



Rapid determination of total metals: synergic effect of ultrasound energy and ionic liquids on the digestion of sediment samples

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Abstract

Purpose The aim of this study was to develop a new and rapid sample digestion procedure for metal extraction using ultrasonic energy together with a combination of an ionic liquid and mineral acids as extractants.

Methods A fixed mass of sediment (about 0.50 g) was extracted with a combination of low volumes of NaHCO₃, HCl, HNO₃, HF and the ionic liquid Bmim[BF₄]. Afterwards, the mixture was sonicated for 20 min. After neutralizing the hydrofluoric acid excess, the extracts were filtered and measured by ICP OES where Cd, Cr, Cu, Ni, Pb and Zn were determined.

Results The recoveries in certified reference materials ranged from 92 to 102% for LGC-6137, from 88 to 98% for IAEA SL-1 and from 81 to 98% for MURST-ISS-A1, with a good precision (relative standard deviation (RSD) < 10.0% for all the certified reference materials). The new digestion procedure was successfully applied to the determination of metals in estuarine sediment samples, with a satisfactory precision (RSD < 9.5%). The results showed no significant statistical differences compared to those obtained by the conventional digestion procedure (with an α -error of 0.05).

Conclusion This approach has led to satisfactory results in the determination of the total metal concentrations for most of the elements studied using shorter analysis times than the conventional procedure, and small volumes of hydrofluoric acid. The new pretreatment method made it possible to satisfactorily assess the total metal concentrations in estuarine sediments.

Keywords Metals · Ultrasound · Ionic liquid · Sediments

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1 Introduction

The occurrence and persistence of potentially toxic metals in the marine environment are being studied around the world due to the increasing accumulation of these pollutants in both sediments and biota (Rajeshkumar et al. 2018). Pollution in aquatic systems is produced either by human activities, by the appearance of compounds that normally would not be present or by an increase in the usual concentrations of existing substances (Jones and Gomes 2014). The presence of metals could affect the environment and the living organisms, and become noxious if they go beyond certain threshold concentrations. Metal toxicity is affected by many factors, including dose, exposure route and chemical form in which metals can accumulate (Tchounwou et al. 2012). Chromium, copper, cadmium, nickel, zinc and lead are potentially toxic metals. These metals are listed in the Priority Pollutants of the Environmental Protection Agency (USEPA 2014) of the United States (United States

Environmental Protection Agency, Appendix A to Part 423 webpage).

In recent years, several researchers have emphasized the need to know the total content of metals with the aim of identifying points with high metal concentrations and thus classifying the polluted places (Sakan et al. 2011). In addition, the total metal concentration is also necessary when evaluation of fractionation studies is carried out (Chand and Prasad 2013). In this regard, it is important to perform an overall mass balance to ensure that the sequential extraction procedures were executed correctly, i.e. the sum of the metal concentrations of all fractions should match the total metal concentration.

On the other hand, it should be noted that sample treatment is a crucial step in most analytical methods dedicated to the determination of total metal concentration in sediment samples (Wang et al. 2016). Instruments used in most of the analytical techniques are not able to deal directly with solid samples, and some pretreatment must be performed to put the sample in the right form. Metal determination in sediment samples requires solid matrix digestion. Thus, the sample must be completely dissolved to ensure that all bound metals are released into the solution. The total dissolution of sediments is achieved by the use of hydrofluoric acid and/or mixtures with other strong acids, such as nitric, hydrochloric and/or perchloric acid (Rao et al. 2008). The treatment involving aqua regia (ISO 1995) is one of the most accepted or recommended methods because, in combination with flame atomic absorption spectrometry (FAAS), it provides analytical performance parameters which are appropriate in nearly all cases (ISO 1995). However, it is noteworthy that the aqua regia procedure is not considered a total digestion, since the metal recoveries do not reach 100% of the metal content in the solid sample (Alsaleh et al. 2018).

For this reason, several methods for the digestion of sediments or soil samples were based on a combination of strong acids with the application of high temperatures. Traditional methods involved sand bath, plate or block heating (Cook et al. 1997; Güngör and Elik 2007; Paul et al. 2018). However, these conventional procedures have certain limitations mainly related to long digestion times and large volumes of strong acids (Güven and Akinci 2011).

Many authors have developed different digestion procedures involving microwave and ultrasound-assisted acid digestion/extraction of metals in environmental solid samples which have several benefits, such as shorter analysis time and lesser contamination risks (Kazi et al. 2009; García-Casillas et al. 2014). Ultrasonic (US) energy as a technique to speed up the extraction of metals from sediments has become a standard practice to improve the digestion procedure (Frena et al. 2014). In a previous work, we have observed that the combination of ionic liquids and chelating extractants accelerates and enhances the extraction efficiency (Álvarez et al.

2017). Ionic liquids (ILs) are organic salts with melting points lower than 100 °C (i.e. they become liquid at room temperature). They consist of an arrangement of organic cations (e.g. ammonium, imidazolium, phosphonium, among others), and both inorganic and organic anions (such as PF₆, BF₄, Cl). ILs show different interesting properties, such as higher thermal and electrochemical stabilities, ionic conductivity, good dissolving ability due to their solvation potential with respect to both polar and non-polar compounds, negligible vapour pressure, non-flammability and non-volatility (Chaban 2015; Rajadurai and Anguraj 2020).

In the last decades, ILs aroused great interest as extractants and, particularly, in the field of metal extraction (Pribylova 2011; Stojanovic and Keppler 2012; Janssen et al. 2015). Several researches have studied the mechanism of interaction between metals and ILs (Stojanovic and Keppler 2012; Janssen et al. 2015) which is based mainly on the ion exchange, the neutral extraction and coextraction and the classical physical adsorption process (Stojanovic and Keppler 2012; Janssen et al. 2015; Rajadurai and Anguraj 2020). The type of interaction mechanism between metal ions and ILs depends largely on the length of the alkyl chain, which confers different hydrophobic/hydrophilic characteristics to ILs (Stojanovic and Keppler 2012; Rajadurai and Anguraj 2020).

The goal of this research is to develop a new digestion procedure for the total metal assessment in sediments. Furthermore, the method aims to achieve satisfactory extractions, while reducing the consumption of acids, particularly HF, and shortening digestion times. This method was performed using an ionic liquid, assisted by ultrasound energy (IL/US). The combination of 1-butyl-3-methylimidazolium tetrafluoroborate and the US irradiation made it possible to decrease the extraction time and the volume of strong acids used in comparison with conventional methods (acid treatment + plate heating). It has to be emphasized that the ultrasound energy tends to accelerate the digestion process.

2 Experimental

2.1 Reagents, samples and instrumentation

All the laboratory material (both plastic and glass) was carefully conditioned using 10% HNO₃ for 24 h, and washed with doubly distilled water before use. Analytical grade reagents and double-distilled water were used throughout this research. 1-Butyl-3-methyl-imidazolium tetrafluoroborate (Bmim[BF₄]) was acquired from Merck. Hydrofluoric, hydrochloric and nitric acids were purchased from Carlo Erba (Erbatron RSE). Multi-element metal standard solutions (Cr, Cu, Cd, Ni, Zn and Pb, purchased from Merck) of 10.00 mg L⁻¹ were prepared by dilution with 0.5 mol L⁻¹ HNO₃ (from Carlo Erba). Quality control standards were

unielemental solutions with a concentration of 1000 mg L^{-1} prepared in 0.1% m/v purified nitric acid. Blank solutions consisted of a 0.5 mol L^{-1} solution of the same solvent.

