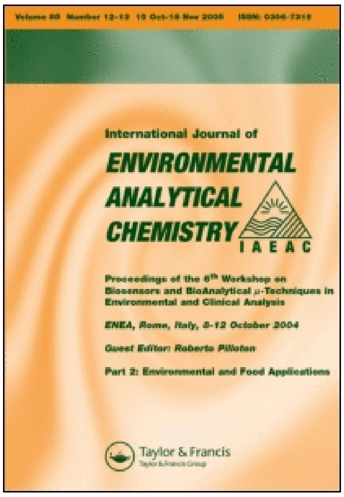

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A MICROWAVE OVEN DIGESTION METHOD FOR THE DETERMINATION OF METALS IN SEWAGE SLUDGES BY ICP-AES AND GFAAS

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An ICP-AES/GFAAS method is described for the determination of metals in sewage sludges following acid digestion in a microwave oven. Application of the method to BCR 144, 145 and 146 sewage sludge standards, gave results in agreement with BCR values. Recoveries were in the range 90–109% for HF/aqua regia digestion. Analysis of aqua regia extracts by ICP-AES was shown to produce data comparable to those reported by BCR.

INTRODUCTION

The characterization of sewage sludge metals is an important requirement prior to sludge disposal or application to farmland which may have beneficial effects,[1] although there is a risk of toxic element accumulating in the soil.[2] The potential hazards associated with contamination of soil, crops or ground water, leading to introduction of toxic elements in the food-chain[3] has caused concern.

For the determination of metals, flame atomic absorption spectrometry (FAAS) is most frequently used in literature.[4–8] However, inductively coupled plasma atomic emission spectrometry (ICP-AES) offers several advantages, e.g., the wide calibration range, the possibility to determine elements simultaneously, the decreased duration of analysis and, therefore, the possibility to analyse more samples in the same time.

Both methods require a digestion to dissolve the metal containing species and remove the matrix. Most digestion methods involve dry ashing,[9–11] aqua regia,[10] nitric acid[12–14] or two or more acids or oxidizing agents;[4,5,15–20] many procedures have been applied which differ with regard to reagent concentrations, temperature, pressure and/or time. The ideal sample preparation procedure would enable a direct, automated sample introduction into a variety of instruments, give a complete recovery of all elements of concern, avoid contamination by reagents and be rapid. Microwave acid digestion is claimed to be suitable for a variety of matrices (21–22). In this paper we report the results obtained by ICP-AES and GFAAS after such a digestion procedure.

EXPERIMENTAL

A Perkin–Elmer ICP/6000 sequential inductively coupled argon plasma-atomic emission spectrometer, equipped with a Perkin–Elmer Model 7500 Data Station and PR-210 Printer, was used.

The instrumental operating parameters are given in ref. 21. The determination of Na and K was carried out on a Perkin–Elmer Model 5000 atomic absorption spectrometer fitted with a standard air-acetylene burner, working in the emission mode.

Most of the work on trace element determinations was carried out on a Perkin–Elmer Zeeman Model 3030 spectrometer, equipped with an HGA-600 graphite furnace and an AS-60 autosampler.

To compare Zeeman-effect and continuum-source background correction, some measurements were taken on a Model 5000 spectrometer equipped with an HGA graphite furnace and an AS-40 autosampler. Pyrolitic graphite tubes with L'vov platform were used exclusively. The graphite furnace programme and matrix modifiers used are the same as previously described.[22]

Electrodeless discharge lamps were used for As, Be, Cd, Sb, Se, Sn and Tl, while hollow cathode lamps were employed for Co, Mo and V.

The microwave oven MDS 81 was used as purchased (CEM, Indian Trail, NC US) with 0–100% full power (600 W) capability in 1% steps. All exposed metallic parts inside the microwave oven were PTFE-coated.

Digestions were carried out in closed 120-ml PTFE vessels which had been cleaned by leaching with hot 0.5 M hydrochloric acid followed by hot 0.5 M nitric acid.

Reagents and calibration

Standard solutions were prepared from a 1000 mg/l standard for atomic absorption spectroscopy (BDH Chemical, Poole, England) by dilution with deionized water.

Hydrochloric acid 32%, nitric acid 65% and hydrofluoric acid 40% were Suprapur reagents (Merck, Darmstadt, FRG). Boric acid was analytical-reagent grade (BDH).

