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Ultrasound and microwave-assisted extraction of metals from sediment: a comparison with the BCR procedure

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Abstract

In this paper we investigate alternatives to mechanical stirring for the extraction of the mobile fraction of metals from sediment, and analyze whether these techniques can reduce extraction time and improve reproducibility. We compare the quantities of metal extracted from BCR601 and BCR701 certified sediments using ultrasound bath, microwave-assisted extraction and the first step in the certified BCR sequential extraction procedure. Some environmentally important not-certified metals such as As, Mn, Co, Fe and Al have been included in this study. In the case of microwave-assisted extraction, we compare tests in which samples are exposed to constant, low power irradiation with tests using pulsed high power.

In the tests using the ultrasound bath, less metal was extracted than with the other extractive techniques and standard deviations were comparable to those obtained with the BCR procedure; in assays using microwaves at constant power, extraction efficiencies were different for different metals and for different reference materials and, in some cases, standard deviations were higher than those for the reference method. In contrast, tests with microwaves and constant temperature produced encouraging results: R.S.D.s lay in the 2–4% range, both for certified and not-certified metals; these values are very low compared to those for the reference method. Extraction efficiencies for certified metals were close to 100% for Cd, Zn, Cu and Ni and around 80% for Pb and Cr.

Keywords: Sequential extraction; Soils and sediments; Leachable metals; Ultrasounds; Microwave

1. Introduction

Scientific interest in the application of sequential extraction to geochemistry has been growing, ever since 1963, when LeRiche and Weir [1] first used the technique to separate chemically bound elements in soil. Since then, researchers have proposed different solvent sequences for the characterization of a broad range of solid environmental matrices. In 1979, Tessier et al. [2] rationalized this work, proposing an extraction protocol that remains a benchmark for the field.

Subsequent work led to the development of alternative extraction procedures [3,4]. These procedures modified specific aspects of Tessier's original protocol, such as the solid/solution ratio, treatment time and washing procedures between steps, attempting in this way to solve problems with specific matrices and to address some of the broader issues with sequential extraction. By now however, it is clear that none of these procedures guarantees solvent selectivity. Furthermore, the lack of standardized procedures means that it is impossible to compare results obtained under different conditions.

Over the years, poor solvent selectivity and difficulties in comparing data from different assays led researchers to abandon sequential extraction. This trend was reversed only when the BCR (the Community Bureau of Reference – now the European Union "Measurement and Testing Programme") initiated a major effort to harmonize extraction procedures. This work led to the definition of an extraction protocol (the BCR protocol) and a purely operational definition of sequential

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fractionation, in which the analytical significance of assay results was tied to the use of specific extraction procedures [3,5,6]. The procedures defined by the BCR protocol are, however, extremely time-consuming and several of the variables which influence extraction efficiency, such as shaking speed and illumination, cannot be defined without ambiguity. The result is poor reproducibility, if not at the intra-laboratory, at least at the inter-laboratory level.

Another result of this harmonization work has been the commercialization of certified materials such as the BCR601 sediment [7], which has been certified for the extraction of Cd, Cr, Ni, Pb and Zn. BCR601 was later replaced by BCR701 [8,9], which included Cu on the list of certified metals.

Certification has only been possible for a limited number of metals where it has been possible to achieve an acceptable level of intra- and inter-laboratory reproducibility. With other environmentally important metals such as As, Mn, Co, Fe, Al, data from assays is highly variable, preventing certification.

In this paper, we investigate alternatives to extraction with mechanical shaking in an end-over-end shaker, showing how these can reduce the time required for assays and improve their reproducibility.

A number of authors have achieved encouraging results, using ultrasound probes to reduce the time required for sequential extraction of metals from sediment [10,11]. The study just cited used Tessier's procedure [2] to achieve sequential extraction of Cu, Cr, Ni, Zn and Pb from non-certified materials. It is well known that exposure of solids to ultrasound leads to structural changes in their surface morphology [12]. The impact of the ultrasound jet and its associated shock wave erodes the solid, leading to localized fragmentation of particles [13–16]. This has predictable consequences on the availability of metals. As a result, while the percentage of materials extracted was comparable to what can be achieved with mechanical shaking, the time required (roughly 10 min per step) was much shorter.

Ultrasound baths are less expensive than probes. We therefore decided to compare the quantities of metal that can be extracted using a bath with the quantities produced by the certified BCR sequential extraction procedure. The test was carried out using a sediment certified for sequential extraction.