An ultrasonic bath with an output power of 160 W (TEST-LAB model TB 04 TA) was used to assist the extraction process. An inductively coupled plasma atomic emission spectrometer (Shimadzu ICPS-1000) operated at 1.2 kW of radio frequency power. An observation height of 12 mm above the load coil (ALC) was selected, with the following argon gas (99.99% purity) flow rates of 1.4, 1.1 and 1.0 L min^{-1} for the plasma, auxiliary and nebulizer (a concentric nebulizer, Conikal U-Series nebulizer, Glass Expansion), respectively. The solution uptake rate was 1.2 mL min^{-1} . A cyclonic spray chamber (Glass Expansion, 50 mL) was used.

The lines used in the determination were 267.80, 327.40, 226.57, 231.6, 213.92 and 220.42 nm for Cr, Cu, Cd, Ni, Zn and Pb, respectively (Alvarez et al. 2011). The integration time was 5 s. The detection limits were estimated from successive determinations of the blank solution. The practical values were calculated as the ratio between three times the standard deviation of the blank signal ($n = 10$) and the slope of the calibration curve obtained for each element, according to Eurachem guidelines (Magnusson Örnemark 2014). The quantification limits (expressed in mg kg^{-1}) were the following: 0.07 (Cr), 0.13 (Cu), 0.03 (Cd), 0.10 (Ni), 0.03 (Zn) and 0.13 (Pb).

Three sediment reference materials were used for validation purposes: estuarine sediment reference material for trace metals LGC-6137 (Laboratory of the Government Chemist, Teddington, UK), Antarctic bottom sediment reference material MURST-ISS-A1 (Italian Research Program in Antarctica) and lake sediment reference material IAEA SL-1 (International Atomic Energy Agency, Analytical Quality Control Services).

Six sediment samples were collected in the Bahía Blanca estuary situated in the southeast of the Buenos Aires province, Argentina (Fig. S1). Three specific zones of the estuary were sampled: Galván harbour, which corresponds to an industrialized area near to the discharges of petrochemical plants (samples S1, S2, S5 and S6); the mouth of the Maldonado stream, which runs through the city of Bahía Blanca (sample S3); and Cuatros port, a recreational fishing area (sample S4). The sediment samples were taken from the top layer (less than 5 cm in depth). The oxic sediments were light brown and scaly in appearance, with no smell of sulphide.

Several portions of sediments were taken at each sampling site, along a zigzagging track, and homogenized in order to obtain representative composite samples, which were maintained at $4 \text{ }^\circ\text{C}$ until further analysis (Alvarez et al. 2011). Prior to the digestion, the samples were air-dried at room temperature for at least 72 h, and sieved with

stainless-steel meshes (size of $63 \text{ }\mu\text{m}$, N° 250). The smaller particles were homogenized by grinding them in an agate mortar. The sediment samples were analyzed in triplicate using the procedures described below (Sec. 2.2.1 and 2.2.2).

2.2 Applied digestion procedures

2.2.1 Total metal concentrations (acid/heating)

In order to obtain the total metal concentrations, the sediment samples (1.0 g of dry material) were treated using the conventional digestion procedure involving 12.0 mL of a mixture of concentrated acids HF/HCl/HNO₃ (5 + 5 + 2) combined with heating by means of a hot plate followed by the addition of 2.0 mL of perchloric acid. Then, 2.0 mL of HNO₃ were added for dissolving of residue, and made up to 25.0 mL with doubly distilled demineralised water. The total digestion time was about 6 h (Alvarez et al. 2011). All the estuarine samples and also the reference materials were treated with this method. The extracts were filtered through $0.45 \text{ }\mu\text{m}$ filter membranes prior to ICP OES measurements.

2.2.2 Ionic liquid-ultrasound assisted digestion (acid/IL/US method)

The parameters selected to enhance the digestion procedure were the sonication time, the volumes of the different acids used, the concentration of ionic liquid Bmim[BF₄] and the presence/absence of salts. The bath ultrasonic power (100 W) was determined calorimetrically by measuring the time–temperature increase. Subsequently, a central composite design (Fernández et al. 2014) was applied to optimize the experimental variables selected by the Plackett–Burman design (PBD). These variables were HF volume and sonication time.

Under the optimized conditions, a fixed mass of sample ($0.50 \pm 0.01 \text{ g}$) was placed into a PTFE tube. Then, an extractant mixture consisting of 0.12 g of NaHCO₃, 4.0 mL of 50 mM Bmim[BF₄], 2.0 mL of HCl, 2.0 mL of HNO₃ and 1.0 mL of HF was added, making up to a final volume of 15 mL. Afterwards, two tubes of sample were sonicated in the ultrasonic bath for 20 min at 100 W, rotating their position after 10 min. This procedure was carried out in order to improve the reproducibility between samples, because the ultrasonic bath has two piezoelectrics. Detergent (0.25% v/v) was added to the water bath to improve the cavitation process (Álvarez et al. 2017). A saturated boric acid solution was directly added after digestion to neutralize the hydrofluoric acid excess (Odika et al. 2020). The extracts were filtered using $0.45 \text{ }\mu\text{m}$ filter membranes and measured by ICP OES.

2.3 Statistical data treatment

The values obtained from the analysis of the three reference materials (i.e. LGC-6137, IAEA-SL-1 and MURST-ISS-A1) using the proposed method were regressed against the corresponding certified values. When these sets of data are consistent, the obtained straight line regression should have a slope of about 1, and an intercept near to 0. The similarity between the obtained regression coefficients and the theoretical value (slope = 1, intercept = 0) could be tested using the statistical joint interval test of slope and intercept. In this test, in the absence of bias, the point (1,0) should fall within the elliptical confidence region centred on the slope and intercept values of the straight regression line obtained (with a confidence level $\alpha = 0.05$) (Massart et al. 1997). The same statistical test was applied to compare the results obtained using the Acid/IL/US method in the analysis of the sediment samples and those recovered when the same samples were treated with the procedure described in Sec. 2.2.1 (Alvarez et al. 2011).

3 Results and discussion

3.1 Ionic liquid/ultrasound-assisted digestion procedure optimization

The proposed Acid/IL/US procedure was optimized by means of experimental design, comparing the efficiency of the digestion techniques with the conventional heating method. Metal recovery was calculated as in Eq. 1.

$$\% \text{Recovery} = 100 \times \left(\frac{\text{metal extracted by acid/IL/US procedure}}{\text{metal extracted by conventional acid/heating method}} \right) \quad (1)$$

3.1.1 Screening step

The selection of the variables in acid/IL/US procedure in sediment samples was carried out according to previously published researches by our group (Alvarez et al. 2001, 2011). In the literature, the ratio extractant volume/sediment mass ranges from 12.5:1 (Álvarez et al. 2017) to 50:1 (Güngör and Elik 2007). However, the more often used ratio is around 25:1. In the current research, the 30:1 relationship was used. The other variables that could potentially affect the procedure were the volumes of each acid, the concentration of the IL, the sonication time and the presence of two salts, NaCl and NaHCO₃. Regarding the latter variables, it has been reported that the use of salts can improve metal extraction efficiency when ILs are used (Álvarez et al. 2017).

