Chemical characterization of municipal solid waste incineration residue: Dissolution of elements with a microwave-dilute acids digestion technique compared to conventional methods

S. Dugenest[*], M. Ollé, A. Ribes and M.F. Grenier-Loustalot

Service Central d'Analyse, Centre National de la Recherche Scientifique,
USR 059, BP. 22, 69390 Vernaison, France

Abstract. The aim of this work was to evaluate the focused microwave technique in an open system for the rapid dissolution of elements in fly ash and filter cakes, in comparison to conventional wet and dry methods. The method involved 15 minutes of heating in microwave system in 2 N nitric or hydrochloric acid. It was tested on different types of samples and led to the dissolution of Ca, Na, K, Zn, Pb, As with 2 N HNO_3 or HCl and Cd, Hg with 2 N HNO_3 for subsequent determination by atomic emission or absorption spectrometry. Thereby this method represents a rapid sample preparation technique for chemical analyses.

Key words. Fly ash   filter cake   microwave acid digestion   ICP-AES   HG-QFAAS.

Introduction

Incineration is an efficient method for treating municipal solid waste (MSW), although it produces fume containing several pollutants. A number of wet, semi-wet or dry processes for scrubbing and neutralizing gases are used before their atmospheric rejection. These processes generate residues: fly ash on the one hand and on the other hand filter cakes only in the first case.

These residues contain major compounds like aluminum and calcium silicates, but also chlorides, sulfates and numerous polluting elements like As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, Co [1]. As a result of their toxicity, they must be stabilized before their disposal in a landfill [2]. Procedures for chemical characterization are thus required to rapidly control the waste at entry into stabilization units and to set up the process formulation.

For this purpose, we have developed techniques for the dissolution of metals in dilute 2 N nitric or hydrochloric acid by focused open microwave system. The microwave technique has many advantages for dissolution in comparison with classical wet methods: rapidity, reproducibility of heating power, reduced quantities of reagents, reduction of sample pollution risks, automatic operation [3,4]. A previous study on soils and sediments, in the laboratory, had shown that this acid normality was the most efficient for the solubilization of many elements and their measurement.

These methods were tested on three samples obtained from different processes. These samples were used as in-laboratory reference materials since few certified samples are currently available. The efficiency of the method was evaluated by comparison with techniques for the total dissolution of elements in the matrix: fusion and digestion with the mixture of hydrofluoric/perchloric/nitric acids and hydrogen peroxide ($HF/HClO_4/HNO_3/H_2O_2$). Focused open microwave dissolution method in 2 N hydrochloric acid was then applied to nine other samples of different origins.

Major and minor elements in solution, Ca, Na, K, Al, Mg, Fe, P, Zn, Pb, Si, Mn, Ti, Cu, Ba, Cr, Cd, Ni, Sr, Sn and Hg above 100 µg/L were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Low concentrations of Hg below 100 µg/L were determined by sample combustion and detection was by atomic absorption photometry. The technique of hydride generation coupled to atomic absorption spectrometry in a quartz furnace (HG-QFAAS) was used to quantify As.

Material and methods

Samples and reagents

Types of samples

Different types of samples were analyzed:

- fly ash from a semi-wet method: HSS (reference), CEC 19/1/93, CEC 2/2/93, CEC 4/2/93,

- fly ash from a wet method: SDP (reference), CEL 1/2/93, CEL 26/10/93, CEL 5/10/93,

- filter cakes from a wet process: GAT 29/10 (reference), GAT 27/1/93, GAT 19/10/93, GAT 26/1/93.

Sample preparation

Samples were dried at 70 °C for 24 h, porphyrized in an agate grinder and then quartered. The particle size of the samples was between 70 and 80 µm.

Reagents

All reagents used were analytical grade:

- 40% hydrofluoric acid (Prolabo Normapur),

- 70% perchloric acid (Prolabo Normapur),

- 36% hydrochloric acid (Prolabo Normapur),

- 65% nitric acid (Baker Analyzed),

- 30% hydrogen peroxide (Prolabo Normapur),

- 98% min sodium hydroxide (Prolabo Normapur).