An alternative technique for accelerating the extraction of metals from sediment is to use microwave ovens. Despite a number of incongruities, recent studies have produced encouraging results in terms of reproducibility and in terms of the time required for the procedure. The literature reports a number of investigations using Tessier's extraction procedure and a range of different reference materials, none of which were certified for sequential extraction. One study [17] has observed differences between the extraction efficiency achieved with microwaves and that of the conventional Tessier procedure. In the fraction bound to carbonates, for example, extraction efficiencies were 10 times higher for Pb, four times higher for Cr, and 2,5 times higher for Fe. The extraction efficiency for Mn, on the other hand, was only half the efficiency of the conventional method. Later investigations [18,19] showed, again for the carbonate fraction, that microwaves lead to reabsorbtion of Ca and Fe, a phenomenon which had not been observed previously. Finally, these studies used a number of different sediments and microwave techniques making it impossible to compare the results. None of these studies considered the effects of temperature, which are very different when microwaves are used instead of mechanical shaking. In microwave irradiation, the efficiency of heating and shaking within the sample are determined by the rotation of the dipole and on ionic conduction, which depend in turn on the viscosity of the medium. At high temperatures, the contribution of dipole rotation decreases while ionic conduction becomes more and more important. During microwave heating of a solution containing ions, dissipation is initially controlled by dipole rotation and later, as the temperature increases, by ionic conduction, which depends closely on the way in which the microwaves are delivered to the sample. We therefore decided to make a systematic study of different techniques for the application of microwaves, by comparing tests in which samples are exposed to constant, low power irradiation with tests using pulsed high power, taking account of the temperature variable and using materials certified for sequential extraction of metals. Given that the largest differences between techniques are those affecting the fraction bound to carbonates (which is also the fraction with the greatest environmental significance), we decided, that we would focus on the first step in the BCR reference procedure.

2. Experimental

2.1. Extraction via the BCR procedure

Before extraction 1 g of certified BCR601 was precisely weighed in a weighing bottle. The sediment was placed in an oven (105 ± 2 °C) until constant weight. This treatment produced a 3.60% loss of weight. Repeating the same operation with BCR701, produced a 2.79% loss of weight. All subsequent measurements were corrected to take account of this loss.

Exactly 0.25 g of certified material (BCR601 or BCR701) were placed in an Erlenmeyer Flask with an emery stopper to which we added 8.5 ml of 0.11 M acetic acid. While the quantity of sediment was lower than in the certified procedure, the ratio of sediment to the volume of extraction solution was the same. In preliminary tests, obstructions in the inductively coupled plasma (ICP) nebulization system made it necessary to replace the centrifuging, required by the BCR protocol, with filtration. Filtration was based on a cellulose nitrate, Whatman millipore filtering system with 0.45 μm pores. Residues were recovered and washed in 2 ml of 0.11 M acetic acid.

The procedure was repeated six times for each certified sediment. Each test used deionized, ultrapure water.

Each time the acetic acid was prepared, the metal content of the extraction solution was measured using the same procedure applied to the samples. Each measurement was repeated three times. In all cases and for all metals the volumes of metal observed in these measurements were stable, and were always less than 5% of those observed for the samples. This value was subtracted from the results.

2.2. *Extraction with ultrasound*

Samples were prepared as described above. They were then placed in an ultrasound bath (28/34 kHz, 80/180 W) for between 15 and 60 min. Immersions longer than 60 min were not investigated, given that they would offer little advantage over mechanical shaking. A Taylor-made rotating plate guaranteed uniform exposure to the ultrasound.

Samples were taken out of the bath three at a time, after different lengths of immersion, filtered using the techniques described earlier and analyzed with ICP-OES.

2.3. *Extraction with microwaves*

Samples were prepared using the procedure described earlier, and placed in the Teflon containers of the microwave oven (Milestone Ethos Touch Control, HPR 1000/6S rotor). Tests were conducted for variable lengths of exposure using both constant, low power irradiation with variable temperature and constant temperature with pulsed high power. Each test was repeated three times.

2.3.1. *Tests with constant power*

In order to obtain a constant and continuous microwave emission, the temperature control of the microwave oven was switched off. As a consequence the sample temperature gradually rises up to values related to the emitting power and to the treatment period. All tests used two step digestion programs. In the first step the emitted power rises linearly from 0 to the maximum fixed value; in the second one this maximum value was kept constant for prefixed time periods. The fist step time period was set to maintain the same slope $\Delta W/\Delta t = 50\ \mathrm{W\,min^{-1}}$. Power ranges and irradiation time periods of the second step were investigated to avoid both too soft conditions resulting in poor recovery extractions and too limit conditions leading to unacceptable sample stress. Table 1 shows the maximum temperatures, which were reached during the studied digestion period.

2.3.2. *Tests with constant temperature*

These tests have been performed at controlled temperature and power was pulsed automatically by the oven to maintain temperature at a constant value. Even in this case two step digestion programs were adopted: the fist step was performed with a programmed temperature curve at $\Delta T/\Delta t = 30\ ^{\circ}\mathrm{C\,min^{-1}}$ up to the maximum temperature; the second step was performed at a constant fixed temperature for prefixed time periods. All these tests used BCR701.

Table 1
Maximum temperatures reached by samples at the end of digestion period as function of power emission and time settings in the second digestion step

Power (W)	MW application time (min)						
	5	8	10	15	30	60	120
20	–	–	–	–	29	32	–
30	–	–	–	–	43	49	–
50	36	38	41	49	68	73	76
70	49	60	63	68	72	78[a]	88
100	52	60	65	98	100	109	125
130	87	90	100	103[b]	115[b]	–	–
200	96[b]	104[b]	111[b]	115[b]	–	–	–

[a] Tests performed with certified material BCR 701.

