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A New Assay for Copper(II) Sulfate by Acidimetry and Its Comparison with Iodometric Assay

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An acidimetric assay for copper(II) sulfate has been developed and compared with iodometric assay. The assay is based on complete precipitation of copper(II) as cupric hydroxide in presence of dilute sodium hydroxide solution; reconstituting the purified precipitate in slight excess of standard H_2SO_4, determining the amount of cupric hydroxide by back-titration of the solution against standard sodium hydroxide solution, wherein copper(II) ions act as self-indicator, and the end-point is characterized by appearance of a faint bluish-white turbidity that does not disappear on shaking and standing. Each mL of 1 N H_2SO_4 consumed is equivalent to 1 mL of 1 N $Cu(OH)_2$ that is equivalent to 31.77 mg of copper(II), or 124.85 mg of copper(II) sulfate pentahydrate. The assay is comparable to iodometric assay with no significant difference between mean per cent purity values ($P > 0.1$), and precisions of two sets of data ($P > 0.1$). Acidimetric assay offers certain advantages over iodometric assay. It is simpler to perform, obviates the use of external indicator, and involves lesser number of chemicals and variables. The technique can be employed for determining per cent purity of commercially produced copper(II) sulfate or other copper salts following their conversion to copper sulfate.

INTRODUCTION

Copper(II) sulfate is commercially prepared for industrial, research and biomedical applications. Iodometric assay is widely employed for determining its purity[1, 2]. Iodometric assays are considered cumbersome with inherent technical problems[2, 3]. A need to develop a simpler titrimetric assay for copper sulfate was mooted on following considerations: (i) copper sulfate can be quantitatively precipitated with dilute sodium hydroxide solution and collected in a purified form as cupric hydroxide/oxide as is done in one of the gravimetric assays for copper(II) sulfate[3, 4], (ii) cupric hydroxide/oxide can be estimated directly by acidimetric technique by back-titration wherein copper(II) acts as a self-indicator to mark equivalence point with turbidity end-point[5] (iii) stoichiometric relation between cupic hydroxide and copper(II) sulfate would enable determination of copper(II)/copper sulfate in an unknown sample and aid in determination of per cent purity of a given sample as each mL of 1 N cupric hydroxide would correspond to 31.77 mg of copper(II), or 124.85 mg of copper sulfate pentahydrate. Therefore, investigations were carried out to compare results obtained with standard iodometric assay with those obtained with standardized acidimetric assay.

EXPERIMENTAL

The chemicals used were of analytical-reagent grade. The experiments were carried out at 21.5 ± 1.5°C. Double-distilled water, freshly boiled and cooled, was used for dilutions, washings and preparation of reagents. Volumetric glassware used was pre-calibrated. Stock copper(II) sulfate pentahydrate (labelled minimum assay 98.5 per cent) was prepared accurately as 5 per cent (w/v) in water in amounts to suffice all the experiments; weighing error was 0.002 per cent. Working sample solution was prepared by dilution as 2% (v/v) in water. Sample sizes taken for comparative assays were 100, 250 and 500 mg. Six assays were conducted at each sample size in a randomized order.

Standard iodometric assay followed was that described elsewhere[2]. Acidimetric assay included following steps: (i) appropriate aliquot size of the working solution of copper sulfate was approximately made 0.5 to 1 per cent with water in 100 to 250 mL titration flask depending upon sample size; (ii) sodium hydroxide solution (*ca.* 0.2 N) was added dropwise with constant shaking till copper(II) ions got completely precipitated—4 to 5 mL of about 0.2 N NaOH were required per 100 mg sample; (iii) the solution was allowed to stand at room temperature for 15 to 20 min; (iv) the precipitate was separated from the solution by filtration using Whatman filter No. 40, and purified off the adhering alkaline residue by 4 to 5 washings with distilled water till filtrate ceased to react to phenolophthalein moistened filter paper strip—20 to 30 mL water was required per 100 mg sample; possibility of any copper ions being lost during purification was ruled out by clarity of the filtrate, and its failure to respond to potassium ferrocyanide test positively that otherwise detects copper ions in traces[6]; (v) precipitate was carefully transferred to original cleansed titration flask employing a jet of distilled water—about 10 mL water was required per 100 mg sample; (vi) the precipitate was dissolved in standard H_2SO_4 (0.4 N)— 10 mL acid was required per 100 mg sample; the acid was standardized against 0.2 N NaOH which had been standardized against 0.2 N succinic acid as primary standard using copper sulfate as indicator[5]; the volume of acid used was noted; and (vii) the sample was titrated against 0.2 N NaOH till equivalence point indicated by the appearance of a faint bluish-white turbidity that did not disappear on shaking and standing[5], in an otherwise clear solution; the volume of the alkali used was noted.

Per cent purity of the sample is given by

$$\frac{A \times 124.85}{w} \times 100$$

where w is apparent weight of the salt in the sample, mg, A is acid consumed by the precipitate, 1 N H_2SO_4 is equivalent to 1 N $Cu(OH)_2$ obtained, and is given by acid used (mL × N) minus alkali used (mL × N).

