Multielement analysis of coal by ICP techniques using solution nebulization and laser ablation

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Abstract

The combination of inductively coupled plasma atomic emission spectrometry and high resolution inductively coupled plasma mass spectrometry for the determination of 70 elements in coal were studied. Four microwave-assisted digestion procedures with different dissolution mixtures (nitric and hydrofluoric acids, aqua regia and hydrogen peroxide), lithium metaborate fusion with and without previous sample ashing as well as direct sampling by laser ablation (LA) have been tested. Examples of spectral interferences are given and different correction procedures are discussed. Detection limits in the low ng g^{-1} range were obtained for most of the elements investigated by using high-purity reagents and by taking special care to prevent sample contamination during preparation. The precision was assessed from replicate analysis (including sample preparation) of coal samples and was found to be, as average values far all elements, 4–5% RSD and 10–15% RSD for procedures including sample digestion and LA sampling, respectively. The accuracy of the overall analytical procedures was estimated by analysis of certified reference materials and of a coal sample obtained from the Interlab Trace round robin test. Among the dissolution mixtures tested, the combination of nitric and hydrofluoric acids with hydrogen peroxide provide the best agreement with certified, recommended, literature-compiled or consensus values, though fusion is necessary to obtain quantitative recoveries for Si, Cr, Hf, W, Zr, Y. In general, results obtained by LA fall within $\pm 20\%$ of those obtained after digestion. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Coal; Laser ablation; High resolution inductively coupled plasma mass spectrometry; Multielement analysis

1. Introduction

Complete chemical characterization of coal is of primary importance in a variety of ecological, industrial and geological applications. The coal mining industry, as well as the combustion of coal for energy production, are well recognised sources of environmental pollution [1,2]. Element flows between coal, bottom ash, fly ash and flue gases are under study with the aim to refine coal combustion technology. The inorganic chemical composition of coal yields information about the

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depositional environment, as well as the sources and differential fixation of elements during coalification processes [3].

Among analytical techniques for the determination of coal-associated elements, inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are interesting due to the combination of multielement capability, wide dynamic range and low instrumental detection limits. Both techniques require sample preparation, the type of which depends mainly on the sample introduction system available. Solution nebulization, which is the most commonly adopted tech-

Table 1
HR-ICP-MS and LA operating conditions and measurement parameters

Rf power/W	1400
Sample uptake rate/ml min^{-1}	0.3 (solution nebulization only)
Argon gas flow rates/l min^{-1}	
Coolant	15
Auxiliary	0.85
Nebulizer	1.15–1.30
Ion sampling depth/mm	9
Ion lens settings	Adjusted to obtain maximum signal intensity
Torch	Demountable with sapphire injector
Nebulizer	Microflow PFE
Spray chamber	Scott type PFE (double-pass)
Sample cone	Nickel, 1.1 mm orifice diameter
Skimmer	Nickel, 0.8 mm orifice diameter
Isotopes	
Low resolution mode	^{7}Li, ^{9}Be, ^{11}B, ^{23}Na, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{98}Mo, ^{101}Ru, ^{103}Rh, ^{105,108}Pd, ^{107,109}Ag, ^{111,114}Cd, ^{115}In[b], ^{120}Sn, ^{121}Sb, ^{126,128}Te, ^{127}I, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{143}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{173}Yb, ^{175}Lu[b], ^{178}Hf, ^{181}Ta, ^{184}W, ^{185,187}Re, ^{191,193}Ir, ^{194,195}Pt, ^{197}Au, ^{201,202}Hg, ^{205}Tl, ^{206,207,208}Pb, ^{209}Bi, ^{232}Th, ^{238}U
Medium resolution mode	^{26}Mg, ^{27}Al, ^{28}Si, ^{31}P, ^{32}S, ^{39}K, ^{44}Ca, ^{45}Sc, ^{47,49}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{62}Ni, ^{63}Cu, ^{64}Zn, ^{69,71}Ga, ^{72,74}Ge, ^{79}Br, ^{115}In[b]
High resolution mode	^{75}As, ^{78}Se, ^{115}In[b]
Acquisition mode	E-scan
No. of scans	15 for each resolution
Acquisition window/%[a]	50 in LRM; 120 in MRM and HRM
Search window/%[a]	50 in LRM; 80 in MRM and HRM
Integration window/%[a]	50 in LRM; 60 in MRM and HRM
Dwell time per sample/ms	10 in LRM; 20 in MRM, 40 in HRM
No. of samples per nuclide	30 in LRM, 25 in MRM and HRM
Laser (Nd:YAG)	
Wavelength/nm	266
Pulse width/ns	3
Pulse energy/mJ	2
Ablation diameter/µm	50
Repetition rate/Hz	20
Number of shots per point	50
Sample scan mode	Zigzag line scan across rectangular area
Distance between points/ mm	0.1

[a] Percent of peak width.
[b] Internal standard.

Table 2
Mathematical correction for non-resolved interferences

Isotope	Interference	Mean degree of correction[a] for NIST SRM 1635 and Interlab samples
[101]Ru	[89]RbO	2.8
[103]Rh	[87]SrO, [87]RbO	2.4
[105]Pd	[89]YO	8.0
[108]Pd	[108]Cd, [92]ZrO, [92]MoO	6.5
[107]Ag	[91]ZrO	1.5
[109]Ag	[93]NbO	1.4
[111]Cd	[95]MoO	<1.01
[114]Cd	[114]Sn, [98]Mo	1.02
[151]Eu	[135]BaO	1.15
[157]Gd	[141]PrO	1.3
[159]Tb	[143]NdO	<1.01
[163]Dy	[147]SmO	<1.01
[165]Ho	[149]SmO	<1.01
[167]Er	[151]EuO	<1.01
[169]Tm	[153]EuO	<1.01
[173]Yb	[157]GdO	<1.01
[175]Lu	[159]TbO	1.06
[178]Hf	[162]DyO	<1.01
[181]Ta	[165]HoO	<1.01
[185]Re	[169]TmO	1.15
[187]Re	[171]YbO	<1.01
[191]Ir	[175]LuO	4.0
[193]Ir	[177]HfO	2.6
[194]Pt	[178]HfO	3.9
[195]Pt	[179]HfO	2.2
[197]Au	[181]TaO	4.2
[202]Hg	[184]WO	1.1

[a] Ratio uncorrected/corrected concentration.

nique, requires transfer of analytes from the solid phase into solution by either acid dissolution or fusion. In the past decade, microwave (MW) assisted dissolution of coal has been developed as a rapid and safe sample preparation method, that requires smaller amounts of acids and that is less prone to contamination than traditional hot-plate protocols. Various acids and acid mixtures, including HNO_3, HCl, HF, $HClO_4$, H_2SO_4, H_3BO_3 and H_2O_2 [2,4–8], have been used for coal samples. Important restrictions may arise from safety considerations ($HClO_4$ and HF), negative effects on instrument parts (HF and H_2SO_4), matrix effects (H_2SO_4 and H_3BO_3) and spectral interferences in ICP-MS (H_2SO_4, $HClO_4$ and HCl). The limitation of acid-based sample preparation is in-

complete digestion while the fusion method enables resistant samples to be dissolved more easily after they have been fused [9]. Using lithium metaborate (LMB) as flux, more than 50 elements were successfully determined in coal ash by Bettinelli and Baroni [10]. However, a significant number of volatile elements, such as Hg, Se, Sb, Cd, Ge, Pb, As, Tl and S, can be completely or partially lost during ashing or fusion. Other problems that are present both in acid digestion and fusion include hydrolysis of refractory elements (e.g. Ta and W) if HF is not used and the low solubilities of the fluoride salts of Y, Pb, Ca, U and Th [11,12].

Alternative techniques of sample pre-treatment that have been applied to ICP-AES and/or ICP-MS coal analysis include slurry nebulization, electrothermal slurry vaporization, and laser ablation (LA). These techniques present several advantages, including simpler sample preparation with lower risks for contamination and analyte losses. Ebdon et al. [13] obtained quantitative results for a large number of minor and trace constituents in coal by slurry nebulization ICP-MS. However, poor results were obtained for Al, Se, Cd, Sb, U and some other elements. Moreover, sample grinding depends on coal type (bituminous or sub-bituminous) and the time necessary to reduce the size of the coal particles to < 5–10 μm can be as long as 24 h [10].

Coal analysis by ultrasonic slurry electrothermal vaporization ICP-MS has been reported by Gregoire et al. [14] and Fonseca and Miller-Ihli [15]. Only a few elements (V, Mn, Ni, Cu, Pb, Cr and Co) have been determined in these studies and it was shown that both the addition of palladium and the oxygen ashing are necessary to improve accuracy.

Chenery et al. [16] reported quantitative determination of 14 trace elements by LA-ICP-MS. Sample preparation was restricted to the polishing of coal blocks and calibration was based on introduction into the ICP of a mixture of ablated material and a nebulized solution, produced in the mixing chamber. A questionable part of this method is the accuracy validation that is obtained by determining trace element contents in a glass reference material.