[b] Test performed with certified materials BCR 701 and BCR 601. All remaining tests were performed with certified material BCR.

2.4. *ICP-OES analysis*

ICP-OES analysis was carried out using VARIAN VISTA MPX CCD Simultaneous ICP-OES with a CETAC U-5000 ultrasound nebulizer. In Table 2 are described the analysis conditions. The lowest quantitation limits (LOQ – error ≤5%) were reported for each metal. The instrument was calibrated using standard solutions in an acetic buffer. To control for spectral interference, the analysis was repeated at two dif-

Table 2
ICP-OES conditions for analysis

ICP–OES instrumental parameters	
Incident plasma power (RF) (kW)	1.00
Plasma gas flow ($\mathrm{L\,min^{-1}}$)	15.0
Auxiliary gas flow ($\mathrm{L\,min^{-1}}$)	1.50
Nebulizer pressure (kPa)	200
Replicate read time (s)	20
Instrument stabilization delay (s)	15
Sample uptake delay (s)	15
Pump rate (rpm)	15
Rinse time (s)	15
Replicates	3

Element	Reading wavelength (nm)	Check wavelength (nm)	LOQ ($\mu\mathrm{g\,L^{-1}}$)
Detection parameters and LOQs (RSD ≤ 5%)			
Al	396.152	308.215	15
As	188.980	193.696	15
Cd	214.439	226.502	0.8
Cr	267.716	284.984	0.8
Co	230.786	238.892	1
Cu	327.395	324.754	1.5
Fe	238.204	259.940	0.15
Mg	279.553	280.270	0.1
Mn	257.610	260.568	0.3
Na	588.995	589.592	0.2
Ni	231.604	227.021	3
Pb	220.353	405.781	5
Si	251.611	288.158	40
Zn	206.200	213.857	1.5

ferent wavelengths. It was shown that the differences were never in excess of 3%. Results at the two wavelengths were averaged.

3. Results and discussion

3.1. The BCR extraction procedure

Prior to the systematic investigation of alternative procedures, we applied the BCR certified extraction procedure to the BCR601 and BCR701 reference samples, measuring the presence of certified metals and of other environmentally significant metals which have not been certified, due to the high variability in the concentrations observed by different laboratories participating in the certification process.

The results of the tests, which were repeated six times, are described in Table 3. Although there are some differences, in general the observed values closely matched the certified values [7–9] and are fully comparable to those obtained by the laboratories, which have taken part to the certification program. The only exception is for Cr, where the observed values were much higher than the certified value, with a very high standard deviation. Careful checks of measurement conditions and of blanks appear to exclude errors during the analysis. In addition the values expressed as total chrome (obtained by direct aqua regia digestion as indicated by BCR protocol) in the two certified materials are in very good agreement with the certified values. The discrepancy is only due to distribution of the metal among the different soluble fraction. It is then possible that the results obtained were due to deterioration of the reference materials during storage or transport.

Table 3 shows the values obtained for uncertified and for certified metals. The values of uncertified metals were used as reference values for the calculation of the percentages of metal recovered by ultrasound and with microwaves.

Table 3
Concentrations obtained with the application of the BCR protocol

	BCR 601		BCR 701	
	Our lab (mg kg^{-1})	Certified (mg kg^{-1})	Our lab (mg kg^{-1})	Certified (mg kg^{-1})
Cd	3.9 ± 0.1	4.1 ± 0.2	7 ± 1	7.3 ± 0.3
Cr	0.7 ± 0.3	0.36 ± 0.04	3.2 ± 0.5	2.3 ± 0.2
Ni	9 ± 1	8 ± 1	17 ± 1	15 ± 1
Pb	2.2 ± 0.1	2.7 ± 0.3	3.5 ± 0.2	3.2 ± 0.2
Zn	232 ± 4	263 ± 5	208 ± 16	205 ± 6
Cu	10 ± 1	–	53 ± 4	49 ± 2
Al	72 ± 4	–	238 ± 37	–
As	2.0 ± 0.1	–	2.1 ± 0.1	–
Co	2.7 ± 0.1	–	2.6 ± 0.1	–
Fe	121 ± 36	–	193 ± 60	–
Mg	1530 ± 20	–	808 ± 39	–
Mn	271 ± 5	–	198 ± 15	–

