

# Vapour-phase Acid Digestion of Inorganic and Organic Matrices for Trace Element Analysis Using a Microwave Heated Bomb

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A vapour-phase microwave pressure digestion technique employing a special polytetrafluoroethylene-based microsampling device was evaluated for the acid digestion of marine sediment and biological tissue samples prior to the determination of their trace and minor element content. Inorganic and organic constituents are almost completely solubilized by vapour-phase attack (with an  $\text{HNO}_3$ -HF mixture for the marine sediment and  $\text{HNO}_3$  for the marine biological tissue) in a perfluoroalkoxy-Teflon pressure bomb. The residue was taken up in 0.5 mol dm<sup>-3</sup>  $\text{HNO}_3$  and analysed by flame and electrothermal atomic absorption spectrometry. Good agreement between the results and certified values for 15 elements was found. The sample preparation time was approximately 45 min for the biological tissue and 90 min for the sediment (including the subsequent cooling time and preparation of the final solution).

**Keywords:** *Vapour-phase microwave digestion; sediment and marine biological standards; elemental analysis; atomic absorption spectrometry*

Conversion of a test portion of sample into solution is a basic operation which, together with the analytical method used, can determine the precision and accuracy of the results obtained. In spite of remarkable progress in the field of measurement techniques, dissolution and decomposition of inorganic and organic materials remain of interest. Digestion of materials represents an important stage in the analysis, and several publications have been devoted to this subject.<sup>1,2</sup>

Two developments are apparent in the sample preparation procedures used or recommended over many years: (1) use of sealed pressure vessels (bombs) to accelerate sample digestion and minimize contamination and losses of volatile elements; and (2) use of microwave radiation to assist in digestion. The merits of pressure digestion in closed vessels are widely recognized<sup>3,4</sup> and it is perhaps not surprising that such techniques are attracting considerable attention. Recently, there has been a great deal of interest in relatively new techniques utilizing microwave technology for the preparation of samples of all types for analysis. As discussed in previous reviews,<sup>5-9</sup> microwave oven digestions are perhaps the most interesting development in sample preparation techniques investigated in the last 20 years. Microwave techniques continue to be developed and compared with the more established methods of sample digestion.

Although utilization of a polytetrafluoroethylene (PTFE) bomb for sample digestion procedures minimizes contamination by reagent(s) during the determination of trace elements, wet digestions at elevated temperature and pressure have the disadvantage that added reagents contribute to the over-all contamination load. In addition, after the samples have been digested, excess of acid(s) must often be removed. A number of papers have appeared on the use of gas-phase reactions to dissolve inorganic and organic matrices as an alternative to conventional PTFE bomb digestion. A recent review by Matusiewicz<sup>10</sup> summarized analytical methods based on vapour-phase attack for the preparation of samples prior to determination of their trace element content. However, no reports on the vapour-phase digestion of materials for their elemental analysis assisted by microwave heating were found. In general, sample attack occurred from the vapour phase only, ensuring that no acid(s) accumulated in the sample, that contamination was minimized and that the method gave very low blank values for impurity elements.

In spite of this, an alternative rapid digestion procedure was sought which would also achieve 'complete' solubilization. For this purpose, the use of vapour-phase digestion coupled

with rapid heating by microwave radiation was investigated to solubilize a marine sediment and biological tissue. The method developed is an extension of the acid vapour-phase thermal pressure decomposition of biological materials previously reported by Matusiewicz<sup>11</sup> and this paper discusses the further application and evaluation of this concept. The proposed method was applied successfully to the determination of 15 elements in two well-characterized reference materials.