Table 3
Method detection limits ($\mu g\ g^{-1}$, based on HR-ICP-MS determination)

Element	Procedure A1	Procedure A2	Procedure A3	Procedure A4	Procedures B	Laser ablation
Si	2.4	5.4	3.2	6.3	24	14000
Al	0.27	0.66	0.23	0.95	2.30	1.80
Ti	0.37	0.47	0.56	0.64	0.57	0.05
Fe	0.32	0.36	0.29	0.36	1.20	0.50
Na	5.7	6.9	11.2	9.5	14	11.0
Ca	4.1	3.9	5.1	4.8	9.6	9.00
Mg	1.8	2.7	2.1	3.6	7.5	17
K	5.2	4.6	7.0	6.2	16	60
S	16	25	23	30	28	26
Ag	0.0038	0.0019	0.0014	0.0019	0.0048	0.001
As	0.032	0.022	0.048	0.052	0.095	0.008
Au	0.0003	0.0005	0.0012	0.0011	0.0002	0.001
B	0.19	0.15	0.19	0.11	Nd	8
Ba	0.013	0.017	0.012	0.022	0.12	0.028
Be	0.0029	0.0015	0.0068	0.0020	0.0016	0.024
Bi	0.0006	0.0001	0.0016	0.0021	0.0004	0.001
Br	9.4	8.4	7.8	6.2	6.6	17
Cd	0.0007	0.0007	0.0016	0.0012	0.0029	0.011
Co	0.015	0.012	0.015	0.021	0.033	0.022
Cr	0.022	0.017	0.019	0.013	0.053	0.001
Cs	0.0003	0.0001	0.0016	0.0011	0.0010	0.0004
Cu	0.031	0.041	0.026	0.034	0.26	0.140
Ga	0.0031	0.0030	0.0057	0.0062	0.055	0.008
Ge	0.007	0.005	0.044	0.076	0.016	0.039
Hf	0.0001	0.0062	0.0007	0.0067	0.0031	0.003
Hg	0.013	0.008	0.014	0.027	0.011	0.060
I	0.11	0.41	0.15	0.16	0.16	0.370
Ir	0.00007	0.00004	0.00009	0.00018	0.00005	ND
Li	0.010	0.028	0.014	0.047	Nd	12
Mn	0.029	0.033	0.045	0.077	0.094	1.200
Mo	0.014	0.024	0.009	0.018	0.009	0.018
Nb	0.0008	0.0012	0.0012	0.0023	0.0039	0.004
Ni	0.073	0.074	0.037	0.083	0.077	0.620
P	0.40	0.37	0.63	0.49	0.44	1.500
Pb	0.0035	0.0090	0.0053	0.0082	0.0056	0.002
Pd	0.0016	0.0033	0.0043	0.0020	0.0024	0.003
Pt	0.0002	0.0004	0.0007	0.0008	0.0007	0.002
Rb	0.005	0.007	0.012	0.013	0.019	0.010
Re	0.00002	0.00002	0.00009	0.00004	0.00005	0.001
Rh	0.00005	0.00009	0.00008	0.00011	0.00020	ND
Ru	0.0002	0.0003	0.0004	0.0003	0.0002	0.004
Sb	0.0019	0.0013	0.0030	0.0012	0.0017	0.007
Sc	0.0003	0.0005	0.0014	0.0026	0.0019	0.003
Se	0.16	0.19	0.22	0.26	0.16	0.111
Sn	0.019	0.034	0.015	0.035	0.015	0.019
Sr	0.004	0.013	0.013	0.025	0.011	0.045
Ta	0.0001	0.0008	0.0002	0.0016	0.0002	0.003
Te	0.0044	0.0047	0.0030	0.0051	0.0054	0.018
Th	0.0007	0.0017	0.0017	0.0043	0.0018	0.001
Tl	0.0006	0.0006	0.0008	0.0007	0.0002	0.004

Table 3 (*Continued*)

Element	Procedure A1	Procedure A2	Procedure A3	Procedure A4	Procedures B	Laser ablation
U	0.0006	0.0005	0.0007	0.0004	0.0007	0.000
V	0.004	0.016	0.006	0.006	0.035	0.005
W	0.0033	0.0054	0.0017	0.0015	0.0018	0.001
Y	0.0012	0.0012	0.0007	0.0010	0.0025	0.006
Zn	0.12	0.15	0.24	0.19	0.48	0.146
Zr	0.008	0.018	0.003	0.017	0.220	0.016
La	0.002	0.001	0.001	0.001	0.016	0.006
Ce	0.08	0.004	0.003	0.012	0.061	0.003
Pr	0.0008	0.0002	0.0004	0.0002	0.0029	0.002
Nd	0.003	0.002	0.004	0.007	0.011	0.005
Sm	0.0007	0.0003	0.0006	0.0002	0.0012	0.003
Eu	0.0002	0.0001	0.0002	0.0002	0.0008	0.003
Gd	0.0006	0.0002	0.0003	0.0004	0.0013	0.014
Tb	0.0001	0.0001	0.0001	0.0001	0.0002	0.001
Dy	0.0002	0.0002	0.0001	0.0002	0.0003	0.003
Ho	0.00005	0.00002	0.00012	0.00003	0.00010	0.0005
Er	0.0002	0.0001	0.0002	0.0002	0.0003	0.002
Tm	0.00002	0.00003	0.00009	0.00003	0.00004	0.000
Yb	0.0002	0.0001	0.0003	0.0002	0.0002	0.006
Lu	0.00005	0.00006	0.00016	0.00006	0.00012	0.002

In another study [17], about 50 elements were determined by LA-ICP-MS after a sample preparation based on the mixing of powdered coal with a binder material (1/1 graphite and cellulose mixture) in a ratio of 1/10 and pressing into a pellet. The results of coal reference materials were, as a rule, within a factor of 5 or better than the reference values. Poor accuracy is the main limitation of this method for multielement analysis of coal.

The present work was undertaken in order to compare different sample dissolution procedures to the determination of about 70 major, minor, trace and ultratrace elements in coal samples, with varying content of bituminous components, by the combination of ICP-AES and double-focusing sector-field ICP-MS. The latter technique, also known as high resolution ICP-MS (HR-ICP-MS), resolves many spectral interferences and provides improved instrumental detection limits in comparison of conventional ICP-MS instruments equipped with quadrupole mass filters (ICP-QMS) [18]. The use of a combination of different analytical techniques permits to obtain, for many elements, two values and this can help to reveal analytical errors.

In this study, two coal reference materials were analysed both after MW dissolution, with different mixtures of HNO_3, aqua regia, HF and H_2O_2 or after LMB fusion, with and without ashing of the samples, and by LA on coal pellets.

2. Instrumental

2.1. Instrumentation

An ARL 3580 (Applied Research Laboratories SA, Ecubilens, Switzerland) ICP-AES instrument was used with a Gilson 100 sample changer. The device has 40 channels for simultaneous multielement detection. Instrument configuration and general experimental conditions are reported elsewhere [19].

The HR-ICP-MS instrument used was an element, equipped with an UV LaserProbe LA system (both from Finnigan MAT, Bremen, Germany). It can be operated in low resolution mode (LRM, $m/\Delta m$ about 300), medium (MRM, $m/\Delta m = 4500$) and high resolution mode (HRM, $m/\Delta m = 9200$). Details of instrumental operating conditions and measuring parameters are given in Table 1.

Table 4
Results for NIST SRM 1635 and comparison with certified and published data