Each mL of 1 N $Cu(OH)_2$ corresponds to 124.85 mg copper sulfate pentahydrate. Estimated copper sulfate pentahydrate in the test sample can be directly obtained by multiplying A and 124.85.

Regression coefficient estimates, b ± S.E., were obtained for two assays in units of mL 1 N cupric hydroxide formed for acidimetric assay, and mL 1 N sodium thiosulfate consumed for iodometric assay per 100 mg copper(II) sulfate pentahydrate to confirm their respective closeness to theoretical stoichiometric values. Differences of mean per cent purity values by two assays were compared by Students' t-test. Precisions of two sets of data were compared by F-test. Accuracy of acidimetric assay was determined as relative mean error of values obtained with acidimetric assay as per cent of values obtained with iodometric assay[2].

RESULTS AND DISCUSSION

The linear relationship between experimental estimates and varying sample sizes for acidimetric and iodometric assays are quite apparent (Table-1). Experimental estimates, b ± S.E., for the two assays were, respectively, 0.793 ± 0.015 and 0.395 ± 0.029 (n = 18, each) which are very close to respective theoretical values of 0.80 and 0.40 units of mL 1 N cupric hydroxide and mL 1 N sodium thiosulfate corresponding to 100 mg copper(II) sulfate pentahydrate in acidimetric and iodometric assays, respectively.

TABLE-1

LINEAR RELATION BETWEEN EXPERIMENTAL ESTIMATES AND SAMPLE SIZES OF COPPER(II) SULFATE PENTAHYDRATE USING IODOMETRIC AND ACIDIMETRIC ASSAYS

Sample size, mg	Iodometric assay, mL 1 N sodium thiosulfate	Acidimetric assay, mL 1 N cupric hydroxide
100	0.386 ± 0.003	0.771 ± 0.005
250	0.973 ± 0.003	1.953 ± 0.008
500	1.965 ± 0.002	3.943 ± 0.003

The values are mean ± S.E. of six observations.

Per cent purity determinations by either assay yield comparable values (Table-2) with no significant differences between mean values obtained over 100 to 500 mg sample size range ($P > 0.1$). There is no significant difference in precisions of two sets of data over test sample size range ($P > 0.1$). Sample size analysis revealed that acidimetric assay is highly accurate as accuracy is better[2] than 1 per cent with relative mean error of the values as 0.10, 0.31 and 0.31 per cent of those obtained with iodometric assay, respectively, at 100, 250 and 500 mg sample sizes. Furthermore, 500 mg sample size is most appropriate for either assay as lower sample sizes affect per cent purity values and precision adversely and significantly ($P < 0.05$). This is in conformity to practice of using about 600 mg sample size in iodometric assay[2].

TABLE-2

PER CENT PURITY COPPER(II) SULFATE PENTAHYDRATE (LABELLED PURITY 98.5 PER CENT) BY IODOMETRIC AND ACIDIMETRIC ASSAYS

Sample size, mg	Iodometric assay	Acidimetric assay
100	96.30 ± 0.77	96.20 ± 0.67
250	97.20 ± 0.30	97.50 ± 0.41
500	98.10 ± 0.13	98.40 ± 0.10

The values are mean ± S.E. of six observations.

The acidimetric technique is a two-step procedure: (i) the quantitative precipitation of copper as copper hydroxide with sodium hydroxide: the step is identical to one used in gravimetrical analysis of copper[3, 4], and (ii) estimating the amount of cupric hydroxide by its capacity to consume standard H_2SO_4, obviating ignition and weighing of CuO as is otherwise done in the gravimetrical assay[3, 4]. The ability of copper ions to act as indicator is based on two facts: (i) copper ions form sparingly soluble cupric hydroxide at pH 6 and above[2], and (ii) solubility product constant of cupric hydroxide is very low[7], 1.6×10^{-19}; thus negligible amounts of hydroxide ions will be required to induce visible turbidity at equivalence point[5]. Phenolphthalein does not work in presence of copper(II) ions as addition of alkali hydroxide precipitates copper, and end-point is erratically delayed (unpublished data).[5]

The study has revealed that the acidimetric assay has accuracy and precision comparable to that of iodometric assay. It can be employed as a better substitute for iodometric assay for offering obvious advantages: (i) the assay is simpler to conduct, (ii) it can be conducted at ease with no haste as is required otherwise in iodometric assay following completion of iodine release[2], (iii) fewer chemicals and variables are involved, (iv) use of external indicator (e.g. starch in iodometric assay) and hazardous chemicals such as concentrated HCl and glacial acetic acid are obviated, and (v) interferences in estimations by any oxidizing/reducing agents, as happens in iodometric assay, are obviated.

The assay has been standardized with respect to copper sulfate, the best known copper salt with wider applications in industry, research, agriculture and veterinary practice. The technique would be applicable to other copper salts, including the subacetate, oxychloride, chloride and oxide, that are employed as fungicides in agricultural practice; the soluble forms can be directly estimated while water-insoluble forms would require preliminary conversion to copper sulfate, and using appropriate stoichiometric factors in final calculations.

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