Talanta 101 (2012) 346–352

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Microwave digestion for the quantification of inorganic elements in coal and coal ash using ICP-OES

Fiona Low, Lian Zhang*

Department of Chemical Engineering, Monash University, Wellington Road, GPO Box 36, Clayton, Victoria 3800, Australia

ARTICLE INFO

Article history:
Received 24 June 2012
Received in revised form
21 September 2012
Accepted 21 September 2012
Available online 28 September 2012

Keywords:
Coal
Coal ash
Microwave digestion
HF amount
Trace elements

ABSTRACT

In this paper, microwave digestion conditions have been optimised to achieve complete recoveries for the ash-forming inorganic elements in coal and coal combustion fly ash, during the analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES). The elements analysed include six major (Al, Ca, Fe, K, Mg and Na) and twelve trace (As, Ba, Be, Co, Cr, Cu, Li, Mn, Ni, Pb, Sr and V). Seven reference samples have been tested, including two standard coal references, SRM1632c and SARM19, their corresponding high-temperature ashes (HTAs), and three coal fly ash references, SRM1633c, SRM2690 and BCR38. The recoveries of individual elements in these samples have been examined intensively, as a function of the amount of hydrofluoric acid (HF, 0–2.0 ml), microwave power (900 W vs. 1200 W) and sample mass (0.05 g vs. 0.1 g). As have been confirmed, the recoveries of these individual elements varied significantly with the microwave digestion condition, elemental type and sample property. For the coal references and their HTAs, the use of HF can be ruled out for most of the elements, except K associated with feldspar, Pb and V. In particular, the recovery of Pb in coal is highly sample-specific and thus unpredictable. The majority of elements in fly ash references require the use of 0.1–0.2 ml HF for a complete recovery. Al in fly ash is the only exceptional element which gave incomplete recoveries throughout, suggesting the use of a complementary technique for its quantification. As has proven to be the only element inconsequential of sample type and digestion conditions, achieving complete recoveries for all cases. On the power parameter, using a higher power such as 1200 W is critical, which has proved to be an ultimatum for the recovery of certain elements, especially in fly ash. Halving sample mass from 0.1 g to 0.05 g was also found to be insignificant.

1. Introduction

Developing a reliable and easy method for accurate quantification of inorganic elements in coal and its combustion/gasification by-products, i.e. fly ash, is pivotal to understand the partitioning behaviour of these elements at high temperatures, and their potential environmental impacts. A variety of spectroscopic techniques have been employed for the quantification of inorganic elements in geological samples. For the instruments based on inductively coupled plasma (ICP), an initial dissolution of coal or coal ash sample in acids to convert all the inorganic elements into ions is essential [1,2]. Of the sample dissolution methods available, microwave digestion is one most promising technique which has been attracting increased attention, due to numerous advantages including a simultaneous treatment of multiple samples, rapid dissolution of solid particles at elevated temperature and pressure, little particle loss in closed vessel and contamination, and being safe for the use of corrosive acids in closed vessels [3–7].

To achieve a satisfactory digestion of coal or its ash sample, the combination of numerous acids is commonly adopted during microwave digestion, including hydrogen peroxide (H_2O_2) to assist the decomposition of coal organic matrix via oxidation [8] and the use of concentrated nitric acid (HNO_3) in conjunction with concentrated hydrofluoric acid (HF) to attack siliceous and aluminosilicate which are the host mineral incorporating a variety of minor and trace elements, particularly in coal ash [3,5]. Although the use of acids for the digestion of coal and coal ash is widely accepted, the acid mixing ratios and microwave digestion conditions necessary to achieve a complete digestion are unique to any laboratory [9,10]. In particular, the use of HF and its optimised amount are still debated. The use of HF is believed to be essential for the dissolution of quartz and kaolinite (or its derivative mullite) to liberate the trace elements embedded inside. However, depending on the quantity of excessive HF, a certain number of the liberated ions can re-precipitate as insoluble fluorides, thereby losing the full recoveries during the subsequent ICP analysis. To solve these two contradictory issues,

---

* Corresponding author. Tel.: +61 3 9905 2592; fax: +61 3 9905 5686.
E-mail address: lian.zhang@monash.edu (L. Zhang).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.09.037

optimising the HF amount is highly required, especially since previous studies only targeted optimising digestion conditions of either entirely coal or ash. It still remains an interest to explore if the optimum conditions achieved for coal are applicable to coal combustion fly ash in which the aluminosilicate slagging matrix is supposed to be more stable and acid-resistant.

The present work is motivated by the above-mentioned critique. Through systematically varying the microwave digestion conditions, the necessity of using HF for a complete digestion of coal and coal ash has been discussed in detail, and consequently, optimised. Apart from varying the HF amount, extra efforts have also been made to vary the microwave power and sample amount. Increase in the first factor is expected to improve temperature and pressure in the coal-/ash-containing closed vessels, which in turn promotes the dissolution of resistant minerals [9,11,12]. On the other hand, reducing ash mass is expected to ensure the concentration of metal fluorides upon the use of HF to be lower than its corresponding solubility. The standard references tested include two coal references, SRM1632c and SARM19, their high-temperature ash (HTA) reference, and three real coal fly ash references, SRM1633c, SRM2690 and BCR38. Examining the HTA samples has two-fold in benefit: its comparison with the corresponding raw coal is helpful in addressing whether or not a prior ashing is beneficial in increasing the recovery of elements by burning off hydrocarbons; and its comparison with real fly ashes provides insight into elucidating the effect of ash matrix on the recovery of elements.

