Critical Review

Microwave digestion procedures for environmental matrices

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Summary of contents

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Introduction

Quantitative analytical techniques are required to determine accurately and rapidly a variety of trace metals with sufficient sensitivity for application to a range of environmental samples. This requirement has led to major technological advances in the development of analytical instrumentation, enabling vast amounts of elemental information to be obtained in a shorter time and with increased sensitivity than was ever possible before. This is especially true of analytical techniques such as inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS), which can obtain multi-element information in a fraction of the time needed to prepare the samples. However, prior to analysis by most analytical techniques there is an intrinsic requirement for the sample to be converted into a liquid form. For solid samples this can be achieved by undertaking some form of digestion procedure.

To be effective, sample digestion methods must efficiently decompose the sample matrix so that the analytes of interest are completely released and solubilised and are in a form compatible with the analytical method of choice. Effective methods of sample digestion are therefore a crucial prerequisite to accurate analysis. However, technological advances in this area have been slow in comparison with the developments in analytical instrumentation. Until relatively recently, sample digestion methods were largely limited to the conventional techniques of wet digestion, dry ashing and fusion techniques. Such methods are often time consuming, may be the source of contamination and losses of analyte and generally require a great deal of operator attention, skill and experience in order to gain accurate and precise results. As a consequence, sample preparation is often regarded as the weak link in sample analysis, and an area which provides much scope for improvement.

Significant improvements in sample preparation techniques have been made since 1975, however, when Abu-Samra[1] first reported the use of microwaves as a heat source for wet digestion methods. Since then the microwave digestion technique has gradually gained widespread acceptance as an effective method of sample preparation. Using this technique, not only have digestion times been dramatically reduced (by a factor of 2–5) but also other benefits such as a reduction in contamination, less reagent and sample usage, a reduction in the loss of volatile species and improved safety have been reported.[2] The advantages of the microwave digestion technique have led to its application as an effective sample preparation method for a wide range of sample matrices. Each year more and more laboratories replace the conventional methods with the new technology, as is reflected in the ever increasing amount of material published on the subject. A number of review articles and books have been published[2–9] detailing the use of the technique for elemental analysis. Kuss[5] listed the applications of microwave digestion techniques for elemental analyses cited in the literature before 1992. Included were references for the digestion of biological, geological, environmental and metallic materials. A publication by Zlotorzynski[3] discusses the fundamental principles of microwave field interaction with the sample matrix, whereas de la Guardia and Morales-Rubio[4] discuss the modern strategies available for the rapid determination of metals in sewage sludges. A review on the use of microwave assisted sample preparation in analytical chemistry has been undertaken by Smith and Arsenault[9] and specifically for analysis by electrothermal atomic absorption spectrometry by Chakraborty *et al.*[6]

This paper reviews the application of microwave energy for the digestion of environmental samples (biological, geological and water) reported since 1992. Where it was felt that the

methodological approach would benefit the reader, matrices which are not strictly environmental are also included, *e.g.*, bovine liver, foodstuffs. Details of the open and closed microwave digestion methods used to digest these samples, including the advantages and disadvantages of each technique, are discussed. The review also attempts to highlight any trends in research and to identify universal digestion procedures for particular matrices or elements.

Tables 1, 2 and 3 summarise the different microwave digestion procedures employed during the review period for biological, geological and water samples, respectively. Each table characterises the matrix digested, elements determined, microwave system used, digestion method, *i.e.*, specific reagents and heating time, and analytical technique used, and finally comments on the effectiveness of the method. In many cases certified reference materials have been used for validation of digestion procedures. It was observed that results are often classed as 'good' when in fact they lie outside the uncertainty limits of the certified value. For clarification, in this review, results described as 'good' indicate that they lie within the uncertainty limits of the certified value. In most cases this is defined as twice the standard deviation of the mean of the certified value. Other results are classified as 'low' or 'high' accordingly. A key to the abbreviations used in Tables 1–3 is given in Table 4.

Open or closed digestion systems?

During the review period, most studies have concentrated on the development of closed digestion methods. Most commonly these are carried out in multimode ovens, in which the microwaves are dispersed into a large cavity, in a similar manner as for domestic microwave ovens. Multimode ovens have also been used for open digestions; however, the majority of open vessel applications utilise monomode (focused) microwave ovens. In the latter case, microwave energy is directly applied to the sample by placing it within the waveguide. Hence, it may be better to describe microwave ovens in terms of the type of applicator used, *i.e.*, 'cavity' for multimode and 'waveguide' for monomode ovens. A commercial closed monomode microwave digestion system is also available.[27] Each microwave digestion system has certain advantages and disadvantages, so it is not possible to suggest either as being the most suitable for all applications.

Closed microwave digestion techniques

The closed digestion technique involves placing the sample in a vial (or bomb), usually constructed of a fluorinated polymer, such as polytetrafluoroethylene (PTFE) or perfluoroalkoxy (PFA). After adding the digestion reagents, the bomb is tightly sealed and placed in the microwave oven for irradiation by microwave energy. Initial closed vessel research was undertaken in domestic multimode microwave ovens. Digestion vessels were often placed inside evacuated desiccators or large plastic jars to contain the evolved acid vapours and improve safety in the event of overheating. In order to prevent damage to the magnetron from reflected microwaves unabsorbed by small samples, an additional load (usually water) was commonly placed in the microwave oven. However, as these auxiliary loads reduce the amount of microwave energy reaching the sample, a constant and reproducible supply cannot be guaranteed. A further disadvantage of the use of domestic microwave ovens is that the power output of the magnetron is static, the output being controlled by cycling the magnetron off and on to obtain an average power level. Domestic ovens typically have a high time base, generally between 10 and 30 s. Hence, to obtain 50% power, the magnetron will only be on for half of the time base. This approach may prove undesirable for analytical work as significant heat losses can occur during the periods of zero

power output. As a result of the unsuitability of domestic ovens for use in analytical chemistry, a number of commercial systems have been specially developed to overcome the problems of acid fume damage, sample power reflection, field inhomogeneity, long time bases and safety.[29,63,75,79,168,169]

The major advantage of the closed microwave digestion technique is the high heating efficiency which can be obtained. Heating causes an increase in pressure, due to the evaporation of digestion acids and the gases evolved during the decomposition of the sample matrix. This is beneficial by increasing the boiling-point of the reagents, which aids the breakdown of the sample matrix. However, the excessive build-up of pressure, especially during the digestion of samples with a high organic content, can lead to the rupture of sealed vessels. For this reason, most digestion bombs are fitted with pressure relief valves, designed to open when the pressure becomes too great, and thus maintain safety. If venting does occur, sample losses are likely and owing to the reduction in acid vapours a less active digestion may result. Considerable research has therefore been undertaken to find ways of controlling or reducing pressure build-up during the digestion process.[31,34,42,47,92,101,112,120,123,128,187]

One method of avoiding excess pressure is to pre-digest the sample, and thus enable the gases evolved from the decomposition of easily oxidised organic matter to escape before commencing the closed digestion procedure. This may be carried out by leaving the samples to pre-digest at room temperature, often overnight.[31,45,47,49,75,80,92,112,123,128] However, if high sample throughput is required this extra step must be taken into account since a large number of digestion vessels will be required. Pre-digestion can also be carried out by microwave heating in an unsealed vessel, prior to the capping and digestion of the sample in the usual manner. Rhoades[49] pre-digested samples by heating for 1 h with a heat lamp. However, an important consideration is that the pre-digestion step should not be too lengthy since it may counteract the benefit of rapid digestion using microwave systems. Also, excessive evaporation of digestion reagents and volatile elements must be avoided. Reid *et al.*[47] overcame these problems by employing an open vessel heptane-cooled reflux pre-digestion step during which oxidation products could escape whilst retaining the analytes and digestion reagents for the ensuing closed digestion.

Heltai and Peresich[101] investigated the idea of controlling the vapour pressure by means of a water cooled spiral inserted into the closed space of the digestion bomb. During the digestion, the acid and water vapours evolved are condensed on the spiral, producing a reflux action which continuously renews the liquid phase over the sample for effective digestion. A different approach involves leaving the closed digestion to continue spontaneously after initial heating to induce the reaction. Using this method temperatures greater than 150 °C and pressures in excess of 150 lb in^{-2} were achieved, sufficient, for example, to digest NIST Bovine Liver.[120]

Another technique reported in order to control pressure build-up is to monitor the pressure or temperature throughout the course of the reaction and subsequently apply microwave power only when the readings are below the required level. In this way the pressure can be controlled, thus minimising venting of the digestion vessel. One commercial company has achieved this by placing a pressure transducer inside one of the digestion vessels to monitor the pressure continuously.[34] Other workers have taken temperature measurements using a non-invasive infrared probe attached to the bottom of the microwave oven.[42] In this case the output from the probe is fed to a computer which switches the magnetron on and off to achieve a pre-set temperature–time programme. The technology for monitoring the temperature or pressure of the digestion offers the potential to produce far more reproducible and controllable procedures.

Table 1 Microwave digestion procedures for biological samples

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Biological tissues	Se	Prolabo (Paris, France) Microdigest 301 (200 W)	Open focused HNO_3–H_2O_2 digestion for 20 min ($n = 1$)	FI-CSV	Good recoveries were obtained for Se in BCR Lyophilised Pig Kidney	10
Marine biological tissues	As	Prolabo A320 (200 W)	Solubilisation: HNO_3 open focused digestion for 10 min. Mineralisation: HNO_3–H_2SO_4–HNO_3–H_2O_2 digestion for 70 min	ICP-MS and HPLC–ICP-MS	Good results were obtained for total arsenic in BCR Cod Muscle after both solubilisation and mineralisation procedures	11
Biological tissues and botanical samples	Se	Prolabo Microdigest A301 (200 W)	Open focused HNO_3 digestion for 20 min, followed by addition of H_2O_2 and further heating for 25 min ($n = 1$)	Se^{VI} is reduced to Se^{IV} prior to analysis by GC-MS	Good agreement with certified values for NIST Bovine Liver and Mixed Diet (Finland), although for NIST Total Diet results were slightly low. Procedure was quicker than a conventional method without needing $HClO_4$	12
Fat-rich foods	Cu, Fe, Ni, Zn	Prolabo Microdigest M300 (200 W) and domestic oven (700 W)	Closed: HNO_3–H_2O_2 PTFE bomb digestion for 20 min. Open focused: HNO_3–H_2SO_4–HNO_3 digestion for 25 min ($n = 1$)	FAAS and ETAAS (for Ni)	For the closed digestion, reasonable agreement was obtained with results from a wet pressure autoclave digestion method (for soybean flour and linseed samples). However, results were generally low for the open microwave method	13
Foods	N	Prolabo Maxidigest MX-350 (350 W)	Open focused H_2SO_4–H_2O_2 Kjeldahl nitrogen digestion for 20–45 min depending on food type ($n = 1$)	NH_3 titration	Substantial time savings over conventional methods were demonstrated, without the need for a catalyst. However, for new matrices each step of the procedure must be re-optimised separately	14
Cereals and cereal products	Cd, Cu, Pb, Se	Prolabo Microdigest A301 and CEM (Buckingham, UK) MDS-2000 (630 W)	(a) Open focused HNO_3–H_2O_2 digestion for 17 min ($n = 1$). (b) Closed HNO_3 digestion for 60 min ($n = 12$)	ETAAS	Generally good results were obtained for the open and closed methods for BCR Brown Bread, NRCCRM Wheat and Rice Flour, CGC Whole Wheat and NIES Rice Flour, Corn Bran, Durum Wheat Flour, Hard Red Spring Wheat Flour, Soft Winter Wheat Flour, Rice Flour and Wheat Flour	15
Marine biological tissues	As, Cd, Cu, Mg, Mn, Ni, Sr, Zn	Prolabo Microdigest A301	Open focused HNO_3 digestion for 17 min, followed by 20 min cooling and further heating with H_2O_2 for 5 min ($n = 1$)	ICP-MS	Generally good results were obtained for NRCC LUTS-1, DORM-1 Dogfish Muscle, DOLT-2 Dogfish Liver and TORT-1 Lobster Hepatopancreas, except for high As and Ni	16
Marine biological tissues and botanical samples	Cd	Prolabo Microdigest A301	Open focused HNO_3–H_2O_2 digestion for 42 min	ETAAS	Good results were obtained for NIST Wheat Flour and Bovine Liver, although for IAEA Fish Flesh Homogenate results were slightly low. Acceptable agreement with results from a conventional wet digestion was obtained for bovine muscle, bovine liver, oyster, barley straw, cabbage, carnations, oak leaves, pine needles, apple-fruit and grass meal	17
Biological tissues	Bi, Cd, Co, Cs, Cu, Fe, Hg, Mn, Mo, Pb, Rb, Sb, Sn, Sr, Tl, Zn	Prolabo Microdigest A301 and Milestone (Sorisole, Italy) MEGA 1200 (1200 W)	HNO_3–H_2O_2 digestion. Closed vessel: 26.5 min. Open focused: 45 min	ICP-MS	Open focused: good results were obtained for NIST Bovine Liver, except for low Cu, Sr and Zn. Closed vessel: Good results were obtained, except for low Cd, Pb and Sr	18
Biological tissues	As, Ba, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, P, Pb, Sr, Zn	Prolabo Microdigest M300 and Floyd (Lake Wylie, SC, USA) RMS-150 (600 W)	Open focused vessel: HNO_3–H_2SO_4–H_2O_2–NH_4EDTA digestion for 30 min ($n = 1$). Closed vessel: HNO_3 digestion for 32 min	ICP-AES and residual carbon content analysis.	Generally good results were obtained for the open digestion of NIST Bovine Liver and Oyster Tissue, IAEA Horse Kidney and NIES Mussel Tissue, although low Na recoveries were slightly low. The residual carbon content of digests following the open method were far superior to those from the closed system	19
Tea leaves	Al, Ba, Ca, Cu, K, Mg, Mn, Zn	Prolabo Microdigest 301	Open focused HNO_3–$HClO_4$ digestion for 35 min ($n = 1$)	ICP-AES	Good agreement with the certified values for NIES Tea Leaves was obtained	20

Table 1 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Marine biological tissues	As	Prolabo Microdigest 301	On-line system incorporating HPLC separation; potassium persulfate–NaOH oxidation and L-cysteine pre-reduction of As species in fish samples following enzymatic extraction	On-line analysis by HG–AAS. Total As can be determined by removal of the HPLC column from the system	The AsBet, DMA, MMA, As^V and total arsenic content of NRCC TORT-1 Lobster Hepatopancreas and DORM-1 Dogfish Muscle were determined by the on-line technique. Results for total arsenic were in good agreement with those obtained by ICP-MS analysis	21
Marine biological samples	As	Prolabo Microdigest 301	Open focused HNO_3–H_2O_2 digestion for 15 min ($n = 1$)	ICP-MS	Good results were obtained for As in NRCC DORM-1 Dogfish Muscle and TORT-1 Lobster Hepatopancreas	21
Marine biological tissues	Hg	Prolabo Microdigest 301	On-line digestion of 0.15% slurries (in 50% HCl), including Br^-–BrO_3^- oxidation of organomercury species	On-line analysis by CV-AFS	A recovery of 97% was obtained for a standard solution of methylmercury chloride. Results for Hg in NRCC DORM-2 Dogfish Muscle were in good agreement with the certified value	22
Marine biological tissues	Hg	Prolabo Microdigest 301	Open focused HNO_3–H_2O_2 digestion for 25 min ($n = 1$)	CV-AAS	Good results were obtained for Hg in NRCC DORM-2	22
Marine biological tissues	As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sr, Zn	Prolabo Maxidigest M401 (300 W)	Open HNO_3 or HNO_3–H_2SO_4 digestion for 20–100 min (depending on sample size) followed by evaporation to a volume of 1 ml	ETAAS	Samples of up to 8 g were successfully digested. Generally good results were obtained for NRCC TORT-1 Lobster Hepatopancreas and LUTS-1	23
Sewage sludge	Hg	Prolabo Microdigest 301	On-line digestion of slurries prepared in nitric acid	On-line Fl-CV-AFS	Good results were obtained for BCR Sewage Sludge (Domestic); however, results for BCR Sewage Sludge Amended Soil were slightly low	24
Marine biological tissues and botanical samples	Al, As, Cd, Co, Cr, Cu, Hg, Mg, Mo, Ni, Pb, Zn	Prolabo Microdigest A300 (200 W)	Open focused digestion with (a) HNO_3–H_2O_2, (b) HCl–HNO_3–H_2O_2, (c) HNO_3–H_2SO_4–H_2O_2	ICP-AES and ICP-MS	Good results were obtained for procedure (a) for BCR Spruce Needles (except low Al, Mg), White Clover, Cod Muscle (except low Hg) and Plankton (except high Hg and low Mn). Procedure (b) gave high As and low Mn, whereas procedure (c) gave low Hg results for BCR Cod Muscle. Results by (b) were generally low for BCR Plankton, except for Cd, Zn	25
Biological tissues	Sb^{III} and Sb^V	Prolabo Microdigest 301	Open focused digestion with (a) 1 M acetic acid (for Sb^{III}), (b) H_2SO_4–KI (for total Sb)	HG–AAS	Good results were obtained for total Sb in spiked calve liver samples. Sb^V was calculated as the difference between total Sb and Sb^{III}	26
Biological tissues	Hg	Prolabo Microdigest A301 and Superdigest (300 W)	Open: HNO_3–H_2SO_4–HNO_3–H_2O_2 digestion for 20 min ($n = 1$). Closed: HNO_3 digestion	CV-AAS	Good results were obtained for Hg in BCR Pig Kidney and IAEA Fish Tissue following both methods. For the open method, digestion with just HNO_3 and with HNO_3–H_2SO_4–HNO_3 resulted in low recoveries	27
Marine biological tissues	Hg	Prolabo Microdigest A301	Open focused microwave assisted extraction for 2 min ($n = 1$) with (a) 25% TMAH, (b) methanolic KOH	HG–CT–GC–ETAAS	Good results were obtained for total Hg and methylmercury in NRCC DORM-1 Dogfish Muscle and TORT-1 Lobster Hepatopancreas and in BCR CRM 463 Tuna Fish Muscle	28
Marine biological tissues	Cd, Cu, Zn	CEM MDS-81D (600 W)	HNO_3 low volume Teflon bomb digestion for 49 min ($n = 24$)	FAAS and ETAAS (for Cd)	Good results were obtained for Cu, Zn and Cd in NIST Oyster Tissue, NRCC DOLT-1 Dogfish Liver and TORT-1 Lobster Hepatopancreas, for Cu and Zn in NRCC DORM-1 and for Zn in NIST Albacore Tuna	29
Botanical samples	Ca, Cu, Fe, K, Mg, Mn, Na, P, Zn	CEM MDS-2100 (950 W)	HNO_3–HCl Teflon bomb digestion for 74 min ($n = 12$)	ICP-AES	Good results were obtained for K, Na, P and Pb in NIST SRM 1572 Citrus Leaves; however Ca, Cu, Mg and Zn results were slightly low and Fe was very low. Results for corn samples were compared with the package label claims of the supplier	30