The study of this large amount of variables or factors would involve a large number of experiments if they were

investigated in a univariate manner. However, the experimental design methodology makes it possible to understand the effect of the variables with minimal experiments (Massart et al. 1997). In a variable screening study, when the influence of a high number of factors is analyzed to determine which of them are relevant, saturated fractional factorial designs could be applied. The PBD is a particular case in which only the main factors affecting the extraction can be estimated with a few experiments, and presumes that the interactions between the variables can be ignored altogether (Myers and Montgomery 2002). Therefore, the number of factors can be evaluated up to $k = N - 1$ independent variables, where N represents the number of experiments. Each variable was investigated in two levels, high (+) and low (−) (coded factor levels), according to preliminary assays (Hibbert 2012).

Therefore, a matrix design involving 11 variables (seven real variables and four dummies) was used. A dummy variable is defined as an imaginary variable, whose variation between the coded levels does not represent an experimental physical change in the design. Therefore, it cannot possibly have an effect on the response. They were used to estimate the standard deviation effects in the statistical meaning (Fernández et al. 2014; Nario et al. 2019). Non-significant imaginary variables for any of the responses demonstrate that there is neither an unknown factor nor a systematic error in the design.

Table 1 shows the Plackett–Burman matrix indicating the 12 random experiments and the levels of each different variable (i.e. HF, HCl and HNO₃ volumes, presence or absence of salt (both NaCl and NaHCO₃), IL concentration and soni-

cation time). The experimental domain, i.e. the range of the studied variables, was selected on the basis of preliminary studies.

The main effects of the variables may be visualized and interpreted by a Pareto chart. The variables are symbolized by individual bars in descending order taking into account their standardized effect, which is the ratio of the estimated effect to its standard error (Aguirre et al. 2020). Significance of the factors was evaluated by a *t*-test. Thus, all the effects larger or equal to 7.51 (*critical value*) were significant. The critical effect is related to the tabulated *t*-value (2.78) and to the estimation of the standard error of the effect (2.71), which was estimated from the dummies' effects (Fernández et al. 2014). Figure 1 shows the Pareto chart corresponding to the effects calculated for each variable after the analysis of the PBD. As it can be seen, the only two variables that have an effect higher than the critical value (7.51) were the

Table 1 Experimental variables and levels of the Plackett–Burman design

	Factor A HF volume (mL)	Factor B HCl volume (mL)	Factor C HNO ₃ volume (mL)	Factor D IL concentration (mM)	Factor E Time sonication (min)	Factor F NaCl (0.1 mol L ⁻¹)	Factor G NaHCO ₃ (0.1 mol L ⁻¹)	Dummies				Response (Cu% recovery)
1	0.2	2	5	10	20	Without	Without	1	-1	1	-1	86.89
2	0.7	5	5	5	20	With	Without	1	-1	-1	-1	85.44
3	0.2	5	5	5	20	Without	With	-1	1	1	1	83.45
4	0.7	5	2	10	20	Without	With	-1	-1	-1	1	102.24
5	0.2	2	2	10	20	With	Without	1	1	-1	1	89.59
6	0.7	2	2	5	20	With	With	-1	1	1	-1	85.44
7	0.2	2	2	5	10	Without	With	-1	-1	-1	-1	79.01
8	0.7	2	5	5	10	Without	Without	1	1	-1	1	82.66
9	0.7	2	5	10	10	With	With	-1	-1	1	1	83.08
10	0.2	5	2	5	10	With	Without	1	-1	1	1	68.1
11	0.2	5	5	10	10	With	With	-1	1	-1	-1	66.78
12	0.7	5	2	10	10	Without	Without	1	1	1	-1	82.25

sonication time and the HF volume, which means that both have significant effects on the response. Besides, both variables have a positive sign. That is to say, when the sign of the effect is positive, the response (i.e. recovery) improves as the variable assumes higher values, and vice versa.

Since the other variables showed no significant effects, the levels of these variables for the next stage of the response surface methodology were set according to the sign of the effects calculated for the PBD. Thus, the values of the variables were fixed as follows: 2 mL of 37% w/w HCl and 2 mL of 65% w/w HNO₃, 10 mM of ionic liquid, absence of NaCl and presence of NaHCO₃.

3.1.2 Optimization strategy

The optimal values for the variables that showed significant effects in the PBD (i.e. HF volume and sonication time) were

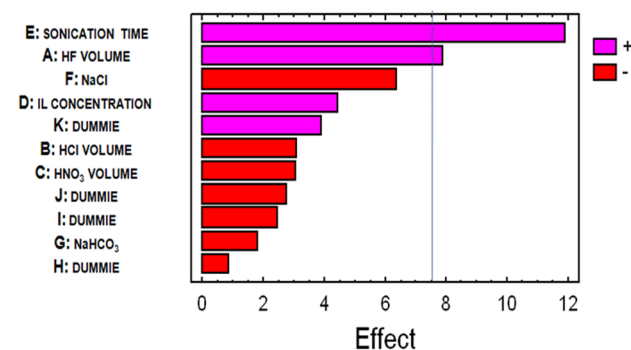


Fig. 1 Pareto chart with the standardized main effects in the Plackett–Burman design. The line indicates the critical value for the significance of effects

found using a central composite design (CCD) for the two factors. The CCD was constituted by a two-level factorial design and two central points with additional star points ($\alpha = \pm 1.41$). Table 2 shows the design involving the selected experiments and the corresponding experimental matrix.

Figure 2 exhibits the Pareto chart of standardized effects at $p = 0.05$ showing the absolute values and indicating which of them are positive or negative. The variables showing an absolute value higher than 2.202 (located on the right of the blue line) were significant. As it can be seen, only the quadratic term of HF volume (AA) showed a significant effect on the digestion recovery. The negative sign of the quadratic term indicates the presence of a local minimum in the response surface (Hibbert 2012).

As it can be seen in Fig. 2, the HF volume and the sonication time showed non-significant effects on the response. However, the interaction between these variables has a positive sign. This indicates that when one variable increases and the other decreases, the best recoveries are obtained. In this study, the best response was obtained when the sonication time and the HF volume were 20 min and 1.0 mL, respectively. This fact concurs with the contour graphic of estimated response surface shown in Fig. S2. From this figure, it can be seen that the recovery increases for higher HF volumes and lower sonication times. A possible explanation of this fact can be attributed to the interaction between the variables (AB) as mentioned before. Other studies published in the literature reported similar optimal conditions in the analysis of ashes samples (Ilander and Väisänen 2007, 2009). They found that the most suitable sonication time for HF digestion was about 20 min, after which a decrease in signal was observed.

Table 2 Experimental variables, levels and star points of the central composite design (CCD)

Factor	Key	Level				
		$-\alpha$	Low	Central	High	$+\alpha$
HF volume (mL)	A	0.50	0.58	0.75	0.92	1.00
Sonication time (min)	B	20	24	30	36	40

Even though the volume of HF established in the experimental design is the highest, it is still a low volume. This is probably related to a kind of synergistic effect between the ILs and the acids used in the extraction process. The mechanism of action of ILs is not yet fully understood (Stojanovic and Keppler 2012). Several authors have suggested that fluoride-containing anions could lead to the in situ generation of hydrofluoric acid under strong acidic conditions (Swatloski et al. 2003; Stojanovic and Keppler 2012; Zimmermann et al. 2020). The hydrolytic degradation of these compounds could potentially contribute to better extraction efficiency in the total metal determination even when low volumes of HF were used.