The elements investigated encompass both major (Al, Ca, Fe, K, Mg and Na) and trace elements (As, Ba, Be, Co, Cr, Cu, Li, Mn, Ni, Pb, Sr and V). The recovery of each element has been discussed as a function of sample property, HF amount, microwave power and sample mass, aiming to address the optimum conditions for maximising the accuracy of ICP-OES coupled with microwave digestion.

2. Experimental

2.1. Coal and fly ash references

The SRM1632c coal reference is a bituminous coal certified by the National Institute of Standards and Technology (NIST), USA, whereas the second coal reference, SARM19, is a sub-bituminous coal certified by the SA Bureau of Standards, South Africa. The ash content of SRM1632c and SARM19 is 7.2% and 29.6%, respectively. The particles size of SRM1632c and SARM19 is less than 250 μm and 106 μm, respectively.

HTA samples were prepared by ashing the two reference coals in a muffle furnace. The muffle furnace was heated in air at a heating rate of approximately 6 °C/min to reach 815 °C and then held for 3 h. The consensus values for the concentrations of major and some trace elements in SRM1632c HTA have been provided with the standard coal together. For ash elemental concentrations that were not provided, their expected concentrations were calculated based on the enrichment factor of the reference material upon ashing.

The first reference coal fly ash, SRM1633c is the product of western Pennsylvania bituminous coal and sourced from a coal-fired plant. Its particle size is less than 74 μm and its constituents were also certified by NIST. Another coal fly ash certified by NIST is SRM2690, a product of Colorado coal with ash particles grounded to pass a 145 μm sieve. For this reference material, only the concentrations of the major constituent elements were certified. The third standard reference ash used, BCR038, was certified by the Community Bureau of Reference (BCR)/ Institute for Reference Materials and Measurements (IRRM). This material particle size is less than 10 μm and was collected at the electrostatic precipitator of a pulverised coal-fired power station in Belgium. All the samples used were dried and stored in a desiccator prior to their analysis.

2.2. Reagents

The acids used are of analytical grade, including HNO_3 (65%, Suprapur), H_2O_2 (30%, Merck), and HF (40%, Fluka). The ultrapure Milli-Q water (Millipore Milli-Q, USA) with a specific resistivity of 18.2 MΩ/cm was used throughout for cleaning purposes and solution preparation. A multi-element standard solution (Perkin Elmer), containing all of the examined elements at a concentration of 10 mg/L in 5% HNO_3 solution, was used for ICP-OES calibration. Both argon and nitrogen gases used for ICP-OES are of ultra high purity grade 5.0. The air used as shear gas was obtained from an air compressor fitted with a pre-dryer filter.

2.3. Microwave digestion

Coal and ash samples were digested using a microwave digestion system (Multiwave 3000, Anton Paar) that permits a maximum of 8 pressure vessels to be simultaneously mounted on the rotor. The pressure vessel used is termed XF100 and consists of a PTFE-TFM liner supported by a ceramic vessel jacket enclosed in a protective casing. The vessel has an operating pressure of 6 MPa, which can withstand a maximum temperature of 260 °C.

For each run, an accurately weighed amount of coal or ash sample was first mixed with 5 ml HNO_3, 2 ml H_2O_2 and a desired amount of HF in a clean vessel. The liner and its contents were then subjected to high-temperature and pressure using the microwave digestion system set at a power of either 900 W or 1200 W. Table 1 lists the conditions tested. The procedures A through to D are for the two coal references without a prior ashing, whereas procedures E through to H are for the HTAs of two coal references. For the HTA samples, 0.1 ml HF was used based on the consideration that the excessive HF could suppress the recoveries of most of the major elements [5]. This will be further explained later. In addition, of these procedures, procedures C and D and procedures E and F demonstrate the influence of varying the microwave power while keeping all other parameters constant, whereas procedures G and H compare the different mass of sample used. This is likewise for procedures I and J for the SRM1633c fly ash reference. The rest of procedures J through to O are a variation of the HF amount used for the digestion of SRM1633c, SRM2690 and BCR038.

Once the vessels have been fully cooled and depressurised, the solution was transferred to individual PTFE (Teflon) sample jars. For a solution where HF is absent, it is subsequently filtered by a

Table 1
Experimental conditions for each procedure.

Sample type	*Raw coal*				*High-temperature ash (HTA)*			
SRM1632c and SARM19								
Procedure label	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)
Mass of sample (g)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.05
Microwave power (W)	900	900	900	1200	900	1200	1200	1200
Amount of HF (ml)	1.0	0.1	–	–	0.1	0.1	–	0.1
Sample type	*Real coal fly ash*							
SRM1633c, SRM2690, BCR38								
Procedure label	(I)[a]	(J)	(K)	(L)	(M)	(N)	(O)	
Mass of sample (g)	0.05	–	–	0.1	0.1	0.1	0.1	
Microwave power (W)	1200	1200	1200	1200	1200	1200	1200	
Amount of HF (ml)	–	–	0.1	0.2	0.5	1.0	2.0	

[a] Only for SRM1633c.

sterilised 0.45 μm syringe filter. In contrast, for the cases of HF used during digestion, the resulting solution was further subjected to an evaporation procedure at 90 °C for approximately 5 h to evaporate the HF, whereby the solution was eventually concentrated into a small drop of thick liquid residue. Consequently, the residue was dissolved within 2% (v/v) HNO_3 to form a solution again, which was then filtrated. All solutions were finally diluted using 2% HNO_3 (which is also the blank solution) at dilution factors (DF) of 150, 2250, and 33,750 for instrumental analysis. All samples for each experimental procedure were performed in four replicates.

