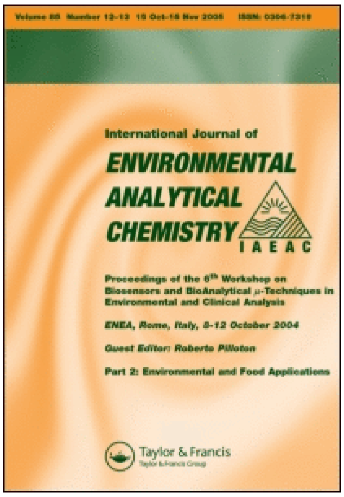

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# USE OF ULTRASONIC ENERGY FOR SHORTENING THE SEQUENTIAL EXTRACTION OF METALS FROM RIVER SEDIMENTS

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Ultrasonic energy delivered by means of a probe was used to reduce the operation time in each of the stages corresponding to the Tessier sequential extraction procedure when it was applied to metal fractionation in a river sediment. The optimum extraction conditions (amplitude and sonication time) were specifically selected in each step for Cu, Cr, Ni, Pb and Zn. Extractable metal contents obtained in each stage by both the conventional and ultrasonic extraction procedures were measured by Flame-Atomic Absorption Spectrometry and the results were statistically compared ($P = 0.95$). Although significant differences were found for Cu in the three first stages and for Pb and Zn in the two last stages, the total extractable metal contents obtained for these elements were similar when using both methods. Ni was always quantitatively extracted and Cr was almost not leached using the proposed accelerated extraction scheme.

*Keywords:* Sequential extraction; ultrasound energy; river sediment; Flame- Atomic Absorption Spectrometry

## INTRODUCTION

The behaviour and possible toxic effects of heavy metals present in environmental samples depends on the chemical form in which the elements appear[1,2]. Several sequential extraction procedures have been used for metal fractionation on different kinds of samples in order to evaluate the possible risk of environment pollution.

The Tessier[3] sequential extraction procedure is one of the most applied methods despite the required high time consumption. However, the overall operation

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time is less than half that required by the most recent three-stage sequential extraction procedure proposed by the Community Bureau of Reference (BCR)[4]. Last method has been introduced in order to harmonise the different fractionation schemes present in the literature[2] and establish a standard procedure.

A great number of applications have been published using both the Tessier and the BCR sequential extraction procedures[5–9], including comparison of the extraction capability between them[10–12], but the long treatment times (e.g. several days) sometimes limit the applicability of both procedures, especially on a routine basis. The use of microwave heating, in the Tessier's extraction scheme, instead of the conventional system (i.e. magnetic shaking and conductive heating) was studied in a few works[13–15]. Mahan et al[13] and Gulmini et al[14] suggested that the results obtained with microwave heating were comparable to those obtained using the traditional treatment. The worst case corresponded to Fe, which was poorly extracted when the microwave heating was used. Recently, the microwave treatment was also used by Ginepro et al[15] for desorption of heavy metals after the oxidation step in the Tessier's scheme. In this case, the traditional treatment was more effective for some elements in comparison with the microwave accelerated one.

Ultrasonic energy, widely known in a large variety of chemical applications such as sample preparation, cell disruption, acceleration of chemical reactions, extraction of adsorbed metals and organic pollutants in solid samples, processing of slurries[16–22], etc. presents an attractive alternative for metal extraction which can replace the traditional sample pretreatment systems. Shortening of the time required for sequential extraction of metals from sewage sludge, using the BCR method, has already been reported by the authors with the use of focused ultrasound energy[23]. In this case, the ultrasound treatment was proposed as a valid alternative to the conventional treatment since information concerning extractable metal contents from sewage sludge was virtually the same.

To the best of our knowledge, no work has been published in the literature where a sequential extraction method applied to sediments is accelerated by ultrasound treatment. The main purpose of this work is to use an ultrasonic probe in order to accelerate the Tessier sequential extraction method for its application to a river sediment. The influence of mechanical parameters (amplitude and sonication time) was specifically studied for copper, chromium, nickel, lead and zinc in order to obtain, in each fraction, extraction conditions that provided the same extraction capability as compared to the conventional Tessier method. Metal determination in the extracts was carried out by Flame Atomic Absorption Spectrometry. The extraction capability obtained with the proposed extraction method was evaluated by comparing analytical results obtained using shaking and conductive heating (conventional Tessier scheme) with those obtained by probe sonication (modified Tessier scheme).

