REINTERPRETATION OF THE FIRST STEP OF THE SEQUENTIAL EXTRACTION PROPOSED BY THE SMT

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(Received: November 3, 2008 - Accepted: July 29, 2009)

ABSTRACT

Samples of sediment from Estero Rungue, north of Santiago, were analyzed during January 2007. The studied zone is affected by acid contamination. Analysis of the sediment by XRD detected the presence of rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The experiments were carried out according to the criterion established for the first Step of the sequential extraction proposed by the SMT, using Ca, Cu, Fe, Ni and Zn sulfates in the form of $\text{M}_x\text{SO}_4 \cdot a\text{H}_2\text{O}$ as a model sediment. The results suggest that it is possible to extract up to ~99% of the sulfates because of the low pH (~3). Analysis of the sediment by XRD before and after the first Step of the sequential extraction showed that the sulfates disappear after the treatment, extending the interpretation of the first Step of the sequential extraction to elements that are interchangeable, adsorbed on carbonates, and present as sulfates.

Keywords: Trace metals, sediments, sequential extraction, sulfates.

INTRODUCTION

For years sequential extraction (SE), proposed originally by Tessier,¹ has been widely used to determine the conditions under which the metals that are being studied will be set free from the mineral matrix. Recently, however, the use of sequential extraction has been modified with the purpose of increasing the method's efficiency, giving rise to a number of variations that have been analyzed by various researchers^{2,3} as well as by the International Union of Pure and Applied Chemistry (IUPAC). In this paper we propose a new interpretation of the first Step of the four-Step sequential extraction proposed by the Standards, Measurements and Testing program of the European Community (SMT, previously BCR), which does not consider the extraction of metals associated with sulfates in the first Step of SE. The four-step SE proposed by the SMT is carried out by extracting metals from the sediment in the following sequential steps: Extraction 1: Trace metals adsorbed on ores or minerals contained in minerals soluble in weak acid (e.g., carbonates). Extraction 2: Trace metals strongly attached to reducible minerals such as Fe and Mn hydroxides. Extraction 3: Trace metals strongly attached to oxidizable minerals such as sulfides, phosphates, and organic matter; Extraction 4: Trace metals in ores such as silicates and/or oxides.

MATERIALS AND METHODS

Sampling

Two river sediment samples were obtained in January 2007 from a single main in the zone of Rungue ($30^{\circ}00'25.55''\text{S}$, $70^{\circ}53'34.68''\text{W}$), 50 km from Santiago (Fig. 1a). In this zone an acid contamination occurs that affects the source of Rungue stream over an extension not larger than 800 m. The physicochemical parameters of the stream are the following: superficial pH ~3.0, Eh ~400 (mV), TDS ~1500 (mg/L), SO_4^{2-} ~3800 (mg/L). From the zone of maximum concentration (Fig. 1b) 250 g of sediment were collected *in-situ* by using a PVC core-type sampler from a depth of 40 cm from the surface, and they were placed in a size A4 high-density polyethylene bag⁴. In a pretreatment, the sample was dried in a convection oven at 60 ± 1 °C for 48-72 h. Once dry, gravel, wood and organic matter were removed from the sample. A 50-g portion of the sample was ground and mixed thoroughly. Major and trace elements were analyzed by X-ray fluorescence spectroscopy (XRF, PANalytical Axios) as follows: 6 g of the sample were heated at 100 °C for 24 h and the sample's moisture was determined. It was then heated at 500 °C for 30 min, 800 °C for 30 min, and 1000 °C for 30 min, and the "loss on ignition" was determined. Finally, 1.00 g of the sample was mixed with lithium borate, melted at 1300 °C, and cooled, yielding a crystallized tablet for XRF analysis (duplicate). The samples were analyzed by X-ray diffraction (XRD, Rigaku RINT 2000) using monochromatic $\text{CuK}\alpha$ radiation at 40 kV and 30 mA in the range of 5° to 50° and 10° to 30° in 2θ . At the same time, analysis by inductively coupled plasma atomic emission spectroscopy with optical detection (ICP-AES, Seiko SPS7700) was carried out on three sediment samples completely digested in acid medium (with a mixture of HNO_3 , HCl and HF)⁵ to determine the trace metals concentration. The detection limits for ICP-AES analysis are (in μg

L^{-1}): 1, 1, 1.5, 20, 4, 3 and 1 for Cr, Zn, Cd, Pb, Ni, Co and Cu, respectively. Finally, and as pattern sediment, quality sulfates (SIGMA®) were used for the analysis, without heating. The pure compounds were: Ca, Cu, Fe, Ni and Zn in the form of $\text{M}_x\text{SO}_4 \cdot a\text{H}_2\text{O}$.

