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Trace element analysis of high-purity graphite following open-focused microwave assisted digestion

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Abstract

Microwave assisted wet digestion of high-purity graphite was successfully accomplished at atmospheric pressure using an open-focused system. Samples of *0.2 - 3* g mass were treated with a 1:2 (*v/v*) mixture of HNO_3 and H_2SO_4. Measurements of the residual organic carbon in the digests, trace element recovery and extent of contamination (magnitude of the blank) were used to characterize the performance of the methodology. A Prolabo Microdigest M 401 unit, fitted with a modified reaction vessel, served to digest samples. Trace element determinations of the graphite were completed by graphite furnace atomic absorption spectrometry (GFAAS). Accuracy was assessed *via* the concurrent digestion and analysis of two certified reference materials (LUTS-1, a lobster hepatopancreas from the National Research Council of Canada; and CRM 1632a, a reference coal material from the National Institute of Standards and Technology). Spike recovery of elements added to graphite samples (As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Sr, and Zn) averaged *88%* [range 79(Pb) - 94(Cd) %]. Limits of detection (ng/g) in the graphite ranged from *0.8* (Cd) to 160 (Se). Precision of replicate determination averaged 10% (relative standard deviation) for trace impurity concentrations (ng/g) of < *2* (Pb) - 190 (As).

Key words: Graphite; microwave digestion; open-focused microwave; reference material; trace elements.

Determinación de elementos trazas en grafito de alta pureza por espectrometría de absorción atómica con horno de grafito luego de digestión con microonda enfocada abierta

Resumen

Digestión húmeda asistida por microonda *de* grafito de alta pureza fue exitosamente lograda a presión atmosférica usando un sistema enfocado abierto. Muestras *de* 0.2-3g se trataron con una mezcla 1:2 (*v/v*) de HNO_3 *y* H_2SO_4. La calidad *de* la metodologia *se* caracterizó a través de mediciones del carbono orgánico residual en los digeridos, de la recuperación de

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los elementos trazas y de la extensión de la contaminación (magnitud de los blancos). Una unidad Prolabo Microdigest M 401, equipada con un recipiente de reacción modificado, sirvió para digerir las muestras. La determinación de los elementos trazas en el grafito se hizo por espectrometría de absorción atómica con horno de grafito (GFAAS). La exactitud se estableció a través de la digestión concurrente y análisis de dos materiales referenciales certificados (LUTS-1, hepatopáncreas de langosta, del Consejo de Investigación Nacional de Canadá; y CRM 1632a, material referencial de carbón, del Instituto Nacional de Standards y Tecnología. La recuperación de los elementos agregados a las muestras de grafito (As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Sr y Zn) promedió un 88% [rango 79 (Pb) - 94 (Cd) %]. Los límites de detección (ng/g) en el grafito oscilaron desde 0.8 (Cd) hasta 160 (Se). La precisión en la determinación replicada promedió un 10% (desviación standard relativa) para concentraciones de impurezas (ng/g) de 2 (Pb) - 190 (As).

Palabras claves: Digestión por microondas; grafito; material de referencia; microonda enfocada abierta.

Introduction

Graphite possesses a number of desirable physico-chemical properties which makes it an attractive material for use in the nuclear industry, for construction where light-weight high-strength composites are required, and in applications demanding high-purity and high-temperature inertness. As such, the control of chemical purity is of paramount importance, as it influences the performance of the product. This is nowhere more significant to the trace element analyst than the quality control evident to guarantee high-purity crucibles and furnaces for use in atomic absorption spectroscopy. Arc spectrography is widely practiced for this purpose (1) but requires suitable reference solids for calibration. Although this is obviated through dissolution of the material prior to analysis by atomic spectrometric techniques, the latter demands high instrumental detection power to compensate for the substantial dilution of the trace impurities which accompanies solubilization. Oxidative ashing at elevated temperature risks losses of the more volatile elements (2). Wet digestion at 200°C in a mixture of periodic and perchloric acid has been used to solubilize 1 g samples of high purity graphite for the purposes of trace element analysis (3). Application of microwaves to assist with the digestion process has been investigated by Nadkarni (4) for the determination of trace elements in coal but difficulties were encountered in extracting full recovery of elements such as Cr, Fe, Ni and Ti. More recently, Koshino and Narukawa (5) successfully decomposed 0.5 g samples of graphite powder with a mixture of HNO_3 and H_2SO_4 acids using a closed digestion vessel heated to 250°C in a thermal oven. At least 72 h were required for complete decomposition. Unfortunately, analyses were undertaken by ICP-AES, and for this reason the detection power for impurities was limited to the 10 - 100 ng/g range. Closed vessel digestion of such material presents several problems, not the least of which is the limitation of sample size in accordance with the safe operating pressure of the device.

