Chemical speciation of heavy metals in the Tigris River sediment

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ABSTRACT

After determination of total heavy metal concentrations in Tigris river sediments, a Tessier sequential extraction technique and a modified form using a microwave heating procedure were applied. Recoveries of total heavy metals from the sediment samples using the microwave and conventional techniques were reasonably comparable, in spite of a big difference in time required. 44–46% of Co, 24–36% of Cu, 69-81 % of Ni, and 55–73% of Zn were found in the residual fraction (*i.e*. not bioavailable).

Keywords: heavy metals, microwave digestion, sediment, sequential extraction, speciation.

INTRODUCTION

Sediments conserve important environmental information (VonGunten *et al.*, 1997), and are increasingly recognised as both a carrier and a possible source of contaminants in aquatic systems (Förstner and Salomons, 1991; Tessier *et al.*, 1994).

To obtain a solution suitable for instrumental element analysis of sediment samples, wet acid digestion procedures are most frequently employed (Achilli *et al.*, 1991; Knapp, 1991). Conventional wet acid digestion procedures can require several hours or even several days to complete sample decomposition, while comparable results have been obtained in a few minutes by microwave wet acid digestion procedures (Krause *et al.*, 1995; Lorentzen and Kingston, 1996; Walter *et al.*, 1997; Wen *et al.*, 1997; Florian *et al.*, 1998).

Much work has been performed on heavy metal pollution in river-lake sediments (Unlü and Gümgüm, 1993; Gulmini *et al.*, 1994; Gümgüm *et al.*, 1994; Leonard *et al.*, 1996; Minissi *et al.*, 1998; Avila-Perez *et al.*, 1999; Liu *et al.*, 1999; Maher *et al*., 1999; Ramos *et al.*, 1999). In the last five years, a number of review articles have been published detailing the use of microwave techniques for analysis of heavy metal pollution in sediments and other environmental samples (Smith and Arsenault, 1996; Wong *et al.*, 1997; Lamble and Hill, 1998).

In order to evaluate the possible toxicity or risk of environmental pollution of heavy metals present in sediments, the types of association between metals and the sediment must be assessed. This can be undertaken by two sequential extraction techniques (Tessier *et al.*, 1979; Commission of European Communities, 1983). The Tessier scheme divides metals into five fractions: (1) exchangeable, (2) carbonate-bounded, (3) iron-manganese oxides-bounded, (4) organic matter-bounded, and (5) residual. In spite of long analysis times (days), many studies have been carried out using this method (Baruah *et al.*, 1996; LopezSanchez *et al.*, 1996; Ginepro *et al.*, 1996; Pempkowiak *et al.*, 1999). Fraction 1 is considered to be the most soluble/bioavailable and the last fraction the least bioavailable or non-anthropogenic (Chapman *et al.*, 1998; Fichet *et al.*, 1998; Rieuwerts *et al.*, 1998; Langston *et al.*, 1999; Mehra *et al.*, 1999). The second technique, three stage BCR sequential extraction procedure were proposed by the Commission of the European Communities Bureau of Reference (BCR – now the Standards, Measurements and Testing Programme–SMT) needs less time than the first one. This procedure was developed and

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improved by SMT (formerly BCR) and it will facilitate comparability of data in the European Union. In this technique, metals were divided into three fractions by the application of following chemicals: (1) CH_3COOH, (2) $NH_2OH.HCl$, (3) H_2O_2 and CH_3COONH_4 (Davidson *et al.*, 1994; Thomas *et al.*, 1994; Quevauviller *et al.*, 1997; Rauret *et al.*, 1999; Sahuquillo *et al.*, 1999).

To overcome long treatment times of the sequential extraction, the use of microwave heating instead of conventional heating in the sequential extraction procedure has been studied and the two techniques compared each other (Gulmini *et al.*, 1994; Ginepro *et al.*, 1996; Perez-Cid *et al.*, 1998). A similar study was performed, using ultrasonic energy (Perez-Cid *et al.*, 1999).

In the present work, the Tigris river sediments were digested by conventional and microwave wet acid procedures and total concentrations of heavy metals (cobalt, copper, nickel and zinc) were determined. After determination of the total concentrations, the Tessier sequential extraction scheme is applied to the sediments by using conventional heating and a modified form, using a microwave heating procedure. The concentrations of the investigated metals were determined by an atomic absorption spectrophotometer (AAS).

EXPERIMENTAL

Nine sediment samples were collected from the eastern side of the Tigris River, Diyarbakyr city/Turkey. The study area is described in our earlier publication (Ünlü *et al.*, 1996). The samples were dried at room temperature, and homogenised. To determine the total metal content 0.2–0.4 g, and for sequential extractions 0.6–0.7 g of the samples were weighed into Teflon beakers and vessels. The experiments were performed on three sets of sub-samples. Conventional decomposition was accomplished on a sandbox, using Teflon beakers, while microwave digestion was performed in a CEM MDS-2000 microwave oven.

The total, and fractionated concentrations of the elements Co, Cu, Ni and Zn were determined by a UNICAM-929 atomic absorption spectrophotometer at the wavelengths (nm) of 240.7; 324.8; 232.0 and 213.9 respectively. Air/acetylene type flame was used for all the elements. All the chemicals used were of analytical reagent grade.

Determination of total metal concentrations by conventional and microwave heating

For conventional dissolution, 10 mL of aqua regia and 5 mL of concentrated hydrofluoric acid were added to the samples, and the mixture was heated to dryness on a sandbox.