2.4. ICP-OES Analysis

A Perkin-Elmer Optima 7000 DV ICP-OES spectrometer with a dual-view (axial-radial) optical system was used for the quantification of six major elements (Al, Ca, Fe, K, Mg and Mn) and fifteen trace elements (As, Ba, Be, Co, Cr, Cu, Li, Na, Ni, Pb, Sr and V). Pre-calibration was conducted through the use of external standard solutions with a maximum concentration of 5 mg/L for individual elements. The instrumental parameters and operating conditions (Table S1) have been optimised to ensure sufficient sensitivity and precision. As evident in Table 2, for the wavelengths of individual elements chosen here, the limit of quantification (LOQ) of an element, as calculated as its concentration equal to ten times the standard deviation of background signal multiplied by a DF of 300 in this study, is comparable to and even better than that has been achieved in the literature [13]. For Ba, the line 233.5 nm was used, rather than the line 455.4 nm adopted in [13] which gave saturated readings even at the low concentration of 1 mg/L. Note that, all the LOQs here were determined based on the analysis of ten replicates of the blank solution, 2% HNO_3.

2.5. ICP-OES result interpretation

Apart from the use of the term 'recovery' to interpret the accuracy for the quantification of individual elements, statistical analysis using homoscedastic student's *t*-test method was also applied to the data of several cases in this study. This is helpful for differentiating the small variation for the concentrations of trace elements. The degree of freedom was fixed at 6 for all cases, on the assumption that the unspecified number of repetitive measurements for the certified data was equal to that adopted for our experiments. Recovered elemental concentrations exceeding 95% confidence (two-tailed $p \leq 0.05$) of the student's *t*-distribution were assumed to be statistically different. This is reflected by a *t*-value of 2.45 based on standard *t*-distribution table. Details for *t*-value calculations are in the supporting information (SI). Negative *t*-values smaller than -2.45 refers to the incomplete recovery of elements. The corresponding digestion method is then deemed unsatisfactory. On the other hand, positive *t*-values over 2.45 were taken as the errors caused by contamination.

Table 2
Analytical wavelengths and limits of quantification (LOQ) of elements in coal.

Element	Wavelength (nm)	LOQ (μg/g) [13]	LOQ (μg/g) This study
Al	396.15	–	3.9
Ca	317.93	–	2.3
Fe	238.20	–	0.3
K	766.49	–	2.5
Mg	285.21	–	0.4
Na	589.59	–	0.7
As	188.98	1.3	1.3
Ba	233.53	0.03[a]	0.05
Be	313.11	0.04	0.03
Co	228.62	0.2	0.2
Cr	267.72	0.5	0.1
Cu	324.75	0.5	0.08
Li	670.78	–	0.05
Mn	257.61	0.06	0.02
Ni	231.60	1.0	0.2
Pb	220.35	1.5	1.5
Sr	407.77	0.01	0.01
V	290.88	0.1	0.5

[a] Determined at a wavelength of 455.4 nm.

3. Results and discussion

3.1. Digestion results for coal and fly ash references

The full ICP-OES results obtained after microwave digestion using procedures A through to D are listed in Tables S2 and S3 in the SI for SRM1632c coal and SARM19 coal, respectively. Apart from the certified and measured concentrations of individual elements, included in the tables are the total relative standard deviation (TRSD) and the instrumental standard deviation (IRSD) for individual elements. The TRSD represents the reproducibility of the sample preparation through the microwave digestion procedures, whereas the IRSD represents the precision of the ICP-OES analysis based on two replicates of a single solution [25]. Irrespective of elemental type, the TRSD values are comparably larger than the corresponding IRSD values, indicative of the large uncertainties caused by sample preparation including the heterogeneity of the mineralogical properties of coal samples and the lower reproducibility of microwave digestion, as expected. For future graph error bar purposes, the two RSDs were combined to give a total single RSD, as described in the SI. Tables S4 and S5 show the results obtained for the two HTA references through microwave digestion procedures E to H. Regarding the three fly ash references, their ICP-OES results are summarised in Tables S6, S7 and S8 for SRM1633c, SRM2690 and BRC038, respectively.

