

Investigations of Sequential Extraction of Chromium from Soil

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Abstract

The sequential extraction of Cr from soil to soil eluates was studied. The influence of conditions of soil sample preparation and conditions of eluates obtained in the final result of Cr extraction from soil and its determination were found. Conditions protecting the total extraction of Cr from soil to solutions were established.

Keywords: chromium, soil, sequential extraction, AAS.

Introduction

Investigations of functional speciation of Cr in soil [1-8] include two stages: the sequential extraction of soil and Cr determination in eluates. The conditions of soil sample preparation for research and carrying out the extraction should protect the total extraction of Cr from soil to solutions and recurrent analytical results. The references describe various procedures for sequential extraction of soil and bottom sediments [9-28] and they concern group extraction of components to solution. In practice they do not protect satisfactory results reproducibility for Cr even though Cr determination in solutions is in detail investigated and described [29-31] and it does not constitute larger difficulty. The cause is probably incomplete Cr extraction from soil to solution in conditions of the sequential extraction. Therefore investigations of influence of soil sample preparation conditions and carrying out the extraction of Cr to solutions becomes purposeful. The research of influence of soil sample preparation (grain diameter, drying temperature) and conditions of carrying out the sequential extraction (time, volume of eluent, temperature) on the final result of Cr extraction from soil and its determination in soil eluates were done. The investigations were performed on surface soil (brown soil) and solutions for the sequential extraction of

soil described in Tessier's method [25,26] or single-stage of soil digestion [29].

Experimental

Soil Preparation and the Sequential Extraction

In experiments surface soil (brown soil) was used, it was brought to air-dried condition or it was dried for 6 hours at a temperature of 20, 30, 50, 80, 100, 150, and 300 °C accordingly, ground to a grain diameter appropriately of 0.1; 0.25; 0.5; 1.02; 2 mm and coarsely ground ($\phi_{\text{soil}} > 2$ mm). There was investigated influence of the sequential extraction time ($t_{\text{extn}} = 15$ min - 20 days), volume of the eluent ($V_{\text{eluate}} = 10 - 100$ ml), temperature of carrying out the sequential extraction process ($t = 20-40^\circ\text{C}$), diameter of soil grain $\phi_{\text{soil}} \geq 0.1$ mm), and drying temperature of soil ($t_{\text{drying}} = 20-300^\circ\text{C}$) on extraction of chromium from soil ($m = 10.00$ g) to solution and the final result of its determination in soil eluates.

The sequential extraction of soil for given conditions (t_{extn} , V_{eluate} , t , ϕ_{soil} , t_{drying}) included 5 steps in order to extract Cr from 5 metal fractions: F(1) - exchangeable metals; F(2) - metals bound to carbonates; F(3) - metals bound to iron and manganese hydrated oxides; F(4)

- metals bound to organic matter; F(5) - residual metals. At steps 1-4 solutions according to Tessier [25,26] were used, in step 5 - the mixture of acids HNO₃ and HClO₄ (2:1) [29].

STAGE 1. To flasks with soil samples 0.5 mol l⁻¹ MgCl₂ solution (pH = 7) was added and the soil was leached. The soil extract (1) was obtained and the G(1) soil residue.

STAGE 2. The acetate buffer: CH₃COOH / CH₃COONa, pH = 5 was added to G(1) residue and leaching of soil was continued. Soil extract (2) and G(2) soil residue were obtained.

STAGE 3. To the G(2) residue 0.04 mol l⁻¹ NH₂OH • HCl in 25% CH₃COOH was added and digestion was performed for an hour on a heating plate at 96°C. A subsequent portion of the solution of hydroxylamine hydrochloride of concentration 0.04 mol l⁻¹ in 25% CH₃COOH was added and digestion was continued for the next hour. The soil extract (3) and the G(3) soil residue were obtained.

STAGE 4. To the G(3) residue small portions of 30% H₂O₂ were carefully added, a flask was covered with a watch glass and the content was being digested for an hour at 85°C. The glass was taken off and the flask content was evaporated to a small volume (1-2 ml). Subsequently a successive portion of 30% H₂O₂ was added, heated for an hour at 85°C and the flask content was evaporated again. To the cooled residue after vaporisation of the solution, 20 ml of 3.2 mol l⁻¹ CH₃COONH₄ in 20% HNO₃ was added. The soil extract (4) and the G(4) residue soil were obtained.

