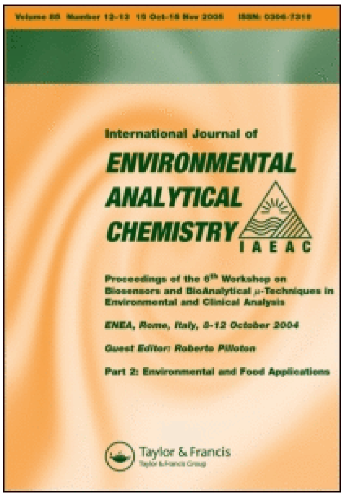

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LEACHING OF HEAVY METALS FROM AN AQUATIC PLANT *(LAGAROSIPHON MAJOR)* USED AS ENVIRONMENTAL BIOMONITOR BY ULTRASONIC EXTRACTION

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Ultrasound energy by means of a probe sonicator was used for leaching metal ions from plant tissue as a possible alternative to conventional digestion methods. The extraction conditions (composition of the extractant agent, sonication power and time and extraction steps) were optimised for copper, lead, manganese and zinc in an aquatic plant with certified metal contents (BCR N° 60 *Lagarosiphon major*). Metal determination in the extracts was carried out by Flame Atomic Absorption Spectrometry. Quantitative recoveries performing two extractions (ranging from 97.6% to 100%) were obtained for all the studied elements except for copper (74.18%). A good precision was also obtained, given that RSD were always lower than 2.5%.

Keywords: Metal leaching; aquatic plant; flame atomic absorption spectrometry; copper; lead; manganese; zinc

INTRODUCTION

Aquatic plants and biological tissues, can be useful for assessing environmental pollution. *Lagarosiphon major* is a typical species found in nearly all European fresh water bodies and as most aquatic plants tends to collect metals from the surrounding water due to its special nutritional functions so that it can be employed as environmental biomonitor.

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The determination of metal ions in these samples by Atomic Absorption Spectrometry frequently requires sample preparation before measurement. The dissolution step is one of the restricting stages in this process[1,2], since it is time-consuming and can cause contamination or losses of the analyte. Automation and shortening of these preliminary operations is actually one of the most important aims in analytical chemistry.

Traditional digestion procedures have been speeded up with the use of the microwave ovens[3–6] and pressure reactors, thus minimising contamination problems and the loss of volatile elements. This digestion system has recently been automated and develops on-line[7,8] so as to avoid manipulation errors (e.g. in the transfer from one vessel to another) and contamination in the digestion bombs, still prevailing in off-line digestion procedures. Energy transmitted through an ultrasonic bath[9,10], has been considered as a valid alternative to the conventional digestion methods, and more economic than the current microwave oven methodology. Another possibility hardly addressed in the literature, consists of exploiting the enormous breaking capability inherent to ultrasound energy transmitted by a titanium probe for leaching of metal ions from solid samples.

In this work, the capability of probe sonicators for the extraction of copper, lead, manganese and zinc was evaluated in an aquatic plant *(Lagarosiphon major),*selected for this study for its exceptionally high content in heavy metals. The different parameters of the extraction process (composition of the extractant solution, sonication power and time, etc.) have been optimised in order to obtain the maximum extraction efficiency for all the considered metals in this study.

EXPERIMENTAL

Instrumentation

The determination of metals in the extracts were carried out using an Atomic Absorption Spectrophotometer (Perkin-Elmer model 2380). Hollow cathode lamps (Cathodeon) were used as a radiation source for all the elements studied. Resonance lines at 324.8, 279.5, 217.0 and 213.9 nm were used for Cu, Mn, Pb and Zn, respectively. Standard instrumental conditions for measurements by Flame-Atomic Absorption Spectrometry (FAAS) were used as recommended by the manufacturer. Extraction was achieved using a 100 W sonicator (Sonics and materials, model VC 100) equipped with titanium probes, allowing us to work with volumes between 200 μl and 100 ml. A Kubota 5100 centrifuge was used to obtain rapid separation of the extracts.