Microwave assisted digestion techniques are now widely practiced throughout the analytical community. In particular, those undertaken using closed Teflon PFA vessels have become accepted methodology utilized in many laboratories for sample preparation, justified by such advantages as rapid processing with a minimal quantity of reagents and potentially improved accuracy and precision as a consequence of the decreased risk of contamination and reduced loss of the more volatile analytes (6). One of the few drawbacks of the methodology, however, is the limited sample size that can be accommodated with existing commercial vessels. The upper limit for biological or geological samples is typically 500 mg and, depending on their organic carbon content, this may be considerably reduced. For graphitic samples, this limit is typically 0.2 - 0.5 g. Often, for trace metal analysis, a larger sample mass is needed to achieve a final solution concentration sufficiently above the detection limit of the instrumental technique to permit precise analysis. Frequently, a larger test portion must be taken to overcome potential inhomogeneity of the sample. An alternative to combining the digests from numerous digestions of smaller sample masses is use of an open-focused microwave digestion system capable of accommodating up to 10 g of material (7-9). This approach to digestion of graphite was examined in this study. Recovery of analyte elements from the sample was verified using spiked samples and accuracy was assessed by processing a coal certified reference material.

Materials and Methods

Apparatus

A commercial open-focused microwave system, the Prolabo Microdigest M 401(Paris France) equipped with a programmable controller, was used for microwave digestions. The lower 10 cm portion of the original Pyrex digestion vessel was replaced with quartz and joined to the upper portion *via* six grades of thermal expansive glass seals. Provision was made for refluxing the sample during long heating times by the addition of a single turn 6 mm od quartz cooling line to the upper internal neck of the vessel, well removed from the microwave field. All vessels were precleaned by refluxing in a mixture of 1:1 HNO_3:H_2SO_4 for 2 h, followed by rinsing in high-purity deionized distilled water (DDW) prepared from a mixed bed ion-exchange system (18.3 MΩ-cm, Barnsted, NanoPure) between every run.

All trace metal determinations in the dissolved graphite samples were performed by graphite furnace atomic absorption spectrometry (GFAAS) using a Varian SpectrAA 30/40 instrument equipped with a GTA 96 graphite tube atomizer and Zeeman background correction. All elements of interest in the coal SRM were determined by flame AAS using a Varian flame atomic absorption spectrometer (Model AA-775) and/or by inductively coupled plasma atomic emission with a Jobin Yvon 38 ICP emission spectrometer. All elements of interest in LUTS-1 samples were determined by GFAAS with the exception of Cd, Cu, Fe, Mn, Sr and Zn, which were determined by ICP-AES. Either a Coulometrics Inc. (Wheat Ridge, CO) total carbon analyzer, Model 5020, or a total organic carbon analyzer, Model TOC 5050 (Shimazi Co., Japan) were used for the determination of residual carbon in the digest solutions and in the parent solid material before digestion.

Reagents

High purity acids were used for sample preparation: concentrated nitric, perchloric and hydrochloric acids were prepared inhouse by sub-boiling distillation in a quartz still using reagent grade acids as feedstocks. High-purity sulphuric acid was supplied by Seastar Chemicals (Sydney,B.C., Canada). Stock standard solutions (1000 mg/l) of As, Cd, Cr, Co, Pb, Se, Sr and Zn were obtained as atomic absorption standards (Seigniory Chemicals, Quebec, Can.) whereas stock solutions of Cu, Fe, Mn and Ni were prepared by dissolution of high-purity metals (99.998%, Ward Hill, MA, U.S.A.). Serial dilutions were made with DDW containing 1-10% (v/v) HNO_3.