Figure 1. (a) Location of the studied zone and quality of the sediment in the high concentration zone. (b) Characteristics of the water and sediment from the high concentration zone.

Sequential extraction proposed by the SMT

According to the methodology proposed by the SMT, the four-Step sequential extraction takes place as follows:

Step 1: Extraction with 0.11 mol/L acetic acid

One gram of the sample is treated with a 0.11 mol/L acid acetic solution at pH~3. The mixture is stirred continuously at 30±10 rpm and 22±5 °C for 16 h. The extractant is separated from the solid residue by centrifuging at 3000 rpm for 20 min. The supernatant is decanted into polyethylene bottles and stored at 4 °C for later analysis. The residue is washed by adding 20 mL of ultrapure water, stirring for 15 min, and centrifuging for 20 min at 3000 rpm. The supernatant is decanted and discarded, taking care not to discard solid particles. In general, trace metals adsorbed on minerals or contained in minerals soluble in weak acid, such as carbonates, can be extracted in this Step.

Step 2: Extraction with 0.5 mol/L hydroxylamine hydrochloride

Forty mL of 0.5 mol/L hydroxylamine hydrochloride solution with the pH adjusted to 1.5 with HNO₃ are added to the residue from Step 1. The mixture is stirred continuously at 30±10 rpm and 22±5 °C for 16 h. The extractant is separated and the residue is treated in the same way as in Step 1. In general, trace metals strongly attached to reducible minerals such as Fe and Mn hydroxides can be extracted in this Step.

Step 3: Digestion with 8.8 mol/L hydrogen peroxide and extraction with 1 mol/L ammonium acetate solution

Ten mL of 8.8 mol/L hydrogen peroxide solution are added carefully to the residue of Step 2. The mixture is digested for 1 h at 22±5 °C and for 1 h at 85±2 °C, until the liquid volume has been reduced to less than 3 mL. A second 10-mL aliquot of 8.8 mol/L hydrogen peroxide is added to the residue and the mixture is digested again for 1 h at 85±2 °C, until the liquid volume is reduced to 1 mL. Finally, 50 mL of 1 mol/L ammonium acetate solution (pH adjusted to 2.0±0.1 with HNO₃) are added to the cold mixture, which is continuously stirred at 30±10 rpm and 22±5 °C for 16 h. The extractant is separated from the solid by centrifugation in the same way as in the previous Steps, collected in polyethylene bottles, and stored at 4 °C until its later analysis. The residue is washed as in the previous Steps and the supernatant is discarded. In general, trace metals strongly attached to oxidizable minerals such as sulfides and phosphates,^{6,7} and organic matter can be extracted in this Step.

Step 4: Digestion with aqua regia (HNO₃ + HCl)

The residue of Step 3 was digested with aqua regia. Trace metals bonded to silicates and/or oxides⁸ can be extracted in this last Step.

Elemental analysis

A sample of the Rungue sediment (M1) was analyzed in triplicate by XRF, ICP-AES and XRD. A second sample from the same initial main (M2) was analyzed by XRD in a range of 10° to 30°. Also, the procedure described above for the first Step of SE was applied in triplicate to one gram of sulfate, as sediment sample. The sulfates were CaSO₄·½H₂O, CaSO₄·2H₂O, CuSO₄·5H₂O, FeSO₄·7H₂O, NiSO₄·6H₂O and ZnSO₄·7H₂O of 90%, 95%, 99%, 99%, 99% and 99% purity, respectively.

