

Investigations of Chemical Fraction of Cr in Soil

J. Kalembkiewicz*, E. Sočo

Department of Inorganic and Analytical Chemistry, Faculty of Chemistry, Rzeszow University of Technology,
Powstańców Warszawy Ave. 6, 35-959 Rzeszów, Poland

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Abstract

The influence of Cr (III) and Cr (VI) on biochemical reactions in the environment depends in part on the possibility of its getting from soil to soil solutions. The various methods of sequential extraction of Cr from soil were studied (Tessier et al. [1, 2], Rudd [3], BCR [4-7], Gatehouse [8], Kersten and Förstner [9], Psenner [10], Sposito [11]) in order to characterize chemical fractions. It was found that chromium determination depends on the method used and varies from 18.2% (BCR) to 96.5% (Tessier) of chromium detection in soil ($34.1 \text{ mg}\cdot\text{kg}^{-1}$). Quantitative evaluation of chemical fraction of Cr in soil by methods of sequential extraction was carried out by Tessier [1-2], Kersten and Förstner method [9] and indicated that Cr desorption increases according to the following order: exchangeable fraction < carbonate < oxide < organic (sulfide). For other procedures studied (Rudd [3], BCR [4-7], Gatehouse [8], Psenner [10], Sposito [11]), no reliable results were obtained for individual chemical fractions. The characterization of fraction of Cr soluble in water and in acids (carbonate and adsorb fractions) was performed. It was found that the Gatehouse method yielded maximum Cr amounts (25.5%) under these conditions. Their method for chromium determination is proposed for highest detectability for fractions of interest.

Keywords: soil, chromium, analysis of chemical fraction, sequential extraction from soil

Introduction

Environmental pollution caused by harmful compounds and chemical element accumulation is a problem relating to soil degradation. Nowadays, the research concerning speciation of metals in the environment, especially of Cr, is acquiring importance [12-21].

In view of various properties and biological activity of chromium in living organisms [22-26], and chromium contribution in the food chain: soil – plant – animal – man [27], it is necessary to determine the amount of chromium in soil, where chromium exists in different oxidation states, and evaluate the methods of separation and determination of various chromium species. Studies on Cr contents and its forms in soil [28-33], conditions of Cr extraction from soil to solutions [21, 32, 33] as well as

extraction methods and investigations of various chemical fraction of Cr have been reported [14, 15, 34-46].

Influence of Cr on the course of biochemical reactions in the environment depends in part on the possibility of its transfer from soil to soil solutions. In practice this process is investigated by performance of the sequential extraction of soil. The Cr sequential extraction for a given soil depends in part on the type of soil, leaching reagent, conditions of the process, and the initial condition of soil (environmental soil, air-dried soil). Recovery factor of chemical fraction of chromium from soil eluates depends on its distribution among various chemical fractions in soil and influences its availability for living organisms. Most often the studies evaluate the chemical fraction of metals in soil as: exchangeable, carbonate, oxide, organic, sulfide and residue forms. Many procedures of sequential extraction of soil and bottom sediments have been described [1-6, 20, 21, 47-52], which include the group extraction of components.

*Corresponding author; e-mail: kalembic@prz.rzeszow.pl

Among various methods of sequential extraction, the Tessier [1, 2], Rudd [3], BCR [4-7], Gatehouse [8], Kersten and Förstner [9], Psenner [10] and Sposito [11] procedures are most often used for environmental samples. The Cr distribution within fractions differs among methods. Therefore, we have attempted to compare those methods in order to establish the optimal sequential method for maximum extractability and reproducibility.

Experimental

Soil Preparation

Surface soil (0-15 cm) growth of grass from the town of Rzeszów, Poland, was used. The samples were collected according to PN-R-04031 [53] norm. A 0.5 kg subsample was obtained from the air-dried soil samples (5 kg), Cr ashes in an agate mortar and a grain diameter subsample of 10.00 g mass (0.25 mm) was utilized for chemical extraction.

Sequential Extraction

Soil was evaluated with a 30 ml portioning of extractant using sequential extraction four replicates. The sequential extraction of Cr from soil was performed in order to determine chemical fractions of Cr. This was done for fractions defined as:

- (1) exchangeable and soluble fraction including Cr forms soluble in water,
- (2) acids soluble fraction (carbonate and adsorbed),
- (3) oxide fraction,
- (4) fraction bound to sulfide and organic matter, and
- (5) so-called residue including the most stable Cr forms.

