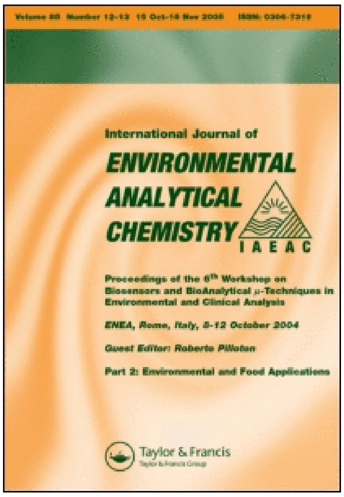

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SEQUENTIAL ULTRASONIC LEACHING OF STRONTIUM FROM SEDIMENTS

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The effects of ultrasonic excitation on the sequential leaching of Sr from sediments have been investigated. The sequential leaching scheme of Tessier partitions metals in sediments into exchangeable, carbonate bound, oxide bound, organic bound, and residual binding fractions. The Sr in the leachates was determined by flame atomic absorption spectrometry. Leaching rate experiments using conventional and ultrasonic leaching showed that the ultrasonic leaching method (ULM) produces comparable results to the conventional procedure. In addition, this method reduces the time required for Tessier fractionation from 21 h to 1.7 h. Sequential ultrasonic leaching procedures were established as a result of the extraction rate experiments.

The precision obtained from 21 replicate ULM yielded an average relative standard deviation % of 9.2, 10.3, 11.7, 8.6, and 12.8 for exchangeable, carbonate, oxide, organic, and residual fractions, respectively. The precision variance between the means of the two leaching methods was not significant at 0.05 probability for Sr. The recoveries of total Sr using NIES CRM-2 ranged from 75 % to 101 % for the conventional procedure and 84 % to 109 % for the ULM.

Keywords: Ultrasonic metal leaching; sequential ultrasonic leaching; sediment; strontium; AAS

INTRODUCTION

In the studies of natural water systems such as stream, lake and sea, the sediment fraction is important and has been investigated extensively. There is interest in the exchange of chemical constituents among the sediment and other primary fractions such as dissolved and suspended and their potential effect on biota and human health. Although sediments are considered to be the ultimate sink for heavy metals released into the environment, relatively little is known about the way that heavy metals are bound to sediments or the ease with which they may be released. For example, if one is interested in the mobility, availability, uptake, and transport of metal in aquatic systems, little information is gained from the

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measurement of total metal in the sediment other than an estimate of the total metal burden in the sink. Knowledge of how a metal is bound in the sediment is necessary to assess accurately the potential modes of transport and future impact on the environment. Such data are obtained from sequential leaching of the sediments. During the various stages of the sequential leaching, the environmental conditions that may be encountered in nature are mimicked. Such procedures are one of the few ways of exploring an important aspect of environmental element chemistry in that they provide useful comparative information about regional variations in sediment chemistry. In particular, the approach of Tessier et al.[1] has been applied widely and has become a bench mark for the evaluation of new developments. Similar schemes have been developed that differ primarily in the leaching conditions used[2–4]. Hence our results were also compared with this method, which will be referred to as conventional leaching (CL).

The scheme developed principally by Tessier et al.[1] partitions metals into five fractions: *1. Exchangeable*. Metals in this fraction are bound to the sediments by weak adsorption onto sediment particles. Changes in ionic strength of the water are likely to affect the adsorption-desorption or ion exchange processes resulting in the uptake or release of metals at the sediment/water interface[5,6], *2. Carbonate Bound*. Metals bound to carbonates are sensitive to pH changes with the lowering of pH being associated with the release of metal cations[7], *3. Oxide Bound*. Metals bound to oxide fraction are unstable under reducing conditions. These conditions result in the release of metal ions to the dissolved fraction[8], *4. Organic Bound*. Degradation of organic matter under oxidizing conditions can lead to the release of soluble metals bound to those materials, *5. Residual*. This fraction should contain naturally occurring minerals, which may hold trace metals within their crystalline matrix. These metals would not be readily released to a soluble state in conditions encountered in nature.

The method of Tessier et al.[1] requires approximately 24 h for leaching and centrifugation to be complete. This characteristic is common to all the sequential leaching procedures and it explains, to a large extent, why the techniques have not been applied more widely to environmental problems. Although microwave digestion techniques appear to offer a solution to the time-consuming problems associated with conventional digestion procedures[1,9–11], their selectivity is poor for very labile metal fractions in the sequential leaching of sediments[9].

