

Letter to Editor

Determination of Chromium in Soil of Łódź Gardens

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Abstract

Our work presents the results of the determination of bioavailable and total chromium (III) and chromium (VI) in the soil of an allotment garden situated in the center of Łódź.

Chromium was determined by the spectrophotometric method in the form of a purple-red Cr (VI) complex with 1,5-diphenylcarbazide in the acid medium, following the establishment of the optimum amounts of the oxidant (ammonium peroxodisulphate (VI)) in the soil solutions. Moreover, the effects of iron and copper ions on the determination results were examined. For comparison, chromium was also determined by atomic absorption spectrometry.

Keywords: chromium (III), chromium (VI), 1,5-diphenylcarbazide, soil.

Introduction

The content of chromium in soils is generally low. The range of mean concentrations of chromium varies from 7 to 150 ppm. and its content and distribution in the soil largely depends on the type of the soil's mother rock. The presence of additional amounts of the element in the soil is caused by human activity, including emission of furnace or coke dust or combustion of fluid fuel or tannery waste water or communal solid waste. The migration of chromium takes place only in a strongly acid and reducing medium, where it occurs in the form of the Cr^{3+} cation, or a strongly basic and oxidizing medium, where it occurs as the CrO_4^{2-} anion. Due to low solubility of its compounds and their high availability to plants, chromium plays an important role in the soil processes [1-3]. To date, no standards are in force in Poland concerning the permissible levels of heavy metals, including chromium, in the soil. It is accepted that the natural content of chromium in the surface layer (0-15 cm) of sandy soil is 2.0-30.0 ppm, in dusty and loamy soil it is 14.8 – 81.0

ppm [4]. The Directive of the Minister of the Environment states that the acceptable content of chromium in built-up and urban areas (at a depth of 0.3-15.0 m) should not exceed 150-190 ppm. [5]

Studies of the effects of chromium on living organisms have indicated its close connection with its oxidation state. Chromium (III) belongs to bioelements; it is an active component of the so-called glucose tolerance factors (GTF). GTF is an active complex of Cr (III) with two molecules of nicotinic acid and three amino acids necessary for proper glucose metabolism. Administration drugs containing Cr (III) proved to be helpful in treatment of diabetes patients. Cr (VI) compounds, on the other hand, are among the strongest carcinogenic and mutagenic agents. The data of the International Cancer Studies Agency classify Cr (VI) as a member of group I – substances with documented strong carcinogenic properties [6, 7, 8]. The present work is a continuation of the wider study on the determination of the content of heavy metals (Cd, Pb, Cu, Fe, Co) in the soils of the Łódź urban agglomeration [9-13].

Experimental

Reagents and Apparatus

- concentrated chloric (VII) acid (Riedwel-de-Haën AG); $d=1.53$ g/ml
- 3% hydrochloric acid; 1m/l and concentrated hydrochloric acid; $d=1.19$ g/ml
- concentrated orthophosphoric acid; $d=1.79$ g/ml
- concentrated sulfuric (VI) acid; $d=1.84$ g/ml
- stock standard solution of Cr (VI), obtained by dissolving 0.2829 g of potassium dichromate (dried to solid mass at 130°C) in 1000 ml of water; 1 ml of thus-prepared solution contained 0.1 mg of chromium (VI)
- working solution of Cr (VI) obtained by diluting 5 ml of the stock standard solution with water to 100 ml. 1 ml of thus-prepared solution contained 0.005 g of chromium (VI)
- 0.5% solution of 1,5-diphenylcarbazide (C_6H_6NHNH)₂CO, obtained by dissolving 0.5 g of 1,5-diphenylcarbazide in 100 ml of acetone
- 1.5% (V/V) solution of ammonium peroxydisulphate (VI)
- 500 µg/ml Fe (III) solution, obtained by dissolving 0.4317 g of ammonium sulfide (VI) and iron (III) Fe (NH_4)(SO₄)₂ · 12H₂O in 100 ml of water with the addition of sulfuric (VI) acid (1: 1) to pH ~ 1-2.
- 5% solution of lanthanum, obtained by dissolving 1.47 g of lanthanum (III) oxide in 25 ml of 3% HCl.
- High-pressure one-stand microwave mineralizer Uni Clever BM-12
- Specord M40 and Specol 11 spectrophotometers with 1 and 5 cm cells
- Atomic absorption spectrophotometer with a chromium cathode lamp

All the solutions used in the experiments were obtained by dissolving analytically pure reagents in redistilled water.