Reagents

The extractant solutions (HNO_3, HCl, and H_2O_2) were prepared from high quality reagents, dissolving them adequately in distilled water. Standard metal solutions (1000 $\mu g\ mL^{-1}$) were obtained from pure metal or from high purity salts. Calibration solutions were done daily, by dissolving the standard solutions correctly. An aquatic plant (BCR N° 60 *Lagarosiphon major*) was used to assess the extraction efficiency of the proposed extraction method. The certified values expressed as $\mu g\ g^{-1}$were 51.2 for Cu, 1759 for Mn, 63.8 for Pb and 313 for Zn.

Extraction procedure

0.2 g of certified material were exactly weighed and placed into a 50 mL capacity centrifuge tubes, together with 5 mL of the corresponding extractant solution. The ultrasonic extraction procedure was then applied to this mixture for a previously selected time and sonication power. Finally, the supernatant liquid was separated from the solid phase by centrifugation for 4 minutes at 2500 rpm and then quantitatively transferred to a 10 mL volumetric flask. The extracts obtained were decanted into polyethylene bottles and stored until their later analysis by FAAS.

Sonication conditions

In order to study the influence of the sonication power and sonication time in the ultrasonic extraction efficiency, a solution of HNO_3 2.5% (w/w) was used as an extractant agent. The sonication powers studied were 10, 20, 50, 70 and 100 W and the optimised sonication time for each of these sonication powers ranged from 1 to 9 min.

Optimization of extractant solution

Acid solutions (HNO_3 and HCl) were used as extractant agents with concentrations in the range of 0.3–15% (w/w). With the aim of improving the extraction efficiency one proceeds to study the behaviour of the following acid combinations: HCl 1% w/w-HNO_3 (0.3–15% w/w), HCl 3% w/w-HNO_3 (0.3–15% w/w) and HCl 6% w/w-HNO_3 (0.3–15% w/w). The effect caused by the addition of increasing concentrations of H_2O_2 (0.3–15% w/w) was studied on the mixture HCl 1% w/w-HNO_3 15% w/w.

Extractant solutions were employed as blank. Concentration values in blanks were lower than the detection limit for all the elements studied.

RESULTS AND DISCUSSION

Metal leaching using a single-step extraction

Optimisation of sonication power and sonication time

The results obtained for all the metals are shown in Figure 1. The sonication power is a scarcely decisive parameter in the leaching of Mn and Zn , given that for values between 10 and 70 W similar recoveries were obtained for identical sonication times. However, for Pb and Cu a greater extraction efficiency was achieved working with a sonication power of 20 W, without regarding the shaking time. Choosing a sonication power of 20 W and a sonication time of 3 minutes, the best recoveries of all the considered metals can be achieved. In any case, the percentage obtained working under these conditions were of about 30% for Cu and between 75–78% for Mn, Pb and Zn.

Optimisation of extractant solution

Recoveries obtained for each metal, working with different extractants and under the most favourable extraction conditions (sonication power/time) can be seen in Figures 2–5. When the extraction was carried out in HNO_3 or HCl medium, Zn and Mn show similar behaviour with regards to both acids, resulting the highest percentage of recovery (78–80%) with extractant concentrations between 1 and 2.5%. However, Cu and Pb show different behaviour. Whilst for Pb recoveries of about 78% can be obtained with HNO_3 solutions (2.5–5% w/w), on the other hand with HCl the better results (recovery 63.28%) were obtained with acid concentration of over 5% (w/w). The most efficient extraction for Cu (recovery of 70%) is obtained by using HNO_3 (5–10% w/w) as extractant agent, whilst for HCl (<2.5% w/w) far lower recoveries were achieved (around 50%).

Summing up, it can be concluded that the best extraction efficiencies (recoveries about 80%) for Mn, Pb and Zn were obtained using HNO_3 2.5% (w/w) as extractant agent. However, the best recovery for Cu (70%) was achieved working with HNO_3 solutions (5–10% w/w). This shows that for the four studied elements the most favourable extraction conditions do not overlap.

