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Spectrophotometric Determination of Copper(II) in Samples of Soil from Selected Allotment Gardens in Lodz

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Abstract

The content of copper in the soil of two allotment gardens in Lodz and a forest area near Lodz were determined. Copper was determined by an adapted extraction - spectrophotometric method in the form of a complex with sodium(I) diethyldithiocarbamate. The influence of the extraction solvent, a masking agent and interfering elements (Fe(III) and Cr(IH)) on determination of copper by this method was examined. Possibilities of elimination of the extraction stage by using a protective colloid for spectrophotometric determination of copper in soil were investigated.

Keywords: copper(II), diethylodithiocarbamate, soil

Introduction

Soil plays an important role in biogeochemical balance of the biosphere. Degradation of soil leads to a reduction or complete loss of its ecological and productive values. It is caused primarily by chemical pollution, especially with excessive, unnatural amounts of trace elements such as cadmium, lead, zinc and copper, which may disturb the function of the complex system of processes occurring in the soil, and cause negative changes in biological activity and physical properties of the soil [1-5]. Chemical degradation of soil is particularly fast when trace elements, which are introduced into it, form easily soluble compounds. Then, their concentration in the water phase of the soil increases and, consequently, their bioaccumulation and migration become easier. Many pesticides, which are perfect ligands for metals present in the soil, form complex compounds with them. Many of these are readily soluble in water, get into the ground water and then, through rivers, into the reservoirs of drinking water.

Copper belongs to elements whose natural content in the soil is most considerably exceeded. Soils which are considered unpolluted may contain (in three classes of granulation and reaction) 5, 25 or 40 mg copper(TJ) per kg of dry substance. In Poland no standards of soil pollution have been established, so the so-called normal concentration of the determined substance in unpolluted soils is frequently used for reference in determination of soil pollution. For copper, normal concentration is 8.8 mg per kg of soil. In polluted soils the value is 50 mg per kg and in contaminated soils it is over 200 mg per kg of soil. According to the guidelines of the Institute of Agriculture, Fertilisation and Pedology in Pulawy, the natural content of copper in the soil is from 15 to 40 mg per kg of dry substance, depending on the type of soil [6]. The Monitor Polski, on the other hand, allows the limit of 50 (for light soil) to 100 mg copper per kg of dry substance (for heavy soil) [7]. Copper is introduced to the environment from natural sources (about $4.0 \cdot 10^8$ kg per year) and as a result of human activity (about $4.5 \cdot 10^9$ kg per year). It is accumulated in the soil (especially in its surface layers) with all its negative consequences [8,9]. Copper is indispensable for normal development of living organisms, but both its excess and deficiency are harmful. Copper deficiency in the diet may cause anaemia, insufficient growth, fertility problems, nervous system disorders and circulatory system diseases. Its excess may lead to changes in the liver and damage kidneys, brain tissue, coronary vessels and myocardium.

Air in large cities, polluted with car exhaust and dust, directly affects soil and cultivated plants [10-13]. Excessive amounts of lead, zinc, cadmium and copper in the surface layers of soil in the allotment gardens in Warsaw and increased content of these elements in plants (especially those grown near arterial roads) have been observed.

The purpose of the present work was to estimate the amount of copper present in the surface layer of soil in two allotment gardens localized in Lodz and a forest area near Lodz.

Experimental

Reagents and Apparatus

- Concentrated perchloric acid (Riedel-de-Haen AG).
- Sodium(I) diethyldithiocarbamate ($C_5H_{10}NS_2Na$-$3H_2O$ - cupral, NaDDTK), - 0.5% solution (m/m) alkalized by means of ammonia (1:1) to reach pH about 8.0. Stored in a dark glass bottle, the solution remains stable for about 1 month. Coloured solution cannot be used.
- Disodium(I) ethylenediaminetetraacetate ($C_{10}H_{14}O_8\ N_2Na_2 \cdot 2H_2O$) - 10% solution (m/m)
- Ammonium citrate - 10% solution (m/m).
- Chloroform.
- 25% ammonia (P.Ch. Odczynniki - Lublin)
- Stock standard solution of copper, concentration lmg/cm^3 was prepared in the following way: 3.9280 g $CuSO_4 \cdot 5H_2O$ was diluted with water in a 1 dm^3 flask, 2 cm^3 of concentrated H_2SO_4 were added, water was added to the mark and the solution was stirred.
- Working standard solution of copper, concentration 0.010 mg/cm^3 was prepared in the following way: 5 cm^3 of stock standard solution were diluted with water in a 500 cm^3 flask and made up to the mark. The solution was pre pared on the day when calibration lines were plotted.
- 5% solution of arabic gum.
- Spekol 11 spectrophotometer with cells 5 cm optical pathlength

NB: All reagents (apart from ammonia and perchloric acid) were produced by POCh-Gliwice.