## EXPERIMENTAL

### Instrumentation

Determination of metals in the extracts was carried by Flame-Atomic Absorption Spectrometry (FAAS) using an Atomic Absorption Spectrophotometer (Perkin-Elmer model 2380). Hollow cathode lamps (Cathodeon) were used as a radiation source for all the studied elements. Resonance lines at 324.8, 357.9, 232.0, 217.0 and 213.9 nm were used for Cu, Cr, Ni, Pb and Zn respectively. Other instrumental parameters were as recommended by the manufacturer. Extraction was achieved using a 100 W, 20 kHz ultrasonic processor (Sonic and Materials, model VC 100), equipped with three titanium microtips having diameters of 3, 6 and 13 mm. The probe sonicator allowed us to work with volumes between 250 µl and 100 ml and sonication power settings in the range of 10–100 % (peak-to-peak tip amplitude). A Kubota 5100 centrifuge was used to obtain a rapid separation of the extracts.

### Reagents

The extractant solutions were prepared from high quality reagents by appropriate dilution in deionized water. The hydroxylammonium chloride solution was prepared prior to use. Standard metal solutions (1000 µg $ml^{-1}$) were prepared from pure metal or from salts considered as as primary standards. Calibration solutions were made daily by appropriate dilution of the standard solutions.

### Sample pre-treatment

The sediment sample was collected from the Barbaña river (Ourense, Spain) and stored in polyethylene containers. Once in the laboratory, the sediment was air dried at room temperature during several days. After this, the sample was sieved (using a nylon sieve) and the particles <100 µm were separated, homogenised and stored in polyethylene vessels in a dry atmosphere (a desiccator). Other soil[5,12] and sediment[6,14,15,24] samples were also air dried before their metal fractionation using sequential extraction procedures. Total metal content in the sample was determined using the microwave digestion procedure optimised in a previous work[11], where the following digestion mixture was used: 4 ml of $HNO_3$ (70 % w/w), 1 ml of HCl (35 % w/w) and 2 ml of HF (48 % w/w).

### Influence of sonication time

Sample treatment was carried out in 50 ml capacity polyethylene tubes, in which 2 g of sediment sample (particle size < 100 µm) was placed.

Exchangeable metals were extracted (a) according the traditional protocol[3] (shaking during 1 hour at room temperature) and (b) using the proposed ultrasonic shaking, operating at 50 % of ultrasound amplitude for a time from 30 seconds to 15 min. Last procedure was carried out introducing the ultrasonic probe in the polyethylene tube and the extraction mixture (extractant/solid sample) was subjected to ultrasounds for a prefixed time. In both conventional and ultrasonic extraction procedures the ratio between the extractant solution and solid sample was kept constant.

Metals bounded to carbonates, Fe and Mn oxides and organic matter were leached in a similar way. Each fraction was obtained by applying the ultrasonic treatment to the residue remaining after removal of metals in the previous stages by means of the conventional procedure. It is important to emphasise that no heating was applied in the third and fourth extracts when the ultrasonic extraction was used. In the fourth fraction, the duration of the final treatment with ultrasound in $NH_4OAc$ was fixed at 2 min since higher sonication times caused some foaming in the extract.

After each extraction step, the supernatant liquid was separated from the solid phase by centrifugation for 5 min at 2500 rpm and then it was decanted and made up to volume. The residue was washed with 10 ml of deionized water, agitated for 15 min and centrifuged once again. The washings were discarded and the extracts were stored in polyethylene vessels until they were measured by FAAS.

### Influence of ultrasound amplitude

When an optimum sonication time was obtained for all metals in each stage of the studied extraction method, the influence of sonication power setting (%) on extraction efficiency was considered. Different values (10, 20, 50, 70 and 100 %) were selected for a prefixed ultrasonic treatment time and the extraction procedure was applied in the same way as described above.