Extraction efficiency was not increased for any of the metals when the nitric acid extractant was replaced by any of the following acid mixtures: HCl 1% w/w-HNO_3 (0.3–15% w/w), HCl 3% w/w-HNO_3 (0.3–15% w/w) and HCl 6% w/w-HNO_3(0.3–15% w/w) (fig. 2–5). Nevertheless, the acid combination of HCl 1% w/w-$HNO_3$15% w/w offers a further advantage for reaching the best extraction conditions for all the metals in the same extract. Recoveries obtained were around 80% for Zn and Mn, 78% for Pb and about 70% for Cu. The addition of H_2O_2 (0.3–15% w/w) to this mixture does not lead to satisfactory results (Fig-

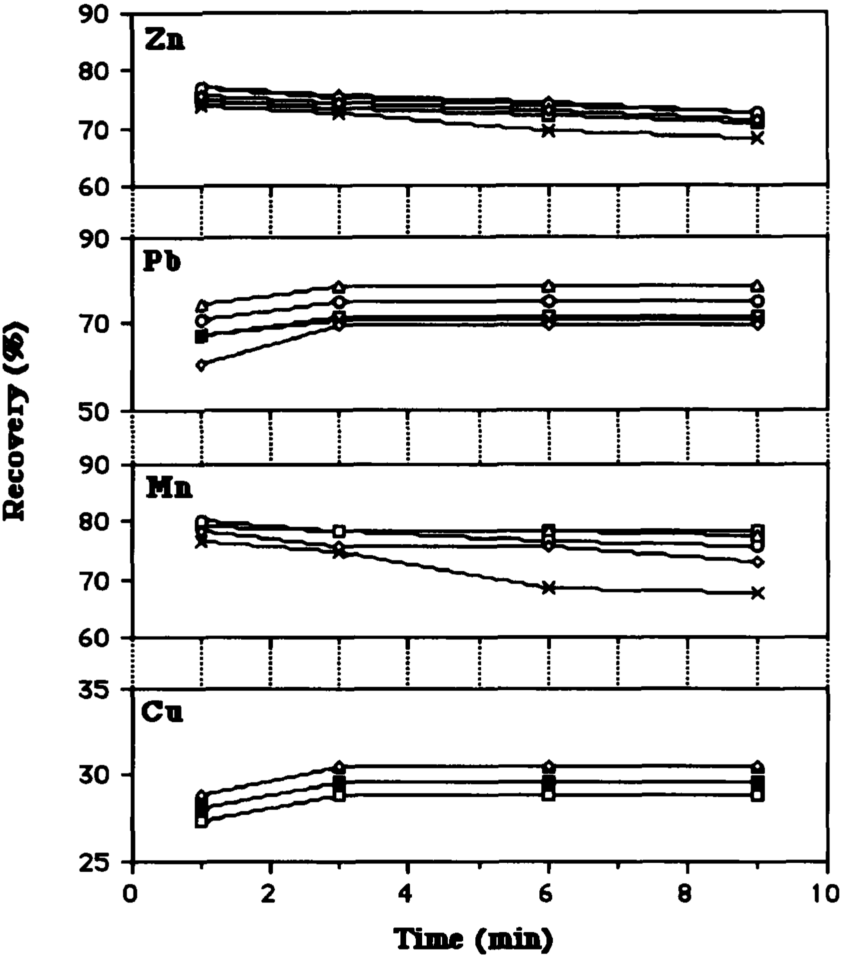

FIGURE 1 Influence of sonication power and sonication time on extraction efficiency in nitric 2.5% (w/w); Sonication power: □,10 W ;Δ,20 W; , O 50 W; ◊,70 W *,100 W

ures 2–5), given that an increase in H_2O_2 concentration results in a reduction of the extraction efficiency for Cu, Mn and Zn.