Table 4
Recovery percentages with ultrasounds as a function of sonication time

	Sonication times					
	5 min	8 min	10 min	20 min	30 min	60 min
Cd	69 ± 3	70 ± 3	72 ± 4	74 ± 6	74 ± 5	74 ± 4
Cr	23 ± 2	25 ± 3	25 ± 4	34 ± 5	38 ± 6	38 ± 2
Ni	53 ± 3	55 ± 3	54 ± 4	63 ± 5	67 ± 6	67 ± 8
Pb	48 ± 1	50 ± 7	50 ± 5	47 ± 6	58 ± 3	54 ± 4
Zn	51 ± 1	53 ± 7	53 ± 5	50 ± 6	62 ± 3	58 ± 4
Cu[a]	49 ± 3	50 ± 4	49 ± 6	60 ± 5	62 ± 6	60 ± 1
Al[a]	38 ± 3	41 ± 5	43 ± 7	48 ± 8	53 ± 8	48 ± 0
As[a]	37 ± 9	44 ± 12	49 ± 7	56 ± 8	61 ± 8	65 ± 3
Co[a]	46 ± 2	48 ± 2	48 ± 3	55 ± 3	60 ± 6	60 ± 6
Fe[a]	16 ± 1	17 ± 2	16 ± 2	20 ± 4	24 ± 6	24 ± 7
Mg[a]	61 ± 2	62 ± 2	62 ± 2	73 ± 4	78 ± 6	76 ± 7
Mn[a]	71 ± 2	72 ± 2	71 ± 2	79 ± 4	79 ± 7	79 ± 4

Tests performed with certified material BCR. Values of uncertified elements are referred to application of BCR protocol in our laboratory.

[a] Uncertified metals.

3.2. Extraction with ultrasound

Table 4 shows the results for extraction with ultrasound. For all metals the percentage of metal extracted was significantly below 100%. Values peaked after 20–30 min, remaining constant for longer periods of immersion. Generally, the results were less reproducible than those obtained with mechanical shaking.

3.3. Extraction with microwaves

3.3.1. Tests with constant power

In these tests, we investigated a range of different experimental conditions, comparing extraction efficiencies and standard deviations with those obtained by our laboratory using the BCR procedure (Table 5). The results showed that experimental parameters have a strong effect on the percentage of metal recovered, presumably because of differences in temperatures during treatment. In the set-up used for the tests, increases in the duration of the procedure or in power both lead to higher sample temperatures (see Table 1). This means that it is not possible to control this variable independently.

Except for Pb, Al and Cu, where it is possible to achieve efficient extraction, even with very mild temperatures, metals cannot be extracted effectively with less than 50 W power. Presumably, this does not produce enough molecular rotation to guarantee effective shaking. More than 50 W power for more than 15 min produces results close to those obtained with the BCR procedure: for most metals, the percentages of metal extracted were close to 100% and standard deviations were comparable to those for the BCR procedure. The only exceptions were Fe and Al, for which extraction efficiencies were low.

With some metals treatment for prolonged periods with high power led to a reduction in the percentage of metal extracted. This was especially true for Cu and to a lesser extent for Ni and Al. Other authors [18,19] have made similar

Table 5
Recovery percentages with microwave at constant power as function of power and erogation time periods set in the second digestion step