## RESULTS AND DISCUSSION

### Optimisation of sonication time

The results of this study are summarised in Figure 1 (a-d) for all the elements in the stages corresponding to the conventional Tessier procedure. Each result was the average value of three determinations performed in separate batches. Recovery, was defined as the ratio, expressed as a percentage, between the amounts of metal leached by the ultrasonic extraction procedure and the conventional Tessier sequential extraction method. It should be highlighted that the goal of this work was to find optimised sonication conditions that provided the same extraction capability as the conventional Tessier method.

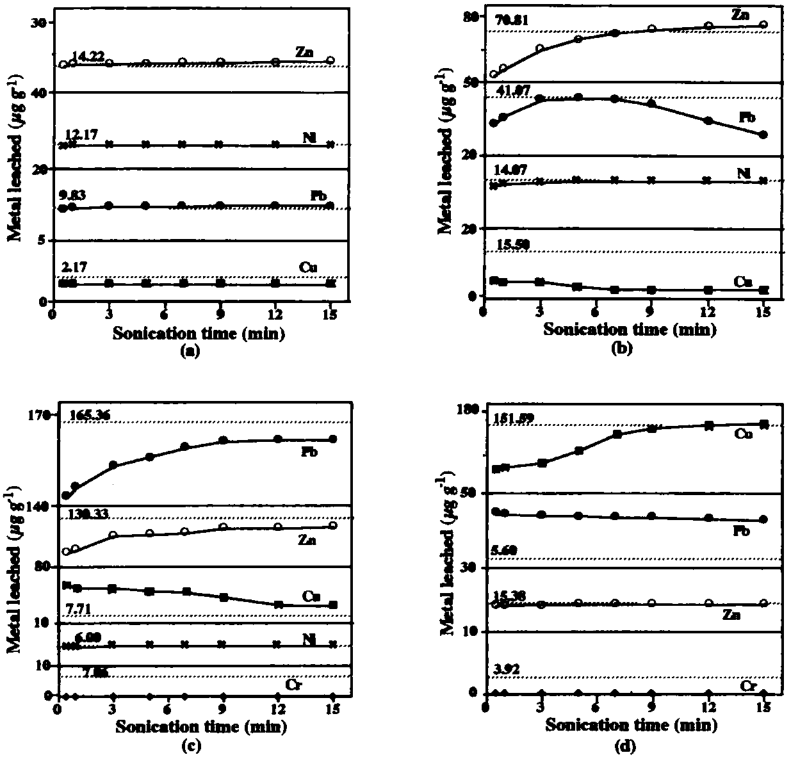

FIGURE 1 Influence of the sonication time on the extraction efficiency. First fraction (a); second fraction (b); third fraction (c); fourth fraction (d). Cu ■; Cr ◆; Ni ×; Pb ●; Zn ○. The discontinuous line indicates metal concentration (μg $g^{-1}$) found with the conventional Tessier sequential extraction method; the solid line indicates metal concentration (μg $g^{-1}$) found with the ultrasound accelerated sequential extraction method

### *First fraction*

In this stage the only detectable metals were Cu, Ni, Pb and Zn. Cu and Ni display a similar behaviour, given that for both elements the reached metal kept constant as the sonication time increased. Recoveries for Cu and Ni were 87.56% and 99.01%, respectively, by applying sonication times of only 1 min. The same extraction efficiency was obtained with sonication times between 1 and 15 min

(Figure 1a). On the other hand, for Pb and Zn recoveries found were around 100 % for both metals. when the ultrasonic extraction procedure was applied for between 30 seconds and 3 min. If the treatment time was prolonged, metal corresponding to the second fraction was also leached and the extraction efficiencies were higher than 100%. Therefore, ultrasonic extraction conditions could be found in order to reach quantitative recovery for Pb, Zn and Ni.

