Comparison of Two Sequential Extraction Procedures for Trace Metal Partitioning in Ore Samples From the Keban Region in Elazığ, Turkey

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INTRODUCTION

Metal mobility powerfully relies on the chemical forms or types of binding of the element in the environment. Determination of total metal concentration in solids does not totally inform about the mobility of metals (1-3). However, it is important to assess the heavy metal burden because metal cations in solids can exist in a variety of physico-chemical forms, i.e., simple or complex ions, easily exchangeable ions, organically bound, occluded by or coprecipitated with metal oxides or carbonates or phosphates and secondary minerals, or ions in crystal lattices of primary minerals (1, 4-7). Besides, it is difficult to determine the particular chemical species or binding forms (8-11). For that reason, sequential extraction procedures are usually practiced since they provide information about the origin, mode of formation, mobilization and presence of trace metals (1, 12). The extractants serve to increase the reactivity of the sequential extraction schemes (SEs) and of the obtained fractions corresponding to metal association forms with lesser mobility. In sequential extraction schemes, the commonly used extractants separate the following groups: unbuffered salts, weak acids, reducing agents, oxidizing agents, and strong acids (13, 14)

In a literature survey, it was found that various chemical extractants can be used and there are numerous sequential extraction

ABSTRACT

The objective of this research was to compare two sequential extraction procedures, modified Tessier and revised BCR, for the fractionation study of Fe, Cu, Co, Pb, Zn, and Mn in ore samples obtained from the Keban Region, Turkey. The efficiency and suitability of these procedures and their corresponding extraction steps for partitioning the heavy metals bound to the solid forms were tested. Metal analysis was carried out by inductively coupled plasma optical emission spectrometer (ICP-OES). The two procedures were examined and showed that there are differences in the bonding forms of the metals to ore and in the properties of the reactants used. Because of these differences, the amount of metals passing through the solution are different in the two procedures.

schemes based on the fractions. These vary in the use of extractants, objective phases, and the order of separation of each particular form of the metal. (15-19) Tessier et al. (19) proposed a five-step procedure which was one of the first SEs and later, most schemes used the five-step procedure (13, 20-22). This scheme has been extensively utilized for the separation of exchangeable metals, metals bound to carbonates, iron manganese oxides, organic matter; and for residual metal which is referred to as exchangeable, weakly absorbed, hydrous oxide-bound, organic bound, and lattice material components, respectively (23-27). One of the other most used sequential

extraction procedures is the modified Tessier procedure. The difference of the modified Tessier procedure is a four-step extraction: exchangeable, carbonates, organic matter and sulfides, and residual (13).

The Community Bureau of Reference (BCR) procedure strongly resembles the Tessier procedure, with the major difference in the first fraction of the procedure. Ure et al. (24, 27, 28) integrate the exchangeable and carbonate-bound steps in the first fraction instead of separately calculating them. Therefore, a three-step SE has been developed as a result of this study in which the metals are divided into acid-soluble/exchangeable, reducible, and oxidizable fractions (1, 13, 23, 29).

The aim of the current study was to compare the two sequential extraction schemes of the modified Tessier procedure (13, 30) and the revised BCR procedure (1, 13, 23, 29) for evaluating metal fractionation in ore samples from the Keban region, Turkey. The extraction steps for heavy metal-bound fractions and the efficiency and suitability of the mentioned procedures were tested.

EXPERIMENTAL

Instrumentation

The metal analyses were performed using an Optima™ 2100 DV inductively coupled plasma optical emission spectrometer (ICP-OES) (PerkinElmer, Inc., Shelton, CT, USA). The instrumental operating parameters are listed in Table I. Spectral detection for metal analysis by ICP-OES was obtained by measuring the absorbance at the maxi-

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mum wavelength of 238.2 nm for Fe, 228.6 nm for Co, 257.6 nm for Mn, 327.4 nm for Cu, 220.4 nm for Pb, and 206.2 nm for Zn. A model MWS-3 microwave digestion system (Berghof Co., Germany) with pressure control was utilized for acid digestion of the samples. Sequential extractions were carried out with a Memmert brand shaker (Memmert GmbH & Co. KG, Germany) and a Heraeus brand Labofuge-200 model centrifuge (Thermo Fisher Scientific, Germany). A Mettler-Toledo pH meter (Schwerzenbach, Zürich, Switzerland) was utilized for pH measurements and adjustment. Ore grinding was done with a Baysan brand jaw crusher and pulverizer (Turkey) and passed through a sieve (Yüksel Kaya Makina, Standard Testing Sieve, Turkey). Ultra-pure water was obtained with a Milli-Q® purifier system (Millipore Corporation, USA) and was used throughout this work.

