EXTRACTION OF COPPER(II) FROM AQUEOUS THIOCYANATE SOLUTIONS INTO CHLOROFORM AND SUBSEQUENT SPECTROPHOTOMETRIC DETERMINATION

KEY WORDS: Extraction, spectrophotometric method, Copper(II), aqueous thiocyanate, 2-benzoylpyridine-2-pyridylhydrazone, 2,2'-dipyridil-2-pyridylhydrazone.

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ABSTRACT
Traces of copper(II) can be quantitatively extracted from aqueous thiocyanate solutions into 2-benzoylpyridine-2-pyridylhydrazone (BPPH) or 2,2'-dipyridil-2-pyridylhydrazone (DPPH) chloroform solution. Optimal conditions given for the extraction are based on a critical study of the relevant factors such as the effect of the pH, thiocyanate and reagent concentration. Very small amounts of copper can be recovered from large sample volumes and determined directly.

INTRODUCTION
The solvent extraction of metal chelates have been used extensively in preconcentration and separation procedures for many metals. The theory of extraction process was developed
The majority of chelating ligands used in extraction are weak acids, $H_L$, which react in the form of their conjugate bases, $L^-$, with metal ions, $M^{n+}$, to give uncharged extractable chelates, $ML_n$. In the last two decades some new organic reagents have become available which can be considered as slightly modified ferroin chromagens. These include certain substituted hydrazones ($-\text{N}=\text{C}-\text{NH}-\text{N}=\text{C}-\text{C}=\text{N}$) that were introduced by Lions et al. Many of these reagents are very sensitive for spectrophotometric determination of metals and some of them have been examined for extraction of cations and their subsequent spectrophotometric microdetermination. It was observed, that some ions such as cyanide, cyanate, thiocyanate etc., increase the extraction of copper(II) complex with pyridine-aldehyde-2-pyridylhydrazone (PAPHY), 2-benzoylpyridine-2-pyridylhydrazone (BPPH) and 2,2'-dipyridyl-2-pyridylhydrazone (DPPH) into organic solvents. An indirect determination of cyanide, cyanate, thiocyanate and selenocyanate by atomic absorption spectroscopy and spectrophotometry was developed. These considerations prompted a study for possible copper preconcentration from aqueous solutions and spectrophotometric microdetermination of copper. A comparison between BPPH and DPPH for extraction of copper(II) and subsequent spectrophotometric microdetermination of copper is reported.

EXPERIMENTAL

Reagents

The synthesis of 2-benzoylpyridine-2-pyridylhydrazone (BPPH) and 2,2'-dipyridyl-2-pyridylhydrazone (DPPH) has been
previously reported (12,13). Solutions of BPPH and DPPH were prepared by dissolving the required weight in chloroform and ethanol. These solutions are stable and can be kept for several weeks in amber-glass bottles.

Standard copper(II) solutions were prepared daily from a stock solution 1000ppm Cu(II) ("Titrisol" Merck). A standard solution of thiocyanate was prepared by dissolving the appropriate amount of potassium thiocyanate in distilled water. The solution obtained was standardized by titration with silver nitrate solution conductometrically.

All other solutions of cations and anions were prepared by dissolving analytical grade reagents in distilled water. Chloroform was also analytical grade reagent (Merck) and it was used without any further purification after being saturated with distilled water and conversely all distilled water used in extraction procedures was saturated with chloroform.

Apparatus

Spectrophotometric measurements were done on Zeiss model PMQ 3 and Unicam SP 700A spectrophotometers with a 10 mm quartz cells. The pH values were measured by a Radiometer model PHM64 Research pH meter calibrated by NBS pH standards at 25±0,5 °C.

Procedure

Into a 50 ml calibrated flask were pipeted in the following order: 0.5-10 ml of a copper standard solution (0.50 ppm, 1.00 ppm, 1.25 ppm, 10.00 ppm or 25.00 ppm according to the experiment), the appropriate amount of the thiocyanate solution, buffered to the required pH by phosphate buffer solution and ionic strength 0.1 by Na₂SO₄ and diluted to
the volume with distilled water. 10 ml of this solution was transferred into a 50 ml separatory funnel, an equal volume of BPPH or DPPH in chloroform (1.2X10^{-4} M or 7.5X10^{-5} M) was added and the two layers were shaken for 30 min. An aliquot of 2.5-3 ml of chloroform extract was transferred to a 10 mm cell and the absorbance at maximum wavelength was measured against the reagent blank.

RESULTS AND DISCUSSION

Absorption spectra

The visible absorption spectra of BPPH-Cu, BPPH-Cu-SCN, DPPH-Cu and BPPH-Cu-SCN in the aqueous and in the chloroform phase are shown in Fig. 1. It can be seen that the copper(II) complexes of BPPH and DPPH give absorption maxima at 480 and 483 nm respectively, whereas their chloroform extracts in the presence of thiocyanate give the corresponding absorption maxima at 535 and 525 nm. There is no effect on the spectra of BPPH-Cu and DPPH-Cu from thiocyanate in the aqueous phase, on the other hand thiocyanates increase the extraction of these complexes and the degree of extraction of BPPH-Cu and DPPH-Cu into the chloroform layer depends on the thiocyanate concentration.

