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Trifluoroethylxanthate as an Analytical Reagent: Spectrophotometric Determination of Cobalt and Copper as Their Trifluoroethylxanthates

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With 2 Figures

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There are a great many colorimetric methods for the determination of cobalt and copper, especially the latter, but in many of the direct methods the reaction conditions are quite rigid. For instance, the determination of cobalt with 2-nitroso-1-naphthol and nitroso-R-salt requires rigid control of pH, reagent concentration and boiling time. The cobalt nitroso-R-salt complex has maximum absorption in aqueous solution at 420 nm, 525 nm and 578 nm, whereas in chloroform it shows absorption at 480—500 nm.

Several reagents, including 2,3-quinoxaline-dithiol, 5,7-dibromo-8-aminoquinoline, 2,2'-dihydroxybenzophenone thiosemicarbazone, (hydroxyaryl)azothiazoles, etc., have been proposed for colorimetric determination of both metals. Xanthates have been tried as complexing agents for the determination of certain metals, but were found to be not very selective, especially for copper, but preliminary experiments have revealed that halogen-substituted xanthates are sensitive and selective reagents for copper as well as for many other metals. In the present communication trifluoroethylxanthate is suggested as a reagent for the direct spectrophotometric determination of cobalt and copper. Its main advantage is that it can be used even

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at very low pH in extraction methods\textsuperscript{14}, resulting in high selectivity, whereas the other xanthates usually decompose under such conditions.

**Experimental**

**Reagents**

Potassium trifluoroethylxanthate was prepared by the method of DeWitt and Roper\textsuperscript{15} and a 0.2\% solution was prepared in a 2\% dimethylformamide solution in distilled water. Solutions of cobalt chloride and copper sulphate were prepared from the analytical grade materials and standardized\textsuperscript{16}. Dimethylformamide, acetone, perchloric acid (70\%\) and ammonia were of analytical grade. Solutions of the interfering ions were prepared in distilled water from analytical grade salts. Acetic acid-acetate buffer solution (pH 6.0) was prepared by mixing 50 ml of 1 M sodium hydroxide with 52.3 ml of 1 M acetic acid and diluting to 500 ml with distilled water.

**General Procedure**

To aliquots of the metal-ion solutions were added 2 ml of 0.2\% reagent solution, 2 ml of pH 6.0 buffer and enough 1 M potassium nitrate solution to give an overall concentration of more than 0.1 M. The metal complexes were then dissolved by adding acetone (5 ml for the cobalt complex, 12 ml for the copper complex), and the solutions were transferred to 25-ml standard flasks and diluted to volume with water. The absorbances were measured (1-cm cells) at the appropriate wavelengths against reagent blanks prepared similarly.

**Results and Discussion**

**Absorption Spectra**

The absorption spectra of potassium trifluoroethylxanthate and its cobalt and copper complexes were recorded in water-acetone solution against water and a reagent blank respectively. The complexes absorb strongly in the ranges 350—355 nm (Co) and 425—435 nm (Cu); the absorption of the reagent is almost negligible at these wavelengths (Fig. 1). For quantitative determinations, the absorbances were measured at 352 and 430 nm for cobalt and copper complexes respectively. The molar absorptivities at $\lambda_{\text{max}}$ were calculated to be $2.9 \times 10^4 \text{L \cdot mole}^{-1} \cdot \text{cm}^{-1}$ and $1.5 \times 10^4 \text{L \cdot mole}^{-1} \cdot \text{cm}^{-1}$ for the cobalt and copper complexes, respectively. Beer's law holds in the concentration ranges (in the final solutions) 0.0—1.7 $\mu$g/ml.