### *Second fraction*

All the elements studied except Cr could be quantified in this stage. Ni and Zn behave in the same way, each improving their extraction efficiency with increasing sonication time. As for Pb, a maximum recovery was achieved using sonication times between 3 and 7 min. For sonication times longer than 7 min the extraction efficiency was progressively decreased, probably due to a re-adsorption process, which increased with increasing sonication time. Ultrasounds applied to the sample could cause disruption of the solid particles, hence changing their surface properties. The same effect was found by Gulmini et al.[14] when the microwave heating was used instead of the conventional procedure in each of the stages corresponding to the Tessier's extraction method. They observed an irreversible adsorption of metal ions in the corresponding residue when the microwave heating time was prolonged. Quantitative recoveries for the three elements (around 100% for Ni and Pb and 98% for Zn) were achieved using ultrasonic treatment for 7 min (Figure 1b). For copper, the extraction efficiency was considerably reduced when the shaking time was prolonged. This behaviour can be attributed to a re-adsorption process and consequently, no satisfactory results (recovery around 30%) was obtained for this element.

### *Third fraction*

In this stage all metals could be detected by FAAS. The extraction efficiency for Ni, Pb and Zn was increased when the shaking time was prolonged. Percentage recoveries of around 100% for Ni, 79% for Pb and 71% for Zn were obtained applying ultrasonic extraction for over 9 min (Figure 1c). Whereas chromium was not extracted for any studied shaking time, copper was strongly leached in this fraction. In conclusion, almost no elements, except Ni, were adequately extracted, in relation to the conventional extraction procedure.

### *Fourth fraction*

In the fourth stage only Cu, Cr, Pb and Zn could be detected by FAAS. In this case Cu and Zn were quantitatively extracted (recoveries around 98%) with treatment times of over 9 min (Figure 1d). However Cr, as in the previous step, was poorly leached using the ultrasonic extraction procedure. In contrast, the extractable content achieved for Pb was considerable higher than that obtained applying the conventional extraction procedure.

Summing up, we can conclude that when using the ultrasonic extraction procedure operating at 50 % amplitude and at different selected shaking times, quantitative recoveries were obtained for Ni, Pb and Zn in the first and second stages, for Ni in the third stage and for Cu and Zn in the fourth stage. However the extraction of Cu in the first and second stages and of Pb and Zn in the third stage was not quantitative and the influence of amplitude must be considered in order to improve the efficiency. The effect of amplitude on the excessive leaching observed for Cu and Pb in the third and fourth stages, respectively, must also be investigated.

## Optimisation of ultrasound amplitude

Taking into account the optimum extraction time selected in the previous phase for each stage, an amplitude study has been made (Figures 2 a-d). The variation of the amplitude values between 10 and 100 % in the first and second stages did not significantly improve the extraction capability for Cu and consequently quantitative recovery for this element was not achieved (Figures 2 a-b). In the third stage (figure 2c), working with an amplitude of 100 %, the best extraction conditions were obtained for Zn (83.25%) and Pb (81.23%). An extraction efficiency about 41% was reached for Cr in this fraction. The extraction percentage obtained for Cu was considerably lower than that obtained using an amplitude of 50%, which means that the extracted metal content was closer to that obtained using the conventional method. The extraction capability for this element was considerably decreased with increasing sonication amplitude. This particular behaviour could be due once again to a re-adsorption process caused by the ultrasonic energy delivered. In the fourth stage (Figure 2d), the extraction percentage for Cu, Pb and Zn was almost unaffected by using different amplitude values between 10 and 100 % and Cr was not extracted.

We can conclude that an amplitude value of 50 % is enough to quantitatively extract Ni, Pb and Zn in the first and second stages and Cu and Zn in the fourth stage. In the third stage the best extraction efficiency was obtained working with an amplitude of 100 %.

