

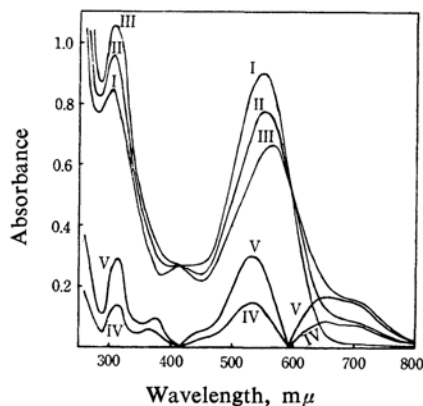
## A New Spectrophotometric Method for the Determination of Copper(II) with Calcichrome

By Hajime ISHII and Hisahiko EINAGA

(Received June 8, 1965)

A new spectrophotometric method for the determination of trace of copper(II) has been developed. It is based upon the formation of a stable bluish-violet copper(II) complex of Calcichrome, which had been reported by some investigators<sup>1-5)</sup> to be a reagent for the determination of calcium.

The absorption spectra of the complex are shown in Fig. 1. The complex spectrum has three absorption maxima with reference to the reagent blank in the visible ( $\lambda_{max}$  535 and 650  $m\mu$ ) and ultraviolet regions ( $\lambda_{max}$  310  $m\mu$ ), and also two isosbestic points, at 415 and 595  $m\mu$ , in the pH range from 3 to 10. As may



Absorption spectra of Cu(II)-Calcichrome complex.

Calcichrome:  $4 \times 10^{-5}$  mol./l., pH: 5. I; Cu 0, II; Cu:C<sub>ch</sub> 1:2, III; Cu: C<sub>ch</sub> 1:1, IV; Difference between I and II, V; Difference between I and III.

- 1) R. A. Close and T. S. West, *Talanta*, **5**, 221 (1960).
- 2) A. M. Lukin, K. A. Smirnova and G. B. Zavarikhina, *J. Anal. Chem. (USSR)*, **18**, 389 (1963).
- 3) M. H.-Lancina and T. S. West, *Anal. Chem.*, **35**, 2131 (1963).
- 4) P. Pakalns and T. M. Florence, *Anal. Chim. Acta*, **30**, 353 (1964).
- 5) H. Ishii and H. Einaga, *Japan Analyst (Bunseki Kagaku)*, **14**, 162 (1965).

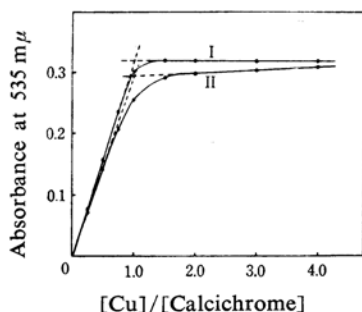


Fig. 2. Determination of mole ratio of Cu(II)-Calcichrome complex by the method of molar ratio.

Calcichrome:  $4 \times 10^{-5}$  mol./l.

I; pH 5, II: pH 4

be seen in Fig. 2, the composition of the complex is 1 to 1. At 535 mμ, the concentration range in which copper(II) obeyed Beer's law is dependent upon the concentration of Calcichrome; for instance, up to 3.5 p. p. m. of copper(II), the law is obeyed when the concentration of Calcichrome is  $6 \times 10^{-5}$  mol. The

molar extinction coefficient is about  $8 \times 10^3$ , and the sensitivity is  $0.008 \mu\text{g. Cu/cm}^2$ , which corresponds to  $\log I_0/I = 0.001$ . At 310 mμ, similar results were obtained. The proposed procedure for the determination is as follows. To a sample solution containing copper(II) in a 50 ml. volumetric flask, 5.0 ml. of a Calcichrome solution ( $6 \times 10^{-4}$  mol./l.) and 5 ml. of a sodium acetate-acetic acid buffer solution (pH 5) are added. After the solution has been diluted to the mark with distilled water, the absorbance of the solution is measured at 535 or 310 mμ with reference to a reagent blank solution. The full color develops instantaneously and is very stable. Copper(I) is also found to behave as copper(II). Some metals, such as vanadium, nickel, and hydroxy group metals, interfere under the conditions proposed.

Further, detailed studies are now in progress.

Central Research Laboratory  
Onoda Cement Co., Ltd.  
Koto-ku, Tokyo