Table 1 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Botanical samples	B, Se	CEM MDS-2000 (630 W)	Se: HNO_3–H_2O_2–H_2O PTFE bomb digestion for 30 min following pre-digestion for 4 h. B: HNO_3–H_2O_2 PTFE bomb digestion for 45 min following pre-digestion for 4 h ($n = 12$)	FAAS (for Se) and ICP-AES (for B)	Se recoveries for NIST Wheat Flour were: 23% with HNO_3, 30% with HNO_3–H_2O_2, 57% with HNO_3–H_2O_2 and 80% with HNO_3–H_2O_2–H_2O. B recoveries for NIST Apple Leaves were: 60% with HNO_3 and 66–96% with HNO_3–H_2O_2. Longer digestion times or adding HCl (for Se) did not increase recoveries	31
Botanical and sludge samples	Pb	CEM SpectroPrep (550 W)	On-line microwave digestion of slurried samples (prepared in 3 M HNO_3 for botanical and HNO_3–$HClO_4$–HF for sludge samples), 10 min per sample	Off-line analysis by ID–ICP-MS	Good results were obtained for Pb in NIST SRM 1547 Peach Leaves and SRM 2781 Domestic Sludge	32
Cocoa	Cu, Fe	CEM MDS-81	HNO_3 bomb digestion for 30 min ($n = 7$)	FAAS	The microwave digestion procedure was four times quicker than a conventional hot-plate method. Results from the two techniques were in good agreement	33
Biological tissues	Ca, Fe, Mg, Zn	CEM MDS-81	HNO_3 bomb digestion for 30 min ($n = 7$)	FAAS	Good results were obtained for Fe and Mg in IAEA Horse Kidney, however, Zn results were slightly high and Ca low	34
Biological tissues and botanical samples	Ca, Cd, Fe, Mg, Zn	CEM MDS-81	On-line stopped-flow digestion (for 5 min) of slurries (prepared in Triton X-100 and HNO_3)	Off-line analysis by AAS	Good Zn results were obtained in IAEA Horse Kidney, but those for Fe and Cd were low and Mg was high. The system was unsuitable for Ca determinations. Results for batch microwave digestion, on-line microwave digestion and hot-plate digestion of cocoa powder were in good agreement. Attempts at slurrying NIST Pine Needles, Oyster Tissue and Bovine Liver at concentrations needed for FAAS detection were unsuccessful	35
Biological tissues and botanical samples	Ca, Fe, Mg, Zn	CEM MDS-81	On-line digestion of HNO_3 slurries	On-line analysis by FAAS	Good recoveries and precision was obtained for the results of NIES Chlorella, Sargasso and Pepperbush and NIST Bovine Liver, although for NIES Mussel, precision was slightly high. At the maximum stable slurry concentration, Zn was not detectable by FAAS in Chlorella and Sargasso, nor was Ca in Bovine Liver	36
Marine biological tissues	Se	CEM MDS-81	HNO_3–H_2O_2 bomb digestion for 24 min followed by evaporation to near dryness (45 min)	ETAAS	Results for Se in lyophilised fish samples were in good agreement with those obtained by a slurry technique	37
Botanical samples	As, Se	CEM MDS-2000	H_2O–HNO_3–H_2O_2 PTFE bomb digestion for 25 min	HG–AAS	Good results were obtained for BCR FD8 Maize Leaves. Spike recoveries of 95 and 105% were obtained for As and Se, respectively	38
Botanical samples	Al, Ca, Cu, Cr, Fe, K, Mg, Mn, Si, Ti, Zn	CEM MDS-81D	Teflon PFA bomb digestion with (a) HNO_3–HCl, (b) HNO_3–HF–H_2O_2	FAAS and DCP-AES (for Cu)	(a) Good Ca, K, Mg, Mn and Zn results were obtained for NIST Citrus Leaves, Pine Needles and IAEA Mixed Diet, but those for Al, Cu and Fe were low. (b) Good results were obtained for Al, Fe and Mg in Citrus Leaves, but Cu results were slightly low	39
Bio-monitors	Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Zn	CEM MDS-2000	HNO_3–H_2O_2 PFA bomb digestion for 15 min (moss and rye grass) and 17 min (humus and hay) ($n = 10$)	FAAS and ETAAS	Good results were obtained for BCR 281 Rye Grass and IAEA V-10 Hay, except for low Fe recoveries. Moss and humus samples were also successfully digested	40
Botanical samples	Ca, Cu, Fe, K, Mn, Mg, Na, P, Zn	CEM MDS-81D	PTFE bomb digestion for 60 min ($n = 12$) with (a) HNO_3 and (b) HNO_3–H_2O_2	AAS and AES (for Na and K)	No significant difference was observed between the results of the two microwave procedures, a conventional dry ashing and a wet ashing technique for lucerne leaves	41
Botanical samples	Ba, Ca, Cu, Mg, Mn, Zn	CEM MDS-81 with IR probe	HNO_3–HF PTFE bomb digestion for 20 min ($n = 6$)	ICP spectrometry	Good results were obtained for NBS Citrus Leaves, except for slightly low Cu	42

Table 1 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Food samples	Na	CEM MDS-2000	PTFE bomb HNO_3–H_2O_2 digestion for 1.5 h ($n = 12$)	AAS, CIE and IC analysis	No CRMs were analysed	43
Sewage sludge	Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sn, Tl, V, Zn	CEM MDS-81D	Closed vessel HNO_3–50% HCl digestion for 20 min	ICP-AES	Results were presented for the acid leachable metals in NIST SRM 2781 Domestic Sludge and used to derive reference values for the sample. Generally results compared well with those of an open vessel hot-plate digestion method. Spike recoveries of 89–120% were obtained for the microwave method	44
Biological tissues and botanical samples	B	CEM MDS-81D	H_2O_2–HNO_3 Teflon bomb digestion for 10 min, following having left samples to pre-digest at room temperature for 10 min	ICP-MS	Generally good results were obtained for B in NIST SRM 1515 Apple Leaves, SRM 1547 Peach Leaves, RM 8433 Corn Bran and RM 8414 Bovine Muscle. Spike recoveries of 90–109% were obtained	45
Botanical samples	As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Tl, V, Zn	CEM MDS-81D	HNO_3 Teflon bomb digestion (18 min) followed by 21 min heating with HF. H_2O_2 is then added and heating continued in a water-bath (15 min) before adding H_3BO_3 for a further 5–10 min heating ($n = 12$)	AAS and ICP-AES	Reasonable agreement with the certified values for NIST SRM 1547 Peach Leaves was obtained, except for low Ba. The method was also used to digest corn leaves	46
Botanical samples	Mn	CEM MDS-81D	HNO_3 Teflon PFA bomb digestion (a) without pre-digestion; (b) with pre-digestion at room temperature (18 h); (c) with microwave pre-digestion and reflux (7 min); (d) with microwave pre-digestion without reflux	FAAS	No significant differences were observed between the results obtained for sweet bay powder by each of procedures (a) to (d). Procedure (c) permits a fast, safe digestion without large evaporation of acids in the pre-digestion step	47
Food samples	Decomposition products	CEM MDS-81D	Bomb digestion with HNO_3, HNO_3–H_2O_2 or HNO_3 followed by H_2O_2–$HClO_4$ treatment on a hot-plate.	Carbon content analysis, IR, TLC	Results illustrated the necessity of employing different sample decomposition methods according to the sample matrix and analytical technique of choice	48
Botanical samples	As, B, Ba, Be, Bi, Ca, Cd, Co, Cu, Cr, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Sr, Te, Zn	CEM MDS-2100	After adding HNO_3 samples are allowed to stand for 35–40 min, heated at 80 °C with a heat lamp (1 h), cooled and capped. Microwave energy is applied in three steps (total 3.5 h, $n = 5$) with cooling and venting between steps. After cooling samples are evaporated at 80 °C under N_2 purge for 4 h	ICP-AES	Generally good results were obtained for NIST SRM 1547 Peach Leaves, 1571 Orchard Leaves and 1572 Citrus Leaves	49
Biological tissues	Ca, Cu, Fe, K, Mg, Mn, P S, Zn	CEM MDS-81D	After initial closed heating with HNO_3–H_2O_2 the digestion is allowed to continue spontaneously without further irradiation	ICP-AES and FAAS	Good recoveries were obtained for Ca, Fe, K, Mg, Mn and S in NIST Bovine Liver. P, Zn and Cu results were just outside the certified range. The heating time required depended on the sample size and amount of H_2O_2 used	50

Table 1 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Sludge samples	As, Se	CEM MDS-81D	PFA bomb digestion for 1–2 h with (a) HNO_3 –HCl, (b) H_2O_2–HCl–H_2SO_4, (c) H_2O_2–H_2SO_4, (d) HNO_3–H_2SO_4	FI–HG–AAS	Method (d) gave the best recoveries (validated using NIST San Joaquin Soil, see Table 2). Good results were obtained for As, but Se recoveries were slightly high. For NIST Domestic Sewage Sludge results agreed well with those of a conventional reflux method, but the microwave method was faster and $HClO_4$ was not required	51
Marine biological tissues	As, Cd, Pb	CEM MDS-2000	HNO_3 Teflon PFA bomb digestion for up to 2 h depending on the sample ($n = 12$)	ICP-AES and ICP-MS	Good results were obtained for NRCC TORT-1 Lobster Hepatopancreas and DORM-1 Dogfish Muscle, except for high As in the former. Spike recoveries were in the range 75–117%.	52
Botanical samples	Ca, Fe, K, Mg, Mn, P, S	CEM MDS-2000	Closed digestion with (a) HNO_3–$HClO_4$ for 1 h 23 min, (b) HNO_3–H_2O_2	ICP spectrometry	Generally good results were obtained for NIES Citrus Leaves, Pine Needles and Corn Leaves	53
Marine biological tissues	Ag, As, Cd, Cr, Cu, Ni, Pb, Zn	CEM SpectroPrep system and Floyd RMS-150	On-line: 0.5% m/v slurries were digested in 20% HNO_3–3% H_2O_2. Batch: Teflon bomb HNO_3–HF digestion for 70 min with cooling step half way through	ID–ICP-MS (standard additions) and ETAAS (for As and Cr)	On-line system: good results were obtained for NRCC LUTS-1 for Cd, Cu, Ni and Pb (Ag and Cr very high). For lobster hepatopancreas, results were in agreement with the closed vessel technique. Slurries of Pacific oyster tissue were not amenable to direct uptake by the SpectroPrep system unless prior digestion was undertaken	54
Botanical samples	Al, B, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, P, S, Sr, Zn	CEM MDS-81D	HNO_3–HF closed digestion for 37 min (including time for cooling steps) followed by open heating with H_2O_2 and SiO_2 for 30 min	ICP-AES	Generally good results were obtained for NIST SRM 1515 Apple Leaves, 1547 Peach Leaves, 1573a Tomato Leaves and 1575 Pine Needles	55
Biological tissues	Al	CEM MDS-81D	HNO_3–HF digestion for 30 min followed by cooling, addition of H_2O_2 and H_3BO_3 and evaporation to dryness for 30 min ($n = 12$)	ICP-AES	Good results were obtained for NIST SRM 1566a Oyster Tissue and NIES 1577b Bovine Liver. However following digestion with HNO_3–$HClO_4$ and HNO_3–H_2O_2 low results were obtained in the former. Spike recoveries of 95–96% were obtained in crab and shrimp meat samples	56
Biological tissues	B	CEM MDS-81D	HNO_3 closed digestion for 35 min followed by cooling, addition of H_2O_2 and evaporation for 30 min	ICP-AES	Spike recoveries of 95–100% were obtained in five meat samples and in NIST Oyster Tissue and Bovine Liver (CRMs not certified for B)	57
Marine biological tissues	Cd, Pb	CEM MDS-2000	HNO_3 digestion for 20–25 min ($n = 12$)	ETAAS	Good results were obtained for Cd and Pb in NRCC DORM-1 Dogfish Muscle	58
Marine biological tissues	Hg	CEM MDS-2000	HNO_3 PTFE bomb digestion for 70 s	CV-AAS	Results were in good agreement with the certified value for NIST RM 50 Albacore Tuna and spike recoveries of 99–102% were obtained	59
Marine biological tissues	As, Cd, Co, Cr, Cu, Hg, Pb, Zn	CEM MDS-81D	HNO_3 Teflon bomb digestion for 2 min followed by preconcentration on a Chelex-100 column	NAA and ETAAS	Good results were obtained for NRCC DORM-1 Dogfish Muscle	60
Biological tissues and botanical samples	Al, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, Zn	CEM MDS-2000	Closed TMAH–EDTA ammoniacal leaching procedure for 30 min with prior stirring step (10 min)	FAAS and ETAAS	Variable results were obtained for NIST SRM 1577b Bovine Liver, NIST SRM 1515 Apple Leaves and NIES CRM No. 1 Pepperbush, No.3 Chlorella, No. 6 Mussel and No. 7 Tea Leaves	61
Marine biological tissues	Hg	Milestone MLS-1200 (1200 W)	HNO_3–H_2O_2 bomb digestion for 6 min	FI–CV-AAS	Good results were obtained for Hg in NRCC DORM-1 Dogfish Muscle	62