RESULTS AND DISCUSSION

The results of the XRF and ICP-AES analysis of sample M1 are shown in Tables 1 and 2; values shown correspond to the averages of the triplicate analysis plus its standard deviation, respectively. The result of the analysis of sample M1 by XRD appears in Figure 2. It is seen that sample M1 corresponds to a normal sediment, with high concentrations of silica, aluminum, magnesium, calcium and iron, in agreement with the values for river sediments⁹ However, the values for copper, zinc and nickel in the sediment are much higher than the values measured in the same place (clean zone with N=30; Table 3), but also compared to other studies of sediments within Chile¹⁰⁻¹², which shows a local contamination; and also to other studies of river sediments in the world¹³. The XRD analysis of sample M1 shows the presence of rozenite (FeSO₄·4H₂O) and gypsum (CaSO₄·2H₂O). In view of the high concentration of copper, zinc, and nickel in the water (TDS ~1500 mg/L) and in the sediment (Table 3), and of the high concentration of SO₄²⁻ in the water (~ 3800 mg/L), it was

assumed that the presence of these sulfates is possible even when they are not detected in the analysis. For the purpose of interpretation, it is assumed that it is possible for these sulfates to exist unconsolidated (not in crystal phase, or amorphous) and that they are present in the analysis at the interference level. Because of the detection of rozenite and gypsum, the first step of the SE was carried out in triplicate by using each time 1g of calcium, copper, iron, nickel and zinc sulfate, simulating the sediment. The results of this extraction are shown in Table 4. It is seen that the results of Step 1 of the SE indicate constant extraction greater than 99% for Cu, Fe, Ni and Zn sulfates. The variable results for the hydrated Ca sulfates can be accounted for either by the low presence of water in the compound or by a pH value above that required for complete dissolving at pH<2.5.¹⁴

Table 1. Results of the XRF analysis of M1 (wt%).

Sample M1 (Wt%)			
	$\bar{X}$	S.D.	
SiO ₂	41.79	±	0.437
FeO	8.773	±	0.135
MgO	11.01	±	0.130
L.O.I.*	6.017	±	0.177
CaO	8.405	±	0.116
Al ₂ O ₃	12.42	±	0.094
MnO	1.602	±	0.022
K ₂ O	2.435	±	0.034
Na ₂ O	2.481	±	0.003
TiO ₂	1.271	±	0.019
P ₂ O ₅	0.300	±	0.003
Total	96.51 %		

S.D. = Standard deviation

*L.O.I. = Loss on ignition. S (carbonates, sulfates, nitrates, etc.)

Table 2. Results of the ICP-AES analysis of M1 (mg L⁻¹) with its concentration and standard deviation.

Element	D.L. (µg L ⁻¹)	Sample M1	
		$\bar{X}$	S.D.
Cr	1	36.15	± 0.72
Zn	1	901.7	± 18
Cd	1.5	17.08	± 0.34
Pb	20	2088	± 41.7
Ni	4	249.4	± 4.99
Co	3	189.3	± 3.79
Cu	1	2968	± 59.4

D.L. = Detection Limits

Table 3. Comparison of the ICP-AES analysis of M1 with the average concentration (mg L⁻¹) and its standard deviation of trace metals along the whole river (N=30).

Elements	M1		Lampa river		Chungara Lake [10]		Laja Lake [10]		Castor Lake [10]		St.R.L. [10]		L.C.S.P. [12]		Rapel Lake [11]	
	$\bar{x}$	S.D.	$\bar{x}$	S.D.	$\bar{x}$	R.S.D.	$\bar{x}$	R.S.D.	$\bar{x}$	R.S.D.	$\bar{x}$	R.S.D.	$\bar{x}$	R.S.D.	$\bar{x}$	R.S.D.
Cu	2968.1 ± 59		191.8 ± 106		18.8 ± 21%		47 ± 12%		22 ± 14%		25.6 ± 8%		54 ± 34%		0.388 ± 1.28%	
Zn	901.8 ± 18		153.3 ± 64		n.m.		n.m.		n.m.		n.m.		n.m.		0.596 ± 1.00%	
Cr	36.15 ± 0.7		54.36 ± 43		37.5 ± 41%		44 ± 9%		41 ± 56%		60.8 ± 3%		64 ± 13%		n.m.	
Cd	17.08 ± 0.3		26.49 ± 7.8		n.m.		n.m.		n.m.		n.m.		n.m.		n.m.	
Pb	2088 ± 41		1744 ± 643		3.40 ± 39%		11 ± 24%		3.4 ± 22%		7.30 ± 25%		40 ± 24%		n.m.	
Ni	249.4 ± 5.0		42.25 ± 25		n.m.		n.m.		n.m.		24.2 ± 8%		30 ± 7%		n.m.	
Co	189.3 ± 3.8		132.7 ± 60		n.m.		n.m.		n.m.		17.8 ± 7%		23 ± 9%		n.m.	

St.R.L. = Saint Rafael Lake; L.C.S.P. = Laguna Chica San Pedro; n.m. = not measured (by the authors).

