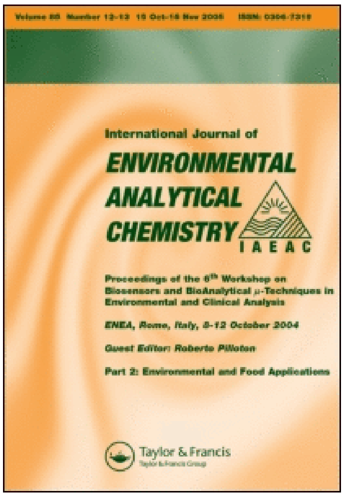

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OPTIMIZATION OF EXTRACTION PROCEDURE FOR DETERMINATION OF TOTAL WATER-SOLUBLE CHROMIUM AND CHROMIUM(VI) IN VARIOUS SOILS

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The parameters influencing the extraction efficiency of total water-soluble chromium and chromium(VI) in clay, peat and sandy soils were investigated. Water and a KH_2PO_4 solution (0.015 mol dm^{-3}) were used as extractants. Samples were ultrasonicated or shaken in classical shakers. Variations of solution volume-to-soil weight ratio, and of shaking time were studied in order to develop the optimal extraction procedure for the determination of total water-soluble chromium and chromium(VI). Soil samples treated with tannery waste continuously for 17 years and soils freshly contaminated with the same waste were studied.

KEY WORDS: Chromium, Chromium(VI), Chelating ion-exchange chromatography, Electrothermal AAS, Extraction procedure, Soil extracts.

INTRODUCTION

Chromium occurs in natural systems mainly in the trivalent and hexavalent oxidation states. Trivalent chromium is an essential element in low concentrations, while chromium is toxic and carcinogenic in the hexavalent state. It is therefore very important, from an environmental and a toxicological point of view, to develop reliable analytical techniques for the determination of chromium in its chemical forms. The relative bond strengths of metals in different soil phases can be determined through sequential extraction procedures. When combined with biological uptake data, the toxicity of metal pollutants could be appraised.

Separation of various chemical forms of a particular element in soil is very important in studies of its distribution and availability to plants. The kinetics and mechanisms of element transformation from one chemical form to another can be studied under different soil conditions, using fractionation techniques. Sequential extraction procedures should achieve efficient removal of an element from a particular phase, so the optimal conditions for an extraction procedure should be studied.

Many investigations have been carried out to develop various fractionation techniques to study the distribution of microelements between different soil or sedimentary phases[1-11]. Calmano and Forstner[1] studied the distribution of heavy metals among major sedimentary phases in polluted rivers by applying a five-step sequential extraction procedure. The weight-to-volume (w/v) ratio used was 0.5 g/50 cm^3. Schuman[2] reported a fractionation scheme for the determination of Zn, Mn and Cu distributed among exchangeable, organic matter, and Fe oxide fractions in various soil samples. Tessier[3] suggested a sequential extraction procedure for the partitioning of particular trace metals among five fractions in river sediments (exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual). In this scheme, 1 g of sediment sample was extracted with 8 cm^3 of $MgCl_2$ (1 mol dm^{-3}) or sodium acetate (1 mol dm^{-3}) to determine the exchangeable metal fraction. In some of the following fractions the w/v ratio was changed. Rauret *et al.*[4] reported the optimization of the Tessier procedure for metal solid speciation in river sediments. In this work, special attention was paid to optimizing the volume-to-weight (v/w) ratio. The exchangeable fraction was disregarded because the amounts of metals released were negligible in comparison to the total metal content. In the second fraction (metals extracted by acetic acid-acetate buffer, pH=5), the v/w ratio proposed by Tessier was increased by ten. At higher v/w ratios a substantial release of lead from the heavily polluted sediments was observed. The differences in release of metals at various v/w ratios were observed also in all other fractions of the Tessier scheme. The study indicated that an optimized v/w ratio procedure or repeated successive extraction procedure should be applied to achieve efficient extraction in a particular phase. Numerous extraction procedures were also studied by other investigators[5-11]. Various v/w ratios, shaking times and extractant types were proposed for the determination of elements in the particular soil phases. Lake *et al.*[5] published a review paper on fractionation, characterization and speciation of heavy metals in sewage sludge and sludge-amended soils. Various extraction procedures were reported and the results of different extraction schemes compared, although variations in reagent strength, volume, and extraction time for different schemes were apparent. Bartlett and James[12] and James and Bartlett[13,14] studied the behaviour of chromium in soils. They proposed $KH_2 PO_4$ (0.01 mol dm^{-3}) to extract efficiently the water-soluble chromate and chromate sorbed on various oxides and clay particles. Applying this procedure, the oxidation[12], reduction[13], and adsorption[14] processes of chromium in various soil samples were studied. Grove and Ellis[15] investigated the fate of Cr(VI), Cr(III) and sludge chromium which had been added to soils. Deionized-distilled water was used as a first extractant in the fractionation scheme. The results reported for the concentration of total water-soluble chromium and chromium(VI) were presumably too low due to the inefficient desorption of chromium(VI) with water.