In our laboratory a modified sequential ultrasonic leaching scheme has been used to study the mobility and transport of Sr in Tecer River (central Anatolia) sediment as a result of pollution from a mine drainage site. In addition, the aim was to develop an alternative technique that would avoid the redistribution of elements into undissolved sediment phases and the time-consuming problems of CL and also the problem of non-selectivity with the microwave technique.

Ultrasonic leaching method[12,13] was thought to be an alternative method to CL. It has been reported that this method gives high recoveries of organics from granular activated carbon[14], sediment[15], fly as[16], biological materials[17] and elements from atmospheric particulates[18]in a much shorter time than is required for other leaching procedures. Besides, the ultrasonic leaching is known to be faster and more effective than the conventional leaching methods to extract the adsorb and remaining metals out of the sediment[12,13]. Similar results may also be expected for labile metal fractions in sediment, from a study of the physical and chemical[19,20] effects of ultrasonication. As anthropogenically produced metals are normally found in the labile fractions[9] rather than in the residual fractions of the sediment, the labile fractions are important from the point of view of environmental pollution.

It was our hypothesis that the ULM could be used to stimulate the rapid release of metals in each of the five binding fractions of sediment. To prove this hypothesis a series of experiments were designed in which the leaching rates of Sr in each of the five fractions could be determined for both the CL and ULM. Once the basic leaching rates were established, procedures for a sequential ultrasonic leaching could be developed.

Strontium was chosen for two reasons. Firstly, as the aim was to study leaching rate an recovery, the problems and uncertainty associated with trace element determination were avoided. In the mine drainage area, selestisid (mainly $SrSO_4$) is handled and, therefore, Sr is present at low levels in the sediment. Secondly, Sr is a heavy nuclear fission product and is distributed on the Earth's surface rather than in the atmosphere after nuclear accidents. From this point of view, the system (the mine drainage site and the river) can act as an analytical model in this instance. The information thus obtained can be used to study the movement of radioactive Sr.

EXPERIMENTAL

Sediments collected from the Tecer River, and the NIES CRM-2 certified reference material which consist 110 μg/g Sr, a pond sediment standard obtained from the NIES (National Institute for Environmental Studies, Japan) were used. The Tecer River sediments were taken from seven sampling points, one before and the others after the drainage water disposal site along the river within a distance of 18 km(see Fig. 1). In general, the sediments for the sequential extractions are dried at approximately 80±10[9]. But, drying at this temperature was not enough for this kind of river sediments which consist high level selestisid and caused problems at grinding and sieving steps. Although there are some drawbacks, e.g. ignorable variation of metal distribution among phases, the sediments were dried at 110 °C overnight to prevent the uncertainty associated with the water content of the samples and were then ground and passed through a 100-mesh screen. The particles passed through the 100-mesh screen were the standard particle size for this type of work. The NIES CRM-2 was used as received from the NIES, except for drying. Sediment samples with a mass of 500±0.1 mg were used for both leaching rate experiments and subsequent ULM experiments. ULM experiments were carried out with an ultrasonic bath, which produced a nominal frequency of 50–60 kHz.

