Acid Digestion of Marine Samples for Trace Element Analysis Using Microwave Heating

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A commercial laboratory microwave - acid digestion system employing two types of closed vessel, (A) completely closed and (B) pressure-relief type, was evaluated for use in sample decomposition prior to the determination of trace elements in marine biological tissue and sediment samples. The decomposition procedure consists in acid digestion in Teflon PFA vessels (with an HNO_3 - $HClO_4$ mixture for marine biological tissues and an HNO_3 - HF - $HClO_4$ mixture for marine sediments) using microwave heating. Subsequent evaporation on a hot-plate was undertaken with the sediment material. The resulting solutions are analysed by flame and graphite furnace atomic absorption spectrometry and by inductively coupled plasma atomic emission spectrometry. Both vessels provide rapid and almost equally satisfactory results for sample dissolution and analysis. Vessel A was judged to be more convenient whereas vessel B is likely to be safer. The sample preparation time was approximately 30 min for the marine biological tissue and 3–4 h for the marine sediment samples (including subsequent evaporation time on a hot-plate following a 30-min microwave digestion).

Keywords: *Microwave digestion; trace metal analysis; graphite furnace atomic absorption spectrometry*

Significant advances have recently been made in analytical instrumentation possessing multi-element capability; however, sample decomposition techniques have not developed as markedly. Current concern over multi-element analyses of biological and sediment materials has resulted in an increasing need for a simple, rapid and accurate method for the preparation of large numbers of such samples. Acid digestion is widely used for the destruction of organic matrices prior to instrumental analysis by such techniques as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). However, wet dissolutions are time consuming and often the slowest step in the analytical procedure. The technique of acid digestion utilising pressure decomposition, well known among workers interested in elemental analyses,[1] is time consuming.

Many problems associated with wet ashing can be minimised if the digestion is performed in a microwave oven using a Teflon vessel. Samples and acid mixtures are heated internally by the oscillating electromagnetic field resulting in very rapid, safe and efficient decomposition. Several papers have appeared[2–10] concerned with the analytical application of microwave energy as the heat source to the acid-digestion system using both open and closed vessels. These papers have reported the successful application of the microwave acid-digestion system to a variety of samples and have demonstrated significant time savings.

Recently, Kingston and Jassie[9] reported the *in situ* measurement of elevated temperature and pressure in closed Teflon PFA (a tetrafluoroethylene with a fully fluorinated alkoxy side-chain) vessels during microwave acid decomposition studies of organic samples and the usefulness of a microwave system for the acid decomposition of biological samples prior to the determination of selenium by GFAAS.[10] Their studies resulted in the development of a more complete and efficient dissolution technique utilising pressurised vessels within a microwave oven.

This paper describes the application and evaluation of a commercial microwave digestion system using two different types of vessel: a completely closed type (CCT vessel) and a pressure-relief type (PRT vessel) for the dissolution of marine biological tissues and sediments prior to the determination of their trace element content. Decomposition utilising either vessel is simple, rapid and reliable and results in solutions suitable for multi-element analysis by FAAS, GFAAS and ICP-AES. The technique is now being routinely used in this laboratory for the dissolution of these and a variety of other samples.

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Experimental

Instrumentation

A Varian Techtron atomic absorption spectrometer, Model SpectrAA-40, equipped with a Varian Techtron GTA-96 graphite-tube atomiser was used for the determination of all elements except arsenic and selenium. Simultaneous background corrections were made using a deuterium lamp. Sample solutions were delivered to the furnace using a Varian Techtron PSC-56 programmable autosampler.

A Perkin-Elmer Model 5000 atomic absorption spectrometer, used for the determination of arsenic and selenium, was fitted with an HGA-500 graphite furnace with Zeeman background correction and an AS-40 autosampler.

Tubes coated with pyrolytic graphite were used exclusively in both AA instruments. Solubilised samples were held in acid-washed polypropylene cups prior to injection.

A Varian Techtron flame atomic absorption spectrometer, Model AA-775, and an Instruments SA (Metuchen, NJ) sequential inductively coupled plasma spectrometer, Model JY 38 VHR, were used for the determination of some elements.

A Coulometrics (Wheat Ridge, CO) total carbon analyser, Model 5020, and a CO_2 coulometer, Model 5010, were used for the determination of total carbon in solutions of digested biological tissue.