Calibration against acidified standard solutions was carried out for all the elements, but an analyte addition technique was also used during method development.

Aliquots of 20 μl of sample and 10 μl of the mixed matrix modifier solution (15 μg Pd + 10 μg $Mg(NO_3)_2$) were used for all determinations. The palladium modifier was prepared by dissolving 300 mg of Pd metal powder (Alpha Products) in 5 ml of concentrated nitric acid and further dilution to 100 ml with deionized water. Magnesium nitrate modifier was prepared by dissolving 200 mg of $Mg(NO_3)_2 \cdot 6H_2O$ (Merck, Suprapur) in 100 ml of deionized water. The mixed palladium and magnesium nitrate modifier was prepared by mixing equal volume of solutions containing 3000 mg/l of Pd and 2000 mg/l of $Mg(NO_3)_2$, respectively.

Certified reference materials

Samples of sewage sludge were obtained from the Community Bureau of Reference

Samples (Brussels, Belgium). The BCR No. 144 Sewage Sludge of Domestic Origin, the BCR No. 145 Sewage Sludge and the BCR No. 146 Sewage Sludge of Mainly Industrial Origin were dried according to BCR suggestions and thoroughly mixed before sampling.

All the sludges were analyzed five times according to both procedures I and II.

Microwave oven decompositions

Procedure (*I*): *HF/aqua regia digestion.* Approx. 250 mg of sample were weighed into a PTFE container and treated with 5 ml of HF and 15 ml of aqua regia. Six containers with the samples were tightly capped and placed on the caroussel in the microwave oven.

The heating program consisted of three stages. The system operated at a power level of 50% for 8 min, at full power for 4 min and at a power level of 80% for 7 min. After completion, the rack was removed from the oven and the containers cooled in a water-bath for about 15 min. When cool, the bottles were opened and 6 ml of boric acid solution were added. The bottles were then closed, returned to the oven and heated at full power for 6 min. The samples with organic residues were filtered, washed with water and the filtrates were diluted to 100 ml.

Procedure (*II*): *aqua regia digestion.* About 250 mg of sample and 15 ml of aqua regia were placed in the PTFE container of the microwave oven. After the heating steps as described above, the bottles were cooled and opened. The contents of the beaker were filtered through a 0.5 μm Fluoropore (R) membrane filter, transferred to a 100 ml calibrated flask and diluted to volume.

Blank determinations were performed by using the same amounts of reagents (acids and salts) but without sludge.

The solutions were finally analyzed by ICP-AES or GFAAS using a blank solution containing the same amount of aqua regia, hydrofluoric acid and boric acid.

RESULTS

The choice of acid mixtures here used is the result of much experimental work carried out to verify the recoveries of toxic metals such as As, Se, Tl, Pb, Cd and Sb in matrices of environmental interest; different acids and mixtures (HNO_3, HCl/HNO_3, $HCl/HNO_3/HF$ and $HCl/HClO_4/HF$) have been used in different devices (PTFE bomb and microwave oven).

In order to verify the volatility of more critical elements under different dissolution conditions, the reference material BCR 145 spiked with 5 $\mu g\,g^{-1}$ of As, Sb and Se, 0.5 $\mu g\,g^{-1}$ of Be and Tl, 10 $\mu g\,g^{-1}$ of Cd and 100 $\mu g\,g^{-1}$ of Pb was analyzed in triplicate.

The percentage recoveries obtained for different elements, on applying the procedures I and II in the microwave oven or the PTFE bomb[22] are reported in Table 1.

Pressure decomposition with aqua regia in the PTFE bomb or microwave oven allows the accurate determination of Se and Sb, but it is not suitable for the determination of As, Be, Tl and Pb. The recovery for these elements is in the 50–

Table 1 Determination of As, Be, Cd, Pb, Sb, Se and Tl (results in $\mu g\,g^{-1}$) in BCR 145 ($n=5$)