Reagents and Standard Solutions

All reagents were of analytical grade; acetic acid (Sigma), hydroxyl ammonium hydrochloride (Sigma), hydrogen peroxide (Merck), ammonium acetate (Merck), magnesium chloride, sodium acetate, hydrofluoric acid and nitric acid (Fluka). Preparation of the standard solutions was done by serial dilution of 1000 mg L⁻¹ stock solution of the desired element.

Preparation of Ore Samples

For this work, the ore samples were obtained from the Keban region in Elazığ, Turkey. The samples were placed into boxes, then dried in an oven at 20 °C for 2 hours, broken with a jaw crusher and pulverizer, milled, and passed through a sieve of 100 mesh.

Sequential Extraction Procedures

Revised BCR Procedure

A revised sequential extraction

procedure for the fractionation of heavy metals, as proposed by the Commission of the European Communities Bureau of Reference (BCR), was applied for the ore sample analysis by ICP-OES.

The revised BCR scheme, a three-step sequential extraction procedure, harmonized and validated the method for the fractionation studies of soils and sediments (13). Compared to the original BCR procedure, the revised protocol involves the use of an increase in concentration of NH₂OH-HCl and a lower pH, as described by Mossop and Davidson (31). These extractions are associated to the exchangeable extraction step 1 where 1 g of ore sample was placed into a 100-mL centrifuge tube, 40 mL 0.11 mol L⁻¹ acetic acid added, then shaken by a mechanical shaker at 20 °C at 30 rpm for 16 hours. The extract was separated from the solid residue by centrifugation at 3000 rpm for 20 minutes, decanted into a volumetric flask, diluted with water to 100 mL, and stored in a refrigerator at 4 °C until subsequent analysis.

Reducible-iron/manganese oxides were extraction step 2, which includes the residue from step 1, to which freshly prepared hydroxylamine hydrochloride (40 mL, 0.5 mol L⁻¹) was added, and the solution pH adjusted to 1.5 with HNO₃. The extraction procedure was then performed in the same way as described in step 1.

Oxidizable-organic matter and sulfides were extraction step 3 where 20 mL hydrogen peroxide (30%, pH 2.0) was added carefully to the residue into the centrifuge tube from step 2, and digested at room temperature for 1 hour with occasional manual shaking. The digestion was continued by heating the vessel to 85 °C in a water bath for 1 hour, then reduced to less than 3 mL volume by further heating of the uncovered tube. A further aliquot of 10 mL of hydrogen peroxide was added and the digestion procedure repeated. Then, 50 mL of ammonium acetate was added to the cool, moist residue and shaken for 16 hours at 20 °C (the pH was adjusted to 2.0 with nitric acid). Following, the extract was separated from the solid residue (as described in step 1).

TABLE I
ICP-OES Instrumental Operating Conditions

Parameters	
RF power	1450 W
Plasma gas flow rate	15 L min ⁻¹
Auxiliary gas flow rate	0.2 L min ⁻¹
Nebulizer gas flow rate	0.8 L min ⁻¹
Sample flow rate	1.5 L min ⁻¹
View mode	Axial
Read	Peak area
Source equilibration time (s)	15 s
Read delay	50 s
Replicates	3
Purge gas	Nitrogen
Shear gas	Air
Plasma gas	Argon
Metal λ max (nm)	Fe 238.2, Co 228.6, Mn 257.6 Cu 327.4, Pb 220.4, Zn 206.2

Finally, step 4 includes a digestion of the residue with aqua regia (HCl/HNO_3 - 3:1) in a microwave oven for 26 minutes. After microwave digestion, the samples of step 4 were filtered through a filter paper (Whatman No. 1 - Cat. No. 1001-010) and diluted to 100 mL with ultrapure water.