D1. Use of a 0.11 mol/L acetic acid solution in the first step of the sequential extraction.

According to the extraction method proposed by the SMT, the reason for the use of acetic acid (HOAc) in the first Step of the SE has to do with the extraction of metals linked to carbonates¹⁵. For that purpose HOAc is used to extract trace metals either specifically adsorbed or bonded to the outer layer in a range of 5% of carbonate.

Figure 2. XRD analysis of sample M1.

Q: quartz, H: hornblende, F: feldspar, G: gypsum, R: rozenite

D2. Differences between the pH values during the use of 0.11 mol/L HOAc

Although the use of HOAc in the sequential extraction is quite common,^{2, 3, 16} the pH values associated with this Step (pH~4.5)^{3, 15, 17-20} do not agree with the values measured in the laboratory during the preparation of the samples (pH~2.80). Acetic acid is a weak acid with a dissociation constant (K_a) 1.75×10^{-5} at 20 °C. Therefore, a 0.11 mol/L solution of HOAc will have a $pH = -\log(\sqrt{(1.75 \times 10^{-5}) \times 0.11}) = 2.85$, a value very close to that found during the preparation of the solution in Step 1 of the SE. This means that the HOAc solution proposed by a number of authors must use a buffer like acetate, for example, to keep the pH~5 as proposed originally by Tessier,¹ something that is not brought up in the papers on SE.

D3. Extraction of sulfates in the first Step of the SE.

With the purpose of determining experimentally if sulfates are extracted in Step 1 of the SE, a second sample (M2) from the same initial main (M1) was analyzed by XRD to determine the constituent minerals before and after the Step 1 extraction. The results of the analysis (Fig. 3) show clearly that the presence of both gypsum and rozenite before (Fig. 3A) and after (Fig. 3B) Step 1 are in full agreement, showing no sulfates after the SE. It is therefore inferred that the sulfates of trace and/or toxic metals are extracted almost completely (see Table 4) in Step 1 of the SE, suggesting that trace metals that are interchangeable, adsorbed on carbonates, and present as sulfates are extracted in this first step of the SE.

Figure 3. XRD analysis of sample M2 before and after the first stage of SE.

G: gypsum, R: rozenite.

Table 4. Results of the extraction with 0.11 mol/L acetic acid solution for different sulfates.

	Molar mass (g/mol)	Cation mass	Purity (%)	Expected value (mg/l)	Sample	Analyzed value (mg L ⁻¹)	Extraction yield
CaSO ₄ ·½H ₂ O	145.15	40.08	90%	4970	A	800	16%
					B	801	16%
					C	800	16%
CaSO ₄ ·2H ₂ O	172.17	40.08	95%	4423	A	2656	60%
					B	2660	60%
					C	2662	60%
CuSO ₄ ·5H ₂ O	249.69	63.55	99%	5039	A	5003	99%
					B	4998	99%
					C	5000	99%
FeSO ₄ ·7H ₂ O	278.02	55.85	99%	3977	A	3959	100%
					B	3960	100%
					C	3961	100%
NiSO ₄ ·6H ₂ O	262.85	58.69	99%	4421	A	4390	99%
					B	4395	99%
					C	4395	99%
ZnSO ₄ ·7H ₂ O	287.56	65.39	99%	4502	A	4491	100%
					B	4489	100%
					C	4491	100%

CONCLUSION

Considering the results obtained from the XRD analysis for sample M2 before and after Step 1 of the sequential extraction, as well as the experiments carried out with Ca, Cu, Fe, Ni and Zn sulfates, it is possible to suggest that most of the sulfates of trace or toxic metals can be extracted in the first Step of the SE because of the low pH value of the HOAc solution. However, this new approximation does not alter what was proposed originally by Tessier or later by other authors, but rather extends the interpretation of the first step of the sequential extraction in the study of sediments that can contain sulfates in their natural states or of basins affected by acid contamination of natural or mining origin.

ACKNOWLEDGEMENTS

The authors wish to thank the government of Japan due its scholarship program Monbukagakusho. Also, the Laboratory of Geochemistry from the University of Tokyo and it's responsible professor, Dr. Takashi Murakami, for his support in the analysis of the samples. Finally, the authors express their tremendous gratitude to E.A., E.L, J.E.F, C.P and S.A. for their kind support in the preparation of this paper.

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