determinations.

†Average of three determinations.

The quantitative displacement of EDTA from Cu-EDTA complex by L-cysteine indicates that the Cu-cysteine complex is more stable than the Cu-EDTA complex at room temperature itself and that EDTA is released instantaneously. For the complete release of EDTA, a slight excess of L-cysteine over and above the molar ratio of 1 : 3 is necessary. Larger excess of the reagent does not have any adverse effect on the results of determination of copper. It is found that L-cysteine forms 1 : 1 complex with copper¹⁰, but during complexation it reduces Cu(II) to Cu(I).

The speciality of the reagent is that it does not form any precipitate with either Cu(II) the metal ion to be estimated or Pb(II) the titrant, in the conc. range of copper studied under the experimental conditions. This facilitates sharp end point. The main advantage of the proposed method is that it does not require heating or cooling before or during the titration. The method does not involve extraction of the Cu-EDTA complex and hence is simple and can be rapidly carried out in a single step. The EDTA solution does not require standardisation and no pH readjustment is required for the final titration.

ACKNOWLEDGEMENT

The authors are thankful to the Professor and Head, Department of Chemistry, Mangalore University, Mangalagangothri for providing necessary laboratory facilities.

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[Received: 18 July 1990; Accepted: 4 April 1991]

AJC-285

NATIONAL SEMINAR ON RAMAN SPECTROSCOPY

May 1992

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