Several authors have reported different relationships between the HF volume and the mass of sediment, either for methods using conventional heating or for microwave- and ultrasound-assisted methods (Table S1). Regarding the conventional heating methods, Paul et al. (2018) employed 3 mL HF for the digestion of 0.100 g of sediment (volume/mass of sediment ratios of 30 mL g⁻¹). They obtained good recoveries for Cu, Ni and Pb, using a digestion at 220 °C for 12 h, which were between 92.9 and 102.6%, and the precision was lower than 8%. Besides, Cook et al. (1997) compared various digestion procedures with diverse HF volume/mass of sediment ratios (10 mL g⁻¹, 8 mL g⁻¹, 4 mL g⁻¹). They analyzed two different sediment samples (one of them with high metal content) and obtained similar results using the different HF volume/mass relationships. However, the recoveries were slightly better for 10 mL g⁻¹

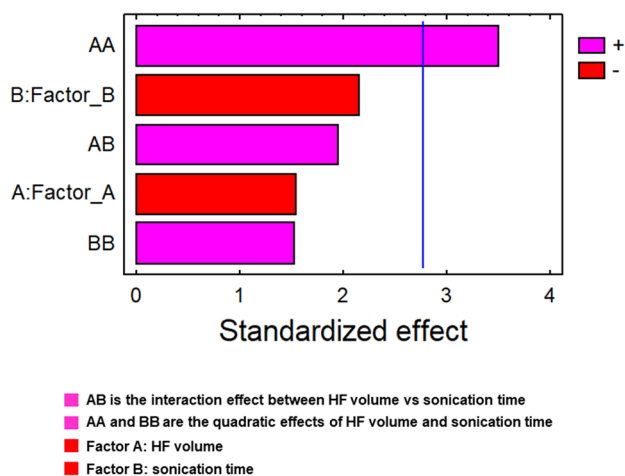
ratio and decreased as the ratio diminished. They argued that the performance of HF-based digestions was different depending on the metal analyzed and the type of sediment. For this reason, comparison between methods is not straightforward. Likewise, Güngör and Elik (2007) used a ratio of 20 mL g⁻¹. The recovery values ranged from 98.6 (obtained for Cu in river sediment samples) to 102% (obtained for Pb in pond sediment samples).

On the other hand, other researchers reported microwave irradiation methods for total metal extraction in sediments. Some methods applied a volume/mass ratio of 6 mL g⁻¹ (USEPA 1996b; Cook et al. 1997). In order to minimize the amount of HF used in the digestion, some authors have made some modifications to the USEPA method. This is the case of Benomar et al. (2012), who adapted the 3052 USEPA method to use smaller amounts of HF, achieving an HF volume/sediment mass ratio of 5 mL g⁻¹. Meanwhile, Lo and Sakamoto (2005) employed a higher ratio (15 mL g⁻¹), since they needed 3 mL of HF for the digestion of 0.2 g of sediment. Finally, Sastre et al. (2002) treated 1.0 g of sediment with a microwave assisted procedure involving 5 steps. In three of them, a HF volume of 10 mL was used. Thus, the volume of HF per gram was 30 mL.

Other methods carried out the digestion process with the aid of ultrasound energy. Güngör and Elik (2007), for example, developed a digestion method involving a mixture of nitric, perchloric and hydrofluoric acids in a 2:1:1 ratio of volumes. Since they used a total volume of 25 mL of acid mixture to treat 0.5 g of sediment, the HF volume/sediment mass ratio was 12.5 mL g⁻¹. Frena et al. (2014), in turn, employed 0.100 g of sediment, and performed the digestion using a volume/mass ratio of about 10 mL g⁻¹.

Compared to all the studies cited above, the Acid/IL/US method proposed in the current investigation used the lowest volume/mass ratio, i.e. 2 mL g⁻¹, since it was able to digest 0.5 g of sediment using 1 mL of HF.

Regarding the pretreatment time, a common feature of conventional methods is the use of long digestion times (Table S1). The methods reviewed in this study oscillated between 1 and 16 h (Cook et al. 1997; Güngör and Elik 2007; Paul et al. 2018). On the other hand, the application of microwave energy to assist the digestion made it possible to considerably reduce the digestion time. In this case, this time varied between 15 and 20 min (USEPA 1996b; Benomar et al. 2012) to 41 min (Cook et al. 1997). The exception was the method proposed by Sastre et al. (2002) that took about

**Fig. 2** Pareto chart of main effects in the central composite design for metal recoveries

91 h. Finally, the time taken for ultrasound-assisted digestion methods is also about 15–25 min. For instance, Frena et al. (2014) reported a digestion time of about 15 min followed by another 15 min of centrifugation. Likewise, Güngör and Elik (2007) developed a method in which ultrasound is applied for 25 min, followed for several steps related to acid evaporation and centrifugation. Furthermore, the method Acid/IL/US takes 20 min, which is within the range of time of the reported ultrasound-assisted digestion methods. It is noteworthy that the total treatment time is 20 min, as no further centrifugation and evaporation operations were necessary. Despite the fact that digestion times are similar for ultrasound and microwave assisted procedures, it is important to take into account the time needed to cool the digestion mixture in microwave assisted methods, which can take up to 20 min using an ice bath (Filgueiras et al. 2000). From this point of view, ultrasound-assisted digestion has an additional advantage, as the temperature in ultrasound-assisted digestion is considerably lower than the one achieved in microwave-assisted digestion.

3.2 Determination of metals in reference materials

Several authors reported that although there are official methods — Method 3050B (USEPA 1996a), Method 3051A (USEPA 2007), Method 3052 (USEPA 1996b) — for metals determination, these methods present certain limitations. In particular, method 3050B (concentrated HNO_3) has the drawback of atmospheric contamination hazard. It is noteworthy that methods 3050B and 3051A ($\text{HCl} + \text{HNO}_3$) are not total digestion techniques, but they are considered pseudo-total extraction methods. In method 3052 ($\text{HNO}_3 + \text{HF}$), the use of microwave-assisted digestion involves overtime cooling of the reactors that needs to be achieved before opening. Da Silva et al. (2014) reported that method 3052 has the highest recoveries and the lowest standard deviations, but overestimated the concentrations, and for this reason it was not recommended. Therefore, it is important to evaluate different strategies to achieve efficient digestion.

Table 3 shows the obtained and certified concentration values for the three sediment reference materials. Overall, the results were satisfactory in both trueness and precision. The recoveries obtained comparing the proposed method with the certified values of the reference material ranged between 81% (Cr in MURST-ISS-A1) and 102% (Cd and Cu in LGC-6137). Precision was evaluated as the percentage relative standard deviation (%RSD), under repeatability conditions, by applying the complete procedure in triplicate to different aliquots of each reference material. Highly satisfactory precision values (less than 10.0%) were obtained for the procedure. The lowest %RSD value was obtained for zinc, whereas the highest one was recorded for cadmium (both in MURST-ISS-A1).

In order to test for the presence of bias, the values obtained by the acid/IL/US method were regressed against the certified values, using bivariate least squares (Massart et al. 1997). The regression equation was $y = 1.05x + 0.04$, and the correlation coefficient 0.996, indicating, in a qualitative manner, that the obtained values fit well to the certified ones. Figure S3 shows that the elliptical region of confidence centred on the obtained regression coefficients (i.e. 1.05 slope and 0.04 intercept) contains the theoretical point (1,0). Therefore, there are no significant statistical differences between both sets of results, considering a significance level of $\alpha = 0.05$, which indicates that the Acid/IL/US digestion procedure attained good metal extraction efficiencies.