The results of various extraction schemes, even those reported for the water-soluble fraction, are often scarcely comparable due to the discrepancies in the procedures used in fractionation studies of soil and sediment samples. The aim of our work was a systematic study and optimization of the most important parameters (soil particle size, type of extractant, shaking time and the way of shaking, v/w ratio) influencing the extraction efficiency for the determination of total water-soluble chromium and chromium(VI) in various soil samples.

EXPERIMENTAL

Instrumentation

An atomic absorption spectrometer (Varian AA 575 with an HGA 76B Perkin-Elmer graphite furnace) was employed for the determination of total water-soluble chromium and separated chromium species in various soil extracts and chromatographic effluents. A peristaltic pump (Ismatec MS4 Reglo) was applied in chelating ion-exchange separations. 38-cm^3 polyurethane tubes were used for extraction of total water-soluble chromium and chromium(VI). A mechanical home-made shaker or Cole-Parmer (4710 Series) Ultrasonic Homogenizer were used for shaking of samples. Soil extracts were centrifuged with a Heraeus Sepatech Biofuge 17S.

Reagents

Merck suprapur acids and doubly distilled water were used for the preparation of samples and standard solutions. All other chemicals were of analytical reagent grade. Standard chromium(VI) (potassium dichromate) and chromium(III) (chromium metal powder (99.99%) dissolved in hydrochloric acid) stock solutions (Cr: 1000 $\mu g\ cm^{-3}$) were used.

Sigma chelating resin Chelex-100, sodium form, 50–100 mesh was used for the separation of chromium species. A mixture of 150 cm^3 HCOOH (0.1 mol dm^{-3}) and 98.5 cm^3 KOH (0.1 mol dm^{-3}), diluted with water to 1000 cm^3 was used to adjust the pH to 4. Sartorius 0.2–0.01 μm cellulose nitrate membrane filters of 25 mm diameter were used in the filtration procedure.

Samples

The concentrations of total water-soluble chromium and chromium(VI) were determined in three different soil types (clay, peat and sandy soil) which were treated with tannery waste and analysed six months after the waste application. Soil samples from the field (silty clay loam texture) treated with the same waste continuously for 17 years were also analysed in the fourth year after the last application. The concentrations of total chromium in these samples before contamination were between 50 and 110 $\mu g\ g^{-1}$. After the application of tannery waste, the concentrations were 2470 $\mu g\ g^{-1}$ in clay soil, 3730 $\mu g\ g^{-1}$ in peat soil, 2360 $\mu g\ g^{-1}$ in sandy soil, and 1400 $\mu g\ g^{-1}$ in field soil. The moisture content of the samples was between 20 and 30%, with the exception of peat soil (about 50%).