Microwave digestion of marine samples was accomplished with the use of a commercial oven, Model MDS-81 (CEM, Indian Trail, NC) equipped with a Teflon-coated oven cavity and removable 12-position sample carousel. The oven has a variable power range (up to 600 W) adjustable in 1% increments. A maximum of three sequential stages of varying power and time intervals are programmable. A variable-speed exhaust fan removed corrosive fumes through a 1 m × 8 cm diameter PVC hose mounted at the back wall of the microwave cavity and vented to a fume-hood. The existing turntable was altered by the supplier to provide a 270° reversing facility operating at 3 rev min^{-1} and a pressure line was installed through the microwave cavity wall to a trans-

ducer. Pressure measurements were made with a CEM Model PM pressure transducer connected to one of the digestion vessels via a length of $\frac{1}{8}$-in o.d. Teflon PFA tubing. The 2 m of tubing ahead of the sensor were filled with de-ionised, distilled water (DDW) to isolate the pressure sensor apparatus from the sample and thus prevent corrosion. A safety valve on the pressure sensor is designed to open if the internal pressure within the line exceeds 100 p.s.i.g.

Teflon PFA digestion vessels of 120-ml capacity were obtained from CEM. Two types of vessel were used: a completely closed type (CCT vessel) and a pressure-relief type (PRT vessel). For the latter vessel, a pressure-relief valve made of Teflon PFA was placed in the top of the vessel. This valve is designed to remain static while the pressure and temperature affect the dimensions of the vessel. If the internal pressure exceeds 75–85 p.s.i.g., the pressure-relief valve opens and the vapours are vented. During normal operation the vessel should not reach pressures sufficient to open the valve. A collection vessel in the centre of the turntable is designed to collect, condense and vent vapours which are released if the relief valve opens. The Teflon vent tubing from each type of vessel is inserted into a hole in the outer ring of the cap of the collection vessel. In each run of both types of digestion vessel, one vessel (120-ml capacity) including sample and acid mixture was used as a pressure monitor during the digestion procedure. This vessel was fitted with a $\frac{1}{8}$-in diameter transfer port and the line secured with a $\frac{1}{8}$-in ferruled Teflon nut. A capping station (CEM) equipped with a tightening collar was used to tighten the cap and to ensure reproducible torque (17 Nm). The digestion vessel with pressure measurement connection and the PRT vessel are shown in Fig. 1. Prior to use, all digestion vessels were conditioned by "annealing." A 20-ml volume of DDW was added to each vessel and the contents were cycled through three 30-min heating intervals during which the internal pressure was maintained at 80 p.s.i.g. A 5-ml volume of nitric acid was added to each vessel and heated in the microwave oven prior to each run of the sample digestion in order to effect cleaning. Calibration of the pressure transducer was accomplished with a commercial two-stage air-pressure regulator gauge at ambient temperature. The calibration was linear over the range 0–90 p.s.i.g. and was in good agreement with the transducer readout.

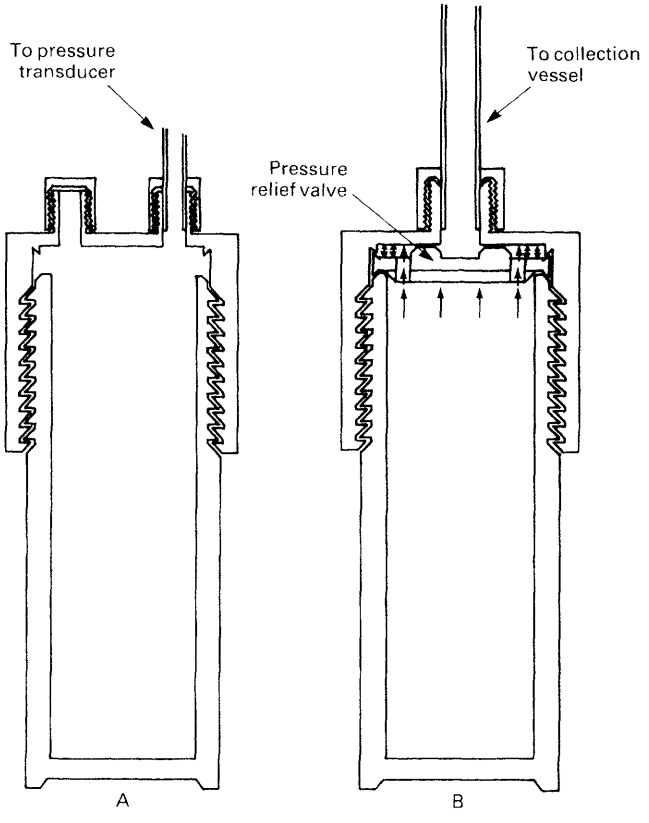

Fig. 1. Digestion vessel, 120-ml capacity: A, vessel for pressure monitoring and B, pressure-relief type vessel

Reagents

All reagents were purified prior to use. Concentrated nitric, perchloric and hydrochloric acids were prepared by sub-boiling distillation in a quartz still using analytical-reagent grade acids as feedstocks. Hydrofluoric acid was distilled in a commercial all-Teflon sub-boiling still.

