

SEQUENTIAL EXTRACTION AND VALUATION OF DIFFERENT FORMS OF CHROMIUM IN SOIL

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Abstract: Influence of chromium on the course of biochemical reactions in the environment depends among others on possibility of its getting from soil to soil solutions. In practice this process is investigated among others by performance of the sequential extraction of soil and characterization of chemical fraction of chromium. Chromium description in soil eluates requires establishing conditions of preparation of a soil sample for researches, performing of the sequential extraction of soil and chromium determination in obtained solutions. Influence of a grain diameter and drying temperature of soil and time of extraction, volume of the eluent and leaching temperature on the final result of Cr extraction from soil to solutions and its determination in eluates were performed. Optimum conditions of Cr extraction from soil and its analysis were established. The estimate of contents of various fraction of Cr in soil was performed as well as it was found not large contents of exchangeable chromium and higher Cr contents in residual.

Key words: soil, sequential extraction of soil, chromium, FAAS

INTRODUCTION

Chromium exists in environment and living organisms first of all in two species, as Cr(III) and Cr(VI). Above two oxidation species of Cr having various properties and biological activity on living organisms. Trivalent chromium is considered as a trace element essential for the proper functioning of living organisms, because it is needful for proper glucose metabolism. Hexavalent chromium has toxic and mutagenic properties related to its oxidizing activity [2]. Presence chromium(VI) in excess, damages circulatory system and causes the carcinogenic changes.

In the view of chromium contribution in food chain: soil-plant-animal-man and its influence on the course of biochemical reactions in the environment depends among others on possibility of its getting from soil to soil solutions. In practice this process is investigated by performance of the sequential extraction of soil, which is one of methods of soil leaching. Obtained aqueous solutions (soil eluates) after the sequential extraction for a given soil have various chemical composition depending among others on a used leaching reagent, conditions of performing the process and the initial condition of soil. Recovery factor of chromium from

soil to soil eluates depends on its distribution among various chemical fractions in soil and projects on its availability for living organisms. Analysis various fraction of chromium constitutes operational or functional approach to the problem of Cr speciation. So far conditions of total chromium determination [3] and conditions of Cr(VI) determination in soil eluates with MgCl_2 and $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ [4] were elaborated. Extraction procedures of soil are used both for the single-stage leaching and the sequential extraction [1,5,7,8]. Among various methods of the sequential extraction of soil, Tessier's method is most often used both in case of soil samples, as well as sediments [8]. Soil eluates (1) - (5) include various metals fractions are obtained by treating soil with solutions in turn: 0.5 M MgCl_2 (pH = 7), the exchangeable fraction; acetate buffer $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ (pH = 5), the carbonates fraction; 0.04 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 25 % CH_3COOH , the oxides fraction - metals bound to iron and manganese oxides; 30 % H_2O_2 (pH = 2) and followed by 3.2 M $\text{CH}_3\text{COONH}_4$ in 20 % HNO_3 , the organic fraction; HF and HClO_4 (5:1) [8] or HNO_3 and HClO_4 (1:2) [3], the final soil digesting. The conditions of sequential extraction of soil are shown in Tab. 1.

The investigations of chromium chemistry with using its fractionation covers among others a stage of soil preparation for the sequential extraction, the sequential extraction of soil and chromium determination in the obtained solutions. The conditions of soil sample preparation for research and carrying out the extraction should protect the total extraction of Cr fraction from soil to solutions and recurrent analytical results.

Table. 1. Conditions of sequential extraction of soil.