Table 1 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Botanical samples	Lanthanides and actinides	Milestone MLS-1200	HNO_3–H_2O_2 PTFE bomb digestion for 14 or 26 min depending on sample size	ICP-MS	Good results were obtained for Ce, Eu, Sm, Tb and ^{238}U in NIST Apple Leaves, but those for ^{232}Th were low. For NIST Orchard Leaves, results were low for ^{232}Th and slightly low for ^{238}U	63
Sewage sludge samples	COD	Milestone MLS-1200	On-line $K_2Cr_2O_7$–H_2SO_4 oxidation (3 min)	FI spectrophotometric detection	Results were in good agreement with those of the standard COD method for sewage samples	64
Marine biological tissues	As	Milestone MLS-1200	HNO_3–H_2O_2 Teflon bomb digestion for 12.5 min	FI–HG–AAS	Recoveries of $13 \pm 10\%$ and $2 \pm 1\%$ were obtained for As in BCR 278 Mussel Tissue and BCR 422 Cod Muscle due to incomplete oxidation of organoarsenicals. Results were compared with those obtained from high-pressure ashing and dry ashing procedures	65
Marine biological tissues	Hg	Milestone MEGA-1200	HNO_3–H_2O_2 closed digestion procedure	FI–CV–AFS	Good agreement with the certified value was obtained for Hg in NRCC DORM-1 Dogfish Muscle and DOLT-1 Dogfish Liver	66
Biological tissues	Ru	Milestone MLS-1200	HNO_3–H_2O_2 PTFE bomb digestion of homogenised samples (in water) for 30 min	ETAAS	Spike recoveries of 95–101% were obtained for liver and kidney samples, but no CRMs were analysed	67
Duck eggs	Cu, Cd, Pb	Milestone MLS-1200	HNO_3–H_2O_2 Teflon bomb digestion for 10 min	FAAS	Recoveries of 82–101% were obtained in egg albumen and yolk samples	68
Biological tissues and botanical samples	B, Cd, Cu, Fe, Mn, P, Pb, Zn	Milestone MLS-1200 MEGA and domestic oven (665W),	Teflon bomb digestion with (a) HNO_3, (b) HNO_3–HF–hot-plate evaporation to dryness–HNO_3, (c) HNO_3–H_2O_2, (d) HNO_3–$HClO_4$	ICP-AES, FAAS, ETAAS	(a) Poor precision. Generally high P and low Fe results were obtained for Comité Inter-Instituts botanical reference materials. (b) Acceptable precision. Fe results were improved but most still outside certified range. (c) and (d) mixed Fe, Cu, Mn, Zn results for NIST Total Diet, NIES Mussel, Pepperbush and BCR Wholemeal Flour (many results too high)	69
Biological tissues	As, Cd, Co, Cu, Fe, Hg, Mg, Mn, Mo, Pb, Se, V, Zn	Milestone MLS-1200 MEGA	HNO_3 digestion (38 min) in dual PTFE containers for sample sizes of 35–45 mg ($n = 20$)	ICP-MS	Good results were obtained for all elements studied in NIST Bovine Liver. Good results were also obtained for As in IAEA MA-A-2 Fish Flesh, however Cd, Cu, Hg, Se and Zn were slightly low	70
Rice flour	Cd, Cr, Fe, Pb	Milestone MLS-1200 MEGA	Closed digestion with (a) HNO_3 for 8 min, (b) HNO_3 for 8 min. Then cool, add HF and $HClO_4$ and heat to dryness at 100 °C. HNO_3 is then added and the sample heated to near dryness	ID–ICP-MS following removal of the Ca matrix by passage through a microcolumn	(a) For the rice flour reference materials NIST SRM 1568, NIES 10a and KRISS A and B, good Cd results were obtained. However, Fe and Cr were low. (b) Good results were obtained for Cr and Fe in the above samples.	71
Biological tissues and botanical samples	Ca, Cu, Fe, K, Mg, Mn, Na, P, Zn	Milestone MLS-1200	HNO_3–H_2O_2 PTFE bomb digestion	ICP-AES and AAS	For NBS Orchard Leaves, Bovine Liver and Spinach low Fe but good Cu, Mn, Na, P and Zn results were obtained. Some Ca, K and Mg recoveries were slightly low	72
Almond kernels	Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Zn	Milestone MLS-1200 MEGA	HNO_3–H_2O_2 Teflon bomb digestion for 22 min ($n = 6$)	ICP-AES	The elemental composition of the kernels of 19 almond cultivars from different origins was determined to investigate the influence of the cultivar on the mineral composition of the sample	73
Marine biological tissues and botanical samples	Al	Milestone MLS-1200	Teflon bomb HNO_3–H_2O_2 digestion for 23 min ($n = 3$)	ETAAS	Good results were obtained for NIST Wheat Flour, but those for Rice Flour were slightly high. Reasonable agreement with the informational values for Total Diet and IAEA Fish Tissue were obtained. The addition of HF to the digestion did not increase recoveries	74

Table 1 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Marine biological samples	Si	Floyd RMS 150 (850 W)	HNO_3–H_2O_2–HF Teflon bomb digestion for 30 min, after having left samples to predigest overnight. HF is neutralised with H_3BO_3	A tertiary amine mixture is added before ICP-AES analysis	Good results were also obtained for NIST 1566 Oyster Tissue. Results were also in acceptable agreement with those obtained by a $LiBO_2$ fusion procedure for a range of food samples	75
Marine biological tissues and botanical samples	As	Floyd RMS 150	HNO_3–H_2O_2 bomb digestion for 32 min ($n = 6$)	ICP-MS	Good results were obtained for NIST Oyster Tissue and Orchard Leaves	76
Marine biological tissues	Ag, Al, As, Cd, Cr, Co, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sn, Th, Zn	Floyd	HNO_3–HF digestion for 42 min, followed by cooling, re-heating for 42 min, evaporation to dryness on a hot-plate (with/without H_2O_2) and re-dissolution in HNO_3/H_2O	ID–ICP-MS and ICP-MS	Good results were obtained for Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sn, Th and Zn in NRCC DORM-2 Dogfish Muscle and DOLT-2 Dogfish Liver	77
Marine biological tissues and botanical samples	Ca, Cu, Fe, Zn	Floyd RMS-150	21 different digestion procedures using HCl–HNO_3–HF in different ratios	DCP-AES	The most suitable procedure was chosen by fractional factorial design. For this procedure, good results were obtained for NRCC TORT-1 Lobster Hepatopancreas and NIST Pine Needles (Ca and Fe only). Spike recoveries of 96–105% were obtained. A detrimental effect of *aqua regia* was reported (HNO_3 and HCl most effective in equal quantities)	78
Biological tissues and botanical samples	As, Cd, Co, Cu, Ni, Pb	PMD, Paar (Graz, Austria)	Quartz tube closed HNO_3–$HClO_4$ digestion (procedure is dependent on the sample)	DP-ASV and HG–AAS (for As)	Mixed results were obtained for Cd, Cu and Pb in BCR Bovine and Cod Muscle, Bovine Liver, Mussel Tissue and Brown Bread. Results for Co in NRCC TORT-1 Lobster Hepatopancreas were good but were slightly low for Ni. For the determination of As in fish and cooking oil (by HG–AAS) addition of H_2SO_4 was needed. Good As results were obtained for BCR Cod Muscle, Mussel Tissue, NIST Orchard Leaves and NRCC TORT-1 Lobster Hepatopancreas	79
Botanical samples	Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, Th, U, V, Zn	Questron (Mercerville, NJ, USA) Q-Wave 1000	HNO_3 PFA bomb digestion for 30 min, after leaving samples to pre-digest overnight ($n = 12$)	ICP-MS	Reasonable agreement with the certified values was obtained for NIST SRM 1515 Apple Leaves and 1547 Peach Leaves, although some results were too high and some too low	80
Biological tissues and botanical samples	Ni	Domestic oven (700 W)	HNO_3–HCl PTFE bomb digestion for 14 min ($n = 3$)	ICP-AES analysis after extraction of Ni complex formed with DPTH into butan-1-ol	Generally good agreement with certified values for BCR Olive Europea, Lagarosiphon Major, Platihpnidium Ripariodides; NRCC DORM-1 Dogfish Muscle, DOLT-1 Dogfish Liver, TORT-1 Lobster Hepatopancreas; NIST Citrus Leaves; BCR Pig Kidney and Bovine Muscle	81
Marine biological tissues and botanical samples	Ni	Domestic oven (700 W)	HNO_3–HCl PTFE bomb digestion for 14 min ($n = 3$)	ICP-AES analysis after extraction of Ni complex formed with BPTH into IBMK	Good agreement with the certified values was obtained for NIST Citrus Leaves, NRCC DORM-1 Dogfish Muscle and NRCC TORT-1 Lobster Hepatopancreas	82
Marine biological tissues	Al	Domestic oven (800 W)	On-line HNO_3 digestion of slurries (in 0.2% HNO_3)	Off-line analysis by ETAAS	90% recovery for Al in NIST SRM 1566a Oyster Tissue was obtained. Five fresh shellfish samples were also analysed	83

Table 1 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Marine biological tissues	Se	Domestic oven (800 W)	On-line digestion of slurries (in 0.2% HNO_3) for 4 min (stopped flow)	Off-line analysis by ETAAS	Good results were obtained for NIST SRM 1566a Oyster Tissue. No significant differences were observed between the results obtained for lyophilised and unlyophilised samples	84
Botanical samples	Hg	Domestic oven (800 W)	HNO_3 PTFE bomb digestion for 3 min at 800 W ($n = 5$)	FANES after reduction with $SnCl_2$ and *in situ* preconcentration	Good agreement with certified values for NIST Citrus Leaves and Pine Needles was obtained	85
Sewage sludge	Cd, Cr, Cu, Ni, Pb, Zn	Domestic oven (662 W)	On-line digestion of 0.2–0.75% m/v slurries prepared in 1.5 M HNO_3	On-line ICP-AES analysis	Generally good results were obtained for BCR Sewage Sludge Industrial	86
Biological tissues	Cu, Fe, Zn	Domestic oven (700 W)	HNO_3–H_2O_2 open digestion for 14 min ($n = 100$)	FI–AAS	Good results were obtained for Cu, Fe and Zn in NBS Bovine Liver and for Zn in BCR Bovine Muscle, although results for Fe and Cu were just outside the certified range	87
Biological tissues and botanical samples	Pb	Domestic oven (700 W)	On-line HCl–HNO_3 digestion of samples (dispersed in Triton X-100 solution)	On-line analysis by FI–ETAAAS	Good results were obtained for BCR Bovine Muscle, Pig Kidney and NIST Bovine Liver. For NIST Pines Needles and BCR Olea Europea results were slightly low	88
Fruit slurries and juices	Pb	Domestic oven (650 W)	On-line HNO_3 digestion of liquid and slurried samples (dispersed in Triton X-100)	On-line analysis by FI–HG-AAS	No significant differences were observed for the results obtained by FI–MW–HG-AAS and a conventional Al heating block digestion (ETAAS analysis)	89
Food and feed crops	Pb	Domestic oven (600 W)	HNO_3 PTFE bomb digestion with V_2O_5 catalyst for 90 s	ETAAS	Good results were obtained for NIST Citrus Leaves	90
Fruit slurries	Cd, Cu, Fe, Pb, Se	Domestic oven (600 W)	HNO_3 PTFE bomb digestion with V_2O_5 catalyst for 90 s	ETAAS	Results were in good agreement with those obtained by a slurry procedure	91
Marine biological tissues	Hg	Domestic oven (700 W)	HNO_3 PTFE bomb digestion for 20 min after leaving samples overnight to partially digest ($n = 10$)	CV-AFS, ICP-MS and ID-ICP-MS	Results obtained after analysis by CV-AFS, ICP-MS (standard additions) and ID-ICP-MS (spike added prior to overnight digestion) were in good agreement with the certified values for BCR Cod Muscle	92
Botanical and sewage sludge samples	Cu, Mn	Domestic oven (650 W)	On-line digestion of HNO_3–H_2O_2 slurries for 2 min (botanical) and 4 min (sewage sludge)	On-line analysis by FAAS	Good results were obtained for Mn in NIST Tomato Leaves. For CBR Sewage Sludge–Domestic and Industrial results were generally in good agreement with the certified values	93
Botanical samples	Co, Cr, Ni	Domestic oven (800 W)	On-line microwave digestion of slurries prepared in 5% HNO_3	Off-line analysis by ETAAS	Good results were obtained for Cr and Ni in NIST Citrus Leaves. Results for Co, Cr and Ni in vegetable samples were compared with those obtained by direct slurry analysis and by a dry ashing method	94
Botanical and sewage sludge samples	Cr	Domestic oven (650 W)	*Aqua regia*–H_2O_2 PTFE bomb digestion	ETAAS	Good results were obtained for Cr in NIST Tomato Leaves and Citrus Leaves. Results were also in agreement with the informational value for BCR Sewage Sludge. Spike recoveries of 98–103% were obtained	95
Biological tissues and sewage sludge samples	Cd	Domestic oven (650 W)	Biological: closed vessel HNO_3 (14 M)–H_2O_2 digestion (12.5 min) Sludge: closed vessel *aqua regia*–HF–H_2O_2 digestion followed by H_3BO_3 treatment	ETAAS	Good results were obtained for BCR Pig Kidney, BCR Sewage Sludge Domestic and for MA-M-2/TM Mussel Tissue (IAEA)	96
Marine biological, botanical and sewage sludge samples	Ni	Domestic oven (1100 W)	*Aqua regia*–HF–H_2O_2 PTFE bomb digestion for 12 min (4 steps) with cooling between each step. After adding H_3BO_3 the sample is heated in a boiling water bath for 10 min	ETAAS	Good results were obtained for Ni in NIES No.10c Rice Flour (unpolished), IAEA No. 325 Mussel Tissue, BCR CRM 143R Sewage Sludge Amended Soil and in CRM 144 Domestic Sewage Sludge	97

Table 1 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Botanical and sewage sludge samples	Cu, Mn, Pb, Zn	Domestic oven (650 W)	Slurries (prepared in HNO_3) are merged on-line with H_2O_2 and digested at 100% power	On-line FAAS	Results were in good agreement with the certified value for Mn in NIST Tomato Leaves, for Cu, Mn and Pb in CBR Sewage Sludge–Industrial and for Pb in Sewage Sludge–Domestic. Results were poor for Cu and Mn in Sewage Sludge–Domestic and for Zn in both sewage CRMs	98
Biological tissues and botanical samples	B	Domestic oven	HNO_3–H_2O_2 PTFE bomb digestion for 1 h ($n = 2$)	Photometry, fluorimetry, ICP-MS and ICP-AES	Good results were obtained for NBS Tomato Leaves and Pine Needles, although recoveries for Bovine Liver were low	99
Marine biological tissues	Cd	Domestic oven	Closed digestion for 135 s ($n = 6$) with (a) HNO_3, (b) H_2SO_4 and (c) HNO_3–H_2SO_4. After cooling H_2O_2 is added, but no heating is applied	FAAS	Spike recoveries of (a) 95–107%, (b) 60–71% and (c) 73–89% were obtained. Digestion (a) was chosen for further study and used to digest NIST SRM 1566a Oyster Tissue. Good agreement with the certified value for Cd was obtained	100
Botanical samples	Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Zn	Domestic oven (550W)	HNO_3–H_2O_2 Teflon bomb digestion with water cooled spiral for 6 min ($n = 1$)	FAAS and FAES	Good results were obtained for Co and Cr in ISS/MMM certified Green Algae. Pb and Ni results were just outside the certified range. Acceptable results were obtained for the 'in-house' reference material Lucerne, except for Fe and Zn	101
Octocorals	Cd, Cu, Ni Pb, Zn	Domestic oven (600 W)	Microwave pre-drying (20–50 min) followed by HNO_3 digestion in pyrex tubes for 1 min (4–6 times) with cooling between steps	ETAAS and FAAS (for Zn)	Good recoveries were obtained for a synthetic CRM prepared from a mixture of 61% NIES Mussel and 39% $CaCO_3$. Eight octocoral species were also analysed	102
Biological tissues and botanical samples	Ca, Cu, Fe, Mg, Mn, Zn	Domestic oven (500 W)	HNO_3–$HClO_4$–HCl–HF PTFE bomb digestion (with polypropylene jacket) for 14 min ($n = 6$)	'One-drop' FAAS	Results were in good agreement with the certified values for NIST Bovine Liver, NIES Pepperbush and Mussel samples. For NIES Tea Leaves, Fe results were high and Ca low. Ca results were also low for NIES Sargasso	103
Botanical samples	Cd	Domestic oven	HNO_3–$HClO_4$–HCl–HF PTFE bomb digestion (with polypropylene jacket) for 9 min ($n = 6$), followed by hot-plate evaporation to dryness and dissolution in $HClO_4$	Fe was removed with HIPT in benzene and the Cd complex formed with APDC was extracted into chloroform for 'one-drop' FAAS analysis	Results were in good agreement with the certified values for NIES Pepperbush and Rice Flour (low and medium) and for NIST Pine Needles, Orchard and Citrus Leaves	104
Marine biological tissues	Se	Domestic oven (600 W)	HNO_3–H_2SO_4–H_2O_2 PTFE bomb digestion	Se^{VI} is reduced to Se^{IV}. The complex $Se(O)SO_3{}^{2-}$ is formed and analysed by DPP	Results were in good agreement with the certified value for Se in NIES No. 6 Mussel sample	105
Marine biological tissues	Se	Domestic oven (600 W)	PTFE bomb digestion with (a) HNO_3–H_2O_2, (b) HNO_3–H_2SO_4–H_2O_2, (c) HNO_3–H_3PO_4–H_2O_2, (d) HNO_3–$K_2S_2O_8$–H_2O_2	Se^{VI} is reduced to Se^{IV} for analysis by HG–AAS	Good results were obtained for NIES Mussel following digestion by procedure (b). Procedures (a), (c) and (d) gave low recoveries	106
Marine biological tissues	As	Domestic oven (700 W)	On-line potassium persulfate–NaOH oxidation, following HPLC separation of As species in sample extracts	On-line analysis by HG–AAS	As^V, MMA, DMA, arsenocholine and arsenobetaine levels were determined in a synthetic fish extract, although no CRMs were analysed. Spike recoveries of 96–110% were obtained	107
Marine biological tissues	As	Domestic oven (750 W)	Sample was heated with HCl–KI in a PTFE bomb for 8 min ($n = 1$). The distilled $AsCl_3$ was collected in hydroxylamine hydrochloride	HG–AAS	Good spike recoveries were obtained for inorganic arsenic in a mussel sample. However, organoarsenic compounds were not decomposed	108