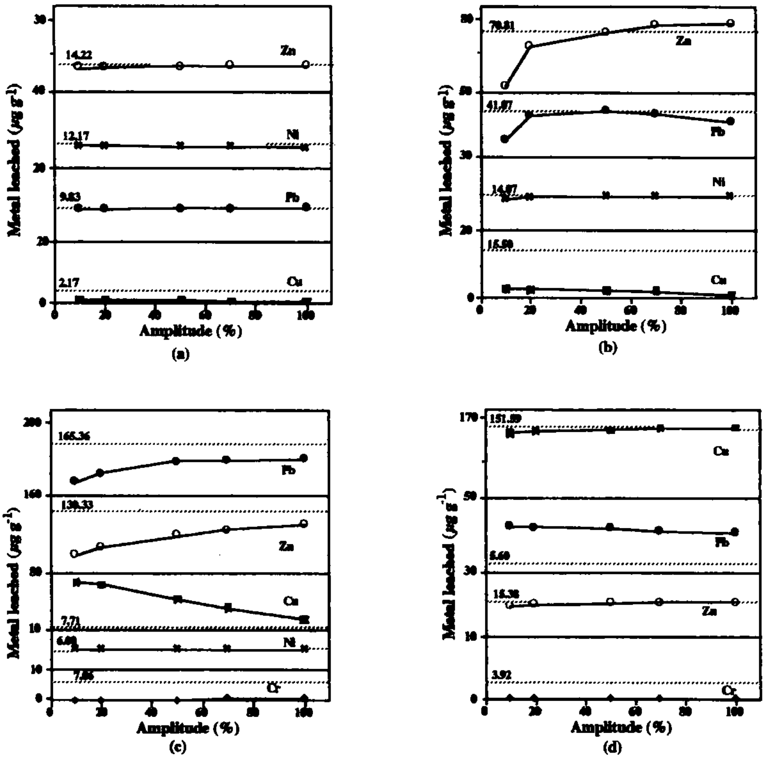

FIGURE 2 Influence of the ultrasound amplitude on the extraction efficiency .First fraction (a); second fraction (b); third fraction (c); fourth fraction (d). Cu ■; Cr ◆; Ni ×; Pb ●; Zn ○. The discontinuous line indicates metal concentration (μg $g^{-1}$) found with the conventional Tessier sequential extraction method; the solid line indicates metal concentration (μg $g^{-1}$) found with the ultrasound accelerated sequential extraction method

## Application of the conventional and the ultrasound accelerated Tessier method to a river sediment

The conventional four-step sequential extraction method and the modified one by means of ultrasonic energy are shown in Table I. Both procedures were applied, in triplicate, for metal partitioning in a freshwater sediment sample collected in the Barbaña river (Orense, Spain). Unlike the optimisation procedure outlined above, in this case, all fractions were successively obtained using ultrasound treatment. Analytical results obtained in each fraction for Cu, Cr, Ni, Pb and Zn by both methods are listed in Table II. Figure 3 shows the partitioning patterns corresponding to the conventional and the ultrasonic accelerated sequential extraction procedures. Analytical results were statistically compared (t-test, p=0.05) and no significant differences were obtained for Ni, Pb and Zn in the first and second stages, for Cu in the fourth stage and for Ni in the third stage. The recoveries achieved in these cases ranged from 97.65% to 100%.

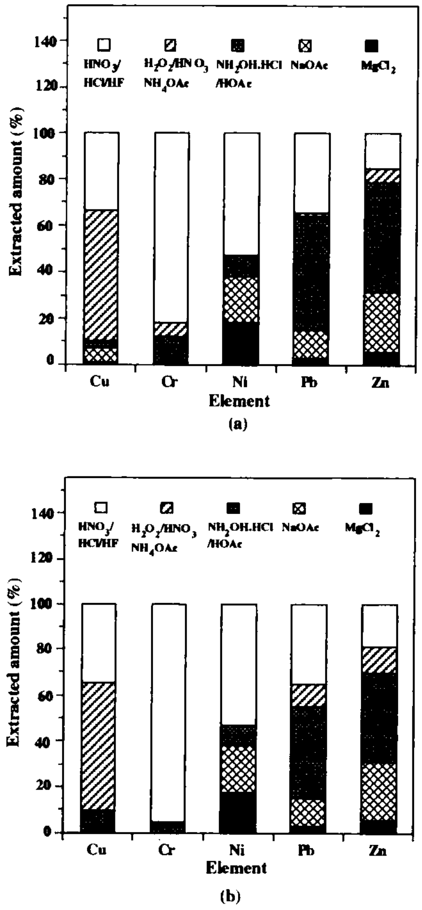

FIGURE 3 Partitioning patterns corresponding to the conventional (a) and the ultrasound accelerated (b) sequential extraction methods