SOIL		
STAGE 1	0.5 M MgCl_2 , pH = 7	Fraction I Exchangeable metals
STAGE 2	$\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$; pH = 5	Fraction II Metals bound to carbonates
STAGE 3	0.04 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 25 % CH_3COOH ; 96 °C	Fraction III Metals bound to iron and manganese hydrated oxides
STAGE 4	a) 30 % H_2O_2 ; pH = 2, HNO_3 ; 85 °C b) 3.2 M $\text{CH}_3\text{COONH}_4$ in 20 % HNO_3	Fraction IV Metals bound to organic matter
STAGE 5	Mineralization – HF and HClO_4 (5:1)	Fraction V Residual metals

The references describe various procedures the sequential extraction of soil and bottom sediments [1,5,7,8] 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 and it does not constitute larger difficulty. The cause is probably incomplete Cr extraction from soil to solution in conditions of the sequential extraction of others metals. Therefore investigations of influence of soil sample preparation conditions and carrying out the extraction of Cr to solutions become purposeful [5]. The researches of conditions of soil sample preparation (a grain diameter, drying temperature) and conditions of carrying out the sequential extraction (time, volume of the eluent, temperature) on the final result of Cr extraction from soil and its determination in soil eluates were done. The optimum conditions of sequential extraction of Cr from soil were established and chemical fraction of Cr in soil were investigated and described.

EXPERIMENTAL

For researches surface soil (0-15 cm, grassy soil) from the Rzeszów town (Poland) and air-dried soil samples were used of a mass of 10.00 g and grain diameter $\phi_{\text{soil}} = 0.25$ mm. Volume of the eluent for every stage of extraction was equal to $V_{\text{eluate}} = 30$ ml. $[\text{Cr}]_{\text{total}}$ by spectrophotometric method with 1,5-diphenylcarbazide (DPC) and FAAS. Measurements were carried out by means of a spectrophotometer of the BECKMAN company, type DU-640 ($\lambda = 545$ nm [6]) and absorption atomic spectrometer model 3100 of the PERKIN-ELMER company ($\lambda = 357.9$ nm for Cr in presence of 1 % NH_4Cl [3]).

Analysis of the total Cr was carried out in established conditions for Cr analysis in reference soil (BPGM-1, brown soil, the certified Cr content: total with HF - $15.8 \text{ mg} \cdot \text{kg}^{-1}$, total direct - $26.3 \text{ mg} \cdot \text{kg}^{-1}$ – The Central Office of Measures, Warsaw), obtaining accuracy $\eta > 98$ %. Determination of total chromium by the FAAS method [3] was performed directly in solutions after soil mineralization and in soil eluates for established optimum conditions of sequential extraction of soil. Possibility of verification of analytical results was also found by drawing up the mass balance of chromium in the research systems.

RESULTS DISCUSSION AND CONCLUSIONS

The results of investigations indicate that degree of soil grinding has essential influence on extraction of chromium from soil to a solution. This influence is particularly visible for grains having a diameter $\phi > 0.5$ mm. Thus grain diameter of soil used for leaching should not

be larger than $0.25 \div 0.5$ mm (Fig. 1). Moreover the investigations results indicate that temperature of soil drying, similarly like previous parameters, influences extraction of chromium from soil to soil eluates (Fig. 2).

Investigations proved influence of the leaching time of soil on the final result of chromium determination in soil eluates. This influence is particularly visible for time $t_{\text{extn}} < 1$ hour. However, for $t_{\text{extn}} = 1$ hour the total chromium practically extracts from soil to eluates. Moreover was investigated influence of the eluate volume and leaching temperature (the working temperature) on the final result of chromium extraction from soil to a solution and its determination. 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 $V_{\text{solution}} [\text{ml}] : m_{\text{soil}} [\text{g}] \geq 3 : 1$. It was found that increase of the extraction temperature in the studied range slightly influences extraction of Cr from soil to F(1) - F(2) water fractions. Since additional heating of the system is burdensome in practice, therefore ambient temperature ($\pm 20^{\circ}$ C) should be accepted as the optimum temperature of soil leaching for F(1) - F(2) fractions.

