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Extraction and Spectrophotometric Determination of Copper(II) with 2-Thenoyltrifluoroacetone

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A highly sensitive method for the spectrophotometric determination of copper(II) with 2-thenoyltrifluoroacetone (TTA) is described. Copper(II) is extracted with TTA in cyclohexane at pH 5.5 and the residual TTA in the organic phase is removed by washing with sodium hydroxide solution containing pyridine. Pyridine is added to the washing solution so that it forms an adduct and prevents the copper-TTA chelate from decomposing during the alkali treatment process. The absorbance of the organic phase is measured at 340 mμ. Beer's law is followed over the concentration range of 0.1 to 1.0 μg of Cu per m*l*, the sensitivity being 0.0023 μg Cu/cm^2 at 340 mμ. The present method was applied to the analysis of natural water.

So-called synergistic extraction of metal chelate has been utilized for various analytical purposes such as separation of metal ions,[1,2] extractive spectrophotometric[3-7] and fluorometric[8] determination of metals. In most cases, enhancement of the extractability could be explained by the formation of an adduct. In the work described below, the adduct formation in the synergistic extraction is shown to be useful for an improvement in the spectrophotometric sensitivity.

Two methods of the spectrophotometric determination of copper(II) with 2-thenoyltrifluoroacetone (TTA) have already been proposed.[9,10] However, the sensitivities of these methods are low compared with that of the well known dithizone method.[11] Although the dithizone method is very popular mainly due to its high sensitivity, it is not always free from interferences caused by coexisting ions and had a defect that the reproducibility of the method depends largely upon the experimental conditions.

Therefore, by the aid of the formation of pyridine adduct, the previous TTA extraction spectrophotometry for copper[10] has been revised into a method for the highly sensitive determination of the element.

Since the low sensitivity of the above mentioned TTA methods is caused by the presence of the residual TTA in the organic phase which interferes with absorption measurement around 340 mμ (an optimum wavelength for the extracted copper-TTA chelate), the residual reagent should be removed by washing the organic phase with an alkali solution. The above purpose can be attained only when pyridine is present in the washing solution, otherwise not only the residual reagent but the copper-TTA chelate is decomposed.

Experimental

Apparatus and Reagents. Absorption measurements were carried out with a Shimadzu Spectronic 20 type photoelectric photometer and 1.17-cm glass cells. The pH value of the aqueous phase was measured after extraction with a Hitachi-Horiba F-5 type pH-meter and a glass electrode. TTA (Wako Pure Chemical Inc.) and cyclohexane (Nippon Rikagakuyakuhin Co.) were used without further purification. Pyridine and all other materials used in this work were of guaranteed grade.

A 0.001M TTA solution was prepared by dissolving a weighed amount of the reagent in cyclohexane. Standard copper solution (100 mg/*l*) was prepared by dissolving copper sulfate pentahydrate in deionized water.

General Procedure. Transfer 50 m*l* of the sample solution containing 1-10 μg of copper to a separatory funnel and adjust the pH of the solution to about 5.5. Then extract with 10 m*l* of 0.001M TTA-cyclohexane solution by shaking for 3 minutes. Allow the phases to separate and remove the aqueous phase. Add 10 m*l* of aqueous solution of sodium

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[1] T. Sekine and D. Dyrssen, *Anal. Chim. Acta*, **37**, 217 (1967).
[2] H. Akaiwa and H. Kawamoto, *ibid.*, **48**, 438 (1969).
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[8] T. Shigematsu, M. Matsui, and R. Wake, *ibid.*, **46**, 101 (1969).
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[10] H. Akaiwa, *Bunseki Kagaku*, **12**, 457 (1963).
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hydroxide (0.005M) containing 1% (v/v) of pyridine and shake the mixture for 3 minutes. Separate the phases and measure the absorbance of the organic phase at 340 mμ against the reagent blank.

Results and Discussion

Absorption Spectrum. The absorption spectrum of copper-TTA-pyridine complex in cyclohexane obtained by the above procedure is shown in Fig. 1. The spectrum of the extracted complex has a maximum absorbance at around 340 mμ, and the intensity is stable for at least 24 hrs. The absorbance of the reagent blank is considerably lowered by washing the organic phase with alkali solution.