TABLE I Operative conditions used in the conventional and modified Tessier sequential extraction schemes

| *Fraction/reagent* | *Conventional conditions (Tessier scheme)* | *Ultrasound conditions (Modified Tessier scheme)* |
|---|---|---|
| ***Exchangeable*** | | |
| 8 ml $MgCl_2$ 1 M (pH=7) | 1 h at 25°C | 1 min at 50 % amplitude |
| ***Carbonate-bound*** | | |
| 8 ml NaOAc 1 M (pH=5) | 5 h at 25 °C | 7 min at 50 % amplitude |
| ***Fe-Mn oxides-bound*** | | |
| 20 ml $NH_2OH.HCl$ 0.04 M in 25% (w/w) HOAc | 6 h at 96 °C | 9 min at 100 % amplitude |
| ***Organic matter-bound*** | | |
| 3 ml $HNO_3$ 0.02 M<br>5 ml $H_2O_2$30% w/v + | 2 h at 85 °C | 9 min at 50 % amplitude |
| 3 ml $H_2O_2$ 30% w/v | 3 h at 85 °C | |
| 5 ml $NH_4OAc$ 3.2 M | 30 min at 25 °C | 2 min at 50 % amplitude |

TABLE II Analytical results obtained applying the conventional and the modified Tessier sequential extraction schemes to a river sediment

| | *Conventional method* $(X \pm s)^*$ | *Ultrasound method* $(X \pm s)^*$ | *Metal recovery*$^\dagger$ *(%)* |
|---|---|---|---|
| **Cu** | 2.17 ± 0.05 | 1.90 ± 0.1 | 87.56 |
| **Cr** | nd | nd | - |
| **Ni** | 12.17 ± 0.29 | 12.08 ± 0.41 | 99.26 |
| **Pb** | 9.83 ± 0.16 | 9.73 ± 0.34 | 98.98 |
| **Zn** | 14.22 ± 0.26 | 14.03 ± 0.42 | 98.66 |
| ***Carbonate-bound*** | | | |
| **Cu** | 15.50 ± 0.47 | 4.21 ± 0.27 | 27.16 |
| **Cr** | nd | nd | - |
| **Ni** | 14.07 ± 0.57 | 13.97 ± 0.21 | 99.29 |
| **Pb** | 41.07 ± 0.37 | 40.55 ± 0.83 | 98.90 |
| **Zn** | 70.81 ± 1.34 | 69.15 ± 1.43 | 97.65 |
| **Fe-Mn *oxides-bound*** | | | |
| **Cu** | 7.71 ± 0.35 | 18.65 ± 0.28 | 241.89 |
| **Cr** | 7.06 ± 0.11 | 2.85 ± 0.10 | 40.37 |
| **Ni** | 6.00 ± 0.23 | 6.00 ± 0.30 | 100.00 |
| **Pb** | 165.36 ± 3.71 | 134.29 ± 0.85 | 81.21 |

| | *Conventional method* $(X \pm s)^*$ | *Ultrasound method* $(X \pm s)^*$ | *Metal recovery*† *(%)* |
|---|---|---|---|
| **Zn** | 130.33 ± 2.79 | 105.94 ± 1.17 | 81.28 |
| ***Organic matter-bound*** | | | |
| **Cu** | 151.59 ± 1.59 | 149.08 ± 3.74 | 98.34 |
| **Cr** | 3.92 ± 0.04 | nd | 0.00 |
| **Ni** | nd | nd | - |
| **Pb** | 5.60 ± 0.36 | 34.58 ± 0.63 | 617.50 |
| **Zn** | 15.38 ± 0.24 | 32.23 ± 0.96 | 209.56 |

* Average of three determinations (expressed in $\mu g\ g^{-1}$) ± standard deviation.
nd= no detected
† The recovery was calculated in the following way: [metal leached using the accelerated method/metal leached using the conventional method] x 100.

According to Table II, Cu was not quantitatively extracted in the first and second stage, when the proposed extraction method was used. However, in the third stage the extraction percentage was abnormally high, which could mean that the unleached metals in the two first stages were released in the third stage. This hypothesis is supported by the observation that the sum of extractable metal contents obtained in the first three stages was similar by both methods. On the order hand, Pb and Zn which were not quantitatively extracted in the third stage, were leached in the fourth stage.

