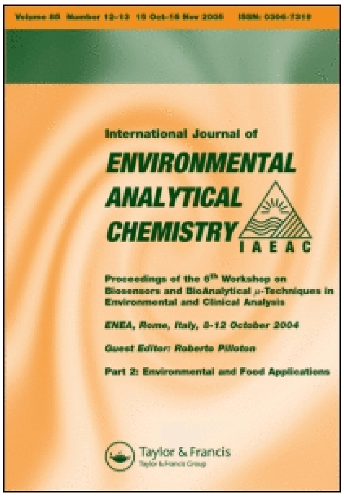

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

A Fractional Factorial Design Applied to the Optimization of Microwave- and Ultrasound-Assisted Acid Leaching Methods for Heavy Metals Determination in Sludges by Flame Atomic Absorption Spectrometry

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To cite this Article Segade, Susana Río , Albor, M. Carmen Diéguez , GÓMEZ, Esperanza FernáNDEZ and LÓPEZ, Elena Falqué(2003) 'A Fractional Factorial Design Applied to the Optimization of Microwave- and Ultrasound-Assisted Acid Leaching Methods for Heavy Metals Determination in Sludges by Flame Atomic Absorption Spectrometry', International Journal of Environmental Analytical Chemistry, 83: 4, 343 — 356

To link to this Article: DOI: 10.1080/0306731031000084013

URL: http://dx.doi.org/10.1080/0306731031000084013

Intern. J. Environ. Anal. Chem., Vol. 83, No. 4, pp. 343–356

Taylor & Francis
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A FRACTIONAL FACTORIAL DESIGN APPLIED TO THE OPTIMIZATION OF MICROWAVE- AND ULTRASOUND-ASSISTED ACID LEACHING METHODS FOR HEAVY METALS DETERMINATION IN SLUDGES BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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(Received 3 May 2002; In final form 12 December 2002)

Microwave-assisted extraction, ultrasound-assisted extraction and microwave-assisted digestion were compared for the determination of chromium, copper, lead and zinc in sludge samples by Flame atomic absorption spectrometry (FAAS) in terms of accuracy, precision, sample throughput and manipulation risk. The complete destruction of the matrix required the use of high temperature, elevated pressure and concentrated acids and the introduction of several time consuming steps, such as a cooling step of the digester and an evaporation step of the concentrated acids. The accelerated extraction procedures using dilute acids as extractants were optimised in order to reduce the treatment time and avoid the risks associated to the use of pressurised digesters. The capabilities of the Plackett–Burman saturated factorial design were explored to study the effect of various parameters on the extraction efficiency. The applicability of both extraction methods for sludge samples analysis of different origin was shown using principal component analysis and cluster analysis.

Keywords: Microwave; Ultrasound; Extraction procedures; Sludge samples; Flame atomic absorption spectrometry; Heavy metals

INTRODUCTION

The physical and chemical composition of sludges remaining after either the purification treatment of wastewaters or the industrial process, which often varies according to the source of the residues, make sludges useful products for agricultural use [1,2]. However, heavy metals concentration in this type of samples must be controlled in order to avoid possible environmental pollution and food chain contamination.

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ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/0306731031000084013

The most widely used technique for the determination of trace metals in a great variety of sample matrices is atomic absorption spectrometry (AAS). Nevertheless, the analysis of sludges by AAS often requires previous sample dissolution, which is usually the most time-consuming step. For this purpose, the dry ashing [3,4] and wet digestion procedures are commonly used. Although the classical methods permit the effective decomposition of the organic matrix and totally dissolve the sample, they also have several disadvantages such as: labourious procedures, long digestion time, analyte losses and sample contamination. Recently, pressurised wet digestion methods based on the use of reactors heated in a sand bath [5], reflux column [6,7], conductive oven [6–8] and microwave oven [1,3–6,9–11] have been developed with the aim of reducing the time required for sludge preparation. Additionally, very few applications of ultrasound energy to diminish the digestion time of sludges have been published [12]. The acceleration to wet digestion procedures by microwave energy is more effective than acceleration by ultrasound energy. While the pressure reactors are submitted to microwave irradiation for several minutes, the sample treatment in an ultrasonic bath requires some hours (1.5 h) [12]. Both approaches markedly improve the drawbacks involved in the classical procedures and nowadays they are considered to be important alternatives to the conventional digestion methods.

Aqua regia [1,6,7,10–12] with or without addition of hydrofluoric acid [1,11] is the medium employed in most publications reported on metal determination in sludges for wet digestion procedures. However, the use of concentrated acids has some drawbacks. Due to elevated acid concentration it cannot be directly introduced into the atomizer of an atomic absorption spectrophotometer, apart from the known problems related to the manipulation of hydrofluoric acid. Therefore, the excessive acid concentration must be eliminated either by evaporation, increasing in this way the number of analytical steps and the time required, or by dilution to an appropriate concentration that should increase the detection limit of the analytical method.

