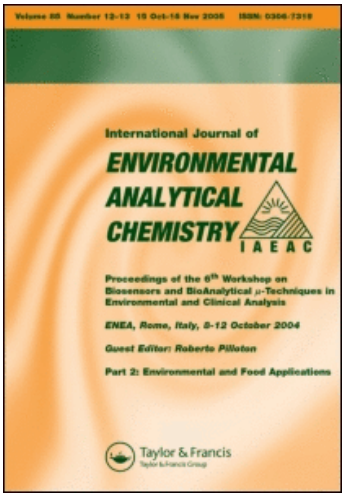

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Simple, fast, and low-contamination microwave-assisted digestion procedures for the determination of chemical elements in biological and environmental matrices by sector field ICP-MS

Beatrice Bocca[a]; Marcelo Enrique Conti[b]; Anna Pino[a]; Daniela Mattei[a]; Giovanni Forte[a]; Alessandro Alimonti[a]
[a] Department of Environment and Primary Prevention, National Institute of Health, Rome, Italy [b] SPES Development Studies, Research Centre at the University 'La Sapienza', Rome, Italy

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Simple, fast, and low-contamination microwave-assisted digestion procedures for the determination of chemical elements in biological and environmental matrices by sector field ICP-MS

BEATRICE BOCCA†, MARCELO ENRIQUE CONTI‡, ANNA PINO†, DANIELA MATTEI†, GIOVANNI FORTE† and ALESSANDRO ALIMONTI*†

†Department of Environment and Primary Prevention, National Institute of Health, Viale Regina Elena, 299, I-00161 Rome, Italy
‡SPES Development Studies Research Centre at the University 'La Sapienza', Via del Castro Laurenziano 9, I-00161, Rome, Italy

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A simple and convenient method for the digestion of animal tissues, lichens, and plants for 33 metals measured by sector field inductively coupled plasma mass spectrometry (SF-ICP-MS) was described. Microwave-assisted acid digestions were performed at atmospheric pressure by means of a multi-samples rotor designed for processing a large number of samples at once in screw-capped disposable polystyrene liners. The digested samples were filled up to final volume directly in the polystyrene liners ready for elemental quantification. Seven certified reference materials, namely BCR 184 (bovine muscle), BCR 186 (pig kidney), DORM-2 (dogfish muscle), BCR 422 (cod muscle), BCR 62 (olive leaves), BCR 100 (beech leaves), and BCR 482 (lichen) were analysed to verify the accuracy of the method. The linearity range, limit of quantification, precision, and recovery by addition of non-certified elements were also assessed. All elements, with the exception of Hg in BCR 184 and As in BCR 186, were above the quantification limit and blank concentrations, and good agreement existed between found and target values in bovine muscle, pig kidney, and cod muscle. Significant deviations were observed for Al, Co, Cr, Mn, and Ni in dogfish muscle and for Ca, Cr, Fe, and Hg in lichens and plants. The proposed digestion procedure offers a low contamination risk, simplicity, speed, low cost, and applicability in routine analysis, and the SF-ICP-MS method allowed metals from a fraction of $ng\,g^{-1}$ to hundreds of $\mu g\,g^{-1}$ to be quantified in one analytical run.

Keywords: Microwave digestion; Certified reference materials; Metals; Sector field inductively coupled plasma mass spectrometry

1. Introduction

Monitoring levels of chemical elements in animal tissues is a key tool for assessing the effect of contamination on animal health and the safety of animal-origin products in human nutrition. Assessment of metal concentrations in plants and lichens is also essential because of their role as bio-indicators of environmental pollution and sources

*Corresponding author. Fax: +39-0649902080. Email: alessandro.alimonti@iss.it

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of information about the fluxes of elements between biota, lithosphere, and atmosphere [1, 2]. For these determinations, there is a growing demand for sample pretreatments characterized by minimum handling and maximum productivity, at the same time combining good accuracy and precision. On the contrary, it often happens that sample pretreatment corresponds with the weak ring of the entire analytical chain, especially for its proneness to altering the analytical information of the samples through contamination or low recovery of analytes [3–5].

In metal analysis, most of the techniques require decomposition of the solid sample and its transformation into an homogeneous liquid phase. Microwave (MW)-based decomposition procedures have been used with increasing success in the treatment of a variety of samples because microwave energy allows the required decomposition temperature to be reached in a short time [6, 7]. In particular, by using MW digestion under pressure in PTFE closed-vessels, contamination from the environment is mostly reduced, and total metal recovery is generally achieved [8–12]. Notwithstanding this, the MW bomb digestion method has several notable drawbacks closely related to the system geometry. It is scarcely applicable for measurements of large number of samples because the available MW rotors allocate only few vessels at every digestion cycle. Moreover, PTFE closed-vessel digestion is labour-intensive and tedious, as samples are transferred between containers, and more than one cleaning cycle is necessary to avoid any memory effects from vessel walls. Finally, the currently used PTFE vessels are too large (100 mL) when small quantities of environmental and biological samples are available.

With the aim of simplifying the entire analytical procedure, limiting sample contamination and low recovery of analytes, increasing efficiency, and lowering analytical costs, alternative digestion procedures for body fluid analysis have recently been developed by the authors [13]. The method was based on the digestion at atmospheric pressure of 80 samples in plastic tubes and on the quantification directly in the liners without any further sample manipulation. In this study, the method was tested for animal tissues, vegetal matrices, and lichen treatment prior to monitoring the metal content.