Other authors reported similar recoveries, ranging from 80 to 117% using different reference material as BCR-146R (Sakan et al. 2011), SRM NIST 2704 (Chand and Prasad 2013) and SRM NIST 2702 (Álvarez-Vázquez et al. 2014), among others. Ghosh and Maiti (2018) also applied the 3051 method to the LGC 6137 certified reference material with good results (recoveries > 88%). Fabri-Jr et al. (2018) used an Antarctic Marine Sediment as certified reference material (MURST-ISS-A1), applying the extraction procedure of Method 3052 (USEPA 1996a, b), with recoveries > 92%. Islam et al. (2020) reported that using Method 3051A (USEPA 2007) in reference material IAEA-SL-1 they obtained recoveries greater than 89%. Furthermore, other authors applied ultrasound-assisted methods for metal extraction in different reference materials. For instance, Mimura et al. (2016) analyzed the certified reference material Buffalo River Sediment 8704 (NIST, MD) to assess Cr, Cu, Zn, Cd and Pb, using an ultrasonic bath for 180 min. The recoveries ranged from 80.1% (Pb) to 93.7% (Zn). Also, Frena et al. (2014) proposed a fast extraction procedure using also an ultrasonic bath. The optimal conditions were applied to three different sediment reference materials (MESS-3, PACS-2 and NCS DC 78,301). The authors reported good results for all the metals in terms of accuracy, although chromium data were not available. Another study was carried out by Fernández-Ortiz de Vallejuelo et al. (2009). They used a glass sonotrode in combination with a mixture of HNO_3 – HCl for 6 min to assess metals concentrations in a NIST 1646a certified reference material with recoveries ranging from 25% (Al) to 125% (Zn). The variation in the recoveries observed in the different published articles seems to be more related to the complex matrix of the certified reference materials than to the concentration levels of the metals in these samples (Sakan et al. 2011; Chand and Prasad 2013).

Also, the same reference sediment samples were analyzed using the conventional acid/heating procedure (Table 3). Normally, conventional heating through a wet digestion procedure uses a combination of some concentrated acids, such as hydrofluoric, hydrochloric, nitric and perchloric. These

Table 3 Total metal concentrations (mg kg^{-1}) (mean \pm s) for different reference materials obtained by both acid/heating treatment and acid/IL/US procedure

	LGC-6137	Cd	Cr	Cu	Ni	Pb	Zn
Certified value	(0.5)*		47 \pm 7	(31.60)*	(31.50)*	73.0 \pm 3.6	231 \pm 16
Acid/heating*	0.47 \pm 0.05		41 \pm 4	27.65 \pm 2.63	26.15 \pm 2.11	68.3 \pm 5.9	208 \pm 12
% recovery	94		87	88	83	94	90
% RSD	10.6		9.8	9.5	8.1	8.6	5.7
Acid/IL/US*	0.51 \pm 0.04		44 \pm 4	32.13 \pm 2.38	28.85 \pm 2.45	70.8 \pm 6.6	230 \pm 12
% recovery	102		94	102	92	97	99
% RSD	7.8		8.5	7.4	8.5	9.3	5.4
Deviation%	-8.5		-7.3	-16.2	-10.3	-3.7	-10.4
	MURST-ISS-A1	Cd	Cr	Cu	Ni	Pb	Zn
Certified value	0.54 \pm 0.02		42.1 \pm 3.5	5.79 \pm 1.15	9.56 \pm 0.76	21.0 \pm 2.1	51.9 \pm 3.2
Acid/heating*	0.50 \pm 0.04		36.2 \pm 3.1	5.38 \pm 0.52	8.12 \pm 0.77	18.0 \pm 1.9	51.4 \pm 1.1
% recovery	93		86	93	85	86	99
% RSD	8.0		8.4	9.7	9.5	10.4	2.1
Acid/IL/US*	0.49 \pm 0.04		33.9 \pm 3.3	5.48 \pm 0.55	8.68 \pm 0.85	18.9 \pm 1.77	50.7 \pm 1.40
% recovery	91		81	95	91	90	98
% RSD	8.2		9.8	10.0	9.8	9.4	2.8
Deviation%	2.0		6.4	-1.9	-6.9	-4.8	1.5
	IAEA-SL1	Cd	Cr	Cu	Ni	Pb	Zn
Certified value	0.26 \pm 0.05		104 \pm 9	30.0 \pm 5.6	44.9 \pm 8.5	37.7 \pm 7.4	223 \pm 10
Acid/heating*	0.23 \pm 0.02		99.1 \pm 9	26.9 \pm 1.95	40.6 \pm 4.1	35.7 \pm 3.5	216 \pm 14
% recovery	88		95	90	90	95	97
% RSD	8.3		8.7	7.3	10.1	9.8	6.6
Acid/IL/US*	0.24 \pm 0.02		91.3 \pm 8	27.1 \pm 1.4	41.3 \pm 3.8	37.0 \pm 3.4	207 \pm 15
% recovery	92		88	90	92	98	93
% RSD	8.3		8.7	5.1	9.2	9.1	7.3
Deviation%	-4.3		7.9	-1.0	-1.7	-9.2	3.9

* All the determinations were performed in triplicate ($n=3$)

combinations were applied for metals determination in sediment samples (Javan et al. 2015; Niedzielski et al. 2015; Maity et al. 2016). In our case, the conventional procedure was sufficient to solubilise most of the metals in the sediment samples of the study area, even those incorporated in stable crystalline lattices of the mineralogical phases. The disadvantage of this procedure is that the digestion time takes at least 6 h (Alvarez et al. 2011). Perhaps, the method should have been re-optimised, but it continued to be used for ICP OES, as it gave good results, and the samples from the Bahía Blanca estuary did not require lower detection limits. Thus, the conventional method was used as designed.

The results obtained by the acid/IL/US digestion method were also compared with those recovered by the conventional acid/heating procedure for the analysis of the three reference materials. Table 3 reports the deviation (expressed as a percentage) of the values obtained with our method with respect to the conventional one. The bias of the concentration values between both sample treatment methods was less than 10% for almost all the elements, which could be considered “negligible” (i.e. less

than 10%) for this kind of samples, as stated by Chand and Prasad (2013). Only in the analysis of LGC-6137 were the deviations slightly higher than 10% for Ni and Zn, and about 16% for Cu, which could still be considered as non-important deviations (Chand and Prasad 2013). In these cases, the deviations were negative, which means that our method obtained better recoveries than the conventional acid/heating method. Furthermore, most of the determinations showed that the acid digestion/IL/US method made it possible to obtain better recoveries than the conventional procedure with respect to the certified values of the reference materials. In fact, the acid/heating procedure led to better results only in five of the eighteen determinations (Cd, Cr and Zn in MURST-ISS-A1, Cr and Zn in IAEA-SL1). Moreover, a t -test for paired data between the recoveries obtained by both the conventional (acid/heating) and the proposed (acid/IL/US) methods was performed. The results showed significant differences between the two methods ($t_{\text{calc}}=2.24$; $t_{\text{crit}}=2.11$) with an α value of 0.05. The results indicate that the proposed method is a good alternative to the conventional procedure.