## Experimental

### Instrumentation

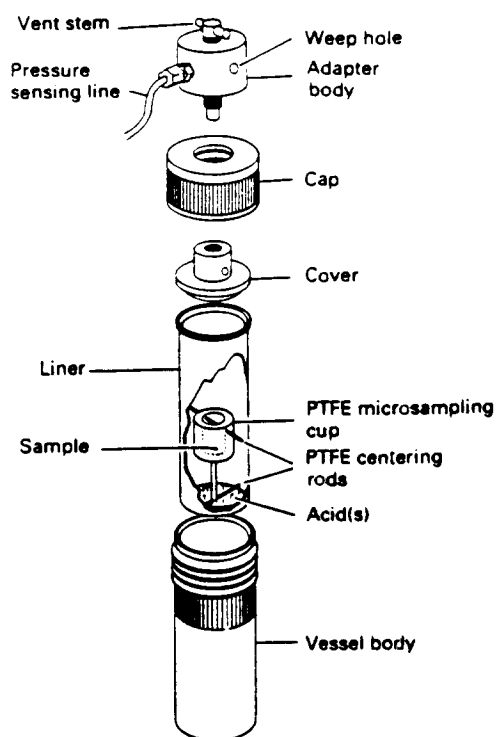
#### *Microwave oven*

A commercially available laboratory oven, Model MDS-81 (CEM, Indian Trail, NC, USA), rated at 600 W was used for microwave digestions. The instrument and its operating conditions have been described previously.<sup>12</sup>

#### *Lined microwave digestion vessel*

A lined digestion vessel of 100 ml volume and manufactured from perfluoroalkoxy (PFA)-Teflon was obtained from CEM. All PTFE materials referred to are manufactured from tetrafluoroethylene with a fully fluorinated alkoxy side-chain (*i.e.*, PFA-Teflon). The bomb can be used at temperatures of up to 250 °C and a maximum pressure of 13.6 atm (1378 020 Pa, 199.9 psi). Venting of digestion or reaction products is controlled with a proprietary sealing and vent stem (a thin fluoroplastic rupture foil is inserted between the body and the cap which acts as a seal) and the vessel can be tightened by hand or opened easily.

A laboratory-built all-PTFE microsampling device based on a design outlined by Matusiewicz<sup>13</sup> was employed for vapour-phase sample digestion. The device was modified so that a relatively large volume sample cup (inner volume 4 ml) could be accommodated in the Teflon vessel described above. A Teflon bar was attached across the top to facilitate removal of the microsampling cup from the PFA-Teflon vessel by means of a Teflon hook. The microwave digestion vessel with a pressure sensor connector (controller adaptor) and the PTFE microsampling device are shown in Fig. 1. Prior to use, the digestion vessel and PTFE microsampling cup were cleaned by leaching with  $\text{HNO}_3$ .



**Fig. 1** Cross-section of the PFA-Teflon vessel with PTFE microsampling cup for vapour-phase microwave digestion

### Measurement apparatus

A Perkin-Elmer Model 5000 atomic absorption spectrometer equipped with an HGA-500 furnace and AS-40 autosampler and a Varian Techtron Model SpectrAA-40 Zeeman atomic absorption spectrometer fitted with a GTA-96 furnace and a PSC-56 autosampler were used for trace element determinations. Operating parameters have been described previously.<sup>12</sup> A Varian Techtron flame (air-acetylene) atomic absorption spectrometer, Model AA-775, was used for the determination of minor elements.

A Coulometrics (Wheat Ridge, CO, USA) Model 5020 total carbon analyser and a Model 5010 CO<sub>2</sub> coulometer were used for the determination of total carbon in the solutions of digested marine materials.

### Reagents

Concentrated HNO<sub>3</sub> was purified prior to use by sub-boiling distillation in a quartz still using the analytical-reagent grade acid as feedstock. 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 Industries, Metuchen, NJ, USA). Serial dilutions were made with high-purity distilled, de-ionized water (DDW) (specific resistivity 18 mΩ cm) (Barnstead Nanopure system) in order to prepare working standards.

### Reference Materials

Validation of the methods described in this work was performed using two certified reference materials (CRMs) from the National Research Council of Canada: NRCC MESS-1 Marine Sediment and NRCC TORT-1 Lobster Hepatopancreas.

### Vapour-phase Microwave Sample Digestion

All sample preparations were conducted in a clean laboratory

equipped with laminar flow benches and fume cupboards providing a class 10 working environment.