Table 1
Typical microwave digestion procedure for 1 g sample of graphite

Step #	Power,%	Time, min	HNO_3,ml	H_2SO_4,ml	Comments
1	95	110	0	0	digestion
2	0	5	4	1	cooling
3	95	180	0	0	digestion
4	60	8	0	0	evaporation
5	0	5	8	0	cooling
6	80	40	0	0	digestion
7	30	2	0	0	evaporation

*Initial acid mixture consists of 5 ml HNO_3 and 4 ml H_2SO_4

Samples

Samples of high-purity graphite were obtained as 6 mm od rod from Ringsdorff -Werke GmbH (Bon, Germany) and were identified for use as dc arc sample electrodes having a maximum concentration of 1 μg/g trace element impurities.

For evaluation of accuracy, a National Institute of Standards and Technology (NIST) coal reference material for trace elements, SRM 1632a, and a National Research Council of Canada (NRCC) lobster hepatopancreas reference tissue for trace elements, LUTS-1, were used. Although the latter material is not at all similar in structure to the graphite samples studied here, it was included in all procedures and analysed as a verification of the overall accuracy of the approach. Whereas the NIST coal sample provided an ideal match to the graphite matrix, this material is only certified for 7 (Cr, Co, Cu, Fe, Mn, Ni and Zn) of the 12 trace elements studied and by itself was insufficient as a check for accuracy of the additional elements studied (As, Cd, Pb, Se and Sr).

Digestion Procedure

All sample manipulations and analyses of digested materials were conducted in a class 100 clean-room environment. Short lengths of graphite rod were placed in precleaned polyethylene bags and carefully crushed with blows from a mallet until a fine powder was achieved. No effort was made to size-fractionate the powder by sieving before use. Contamination was minimized by ensuring that no sample was exposed to any surface other than that of the polyethylene bags. The resultant graphite powder was subsequently leached by immersion in a mixture of 15% HCl and 5% HNO_3 (*v/v*) for varying periods of time before being rinsed with DDW and carefully dried to constant weight under a heat lamp in a class 10 hood. Samples of 1632a coal were weighed out directly from the parent material.

Typically, a 1 g mass of the powdered sample was placed in the bottom of the digestion vessel, 5 ml of HNO_3 and 4 ml H_2SO_4 added, and the sample subjected to the digestion procedure outlined in Table 1. The mixture was heated at 95% power output for 110 min to effect the initial digestion. Following a brief cooling period (step 2) to

Table 2
Digestion conditions for different masses of graphite

Sample mass, g	Repeats of steps 2 and 3*	Time at 95% power, min	Total ml HNO_3	Total ml H_2SO_4
0.2	1	470	11	5
0.5	3	830	27	7
1	6	1370	39	10
2	13	2630	67	17
3	19	3710	88	23

*Number of times steps 2 and 3 of the digestion cycle reported in Table 1 are repeated.

examine the contents, an additional 4 ml of HNO_3 and 1 ml H_2SO_4 were added and the sample further digested at 95% power for 180 min. Steps 2 and 3 were repeated 6 times for a 1 g sample (Table 2). Despite the presence of the reflux coil in the neck of the vessel, nitric acid vapor escapes, necessitating its replenishment after a lengthy period of heating. Subsequently, (step 4) the cooling reflux is halted and the nitric acid is evaporated, thereby raising the temperature of the digestion mixture to permit a more aggressive attack of the graphite by the H_2SO_4, which is also permitted to almost completely evaporate. A brief cooling period is introduced (step 5) to permit visual inspection of the sample and allow for the addition of a further 8 ml of HNO_3. The sample is then further digested at 80% power for 40 min (step 6) and finally subjected to a short 2-minute low-power evaporation (step 7) during which the solution volume was reduced to about 3 ml. Following a 5-minute cooling period, the sample was quantitatively transferred to a 50 ml calibrated flask and diluted to volume. The final solution was clear and colorless and was stored in a precleaned screw-capped polyethylene bottle prior to analysis.