3.3 Metal concentrations of estuarine sediment samples

The acid/IL/US method was applied to the six estuarine sediment samples to assess the concentrations of Cd, Cr, Cu, Ni, Pb and Zn. The obtained results are summarized in Table 4. The %RSD values for the acid/IL/US method ranged from 4.1 to 9.5%, which could be considered “acceptable” (i.e. RDS lower than 20%) for this type of samples (Chand and Prasad 2013; Niedzielski et al. 2015). Looking at the precision per

element, it can be seen that chromium, nickel and lead showed a larger dispersion in the results than the other metals. The %RSD values ranged from 6.7 to 9.4% for chromium, 7.5 to 9.4% for nickel and 6.1 to 9.5% for lead. On the contrary, zinc showed the lowest %RSD values (between 4.1 and 6.8%), which is to be expected as it is well known that precision is concentration-dependent, and is better at higher concentrations (Thompson 2012). Indeed, the amount of zinc in the samples is, at least, one order of magnitude higher than the concentrations found for the other metals. In the same way, the relatively

Table 4 Total metal concentrations (mg kg^{-1}) and % RSD ($n=3$) for different sediment samples

		Acid/IL/US		Acid/heating		Deviation (%)
		Metal concentration* (mg kg^{-1})	RSD%	Metal concentration* (mg kg^{-1})	RSD%	
S1	Cd	4.75	6.7	4.70	8.7	-1.1
	Cr	48.33	6.7	54.47	9.3	11.3
	Cu	70.82	6.7	70.63	9.3	-0.3
	Ni	39.46	7.9	40.25	9.4	2.0
	Pb	36.12	8.4	39.75	9.5	9.1
	Zn	235.7	5.3	228.1	7.5	-3.3
S2	Cd	3.58	5.9	3.42	8.2	-4.7
	Cr	34.36	9.1	39.05	9.1	12.0
	Cu	79.84	7.9	85.07	9.2	6.1
	Ni	43.08	7.5	45.12	7.7	4.5
	Pb	67.85	6.1	73.86	9.1	8.1
	Zn	198.2	5.7	183.7	8.2	-7.9
S3	Cd	3.98	6.3	4.03	7.9	1.2
	Cr	45.38	8.9	50.68	9.6	10.5
	Cu	103.8	6.1	109.7	8.7	5.4
	Ni	35.39	8.4	38.05	8.8	7.0
	Pb	65.53	9.2	70.28	8.9	6.8
	Zn	150.7	4.9	143.8	6.8	-4.8
S4	Cd	2.93	6.8	2.98	9.1	1.7
	Cr	27.48	8.1	30.15	9.3	8.9
	Cu	79.95	7.5	80.30	9.8	0.4
	Ni	25.14	9.4	26.15	7.9	3.9
	Pb	37.62	8.4	39.76	8.2	5.4
	Zn	402.6	4.1	388.2	6.3	-3.6
S5	Cd	1.97	6.1	1.85	9.7	-6.5
	Cr	22.69	9.4	26.08	9.5	13.0
	Cu	86.11	8.9	91.05	8.4	5.4
	Ni	29.25	9.1	31.12	9.7	6.0
	Pb	30.55	9.5	32.85	9.7	7.0
	Zn	149.8	6.8	152.6	8.1	1.8
S6	Cd	2.22	6.8	2.13	9.4	-4.2
	Cr	17.95	7.5	19.85	9.4	9.6
	Cu	102.2	6.1	100.8	8.9	-1.4
	Ni	22.06	8.5	21.98	8.7	-0.4
	Pb	24.62	9.5	27.05	9.8	9.0
	Zn	246.8	4.1	245.3	5.2	-0.6

*Values obtained as the average of the triplicate analysis of the samples

low %RSD values obtained for cadmium (5.9 to 6.8%), which is present in very low concentrations in the sediment samples, are noticeable. In fact, concentrations of cadmium found in the sediment samples were as low as 1.97 mg kg^{-1} , which is about 65 times the limit of quantification for Cd in the ICP OES determination carried out in the current research (0.03 mg kg^{-1}). On the other hand, the lowest concentration for Zn (the most abundant element in the samples) is about 5000 times the limit of quantification for this element (also 0.03 mg kg^{-1}).

The values recovered by both digestion procedures were also compared on an element-by-element basis. Table 4 shows the percentage deviation values obtained for Acid/IL/US with respect to the conventional digestion procedure. The deviation values for all the elements were lower than 10%, except for chromium, for which the bias ranged between 9.6 to 13%. Even though these values could be considered as acceptable (Chand and Prasad 2013; Niedzielski et al. 2015), there were statistical significant differences ($\alpha = 0.05$) between both methods for chromium. This fact would indicate that the extraction ability of the proposed method is lower than the conventional one. Other studies on the determination of total metals also reported difficulties in determining chromium (Hornberger et al. 1999; Ilander and Väisänen 2009; Kumkrong et al. 2021). Moreover, the results obtained with the conventional method in the current study also show low recoveries for MURST-ISS-A1 and LGC-6137.

Regarding precision, Table 4 shows that the Acid/IL/US procedure presented lower RSD% values than the conventional digestion method, where the RSD% was lower for the Acid/heating procedure only in four of the 36 samples. However, a statistical comparison between the variances, corresponding to the determination of each element in each sample, showed that there were no statistically significant differences between the precision of the two methods ($n = 3$; $\alpha = 0.05$).

It is important to note that, according to the sediment quality guidelines (SQG), if metal concentrations in the sediments are less than the threshold effect concentration (TEC), this indicates that there are no harmful effects on biota. However, if the concentrations are higher than the probable effect concentration (PEC) this indicates probable harmful effects (MacDonald et al. 2000). In this study, the total concentrations are below this value for all metals at all sampling points (Fig. S4). However, Cd should be monitored at sampling point S1, since its value is close to PEC.

4 Conclusions

The obtained results point out that the proposed acid/IL/US procedure is a fast and accurate method for total trace metal determination in estuarine sediments. The combination

of ionic liquids and ultrasound assistance technologies for improving the digestion method makes it possible to obtain satisfactory results, which showed good correspondence with the certified reference materials for the analyzed metals. In addition, the acid/IL/US method exhibits such a digestion efficiency that makes it suitable to estimate the total metal concentration in sediment samples from potentially polluted environments. Notably, at all sampling points studied, none of the metals exceeds the probable effect concentration (PEC).

In addition, the volume of hydrofluoric acid is 60% less than the one used in conventional digestion procedure, considering the same mass of sediment, and the net digestion time of analysis is 20 min. Moreover, there are certain post-digestion operations (e.g. evaporation) which are commonly performed in most of the reported methods and are not present in our method. Besides, digested samples do not need a waiting time for cooling before further analysis.

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References

- Aguirre MA, Canals A, López-García I, Hernández-Córdoba M (2020) Determination of cadmium in used engine oil, gasoline and diesel by electrothermal atomic absorption spectrometry using magnetic ionic liquid-based dispersive liquid-liquid microextraction. *Talanta* 220:121395. <https://doi.org/10.1016/j.talanta.2020.121395>
- Alsaleh KA, Meuser H, Usman AR, Al-Wabel MI, Al-Farraj AS (2018) A comparison of two digestion methods for assessing heavy metals level in urban soils influenced by mining and industrial activities. *J Environ Manage* 206:731–739. <https://doi.org/10.1016/j.jenvman.2017.11.026>
- Alvarez MB, Domini CE, Garrido M, Lista AG, Fernández Band BS (2011) Single-step chemical extraction procedures and chemometrics for assessment of heavy metal behaviour in sediment samples from the Bahía Blanca estuary, Argentina. *J Soils Sediments* 11:657–666. <https://doi.org/10.1007/s11368-011-0350-7>
- Alvarez MB, Malla ME, Batistoni DA (2001) Comparative assessment of two sequential chemical extraction schemes for the fractionation of cadmium, chromium, lead and zinc in surface coastal sediments. *Fresenius J Anal Chem* 369:81–90. <https://doi.org/10.1007/s002160000592>
- Álvarez SM, Llamas NE, Lista AG, Álvarez MB, Domini CE (2017) Ionic liquid mediated extraction assisted by ultrasound energy of available/mobilizable metals from sediment samples. *Ultrason Sonochem* 34:239–245. <https://doi.org/10.1016/j.ultsonch.2016.05.044>