Microwave digestion was performed using 5 mL of aqua regia with a satisfactory modified programme; power 30%, pressure 40% and time 10 min. The analytical results are shown in Table 1.

Sequential extraction of metals by conventional and microwave heating

The Tessier sequential extraction scheme (conventional), and a modified form (microwave heating procedure) were applied to the Tigris river sediments. During the microwave extractions closed vessels were used, and 30% power and 40% pressure were applied. Working conditions (including reagents) used in the conventional Tessier scheme and the modified form are shown in Table 2. Both procedures were repeated with three sets of subsamples, and metal concentrations obtained in each leachate are shown in Table 3.

RESULTS AND DISCUSSION

Table 1 gives the average results of total metal concentrations in the Tigris river sediment by conventional and microwave digestion techniques. The results show that there is a good agreement between the two applied digestion techniques.

Sequential extraction conditions for conventional and microwave heating techniques can be seen in Table 2. This shows the maximum conventional sequential extraction times are not suitable for daily work. In practice, it is believed that approximately 31 h are required for conventional handling (Gulmini *et al.*, 1994).

None of the investigated metals (Co, Cu, Ni, Zn) were extracted in the classical exchangeable fraction and the microwave procedure was not applied for this stage (Table 3).

It can be seen from Table 3 that, only Ni and Zn were found in the leachate of carbonate bound metals. The average concentrations of Ni and Zn (using both techniques) were approximately 1 mg kg^{-1} and 10 mg kg^{-1}, respectively. The ratio of microwave /conventional extractions were calculated as 98.06% for Ni and 96.18% for Zn.

In the iron–manganese oxides fraction, for all of the investigated metals higher results were obtained in the microwave extraction technique than the conventional one. The extraction rates (as a proportion of total concentration) were found to decrease in the sequence: Zn>Co>Ni>Cu for both conventional and microwave applications. Approximately 25% of the zinc and cobalt in the sediments were found in this fraction, compared approximately 10% for copper and nickel. Zinc has the highest proportion in this fraction (28.85%) and copper the least (6.97%).

The organic matter-bound stage, accounted for the lowest proportion of total nickel (6.36% and 9.80%) and the highest proportion of total copper (43.88% and 40.81%) for conventional and microwave applications respectively.

Table 1 Concentrations of heavy metals in the Tigris river sediment

Sample/Method	Heavy metals (mg kg^{-1} ± SD*)			
	Co	Cu	Ni	Zn
Conventional	32.01 ± 1.16	728.96 ± 14.75	66.35 ± 4.01	369.14 ± 12.24
Microwave	30.78 ± 1.23	719.22 ± 16.13	63.72 ± 3.21	358.27 ± 15.12

*SD: standard deviation.

Table 2 Working conditions used in the conventional and microwave sequential extraction of heavy metals from the Tigris river sediment

Fractions and Reagents	Conventional conditions (Tessier scheme)	Microwave conditions (Modified scheme)
Exchangeable		
25 mL 1M $MgCl_2$ (pH: 7.05)	1 h, 25°C	–
Carbonate-bound		
25 mL 1M CH_3COONa (pH: 5.22)	5 h, 25°C	10 min
Fe-Mn oxides-bound		
25 mL 0.04M $NH_2OH.HCl$ (in 25% (v/v) CH_3COOH)	6 h, 96(C	15 min
Organic matter-bound		
9 mL 0.02M HNO_3 + 16 mL 30% H_2O_2	5 h, 96°C	10 min

Table 3 Heavy metal concentrations obtained applying the conventional and microwave extraction schemes to the Tigris river sediment

Sample/method	Heavy metals (mg kg^{-1} ± SD*)			
	Co	Cu	Ni	Zn
Conventional				
Exchangeable	ND	ND	ND	ND
Carbonate-bound	ND	ND	1.03 ± 0.07	10.22 ± 0.41
Fe-Mn oxides-bound	7.42 ± 0.37	50.82 ± 1.52	7.41 ± 0.52	104.42 ± 5.02
Organic mat.-bound	10.13 ± 0.73	319.90 ± 12.80	4.22 ± 0.38	51.49 ± 3.04
Microwave				
Carbonate-bound	ND	ND	1.01 ± 0.05	9.83 ± 0.47
Fe-Mn oxides-bound	7.81 ± 0.40	79.39 ± 1.61	8.12 ± 0.38	106.50 ± 4.85

Differences between the total metal concentrations and sum concentrations of the four sequential leachates were calculated as residual fractions, and thus residual concentrations of the conventional and microwave extractions were respectively, (mg kg^{-1}) 14.46 and 14.57 for Co, 358.24 and 342.32 for Cu, 53.69 and 48.09 for Ni and 203.01 and 194.62 for Zn.

CONCLUSION

Analytical results obtained using conventional and microwave digestion techniques show that, there is a good agreement between the two techniques for all of the investigated metals in the Tigris river sediment. 44–46 % of Co, 24–36 % of Cu, 69–81 % of Ni, and 55–73 % of Zn were calculated to be in the residual fraction (not bioavailable).

This work shows that Tigris river sediment was contaminated by heavy metals Co, Cu, Ni, Zn and that microwave heating techniques can be valuable in studies of total metal concentration and the speciation of metals within fractions of sediments. The proposed scheme allows shortening the sequential extraction time from days to minutes.

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