All solutions were prepared with deionized water. To limit risks of sample pollution, glassware was thoroughly washed with nitric acid and deionized water before use.

Solution of 0.2% sodium borohydride (Prolabo) was prepared in 0.05% sodium hydroxide.

Digestion methods

Fusion and digestion by H_2SO_4 /HNO_3 /$KMnO_4$

The fusion and the digestion by H_2SO_4/HNO_3/$KMnO_4$ of the samples were conducted by the Service d'Analyse des Roches et des Minéraux (SARM) of the Centre de Recherche Pétrographique et Géochimique (CRPG), UPR 6709. Sample of 100 mg was fused in a gold-platinum-rhodium crucible with a mixture of lithium metaborate and boric acid. The fusion cycle was carried out at 1080 °C for 3 hours in an automated tunnel oven. The acid and oxidizing digestion was used for mercury dissolution.

Digestion by HF/$HClO_4$ /HNO_3 /H_2O_2

Sample of 50 or 100 mg was treated in a Teflon beaker on a hot plate. This mixture totally attacks the matrix by dissolution of the silicate matrix with loss of Si by SiF_4 volatilization and volatile species such as Sn, Hg, As [5].

Open microwave system

The focused open microwave system used (A301, Prolabo) enabled 16 samples to be consecutively and automatically processed, as well as the automatic addition of reagents at any time. A 1 or 2 g sample was added to a digestion flask, followed by 25 mL of reagent, 2 N HCl or HNO_3. Heating power was set up at 40 W for 15 min. The resulting solution was filtered and the digestion flask was rinsed several times with deionized water, then the final volume was adjusted to 50 mL. It means that it's not a total digestion, resulting so in poor recovery of certain elements.

Apparatus

Apparatus employed by the SARM of the CRPG

The measurement of Ca, Na, K, Al, Mg, Fe, P, Si, Mn and Ti in the solutions resulting from samples fusion was realized by ICP-AES, with a Jobin-Yvon Model JY 70 type II apparatus, while the measurement of Zn, Pb, Cu, Ba, Cr, Cd, Ni, Sr, Sn and As was achieved by ICP-MS with a Perkin Elmer Model Elan 5000 apparatus. The Hg assay in solutions obtained by samples digestion with H_2SO_4/HNO_3/$KMnO_4$ was conducted by atomic absorption spectrometry (AAS) with the amalgam method.

Inductively coupled plasma-atomic emission spectro-metry (ICP-AES) for the measurement of Ca, Na, K, Al, Mg, Fe, P, Zn, Pb, Si, Mn, Ti, Cu, Ba, Cr, Cd, Ni, Sr, Sn and Hg (>100 µg/L).

A sequential ARL 3520 and a combined sequential-simultaneous ARL 3580 instruments were used. Experimental analysis conditions are described in table I.

Mercury in fly ash extraction solutions could not be determined by ICP-AES because of the high detection limit of this element, about 50 µg/L, and the high spectral background resulting from the solubilization of the matrix. This last phenomenon also made it impossible to determine arsenic by ICP-AES.

Quartz furnace atomic absorption spectrometry coupled with hydride generation (HG-QFAAS) for measuring As

The principle of this coupling is based on the transformation of arsenic into a volatile hydride after reduction of AsV to AsIII by a mixture of potassium iodide-ascorbic acid (5% *m/v*), atomizing arsines formed in an electrically heated quartz cell and their detection by atomic absorption spectrometry.

Sample introduction (200 or 500 µL) and hydride generation were achieved in a Perkin Elmer Model FIAS 200 segmented flow injection apparatus. Hydrides were generated by addition of 10% hydrochloric acid and 0.2% sodium

Table I. Instrumental conditions for the spectrometric determination of elements.