Table 1 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Botanical samples	Ca, K, Mg, P, S	Domestic oven (750 W)	HNO_3–$HClO_4$ open digestion for 15–30 min depending on the sample ($n = 25$)	ICP-AES analysis	Good results were obtained for P in NBS Pine Needles and Citrus Leaves, although results for Ca and K in the former were slightly outside the certified range	109
Biological tissues	As	Domestic oven (650 W)	HNO_3–H_2SO_4–H_2O_2 PTFE bomb digestion	HG–AAS with a modified electrical heating system	Good results for As in NIST Bovine Liver and spike recoveries of 91–108% were obtained	110
Food samples	Bromide ions	Domestic oven	NaOH (0.5 M) bomb digestion for 4 min. After cooling, H_2O_2 is added and heating continued for a further 2 min ($n = 2$)	Ion-exchange chromatography (UV spectrometric detection), following cation exchange removal of Na	Bromide ions were determined in total diet samples. Spike recoveries of 87–119% were obtained in four different food samples	111
Marine biological tissues	Hg	Domestic oven (750 W)	HNO_3–H_2O_2 PTFE bomb digestion for 5 min, after leaving the sample to predigest overnight	CV-AAS	Good results were obtained for total Hg in NRCC DORM-1 Dogfish Muscle. Tuna fish samples were also analysed and spike recoveries of 91–93% were obtained	112
Marine biological tissues	As	Domestic oven (600 W)	HNO_3 PTFE bomb digestion with catalyst of V_2O_5 for 90 s	HG–AAS	Results were in good agreement with the certified value for BCR Mussel Tissue and spike recoveries of 93–101% were obtained	113
Marine biological tissues	Hg	Domestic oven (600 W)	HNO_3 bomb digestion of samples and standards for 90 s	CV-AAS	Good results for BCR Mussel Tissue and spike recoveries of 95–106% were obtained	114
Botanical samples	As	Domestic oven (600 W)	HNO_3 bomb digestion with catalyst of V_2O_5 for 90 s	HG–AAS	Results were in good agreement with the certified values for NBS Citrus Leaves	115
Total diet samples	Al, Ca, Cu, Fe, K, Mg, Na, P, Zn	Domestic oven (750 W)	Digestion (quartz vessel) with (a) HNO_3, (b) HNO_3–H_2O_2, (c) HNO_3–H_2SO_4, (d) HNO_3–HCl	ICP-AES	Good results were obtained for NIST Total Diet except for (a) slightly low K and Zn, (b) slightly low K, (c) slightly high P and slightly low Al, K and Zn	116
Marine biological tissues	As	Domestic oven	HNO_3 Teflon bomb digestion for 90 s	ETAAS	Good results were obtained for NIST Oyster Tissue	117
Biological tissues	Se	Domestic oven (650 W)	HNO_3 Teflon bomb digestion (3 min) followed by evaporation to dryness with $HClO_4$ (twice) and re-dissolution in H_2O	SW-CSV following reduction of Se^{VI} to Se^{IV}	Results were in good agreement with the certified values for NIST Bovine Liver (sample amount 5 mg)	118
Biological tissues and botanical samples	Ca, Fe, Mg, Zn	Domestic oven (800 W)	HNO_3 closed digestion for 7 min ($n = 2$)	ICP-AES	Good results were obtained for NIST 1577 Bovine Liver (except slightly high Mg and Zn) and for 1570 Spinach (except slightly low Ca and Fe)	119
Food samples	Al	Domestic oven	HNO_3 PTFE bomb digestion (32 min)	ICP-AES	Generally low results were obtained for total diet samples. Higher recoveries were obtained by a HNO_3–HF–HNO_3–$HClO_4$ digestion in a drying oven	120
Botanical samples	Cd, Cu, Pb, Zn	Domestic oven (850 W)	HNO_3–$HClO_4$ digestion in quartz crucible placed inside Teflon bomb for 29 min ($n = 4$) followed by hot-plate evaporation to dryness	DP-ASV	Good results were obtained for NIST Citrus Leaves, Lucerne P-alfalfa (Slovakia) and CL-1 Cabbage leaves (Poland) (except low Cu). Cu, Pb and Zn results were low for NIST Apple Leaves	121
Biological tissues and botanical samples	Cd, Cu, Pb, Zn	Domestic oven	HNO_3–$HClO_4$ digestion in quartz crucible placed inside Teflon bomb for 11 min ($n = 10$)	DP-ASV	Generally good results were obtained for CL-1 Cabbage Leaves (Poland), P-alfalfa Lucerne (Slovakia), BCR Rye Grass, SRM Apple Leaves, BCR and SRM 1577b Bovine Liver	122

Table 1 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Sewage sludge	Cd, Cr, Pb	Domestic oven	HCl–HNO$_3$ Teflon bomb digestion (20 min) following pre-digestion overnight	ETAAS	Good results were obtained for Pb and Cr in BCR Sewage Sludge (CRM 145R) but Cd results were slightly low	123
Biological tissues	Po	Domestic oven (650 W)	HNO$_3$ PFA bomb digestion (1h for plants and 2 h for animal tissue, $n = 4$), followed by evaporation to dryness and re-dissolution in HCl	Alpha spectrometry after plating on silver discs	A good level of precision for results was achieved with no loss of Po during the digestion	124
Marine biological tissues and botanical samples	Cd, Co, Cu, Ni, Pb	Domestic oven	HNO$_3$–HCl–HClO$_4$–HF PTFE bomb digestion	ICP-AES	Good Cu and Pb, but low Cd, Co and Ni results were obtained for NIES Pepperbush. Results were also good for Cd, Cu and Pb in Chlorella. For NIES Mussel, Cd, Co and Cu results were good, however Ni and Pb were low. Generally low results were obtained for NIES Tea Leaves	125
Marine biological tissues	Cd, Cu, Pb, Zn	Domestic oven	HNO$_3$ PTFE bomb digestion for 6.5 min ($n = 4$)	FAAS and ETAAS	Generally good results were obtained in NRC-D Dogfish (except low Cu), NRC-E Scallop (except low Cd) and NRC-F Swordfish (except low Cu)	126
Botanical samples	Co	Domestic oven	HNO$_3$–HCl bomb digestion for 10 min followed by hotplate evaporation to dryness	FI–spectrophotometric determination following complexation with PSAA	Results were in good agreement with the certified values for NIES Pepperbush	127
Biological tissues and botanical samples	Cd, Cu, Fe, Mn, Pb	—	Open HNO$_3$–H$_2$O$_2$-digestion, following having left the sample to pre-digest overnight	ETAAS	Generally good results were obtained for BCR Bovine Mussel, Olea Europea (except high Cu), Lagarosiphoumajur (except low Cu), Pig Kidney (except low Cu, Fe, Zn) and for NBS Citrus Leaves (except high Cu), Pine Needles (except low Pb) and Wheat Flour	128
Marine biological tissues	As	—	H$_2$SO$_4$–HNO$_3$–H$_2$O$_2$ closed digestion for 30 min	ICP-AES	A selection of fish and shellfish samples were analysed; however, no CRMS were included	129
Botanical samples	Al, Fe, Si	—	HNO$_3$–H$_2$O$_2$–HF digestion for 13 min	ICP spectrometry	UCD 155 (Avocado); 176 (Citrus); 124 (Barley Hulls) and 190 (Rice Straw) and NIST 1547 (Peach) samples were analysed	130
Food samples	Amino acids	—	Hydrolysis performed by heating with 6 M HCl in a closed vessel	—	The amino acid sequence obtained from microwave digestion and a conventional method were compared in bovine serum albumin and Durum wheat samples	131
Botanical samples	Phenolic acids	—	Teflon bomb NaOH digestion at 700 W for 90 s	HPLC	The liberation of β-ether bound phenolic acids from plant cell walls of maize, wheat, oilseed rape stems and barley was an order of magnitude more effective than with a dioxane—HCl procedure and as effective, but far quicker than high-temperature alkaline digestions	132
Botanical samples	P	—	HNO$_3$–H$_2$O$_2$–HCl digestion	ICP-AES	Results were in good agreement with the certified value for NIST Citrus Leaves	133
Biological tissues and botanical samples	Ag, Ba, Cd, Cs, Hg, Mo, Pb, Rb, Sb, Sn, Sr	—	HNO$_3$ PTFE bomb digestion for 40 min	ICP-MS	Good results were obtained for Ag, Mo, Pb and Rb in NIST Bovine Liver (Sr slightly high), for Rb in NIST Wheat Flour (Mo slightly high) and for Cd and Hg in BCR Pig Kidney	134
Marine biological tissues and botanical samples	Al	—	HNO$_3$ PTFE bomb digestion with seven heating steps (total 56 min), with cooling between each step	ETAAS	Results were in good agreement with the certified values for Al in NIES Mussel, NIST Citrus Leaves and Oyster Tissue. Spike recoveries of 92–104% were also obtained	135

Table 2 Microwave digestion procedures for geological samples

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Sediment samples	Hg	Prolabo Microdigest 301	On-line digestion of 0.15% slurries (in 50% HCl), including Br^-–BrO_3^- oxidation of organomercury species	On-line analysis by CV-AAS	A recovery of 97% was obtained for a methylmercury standard. Good results were obtained for Hg in NRCC PACS-1 Harbour Marine Sediment	22
Sediment samples	Hg	Prolabo Microdigest 301	Open focused HNO_3–H_2SO_4–H_2O_2 digestion for 10 min ($n = 1$)	CV-AAS	Results were in agreement with the certified value for NRCC PACS-1 Harbour Marine Sediment	22
Soil and sediment samples	Hg	Prolabo Microdigest 301	On-line digestion of slurries prepared in nitric acid	On-line FI–CV–AFS analysis	Good results were obtained for State Bureau of Metrology (China) Polluted Farm Soil and Canadian Centre for Mineral and Energy Technology Lake Sediment	24
Soil and sediment samples	As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Zn	Prolabo Microdigest A300 and CEM MDS-81D	(a) Closed vessel HCl–HNO_3–HF digestion. Open focused digestion with: (b) HNO_3–H_2O_2; (c) HCl–HNO_3–H_2O_2	ICP-AES and ICP-MS	Good results were obtained for BCR Amended Soil using procedure (b) and for Estuarine Sediment (except high Hg and Pb) using procedures (a) and (c)	25
Soil samples	Hg	Prolabo Maxidigest MX350 and CEM MDS-81D	Open and closed digestion with (a) 1 M HCl, (b) 50% HNO_3, (c) HNO_3, (d) *Aqua regia*	CV-AAS and ETAAS	For the open digestion, results were low for NIST Montana Soil whereas good results were obtained for the closed digestion [procedures (a), (b) and (d)]	136
Sediment samples	As	Prolabo A300 and CEM MDS-81D	Open focused digestion with (a) HCl–HNO_3–H_2O_2 for 35 min (total As), (b) HNO_3–HCl for 12 min (As speciation). Closed digestion with: (c) HNO_3–$HClO_4$–HF–HCl for 1h (total As)	ICP-MS and ICP-AES (for total arsenic) HPLC–ICP-MS (for As speciation)	In the lake sediment analysed, the As species DMA, MMA and As^V were stable during the microwave extraction procedure. As^{III} was oxidised to As^V, but this was reduced by extraction with orthophosphate or ammonium oxalate. An extraction yield for total As of 100% was obtained for the microwave extraction procedure (calculated as % of the yield obtained by the total As procedures)	137
Sediment samples	Hg	Prolabo Maxidigest (300 W)	On-line digestion of slurries prepared in *aqua regia*–$KMnO_4$	On-line analysis by FI mercury system	Good results were obtained for NIST Buffalo Sediment, although those for NRCC BCSS-1 Marine Sediment were slightly high. Good spike recoveries were also obtained	138
Soil samples	Cu, Fe, Zn	Prolabo Microdigest 301	Automated DTPA–$CaCl_2$–triethanolamine extraction using a robotic station (5 samples h^{-1})	Automated centrifugation and transport to FAAS	The extraction efficiency of Zn is comparable to the conventional technique, whereas a greater efficiency resulted for Fe and Cu	139
Sediment samples	Hg	Prolabo Microdigest A301	Open focused HNO_3 digestion for 5 min, followed by 5 min cooling and heating with H_2O_2 (5 min)	FI–ICP-MS	Good results were obtained for Hg in NRCC PACS-1 Harbour Marine Sediment, IAEA-356 and BCR S19 sediment samples. Samples from Arcahon Bay were also analysed	140
Dust and air filters	Pb	CEM SpectroPrep	On-line microwave digestion of slurried samples (prepared in 3 M HNO_3); 10 min per sample	Off-line analysis by ID–ICP-MS	Good results for Pb were obtained in NIST SRM 2676d Toxic Metals on Filters	32
Coal samples	Ca, Cd, Fe, Mg, Zn	CEM MDS-81	On-line stopped-flow digestion of slurries (in Triton X-100 and HNO_3) for 5 min per sample	Off-line analysis by AAS	Incomplete digestion of coal resulted	35
Soil samples	As, Se	CEM MDS-2000	H_2O–HNO_3–HCl–HF PTFE bomb digestion for 30 min	HG–AAS	Good results for MRG-1 silicated rocks (Canada Centre for Mineral and Energy Technology) and spike recoveries of 95% were obtained	38

Table 2 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Geological samples	As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Tl, V, Zn	CEM MDS-81D	HNO_3 Teflon bomb digestion (18 min) followed by 21 min heating with HF. H_2O_2 is then added and heating continued in a water-bath (15 min) before adding H_3BO_3 for a further 5–10 min ($n = 12$)	AAS and ICP-AES	Good results were obtained for NIST SRM 2704 Buffalo River Sediment, except for high Sb and Tl, slightly low Co and Cu and slightly high As, Cr and Mn. The method was developed to analyse fertilizers and soil amendments including rock phosphates, liming materials organic material and sandy loam soil	45
Soil samples	As, Se	CEM MDS-81D	PFA bomb digestion for 1–2 h with: (a) HNO_3–HCl, (b) H_2O_2–HCl–H_2SO_4, (c) H_2O_2–H_2SO_4, (d) HNO_3–H_2SO_4	FI–HG–AAS	Method (d) gave the best recoveries (validated using NIST San Joaquin Soil). Good results were obtained for As, but Se recoveries were slightly high. Method used to analyse sewage sludge (see Table 1)	51
Sediment samples	As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn	CEM SpectroPrep system	On-line digestion of 1% slurries (in 20% HF, 50% HNO_3 and 10% HCl)	ICP-MS, ICP-AES (for Fe and Al) and ETAAS (for As)	Good results were obtained for As, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn in NRCC BCSS-1 Marine Sediment, however, results for Cr and Al were low	54
Sediment samples	Hg	CEM MDS-2000	HNO_3 PTFE bomb digestion for 70 s	CV-AAS	Results were in good agreement with the provisional value for NIES No. 2 Pond Sediment	121
Phosphatic fertilisers and animal feedstuffs	As, B, Ba, Bi, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Se, Sb, V, W, Zn	CEM MDS-81D	PTFE bomb digestion with (a) HNO_3, (b) HCl–HNO_3–$HClO_4$–HF	ICP-MS	For NIST Buffalo River Sediment: (a) Results for As, Cd, Co, Cu, Ni and Pb were good, but those for Ba, Cr, Mn, Sb, V, Zn were low and Hg was high; (b) Results for As, Co, Cu and Ni were good; Ba, Hg and V results were better than for (a), but Ni, Zn and Sb were high and Cr low. Results for NBS Florida Phosphate Rock by procedure (a) generally agreed well with the certified and informational values	141
Sediment samples	Co, Cu, Mn, Pb, Zn	CEM MDS-81D	18 digestion procedures with different combinations of HNO_3, H_2O_2, HF and HCl	FAAS and L'vov platform (for Co)	PCA and multicriteria decision making methods PROMETHEE and GAIA selected an HCl–HNO_3–HCl digestion as the best for NBS Buffalo River Sediment	142
Sediment and rock samples	Co, Cr, Cu, Ni, Pb, Zn	CEM MDS-81D	14 digestion procedures with different combinations of HF, HNO_3, HCl, H_2O_2 and acetic acid	FAAS	PCA, SIMCA, PROMOTHEE, GAIA and Fuzzy Clustering chemometric techniques selected an HNO_3–HF digestion as the best procedure for NBS Buffalo River Sediment and 'In House' secondary rock standard	143
Sediment samples	Cd	CEM MDS-81D	HNO_3 Teflon bomb digestion for 80 min ($n = 12$)	ETAAS	Good results were obtained for NIST Sediments 1646 and 2704. Results were in good agreement with those obtained from a conventional HF–$HClO_4$ digestion undertaken in platinum crucibles	144
Sediment samples	Cr	(a) CEM MDS-81, (b) Floyd RMS-150, (c) Milestone MLS 1200 MEGA	HCl–HNO_3–HF–$HClO_4$ PTFE bomb digestion: (a) heated to 1200 psig, cooled and repeated ×2, (b) heated for 20 min at medium pressure, (c) heated for 26.5 min at high pressure. After cooling all samples were evaporated to dryness on a hot-plate and solubilised in HNO_3	FAAS and ICP-AES	Using procedure (b), results were obtained in agreement with the certified value for NIST SRM 2704 Buffalo River Sediment. A mean spike recovery (for all procedures) of 98% was obtained. However, low results were obtained for Cr in NRCC BCSS-1 Marine Sediment following procedures (a), (b) and (c) and also by an open hot-plate method. It was concluded that no acid dissolution procedures are adequate for the determination of Cr in this sample	145
Sediment samples	Cr, Cu, Hg, Mn, Ni, Pb, Zn	CEM MDS-81D	PTFE bomb digestion ($n = 12$) with (a) *aqua regia* (80 min), (b) *aqua regia*–HF (80 min)	AAS and CV-AAS (for Hg)	For procedure (a), results were generally low for NRCC MESS-1 Estuarine Sediment and PACS-1 Harbour Marine Sediment. Results were slightly improved after digestion by procedure (b), but most results were still not in good agreement with the certified values	146