Standard solutions of the elements were prepared by dissolution of the pure metals or their salts (Spex, Metuchen, NJ). Serial dilutions were made with high-purity DDW in order to prepare working standards.

Standards

Validation of the methods presented in this study was performed by using two certified reference materials from the National Research Council of Canada: NRCC lobster hepatopancreas (TORT-1) and NRCC marine sediment (MESS-1).

Procedures

All sample preparations were carried out in a clean laboratory equipped with laminar flow benches and fume cupboards providing a class-10 working environment.

Marine biological reference material TORT-1 was decomposed as follows: a 0.25-g dry sample was placed in a CCT or PRT digestion vessel and 6 ml of nitric and 0.5 ml of perchloric acids were added. A relief valve was placed in the top of the PRT vessel, the cap screwed down finger-tight and subsequently fastened tightly using the capping station. The sealed vessel was then positioned in the carousel of the microwave oven. Exhaust tubing from the vessel was secured through the hole in the outer ring of the cap of the collection vessel. For one vessel, used as the pressure monitor, the pressure sensor line was mounted through the transfer port of the vessel. The contents of the vessel were rapidly heated until the internal pressure reached 60–65 p.s.i.g. using full power (100%). This pressure was maintained for 20 min by heating at reduced power. If the pressure exceeded 65 p.s.i.g. during decomposition, the power was reduced in order to maintain a constant 60–65 p.s.i.g. After cooling, the vessel cap was loosened and the interior gas expelled into a fume hood. The cap was then removed and the vessel allowed to stand for *ca.* 2 min to release any further gas. The inside of the cap (and the pressure-relief valve in the case of the PRT vessel) was washed with small volumes of DDW and the contents were transferred into a 25-ml calibrated flask and diluted to volume with DDW. The sample solutions were stored in 30-ml screw-capped polypropylene bottles prior to the analysis for all elements. Up to 0.5 g of TORT-1 could be digested using 6 ml of nitric and 1 ml of perchloric acids at 70–75 p.s.i.g. Sample preparation for the biological tissue required about 30 min, including cooling time.

Several additional decomposition schemes were evaluated for the digestion of TORT-1 samples using CCT vessels. (1) Two-stage digestions were undertaken in which samples were heated at 80 p.s.i.g. for 20 min and then cooled. The cap was loosened and excess gas released. The vessel was then tightly re-sealed and the samples were again heated in the same manner. For comparison, three additional procedures were included: (2) a conventional single-stage microwave digestion at 70 p.s.i.g. for 20 min; (3) single-stage microwave digestion with subsequent hot-plate open digestion of the resultant solution; and (4) open beaker digestion on a hot-plate.

Corresponding blanks were also prepared according to each procedure.

The total residual carbon content in the resultant solutions was determined and used as a measure of the efficiency of the wet digestion procedure.

Marine sediment reference material MESS-1 was decomposed as follows: a 0.2-g dry sample (up to 0.6 g of MESS-1 could also be decomposed under the following conditions) was placed in a CCT or PRT vessel and 3 ml of nitric, 3 ml of hydrofluoric and 1 ml of perchloric acids were added. Then the same procedure cited for the decomposition of TORT-1 was followed. For the sediment material, an additional digestion was carried out following that in the microwave oven. The vessel, without cap, was placed on a hot-plate at *ca.* 180 °C and the solution was evaporated nearly to dryness under a heat lamp to remove the hydrofluoric acid. A 2-ml volume of hydrochloric acid was added to dissolve the residue and the solution heated further. A small volume of DDW was added and the contents were quantitatively transferred into a 50-ml calibrated flask and diluted to volume with DDW. The sample solutions were stored in 50-ml screw-capped polypropylene bottles prior to analysis. The digestion procedure for the sediment sample could be performed on a 3–4 h cycle (depending on the temperature of the hot-plate).

Blanks for the biological tissue and sediment samples were also prepared using these procedures in a manner identical with that for the samples.