As regards quantification techniques for metals, inductively coupled plasma atomic emission spectrometry (ICP-AES) and ICP-mass spectrometry (MS) have proved to be advantageous with respect to more traditional techniques such as atomic absorption spectrometry because of characteristics such as simultaneity, wide dynamic concentration range, and low detection limits. In addition, the application of sector field (SF) ICP-MS permitted further improvements with respect to quadrupole ICP-MS because, working at higher mass resolutions, spectral interferences can be physically shifted away from the analyte peak [14–16]. When the analytical interest is focused on both essential and toxic elements, the combination of ICP-AES and ICP-MS techniques becomes mandatory due to the different concentration of metal in matrices, involving a double analytical sample cycle with an obvious large consumption of sample solution and chemical reagents as well as a waste of time. The use of a single analytical sequence, i.e. single equipment, becomes mandatory in the case of samples where the amount is very limited.

In this work, the possibility of determination by SF-ICP-MS of up to 33 elements in concentrations varying from tens of nanograms per gram (i.e. Ag, As, Au, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Hg, Li, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Tl, U, V, W, and Zr) to thousands of micrograms per gram (i.e. Al, Ca, Fe, K, Mg, Na, and Zn) was explored. The main method performances investigated were linearity range, blank concentration, limits of quantification, accuracy and precision on different animal tissue, plant, and

lichen certified reference materials (CRMs). The main purpose was, thus, to develop a routine, multi-elemental method that would be useful for monitoring campaigns in which a high number of samples and large number of analytes have to be used, at the same time maintaining a good performance level.

2. Experimental

2.1 *Samples*

Both biological and environmental samples chosen for this study were CRMs, as diverse as animal tissues, plants, and lichens. For tissues, the BCR 184 (bovine muscle), BCR 186 (pig kidney), DORM-2 (dogfish muscle), and BCR 422 (cod muscle) were selected. The BCR 482 (lichen), BCR 62 (olive leaves), and BCR 100 (beech leaves) were also considered. All the BCR CRMs were purchased from the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium). The DORM-2 was available from National Research Council of Canada (NRCC, Ottawa, Canada).

2.2 *Reagents and instrumentation*

Single-element standard solutions (SPEX, Edison, NJ) at the concentration of $1\,mg\,mL^{-1}$ were used to prepare calibrants and internal standards (ISs). High-purity deionized water (EASY-pure, PBI, Milan, Italy) for dilution of samples and standards, and 67% HNO_3 and 65% $HClO_4$ of ultrapure-grade (Carlo Erba, Milan, Italy), 40% HF and 99.8% H_3BO_3 (solid) of suprapure-grade (Merck, Darmstadt, Germany) for digestions were used.

The CRMs were MW-digested in a Milestone Ethos 900-Mega II oven (FKV Milestone, Milan), loading a carousel (Milestone MultiPREP 80) with a capacity of 80 samples. The digestions were carried out at atmospheric pressure in 15-mL Falcon® screw-capped polystyrene liners (Becton Dickinson Labware, Franklin Lakes, NJ). One liner allowed the connection of a temperature sensor so as to monitor the progress of digestion conditions. The SF-ICP-MS system used was a Thermo Finnigan Element II model (Bremen, Germany) working with a standard sample-introduction system (Meinhard-type glass nebulizer; water-cooled Scott spray chamber; torch with guard electrode device; platinum interface cones). The following ICP-MS operating conditions were used: RF power, 1200 W; gas flow rates, $14.0\,L\,min^{-1}$ (plasma), $0.90\,L\,min^{-1}$ (auxiliary), and $0.85\,L\,min^{-1}$ (nebulizer); mass resolution, $300\,m/\Delta m$ (low resolution, LR, for Ag, Au, Ba, Be, Bi, Cd, Cs, Hg, Li, Mo, Pb, Sb, Sn, Sr, Tl, U, W, and Zr), $4000\,m/\Delta m$ (medium resolution, MR, for Al, Co, Cr, Cu, Mn, Ni, and V), and $10\,000\,m/\Delta m$ (high resolution, HR, for As, Ca, Fe, K, Mg, Na, Se, and Zn); acquisition mode, electric scan; mass window (%), 100 in LR, 80 in MR and HR; search window (%), 80 in LR, 60 in MR and HR; integration window (%), 60 in LR, MR and HR; numbers of scan, six for each resolution; total time of analysis sequence, 2 min. For metal quantification, the standard addition approach on at least five concentration levels was used. Three different ISs were used: in LR mode, ^{115}In for Ag, Au, Ba, Be, Cd, Cs, Li, Mo, Sb, Sn, Sr, and Zr, and ^{195}Pt for Bi, Hg, Pb, Tl, W, and U; in the MR mode, ^{45}Sc for Al, Co, Cr, Cu, Mn, Ni, and V; in HR mode, ^{115}In for As, Ca, Fe, K,

Table 1. Main SF-ICP-MS parameters.