Table 2 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Dust, ashes and sediments	Al, As, Ba, Be, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, S, Sb, Ti, V, Zn	CEM MDS-81D	Teflon PFA bomb digestion for 22 min (n = 6) with (a) HNO_3–HCl (acid soluble elements), (b) HNO_3–HCl–HF with H_3BO_3 neutralisation (total digestion)	ICP-AES	(a) Recoveries obtained for different elements in the range: NRCC MESS-1 Estuarine Sediment 25–103%, NRCC PACS-1 Harbour Marine Sediment 38–99%, NIST Coal Fly Ash: 60–103%, 'in-house' dust: 23–100%. (b) Good results were obtained for Coal Fly Ash (except low Co) and for MESS-1 (except low Ti). For PACS-1 results were good, except for Al, Fe, Ca, Mg, Ni and S (just outside certified range)	147
Sediment samples	As, Hg, Se	CEM MDS-81D	PFA bomb digestion with (a) H_2SO_4–HNO_3–HCl (As and Se), (b) HNO_3 (Hg)	FI–AAS (As and Se) and CV-AAS (Hg)	Good results were obtained for proposed NIST SRM 1646a Estuarine Sediment and SRM 2704 Buffalo River Sediment. Results were in good agreement with those of a traditional reflux digestion	148
Molybdenite mineral	Os	CEM MDS-81D	HNO_3–H_2SO_4 PTFE bomb digestion for 45 min followed by heating with $K_2Cr_2O_7$.	Os distillation prior to ICP-MS analysis	The technique was applied to Re–Os age determination in a natural molybdenite sample. Results were in agreement with those obtained by a U–Pb method for zircon (associated mineral)	149
Marine sediment samples	Al, Ca, Cr, Cu, Fe, Mn, Ni, Pb, Zn	CEM MDS-2000 and Milestone LAVIS-1000 multiMOIST microwave drying system	HNO_3 bomb digestion following microwave drying of the sample by the two methods (15 min)	ICP-AES and FAAS (for Pb)	No significant differences were found between the moisture content of marine sediment dried by traditional oven and vacuum microwave drying techniques. Similar results were obtained for the trace metal and total carbon content of marine sediments dried by the two methods	150
Geological samples	Ba, Be, Co, Cr, Cs, Cu, Hf, Mo, Ni, Nb, Pb, Rb, Sb, Sc, Sn, Sr, Ta, Th, Tl, U, W, Zn, Zr and REEs	CEM MDS-81D	PFA bomb HNO_3–HF–$HClO_4$ digestion for 63 min (n = 4), followed by hot-plate evaporation to dryness with $HClO_4$ and dissolution in HNO_3	ICP-AES and ICP-MS	Generally acceptable results were obtained for Ba, Be, Co, Cs, Cu, Ni, Nb, Pb, Rb, Sb, Sn, Sr, Ta, Th, Tl, U, W, Zn and for most of the REEs in a range of geological CRMs (sediments and rocks). The accuracy of Cr, Hf, Mo, Sc, Zr determinations varied with the sample type, whereas Y recoveries were low in the nine CRMs analysed	151
Geological samples	Au, Ir, Pd, Rh, Ru, Pt	CEM MDS-81D	(a) Low pressure HNO_3–HCl–HF–$HClO_4$ digestion. (b) High pressure *aqua regia*–HF digestion. Residues were fused with Na_2CO_3–Na_2O_2	ICP-MS	Procedure (a) was employed for the digestion of sulfide-rich samples and procedure (b) for silicate, sulfide and chromite samples. CRMs were also analysed	152
Airborne particulates on Teflon filters	Al, As, Ba, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, V, Zn	CEM MDS-2000	HCl–HNO_3–$HClO_4$–HF digestion (32 min) followed by open vessel evaporation of HF (25 min) (n = 12)	ICP-MS	Generally low results were obtained for NIST Urban Particulate Matter [accredited in part to the low mass of sample used (0.1 mg)]. Higher recoveries were obtained with a conventional pressure bomb digestion although the digestion time was 10 times higher	153, 154
Airborne particulates on glass-fibre filters	Al, Fe, K, Mg, S, Zn	CEM MDS-2000	HNO_3–$HClO_4$ PTFE bomb digestion for 9 min followed by cooling, removal of filter residue, heating with HF (9 min) and H_3BO_3 neutralisation of HF	ICP-AES	Recoveries of 90–101% were obtained for Al, Fe, K, Mg, S and Zn in NIST Urban Particulate Matter	155
Airborne particulate matter on filters	As	CEM MDS-2000	HNO_3–$HClO_4$ PTFE bomb digestion, followed by cooling, removal of filter and further heating with $HClO_4$–HF (total 18 min). HF removed by evaporation	ICP-MS	A recovery for As of 107.4% was obtained in NIST (SRM 1648) Urban Particulate Matter	156

Table 2 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Rock samples	59 major and trace elements	CEM MDS-2000	HNO_3–HF–$HClO_4$ Teflon bomb digestion for 0.5–1 h ($n = 9$). After cooling samples are transferred to beakers for hot-plate evaporation to dryness. HNO_3 is then added, and samples taken to dryness again	ICP-MS	Results were presented for 59 elements in Geological Society of Japan rock reference materials JB-1 Basalt, JB-3 Basalt, JG-1 Granodiorite, JR-2 Rhyolite, JGb-1 Gabbro and JA-2 Andesite	157
Sediment samples	Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, Se, Zn	CEM MDS-2000	HF–HCl–HNO_3 PTFE bomb digestion for 15 min ($n = 12$)	FAAS and ETAAS	Orthogonal array design was applied to the optimisation of digestion parameters. Generally good results were obtained for NBS Buffalo River Sediment, NRCC BCSS-1 Marine Sediment and NIES Pond Sediment	158
Sediment samples	Hg	CEM MDS-2000	PTFE bomb closed digestion for 30 min ($n = 12$) with (a) HNO_3–H_2SO_4, (b) HNO_3–$HClO_4$ (c) HNO_3–HCl, (d) HNO_3–HCl–HF	FI–CV-AAS	Good results were obtained for NIST SRM 1645 River Sediment, NRCC BCSS-1 Marine Sediment, NIES CRM No. 2 Pond Sediment and in a mixture of the latter and NIST SRM 1515 Apple Leaves (chosen to give the sample an organic matter content of 10%). Procedures (c) and (d) were the most effective. Spike recoveries of 94–104% were obtained for sediment and soil samples	159
Soil and sediment samples	Cu, Cr, Mn, Pb, Zn	CEM MDS-2000	HCl–HNO_3–HF PTFE bomb digestion for 30 min ($n = 12$)	FAAS and ETAAS	Mixed-level orthogonal array design was applied to the optimisation of digestion parameters. For the optimised procedure, generally good results were obtained for NBS SRM 1645 River Sediment, NIES No. 2 Pond Sediment (except low Cr) and NRCC BCSS-1 Marine Sediment	160
Sediment samples	As, Se	CEM MDS-2000	Closed digestion for 30 min ($n = 12$) with (a) HNO_3–H_2SO_4, (b) HNO_3–$HClO_4$, (c) HNO_3–HCl, (d) HNO_3–HCl–HF, (e) HNO_3–H_2SO_4–$HClO_4$	FI–HG-AAS	Good results were obtained by all procedures for NIST SRM 1645 River Sediment, however procedures (a), (b) and (e) were not recommended owing to the potential hazardous nature of the digestion environment. No effect to the digestion was observed following the addition of SRM 1515 Apple Leaves (to give an organic content of 10%). Good results were obtained by procedures (c) and (d) for NRCC BCSS-1 and NIES CRM No. 2 Pond Sediment. Spike recoveries of 94–104% were obtained for sediment samples	161
Coral soil samples	Si	Floyd RMS-150	HNO_3–H_2O_2–HF Teflon bomb digestion for 25 min	ICP-AES following addition of H_3BO_3 and a tertiary amine mixture	Acceptable agreement with the results obtained from an $LiBO_2$ fusion procedure was obtained following microwave digestion of five coral soil samples. The average precision of the method was 7%	19
Soil and dust	As	Floyd RMS-150	HNO_3–H_2O_2 bomb digestion for 32 min ($n = 6$)	ICP-MS	Good results were obtained for NIST Urban Particulate Matter and IAEA Soil 7	77
Sediment samples	Cd, Cr, Cu, Pb, Ni, Sb, Sn, Th	Floyd	Samples were digested with HNO_3–HF for 52 min, evaporated to dryness on a hot-plate and dissolved in HNO_3–H_2O	ID–ICP-MS, ICP-MS and ETAAS	Good results were obtained for Cd, Cr, Cu, Pb, Ni, Sb, Sn and Th in a Mississippi River delta sediment sample (NOAA/7)	78
Dust samples	Cd, Pb	Floyd RMS-150	Teflon bomb digestion for 20 min with (a) HNO_3, (b) HCl–HNO_3, (c) HNO_3–HF	DP-ASV and FAAS	Digestion efficiencies of 85–95% were obtained (RSD = 10%) for NBS Urban Particulate Matter, BCR City Waste Incineration Ash and River Sediment. No significant differences were found between the results of the three microwave methods and a standard hot-plate digestion method	162

Table 2 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Geological samples	Al, Fe, K, Mg, Na, Si	Milestone MLS-1200	PTFE bomb digestion. Coal: HNO_3–H_2O_2–HF–$HClO_4$. Limestone: HCl–HF. Iron Ores: HCl	ICP-AES and AAS	Results for limestone samples were in good agreement with those obtained by XRF. Fe levels in BCS NIMBA Fe Ore, Fe Ore Sinter and Lincolnshire Fe Ore were within the certified range	72
Sediment samples	As, Al, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, Sn, Ti, Zn	Milestone MLS-1200 MEGA	Teflon bomb digestion for 25 min ($n = 6$) with (a) HNO_3–HF–H_3PO_4–H_3BO_3, (b) HNO_3–HCl–HF–H_3BO_3, (c) Extraction with HNO_3	ICP-AES [for (a) and (b)] and TXRF [for (c)]	Results for BCR 320 River Sediment were follows: (a) good for Al, Fe, Mn, low for Cr, Cu and Zn and high for Co; (b) good for Al, Fe, Cu; high for Co and slightly low for Cr, Mn, Zn; (c) good for As, high for Ni, slightly low for Cu, Fe, Pb and Zn and very low for Cr and Sn	163
Sediment samples	50 elements	Milestone MLS-1200	HNO_3–HF Teflon bomb digestion for 19 min, followed by evaporation to dryness (90 min) and dissolution in HCl	ICP-MS and TXRF	Good results were obtained for Al, Ca, Fe, K, Mg, Na, Pb, Rb, Sr, Ti and V in NRCC MESS-1 Estuarine Sediment; however, Ba results were high and Zn low	164
Rock and sediment samples	Th, U, Y and lanthanides	Milestone MLS-1200 MEGA	HF–HNO_3–HCl Teflon bomb digestion for 16 min, followed by heating with H_3BO_3 and EDTA for 8 min	ICP-MS	Results were presented for USGS Andesite (AGV-1), Basalt (BCR-1, BHVO-1), Diabase (W-2, DNC-1), Granite (G-2), Marine Mud (MAG-1), for CCRMP Syenite (SY-2), Gabbro (MRG-1), Lake Sediments (LKSD-1,4), Stream Sediments (STSD-1,4) and for NIM-G Granite, BE-N Basalt, GSD-1,5,6 Stream Sediment and NBS SRM 1645 River Sediment	165
Airborne particulates on PTFE filters	Al, As, Cd, Cr, Cu, Fe, K, Mg, Ni, Pb, S, Sb, V, Zn	Milestone MLS-1200	HNO_3–$HClO_4$–HF PTFE bomb digestion for 8 min	FAAS, ETAAS, ICP-AES and ICP-MS	Good results were obtained for As, Cd, Cu, Fe, Mg, Ni, S, Sb and Zn in NIST Urban Particulate Matter; however K, Pb and V results were slightly low and Al and Cr very low	166
Coal samples	REEs	Milestone MLS-1200	PTFE bomb digestion with HNO_3–H_2O_2–HF–HCl	HPIC with UV/VIS detection and on-line preconcentration	Acceptable agreement was obtained with the published values for NBS 1632a, SARM-18, 19 and 20 coal CRMs (not certified)	167
Baghouse dust	Hg	Questron Q-Wave 1000	HNO_3 Teflon bomb digestion	CV-AAS	No statistical difference was observed between the results for a traditional water bath method and the microwave digestion method	168
Geological samples	Al, Ag, As, Ba, Bi, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Sr, Th, Ti, Tl, U, V, Zn	Questron Q-Wave 1000	HNO_3–HF–H_2O_2 Teflon bomb digestion for 25 min. After cooling, H_3BO_3 is added and heating continued for a further 15 min ($n = 12$)	ICP-MS	Results were presented for NIST SRM 1633b Coal Fly Ash, SRM 1648 Urban Particulate Matter, SRM 1646 Estuarine Sediment, SRM 2704 Buffalo River Sediment, SRM 2711 Montana Soil San Joaquin Soil Baseline Trace Element, SRM 2709 San Moderately Elevated Trace Element and SRM 2700 Montana Soil Highly Elevated Trace Element	169
Marine sediments	Pb	Portland DMR-140	HNO_3–HCl PTFE bomb digestion for 10 min	ETAAS	Results for NRCC PACS-1 Harbour Marine Sediment were good and spike recoveries of 95–99% were obtained. Results were compared with those obtained by a slurry method	170
Coal fly ash	As, Se	Commercial oven (650W)	HCl–HNO_3–H_2SO_4 Parr bomb digestion for 2 × 3 min with interim cooling step (15 min). Sample then heated in a water-bath for 30 min to remove nitrates	HG–AAS analysis following pre-reduction with KI and ascorbic acid	Results for As and Se in NIST 1633b Coal Fly Ash were in good agreement with the certified values and with the results obtained by an NaOH fusion procedure	171
Sediments, geological samples	Hg	Domestic oven (800 W)	HNO_3 PTFE bomb digestion for 3 min at 800 W ($n = 5$)	FANES after reduction with $SnCl_2$ and *in situ* preconcentration	Results for NIST River Sediment were slightly low	85

Table 2 *Continued*

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Sediments samples	Cr	Domestic oven (650 W)	Aqua regia–HF–H_2O_2 PTFE bomb digestion, followed by 10 min heating with H_3BO_3 in a water-bath	ETAAS (no modifier)	Results were in good agreement with the certified value for Cr in BCR River Sediment. Spike recoveries of 101–102% were obtained	95
Sediment and soil samples	Ni	Domestic oven (1100 W)	Aqua regia–HF–H_2O_2 PTFE bomb digestion for 12 min (4 steps) with cooling between each step. After adding H_3BO_3 the sample is heated in a boiling water-bath for 10 min	ETAAS	Good results were obtained in BCR CRM 143R Sewage Sludge Amended Soil, BCR CRM 320 River Sediment, NIES No. 2 Pond Sediment; Canada Centre for Mineral and Energy Technology LKSD 4 Lake Sediment; MAFF North Sea Sandy Sediment COR 5A/91 and Geological Survey of Japan JB 2 Tholeiitic Basalt	97
Sediment samples	As	Domestic oven (700 W)	On-line potassium persulfate–NaOH oxidation following HPLC separation of As species (prior digestion of samples is necessary)	On-line analysis by HG–AAS	As^V, MMA and DMA species were determined in a sediment extract. No CRMs were analysed	107
Sediment samples	Hg	Domestic oven (750 W)	PTFE bomb HNO_3–H_2SO_4–H_2O_2 digestion for 4 min following pre-digestion overnight	CV-AAS	Good results were obtained for Hg in MESS-2 Estuarine Sediment. Spike recoveries of 91–108% were obtained in River Mersey sediment samples	112
Dust wipe and air filters	Pb	Domestic oven (800 W)	Teflon PFA HNO_3 digestion for 6 min ($n = 12$)	ETAAS	Recoveries of 96–114% were obtained for the NIOSH and ELPAT wipe samples. For air filter samples, spike recoveries of 94–103% were obtained	172
Soil and sediment samples	Cd, Cu, Pb	—	Open HNO_3–H_2O_2–aqua regia–HF digestion following overnight pre-digestion	ETAAS	Generally low results were obtained for BCR Calcareous Loam Soil, River Sediment and NBS Urban Particulate Matter	128
Silicate rocks	Fe oxidation states	—	HF–H_2SO_4 PTFE bomb digestion under Ar atmosphere	Absorbance at 560 nm of Fe^{III}–Tiron complex followed spectrophotometrically with time	FeO and Fe_2O_3 results were compared with those from the static o-phenanthroline method	173
Soils and clays	Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Ti	—	HF–aqua regia Teflon bomb digestion for 10 min	ICP-AES	Generally good results were obtained for NIST SRM 1646 Estuarine Sediment, SRM 278 Obsidian and SRM 688 Basalt	174