ICP-AES conditions			
Nebulizer	Type "Meinhardt"		
R.f. power	1250 W		
Plasma gas flow rate	1 L/min		
Coolant gas flow rate	12 L/min		
Nebulization gas flow rate	1 L/min		
Sample uptake	1 mL/min		
Element	Wavelength (nm)	Element	Wavelength (nm)
Ca	317.93	Mn	257.61
Na	589.59	Ti	337.28
K	766.49	Cu	324.75
Al	308.22	Ba	233.53
Mg	279.08	Cr	267.72
Fe	259.94	Cd	231.60
P	178.29	Ni	346.45
Zn	213.86	Sr	214.44
Pb	220.35	Sn	189.99
Si	251.61	Hg	194.23

HY-QFAAS conditions (As)	
Wavelength	193.7 nm
Slit width	0.7 nm (high)
Atomization temperature	900 °C
Argon gas flow rate	70 mL/min

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borohydride ($NaBH_4$ in 0.05% sodium hydroxide solution). They were then separated from the liquid mixture by argon gas flow in a liquid-gas separator, and carried in the quartz cell of a Perkin Elmer Model 3100 atomic absorption spectrometer, equipped with an electrodeless discharge lamp. The experimental detection conditions are described in table I.

AMA 254 analyzer for measuring Hg (<100 µg/L)

The principle of the technique is based on sample combustion at 750 °C, the decomposition of the combustion gases by a catalyst and the amalgamation of Hg vapors in a gold trap. Desorbed Hg vapors were then detected by atomic absorption photometry with a low pressure mercury vapor lamp and a silicon detector. This instrument can be used to analyze solid, powdered or liquid samples. A prior study on different types of certified samples, furnished by the Bureau of Community Reference, and MSW incineration residues had given validated results independently of the physical state of the sample (unpublished results). The assay limit in that work was evaluated at 0.5 ng of Hg.

Mercury in solutions obtained by extracting fly ash with 2 N HNO_3 was determined using 100 µL samples. It could not be realized in hydrochloric acid extracts because of the risk of destroying the analyzer catalyst and trap with chloride ions.

Results and discussion

Determination of elements by conventional digestion methods

The dissolution of elements by the mixture of $HF/HClO_4/HNO_3/H_2O_2$ was investigated on eight replicate samples, four weighing 50 mg and four weighing 100 mg, of three different materials: HSS, SDP and GAT29/10. All elements were determined in each solution. Mean of the determination results of each element and its standard deviation are listed in table II for each sample. The table also lists the concentrations of elements, obtained by fusion and spectrometric determination ICP-AES or ICP-MS by the SARM of the CRPG; the determination results of Hg in HSS, SDP and GAT 29/10 were respectively 5.3 µg/g, 4.2 µg/g and 1106 µg/g.

The determination results of elements solubilized with the wet process in each sample are in overall good agreement with the results found by dissolution with the dry method. Digestion by the mixture of strong acids quantitatively solubilizes most of the elements in the matrix: Ca, Na, K, Al, Mg, Fe, Pb, Ba, Cd, Ni. However the determination of Na and K in the filter cake by acid digestion furnished highly dispersed overestimated results in spite of precautions taken to avoid sample pollution.

Acid digestion could not be used to determine Ti, probably because of its partial presence in the form of oxides in the matrix.

The determined concentrations of P in the three samples were lower than those obtained by fusion. According to published data [5], this could result from volatilization of H_3PO_4 formed in HF, starting at 100 °C. The incomplete solubilization of P by acid digestion could also be related to the

Table II. Results of determination of elements in HSS, SDP and GAT29/10 by wet and dry digestion techniques.