Element	Abundance (%)	Resolution used (m/Δm)	Interference separated with the selected resolution
^{109}Ag	48.2	300	[a]
^{27}Al	100	4000	$^{11}B^{16}O$, $^{10}B^{16}OH$, $^{13}C^{14}N$, $^{12}C^{15}N$, $^{12}C^{14}NH$, $^{54}Fe^{2+}$
^{75}As	100	10,000	$^{40}Ar^{35}Cl$, $^{38}Ar^{37}Cl$, $^{36}Ar^{39}K$, $^{59}Co^{16}O$, $^{36}Ar^{38}ArH$,
^{197}Au	100	300	[a]
^{138}Ba	71.7	300	[a]
^{9}Be	100	300	[a]
^{209}Bi	100	300	[a]
^{44}Ca	2.1	10,000	$^{28}Si^{16}O$, $^{88}Sr^{2+}$, $^{27}Al^{16}OH$, $^{12}C^{16}O^{16}O$, $^{14}N^{14}N^{16}O$
^{111}Cd	12.8	300	[a]
^{59}Co	100	4000	$^{40}Ar^{19}F$, $^{43}Ca^{16}O$, $^{41}K^{18}O$, $^{36}Ar^{23}Na$, $^{40}Ar^{18}OH$, $^{42}Ca^{16}OH$
^{52}Cr	83.8	4000	$^{40}Ar^{12}C$, $^{36}Ar^{16}O$, $^{38}Ar^{14}N$, $^{35}Cl^{17}O$, $^{37}Cl^{15}N$, $^{35}Cl^{16}OH$
^{133}Cs	100	300	[a]
^{63}Cu	69.2	4000	$^{40}Ar^{23}Na$, $^{31}P^{16}O^{16}O$, $^{27}Al^{36}Ar$, $^{44}Ca^{19}F$
^{56}Fe	91.7	10,000	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$
^{202}Hg	29.8	300	[a]
^{39}K	93.3	10,000	$^{23}Na^{16}O$, ^{38}ArH
^{7}Li	92.5	300	[a]
^{24}Mg	79	10,000	$^{12}C^{12}C$, $^{48}Ca^{2+}$
^{55}Mn	100	4000	$^{37}Cl^{18}O$, $^{40}Ar^{15}N$, $^{39}K^{16}O$, $^{40}Ar^{14}NH$
^{98}Mo	24.1	300	[a]
^{23}Na	100	10,000	[a]
^{60}Ni	26.1	4000	$^{44}Ca^{16}O$, $^{23}Na^{37}Cl$, $^{36}Ar^{24}Mg$, $^{120}Sn^{2+}$
^{208}Pb	52.4	300	[a]
^{121}Sb	57.3	300	[a]
^{82}Se	9.20	10,000	$^{66}Zn^{16}O$, $^{40}Ar^{42}Ca$, $^{64}Zn^{18}O$, $^{65}Cu^{16}OH$, $^{63}Cu^{18}OH$, $^{64}Zn^{17}OH$
^{118}Sn	24.2	300	[a]
^{88}Sr	82.6	300	[a]
^{205}Tl	70.5	300	[a]
^{238}U	99.3	300	[a]
^{51}V	99.8	4000	$^{35}Cl^{16}O$, $^{37}Cl^{14}N$, $^{40}Ar^{11}B$, $^{36}Ar^{14}NH$
^{184}W	30.7	300	[a]
^{64}Zn	48.6	10,000	$^{40}Ar^{24}Mg$, $^{48}Ca^{16}O$, $^{36}Ar^{28}Si$
^{90}Zr	51.5	300	[a]

[a]No relevant interference.

Mg, Na, Se, and Zn. All the ISs were at the concentration of 1 ng mL^{-1} in the analytical solutions. Details on the chosen isotopes are reported in table 1.

2.3 *Sample treatment*

All the samples were directly weighed into the plastic liners, added with digestion reagents, predigested overnight and digested in the MW oven following a selected temperature ramp. In order to minimize the contamination from collection devices, the liners were previously cleaned with a mixture of 10% (v/v) of HNO_3 followed by repeated rinses with deionized water.

Aliquots of ca 100 mg of the BCR 184, BCR 186, DORM-2, and BCR 422 were predigested overnight at room temperature with 1.5 mL of HNO_3 and then MW digested after a further addition of 1.0 mL of HNO_3. The reduced amounts of the utilized CRMs (100 mg) better simulated the small sizes of the real samples, representing, at the same time, a sufficiently homogenous sub-sampling. The following temperature ramp was

used: 30 min to reach 80°C, at 80°C for 30 min, then in 10 min up to 90°C, and at 90°C for 2 h to complete the digestion. Afterwards, the digested solutions were diluted with deionized water up to 10 mL. For the SF-ICP-MS analysis, samples were further diluted 1:2 v/v with water.

With reference to lichens and vegetal-based CRMs (BCR 482, BCR 62, and BCR 100), ca 100 mg of each CRM was predigested for 24 h at room temperature with 4.0 mL of HNO_3 and 0.2 mL of $HClO_4$. The next day, lichens and plants were MW-digested with the same temperature ramp programmed for animal tissues. On the basis of preliminary trials, the digestion solutions were simultaneously added with 0.1 mL of HF and 0.3 mL of H_3BO_3 0.45 M and again subjected to MW irradiation under the same conditions. This procedure was also in line with the main objective to handle samples as little as possible. The solutions were diluted up to 10 mL with water and analysed by SF-ICP-MS at a ratio of 1:5 v/v with water. Blank samples were run together with matrices and were considered in the final evaluation.

3. Results and discussion

3.1 *Optimization of digestion procedures*

Microwave digestion at atmospheric pressure with HNO_3 took 3 h approximately to decompose 80 samples of animal tissues in one cycle. The H_2O_2 was not used because studies found HNO_3 alone to be equally effective in digesting soft tissues (such as muscle) [17, 18]. Compared with animal tissues, lichens and plants required a more complete decomposition, including an HF treatment for the decomposition of silica. For this reason, the mineralization time for lichens and plant-based CRMs was doubled in order to totally dissolve the matrices and avoid any possible residues. To improve the oxidizing power of the digestion mixture, the H_2O_2 was tentatively added to plants, but the contact of this reagent with samples produced foaming. Alternatively to the H_2O_2, the $HClO_4$ was adopted in digesting plants, and it was able to bring the necessary oxygen to destroy the organic matter and allowed to reduce the volatility of elements such as Cr by the formation of soluble complexes [19]. The HF was indispensable in complexing elements as their stable fluorides. The addition of 0.05 mL of HF resulted in undigested residue in the form of blank solid particles visible at the bottom of the liners. When 0.2 mL of HF was added, low recoveries were observed for elements such as Se, V, and Zn [20]. For these reasons, the quantity of 0.1 mL was selected as the best compromise between the complete destruction of silicates without degrading the recoveries of some elements. The addition of H_3BO_3 was indispensable in neutralizing the residual HF which could be corrosive for the quartz introduction devices used in the ICP. The addition of H_3BO_3 helped also to prevent insoluble fluorides especially of Al, Ca, and Mg, which otherwise were removed from the solution leading to very low recoveries.