Effects of experimental conditions

Measurements of absorbance were repeated at least twice and the average of the three absorbance values was taken in calculating R, degree of extraction. Since the volumes of the two phases were equal, \( R = \frac{A_1}{A_0} \), where \( A_0 \) = absorbance for 100% extraction, \( A_1 \) = the absorbance for the first extract. \( A_0 \) was taken as the sum of the absorbance measured after successive extraction of the same aqueous phase containing a known
Fig 1. Absorption spectra of: BPPH-Cu in aqueous phase (1), BPPH-Cu in extract (2), extract of BPPH-Cu-SCN (3), DPPH-Cu in aqueous phase (4), DPPH-Cu in extract (5), extract of DPPH-Cu-SCN (6). $[\text{Cu}^{II}] = 3.95 \times 10^{-5}$M. $[\text{BPPH}] = 1.2 \times 10^{-4}$M, $[\text{DPPH}] = 1.2 \times 10^{-4}$M, $[\text{SCN}^-] = 4 \times 10^{-4}$M, pH = 7.0 ± 0.2.

quantity of metal with several aliquots of ligand (BPPH or DPPH) in chloroform. In presence of thiocyanate ions, the absorbance of the second extract was generally very low and near to zero. No independent measurement of the concentration of metal left in the aqueous phase was made, hence very high and very low values of R may be in error.

The effect of pH on the extraction of copper as BPPH-Cu and DPPH-Cu from aqueous solutions into chloroform layer is shown in Figure 2.

The optimum pH range for the determination of copper(II) after extraction as BPPH-Cu is 3.8-9.0 and as DPPH-Cu is 5.6-10.5 in presence of thiocyanate (curve 2 and 4, Fig 2) and the extraction of copper(II) with BPPH or DPPH can be done
better and over a wider pH range when thiocyanate is in excess in the aqueous solutions. The pH of aqueous solutions was used to be 7.0±0.2. The effect of ligands concentration and the effect of thiocyanates concentration on the extraction of copper(II) were studied.

Figure 3 shows the effect of ligands concentration. The concentration of BPPH or DPPH must be 2.2 times greater than copper(II) concentration for quantitative extraction. The ligand concentration was used to be threefold molar excess over copper(II) concentration.

Figure 4 Shows the effect of thiocyanate concentration.

**Conformance with Beer's law**

The extraction of copper(II) from aqueous thiocyanate solutions is nearly complete, 97% extraction as BPPH-Cu-SCN,
Fig. 3. Effect of the ligands concentration on the extraction of copper(II). Curve 1: effect of BPPH concentration, curve 2: effect of DPPH concentration, $[Cu^{2+}] = 3.95 \times 10^{-5} \text{M}$, $[SCN^-] = 4 \times 10^{-4} \text{M}$, pH = 7.0±0.2.

Fig. 4. Effect of the thiocyanate concentration on the extraction of copper(II). Curve 1 in presence of BPPH, curve 2 in presence of DPPH. $[Cu^{2+}] = 3.95 \times 10^{-5} \text{M}$, $[BPPH] = 1.2 \times 10^{-4} \text{M}$, $[DPPH] = 1.2 \times 10^{-4} \text{M}$, pH=7.0±0.2.
95% extraction as DPPH-Cu-SCN under optimum conditions. To increase accuracy and sensitivity of copper(II) determination a single extraction was carried out. The lowest effective volume ratio of aqueous solution to organic solvents for a single extraction was determined. This ratio was found to be 10:1. Figure 5 shows the results for single extraction.

**Color stability and precision**

The color intensity of chloroform extracts remains constant at least for 3 hours. The reproductibility of the measurements expressed as relative standard deviation is 1.02% for BPPH-Cu-SCN system ($\lambda=535\text{nm}$) and 1.51% for DPPH-Cu-SCN system ($\lambda=525\text{nm}$). The detection limit for both extraction systems is 5 ppb ($V_w: V_o = 50:5$).

**Effects of diverse ions**

Diverse ions studies carried out on BPPH-Cu-SCN and DPPH-Cu-SCN for copper(II) determination showed that practical analytical procedures were feasible. 0.20 parts per million concentration of copper(II) can be measured without interference in the presence of 100 ppm of $\text{Al}^{3+}$, $\text{As}^{3+}$, $\text{As}^{5+}$, $\text{Na}^+$, $\text{K}^+$, $\text{NH}_4^+$, $\text{Ca}^{2+}$, $\text{Ba}^{2+}$, $\text{Cl}^-$, $\text{Br}^-$, $\text{I}^-$, $\text{CN}^-$, $\text{SCN}^-$, $\text{NO}_3^-$, $\text{PO}_4^{3-}$, $\text{SO}_4^{2-}$, $\text{Zn}^{2+}$, $\text{Co}^{2+}$, $\text{Ni}^{2+}$, $\text{Hg}^{2+}$, interfere completely at the level of 2 ppm. $\text{Mn}^{2+}$ interferes at the level of 5 ppm the determination of copper(II) through the BPPH-Cu-SCN extraction system, but it does not interfere when copper(II) is determined through the DPPH-Cu-SCN system.

**Comparison between BPPH and DPPH for copper extraction**

Both of the ligands have approximately the same analytical properties. The synthesis of BPPH is more difficult than that
Fig. 5. Calibration graphs for Cu(II) determination. Curve 1 for BPPH-Cu-SCN system, curve 2 for DPPH-Cu-SCN system.

\[ [\text{SCN}^-] = 2 \times 10^{-4} \text{M}, \quad [\text{BPPH}] = 1.2 \times 10^{-4} \text{M}, \quad [\text{DPPH}] = 1.2 \times 10^{-4} \text{M} \]

\[ V_w = 50 \text{ml, } V_o = 5 \text{ml.} \]

of DPPH. On the other hand BPPH-Cu-SCN degree of extraction is slightly higher than that of BPPH-Cu-SCN and the system BPPH-Cu-SCN gives better reproducibility, lower standard deviation, for determination of copper(II).

REFERENCES


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