Soil Sampling, Soil Extraction and Mineralization

The primary soil samples were collected according to the recommended standard by means of a soil sampler from the surface layer of soil (0-20 cm) in the "Krokus" allotment garden situated in the center of Łódź. After drying them in air, laboratory samples were prepared.

The soil for extraction was ground and sifted through a screen with 2 mm mesh diameter, whereas the soil samples prepared for mineralization were ground more finely and sifted through a screen with 0.1 mm mesh diameter [14].

Total chromium was determined in the mineralized soil samples. Mineralization of the laboratory soil samples of approximately 0.500 g was carried out in concentrated chloric (VII) acid using a microwave mineralizer [15].

Bioavailable chromium was determined in soil extracts prepared in the same way as those used for deter-

mination of the level of bioavailable forms of other heavy metals.

Chromium was determined spectrophotometrically in the form of a complex with 1,5-diphenylcarbazide in the soil solutions and the results were compared with the results of the determination by the atomic absorption method – FAAS.

Principle of Chromium Determination by Spectrophotometric Method

The diphenylcarbazide method involves the formation of a purple-red complex of chromium (VI) with 1,5-diphenylcarbazide in the acid medium. Its molar absorption coefficient at $\lambda=545$ nm is $4.3 \cdot 10^4$. The obtained color is a result of a reaction of chromium (III) *in statu nascendi*, still not hydrated with water molecules, produced in the process of the reduction of Cr (VI) with 1,5-diphenylcarbazide, which is at the same time oxidized to form the diphenylcarbazone.

Oxidation of Cr³⁺ to Cr₂O₇²⁻ is of key importance in the determination of chromium by this method. The following compounds were used as oxidizing agents: sodium peroxide, hydrogen peroxide, chloric (VII) acid, bromine, sodium bismuthate (V), ammonium peroxydisulfate (VI) and potassium manganate (VII).

The acidity of the analyzed solution influences the intensity of the color, so it should be maintained at the same level. The recommended pH is about 1-2 since it ensures high sensitivity of the reaction. The color is stabilized by the presence of phosphates (V).

The diphenylcarbazide method of determination of Cr (VI) can be considered selective. The determination is disturbed only by Fe, V, Mo and Hg ions if their amount considerably exceeds the amount of chromium. Higher amounts of Fe (III) are masked by the addition of orthophosphoric (V) acid or sodium versenate. It can also be separated by extraction or in the form of Fe (OH)₃. Vanadium should be separated prior to chromium determination if its amount is 10 times higher than the amount of chromium. After the oxidation of chromium, 8-hydroxyquinoline (pH ≈ 4) is added and vanadium is extracted with chloroform. At the same time, iron, molybdenum and copper oximes are extracted. The disturbing molybdenum is masked with oxalic acid. The addition of chlorine is bound with Hg²⁺ to form a non-dissociated HgCl₄²⁻ and prevents a reaction between mercury and diphenyl carbazide. The method is very sensitive, so it can be used for the determination of very small amounts of chromium in biological samples, water, industrial waste water and minerals [16-18].

Determination Procedure

In order to plot the calibration line, 0.0, 0.2, 0.4, 0.8, 1.4, 2.0, 3.0, 4.0 and 5.0 ml of the working Cr (VI) solutions

were measured in turns into 50 ml flasks, which corresponded with the Cr (VI) content in a sample ranging from 0.0 to 0.025 mg. 1.0 ml of H_2SO_4 (1:1) and 0.3 ml of concentrated H_3PO_4 were added and the solution was diluted with distilled water up to the mark. After 5 minutes, 1.0 ml of 1,5-diphenylcarbazide was added to each sample. After another 10 minutes, the absorbance of the solutions was measured in 5 cm cells at $\lambda=543.5$ nm against blank test. (We had determined analytical wavelength and complex stability earlier). The dependence between the concentration of chromium (VI) and absorbance is rectilinear over the whole range of the examined concentrations (Fig. 1) and its correlation coefficient is 0.9996.

