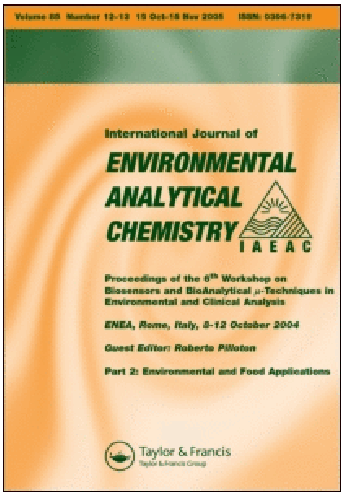

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INTERCOMPARISON OF TRACE ELEMENT DETERMINATION IN SAMPLES FROM A COAL-FIRED POWER PLANT

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The combustion of fossil fuels, e.g. coal, is one of the anthropogenic sources of hazardous trace element emissions. This interlaboratory study was arranged to test and improve the quality of trace element analysis of different types of samples from a coal-fired power plant. Samples of coal, fly ash, by-product from flue gas desulphurisation (=FGD product, consisting mainly of $CaSO_3$ and $CaSO_4$), and two different absorption media used for the sampling of vaporous metals and metalloids in flue gases were sent to be analyzed for Al, As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, Tl, V and Zn by different Finnish laboratories using mainly atomic spectroscopic methods. In addition, neutron activation analysis and X-ray fluorescence spectroscopy were employed. 12 laboratories took part in the analysis of a HNO_3 sample, 5 in the analysis of a $K_2Cr_2O_7/HNO_3$ sample, 15 in the analysis of a fly ash sample, 9 in the analysis of a coal sample, and 7 in the analysis of a sample of the by-product from flue gas desulphurisation. The results were evaluated both in terms of interlaboratory agreement and in comparison with different digestion and analytical methods used in the intercomparison. The magnitude of the deviations of the results clearly indicated a need to develop the quality of power plant sample analysis. Considering the methods used, it was concluded that the composition of the acid mixture used for the digestion of solid samples is more decisive than the method of heating during the digestion.

KEY WORDS: Trace element, intercomparison, coal, fly ash, flue gas desulphurisation, power plant.

INTRODUCTION

The combustion of fossil fuels, e.g. coal, is one of the most important anthropogenic sources of toxic trace element emissions. Many trace metals or metalloids, e.g. Be, Cd and Hg, accumulate in nutrient cycles. Therefore, they may be extremely hazardous to living organisms. The development of environmental legislation calls for the reduction of trace element emissions into the environment. In order to control these emissions from a coal-fired power plant, and to assess the environmental risks of such a plant, the behaviour of hazardous elements in the plant must be understood. This is also required when making decisions concerning the utilization of waste products from such a plant. Reliable information about the total concentrations of environmentally hazardous elements in the mass flows of the plant is a prerequisite for overall understanding of the behaviour of these elements and their transport through the process. To obtain this information, reliable sampling and analytical methods are necessary.

It has become evident in many of our emission measurement campaigns that a lot of expertise and long experience are required to determine trace elements reliably in power plant samples. A great deal of method development and testing has been reported in the literature over many years[1-3]. However, as discussed by Schlums *et al.*[4] the determination of trace elements in e.g. ash samples has not yet been satisfactorily harmonized. Even if the sampling can be performed faultlessly, inaccuracy and irreproducibility of further analytical steps such as digestion and final determination may cause serious uncertainty in emission and mass balance determinations. From the viewpoint of the organization in charge of emission measurements and power plant studies, this makes the evaluation of the results very complicated and, in the worst case, whole sampling campaigns worthless. Accordingly, we considered it necessary to test sample digestion methods for solid samples from energy producing plants along with our own method development projects[5,6].

As discussed by Quevauviller *et al.*[7], participation in interlaboratory studies is one of the most powerful tools in detecting and removing error sources. While the improvement of the precision of the analyses can be dealt within the laboratory itself, accuracy of the results can only be achieved by comparison with other laboratories by means of interlaboratory studies or use of certified reference materials[8]. This intercomparison was arranged in order to measure and improve the quality of trace element determination of different types of samples from a coal-fired power plant in Finland. In this first round of the intercomparison, no specific analytical methods were recommended or required. According to Schlums *et al.*[4], this kind of intercomparison belongs to the first stage of quality control procedures, and its aim is to compare different methods and to exchange information. Confirming the best analytical method or the establishment of certified concentration values for a reference sample are subjects for further intercomparison rounds.

SCOPE OF THE INTERCOMPARISON

Participants

Before preparing the samples, a questionnaire was sent to 20 Finnish chemical laboratories selected for their experience in trace element determination. The questionnaire contained information about the intercomparison and an invitation to take part in the analyses of the samples for Al and for As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, Tl, V and Zn. Fifteen laboratories participated in the intercomparison. The samples and elements analyzed and the methods used by different laboratories are shown in Table 1.

Recommendations to the participants

The participants were asked to make at least three replicate analyses of each sample type and to report the individual results, the mean values and the relative standard deviations. A minimum sample size of 100 mg was recommended in the case of solid samples. In order to assure a uniform way of removing moisture from solid samples, drying at 40°C to constant mass (not less than 24 h) was recommended. The temperature was low in order to avoid losses of any volatile trace elements. The participants were asked to report the trace metal contents on a dry-weight basis.

Table 1 A summary of the samples analyzed, and the analytical and digestion techniques used by the participants of the intercomparison; ETAAS = electrothermal atomic absorption spectrometry, FAAS = flame AAS, HGAAS = hydride generation AAS, CVAAS = cold vapour AAS, ICP-AES = inductively coupled plasma atomic emission spectrometry, ICP-MS=ICP mass spectrometry, XRF=X-ray fluorescence spectrometry, NAA = neutron activation analysis.