W	Time (min)						
	5	8	10	15	30	60	120
(a) Certified metals							
Cd							
20					51 ± 1	53 ± 1	
30				58 ± 4	62 ± 2		
50	69 ± 3	69 ± 1	79 ± 7	67 ± 1	69 ± 1	85 ± 7	81 ± 3
70	63 ± 1	77 ± 1	66 ± 2	76 ± 4	73 ± 2	85 ± 4	83 ± 2
100	65 ± 2	71 ± 2	66.1 ± 0.3	71 ± 1	68 ± 4	78 ± 5	70 ± 2
130	70 ± 2	64 ± 1	70 ± 2	106 ± 1	98 ± 8		
200	96 ± 2	93 ± 4	97 ± 2	92 ± 2			
Cr							
20					47.4 ± 0.3	48 ± 1	
30					50 ± 4	55 ± 5	
50	10 ± 2	57 ± 3	61 ± 1	59 ± 2	65 ± 1	64 ± 7	60 ± 2
70	58 ± 1	63 ± 1	59 ± 1	68 ± 3	67 ± 3	65 ± 3	63 ± 5
100	57 ± 3	56 ± 2	63 ± 5	65 ± 2	66 ± 5	58 ± 5	65 ± 6
130	55 ± 3	55 ± 3	59 ± 5	61 ± 2	88 ± 6		
200	49 ± 1	59 ± 3	75 ± 4	96 ± 6			
Ni							
20					22 ± 1	29 ± 1	
30					36 ± 4	45 ± 3	
50	30 ± 1	37 ± 2	40 ± 1	47 ± 2	61 ± 3	86 ± 9	94 ± 3
70	38 ± 1	67 ± 3	55 ± 5	63 ± 1	72 ± 5	101 ± 8	100 ± 8
100	40 ± 2	60 ± 1	57 ± 4	68 ± 7	65 ± 1	77 ± 5	60 ± 6
130	55 ± 4	98 ± 2	98 ± 3	111 ± 4	102 ± 7		
200	102 ± 2	102 ± 3	102 ± 4	102 ± 7			
Pb							
20					91 ± 7	77 ± 3	
30					83 ± 5	83 ± 6	
50	71 ± 4	73 ± 7	76 ± 4	63 ± 4	69 ± 1	93 ± 9	89 ± 8
70	57 ± 3	60 ± 3	60 ± 3	67 ± 9	64 ± 5	89 ± 3	98 ± 8
100	81 ± 4	70 ± 7	77 ± 4	76 ± 13	71 ± 7	80 ± 6	62 ± 8
130	66 ± 3	82 ± 7	62 ± 4	98 ± 5	77 ± 10		
200	87 ± 4	88 ± 11	88 ± 7	63 ± 8			
Zn							
20					38 ± 2	42 ± 4	
30					46.1 ± 0.1	51 ± 1	
50	56 ± 2	59 ± 1	61.1 ± 0.2	58 ± 2	60 ± 2	76 ± 6	70 ± 1
70	55.0 ± 0.4	69 ± 1	58 ± 2	67 ± 4	63 ± 1	72 ± 3	63 ± 1
100	54 ± 3	63 ± 2	57 ± 3	60 ± 2	57 ± 5	59 ± 3	48 ± 2
130	60 ± 3	54 ± 1	66 ± 5	100 ± 3	87 ± 10		
200	90 ± 2	86 ± 2	90 ± 1	83 ± 6			
Cu[a]							
20					79 ± 1	84 ± 2	
30					89 ± 7	98 ± 2	
50	92 ± 9	103 ± 9	106 ± 10	105 ± 9	101 ± 4	105 ± 8	92 ± 7
70	98.2 ± 0.1	107 ± 9	92 ± 3	98 ± 3	79 ± 2	81 ± 8	31 ± 5
100	107 ± 9	96 ± 2	107 ± 2	77 ± 7	50 ± 4	21 ± 7	6.9 ± 0.4
130	104 ± 3	61 ± 9	82 ± 3	60 ± 3	11 ± 10		
200	60 ± 6	31 ± 3	60 ± 8	4 ± 3			
(b) Uncertified metals							
Al							
20					71 ± 2	67 ± 4	
30					65 ± 6.2	61 ± 4	
50	67 ± 6	64 ± 3	66 ± 1	50 ± 1	40 ± 1	64 ± 3	73 ± 4
70	55 ± 1	59 ± 2	42 ± 1	49 ± 2	39 ± 2	45 ± 1	44 ± 2
100	40 ± 5	47 ± 2	34 ± 2	36 ± 1	34 ± 2	50 ± 1	60 ± 0
130	50 ± 3	33 ± 2	42 ± 3	45 ± 1	46 ± 3		
200	36 ± 2	34 ± 1	38 ± 2	54 ± 5			

Table 5 (*Continued*)

W	Time (min)						
	5	8	10	15	30	60	120
As							
20					45 ± 8	45 ± 6	
30					57 ± 3	70 ± 4	
50	58 ± 6	66 ± 5	74 ± 2	74 ± 8	89 ± 4	151 ± 5	165 ± 7
70	62 ± 4	98 ± 5	82 ± 4	99 ± 2	115 ± 4	165 ± 7	181 ± 6
100	75 ± 5	94 ± 8	97 ± 5	107 ± 6	136 ± 2	184 ± 9	195 ± 2
130	91 ± 3	112 ± 6	111 ± 3	175 ± 7	227 ± 10		
200	148 ± 4	190 ± 8	219 ± 8	242 ± 10			
Co							
20					28 ± 2	31.5 ± 0.4	
30					39 ± 3	46 ± 1	
50	45 ± 1	49 ± 1	52 ± 1	54 ± 1	66 ± 1	101 ± 5	115 ± 4
70	46 ± 1	50 ± 1	58 ± 2	73 ± 4	88 ± 1	113 ± 4	124 ± 2
100	49 ± 2	59 ± 4	66 ± 1	81 ± 1	93 ± 1	112 ± 5	95 ± 5
130	66 ± 1	76 ± 2	82 ± 2	113 ± 1	120 ± 7		
200	95 ± 4	99 ± 4	115 ± 2	117 ± 2			
Fe							
20					22 ± 2	22 ± 1	
30					21 ± 2	25 ± 2	
50	22 ± 1	24.3 ± 0.4	25 ± 2	21 ± 1	27 ± 1	59 ± 3	64 ± 3
70	20.3 ± 0.1	33 ± 1	24 ± 1	31 ± 2	36 ± 1	29 ± 8	33 ± 1
100	22.2 ± 0.4	32 ± 4	31 ± 1	38 ± 1	40 ± 1	25 ± 9	39 ± 2
130	31 ± 4	41 ± 8	41 ± 3	95 ± 8	126 ± 10		
200	79 ± 4	103 ± 7	140 ± 10	201 ± 24			
Mg							
20					36 ± 1	38 ± 1	
30					40 ± 2	44 ± 2	
50	46 ± 1	48.1 ± 0.2	50.8 ± 0.4	50 ± 1	56 ± 1	77 ± 4	81 ± 2
70	45.7 ± 0.4	63 ± 3	51 ± 2	59 ± 1	61 ± 2	79 ± 2	86 ± 1
100	45 ± 1	57 ± 1	50 ± 1	56 ± 1	57 ± 3	74 ± 2	76 ± 1
130	54 ± 1	52 ± 1	61 ± 1	97 ± 1	100 ± 2		
200	85 ± 1	88 ± 2	96 ± 1	98 ± 4			
Mn							
20					47 ± 1	50 ± 1	
30					59 ± 3	64 ± 2	
50	70 ± 1	73 ± 1	75.9 ± 0.5	71 ± 1	79 ± 1	94 ± 8	100 ± 2
70	67 ± 1	88 ± 1	74 ± 2	86 ± 2	93 ± 1	109 ± 3	117 ± 3
100	69 ± 2	85 ± 2	79 ± 1	89 ± 2	95 ± 1	115 ± 4	114 ± 3
130	82 ± 3	87 ± 2	91 ± 1	112 ± 2	119 ± 3		
200	103 ± 2	106 ± 4	116 ± 2	121 ± 6			