When digesting sample masses smaller or larger than 1 g, it is necessary to modify the above program in accordance with the mass of the sample. Table 2 summarizes the number of times additional reagents are added to the digestion vessel and the total time that the sample is subjected to the primary digestion phase (steps 1 and 3) at 95% power levels.

Trace element recovery from the digestion process was verified by running spiked samples through the procedure in addition to analytical blanks.

Digestion of graphite was also accomplished with a 1:2 (*v/v*) mixture of $HClO_4$ and HNO_3 using an identical heating program to that outlined in Table 1. Residual $HClO_4$ was carefully removed during the evaporation step (step 4) and 10 ml HNO_3 added (step 5) prior to the final digestion in which the solution volume was reduced to 3 ml.

Accuracy of the results was assured by the digestion of NIST 1632a coal reference material in a manner identical to that described for the graphite. In this instance, 1 g samples of coal could be completely solubilized (digested) under the same conditions as for 0.2 g graphite. Additionally, samples of NRCC LUTS-1 lobster hepatopancreas reference material were digested and analyzed according to the procedures outlined in ref. 9 in an effort to provide certified data for additional elements of interest.

Analyses

Trace element analyses were accomplished using flame-AAS and ICP-AES for coal samples, and GFAAS for graphite and LUTS-1 samples. The instruments were operated under the usual conditions as recommended by the manufacturers.

The efficiency of sample digestion was assessed through measurement of the total residual carbon in the digest solutions. Standardization of the measurement apparatus was performed using potassium hydrogen phthalate and polyethylene glycol.

Results and Discussion

Graphite is a difficult material to digest in acidic solutions owing to the relatively inert nature of the basal plane of this structure. Intercalation of sulphate and chloride anions serves to open up the material and increase the surface area available for oxidation. Attempts to digest the graphite solely in HNO_3 were relatively unsuccessful (as judged from the excessive digestion time required), perhaps owing in part to the passivation of the surfaces which may occur following oxidation of the numerous carbonaceous moieties usually present. A mixture of HNO_3 and H_2SO_4 provided the most satisfactory results. Although $HClO_4$ could also be used, it was found not necessary and is best avoided, unless a special fume hood is available for dealing with the vapours from this acid.

Although an approximately 1:1 (*v/v*) starting mixture of $HNO_3 : H_2SO_4$ was used, it is difficult to control this ratio during the digestion because, despite the presence of the added reflux coil, the higher vapour pressure of HNO_3 slowly depletes the concentration of this component and subsequent additions are necessary. It was deemed prudent to remove the majority of the H_2SO_4 from the final mixture at the completion of the digestion, as this acid is particularly corrosive to graphite tubes used in the GFAAS analysis of the digests. Completion of digestion process was confirmed through visual inspection of the solution in that there was no particulate material evident. Removal of the H_2SO_4 at this point served to ensure that the solubilization was complete. The final solutions contained 5 - 6% (*v/v*) HNO_3. As the graphite is completely converted to carbon dioxide during the digestion, only low level impurities are expected to constitute the matrix of these solutions, hence no interferences are to be expected and none were encountered.

It is clear from the data of Koshino and Narukawa (5) that HNO_3 is necessary for the efficient digestion of graphite. Additionally, in a closed system, 72 hours were required to achieve digestion efficiencies of 98 - 100% using 0.5 - 1.0 g samples. The data in Tables 1 and 2 also show that the oxidative dissolution of graphite in an open system is also extremely difficult. However, with the open-focused system, much larger sample masses can be accommodated and the time taken for digestion of 0.5 g samples is 5-fold less than when thermally heated closed bombs are used.

The efficiency of decomposition or oxidation of the sample was evaluated through measurement of the residual carbon which remained in the digest solutions (no particulate matter was evident, as judged from eye observation and scattering of light). For sample masses from 0.2 - 3.0 g, the efficiency of digestion was never less than 98% [average 99.4 ± 0.7%, n=11]. Samples processed with a mixture of HNO_3 and $HClO_4$ exhibited equally efficient digestion capability.