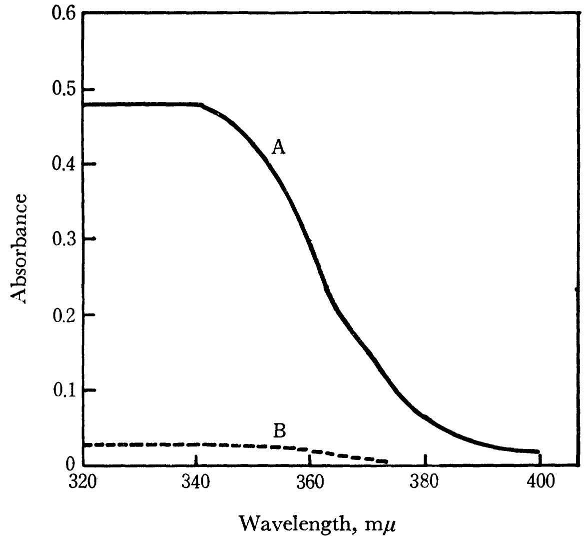

Fig. 1. Absorption spectra of copper-TTA-pyridine chelate (A) and the reagent blank (B).

Effect of pH. The extraction of copper into benzene proceeds according to the reaction: $Cu^{2+}+2HTTA_{,org.}=Cu(TTA)_{2,org.}+2H^+$, for which the extraction constant was reported to be 4.8×10^{-2}.12) The above reaction indicates that the extractability of copper is affected by the TTA concentration and the pH.

Copper can be extracted quantitatively at pH 4.0 by using 0.01 M TTA in benzene.10) However, since the residual TTA in the organic phase interferes with the absorption measurement, the TTA concentration for the extraction of copper was required to be as low as possible. Considering the above situation, the 0.001M TTA solution was adopted. The extraction curve obtained at the TTA concentration of 0.001M is shown in Fig. 2. As can be seen in the extraction curve, an increase in pH leads to an increase in the extractability of copper, and above 5.2 the absorbance becomes constant. Accordingly, a pH value of 5.5 was adopted.

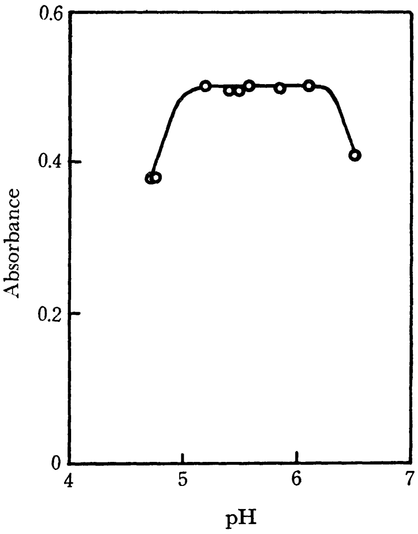

Fig. 2. Effect of pH on the absorbance of the organic phase.

Removal of Residual TTA. TTA has a strong absorption at around 340 mμ, and interferes with the absorption measurement of the extracted complex in the cyclohexane phase. In order to increase the spectrophotometric sensitivity, the residual TTA which does not combine with copper should be removed from the organic phase.

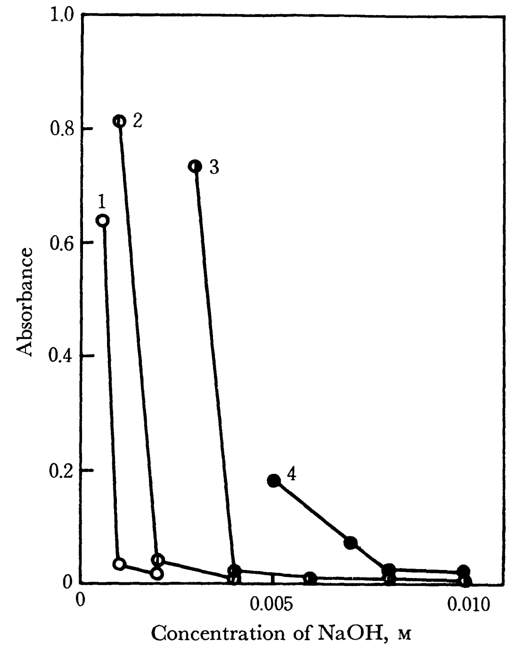

Fig. 3. Removal of the residual TTA.
TTA concentration – 1: 5×10^{-4}M, 2: 1×10^{-3}M, 3: 2×10^{-3}M, 4: 5×10^{-3}M.