Sample preparation and determination of total water-soluble chromium and chromium(VI)

Samples were stored in closed polyethylene bags at 277 K and were analysed within seven days after storage. All analyses were done in triplicate. 2.00 g of moist soil samples were shaken with 20 cm^3 of water or KH_2PO_4 solution (0.015 mol dm^{-3}). Samples were shaken either in a classical shaker (1–8 h) or in an ultrasonic immersion device (12 W ultrasonic power output, 5 min ultrasonic agitation). Samples were then centrifuged (10.000 rpm, 20 min), decanted and filtered through membrane filters of various pore sizes (0.2–0.01 μm). The concentrations of total water-soluble Cr in these extracts were determined by electrothermal atomic absorption spectrometry (ETAAS) at optimal measurement conditions[16]. Aliquots of these solutions were used to separate chromium species on Chelex-100 chelating ion-exchange resin[16]. This method was chosen because of its high sensitivity and short time of analysis. The (ammonium-form) resin[17] was slurried with water and transferred to the column (1 cm^3 plastic pipette tip) connected to a peristaltic pump. The column resin was equilibrated with buffer solution (pH=4), followed by passage of a buffered sample (5 cm^3 of sample and 5 cm^3 of buffer) at a flow rate of 1 cm^3 min^{-1}. The eluate was washed with 15 cm^3 of buffer at a flow rate of 4.5 cm^3 min^{-1}. Sample eluent was collected into 50 cm^3 beakers, acidified with 0.2 cm^3 of nitric acid (1 + 1) and evaporated to approx. 2 cm^3. The evaporated samples were transferred to 5 cm^3 volumetric flasks, and diluted with water to the mark. The same procedure was applied to the blank solution. Chromium(III) species were retained by the column resin while chromium(VI) passed through and was measured by ETAAS in the eluate. Some moderately labile Cr(III) organic complexes could partially pass through the resin column and yield apparently higher Cr(VI) values. The latter may produce positive systematic errors in the determination of chromate in soil extracts, the extent of which is evident from our previous work[16].

RESULTS AND DISCUSSION

Influence of particles on determination of total water-soluble chromium in soil extracts

The influence of particles in soil extracts on the determination of total water-soluble chromium was investigated. 2.00 g of moist soil samples were extracted with 20 cm^3 of water or KH_2PO_4 (0.015 mol dm^{-3}) by shaking in a classical shaker for 2 h, centrifuged, decanted and filtered through membrane filters of various pore size (0.2, 0.1, 0.05 and 0.01 μm). Total water-soluble chromium in these extracts was determined by ETAAS. The results are presented in Figure 1A and Figure 1B. It can be seen from these figures that filtering through 0.2 μm membrane filters did not remove particles and colloids from the solution efficiently. These fine particles and colloids contain chromium and contribute to the AAS signal. This effect is particularly pronounced in soils with a high clay fraction and is larger when water is used as an extractant: obviously, KH_2PO_4 is an electrolyte which inhibits the formation of colloids in the extracting solution. It is also evident that when water is used as an extractant (Figure 1A), filtering through 0.05 μm membrane filters should be employed to efficiently remove particles and colloids from soil extracts. The only exception is sandy soil with coarser particles where filtering through 0.1 μm membrane filters is sufficient. When extraction with KH_2PO_4 (0.015 mol dm^{-3}) is applied (Figure 1B), the efficient removal of particles from soil extracts is achieved with filtering through 0.1 μm membrane filters.