Reference		Found						
		Procedure A1	Procedure A2	Procedure A3	Procedure A4	Procedure B1	Procedure B2	Laser ablation
Macroelements (%)								
Si	0.65[c]	0.022 (0.004)	0.502 (0.012)	0.120 (0.005)	0.507 (0.008)	0.708 (0.014)	0.715 (0.009)	ND
Al	0.32[b], 0.195[d]	0.122 (0.003)	0.296 (0.004)	0.247 (0.018)	0.314 (0.008)	0.319 (0.006)	0.309 (0.008)	0.261 (0.028)
Ti	0.02[b], 0.0205[d]	0.018 (0.001)	0.021 (0.001)	0.017 (0.001)	0.020 (0.001)	0.021 (0.001)	0.021 (0.001)	0.019 (0.002)
Fe	0.239 (0.005)[a], 0.221[d]	0.216 (0.006)	0.225 (0.004)	0.219 (0.006)	0.218 (0.003)	0.231 (0.005)	0.226 (0.009)	0.190 (0.004)
Na	0.24[b]	0.244 (0.002)	0.242 (0.004)	0.236 (0.008)	0.242 (0.004)	0.239 (0.002)	0.235 (0.005)	0.240 (0.030)
Ca	0.54[c]	0.493 (0.007)	0.493 (0.003)	0.507 (0.022)	0.526 (0.009)	0.537 (0.015)	0.526 (0.009)	0.420 (0.061)
Mg	0.1[c], 0.082[d]	0.084 (0.001)	0.086 (0.004)	0.088 (0.003)	0.087 (0.002)	0.091 (0.005)	0.090 (0.004)	0.095 (0.009)
K	0.012[c]	0.008 (0.001)	0.011 (0.001)	0.013 (0.001)	0.013 (0.001)	0.012 (0.001)	0.011 (0.001)	0.007 (0.002)
S	0.33 (0.03)[a]	0.330 (0.010)	0.336 (0.013)	0.271 (0.024)	0.278 (0.018)	0.004 (0.001)	0.042 (0.006)	0.390 (0.030)
Trace elements (µg g^{-1})								
Ag		0.0159 (0.0026)	0.0148 (0.012)	0.0156 (0.0008)	0.0176 (0.0012)	<0.0048	0.0053 (0.0041)	0.0281 (0.0094)
As	0.42 (0.15)[a], 0.6[d]	0.419 (0.027)	0.449 (0.016)	0.411 (0.031)	0.426 (0.012)	0.123 (0.019)	0.403 (0.012)	0.45 (0.09)
Au	<0.006[c]	<0.0011	<0.0015	<0.0011	<0.0013	<0.0027	<0.0045	ND
B	105[c]	128 (3)	126 (1)	134 (15)	130 (7)	ND	ND	119 (12)
Ba	84[c], 75[d]	81.5 (7.1)	84.9 (6.6)	83.2 (6.4)	84.2 (1.8)	84.7 (2.2)	83.1 (5.4)	86 (17)
Be	0.5[d]	0.582 (0.051)	0.552 (0.012)	0.558 (0.033)	0.563 (0.010)	0.572 (0.011)	0.552 (0.006)	0.680 (0.005)
Bi		0.0771 (0.0029)	0.0701 (0.024)	0.0682 (0.0025)	0.0724 (0.0023)	<0.0004	0.0043 (0.0009)	0.085 (0.006)
Br	1.6[c]	13.2 (15.4)	15.3 (6.3)	<7.8	<6.2	<6.6	<6.6	<17
Cd	0.03 (0.01)[a], 10.6[d]	0.0253 (0.0037)	0.0281 (0.0041)	0.0317 (0.0011)	0.0312 (0.0029)	0.0032 (0.0002)	0.0137 (0.0007)	0.033 (0.003)
Co	0.65[b], 1.3[d]	0.649 (0.021)	0.649 (0.034)	0.631 (0.027)	0.667 (0.027)	0.656 (0.01)	0.621 (0.032)	0.62 (0.06)
Cr	2.5 (0.3)[a], 6.7[d]	2.19 (0.04)	2.55 (0.03)	2.05 (0.06)	2.32 (0.11)	2.68 (0.12)	2.62 (0.09)	2.8 (0.4)
Cs	0.053[c], 0.08[d]	0.048 (0.002)	0.060 (0.001)	0.054 (0.003)	0.059 (0.002)	0.058 (0.002)	0.055 (0.001)	0.104 (0.024)
Cu	3.6 (0.3)[b]	3.43 (0.06)	3.45 (0.04)	3.28 (0.04)	3.42 (0.09)	3.28 (0.05)	3.17 (0.18)	4.1 (0.9)
Ga	1.05[b], 7.9[d]	0.879 (0.010)	0.979 (0.016)	0.846 (0.028)	0.878 (0.015)	1.02 (0.04)	1.01 (0.02)	1.0 (0.1)
Ge	2.5[d]	0.241 (0.005)	0.289 (0.020)	0.754 (0.055)	0.821 (0.072)	0.269 (0.051)	0.289 (0.014)	0.73 (0.41)
Hf	0.29[a]	0.148 (0.001)	0.193 (0.02)	0.092 (0.014)	0.163 (0.003)	0.276 (0.009)	0.268 (0.011)	0.26 (0.04)
Hg	0.02[a]	0.028 (0.008)	0.019 (0.001)	0.029 (0.004)	0.028 (0.002)	<0.011	<0.011	0.018 (0.015)
I	0.6[c]	1.60 (0.02)	1.45 (0.06)	1.72 (0.46)	1.66 (0.17)	<0.16	0.31 (0.02)	1.72 (0.02)
Ir		<0.0002	<0.0002	<0.0002	<0.0002	<0.0003	<0.0004	IS[e]
Li	0.83[c], 2.6[d]	1.04 (0.13)	1.44 (0.11)	1.39 (0.12)	1.69 (0.16)	ND	ND	<11
Mn	21.4 (1.5)[a], 21.4[d]	21.5 (0.3)	21.8 (0.3)	21.1 (0.6)	21 (0.2)	20.9 (0.4)	21.3 (0.9)	19.8 (1.5)
Mo	0.27[c], 0.5[d]	0.351 (0.019)	0.352 (0.015)	0.327 (0.008)	0.357 (0.012)	0.367 (0.003)	0.349 (0.013)	0.41 (0.03)
Nb	0.9[d]	0.648 (0.014)	0.723 (0.006)	0.616 (0.065)	0.768 (0.025)	0.742 (0.013)	0.713 (0.018)	1.09 (0.06)
Ni	1.74 (0.10)[a], 4.9[d]	1.72 (0.02)	1.71 (0.03)	1.83 (0.09)	1.86 (0.14)	1.85 (0.14)	1.83 (0.06)	1.6 (0.1)
P	60[c]	61.4 (1.8)	66.1 (1.9)	67.3 (1.2)	66.6 (2.7)	63.5 (1.1)	61.6 (0.9)	83 (26)
Pb	1.9 (0.2)[a], 2.1[d]	1.96 (0.015)	1.91 (0.12)	1.84 (0.04)	1.88 (0.03)	0.128 (0.011)	0.313 (0.024)	1.86 (0.24)
Pd		<0.045	<0.056	<0.037	<0.052	<0.047	<0.051	ND
Pt		<0.0013	<0.0011	<0.0016	<0.0018	<0.0015	<0.0018	ND
Rb	0.7[d]	0.309 (0.023)	0.635 (0.027)	0.484 (0.061)	0.667 (0.017)	0.626 (0.013)	0.618 (0.022)	0.44 (0.05)

Table 4 (*Continued*)

Reference		Found						
		Procedure A1	Procedure A2	Procedure A3	Procedure A4	Procedure B1	Procedure B2	Laser abla-tion
Re		0.00083 (0.00006)	0.00079 (0.00007)	0.0007 (0.0002)	0.0008 (0.0001)	0.0002 (0.0001)	0.0006 (0.0001)	0.0065 (0.0045)
Rh		<0.0112	<0.0137	<0.0149	<0.0147	<0.0139	<0.0129	IS[e]
Ru		<0.0014	<0.0018	<0.0014	<0.0016	<0.0015	<0.0012	Nd
Sb	0.14[b], 0.20[d]	0.118 (0.003)	0.121 (0.002)	0.129 (0.005)	0.139 (0.006)	0.086 (0.008)	0.136 (0.012)	0.12 (0.01)
Sc	0.63[b]	0.585 (0.007)	0.635 (0.012)	0.567 (0.022)	0.596 (0.009)	0.626 (0.013)	0.614 (0.012)	0.56 (0.08)
Se	0.9 (0.3)[a], 4.0[d]	0.751 (0.101)	0.826 (0.059)	0.871 (0.052)	0.935 (0.068)	<0.16	0.326 (0.031)	0.93 (0.05)
Sn	0.2[d]	0.096 (0.008)	0.086 (0.005)	0.088 (0.004)	0.097 (0.010)	<0.015	<0.015	0.40 (0.08)
Sr	135[c], 110[d]	130 (4)	133 (4)	136 (3)	138 (3)	141 (3)	134 (3)	105 (11)
Ta	0.049[c]	0.0331 (0.0009)	0.0491 (0.0010)	0.0170 (0.0032)	0.0497 (0.0016)	0.0463 (0.0026)	0.0507 (0.0011)	0.074 (0.011)
Te		0.0227 (0.0025)	0.0223 (0.0005)	0.0262 (0.0035)	0.0274 (0.0009)	<0.005	<0.005	0.065 (0.016)
Th	0.62 (0.04)[a], 3.3[d]	0.570 (0.006)	0.640 (0.012)	0.498 (0.035)	0.567 (0.036)	0.628 (0.017)	0.641 (0.028)	0.68 (0.09)
Tl		0.0147 (0.0007)	0.0153 (0.0008)	0.0150 (0.0004)	0.0160 (0.0016)	<0.0002	<0.0002	0.036 (0.011)
U	0.24 (0.02)[a], 1.4[d]	0.242 (0.018)	0.232 (0.006)	0.178 (0.003)	0.211 (0.003)	0.225 (0.003)	0.228 (0.006)	0.27 (0.03)
V	5.2 (0.5)[a], 3.8[d]	4.96 (0.02)	5.37 (0.21)	4.47 (0.15)	5.07 (0.32)	5.38 (0.09)	4.94 (0.34)	4.2 (0.6)
W	<0.9[c]	0.155 (0.004)	0.201 (0.003)	0.157 (0.010)	0.178 (0.005)	0.358 (0.021)	0.339 (0.024)	0.36 (0.04)
Y	12.2[d]	1.82 (0.01)	1.93 (0.04)	1.78 (0.14)	1.89 (0.02)	2.13 (0.11)	2.14 (0.02)	2.5 (0.3)
Zn	4.7 (0.5)[a], 8.8[d]	4.08 (0.26)	4.69 (0.07)	4.95 (0.16)	4.74 (0.3)	4.13 (0.19)	4.13 (0.05)	4.6 (0.5)
Zr	16[c]	4.32 (0.11)	5.61 (0.03)	3.15 (0.50)	5.42 (0.09)	6.26 (0.19)	6.12 (0.35)	8.1 (2.2)
Rare-earth elements ($\mu g\ g^{-1}$)								
La	2.1[c]	1.82 (0.02)	1.98 (0.04)	1.77 (0.14)	1.91 (0.07)	1.95 (0.04)	1.95 (0.03)	2.23 (0.37)
Ce	3.6[b], 4.2[d]	3.27 (0.07)	3.63 (0.08)	3.11 (0.24)	3.43 (0.10)	3.54 (0.09)	3.51 (0.02)	3.39 (0.53)
Pr		0.384 (0.015)	0.411 (0.009)	0.365 (0.030)	0.395 (0.006)	0.393 (0.006)	0.387 (0.002)	0.36 (0.07)
Nd	1.4[c]	1.44 (0.04)	1.56 (0.043)	1.34 (0.09)	1.47 (0.05)	1.49 (0.05)	1.45 (0.03)	1.3 (0.1)
Sm	0.25[c], 0.5[d]	0.286 (0.006)	0.298 (0.007)	0.259 (0.021)	0.279 (0.005)	0.286 (0.010)	0.278 (0.008)	0.30 (0.04)
Eu	0.06[b], 0.15[d]	0.0618 (0.0023)	0.0680 (0.0037)	0.0567 (0.0047)	0.0623 (0.0016)	0.0662 (0.0031)	0.0658 (0.0006)	0.078 (0.012)
Gd	0.23[c]	0.243 (0.002)	0.264 (0.005)	0.236 (0.017)	0.247 (0.006)	0.262 (0.009)	0.274 (0.005)	0.298 (0.023)
Tb	0.045[c], 0.17[d]	0.0436 (0.0006)	0.0450 (0.0014)	0.0357 (0.0029)	0.0391 (0.0012)	0.0468 (0.0011)	0.0471 (0.0012)	0.052 (0.008)
Dy	0.31[c]	0.260 (0.005)	0.280 (0.008)	0.229 (0.016)	0.250 (0.007)	0.282 (0.010)	0.286 (0.005)	0.312 (0.028)
Ho		0.0561 (0.0011)	0.0621 (0.0016)	0.0493 (0.0034)	0.0549 (0.0008)	0.0618 (0.0006)	0.0583 (0.0013)	0.066 (0.007)
Er		0.159 (0.02)	0.173 (0.002)	0.140 (0.012)	0.153 (0.005)	0.174 (0.005)	0.168 (0.004)	0.179 (0.024)
Tm		0.0231 (0.0004)	0.0271 (0.0009)	0.0205 (0.0010)	0.0232 (0.0005)	0.0271 (0.0003)	0.0258 (0.0007)	0.033 (0.006)
Yb	0.14[c]	0.135 (0.001)	0.152 (0.004)	0.152 (0.012)	0.160 (0.002)	0.152 (0.006)	0.161 (0.004)	0.178 (0.019)
Lu	0.027[c]	0.0202 (0.0004)	0.0228 (0.0003)	0.0191 (0.0014)	0.0209 (0.0003)	0.0229 (0.0006)	0.0215 (0.0005)	0.031 (0.006)

