

# A NEW SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF COPPER WITH SODIUM VERSENATE

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## INTRODUCTION

ESTIMATION of copper in solutions<sup>1,2</sup> and in a number of alloys<sup>3,4</sup> and metals,<sup>5,6</sup> as also in semi-conductors<sup>7</sup> has been the subject of recent interest. For this purpose a series of reagents like dithizone,<sup>8</sup> thiobenzamide,<sup>1</sup> 2-methyl-8-quinolinol,<sup>9</sup> nitrilotriacetic acid,<sup>10</sup> diethyldithiocarbamate,<sup>5</sup> ethylenediaminetetra-acetic acid (EDTA),<sup>11,12</sup> etc., have been developed for colorimetric estimation of copper. A resumé on the work done, during a period of two years (from August 1953 to August 1955) amounting to a few scores of papers, has been given by Mellon and Boltz.<sup>13</sup>

It is known that EDTA forms a soluble complex with copper<sup>14</sup>; using this property, simple methods for estimation of copper in steel, bronze and other alloys, have been developed. Thus Sedivec and Vasak<sup>15</sup> determined copper in steel by complexing the mixture with EDTA and later precipitating copper with diethyldithiocarbamate. Similarly Byrn and Robertson<sup>16</sup> precipitated copper quantitatively in the presence of EDTA from a solution of nickel copper alloy or bronze by 2-(0-hydroxy phenyl) Benzole. Direct spectrophotometric methods for determining copper with EDTA have also been developed. Malmstadt and Gohrbandt<sup>17</sup> recorded the absorption of copper nitrate versenate and copper versenate solutions in the ultraviolet region and used the absorption at  $\lambda = 320 \text{ m}\mu$  for estimation of copper with versenate and *vice-versa*. Similarly in the near infra red region Hughes and Mortell<sup>18</sup> showed that copper versenate has its maximum absorption between  $\lambda = 700\text{--}750 \text{ m}\mu$ ; employing the absorption of copper at  $\lambda = 745 \text{ m}\mu$ , Underwood<sup>19</sup> titrated copper solution with EDTA; and Nielsch and Boltz<sup>12</sup> estimated copper with EDTA using the absorption maximum at  $\lambda = 720 \text{ m}\mu$ .

In the course of a series of investigations on the easy estimation of calcium in sugar solutions and sugarcane juices, which is a problem in sugar technological laboratories, a new method for the estimation of copper spectrophotometrically has been evolved. This method appeared usefu<sub>1</sub>

on account of the possibility of using the characteristic absorption of copper in the visible region (at  $\lambda = 630 \text{ m}\mu$ , *vide infra*). It may be added that there have been similar simple methods worked out (*vide supra*) which involved the use of absorption of copper in the ultraviolet region or in the near infrared. Non-availability of the ultraviolet and other spectrophotometers in our Laboratory set a limitation to the use of these methods. The present communication describes a method for estimation of copper in ammoniacal medium by disodium salt of ethylenediaminetetra-acetic acid using Unicam SP 350 DG Spectrophotometer, which has a continuous variation of wavelength in the region 400–700  $\text{m}\mu$ .

#### EXPERIMENTAL

The spectrophotometer employed, *viz.*, Unicam SP 350 DG Spectrophotometer has an one cm. light path.

The substances used were of the following grade: Copper sulphate used was of BDH Analar quality; this was purified by recrystallisation in distilled water.

The sodium versenate employed was of Merck quality.

The method for carrying out the spectrophotometric titrations was as follows: Solutions were made in such a way that the final volume (25 ml.) contained a fixed quantity of copper and ammonia and varying quantities of the titrant, *viz.*, the sodium versenate. The absorption of these solutions was studied in a few cases, in the range 400–700  $\text{m}\mu$  and in the subsequent experiments at  $\lambda = 630 \text{ m}\mu$  (*vide infra*).

#### RESULTS AND DISCUSSION

Figure 1 gives a typical series of results on the absorption of ammoniacal copper solution in the range 400–700  $\text{m}\mu$ . In this, curves 1, 2 and 3 refer respectively to 20, 16 and 10 mM. concentration of copper solution containing 1.15 M. of ammonia. It was interesting to note that ammoniacal copper solution exhibits well-defined characteristic maximum at  $\lambda = 630 \text{ m}\mu$ ; the absorption at this wavelength obeys Beer's law (*see* Fig. 2) with a value of  $50 \text{ mole}^{-1} \text{ litre cm.}^{-1}$  for the corresponding constant. Further, it was instructive to note that the absorption of copper versenate at  $\lambda = 630 \text{ m}\mu$  also obeyed the Beer's law (Fig. 3); the Beer's constant for copper versenate under the experimental condition, *viz.*, in the ammoniacal medium was  $16.7 \text{ moles}^{-1} \text{ litre cm.}^{-1}$ . This appreciable difference between the Beer's constants of copper and copper versenate solutions facilitated the execution of the titrations under investigation.