	HSS		SDP		GAT29/10	
	DD [a] (n=1) [c]	WD [b] (n=8) [c]	DD [a] (n=1) [c]	WD [b] (n=8) [c]	DD [a] (n=1) [c]	WD [b] (n=8) [c]
Ca (%)	34.86	36.77±0.22	13.74	14.90±0.42	13.84	14.67±0.50
Na (%)	1.17	1.19±0.05	2.83	2.78±0.05	0.06	0.17±0.03
K (%)	2.25	2.32±0.11	3.88	3.86±0.08	0.36	0.55±0.24
Al (%)	1.41	1.33±0.08	6.79	6.66±0.10	5.51	5.38±0.09
Mg (%)	0.56	0.52±0.04	1.51	1.41±0.06	3.64	3.44±0.13
Fe (%)	0.52	0.54±0.03	2.27	2.17±0.08	2.16	2.11±0.09
P (%)	0.22	0.17±0.01	0.87	0.61±0.04	0.40	0.33±0.02
Zn (%)	0.71	0.81±0.03	0.97	1.07±0.03	1.70	1.90±0.08
Pb (%)	0.25	0.23±0.02	0.69	0.60±0.05	0.96	0.90±0.03
Si (%)	3.29	NR [d]	15.95	NR [d]	9.27	NR [d]
Mn (µg/g)	232	380±26	542	929±53	697	976±20
Ti (µg/g)	1980	1700±56	9700	6697±502	4700	3377±165
Cu (µg/g)	365	314±31	767	797±70	1490	1654±48
Ba (µg/g)	279	284±12	1393	1384±101	210	215±9
Cr (µg/g)	189	168±34	722	435±113	388	444±28
Cd (µg/g)	124	120±12	227	220±9	445	395±55
Ni (µg/g)	20	20±1	122	110±8	81	81±11
Sr (µg/g)	324	394±50	324	389±26	80	125±25
Sn (µg/g)	804	NR [d]	1268	NR [d]	2820	NR [d]
As (µg/g)	22	NR [d]	38	NR [d]	61	NR [d]

[a] DD: dry digestion (fusion).

[b] WD: wet digestion (by $HF/HClO_4/HNO_3/H_2O_2$).

[c] n: replicate number. For n = 8, standard deviation (± SD) on the mean is indicated.
[d] NR: non-realizable.

presence of insoluble salts in the matrix, such as calcium metaphosphates $Ca(PO_3)_2$.

Regardless of the sample, the determined values of Zn appear to be overestimated in comparison with the values provided by fusion, in spite of good analysis accuracy, relative standard deviation varying from 3 to 5%.

The results of Mn and Sr assays by wet digestion were much higher than those obtained with the dry method. They did not arise from spectral interference by co-solubilized elements, however, and it is probable that these two elements were not totally solubilized by fusion.

There was high dispersion, about 10%, of the Cu contents in the three samples. The determination of Cr after acid digestion also provided dispersed results (relative standard deviation >20%). This may have arisen from the non-repeatable dissolution of Cr oxides, which are not easily solubilized. In addition, the Cr content determined in the SDP sample was not in agreement with the value obtained by fusion.

Most of the contents of elements in samples treated by fusion were confirmed by acid digestion. These values were thus taken as reference for the three samples, and were compared to the values obtained by dissolution using the focused open microwave system in dilute acid. For Mn and Sr, the concentrations used were those determined by acid

digestion, not by fusion. In the case of Ti, P, Zn, Cu and Cr, the retained values were obtained by fusion.

Determination of elements by microwave-dilute acids digestion techniques

The methods of dissolution combining dilute acids and microwave heating were evaluated in the three samples of waste for which the concentrations of elements were determined after the complete dissolution of the matrix (reference materials). The microwave dissolution of the material was carried out in both 2 N HNO_3 and 2 N HCl using five replicate of each sample. Mean recovery of the elements from each sample shows generally low standard deviation (Tab. III).

These two procedures lead to the partial or complete solubilization of elements initially present in the matrix. Regardless of the nature of acid, focused open microwave system led to the total solubilization of Zn, Pb and Ca, their recoveries exceeding 90%. These methods could also be used to determine Cu, Mn and Sr, with a maximal error of 20% by default. 2 N nitric acid would solubilize Sr with more efficiency. The results show that Na and K are extracted from HSS and SDP fly ash by more than 85%. The results of the determination of Na in the filter cake were dispersed and unusable, probably because of pollution by reagents or handling, and the solubilization of K was not complete.

These techniques lead to the total dissolution of Mg, P, Fe from the filter cake but only their partial solubilization in fly ash. 2 N hydrochloric acid seems to be better suited for dissolving Fe. These findings suggest a speciation difference of these elements between fly ash and filter cakes. The dissolution of P by these methods is equal to or higher than acid digestion (Tab. II), which would verify the loss of P during digestion by HF.

Combined with HG-QFAAS coupling, these dissolution techniques enable As to be assayed in the waste tested. Actually, As contents of HSS and SDP have been undoubtly overestimated by fusion and ICP-MS detection method.