Table 3
Recovery of element spikes, %*

Element	Graphite $HNO_3 + HClO_4$	Graphite $HNO_3 + H_2SO_4$	CRM 1632a $HNO_3 + H_2SO_4$	Luts-1 $HNO_3 + H_2SO_4$
As	89 ± 6	83 ± 4	91 ± 3	96 ± 2
Cd	92 ± 3	94 ± 2	94 ± 2	98 ± 3
Cr	90 ± 2	86 ± 3	94 ± 3	96 ± 1
Co	91 ± 3	87 ± 2	94 ± 3	99 ± 2
Cu	89 ± 4	92 ± 3	96 ± 3	99 ± 2
Fe	89 ± 3	94 ± 4	97 ± 4	96 ± 3
Pb	87 ± 4	79 ± 3	81 ± 5	97 ± 2
Mn	92 ± 3	84 ± 2	90 ± 2	99 ± 2
Ni	93 ± 4	89 ± 4	94 ± 3	97 ± 3
Se	93 ± 3	90 ± 4	92 ± 2	95 ± 3
Sr	87 ± 4	82 ± 4	93 ± 3	95 ± 3
Zn	92 ± 3	87 ± 3	96 ± 3	98 ± 2

*Recoveries of element spikes added to nominal 1 g samples. Average and standard deviation for 4 replicate runs.

Trace element recovery

Recovery of element spikes added to samples of powdered graphite was used in conjunction with the analysis of reference materials to assess the overall accuracy of the analytical approach. Table 3 summarizes the results for element spikes added (total of 50-500 ng amounts of individual elements added) to nominal 1 g samples of graphite digested in both HNO_3 - H_2SO_4 and -$HClO_4$ media as well as to NIST coal and NRCC lobster hepatopancreas reference materials in an HNO_3 - H_2SO_4 mixture. Results reflect measurements from 4 replicate digestions in each case. The average recovery of the 12 elements from graphite samples is 88% in the H_2SO_4 media and 90% in the $HClO_4$ mixture. Significantly higher recovery of Pb is noted for the perchloric acid digestion as compared to the sulphuric acid digestion. Krushevska et al. (8) used H_2SO_4 , in a similar microwave system, to study the digestion of biological samples, and cautioned against incomplete recovery of Pb, Ca and Sr due to the formation of low-solubility sulphates. Lead (in addition to Sr and Ca) was also susceptible to coprecipitation loss in the presence of Ba (when present at concentrations above 0.1 g/ml) in H_2SO_4 media (4%). This problem was not evident in an earlier study from this laboratory (9) focusing on the digestion of biological materials, although in the present case, the enhanced recovery of Pb in the

Table 4
Methodological blank and estimated limits of detection

	Relative blank, ng/ml*		
Element	HNO_3 - H_2SO_4	HNO_3 - $HClO_4$	LOD**, ng/g
As	3.4 ± 0.5	3.4 ± 0.5	70
Cd	<0.016	<0.016	0.8
Cr	<0.09	<0.09	5
Co	<0.27	<0.27	17
Cu	0.33 ± 0.03	0.49 ± 0.04	5
Fe	0.24 ± 0.02	0.48 ± 0.05	3
Pb	0.13 ± 0.01	0.38 ± 0.03	2
Mn	0.084 ± 0.006	0.084 ± 0.007	1
Ni	0.57 ± 0.06	1.1 ± 0.2	9
Se	<3	<3	160
Sr	0.37 ± 0.04	0.49 ± 0.07	6
Zn	0.20 ± 0.02	0.23 ± 0.02	3

* Mean and standard deviation of results (n = 5) based on the digestion of 1 g graphite with dilution to 50 ml.
** Estimated LOD based on $3\sigma_{blank}$.

$HClO_4$ mixture is apparent and may arise as a result of the loss of Pb as the insoluble sulphate. In all cases, however, recovery factors were taken into account in deriving the final analytical results.