Lab#		*Analytical method*		*Digestion method*	*Digestion reagents*
1	A:	ETAAS:	As, Cd, Cr, Cu, Ni, Pb		
		FAAS:	Zn		
		ICP-AES:	Al, Co, Mn, V		
	C:	XRF:	Al, As, Co, Cr, Cu, Mn, Ni, Pb, Zn		
2	A:	ETAAS:	As, Cd, Co, Cr, Ni, Pb, Se, V	C–E: Pressurized microwave heating	C–E: aq.reg ; Hg
		FAAS:	Al, Cu, Mn, Zn		C,D: HNO_3+HF;H_3BO_3: Others
	C,D:	ETAAS:	As, Cd, Co, Cu, Ni, Pb, Se, V		
		FAAS:	Al, Cr, Mn, Zn		
	E:	ETAAS:	As, Cd, Co, Ni, Pb, Se, V		E: HNO_3: Others
		FAAS:	Al, Cr, Cu, Mn, Zn		
	A,C–E:	Au-film :	Hg		
3	C,D:	ETAAS:	As, Cd(D), Cr, Pb, V, Zn	C,D: Pressurized microwave heating	C,D: HNO_3+HF
		FAAS:	Cd(C), Co, Cu, Mn, Ni		
		CVAAS:	Hg		
4	A,C:	ETAAS:	As, Cd, Cr, Co, Ni, Pb	C: Pressurized autoclave heating	C: HNO_3+HF: Hg
		CVAAS:	Hg		C: HNO_3: Others
		ICP-AES:	Al, Cu, Mn, Zn		
5	A–E:	ETAAS:	As, Cd, Cu, Pb, Tl	C–E: Refluxion: Hg	C,E: HNO_3+H_2SO_4: Hg
		FAAS:	Mn	C–E: Pressurized microwave heating: Others	
		CVAAS:	Hg		D: HNO_3+HCl : Hg
		ICP–AES:	Be, Cr, Co, Ni, Se,V, Zn		C,D: HNO_3+HF;H_3BO_3: Others
					E: HNO_3: Others
6	A–E:	ETAAS:	Cd, Co, Cr, Cu, Ni, Pb	C–E: Pressurized microware heating	C,D: HNO_3+HF
		FAAS:	Zn		E: aq.reg.
7	C,D:	CVAAS:	Hg	C,D: Parr oxygen bomb	C,D: Dry combustion
8	A:	ICP–MS:	Al, As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Tl, V, Zn		
	C–E:	NAA:	As, Co, Cr, Ni		
9	A,C:	ETAAS:	Cd, Co, Cr, Cu, Mn, Pb, V	C: Pressurized microware heating	C: HNO_3+HF; H_3BO_3
		FAAS:	Zn		
10	A:	ICP–MS:	Al, As, Be, Co, Cr, Cu, Mn, Ni, Pb, Tl, V, Zn	C,E: Non-pressurized, heating vessel: Al, Mn	C,E: HF+aq.reg.+$HClO_4$:Al, Mn
	B:	CVAAS:	Hg		
	C,E:	ICP–AES:	Al, Mn	C,E: Room temperature, test tube: Others	C,E: HNO_3+HF: Others
		ICP–MS:	As, Be, Cd, Co, Cr, Cu, Ni, Pb, Se, Tl, V, Zn		
11	A:	ETAAS:	As, Al, Cd, Cr, Cu, Mn, Pb	C–E:	C–E:
	C–E:	ETAAS:	As, Cd, Cr, Cu, Mn, Pb	a) Hot-plate heated non-pressurized vessel	a) HNO_3+HCl+HF+$HClO_4$
		FAAS:	Al	b) Pressurized microwave heating	b) HNO_3+HF;H_3BO_3
12	A–C,D:	ETAAS:	Cd, Cr, Cu, Pb, Tl, V(A)	C,E: Pressurized vessel, steam bath	C,E: aq.reg.+HF;H_3BO_3
		FAAS:	Co, Mn, Ni, V(A,C), Zn		
		CVAAS:	Hg		
		HGAAS:	As, Se		
13	A,C:	ETAAS:	As, Cd, Cr, Cu, Mn, Ni, Pb, V, Zn	C: Ultrasonic: As	C: HNO_3: As
				C: Pressurized microwave heating: Others	C: HNO_3+HF:Others
14	A,C,D:	ETAAS:	Cd, Cr, Cu, Mn, Ni, Pb	C,D: Pressurized microwave heating	C,D: HNO_3+HCl+HF; H_3BO_3
15	C,D:	XRF:	Al, As, Co, Cr, Cu, Mn, Ni, Pb, V, Zn		

No restrictions were imposed with respect to sample handling or analytical techniques.

Description of the samples

HNO_3 solution (sample A) Strongly acidic HNO_3 solutions are often used as absorption media for the sampling of vaporous metals and metalloids in flue gases. 2 l of 7.4 M (38% -weight) HNO_3 was prepared in the laboratory from 14.4 M HNO_3 (suprapur® 65%, Merck) and water purified in a Nanopure II (Barnstead) system. Solutions of Al, As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, Tl, V and Zn were prepared from Titrisol® commercial solutions (Merck) and added in exactly measured volumes to the 7.4 M HNO_3. The concentration range was chosen to be 5–200 µg/l. This concentration range is typical in the sampling of vaporous metal emissions from a coal-fired power plant by means of liquid absorption. The resultant solution was distributed into 100 ml vessels made of high-density polyethylene (HDPE) and stored in a refrigerator before despatch to the participants. Random samples were analysed for Cd, Cu and Zn by means of electrothermal atomic absorption spectrometry (ETAAS) in order to check the concentration levels and to make sure that the sample had not been contaminated during the preparation. A good agreement with the calculated values was observed. Due to the strong acidity of the solution, the samples were regarded to remain stable during the course of the intercomparison.

$K_2Cr_2O_7/HNO_3$ solution (sample B) A 0.16 M (4% -weight) solution of $K_2Cr_2O_7$ in 3.5 M (20% -weight) HNO_3 has been found to be an efficient sampling medium for vaporous mercury in flue gases[9]. 2 l of this solution was prepared in the laboratory from $K_2Cr_2O_7$ (p.a., Hg free, Merck), HNO_3 (p.a. Hg free, 65%, Merck) and water purified in a Nanopure II (Barnstead) system. A solution of mercury was prepared from a Titrisol® Hg commercial solution (Merck) and added to the $K_2Cr_2O_7/HNO_3$ solution. The resultant solution was distributed into 100 ml vessels made of HDPE and stored in a refrigerator before despatch to the participants. Random samples were analysed for Hg by means of cold vapour atomic absorption spectrometry in order to check the concentration level. A good agreement with the calculated value was obtained. Due to the strong acidity and high $K_2Cr_2O_7$ concentration of the solution, the samples were regarded to remain stable during the course of the intercomparison.

