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Some Aspects of the Solvent Extraction-spectrophotometric Determination of Copper Dithiocarbamate Complex in Strongly Acidic Media

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Synopsis. The time stability of the extracted complexes in isobutyl methyl ketone depends on the pH of the washing solution of the extract and on the stability of the metal complex. The extract is stable to concentrated acid when the organic extract is separated rapidly and washed with water. Copper(II) tetramethylenedithiocarbamate is quantitatively extracted from 1—6 and 1—2 mol dm^{-3} hydrochloric and nitric acid media respectively.

Sodium diethyldithiocarbamate(DDTC) and ammonium tetramethylenedithiocarbamate(Ammonium 1-pyrrolidinecarbodithioate, APCD) have been widely used as extraction and colorimetric reagents for many metal elements. There are a number of publications about the determination of copper(II) with those complexing agents.[1-8)] The general principles are based on Sandell and others.[9-10)] Many analytical procedures require precise adjustment of pH, usually in the range 2—4, and APCD is often preferred to DDTC when extractions are performed in acidic solution. However, some studies indicate that the pH-range for extraction with APCD is different for copper.[6-8)] Moreover, these papers do not provide any information on the optimum range of strongly acidic concentration required for the extraction of copper(II). We have studied the time stability of copper(II)–DDTC and –PCD complexes in isobuthyl methyl ketone(IBMK) with the different acidities of the aqueous phase and the effect of pH of the washing solution on the extract, and we have applied this result to determine trace amounts of copper(II).

Experimental

Reagents. All solutions were prepared by dissolving analytical reagent grade chemicals in doubly distilled water. A 0.01 mol dm^{-3} copper(II) standard solution was prepared by dissolving recrystallized copper(II) sulfate pentahydrate in water, and diluted with water to give an adequate concentration before use. A 1% aqueous solution of DDTC and APCD were prepared. All other solvents were used without further purification.

Recommended General Procedure. The aqueous phase containing standard or sample should be acidified with hydrochloric or nitric acid; then adjust the acidity to the desired value. Add 10 cm^3 of the 1% DDTC or APCD solution, mix and allow to stand for 30 s. Extractions should be done in separatory funnels shaken for 7—10 min with 25 cm^3 of IBMK. After the aqueous phase is withdrawn, the organic phase should then be shaken with 50 cm^3 of water for about 5 min. After separating the two phases, the absorbance of the yellow copper complex in the IBMK phase can be measured at 435 nm against a reagent blank prepared in an identical manner.

Results and Discussion

Effect of Washing Solution on the Stability of the Extracts. The extraction of metal complex into the organic phase depends upon the hydrogen-ion concentration of the aqueous phase. If the pH is less than some critical value, the amount of the metal ion extracted decreases steeply. Therefore, when the IBMK phase is not separated from the aqueous phase, the decomposition of the metal complex will be faster and will depend on the treatment of the extracts.

Figure 1 show that the time stability of the copper–PCD and –DDTC complexes in IBMK depends on the treatment of the extracts. In this experiment, the aqueous phase was adjusted to acidity 4 mol dm^{-3} with hydrochloric acid. It is seen that the absorbances of both extracts remain almost constant for at least 2 h after washing with water, whereas the use of 4 mol dm^{-3} hydrochloric acid as washing solution causes the very rapid change of the absorbance with time. It was thought that the copper–PCD and –DDTC complexes might be made stable in the IBMK if, after the extraction, the organic phase was washed with neutral water to prevent decomposition of extract by hydrogen ion attack.

Extraction Behavior in Hydrochloric Acid. The extractions of copper(II) with APCD and DDTC in

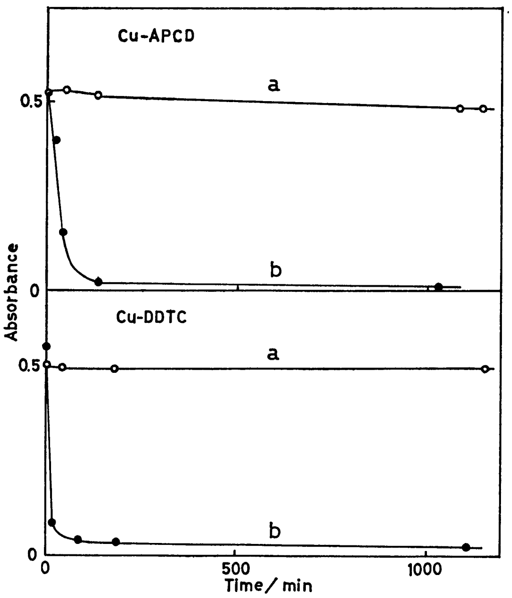

Fig. 1. Effect of acidity of washing solution on the absorbance of Cu-APCD and -DDTC complexes in IBMK.
a: Wash with 50 cm^3 of water, b: wash with 50 cm^3 of 4 M HCl, IBMK: 25 cm^3, Cu: 4×10^{-4} M.