[a] Certified metals.

observations for Ca and Fe, noting that with these metals, microwaves produce a reabsorbtion effect.

Readers should note that data shown in italics was obtained using BCR701 rather than BCR601. For most metals, extraction efficiencies were similar for both reference materials. However, in some cases, such as Fe and Cu, there were significant differences. These were probably due to differences in the way the composition of the materials affected reactivity under the test conditions.

It was not possible to identify a single set of conditions optimal for all metals but, in nearly all cases, 70 W of power for 60 min produced acceptable results. It was these conditions that were used for later comparisons.

3.3.2. *Test with constant temperature*

In these tests, we investigated the effects of temperature and length of exposure. In initial trials, we used a maximum power of 250 W. However, this did not allow immediate establishment of the desired temperature profile. In subsequent tests, maximum power was set to 500 W. As in the tests reported earlier, the percentages of metal extracted were compared with those from the BCR procedure. Table 6 shows that the results for Mn, Mg, Cd, Zn, Ni and Pb, were relatively insensitive to changes in the experimental conditions. For these metals, it was possible to identify plateau conditions under which the percentages of metal extracted were very close to 100%.

Table 6
Recovery percentages with microwave at constant temperature as function of teperature and erogation time periods set in the second digestion step

T (°C)	Time (min)					
	5	8	10	15	30	60
(a) Certified metals						
Cd						
50	84 ± 3	93 ± 2	87 ± 2	97.2 ± 0.4	99 ± 3	104 ± 6
60	99 ± 2	94 ± 3	96 ± 1	100 ± 1	104 ± 3	107 ± 1
70	103 ± 2	98 ± 1	105 ± 2	102 ± 2	92 ± 3	99 ± 1
90	99 ± 9	103 ± 1	98 ± 8	102 ± 2		
Cr						
50	35 ± 2	38 ± 1	40 ± 2	44 ± 1	46 ± 2	56 ± 3
60	42 ± 1	41 ± 1	45 ± 2	50 ± 1	55 ± 7	60 ± 4
70	47 ± 4	42 ± 1	57 ± 2	53 ± 1	54 ± 2	53 ± 1
90	53 ± 5	65 ± 3	68 ± 6	78 ± 5		
Ni						
50	74 ± 2	80 ± 1	82 ± 3	90 ± 1	93 ± 3	106 ± 7
60	95 ± 2	89 ± 2	96 ± 3	102 ± 3	110 ± 5	116 ± 6
70	103 ± 3	95 ± 3	116 ± 3	110 ± 3	106 ± 5	112 ± 2
90	106 ± 9	117 ± 3	113 ± 8	121 ± 2		
Pb						
50	70 ± 5	80 ± 5	71 ± 3	97 ± 2	91 ± 6	110 ± 6
60	99 ± 7	91 ± 7	71 ± 6	100 ± 8	109 ± 6	112 ± 6
70	87 ± 8	103 ± 7	96 ± 4	99 ± 3	94 ± 8	96 ± 4
90	100 ± 9	74 ± 1	85 ± 1	81 ± 10		
Zn						
50	82 ± 3	88 ± 3	72 ± 2	90 ± 2	92 ± 3	98 ± 6
60	91 ± 2	87 ± 2	88 ± 1	93 ± 1	97 ± 4	101 ± 1
70	96 ± 3	90 ± 2	100 ± 2	96 ± 1	88 ± 3	93 ± 1
90	88 ± 7	93 ± 2	87 ± 6	93 ± 3		
Cu						
50	72 ± 3	75 ± 1	78 ± 3	82 ± 2	86 ± 4	92 ± 6
60	82 ± 1	78 ± 1	81 ± 1	86 ± 2	89 ± 4	95 ± 1
70	86 ± 4	80 ± 2	88 ± 3	87 ± 2	78 ± 4	85 ± 1
90	62 ± 4	54 ± 2	38 ± 7	36 ± 8		
(b) Uncertified metals						
Al						
50	41 ± 3	39 ± 2	46 ± 4	42 ± 1	43 ± 2	42 ± 3
60	36 ± 1	35 ± 2	36 ± 1	37 ± 1	40 ± 2	43 ± 2
70	35 ± 3	38 ± 2	53 ± 2	42 ± 2	39 ± 3	42 ± 1
90	30 ± 2	43 ± 1	31 ± 5	47 ± 8		
As						
50	74 ± 3	68 ± 6	83 ± 6	85 ± 6	90 ± 5	105 ± 4
60	96 ± 8	90 ± 5	100 ± 5	100 ± 8	117 ± 7	129 ± 9
70	103 ± 8	98 ± 1	123 ± 1	123 ± 3	138 ± 7	129 ± 2
90	168 ± 10	179 ± 11	183 ± 11	183 ± 5		
Co						
50	62 ± 3	68 ± 1	71 ± 2	76 ± 1	80 ± 4	94 ± 7
60	84 ± 2	77 ± 1	84 ± 2	91 ± 4	99 ± 9	107 ± 9
70	101 ± 3	92 ± 2	119 ± 3	113 ± 4	101 ± 6	101 ± 1
90	100 ± 8	113 ± 3	111 ± 10	122 ± 1		
Fe						
50	22 ± 1	28 ± 1	29 ± 2	36 ± 1	39 ± 3	57 ± 5
60	46 ± 5	39 ± 3	49 ± 3	55 ± 3	68 ± 14	61 ± 6
70	50 ± 2	43 ± 6	72 ± 4	66 ± 3	80 ± 4	73 ± 5
90	94 ± 9	115 ± 6	117 ± 9	134 ± 6		
Mg						
50	76 ± 4	81 ± 1	84 ± 2	88.1 ± 0.4	91 ± 3	100 ± 4
60	86 ± 3	83 ± 2	88 ± 2	94 ± 1	98 ± 3	102 ± 3
70	90 ± 5	84 ± 2	97 ± 2	93 ± 2	91 ± 2	92 ± 2
90	89 ± 7	99 ± 2	95 ± 8	102 ± 1		
Mn						
50	81 ± 3	86 ± 1	85 ± 2	89 ± 1	92 ± 3	99 ± 5
60	94 ± 2	89 ± 1	92 ± 3	96 ± 2	100 ± 4	104 ± 3
70	102 ± 2	97 ± 2	107 ± 3	105 ± 3	96 ± 4	99 ± 1
90	100 ± 8	109 ± 3	106 ± 9	111 ± 2		