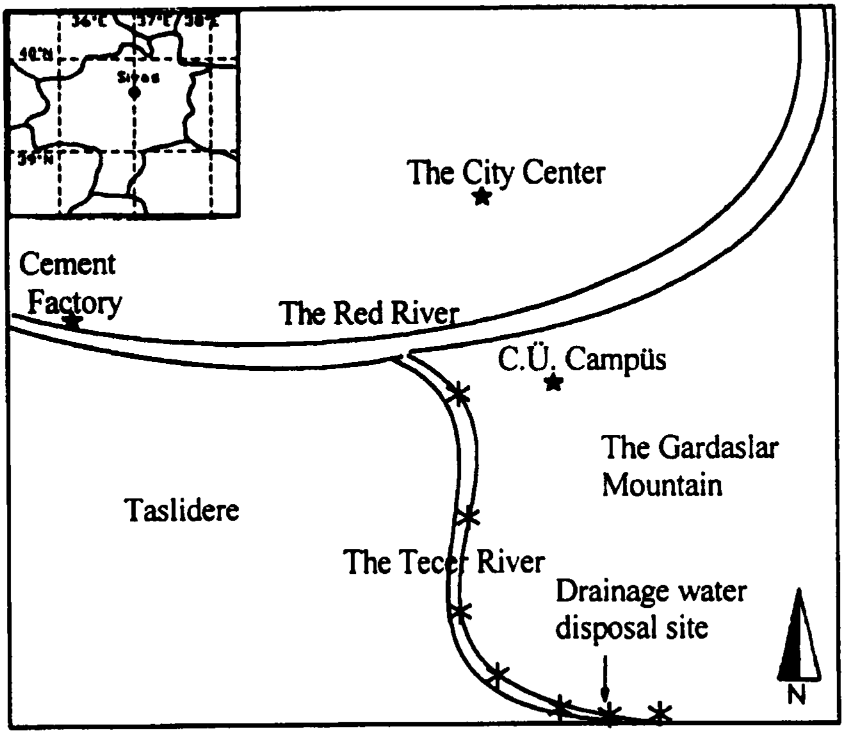

FIGURE 1 The sampling stations of the Tecer River

The reagents used for the leaching of each fraction were identical with those recommended by Tessier et al.[1] for the CL.

The separation of the extracts from the solid residue at the end of each leaching was accomplished by centrifugation at 5000 rpm for 10 min with a laboratory-built centrifuge. The Sr in the extracts was determined by flame atomic absorption spectrometry using a UNICAM 929 spectrometer. A 1.0 ml volume of a 1 % m/V La^{+3} solution was added to the extracts as a ionization buffer and Sr was determined at 460.7 nm using an air-acetylene flame. The concentrations were obtained directly from calibration graphs after correction of the absorbance for the signal from an appropriate reagent blank. Only matrix interferences were monitored for Sr at each fraction using standard additions analysis while all quantification of Sr was performed using calibration method.

Before a procedure could be established for ultrasonic leaching of sediments, leaching rate experiments were performed to establish the ultrasonication times required to reach the recoveries that are obtained by CL using the recommended times for each fraction. The ultrasonic leaching rates were determined by performing repeated ultrasonic leaching of samples for periods of between 10 and 30 min.

By using the graphs obtained from the ULM rate experiments, the following procedures were established for ULM and were compared with the appropriate reference method[1] (see Fig. 2).

Procedures for the sequential ultrasonic leaching of strontium

Fractions

Exchangeable. The sediment samples were transferred into 100 ml centrifuge bottles and 50.0 ml of 1 M $MgCl_2$ adjusted to pH 7 were added to each sample. The sediments were then leached for 20 min under ultrasonic excitation in an open container. After ultrasonication the mixtures were centrifuged and the supernatants were removed using transfer pipettes.

Carbonate Bound. A 50.0 ml volume of a freshly prepared solution of 1 M $NaCH_3COO$ adjusted to pH 5 with CH_3COOH was added to the residue from the exchangeable Sr fraction. The mixtures were subjected to ultrasonic excitation for 20 min and the supernatants were separated as before.

Oxide Bound. To the residue from the carbonate bound Sr fraction, 50.0 ml of 0.04 M $HONH_2HCl$ (hydroxylamine hydrochloride) in 25 % (V/V) CH_3COOH was added and ultrasonicated for 20 min and the supernatants were separated as before.

Organic Bound. To the residue from the oxide bound Sr fraction, 19.0 ml of 0.02 M HNO_3 and 31.0 ml of 30 % H_2O_2 adjusted to pH 2 were added this mixture was ultrasonicated for 20 min, centrifuged, and decanted.

Residual. A 50.0 ml volume of a freshly prepared solution of HCl-$HClO_4$-HF (2:1:1, V/V) was added to the residue from the organic bound Sr fraction. The mixtures were subjected to ultrasonication for 20 min and the supernatants were separated as before.