Overnight pre-digestion before absorption of the MW irradiation and a relatively long initial increase in the decomposition temperature were used to prevent exothermic oxidation reactions from leading to vigorous overheating of the mixture. The temperature setting was chosen to heat the mixture to a temperature no higher than that required to achieve gentle boiling and to avoid excess acid fumes carrying

volatile elements. By making sure the screw caps of the tubes were not completely closed, a decomposition temperature of 90°C could be reached without any visible deterioration of the plastic containers. Under these conditions, sufficient mineralization efficiency was achieved (maximum total organic carbon remaining, 3.5 g L^{-1}). After the digestion, samples were filled up to a final volume directly in the polystyrene liners ready for elemental quantification, thus minimizing the risk of exogenous contamination and simplifying the overall procedure.

3.2 *Interference*

Table 1 shows the elements, measured m/z ratios, isotopic abundances, and resolution selected for separating the significant interferences.

Elements not hampered by any relevant interference were quantified in the LR resolution and, apart from Ag, Cd, and Sn, by using their most abundant isotopes. Silver was quantified at the lowest abundant mass because the signal at mass 107 (abundance of 52%) was interfered with by $^{40}Ar^{67}Zn$; Cd was not determined at mass 114 (abundance of 28.7%) because of the isobaric interference of ^{114}Sn; and Sn was quantified at mass 118 because the contribution from $^{38}Ar^{82}Se$ on mass 120 (abundance of 32.6%) was not negligible (i.e. 50% of the total signal).

Elements such as Al, Co, Cr, Cu, Mn, Ni, and V were heavily interfered with by polyatomic ion species produced by a combination of isotopes coming from plasma, reagents, and matrices. In particular, the addition of HNO_3, $HClO_4$, HF, and H_3BO_3 created interferences that were not negligible, as $^{12}C^{15}N^+$ which overlapped the signal of ^{27}Al, $^{38}Ar^{14}N^+$ on ^{52}Cr, $^{40}Ar^{15}N^+$ on ^{55}Mn, and $^{36}Ar^{14}NH^+$ on V; the species $^{35}Cl^{17}O^+$, $^{37}Cl^{18}O^+$, and $^{35}Cl^{16}O^+$, which fell on ^{52}Cr, ^{55}Mn, and ^{51}V, respectively; and $^{23}Na^{37}Cl^+$ which hampered the ^{60}Ni signal. As regards fluorine, its argide heavily covered the signal of Co, while the specie $^{44}Ca^{19}F^+$ interfered with the chosen mass of ^{63}Cu. The presence of boron in the digestion mixture produced $^{11}B^{16}O^+$ and $^{40}Ar^{11}B^+$, affecting the signal of Al and V at masses 27 and 51, respectively. The high content in the matrices of elements such as Ca, K, Na, and Mg—forming several oxides, argides, and chlorides—also posed problems for the quantification of Co, Cu, Mn, and Ni leading to falsely high values. In this study, by using the MR mode all these interferences were shifted far from the analytical peak and thus unequivocally separated. This instrumental setting allowed us to avoid the use of mathematical correction factors usually applied in quadrupole ICP-MS analyses which would have been inadequate anyway in case of a high amount of interference. As for the LR, the most abundant isotopes were selected for each element with the exception of Ni which was interfered by the isobaric ^{58}Fe at its most abundant isotope.

To determine As and Se, the use of the HR mode was mandatory to separate their signal from interference. Among all the available isotopes of Se, those at mass 76, 78, and 80 could not be selected because of the huge signal from the Ar dimers. Between mass 77 and 82, the latter was chosen because it was completely free from $ArCl^+$ and ArK^+. Moreover, the HR setting was also used for the analysis of Ca, Fe, K, Na, Mg, and Zn because, besides its main use in eliminating relevant interferences, it helped to reduce the signal intensity, since these elements are present at very high concentrations in the considered matrices. Except for Ca, which could not be detected at mass 40

Table 2. Blanks concentration and LOQs in polystyrene liners expressed in $ng\,mL^{-1}$ for different digestion mixture.

	Animal tissues		Plants and lichens	
Element	Blank	LOQ[a]	Blank	LOQ[a]
Ag	0.03	0.01	nd	nd
Al	2.0	1.0	11.2	7.0
As	<LOQ	0.20	<LOQ	0.60
Au	<LOQ	0.01	nd	nd
Ba	0.04	0.04	<LOQ	0.20
Be	0.04	0.02	nd	nd
Bi	0.06	0.02	nd	nd
Ca	10	1.0	23	13
Cd	<LOQ	0.005	<LOQ	0.006
Co	<LOQ	0.01	<LOQ	0.02
Cr	0.07	0.05	<LOQ	0.04
Cs	<LOQ	0.001	0.002	0.001
Cu	0.50	0.40	0.15	0.13
Fe	3.5	1.0	<LOQ	2.4
Hg	0.10	0.07	0.2	0.06
K	11	5.0	15	2.1
Li	0.03	0.01	nd	nd
Mg	2.0	0.50	3.0	1.6
Mn	0.05	0.03	0.26	0.21
Mo	<LOQ	0.005	0.005	0.004
Na	23	15	14	8.0
Ni	0.20	0.10	<LOQ	0.07
Pb	0.05	0.025	<LOQ	0.12
Sb	<LOQ	0.009	<LOQ	0.003
Se	<LOQ	0.30	<LOQ	0.25
Sn	<LOQ	0.14	<LOQ	0.043
Sr	<LOQ	0.15	<LOQ	0.06
Tl	<LOQ	0.001	<LOQ	0.001
U	<LOQ	0.008	<LOQ	0.007
V	<LOQ	0.02	<LOQ	0.02
W	<LOQ	0.02	<LOQ	0.02
Zn	1.5	0.50	<LOQ	1.0
Zr	0.07	0.015	nd	nd