A similar procedure was used to determine the content of chromium in the soil samples: 0.1 ml of mineralized soil or 5.0 ml of extracted soil were added to the flasks. Since chromium can occur in different oxidation states, $(NH_4)_2S_2O_8$ was added as an oxidizing agent, which guaranteed that chromium was present in the solutions only in the form of $Cr_2O_7^{2-}$. The content of chromium in the soil was calculated according to the following equation:

$$x = C_x \frac{V_1 \cdot 1000}{V_2 \cdot m} [ppm]$$

where x – the content of Cr in the soil [ppm]

C_x – the concentration of the metal read on the calibration line [mg]

V_1 – the total volume of the mineralized or extracted soil sample [ml]

V_2 – the volume of the soil solution used for the analysis [ml]

m – the weighed portion of soil used for mineralization or extraction [g]

The Principle of Chromium Determination by FAAS Method [19-21]

Chromium was determined by flame atomic absorption spectrometry (FAAS) in a reducing air/acetylene flame at a wavelength of 357.9 nm. Prior to each series

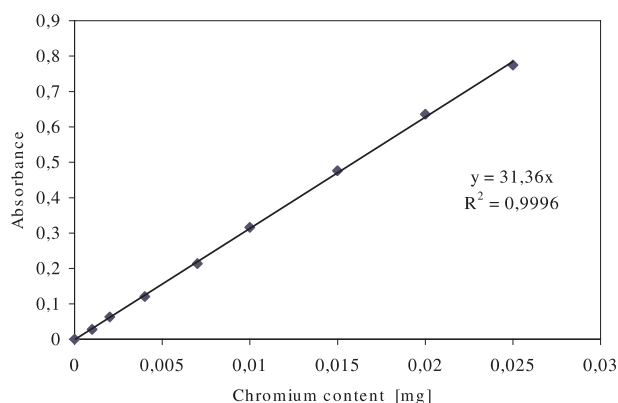


Fig. 1. Calibration line for determination of Cr (VI) in the form of a complex with 1,5-diphenylcarbazide.

of measurements a calibration line was plotted. For this purpose, 0.00; 0.125; 0.50; 1.25 and 2.50 ml of stock standard solution of Cr (VI) were placed in 50 ml flasks and 10.0 ml of 5% lanthanum solution was added and the volume was filled up to the mark with 1 M solution of hydrochloric acid. The following concentrations of Cr (VI) in the sample correspond with thus prepared standard solutions: 0.00; 0.25; 0.50; 1.00; 2.50 and 5.0 $\mu\text{g/ml}$. An example of the calibration line is presented in Fig. 2.

A similar procedure was used to determine the content of chromium in soil samples, adding 10.0 ml of 5% solution of lanthanum to the flasks containing the soil mineralizate or electrolyte and then adding 1M solution of hydrochloric acid to the mark.

Discussion

The spectrophotometric method for the determination of chromium in soil was developed with the use of the recommendations for its determination in water and waste water. The recommendations include the use of 1,5-diphenylcarbazide as the complexing agent.

Iron (III) ions begin to disturb the method if their content is 20 times higher than the content of chromium. As the mean content of chromium in soils is 7-150 ppm, (usually 20-50 ppm), while the mean content of iron is 2,000 to 20,000 ppm, it was necessary to mask Fe (III) ions present in the soil solutions by means of orthophosphoric acid. The results are presented in Table 1. The above-mentioned recommendations show that even at high concentrations of Fe (III) ions in the solution, 0.3 ml of concentrated H_3PO_4 solution per sample are sufficient to mask them. Our results, however, indicate that this amount is too low; at high Fe (III) concentration levels the determination error exceeded 50%. The error in the determination of chromium was the lowest (about $\pm 2.0\%$) when 2.0 ml of concentrated H_3PO_4 were introduced to the reducing solution and in our study we used this amount of the masking agent in the determination of chromium in mineralized and extracted soil samples.

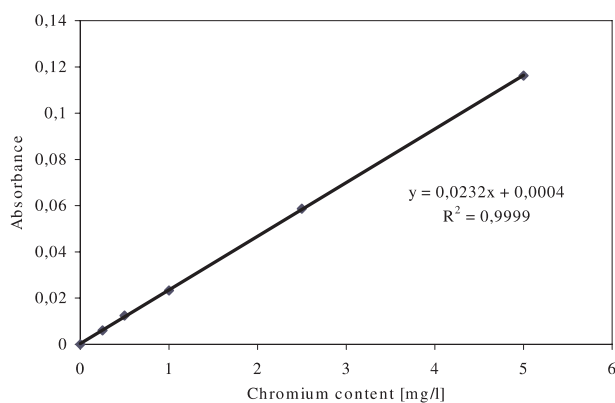


Fig. 2. Calibration line for determination of Cr (VI) by flame atomic absorption spectrometry.