3.2. Influence of HF addition on the recovery of major elements

Based on the results in Tables S2 and S3, Fig. 1 plots the recoveries of six major elements in the two coal references. It is evident that the recoveries of these elements are highly dependent on coal sample type, with SRM1632c in *panel* (a) giving better overall recoveries than SARM19 in *panel* (b). Ascertaining this are the *t*-test results in Table S9, indicating that while only the case of 'no HF' for Ca and Mg gave unsatisfactory recoveries for the SRM1632c, majority of the cases gave poor recoveries for the SARM19. The difference in recovery behaviour can be attributed to the difference in mineralogical properties of the two coals, i.e. mode of occurrence of individual elements. For instance, the use of HF is essential for the decomposition of feldspar inherent in the SARM19 coal [13]. In addition, the unique recovery trend of K in the SARM19 coal with respect to amount of HF used implies an optimised HF quantity at approximately 0.1 ml. The use of excessive amounts of HF is supposed to promote secondary reactions between fluorosilicic acid, a by-product of the primary reaction between HF and the feldspar, and aluminium silicates, clays and feldspar. These reactions are believed to have adverse effects because they retard HF reactions [14]. For Al and Mg in the SARM19 coal, a continuous reduction in their recoveries with increase in HF amount can be attributed to the formation of insoluble metal fluorides [13]. In addition, the asterisk symbols for the case of 'no HF and 1200 W power' in Fig. 1 confirms the possibility of eliminating the use of HF for the recovery of certain elements in coal.

Fig. 2 depicts the recoveries of major elements in three fly ash references as a function of the amount of HF used for digestion. Irrespective of fly ash type, the major elements within them are

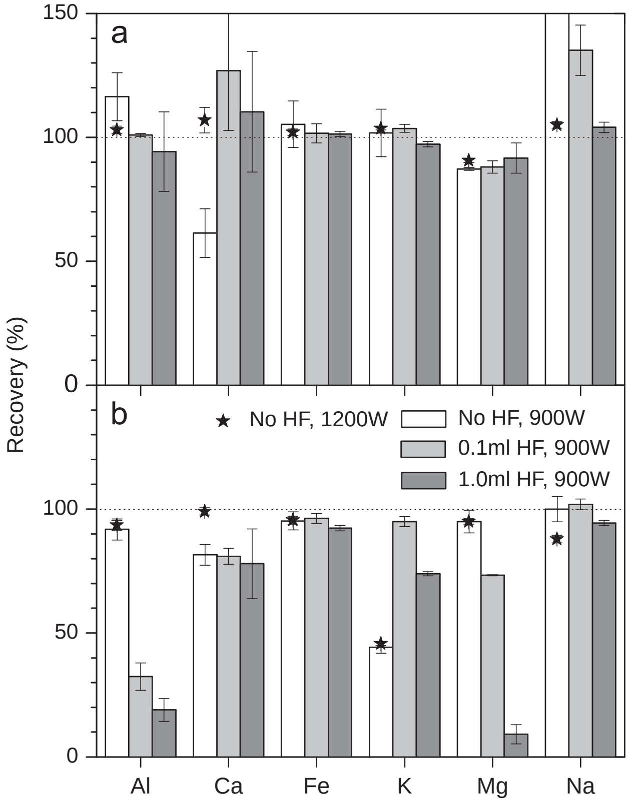

Fig. 1. Effects of HF amount and microwave power on the recoveries of major elements in coal references (a) SRM1632c and (b) SARM19.

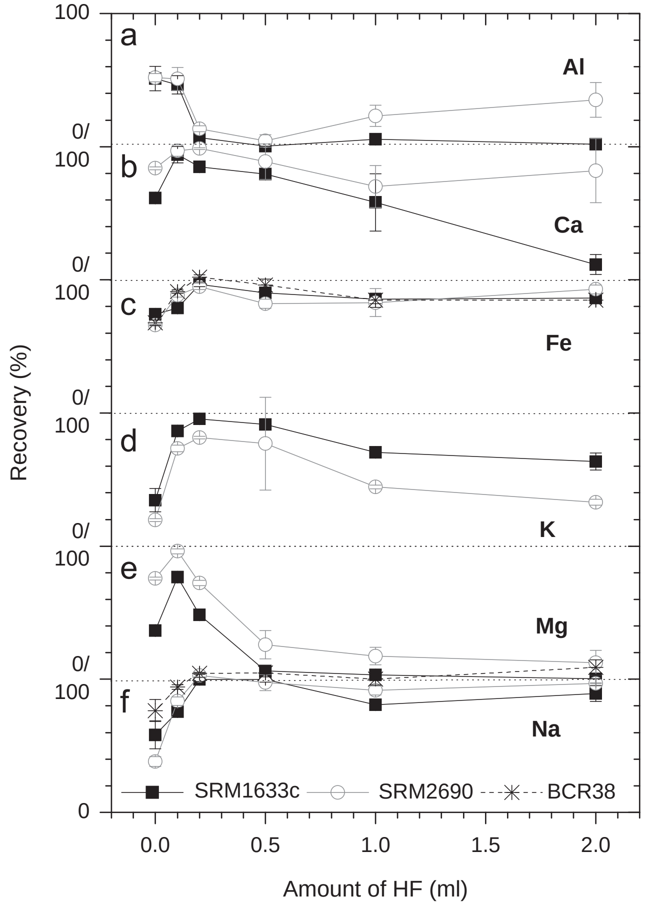

Fig. 2. Effects of HF amount on the recoveries of major elements in three fly ash references.