STAGE 5. The G(4) residue was subjected to digestion in a mixture of concentrated HNO₃ and HClO₄ acids (2 : 1). The flask was covered with a watch glass, put on a heating plate (temp. 90°C) and heated for an hour. After lapse of this time the flask content was evaporated to dryness. To the dry cooled residue 15 ml of HCl solution (1:1) was added, it was put again on a heating plate and heated as before. The flask content was hot-filtered by a medium quantitative filter paper, decanting sediment traces with the help of the hot 1% HCl. The soil solution (5) was obtained.

Determination and Balance of Cr

Chromium concentration in soil eluates and in solutions after soil mineralization was determined appropriately by diphenylcarbazide method and FAAS. Measurements were carried out by means of a spectrophotometer of the BECKMAN company, type DU-640 with $\lambda = 545$ nm and absorption atomic spectrometer model 3100 of the PERKIN-ELMER company, with the wavelength of 357.9 nm in presence of 1% NH₄Cl [29]. The control of results of Cr determination was performed by checking the Cr mass balance in soil eluates and soil and total Cr determination in soil in settled conditions for analysis of the Cr in reference soil (single-stage soil digestion with the mixture of nitric(V) acid and chloric(VII) acid, Cr determination by the FAAS method in the presence of 1% NH₄Cl). The sequential extraction of soil and mineralization of the studied sample and reference soil was carried out appro-

priately on four and six parallel samples. Measurement of Cr concentration in the final solution was performed three times. The determined Cr concentration in soil eluates was recalculated to Cr concentration in appropriate metal fractions F(1) - F(5). The results are shown in Tables 1-5.

Reagents

Reagents POCh Gliwice (Poland), Fluka Garantie, Germany and Aldrich Chemie, Germany: magnesium chloride (a.p., POCh), acetate buffer (a.p., Fluka), hydroxylamine hydrochloride (a.p., POCh), 30% solution of H₂O₂ (a.p., POCh), nitric(V) acid (a.p., POCh), chloric(VII) acid (a.p., POCh), hydrofluoric acid (a.p., POCh), acetic acid (a.p., Aldrich), ammonium acetate (a.p., Aldrich), ammonium chloride (a.p., POCh), 1,5-diphenylcarbazide (a.p., Fluka) and standard chromium solution (Central Office of Measures, Warsaw) were used, as well as the certification reference material BPGM-1 (brown soil, the certified Cr content: total with HF - 15.8 $\mu\text{g g}^{-1}$, total direct - 26.3 $\mu\text{g g}^{-1}$) - The Central Office of Measures, Warsaw.

Results and Discussion

Influence of Sequential Extraction Time

Extraction was performed for soil samples having mass $m = 10.00$ g, grain diameter $\phi = 0.25$ mm, volume of the eluent $V = 30$ ml and process working time: 5, 10, 15, 30 minutes, 1 hour (all fractions) and 2, 5, 10, 18 hours; 1, 2, 5, 10 and 20 days (F(1) - F(2) fractions).

Investigations proved influence of the leaching time of soil on the final result of chromium determination in soil eluates (Table 1). This influence is particularly visible for time $t_{\text{extn}} < 1$ hour for F(3) - F(5) fractions. However, for $t_{\text{extn}} \geq 1$ hour total Cr practically extracts from soil to eluates. Thus, increasing time of soil extraction over 1 hour does not have influence on extraction of Cr from soil to solution.

Influence of Eluate Volume

Investigations were performed for soil samples having mass $m = 10.00$ g, grain diameter $\phi = 0.25$ mm, extraction time $t = 1$ hour and the eluate volume $V = 10, 14, 20, 30, 50, 75, 100$ ml. It was found that change of the leaching solution volume from 30 to 100 ml [F(1) - F(2) fractions], as well as from 20 to 100 ml [F(3) - F(5) fractions] does not cause larger changes in the determined Cr concentration in a given fraction (Table 2). Taking into consideration the obtained results, it ought to be stated that the total Cr extraction from soil to solutions was obtained for the ratio $V_{\text{solution}} [\text{ml}] : m_{\text{soil}} [\text{g}] > 3 : 1$.