Table 3 Microwave digestion procedures for water and waste water samples

Matrix	Elements	Microwave system	Digestion method	Analysis Technique	Comments	Ref.
Water samples	Se^{IV} and Se^{VI}	Prolabo Microdigest 301	On-line microwave assisted HCl pre-reduction of Se^{VI} to Se^{IV}	On-line analysis by FI–CSV	Se^{VI} was calculated as the difference between the Se^{IV} concentration after pre-reduction and the initial Se^{IV} concentration. For a BCR candidate water sample, results were low for Se^{VI} and therefore high for Se^{IV}. The total Se concentration was however in good agreement with the proposed value	10
Water and waste water samples	Hg	Prolabo Maxidigest	On-line digestion of samples prepared in H$_2$SO$_4$–HNO$_3$–KMnO$_4$–K$_2$S$_2$O$_8$ with HCl carrier	FI–mercury system	Generally good spike recoveries were obtained for inorganic and methylmercury in drinking water and waste water samples	138
Water samples	Se	Prolabo Microdigest M301	On-line HBr–KBrO$_3$ pre-treatment of Se^{VI} to Se^{IV} (30 samples h^{-1})	On-line analysis by HG–AAS	Total Se was determined following application of microwave energy to the sample, whereas Se^{IV} was determined in its absence. Se^{IV} was calculated by difference. No CRMs were analysed	175
Water samples	Se	Prolabo Microdigest M301	On-line HBr–KBrO$_3$ pre-treatment of Se following HPLC separation of species	On-line analysis by HG–AAS	The determination of selenite, selenate and selenoamino acids (selenocystine, selenomethionine and selenoethionine) in urine was undertaken	176
Water samples	Se	Prolabo Microdigest 301	On-line HCl (6 M) reduction of Se^{VI} to Se^{IV}	On-line analysis by HG–AAS	The Se^{VI} concentration was calculated as the difference between the total Se content (microwave on) and the Se^{IV} content (microwave off). Good results were obtained for NIST 1643c Trace Elements in Water	177
Water samples	Se	Prolabo Microdigest 301	On-line HCl reduction of Se^{VI} to Se^{IV} following HPLC separation of Se^{VI} and Se^{IV}	On-line analysis by HG–AFS	Results were in good agreement with the total Se content of NIST 1643c Trace Elements in Water	178
Water samples	As, Bi, Hg, Pb, Sn	Prolabo Maxidigest MX-350	On-line digestion of samples mixed with a suitable oxidising agent (dependent on element)	FI–CV-AAS and HG–AAS	Good Bi and Hg results were obtained, although problems were experienced for As, Pb and Sn determinations	179, 180
Water samples	Hg	Prolabo Maxidigest MX-350	On-line KBrO$_3$–KBr digestion (7 samples h^{-1})	FI–CV-AAS in amalgamation mode	Good recoveries were obtained for the seven Hg species investigated. The results for 22 water samples were in acceptable agreement with those obtained from an external laboratory	181
Water samples	Total N and P	CEM MDS-81D	Teflon bomb potassium persulfate and NaOH digestion for 45 min (n = 12)	Colorimetric determination	Good recoveries were obtained for all P and N compounds tested except for aminoantipyrine (60–73%). Spike recoveries of 98.4–105.9% were obtained in real samples	182
Waste water samples	Total P	CEM MDS-81D	On-line HNO$_3$ digestion with prior addition of pyrophosphatase (25 samples h^{-1})	Colorimetric detection of molybdenum blue complex	Results were in good agreement with those obtained form a batch 'block' digestion (3 h). Complete recoveries of tetrameta-, trimeta-, ortho- and pyrophosphate as orthophosphate were obtained	183
Water samples	COD	Milestone MLS 1200	On-line K$_2$Cr$_2$O$_7$–H$_2$SO$_4$ oxidation (3 min)	FI–spectrophotometric detection	Results were in good agreement with those of the standard COD method for a range of water samples and food industry waste	64
Water samples	Se	Milestone MLS-1200 MEGA	On-line KBr–HCl pre-treatment of Se^{IV}, Se^{VI} and Se-Met, following seperation by anion-exchange chromatography	HG–AAS	The seperation of Se^{IV}, Se^{VI} and Se-Met was demonstrated; however, no CRMs were analysed	184
Water samples	As	Domestic oven (700 W)	On-line potassium persulfate–NaOH oxidation, following HPLC separation of As species	On-line analysis by HG–AAS	As^{III}, As^{V} and arsenobetaine were determined in mineral, sewage and harbour sea water samples although no CRMs were analysed	107
Water, waste water and sewage effluents	Total P	Domestic oven (700 W)	On-line potassium peroxodisulfate digestion	FI–colorimetric detection of phosphomolybdenum blue complex	Complete digestion of all P compounds tested was achieved, except for condensed phosphates. No significant differences were observed between the results of the on-line and batch methods, although the former had a small positive bias	185
Waste water samples	COD	Domestic oven (662 W)	On-line oxidation of sample, previously mixed with K$_2$Cr$_2$O$_7$ (up to 50 samples h^{-1})	On-line FAAS analysis of unoxidised Cr following anion-exchange seperation	The COD values obtained for 12 different organic compounds and for urban and industrial waste water samples were not significantly different to those obtained by a closed reflux method	186

Table 4 Key to abbreviations used

Analysis Techniques	
AFS	Atomic fluorescence spectrometry
CIE	Capillary ion electrophoresis
CV-AAS	Cold vapour atomic absorption spectrometry
DCP-AES	Direct current plasma atomic emission spectrometry
DP-ASV	Differential-pulse anodic stripping voltammetry
DPP	Differential-pulse polarography
ETAAS	Electrothermal atomic absorption spectrometry
FAAS	Flame atomic absorption spectrometry
FAES	Flame atomic emission spectrometry
FANES	Furnace atomic non-thermal excitation spectrometry
FI	Flow injection
HG–AAS	Hydride generation atomic absorption spectrometry
HPIC	High-performance ion chromatography
HPLC	High-performance liquid chromatography
IC	Ion chromatography
ICP-AES	Inductively coupled plasma atomic emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ID	Isotope dilution
IR	Infrared spectrometry
NAA	Neutron activation analysis
SW-CSV	Square-wave cathodic stripping voltammetry
TLC	Thin-layer chromatography
TXRF	Total reflection X-ray fluorescence spectrometry
XRF	X-ray fluorescence spectrometry

Compounds	
APDC	Ammonium pyrrolidin-1-yldithioformate
BPTH	1,5-Bis[phenyl-(2-pyridyl)methylene]thiocarbonohydrazide
DPTH	1,5-Bis(di-2-pyridylmethylene)thiocarbonohydrazine
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
HIPT	2-Hydroxy-4-isopropylcycloheptatrienone
IBMK	Isobutyl methyl ketone
PSAA	2-(5-Bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulfopropyl-amino)aniline
TMAH	Tetramethylammonium hydroxide

Reference Material Suppliers	
BCR	Community Bureau of Reference
CCRMP	Canadian Certified Reference Materials Project
CGC	Canadian Grain Commission
ELPAT	Environmental Lead Proficiency Analytical Testing Program
IAEA	International Atomic Energy Agency
ISS/MMM	Istituto Superiore di Sanità, Rome, Italy
KRISS	Korea Research Institute of Standards and Science
MAFF	Ministry of Agriculture, Fisheries and Food, UK
NBS	National Bureau of Standards, USA
NIES	National Institute of Environmental Studies
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology, USA
NRCC	National Research Council of Canada
NRCCRM	National Research Centre for Certified Reference Materials, Beijing
USGS	United States Geological Survey

Others	
COD	Chemical oxygen demand
CRM	Certified reference material
MW	Microwave
REEs	Rare earth elements
RM	Reference material

Reid *et al.*[187] described a method for the rapid cooling of Teflon pressure vessels using liquid nitrogen. Cooling in the microwave unit itself, although considerably decreasing reaction rates, was useful in some cases to prevent uncontrollable increases in pressure. However, a more effective method involved cooling, subsequent to or between heating cycles. This approach saved considerable time and additionally prevented pressure build-up occurring after the microwave process had ceased, which could otherwise lead to venting of the vessel.

Open digestion techniques

Open digestion systems operate at atmospheric pressure and so do not suffer from the problems associated with pressure build-up. However, they do require an effective fume removal system. Most open vessel work has been carried out using monomode (focused) microwave systems.[10–28,136–140,175–181] Heating is more efficient than with conventional microwave designs (multimode) because the sample is placed within the waveguide, and thus directly within the path of the microwave energy. The potential loss of volatile species is controlled by condensation of vapours in a reflux column situated above the sample flask. The open vessel approach can generally accommodate larger samples (up to 15 g) than the closed technique and allows the delivery of digestion reagents at any stage of the procedure. The latter may be beneficial for the effectiveness of the digestion, and is a distinct advantage over closed methods where the addition of reagents cannot readily be achieved without cooling and opening the vessels. Also, the system can quickly and effectively evaporate to dryness, a particular

advantage for the removal of HF during the digestion of geological samples. Another advantage is that the power output of the magnetron can be controlled more readily than for domestic ovens. For example, at 50% power the output of the magnetron is actually reduced to 50% rather than pulsing on and off to produce an overall mean of 50% power (see the previous section). Direct temperature measurements and temperature control to follow a previously defined programme are also possible.[188]

A potential disadvantage of the open monomode system is that only one sample can be digested at a time, although this can be overcome by use of an autosampler unit with the ability to run up to 16 samples.[189] A multicavity monomode system is also available for the digestion of up to four samples for the determination of Kjedahl nitrogen.[190] A more recent addition to the commercial market is a two- or six-cavity open microwave digestion unit with the ability to programme the power output/desired temperature to each sample independently.[191] Another point for discussion is that many open digestion procedures, by virtue of operating at atmospheric pressure, must use a high boiling-point acid, such as sulfuric acid, in order to decompose completely organic material in the sample. Many workers overcome the use of highly corrosive sulfuric acid by utilising perchloric acid or hydrogen peroxide instead.

A less common approach is the use of conventional microwave ovens[87,109,128] for open digestions. Burguera *et al.*[87] demonstrated that the digestion of biological samples could be effectively achieved for 100 samples placed in polyethylene test-tubes (covered with a Teflon sheet) in only 14 min. However, no comment was made as to the lifetime of the oven.

On-line digestion techniques

There is a growing trend towards the development of on-line microwave digestion and analysis techniques, for both solid[22,24,32,35,36,54,83,84,86,88,89,93,94,98,138] and liquid[10,21,107,138,175–181,183–186] samples. Such techniques can lead to considerable time savings compared with batch microwave digestions and thus the benefits over conventional techniques are even more impressive. However, for solid samples it is usually necessary to prepare a slurry of the sample before analysis. This is undertaken to ensure effective sample transport into the digestion manifold. Most workers have reported the necessity for further grinding of the sample, sometimes with the addition of surfactants,[35,89] in order to produce a stable slurry. Samples can then be digested in either a continuous or stopped flow system for on-line analysis[22,24,35,36,86,88,89,93,98,138] or collected for separate treatment.[32,35,54,83,84,94] Hulsman *et al.*[192] investigated the dispersion behaviour of solid particles in flow injection analysis in order to help achieve reproducible pre-treatment procedures.

On-line microwave digestion of slurries has been successful for the determination of Al, As, Cd, Cu, Co, Cr, Fe, Hg, Mg, Mn, Ni, Pb and Zn in biological, soil and sediment samples. However, incomplete digestion has been reported for coal samples.[35] It has also been noted that for some detection systems, *e.g.*, flame atomic absorption spectrometry (FAAS), that the mass of sample required for trace analysis may be incompatible with the slurry approach.[35,36] Other workers have reported blocking of the transfer lines for some samples, therefore necessitating a pre-digestion before on-line treatment.[54] An alternative method to the slurry approach has been reported by Legere and Salin,[193] who proposed encasing the sample in a digestible capsule for easy transfer into the digestion tube. Once in place the reagents could be added, the tube sealed and the digestion allowed to continue in a fully automated system. Torres *et al.*[139] developed a microwave-assisted robotic method for the extraction of Cu, Fe and Zn from soil samples. The system was capable of the weighing, extraction, centrifugation and transport of the sample to the flame atomic absorption spectrometer.

In contrast to the problems associated with solids, water samples are more compatible with the on-line digestion process. Techniques suitable for the determination of the chemical oxygen demand (COD),[64,186] total P,[183,185] As,[107] Bi[179,180] and Hg[138,179–181] and the speciation of Se[175–178,184] have been developed. These procedures result in considerable time savings on the batch techniques, especially if the system can be combined with an autosampler. Open monomode (focused) microwave digestion systems are particularly suited to on-line applications, having been successfully used by a number of workers for this purpose.[21,22,138,175–179,181]

Chemometrics

Chemometrics and factorial designs[78,142,143,159,160] have been used to select the best digestion technique for a particular purpose, *i.e.*, to chose the best combination of reagents, reagent volumes, digestion times and power settings. This is of particular value in a multi-element situation when no single digestion procedure gives good results for all the elements required and a method is needed to obtain the best overall performance. In addition, Feinberg *et al.*[67] related digestion programmes with the nature of the sample matrix using an empirical modelling approach. A preliminary study using Kjedahl nitrogen determinations in food samples to define reference digestion procedures was found to be very effective for precisely defined samples. However, for complex foods the model needed further development.

Universal digestion procedures

This section discusses the use of microwave digestion systems for the digestion of biological, geological and water samples, in order to identify potential 'universal' digestion procedures for a particular matrix or element. Tables 5, 6 and 7 summarise the different reagent combinations that have been used for the determination of different elements in biological, geological and water samples respectively.

Biological samples

Many papers have been published reporting the use of microwave digestion procedures for biological samples[10–135] (Table 1). A wide range of samples have been investigated, the diversity of which is nearly matched by the number of different digestion methods used. A wealth of different combinations of acids and oxidising agents are commonly employed for the determination of different elements in biological samples (Table 5). Few trends seem to exist with good results being obtained for the same element in the same matrix after digestion with a range of different reagents. Conflicting evidence also exists as to the efficacy of the same reagent combination for the digestion of a particular matrix.

For the determination of aluminium in biological samples there is disagreement as to whether digestion with HF is necessary. In support is the work of Lajunen and Piispanen,[39] who reported low Al recoveries in NIST Citrus Leaves and Pine Needles and IAEA Mixed Diet after a closed nitric–hydrochloric acid digestion. Recoveries were improved by employing nitric and hydrofluoric acid in combination with hydrogen peroxide. Low recoveries were also obtained in BCR Spruce Needles following a nitric acid–hydrogen peroxide digestion[25] and in shellfish,[83] total diet samples[120] and NIST Apple and Peach Leaves[80] following closed digestion procedures with just nitric acid. For marine biological tissue (NIST Oyster Tissue), closed digestion procedures with nitric and perchloric acid, and nitric acid and hydrogen peroxide, also resulted in low results for Al.[56] However, good results were again achieved by the addition of hydrofluoric acid to the nitric acid and hydrogen peroxide digestion mixture.