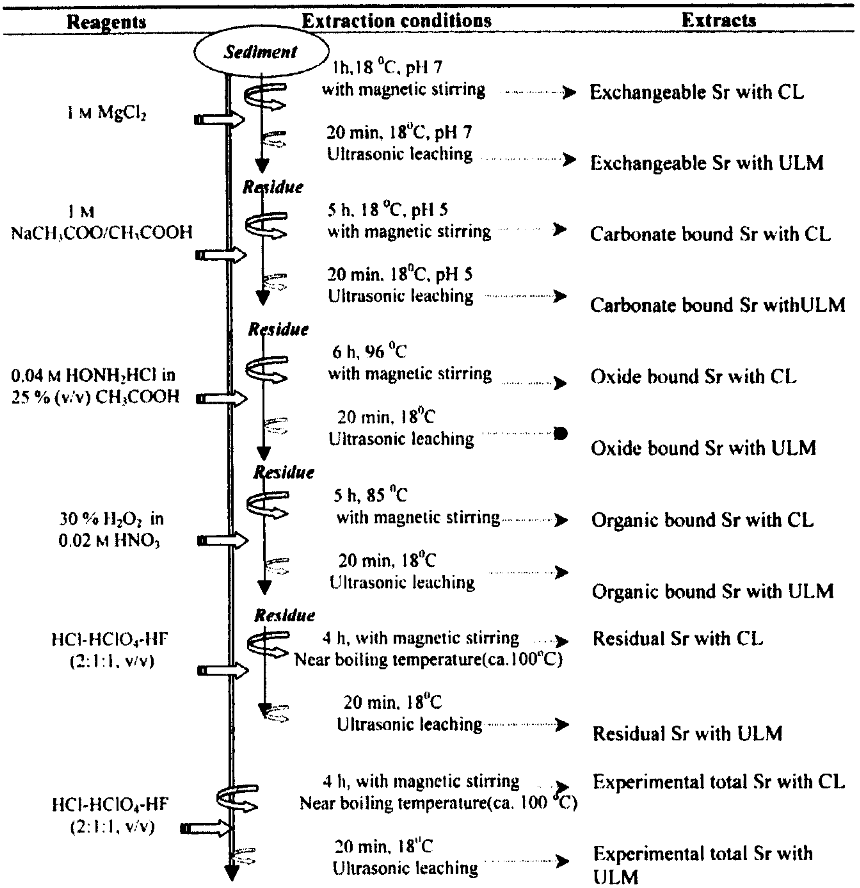

FIGURE 2 Scheme for the sequential leaching of exchangeable, carbonate bound, oxide bound, organic bound, residual and total Sr from river sediments with ULM and CL

Total. The procedure described above for the residual fraction was repeated using a raw sediment sample. The total leaching times were 2 h and 25 h for ULM and CL, respectively.

RESULTS AND DISCUSSION

The ultrasonic leaching rate curves with ULM and the recoveries at recommended times with CL for Sr fractions in river sediments were compared in Fig. 2. While there were some variations in leaching time from fraction to fraction, the ULM required maximum 10 min to reach the same recoveries given for each fraction by CL.

By use of leaching rate studies to establish the ultrasonic leaching times for each of the fractions, a leaching time was chosen that corresponded to a point on the plateau that was just beyond the point of inflection on the leaching rate curves. The corresponding time required to satisfy this condition was approximately 20 min for all fractions.

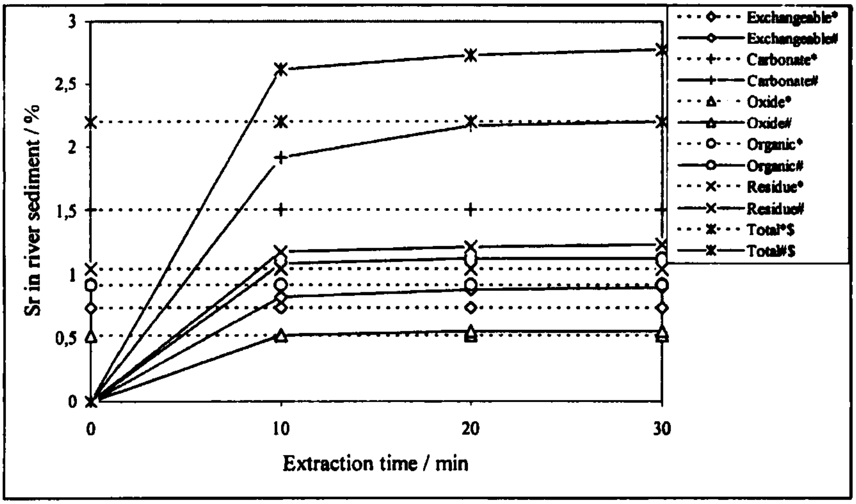

FIGURE 3 Comparison of ULM rate curves and recoveries at recommended times with CL (time as hours 1, 5, 6, 5, 4, and 4 for exchangeable, carbonate, oxide, organic, residue, and total fractions, respectively) for Sr fractions in river sediment, *: CL, #: ULM, $: Experimental total (total =graphic value × 2)

Comparison of the recoveries of Sr fractions from various sediment samples using ULM and CL are shown in Table I. Each value in Table I is the mean of three or four replicate measurements and RSDs %(as average relative standard deviation %) were calculated from pooled data for each leaching method. The statistical analysis[21] (*t* and *F* significance tests at 0.05 probability) based on these data showed that the differences between the means of the two leaching methods were not statistically significant. The reproducibility in total Sr was acceptable in such studies for both methods, the average RSDs % being 12.8 [n(degree of freedom)=14] and 14.7 (n=14), for ULM and CL, respectively. In the recoveries of total Sr from NIES CRM-2, a 1 % positive and a 25 % negative error were found with CL, whereas a 9 % positive and a 16 % negative error were found with ULM.