Total extractable metal contents obtained for each metal using both methods are summarised in table III. It can be observed that, except for Cr, a good overall extraction efficiency was obtained (ranging from 98.23 % to 99.41%) with the proposed ultrasonic extraction procedure for all the studied elements. The RSD values were always lower than 5% except for Cu in the first and second extracts, where values of 5.26 and 6.41% were obtained, respectively.

TABLE III Total extractable metal contents obtained in a sediment sample applying the conventional and the modified Tessier sequential extraction schemes

| | *Total extractable metals (conventional method)** | *Total extractable metals (ultrasound method)** | *Recovery*† *(%)* |
|---|---|---|---|
| **Cu** | 176.97 | 173.84 | 98.23 |
| **Cr** | 10.98 | 2.85 | 25.93 |
| **Ni** | 32.24 | 32.05 | 99.41 |
| **Pb** | 221.86 | 219.15 | 98.78 |
| **Zn** | 230.74 | 221.35 | 95.93 |

* Sum of metal contents extracted in the fourth fractions (expressed in $\mu g\ g^{-1}$)
†The recovery was calculated in the following way: [metal leached using the accelerated method/metal leached using the conventional method] x 100.

Other attempts, using microwave energy, have been made to shortening the operation time in all stages[14] (or in a particular one[15]) of the Tessier sequential extraction procedure when it was applied to metal fractionation from sediment samples. When the results shown in this work are compared with those reported by using microwave energy (e.g. Ref. 14), it can be concluded that similar extraction efficiency relative to the global extraction process, were provided by both acceleration strategies (microwave and ultrasonic energy). However, partitioning patterns with ultrasonic extraction were closer to those obtained by the conventional sequential extraction procedure.

Total metal content in the sediment sample was determined using microwave digestion. The results obtained were ($\mu g\ g^{-1}$) 265.84±9.19, 61.22±4.32, 68.28±4.74, 337.41±10.64, 271.82±8.20 for Cu, Cr, Ni, Pb and Zn, respectively. In all cases the results where expressed as mean value ± standard deviation of three determinations.

Taking into account Table III and Figure 3, it is possible to conclude that both procedures provide similar total extractable metal contents, except for Cr, when they are applied to a sediment sample. The residual fraction was calculated by difference between the total content and the extractable one.

In this sample, Zn was the most leachable element, since it was mainly distributed (around 85 %) among the extractable fractions of the sediment, and especially associated with carbonates and Fe-Mn oxides. About 53 % of the total Ni content corresponds to the residual fraction and the rest of this element was mainly bound to the carbonate and exchangeable fractions. Around 67 % of Pb and Cu are associated to the non-residual fractions and particularly bound to carbonates/Fe-Mn oxides and organic matter, respectively. Cr is mainly located in the residual fraction (about 82 %) and consequently, a low mobility was expected for this element.

According to the above, we could predict for this sediment sample a low metal mobilization, especially for Cr. Ni, Pb and Zn could be more mobilizable than Cr, since they were significantly associated with extractable fractions. This behaviour was also reported for Cu, Pb and Zn in other sediment samples previously studied[10,24]. Cu appears principally associated with the organic matter of the sediment. Pb and Zn are mainly bound to Fe-Mn oxides and carbonates and to a lesser degree, to the organic matter.

## CONCLUSIONS

Analytical results obtained using an ultrasound accelerated extraction scheme show that for some elements, significant differences with respect to those obtained by the conventional scheme are observed. However, both schemes provide similar information about the possible mobility of heavy metals in the environment since total extractable amounts of metals were virtually the same. According to this, ultrasonic energy could be considered as a valid alternative to reduce drastically the operating time involved in the Tessier sequential extraction method. When this accelerated extraction scheme was applied to metal fractionation in sediment samples the following advantages can be considered: i) in the first and second stages, the shaking time was reduced from 1 and 5 h to 1 min and 7 min, respectively; ii) in the third and fourth stages the extraction time was reduced from 6 and 5 h, respectively, to 9 min, with the additional advantage that both conductive heating and strict temperature control was avoided; iii) the final addition of $NH_4OAc$ only required 2 min. In conclusion, the proposed scheme allowed us to shorten the total extraction time from 17 h and 30 min to 28 min.

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