Modified Tessier Procedure

In exchangeable step 1, the fractions extracted were approximately 1 g ore sample with 10 mL of 1 M ammonium acetate (pH 7.0). The sample was shaken for 1 hour at 150 rpm at 20 °C, then centrifuged at 4000 rpm for 10 minutes. The liquid phase was decanted into a volumetric flask and diluted with 100 mL ultrapure water. The carbonates were extracted in step 2. For this purpose, 1 M 10 mL acetic acid was added to the residue of fraction 1. The solution was shaken at 150 rpm for 1 hour, then centrifuged for 10 minutes at 4000 rpm at 20 °C. The liquid phase was decanted into a volumetric flask and diluted with ultrapure water to 100-mL volume. Oxidizable-organic matter and sulfides were extracted in step 3. The residue from fraction 2 was treated with 5 mL of a 30% solution of H_2O_2 , the pH was

adjusted to 2.0 with nitric acid solution. The sample was shaken for 3 hours at 150 rpm at 35 °C. After the sample was centrifuged at 10.000 rpm, it was filtered with filter paper (Whatman No. 1 - Cat No. 1001-010) and diluted to 100 mL with ultrapure water. Then, 10 mL aqua regia, 2.5 mL HNO_3 (65%), and 7.5 mL HCl (37%) were added to the residue and filtered from fraction 3. After microwave digestion, the samples were filtered and diluted to 100 mL with ultrapure water (13).

RESULTS AND DISCUSSION

Revised BCR Procedure

Step 1: 40 mL CH_3COOH (0.11 M, pH=7.0)

This step was applied to produce acetate salts of Fe, Cu, Zn, Pb, and Mn and to determine the solubility ratio of these salts in solution. In Table II, it can be seen that these ions in the ore structure could pass to solution at different ratios according to their solubility.

Step 2: 40 mL $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.5 M, pH=1.5)

In this step, the aim was to create conditions for the passage of metal ions, which includes a high

ratio of Fe and Mn to solution by addition of hydroxylamine, a reducing reagent, and hydrochloric acid, both a proton donor and complexing agent. The procedure was chosen due to the fact that Fe mineral is both in hematite and magnetite structure and manganese can be found as MnO compound.

Step 3: 20 mL H_2O_2 (30%, pH=2.0) and 50 mL $\text{CH}_3\text{COONH}_4$ 1 M, pH=2.0

The addition of H_2O_2 allows decomposition of the organic substances (CO_2 , H_2O , NO_x) due to its high oxidizing activity which causes a reduction electrode potential of 1.70 V. This step was carried out to convert sulfur in the sulfur compounds to its elemental form and dissolution of the metal ions by converting them to the highest oxidation state. Since the pH of the medium is fixed at around 2.0, the acetate salts of the metal compounds may dissolve and pass into the aqueous medium. However, as can be seen from Table II, all metal ions except Cu^{1+} cannot be dissolved in solution due to the existence of $\text{NH}_4\text{CH}_3\text{COO}$. Furthermore, it is also thought that all Cu^{1+} in the ore structure became and dissolved as Cu^{2+} ions in $\text{NH}_4\text{CH}_3\text{COO}$ solution.

TABLE II
Results Obtained (mean $\pm$ standard deviation, n=3)
for Sequential Extraction Procedures

Revised BCR	Fe (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Co (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Mn (mg kg ⁻¹)
Step 1	7.10 $\pm$ 0.14	3438 $\pm$ 103	Nd	0.06 $\pm$ 0.0013	6.10 $\pm$ 0.12	173 $\pm$ 5
Step 2	2514 $\pm$ 50	3286 $\pm$ 66	13.14 $\pm$ 0.26	8.26 $\pm$ 0.16	7.74 $\pm$ 0.14	736 $\pm$ 20
Step 3	Nd	36.3 $\pm$ 0.72	Nd	Nd	Nd	Nd
Step 4	458000 $\pm$ 7246	7020 $\pm$ 158	34.78 $\pm$ 0.69	73 $\pm$ 1	118 $\pm$ 2	603 $\pm$ 12
Modified Tessier	Fe (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Co (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Mn (mg kg ⁻¹)
Step 1	2.82 $\pm$ 0.06	1028 $\pm$ 23	Nd	Nd	1.18 $\pm$ 0.02	17.48 $\pm$ 0.35
Step 2	589 $\pm$ 13	5286 $\pm$ 140	3.92 $\pm$ 0.08	244 $\pm$ 7	15.02 $\pm$ 0.45	375 $\pm$ 10
Step 3	792 $\pm$ 24	718 $\pm$ 18	1032 $\pm$ 30	11.36 $\pm$ 0.22	7.10 $\pm$ 0.14	605 $\pm$ 13
Step 4	365800 $\pm$ 6975	668 $\pm$ 17	34.72 $\pm$ 0.67	68 $\pm$ 1	114 $\pm$ 3	648 $\pm$ 15

Nd: not detected.