For many biological and sediment samples, the sample solutions can be analysed directly by FAAS, GFAAS or ICP-AES. For the determination of arsenic and selenium by GFAAS, nickel was added as a matrix modifier. The furnace conditions for the atomisation of the sample solutions were as recommended by the manufacturer (or slightly modified).

Results and Discussion

The amount of sample which can be digested is often an important consideration. It is preferable to use as much sample as possible for some trace element determinations but the amount is limited by the maximum gas pressures which result from the decomposition of organic materials.

The microwave oven - acid dissolution system used in this study is the same as that used by Kingston *et al.*[9,10] These workers employed a completely closed vessel of small capacity (60 ml) for the destruction of biological samples. As Kingston *et al.* remarked,[9] the pressure rather than the temperature within the vessel is more often the limiting parameter with microwave oven closed-vessel digestion systems. Compared with sediment samples, biological samples produce more gaseous degradation products which increase the pressure in the system during heating. Therefore, prior to placement in the microwave oven, these workers pre-digested their samples with acid using a hot-plate until nearly dry. The CCT and PRT vessels tested in this study have a 120-ml capacity. In both instances pre-digestion was not required to decompose biological tissue samples weighing up to 0.5 g because of the low pressure rise during microwave heating compared with that which would occur using a small capacity (60 ml) digestion vessel. After microwave heating and cooling, using the experimental conditions described earlier, the residual pressure was close to 0 p.s.i.g. for the sediment sample, but remained at about 20 p.s.i.g. for the biological sample.

Kingston and Jassie[9] reported efficient decomposition of biological and botanical samples in the microwave oven using only nitric acid. In this study, perchloric acid was used in addition to nitric acid for decomposition as this mixture has a higher oxidising power and accelerates the digestion of samples, particularly biological tissue. Up to 0.5 g of biological tissue (TORT-1) could be decomposed in either type of vessel using 6 ml of nitric acid and 1 ml of perchloric acid at 70–75 p.s.i.g. with no pressure-release problems.

Table 1. Analysis of NRCC biological standard TORT-1

Element	Concentration/mg kg^{-1}* CCT vessel†	PRT vessel‡	Certified value/mg kg^{-1}§
As	25.6 ± 2.7	22.2 ± 1.3	24.6 ± 2.2
Cd	26.9 ± 1.8	27.5 ± 2.0	26.3 ± 2.1
Co	0.46 ± 0.05	0.40 ± 0.03	0.42 ± 0.05
Cr	2.2 ± 0.3	2.2 ± 0.4	2.4 ± 0.6
Cu	428 ± 57	390 ± 4¶	439 ± 22
	383 ± 6¶		
Fe	192 ± 20	181 ± 16¶	186 ± 11
	171 ± 16¶		
Mn	22.8 ± 2.0	20.9 ± 1.4	22.4 ± 1.0
Ni	2.2 ± 0.2	2.0 ± 0.2	2.3 ± 0.3
Pb	8.8 ± 0.7	8.7 ± 1.3	10.4 ± 2.0
Se	7.1 ± 0.4	7.1 ± 0.2	6.88 ± 0.47
Zn	163 ± 6	166 ± 4¶	177 ± 10

* Determined by GFAAS unless indicated otherwise.
† Mean and standard deviation of seven replicates.
‡ Mean and standard deviation of five replicates.
§ Precision expressed as 95% tolerance limits.
¶ Determined by FAAS.

Table 2. Analysis of NRCC sediment standard MESS-1

Element	Concentration/mg kg^{-1}* CCT vessel†	PRT vessel‡	Certified value/mg kg^{-1}§
As	10.9 ± 0.7	10.4 ± 0.7	10.6 ± 1.2
Cd	0.69 ± 0.06	0.63 ± 0.08	0.59 ± 0.10
Co	11.2 ± 0.8	10.4 ± 0.9	10.8 ± 1.9
Cr	59 ± 5	59 ± 1	71 ± 11
	62 ± 3¶	65 ± 2¶	
Cu	28.3 ± 2.0	27.4 ± 3.0 ‖	25.1 ± 3.8
	26.7 ± 0.8¶	27.9 ± 1.1¶	
Fe**	3.04 ± 0.06‖	3.01 ± 0.10‖	3.05 ± 0.18
	2.91 ± 0.06¶	3.14 ± 0.05¶	
Mn	480 ± 14‖	489 ± 21‖	513 ± 25
	513 ± 9¶	564 ± 12¶	
Ni	27.1 ± 1.5	26.4 ± 3.2	29.5 ± 2.7
	32.0 ± 5.6¶	29.6 ± 3.6¶	
Pb	33.7 ± 3.1	31.4 ± 2.7	34.0 ± 6.1
Zn	183 ± 4	185 ± 7‖	191 ± 17
	179 ± 6¶	197 ± 6¶	

* Determined by GFAAS unless indicated otherwise.
† Mean and standard deviation of six replicates (FAAS, GFAAS) or three replicates (ICP-AES).
‡ Mean and standard deviation of five replicates.
§ Precision expressed as 95% tolerance limits.
¶ ICP-AES.
‖ FAAS.
** Expressed as a percentage by mass.