By shaking TTA-cyclohexane solution with sodium hydroxide solution, the absorbance of the cyclohexane phase at 340 mμ decreases with increasing alkali concentration (Fig. 3). This decrease in the absorbance indicates the removal of the TTA from the cyclohexane solution, and shaking for 3 min with 0.005M sodium hydroxide solution is sufficient for the present purpose.

Effect of Pyridine. The copper-TTA chelate was decomposed by the alkali treatment of the cyclohexane phase in the absence of pyridine and copper was stripped into the alkali solution. However, the stripping of copper could be avoided by adding pyridine. As is shown in Fig. 4, the absorbance of the cyclohexane

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12) R. A. Bolomey and L. Wish, *J. Amer. Chem. Soc.*, **72**, 4483 (1950).

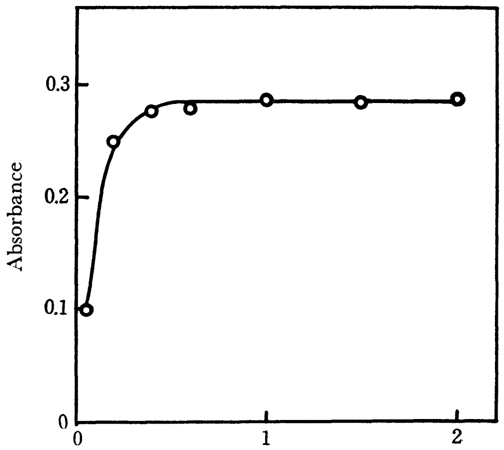

Fig. 4. Effect of pyridine concentration on the absorbance of the organic phase.

phase containing copper-TTA chelate increases along with an increase in the pyridine concentration in the alkali solution, and finally reaches a constant value in the pyridine concentration range above 0.5%. This indicates that the copper-TTA chelate in cyclohexane phase is stabilized by the presence of pyridine and the chelate was prevented from decomposition.

Pyridine Adduct. Visible spectra of benzene solutions of the copper-TTA chelate with various amounts of pyridine were measured and are shown in Fig. 5. The systematic variation in the spectra and the presence of two isosbestic points furnish the evidence for the formation of the pyridine adduct (1:1). The formation constant for the adduct was estimated to be $10^{3.45\pm0.25}$ by the method proposed by Ke and Li.[13]

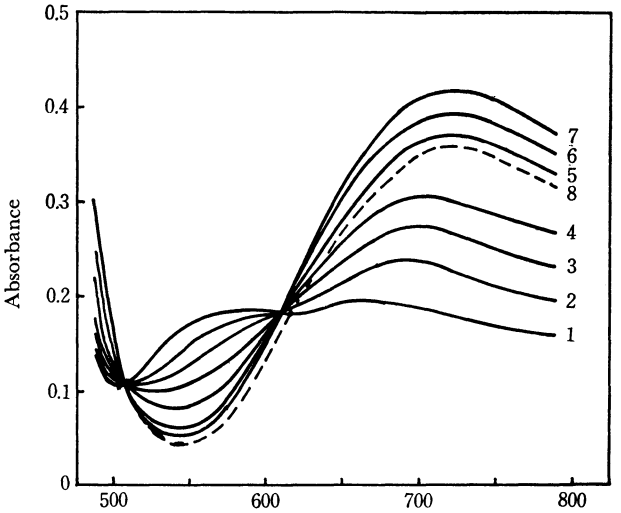

Fig. 5. Effect of pyridine concentration on the spectra of 5×10^{-3}M Cu (TTA)$_2$ in benzene.
Pyridine concentration - 1: 0, 2: 1×10^{-3}M, 3: 2×10^{-3}M, 4: 3×10^{-3}M, 5: 5×10^{-3}M, 6: 1×10^{-2}M, 7: 5×10^{-2}M, 8: 2.5×10^{-1}M.