Ultrasound-assisted extraction in dilute acids has become an accepted sample treatment procedure for the determination of lead in a variety of environmental media. An aim of this work is to study the potential utility of microwave- and ultrasound-assisted extraction in dilute acids for the extraction of several metals from sludge samples. The influence of extraction parameters on extraction efficiency was investigated due to the experimental conditions for the use of dilute acids as extraction solutions of metals from sludge samples have not been previously reported in the literature to our knowledge.

In this article, the simple, rapid and inexpensive microwave- and ultrasound-assisted acid leaching procedures were optimised in terms of maximum extraction efficiency of chromium, copper, lead and zinc from a sewage sludge in a minimum time using a mixture of dilute hydrochloric and nitric acids as extraction solutions. The Plackett–Burman fractional factorial design [5,13] allowed the quantification of the influence of the extraction parameters in obtaining the best conditions for the extraction of the above mentioned heavy metals from sludges. The extractions were carried out in open vessels without reflux columns, avoiding the risks associated to the use of concentrated acids, the application of high temperatures and pressures and long cooling time. Metal concentrations were directly determined in the acid extracts by Flame atomic absorption spectrometry (FAAS) without previous evaporation of the extracts. Both extraction methods were applied to the analysis of sludges from a variety of sources and the results obtained were compared. The accuracy of the methods was checked by the analysis of the samples studied following a previously validated method based on acid digestion of sludge samples in a medium-pressure reactor heated by microwave irradiation. The three sample treatment procedures were compared in relation to their accuracy, precision, sample throughput and safety.

EXPERIMENTAL

Instrumentation

The extractions were performed with a Selecta ultrasonic bath operated at a power of 150 W or a Moulinex domestic microwave oven (900 W). A Kubota model 5100 centrifuge was used for rapid supernatant separation from the extracts. The sludges were digested in Parr-type model 4782 medium-pressure reactor heated in the above mentioned microwave oven.

Absorbance was measured with a Perkin-Elmer model 2380 atomic absorption spectrophotometer. Cathodeon hollow-cathode lamps were used as the radiation source. The instrumental parameters are listed in Table I.

Reagents

All chemicals were of analytical-reagent grade. The extractants were prepared by dilution of concentrated reagents with deionised water. The stock standard solutions of the metals (1000 mg L^{-1}) were prepared by dissolving the appropriate amount of pure metal or high purity salts and stored in a refrigerator. Working standard solutions were prepared just before use by appropriate dilution of the stock standard solutions.

Sample Preparation

Six sludge samples (I–VI) from different sources were analysed. Samples I and II were obtained from a treatment plant of wastewaters and they are the solid wastes remaining after the purification process of residual waters. Samples III and IV were collected from a viticulture industry. The sludge IV was subjected to a purification process. The samples V and VI were obtained from an oil industry. The sample preparation was as follows: the sludges were oven dried at 110°C for 48 h and the dry samples were afterwards ground and sieved (< 70 μm).

Microwave Digestion [5]

0.1 g of sludge sample was accurately weighed and placed into a 45 mL capacity Teflon vessel. Then, 4 mL of 70% m/m nitric acid, 1 mL of 37% m/m hydrochloric acid and

TABLE I Instrumental parameters

Parameter	*Cr*	*Cu*	*Pb*	*Zn*
Wavelength (nm)	357.9	324.8	217.0	213.9
Slit (nm)	0.7	0.7	0.7	0.7
Air/acetylene flow-rate (L min^{-1})	11/2	11/1	11/1	11/1
Lamp intensity (mA)	30	30	10	15
Linear interval (mg L^{-1})	0–5	0–5	0–20	0–1

2 mL of 48% m/m hydrofluoric acid were added into the vessel. The Parr reactor was carefully sealed and exposed to microwave irradiation at 540 W for 2 min. The reactor was then cooled to room temperature in an ice bath before opening. The solution obtained was quantitatively transferred into a Teflon beaker and evaporated to dryness in a sand bath. The residue was dissolved in 1 mL of concentrated hydrochloric acid and the resulting solution was again quantitatively transferred into a 10 mL volumetric flask and diluted to volume with deionised water. The blanks were prepared exactly the same as the samples.

Microwave-assisted Extraction Procedure

A 0.1–0.6 g portion of sludge sample and 5 mL of a mixture of 0.7–4 mol L^{-1} hydrochloric acid and 0–2 mol L^{-1} nitric acid were placed in a 50 mL capacity centrifuge tube. The slurry was homogenised by agitation and exposed to microwave irradiation at 75–170 W for 0.5–2 min. The supernatant liquid was separated from the solid residue by centrifugation at 2500 rpm for 5 min. Then, the liquid phase was quantitatively transferred into a 10 mL volumetric flask and the solid phase could be again submitted to the same treatment with the acid mixture. The supernatant liquid was also separated from the solid residue by centrifugation at 2500 rpm for 5 min. The acid extracts were combined and diluted to volume with deionised water. The blanks were prepared exactly the same as the samples.