The PFA-Teflon bomb and PTFE microsampling device were hot-leached with concentrated HNO<sub>3</sub> for 5 min, during which time the internal pressure was maintained at 5 atm (506 625 Pa, 73.5 psi). Suitable sample masses of MESS-1 and TORT-1 (approximately 0.250 g) were transferred into the PTFE cup of the microsampling device, which was then lowered into the 100 ml PFA-Teflon vessel containing concentrated acid or a mixture of acids. For MESS-1, the PFA-Teflon vessel contained 1 ml of HNO<sub>3</sub> and 5 ml of HF. For the digestion of TORT-1, 6 ml of HNO<sub>3</sub> were used. In addition, the sample in the PTFE cup was initially wetted with 600 μl of HNO<sub>3</sub> to prevent charring of organic material, as had been noted previously.<sup>14</sup> The vessel cap was tightly secured by hand and the complete assembly was then heated in a microwave oven for 25 min at 35% power (210 W) (for MESS-1) or for 5 min at 10% power (60 W) followed by 5 min at 15% power (90 W) and 15 min at 25% power (150 W) (for TORT-1). The maximum pressure achieved in the sealed vessel during microwave irradiation was approximately 13 atm (1317 225 Pa, 191 psi). After cooling the vessel to room temperature in an ice-bath in order to reduce the internal pressure, unscrewing the cap and removing the inner PTFE microsampling device, an almost dry and light-coloured (MESS-1) or light brownish yellow coloured (TORT-1) residue was observed. The residue (MESS-1) was washed with small volumes of DDW and the contents were transferred into a beaker and heated for about 30 min. After cooling, the contents were transferred into a 25 ml calibrated flask and diluted to volume with 0.5 mol dm<sup>-3</sup> HNO<sub>3</sub>. Sample solutions were stored in 30 ml screw-capped polypropylene bottles prior to analysis. The TORT-1 residue was completely soluble in 0.5 mol dm<sup>-3</sup> HNO<sub>3</sub>. The contents were transferred into a 25 ml calibrated flask and diluted to volume with DDW. Sample solutions were stored in 30 ml screw-capped polypropylene bottles prior to analysis.

Sample preparations for these marine materials required about 90 min for MESS-1 and 45 min for TORT-1, including the subsequent cooling time and preparation of the final solution. Corresponding blanks were also prepared according to the above procedure.

### Analysis

The total residual carbon content in the resulting solutions was determined and used as a measure of the efficiency of vapour-phase digestion.

Sample solutions were analysed directly by flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ETAAS). For the determination of As and Se by ETAAS, Pd (10 μg) was added as a chemical modifier. The furnace conditions for the atomization of the sample solutions were as recommended by the manufacturer or were modified slightly.<sup>12,14</sup>

## Results and Discussion

### Pressure Evaluation

Pressure, rather than temperature within the vessel, is more often the limiting parameter with microwave oven closed-vessel digestion systems.<sup>15</sup> In both instances (MESS-1 and TORT-1) initial experiments were undertaken in order to assess the pressure generated during vapour-phase digestion. Using a 100 ml PFA-Teflon vessel, samples of MESS-1 and TORT-1 were vapour-phase digested with different volumes of HNO<sub>3</sub>-HF or HNO<sub>3</sub>, respectively. With low applied power, a gentle, continuous rise in pressure was observed during digestion. The objective was to obtain conditions which resulted in a clear, colourless solution (after dissolution of the residue

left in the PTFE cup) with maximum carbon oxidation efficiency. A mixture of 5 ml of HF and 1 ml of HNO<sub>3</sub> (for MESS-1) and 6 ml of HNO<sub>3</sub> (for TORT-1) proved to be the most satisfactory for samples of 250 mg. A maximum pressure of 13 atm (1317225 Pa, 191 psi) was achieved slowly (after about 12–18 min). After microwave heating and cooling to room temperature, the residual pressure was approximately 0.5 atm (50663 Pa, 7.4 psi) for the sediment sample, but remained at about 2.5 atm (253313 Pa, 36.7 psi) for the biological sample.

### Effect of Heating Time and Digestion Power

Microwave energy produces an intense internal heating, together with a differential polarization effect.<sup>7</sup> This can agitate and rupture sample surface layers and expose new surfaces to the attacking acid vapours. Full power (600 W, 100% output) heating could not be used to digest the samples. In order to avoid a violent digestion reaction in the pressure vessel, a very mild and safe heating programme was used for vapour-phase sample digestion. The time necessary for complete digestion with the selected acid mixtures was examined over the range 5–30 min (at 35 and 25% power output for MESS-1 and TORT-1, respectively). At a heating time longer than 25 min, with the 100 ml PFA-Teflon vessel, no further changes in digestion efficiency were observed. For TORT-1, digestion was performed using a microwave programme of 10% power (60 W) for 5 min followed by 15% power (90 W) for 5 min and 25% power (150 W) for 15 min in order to avoid sample charring. Under optimum conditions the entire procedure, including heating and cooling steps and also sample preparation, took about 45 min for TORT-1. The procedure was found to be safe if overheating was avoided. When microwave vapour-phase digestion of MESS-1 was judged to be complete, it was found that the matrix had not completely dissolved in 0.5 mol dm<sup>-3</sup> HNO<sub>3</sub>. This problem was overcome by heating the sample for about 30 min on a hot-plate until almost complete dissolution of the residue was achieved. Approximately 1 mg of insolubles (probably silica) remained. The entire procedure required about 90 min.