Analytical Results

Although most trace elements in the solubilised samples of TORT-1 and MESS-1 were determined by GFAAS, FAAS or ICP-AES techniques were used for some elements. With the exception of Cr in MESS-1, analytical results for the determination of a number of trace elements in both samples are given in Tables 1 and 2 and are seen to be in good agreement with the NRCC certified values. The results for Cr in MESS-1 are biased low. Total dissolution of (presumably) chromite species in this sample using closed-vessel decomposition techniques is difficult[11] unless multiple addition - evaporation cycles of $HClO_4$ - HNO_3 are made to the sample residues following the initial closed-vessel decomposition.[12]

During *in situ* pressure monitoring using the PRT vessel connected to the transducer, an initial early release of pressure was detected in most vessels (presumably as the relief valve became seated). Despite this, even volatile elements such as arsenic and selenium exhibited no significant loss of analyte

during sample digestion using either type of decomposition vessel. The small relative standard deviations obtained for each element in TORT-1 and MESS-1 reflect the good reproducibility achieved with these digestion techniques. Comparison of the analytical results (Tables 1 and 2) reveals no significant difference between the performance of the CCT and PRT vessels with either sample. Therefore, the PRT vessel system can be used if the digestion pressure is kept below 75 p.s.i.g. However, caution is advised because of the pressure rise and potential leakage of liquid through the relief valve when using the PRT vessel system if this pressure is exceeded.

Blanks

As this procedure can reduce the amount of acids required for the decomposition of samples compared with open-beaker acid-digestion techniques, contamination from added reagents is reduced.

Procedural blank values obtained for biological tissue and sediment samples, given in Table 3, are almost identical for both types of vessels. These blank values did not contribute significantly to the trace element content of the samples studied here. The worst situation is that of chromium for which the blanks contribute approximately 13 and 1% of the indigenous element content of TORT-1 and MESS-1, respectively. Notably, both iron and chromium are frequent contaminants in Teflon material and, as such, probably reflect contamination from the decomposition vessels rather than the reagents. Blanks for cadmium, copper and lead obtained in this study were remarkably improved (reduced to below the detection limit), compared with those resulting from an open-beaker hot-plate digestion procedure of the same samples.[12]

Efficiency of Digestion

Kingston and Jassie[9] attempted to evaluate the completeness of dissolution of several biological and botanical samples wet digested with a similar microwave oven - pressurised vessel system. Free amino acid concentrations in the digests were measured and compared with those resulting from standard hot-plate wet-oxidation procedures (for human urine samples). The results of this approach reflect the comparative efficiency of protein hydrolysis in the samples and not necessarily that of total carbon oxidation efficiency.

In this study, the total residual carbon in a number of digested samples of TORT-1 was determined and used as a relative measure of the efficiency of the various digestion schemes. The results are summarised in Table 4. It is clear that digestion schemes which utilise the hot-plate to fume off the perchloric acid and take the sample to incipient dryness are the most efficient in terms of the total destruction of organic matter. Two-stage digestions undertaken in the microwave oven are clearly superior to single-stage techniques (without the hot-plate) and result in clear, colourless digests. By contrast, solutions recovered using single-stage microwave digestions were slightly yellow - green. It is concluded that, despite the 24% residual carbon content in the two-stage digests, the oxidation state of the carbon is higher than that in the single-stage digests.

Considering the need for close attention by the analyst, the lengthy time required (*ca.* 4 h) and the possible loss of volatile elements when subjecting samples to open-beaker wet digestions, the efficiency and speed of two-stage microwave digestion procedures clearly point to the superiority of this approach.

In terms of convenience and ease of use, the CCT vessel digestion system is preferred. In contrast to the PRT vessel system, where one needs to wash the cap and relief valve, the CCT vessel requires only a small volume of water to wash the inside of the cap after decomposition. If the CCT vessel is used, a final volume of 10 ml can easily be achieved. Therefore, for the determination of low concentrations of elements in biological samples this vessel is advantageous.