Influence of Leaching Temperature

Investigations were performed on soil ($m = 10.00$ g), grain diameter 0.25 mm, using 30 ml of the eluate and

Table 1. Influence of sequential extraction time on chromium extraction from soil to eluting: MgCl₂ (1), CH₃COOH/CH₃COONa (2), NH₂OH • HCl (3), H₂O₂ (4), HNO₃, HClO₄ (5).

$m_{\text{Soil}} = 10.00 \text{ g}$, $V_{\text{solution}} = 30 \text{ ml}$, $\phi_{\text{Soil}} = 0.25 \text{ mm}$. Average chromium concentration for $n = 4$ and $p = 95 \%$.

Time	Concentration of chromium in soil [$\mu\text{g g}^{-1}$]					
	Metals fractions					$\sum_{i=1}^5 [\text{Cr}]_i$
	F(1)	F(2)	F(3)	F(4)	F(5)	
minutes: 5	0.00	0.00	0.95 ± 0.18	1.70 ± 0.47	2.80 ± 0.38	5.45 ± 1.03
10	0.00	0.00	1.65 ± 0.31	2.50 ± 0.37	3.50 ± 0.29	7.65 ± 0.97
15	0.00	0.00	2.15 ± 0.34	3.30 ± 0.51	4.90 ± 0.42	10.35 ± 1.27
30	0.00	0.00	2.75 ± 0.19	4.55 ± 0.62	7.25 ± 0.54	14.55 ± 1.35
hours: 1	0.00	0.00	3.05 ± 0.12	4.90 ± 0.50	8.75 ± 0.58	16.70 ± 1.20
2	0.00	0.00	3.05 ± 0.12	4.85 ± 0.45	8.70 ± 0.53	16.60 ± 1.10
5	0.00	0.00	Not investigated			
10	0.00	0.00				
18	0.00	0.00				
days: 1	0.00	0.00				
2	0.00	0.00				
5	0.00	0.00				
10	0.00	0.00				
20	0.00	0.00				

Table 2. Influence of eluting solution volume: MgCl₂ (1), CH₃COOH/CH₃COONa (2), NH₂OH • HCl (3), H₂O₂ (4), HNO₃, HClO₄ (5) on chromium extraction from soil to eluting.

$m_{\text{Soil}} = 10.00 \text{ g}$, $t_{\text{extn}} = 1 \text{ h}$, $\phi_{\text{Soil}} = 0.25 \text{ mm}$. Average chromium concentration for $n = 4$ and $p = 95 \%$.

Volume of solution [ml]	Concentration of chromium in soil [$\mu\text{g g}^{-1}$]					
	Metals fractions					$\sum_{i=1}^5 [\text{Cr}]_i$
	F(1)	F(2)	F(3)	F(4)	F(5)	
10	0.00	0.00	2.75 ± 0.14	3.95 ± 0.34	8.45 ± 0.63	15.15 ± 1.11
14	0.00	0.00	2.75 ± 0.20	4.15 ± 0.22	8.80 ± 0.67	15.70 ± 1.09
20	0.00	0.00	2.80 ± 0.35	4.40 ± 0.28	8.90 ± 0.74	16.10 ± 1.37
30	0.00	0.00	3.05 ± 0.12	4.90 ± 0.50	8.75 ± 0.58	16.70 ± 1.20
50	0.00	0.00	3.00 ± 0.19	4.75 ± 0.47	8.65 ± 0.62	16.40 ± 1.28
75	0.00	0.00	3.05 ± 0.24	4.85 ± 0.32	8.75 ± 0.70	16.65 ± 1.26
100	0.00	0.00	3.05 ± 0.21	4.75 ± 0.37	8.80 ± 0.61	16.60 ± 1.19

Table 3. Influence of sequential extraction temperature on chromium extraction from soil to eluting: MgCl₂ (1), CH₃COOH/CH₃COONa (2), NH₂OH • HCl (3), H₂O₂ (4), HNO₃, HClO₄ (5).