Figure. 4 gives a typical set of curves representing the variation of the absorbency of ammoniacal copper at  $\lambda = 630 \text{ m}\mu$  during the progress of the

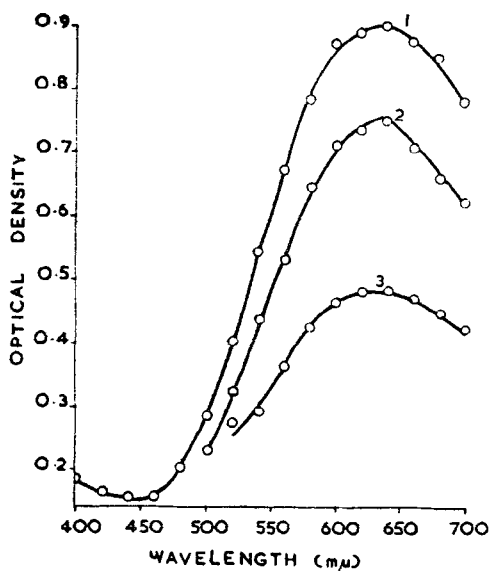


FIG. 1.

FIG. 1. Absorption spectra of copper ammonium complex in the visible region. Concentration of ammonia: 1.15 M. Curve 1 refers to 20 mM.; Curve 2, to 16 mM.; and Curve 3, 10mM. of  $\text{Cu}^{++}$ .

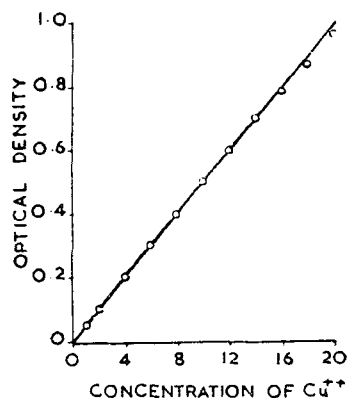


FIG. 2.

FIG. 2. Variation of optical density with the concentration of  $\text{Cu}^{++}$  at  $\lambda = 630 \text{ m}\mu$ . Concentration of ammonia: 1.15 M. The scale on the X-axis refers to mM.

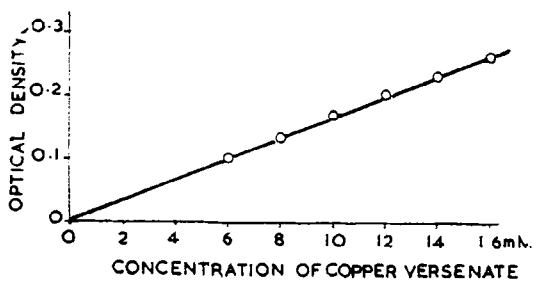


FIG. 3.

FIG. 3. Variation of optical density with the concentration of copper versenate complex at  $\lambda = 630 \text{ m}\mu$ .

Concentration of ammonia: 1-15 M.

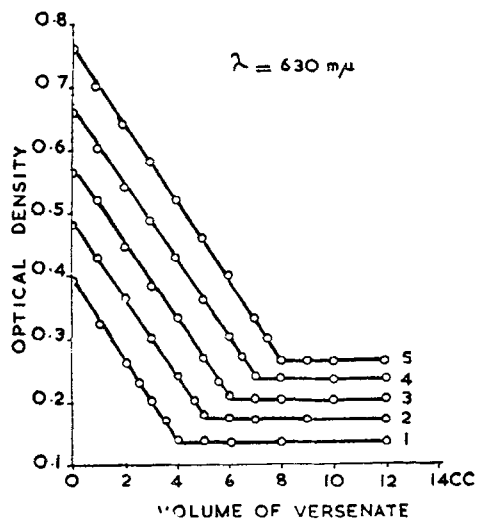


FIG. 4.

FIG. 4. Spectrometric titration of  $\text{Cu}^{++}$  with sodium versenate at  $\lambda = 630 \text{ m}\mu$ .

Concentration of ammonia: 1.15 M. Concentration of sodium versenate: 50 mM. Curve 1 refers to 8 mM.; Curve 2, to 10 mM.; Curve 3, to 12 mM.; and Curve 4, to 16 mM. of  $\text{Cu}^{++}$

titration. It was instructive to note that optical density of copper decreased progressively with the addition of versenate till the end point; further addition of versenate effected little the optical density. It may be noted that the end points were very sharp; the error involved in the determination of copper by versenate is less than 1%.

#### SUMMARY

Employing the absorption at  $\lambda = 630 \text{ m}\mu$  of copper ammonium complex, a new method for determination of  $\text{Cu}^{++}$  by sodium versenate was described. The experimental error involved in the method was less than 1%.

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