TABLE I Recoveries of Sr fractions in Tecer River sediments and determination of total Sr in NIES CRM-2 with ULM (20 min) and CL (time as hours 1, 5, 6, 5, and 4 for exchangeable, carbonate, oxide, organic, and residual binding fractions, respectively)

Fractions	*Distance from drainage water disposal site/km*	*Sr recoveries/ g per 100 g*	
		CL	***ULM***
Exchangeable	2.0 (before)	0.21 ± 0.02	0.38 ± 0.03
	0.0 (at stream)	0.74 ± 0.08	0.88 ± 0.08
	1.5 (after)	2.03 ± 0.25	3.12 ± 0.29
	3.5 (after)	2.24 ± 0.28	4.07 ± 0.37
	6.5 (after)	2.83 ± 0.31	3.86 ± 0.35
	11.5 (after)	1.51 ± 0.17	2.77 ± 0.2
	18.0 (after)	0.67 ± 0.08	1.24 ± 0.11
Carbonate Bound	2.0 (before)	0.11 ± 0.01	0.11 ± 0.01
	0.0 (at stream)	1.51 ± 0.15	2.17 ± 0.22
	1.5 (after)	1.15 ± 0.11	2.10 ± 0.21
	3.5 (after)	1.07 ± 0.10	1.91 ± 0.19
	6.5 (after)	0.73 ± 0.07	1.56 ± 0.16
	11.5 (after)	0.41 ± 0.04	1.04 ± 0.10
	18.0 (after)	0.23 ± 0.02	0.29 ± 0.03
Oxide Bound	2.0 (before)	BDL[a]	BDL[a]
	0.0 (at stream)	0.52 ± 0.05	0.55 ± 0.06
	1.5 (after)	0.64 ± 0.09	0.67 ± 0.08
	3.5 (after)	0.64 ± 0.09	0.65 ± 0.08
	6.5 (after)	0.72 ± 0.10	0.74 ± 0.09
	11.5 (after)	0.41 ± 0.06	0.52 ± 0.06
	18.0 (after)	0.13 ± 0.02	0.15 ± 0.02
Organic Bound	2.0 (before)	BDL[a]	BDL[a]
	0.0 (at stream)	0.92 ± 0.11	1.12 ± 0.10
	1.5 (after)	0.78 ± 0.09	1.06 ± 0.09
	3.5 (after)	0.89 ± 0.11	1.09 ± 0.09
	6.5 (after)	0.69 ± 0.08	0.74 ± 0.06
	11.5 (after)	0.35 ± 0.04	0.41 ± 0.04
	18.0 (after)	0.21 ± 0.03	0.28 ± 0.02

Fractions	*Distance from drainage water disposal site/km*	*Sr recoveries/ g per 100 g*	
		CL	***ULM***
Residual	2.0 (before)	BDL[a]	BDL[a]
	0.0 (at stream)	1.04 ± 0.15	1.21 ± 0.15
	1.5 (after)	1.45 ± 0.21	1.46 ± 0.19
	6.5 (after)	1.48 ± 0.22	1.64 ± 0.21
	18.0 (after)	0.77 ± 0.11	0.91 ± 0.12
Total[d]	2.0 (before)	3,20(± 0.47)10^{3}[b]	4.92(± 0.63))10^{3}[b]
		2,82(± 0.41)10^{3}[c]	3.94(± 0.50)10^{3}[c]
	0.0 (at stream)	47.33(± 6.95)10^{3}[b]	59.31(± 7.59)10^{3}[b]
		44.10(± 6.48)10^{3}[c]	54.63(± 6.99)10^{3}[c]
	1.5 (after)	60.52(± 8.90)10^{3}[b]	84.14(± 10.77)10^{3}[b]
		53.71(± 7.89)10^{3}[c]	69.82(± 8.94)10^{3}[c]
	6.5 (after)	64.54(± 9.49))10^{3}[b]	86.40(± 11.06)10^{3}[b]
		56.51(± 8.31)10^{3}[c]	78.22(± 10.01)10^{3}[c]
	18.0 (after)	20.14(± 2.96)10^{3}[b]	28.70(± 3.67)10^{3}[b]
		17.44(± 2.56)10^{3}[c]	23.41(± 3.00)10^{3}[c]
	NIES CRM-2[e]	97 ± 14[dc]	106 ± 13[dc]