Metal included in this fraction is chemical by passive and biologically inactive.

Analysis of Total Chromium

Analysis of total Cr was carried out in conditions for Cr analysis in certification reference soil BPGM-1 (brown soil, the certified Cr content: total with HF – 15.8 $\mu\text{g g}^{-1}$, total direct – 26.3 $\mu\text{g g}^{-1}$). Single-stage soil digestion with the mixture of nitric(V) acid and chloric(VII) acid (2:1) in the presence of 1% NH_4Cl with accuracy $\eta > 98\%$. Six replicates were used.

Chromium Determination

Determination of total chromium by flame atomic absorption spectrometry (FAAS) was performed directly in solutions in the presence of 1% NH_4Cl [31] with three replicates. Cr concentration in soil eluates was recalculated to Cr concentration in appropriate metals fractions

F (1) – F (5) and Cr concentration in soil. The results are shown in Table 1.

Statistical Analysis

Statistical analysis was performed using MS Excel 2000 (Microsoft). Relative standard deviation (RSD)% and Student correlation coefficient were calculated, significance was set at $p=95\%$ and $n=4$. Obtained results have the following value of relative standard deviation $\text{RSD} < 2\%$ (single measurement) [54].

Instrumentation

Measurements were carried out by means of atomic absorption spectrometer model 3100 (PERKIN-ELMER) ($\lambda = 357.9 \text{ nm}$ for Cr in presence of 1% NH_4Cl [31]). The pH measurements were conducted using pHmeter (E-metron, CPI-551 model). A universal shaker Model 358 A of the ELPIN-PLUS company (Poland) and electric hotplate with temperature control and digital display to 1°C Model SD 300 of the STUART company (England) were used for the extraction. The heating digester with programmable increase of temperature from 25 to 450°C Model DK6 with mineralizations groups finalized to heavy metals trace determinations Model TMD6 of the VELP Company (Italy) was used. A centrifuge test tube Model WE-6 (Precision Engineering, Poland) was used for centrifuging of the soil extracts at 2500 rpm. The soil samples were dried with electric drier model KBC-65G of the WAMED Company (Poland). The deionizator of the Cobrabid-AQUA Company (Poland) was used for the deionization of water.

Results and Discussion

Analysis of Total Chromium

Soil samples were pulped with nitric(V) and chloric(VII) acids. Total chromium was determined in those solutions. Total chromium content was found to be $34.1 \pm 1.6 \text{ mg kg}^{-1} \text{ Cr}$.

Evaluation of Cr Amount Obtained from Sequential Extraction

The sum of Cr content in appropriate chemical fractions for various sequential extraction methods were compared (Fig. 1). It was found that applied methods extract Cr from soil to solutions to a various extent. Summary concentration of Cr ($\sum_{i=1}^n [\text{Cr}_i]$) for individual sequential extraction appropriately equaled: 32.9 (Tessier), 31.2 (Kersten and Förstner), 29.7 (Gatehouse), 18.3 (Sposito), 17.9 (Rudd), 11.6 (Psenner) and 6.2 (BCR) mg kg^{-1} . Taking into account

Table 1. Chromium concentration in various chemical fractions for given sequential extraction methods.