Step 4: 10 mL demineralized water and 10 mL aqua regia (HCl/HNO₃, 3:1)

In this step, HCl/HNO₃ solution (3:1), which was diluted by half with demineralized water, was added to the remaining ore structure (includes the metals that were not dissolved in the previous steps), then the solution was treated in the microwave oven to dissolve them.

Modified Tessier Procedure

Step 1: 10 mL NH₄CH₃COO (1 M, pH = 7.0)

This study was performed to determine the ions that can pass to the solution by an effective buffering with the addition of NH₄CH₃COO at pH 7.0. The values obtained in this study were lower than those obtained by buffering with CH₃COOH at pH 7.0.

Step 2: 10 mL CH₃COOH (1 M, pH = 5.5)

In order to detect the presence of carbonated compounds in the structure, the pH of CH₃COOH medium was adjusted to 5.5 and dissolution was performed. As can be seen from Table II, it was observed that Fe, Cu, Co, Zn, Pb, and Mn were passed to the solution medium.

Step 3: 5 mL H₂O₂ (30%, pH = 2.0)

In this step, H₂O₂ was added to decompose the organic substances (CO₂, H₂O, NO_x) by its high oxidizing activity which causes a reduction electrode potential of 1.70 V. It is aimed to convert the sulfur in the sulfur compounds to its elemental form and dissolve the metal ions by converting them to the highest oxidation state. The acetate salts of the metal compounds can be dissolved and passed into the aqueous medium since the pH is fixed around 2.0.

Step 4: 10 mL demineralized water and 10 mL aqua regia (HCl/HNO₃, 3:1)

This step is the same as step 4 in the revised BCR procedure. The remaining ore structure was also treated with HCl/HNO₃ solution (3:1), which was diluted by half with demineralized water for the metals that were not dissolved in the previous steps, and then the solution was put in a microwave oven to dissolve them.

CONCLUSION

When the two studied procedures are examined, it can be seen that there are differences in the bonding forms of the metals to the ore and the properties of the reactants. Because of these differences, the amount of metals passing to the solution are different for both procedures.

When the first steps of the modified Tessier and the revised BCR procedures are compared, it can be seen that the ions pass to the solution at lower values in the modified Tessier procedure. In the second step of the revised BCR procedure, it is thought that the ions can pass to the solution depending on their reduction, oxidation, and complexation properties. Mn is more likely to be dissolved in the second step of the revised BCR than in the other steps. The reason may be that Mn changes to MnO due to the hematite and magnetite structure of the ore. In the second step of the modified Tessier procedure, the presence of carbonated compounds in the ore structure and the passage of all studied ions to solution were observed. If the second steps are compared, it can be seen that the revised BCR procedure is better for dissolution of the Fe, Co, and Mn ions; however, the modified Tessier procedure for dissolution of Cu, Pb, and Zn. In the third step of the revised BCR procedure, only the Cu ion passes to the solution. The rea-

son may be that all Cu¹⁺ in the ore structure became and dissolved as Cu²⁺ ions in the NH₄CH₃COO solution. However, in the third step of the modified Tessier procedure, all of the metal ions in the sample dissolved and passed to the solution due to H₂O₂ which is a strong oxidizing agent, and the pH of the solution is fixed at around 2.0. The final steps of both procedures were carried out to pass the ions to the solution which are found as mineral structure and cannot dissolve.

All in all, if the revised BCR and the modified Tessier procedures are compared, it seems that the modified Tessier procedure has more advantages due to the fact that the revised BCR procedure needs more chemicals and takes a longer time to complete. However, the appropriate procedure changes depending on the metal. According to the results of this study, Cu, Pb, and Mn ions passed to solution better in the modified Tessier procedure, but the Fe, Cu, Zn ions were more dissolved in the revised BCR procedure.

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