

EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN SOIL AND IN PLANT MATERIAL USING *ISO*-PROPYL ETHER

Naoharu MIZUNO† Kenjiro HAYASHI†† & Toshio HASEBE†

イソプロピルエーテルによる土壌および植物中の 銅の溶媒抽出—吸光光度定量

水野直治・林謙次郎・長谷部俊雄

A modified method for the determination of the copper content in soil and in plant material was studied.

The improved method, in which *iso*-propyl ether is used as an extracting reagent, is especially suitable for the separation of microgram amounts of copper in the presence of substantial amounts of other ions.

It was found that large amounts of both calcium and phosphate can be tolerated.

It was also found that the color of copper-diethyldithiocarbamate complex in *iso*-propyl ether is more stable than that in chloroform or in carbon tetrachloride under diffused daylight.

Only one extraction was necessary to remove all copper from the aqueous layer and the second extract was colorless.

I INTRODUCTION

Copper is frequently determined colorimetrically by carbon tetrachloride or chloroform extraction of copper-diethyldithiocarbamate¹⁾. However, there are some defects, such as : 1) The extraction with carbon tetrachloride or chloroform must be repeated several times²⁾. 2) In general, the extract is cloudy. 3) Large amounts of both calcium and phosphate form a

turbid solution and the results for copper tend to be low¹⁾.

When many samples of soil or plant material need to be analyzed for their total copper content, the carbon tetrachloride or the chloroform extraction methods are unsuitable.

The objective of this paper is to present the results of a method that will eliminate these defects and to propose a simple and rapid method for determining copper in soil and in plant material.

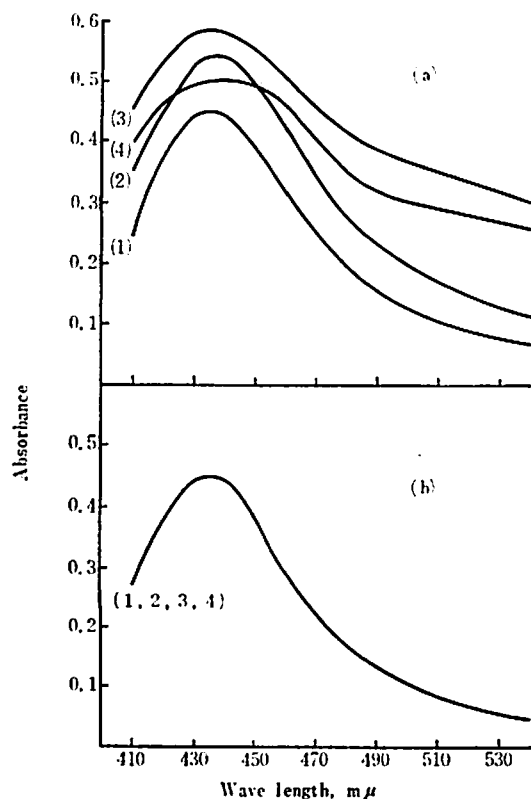
II PROCEDURE AND RESULTS OF THE EXPERIMENT

† Hokkaido Central Agricultural Experiment Station.

†† Chemical Department, Faculty of Science, Yamaguchi University, Yamaguchi.

Procedure-followed : In a suitable separatory funnel, 20 to 50 ml of the solution to be analyzed, containing not more than 50 μg of copper was placed. To this solution, 10 ml of ethylenediamine tetraacetic acid (EDTA) and citrate mixture (made by dissolving 20 grams of ammonium citrate and 5 grams of the disodium salt of EDTA in 100 ml of conductivity water) and 2 to 3 drops of cresol red were added, followed by concentrated ammonia until the indicator showed its alkaline color¹⁾. This was diluted to about 70 ml with water. After mixing 1 ml of 1 per cent sodium diethyldithiocarbamate solution was added. This was shaken vigorously for 2 minutes

Fig. 1 The effects of organic solvents on the absorption spectra conducted near the window on a cloudy day, at 20°C with Cu : 20 $\mu\text{g}/10$ ml on (a) Carbon tetrachloride and (b) *Iso*-propyl ether.