$m_{\text{soil}} = 10.00 \text{ g}$, $V_{\text{solution}} = 30 \text{ ml}$, $t_{\text{extn}} = 1 \text{ h}$, $\phi_{\text{Soil}} = 0.25 \text{ mm}$. Average chromium concentration for $n = 4$ and $p = 95 \%$.

Temperature of extraction [°C]	Concentration of chromium in soil [$\mu\text{g g}^{-1}$]		
	Metals fractions		$\sum_{i=1}^5 [\text{Cr}]_i$
	F(1)	F(2)	
20	0.00	0.00	0.00
30	0.10 ± 0.04	0.00	0.10 ± 0.04
40	0.20 ± 0.05	0.10 ± 0.02	0.30 ± 0.07

extraction time of 1 hour. Leaching of soil was carried out at 20, 30 and 40°C for the first two steps of extraction. Subsequent stages of soil extraction, according to the sequential extraction procedure, are performed at 96, 85 and 90°C.

It was found that increasing the extraction temperature in the studied range slightly influences extraction of Cr from soil to F(1) - F(2) water fractions. Thus, temperature increases from 20 to 40°C causes increase of Cr concentration getting to solutions accordingly for F(1) from 0.00 to $0.20 \pm 0.05 \mu\text{g g}^{-1}$, for F(2) from 0.00 to $0.10 \pm 0.02 \mu\text{g g}^{-1}$, (Table 3). Since additional heating of the system is burdensome in practice ambient temperature (+ 20°C) should be accepted as the optimum temperature of soil leaching for F(1) - F(2) fractions.

Table 4. Influence of grain diameter of soil on chromium extraction from soil to eluting: MgCl₂ (1), CH₃COOH/CH₃COONa (2), NH₂OH • HCl (3), H₂O₂ (4), HNO₃, HClO₄ (5).

m_{Soil} = 10.00 g, V_{solution} = 30 ml, t_{extn} = 1 h. Average chromium concentration for n = 4 and p = 95 %.

Grain diameter of soil ϕ [mm]	Concentration of chromium in soil [$\mu\text{g g}^{-1}$]					
	Metals fractions					$\sum_{i=1}^5 [\text{Cr}]_i$
	F(1)	F(2)	F(3)	F(4)	F(5)	
0.10	0.00	0.00	3.10 ± 0.10	4.80 ± 0.52	8.70 ± 0.61	16.60 ± 1.23
0.25	0.00	0.00	3.05 ± 0.12	4.90 ± 0.50	8.75 ± 0.58	16.70 ± 1.20
0.50	0.00	0.00	1.90 ± 0.22	3.50 ± 0.44	11.20 ± 0.53	16.60 ± 1.19
1.02	0.00	0.00	1.35 ± 0.19	2.45 ± 0.42	12.55 ± 0.64	16.35 ± 1.25
2.00	0.00	0.00	0.95 ± 0.24	2.05 ± 0.39	13.40 ± 0.67	16.40 ± 1.30
> 2.00	0.00	0.00	0.45 ± 0.27	1.55 ± 0.36	14.60 ± 0.59	16.60 ± 1.22

Table 5. Influence of soil drying temperature on chromium extraction from soil to eluting: MgCl₂ (1), CH₃COOH/CH₃COONa (2), NH₂OH • HCl (3), H₂O₂ (4), HNO₃, HClO₄ (5).

m_{Soil} = 10.00 g, V_{solution} = 30 ml, t_{extn} = 1 h, ϕ_{Soil} = 0.25 mm. Average chromium concentration for n = 4 and p = 95 %.

Drying temperature of soil [°C]	Concentration of chromium in soil [$\mu\text{g g}^{-1}$]					
	Metals fractions					$\sum_{i=1}^5 [\text{Cr}]_i$
	F(1)	F(2)	F(3)	F(4)	F(5)	
Not dried soil	0.00	0.00	2.75 ± 0.11	4.80 ± 0.44	8.95 ± 0.62	16.50 ± 1.17
20	0.00	0.00	3.05 ± 0.12	4.90 ± 0.50	8.75 ± 0.58	16.70 ± 1.20
30	0.00	0.00	3.05 ± 0.23	4.55 ± 0.57	8.95 ± 0.51	16.55 ± 1.31
50	0.00	0.00	2.95 ± 0.29	4.05 ± 0.53	9.30 ± 0.49	16.30 ± 1.28
80	0.00	0.00	2.90 ± 0.35	3.90 ± 0.41	9.30 ± 0.47	16.10 ± 1.23
100	0.00	0.00	2.90 ± 0.10	3.90 ± 0.46	9.35 ± 0.54	16.15 ± 1.10
150	0.00	0.00	2.80 ± 0.18	3.90 ± 0.39	9.70 ± 0.62	16.40 ± 1.19
300	0.00	0.00	2.80 ± 0.14	3.90 ± 0.43	9.70 ± 0.57	16.40 ± 1.14