These methods lead to only the partial solubilization of Si, Al, Ti, Cr, Ni, Sn, Ba. These elements are probably present as insoluble silicoaluminates or oxides in the matrix.

2 N nitric acid combined with microwave heating provided the total dissolution of Cd and Hg in the residues. Yields obtained with hydrochloric acid were lower.

The techniques of dissolution by focused microwave in dilute acids would thus enable Zn, Pb, As, Cd, Hg, Ca, Na, K to be determined in fly ash and filter cakes (except Na and K).

Application of microwave-hydrochloric acid digestion technique to the characterization of different fly ash and filter cakes

On the basis of the above results, the microwave-2 N HCl dissolution method was applied to nine other samples for the determination of Zn, Pb, As, Ca, Na and K. The results and the values obtained with fusion by the CRPG are listed in table IV. In this way, the efficiency of the method for the determination of Zn, Pb, As and Ca in the different types of

Table III. Microwave-nitric or hydrochloric acid digestion methods efficiency on HSS, SDP and GAT29/10; results are expressed as mean recoveries and standard deviations.

	HSS		SDP		GAT29/10	
	HNO_3 (n = 5)[a]	HCl (n = 5)[a]	HNO_3 (n = 5)[a]	HCl (n = 5)[a]	HNO_3 (n = 5)[a]	HCl (n = 5)[a]
Zn	99±1.5	100±1.9	92±2.0	94±0.4	104±2.5	109±6.1
Pb	96±7.2	100±9.8	91±2.8	93±2.8	98±3.1	101±5.5
Ca	97±2.1	101±1.3	94±3.3	101±0.8	98±4.0	106±4.5
Cu	78±1.1	81±2.0	97±1.7	101±1.9	100±2.4	116±4.8
Mn	78±3.0	78±2.3	86±3.2	88±1.5	101±3.8	101±4.2
Sr	93±6.0	81±1.5	91±3.5	80±1.1	87±4.6	81±4.2
Na	94±3.6	96±3.7	88±3.8	86±0.9	157±12.1	147±1.9
K	98±6.3	95±2.8	86±1.7	86±3.5	57±1.0	60±3.6
Mg	77±6.6	75±5.8	66±3.4	62±1.7	90±2.2	96±5.4
P	77±3.3	82±2.2	72±2.2	74±1.8	95±3.6	98±8.3
Fe	69±2.0	79±0.9	47±0.4	63±1.4	96±2.6	100±5.1
As	82±3.5	82±2.8	82±1.9	82±2.5	92±7.2	98±10
Si	35±0.8	35±1.5	20±2.0	27±1.6	3±0.2	3±0.1
Al	67±2.5	66±2.1	67±0.5	69±1.1	80±2.4	85±4.1
Ti	24±0.7	24±0.5	22±0.4	22±0.3	23±0.6	24±0.7
Cr	31±4.0	33±4.0	20±1.3	26±0.5	61±4.0	69±5.0
Ni	51±6.2	56±5.6	47±2.5	50±1.1	84±5.3	80±4.8
Sn	31±2.3	34±1.8	24±0.9	34±1.0	16±0.7	22±1.0
Ba	76±3.1	72±2.2	76±2.2	40±1.3	74±2.1	76±2.1
Cd	96±7.6	81±3.0	93±5.4	81±2.1	96±5.2	84±5.0
Hg	103[b]	ND[c]	98[b]	ND[c]	89±1.5	59±4.5

[a] n: replicate number.
[b] n = 1.
[c] ND: not determined.

residues was verified. This technique could also be used to assay Na in fly ash. Precautions preventing sample pollution must be taken for the determination of K.

The results obtained with these samples showed the efficiency of the method for the determination of P in filter cakes but in fly ash as well. This method would thus also be applicable to the assay of P in all the residues studied.

Conclusions

None digestion method allows the total solubilization of all the elements contained in such matrices, even the wet and dry conventional methods which were investigated in this work.