Both microwave digestion vessels described here are safe to operate as they allow the monitoring of pressure during the digestion. The manufacturer of the microwave heating equipment (CEM) advises that a completely closed vessel should not be used in the MDS-81 microwave oven. Our experience suggests that even a closed vessel can be operated safely if the pressure within the vessel containing a representative sample is monitored during digestion. To date, there have been no bursting problems during the digestion of a large number of biological and sediment materials using either vessel under the conditions mentioned above. However, for safe operation careful attention should be given to the nature and size of the sample and operating pressure, particularly when using the CCT vessel. In the case of the PRT vessel, the pressure-relief valve will open if the internal pressure reaches 75 to 85 p.s.i.g. and sometimes the liquid in the digestion vessel will also be vented into the collection vessel. Therefore, care should be taken to operate the PRT vessel below about 75 p.s.i.g.

At present, the Teflon vessels have been used for approximately 50–100 digestions with no apparent signs of fatigue under the conditions described. Hence, both digestion-vessel

Table 3. Absolute blank values. Mean and standard deviation of five determinations. Data were obtained by GFAAS

Element	Biological tissue/ng		Sediment/ng*	
	CCT vessel	PRT vessel	CCT vessel	PRT vessel
As	<10	<10	<20	<20
Cd	< 1	< 1	< 1	< 1
Co	< 5	< 5	< 5	< 5
Cr	71 ± 14	71 ± 12	110 ± 18	98 ± 24
Cu	< 2	< 2	< 5	< 5
Fe	36 ± 9	33 ± 9	68 ± 27	57 ± 27
Mn	< 6	< 6	< 2	< 2
Ni	< 5	< 5	<10	<10
Pb	< 5	< 5	< 5	< 5
Se	<20	<20	ND†	ND†
Zn	21 ± 12	31 ± 14	57 ± 13	42 ± 7

* Major constituents : SiO_2, 67.5 ± 1.9%; Al_2O_3, 11.03 ± 0.38%; and Fe_2O_3, 4.36 ± 0.25%.

† Not determined.

Table 4. Total residual carbon in digested samples of TORT-1

Method	Residual carbon*		Efficiency of oxidation, %
	In digestate/ μg ml^{-1}†	In dry sample/ mg g^{-1}	
Two-stage microwave digestion	1080 ± 110(3)	108 ± 11(3)	76
Single-stage microwave digestion	1630 ± 70(3)	163 ± 7(3)	64
Single-stage and hot-plate digestion	410 ± 60(4)	41 ± 6(4)	91
Open-beaker digestion	1070 ± 160(5)	54 ± 8(5)	88

* Total carbon content of undigested sample, 448 ± 6 mg g^{-1} (n = 3), dry mass basis. Mean and standard deviation reported. Number in parentheses is the number of replicates.

† Sample mass, 0.25 g (1.0 g for open-beaker digestion); final volume, 25 ml (50 ml for open-beaker digestion).

systems are well suited for the rapid preparation of samples prior to multi-element determinations in marine samples by FAAS, GFAAS or ICP-AES.

Conclusion

Use of either a CCT or PRT vessel in conjunction with microwave heating has proved to be a rapid and accurate dissolution technique for a wide range of marine samples including biological tissues and sediments prepared for multi-element trace analysis. This method is particularly suitable for the determination of volatile elements such as arsenic and selenium. The resultant solutions are suitable for use with a number of instrumental methods of analysis including FAAS, GFAAS, ICP-AES, ICP-MS and ASV (using two-stage digests). Additional advantages of the method include: (i) high efficiency of destruction of organic material under pressure; (ii) no need for sample pre-digestion; (iii) relatively small amounts of acid are required for digestion which reduces potential contamination from acids; and (iv) safe operation.

The sample preparation time for the microwave acid-digestion technique was about 30 min including subsequent cooling time for the biological tissue sample, and 3–4 h including subsequent heating time on the hot-plate after microwave digestion for the sediment sample.

If the contents of the digestion vessel for the sediment sample are transferred into a Teflon PFA beaker prior to heating on the hot-plate, the lifetime of the digestion vessel may be increased and the sample preparation time reduced further.

The authors thank H. M. Kingston for helpful advice, M. R. Miedema for ICP-AES results and V. P. Clancy for total carbon analyses.

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Paper A7/234
Received June 9th, 1987
Accepted July 14th, 1987