Ultrasound-assisted Extraction Procedure

0.1–0.6 g of sludge sample were accurately weighed in a 50 mL capacity centrifuge tube and 5 mL of a mixture of 0.7–4 mol L^{-1} hydrochloric acid and 0–2 mol L^{-1} nitric acid were added. The slurry was homogenized by agitation and subjected to ultrasonic agitation during 0.5–20 min. The supernatant liquid was separated from the solid residue by centrifugation at 2500 rpm for 5 min. Both phases were then treated in the same way as in the microwave-assisted extraction procedure. The blanks were prepared exactly the same as the samples.

Plackett–Burman Design

The Plackett–Burman fractional factorial design was used to known the influence of some variables on extraction efficiency of heavy metals from sludges by both microwave- and ultrasound-assisted extraction procedures and thus, to eliminate those that were not significant variables. A Plackett–Burman design for seven factors (Table II) was selected using as many columns as variables studies. Therefore, only eight experiments were carried out. The variables investigated with their factor designators and the lower (−) and upper (+) levels for each one of them are shown in Table III. A variable was considered as significant when the difference between the average value of the results obtained for upper and lower levels was higher than the double of the average standard deviation. Only the significant variables were optimised afterwards.

TABLE II Plackett–Burman design

Experiment	*A*	*B*	*C*	*D*	*E*	*F*	*G*
1	+	+	+	−	+	−	−
2	+	+	−	+	−	−	+
3	+	−	+	−	−	+	+
4	−	+	−	−	+	+	+
5	+	−	−	+	+	+	−
6	−	−	+	+	+	−	+
7	−	+	+	+	−	+	−
8	−	−	−	−	−	−	−

TABLE III Variables studied for both microwave- and ultrasound-assisted extraction procedures

Variable	*Factor*	*Lower level* (−)	*Upper level* (+)
Microwave-assisted extraction			
Microwave power (W)	A	75	170
Extraction time (min)	B	0.5	2
HCl concentration ($\mathrm{mol\,L^{-1}}$)	C	0.7	4
Second extraction	D	No	Yes
$2\,\mathrm{mol\,L^{-1}}$ HNO_3 addition	E	No	Yes
Ultrasound-assisted extraction			
Extraction time (min)	A	0.5	20
HCl concentration ($\mathrm{mol\,L^{-1}}$)	B	0.7	4
Second extraction	C	No	Yes
$2\,\mathrm{mol\,L^{-1}}$ HNO_3 addition	D	No	Yes

RESULTS AND DISCUSSION

Study of the Influence of the Variables

The effect of each variable on the extraction efficiency of chromium, copper, lead and zinc from the sludge sample I was evaluated following the Plackett–Burman design (Figure 1). The results obtained for the eight experiments corresponding to the microwave-assisted extraction procedure indicated that only the microwave power and hydrochloric acid concentration were not significant variables; the extraction time had a positive effect on the extraction yield of chromium and copper; a two stage extraction significantly increased the extraction efficiency of chromium, copper and zinc and finally, the addition of nitric acid showed an opposite effect on the extraction yield of copper and lead. The Plackett–Burman design confirmed the significance of the extraction time, two stage extraction and addition of nitric acid. Thus, the extraction time and nitric acid concentration were afterwards optimised using a two stage sequential extraction method. The microwave power and hydrochloric acid concentration were maintained constant at 75 W and $0.7\,\mathrm{mol\,L^{-1}}$, respectively.

On the other hand, the results obtained for the eight experiments corresponding to the ultrasound-assisted extraction procedure showed that all the variables were significant. So, the extraction time had a positive effect on the extraction yield of chromium and copper. In relation to hydrochloric acid concentration, its influence depended on