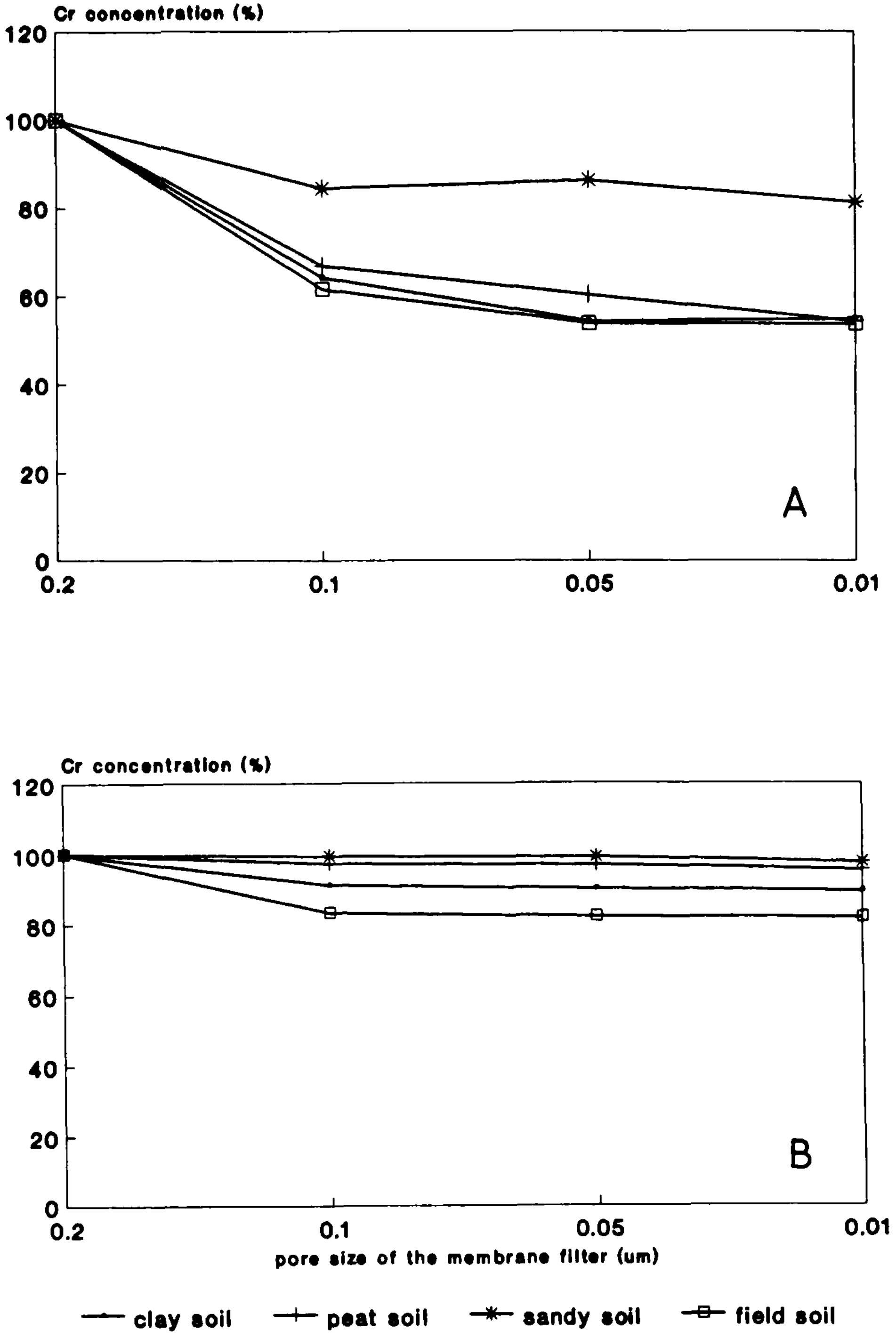

Figure 1 The influence of filtration on concentration of: (A)—total water-soluble chromium; (B)—total KH_2PO_4 soluble chromium (2.00 g moist soil in 20 cm^3 of extractant).