At high pyridine concentration (0.25M), the isosbestic points disappear probably because of the formation of the adduct (1:2), Cu(TTA)$_2$ (pyridine)$_2$.

In order to obtain further confirmation of the formation of pyridine adduct, the copper-TTA chelate Cu(TTA)$_2$ was prepared by adding the TTA-ethanol solution to the aqueous solution of copper and recrystallizing the resulting chelate from ethanol. The green crystalline solid was obtained by heating the copper-TTA chelate together with pyridine. Elemental analysis of the solid was given in Table 1. As is seen in Table 1, the analytical results showed good agreement with the calculated value for Cu(TTA)$_2$-(pyridine)$_2$. These results indicate that the pyridine adduct is formed when the organic phase is treated with alkali solution containing pyridine and the formation of the adduct may prevent the copper-TTA chelate from decomposition.

TABLE 1. ELEMENTAL ANALYSIS OF THE ADDUCT

	Cu(%)	C(%)	H(%)
Calculated*	9.56	46.7	2.71
Found	9.59	46.8	2.77

* Values for Cu(TTA)$_2$(pyridine)$_2$

Synergistic effect in the extraction of copper with TTA has been explained by the formation of an adduct.[14,15] Although the effect enhances the extractability of copper, the synergistic extraction is not suitable for the present case because co-extraction of divalent metal ions occurs. Therefore, the formation of the pyridine adduct should be performed at the stage after the completion of the extraction of the copper-TTA chelate.

Calibration Curve. Calibration curve obtained by the above mentioned procedure is linear for 0—1 ppm of copper in the organic phase and passes through the origin. The reproducibility of absorption mesurements is better than 1%. The sensitivity represented by Sandell's definition is 0.0023 μg/cm^2 at 340 mμ, which is nearly equal to that of the most sensitive dithizone method.[11] The sensitivity of the previous TTA method (0.7 μg/cm^2 at 430 mμ)[10] is remarkably improved. The present method is highly sensitive compared with the neocuproine method (0.008 μg/cm^2 at 457 mμ),[11] the diethyldithiocarbamate method (0.0046 μg/cm^2 at 436 mμ)[11] and the thiothenoyltrifluoroacetone method (0.01 μg/cm^2 at 490 mμ).[16]

Diverse Ions. The effect of diverse ions on the determination of copper was investigated by adding the known amount of test ion to a standard copper solution and by comparing the final absorbance with the standard. One milligram each of Ag(I), Ca(II), Cr(III), Mg(II), Mn(II), Pb(II), Sr(II), Tl(I), Zn(II), and 10 μg of Co(II) and Ni(II) gave no interference in the present method. Two hundred micrograms

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each of Al(III), Ce(III), Fe(III), Th(IV) interfered with the determination because of the formation of precipitate. However, these elements could be masked and kept in solution by adding 100 mg of fluoride ion.

Among anions, 100 mg each of fluoride and phosphate ions gave no interference, but the same amount of thiosulfate, thiocyanide, cyanide, tartrate and citrate ions interfered with the determination and could not be used for masking purpose.

Determination of Copper in Natural Waters. For determination of copper in natural water samples, 50 m*l* of the sample solution was taken and the general procedure was modified by adding 100 mg of fluoride ion (as NaF) before adjusting the pH. The analytical results are shown in Table 2. Recovery test and reproducibility indicate that the present procedure is applicable to these samples.

TABLE 2. ANALYTICAL RESULTS OF NATURAL WATER SAMPLES

Sample no.[a]	Cu present[b] (μg/m*l*)	Cu added (μg/m*l*)	Cu found[c] (μg/m*l*)
1	0.102 ±0.009	0.100	0.201±0.004
2	0.0516±0.0039	0.100	0.154±0.015
3	0.0528±0.0022	0.100	0.154±0.002
4	0.0246±0.0041	0.100	0.135±0.045
5	0.0596±0.0035	0.250	0.335±0.017

a) Samples taken from the Watarase river.

b) Average value of 5 determinations and 95% confidence limit.

c) Average value of 3 determinations and 95% confidence limit.

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