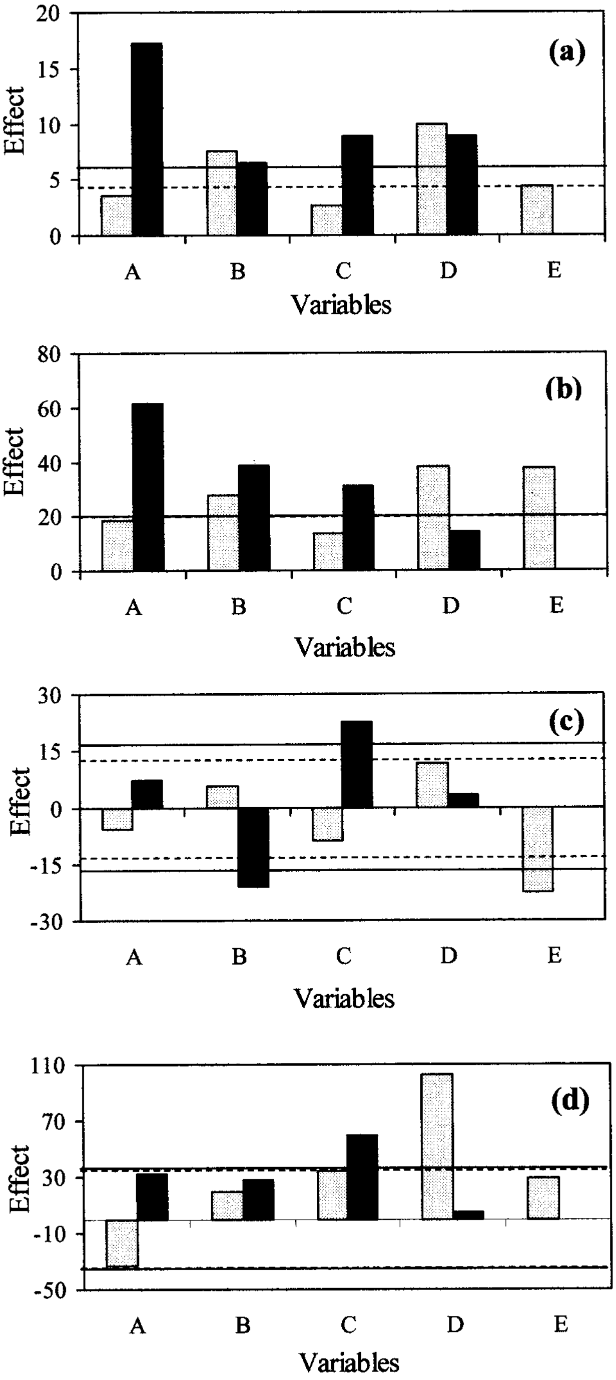

FIGURE 1 Effect of the variables on the extraction efficiency of chromium (a), copper (b), lead (c) and zinc (d) using both microwave-assisted extraction ( ) and ultrasound-assisted extraction (■) procedures. The effect was calculated as the difference between the average value of the results obtained for upper and lower levels. The continuous and dashed lines show double the average standard deviation for microwave- and ultrasound-assisted procedures, respectively.

the metal determined. The extraction efficiency increased significantly with hydrochloric acid concentration for chromium and copper, whereas it decreased significantly for lead. The addition of nitric acid had a positive effect on the extraction yield of chromium. The two stage sequential extraction method was used for further experiments due to its positive effect on all the metals determined. Therefore, the conditions required for the ultrasound-assisted extraction procedure were more drastic than the microwave-assisted extraction procedure.

The extraction conditions had a greater influence on the extraction efficiency of chromium and copper when both microwave and ultrasonic energies were used for the acceleration of the extraction procedure. Furthermore, chromium could not be quantitatively extracted from the sludge sample I under the extraction conditions selected in the Plackett–Burman design.

Optimisation of Microwave- and Ultrasound-assisted Extraction Procedures

Both extraction procedures were optimised in terms of quantitative recovery of chromium, copper, lead and zinc from the sludge sample I in a minimum time. The effect of the extraction time on the recovery of chromium, copper and lead was investigated when the extraction procedure was carried out under a microwave field and different extractants were used. The extraction medium was a mixture of hydrochloric and nitric acids in which hydrochloric acid concentration was maintained constant at 0.7 mol L^{-1} and nitric acid concentration was modified from 0 to 2 mol L^{-1}. As can be seen in Figure 2, optimum nitric acid concentration was 0.5 mol L^{-1}. The extraction yield of copper increased about 15% with increasing nitric acid concentration from 0 to 0.5 mol L^{-1}. Additionally, the recovery of lead also increased to around 15% when nitric acid concentration was decreased from 2 to 0.5 mol L^{-1}. The extraction time affected in decreasing the extraction efficiency

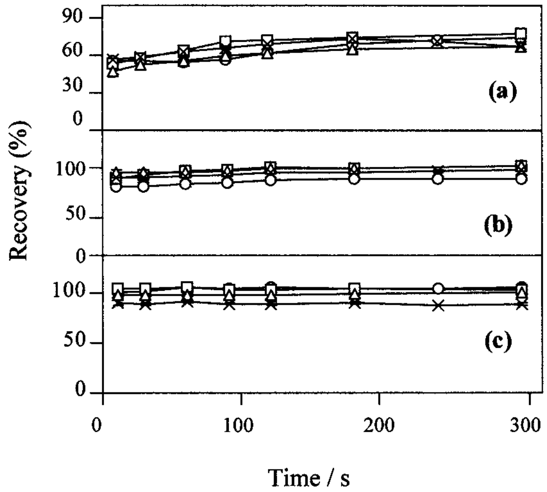

FIGURE 2 Influence of extraction time on recovery of chromium (a), copper (b) and lead (c) using as extractant 0.7 mol L^{-1} hydrochloric acid (○), 0.7 mol L^{-1} hydrochloric acid + 0.5 mol L^{-1} nitric acid (□), 0.7 mol L^{-1} hydrochloric acid + 1 mol L^{-1} nitric acid (Δ), 0.7 mol L^{-1} hydrochloric acid + 2 mol L^{-1} nitric acid (×) for the microwave-assisted extraction procedure.

of chromium, copper and lead from the sludge sample. The increase in chromium recovery with the extraction time was more accused for a nitric acid concentration of 0.5 mol L^{-1} in the extractant. The slurries were submitted to a microwave field during 180 s for further studies.

