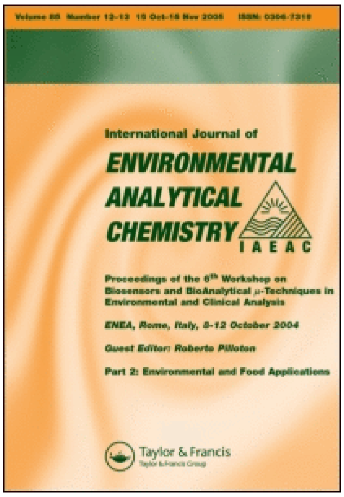

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MICROWAVE DESORPTION TREATMENT AFTER THE OXIDATION STEP IN TESSIER'S SEQUENTIAL EXTRACTION SCHEME

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Microwave desorption of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn after the oxidation step in Tessier's sequential extraction scheme was studied. Metals were determined by atomic absorption spectrometry in solutions obtained after traditional or microwave desorption and results were compared using the Kruskal-Wallis statistical test.

Besides Cr, Cu and Pb, for which the two treatments gave the same results, the traditional treatment was more effective in extracting the considered trace metals from the oxidised surface of the sediment.

KEY WORDS: Microwave heating, Tessier's sequential extraction, sediment analysis.

INTRODUCTION

Metals are not permanently bonded to aquatic sediments. They can be released due to modifications of the physical—chemical conditions at the solid—liquid interface[1]. Therefore, the determination of total concentrations is not sufficient for determining the availability of pollutants to the environment or to the living organisms[2]. The type of association between trace metals and the sediment must be assessed. This can be done by sequential extraction techniques that, despite some limitations, permit to determine various chemical fractions related to a gradient in association stability[3].

So far, many sequential extraction schemes have been proposed[4], but almost all of them need a very long time (days) to treat samples for analysis. Among these, Tessier's[5] method has been widely used enabling comparison with published results[6]. To overcome long treatment times, which sometimes limit the application of sequential extraction techniques, the use of microwave (mw) heating instead of the traditional procedure (shaking at room temperature and heating in a thermostatic bath) in Tessier's extraction scheme was studied by Mahan *et al.*[7]. Using a domestic apparatus, they proved that mw treatment produces results comparable to those of the traditional treatment in a considerably shorter time.

Nowadays mw heating has a widespread application for analytical purposes[8] and many mw laboratory digesters are available. In a previous work[9] a laboratory mw digester was used to follow Tessier's sequential extraction scheme, getting substantially Mahan's results, but poor recoveries of iron after the oxidation step. As the percentage of

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C in the residue after traditional or mw oxidation was the same, the low recovery of iron was probably due to readsorption of ions on the new created solid—solution interface and not to an uncomplete oxidation of organic matter.

To avoid readsorption after the oxidation, Tessier suggested in his extraction scheme a desorption treatment, that was shaking for 30 min at room temperature with NH_40Ac 3.2 mol dm^{-3} in HNO_3 20% v/v; although this desorption treatment was adopted also after mw oxidation, iron was poorly recovered, suggesting that mw oxidation created a surface that was more active in adsorbing released ions and that a stronger desorption treatment was needed.

In this work the application of mw heating to desorption treatment was studied, trying to improve metal recovery after oxidation of organic matter. As the attention was concentrated on the oxidation step, a simplified "microwave Tessier's extraction scheme" was adopted; trace metals were partitioned in 3 fractions:

i. reducible fraction (Red.): encompassing the so called exchangeable metals, carbonate bond and Fe/Mn oxides bond metals of Tessier's traditional extraction scheme.
ii. oxidable fraction (Ox.): corresponding to the fraction bonded to organic matter and sulphides in Tessier's scheme.
iii. residual fraction (Res.).

Subsamples of sediment from the Po river were previously microwaved to extract the reducible fraction and then the oxidable fraction was extracted by two different treatments:

i. microwave oxidation and traditional desorption.
ii. microwave oxidation and microwave desorption.

Results from the different procedures were compared by the Kruskal Wallis statistical test[10] to objectively point out differences.

In the present work, the behaviour of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn was considered. The metals were determined by AAS in each fraction of the sequential extraction scheme and in solutions obtained after total digestion. Mass balance was verified by comparing the sum of each fraction with total metal content.

EXPERIMENTAL

Sampling and pretreatment

The sediment was collected in Po river, from a depth of 0–5 cm. Immediately after sampling, the mud was centrifuged and the solid material obtained was dried at room temperature in a laminar flow hood. The dry sediment was sieved through a nylon sieve and the fraction ≤ 63 μm was studied[11]. The material was stored in a plastic bottle containing a Teflon ball at +4°C until treatment. Before drawing subsamples, the bottle was shaken for at least 4 min[12]; to standardise residual humidity, the material was then left overnight in a desiccator before weighing.