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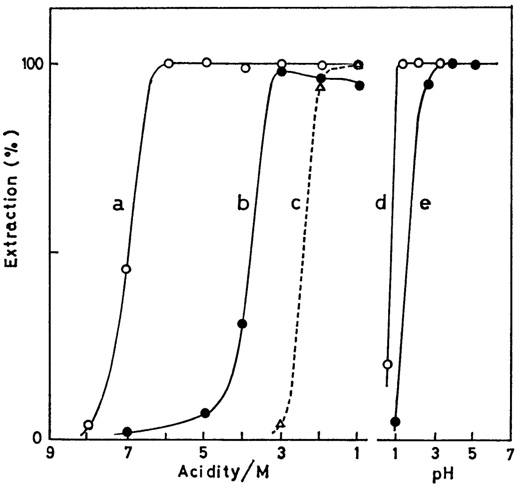

Fig. 2. Effect of acidity on the extraction of Cu(II) with APCD and DDTC in IBMK.
a: Cu–APCD–HCl system, b: Cu–DDTC–HCl system, c: Cu–APCD–HNO_3 system, d: Cu–APCD–HCl system, e: Cu–DDTC–HCl system. In the a, b, and c system, IBMK phase was washed with 50 cm^3 water, but in the d and e system, IBMK phase was not washed.
IBMK: 25 cm^3, Cu; 8×10^{-4} M.

IBMK were studied over the acidity range 1—8 mol dm^{-3}. The effects of acidity and the degree of extraction are shown in Fig. 2. With DDTC, the extraction is quantitative at acidity 1—3 mol dm^{-3}, but is incomplete at higher acid concentration. With APCD, copper(II) is completely extracted over the acidity range 1—6 mol dm^{-3}, but extraction is incomplete outside this acidity range. The decomposition of copper–PCD complex will be faster in the acidity range more than 6 mol dm^{-3} and will depend on the increase in the acidity of the aqueous phase.

Extraction Behavior in Nitric Acid. With APCD, copper(II) is extracted into IBMK at acidity less than 3 mol dm^{-3}, but the extraction of copper–DDTC complex is incomplete for acidity values. The oxidation decomposition of the dithiocarbamate complex with nitric acid is considered to occur in both the aqueous and organic phases. However, although the extraction range in nitric acid is very narrow compared to that in hydrochloric acid, it is noticeable that the stability of the copper–PCD complex in the organic phase is rather higher than that of the copper–DDTC complex.

Interferences. Synthetic mixtures were prepared with cations commonly found with copper in cadmium metal. No interference was observed in the determination of 5 μg of copper(II) with 1 mg of zinc(II), lead(II), iron(III), and thallium(II), and 10^6 times of cadmium(II).

Determination of Copper in Cadmium Metal. The method has been applied to the determination of a trace amount of copper in cadmium metals as follow: Dissolve 5 g of the sample into 100 cm^3 of 4 mol dm^{-3} nitric acid and rinse the beaker with 5 cm^3 of water. Transfer the solution to a 300 cm^3 separating funnel with 160 cm^3 of water. Add 10 cm^3 of 0.1% APCD solution. Shake the funnel for 8 min with 25 ml of IBMK. The two phases should be allowed to settle for 30 s; the aqueous phase was rapidly separated. The organic phase should then be shaken with 50 cm^3 of water for 5 min. The two phases thus separated. The yellow copper complex in the IBMK phase was measured photometrically at 435 nm against the reagent blank. Amounts of copper in various types of cadmium metals were determined and results were compared with those obtained by the atomic absorption method. The values were in good agreement. A study of the precision at 0.1 ppm level of copper showed the relative standard deviation of 1.3% for five replicates.

The procedure described in this paper is special additional step is unnecessary for stabilization of the extract; it is simple and permits the direct extraction of copper in various metals after decomposition of the metals with concentrated hydrochloric or nitric acid.

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