Similar investigations were performed in order to study the influence of the extraction time on the extraction yield of chromium, copper and lead using ultrasound energy for the acceleration of the extraction procedure as well as several extraction mediums. The extractants employed were also mixtures of dilute hydrochloric and nitric acids. An increase in extraction time or hydrochloric acid concentration clearly improved the extraction yield of chromium. So, the recovery of chromium increased between 15 and 20% with increasing hydrochloric acid concentration from 0.7 to 2 mol L^{-1} and the extraction time from 1 to 10 min, respectively. The variation of the recovery of copper and lead was less pronounced than that of chromium. Furthermore, as can be seen in Figure 3, chromium recovery increased when nitric acid concentration was varied from 0 to 2 mol L^{-1}. However, nitric acid concentrations higher than 1 mol L^{-1} caused a negative effect on lead recovery. As a consequence, ultrasound-assisted extraction was performed in 2 mol L^{-1} hydrochloric acid and 1 mol L^{-1} nitric acid medium for 10 min.

With the aim of improving the recovery of chromium, the influence of hydrogen peroxide concentration in the extraction medium was investigated for both extraction procedures. Figure 4 shows that the effect of hydrogen peroxide concentration on the extraction yield of chromium was clearly unfavourable. Hence, the addition of hydrogen peroxide to the extractants markedly reduced the recovery of chromium. As a result, the above mentioned acid mixtures were used as extractants.

The effect of the sample amount on the recovery of chromium, copper, lead and zinc was also studied. In general, when the sample amount submitted to both microwave- and ultrasound-assisted treatments was increased using the same volume of acid extractant, the extraction efficiency decreased for all of the metals previously cited as shown in Figure 5. A sample amount of 0.2 g was selected for further work, because high standard deviations could be using sample sizes of less than 0.2 g for inhomogeneous samples.

On the other hand, the time required for sample treatments was reduced by performing simultaneous extractions. The recoveries, calculated as the quotient between the concentrations obtained with individual and simultaneous treatments, obtained for

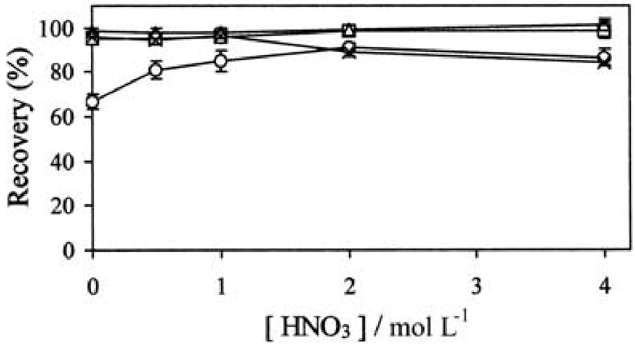

FIGURE 3 Influence of nitric acid concentration in the extractant on recovery of chromium (○), copper (□), lead (×) and zinc (Δ) using the ultrasound-assisted extraction procedure.

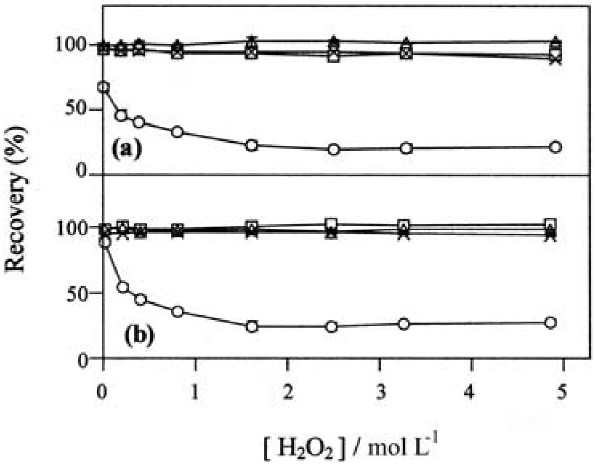

FIGURE 4 Influence of hydrogen peroxide concentration in the extractant on recovery of chromium (○), copper (□), lead (×) and zinc (Δ) using both microwave-assisted extraction (a) and ultrasound-assisted extraction (b) procedures.