Evidence also exists, however, to suggest that digestion with HF is unnecessary for some samples. For example, good results have been obtained for Al in NIST Total Diet[116] and in NIST Citrus Leaves[135] after a simple nitric acid digestion. A combination of nitric acid and hydrogen peroxide was used for the digestion of NIST Wheat Flour, although results for NIST Rice Flour were slightly high.[74] Recoveries were not increased, however, by the inclusion of HF in the procedure. We have reported the successful determination of aluminium in tea leaves following an open nitric and perchloric acid digestion, although low recoveries were obtained with nitric acid, alone and in combination with hydrogen peroxide.[20]

Similar discrepancies exist for the determination of iron. A simple nitric acid digestion was used successfully for the determination of iron in cocoa,[33] IAEA Horse Kidney,[34] NIST Total Diet,[116] NIST Bovine Liver,[36,70,119] and NIES Mussel,[36] Chlorella,[36] Sargasso[36] and Pepperbush[36] samples. However, Mingorance *et al.*[69] obtained low and imprecise results for botanical samples using a similar method. A slight improvement was obtained with a nitric and hydrofluoric acid digestion, but the results were still outside the certified range. Good results were obtained with nitric acid and hydrogen peroxide for NIST Total Diet and with nitric and perchloric acid for NIES Pepperbush and Mussel samples.[69] However, low results were obtained following both procedures for the determination of Fe in BCR Wholemeal Flour. A nitric acid and hydrogen peroxide digestion was also employed by Burguera *et al.*[87] to give good results for NBS Bovine Liver, but for BCR Bovine Muscle the results were slightly high. Using a similar procedure, good

Table 5 Reagents for the microwave digestion of biological samples

Samples	Reagents used	Elements determined	Ref.
Marine Biological Tissues	HNO_3	Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Se, Sr, Zn	23, 27, 29, 52, 58, 59, 60, 70, 74, 83, 84, 92, 100, 102, 114, 117, 135
	HNO_3 with V_2O_5 catalyst	As	113
	HNO_3–H_2O_2	Ag, Al, As, B, Cd, Cr, Cu, Hg, Mg, Mn, Ni, Pb, Se, Sr, Zn	16, 17, 21, 25, 37, 54, 57, 62, 65, 66, 76, 112
	HNO_3–HCl	Ni	81, 82
	HNO_3–H_2SO_4	As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sr, Zn	23
	HNO_3–HF	Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sn, Th, Zn	54, 77
	HNO_3–HF–H_2O_2–H_3BO_3	Al	56
	HCl–HNO_3–H_2O_2	Cd, Fe, Zn	25
	HNO_3–$HClO_4$	Co, Cu, Fe, Pb	79
	HCl–HNO_3–HF	Ca, Cu, Fe, Zn	78
	HNO_3–H_2SO_4–H_2O_2	As, Hg, Se	22, 105, 106, 129
	HNO_3–H_2SO_4–HNO_3–H_2O_2	Hg	11, 27
	HNO_3–$HClO_4$–HCl–HF	Ca, Cd, Co, Cu, Fe, Mg, Mn, Zn	19, 103, 125
	HNO_3–H_2SO_4–H_2O_2–NH_4EDTA	Ca, Cd, Cu, Fe, K, Mg, Mn, P, Sr, Zn	19
	HNO_3–H_2O_2–HF	Si	75
	HCl–Br^-/BrO_3^-	Hg	22
	Aqua regia–HF–H_2O_2	Ni	97
	$K_2S_2O_8$–NaOH	As	21, 107
	TMAH	Hg, methyl-Hg	28
	Methanolic KOH	Hg, methyl-Hg	28
Other biological tissues	HNO_3	As, Ag, Cd, Co, Cu, Fe, Hg, Mg, Mn, Mo, Po, Pb, Rb, Se, V, Zn	27, 34, 35, 36, 70, 119, 124, 134
	HNO_3–HCl	Ni, Pb	81, 88
	HNO_3–$HClO_4$	Cd, Cu, Pb, Se	79, 118, 122
	HNO_3– H_2O_2	B, Bi, Ca, Cd, Co, Cs, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, P, Pb, Rb, Ru, S, Sb, Se, Sn, Sr, Tl, Zn	10, 12, 17, 18, 45, 50, 57, 67, 72, 87, 96, 99, 128
	HNO_3–$HClO_4$–HCl–HF	Ca, Cu, Fe, Mg, Mn, Zn	103
	HNO_3–H_2SO_4–H_2O_2	As	110
	HNO_3–H_2SO_4–HNO_3–H_2O_2	Hg	27
	HNO_3–H_2SO_4–H_2O_2–NH_4EDTA	Ca, Cd, Cu, Fe, K, Mg, Mn, P, Sr, Zn	19
	HNO_3–HF–H_2O_2–H_3BO_3	Al	56
	H_2SO_4–KI	Sb	25
	Acetic acid	Sb^{III}	25
Botanical samples (terrestrial)	HNO_3	Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Eu, Fe, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Po, Rb, S, Se, Sm, Sr, Tb, Te, Th, U, V, Zn	15, 32, 33, 35, 41, 47, 49, 71, 74, 80, 85, 89, 90, 116, 119, 134, 135
	HNO_3–H_2O_2	Al, As, B, Ca, Cd, Ce, Cr, Co, Cu, Eu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Se, Sm, Tb, ^{232}Th, ^{238}U, Zn	12, 13, 15, 17, 25, 31, 38, 40, 41, 45, 63, 72, 73, 76, 93, 98, 99, 101, 116, 128
	HNO_3–HCl	Ca, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn	30, 39, 81, 82, 88, 116, 127
	HNO_3–$HClO_4$	Al, Ba, Ca, Cd, Cu, Fe, K, Mg, Mn, P, Pb, S, Zn	20, 53, 79, 109, 121, 122
	HNO_3–$HClO_4$–HCl–HF	Ca, Cd, Cu, Fe, Mg, Mn, Pb, Zn	103, 104, 125
	HCl–HNO_3–HF	Ca, Fe	78
	HNO_3–HF–H_2O_2	Al, Fe, Mg, Si	39, 130
	HNO_3–HF–H_2O_2–H_3BO_3	As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Tl, V, Zn	46
	HNO_3–HF–$HClO_4$–HF	Cr, Fe	71
	HNO_3–H_2SO_4	Al, Ca, Cu, Fe, Mg, Na, Zn	116
	H_2SO_4–H_2O_2	Kjeldahl N	14
	HNO_3–HF	Ba, Ca, Mg, Mn, Zn	42
	HNO_3 with V_2O_5 catalyst	As, Cd, Cu, Fe, Pb, Se	91, 115
	HNO_3–H_2O_2–HCl	P	133
	HNO_3–HF–H_2O_2–SiO_2	Al, B, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, P, S, Sr, Zn	55
	Aqua regia–HF–H_2O_2	Ni	97
	Aqua regia–H_2O_2	Cr	95
	NaOH–H_2O_2	Br^-	111
Botanical samples (marine)	HNO_3	Cd, Fe, Mg	36
	HNO_3–H_2O_2	Co, Cr	101
	HNO_3–$HClO_4$–HCl–HF	Cd, Cu, Pb	103, 125

Table 5 *Continued*

Sewage sludge samples	HNO_3	Cd, Cr, Cu, Hg, Ni, Pb, Zn	24, 32, 44, 86
	$HCl–HNO_3$	Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sn, Ti, V, Zn	44, 123
	$HNO_3–H_2O_2$	Cu, Mn, Pb	93, 98
	$HNO_3–H_2SO_4$	As, Se	51
	Aqua regia–H_2O_2	Cr	95
	Aqua regia–HF–H_2O_2	Ni	97
	Aqua regia–HF–H_2O_2–H_3BO_3	Cd	96
	$K_2Cr_2O_7–H_2SO_4$	COD	64

results have been obtained for BCR Pig Kidney,[128] Bovine Muscle[128] and Liver[18,50] and NBS Citrus Leaves,[128] Pine Needles[128] and Wheat Flour.[128] However, low iron recoveries have been reported using the same reagent combination for NBS Orchard Leaves, Spinach Leaves and Bovine Liver,[72] BCR Rye Grass,[40] IAEA Hay[40] and for fat-rich foods.[13] For the last samples, recoveries were improved by use of a closed nitric–sulfuric–nitric acid digestion. Sulfuric acid has also been used by Krushevska *et al.*[19] in combination with nitric acid, hydrogen peroxide and NH_4EDTA to give good results for NIES Mussel Tissue, IAEA Horse Kidney and NIST Bovine Liver and Oyster Tissue. For NIST Citrus Leaves the use of nitric and hydrochloric acid gave low recoveries for Fe, but good results were obtained for a variety of other metals.[30]

A number of workers, however, have reported that to obtain complete iron recoveries, digestion with HF was necessary. For example, for the digestion of NIST Citrus Leaves, Lajunen and Piispanen[39] found hydrogen peroxide, nitric and hydrofluoric acid to be more effective than a simple nitric and hydrochloric acid digestion. Park and Suh[71] reported that a nitric acid digestion was unsuitable for the determination of Fe and Cr in rice flour samples, but in combination with hydrofluoric and perchloric acids complete recoveries were obtained. A nitric, perchloric, hydrochloric and hydrofluoric acid digestion was successfully developed by Kojima *et al.*[103] for the determination of iron in NIST Bovine Liver and NIES Pepperbush and Mussel samples, although for NIES Tea Leaves the results were slightly high. Sun *et al.*[55] obtained complete recoveries for iron in NIST Pine Needles and Apple, Tomato and Peach Leaves following digestion with nitric acid, hydrofluoric acid and hydrogen peroxide. Mohd *et al.*[78] used a chemometrics technique to select the best reagent combination for the digestion of NRCC TORT-1 and NIST Pine Needles. The chosen procedure involved digestion with hydrochloric, nitric and hydrofluoric acid in which the hydrochloric and nitric acid were present in equal proportions rather than as *aqua regia*.

A number of different techniques for the determination of selenium have also been suggested. Banuelos and Akohoue[31] investigated a number of different reagent combinations with and without a pre-digestion stage. Using a simple nitric acid digestion, a selenium recovery of only 23% was obtained for NIST Wheat Flour. Recoveries were improved to 80% after a nitric acid and hydrogen peroxide digestion with a 4 h pre-digestion step (57% without pre-digestion). However, further heating or the addition of hydrochloric acid did not increase the recoveries. In another publication,[70] the determination of selenium in NIST Bovine Liver was successfully achieved by digestion with nitric acid, but results for IAEA Fish Flesh were low. Selenium determinations have also been successfully carried out using open nitric acid and hydrogen peroxide digestion procedures for BCR Lyophilised Pig Kidney,[10] cereal reference materials[15] and NIST Bovine Liver[12] and Mixed Diet[12] samples. However, results for NIST Total Diet[12] were slightly low. Good results have also been obtained in closed digestions using nitric acid and hydrogen peroxide for BCR Maize Leaves[38] and lyophilised fish samples.[37] An alternative

technique, for the digestion of NIST Bovine Liver, was offered by Prasad *et al.*[118] This involved a closed nitric acid digestion, followed by evaporation to dryness with perchloric acid to remove organics and analysis by square-wave cathodic stripping voltammetry. However, for analysis by hydride generation–atomic absorption spectrometry (HG–AAS) a similar procedure was found to be ineffective. This was also the case when phosphoric acid or potassium persulfate was added.[106] Good results were obtained, however, for NIES Mussel Tissue by using nitric and sulfuric acid with hydrogen peroxide;[105,106] for NRCC DORM-2 and DOLT-2 after digestion with nitric and hydrofluoric acid[66] and by a semi-on-line nitric acid digestion method for NIST Oyster Tissue[84].

For arsenic, good results have been obtained using a nitric acid digestion for BCR Cod Muscle,[11] NIST Oyster Tissue,[117] NIST Orchard Leaves,[49] NIST Bovine Liver[70] IAEA Fish Flesh[70] and NRCC DORM-1,[52] although for NRCC TORT-1 results were slightly high.[52] Yusof *et al.*[60] and Liu *et al.*[23] obtained good results for TORT-1 using a similar digestion procedure. A nitric acid digestion was also carried out by Navarro and co-workers,[113,115] in combination with a catalyst of V_2O_5, to obtain good results for BCR Mussel Tissue and NBS Citrus Leaves. A nitric acid and hydrogen peroxide digestion was successfully employed for the digestion of NIST Oyster Tissue and Orchard Leaves,[76] for NRCC TORT-1 and DORM-1,[21] for BCR Maize Leaves[38] and for BCR Spruce Needles, White Clover, Cod Muscle and Plankton samples.[25] However, El Moll *et al.*[129] required the use of a more vigorous multi-step procedure with nitric and sulfuric acid and hydrogen peroxide for the open vessel digestion of a range of fish samples. Krushevska *et al.*[19] also employed a mixture of nitric acid, sulfuric acid and hydrogen peroxide, but in combination with NH_4EDTA, for a range of biological samples. Schramel and Hasse[79] reported that a nitric acid procedure was successful for the digestion of NIST Orchard Leaves, although for the determination of arsenic in fish by HG–AAS a nitric, perchloric and sulfuric acid digestion was necessary, presumably to break down organoarsenic compounds in the sample. In the work of Edwards *et al.*[66] the very low recoveries obtained for As in marine biological samples, following digestion with nitric acid and hydrogen peroxide and HG–AAS analysis, was attributed to the incomplete breakdown of organoarsenicals. For analysis by HG–AAS, Mayer *et al.*[110] found a nitric acid, sulfuric acid and hydrogen peroxide mixture to be successful for the determination of As in NIST Bovine Liver. McLaren *et al.*[77] developed a nitric and hydrofluoric acid digestion followed by hot-plate evaporation to dryness and dissolution of the sample in nitric acid for the determination of a range of elements, including arsenic, in NRCC DORM-2 and DOLT-2. For the determination of As and Se sewage sludge[51] by HG–AAS, digestion with nitric and sulfuric acid has been found to be the most effective procedure. An alternative approach for the breakdown of organoarsenic compounds is to undertake an on-line potassium persulfate–sodium hydroxide digestion.[21,107] Speciation of arsenic may then be achieved by the coupling of an HPLC column to the system. Using the former system we have also

Table 6 Reagents for the microwave digestion of geological samples

Samples	Reagents used	Elements determined	Ref.
Sediments	HNO₃	Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn	24, 85, 121, 141, 144, 148, 150, 162
	HNO₃–H₂O₂	Cd, Hg	140
	HCl–HNO₃	As, Cd, Hg, Pb, Se	161, 162, 170
	HNO₃–HF	Al, Ca, Co, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Rb, Sr, Ti, V, Zn	143, 162, 164
	HCl–HNO₃–H₂O₂	As, Cd, Cr, Cu, Ni, Zn	25, 137
	H₂SO₄–HNO₃–HCl	As, Se	148
	HNO₃–H₂SO₄–H₂O₂	Hg	22, 112
	HNO₃–HClO₄–HF	As, Ba, Co, Cr, Cu, Ni, Nb, Pb, Rb, Sb, Sn, Sr, Ta, Th, Tl, W, Zn, REEs	141, 145
	HNO₃–HCl–HF	Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, S, Se, Th, Ti, U, V, Y, Zn, lanthanides	25, 54, 142, 147, 158, 159, 160, 161, 163, 165
	HNO₃–HF–HNO₃	Cd, Cr, Cu, Ni, Pb, Sb, Sn, Th	78
	HNO₃–HClO₄–HF–HCl	As	137
	HNO₃–HF–H₂O₂–H₃BO₃	Ag, Al, As, Ba, Bi, Cd, Co, Cr, Cu, Fe, Hg, Li, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Sr, Th, Ti, Tl, U, V, Zn	45, 169
	HF–*aqua regia*	Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Ti	174
	Aqua regia–KMnO₄	Hg	138
	Aqua regia–HF–H₂O₂	Cr, Ni	95, 97
	HCl–Br⁻/BrO₃⁻	Hg	22
Rocks/minerals	HNO₃	Co, Cr, Cu, Mn, Mo, Ni, V	141
	HCl	Fe	72
	HNO₃–HF	Co, Cr, Cu, Ni, Pb, Zn	143
	HCl–HF	Al, K, Mg, Si	72
	HNO₃–HClO₄–HF	Al, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, K, Hf, Ho, In, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Nb, Pr, Pb, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, REEs	151, 157
	HF–H₂SO₄	Fe	173
	HNO₃–H₂SO₄–K₂Cr₂O₇	Os	149
	HF–HNO₃–HCl	As, Se, Th, U, Y, lanthanides	38, 165
	HNO₃–HCl–HF–HClO₄	Au, Ir, Pb, Pt, Rh, Ru	152
	Aqua regia–HF–H₂O₂	Ni	97
	HF–*aqua regia*	Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Ti	174
Soil	HNO₃	Hg	24, 136
	HNO₃–H₂O₂	As, Cd, Cu, Ni, Pb, Zn	25, 77
	HNO₃–H₂SO₄	As	51
	HCl	Hg	136
	HNO₃–H₂O₂–HF	Si	19
	HNO₃–HF–H₂O₂–H₃BO₃	Al, Ag, As, Ba, Bi, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Sr, Th, Ti, Tl, U, V, Zn	169
	Aqua regia	Hg	136
	Aqua regia–HF–H₂O₂	Ni	97
Dust, ashes and airborne particulate matter	HNO₃	Cd, Hg, Pb	32, 162, 168, 172
	HNO₃–H₂O₂	As	77
	HNO₃–H₂SO₄	As, Se	171
	HCl–HNO₃	Cd, Pb	162
	HNO₃–HF	Cd, Pb	162
	HNO₃–HCl–HF	Al, Ba, Ca, Cr, Cu, Fe, Mg, Mg, Ni, Ti, V, Zn	147
	HNO₃–HClO₄–HF	Al, As, Ba, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Sb, V, Zn	153, 154, 155, 156, 166
	HNO₃–HF–H₂O₂–H₃BO₃	Al, Ag, As, Ba, Bi, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Sr, Th, Ti, Tl, U, V, Zn	169
Coal	HNO₃–H₂O₂–HF–HCl	REEs	

shown that the determination of total arsenic was possible by virtue of an L-cysteine pre-reduction step.[21]

The more readily released elements from biological matrices such as Cu and Zn have been determined after digestion with a vast number of different reagents ranging from nitric acid alone[19,23,29,33–36,40,41,49,60,70,91,98,119,126] and in combination with hydrogen peroxide[13,15,16,18,25,41,50,72,87,93,98,101,116] to combinations of nitric, perchloric, hydrochloric and hydrofluoric acids.[103,122]

Methods for the determination of mercury are, however, slightly in agreement, with many workers employing a closed nitric acid digestion procedure. Good results have been obtained

Table 7 Reagents for the microwave digestion of water and waste water samples

Reagents used	Elements determined	Ref.
$K_2S_2O_8$	Total P	185
$K_2S_2O_8$–NaOH	As, total P and N	107, 182
H_2SO_4–HNO_3–$KMnO_4$–K_2SO_8	Hg	138
HNO_3 and pyrophosphatase	Total P	183
$KBrO_3$–KBr	Bi, Hg	179, 180, 181
$KBrO_3$–HBr	Se	175, 176
HCl	Se	10, 177, 178
$K_2Cr_2O_7$–H_2SO_4	COD	64, 186
KBr–HCl	Se	184

for BCR Pig Kidney,[27,134] Mussel Tissue[114] and Cod Muscle[92] NIST Citrus Leaves,[85] Pine Needles[85] and Albacore Tuna,[59] IAEA Fish Tissue[27] and NRCC TORT-1[62] using this procedure. However, a number of workers have reported the use of strong oxidising reagents such as sulfuric acid and hydrogen peroxide for the determination of mercury using open[22,27] and closed microwave digestion systems.[62,66,111] An on-line system developed in our own studies for the determination of Hg in biological and sediment samples has been reported.[22] The system was suitable for the analysis of samples containing organomercury compounds by the utilisation of a bromide–bromate oxidation reaction. For the speciation of mercury, Tseng *et al.*[28] have developed an open focused microwave assisted extraction procedure for analysis by HG–CT–GC–ETAAS.