Soil Sample Taking and Mineralization

The original samples of soil were collected according to the standard [14], using a soil stick at two depths: 5 cm and 20 cm. Laboratory samples were prepared according to the standard [15]. Prior to mineralization, in order to bring the soil to the "state of air dryness", it was stored for two weeks in a dry and airy place.

Mineralization was carried out using perchloric acid at boiling point. Soil samples of 2 g each (weighed with an accuracy of 0.001 g) were placed in a Kjeldahl flask and 20 cm^3 of concentrated perchloric acid were added. Then they were heated in a sand bath under reflux condenser for 8-9 hours. After mineralization, the solution was filtered into 50 cm^3 measuring flasks and redistilled water was added to the mark. Copper concentration was determined in prepared samples.

Principle of the Method [16]

Sodium(I) diethyldithiocarbamate (Na-DDTK, cupral) and copper ions form a yellow-brown neutral chelate $Cu(DDTK)_2$ at pH range 4-11. The complex is sparingly soluble in water, but dissolves more readily in organic solvents such as chloroform, carbon tetrachloride or amyl acetate.

Table 1. Selection of optimal amounts of agents masking the metals interfering with the determination of Cu(II) by the method using sodium(I) dithyldithiocarbamate.

Content [mole/50 cm^3]		Content of Cu(II) in different soil samples [mg/kg dry mass]				
EDTA	ammonium citrate	1	2	3	4	5
$5.3 \cdot 10^{-4}$	$2.2 \cdot 10^{-3}$	28.41	57.27	54.51	143.23	81.42
$8.0 \cdot 10^{-4}$	$2.6 \cdot 10^{-3}$	26.05	44.71	45.24	128.24	59.19
$1.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	24.72	35.21	34.02	108.24	40.72
$1.3 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$	25.01	35.52	34.14	108.82	41.21
$1.6 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$	24.87	35.07	34.82	108.57	41.12

Spectrophotometric determination of microgram amounts of copper(II) consists in extraction of the formed copper(II) diethyldithiocarbamate by means of CCI4 or CHClj and measurement of the absorbance of the solution at wavelength 436 nm. Metal ions which form coloured complexes with cupral (e.g. Fe(III), Bi(III), Mn(II), Ni(Il), Co(II)) interfere with the determination. The interfering ions are masked by means of EDTA solution with the addition of tartrate or citrate at pH 8-9.

Determination

In order to make the calibration line, 1-7 cm^3 of copper(II) working standard solution (equivalent to 0.01-0.07 mg copper) were measured into separatory funnel, 7 cm^3 of 10% ammonium citrate and 4 cm^3 of 10% EDTA solutions were added, pH was brought to about 8.5 using 25% ammonia solution, and 5 cm^3 of 0.1% NaDDTK solution were added. The copper(II) diethyldithiocarbamate complex formed in this way was extracted three times with 10 cm^3 chloroform portions (shaking time for each portion of CHCI3 was about 1 minute). The extracts were joined and chloroform was added to the mark in a 50 cm^3 measuring flask. Absorbance of $Cu(DDTK)_2$ solution was measured against blank test at 436 nm and the calibration line was plotted.

In order to determine the content of copper in the soil, 10 cm^3 of the solution obtained after mineralization of samples were transferred to separatory funnel, all reagents (apart from the standard solution of copper) were added consecutively in a way similar to that used for the plotting of the calibration line. The solution was extracted with chloroform and absorbance of the complex was measured at the organic phase against a reagent blank. The concentration of copper C_x [in mg/50 cm^3] was read from the calibration line. The content of copper(II) x in the soil was calculated according to the following formula:

$$x = C_x \frac{V_1 \cdot 1000}{V_2 \cdot m} \text{ [mg Cu per kg of dry mass]}$$

where:

C_x - concentration of copper read from the calibration line [mg/50 cm^3];

V_1 - total volume of solution after mineralization [cm^3];

V_2 - volume of the solution after mineralization taken for analysis [cm^3];

m - weighed sample of soil [g].