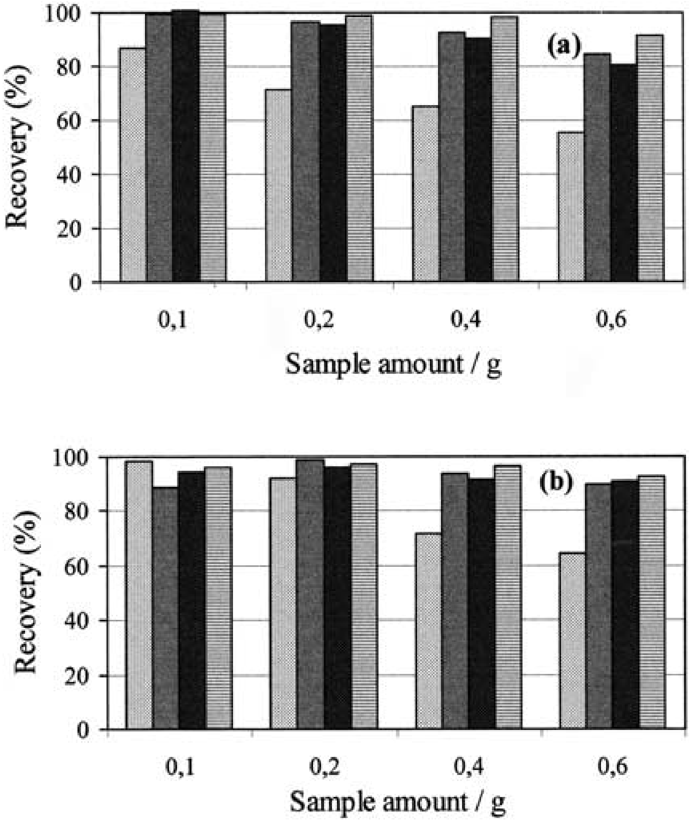

FIGURE 5 Influence of sample amount on recovery of chromium (▒), copper (▓), lead (■) and zinc (▤) using both microwave-assisted extraction (a) and ultrasound-assisted extraction (b) procedures.

TABLE IV Simultaneous microwave- and ultrasound-assisted extractions

Metal	*Recovery* (%)[a,c]	*RSD* (%)[a]	*Recovery* (%)[b,c]	*RSD* (%)[b]
Simultaneous microwave-assisted extractions				
Cr	99.9	3.4	89.1	9.9
Cu	99.5	1.2	89.8	2.4
Pb	100	0	99.9	0.5
Zn	94.3	2.9	95.4	2.5
Simultaneous ultrasound-assisted extractions				
Cr	90.4	2.3	72.4	4.0
Cu	99.1	0.7	100	1
Pb	10.1	1	99.9	1.0
Zn	96.1	0.4	98.5	1.6

[a] Three simultaneous extractions were carried out; [b] six simultaneous extractions were carried out; [c] recovery was calculated as the quotient between the concentrations obtained with individual treatment and simultaneous treatment.

three or six simultaneous extractions are summarised in Table IV. When three simultaneous extractions were carried out, the recoveries were higher than 90% for all of the metals extracted by both proposed procedures. The chromium recovery was only 72% for six simultaneous ultrasound-assisted extractions and recovery of some metals was higher than 89% for six simultaneous microwave-assisted extractions.

Analysis of Real Samples

In order to check the applicability of the developed extraction procedures, six real sludge samples (I–VI) of different composition were analysed in triplicate using both microwave- and ultrasound-assisted procedures. The calibration graph and the standard additions methods were compared (t-test; $p = 0.05$) by means of the slopes for all the metals determined by both proposed methods in different sludge samples. No significant differences were obtained using both calibration methods. Therefore, the calibration with aqueous standards was chosen for further analysis. With the aim of validating both extraction procedures, the results obtained were statistically compared with those obtained by a previously validated method based on a microwave-assisted digestion [5]. Table V summarises the results found for the proposed extraction procedures, which have been tested by comparing them with those obtained by using the reference digestion procedure. The F-test has been applied in order to check if both extraction procedures provide standard deviations which are not significantly different from those obtained by the reference method, and the t-test has been used to verify whether the differences between the means obtained by the proposed extraction procedures and the reference method differ significantly from zero.

The values of concentration determined using microwave- and ultrasound-assisted extraction procedures were in good agreement with the concentrations determined using the microwave-assisted digestion procedure for copper, lead and zinc and for all sludge samples analysed, except in the case of the sludge sample II for the zinc extraction by the microwave-assisted procedure. The results obtained indicated no dependence on the material. However, when the results found for chromium using both extraction procedures were compared with those obtained using the digestion