Multiple samples could be prepared concurrently, limited only by the number of digestion bombs and PTFE microsampling devices available.

### Impurity Transport and Element Volatility Study

Although acid vapour-phase digestion procedures have been used previously,<sup>10</sup> no data are available on the possible transfer of trace elements from reagents to sample during the digestion process during microwave heating.

In order to ascertain whether such a transfer could occur, it was desirable to use comparatively large amounts of trace element impurities in the acid solution. Trace amounts of the 15 elements to be determined were added (in artificially contaminated acid) to the acid mixture (HF–HNO<sub>3</sub>) before use in amounts which contained up to 10 ppm of each element. These amounts were sufficiently large to allow the results of any contaminant transfer to be easily observed. Trace element levels in the condensate within the microsampling cup were measured as was the reagent acid mixture after the vapour-phase treatment. All of the trace elements added remained in the acid mixture, indicating that no trace elements had been volatilized and transferred into the sample cup. Therefore, it can be concluded that no detectable transfer of reagent impurity occurs during the vapour-phase microwave digestion process. It is noteworthy that the purity (and the grade) of the initial acid(s) used does not have any significant effect and is not important in the proposed digestion method.

**Table 1** Procedural blank values. Determined by ETAAS: means of six determinations; fixed volume, 25 ml

Element	Sediment/ng	Biological tissue/ng
As	<8	<4
Cd	<1	<0.5
Co	<4	<2
Cr	<10	<4
Cu	<4	ND*
Mn	ND	<5
Mo	<10	<6
Ni	<8	<4
Pb	<6	<4
Se	<10	<8
V	<10	<6

\*ND = Not determined.

**Table 2** Analysis of NRCC CRM MESS-1

Element	Concentration*/µg g <sup>-1</sup>	Certified value†/µg g <sup>-1</sup>
As	10.2 ± 1.0	10.6 ± 1.2
Cd	0.69 ± 0.11	0.59 ± 0.10
Co	11.5 ± 2.0	10.8 ± 1.9
Cr	51 ± 10	71 ± 11
Cu	28.8 ± 4.5	25.1 ± 3.8
Mn‡	490 ± 20	513 ± 25
Ni	31.5 ± 3.5	29.5 ± 2.7
Pb	32.1 ± 5.2	34.0 ± 6.1
Sn	3.6 ± 0.5	3.98 ± 0.44
V	75 ± 15	72.4 ± 17
Zn‡	180 ± 14	191 ± 17

\* Determined by ETAAS unless indicated otherwise; mean ± standard deviation of six replicates.

† Precision expressed as 95% tolerance limits.

‡ Determined by FAAS.

### Blanks

With each new digestion technique designed for trace level determination, the element blank contributed by the digestion vessel and reagents must be documented by the analyst for accurate analysis. The accuracy of the data will be highly dependent on the quality of blank determinations.

Blanks were prepared and analysed by subjecting them to the same procedures as the samples. Procedural blank values obtained for sediment and biological tissue samples for all the analytes of interest are summarized in Table 1. In all instances, blank levels in the resulting solutions were below the detection capability of ETAAS, leading to the conclusion that contamination appears to make no significant contribution to the total content of analytes in MESS-1 and TORT-1.

This procedure offers an alternative to thermal vapour-phase bomb digestion and has the advantage of extremely low blank values. Low blanks were obtained because distilled HF and/or HNO<sub>3</sub> vapour was the main oxidant or reagent, and trace impurities in the liquid reagent did not reach the sample.

### Accuracy

In order to evaluate the reliability of the data and the accuracy of the methodology, two NRCC marine CRMs were analysed.