[a] From NIST certificate (certified values).

[b] From NIST certificate (recommended values).

[c] From references [26–29].

[d] From reference [13].

[e] Element used as internal standard.

Table 5
Results for Interlab coal sample

Reference[a]		Found						
		Procedure A1	Procedure A2	Procedure A3	Procedure A4	Procedure B1	Procedure B2	Laser ablation
Macroelements (%)								
Si		0.040 (0.032)	1.33 (0.06)	0.290 (0.030)	1.18 (0.05)	2.13 (0.07)	2.03 (0.05)	ND
Al		0.147 (0.013)	0.940 (0.090)	0.721 (0.065)	0.961 (0.042)	0.933 (0.022)	0.944 (0.040)	0.97 (0.04)
Ti		0.035 (0.01)	0.049 (0.002)	0.035 (0.002)	0.050 (0.002)	0.050 (0.001)	0.051 (0.001)	0.052 (0.004)
Fe		1.64 (0.03)	1.69 (0.06)	1.63 (0.03)	1.67 (0.05)	1.63 (0.03)	1.65 (0.03)	1.4 (0.1)
Na		0.014 (0.001)	0.020 (0.001)	0.019 (0.002)	0.021 (0.001)	0.020 (0.001)	0.020 (0.001)	0.022 (0.002)
Ca		0.236 (0.002)	0.236 (0.001)	0.246 (0.002)	0.246 (0.006)	0.246 (0.007)	0.240 (0.012)	0.193 (0.018)
Mg		0.073 (0.002)	0.097 (0.002)	0.095 (0.003)	0.102 (0.002)	0.097 (0.002)	0.098 (0.003)	0.090 (0.009)
K		0.068 (0.006)	0.169 (0.005)	0.148 (0.012)	0.166 (0.004)	0.173 (0.002)	0.166 (0.004)	0.14 (0.01)
S		2.70 (0.050)	2.68 (0.050)	2.19 (0.100)	2.15 (0.050)	0.020 (0.008)	0.250 (0.020)	3.5 (0.2)
Trace elements ($\mu g\ g^{-1}$)								
Ag		0.0536 (0.0045)	0.0491 (0.0039)	0.0559 (0.0056)	0.0497 (0.0024)	0.0133 (0.0016)	0.0224 (0.0020)	0.055 (0.005)
As	4.5	4.44 (0.11)	4.49 (0.09)	4.28 (0.19)	4.35 (0.12)	1.54 (0.05)	3.67 (0.01)	3.3 (0.3)
Au		<0.0013	<0.0015	<0.0018	<0.0027	<0.0032	<0.0036	0.011 (0.006)
B		25.9 (1.5)	29.6 (0.5)	24.5 (2.0)	32.8 (1.4)	ND	ND	26 (4)
Ba		15.1 (3.2)	30.7 (1.9)	26.1 (4.8)	30.1 (0.9)	32.1 (1.6)	31.1 (1.4)	30 (1)
Be	1.98	2.12 (0.07)	2.23 (0.15)	2.19 (0.13)	2.19 (0.18)	2.01 (0.05)	1.95 (0.07)	2.9 (0.2)
Bi		0.0670 (0.0029)	0.0651 (0.0004)	0.0700 (0.0031)	0.0679 (0.0011)	0.0041 (0.0001)	0.0161 (0.0018)	0.067 (0.012)
Br		59.5 (0.2)	56.6 (3.5)	15.0 (1.0)	15.2 (2.1)	<6.6	<6.6	42 (20)
Cd	1.5	1.54 (0.13)	1.62 (0.12)	1.53 (0.04)	1.59 (0.07)	0.16 (0.01)	0.27 (0.02)	1.3 (0.04)
Co	3.45	4.77 (0.21)	4.62 (0.37)	3.83 (0.09)	4.01 (0.15)	4.26 (0.1)	4.23 (0.12)	4.6 (0.3)
Cr	15.7	8.8 (0.3)	12.9 (0.9)	11.0 (1.3)	11.7 (0.7)	16.6 (0.6)	15.9 (0.6)	13.1 (0.5)
Cs		0.708 (0.041)	0.974 (0.015)	0.896 (0.013)	0.965 (0.031)	0.954 (0.023)	0.929 (0.026)	0.94 (0.12)
Cu	8.7	7.74 (0.26)	7.62 (0.07)	7.95 (0.31)	7.71 (0.28)	7.74 (0.41)	7.46 (0.23)	6.2 (0.5)
Ga		1.56 (0.07)	2.51 (0.07)	2.37 (0.08)	2.68 (0.04)	2.84 (0.08)	2.68 (0.03)	2.6 (0.1)
Ge		0.25 (0.03)	2.28 (0.14)	1.61 (0.1)	2.94 (0.27)	1.85 (0.09)	1.99 (0.05)	9.0 (2.5)
Hf		0.217 (0.007)	0.385 (0.011)	0.192 (0.045)	0.355 (0.019)	0.677 (0.013)	0.739 (0.019)	0.72 (0.09)
Hg	0.09	0.118 (0.009)	0.117 (0.009)	0.101 (0.016)	0.099 (0.009)	<0.011	0.012 (0.005)	0.19 (0.05)
I		20.2 (1.2)	22.3 (1.2)	19.0 (1.2)	20.6 (0.9)	0.22 (0.04)	0.42 (0.02)	18.9 (0.4)
Ir		<0.0006	<0.0006	<0.0005	<0.0005	<0.0006	<0.0008	IS[b]
Li		3.4 (0.7)	11.2 (0.3)	9.6 (0.7)	11.4 (0.5)	ND	ND	<17
Mn	34.6	35.2 (0.5)	35 (1.4)	35.4 (1.6)	35.6 (0.9)	35.9 (1.1)	34.6 (0.6)	34 (3)
Mo	9.65	6.91 (0.29)	7.17 (0.13)	6.86 (0.19)	6.99 (0.23)	7.09 (0.16)	6.81 (0.26)	5.2 (0.3)
Nb		1.47 (0.05)	1.81 (0.02)	1.24 (0.37)	1.66 (0.12)	1.55 (0.02)	1.46 (0.03)	3.5 (0.4)
Ni	19	17.5 (0.5)	19.1 (1.6)	19.1 (1.1)	19.1 (0.8)	18.7 (0.6)	18.3 (0.3)	24 (2)
P		63.1 (6.2)	65.8 (3)	67.5 (1.3)	65.5 (3.2)	64.9 (2.6)	64.1 (1.9)	81 (14)
Pb	47	51.3 (1.8)	49.1 (0.8)	49.4 (1.2)	50.6 (1.4)	9.6 (1.1)	14.7 (1.3)	53 (2)
Pd		<0.082	<0.097	<0.054	<0.084	<0.124	<0.166	ND
Pt		<0.0021	<0.0027	<0.0022	<0.0025	<0.0023	<0.0034	ND
Rb		7.3 (0.5)	13.3 (0.4)	12.7 (0.5)	13.4 (0.5)	13.2 (0.7)	12.8 (0.5)	12 (1)
Re		0.0138 (0.0005)	0.0137 (0.0004)	0.0137 (0.0006)	0.0130 (0.0009)	0.0009 (0.0001)	0.0086 (0.0004)	0.0148 (0.0035)
Rh		<0.0041	<0.0045	<0.0033	<0.0039	<0.0027	<0.0035	IS[b]
Ru		<0.0017	<0.0035	<0.0025	<0.0044	<0.0019	<0.0028	ND
Sb	0.84	0.138 (0.011)	0.438 (0.004)	0.414 (0.012)	0.453 (0.018)	0.263 (0.005)	0.417 (0.014)	0.49 (0.06)
Sc		1.83 (0.05)	1.98 (0.09)	1.69 (0.20)	1.68 (0.08)	2.08 (0.05)	1.97 (0.04)	2.2 (0.3)
Se	2.3	1.77 (0.21)	1.94 (0.16)	2.31 (0.16)	2.55 (0.17)	0.32 (0.02)	0.56 (0.02)	4.0 (0.7)
Sn		0.151 (0.021)	0.356 (0.008)	0.314 (0.026)	0.347 (0.016)	<0.015	0.080 (0.002)	0.49 (0.07)
Sr		34.0 (1.8)	38.9 (0.4)	37.1 (2.8)	38.2 (0.9)	38.6 (0.7)	37.6 (0.6)	33 (1)