[a]LOQ, calculated as 10σ criterion of the blank values.
nd: not determined.

because of the presence of ^{40}Ar, all the other metals were quantified at their most abundant mass.

3.3 *Method performances*

Table 2 shows the concentration levels of blanks along with the limits of quantification (LOQs) expressed as 10 times the standard deviation (SD) of 10 replicated measurements of blanks, including the dilution factor. Blanks related to the digestion of tissues were 12.5% HNO_3, and those of plants and lichens were given in a mixture of 8% HNO_3, 0.4% $HClO_4$, 0.2% HF, and 0.6% H_3BO_3. In both cases, procedural blanks do not actually contribute to the analytical signal for most of the elements, being lower than or very close to the LOQ values, with the exception of Al, Ca, Fe, K, Mg, Na, and

Zn, whose blank concentrations ranged between 1.5 and 23 ng mL^{-1}. This fact was not a problem as the level of these elements was usually much higher in all the considered matrices. The addition of $HClO_4$, HF, and H_3BO_3 in the vegetable matrices worsened the levels of blanks only for Al, Ca, and Mn (see table 2).

The method linearity range was determined by measuring 10 spiked digested samples with concentrations spanning the range 0.5–500 ng mL^{-1} for all elements, 5–5000 ng mL^{-1} for Al, Cu, Fe, Mg, and Zn, and 2500 ng mL^{-1} to 100 μg mL^{-1} for Na, K, and Ca. Frequently, R^2 values were found to be better than 0.9990, with the only exceptions for As in DORM-2, Se in BCR 482, and V in BCR 422, whose R^2 values were equal to 0.992, 0.989, and 0.993, respectively. Because the approach of the standard addition calibration in the matrix was used, the resulting goodness of these values also reflected the fact that the matrix-effect influence was under control.

Table 3 shows the accuracy and precision (i.e. 10 replicated measurements of the same CRM solution containing certified or spiked concentration of a particular element) for bovine muscle and pig kidney, table 4 lists the results for dogfish and cod muscle, and table 5 reports the data on lichens, olive, and beech leaves. In the case of bovine muscle, all elements matched the CRM values well, with results ranging between 91 and 106%. An exception was Hg, which could not be detected with sufficient accuracy because in the final solutions, the concentrations were below the LOQ. Recoveries for spiked elements—in the interval 82–114%—were quite satisfactory considering that they are calculated on a concentration of 5 ng mL^{-1} in the analytical solution. Precision was below 10% for all the elements, with the highest RSD observed for As, Be and Zr. The MW digestion method developed succeeded also with pig kidney. All elements showed recoveries around 100%, only As value was 21% too low, while Cs and Ni were 17% and 15% too high, respectively. For As, the deviation from the certified value could be due to the fact that quantification was performed very close to its LOQ. For Cr, the value found was lower than the low limit of the indicated range, but this range was obtained only by one laboratory, using a different analytical method (i.e. the RNAA). Moreover, this CRM (BCR 186, pig kidney) was suspected to be inhomogeneous also by other authors [21]. The results on pig kidney showed a trend to a lower precision probably because the content in fatty acid material was higher in kidney than in muscle. In general, the proposed method works very well with meat-based materials. Efficiencies were comparable with—and for some elements such as Fe, Zn, and Mg even higher than—that achieved with focused MW-assisted digestion and ultrasound-assisted leaching tested as new extraction techniques for meat [22].

In dogfish muscle (see table 4), acceptable accuracies were obtained for some elements, including volatile elements (i.e. As, Se, and Hg), but partial recoveries were observed for Al (80%), Co (78%), Cr (71%), Mn (74%), and Ni (78%). Similarly low results for Cr and Ni were obtained also by other authors, who suggested that a possible inhomogeneous contamination of these metals occurred from the stainless steel blades used to break up the raw material in the preparation of the CRM [23, 24]. Moreover, Sn showed a significant positive deviation from the value which was given as indicative, and Cd presented a value higher than 16% from the reference value. Data for cod muscle were in agreement with the target values with recoveries ranging between 92% (Pb) and 119% (Co). In comparison with the results obtained in dogfish muscle, recoveries for Al, Co, Cr, Mn, and Ni were quantitative. This demonstrates that the treatment procedure did not work similarly with different fish tissues, being less efficient with dogfish than with cod muscle. On the other hand, the data on precision, which

Table 3. Values obtained in the analysis of CRMs based on bovine and pig tissues (values in parentheses are indicative only).