Fly ash (sample C), coal (sample D) and FGD product (sample E) Solid samples were taken from a coal-fired power plant (160 MW electricity, 270 MW district heating) equipped with electrostatic precipitators and a spray-dryer-type flue gas desulphurisation unit with fabric filters. Fly ash was collected from an intermediate reservoir containing ash from all the hoppers of the electrostatic precipitator. Coal samples were collected from the coal suppliers of the mills. Samples of the by-product from the flue gas desulphurisation unit (FGD product) were collected from the transmitters downstream of the fabric filters.

Before further treatment, the gross sample of coal (a few hundred kilograms) was first ground so that the grain size was less than 5 mm. Then the sample was dried in air. Laboratory samples of 3–5 kg were taken from the gross sample. These laboratory samples were ground to a grain size of less than 0.1 mm and divided into smaller samples. To obtain a sample for this intercomparison, a number of the small samples were combined.

The grain size of the solid samples was confirmed to be less than 0.2 mm by means of ball mill grinding using agate and/or ZrO_2 balls. The homogeneity of the samples was confirmed by means of a combined ball milling and sample dividing program. Gross samples of fly ash, coal and FGD product were divided using a Retsch PZT laboratory sample divider according to the following scheme: The sample was divided into eight vessels. Each of these subsamples was further divided into eight smaller samples. These smaller samples were again combined so that eight new subsamples resulted. Three of these subsamples were chosen at random and divided into eight small samples of 20–30 g into wide-mouthed 30 ml polypropylene sample vessels. A smaller sample of about 5 g was then taken from each of these vessels and sent to the participants.

The homogeneity of these small samples, both within themselves and between individual samples, was checked by means of neutron activation analysis (NAA) and X-ray fluorescence spectroscopy (XRF) before sending the samples to the participants. These methods are the most suitable and widely used for the verification of homogeneity, because they are multi-element methods and do not require digestion of the sample[8,10–12].

Samples for homogeneity testing using NAA were taken from ten different sample vessels chosen at random from the whole population of each sample type. An additional ten samples were taken from the tenth vessel. The average sample size was 100 mg. This sample size was also used by Abraham and Schlums[13] in their study. Other details about the homogeneity check using NAA are described in previous work by Rosenberg *et al.*[14]. The relative standard deviations of the analyzed concentrations of Cr, Fe and Co in the fly ash and the coal samples chosen at random were even smaller than those of reference samples, which indicates that the homogenization had been successful. This was further confirmed by consideration of the analyzed concentrations of Sc and La. In the case of FGD product, the Cr, Fe and Co concentrations were so low that only the deviations in the results for Na, Sc and La were used as an indicator of satisfactory homogeneity.

Samples for XRF analysis were taken from five sample vessels of each sample type. The samples were mixed (2:1) with microcrystalline cellulose (Avicell), and of this mixture 1.5 g was pressed into pellets. Each sample was measured twice using a Philips PW 1480 X-ray fluorescence spectrometer with a Mo/Sc dual anode. The small relative standard deviations of the results for Fe, Zn, Ti, Ca, K and Al contents further confirmed the homogeneity of the samples (see Table 2).

The stability of the solid samples studied in this intercomparison was regarded to be good during the short period of time between despatch to the participants and requested deadline of the reports. Certain ash samples have been observed to remain stable at least for four years[15].

The moisture content of the coal samples was determined separately. Drying in a N_2 atmosphere at 40°C for 24 h reduced the weight of the sample by 1.6% on average. When the sample was further dried at 105°C for 1 h, the total reduction in weight was

Table 2 Homogeneity testing of samples of fly ash, coal and by-product from flue gas desulphurisation (FGD product). Relative standard deviations (%) of the analyses of five random samples for Fe, Zn, Ti, Ca, K and Al by means of XRF are given as a measure of the homogeneity of the samples. The Zn and Ti contents in the FGD product samples were below the detection limit.

	Fe	*Zn*	*Ti*	*Ca*	*K*	*Al*
Fly ash	1.0	4.2	1.0	0.9	0.9	1.3
Coal	1.2	4.5	1.3	3.4	0.8	1.1
FGD product	1.7	–	–	0.9	1.9	3.7

2.6%. The ash content of the coal samples was determined by ashing at 550°C for 3 h + 1.5 h. The average ash content was 13.1%.

EXPERIMENTAL TECHNIQUES USED BY THE PARTICIPANTS

Digestion methods

A summary of the digestion methods with information about the acids used is given in Table1.

Pressurized microwave digestion was the most widely used method for the dissolution of solid samples for atomic spectroscopic analysis. For instance, in the analysis of the fly ash sample, eight of the participating laboratories employed a microwave oven. In most cases the digestion was controlled by adjusting the time for which the samples were subjected to microwave heating. It was very common that the total time was about 1 hour or slightly less. In two cases, a pressure control system was used.

In addition to microwave heating, digestions were done in a closed vessel in a steam bath, in a closed vessel in an autoclave and in an open vessel on a hot-plate. Digestion in a test tube in room temperature was also employed. For the determination of mercury, specific digestion methods were used.

Sample sizes varied from 0.2 to 0.5 g. For mercury analysis, the sample size was bigger in some cases. The volume of the acid or acid mixture used for the digestion was about 10 ml. Before the analysis, the digested sample was in most cases diluted with water.

Analytical techniques

The analytical methods used for the analysis of different elements in different samples are also summarized in Table 1.

Most of the laboratories employed electrothermal atomic absorption spectrometry (ETAAS) in their analyses. A few analyses were performed by means of flame atomic absorption spectrometry (FAAS) and hydride generation atomic absorption spectrometry (HGAAS). Two laboratories had access to inductively coupled plasma mass spectrometry (ICP-MS). Four laboratories used inductively coupled plasma atomic emission spectrometry (ICP-AES), but this method was mainly used in addition to ETAAS or ICP-MS for certain elements (Al, Be, Co, Cr, Cu, Mn, Ni, Se, V, Zn). One laboratory analyzed the fly ash and coal samples by means of X-ray fluorescence spectrometry, while another used this technique only for the analysis of the fly ash sample. One set of results for fly ash, coal and FGD product was reported on the basis of neutron activation analysis.

Hg analyses were performed by means of cold vapour atomic absorption spectrometry (CVAAS). One laboratory used a Au-film mercury analyzer.