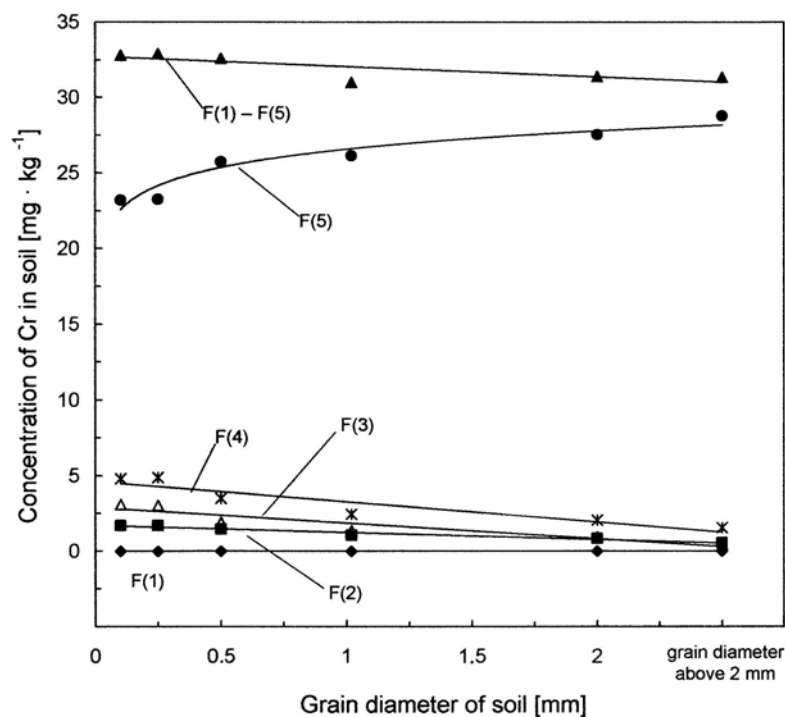


Fig. 1. Influence of grain diameter of soil on chromium extraction from soil to solution in process sequential extraction by Tessier's method. The number of Cr fraction: F(1) – exchangeable fraction, F(2) – carbonates fraction, F(3) – oxides fraction, F(4) – organic fractions, F(5) – residual fractions, ▲ - [Cr] total.

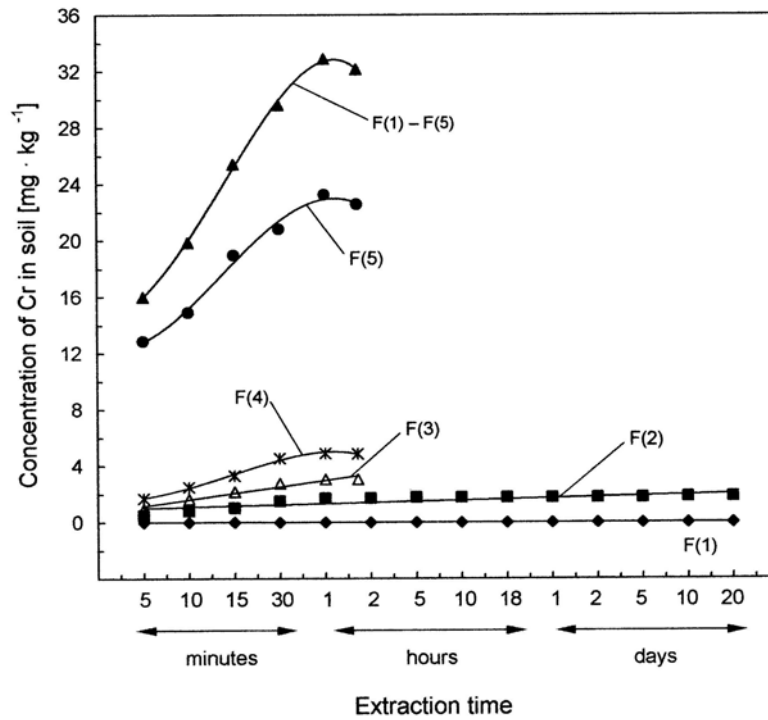


Fig. 2. Influence of sequential extraction time (by Tessier's method) on chromium extraction from soil to solution.
 The number of Cr fraction: F(1) – exchangeable fraction, F(2) – carbonates fraction, F(3) – oxides fraction, F(4) – organic fractions, F(5) – residual fractions, ▲ - [Cr] total.

