

Determination of Copper by Isotopic Dilution

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ABSTRACT

A rapid and selective method was used for the determination of copper by isotopic dilution employing substoichiometric extraction with dithizone in carbon tetrachloride. The appropriate pH range for the substoichiometric extraction was 2-7. In the analysis, even a large excess of elements forming extractable complexes with dithizone does not interfere. The accuracy and precision of the method were evaluated. The method has been applied to analysis of reference materials, wheat flour, wine, and beer.

Index Entries: Copper; isotopic dilution; substoichiometry; copper dithizonate; application of tracers; environmental samples.

INTRODUCTION

Copper is one of the elements that has biological interest at trace and ultratrace levels. Analytical difficulties often seem to increase drastically when analyzing materials with very low contents of trace elements (1). Thus, the availability of sensitive and selective methods is of great importance for biological and environmental samples. Neutron activation analysis with inherent sensitivity is the obvious method of choice. However, the ^{64}Cu isotope can also be produced by the reaction $^{64}\text{Zn}(n, p)^{64}\text{Cu}$, which has a cross-section of 390 mb and ^{64}Zn has 48.9% natural abundance. Since most biological samples contain amounts of Zn

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comparable to those of copper, this reaction may cause some interference in the determination of copper. In this context, substoichiometric isotopic dilution analysis proposed by Suzuki (2) and Ruzicka and Stary (3) is a very attractive analytical method to determine copper in these kinds of samples.

The method offers an accurate and precise determination of trace and ultratrace amounts of elements by measurements of radioactivity alone, without corrections for chemical yield. The advantages of substoichiometric separation are that it is highly selective, quick, and reproducible. The principles of the method were treated in several papers (4-7). This article describes a simple procedure for the determination of copper in biological and environmental samples by isotope dilution analysis involving the substoichiometric extraction technique with dithizone into carbon tetrachloride.

MATERIALS AND METHODS

Counting Apparatus

A nuclear Chicago single-channel analyzer coupled to a 3.7×6.2 cm well-type NaI (Tl) crystal was used for the measurements of the activity.

Reagents

All the chemicals, reagents, and solvents used were of A.R. grade. The acids and ammonium hydroxide were purified by distillation.

Radio-Copper Solution

^{64}Cu was produced by the neutron irradiation of metallic copper for 30 min or 8 h at a neutron flux of 10^{12} n/cm²/s. The irradiated target was dissolved in nitric acid, and excess acid was eliminated by evaporation. The radioactive solution was transferred and diluted to give a concentration of 1 mg/mL.

Dithizone Solution

The solution was prepared dissolving dithizone in CCl_4 to give a concentration of 10^{-3} mol/L. The solution was transferred into an amber flask and kept in the refrigerator, since it decomposes rapidly with formation of carbodiazone if exposed to strong light and subjected to relatively high temperatures.

Buffer Solution

Buffer solution was prepared by the dissolution of 15 g of potassium iodide, 13 g of ammonium acetate in 100 mL of water, and the addition

of glacial acetic acid to attain a pH value of 4.8 (8). It was purified by shaking with a concentrated solution of dithizone in CCl_4 .

Interfering Elements Solutions

Appropriate amounts of the elements; salts, oxides, or metals were dissolved in acid or deionized distilled water. The excess acid was eliminated by evaporation. The solutions were transferred to give a concentration of 1 mg/mL. The procedure was applied to prepare As(III), Au(III), Bi(III), Cd(II), Co(II), Hg(II), In(III), Mn(II), Ni(II), Pb(II), Pd(II), Pt(II), Sb(III), Se(II), Sn(IV), and Zn(II).

Sodium Thiosulfate Solution 2%

An amount of sodium thiosulfate was dissolved in distilled water.

COPPER EXTRACTION

The high selectivity and simplicity of the method that give optimum conditions for the determination of copper were studied. The influence of hydrochloric, sulfuric, and nitric acids was examined because of the possibility of using these acids in the digestion process of samples.

EQUILIBRIUM TIME

A series of solutions, pH 5, with the same amounts of ^{64}Cu were shaken with dithizone in CCl_4 for different times. The γ activity of the extracted copper was measured and plotted against shaking time. The equilibrium was reached after 2 min of shaking.