Table 5 (*Continued*)

Reference[a]	Found						
	Procedure A1	Procedure A2	Procedure A3	Procedure A4	Procedure B1	Procedure B2	Laser ablation
Ta	0.005 (0.003)	0.121 (0.002)	0.002 (0.001)	0.124 (0.006)	0.131 (0.003)	0.142 (0.012)	0.26 (0.04)
Te	0.0169 (0.0027)	0.0181 (0.0015)	0.0270 (0.0010)	0.0259 (0.0022)	<0.0054	<0.0054	0.086 (0.017)
Th	1.46 (0.01)	1.75 (0.02)	1.36 (0.16)	1.44 (0.09)	1.70 (0.05)	1.79 (0.03)	1.9 (0.2)
Tl	0.676 (0.027)	0.704 (0.016)	0.642 (0.016)	0.682 (0.019)	0.185 (0.007)	0.272 (0.003)	0.63 (0.08)
U	2.19 (0.09)	2.25 (0.18)	2.18 (0.17)	2.27 (0.008)	2.18 (0.08)	2.16 (0.03)	2.8 (0.4)
V 37.7	33.5 (0.07)	38.1 (2.3)	33.8 (0.8)	35.8 (1.6)	38.1 (0.6)	36.1 (2.4)	33 (5)
W	0.252 (0.037)	0.743 (0.167)	0.567 (0.072)	0.730 (0.082)	0.817 (0.028)	0.902 (0.079)	0.95 (0.14)
Y	4.85 (0.04)	5.18 (0.06)	3.81 (0.32)	4.25 (0.14)	6.12 (0.11)	5.85 (0.28)	6.3 (0.3)
Zn 284	273 (22)	289 (29)	272 (16)	283 (21)	226 (8)	233 (11)	240 (20)
Zr	8.7 (0.3)	13.6 (0.3)	7.3 (2.1)	12.5 (0.6)	13.1 (0.1)	13.7 (1.2)	20 (4)
Rare-earth elements ($\mu g\ g^{-1}$)							
La	4.55 (0.16)	6.39 (0.14)	5.99 (0.37)	5.76 (0.21)	6.38 (0.27)	6.47 (0.34)	6.3 (0.8)
Ce	11.7 (0.3)	14.8 (0.4)	14.1 (0.7)	13.5 (0.5)	14.8 (0.1)	15.3 (0.9)	15 (1)
Pr	1.47 (0.05)	1.81 (0.05)	1.71 (0.10)	1.61 (0.08)	1.78 (0.05)	1.77 (0.02)	2.2 (0.3)
Nd	6.00 (0.20)	7.17 (0.30)	6.86 (0.35)	6.47 (0.18)	7.15 (0.11)	7.12 (0.28)	7.5 (0.8)
Sm	1.40 (0.04)	1.55 (0.02)	1.43 (0.09)	1.33 (0.04)	1.51 (0.02)	1.50 (0.03)	1.3 (0.1)
Eu	0.256 (0.005)	0.280 (0.002)	0.289 (0.024)	0.270 (0.011)	0.281 (0.008)	0.273 (0.008)	0.248 (0.017)
Gd	1.18 (0.05)	1.16 (0.02)	0.94 (0.09)	0.87 (0.03)	1.17 (0.02)	1.13 (0.06)	1.4 (0.1)
Tb	0.180 (0.003)	0.188 (0.002)	0.150 (0.022)	0.148 (0.007)	0.188 (0.011)	0.191 (0.013)	0.20 (0.01)
Dy	0.98 (0.02)	1.06 (0.01)	0.83 (0.12)	0.89 (0.03)	1.07 (0.04)	1.06 (0.04)	1.1 (0.1)
Ho	0.193 (0.009)	0.211 (0.002)	0.161 (0.026)	0.152 (0.009)	0.213 (0.004)	0.216 (0.009)	0.22 (0.02)
Er	0.510 (0.012)	0.570 (0.008)	0.419 (0.080)	0.407 (0.016)	0.575 (0.009)	0.581 (0.026)	0.68 (0.13)
Tm	0.0749 (0.0015)	0.0855 (0.0017)	0.0618 (0.0111)	0.0600 (0.0022)	0.0865 (0.0023)	0.0868 (0.0002)	0.10 (0.01)
Yb	0.415 (0.012)	0.471 (0.003)	0.369 (0.068)	0.368 (0.013)	0.468 (0.010)	0.475 (0.016)	0.56 (0.02)
Lu	0.0568 (0.0010)	0.0673 (0.0017)	0.0489 (0.0095)	0.0495 (0.0034)	0.0667 (0.0026)	0.0677 (0.0028)	0.081 (0.006)

[a] Median results from Interlab Trace program.
[b] Element used as internal standard.

HR-ICP-MS optimization and mass calibration was carried out using solution nebulization, as reported previously [20]. System optimization for solid sampling was performed for ^{115}In signal intensity during continuous ablation of pressed coal powder doped with In at 100 $\mu g\ g^{-1}$. The only ICP parameter that has to be changed when shifting from liquid to solid introduction is sample gas flow (the optimum for LA being about 0.2 l min^{-1} higher than for conventional nebulization).

The major laser parameters that have to be optimized are energy and sampling (i.e. ablation crater) diameter. Generally, higher energy results in enhanced signal intensity, but it produces a noise, resulting from the release of large fragments of the solid to the plasma. This effect can, to some extent, be overcome by using a defocused laser beam (i.e. larger sampling diameter). The optimum signal to noise ratio was found with 2 mJ laser energy and 50 μm sampling diameter. Signal stability is further improved by including a Scott type double pass spray chamber between the ablation chamber and the ICP torch [21]. The use of a spray chamber facilitates some control of the particle size of ablated material and results in more uniform particle size distribution, thereby improving precision and preventing deposition of material in the torch injector and on the sampling cone [22].

For MW dissolution a microwave system (MDS-2000, CEM, Matthews, USA), equipped with 12 perfluoroalcoxy (PFA) vessels with safety rupture membranes (maximum operating pressure 1380 kPa), was used. The vessels are located on a rotating turntable to ensure even sample heating.

Before use and between each batch of samples, PFA utensils were thoroughly acid cleaned and then rinsed with deionized water.

2.2. Reagents

All calibration and internal standard solutions used were prepared by diluting 1 mg ml^{-1} single-element standard solutions (SPEX Plasma Standards, Edison, NJ), taking into account inter-element compatibility. Concentrations in the calibration standards were checked using quality control samples prepared by diluting 10 mg l^{-1} multi-element standard solutions (PE Pure Plus Atomic Spectroscopy Standard, Norwalk, USA).