RESULTS AND DISCUSSION

12 laboratories reported results on the HNO_3 sample, 5 on the $K_2Cr_2O_7/HNO_3$ sample, 15 on the fly ash sample, 9 on the coal sample, and 7 on the sample of FGD product (i.e. by-

product from flue gas desulphurisation). Most laboratories reported the results as mean values of three determinations. In some cases the analyses had been repeated even more than ten times. Three sets of results for the liquid samples and one set of results for the fly ash sample were given as single values only. The highest number of laboratory results were received for Cd, Cr, Cu and Pb. These are shown as examples in Figure 1. Unfortunately, only few laboratories reported results for Be, Hg, Se and Tl, which made any conclusions about the reliability of the determination of these elements partly uncertain.

Because the aim of this intercomparison was not to prepare reference materials with certified concentrations but to evaluate and improve the quality of trace element determination in samples from a coal-fired power plant, the results were not subjected to extensive statistical analysis. The use of conventional statistical methods may not even be reasonable, because different digestion methods may cause systematically erroneous results that do not follow a Gaussian distribution[3,13]. The range of different laboratory values is given in Table 3 as an indicator of the interlaboratory agreement of concentrations measured. The medians, corrected means and relative standard deviations of the different laboratory means were determined for each element concentration in each type of sample (see Table 3) in order to obtain an estimate for the correct concentration values. In the determination of the corrected mean, the results that were distinctly different from all other laboratory means were rejected as outliers. This kind of outliers are called Type 2 outliers by de Voogt *et al.*[16]. In the determination of the ranges, the medians and the corrected means, the values reported to be below the detection limit were not considered.

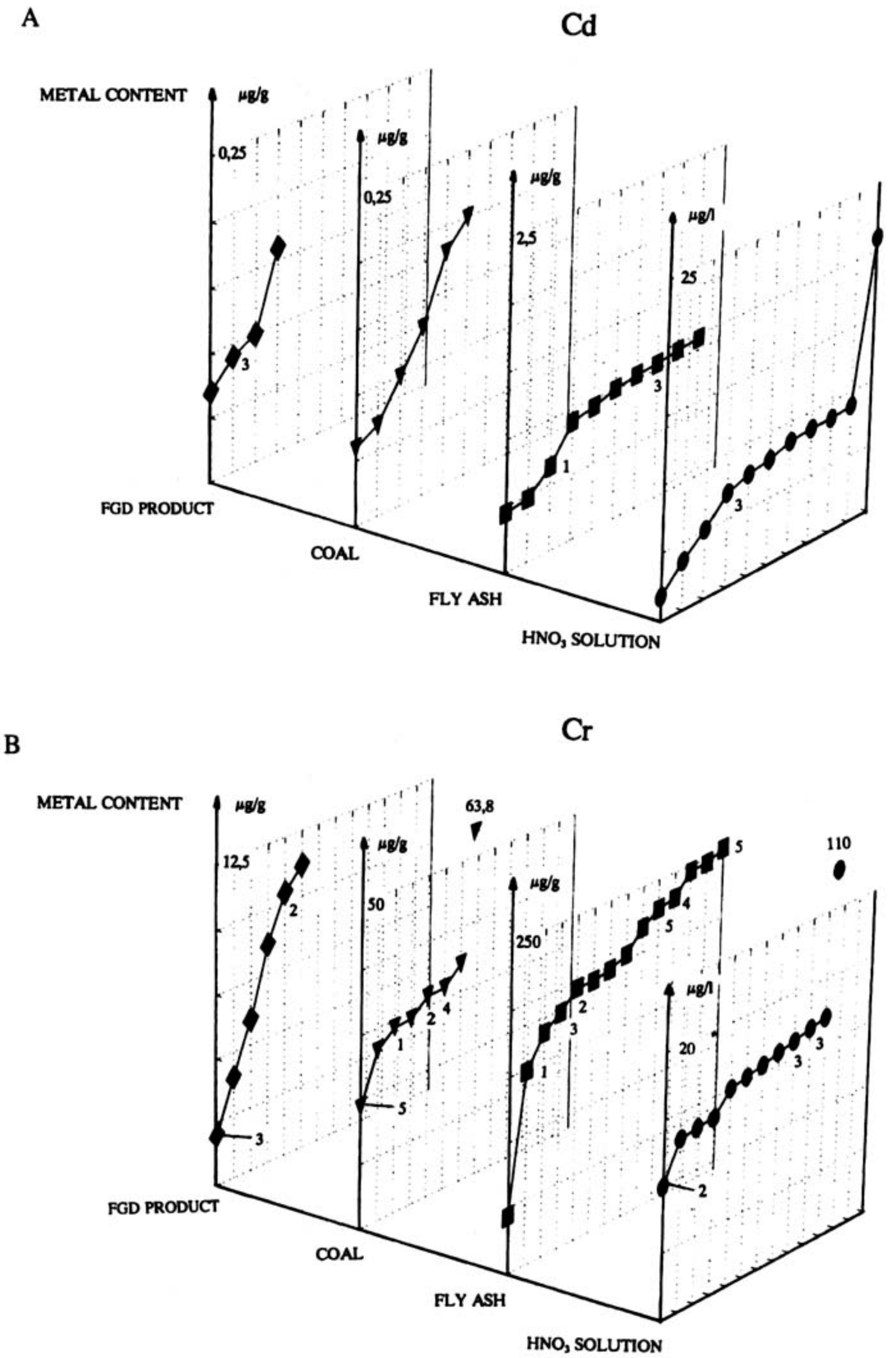
The results were also grouped and examined according to the analytical method used and the digestion method of the solid sample. These considerations are summarized in Tables 4 to 7. The contents reported to be below the detection limit are not included in the mean values given in these tables. The results for mercury are presented separately in Tables 5 and 7. It has to be taken into account that the results shown in Tables 4 to 7 must not be interpreted independently of each other, because the digestion method has an influence on the results of Tables 4 and 6, and the analytical method has an influence on the results of Tables 5 and 7.

In the following sections the results are discussed sample by sample.