Table 1. The effect of a masking agent – H_3PO_4 – on the determination of Cr (VI) content in the presence of different amounts of iron.

Iron content [µg/ml]	Amount of introduced concentrated H_3PO_4 [ml]	Content of chromium (VI) [µg/ml]		Determination error [%]	Content of chromium (VI) [µg/ml]		Determination error [%]
		introduced	found		introduced	found	
0.0	1.5	10.00	10.20	2.00	20.00	21.01	5.05
	1.8		10.16	1.60		20.99	4.95
	2.0		10.14	1.40		20.96	4.80
	2.3		10.14	1.40		21.24	6.20
1000	1.5	10.00	10.84	8.40	20.00	22.51	12.55
	1.8		10.14	1.40		20.89	4.45
	2.0		9.95	- 0.50		20.12	0.60
	2.3		9.47	- 5.30		19.42	- 2.90
3000	1.5	10.00	11.29	12.90	20.00	21.75	8.75
	1.8		10.62	6.20		20.12	0.60
	2.0		10.17	1.70		19.96	- 0.20
	2.3		9.57	- 4.30		19.04	- 4.80
9000	1.5	10.00	11.72	17.20	20.00	22.90	14.50
	1.8		10.79	7.90		20.70	3.50
	2.0		10.17	1.70		19.74	- 1.30
	2.3		9.73	- 2.30		19.36	- 3.20
11000	1.5	10.00	12.47	24.70	20.00	24.94	24.70
	1.8		10.81	8.10		21.65	8.25
	2.0		10.20	2.00		21.73	3.65
	2.3		9.79	- 2.10		18.75	- 6.25

Table 2. The effect of Cu (II) ions on the determination of Cr (VI) content in the form of a complex with 1,5-diphenylcarbazide.

Cu(II) concentration [µg/ml]	Cr(IV) concentration [µg/ml]		Determination error [%]
	introduced	found	
0.00	20.0	20.58	2.9
12.50	20.0	20.62	3.1
18.75	20.0	20.61	3.1
25.00	20.0	20.63	3.1
37.50	20.0	20.62	3.1
50.00	20.0	20.81	4.0
75.00	20.0	20.94	4.7
100.00	20.0	21.51	7.5

Other metals disturbing chromium determination are copper, vanadium, molybdenum and mercury. The content of the latter three of them in soil is so low that they do not affect the results of the determination of chromium. However, in cases where the concentration of chromium is low, the natural content of copper (5 to 140 ppm) may disturb its determination by the method under discussion. Therefore, the influence of different amounts of copper on the results of chromium determination was examined. The results are listed in Table 2. They show that even a 4-fold excess of Cu (II) in relation to Cr (VI) ions does not result in a determination error higher than 5.0%. Taking into account the natural contents of Cr and Cu in soil, we did not use a masking agent for copper in the soil solutions.

Chromium with oxidation state +6 can be determined by the diphenylcarbazide method, but Cr^{3+} ions, which are also present in soil, do not form a colored compound with diphenyl carbazide. Thus, an important stage in the determination of chromium in soil is bringing it to oxidation state +6.

Ammonium peroxydisulphate (VI) was used as an oxidant in the acid medium. According to literature data its concentration in the determined sample should be 0.1% V/V. In the case of the soil samples these amounts proved to be too low, which is demonstrated in the data listed in Table 3 (Cr content found by means of AAS is given for comparison). It can be agreed that the optimum concentration is 1.5% V/V and thus, when determining chromium by spectrophotometry, we added enough $(NH_4)_2S_2O_8$ to all the soil solutions to bring its concentration to 1.5% V/V.

When the conditions of determination of chromium in the form of its complex with diphenylcarbazide in soil solutions were established, total and bioavailable chromium was determined in samples collected at six different sites (collected according to the recommended standard) in the "Krokus" allotment gardens in Łódź. The results are listed in Table 4. The content of total chromium determined by this method was from 22.14 to 30.81 ppm, depending on the sample collection site. Relative standard deviation (RSD) was from 0.62% to 2.04% ($n = 5$) and the confidence interval was from ± 0.28 to ± 0.67 mg (for 95% probability).

To examine the reliability of the determination, comparative determination of chromium was carried out in the same soil solutions by flame atomic absorption spec-

Table 3. The effect of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ concentration on the determination of Cr (VI) in selected soil samples.