Reading were as follows:

(1) Immediate reading. (2) Reading after 30 min ~ 1 hr. (3) Reading after 3 hr. and (4) Reading after 5 hr.

with 10 ml of *iso*-propyl ether. The phases were allowed to separate and the absorbance of the *iso*-propyl ether extract at 432 $m\mu$ was compared with the control. Copper was separated quantitatively by a single extraction.

Stability of the color of extracts : The color of the copper-diethyldithiocarbamate complex in *iso*-propyl ether is more stable than that in carbon tetrachloride or in chloroform. In this investigation no color change occurred during 8 hours of exposure to diffused daylight (Fig.1).

Wave length selection for the measurement of transmittancy : The absorption curve for the copper carbamate complex in *iso*-propyl ether has a maximum at 432 $m\mu$ ¹²⁾. No deviations from Beer's law were found up to 60 μg of copper in 10 ml of *iso*-propyl ether.

Interference effects : The procedure used in this work was to compare the absorbancies of the extracts from the solutions containing the extraneous ion with that given by a solution of the same copper ion concentration containing no added ion. Table 1 summarizes the effects of the suspected interfering ions.

Table 1 Effect of diverse ions

Ion	Added as	Added (mg)	Absorbance*
—	—	—	0.452
Zn	ZnSO ₄	0.10	0.453
Ni	NiCl ₂	2.0	0.452
Co	CoSO ₄	1.0	0.451
Mn	MnSO ₄	1.0	0.453
Fe	FeCl ₃	20.0	0.451
Ca	CaCl ₂	40.0	0.452
Na	NaCl	1.0 × 10 ³	0.453
PO ₄	(NH ₄) ₂ HPO ₄	360.0	0.452

Copper : 20 $\mu\text{g}/10$ ml of *iso*-propyl ether.

* Each result is the mean of duplicates.

Determination of copper in synthetic sample solutions by the improved method : In order to check the accuracy of the improved proce-

dure, known amounts of copper in synthetic solution were determined, and the amounts recovered were found satisfactory (Table 2). The amounts of diverse ions present in the synthetic solutions were much more than those normally present in soils, rocks, and plants.

Table 2 Recovery of copper in the synthetic solution

Ion		Copper, micrograms	
Present*	(mg)	Added	Recovered**
Zn	0.1	10.0	9.9 ± 0.14
Ni	2.0		
Co	1.0	20.0	19.9 ± 0.16
Mn	1.0		
Fe	20.0	30.0	29.9 ± 0.29
Ca	40.0		
Na	1.0 × 10 ³		
PO ₄	360.0		

* These ions and the indicated amounts were present in 20 ml of solution.

** 99% Confidence.

This procedure may be used to determine copper in any soil, rock, or plant material containing large amounts of both calcium and phosphate.

Determination of copper in soil and rock samples : Two grams of finely ground soil or rock (1 mm mesh) were dissolved with 10 grams of sodium carbonate³. The silica was separated with hydrochloric acid and then the filtrate was diluted to 100 ml with water. A suitable aliquot of the filtrate was put into a separatory funnel and then the copper content was determined using the improved method. The results are shown in Table 3.

Table 3 Recovery of copper from soil or rock samples

Samples	Original copper in soil or rock (%)	Recovered*		
		μg	%	
Serpentine soil No.	1	6.9 × 10 ⁻³	19.5	97.0
	2	2.5 × 10 ⁻³	19.0	95.0
Serpentine rock No.	1	4.0 × 10 ⁻³	20.5	102.5
	2	8.0 × 10 ⁻³	19.5	97.5

* Recovery of 20 μg of copper added to soil or rock samples.