	BCR 184, bovine muscle				BCR 186, pig kidney			
	Accuracy (mean ± SD) (ng g^{-1})				Accuracy (mean ± SD) (ng g^{-1})			
Element	Certified	Found	Recovery (%)	Precision (%)	Certified	Found	Recovery (%)	Precision (%)
Ag	1000[a]	846 ± 112	84.6	5.00	1000[a]	966 ± 74	96.6	6.54
Al	1000[a]	1040 ± 66	104	6.27	1000[a]	950 ± 62	95.0	6.49
As	1000[a]	850 ± 45	85.0	8.50	63 ± 9	49.8 ± 5.2	79.0	9.30
Au	1000[a]	840 ± 112	84.0	5.23	1000[a]	986 ± 68	98.6	6.34
Ba	1000[a]	970 ± 50	97.0	3.64	1000[a]	1022 ± 30	102	2.46
Be	1000[a]	1064 ± 38	106	9.80	1000[a]	1128 ± 42	113	13.7
Bi	1000[a]	1140 ± 70	114	5.61	1000[a]	1130 ± 54	113	6.43
Ca[b]	(150)	152 ± 10	101	3.60	(295)	285 ± 19	96.6	3.44
Cd	13 ± 2	13 ± 1	100	3.56	2710 ± 150	2532 ± 127	93.4	3.63
Co	1000[a]	900 ± 124	90.0	7.23	1000[a]	998 ± 26	99.8	8.50
Cr	(76–153)	94.7 ± 10	–	3.69	(58–142)	42.7 ± 6.1	–	4.91
Cs	1000[a]	1026 ± 104	103	1.80	1000[a]	1172 ± 62	117	1.29
Cu	2360 ± 60	2342 ± 38	99.2	3.28	31,900 ± 400	31,026 ± 1657	97.3	3.86
Fe[b]	79.0 ± 2	77.3 ± 3.5	97.8	2.25	299 ± 10	321 ± 17	107	3.84
Hg	2.6 ± 0.6	< LOQ			1970 ± 400	1899 ± 124	96.4	1.20
K[b]	(16,600)	15,389 ± 1250	92.8	4.03	(12,600)	11,828 ± 1075	93.8	3.14
Li	1000[a]	930 ± 80	93.0	3.15	1000[a]	1118 ± 28	112	2.42
Mg[b]	(1020)	1080 ± 90	106	3.04	(829)	789 ± 59	95.2	3.28
Mn	334 ± 28	304 ± 31	91.0	7.55	8500 ± 300	8805 ± 286	104	8.70
Mo	1000[a]	1052 ± 11	105	3.85	1000[a]	980 ± 24	98.0	4.29
Na[b]	(2000)	2105 ± 189	105	3.50	(7100)	6976 ± 475	98.2	3.24
Ni	(270)	282 ± 13	104	5.10	(420)	492 ± 36	117	5.48
Pb	239 ± 11	233 ± 10	97.5	1.50	306 ± 11	283 ± 18	92.5	1.70
Sb	1000[a]	820 ± 102	82.0	5.30	1000[a]	1010 ± 52	101	6.44
Se	183 ± 12	189 ± 17	103	3.50	10,300 ± 500	11,111 ± 563	108	1.37
Sn	1000[a]	1042 ± 126	104	6.52	1000[a]	982 ± 46	98.2	5.15
Sr	1000[a]	930 ± 62	93.0	3.10	1000[a]	1002 ± 36	100	4.50
Tl	1000[a]	840 ± 44	84.0	2.03	1000[a]	1042 ± 56	104	2.38
U	1000[a]	1060 ± 32	106	3.26	1000[a]	94.2 ± 3.4	94.2	4.66
V	1000[a]	886 ± 66	88.6	7.50	1000[a]	1086 ± 58	109	8.48
W	1000[a]	1100 ± 102	110	5.89	1000[a]	91.4 ± 7.8	91.4	7.66
Zn[b]	166 ± 3	153 ± 7	92.2	1.52	128 ± 3	135 ± 13	106	1.69
Zr	1000[a]	1084 ± 64	108	8.20	1000[a]	1024 ± 44	102	9.60

[a]Amount (ng g^{-1}) spiked on the raw CRM mass for recovery test. [b]Concentration in μg g^{-1}.

were similar in both materials, did not indicate differences in the homogeneity of the digests. The elements with the worst precisions were Co, Ni, Sb, Se, V, and W.

Values found for lichens and plants (see table 5) were generally in line with those certified or indicative, suggesting a good method accuracy. Nevertheless, there were some cases in which deviations occurred. Low recoveries of Cr were observed in lichens (−32%), while recoveries around 100% were observed both in olive leaves and in beech leaves. The results on Cr in lichens agreed better with the data obtained with ICP-MS (3.4–3.7 μg g^{-1}) during the certification process which, in any case, were not considered for the certification. Previous experiments proved that Cr total recovery from the plant matrix needed a sufficiently strong digestion procedure and was only stabilized after a long mineralization time [14]. Similarly low recoveries of Cr were also obtained after

Table 4. Values obtained in the analysis of fish-based CRMs.