Soil sample	$(\text{NH}_4)_2\text{S}_2\text{O}_8$ concentration in the analyzed sample [% V/V]	mean Cr(VI) content [ppm]	
		determined by the spectrophotometric method	determined by FAAS method
6	0.1	2.23	3.40
	0.5	2.27	
	1.0	2.83	
	1.5	3.29	
	2.0	3.08	
5	1.0	10.93	12.91
	1.5	12.72	
	2.0	11.67	
2	1.0	3.09	4.27
	1.5	4.18	
	2.0	3.27	

Table 4. The content of bioavailable and total chromium in the soil of the "Krokus" allotment gardens.

Soil sample	Bioavailable chromium content [ppm]		Total chromium content [ppm]	
	determined by the spectrophotometric method	determined by FAAS method	determined by the spectrophotometric method	determined by FAAS method
1.	3.57	3.75	25.02	25.86
2.	4.15	4.27	22.14	22.73
3.	1.51	1.62	22.59	22.93
4.	2.02	2.08	22.51	22.84
5.	12.84	12.91	30.81	32.33
6.	3.29	3.40	22.44	25.29

trometry. The results are presented in Table 4. The total content of chromium found using this method is from 22.73 to 32.33 ppm, depending on the site of the sample collection. Relative standard deviation (RSD) is from 0.92 to 1.50% ($n = 5$), and the confidence interval varies from ± 0.29 to ± 0.42 ppm (for 95% probability).

The results obtained by the FAAS method were always from 0.5 to 10.0% higher than those obtained by the spectrophotometric method. This suggests that both methods can be treated as equally appropriate for the determination of this element.

Chromium has been previously determined in the soils of the city of Łódź; the content of heavy metals has been measured in the samples collected in green areas situated next to streets and in parks [22]. In the surface layer of the soil 6 to 66 ppm of chromium was found (mean content 26 ppm), the amount comparable with its content in the soil of the "Krokus" gardens. Similar contents of total chromium were found by J. Czekala [23,24]; at depths of 0-30 cm they varied from 9.7 to 32.5 ppm, depending on the type of the examined soil.

In the soils of the Małopolskie Voivodeship [25] the content of chromium, close to total chromium, was found to be from 4.34 to 45.81 ppm, while the geometric mean is 18.11 ppm. Similarly, in the soils of other regions of Poland [26-28] the level of this element in the surface layer was from 10.33 to 76.00 ppm. No relationship was found between the vicinity of roads with heavy traffic

and the content of chromium in the soil [29]; 10 to 50 ppm of chromium were found in the soils collected in the areas close to such roads. The method of preparation of the soil samples for analysis (chloric (VII) acid [26], a mixture of concentrated chloric (VII) and nitric (V) acids [27], a mixture of acid and concentrated nitric (V) acid [24], and concentrated nitric (V), sulfuric (VI) and hydrochloric acids [22] were used for this purpose) and the determination method affected the results of chromium determination.

Baryłkiewicz and Siepak [30] have observed that Polish light soils contain from 2 to 60 ppm, and heavy soils from 14 to 80 ppm of chromium. The Directive of the Minister [5] informs that the content of chromium in built up or urbanized areas (at depths of 0.3-15 m) should not exceed 150-190 ppm. According to the literature data presented, it should be accepted that the soil of the allotment garden in the center of Łódź contains natural, most commonly observed amounts of the element.

Table 4 shows the results for bioavailable chromium. The proportion of soluble forms of chromium varied greatly and, depending on the site of sample collection, was from 7 to 36% of its total content in the soil. These values are in agreement with the literature data [23, 27], if the element was determined in the extract of 1 M hydrochloric acid. The content of bioavailable chromium was not comparable when it was determined in the extract of 0.1 M hydrochloric acid.

Table 5. Proportions of Cr (III) and Cr (VI) in the bioavailable chromium in "Krokus" gardens soil.

Soil sample	Bioavailable chromium content [ppm]	
	Cr(III)	Cr(VI)
1	1.91	1.67
2	1.93	2.19
3	0.80	0.73
4	0.75	1.26
5	6.40	6.44
6	1.69	1.63

As Cr (III) and Cr (VI) ions play very different roles in living organisms, their proportion in the soil solutions was measured (Table 5). The content of both forms is given only for bioavailable chromium, because in the course of mineralization with chloric (VII) acid Cr (III) is partly oxidized to Cr (VI) and the results may not correspond with the real proportions. The results show that Cr (III) accounts only from 37 to 50% of bioavailable chromium, so that the amount of the form of chromium which has a harmful influence on living organisms prevails in the soil extracts.

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