Influence of shaking time (classical shaking) on determination of total water-soluble chromium and chromium(VI) in soil extracts

The influence of shaking time on the concentration of total water-soluble chromium and chromium(VI) was studied. 2.00 g of moist soil samples were extracted with 20 cm^3 of water or KH_2PO_4 (0.015 mol dm^{-3}) by shaking in a classical shaker for 1, 2, 4 or 8 h. Total water-soluble chromium and chromium(VI) were determined using the procedure described above at optimal conditions of measurement. The results for all samples are presented in Figures 2A–2D. When samples were extracted with KH_2PO_4 (0.015 mol dm^{-3}), equilibrium of total soluble chromium and chromium(VI) between the solid and liquid phases was established after 2 h when shaking clay (Figure2A) and field (Figure 2D) soils. Equilibrium

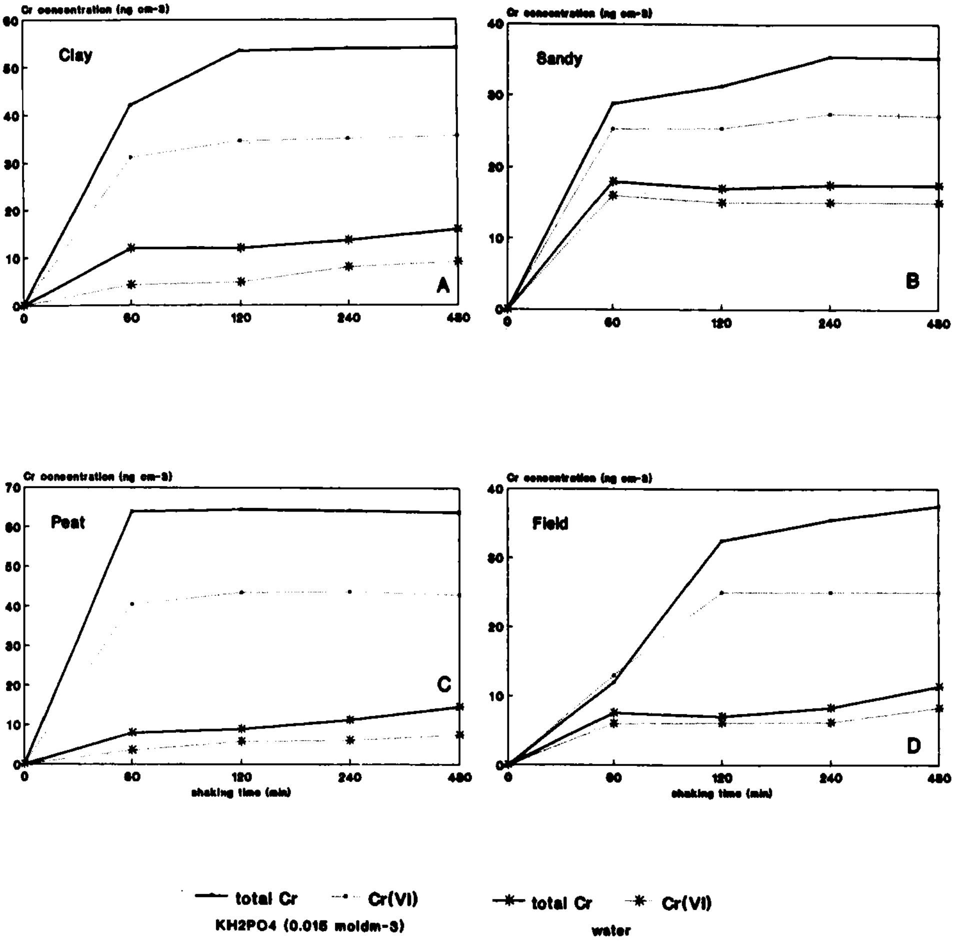

Figure 2 The influence of shaking time on concentration of total water-soluble and total KH_2PO_4 soluble chromium and chromium(VI) in: (A)—clay soil; (B)—sandy soil; (C)—peat soil; (D)—field soil (2.00 g moist soil in 20 cm^3 of extractant).