Instruments and reagents

Fe, Zn and Mn were determined by FA/AAS with air/acetylene flame using a Perkin Elmer 1100 B spectrophotometer. Cd, Cr, Cu, Ni and Pb were determined by ETA/AAS with a Perkin Elmer 5000 spectrophotometer equipped with a HGA 400 graphite furnace unit and an AS40 automatic sampler. Atomization conditions were those indicated by the manufacturer, slightly modified to obtain maximum signal.

A CEM MDS 2000 microwave digester was used. For total dissolution, which were made in sealed vessels, the oven was equipped with an automatic pressure control device.

Reagents were Merk Suprapur when available or analytical grade.

Aqua regia digestion and extraction of residual fraction

To determine total metal content and to extract the residual fraction in the three step microwave sequential extraction scheme, aqua regia digestion under pressure using microwave heating was adopted[3]. The same digestion technique was also adopted to attack a reference sediment (RS) in order to verify the accuracy of total metal determinations.

Desorption procedures

About 1 g of sediment was treated to extract the reducible fraction and to oxidise the organic matter according to the procedure described elsewhere[9].

After the H_2O_2 oxidation the microwave (a) and traditional (b) desorption procedures were performed as follows:

a) 5 cm^3 of CH_3COONH_4 3.2 mol dm^{-3} were added to sample suspensions and they were microwaved for 5, 7, 11, 13, 15 and 17 min at 20% power (4 samples simultaneously for each treatment time). After cooling, samples were centrifuged, solutions were decanted, diluted to 50 ml with HNO_3 1% and stored at +4°C. Residues after 13 min of mw desorption treatment were digested to extract the residual fraction and to determine the mass balance. Residues from other treatment times were discarded.

b) 5 cm^3 of CH_3COONH_4 3.2 mol dm^{-3} were added to sample suspensions, shaken continuously for 30 min and centrifuged. Decanted solutions were diluted to 50 ml with HNO_3 1% and stored at +4°C, residues were discarded.

Accuracy of metals determination

Accuracy for total metal determination was verified by carrying out digestion and analysis of the sample at the same time with a sediment with a certified content of metals (RS). As results for the RS were in the certified range for all metals determined, it was reasonable to assume that also determinations on Po river sediment were accurate.

As it was impossible to find a RS to verify the accuracy of each extraction step, mass balance was used as an index of the accuracy of metals determination in each fraction.

RESULTS AND DISCUSSION

Mass balance

As reported in Table 1, the metals mass balance was verified for a set of samples that were mw heated for 13 min in the desorption step. For all metals considered, there was a good agreement between total metals determination and the sum of each fraction.

As the matrix was the same for each set of samples (mw heated for different times and

Table 1 Metals mass balance (standard deviations are indicated in parenthesis).

	Cd (μg/g)	Cr (μg/g)	Cu (μg/g)	Fe (mg/g)	Mn (μg/g)	Ni (μg/g)	Pb (μg/g)	Zn (μg/g)
Red.[a]	0.772	7.23	6.08	3.39	237	9.61	89.1	113
	(0.050)	(0.57)	(0.38)	(0.27)	(0.7)	(0.45)	(0.1)	(0.8)
Ox.[b]	0.978	6.27	21.3	0.13	14.0	4.43	14.3	6.44
	(0.770)	(0.31)	(0.8)	(0.01)	(1.1)	(0.05)	(1.0)	(0.40)
Res.[b]	1.01	128	29.6	26.6	343	103	50.3	82.4
	(0.09)	(3)	(4.6)	(2.1)	(7)	(9)	(0.7)	(1.2)
Σ	2.76	142	57.0	30.1	594	117	154	202
Total[a]	2.63	152	50.2	29.9	593	120	151	206
	(0.16)	(16)	(3.4)	(1.7)	(4)	(7)	(2)	(6)
Δ%	+4.90	−6.58	+13.5	+0.669	+0.168	−2.50	+1.99	−1.94

[a] 6 independent subsamples
[b] 4 independent subsamples

traditionally desorbed) the good agreement in mass balance for the chosen set of samples was assumed to be representative of the accuracy of the method.

Comparison between microwave and traditional desorption procedures

Metals were determined on 4 subsamples after each oxidation + desorption step and results of the determinations are shown in Table 2. Data referring to each desorption treatment were compared by the Kruskal-Wallis statistical test, checking the null

Table 2 Metal contents in oxidable fraction after traditional (trad.) and different microwave (mw) desorption treatments.