Geological samples

Less work has been carried out for the digestion of geological samples than for biological samples, although a wide range of matrices have been digested by a number of different digestion procedures (see Tables 2 and 6). Included are sediment, soil, rock, coal, ash and dust samples.

For the determination of some elements simple nitric or hydrochloric acid digestions will suffice for some samples. For example, good Fe recoveries in Fe ore samples were obtained using a simple hydrochloric acid digestion, but for limestone samples the additional use of hydrofluoric acid was required.[72] Lead in dust wipe and air filters[172] has been determined after a nitric acid digestion. Mercury was also determined using a similar procedure in NIES Pond Sediment,[121] baghouse dust[168] and NIST SRM Estuarine Sediment and Buffalo River Sediment.[148] However, other workers reported high results for NIST Buffalo Sediment[141] and slightly low results for NIST River Sediment.[85] Following both an open and closed nitric acid digestion procedure, results were also low for mercury in NIST Montana Soil.[136] However good results were obtained for Hg in NRCC PACS-1, IAEA-356 and BCR S19 sediment samples following open digestion with nitric acid.[140] Morales-Rubio *et al.*[24] have found the on-line digestion of slurries prepared in nitric acid to be successful for the determination of Hg in soil and sediment samples. An alternative system for the determination of mercury has been proposed by Hanna and McIntosh.[138] Sediment slurries, prepared in *aqua regia* and potassium permanganate, were digested on-line for analysis in a flow injection mercury system. In addition, an on-line system employing a bromide–bromate oxidation reaction has been developed in our studies for the determination of mercury in sediment samples.[22]

Feng and Barratt[162] observed no significant differences between the results obtained after digestion with nitric acid, with hydrochloric and nitric acid or with nitric and hydrofluoric

acid for the determination of Cd and Pb in BCR City Waste Incineration Ash, BCR River Sediment and in NBS Urban Particulate Matter. However, using a nitric acid and hydrogen peroxide digestion, low Cu and Pb (but good Cd) results were obtained in the last two samples and in BCR Calcareous Loam Soil by Chakraborti *et al.*[128] The results were improved by employing an extra heating step with *aqua regia* and HF. Good results for cadmium in sediment samples were obtained following digestion with just nitric acid.[144] A nitric acid digestion was also employed by Averitt and Wallace[141] to obtain good results for As, Cd, Co, Cu, Ni and Pb in NIST Buffalo River Sediment, although the Ba, Cr, Mn, Sb, V and Zn results were low and Hg results were high. Barium, Hg and V results were improved using a nitric, perchloric, hydrofluoric acid digestion procedure, but Cr was still low and Zn and Sb high. Marr *et al.*[146] reported a benefit from the addition of HF to an *aqua regia* digestion for the analysis of the sediments NRCC MESS-1 and PACS-1, but again the results for Cr and Mn were low.

In environmental analysis, it is often useful to acquire information on the bioavailable rather than the total elements present. This can often be achieved by using a mild leaching procedure. Paudyn and Smith[147] carried out such a procedure for NRCC MESS-1 and PACS-1 and NIST Coal Fly Ash. This work also demonstrated how the digestion conditions required for the total release of different elements varies from sample to sample. For example, complete recoveries of Mn were obtained for NIST Fly Ash, compared with only 63% for MESS-1 sediment. Total recoveries were also obtained for Cu and Zn in all samples whereas for other elements recoveries were much lower, *e.g.*, 35–60% for chromium, thus warranting a more vigorous digestion procedure.

Low Cr and Al values were obtained for NRCC BCSS-1 sediment following an on-line hydrofluoric, nitric and hydrochloric acid digestion, although recoveries for As, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn were good. Using a similar combination of reagents, good results were obtained for Cr in NRCC BCSS-1, although the results for NIES No. 2 Pond Sediment were low. Following disappointing results using a number of medium- and high-pressure digestion procedures for Cr in NRCC BCSS-1, Liu *et al.*[145] concluded that no acid dissolution procedures were adequate for this sample. Low Al and Cr results have also been reported for NIST Urban Particulate Matter after digestion with nitric, perchloric and hydrofluoric acids, however results for As, Cd, Cu, Fe, Mg, Ni, S, Sb and Zn were good.[166] Complete recoveries of Cr have been obtained for NIST Fly Ash, NRCC MESS-1 and PACS-1 following a nitric, hydrochloric and hydrofluoric acid digestion.[147] Good recoveries were also obtained for Cr in Mississippi River delta sediment following a nitric and hydrofluoric acid digestion[77] and by an *aqua regia*, hydrofluoric acid and hydrogen peroxide digestion for BCR River Sediment.[95] However, good Cr recoveries were obtained without the use of HF following an open hydrochloric, nitric acid and hydrogen peroxide digestion (and in a closed hydrochloric, nitric and hydrofluoric acid digestion) in BCR Estuarine Sediment.[132] Good As, Cd, Cu, Ni and Zn recoveries were also obtained, although Hg and Pb levels were high. Totland *et al.*[151,152] also employed HF in combination with nitric and perchloric acid for the successful digestion of nine rock and sediment samples.

For the determination of As and Se in soil[51] and in coal fly ash[171] by HG–AAS, digestion with nitric and sulfuric acids has been found to be the most effective procedure. Lasztity *et al.*[76] employed a nitric acid and hydrogen peroxide digestion for the determination of As in NIST Urban Particulate Matter and IAEA Soil 7, whereas a nitric, hydrochloric and hydrofluoric acid digestion was successfully employed by Jimenez de Blas *et al.*[38] for the determination of As in soil samples. The determination of As in airborne particulate matter has been

undertaken by digestion with nitric, hydrofluoric and perchloric acids[156].

For the determination of rare earth elements in coal, Watkins *et al.*[167] employed a closed nitric acid, hydrogen peroxide, hydrofluoric and hydrochloric acid digestion. Sen Gupta and Bertrand[165] developed a hydrofluoric, nitric and hydrochloric acid digestion for the determination of Th, U, Y and the lanthanides in a large number of sediment and rock samples.

The use of a chemometrics technique for the selection of the best technique for the determination of Co, Cu, Mn, Pb and Zn in NBS Buffalo River Sediment was reported by Kokot *et al.*[142] A digestion procedure with hydrofluoric, nitric and hydrochloric digestion was selected, whereas for Co, Cr, Cu, Ni, Pb and Zn a nitric and hydrofluoric acid digestion was found to be most effective.[143] A hydrofluoric, hydrochloric and nitric acid digestion procedure was selected by an orthogonal array design for the digestion of sediment samples.[158,160]

Water Samples

Relatively few publications have reported the application of microwave digestion to the determination of elements in water samples (see Table 3).[10,107,138,175–185] Benson *et al.*[185] successfully employed an on-line potassium persulfate digestion for the determination of total phosphorus, although incomplete digestion of condensed phosphates was observed. A similar digestion procedure, but in batch mode, was applied for the determination of total phosphorus and nitrogen by Johnes and Heathwaite.[182] Complete recoveries for phosphorus were obtained but for nitrogen the breakdown of aminoantipyrine was incomplete. The determination of phosphorus was also carried out using a nitric acid digestion with prior addition of pyrophosphate to give complete recoveries of tetrameta-, trimeta-, ortho- and pyrophosphate.[183] Arsenic speciation has been achieved by on-line HPLC separation followed by a potassium persulfate and sodium hydroxide microwave digestion and analysis by HG–AAS.[107] Pitts *et al.*[177] developed an on-line microwave reduction system for the conversion of Se^{VI} to Se^{IV} prior to analysis by HG–AFS. In a subsequent study by the same authors, the system was used for the speciation of Se^{VI} and Se^{IV} following separation by HPLC.[178] A similar system for the pre-reduction of Se^{VI} to Se^{IV}, but for analysis by FI–CSV, was reported by Bryce *et al.*[10] The determination of Se has also been addressed using on-line HBr–KBrO$_3$ pre-reduction methods, developed by Gonzalez LaFuente *et al.*[175] and coupled with HPLC separation by Marchante-Gayon *et al.*[176] Ellend *et al.*[184] have also developed an on-line separation and pre-treatment method for the speciation of Se. For the determination of mercury by CV-AAS, digestion with KBrO$_3$–KBr is commonly used. Welz *et al.*[181] developed an on-line system for Hg and Bi, although problems were encountered in the determination of As, Pb and Sn. As described previously, a system for the on-line determination of Hg in sediments, water and waste water samples was proposed by Hanna and McIntosh.[138] For COD determinations, Balconi *et al.*[64] and Cuesta *et al.*[186] developed on-line methods employing a K$_2$Cr$_2$O$_7$–H$_2$SO$_4$ digestion.

Conclusions

Biological samples consist of a complex mixture of carbohydrates, proteins and lipids and so are not completely soluble in water or organic solvents. Before analysis it is therefore necessary to decompose the organic matter and release the metals from the sample matrix. The majority of the digestion procedures used to date involve the initial use of strong oxidising agents such as nitric acid to decompose the organic matrix of the sample. Many elements are then liberated as soluble nitrate salts. Other acids can be employed to break down the sample further, according to the elements that need to be

determined and the analysis technique chosen. For example, hydrochloric acid is a good solvent for many metal oxides, for metals that are oxidised more easily than hydrogen and for some organometallic compounds. The use of hydrofluoric acid is necessary for the determination of a number of elements which are associated with siliceous minerals.

For the determination of iron and aluminium in biological samples, a wide variety of reagents have been successfully employed. For the former, digestions with nitric acid alone and in combination with hydrogen peroxide are very common and generally effective for the digestion of biological samples. However, the requirement for HF during the digestion of some botanical samples has been reported. For the determination of aluminium many workers have reported that the low results generated from digestion with just nitric acid or nitric acid and hydrogen peroxide can be improved by the addition of HF. However other workers have found this step unnecessary. Therefore, no steadfast rules regarding the need for HF during the determination of Al and Fe can be made, since it depends on the exact sample type and the amount of siliceous material present. The determination of Al is also hindered by high background levels, which can be prohibitive for trace analysis. Hence measures to control background contamination, in addition to the preparation of sample blanks, should be routinely adopted to minimise this problem.

For the determination of arsenic, digestion with nitric acid may be used successfully in many cases, although for the analysis of fish samples by HG–AAS more vigorous conditions are usually required. Sulfuric acid is often employed to break down organoarsenic compounds which are not reduced and thus not hydride forming upon reaction with sodium borohydride. Similar findings have also been observed for the determination of Hg and Se. For the latter, nitric acid and hydrogen peroxide digestions have been used successfully to replace the conventional nitric and perchloric acid and sulfuric acid procedures. However, when analysis by hydride generation is desired, sulfuric acid is still required to break down the more resistant organoselenium compounds. For the less strongly bound elements in biological materials, such as Cu and Zn, the digestion procedure is less critical with a wide range of different reagent combinations giving good results.

The wide range of sample compositions represented by geological materials preclude the use of any single digestion procedure. For example, sediment samples consist of a combination of different materials, *e.g.*, clay, organic material, siliceous and other minerals, and are therefore one of the most difficult sample matrices to digest. Hence in many cases, to attain complete digestion the use of HF is necessary to decompose resistant minerals, in addition to strong oxidising reagents such as nitric acid and sometimes perchloric acid to break down organic matter. In the literature there is evidence to suggest that a number of elements such as Cd, Cu, Hg, Pb and Zn can be easily released after digestion with just nitric or hydrochloric acid. This is because in many cases they are sorbed on clay minerals or are in other readily decomposed phases, rather than within the resistant framework-lattice silicates. However, other elements are more strongly bound, either as part of resistant minerals or associated with other minerals, and so in such cases the use of HF may be required. For example, some Cr bearing minerals, notably chromite, are very difficult to decompose even with the use of HF–HClO$_4$ under pressure, although complete Cr recoveries have been reported without the use of HF. The need for HF is therefore very much dependent on the nature of the minerals present in the samples. Because real samples will vary in composition from that of the certified reference materials used for validation of a procedure, it would seem prudent to suggest that for the determination of all but the most weakly bound elements in sediments, digestion with HF is recommended.

The digestion reagents required for the efficient digestion of a particular sample type are very much dependent on the exact sample matrix and the elements to be determined. Excluding water samples there is generally little agreement in the literature, with often conflicting evidence as to which reagent combinations are most effective for the same matrix. This may reflect the fact that the digestion is influenced by factors other than just the choice of reagents, *e.g.*, the relative proportions of each reagent, heating times and the pressure and temperature reached during the procedure. In many cases good results for the same matrix have been reported by a number of different methods. In addition, the literature suggests that no standard digestion procedures can be employed for the determination of a specified element in all samples of the same type, *e.g.*, Fe in all biological samples, or for the determination of all the elements in a particular sample, *e.g.*, all the elements in mussel tissue. Therefore, it may not be justified to extrapolate a technique designed for the determination of just a few elements to a multi-element determination.

The choice of sample preparation method may, however, be influenced by a number of practical considerations in addition to the type of sample and elements to be determined. These may include the number of samples to be analysed, method of analysis, safety aspects, capital and operating costs of equipment, operator skill and the degree of accuracy and precision required. The method of final analysis is an important factor, influencing the extent of the digestion required, *e.g.*, for electroanalytical techniques complete breakdown of the organic components is necessary, whereas ICP-AES can tolerate dissolved solid contents of up to 1–2%. Also, the addition of certain reagents during the reaction can be considered. For example, the addition of boric acid for HF neutralisation may cause the final solution to possess a high solids content, which can give problems in sample introduction systems in addition to increasing the background signal and thus degrading sensitivity. ICP-MS suffers from a number of interferences, particularly polyatomic ion interferences. Hence the presence of a number of acids, including hydrochloric and sulfuric acid, in the final solution is not recommended for the determination of some elements. Therefore, adapting a digestion method for analysis by a different technique to that originally intended may not prove successful.

When considering the speed of a particular procedure, it is not just the time for the actual digestion that should be considered. Other factors should also be taken into account, *e.g.*, sample preparation before analysis, including grinding and slurry formation; pre-digestion and cooling times, including those necessary between reagent additions/heating cycles; and the washing of digestion vessels. These factors are often overlooked.

A standard method of validating a procedure is to use a suitable certified reference material. However, as discussed previously, there seems to be a lack of consistency in the 'grading' of these results. Often results are classed as 'good' even though they do not lie within the uncertainty limits of the certified values.

As mentioned above, it is not just digestion procedures which lend themselves to automation, but also the choice of digestion method. Chemometrics and factorial designs have been used effectively to help choose the best digestion procedure for a particular purpose. Models have also been developed to predict digestion methods depending on the composition of the sample of interest. This undoubtedly is a useful step forward, especially to predict digestion conditions for new samples.

For batch digestions, many closed digestion procedures are developed in terms of heating at a particular power setting for a certain period of time, usually optimised to maximise energy input without causing venting of the vessels. These procedures are therefore operational, *i.e.*, specific to the particular micro-wave system and bomb design used. Adaptation for use in a different laboratory may not be straightforward unless the same equipment is used, as re-optimisation of the original power settings and heating times may be necessary. The optimum power and time settings may also vary considerably according to the exact nature of the sample owing to the amount of organic matter present, which influences the amount of gaseous products evolved during the reaction.

It has been shown that direct temperature and pressure measurements during the course of the digestion are possible. Such measurements can then be fed to a computer controlling the magnetron to achieve a pre-set temperature or pressure programme. This technology offers the potential to produce far more reproducible and controllable procedures, reducing the possibility of venting of digestion vessels. In closed systems it also enables the system to be operated to its full digestion potential, *i.e.*, at its maximum pressure level without venting, regardless of the exact level of organic matter. Following this approach, digestion procedures can be transferred far more easily between similar samples and between different workers, and could potentially lead to the establishment of standard digestion procedures, in addition to improving the overall safety of this technique.

There has been a growing trend in recent years towards the development of fully automated on-line microwave digestion and analysis techniques. This area is well suited to water and waste water samples, of which a large number are routinely analysed in many laboratories. Open monomode (focused) systems have been found to be particularly useful for on-line applications. Further developments are likely through both the adaptation of standard batch digestion methods to on-line applications and in the development of new chemistries suited to the on-line approach. The digestion of solids is complicated by the method of introducing the sample into the system. Introduction in the form of a slurry is one approach; however, the determination of low levels of analyte may be problematic owing to limitations in the maximum stable slurry concentration. However, despite the initial problems encountered with on-line microwave digestion systems for solid samples, good results have been obtained for a number of biological and geological materials. This approach to sample digestion would seem to offer much potential for further development and could result in dramatic time savings over batch microwave and conventional digestion techniques.

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