	DORM 2, dogfish muscle				BCR 422, cod muscle			
	Accuracy (mean ± SD) (ng g^{-1})				Accuracy (mean ± SD) (ng g^{-1})			
Element	Certified	Found	Recovery (%)	Precision (%)	Certified	Found	Recovery (%)	Precision (%)
Ag	41 ± 13	41.6 ± 8.1	101	4.12	1000[a]	1050 ± 36	105	6.88
Al	10.900 ± 17.0	8750 ± 221	80.3	10.8	1000[a]	1124 ± 56	112	9.35
As[b]	18.0 ± 1.1	16.5 ± 1.3	91.9	8.46	21.1 ± 0.5	19.8 ± 1.3	93.8	7.73
Au	1000[a]	1050 ± 62	105	9.10	1000[a]	1064 ± 52	106	8.35
Ba	10,000[a]	9740 ± 280	97.4	2.00	1000[a]	1072 ± 28	107	1.98
Be	1000[a]	1102 ± 22	110	9.90	1000[a]	1038 ± 14	104	7.80
Bi	1000[a]	1050 ± 20	105	9.79	1000[a]	1080 ± 22	108	6.21
Ca[b]	nc			2.93	(330)	337 ± 2	102	3.80
Cd	43 ± 8	50.3 ± 0.2	117	5.83	17 ± 2	16.2 ± 1.1	95.3	6.10
Co	182 ± 31	143 ± 8	78.6	12.3	(15)	17.2 ± 1.7	115	10.7
Cr	34.7 ± 5.5[b]	24.6 ± 1.4[b]	70.8	6.61	1000[a]	1102 ± 58	110	5.35
Cs	1000[a]	950 ± 50	95.0	3.56	1000[a]	1074 ± 56	107	2.87
Cu	2340 ± 160	2252 ± 1.75	96.2	5.72	1050 ± 70	1166 ± 116	111	4.43
Fe	142 ± 10[b]	126 ± 4[b]	88.9	8.75	5460 ± 30	5228 ± 613	95.6	7.57
Hg	4640 ± 260	4435 ± 3.8	95.6	8.28	559 ± 16	541 ± 33	96.8	4.80
K[b]	nc			2.04	(21, 700)[b]	20,364 ± 1989	93.8	2.73
Li	1000[a]	1170 ± 22	117	2.87	1000[a]	1158 ± 28	116	2.96
Mg[b]	nc			3.93	(1400)	1302 ± 169	93.0	2.61
Mn	3660 ± 340	2712 ± 168	74.1	9.52	543 ± 28	532 ± 24	98.0	10.5
Mo	1000[a]	1128 ± 42	113	6.63	1000[a]	1148 ± 70	115	8.82
Na[b]	nc			3.77	(2200)	2227 ± 245	101	2.68
Ni	19,400 ± 3100	15,020 ± 1098	77.4	14.1	1000[a]	984 ± 54	98.4	9.72
Pb	65 ± 7	58.7 ± 4.7	90.3	6.80	85 ± 15	77.9 ± 10.3	91.6	5.47
Sb	1000[a]	1052 ± 38	105	9.69	1000[a]	1038 ± 54	104	13.2
Se	1400 ± 90	1329 ± 200	94.9	10.6	1630 ± 70	1734 ± 121	106	12.2
Sn	(23)	30.1 ± 2.8	130	10.0	1000[a]	982 ± 30	98.2	2.53
Sr	10,000[a]	11,120 ± 9.0	111	8.24	(700)	806 ± 20	115	8.77
Tl	(4)	4.21 ± 0.31	105	5.20	1000[a]	976 ± 16	97.6	8.15
U	1000[a]	928 ± 38	92.8	6.08	1000[a]	958 ± 36	95.8	4.26
V	1000[a]	1150 ± 16	115	9.45	1000[a]	1072 ± 52	107	13.2
W	1000[a]	934 ± 56	93.4	9.47	1000[a]	962 ± 62	96.2	11.5
Zn[b]	25.6 ± 2.3	24.5 ± 1.7	95.5	6.27	19.6 ± 0.5	19.7 ± 1.0	100	6.52
Zr	1000[a]	978 ± 44	97.8	8.30	1000[a]	966 ± 32	96.6	7.22

Values in brackets are indicative only; nc, not certified.
[a]Amount (in ng g^{-1}) spiked on the raw CRM mass for recovery test; [b]Concentration in μg g^{-1}.

treatment with MW digestion in closed vessels [19] or with MW extraction using HCl or EDTA as extractants [25]. Also, Ca, Fe, Na, and K appeared to be not completely solubilized, and this is quite surprising as Ca and Fe are quantitatively extractable by the use of HF and HCl combined to HNO_3, and Na and K are generally easily mobilizable in solution [26, 27]. An underestimation was also observed for Ni and Sb in beech leaves only, and U in all the matrices, but any conclusion about these data is questionable because the provided values were indicative, mainly determined by a single laboratory.

However, in classic procedures using MW digestion in PTFE vessels, the same results for Ni occurred [19]. Half Mo compared with the indicative value in lichens was found, but this was in accordance with the values in olive and beech leaves. Arsenic always gave good results, while Se showed an overestimation (+30%) only in olive leaves with

Table 5. Values obtained in the analysis of lichens and plant-based CRMs (values in parentheses are indicative only).