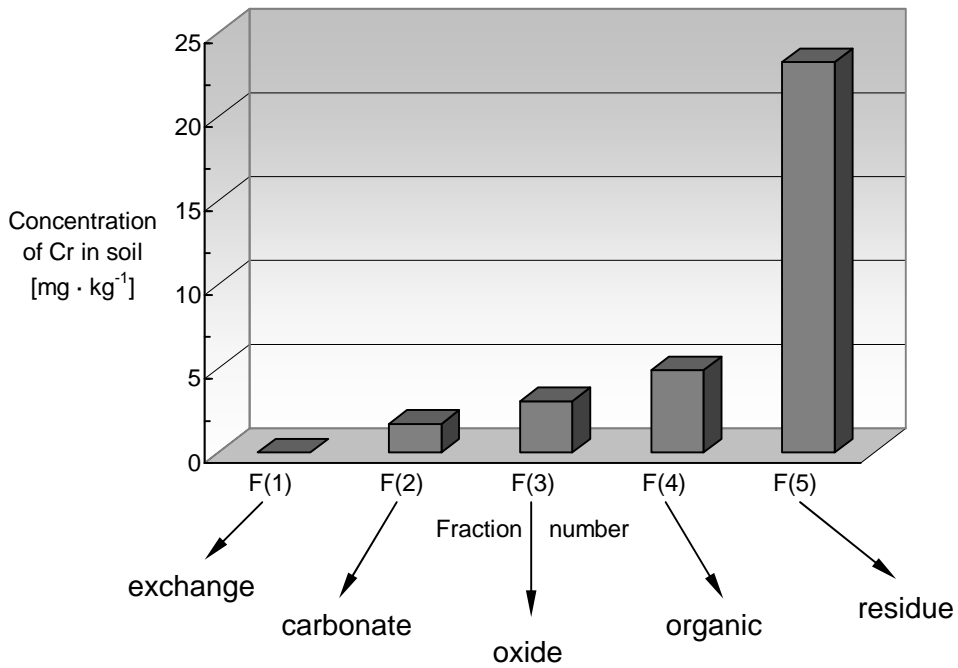


Fig. 3. Distribution of Cr in surface soil (depth of 5 cm, from the Rzeszow town, Poland) after the sequential extraction by Tessier's method.

The quantitatively estimate of chemical fraction of Cr in soil. Distribution of Cr in surface soil is shown in Fig. 3. It was found that Cr occurs first of all in the organic fraction ($4.7 \text{ mg} \cdot \text{kg}^{-1}$) and the soil residue ($23.0 \text{ mg} \cdot \text{kg}^{-1}$) as well as in not larges concentrations in the exchangeable, carbonate and oxide fraction (0.7 , 1.8 and $2.7 \text{ mg} \cdot \text{kg}^{-1}$). The verification of analytical results was performed by comparing the total content of chromium in soil ($[\text{Cr}]_{\text{total}} = 33.4 \pm 3.7 \text{ mg} \cdot \text{kg}^{-1}$, $n = 6$ and $p = 95 \%$) with the sum of Cr contents in appropriate chemical fractions ($\sum_{i=1}^5 [\text{Cr}]_i = 32.9 \pm 2.2 \text{ mg} \cdot \text{kg}^{-1}$, $n = 4$ and $p = 95 \%$) obtaining relative scatter of results doesn't exceed 2 %. The obtained results in the scope of the mass balance of Cr also indicate the possibility of using this procedure to verification of analytical results.

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