METHOD	STEP	Cr FRACTION	$[\text{Cr}]_{\text{total}}$, $\text{mg} \cdot \text{kg}^{-1}$	$\sum_{i=1}^n [\text{Cr}]_i$ $\text{mg} \cdot \text{kg}^{-1}$
TESSIER	1	exchangeable	0 ± 0.1	32.9 ± 1.4
	2	carbonate	1.7 ± 0.5	
	3	Fe-Mn oxides (or reducible)	3.0 ± 0.2	
	4	organic and sulfide (or oxidizable)	4.9 ± 0.7	
	5	residual	23.3 ± 3.4	
RUDD	1	exchangeable	5.9 ± 2.2	17.9 ± 1.3
	2	adsorbed	1.7 ± 0.8	
	3	organic	1.0 ± 0.5	
	4	carbonate	4.1 ± 0.9	
	5	sulfide	5.2 ± 1.1	
BCR	1	carbonate (acid soluble)	2.3 ± 0.7	6.2 ± 0.6
	2	Fe-Mn oxides (reducible)	2.0 ± 0.8	
	3	organic and sulfide (oxidizable)	1.9 ± 0.7	
GATEHOUSE	1	water-extractable (water soluble)	0.6 ± 0.1	29.7 ± 1.1
	2	ion- exchangeable	8.1 ± 1.4	
	3	Mn-Fe oxides (reducible)	9.6 ± 1.3	
	4	organic and sulfide (oxidizable)	1.2 ± 0.8	
	5	residual	10.2 ± 2.6	
KERSTEN AND FÖRSTNER	1	ion- exchangeable	1.2 ± 0.5	31.2 ± 1.8
	2	carbonate	4.5 ± 1.1	
	3	Mn oxides (easily reducible)	1.8 ± 0.4	
	4	Fe oxides (moderately reducible)	4.2 ± 1.3	
	5	organic and sulfide (oxidizable)	12.3 ± 2.7	
	6	residual (lithogenic crystalline minerals)	7.2 ± 1.6	
PSENNER	1	water soluble	0.5 ± 0.1	11.6 ± 0.7
	2	organic and humus	1.4 ± 0.6	
	3	humus	0.8 ± 0.1	
	4	carbonate, hydroxide Fe and sulfide	1.1 ± 0.5	
	5	clay	7.8 ± 1.0	
SPOSITO	1	ion- exchangeable	4.7 ± 0.7	18.3 ± 0.9
	2	adsorbed	0.6 ± 0.1	
	3	organic	1.0 ± 0.3	
	4	carbonate	0.8 ± 0.1	
	5	sulfide	11.2 ± 1.3	

the total contents of Cr in soil (34.1 mg kg^{-1}), the percentage contents (%) of chromium in soil according to applied methods can be put in order:

BCR (18.2%) < Psenner (34.0%) < Rudd (52.5%) ~ Sposito (53.7%) < Gatehouse (87.1%) < Kersten and Förstner (91.5%) < Tessier (96.5%)

The results indicate that the most reliable method for determination of chemical fraction of Cr in soil are Tessier's as well as Kersten and Förstner's method.

Chemical Fraction of Cr in Soil

Distribution of Cr in soil indicate that its content in various fractions is variable (Fig. 2). It was found that Cr occurs first of all in the organic and sulfide fraction ($12.3 \text{ mg} \cdot \text{kg}^{-1}$ – Kersten and Förstner, 11.2 – Sposito, 5.2 – Rudd) and the residue ($23.3 \text{ mg} \cdot \text{kg}^{-1}$ – Tessier, 10.2 – Gatehouse, 7.2 – Kersten and Förstner), acid soluble, carbonate and adsorbed fraction (1.7 – $\text{mg} \cdot \text{kg}^{-1}$ – Tessier, 2.3 – BCR, 1.7 – Rudd, 4.5 – Kersten and Förstner, 1.1 – Psenner, 1.4 – Sposito), oxide fraction ($3.0 \text{ mg} \cdot \text{kg}^{-1}$ – Tessier, 2.0 – BCR, 1.8 – Kersten and Förstner) as well as in small concentrations in the water soluble and exchangeable fraction (0 – $\text{mg} \cdot \text{kg}^{-1}$ Tessier, 0.6 – Gatehouse, 0.5 – Psenner).

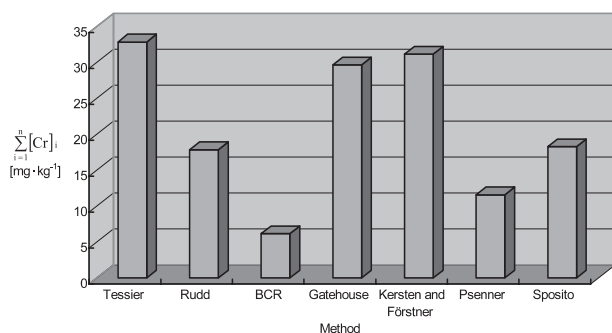


Fig. 1. Summary concentration of Cr in soil ($\sum [Cr]_i$) for individual procedures of sequential extraction.