Influence of Conditions of Soil Sample Preparation

Influence of degree of soil grinding (grain diameter) and temperature of its drying on the final result of Cr determination in soil eluates after the sequential extraction was studied.

In the first part air-dried, surface soil samples were used for investigations with grain diameter: 0.1; 0.25; 0.5; 1.02; 2 mm and coarsely ground $\phi > 2$ mm). In the second part soil was subjected to drying at 20, 30, 50, 80, 100, 150 and 300°C for 6 hours and it was ground till a grain diameter of 0.5 mm was obtained. Investigations were performed for m = 10.00 g of soil, volume of the eluent V = 30 ml and extraction time t = 1 hour.

The results of investigations indicate that degree of soil grinding has essential influence on extraction of Cr from soil to a solution. This influence is particularly visible for grains having a diameter $\phi > 0.25$ mm (Table 4). It was found that with an increase of grain diameter the Cr concentration in eluates (3) and (4) decreases. Thus, grain diameter of soil used for leaching should not be larger than 0.25 mm. Moreover, investigation results indi-

cate that drying temperature of soil, similarly to previous parameters, influences Cr extraction from soil to soil eluates (Table 5). This influence is especially observed for the third and fourth fraction, for which increase of drying temperature of soil from 30 to 300°C lowers Cr extraction from soil to a solution. This effect is levelled only by the final stage of soil digestion in the mixture of acids HNO₃ and HClO₄. It was found that in optimum conditions of sequential extraction of soil the air-dried soil or drying of soil at 20-30°C should be used for effective determination of Cr in soil eluates. In higher drying temperatures Cr contained in soil creates probably sparingly soluble compounds, which do not get easy into eluates with NH₂OH • HCl and H₂O₂, causing distortion of pattern of the actual chromium distribution in various metals fractions.

Balance of Cr

The mass balance of Cr was checked in the researched systems by comparing the total content of chromium

in soil ($[Cr]_{total}$) with the sum of Cr contents in appropriate metals fractions $\left(\sum_{i=1}^5 [Cr]_i\right)$. Determination of $[Cr]_{total}$ in soil was performed in analysis conditions $[Cr]_{total}$ in the reference soil (certification reference material BPGM-1), for which the result of Cr analysis was obtained with accuracy $\eta > 98\%$ in relation to the certification value. The results on Cr determination in soil eluates were obtained for optimum conditions of sequential extraction of Cr from soil. It was found that in the studied systems the total chromium concentration in soil and in metals fractions appropriately amounts to:

$$([Cr]_{total} = (16.80 \pm 0.90) \mu\text{g g}^{-1}, n = 6 \text{ and } p = 95\% \text{ and } \sum_{i=1}^5 [Cr]_i = (16.70 \pm 1.20) \mu\text{g g}^{-1}, n = 4$$

Conclusions

The influence of conditions of soil sample preparation (brown soil) and conditions of soil eluates obtained in the Cr extraction from soil was studied. It was found that influence of extraction time, volume of the eluent, leaching temperature, diameter of soil grains and drying temperature of soil on the final of Cr concentration in soil eluates after 5-step sequential extraction of soil. Optimum conditions protecting total Cr extraction from soil to solutions were established: a diameter of soil grains $\phi < 0.25$ mm, drying temperature (coming to air-dried condition) of soil 20-30°C, time of soil extraction - 1 hour, ratio of the eluent volume V [ml] to the soil mass m [g] 3 : 1, temperature of the sequential extraction - about 20°C for F(1) - F(2) fractions, for F(3) - F(5) fractions - according to the leaching procedure of soil 96, 85 and 90°C.

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