Metal leaching using a two-stage sequential extraction

In order to improve the extraction efficiency and achieve quantitative recoveries for all the studied elements, it was found necessary to apply a two stage extrac-

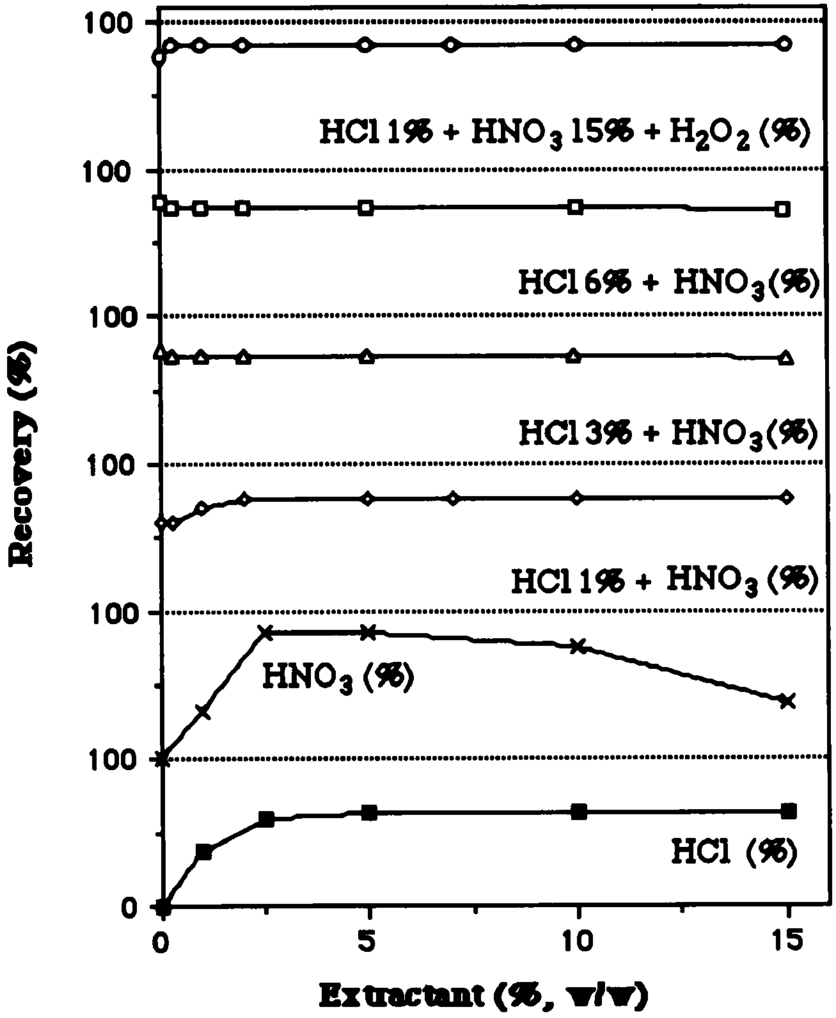

FIGURE 2 Influence of both extractant and extractant concentration on recovery for copper

tion method, developed consecutively on the same sample. The operational procedure can be seen in detail in Figure 6. A second experiment was set up carrying out the extraction in a similar way, only modifying the composition of the extractant agent (HCl 1% w/w-HNO_3 15% w/w-H_2O_2 2% w/w). Once again the addition of H_2O_2 reduces the extraction efficiency for all the metals, obtaining recoveries 9–18% lower than those obtained with the mixture of HCl 1% w/w-HNO_3 15% w/w.