EFFECT OF ACIDS

The influence was verified by the addition of an aqueous solution to the tracer dissolved in HCl, HNO_3 , or H_2SO_4 separately. The excess of acid was eliminated by evaporation, and the pH was adjusted to 4.8 with buffer solution. The solution was shaken for 2 min with the dithizone solution. The phases were separated, and the activity of the organic aliquot was measured. The results showed that copper is quantitatively extracted independently on the acid used.

SUBSTOICHIOMETRIC EXTRACTION

A known amount of ^{64}Cu and a substoichiometric amount of dithizone in CCl_4 solution were added to an aqueous solution. A series of preliminary experiments were carried out to ascertain the best conditions of

Table 1
Effect of pH on the Substoichiometric Extraction of Copper^a

pH	Percentage of extraction (%)
0.5	67.8
1.0	84.5
1.5	87.1
2.0	89.4
3.0	89.0
4.0	90.9
5.0	93.3
6.0	95.4
7.0	95.3
8.0	64.9

^aDithizone concentration 10^{-3} mol/L, 6.3×10^{-3} mol/L ^{64}Cu . Shaking time: 3 min.

pH range and influence of masking agent for finding the reproducibility of the substoichiometric extraction.

pH RANGE

A series of solutions with known amounts of radio-copper with a constant, but substoichiometric amount of dithizone in CCl_4 were prepared and investigated at different pHs. The dependence of the substoichiometric extraction of Cu with dithizone on the pH can be seen in Table 1. Copper could be extracted substoichiometrically from pH 2 to 7, which is in agreement with the predicted value (9).

REPRODUCIBILITY OF SUBSTOICHIOMETRIC EXTRACTION

The reproducibility of the substoichiometric extraction of copper with dithizone into CCl_4 was examined in solutions containing different

Table 2
 Substoichiometric Extraction of Cu(II) with Dithizone into CCl₄^a

⁶⁴ Cu(II) (ug)	Activity of 1mL aliquot of organic phase (cpm)
8.09	4003
12.13	5967
16.18	7720
24.27	8391
32.36	8550
36.40	8835
40.45	8841
50.56	9016

Dithizone concentration 10⁻⁴ mol/L, shaking time: 3 min.

amounts of radioactive Cu(II). A graph was plotted of the activity of an aliquot of the organic phase vs the amount of Cu(II) taken. As shown in Table 2, the activity of the organic phase increased with the growing amount of Cu(II); after the point, which corresponds to a copper-dithizone ratio of 1:2, the amount of copper in the organic phase remained constant. The aqueous solution containing excess labeled copper was treated repeatedly with dithizone in CCl₄. In each case, the activity of the organic phase was noted to be the same as that of the other extracts. This shows that the same amount of copper was extracted in each extraction.

INTERFERENCES OF OTHER ELEMENTS IN THE SUBSTOICHIOMETRIC EXTRACTION OF Cu(II)

The study of the selectivity of substoichiometric separation of Cu(II) was carried out by means of a series of solutions containing known amounts of nonactive copper and active copper and substoichiometrically extracted with dithizone in CCl₄, in the presence of As(III), Au(III), Bi(III), Co(II), Cd(II), Hg(II), In(III), Mn(II), Ni(II), Pb(II), Pd(II), Pt(II),

Table 3
Interference with Extraction of Copper Caused by Addition
of Nonactive Elements

Copper taken (μg)	Active copper (μg)	Other cations present (μg)	Copper found (μg) [*]
1.0	1.0	—	1.17 \pm 0.02
		25.0 μg Hg	1.01 \pm 0.02
1.0	1.0	—	1.25 \pm 0.03
		1.01 μg Au	1.44 \pm 0.04
		0.95 μg Pd	3.12 \pm 0.08
		1.04 μg Pt	1.33 \pm 0.03
1.0	1.0	—	1.22 \pm 0.03
		93.2 μg Bi	1.10 \pm 0.03
		98.5 μg In	1.40 \pm 0.03
		100.8 μg Mn	1.31 \pm 0.03
		98.7 μg Se	1.38 \pm 0.03
1.0	1.0	—	1.01 \pm 0.03
		100.0 μg As	1.12 \pm 0.04
		100.0 μg Cd	1.05 \pm 0.03
		100.0 μg Co	1.01 \pm 0.03
		100.0 μg Ni	1.05 \pm 0.03
		100.0 μg Pb	1.00 \pm 0.03
		100.0 μg Sb	1.10 \pm 0.03
		100.0 μg Sn	1.08 \pm 0.03
		100.0 μg Zn	1.09 \pm 0.03

*Arithmetic mean, $n = 4$.