Determination of copper in plant samples :

From 0.5 to 1.0 grams of oven-dried (24 hours at 60°C), finely ground plant material was weighed and placed in a 300 ml tall beaker. 10 ml of fuming nitric acid was added and the beaker was covered with a watch-glass and allow to stand overnight. Then 5 ml of concentrated sulphuric acid was added and dissolved using a low heat. If at this stage the solution was still colored, 3 to 4 ml of a mixed acid solution (fuming nitric acid : 70 per cent perchloric acid = 1 : 1) was added and again heated until fumes of sulphuric acid were given off. After cooling, 30 ml of water was added and again cooled. The solution was filtered the filtrate was diluted to 100 ml with water. An aliquot of this solution was used for the determination of copper. The results are shown in Table 4.

Table 4 Recovery of copper from plant materials

Plant material	Original copper found %	Copper recovered*	
		μg	%
Orchard grass	1.0 × 10 ⁻³	20.0	100
Alfalfa	2.4 × 10 ⁻³	20.0	100
Sugar beet	2.6 × 10 ⁻³	19.7	98.5
Soybean (top)	2.4 × 10 ⁻³	20.5	102.5
Radish	4.0 × 10 ⁻³	20.3	101.5
Red clover	1.68 × 10 ⁻²	19.5	97.5
Ladino clover	1.82 × 10 ⁻²	20.5	102.5
Potato (top)	1.94 × 10 ⁻²	20.0	100

* Recovery of 20 μg of copper added to plant samples.

The recovery of copper was tested by the addition of 20 μg of copper to aliquots of the sample solution. The results gave a recovery range of 19 to 20.5 μg. It was shown that the error is low (Table 3 and 4).

III CONCLUSIONS

This method is a simple and rapid one for determining the copper content and is especially

suitable for the determination of microgram amounts of copper in the presence of large amounts of both calcium and phosphate.

It was found that only one extraction was necessary to remove all copper from the aqueous layer.

Separation of the organic layer from the aqueous one after mixing is easier in *iso*-propyl ether than in chloroform or in carbon tetrachloride.

REFERENCES

- 1) CHENG, K. L., and R. H. BRAY, 1953; Two specific methods of determining copper in soil and in plant material, *Anal. Chem.*, 25, 655-659.
- 2) CHILTON, J. M., 1953; Simultaneous colorimetric determination of copper, cobalt, and nickel as diethyldithiocarbamates, *ibid.*, 25, 1274-1275.
- 3) PURVIS, E. R., and N. K. PETERSON, 1956; Methods of soil and plant analyses for molybdenum, *Soil Science*, 81, 223-228.
- 4) SANDELL, E. B., 1959; *Colorimetric Determination of Traces of Metals*, Third Edition, Interscience Publishers, Inc., New York, p. 444.

摘 要

土壌および植物中の銅の定量法を検討した。銅は一般に銅—ジエチルジチオカルバミン酸錯体にして、四塩化炭素またはクロロホルムに抽出し、吸光光度法によって定量されている¹⁾。しかしながら、これにはつぎに示すような欠点が認められる。

- 1) 四塩化炭素またはクロロホルムでは抽出操作を反復する必要がある²⁾。
- 2) 抽出液が曇ることがある。特に土壌または植物などの試料に応用した場合にこの現象は著しい。
- 3) カルシウムと磷酸が多量に存在する場合は溶液に濁りを与え、また銅の定量値を低くしがちである³⁾。

以上のことから、土壌中または植物中の銅をジエチルカルバミン酸法でする際に四塩化炭素やクロロホルムを抽出溶媒に用いるのは不適當である。

ここに提出した改良法はイソプロピルエーテルを抽出溶媒に使用するものである。その特徴は、ほかのイオンが多量に存在してもミクログラム単位の銅の分離に適すること、また抽出された銅錯体は、クロロホルムまたは四塩化炭素中におけるよりも安定で、長時間吸光度に変化がないことである。

抽出操作は一度でよく、二度目の抽出液に銅錯体の存在が認められない。