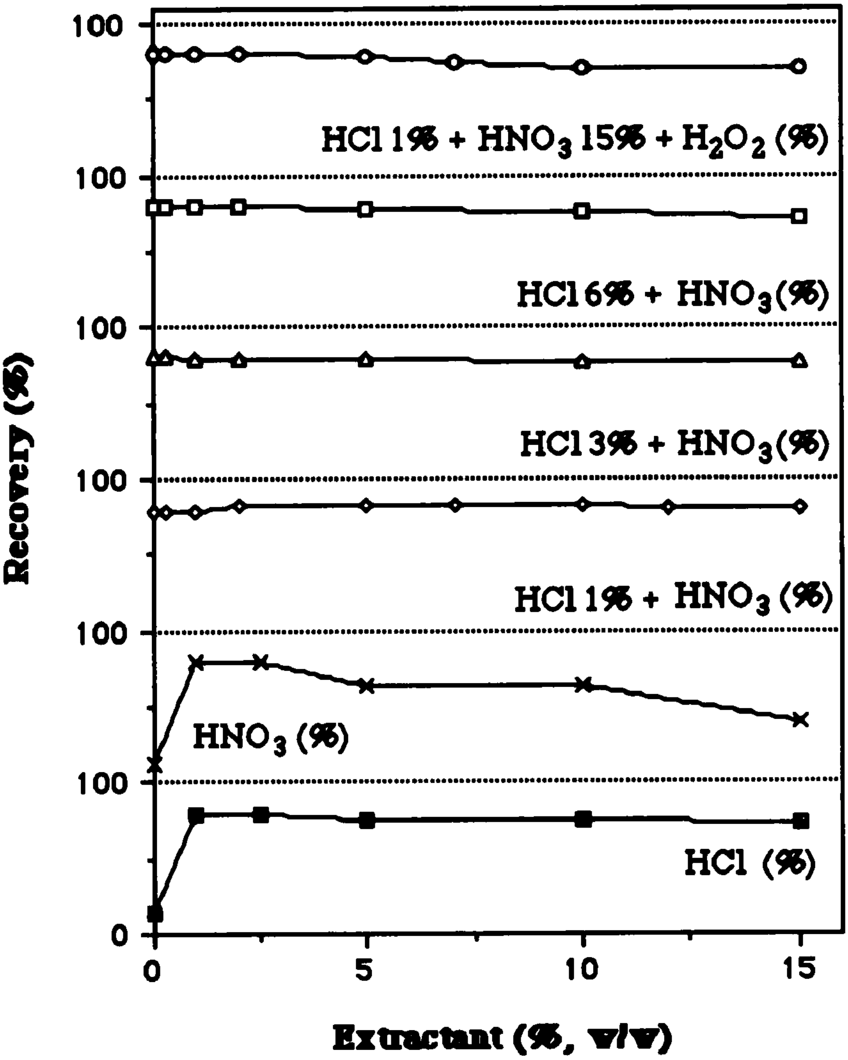

FIGURE 3 Influence of both extractant and extractant concentration on recovery for manganese

Table I shows the recoveries obtained using this two step extraction method and quantitative results can be asserted for all metals (97.62–100.09%) with the exception of copper (74.18%). LODs values were calculated as 3 σ/m, where σ is the standard deviation of blank (n=10) and m the slope of the calibration curve. These values expressed as μg g^{-1} were 0.83, 0.45, 3.57 and 0.26 for Cu, Mn, Pb and Zn, respectively. The application of t-test (p=0.05) allows to assure that, except for copper, no significant difference exists between the certified values and those obtained experimentally (n=3). However, given that the RSD obtained are lower than 2.5% this method can be considered sufficiently precise. The comparison of variance obtained with the proposed method and that the certified material allowed us to conclude that no significant differences occur.