Methodological blank and limit of detection (LOD)

One of the principal advantages of undertaking microwave assisted digestion techniques in closed vessels is the significant reduction in the magnitude of the methodological blank, in that the air-borne contamination is virtually eliminated during the reaction, only small amounts of reagent are consumed, and minimal operator intervention and manipulation are required. The open-focussed vessel used in this study is somewhat intermediate in performance between that of the closed vessel and open beaker hot plate techniques. Table 4 summarizes the methodological blanks which arise for both HNO_3 - H_2SO_4 and HNO_3 - $HClO_4$ digestions as well as the estimated limits of detection for the trace impurities in graphite. The latter is defined as three times the standard deviation of the blank. Elemental concentrations in the blanks for Cd, Cr, Co and Se could not be detected and were limited by instrument LOD. For these elements, the methodological LOD was calculated from the precision

Table 5
Effect of acid leach time on trace element content of graphite powder*, ng/g

Element	Leach time, h			
	0	0.5	1	2
As	340 ± 50	167 ± 13	124 ± 10	116 ± 12
Cd	16.6 ± 1.4	2.4 ± 0.2	2.0 ± 0.2	1.9 ± 0.2
Cr	73.8 ± 6.7	12.0 ± 0.9	10.4 ± 1.1	10.2 ± 1.0
Co	<17	<17	<17	<17
Cu	26.2 ± 2.1	<5	<5	<5
Fe	820 ± 60	169 ± 19	157 ± 13	141 ± 12
Pb	18.9 ± 1.5	<2	<2	<2
Mn	16.8 ± 1.5	4.2 ± 0.5	4.1 ± 0.4	4.0 ± 0.3
Ni	85.7 ± 6.8	<9	<9	<9
Se	<160	<160	<160	<160
Sr	171 ± 14	49.9 ± 3.2	48.8 ± 4.7	46.4 ± 4.9
Zn	85.4 ± 5.9	29.5 ± 1.9	27.8 ± 2.0	24.6 ± 1.6

* Mean and standard deviation (n=5) of data for room temperature leach in (*v/v*) 5 % HNO_3 / 15 % HCl.

of measurement of a blank solution spiked to contain a level of the element close to the estimated LOD. These limits of detection are generally an order of magnitude superior to those reported by Koshino and Narukawa (5), because these authors used ICP-AES as the method of quantitation and their LODs were likely all instrument limited. Blanks for Cu, Fe, Pb, Ni and Sr are slightly higher in $HClO_4$ digested samples than in those treated with H_2SO_4 and likely reflect the impurity level differences present in the two acids. It is clear from the data in Table 4 that sufficient detection power is available with this analytical approach to be able to accurately analyze high-purity graphites.

Effect of acid pre-leach

As noted in the experimental section, samples of crushed graphite powder were subjected to a mild surface leaching at room temperature in a mixture of 5% HNO_3 / 15% HCl (*v/v*) for varying periods of time prior to washing with DDW and complete digestion. This was done in order to remove surface contamination. It is clear from the experiments of Hashitani et al. (3) that extensive (3 hour) "leaching" of graphite in a 1:1 HNO_3:HCl mixture at elevated temperature is capable of removing about 95% of the impurity content from graphite because of the porous nature of this material. Data presented in Table 5 illustrate the effect of the acid leaching time on the results of the

Table 6
Analytical results for high-purity graphite*

Element	Concentration, ng/g	
	HNO_3 - H_2SO_4	HNO_3 - $HClO_4$
As	167 ± 13	190 ± 17
Cd	2.4 ± 0.2	2.3 ± 0.2
Cr	12.0 ± 0.9	16.5 ± 1.2
Co	<17	<17
Cu	<5	<5
Fe	169 ± 19	182 ± 14
Pb	<2	<2
Mn	4.2 ± 0.5	4.0 ± 0.3
Ni	<9	<9
Se	<160	<160
Sr	49.9 ± 3.2	53.8 ± 4.9
Zn	29.5 ± 1.9	27.8 ± 2.4