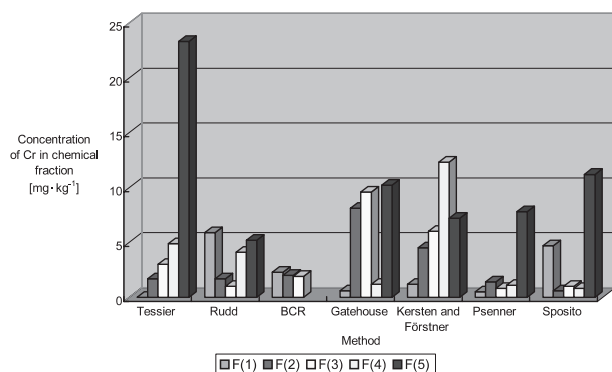


Fig. 2. Distribution of Cr concentration in chemical fraction in soil for various procedures of sequential extraction.

F (1) – exchangeable fraction, F (2) – carbonate fraction, F (3) – oxide fraction, F (4) – organic or sulfide fraction, F (5) – residue.

For Tessier and Kersten and Förstner procedures the Cr fractions can be put in order (except for 5th fraction i.e. residue):

Cr (exchangeable) < Cr (carbonate) < Cr (oxide) < Cr (organic, sulfide)

For remaining procedures: Rudd, BCR, Sposito, Psenner and Gatehouse no regular dependences of Cr amount in individual chemical fraction was obtained.

Results indicate the possibility of transfer of Cr from soil to soil environment in conditions of neutral condition or weak acid condition (pH=5). Obtained order of Cr fraction in soil can change in time depending on physicochemical parameters of soil, special pH and temperature, that lead to change of solubility of Cr compounds and their tendency to extract from soil to soil environment.

Characterization of Water- and Acid-Soluble Cr

Fractions of Cr: soluble in water and soluble in acids adequately equals to ($\text{mg} \cdot \text{kg}^{-1}$): 0.5 (Psenner), 1.7 (Tessier), 2.3 (BCR), 5.3 (Sposito), 5.7 (Kersten and Förstner), 7.6 (Rudd) and 8.7 (Gatehouse) – Table 1. Considering total amount of Cr extracted from soil to solution in the form of exchangeable fraction in ratio of total content of Cr in soil ($34.1 \text{ mg} \cdot \text{kg}^{-1}$), the results attributed to studied methods can be put in order:

Psenner (1.5%) < Tessier (5.0%) ~ BCR (6.7%) < Sposito (15.5%) ~ Kersten and Förstner (16.7%) < Rudd (22.3%) < Gatehouse (25.5%)

This indicated that maximum amounts of Cr as exchangeable fraction and soluble in acids fraction are obtained by the use of Rudd and Gatehouse method.

Conclusions

The various methods of sequential extraction of Cr from soil (Psenner, Tessier et al., BCR, Sposito, Kersten and Förstner, Rudd, Gatehouse) were studied in order to characterize chemical fraction and was it found the yield of extraction varied from 18.2% (BCR) to 96.5% (Tessier) of chromium content in soil (34.1 mg kg^{-1}).

The chromium content in particular fractions using sequential extraction methods was in order exchangeable fraction < carbonate < oxide < organic (sulfide) by Tessier, Kersten and Förstner methods, while other studied procedures (Rudd, Gatehouse, Psenner, BCR, Sposito) did not give any regular trends in Cr amount for individual chemical fraction.

The best method for determination of fractions soluble in water and soluble in acids (carbonate and adsorbed) was obtained by Gatehouse method. This seems to be important in the context of the important issue of transfer of chromium from soil to soil solutions in natural conditions.

Optimum conditions of Cr chemical fraction extraction were established. In order to extract exchangeable fraction of chromium (pH = 7) $1 \text{ mol l}^{-1} \text{ KNO}_3$ solution

(16 h in 25°C – Rudd) should be applied. Next, in order to elute adsorbed and carbonate fraction the extraction by means of acetate buffer (pH = 5, 5h in 25°C – Kersten and Förstner) is recommended to apply. In order to extract oxide fraction of chromium the use of 0.1 mol l⁻¹ NH₂OH HCl in CH₃COONH₄/CH₃COOH (pH = 4.5, 20 min in 25°C – Gatehouse) is recommended, which should be followed by extraction with 4 mol l⁻¹ HNO₃ (16 h in 80°C – Sposito) for sulfide fraction and 30% H₂O₂ in HNO₃ (pH = 2, 5h in 80°C) for organic fraction and finally followed by extraction with 3.2 mol l⁻¹ CH₃COONH₄ in 20% HNO₃ (30 min in 25°C – Tessier). The extraction of Cr from soil residue should be performed by mineralization in HNO₃/HClO₄ (2 h in 90°C) by Tessier's method.

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