Analytical grade nitric acid (65%, Merck, Darmstadt, Germany) was used after additional purification by sub-boiling distillation in a quartz still (Heraeus, Karlsruhe, Germany). Suprapure grade hydrochloric (37%) and hydrofluoric (40%) acids,

Table 6

Results for NIST SRM 1633b and comparison with certified and recommended data

| Reference		Found		Reference		Found	
		Procedure A2	Procedure B2			Procedure A	Procedure B
Macroelements				Pb	68.2 (1.1)	68.8 (1.4)	19.8 (2.1)
Si	23.02 (0.08)	5.53 (0.71)	22.8 (0.4)	Pd		<0.142	<0.078
Al	15.05 (0.27)	6.36 (0.27)	15.0 (0.4)	Pt		<0.016	<0.021
Ti	0.791 (0.014)	0.782 (0.009)	0.781 (0.016)	Rb	140	136 (6)	134 (4)
Fe	7.78 (0.23)	6.59 (0.20)	7.83 (0.26)	Re		0.0040 (0.0004)	0.0032 (0.0004)
Na	0.201 (0.003)	0.196 (0.005)	0.209 (0.006)	Rh		<0.028	<0.042
Ca	1.51 (0.06)	1.49 (0.04)	1.54 (0.05)	Ru		<0.061	<0.087
Mg	0.482 (0.008)	0.210 (0.015)	0.479 (0.022)	Sb	6	5.42 (0.21)	3.49 (0.45)
K	1.95 (0.03)	1.92 (0.03)	1.94 (0.06)	Sc	41	16.1 (1.1)	37.8 (1.5)
S	0.208 (0.001)	0.200 (0.04)	0.012 (0.003)	Se	10.26 (0.17)	10.9 (1.0)	<0.16
Trace elements				Sn		6.13 (0.34)	0.89 (0.13)
Ag		0.754 (0.027)	0.238 (0.034)	Sr	1041 (14)	1050 (10)	1020 (20)
As	136.2 (2.6)	135 (6)	108 (8)	Ta	1.8	1.52 (0.12)	1.88 (0.15)
Au		<0.012	<0.015	Te		0.214 (0.005)	<0.054
B		87.8 (7.0)	ND	Th	25.7 (1.3)	14.9 (0.8)	24.3 (0.9)
Ba	709 (27)	709 (31)	689 (21)	Tl	5.9	6.07 (0.12)	0.22 (0.04)
Be		13.4 (0.3)	12.9 (0.5)	U	8.79 (0.36)	8.87 (0.08)	8.71 (0.14)
Bi		1.29 (0.03)	0.09 (0.02)	V	295.7 (3.6)	294 (6)	287 (9)
Br	2.9	<8.4	<6.6	W	5.6	4.92 (0.31)	6.21 (0.45)
Cd	0.784 (0.006)	0.793 (0.023)	0.141 (0.029)	Y		34.3 (2.3)	79.9 (3.8)
Co	50	46.2 (1.7)	44.9 (2.1)	Zn	210	192 (3)	162 (10)
Cr	198.2 (4.7)	198 (7)	205 (5)	Zr		185 (8)	212 (9)
Cs	11	10.9 (0.4)	10.8 (0.4)	La	94	60.2 (0.34)	84.8 (2.1)
Cu	112.8 (2.6)	111 (3)	56.2 (5.2)	Ce	190	149 (6)	181 (4)
Ga		58.3 (1.4)	56.4 (2.6)	Pr		15.2 (1.4)	19.8 (1.1)
Ge		16.1 (0.7)	29.7 (1.3)	Nd	85	57.1 (3.1)	81.8 (1.6)
Hf	6.8	5.63 (0.49)	6.74 (0.31)	Sm	20	13.7 (1.0)	18.8 (0.6)
Hg	0.141 (0.019)	0.153 (0.023)	<0.011	Eu	4.1	3.12 (0.23)	3.87 (0.18)
I		0.848 (0.123)	<0.16	Gd	13	9.53 (0.83)	12.1 (0.34)
Ir		<0.0043	<0.0075	Tb	2.6	1.95 (0.09)	2.39 (0.16)
Li		64.1 (3.7)	ND	Dy	17	11.5 (0.3)	16.5 (0.7)
Mn	131.8 (1.7)	131 (3)	136 (6)	Ho	3.5	2.25 (0.16)	3.24 (0.14)
Mo		20.7 (0.9)	19.2 (1.1)	Er		5.73 (0.31)	7.79 (0.16)
Nb		21.3 (1.6)	25.9 (1.9)	Tm	2.1	1.27 (0.07)	1.81 (0.11)
Ni	120.6 (1.8)	119 (1)	96.9 (4.7)	Yb	7.6	4.60 (0.32)	7.29 (0.33)
P	2300	2240 (130)	2230 (90)	Lu	1.2	0.778 (0.064)	1.05 (0.07)
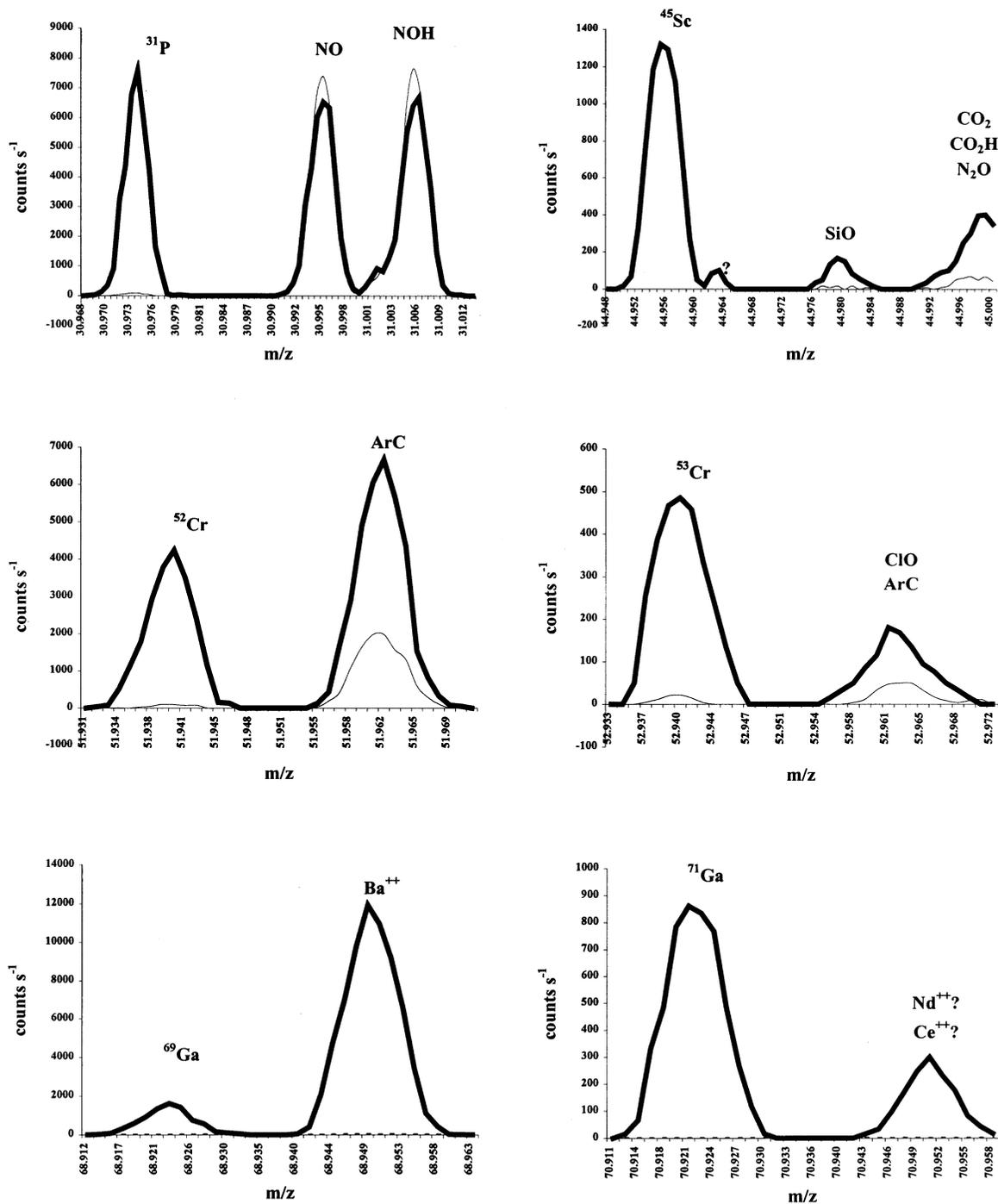
Fig. 1. Medium resolution ICP mass spectra obtained for NIST SRM 1635 (bold line) and for blank prepared according to procedure A2.
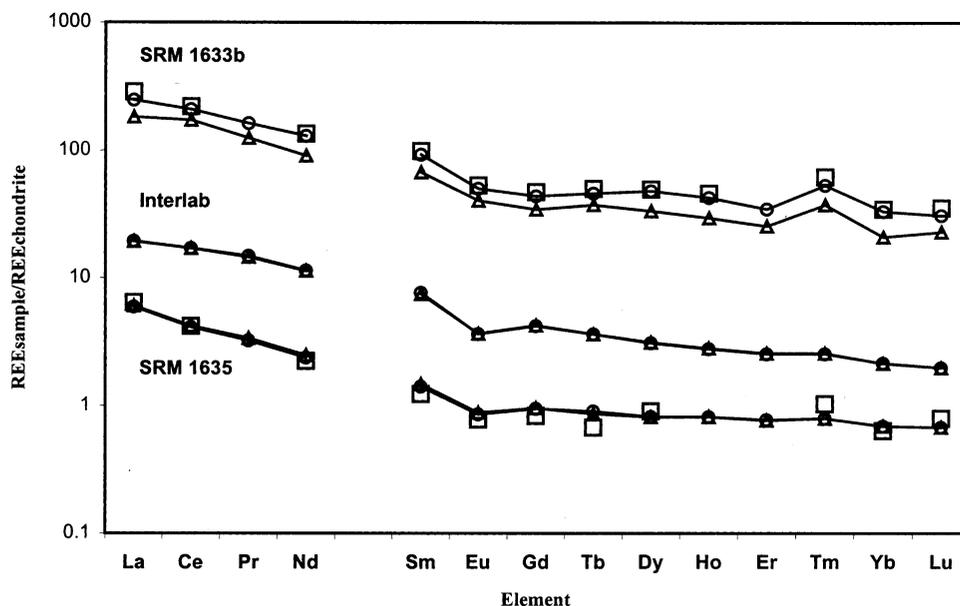
Fig. 2. Chondrite-normalized REE patterns for coal and coal fly ash samples. (squares, recommended or published values; circles, HR-ICP-MS results after LMB fusion; triangles, HR-ICP-MS results after A2 MW treatment).

as well as analytical grade hydrogen peroxide (30%) and tartaric acid (all from Merck), were used without additional purification. Lithium metaborate (J.T. Baker B.V., Deventer, Holland) was of analytical grade.