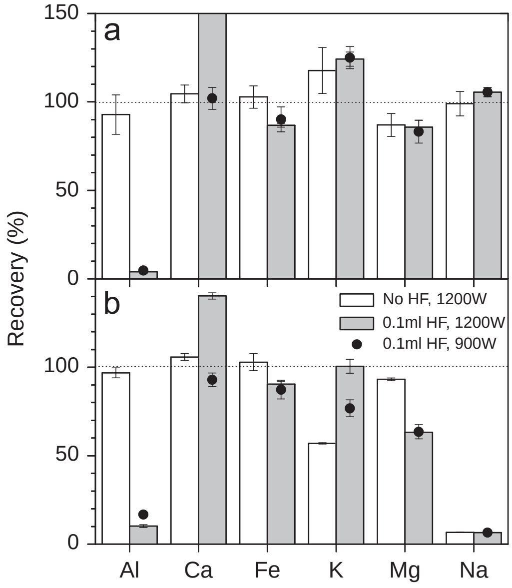

Fig. 3. Effects of HF amount and microwave power on the recoveries of major elements in HTAs (a) SRM1632c and (b) SARM19.

more sensitive towards HF applications than coal references. Each of these major elements in the fly ash possesses its own unique recovery trend. For Al, its recovery in the absence of HF reached up to 50%. Adding an amount of HF from 0.2 ml onwards to the fly ash caused the precipitation of nearly the entire Al. Clearly, the microwave digestion method discussed here is incapable of quantifying Al in coal combustion fly ash, the reason of which can be due to the incorporation of Al in a stable slagging phase formed at high temperatures. A different technique such as X-ray Fluorescence (XRF) should be considered to supplement ICP-OES for Al measurement. Secondary to this is the drop in the recoveries of Mg, Ca, K and Fe past their optimum HF points of 0.1–0.2 ml. Indeed, a trend emerges on the extent of major element suppression by HF, i.e. insoluble metal fluoride formation, which can be attributed to their preference order for reaction as shown in Fig. S1. This also explains the different effects of HF addition on Ca recovery between coal and fly ash references. Typically in fly ash, Ca is present in an oxide form, which is much more likely to form insoluble Ca fluoride compared to the carbonate form of Ca, a common Ca mode of occurrence in coal, as substantiated by thermodynamic predictions using Gibbs energy minimisation function. The formation of Na fluoride is not an issue, as it is highly soluble in aqueous solutions.

Fig. 3 further describes the recovery of the major elements for the two HTA samples, which were digested by microwave under the perceived optimum HF amount (0.1 ml), and a blank case of using no HF. Interestingly, except K in SARM19 HTA, the other major elements in HTA samples showed no requirement on the use of a minimum amount of HF for digestion, as confirmed by *t*-test results in Table S10. Indeed, the use of no HF at 1200 W is good enough for a full recovery of Al. Here again, this is a strong indicator of the formation of a stable structure for Al-bearing species in a real coal fly ash collected from pulverised coal-fired power plants. The slagging phase is very likely formed for Al in fly ash. In contrast, high-temperature ashing at 815 °C is not a step-change process to affect the structure of Al-bearing species in coal.

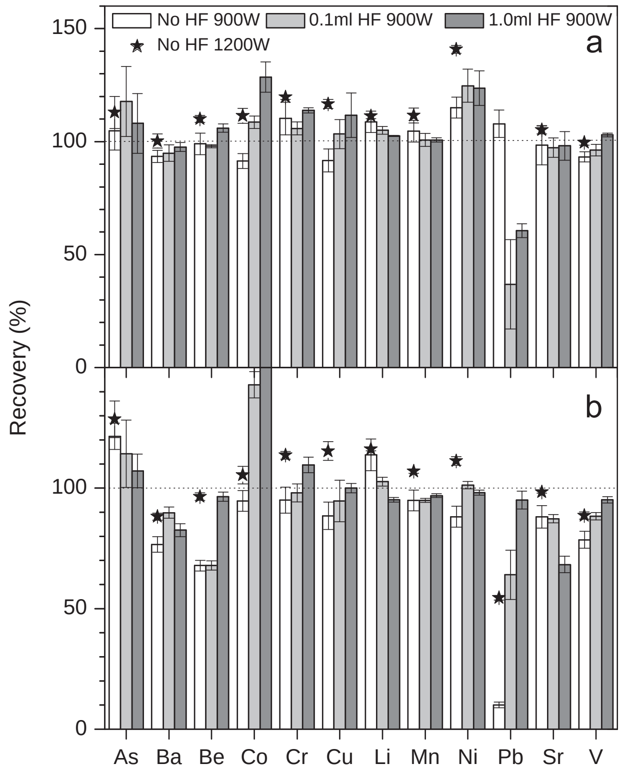

Fig. 4. Effects of HF amount and microwave power on the recoveries of trace elements in coal references (a) SRM1632c and (b) SARM19.

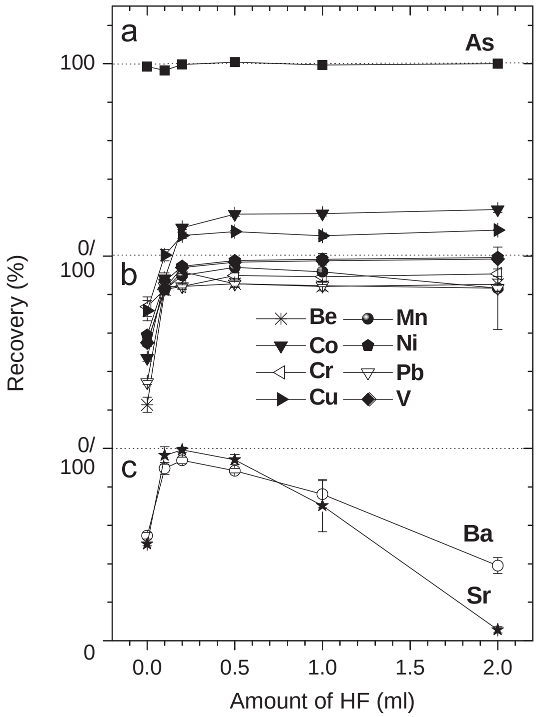

Fig. 5. Effects of HF amount on the recoveries of trace elements in fly ash reference SRM1633c.