Discussion

The extraction spectrophotometric method with sodium® diethyldithiocarbamate as the complexing agent (described in literature [16-18]) was used to determine total content of copper(II) in soil. Preliminary investigation was carried out to establish measurement conditions (selection of extraction solvent, masking agents). According to literature data solubility of copper(II) diethyldithiocarbamate complex is much better in carbon tetrachloride than in chloroform recommended due to its lower toxicity. In order to investigate the effect of organic solvents (CCl_4 $CHCl_3$) on the accuracy of the results of copper(II) determination, a series of tests was carried out, in which either chloroform or carbon tetrachloride were used as solvents. The results indicate that the type of extraction solvent does not have a significant influence on the accuracy of determination (relative error of determination did not exceed 3.5%). For further analysis the less toxic chloroform was used.

Ions (Fe(III), Cr(III), Mn(II), Co(II), Ni(II)) form coloured complexes with cupral, therefore interfere with determination of copper(II) with this agent. A masking agent recommended in literature is EDTA in the medium of ammonium citrate. The amount of the complexing agent depends on the content of interfering metals in the soil. To establish the amount of masking agents, different amounts of EDTA and ammonium citrate were added to the analyzed solutions of mineralized soil samples, and then $Cu(DDTK)_2$ complex was extracted. The results are presented in Table 1. They show that in order to mask the interfering ions completely, the amount of EDTA and ammonium citrate added should be $1.0\text{-}10^{-3}$ mole and $3.0\text{-}10^{-3}$ mole, respectively, per 50 cm^3 of final volume of copper(II) complex. Another series of measurements was carried out to confirm the proper selection of amounts of masking agents. The amount of Fe(III) added to the analyzed solutions of mineralized soil was 30 and 60 times higher, and the amount of Cr(III) was 30 times higher than the determined amount of Cu(II). Then the masking agents were introduced in amounts established beforehand. It was found that the addition of the high excess of the above-mentioned ions does not significantly affect the determination of copper(II) in soil samples (relative error of determination < 2%). This suggests that the proposed amounts of EDTA and ammonium citrate bind all interfering ions into complexes.

Since the extraction method is relatively time-consuming and expensive (due to large amounts of organic reagents used), we tried to determine copper(II) in the form of copper(II) diethyldithiocarbamate pseudosolution stabilized by the addition of arabic gum and without extraction [19]. The content of copper found with the use of protective colloid was about 2-3 times higher than that determined by the extraction method. The investigation of standard solutions demonstrated that the addition of 10-30-fold excess of Fe(III) or Cr(III) over Cu(II) significantly elevates the results of copper(II) determination by the cupral method using the protective colloid (Table 2). The results show that this method is not suitable for analysis of soil.

Eventually, the extraction spectrophotometric variety of the diethyldithiocarbamate method was used to determine copper(II) in the soil of two allotment gardens in Lodz and a forest area near Lodz. Table 3 presents the results of the analysis of the soil samples collected at a depth of 5.0 cm. Their comparison demonstrates that the content of copper(II) in the soil depends on localization of the area from which the soil samples were collected. The soil of the forest area in Lublinek, localized at a considerable distance from the city and uncultivated, contains amounts of copper(II) characteristic of soils which are not polluted with this metal. In the area of allotment gardens the concentration of the metal is higher. Copper(II) concentration in the "Nowe Rokicie" is on average 1.5 times higher than in "Uniontex", which results from their localization. The "Nowe Rokicie" gardens lie directly beside roads with heavy **traffic, while** "Uniontex" gardens are further from arterial roads and consequently, their exposure to heavy metals such as Pb, Cd, Cr, or Cu is lower. Table 4 shows results of Cu(II) determination in the soil samples from the "Nowe Rokicie" gardens collected from depths of 5.0 and 20.0 cm. The copper which is present in the soil at 20.0 cm constitutes 80-90% of the ions of the metal present in the higher layers of the soil.

According to the guidelines of the Pulawy Institute of Agriculture, Fertilization and Pedology, the results

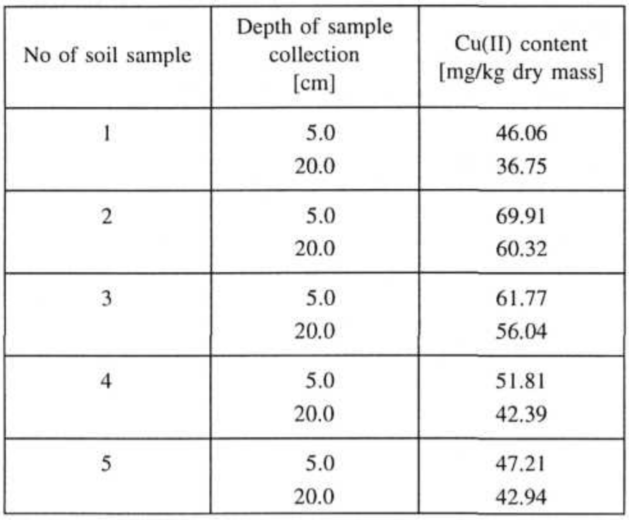
Table 2. Influence of Fe(III) and Cr(III) ions on determination of Cu(II) content in the standard solution in the form of copper(II) diethyldithiocarbamate pseudosolution stabilized with arabic gum solution.