was achieved after 1 h of shaking for sandy (Figure 2B) and peat (Figure 2C) soil samples. During extraction with water, the concentration of total water-soluble chromium and chromium(VI) was moderately increased and the equilibrium between the solid and liquid phases established after about 8 h of shaking in all samples (Figures 2A–2D). This was a result of a gradual desorption of chromate from clay particles. The discrepancies observed in clay, peat and field soils were presumable due to the experimental error. However, even after 8 h of shaking the concentrations of total water-soluble chromium and chromium(VI) were substantially lower than those obtained by KH_2PO_4 (0.015 mol dm^{-3}) extraction. These findings are in agreement with those of Bartlett and James[12], who proposed KH_2PO_4 for efficient extraction of water-soluble chromium and chromium(VI) sorbed on various oxides and clay particles.

Comparison between classical shaking and ultrasonic agitation on determination of total water-soluble chromium and chromium(VI) in soil extracts

Classical shaking (2 h) and ultrasonic agitation (5 min of immersion ultrasonic agitation) were compared with the extraction of 2.00 g of moist soil samples with 20 cm^3 of KH_2PO_4 (0.015 mol dm^{-3}). After filtration through 0.2 μm and 0.05 μm membrane filters, the total water soluble chromium and chromium(VI) in soil extracts were determined. The results are presented in Table 1. In the case of ultrasonic agitation, filtering through a 0.2 μm membrane filter did not remove particles and colloids efficiently, as was found previously with classical shaking. Table 1 also shows that the concentrations of total water-soluble chromium and chromium(VI) were higher in extracts of the freshly contaminated soil samples than in those of the field soil sample. Obviously, during long-term application, chromium present in the tannery waste in the field soil was transformed and incorporated into the less soluble fractions of the soil, while in freshly contaminated samples more chromium was bound to the labile, easily soluble fractions of the soil and of the waste itself. It is also evident that the observed concentrations of total water-soluble chromium and chromium(VI) in freshly contaminated soil samples are higher with classical shaking than with ultrasonic agitation. When ultrasonic agitation is applied for 5 min, the equilibrium concentration of chromium (total water-soluble chromium and chromium(VI)) is not achieved between the solid and liquid phases. For total equilibration in the liquid phase of soil samples freshly contaminated with tannery waste, a longer ultrasonic agitation time should be applied. The concentrations of total water-soluble chromium and chromium(VI) in the field soil sample from Table 1. are comparable for ultrasonic agitation and classical shaking. The chromium from tannery waste in this sample is almost transformed and incorporated into the soil, so 5 min of ultrasonic agitation is enough to achieve equilibrium between the solid and liquid phases. Ultrasonic agitation is very convenient due to its short shaking time (5 min) needed for various soil samples. The exception are soil samples freshly contaminated with different waste materials. In those samples, either longer ultrasonic agitation times or 2 h of classical shaking should be applied.

Table 1 Comparison between classical shaking and ultrasonic homogenization on determination of total KH_2PO_4 soluble chromium and chromium(VI) in various soil samples (2.00 g moist soil in 20 cm^3 KH_2PO_4 0.015 mol dm^{-3}).

Soil sample	*Shaking**	*TOTAL SOLUBLE CHROMIUM***		*CHROMIUM(VI)****
		0.2μm filter (ng cm^{-3})	*0.05 μm filter (ng cm^{-3})*	*0.05 μm filter (ng cm^{-3})*
Clay soil	C	425	163	72
	U	91	89	52
Sandy soil	C	426	95	46
	U	79	53	31
Peat soil	C	163	40	30
	U	47	31	22
Field soil	C	44	39	33
	U	46	36	32

*C—classical shaking (2 h); U—immersed ultrasonic agitation (5 min)
**ETAAS.
***Chelating ion-exchange—ETAAS.