With Co, Fe and As, extraction efficiency was tightly dependent on the test conditions. The application of high temperatures for prolonged periods gave values in excess of 100%. For Al and Cr, on the other hand, extraction efficiencies were very low. In the case of Cu, tests at high temperatures led to reabsorbtion (as already observed during the tests with constant power). At 60 and 70 °C, on the other hand, it was possible to extract about 80% of metal.

For all metals, standard deviations were significantly lower than those for the other procedures discussed.

As with the tests at constant power, it was not possible to identify a single set of test conditions, optimal for all metals. A good compromise was to use $T = 70\,^{\circ}\mathrm{C}$ and $t = 10$ min. Under these conditions, it was possible to achieve close to 100% extraction and/or plateau extraction values for the majority of metals.

The use of constant temperatures made it possible to separate the effects of time and temperature on dissolution. In this way we were able to obtain information on the solubilization of the metals under investigation.

An analysis of extraction efficiency as a function of temperature and time shows that for some metals (Al, and Zn), extraction efficiency was nearly constant over the range of values used in the tests. We hypothesize that in these cases equilibrium was achieved rapidly and that enthalpic effects were small.

For all other metals extraction efficiency increased to a plateau. The higher the temperature the less time was required to reach the plateau. This behavior is typical of processes with slow kinetics, where reactions become faster with increases in temperature.

For some metals (Ni, Cd, Mg and Mn) the percentage of metal recovered increased over time until it reached a plateau. This behavior was nearly independent of temperature. This suggests that temperature had little effect on the equilibrium state and that the enthalpic contribution was small.

In some cases (Pb, As and Co), the plateau for extraction efficiency varied with temperature. It was observed that in the case of As, extraction became significantly more efficient at higher temperatures. This suggests endothermic behavior. Similar, though weaker effects were observed for Co. With Pb, on the other hand, maximum extraction efficiencies fell with increasing temperature – suggesting that the dissolution process is exothermic.

The results for Cu and Fe are particularly interesting. Here, the results at 90 °C were very different from those at other temperatures. At temperatures below 70 °C results were similar to those for other metals. At 90 °C, however, they were very different, suggesting differences in the underlying processes.

In the case of Fe, we observed a significant increase in the quantity of dissolved metal, while with Cu, the efficiency of the extraction process was significantly lower. This was probably due to reabsorbtion or precipitation – effects also observed in the tests with constant power.

Readers will note that for some metals there are discrepancies between the results with constant temperature and those with constant power (see Table 5). There are several possible reasons. First, the tests did not use the same reference materials; in these conditions the same extraction technique can produce different results. Unfortunately, a further comparison between two materials was not possible because the BCR601 material is now not commercially available. Second, the first series of tests used constant, relatively low power while the second series involved pulses at high power. These alternative modes of operation may have produced different pattern of collisions between molecules in the solvent and the reference material. This would produce significant effects on the dissolution process.