- Álvarez-Vázquez MA, Bendicho C, Prego R (2014) Ultrasonic slurry sampling combined with total reflection X-ray spectrometry for multi-elemental analysis of coastal sediments in a ria system. *Microchem J* 112:172–180. <https://doi.org/10.1016/j.microc.2013.09.026>
- Benomar M, Mendiguchía C, Er-Raioui H, Marhraoui M, Lafraoui G, Oulad-Abdellah MK, García-Vargas M, Moreno C (2012) Analysis of heavy metals in sediments from northern Moroccan coast using simple and low-cost methodology. *Open Environ Pollut Toxicol J* 3:47–54. <https://doi.org/10.2174/1876397901203010047>
- Chaban V (2015) Hydrogen fluoride capture by imidazolium acetate ionic liquid. *Chem Phys Lett* 625:110–115. <https://doi.org/10.1016/j.cplett.2015.02.041>
- Chand V, Prasad S (2013) ICP-OES assessment of heavy metal contamination in tropical marine sediments: a comparative study of two digestion techniques. *Microchem J* 111:53–61. <https://doi.org/10.1016/j.microc.2012.11.007>
- Cook JM, Gardner MJ, Griffiths AH, Jessep MA, Ravenscroft JE, Yates R (1997) The comparability of sample digestion techniques for the determination of metals in sediments. *Mar Pollut Bull* 34:637–644. [https://doi.org/10.1016/S0025-326X\(96\)00186-5](https://doi.org/10.1016/S0025-326X(96)00186-5)
- da Silva YJAB, do Nascimento CWA, Biondi CM, (2014) Comparison of USEPA digestion methods to heavy metals in soil samples. *Environ Monit Assess* 186:47–53. <https://doi.org/10.1007/s10661-013-3354-5>
- Fabri-Jr R, Krause M, Dalfior BM, Salles RC, de Freitas AC, da Silva HE, Licinio MVVJ, Carneiro MTW (2018) Trace elements in soil, lichens, and mosses from Fildes Peninsula, Antarctica: spatial distribution and possible origins. *Environ Earth Sci* 77:1–10. <https://doi.org/10.1007/s12665-018-7298-5>
- Fernández E, Vidal L, Iniesta J, Metters JP, Banks CE, Canals A (2014) Screen-printed electrode-based electrochemical detector coupled with in-situ ionic liquid-assisted dispersive liquid–liquid microextraction for determination of 2,4,6-trinitrotoluene. *Anal Bioanal Chem* 406:2197–2204. <https://doi.org/10.1007/s00216-013-7415-y>
- Fernandez-Ortiz de Vallejuelo S, Barrera A, Arana G, de Diego A, Madariaga JM (2009) Ultrasound energy focused in a glass probe: an approach to the simultaneous and fast extraction of trace elements from sediments. *Talanta* 80:434–439. <https://doi.org/10.1016/j.talanta.2009.07.002>
- Filgueiras AV, Capelo JL, Lavilla I, Bendicho C (2000) Comparison of ultrasound-assisted extraction and microwave-assisted digestion for determination of magnesium, manganese and zinc in plant samples by flame atomic absorption spectrometry. *Talanta* 53:433–441. [https://doi.org/10.1016/S0039-9140\(00\)00510-5](https://doi.org/10.1016/S0039-9140(00)00510-5)
- Frena M, Quadros DP, Castilho IN, de Gois JS, Borges DL, Welz B, Madureira LA (2014) A novel extraction-based procedure for the determination of trace elements in estuarine sediment samples by ICP-MS. *Microchem J* 117:1–6. <https://doi.org/10.1016/j.microc.2014.05.014>
- García-Casillas D, García-Salgado S, Quijano MÁ (2014) Accuracy evaluation of ultrasound probe sonication and microwave-assisted extraction systems for rapid single extraction of metals in soils. *Anal Methods* 6:8403–8412. <https://doi.org/10.1039/C4AY01788A>
- Ghosh SP, Maiti SK (2018) Evaluation of heavy metal contamination in roadside deposited sediments and road surface runoff: a case study. *Environ Earth Sci* 77:1–13. <https://doi.org/10.1007/s12665-018-7370-1>
- Güngör H, Elik ADIL (2007) Comparison of ultrasound-assisted leaching with conventional and acid bomb digestion for determination of metals in sediment samples. *Microchem J* 86:65–70. <https://doi.org/10.1016/j.microc.2006.10.006>
- Güven D, Akinci G (2011) Comparison of acid digestion techniques to determine heavy metals in sediment and soil samples. *G U J Sci* 24:29–34
- Hibbert DB (2012) Experimental design in chromatography: a tutorial review. *J Chromatogr B* 910:2–13. <https://doi.org/10.1016/j.jchromb.2012.01.020>
- Hornberger MI, Luoma SN, van Geen A, Fuller C, Anima R (1999) Historical trends of metals in the sediments of San Francisco Bay, California. *Mar Chem* 64:39–55. [https://doi.org/10.1016/S0304-4203\(98\)80083-2](https://doi.org/10.1016/S0304-4203(98)80083-2)
- Ilander A, Väisänen A (2007) An ultrasound-assisted digestion method for the determination of toxic element concentrations in ash samples by inductively coupled plasma optical emission spectrometry. *Anal Chim Acta* 602:195–201. <https://doi.org/10.1016/j.aca.2007.09.015>
- Ilander A, Väisänen A (2009) The determination of trace element concentrations in fly ash samples using ultrasound-assisted digestion followed with inductively coupled plasma optical emission spectrometry. *Ultrason Sonochem* 16:763–768. <https://doi.org/10.1016/j.ultsonch.2009.03.001>
- Islam MA, Das B, Quraishi SB, Khan R, Naher K, Hossain SM, Karmaker S, Latif SA, Hossen MB (2020) Heavy metal contamination and ecological risk assessment in water and sediments of the Halda river, Bangladesh: a natural fish breeding ground. *Mar Pollut Bull* 160:111649. <https://doi.org/10.1016/j.marpolbul.2020.111649>
- ISO (1995) International Standard. ISO 11466:1995. Soil quality — extraction of trace elements soluble in aqua regia
- Janssen CH, Macias-Ruvalcaba NA, Aguilar-Martinez M, Kobrak MN (2015) Metal extraction to ionic liquids: the relationship between structure, mechanism and application. *Int Rev Phys Chem* 34:591–622. <https://doi.org/10.1080/0144235X.2015.1088217>
- Javan S, Hassani AH, Ahangar AG, Soltani J (2015) Fractionation of heavy metals in bottom sediments in Chahnimeh 1, Zabol. *Iran Environ Monit Assess* 187:1–11. <https://doi.org/10.1007/s10661-015-4510-x>
- Jones OAH, Gomes RL (2014) Chemical pollution of the aquatic environment by priority pollutants and its control. In: Harrison RM (ed) *Pollution causes-effects and control*, 5th edn. RSC Publishing, Birmingham, pp 1–28
- Kazi TG, Jamali MK, Arain MB, Afridi HI, Jalbani N, Sarfraz RA, Ansari R (2009) Evaluation of an ultrasonic acid digestion procedure for total heavy metals determination in environmental and biological samples. *J Hazard Mater* 16:1391–1398. <https://doi.org/10.1016/j.jhazmat.2008.04.103>
- Kumkrong P, Mercier PHJ, Gedara IP, Mihai O, Tyo DD, Cindy J, Kingstom DM, Mester Z (2021) Determination of 27 metals in HISS-1, MESS-4 and PACS-3 marine sediment certified reference materials by the BCR sequential extraction. *Talanta* 221:121543. <https://doi.org/10.1016/j.talanta.2020.121543>
- Lo JM, Sakamoto H (2005) Comparison of the acid combinations in microwave-assisted digestion of marine sediments for heavy metal analyses. *Anal Sci* 21:1181–1184. <https://doi.org/10.2116/analsci.21.1181>
- MacDonald DD, Ingersoll CG, Berger TA (2000) Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Arch Environ Contam Toxicol* 39:20–31. <https://doi.org/10.1007/s002440010075>
- Magnusson B, Örnemark U (Eds.) (2014) *Eurachem guide: the fitness for purpose of analytical methods – a laboratory guide to method validation and related topics* (2nd ed. 2014) https://www.eurachem.org/images/stories/Guides/pdf/MV_guide_2nd_ed_EN.pdf. Accessed 24 March 2021
- Maity S, Sahu SK, Pandit GG (2016) Determination of heavy metals and their distribution in different size fractionated sediment samples using different analytical techniques. *Soil Sediment Contam* 25:332–345. <https://doi.org/10.1080/15320383.2016.1137862>
- Massart DL, Vandeginste BGM, Buydens LMC, de Jong S, Lewi PJ, Smeyers-Verbeke J (1997) *Handbook of chemometrics and*