Element	*Reported values*	*PTFE bomb (AR)*	*Microwave (AR)*	*PTFE bomb (I)*	*Recov.* (%)*	*Microwave (I)*	*Recov.* (%)*
As[a]	(3.7–3.8)	2.6±0.3	2.5±0.2	3.3±0.3	99.6	3.3±0.2	99.5
Be[b]	(0.87)	0.20±0.1	0.27±0.2	0.41±0.1	98.9	0.50±0.2	99.1
Cd	18.0±1.2	16.2±1.5	15.7±0.9	17.0±1.2	99.4	17.2±1.0	98.6
Pb	394±15	287±9	299±7	385±10	101.2	375±8	99.2
Sb[a]	(6.1–17.7)	8.0±0.5	8.4±0.3	8.2±0.5	89.7[c]	8.6±0.4	95.1
Se[a]	(1.2–1.4)	3.2±0.4	3.9±0.2	4.2±0.3	99.0	4.1±0.2	98.7
Tl[a]	(0.16–0.46)	0.15±0.08	0.20±0.06	0.20±0.07	85.4[c]	0.30±0.05	99.2

*Percentage recovery calculated on three replicate determinations of BCR 145 spiked with 5 $\mu g\,g^{-1}$ of As, Sb and Se, 0.5 $\mu g\,g^{-1}$ Be and Tl, 10 $\mu g\,g^{-1}$ of Cd and 100 $\mu g\,g^{-1}$ of Pb.

[a] Minimum and maximum values reported by BCR.

[b] Only one value reported by BCR.

[c] Occasional losses during the drying step.

Table 2 Analysis of major constituents (%) in BCR certified sludges[a]

Element	*BCR 144*		*BCR 145*		*BCR 146*	
	Values reported[b]	*Values found*	*Values reported*[b]	*Values found*	*Values reported*[b]	*Values found*
Al	(18.5)	18.3±0.6	(18.1–19)	17.0±0.7	(29.3–29.5)	28.7±1.2
Ca	(24–41)	42.7±0.3	(53–107.5)	99.2±0.5	(46–99.3)	95.0±0.4
Mg	(4–4.7)	4.64±0.2	(14.0–15.6)	15.4±0.7	(14–16.3)	15.1±0.6
Fe	(44.0–48.5)	45.7±1.8	(7.7–8.6)	8.2±0.5	(16.9–18.5)	17.8±0.3
Ti	(1.21–1.25)	1.10±0.08	(1.9)[c]	1.61±0.06	(18–19.9)	19.1±1.2
Na	(0.5–1)	1.20±0.05	(0.8–1.9)	1.70±0.07	(0.6–2.2)	1.93±0.5
K	(0.9–2.7)	2.30±0.2	(1.3–3.6)	2.95±0.3	(1.4–5.1)	3.52±0.2

[a] Mean value of five replicates.

[b] Minimum and maximum values reported by BCR.

[c] Only one value reported by BCR.

80% range. Dissolution by procedure I yields accurate results both in the PTFE bomb and in the microwave oven for all elements showing, however, occasional and non-reproducible losses of Tl and Sb in the bomb procedure, some contamination caused by the metallic parts of the bomb and prolonged times required for the complete dissolution of some samples.

The use of $HClO_4$, tested in the PTFE bomb procedure, was rejected for safety reasons and also because it requires an additional step ($HClO_4$ decreases the lifetime of the GFAAS graphite tubes and must be eliminated before the instrumental analysis).

HF/aqua Regia Digestion

Results relative to the major constituents and trace elements for replicate digestions of the BCR sludges are shown in Tables 2 and 3, respectively. In these tables, beside the "found" values, the "certified" or "indicative only" values are given as reported by BCR.[23–25]

In some cases, when large discrepancies were present for the indicative values or when only a limited number of results were given in the appropriate BCR report, the indicated minimum and maximum values are given in the tables.

The within-batch precision of the method was determined by replicate analysis of the BCR 144, BCR 145 and BCR 146 certified reference materials. It should be noted that each replicate was taken through the entire procedure; at is, the precision data represent the combined precision of sub-sampling, digestion, dilution and analysis.

The bias of the technique was determined by reference to the certified value of all three reference samples. Tables 2 and 3 indicate that the precision (as CV) of ICP-AES for major constituents is 5–7% or better, and for trace elements approx. 2–5%.

For the major elements (not certified by BCR) we can not calculate the recovery but, in any case, our results are within the range of values given in Table 2.

The CV's for Cr, Cu, Ni, Pb and Zn in BCR 144 are comparable to those reported by Hawke[26] for the same sample treated with nitric acid only; therefore there is no indication for a decrease of precision owing to a higher concentration of acids and salts in the solutions analysed.

The *t*-test applied to verify if our experimental results for Cu, Mn, Ni, Pb and Zn are significantly different from the certified values confirmed that, at a significance level of 0.05, there is no evidence of a systematic error. This means that there is no difference between the observed and known values other than that which can be attributed to random variation.