		trad.	mw 5'	mw 7'	mw 11'	mw 13'	mw 15'	mw 17'
Cd (μg/g)	mean	0.743	0.916	1.02	0.877	0.978	1.02	0.969
	sd	0.019	0.050	0.040	0.36	0.77	0.737	0.074
	RSD%	2.59	5.47	3.87	4.10	7.91	7.23	7.64
Cr (μg/g)	mean	5.93	5.69	6.20	6.39	6.27	6.60	7.20
	sd	0.391	0.338	0.615	0.195	0.314	0.321	0.396
	RSD%	6.60	5.93	9.92	3.06	5.01	4.86	5.50
Cu (μg/g)	mean	22.7	19.2	18.7	19.6	21.3	22.9	21.1
	sd	3.44	1.61	0.271	1.09	0.792	0.906	0.137
	RSD%	15.1	8.37	1.45	5.55	3.71	3.96	0.651
Fe (μg/g)	mean	280	120	110	130	131	130	124
	sd	25.1	5.95	6.19	6.47	8.57	8.26	7.10
	RSD%	8.99	4.97	5.65	4.96	6.51	6.35	5.74
Mn (μg/g)	mean	17.7	10.2	10.7	11.7	14.01	13.2	13.4
	sd	2.97	0.669	0.673	0.422	1.06	0.461	0.532
	RSD%	16.8	6.55	6.29	3.72	7.56	3.50	3.97
Ni (μg/g)	mean	6.84	3.38	3.44	4.01	4.43	4.42	4.50
	sd	1.34	0.124	0.255	0.116	0.0539	0.162	0.145
	RSD%	16.6	3.66	7.41	2.90	1.21	3.67	3.21
Pb (μg/g)	mean	9.58	14.9	14.3	14.5	14.3	13.1	14.0
	sd	0.904	2.54	0.889	1.78	0.974	1.41	0.432
	RSD%	9.44	17.1	6.20	12.3	6.82	10.7	3.09
Zn (μg/g)	mean	10.7	4.76	5.59	5.71	6.44	7.42	6.77
	sd	1.98	0.153	0.277	0.277	0.399	0.38	0.387
	RSD%	18.5	3.21	4.86	4.86	6.11	5.12	5.72

hypothesis (that was "each treatment yields to the same results") for significance levels α of 0.1 and 0.05.

For the determined metals (excepted for Pb), the value of Hc (calculated discriminant function) calculated from analytical data was > of Ht (tabulated discriminant function) tabulated on the X^2 distribution table for both $\alpha = 0.05$ and 0.1. This means that for each metal there was at least one group of data (treatment) whose mean was significantly different from those of the other groups. After that, a multiple comparison[10] among groups was executed. With this statistical test each group was compared sequentially with all others and possible differences were pointed out for each couple for a given significance level. Significance levels $\alpha = 0.05$, $\alpha = 0.1$ and $\alpha = 0.01$ were considered and the value of 0.05 was chosen as optimal for this set of experimental data, as value of 0.1 and 0.01 were respectively too severe and too large to satisfactorily discriminate between groups. The test was not applied to Pb, as no significant difference among treatments was pointed out by the Kruskal—Wallis test, although matrix problems yielded scattered data and the efficiency of the test might be reduced.

Results of multiple comparison with a significance level $\alpha = 0.05$ are reported in Table 3. For each microwave desorption time is indicated whether the results differ from those obtained with traditional desorption. After the statistical test it was possible to subdivide the considered metals into two groups:

i. Cr, Cu and Pb for which was impossible to discriminate between traditional and microwave desorption with a heating time between 11 and 15 min;

ii. Cd, Fe, Mn, Ni and Zn for which traditional desorption was generally more effective in extracting metals from the oxidised surface of the sediment even with long microwave heating times.

CONCLUSION

Contrary to expectation, experimental data showed that microwave heating was not able to improve metal recovery after organic matter oxidation and for Cd, Fe, Mn, Ni and Zn the recovery was even lower that with traditional desorption. Only for Cr, Cu and Pb the two methods yield similar results. Therefore, mw desorption is not advisable for metal speciation with Tessier's sequential extraction scheme as it could bring to underestimate organic fraction.

From the obtained data it seems that the metal—sediment interaction becomes

Table 3 Multiple comparison test ($\alpha = 0.05$) between traditional desorption and each mw desorption treatment.

	mw 5'	mw 7'	mw 11'	mw 13'	mw 15'	mw 17'
Cd	yes	yes	no	yes	yes	yes
Cr	no	no	no	no	no	yes
Cu	yes	yes	no	no	no	no
Fe	yes	yes	yes	yes	yes	yes
Mn	yes	yes	yes	no	yes	yes
Ni	yes	yes	yes	yes	yes	yes
Zn	yes	yes	yes	yes	yes	yes

yes: trad. and mw treatment (for the indicated heating time) are different for a significance level of 0.05
no: trad. and mw treatment (for the indicated heating time) are not different for a significance level of 0.05

stronger with microwave heating, probably due to a modification of the sediment surface, which plays a very important role in the oxidation step of the sequential extraction. A better understanding of metal—sediment interaction will probably help to explain the behaviour of metal desorption with mw heating.

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