Influence of v/w ratio on concentration of total water-soluble chromium in soil extracts

1.00 g of moist soil sample was mixed with 5–300 cm^3 of water or KH_2PO_4 (0.015 mol dm^{-3}) and shaken for 2 h on a classical shaker. The concentration of total water-soluble chromium in soil extracts was determined by the procedure described above. The results for clay, sandy, peat and field soils are presented in Figures. 3A,B–6A,B. The influence of the

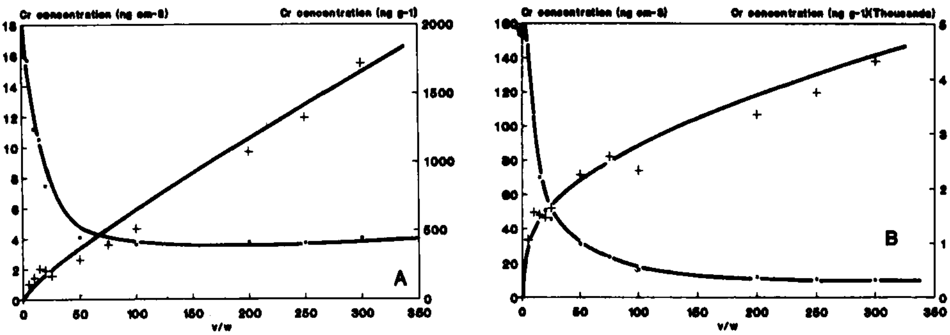

Figure 3 The influence of v/w ratio in clay soil on concentration of: (A)—total water-soluble chromium; (B)—total KH_2PO_4-soluble chromium (1.00 g of moist soil).

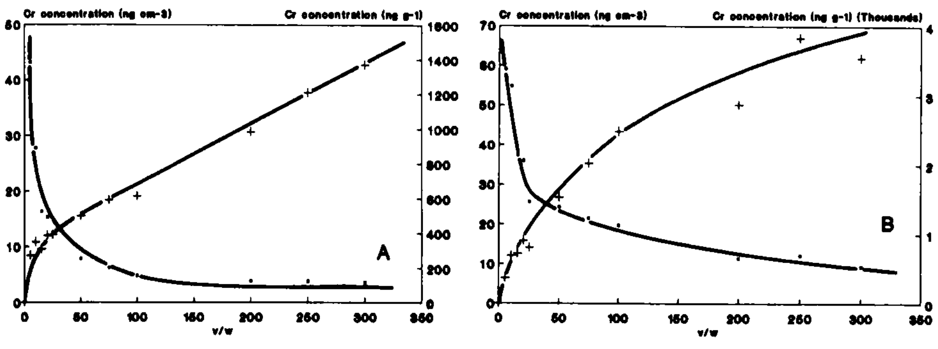

Figure 4 The influence of v/w ratio in sandy soil on concentration of: (A)—total water-soluble chromium; (B)—total KH_2 PO_4-soluble chromium (1.00 g of moist soil)

v/w ratio is the same in all soil samples. The concentration of total water-soluble chromium applying extraction with water or KH_2 PO_4 (0.015 mol dm^{-3}), expressed in ng cm^{-3}, seems to decrease exponentially with an increasing v/w ratio. Lower concentrations of total water-soluble chromium appear to be due to inefficient desorption of chromium(VI) bound to clay minerals and humic substances, when water is used as extractant. Concentration of total water soluble chromium in extracts is practically constant at v/w ratios higher than 75. As a result the concentration of total water soluble chromium in soil expressed in ng/g increases almost linearly with v/w ratio. Taking into consideration the homogeneity of the soil samples, and to avoid large volumes, a v/w ratio of 10 is proposed for analytical use (20 cm^3 of extractant and 2.00 g of soil sample).