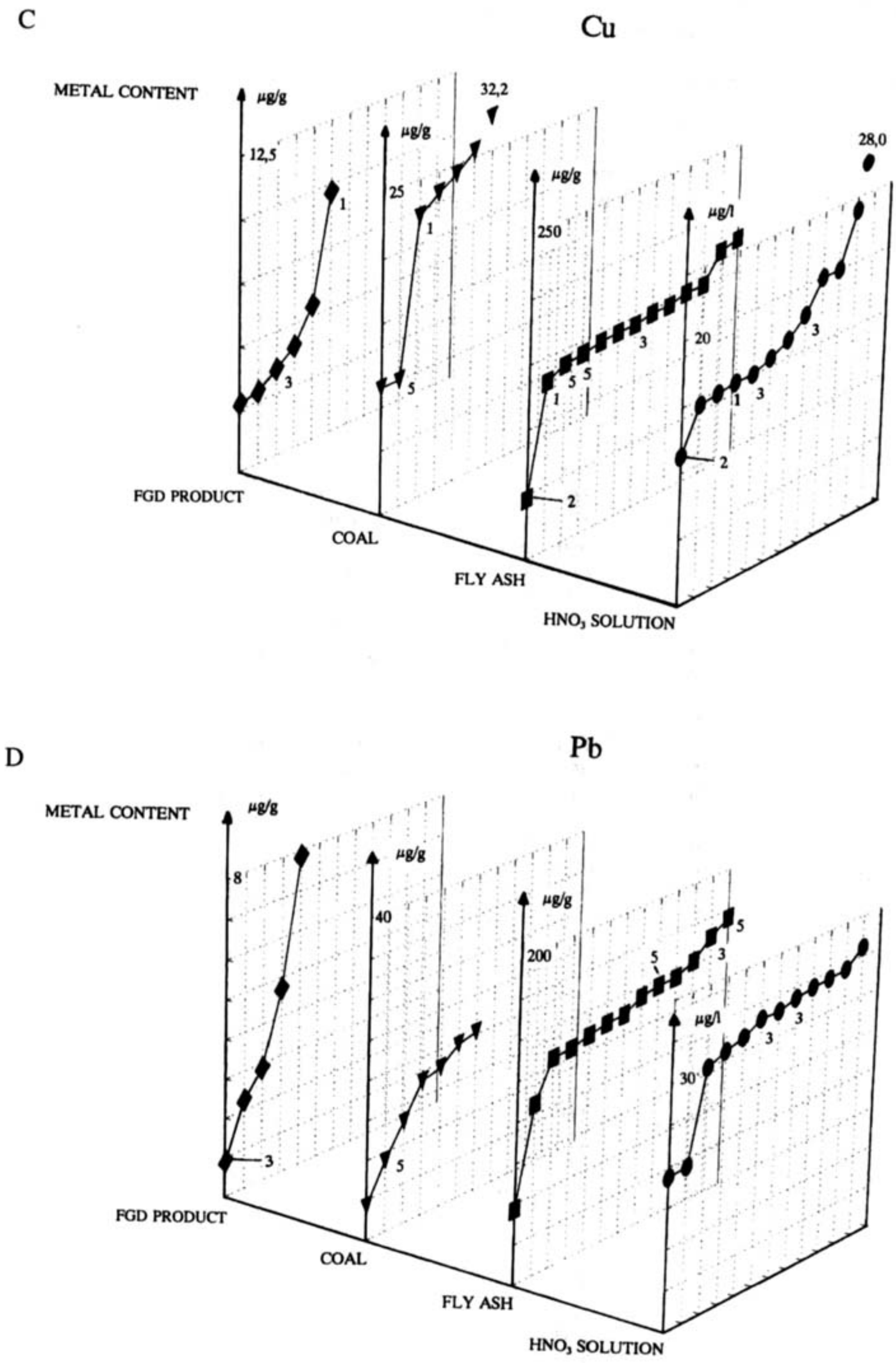
HNO_3 sample (sample A)

The ranges of the concentration values shown in Table 3 for the HNO_3 sample suggest that there is a need to improve the quality of trace element determination in liquid samples. After rejecting type 2 outliers discussed above, the relative standard deviations for Co, Ni, Pb, Se and Tl were below 10% (However, for Se and Tl, only a few results were reported). For Al, As, Cd, Cr, Cu, V and Zn the relative standard deviations were higher than 10%, for Mn almost 30%, and for Hg almost 90%. In the work of Abraham *et al.*[3], the analysis of As, Cd, Co, Cr, Fe, Ni, Pb and Zn was studied. The highest standard deviations in dilute HNO_3 samples were reported for Co and Ni, but this was not the case in this intercomparison.

The results given in Table 4.1 show that both laboratories employing an ICP-MS instrument obtained results in good agreement with the median and the corrected mean value of all the results given in Table 3. Also the relative standard deviations for this method were low. ETAAS generally gave good results, but a few obviously erroneous results caused high relative standard deviations and made an unfavourable impression.



Figures 1 The laboratory means obtained for Cd, Cr, Cu and Pb given as µg/l for sample A (HNO_3 solution) and as µg/g for samples C (fly ash), D (coal) and E (by-product from flue gas desulphurisation, i.e. FGD product); ETAAS was mainly used, except for results marked with 1) FAAS, 2) ICP-AES, 3) ICP-MS, 4) NAA, 5) XRF was employed.



Figures 1 *Continued*

Table 3 Summary of the results of the intercomparison; concentrations given as µg/l for HNO_3 (=A) and $K_2Cr_2O_7/HNO_3$ (=B) samples, and as µg/g for samples of fly ash (=C), coal (=D) and FGD (flue gas desulphurisation) product (=E).