Tables 2 and 3 present results for trace and minor element content determined after using the proposed vapour-phase microwave digestion procedure. Agreement between the results obtained in this work and certified values is good, with one exception; values for Cr in MESS-1 are biased lower than the certified value. It is possible that this element is bound in several forms and its low recovery might be due to incomplete dissolution of (presumably) chromite species<sup>12</sup> or to the

Table 3 Analysis of NRCC CRM TORT-1

Element	Concentration*/ $\mu\text{g g}^{-1}$	Certified value†/ $\mu\text{g g}^{-1}$
As	25.2 ± 1.5	24.6 ± 2.2
Cd	28.0 ± 1.9	26.3 ± 2.1
Co	0.40 ± 0.06	0.42 ± 0.05
Cr	2.1 ± 0.4	2.4 ± 0.6
Cu‡	422 ± 20	439 ± 22
Fe‡	190 ± 13	186 ± 11
Mn	22.5 ± 2.0	23.4 ± 1.0
Mo	1.5 ± 0.3	1.5 ± 0.3
Ni	2.1 ± 0.3	2.3 ± 0.3
Pb	11.0 ± 1.9	10.4 ± 2.0
Se	6.5 ± 0.6	6.88 ± 0.47
Sr‡	119 ± 10	113 ± 5
V	1.1 ± 0.3	1.4 ± 0.3
Zn‡	170 ± 12	177 ± 10

\* Determined by ETAAS unless indicated otherwise: mean ± standard deviation of six replicates.

† Precision expressed as 95% tolerance limits.

‡ Determined by FAAS.

existence of some chemical forms of Cr that are resistant to acid vapour-phase digestion.

In general, however, these data support the validity of the proposed digestion procedure and operating conditions and confirm the suitability of the system for trace and minor element determinations in inorganic and organic matrices.

Additionally, it is clear that none of the elements, including volatile elements such as As and Se, is lost from the samples with this type of digestion procedure.

### Efficiency of Vapour-phase Digestion

Relatively few observations have been reported concerning the completeness of microwave sample digestion<sup>7</sup> and emphasis should be placed on increased exploitation of the efficiency of the microwave digestion technique. One way of evaluating the completeness of a digestion procedure is to determine the residual carbon content in the samples after decomposition.

In this work, the total residual carbon in digested samples of TORT-1 was determined and used as a relative measure of the efficiency of vapour-phase microwave digestion. The results, summarized in Table 4, clearly show that the organic matrix has been almost completely oxidized during pressurized vapour-phase microwave digestion. This implies that about 3% of the carbon originally present in the sample remains incompletely oxidized in the digest. It has been reported<sup>16,17</sup> that the isomers of nitrobenzoic acid are common oxidation-resistant products of the high temperature attack of biological materials with  $\text{HNO}_3$ . These species might account for the residual carbon noted in this work. Enhanced efficiency of digestion was obtained with the proposed vapour-phase  $\text{HNO}_3$  procedure compared with the use of a conventional  $\text{HNO}_3$ - $\text{H}_2\text{O}_2$  mixture<sup>14</sup> or with  $\text{HNO}_3$ - $\text{HClO}_4$ .<sup>12</sup> Experiments with two-stage vapour-phase digestions undertaken in the microwave oven did not yield any significant increase in the oxidation efficiency.

In this work,  $\text{HClO}_4$  was not used because it has been shown that this acid is not effective for the decomposition of organic matter in the vapour phase.<sup>18</sup> This is because the boiling-point of  $\text{HClO}_4$  is higher and its vapour pressure lower than those of the other acids.

### Conclusions

A recent review of acid vapour-phase sample digestion by Matusiewicz<sup>10</sup> has highlighted one interesting problem for future study. A comment in the final section of that paper is

Table 4 Total residual carbon in vapour-phase microwave digested samples of TORT-1

Method	Sample mass/g	Final volume/ml	Time/min	Efficiency of oxidation*(%)
Single-stage digestion	0.25	25	25	97.4 ± 1.5
Two-stage digestion‡	0.25	25	40	97.1 ± 1.5

\* Five measurements from a sample preparation; total carbon content of undigested sample: 423 ± 10  $\text{mg g}^{-1}$  ( $n=3$ ), dry mass basis.

† Digestion scheme which utilizes digestion for 25 min and, after venting, a further digestion period of 15 min.

particularly pertinent to the work reported here: 'Emphasis should be placed on an evaluation and investigation of vapour-phase microwave digestion of inorganic and organic materials'. In this respect, we believe that vapour-phase microwave digestion can make a significant contribution.