4. Conclusions

To evaluate the practical usefulness of the techniques we have been discussing, we compared extraction efficiency and reproducibility (under optimal test conditions) with the certified BCR values, the values obtained by laboratories participating in the certification process, and our own results for the BCR procedure.

Fig. 1 compares normalized with the certified values extraction efficiency and standard deviations. The normalization of the extraction efficiency made it possible to compare the data from the two distinct reference materials used in the tests. The comparison was then extended to non-certified metals. In this case, the extraction efficiency were normalized with respect to the average values obtained by our laboratory during the application of the BCR procedure (Fig. 2). The evaluation focussed on the percentages of metal recovered using different techniques and on the reproducibility of the results.

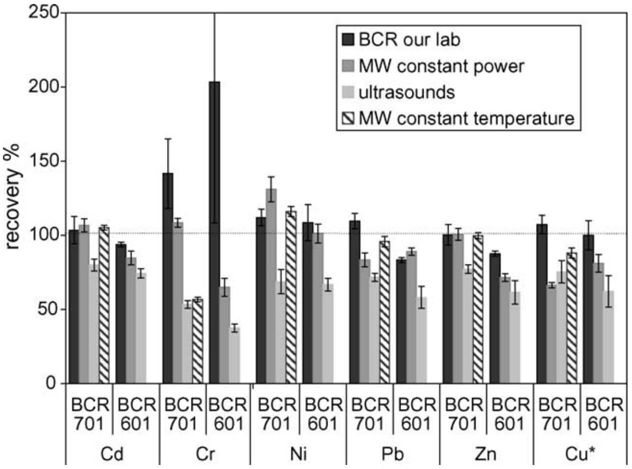

Fig. 1. Comparison of recoveries obtained with the MW (constant power: power, 70 W; $t = 60$ min – constant temperature: $T = 70\,^{\circ}\mathrm{C}$; $t = 10$ min), US ($t = 30$ min) and BCR protocol from reference materials 601 and 701 – certified metals.

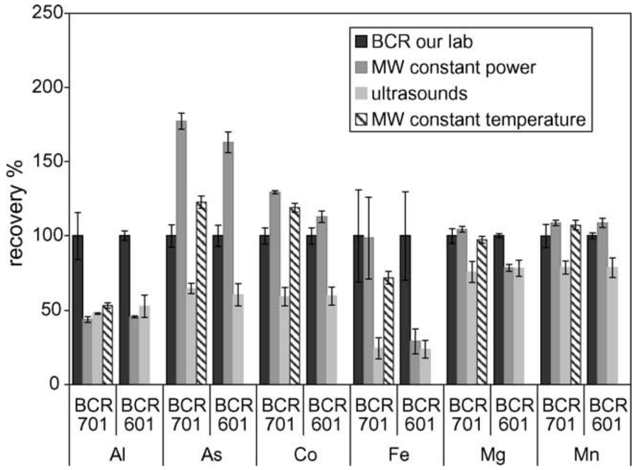

Fig. 2. Comparison of recoveries obtained with the MW (constant power: power, 70 W; $t = 60$ min – constant temperature: $T = 70\,^{\circ}$C; $t = 10$ min), US ($t = 30$ min) and BCR protocol from reference materials 601 and 701 – uncertified metals.

As already shown the standard deviations obtained by the application of the BCR protocol in our laboratory are indistinguishable from those obtained by the laboratories, which participated in the certification work.

For the test with ultrasound the best results were obtained by immersion for 30 min in a homogenous ultrasound bath. For all metals, the efficiency of extraction was significantly below the levels achieved with other extraction techniques. Standard deviations were comparable to those for the BCR procedure.

It should be noted that to date we have not been able to eliminate sources of random error such as uncontrolled variations in temperature and variations in shaking efficiency. There are, however, many ways in which it might be possible to optimise the procedure. This could lead to significant improvements, at least in terms of reproducibility.

As far as concerns the microwave-based test at constant power, extraction efficiency was sometimes significantly less than 100%; values varied from metal to metal and were strongly dependent on the choice of reference material. In several cases, standard deviations were higher than those for the reference method. It follows that this extraction procedure is not competitive.

In contrast with these findings, the results from the microwave test with constant temperature were extremely encouraging. Both for certified and non-certified metals, the reproducibility of the data lay in the 2–4% range. This compares very well with the reference method (BCR*n*) whose reproducibility values varied between 5 and 10% for certified metals, with values as high as 30% for uncertified metals.

These positive results for reproducibility can be explained if we consider that the microwave test with constant temperature eliminates most sources of random error. We are therefore hopeful that it will be possible to obtain low variability in inter-laboratory as well as inter-laboratory comparisons.

For certified metals, we achieved close to 100% recovery for Cd, Zn, Cu and Ni and around 80% for Pb and Cr. Microwave testing with constant temperature could thus represent a valid alternative to the BCR method, though further work will be required to ensure that extraction efficiencies do not vary between different materials.

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