		N	<	*Range*	*Median*	*a*	$\bar{x}$	*rel σ*
Al	A	6	1	46.3...210	50	4	51	13
	C	6	0	21900...146700	135000	5	138000	7
	D	3	0	19700...21000	20500	3	20400	3
	E	3	0	2220...2783	2330	3	2440	12
As	A	9	0	14.6...40.0	25	6	24	14
	C	11	0	12.8...110	35	8	33	17
	D	5	0	4.50...14.8	4.4	4	3.1	62
	E	6	1	0.88...3.90	1.5	4	1.3	25
Be	A	3	2	—	4.3	1	4.3	—
	C	2	0	10.8...17.5	14	2	14	33
	D	1	1	—	—	1	1.0	—
	E	2	1	—	0.05	1	0.1	—
Cd	A	11	0	1.80...21.0	7.9	8	7.8	16
	C	11	1	0.45...1.07	0.97	7	1.0	7
	D	6	0	0.06...0.20	0.12	6	0.1	47
	E	6	2	0.07...0.16	0.95	4	0.1	37
Co	A	9	2	10.0...25.3	25	7	24	4
	C	10	0	10.0...70.5	51	7	49	9
	D	6	0	2.00...10.4	8.1	4	9.1	13
	E	6	1	0.86...4.00	1.3	5	1.3	63
Cr	A	12	0	10.0...110	16	11	15	14
	C	14	0	44.3...253	201	13	209	15
	D	8	0	19.0...63.8	31	6	30	9
	E	7	0	4.00...12.5	7.3	5	8.0	38
Cu	A	12	0	11.3...28.0	16	9	17	13
	C	13	0	46.9...176	144	10	144	4
	D	7	0	10.0...32.2	23	4	24	6
	E	6	0	2.75...9.69	3.8	5	3.7	29
Hg	A	3	0	0.74...23.0	3.3	2	2.0	90
	B	5	0	0.20...5.00	2.4	4	3.2	38
	C	5	0	0.16...1.70	0.28	4	0.3	31
	D	2	0	0.04...0.13	0.09	2	0.1	72
	E	3	0	0.15...0.97	0.42	3	0.5	81
Mn	A	11	1	20.0...50.0	29	9	35	29
	C	12	0	414...899	789	9	781	7
	D	6	0	49.0...91.1	88	5	89	3
	E	5	0	75.5...92.3	84	5	85	8
Ni	A	10	1	26.5...50.0	41	7	41	5
	C	12	0	49.0...158	141	11	140	8
	D	7	0	2.00...25.1	22	6	22	14
	E	5	1	2.80...10.0	3.4	3	3.7	23
Pb	A	12	0	18.7...36.1	33	10	33	5
	C	13	0	46.3...170	138	12	142	12
	D	7	0	4.30...20.3	17	6	16	27
	E	6	1	0.89...7.9	2.9	3	3.3	39
Se	A	3	0	9.00...22.3	10	2	10	7
	C	3	1	2.60...11.5	7.0	1	2.6	—
	D	1	1	—	—	1	1.0	—
	E	3	1	8.35...14.5	11	2	11	38
Tl	A	4	0	16.6...29.0	18	3	17	5
	C	3	1	2.69...2.90	2.8	2	2.8	5
	D	1	0	—	0.9	1	0.9	—
	E	3	1	0.11...0.80	0.5	2	0.5	107

(Continued on next page)

Table 3 *(Continued)*

		N	<	*Range*	*Median*	*a*	$\bar{x}$	*rel* σ
V	A	8	1	66.0...92.0	78	6	63	11
	C	8	0	276...382	312	6	301	6
	D	4	0	25.3...54.4	52	3	53	3
	E	4	0	3.50...13.1	7.5	3	6.2	40
Zn	A	10	0	83.0...187	157	8	161	14
	C	11	0	69.8...318	243	8	253	9
	D	4	0	24.1...31.5	25	3	24	4
	E	5	0	7.67...18.7	13	5	13	32

N = number of laboratory means
< = number of lab. means below the detection limit
a = number of laboratory means accepted for the corrected overall mean
$\bar{x}$ = corrected overall mean of laboratory means
rel σ = relative standard deviation of accepted lab. means (%)

Table 4.1 Results of the intercomparison (except for Hg) grouped according to the analytical techniques used; concentrations given as μg/l for HNO_3 sample (Table 4.1), and as μg/g for samples of fly ash (Table 4.2), coal (Table 4.3) and FGD (flue gas desulphurisation) product (Table 4.4).

	ET AAS			*Other AAS**			*ICP-AES*			*ICP-MS*		
	N	$\bar{x}$	*rel* σ	*N*	$\bar{x}$	*rel* σ	*N*	$\bar{x}$	*rel* σ	*N*	$\bar{x}$	*rel* σ
Al	1	50	–	1	210	–	1	46.3	–	2	54.0	12.9
As	6	26.3	26	1	14.6	–	–	–	–	2	26.1	4.2
Be	–	–	–	–	–	–	–	–	–	1	4.3	–
Cd	10	8.2	59	–	–	–	–	–	–	1	7.0	–
Co	3	24.3	3.9	1	25.0	–	1	10.0	–	2	24.0	4.0
Cr	9	25.4	118	–	–	–	1	10.0	–	2	16.4	2.1
Cu	8	19.2	23	1	15.0	–	1	11.3	–	2	16.4	8.3
Mn	4	32.3	23	3	31.7	41	1	47.7	–	2	29.7	4.4
Ni	6	38.2	14	–	–	–	1	50.0	–	2	42.3	5.3
Pb	10	30.2	20	–	–	–	–	–	–	2	33.3	0.9
Se	1	22.3	–	1	10.0	–	–	–	–	1	9.0	–
Tl	2	22.8	27	–	–	–	–	–	–	2	17.7	4.0
V	3	79.0	16	1	75.0	–	1	70.0	–	2	79.9	2.4
Zn	1	181.6	–	5	129	31	2	167	7.7	2	152	9.1

*As: HG AAS
Others: F AAS

N = number of laboratory means
$\bar{x}$ = mean of laboratory means (all lab. means included)
rel σ = relative standard deviation of laboratory means (%)

The poor accuracy of the results obtained using ICP-AES might be due to the fact that the analyses were performed at a concentration range close to the detection limit of this technique.

The result obtained for Hg by means of Au-film analyzer differed significantly from the ones obtained using CVAAS (see Table 5).

.2 *(Continued)*

ET AAS			*Other AAS*ᶠ			*ICP-AES*			*ICP-MS*			*NAA*			*XRF*	
N	*x̄*	*rel σ*	*N*	*x̄*	*rel σ*	*N*	*x̄*	*rel σ*	*N*	*x̄*	*rel σ*	*N*	*x̄*	*rel σ*	*N*	*x̄*
–	–	–	2	139500	5	2	77950	72	–	–	–	–	–	–	2	13800
6	51.5	57	1	12.8	–	–	–	–	1	35.8	–	1	34.0	–	2	3
–	–	–	–	–	–	1	10.8	–	1	17,5	–	–	–	–	–	
8	0.87	30	1	0.64	–	–	–	–	1	1.0	–	–	–	–	–	
4	37.9	43	2	52.3	4.7	1	70.5	–	1	51.4	–	1	50.9	–	1	1
8	190	34	1	149	–	1	195	–	1	182	–	1	231	–	2	24
8	154	8.4	1	131	–	1	46.9	–	1	144	–	–	–	–	2	13
4	835	7.4	4	711	18	2	606	32	–	–	–	–	–	–	2	73
5	118	34	2	134	7.7	1	150	–	1	140	–	1	158	–	2	14
0	127	24	–	–	–	–	–	–	1	163	–	–	–	–	2	15
	–	–	1	2.60	–	–	–	–	1	11.5	–	–	–	–	–	
1	2.90	–	–	–	–	–	–	–	1	2.7	–	–	–	–	–	
4	332	10	1	307	–	1	342	–	1	279	–	–		–	1	27
3	253	18	4	245	25	2	171	59	1	276	–	–	–	–	2	23