- qualimetrics: part A. Elsevier, Amsterdam <https://www.elsevier.com/books/handbook-of-chemometrics-and-qualimetrics/massart/978-0-444-89724-4>
- Mimura A, Oliveira MA, Ciminelli VS, Silva JC (2016) Optimization of ultrasound-assisted extraction of Cr Cu Zn Cd and Pb from sediment followed by FAAS and GFAAS analysis. *J AOAC Int* 99:252–259. <https://doi.org/10.5740/jaoacint.15-0090>
- Myers RH, Montgomery DC (2002) Response surface methodology. Wiley, New York
- Nario NA, Insausti M, Domini CE, Grünhut M (2019) Free glycerol sensing in biodiesel: automatic system based on sequential enzymatic reactions using a fit-for-purpose chemiluminescence detection chamber. *Energy Fuels* 33:9925–9933. <https://doi.org/10.1021/acs.energyfuels.9b02303>
- Niedzielski P, Kozak L, Wachelka M, Jakubowski K, Wybierska J (2015) The microwave induced plasma with optical emission spectrometry (MIP–OES) in 23 elements determination in geological samples. *Talanta* 132:591–599. <https://doi.org/10.1016/j.talanta.2014.10.009>
- Odika PO, Anike OL, Onwuemesi AG, Odika NF, Ejeckam RB (2020) Assessment of environmental geochemistry of lead-zinc mining at Ishiagu area, lower Benue trough, southeastern Nigeria. *Earth Sci Res* 9:1–31. <https://doi.org/10.5539/esr.v9n1p31>
- Paul SA, Gaye B, Haeckel M, Kasten S, Koschinsky A (2018) Biogeochemical regeneration of a nodule mining disturbance site: trace metals, DOC and amino acids in deep-sea sediments and pore waters. *Front Mar Sci* 5:117. <https://doi.org/10.3389/fmars.2018.00117>
- Pribylova G (2011) Influence of ionic liquids on actinides extraction by diphenyl (dibutyl) carbamoylmethylphosphine oxide in different solvents from nitric acid solution. *J Radioanal Nucl Chem* 288:693–697. <https://doi.org/10.1007/s10967-011-1014-1>
- Rajadurai V, Anguraj BL (2020) Ionic liquids to remove toxic metal pollution. *Environ Chem Lett* 19:1173–1203. <https://doi.org/10.1007/s10311-020-01115-5>
- Rajeshkumar S, Liu Y, Zhang X, Ravikumar B, Bai G, Li X (2018) Studies on seasonal pollution of heavy metals in water, sediment, fish and oyster from the Meiliang Bay of Taihu Lake in China. *Chemosphere* 191:626–638. <https://doi.org/10.1016/j.chemosphere.2017.10.078>
- Rao, RM, Sahuquillo A, Sanchez JL (2008) A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials. *Water Air Soil Pollut* 189:291–333. <https://doi.org/10.1007/s11270-007-9564-0>
- Sakan S, Dordevic D, Devic G, Relic D, Anđelkovic I, Duricic J (2011) A study of trace element contamination in river sediments in Serbia using microwave assisted aqua regia digestion and multivariate statistical analysis. *Microchem J* 99:492–502. <https://doi.org/10.1016/j.microc.2011.06.027>
- Sastre J, Sahuquillo A, Vidal M, Rauret G (2002) Determination of Cd, Cu, Pb and Zn in environmental samples: microwave-assisted total digestion versus aqua regia and nitric acid extraction. *Anal Chim Acta* 462:59–72. [https://doi.org/10.1016/S0003-2670\(02\)00307-0](https://doi.org/10.1016/S0003-2670(02)00307-0)
- Stojanovic A, Keppler BK (2012) Ionic liquids as extracting agents for heavy metals. *Sep Sci Technol* 47:189–203. <https://doi.org/10.1080/01496395.2011.620587>
- Swatloski RP, Holbrey JD, Rogers RD (2003) Ionic liquids are not always green: hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate. *Green Chem* 5:361–363. <https://doi.org/10.1039/b304400a>
- Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ (2012) Heavy metal toxicity and the environment. In: Luch A (ed) *Molecular, Clinical and Environmental Toxicology*, vol 3. Environmental Toxicology. Springer, Basel, pp 133–164
- Thompson M (2012) Precision in chemical analysis: a critical survey of uses and abuses. *Anal Methods* 4:1598–1611. <https://doi.org/10.1039/C2AY25083G>
- USEPA (1996a) United States Environmental Protection Agency. Method 3050B acid digestion of sediments, sludges, and soils 1.0 scope and application. Washington, DC, USA, Revision 2. <https://www.epa.gov/sites/production/files/2015-06/documents/epa-3050b.pdf>. Accessed 28 December 2020
- USEPA (1996b) United States Environmental Protection Agency. Method 3052 microwave assisted acid digestion of siliceous and organically based matrices. Revision 0. <https://www.epa.gov/sites/production/files/2015-12/documents/3052.pdf>. Accessed 28 December 2020
- USEPA (2007) United States Environmental Protection Agency. Method 3051A—microwave assisted acid digestion of sediments, sludges, soils and oils; United States Environmental Protection Agency: Washington, DC, USA, Revision 1. <https://www.epa.gov/sites/production/files/2015-12/documents/3051a.pdf>. Accessed 28 December 2020
- USEPA (2014) United States Environmental Protection Agency. Appendix A to part 423–126 priority pollutants. <https://www.epa.gov/sites/production/files/2015-09/documents/priority-pollutant-list-epa.pdf>. Accessed 04 January 2021
- Wang H, Ding J, Ren N (2016) Recent advances in microwave-assisted extraction of trace organic pollutants from food and environmental samples. *Trends Anal Chem* 75:197–208. <https://doi.org/10.1016/j.trac.2015.05.005>
- Zimmermann T, von der Au M, Reese A, Klein O, Hildebrandt L, Pröfrock D (2020) Substituting HF by –an optimized digestion method for multi-elemental sediment analysis via ICP-MS/MS. *Anal Methods* 12:3778–3787. <https://doi.org/10.1039/D0AY01049A>

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