Deionized 'Milli-Q water' (Millipore Milli-Q, Bedford, USA) was additionally purified by sub-boiling distillation in a Teflon still (Savillex Corp., Minnetonka, Minnesota, USA).

2.3. Samples and standards

Two coal samples were used in the present study, namely, the certified reference material SRM 1635 (sub-bituminous coal, NIST, Gaithersburg, USA) and a bituminous coal sample supplied for a round robin test by the Interlab Trace program (Ashland, USA). NIST SRM 1633b (coal fly ash) was used for testing selected preparation procedures on ashed coal matrix. For HR-ICP-MS optimization and calibration using LA, a set of three in-house carbon standards was prepared from active carbon (intended for medical use, Pharmasorb, Perm, Russia), by doping 0.5 g sub-samples with internal standard solution (Rh,

In and Ir) together with PE Pure Plus Atomic Spectroscopy Standard and SPEX standard solutions, followed by drying at 50°C for 12 h and homogenization. One sub-sample was not doped with analyte elements, as it is necessary to correct for the elemental content of the carbon. For the highest standard, this doping procedure results in an increase from the initial concentration by 5 µg g^{-1} for trace elements, and by up to 5000 µg g^{-1} for major elements. Internal standard (IS) elements (Rh, In, Ir) were added to all three sub-samples at 100 µg g^{-1} levels. It appears that the host matrix contained significant concentrations of Ba, Rb and Cr, resulting in poor linearity of calibration graphs for these elements.

2.4. Description of analytical procedures

2.4.1. MW dissolution

For MW dissolution, a sample weight of about 0.1 g and reagent volumes in the range from 5 to 6 ml were used. In preliminary experiments it appeared that the increasing sample weight while maintaining a constant sample/reagent ratio, may cause overpressure during the MW dissolution.

The increased sample/reagent ratio results in poor recoveries for some elements, as well as in difficulties when pouring the solutions from the MW vessel. The coal is weighed and transferred to MW vessels and reagent mixture is added. The vessels are then closed, mounted in sleeves (outer vessels) and heated in the MW oven at 325 W power for 1 h. The vessels are carefully vented in a fume hood after cooling to room temperature. The solution is then transferred to an acid-cleaned (hot mixture of HNO_3/HCl followed by soaking in 10% HNO_3 overnight) 10 ml polystyrene test tube (Nalge Nunc International, Rochester, NY). Four different reagent mixtures were used for MW assisted treatment: 5 ml HNO_3 + 1 ml H_2O_2 (procedure A1); 5 ml HNO_3 + 1 ml H_2O_2 + 0.1 ml HF (procedure A2); 5 ml aqua regia (procedure A3); 5 ml aqua regia + 0.1 ml HF (procedure A4). The choice of the volume of HF is based on Ikävalko et al. [8] findings. They showed that addition of HF to the sample in a ratio of about 1:1 (v/w) is sufficient for the dissolution of the silicates in coal samples. It should be noted that a significant part of the coal matrix remains unaffected by any of the reagent mixtures tested. Hence, this sample preparation results in leaching rather than in complete dissolution and, consequently, in significant losses. After sedimentation of undigested particles to the bottom of the tube, two particle-free aliquots of the solutions were diluted with ultrapure water, resulting in dilution factors of 500 and 2000 for ICP-AES and HR-ICP-MS determinations, respectively. Though it is advisable to use acid evaporation or addition of H_3BO_3 when applying acid mixtures containing HF for sample dissolution [3,8], these procedures were avoided in the present study as they are likely to cause losses of some analytes (evaporation), to increase matrix effects (H_3BO_3) as well as to introduce additional contamination. In HR-ICP-MS, using an acid-resistant sample introduction system eliminated negative effects caused by HF. After the sample dilution, the remaining of HF traces ($< 0.2\%$) caused only moderate increases in ICP-AES blanks for Si.

2.4.2. LMB fusion

Two slightly different LMB fusion procedures were applied to the coal samples following, in general, the method described by Ödman et al. [23]. In the first procedure (B1), 1 g of coal is weighed and placed in a porcelain combustion crucible (LECO, Upplands Väsby, Sweden), which is then heated in a furnace at 550°C overnight. The ash is weighed with 0.1 mg resolution. An amount of LMB double with respect to ash is added and carefully mixed with the ash. The mixed sample/ LMB powder is then transferred to a carbon crucible (Schunk, Lenhouda, Sweden) and heated in a furnace at 1000°C for 30 min. After cooling the bead is transferred from the crucible to a 10-ml acid-cleaned polystyrene test tube and 10 ml of a nitric/tartaric acid mixture (5%/1% v/v in ultrapure water) is added to the tubes. The tubes are placed on a laboratory shaker overnight till complete dissolution. Two aliquots of the resulting solution are diluted using 5% HNO_3 for ICP-AES and 2% HNO_3 for HR-ICP-MS. For ICP-AES the concentration of LMB in the final solution should be 2% w/v (this enables the use of B as an internal standard in the instrumental detection step). For HR-ICP-MS the dilution factor is approximately 2000 relative to the coal mass before ashing.

The ashing step is excluded in the second fusion procedure (B2). Approximately 1 g of coal powder is mixed with LMB, followed by fusion. Otherwise, this procedure is similar to that described above. Together with significantly shorter preparation time, the second fusion procedure eliminates losses of volatile elements during ashing. The presence of fluxing agent stabilizes some, but not all, of the more volatile elements during high temperature treatment. The need for greater sample dilution prior to analysis by ICP-AES (owing to the higher amount of LMB used) is the major drawback of the B2 procedure.

Coal samples were prepared in triplicate together with six preparation blanks for each procedure. The final solutions for HR-ICP-MS were spiked with IS solution (In) to 25 µg l^{-1}. Sample and blank solutions from each preparation procedure were separately analysed by ICP-AES and HR-ICP-MS using synthetic blanks and standards matching sample solutions in terms of reagents mixture and acid strength. All sample handling and analyses were performed in clean (class 1000) laboratory.

Results were corrected for moisture content which was determined on separate 0.2 mg sub-sam-

ples (being 15.5% and 0.6% for SRM 1635 and Interlab samples, respectively).

2.4.3. Laser ablation

Sample preparation for LA was restricted to doping to 100 μg g^{-1} 0.5 g coal powder with IS following the same procedure as described for in-house carbon standards (see Section 2.3). Coal and carbon powders so prepared were pressed into pellets (12 mm in diameter and 2–3 mm thick) at a total thrust of 10 t in a press Herzog TP20 (Osnabruck, Germany) designed for sample preparation for IR spectroscopy. All sample manipulations were performed using plastic gloves and plastic tweezers.

The samples and standards were placed in the ablation cell and the sequence started with analysis of the carrier gas without LA (gas blank). The laser had been programmed to perform continuous ablation for about 15 min on six areas for each pellet in sequence on samples and standards. A 30 s delay, after the ablation start was included before commencing HR-ICP-MS data acquisition, so that the analyte can reach the plasma and the signal can stabilize. Raw intensity data were transferred to a personal computer and subsequent data manipulation was performed off-line using statistical software. At the beginning, the intensities of analytes were corrected for the variations in ablation efficiency and plasma instability, using intensities for IS. For each isotope the IS that is closest in mass was used. The corrected intensities were summarized for each ablation area and within-pellet mean intensity and standard deviation were calculated. Calibration performed by means of carbon standards resulted in linear calibration graphs for the majority of elements with correlation coefficients better than 0.98.

2.5. Spectral interferences

For the ICP-AES data, mathematical corrections for spectral overlaps were carried out by the instrument software. These calculations are based on measured intensities for interfering elements, and provide both corrected results and correction factors which enable the detection of potentially inaccurate results for which the degree of correction is unacceptably high.