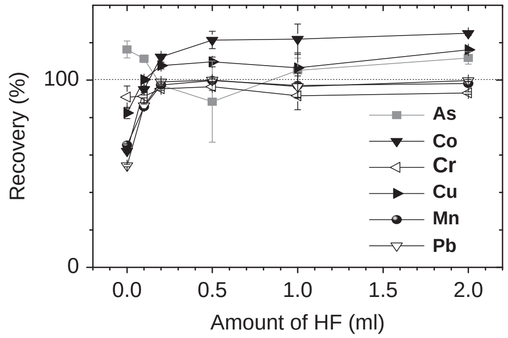

Fig. 6. Effects of HF amount on the recoveries of trace elements in fly ash reference BCR38.

3.3. Influence of HF addition on the recovery of trace elements

Fig. 4 plots the recoveries of trace elements in the coal references as a function of HF amount and microwave power. With the exception of Pb and V in SARM19 coal, addition of HF seems to bring no extra benefit to their quantitative analysis, provided that the microwave power parameter is optimised. Specifically for Pb dissolution, the use of approximately 1.0 ml HF is essential. Such an observation is contradictory to Pb in the SRM1632c coal which showed a negative reaction to any amount of HF. Clarifying the reason for this discrepancy is beyond the scope of this study. However, it demonstrates a strong sample-specific dependency for Pb measurement. In this sense, it is unlikely to standardise the digestion conditions for the quantification of Pb in coal.

The observations above are in contrast to the majority of the trace elements in fly ash references which require at least 0.1–0.2 ml HF to achieve sufficient liberation, see Fig. 5. Of all the trace elements tested, As is the sole element appearing to be independent of digestion conditions employed (*panel* (a)). This demonstrates its weak association in fly ash and thus, the easiness to decompose during microwave digestion. Such a finding is in agreement with literature [15,16]. For the rest of the trace elements, they are apparently incorporated into a stable matrix, such as aluminosilicate slag, which cannot be decomposed unless the HF is used. Additionally, these elements can be further segregated into two groups based on their recovery behaviour with respect to addition of excess HF; one, inconsequential (*panel* (b)), and the other, suppressed by it (*panel* (c)). The rationalisation for the former group in behaving as such is that they possess no tendency to form insoluble metal fluorides. Fig. 6 for the BCR38 fly ash reference provides validation to the behaviour of As and the elements belonging to the second group. For Ba and Sr in *panel* (c) of Fig. 5, the dip in recovery passing their optimum point of 0.2 ml HF is obviously caused by the formation of insoluble metal fluorides. Their aversion towards excess HF is also documented in Fig. S2 (panel (c)) using reference values of SARM2690. The other trace elements in BCR38 were not discussed here, because their certified values are not available.

The recoveries of trace elements in the HTAs are summarised in Fig. 7 for the three typical digestions conditions, same as that for the major elements in Fig. 3. For the SRM1632c HTA, only Pb and V showed a strong request for the use of 0.1 ml HF. The rest of the elements satisfactorily recovered under the blank condition of using no HF at 1200 W. Back to the results in Fig. 4(a), it is apparent that the original Pb in the SRM1632 coal is mostly present as a loose structure such as oxide or organically bound metal, the majority of which however is apparently incorporated into a stable matrix upon 815 °C ashing. Such an inference is not applicable to the SARM19 coal, in which the original Pb should already be incorporated into aluminosilicate during coalification, hence requiring the use of HF for digestion of Pb in both raw coals and their HTAs. The discrepancy of Pb between two coals and their HTA samples is clearly indicative of the difficulty for standardising the microwave digestion procedure for the quantification of this metal by ICP. In other words, a complementary method should be considered. In addition to Pb and V requiring HF, recoveries of Ba and Be in the