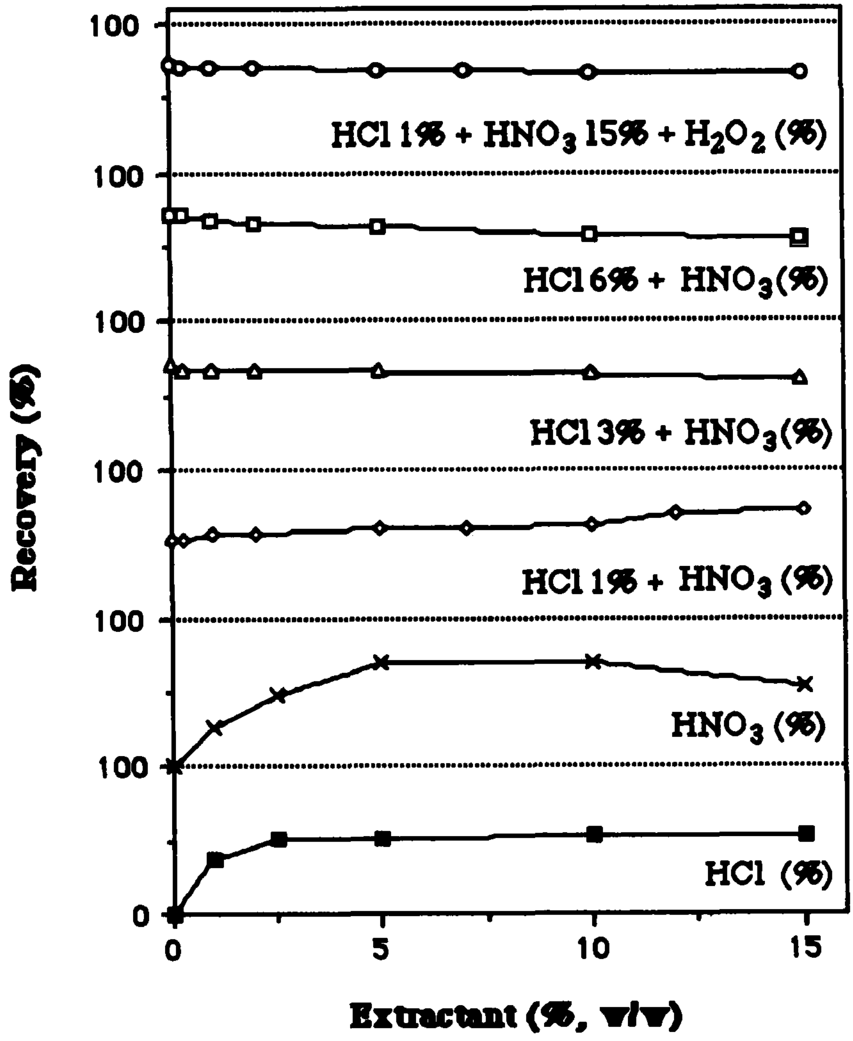

FIGURE 4 Influence of both extractant and extractant concentration on recovery for lead

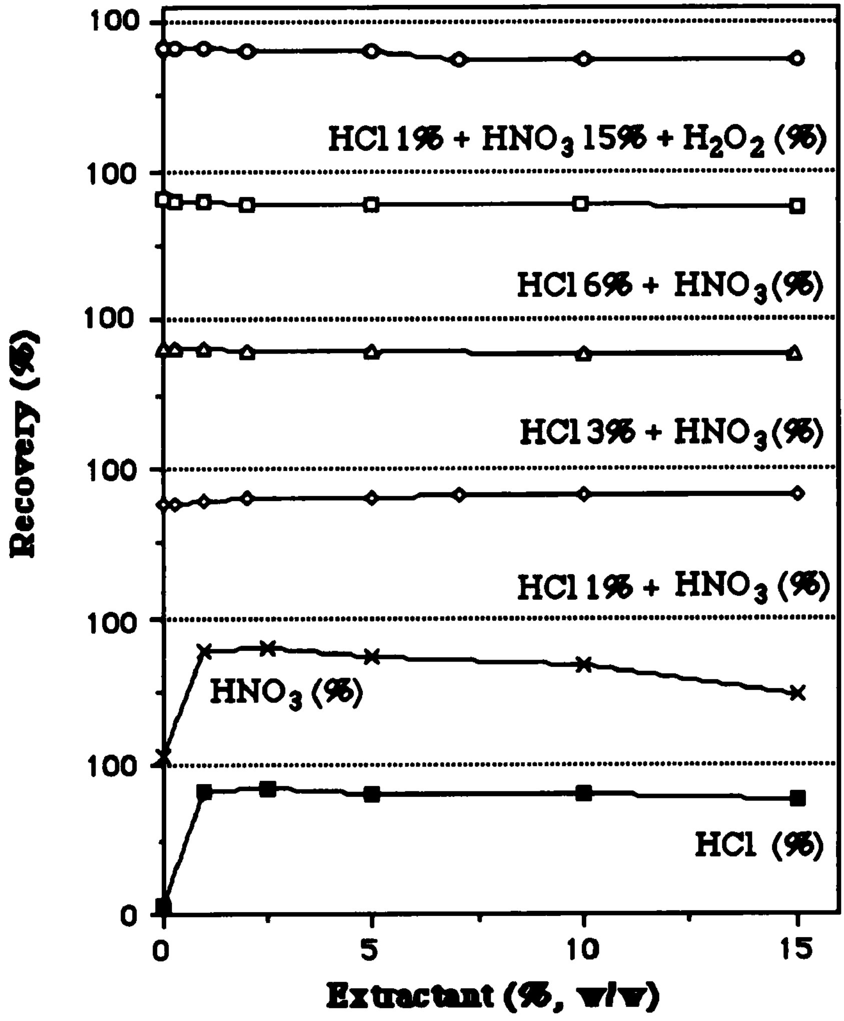

FIGURE 5 Influence of both extractant and extractant concentration on recovery for zinc