3 *(Continued)*

ET AAS			*Other AAS*ᶠ			*ICP-AES*			*NAA*			*XRF*	
	x̄	*rel σ*	*N*	*x̄*	*rel σ*	*N*	*x̄*	*rel σ*	*N*	*x̄*	*rel σ*	*N*	*x̄*
–	–	–	2	20000	2.7	–	–	–	–	–	–	1	21000
4	7.0	73	–	–	–	–	–	–	1	4.2	–	–	–
6	0.12	47	–	–	–	–	–	–	–	–	–	–	–
2	5.7	56	1	8.2	–	1	10.4	–	1	9.9	–	1	2.0
4	38.5	45	1	29.1	–	1	31.6	–	1	31.7	–	1	19
5	23.1	35	1	22.2	–	–	–	–	–	–	–	1	10
2	89.9	0.9	3	87.6	3.9	–	–	–	–	–	–	1	49
3	20.7	19	1	21.9	–	1	24.5	–	1	25.0	–	1	2
6	15.3	39	–	–	–	–	–	–	–	–	–	1	9
1	0.90	–	–	–	–	–	–	–	–	–	–	–	–
2	38.3	48	–	-	–	1	54.4	–	–	–	–	1	52
	25.5	–	2	23.9	1.2	1	31.5	–	–	–	–	–	–

Table 4.4 *(Continued)*

	ET AAS			*Other AAS*^{a}			*ICP-AES*			*ICP-MS*		
	N	$\bar{x}$	*rel* σ	N	$\bar{x}$	*rel* σ	N	$\bar{x}$	*rel* σ	N	$\bar{x}$	*rel* σ
Al	–	–	–	2	2560	13	1	2220	–	–	–	–
As	3	2.4	57	1	0.88	–	–	–	–	1	1.3	–
Cd	3	0.11	42	–	–	–	–	–	–	1	0.09	–
Co	2	1.0	24	1	4.0	–	1	2.7	–	1	1.3	–
Cr	3	6.2	38	1	11.2	–	1	10.4	–	1	2.0	–
Cu	4	3.8	33	1	9.7	–	–	–	–	1	3.5	–
Mn	1	84.0	–	3	83.3	10	1	91.0	–	–	–	–
Ni	2	2.7	90	–	–	–	1	2.8	–	1	3.9	–
Pb	4	4.4	57	–	–	–	–	–	–	1	0.89	–
Se	–	–	–	1	8.35	–	–	–	–	1	14.5	–
Tl	1	0.80	–	–	–	–	–	–	–	1	0.11	–
V	1	6.7	–	1	13.1	–	1	8.3	–	1	3.5	–
Zn	–	–	–	3	13.0	43	1	10.8	–	1	14.3	–

Table 5 Results of the intercomparison for Hg grouped according to the analytical techniques used; concentration given as µg/l for HNO_3 (=A) and $K_2Cr_2O_7/HNO_3$ (=B) samples, and as µg/g for samples of fly ash (=C), coal (=D) and FGD (flue gas desulphurisation) product (=E).

	CVAAS			*Au-film Hg analyzer*		
	N	$\bar{x}$	*rel* σ	N	$\bar{x}$	*rel* σ
A	2	13.2	75	1	0.74	–
B	4	2.7	64	1	2.4	–
C	4	0.60	107	1	0.36	–
D	2	0.09	72	–	–	–
E	2	0.56	73	1	0.42	–

N = number of laboratory means
$\bar{x}$ = means of laboratory means (all lab. means included)
rel σ = relative standard deviation of laboratory means (%)

$K_2Cr_2O_7/HNO_3$ sample (sample B)

At first sight it seemed obvious that one much too low value was reported for Hg in the $K_2Cr_2O_7/HNO_3$ sample, but the rest of the results were in better agreement with each other. However, the relative standard deviation even after rejecting the outlier was approximately 40% (see Table 3), which cannot be considered satisfactory.

The mean of results obtained using cold vapour atomic absorption spectroscopy was very close to the value obtained using a Au-film Hg analyzer (see Table 5). Two of the three values that were closest to the median and the corrected mean were obtained using CVAAS, the third being obtained with a Au-film analyzer.

Fly ash (sample C)

The ranges of the concentration values for the solid fly ash sample were very large. However, when the outliers were omitted, the relative standard deviations were even smaller than in the case of the HNO_3 sample (Table 3). For Al, Cd, Co, Cu, Mn, Ni, Tl, V

Table 6.1 Results of the intercomparison (except for Hg) grouped according to the digestion techniques used; concentrations given as μg/g for samples of fly ash (Table 6.1), coal (Table 6.2) and FGD (flue gas desulphurisation) product (Table 6.3).

	Pressurized digestion							*Non-pressurized digestion*						
	Microwave			*Autoclave*		*Steam bath*		*Hot-plate heating*			*Room temperature*		*Ultrasonic*	
	N	$\bar{x}$	*rel σ*	*N*	$\bar{x}$	*N*	$\bar{x}$	*N*	$\bar{x}$	*rel σ*	*N*	$\bar{x}$	*N*	$\bar{x}$
Al	2	136700	4.5	1	21900	–	–	2	140400	6.4	–	–	–	–
As	4	50.6	80	1	27.7	1	12.8	1	31.0	–	1	35.8	1	68.1
Be	1	10.8	–	–	–	–	–	–	–	–	1	17.5	–	–
Cd	8	0.85	28	1	0.48	–	–	1	1.00	–	1	1.04	–	–
Co	5	52.4	21	1	14.1	1	50.5	–	–	–	1	51.4	–	–
Cr	8	197	15	1	44.3	1	247	1	172	–	1	182	–	–
Cu	8	151	11	1	46.9	1	143	1	143	–	1	144	–	–
Mn	7	769	16	1	414	1	805	2	774	4.4	–	–	–	–
Ni	6	139	8.5	1	49.0	1	127	–	–	–	1	140	–	–
Pb	8	140	5.1	1	46.3	1	107	1	130	–	1	163	–	–
Se	–	–	–	–	–	1	2.60	–	–	–	1	11.5	–	–
Tl	–	–	–	–	–	–	–	–	–	–	1	2.69	–	–
V	5	334	8.9	–	–	1	307	–	–	–	1	279	–	–
Zn	6	252	21	1	69.8	1	243	–	–	–	1	276	–	–