The technique of focused microwave in an open system combined with the use of 2 N nitric or hydrochloric acid, could be used to determine alkaline and alkaline earth elements, Ca, Na and K, in fly ash and filter cakes. It was difficult, however, to measure Na and K at low concentrations, below 1 µg/g. The method also enable polluting elements to be assayed: Zn, Pb, As with 2 N HNO_3 or HCl and Cd, Hg with 2 N HNO_3. The technique is a simple and rapid (15 min) method for the preparation of sample, for the

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Table IV. Results of determination of elements in CEC, CEL and GAT samples by microwave-hydrochloric acid digestion technique.

	Zn (%) DD[a] (n=1)[c]	Zn (%) MD[b]	Pb (%) DD[a] (n=1)[c]	Pb (%) MD[b]	Ca (%) DD[a] (n=1)[c]	Ca (%) MD[b]	Na (%) DD[a] (n=1)[c]	Na (%) MD[b]	K (%) DD[a] (n=1)[c]	K (%) MD[b]	P (%) DD[a] (n=1)[c]	P (%) MD[b]	As (µg/g) DD[a] (n=1)[c]	As (µg/g) MD[b]
C 19/1/93	0.68	0.66±0.02 (n=2)[c]	0.26	0.30±0.01 (n=2)[c]	27.5	27.4±0.2 (n=2)[c]	1.60	1.47±0.03 (n=2)[c]	1.68	2.35±0.05 (n=2)[c]	0.35	0.39±0.02 (n=2)[c]	17	14.1±0.2 (n=2)[c]
E 2/2/93	0.79	0.74 (n=1)[c]	0.25	0.25 (n=1)[c]	29.7	25.5 (n=1)[c]	1.33	1.33 (n=1)[c]	1.34	2.15 (n=1)[c]	0.28	0.28 (n=1)[c]	18	15 (n=1)[c]
C 4/2/93	0.85	0.76 (n=1)[c]	0.24	0.22 (n=1)[c]	27.6	24.7 (n=1)[c]	1.46	1.24 (n=1)[c]	1.71	2.17 (n=1)[c]	0.33	0.32 (n=1)[c]	18	15 (n=1)[c]
C 1/2/93	0.72	0.62±0.01 (n=4)[c]	0.26	0.25±0.02 (n=4)[c]	16.2	14.8±0.3 (n=4)[c]	2.75	2.40±0.10 (n=4)[c]	3.03	3.19±0.07 (n=4)[c]	0.67	0.63±0.02 (n=4)[c]	23	17.8±0.3 (n=2)[c]
E 26/10/93	0.59	0.51±0.01 (n=2)[c]	0.19	0.17±0.02 (n=2)[c]	18.1	16.7±0.3 (n=2)[c]	1.97	1.70±0.02 (n=2)[c]	2.27	2.40±0.07 (n=2)[c]	0.62	0.61±0.02 (n=2)[c]	23.4	19.6 (n=1)[c]
L 5/10/93	0.68	0.54 (n=1)[c]	0.23	0.19 (n=1)[c]	17.5	17.0 (n=1)[c]	2.24	2.05 (n=1)[c]	2.40	2.74 (n=1)[c]	0.60	0.57 (n=1)[c]	20.3	16.5 (n=1)[c]
G 27/1/93	1.35	1.65 (n=1)[c]	0.74	0.81 (n=1)[c]	18.1	15.5 (n=1)[c]	ND[d]	ND[d]	ND[d]	ND[d]	0.22	0.26 (n=1)[c]	45.5	46.2 (n=1)[c]
A 19/10/93	1.83	1.73 (n=1)[c]	0.71	0.99 (n=1)[c]	18.3	16.0 (n=1)[c]	ND[d]	ND[d]	ND[d]	ND[d]	0.33	0.27 (n=1)[c]	51.5	42.5 (n=1)[c]
T 26/1/93	1.26	1.50 (n=1)[c]	0.71	0.87 (n=1)[c]	15.6	16.7 (n=1)[c]	ND[d]	ND[d]	ND[d]	ND[d]	0.19	0.24 (n=1)[c]	48.1	49.7 (n=1)[c]

[a] DD: dry digestion (fusion).

[b] MD: microwave digestion (with 2N HCl).

[c] n: replicate number. For n>1, standard deviation (± SD) on the mean is indicated.

[d] ND: not determined.

spectrometric determination of different elements of interest in this type of waste.

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