The literature[9,10] shows that metal leaching by means of sonication ultrasonic bath represents an alternative to both conventional (because of their greater rapidity and operational simplicity) and microwave digestion methods (because of their significantly lower cost). The proposed method, for the extraction of metal ions from plant tissues, shares both advantages in the complete way.

TABLE I Analytical results obtained for Cu, Mn, Pb and Zn in the certified material (Lagarosiphon major) using the two-step ultrasonic extraction method

Element	*Certified value* ($\mu g\ g^{-1}$)†	*Found value* ($\mu g\ g^{-1}$)†	*RSD (%)*	*Recovery (%)*
Cu	51.00±1.90	37.83±1.44	1.53	74.18*
Mn	1759.00±51.0	1717.07±53.56	1.25	97.62
Pb	63.80±3.2	63.86±3.95	2.49	100.09
Zn	313.00±8.0	309.65±5.89	0.76	98.93

† The uncertainty is taken as the 95% confidence interval of the mean.

* No quantitative recovery for copper was obtained.

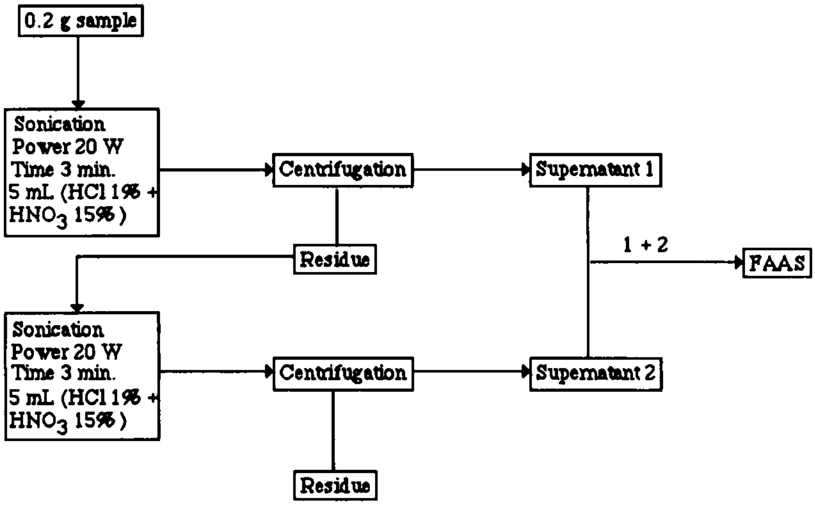

FIGURE 6 Two-step extraction method for the determination of Cu, Mn, Pb and Zn in an aquatic plant

CONCLUSIONS

The extraction of metal ions employing ultrasonic probes from plant tissues, supposes an alternative to conventional digestion methods and offers certain advantages over the actual microwave digestion methods: i) in contrast to what occurs in pressure reactors, the mass of sample to be treated is neither a limiting or decisive factor, which offers an advantage when treating only slightly contaminated samples; ii) extraction time (7 minutes) is even slightly less than required in the majority of microwave digestion procedures; iii) extracts are obtained immediately after the sonication stage thus avoiding the cooling time (approx. 30 minutes) required by pressure bombs before opening, which means a slowing up in the overall process of sample dissolution; iv) less consumption of reagents, replacing the use of concentrated acids by diluted solutions; v) the initial cost of the necessary equipment, as well as the later maintenance, can be considered as slightly lower than that required for digestions carried out with traditional microwave ovens.

Despite all the advantages that this method shows with respect to its application to plant tissue, its application in the complete leaching of metal ions from samples with high silica contents (soils, sediments, etc.) is restricted by the unability of using HF as an extractant agent.

Acknowledgements

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