Sb(III), Se(II), Sn(IV), and Zn(II). As shown in Table 3 even a large excess of metals that form extractable complexes with dithizone when iodide is present in the aqueous phase will not inhibit the extraction. It can be seen that only Au, Pd, and Pt interfere.

Table 4
Results of Copper Determination

Material	Certified value ($\mu\text{g/g}$)	Experimental value ($\mu\text{g/g}$) [*]	RSD	Deviation from the certified value %
SRM 1567a	2.1 \pm 0.2	1.79 \pm 0.16	0.057	-14.6
SRM 1568	2.2 \pm 0.3	2.04 \pm 0.22	0.043	-7.4
SRM MA-A-2 621	4.0 \pm 0.1	4.83 \pm 0.6	0.078	20.8
SRM 1572	16.5 \pm 1.0	17.0 \pm 0.6	0.022	3.0
Wheat flour		1.00 \pm 0.09	0.053	
Wine ($\mu\text{g/mL}$)		0.17 \pm 0.01	0.051	
Beer ($\mu\text{g/mL}$)		0.28 \pm 0.02	0.063	

*Arithmetic mean ($n = 4$) and its confidence limits ($\bar{x} \pm 0.05 \text{sn}^{-1/2}$).

APPLICATIONS

The method described has been applied to the determination of copper in reference materials (RMs): citrus leaves: NBS-SRM-1472; wheat flour: NBS-SRM-1567a; rice flour: NBS-SRM-1568; fish homogenate: MA-A-2 621, wine, beer, and wheat flour.

Sample Preparation

RMs

An amount of 200 mg of sample was added to 2–3 mL of HNO_3 and a known amount of ^{64}Cu in a microwave acid digestion bomb. The sample was digested in a microwave furnace at medium power for 2 min and cooled for 1 h. The sample solution was evaporated to eliminate the excess acid.

Wine and Beer

The procedure used was described by Kumar et al. (10). An aliquot of 50 mL of wine or beer was evaporated to dryness, and the residue was dissolved in 100 mL of HNO₃.

Substoichiometric Determination of Copper

The appropriate amount of dilute HNO₃ or NH₄OH was added to the sample and standard solutions to adjust the pH to 4.0–5.0. After adjusting the acidity, 2 mL of buffer solution and 0.5 mL of sodium thio-sulfate solution 2% were added. The solutions were simultaneously extracted with equal substoichiometric portions of dithizone in CCl₄. The activity of the organic layer was measured. Table 4 shows the results obtained.

DISCUSSION

As shown above, Cu(II) could be extracted with a substoichiometric amount of dithizone in CCl₄ solution between pH 2 and 7. Above and below this pH range, the extraction is not quantitative. To examine the influences of other elements, the substoichiometric extraction with 1×10^{-5} mol/L dithizone was applied to the synthetic samples solutions containing a small amount of copper and large amounts of other elements. As presented in Table 3, the substoichiometric determination of copper is possible together with other elements that have higher extraction constants than copper. The logarithm of the extraction constant of mercury with dithizone is 26, 85. However, the results showed that mercury does not interfere with the extraction of copper. This occurs because a buffer solution containing iodide was added to the aqueous solution to form an HgI₄²⁻ complex, which keeps mercury in the aqueous phase. The thiosulfate present prevents oxidation of the dithizone by free iodine.

This method is found to be reasonably selective for Cu(II). The elements Au, Pt, and Pd are extracted, but they may be left out of consideration because of their rarity in these kinds of samples.

The precision and accuracy of the method were tested with reference materials. From Table 4, the good precision of the method is shown. Even for materials with the lowest copper contents, relative standard deviation does not exceed 8%. The precision of substoichiometric analysis has mainly two components: one associated with substoichiometric separation and the other associated with radioactivity measurements. Since the latter component can be improved by use of a radioisotope with a high specific activity, the precision depends primarily on the former component.

The detection limit was found to be < 13 ng, which was obtained with radio-copper produced by irradiation of Cu(II) in a thermal neutron flux of 10^{12} n/cm²/s for 8 h applying the substoichiometric radiochemical separation procedure.

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