TABLE V Determination of chromium, copper, lead and zinc in sludge samples

Sample	*Cr* $\bar{x} \pm s$ ($\mu g\,g^{-1}$)[a]	*Cu* $\bar{x} \pm s$ ($\mu g\,g^{-1}$)[a]	*Pb* $\bar{x} \pm s$ ($\mu g\,g^{-1}$)[a]	*Zn* $\bar{x} \pm s$ ($\mu g\,g^{-1}$)[a]
Microwave-assisted digestion				
I	63.7 ± 1.9	449 ± 3	399 ± 14	886 ± 10
II	98.4 ± 1.4	478 ± 5	488 ± 2	979 ± 12
III	27.8 ± 2.4	884 ± 27	< LOD	32.6 ± 1.2
IV	61.1 ± 2.7	925 ± 1	15.5 ± 4.2	221 ± 5
V	119 ± 9	46.0 ± 1.1	< LOD	75.1 ± 2.6
VI	13.5 ± 0	34.5 ± 1.8	< LOD	40.3 ± 0.8
Microwave-assisted extraction				
I	43.8 ± 2.1	435 ± 11	414 ± 23	875 ± 2
II	74.0 ± 2.6	471 ± 2	486 ± 16	1018 ± 7
III	29.2 ± 1.9	917 ± 23	< LOD	32.5 ± 0.3
IV	47.5 ± 0.6	893 ± 13	15.7 ± 1.2	216 ± 3
V	55.8 ± 2.4	41.6 ± 3.4	15.7 ± 2.2	69.2 ± 4.1
VI	10.3 ± 1.4	37.2 ± 1.3	< LOD	37.9 ± 2.3
Ultrasound-assisted extraction				
I	59.9 ± 2.6	443 ± 11	386 ± 15	870 ± 13
II	78.3 ± 3.5	471 ± 13	475 ± 11	979 ± 15
III	25.7 ± 1.9	862 ± 25	< LOD	30.0 ± 0.1
IV	55.1 ± 7.2	898 ± 10	15.3 ± 2.9	219 ± 3
V	58.8 ± 8.8	42.4 ± 2.3	< LOD	75.3 ± 4.3
VI	13.9 ± 1.2	38.0 ± 3.2	< LOD	36.0 ± 5.1

[a] Average value ± standard deviation ($n = 3$).

method, they differed significantly. Furthermore, the recovery of chromium depended on the sample investigated. So, it is known that recovery rates of certain elements such as chromium depended on the amount and nature of the alumosilicate matrix [14]. On the other hand, when comparing the averages of data obtained by the use of microwave- and ultrasound-assisted extraction procedures, the between-methods differences of the averages were greater than 10% only for chromium. The best recoveries of chromium corresponded to the ultrasound-assisted extraction method. So, chromium recoveries higher than 90% were achieved by ultrasound-assisted extraction procedure in four sludge samples (I, III, IV, VI) while quantitative recoveries of chromium were only obtained for the sludge sample III by microwave-assisted extraction procedure. The results found evidence that the lowest chromium recoveries corresponded to the samples containing the highest chromium concentrations.

Both microwave- and ultrasound-assisted extraction methods permitted to reduce the time involved in sample treatment respect to microwave-assisted digestion using pressurised digesters due to the avoiding of the cooling step and evaporation step of concentrated acids. The sample throughout was 15, 5 and 1 samples/h for microwave-assisted extraction, ultrasound-assisted extraction and microwave-assisted digestion, respectively. On the other hand, the use of mixture of dilute nitric and hydrochloric acids for metal extraction in opened vessels avoids the risks associated to elevated temperatures and pressures and those corresponding to the work with concentrated acids, especially hydrofluoric acid.

The detection limit values were calculated as $3s\,\mathrm{m}^{-1}$, where s is the standard deviation of the blank ($n = 10$) and m is the slope of the calibration curve. The detection limit found for chromium, copper, lead and zinc determinations was 0.014, 0.017, 0.071

and 0.0052 mg L^{-1}, respectively. Thus, a minimum concentration of 0.68, 0.83, 3.6 and 0.26 µg g^{-1} in the solid sample was for chromium, copper, lead and zinc, respectively. The relative standard deviation obtained for three independent analysis of the same sample was within the range 1.3–15% for chromium, 0.43–8.4% for copper, 2.3–1.9% for lead and 0.23–14% for zinc, as a function of the different nature of the samples and the different concentration of the elements to be determined. However, in general there were no significant differences (*F*-test) between the variances found for both extraction procedures and those obtained for the digestion method. The best accuracy and satisfactory precision were obtained when the ultrasound-assisted extraction procedure was used for sample treatment.

Principal component analysis (PCA) was applied to the results obtained in order to obtain more information about the applicability of both microwave- and ultrasound-assisted extraction methods for heavy metals determination in sludge samples of different origin. PCA was performed on a matrix composed of eight columns (the four metals extracted by microwave and ultrasound energy) and six rows (the sludge samples). The data were taken to extract three principal components, which explain 96.6% of the total variance of data on metals of these samples. The loading values of the initial variables are shown in Figure 6. As can be observed, chromium, lead and zinc gave a high contribution to Factor 1, which accounts for 61.7% of the total variance. Nevertheless, copper was the most significant for Factor 2, being its contribution to the total variance of 24.5%.