*Mean and standard deviation for results from 5 digestions of 1 g samples subjected to 0.5 h preleach.

total analysis of the high-purity powder used in this study. Analysis of the unleached material revealed higher concentrations of nearly all elements as compared to the leached material. Trace impurities in the graphite selected for this study are significantly lower than those reported elsewhere for other graphites (3, 5). A 30 minute leach in dilute acid appears to be sufficient to clean the easily adsorbed surface contamination from the samples; a more extended leach does not significantly alter the impurity levels and likely does so by removing trace elements from the porous bulk of the sample. All subsequent analytical results to be presented for graphite are based on the analysis of samples that have been subjected to a dilute acid leach of surface impurities for 30 min.

Analytical results

Table 6 summarizes the results of analysis of the high-purity graphite by GFAAS techniques. Data are presented for both the H_2SO_4 and $HClO_4$ digestions. Apart from Cr, the results are, within the precision of the measurements, independent of the acid medium. When $HClO_4$ is used, the results for Cr are elevated because this acid is more effective in solubilizing the more non-labile forms of this element which may be present in the sample (10), suggesting that the true value for the concentration of Cr is that obtained with the $HClO_4$ digestion process. As noted earlier, the impurity levels in this sample of graphite are significantly lower than those reported by others analyzing similar materials (3,5). The precision of analysis of replicate 1 g samples (n=5) is seen to average 10% (ex-

Table 7
Analytical results for certified reference materials

	NIST coal 1632a		NRCC LUTS-1	
	Concentration*, µg/g			
Element	Found	Certified	Found	Certified
As	115 ± 13		2.95 ± 0.24	2.83 ± 0.13
Cd	1.88 ± 0.17		2.01 ± 0.30	2.12 ± 0.15
Cr	27.1 ± 2.8	34.4 ± 1.5	0.065 ± 0.014	0.079 ± 0.012
Co	5.89 ± 0.47	6.8**	0.052 ± 0.008	0.052 ± 0.006
Cu	15.4 ± 1.7	16.5 ± 1	14.4 ± 1.5	15.9 ± 1.2
Fe	1.15 ± 0.09***	1.11 ± 0.02**	10.5 ± 1.2	11.6 ± 0.9
Pb	30.7 ± 3.1		0.008 ± 0.003	0.010 ± 0.002
Mn	27.3 ± 1.9	28 ± 2	1.14 ± 0.12	1.20 ± 0.13
Ni	18.1 ± 1.5	19.4 ± 1	0.189 ± 0.025	0.200 ± 0.034
Se	39 ± 6		0.616 ± 0.068	0.641 ± 0.054
Sr	71 ± 8		2.02 ± 0.31	2.46 ± 0.28
Zn	30.3 ± 2.9	28 ± 2	10.3 ± 1.0	12.4 ± 0.8

*Mean and standard deviation for 4 replicate samples of each material.
**For information only, not certified.
***% content.

pressed as a relative standard deviation). This can be considered more than adequate for the levels of impurities measured.

The accuracy of the results was verified through the recovery of spikes added to the samples (Table 3), and through the analysis of two certified reference materials - a NIST coal sample (1632a), and an NRCC biological material (LUTS-1, lobster hepatopancreas). The coal sample was processed using the same procedure as outlined for the graphite. Digestion of the LUTS-1 material was as described earlier (9). Results of these analyses are summarized in Table 7. Excellent agreement between certified and measured contents is evident for both samples with the exception of Cr in the NIST coal, indicating the absence of any systematic errors in the measurement process. The low recovery of Cr in the coal sample is likely due to the difficulty associated with the complete dissolution of this element in the HNO_3 - H_2SO_4 mixture, as noted earlier for the digestion of the graphite samples.

It may be concluded that an open-focused microwave assisted acid digestion system is useful for the dissolution of high-purity graphite. Relatively large sample masses can be conveniently processed in significantly shorter periods of time as compared to conventional closed vessel systems (6 hour *vs* 72 hours). There is no danger of loss of volatile element impurities and analytical blanks are sufficiently low that ultratrace levels can be addressed.

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