During analysis of complicated matrices by ICP-MS, spectral interferences are known to present one of the major obstacles to achieve accurate results [24]. As a result, several matrix elements (Si, P, S, K, Ca and Fe) are considered as 'problematic' in ICP-QMS. Due to high mass resolution capability, HR-ICP-MS allows accurate determination of many elements even in such a complicated matrix as seawater [20]. In the present study, MRM was used for 20 elements (Mg, Al, Si, P, S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, and Br) while the determination of As and Se required HRM. Examples of spectra recorded in MRM for selected isotopes in NIST SRM 1635 digest (procedure A2) are presented in Fig. 1. Though it may appear that interferences on P originating from NO^+ and NOH^+ can be overcome by blank subtraction when applying ICP-QMS, this will actually result in erroneously low P concentrations. This is because lower levels of interfering signals are observed in the sample matrix when compared to the blank solution, owing to evaporative losses of nitrogen species from the former during digestion. Another monoisotopic element, Sc, is affected by numerous interferences, especially of carbon-containing molecules. These data are opposite to those of Fadda et al. [3] who stated that the determination of Sc did not suffer from increased carbon content in the sample solution. The spectra nearby Cr and Ga isotopes represent two examples where a minor isotope appears to be less affected by spectral interferences than the major isotope.

When performing MW dissolution, the use of HCl in the digestion mixture results in severe interferences on V, Cr, Ga, Ge, As, Se and Yb isotopes. Though it is possible to overcome the majority of spectral interferences using a resolution that is sufficient to isolate the analyte signals from interfering peaks in the mass range from 24 to 81 amu, a significant number of interferences originating from oxides in the higher mass region can not be resolved, even in HRM. Moreover, an increase in resolution is joined to a decrease in sensitivity owing to the reduced ion transmission. In order to assess the severity of these interfer-

ences, the oxide formation ratios for potentially interfering elements were determined by analyzing a set of single-element standards in LRM (solution nebulization) and these data were used for mathematical correction. The mean degree of correction (i.e. the ratio uncorrected/corrected concentration) values for selected isotopes in the NIST and Interlab coal samples are presented in Table 2. For ten elements the degree of correction was less than 1.05, and for them the contribution from oxide peaks on the analyte signal was assumed to be negligible. For the remainder, the results were corrected mathematically using oxide formation ratios that were determined experimentally on a daily basis. For the most severely affected isotopes (degree of correction higher than 2), small variations in oxide formation owing to changes in plasma parameters during the analytical procedure are expected to yield inaccurate results. Hence, results for such elements (Ru, Rh, Pd, Ir, Pt and Au) are reported as less than the uncorrected value.

It must be noted that the mathematical corrections discussed here ignore interferences originating from hydroxide and chloride species. The former is neglected as it was shown [25] that hydroxide formation is about 10-fold lower than oxide formation. Correction for chloride interferences is complicated as, for example, correction for BaCl interferences on Tm and Yb isotopes depends on the contents of both Cl and Ba in the sample solution.

Oxide formation while using LA is significantly lower if compared to the solution nebulization, owing to the reduced amount of oxygen that reaches the ICP as water vapour and aerosol. For example, the ratio UO/U decreases from about 0.03 (solution nebulization) to less than 0.01 (LA). Hence, no corrections for oxide interferences were performed for LA-ICP-MS, though the results for elements that might be severely affected (Ru, Pd and Au) were excluded from evaluations.

For both solution nebulization and LA, isobaric interferences such as from ^{114}Sn on ^{114}Cd were corrected mathematically using the intensity of an alternative isotope for the interfering element and its relative abundance.

3. Results and discussion

Detection limits, calculated as three times the standard deviation for preparation blanks (gas blanks for LA) for each procedure, are given in Table 3. For major elements they are in the low µg g^{-1} range, except for Si if using LA. High values caused by a large and unstable Si blank are probably due to torch overheating when switching it to a dry plasma. Poor detection limits for Li and B with LA are attributed to the high instrumental blank levels of these elements caused by the contamination from previous analyses of fusion solutions containing large quantities of LMB. Cleaning or replacement of the sample introduction system (including tubing, nebulizer, spray chamber, torch and cones) do not eliminate these high blanks completely. It seems that deposition of LMB on the internal parts of the instrument is responsible for long-lasting memory effects. Detection limits are below 10 ng g^{-1} for about 40 minor and trace elements in all procedures, though blank levels for fusion were significantly higher for elements such as Al, Ag, Ba, Cu, V and Ce, reflecting more extensive sample handling and possibly impurities in the LMB.

Results for NIST SRM 1635 and Interlab coals obtained by different approaches are summarized in Tables 4 and 5, respectively. As differences between ICP-AES and HR-ICP-MS results were, as a rule, insignificant (when not limited by instrumental detection limits in the former technique), the more precise data are reported. The accuracy of the results for NIST SRM 1635 can be evaluated by comparison with certified and recommended values, which are available for 25 elements for this material. Concentrations of 31 additional elements in this coal sample have been previously reported [17,23–25], but the significance of differences between found concentrations and literature values are difficult to evaluate. For the Interlab sample, median concentrations based on results received from all participants in the Interlab Trace program are available for 15 elements. These consensus values are to be treated with caution because of their great scatter, for some elements covering five orders of magnitude. This variability in the reported values is, however,

not unusual in trace element determinations with different analytical techniques. For the others elements, no independent check of accuracy is possible and applied procedures can be compared only with respect to relative recovery.

From the data obtained with different MW dissolutions, it appears that the recovery of Fe, Na, Ca, Mg, Ag, Be, Cu, Mn, Mo, Ni, P, B, Bi, Pb, Sb and Tl is independent of the acid mixture and that results for these elements fall within $\pm 10\%$ of certified/recommended values, where available. Recovery of the other elements are influenced by both the acid mixtures and the coal types. The addition of a minor amount of HF to $HNO_3 + H_2O_2$ or aqua regia results in higher recovery for many elements that are associated with siliceous materials in coal. Generally, procedure A2 provides the best accuracy (good agreement for 22 out of 25 elements for NIST SRM 1635 and for 13 out of 15 elements for Interlab, for which certified or recommended values are available). It should also be noted that, when applying procedure A2, good agreement with literature data was found for Ca, Mg, Ba, Cs and Sr. Poor recoveries for these elements when using HF in MW dissolution have been reported previously [10].

LMB fusion results in further improvement for the recovery of elements such as Si, Hf, Cr, W, Zr, Y, accompanied, however, by obvious losses for Ag, As, Cd, Cu, Bi, Hg, I, Se, Sn, Tl, Pb, Re, Te, S and Zn. Though it is possible to improve the recovery of selected elements, by excluding sample ashing from the fusion procedure (B2), results for the majority of volatile elements are still significantly lower if compared to MW dissolution.

Complete recovery of As, Cu and Zn in the LMB fusion of coal ash has been reported previously [10]. An explanation for this discrepancy might be that retention of volatile elements in coal is dependent upon the exact mineral matter composition.

Though no single sample preparation method can provide accurate results for all the elements under consideration, by using a combination of the A2 and B2 procedures, one can avoid negative effects related to acid-resistant mineral phases as

well as to losses of volatile elements. In order to evaluate the suitability of these two sample preparation methods for other sample types, they have been applied to SRM 1633b coal fly ash (Table 6). Although recoveries in the MW procedure for elements such as Sc, Th and the REE were lower compared to coal samples (Fig. 2), accurate results were obtained for 46 out of 47 elements for which certified or recommended values are available. Smooth chondrite-normalized patterns in Fig. 2 also reflect internal consistency in REE results.

The precision, as determined by the analysis of coal samples prepared in triplicate, was generally better than 3–5% for all MW and fusion procedures. It was, however, significantly worse for LA, being in the range 10–20% of RSD for most of the elements. Possible reasons for this variation, other than the obvious problem of heterogeneous analyte distributions, include inhomogeneous mixing of coal powder with IS solution or density differences between different points in the pressed coal tablets. For about 50 elements, results obtained with LA fall within 20% of those obtained by MW digestion or fusion. In spite of relatively poor agreement for elements such as As, Se, Sn, Re, Te and Tl, accuracy obtained with LA in the present study is superior to that reported for this technique in other studies [16,17], as well as for slurry nebulization [13].

4. Conclusions

The combination of ICP-AES and HR-ICP-MS is an useful approach to the simultaneous determination of a wide range of major, minor, and trace elements in coal. Even if a significant number of elements affected by spectral interferences can be accurately determined by HR-ICP-MS, unresolved interferences caused by oxide species are still the major obstacle for quantification of Rh, Ru, Pd, Pt, Ir and Au. Accurate results for these elements at low ng g^{-1} levels can be obtained only after chemical separation of interfering elements or by minimizing oxide formation by using aerosol desolvation. For elements such as Ca, Fe, Ti, Mg, Cu, Be, Mn, Ba, Sr, Ni, B, Mo,

Sn, Bi and P, recovery is over 90% independent of the acid mixture used in MW dissolution. Extraction efficiency for certain elements is strongly dependent on the applied leaching mixture and varies among different coal types. Though elemental recoveries obtained with a mixture of nitric and hydrofluoric acids with hydrogen peroxide were superior to those obtained with other mixtures, recoveries for Si, Hf, W, Zr, REE and Nb were low. Hence, a combination of this procedure and LMB fusion without ashing should be applied to coal analysis in order to obtain accurate data for as many elements as possible. It appears that the use of aqua regia provides no improvement in recovery and that hydrochloric acid must be avoided in coal digestion.

LA is ideally suited for rapid screening of element concentration ranges in coal if a 15–20% accuracy is acceptable. Though it was possible to evaluate accuracy for more than 50 elements, new coal reference materials with certified values for a larger number of elements are needed in order to facilitate method validation.

Acknowledgements

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