a. BDL: below detection limit.
b. Calculated total Sr (from sum of five fractions).
c. Experimental total Sr (from direct raw sediment leaching).
d. Values in µg/g.
e. Reference value of Sr is 110 µg/g.

The ULM recoveries of exchangeable Sr are 1.2–1.9 times greater than the CL recoveries. One of the problems with sequential leaching procedures is the redistribution of dissolved elements between phases during the leaching. We therefore concluded that high ULM recoveries depended on preventing this re-adsorbtion. The reproducibility (as average RSD %) of ULM for exchangeable Sr fraction is 9.2 (n=14), which is slightly higher than CL, which has an average RSD % of 12.4 (n=17). The exchangeable Sr in river sediment is 2.3–3.5 times greater than in sediment collected from the immediate vicinity of the drainage water disposal site. The results are in accordance for both methods. The exchangeable Sr fraction reached its maximum value within 6.5 km of this site and then gradually decreased. This can be explained as following;

Before, Sr might undergo dissolving-adsorption on the sediment and it might transformed from chemical bound to physical bound. After then(6.5 km) Sr might bound to sediment as a crystal structure component.

The exchangeable Sr in the leachat of NIES CRM-2 could not be determined with either ULM or CL. The amount of exchangeable Sr from NIES CRM-2 was below our detection limits.

The recoveries for the CL and ULM of the carbonate and organic bound Sr fractions are compared in Table I. The recoveries of the carbonate bound and organic bound Sr in river sediment are the highest in sediment collected from the immediate vicinity of the drainage water disposal site and then gradually decreased. The organic bound Sr could not be determined before the drainage water disposal site. The reproducibility for carbonate bound Sr was acceptable for both methods, the average RSD % being 10.3 (n=14) and 9.7 (n=17), for ULM and CL, respectively. Again, average RSD % was obtained in organic bound Sr fraction 8.6 (n=12) and 12.2 (n=12), for ULM and CL, respectively.

Although it appears that the recoveries with ULM of oxide bound and residual Sr are slightly higher than those with CL (see Table I), there is actually no significant difference between the recoveries of the two methods. The oxide bound and residual Sr in river sediment reached its maximum value within 6.5 km of distance from drainage water disposal site and then decreased. The reproducibility (as average RSD %) of ULM for oxide bound fraction is 11.7 (n=12), which is also slightly higher than CL, which has an average RSD % of 14.2 (n=12). Again, average RSD % was obtained in residual Sr 12.8 (n=12) and 14.7 (n=12) for ULM and CL, respectively. Residual and oxide bound Sr could not be determined before the drainage water disposal site was reached.

Because of the amount of fractional Sr from NIES CRM-2 was below our detection limits, the fractional Sr in the NIES CRM-2 extracts could not be determined with either ULM or CL.

The calculated total Sr which was determined by summing the exchangeable, carbonate, oxide, organic and residual Sr fractions, and experimental total Sr determined from direct leaching of raw sediment are also summarized in Table I for both methods. The calculated total Sr values were always higher than the experimental values. This could be due to the number of leaching performed, which of course affects the recovery of Sr. The calculated total Sr values were obtained from five leaching whereas the experimental total Sr values were obtained from a single leaching; hence the results are reasonable.

The accuracy of the ULM was assessed by measuring of total Sr in leachat of NIES CRM-2 standard, and the results obtained are given in Table I. We concluded that the solvent system used was responsible for the low recoveries and poor reproducibility in the total metal leaching, because the results were approximately the same for both leaching methods.

Although there was no standard reference material available for comparison of the accuracy of Sr fractions with ULM, this works shows that ULM can be valuable in the study of the speciation of metals within binding fractions of sediments. Use of the ULM reduces the time required for fractionation from 21 h to 1.7 h, while providing the results, which are comparable to the CL. It is clear that the ULM is a rapid, inexpensive, easy, reproducible and selective technique for sequential leaching of Sr metal in sediment, which are important in environmental pollution.

Acknowledgements

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