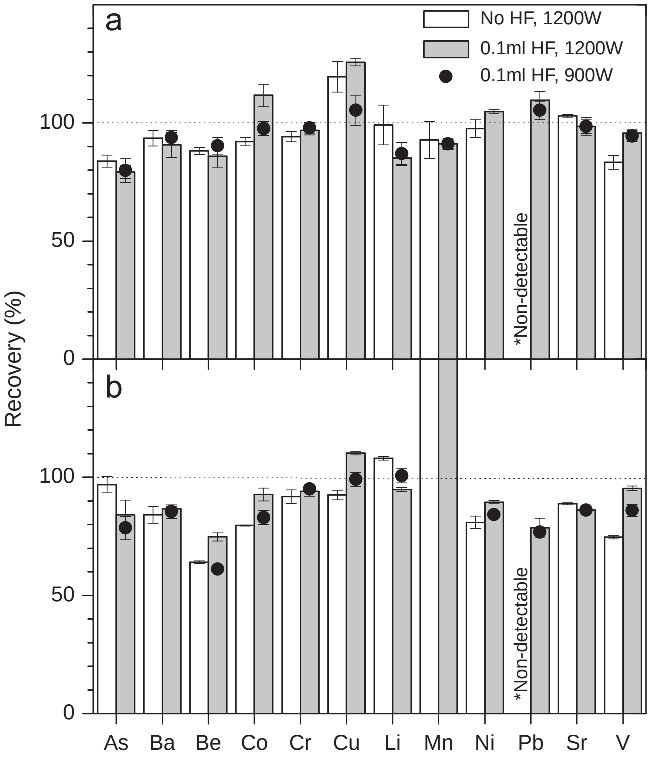

Fig. 7. Effects of HF amount and microwave power on the recoveries of trace elements in HTAs (a) SRM1632c and (b) SARM19.

SARM19 HTA were incomplete throughout, which is the same for these two metals in the raw coal, Fig. 4(b). Apparently, these two metals in SARM19 coal are also incorporated into a stable structure, which bear little change upon high-temperature ashing. For further clarity, *t*-test results for the trace elements in the two HTAs are presented in Fig. S3. Note that the disproportionate results of Li here are due to the unavailability of certified error.

3.4. Influence of microwave power on inorganic element recovery

Fig. S4 depicts typical heating profiles for microwave digestion procedures using 900 W (e.g. procedure C) and 1200 W (e.g. procedure D). The temperatures achieved at 900 W ranged between 150 °C to 200 °C, relative to a mean vessel temperature above 200 °C at the microwave power of 1200 W. Likewise with pressure readings, setting the microwave power at 900 W gave a max pressure of 53.5 bars, relative to a max pressure reading of 60.0 bars at 1200 W.

Back to Figs. 1 and 3 for major elements in the two coals and HTAs, one can conclude the significance of using a higher microwave power on elemental recoveries. In some cases, it can offset the necessity for the use of HF, such as that observed for the recovery of Ca in the SRM1632c coal in Fig. 1(a). The use of a higher microwave power may even be a prerequisite for complete elemental recovery e.g. SARM19 Ca in Fig. 1(b). Likewise, for the recovery of K in SARM19 HTA in Fig. 3(b), a combined use of 1200 W and 0.1 ml HF is essential. Such a power dependency is additionally evident for trace elements in Fig. 4, as attested by their complete recovery in the SRM1632c coal and overall improved recovery in the SARM19 coal on increasing the power to 1200 W. Even so, one has to be cautious that for some elements such as Pb in SARM19 coal, increasing microwave power is still incapable of completely replacing the use of HF. This is substantiated in Fig. 4(b), where the recovery of Pb at 1200 W without HF was only improved to around 50%, in comparison to nearly 100% achieved in the case of 1.0 ml HF and 900 W. Here again, the majority of Pb in SARM19 coal is incorporated into a stable host mineral such as aluminosilicate and/or quartz, which rarely changes upon ashing. The results for digestion tests on the three fly ash references at 900 W witnessed the incomplete dissolution of a large quantity of sample material, and hence were not discussed here. In other words, the use of a higher microwave power, e.g. 1200 W tested here, is essential for real fly ash samples collected from power plants.

3.5. Influence of sample mass on inorganic element recovery

A mass amount of approximately 0.1 g for a coal sample, in consistence with [13], was analysed throughout in this study. To mimic a worst-case scenario that the availability of sample is scarce, procedure H and procedure I for halving ash quantity were further conducted to assess the influence of sample mass on the recovery of elements. Fig. 8 describes the comparison between the two sample mass tested for SRM1633c real fly ash in *panel* (a), SRM1632c HTA in *panel* (b) and SARM19 HTA in *panel* (c). All other parameters were kept constant. For Fig. 8(a), HF was not added to examine the sole contribution of halving the sample mass, whereas procedures in Fig. 8(b) and (c) entail the addition of 0.1 ml HF. Irrespective of sample property, the negligible difference was confirmed for the recovery of nearly all the elements between the two sample masses. The use of a small amount of reference sample is thus reasonable, and is beneficial in reducing the cost for the purchase of reference samples.

4. Conclusions

The optimum digestion conditions in terms of HF amount, microwave power, and sample mass to achieve reliable elemental recoveries have been examined systematically in this study, using two coal references and their HTAs, SRM1632c and SARM19,