The mean recoveries for the certified elements (Cu, Ni, Pb and Zn) are in the 90–109% range confirming that the microwave oven dissolution procedure and ICP-AES give a quantitative recovery of the elements investigated.

The results for Zr given in Table 3, are outside the range of indicative values reported for BCR 144 and 145, while for sludge BCR 146 they are quite high. These discrepancies can be due to an incomplete digestion of the Zr compounds by the microwave procedure, as previously shown for coal fly ash and geological materials,[27] while for BCR 146 only one value is reported. Our Sc results are lower than those reported by BCR for all three sludges; we are not able to offer a valid explanation for this.

The GFAAS technique with a Stabilized Temperature Platform Furnace (SPTF) protocol and an appropriate modifier was used to analyse the sludge samples for As, Be, Cd, Sb, Se, Sn and Tl as previously reported;[22] wall atomization was employed for Co, Mo and V. The values shown in Table 3 indicate that no significant differences were found for Cd and Co (the observed t values are less than the critical value at $p = 0.05$) and that the As, Sb, Mo and Tl results are well within the range of values reported by BCR.

The Se values obtained with the microwave dissolution procedure are slightly higher than those reported in Table 3, which may indicate a slight positive bias in the determination of this element. The Sn results are lower than the reported values, indicating low recoveries for this element.

An anomalous value for Be in BCR 146 is given in Table 3. The value provided by BCR was obtained in one laboratory only and only by means of the ICP technique. Considering the two more sensitive Be lines at 313.04 nm and 234.86 nm

Table 3 Analysis of trace elements (μg/g) in BCR certified sludges[a]

Element	*BCR 144*		*BCR 145*		*BCR 146*	
	Values certified[b]	*Values found*	*Values certified*[b]	*Values found*	*Values certified*[b]	*Values found*
As	(5.9–7.4)	5.0±0.6	(3.7–3.8)	3.3±0.3	(2.0–5.6)	4.1±0.3
Be	(0.66)	0.45±0.1	(0.87)	0.46±0.1	(5.4)	0.8±0.1
Cd	4.82±0.97	5.71±0.8	18.0±1.2	17.2±1.0	77.7±2.6	80.6±2.8
Co	9.06±0.6	8.70±0.3	8.38±0.71	8.31±0.45	11.8±0.7	12.7±0.5
Cr	(325–662)	435±11	(60–124)	78±6	(678–1002)	792±16
Cu	713±26	665±36	429±10	409±20	934±24	915±20
Mn	449±13	407±7	241±12	225±19	588±24	576±12
Mo	(4–4.5)	4.5±0.5	(4–6.7)	6.7±0.4	(7.8–12.8)	16.9±0.7
Ni	942±22	1010±25	41.4±2.4	39.6±2.2	280±18	297±14
Pb	495±19	501±9	394±15	385±8	1270±28	1257±30
Sb	(2.5–18.4)	4.9±0.3	(6.1–17.7)	8.6±0.4	(55–112)	100±3
Sc	(1.38–1.68)	<1	(1.58–2.00)	<1	(1.7–2.89)	<1
Se	(1.49–2.7)	3.2±0.1	(1.20–1.40)	4.1±0.2	(1.01–2.2)	2.7±1.5
Sn	(95–100)	68±5	(128–140)	85±6	(165–600)	114±9
Tl	(0.28–0.526)	0.34±0.05	(0.16–0.46)	0.30±0.05	(0.57–1.30)	1.27±0.7
V	(12.9–17.5)	11.5±1.1	(16.6–39.8)	19.9±1.2	(18.8–38)	37.0±1.7
W	(3.4–8)	<1	(13–20)	<1	(4.1–8.5)	<1
Zn	3143±103	3025±56	2843±64	2784±39	4059±59	4130±75
Zr	(53–58)	25±4	(60–78)	25±4	(9.0)	49±5

[a] Mean value of five replicates.

[b] Values in brackets are minimum and maximum values reported by BCR and are indicative only; occasionally, only one value has been reported.

(probably used in the ICP analysis), the interferences reported by Pougnet[28] due to the presence of iron, vanadium and titanium, and the higher concentration of iron and titanium in BCR 146 compared with BCR 144 and BCR 145, high difference between our value and that reported by BCR may be considered explained.