	BCR 482, lichens				BCR 62, olive leaves				BCR 100, beech leaves			
	Accuracy (mean ± SD) ($ng\,g^{-1}$)				Accuracy (mean ± SD) ($ng\,g^{-1}$)				Accuracy (mean ± SD) ($ng\,g^{-1}$)			
Elements	Certified	Found	Recovery (%)	Precision (%)	Certified	Found	Recovery (%)	Precision (%)	Certified	Found	Recovery (%)	Precision (%)
Al[b]	1103 ± 24	1092 ± 138	99.1	4.94	450 ± 20	468 ± 39	104	3.10	435 ± 4	443 ± 9	102	8.36
As	850 ± 70	901 ± 6	106	7.17	(200)	196 ± 14	98.0	3.82	(510)	535 ± 167	105	24.1
Ba[a]	(14.9)	14.5 ± 8.4	97.2	7.74	10.0[b]	10.9 ± 1.0	109	5.88	10.0[b]	10.2 ± 1.0	102	5.98
Ca[a]	(2624)	1815 ± 479	69.1	5.31	nc			4.71	5300 ± 50	4567 ± 519	86.1	4.24
Cd	560 ± 20	483 ± 13	86.3	6.01	100 ± 20	103 ± 14	103	6.58	(340)	326 ± 38	95.9	6.12
Co	(320)	323 ± 30	101	7.72	(200)	187 ± 24	93.5	10.8	1000[b]	800 ± 20	80.0	8.09
Cr	4120 ± 150	2794 ± 79	67.8	8.46	(2000)	1793 ± 127	89.7	3.50	8000 ± 600	8266 ± 1215	103	10.5
Cs	(190)	196 ± 17	103	8.92	(100)	104 ± 9	104	4.34	1000[b]	995 ± 52	99.5	6.33
Cu	7030 ± 190	7712 ± 595	110	6.76	46.6 ± 1.8[a]	50.9 ± 8.6[a]	109	6.89	(12.0) [a]	12.2 ± 0.9[a]	102	2.58
Fe[a]	(804)	664 ± 51	82.5	8.77	nc			4.65	(550)	428 ± 25	77.8	6.13
Hg	480 ± 20	825 ± 13	172	4.72	280 ± 20	485 ± 35	173	3.55	(260)	316 ± 33	121	3.38
K[a]	(3900)	3392 ± 119	87.0	5.84	nc			4.78	9940 ± 2000	8614 ± 552	86.7	3.65
Mg[a]	(578)	508 ± 13	87.9	5.45	nc			7.95	878 ± 17	818 ± 19	93.2	9.98
Mn[a]	(33.0)	33.1 ± 2.1	100	3.66	57.0 ± 2.4	53.8 ± 1.5	94.3	6.24	(1300)	1325 ± 65	102	5.18
Mo	(850)	348 ± 6	41.0	1.15	(200)	198 ± 17	99.0	4.06	(500)	503 ± 14	101	2.87
Na[a]	(119)	97.0 ± 8.6	81.5	5.41	nc			6.35	(255)	261 ± 59	102	10.9
Ni	2470 ± 70	2613 ± 23	106	6.68	(8000)	2374 ± 297	29.7	5.40	10,000[b]	10,710 ± 109	107	5.99
Pb[a]	40.9 ± 1.4	40.6 ± 1.1	99.4	3.75	25.0 ± 1.5	24.3 ± 1.3	97.3	2.95	(16.3)	16.5 ± 0.5	102	2.36
Sb	(350)	284 ± 6	81.1	12.2	(3000)	70 ± 7	2.33	4.67	(359)	327 ± 11	91.1	3.72
Se	(600)	617 ± 64	103	14.4	(100)	131 ± 39	131	10.4	(150)	159 ± 28	106	15.4
Sn	(1310)	1250 ± 123	95.4	7.14	(1000)	998 ± 192	99.8	4.31	1000[b]	976 ± 12	97.6	4.98
Sr[a]	(10.35)	9.14 ± 0.9	88.3	7.76	10.0[b]	11.0 ± 1.0	110	6.04	(13.3)	11.6 ± 2.8	87.1	5.04
Tl	(61)	58 ± 20	95.1	15.2	(30)	24 ± 3	80	5.49	1000[b]	1062 ± 82	106	3.67
U	(137)	41 ± 2	30.0	18.8	(200)	21 ± 5	10.5	6.64	1000[b]	967 ± 22	96.7	3.27
V	(3740)	3720 ± 550	99.5	7.55	(1000)	1072 ± 48	107	7.53	1000[b]	1024 ± 778	102	17.6
W	1000[b]	920 ± 25	92.0	11.9	(200)	156 ± 21	78.0	2.37	1000[b]	950 ± 20	95.0	2.75
Zn[a]	100.6 ± 2.2	102 ± 9.5	102	3.33	16.0 ± 0.7	16.1 ± 0.7	101	9.14	(69.0)	68.9 ± 2.6	99.8	8.11

[a]Concentration in $\mu g\,g^{-1}$. [b]Amount (in $ng\,g^{-1}$) spiked on the raw CRM mass for recovery test. nc, not certified.

respect to an indicative value obtained by NAA. The mercury level was much higher than that certificated in lichens and in olive leaves, while it matched the indicative value in beech leaves. Mercury contamination of samples was excluded because of the low levels of related blanks, but it can only be suggested to be a possible memory effect in the ICP-MS interfaces [28]. On the other hand, in contrast with previous works, the combination of $HNO_3/HF/HClO_4$ allowed to obtain quantitative recoveries for Al in the three reference materials [14]. Also, data on V agreed completely with the indicative values, while some extraction methods found its extraction from plants to be quite difficult [25]. The procedure applied to lichens and vegetal CRMs offered a good precision with several values less than 10%, except for Se in all the materials, for U, Tl, and W in lichens and for As and V in beech leaves.

4. Conclusions

The proposed atmospheric-pressured MW acid digestion proved to be suitable for efficient decomposition of animal tissues, lichens, and vegetal-derived materials. The determined recoveries were generally in good agreement with the target values for all the tested CRMs, although the best performances were obtained for bovine muscle, pig kidney, and cod muscle. In dogfish muscle, low recoveries of Al, Co, Cr, Mn, and Ni were observed, while in lichens and plants, recoveries for Ca, Cr, and Fe were not quantitative, and Hg was overestimated. The procedure has the advantage of greatly reducing digestion time, enabling a start-to-finish preparation of up to 80 samples of animal tissues and plants in a maximum of 6 h. The main advantage of the proposed digestion method is the decrease in contamination risk of samples as they were prepared for the analysis in the same plastic containers in which they were originally collected. As regards the SF-ICP-MS method, it was able to determine in one run elements present at ultra-trace levels and also those at parts per million concentrations by working at three different resolution settings. In view of its simplicity and efficiency, the entire procedure seems to be very attractive for routine analysis, combining the possibility of producing a general picture of the elemental state in many samples with a sufficiently good performance.

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