The sludge samples can be defined by the values of their scores on Factors 1 and 2. The Cluster analysis (Figure 7) showed three classes separated in relation to the contents of metals in the sludge samples that correspond to sewage sludge samples (I and II), sludge samples proceeding from viticulture industry (III and IV) and sludge samples proceedings from oil industry (V and VI), respectively. It can be concluded that the sludge samples that are similar in origin tend to associate in the same group. Therefore, the applicability of both microwave- and ultrasound-assisted

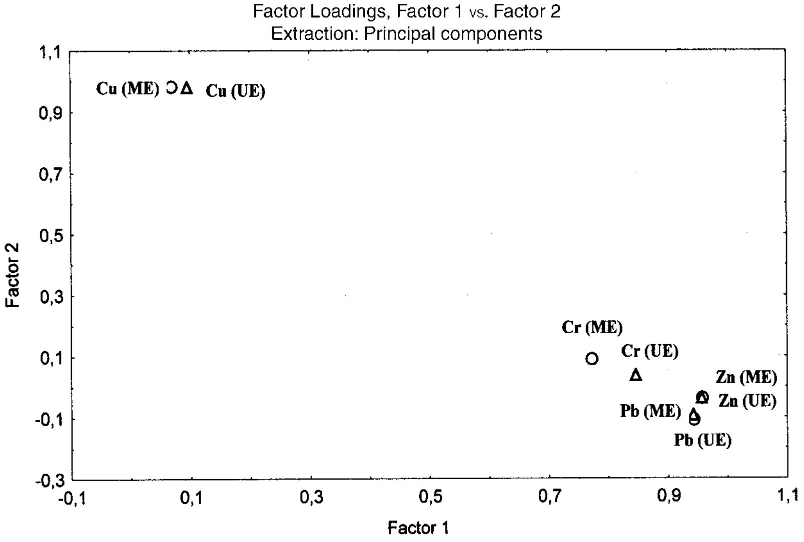

FIGURE 6 Loading values of the metals extracted by microwave- (ME) and ultrasound- (UE) assisted extraction methods.

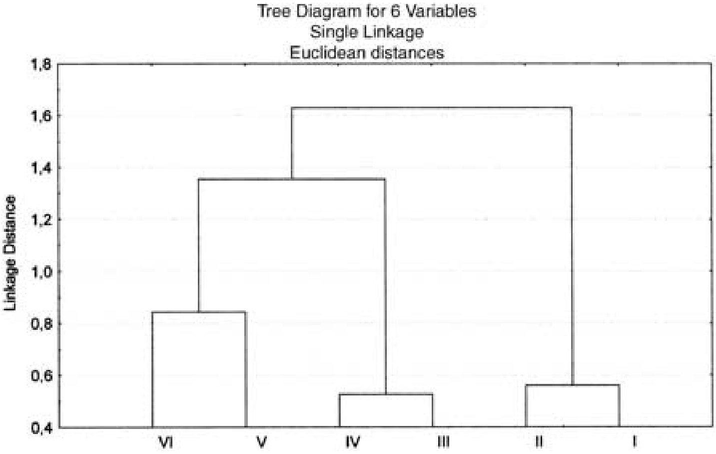

FIGURE 7 Classification of the sludge samples based on the cluster analysis.

extraction methods for the analysis of sludge samples with different composition was confirmed by the separation between the groups.

CONCLUSIONS

The digestion of samples is the most time-consuming step in the analysis of solids by atomic spectrometry, so various alternatives to the traditional wet digestion have been proposed. Two simple and rapid extraction procedures, microwave- and ultrasound-assisted extraction procedures, were optimised for sludge sample pre-treatment by using a mixture of dilute hydrochloric and nitric acids in order to achieve complete leaching of chromium, copper, lead and zinc from sludge samples in a minimum time. The most attractive advantages of both microwave- and ultrasound-assisted extraction procedures over conventional methods can be briefly summarised as follows: (i) the sludge samples suspended in the acid mixture were exposed to microwave irradiation or subjected to ultrasonic agitation for only a few minutes, which permitted the increase of the speed of the whole analytical method, (ii) simultaneous extractions were performed with the aim of shortening the sample pre-treatment time, (iii) the extraction procedure accelerated by microwave energy was less time consuming than the ultrasound-assisted extraction procedure and has opened up new possibilities to the full automation of the sample pre-treatment, (iv) no extract was treated afterwards because neither hydrofluoric acid was added nor the extractants used were concentrated acids, (v) the highest concentration of both hydrochloric acid and nitric acid in the extractant was used for the ultrasound-assisted extraction procedure, (vi) adequate calibration with aqueous standards and (vii) good precision and accuracy for copper, lead and zinc.

The principal drawback of both extraction procedures was the incomplete leaching of chromium from sludge samples. However, the extraction efficiency of chromium depended on the sample matrix and the extraction procedure used. The ultrasound-assisted extraction procedure permitted the achievement of quantitative recovery of chromium in four sludge samples while the microwave-assisted extraction procedure only permitted the quantitative recovery of chromium from one sludge sample. In summary, the ultrasound-assisted extraction procedure provided better results than the microwave-assisted extraction procedure, while the first procedure was more time consuming than the second procedure.

Acknowledgement

The authors acknowledge the financial support (Project 64102K007) of the University of Vigo (Spain).

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