No of soil sample	Introduced [mg/50 cm^3]			Determined [mg/50 cm^3]	Relative error [%]
	Cr(III)	Fe(III)	Cu(II)	Cu(II)	
1	0.00	0.00	0.050	0.050	0.0
2	0.52	0.00	0.050	0.061	22.0
3	1.04	0.00	0.050	0.065	30.0
4	1.56	0.00	0.050	0.071	42.0
5	0.00	0.56	0.050	0.062	24.0
6	0.00	1.12	0.050	0.064	28.0
7	0.00	1.40	0.050	0.070	40.0
8	0.52	0.56	0.050	0.070	40.0

Table 3. Content of copper(II) in soil samples collected at a depth of 5.0 cm in different areas of Lodz.

No of soil sample	Content of Cu(II) [mg/kg dry mass]		
	"Uniontex"	"Nowe Rokicie"	Lublinek
1	25.92	48.06	12.34
2	37.14	69.91	11.65
3	30.07	59.87	14.97
4	39.41	60.32	25.91
5	37.23	61.77	17.24
6	38.26	57.04	
7	30.89	51.81	
8	77.17	45.39	
9	39.12	47.21	
10	28.57	46.97	

Table 4. Content of Cu(II) in soil samples from the "Nowe Rokicie" allotment gardens collected at two different depths.



No of soil sample	Depth of sample collection [cm]	Cu(II) content [mg/kg dry mass]
1	5.0	46.06
	20.0	36.75
2	5.0	69.91
	20.0	60.32
3	5.0	61.77
	20.0	56.04
4	5.0	51.81
	20.0	42.39
5	5.0	47.21
	20.0	42.94

obtained in the "Uniontex" gardens and the forest area are within the limits of natural content of copper(II) in soil. The "Nowe Rokicie" gardens may be classified as being slightly polluted with this metal.

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References

1. KABATA-PEND1AS A. Wybrane zagadnienia zwiazane z chemicznym zanieczyszczeniem gleb, Wyd. PAN **1989.**
2. KABATA-PENDIAS A., PENDIAS H. Biogeochemia pierwiastkow sladowych, PWN, Warszawa **1993.**
3. PAWLOWSKI L. Wiad. Chem. **43,** 451, **1984.**
4. PAWLOWSKI L. Wiad. Chem. **38,** 451, **1984.**
5. MACIAK F. Ochrona i rekultywacja srodowiska, Wyd. SGGW, Warszawa, **1996.**
6. DUDKA S. Ocena calkowitych zawartosci pierwiastkow glownych i sladowych w powierzchniowej warstwie gleb Polski 1. U. N. G., R (293), Pulawy.
7. Monitor Polski, **23,** (285), zal. 3, **1986.**
8. WACHWIK A. Rocz. PZH, **38,** 363, **1987.**
9. WACHWIK A. Rocz. PZH, **38,** 491, **1987.**
10. GOLDA T., GRUSZCZYNSKI S., TRAFAS M. Arch. Ochr. Srod. **3-4,** 171, **1994.**
11. KOWALSKA-PYLKA H. i inn. Rocz. PZH, **46,** 3, **1995.**
12. TERELAK H. i inn. Arch. Ochr. Srod. 3-4, 167, **1997.**
13. SZRZECHINSK1 I., GOZLINSK1 H., SIKORA I., KLECZKOWSKI M. Bromat. Chem. Toksykol. **16,** 3-4, **1986.**
14. BN-76/9180-06, Gleby i utwory mineralne. Pobieranie probek gleby i oznaczanie skladu mechanicznego.
15. BN-74/9190-02, Pobieranie probek gleby i przygotowywanie sredniej probki laboratoryjnej.
16. MARCZENKO Z. Spektrofotometryczne oznaczanie pierwia stkow, PWN Warszawa, **1979.**
17. PN-C-04611-2 Badania zawartosci miedzi; Oznaczanie **miedzi** w zakresie 0.001-2.000 mg/ml metod kolorymetryczna. z dwuetylodwutiokarbaminianem sodowym.
18. STRUSINSK1 A., WYSZYNSKA H. Rocz. PZH, 22, 649, **1971.**
19. MINCZEWSKI J., MARCZENKO Z. Chemia analityczna, PWN Warszawa, **1965.**