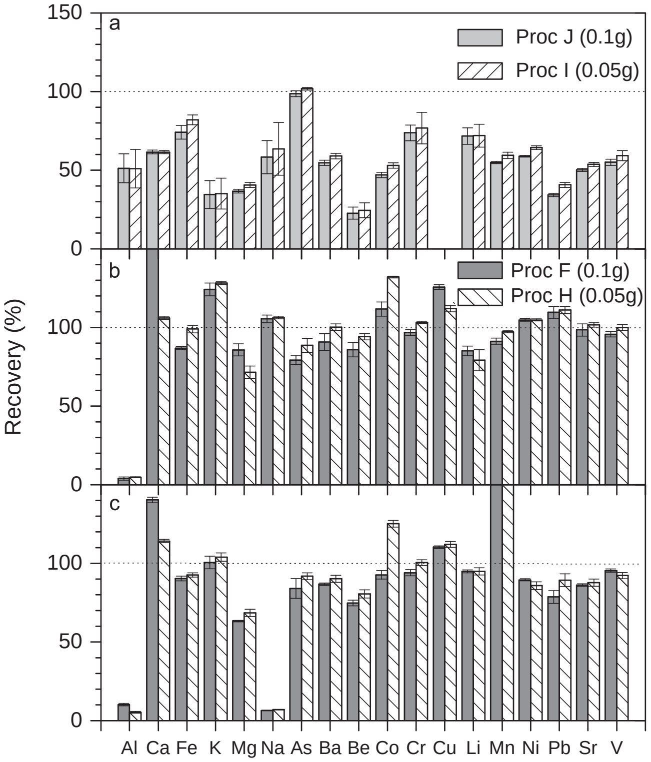

Fig. 8. Comparison between the different mass of sample used in procedure J/F—0.1 g and procedure I/H—0.05 g for (a) SRM1633c, (b) SRM1632c HTA, and (c) SARM19 HTA.

as well as three real coal fly ash references, SRM1633c, SRM2690 and BCR38. The major conclusions can be drawn as follows.

1. For the recovery of major elements in coal and HTAs, HF is only necessary for K associated with the presence of feldspar. In contrast, for the fly ashes, an optimum HF amount of 0.1 ml and 0.2 ml is required for the two groups, Ca and Mg, and Fe, K and Na, respectively. The element recovery suppression past this point is attributed to the formation of insoluble metal fluorides. Al in fly ash references is the sole element showing a consistently lower recovery under all the conditions tested here, suggesting the necessity of using a different technique to complement ICP-OES.
2. With the exception of Pb and V in coals and HTAs, the rest of the trace elements in these two sample types can forego the need of HF to achieve acceptable recoveries. Likewise, As in the fly ash references have proven to be independent of digestion conditions throughout. The quantification of Pb in coal samples is highly sample-specific. For the remaining trace elements in fly ash references, an optimum amount of 0.1–0.2 ml HF is essential to ensure a full recovery. Adding excessive HF is insignificant for Be, Co, Cr, Cu, Mn, Ni, Pb and V, irrespective of fly ash type. However, Ba and Sr tend to form insoluble fluorides in excess HF, worsening their recoveries.
3. Microwave power (i.e. digestion temperature) is a critical factor in determining HF necessities and overall elemental recoveries. The use of 1200 W power in this study is preferred over 900 W, irrespective of the presence of HF. Decreasing the sample mass of 0.1 g here by half is insignificant in the recovery of all the elements.

Acknowledgements

The authors are grateful to the Australian Research Council Future Fellowship grant (FT0991010) and Australian national low emission coal (ANLEC) R&D for financial support.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.09.037.

References

[1] J. Wang, T. Nakazato, K. Sakanishi, O. Yamada, H. Tao, I. Saito, Talanta 68 (2006) 1584–1590.
[2] E. Hatanpää, K. Kajander, T. Laitinen, S. Piepponen, H. Revitzer, Fuel Process. Technol. 51 (1997) 205–217.
[3] A. Saydut, Energy, Explor. Exploit 28 (2010) 105–116.
[4] F.A.C. Amorim, B. Welz, A.C.S. Costa, F.G. Lepri, M.G.R. Vale, S.L.C. Ferreira, Talanta 72 (2007) 349–359.
[5] Y.H. Xu, A. Iwashita, T. Nakajima, H. Yamashita, H. Takanashi, A. Ohki, Talanta 66 (2005) 58–64.
[6] T. Wondimu, W. Goessler, K.J. Irgolic, Fresenius J. Anal. Chem. 367 (2000) 35–42.
[7] V. Sandroni, C.M.M. Smith, Anal. Chim. Acta 468 (2002) 335–344.
[8] A. Montaser, in: H.M. Kingston, P.J. Walter (Eds.), Inductively Coupled Plasma Mass Spectrometry, Wiley-VCH, United States of America, 1997, pp. 34–78.
[9] S.J. Hill, T.A. Arowolo, O.T. Butler, J.M. Cook, M.S. Cresser, C. Harrington, D.L. Miles, J. Anal. Atom. Spectrom. 19 (2004) 301–330.
[10] V. Roje, Chem. Pap. 64 (2009) 409–414.
[11] Z. Yu, P. Robinson, A.T. Townsend, C. Mnker, A.J. Crawford, Geostand. Newsletter 24 (2000) 39–50.
[12] W. Diegor, H. Longerich, T. Abrajano, I. Horn, Anal. Chim. Acta 431 (2001) 195–207.
[13] J. Wang, T. Nakazato, K. Sakanishi, O. Yamada, H. Tao, I. Saito, Anal. Chim. Acta 514 (2004) 115–124.
[14] E. Huenges, in: T. Schulte, G. Zimmermann, F. Vuataz, S. Portier, T. Tischner, R. Junker, R. Jatho, E. Huenges (Eds.), Geothermal Energy Systems: Exploration, Development, and Utilization, Wiley-VCH, Germany, 2010, pp. 173–240.
[15] Y.H. Xu, T. Nakajima, A. Ohki, Toxicol. Environ. Chem. 81 (2001) 55–68.
[16] F.E. Huggins, G.P. Huffman, A. Kolker, S.J. Mroczkowski, C.A. Palmer, R.B. Finkelman, Energ Fuel 16 (2002) 1167–1172.