Vapour-phase sample digestion in pressurized PFA-Teflon vessels using microwave radiation has proved to be an extremely effective method for the digestion of organic and inorganic material. Results obtained using  $\text{HNO}_3$  and  $\text{HF-HNO}_3$  digestion yield trace and minor element data that are in good agreement with certified values, with the exception of Cr in inorganic matrices.

In addition to the obvious advantages of low blanks, the vapour-phase microwave digestion method, when used for the dissolution of marine sediment and for the decomposition of marine biological tissue, has the advantage of producing a dry digestion product that is soluble in water or slightly acidified water. Therefore, tedious evaporation of excess of acid(s) is avoided. The disadvantages are that the samples might not be totally dissolved and that care must be taken not to over-pressurize the closed digestion vessel. Hence, the microwave heating programme must be carefully selected. An additional way to avoid rapid and uncontrolled heating might be to use a glass insert (tube) or special liner which is a heavy absorber of microwave energy. Such an insert or liner allows a combination of microwave/thermal heating to be applied to the sample. In this instance, the walls of the vessel will attain a higher temperature, minimizing condensation of vapour. This should produce higher pressure in the closed vessels and a higher temperature in the solution phase, even with reduced microwave power.

The primary advantage of the proposed method is that the closed PFA-Teflon vessel enables higher pressure and presumably a higher temperature to be reached while lowering the blank by application of isopiestic distillation of the reagents. Therefore, requirements with respect to the purity of the acid(s) can be less stringent. However, this advantage might be partly offset by the requirement of a longer digestion time or by the introduction of contamination during weighing of the Teflon cup. Additionally, the effects of pressure and temperature during vapour-phase digestion remain to be evaluated. The proposed method could be applied to the determination of major, minor, trace and ultratrace elements in samples and should find application in the analysis of other types of inorganic and organic materials.

Further work using different types of closed vessels, other reagent combinations and other reaction conditions in order to achieve complete decomposition of organic matrices is currently in progress.

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### References

- 1 Bock, R., *A Handbook of Decomposition Methods in Analytical Chemistry*. International Textbook Co., London, 1979.
- 2 Sulcek, Z., and Povondra, P., *Methods of Decomposition in Inorganic Analysis*. CRC Press, Boca Raton, FL, 1989.
- 3 Jackwerth, E., and Gomiscek, S., *Pure Appl. Chem.*, 1984, **56**, 479.
- 4 Griepink, B., and Tölg, G., *Pure Appl. Chem.*, 1989, **61**, 1139.
- 5 *Introduction to Microwave Sample Preparation: Theory and Practice*, eds. Kingston, H. M., and Jassie, L. B., American Chemical Society, Washington, DC, 1988.
- 6 de la Guardia, M., Salvador, A., Burguera, J. L., and Burguera, M., *J. Flow Injection Anal.*, 1988, **5**, 121.
- 7 Matusiewicz, H., and Sturgeon, R. E., *Prng. Anal. Spectrosc.*, 1989, **12**, 21.
- 8 Sulcek, Z., Novak, J., and Vyskocil, J., *Chem. Listy*, 1989, **83**, 388.
- 9 Kimber, G. M., and Kokot, S., *TrAC, Trends Anal. Chem. (Pers. Ed.)*, 1990, **9**, 203.
- 10 Matusiewicz, H., *Spectrosc., Int.*, 1991, **3**, 22.
- 11 Matusiewicz, H., *J. Anal. At. Spectrom.*, 1989, **4**, 265.
- 12 Nakashima, S., Sturgeon, R. E., Willie, S. N., and Berman, S. S., *Analyst*, 1988, **113**, 159.
- 13 Matusiewicz, H., *Chem. Anal. (Warsaw)*, 1988, **33**, 173.
- 14 Matusiewicz, H., Sturgeon, R. E., and Berman, S. S., *J. Anal. At. Spectrom.*, 1989, **4**, 323.
- 15 Kingston, H. M., and Jassie, L. B., *Anal. Chem.*, 1986, **58**, 2534.
- 16 Pratt, K. W., Kingston, H. M., MacCrehan, W. A., and Koch, W. F., *Anal. Chem.*, 1988, **60**, 2024.
- 17 Würfels, M., Jackwerth, E., and Stoeppler, M., *Anal. Chim. Acta*, 1989, **226**, 31.
- 18 Kojima, I., and Iida, C., *Anal. Sci.*, 1986, **2**, 567.

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