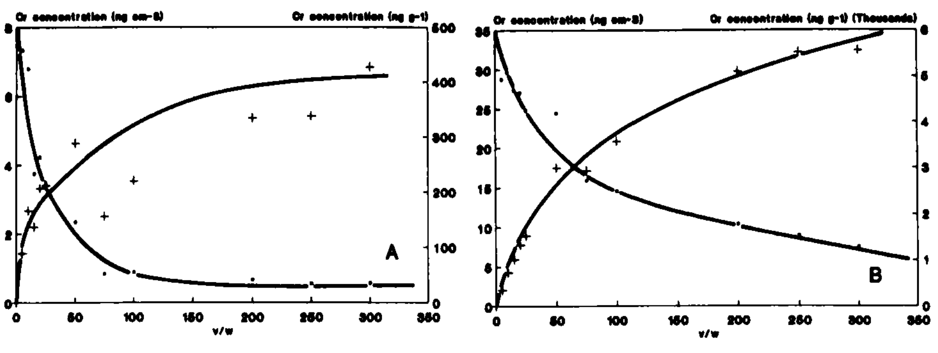

Figure 5 The influence of v/w ratio in peat soil on concentration of: (A)—total water-soluble chromium; (B)—total KH_2 PO_4-soluble chromium (1.00 g of moist soil).

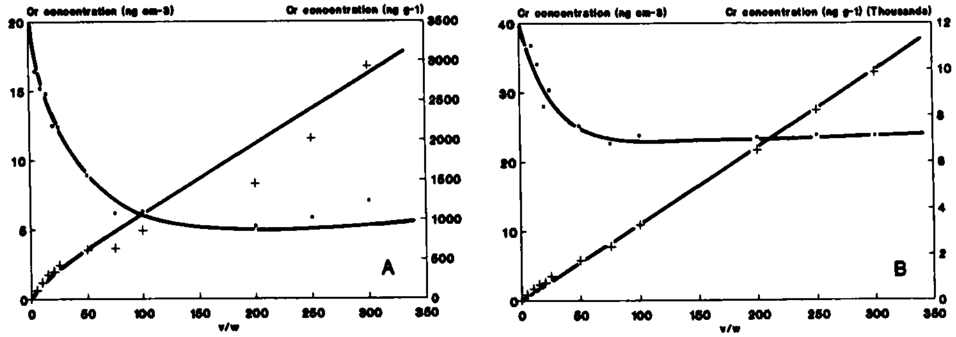

Figure 6 The influence of v/w ratio in field soil on concentration of: (A)—total water-soluble chromium; (B)-total KH_2PO_4-soluble chromium (1.00 g of moist soil).

CONCLUSIONS

The parameters influencing the extraction efficiency of total water-soluble chromium and chromium(VI) were investigated in clay, peat and sandy soils, freshly contaminated with tannery waste, and in field soil, contaminated with the same waste, four years after the last waste application. Water or a KH_2PO_4 solution (0.015 mol dm^{-3}) were used as extractants. The latter, being an electrolyte, desorbs chromium(VI) from clay particles and humic substances more efficiently than water, so it should be used as extractant in the determination of total water-soluble chromium and chromium(VI) in soil samples. Particles and colloids carrying chromium in soil extracts should be removed prior to analysis, otherwise too high results of total water-soluble chromium and chromium (VI) are obtained. Filtering through 0.1 μm membrane filters is recommended for the efficient removal of particles and colloids when using KH_2PO_4 as an extractant, and 0.05 μm filters for water extraction. The equilibration of total water-soluble chromium between solid and liquid phases is achieved after 2 h of shaking in a classical shaker when using KH_2PO_4 (0.015 mol dm^{-3}) as an extractant, and after 8 h when using water. 5 min of immersion ultrasonic agitation is very convenient for many soil samples. However, with samples freshly contaminated with tannery waste, longer ultrasonic agitation should be applied to ensure equilibrium of total water-soluble chromium and chromium(VI) between solid and liquid phases of untransformed waste material. The influence of the $^v/w$ ratio was also studied in order to develop the optimal extraction procedure for total water-soluble chromium and chromium(VI). In actual praction, 20 cm^3 of extractant and 2.00 g of soil samples are used for the determination of total water-soluble chromium and chromium(VI).

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