According to the procedure reported in the literature[29] employing the STPF protocol and the modifier, we verified the Be content of the BCR samples by using two different atomic absorption instruments, one equipped with a D_2 background corrector and the other with a Zeeman effect background system. The results obtained were respectively $0.44 \pm 0.10\,\mu$g/g and $0.45 \pm 0.12\,\mu$g/g for BCR 144, $0.46 \pm 0.15\,\mu$g/g and $0.36 \pm 0.10\,\mu$g/g for BCR 145, and $0.77 \pm 0.13\,\mu$g/g and $0.63 \pm 0.12\,\mu$g/g for BCR 146.

This is conclusive evidence that the Be content in sludge samples can be determined, without interferences, by GFAAS, after microwave oven dissolution, either with D_2 or Zeeman background correction. In comparison with ICP-AES analysis, the GFAAS determination of such low Be contents offers, in our opinion, more reliable and accurate results.

Aqua Regia Digestion

Many laboratories involved in agricultural analysis frequently do not determine

Table 4 Values for aqua-regia-soluble element contents in BCR certified sludges (μg/g)[a]

Element	*BCR 144*		*BCR 145*		*BCR 146*	
	Values reported[b]	*Values found*	*Values reported*[b]	*Values found*	*Values reported*[b]	*Values found*
Al[b]	11.4±0.6	11.4±0.3	8.6±0.3	9.4±0.2	13.9±0.5	13.9±0.2
Fe[b]	43.1±1.3	44.3±1.2	8.1±0.2	7.9±0.2	—	17.6±0.1
Ti	86±3	89±4	149.6±5.3	152±5	277.6±8.8	409±7
Cu	694±44	682±12	415±23.5	409±9.1	921±47.5	902±23
Cr	494±61	480±13	85.2±16.3	79±5.2	769±79	735±36
Mn	436±30	426±14	219.6±14.0	212±10	555±32	558±8
Ni	947±65	945±15	38.5±3.6	39±2	269±7	258±11
Pb	479±51	474±15	332±22	318±20	1255±41	1264±25
Zn	3090±266	3042±50	2772±209	2690±69	4002±296	3897±95

[a] Mean of five determination.
[b] Values reported as mg/g.

the total content of certain trace elements, but they determine the nitric-acid or aqua-regia-soluble content according to suggestions of Muntan[30] and Cottenie.[31]

It is therefore highly significant to compare the "total metal content" determined by HF/aqua regia digestion (procedure I) and the aqua-regia-soluble content obtained by procedure II.

For considerations such as speed of analysis and need for an accurate, safe and simple method of digestion that can be readily applied to a large number of samples, we compared the aqua regia microwave oven procedure with the standardized procedure as reported by BCR.[23–25] Table 4 presents the results found for the elements Al, Fe, Ti, Cu, Cr, Mn, Pb and Zn by the microwave oven procedure and those given by BCR. The *t*-test applied to our results gave, except for Al in BCR 145 and for Ti in BCR 146, an observed value of *t* less than the critical value at a significance level of 0.05. The recoveries for most elements are in the range of 92–106%, indicating a satisfactory accuracy for the dissolution procedure. Obviously, the solubilization of Fe, Cu, Cr, Mn, Ni, Pb and Zn-containing compounds present in the sludges, by the aqua regia procedure, is almost quantitative, while the results for the macrocostituents Al and Ti leave something to be desired.

The CV's for procedure II are of the same order as those obtained by HF/aqua regia dissolution previously reported.

Satisfactory results can be obtained in only about 35 min of dissolution time, whereas the 'conventional' procedure requires not less than 3–5 h. As we normally analyse six samples at the same time, the time required for the digestion step is considerably reduced as compared to that required for conventional digestions. The final solution prepared by our procedure is suited for multielemental analysis by ICP-AES and for trace element analysis by GFAAS.

CONCLUSIONS

The digestion of sewage sludges with aqua regia/HF in a microwave oven allows good recoveries of several metals of environmental interest and can easily be applied in routine laboratories. The simple aqua regia digestion in a microwave oven is an accurate and rapid dissolution technique for the determination of Cu, Cr, Mn, Ni, Pb and Zn, but not for the macrocostituents. The coefficients of variation for both procedures are 1–6%. The time required for the digestion stage is notably reduced compared with that of conventional dissolution procedures. The digests can be used for ICP-AES and GFAAS analysis.

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