N = number of laboratory means
$\bar{x}$ = means of laboratory means (all lab. means included)
rel σ = relative standard deviation of laboratory means (%)

Table 6.2 *(Continued)*

	Pressurized digestion			*Non-pressurized digestion*	
	Microwave			*Hot-plate heating*	
	N	$\bar{x}$	*rel σ*	*N*	$\bar{x}$
Al	2	19500	7.1	1	19700
As	4	6.8	78	1	4.4
Cd	6	0.11	42	1	0.20
Co	4	7.5	39	–	–
Cr	6	36.0	38	1	26.5
Cu	6	23.0	32	1	24.3
Mn	5	86.0	6.7	1	89.3
Ni	5	21.7	15	–	–
Pb	6	15.1	38	1	20.3
Tl	1	0.9	–	–	–
V	3	43.7	37	–	–
Zn	4	26.2	14	–	–

and Zn the relative standard deviation was below 10%, while only for As, Be, Cr, Hg and Pb it was higher than 10%. For Hg, the magnitude of the relative standard deviation was 31%. Lower standard deviations compared to the HNO_3 sample seem a bit surprising, and they are not in agreement with the results reported by Abraham *et al.*[3]. They stated that the main problems in the determination of metals in ash arise from the digestion, because a digestion step may cause more sources of error due to sample loss, contamination, etc. In the work of Abraham *et al.*[3] the determination of As, Cd, Co, Cr, Fe, Ni, Pb and Zn in

Table 6.3 *(Continued).*

	Pressurized digestion					*Non-pressurized digestion*				
	Microwave			*Steam bath*		*Hot-plate heating*			*Room temperature*	
	N	$\bar{x}$	*rel σ*	*N*	$\bar{x}$	*N*	$\bar{x}$	*rel σ*	*N*	$\bar{x}$
Al	2	4590	56	–	–	2	2280	3.4	–	–
As	2	1.6	7.1	1	0.88	1	1.6	–	1	1.3
Be	–	–	–	–	–	–	–	–	1	0.05
Cd	3	0.13	64	–	–	1	0.16	–	1	0.09
Co	3	1.6	61	1	4.0	–	–	–	1	1.3
Cr	4	8.2	38	1	4.0	1	8.7	–	1	2.0
Cu	4	5.2	59	1	2.8	1	5.5	–	1	3.5
Mn	3	81.9	11	1	82.0	2	87.5	5.7	–	–
Ni	3	2.8	63	–	–	–	–	–	1	3.9
Pb	3	5.1	47	1	2.3	1	7.9	–	1	0.89
Se	–	–	–	1	8.4	–	–	–	1	14.5
Tl	1	0.8	–	–	–	–	–	–	1	0.11
V	2	7.5	15	1	13.1	–	–	–	1	3.5
Zn	3	12.4	46	1	12.5	–	–	–	1	14.3

Table 7 Results of the intercomparison for Hg grouped according to the digestion techniques used; concentrations given as μg/g for samples of fly ash (=C), coal (=D) and FGD (flue gas desulphurisation) product (=E).

	Pressurized digestion						*Non-pressurized*			
	Microwave		*Autoclave*		*Steam bath*		*Oxygen bomb*		*Refluxion*	
	N	$\bar{x}$	*N*	$\bar{x}$	*N*	$\bar{x}$	*N*	$\bar{x}$	*N*	$\bar{x}$
C	1	0.36	1	0.28	1	1.70	1	0.16	1	0.25
D	–	–	–	–	–	–	1	0.13	1	0.04
E	1	0.42	–	–	1	0.97	–	–	1	0.15

N = number of laboratory means
$\bar{x}$ = mean of laboratory means (in this case, $\bar{x}$ refers to the laboratory mean, i.e., N = 1)

ash samples in different laboratories was compared, while in the work of Abraham and Schlums[13] also Be, Cu, Hg, Mn, Sb, Se, V and a few other trace elements were included. It was observed that the determination of Cd, Co, Hg and Se results in the highest relative standard deviations. In the study reported by Ondov *et al.*[1], the determination of Cr, Mn, Ni and V using atomic spectrometric techniques gave the highest relative standard deviation for Cr. In our intercomparison, the highest relative standard deviations were observed for Hg and As. (The standard deviation reported for Be in Table 3 is also high, but it is based on only two laboratory results. Therefore, it cannot be compared to the standard deviations of the other elements.)

No analytical technique seemed superior to the others, as shown in the results in Table 4.2 The results of XRF and NAA were comparable to those of atomic spectroscopic methods. A few ICP-AES results differed from the other values, which is in agreement with the observations of Kimbrough and Wakakuwa[17] concerning element determination in solid samples: the use of ICP-AES gave more often too low and too high values. This, however, may be due to an inefficient sample digestion. The use of HGAAS resulted in a low value for As. This is in agreement with the statement of Kimbrough and Wakakuwa[17], who considered HGAAS as an inaccurate and irreproducible method for the analysis of acid digests of solids. In the case of mercury (see Table 5), the results obtained using CVAAS showed a high relative standard deviation, as indicated above.

Table 6.1 shows that not only microwave digestion but also digestion under conventional heating or even without any heating can give a good yield in the determination of trace elements. Surprisingly good results were obtained for the fly ash sample by the combination of digestion in a test tube at room temperature and ICP-MS analysis. This digestion method requires a relatively long time, but seems to be very efficient indeed. Autoclave heating seemed to result in poor values. This, however, is most likely due to the fact that HF was not used in the digestion. The composition of the acid mixture used for the digestion seemed to be more decisive than the heating. The role of HF is important, and a combination of HNO_3 and HF gave good yields, as reported already on the basis of our method development[5,6]. The use of HCl did not change the yield to any significant extent.

On the basis of the results obtained for Hg using different digestion methods (Table 7), it seems possible that in one case (steam bath heating) contamination has occurred. Other results are in reasonable agreement with each other.

Coal (sample D)

The results for coal (see Table 3) are fewer than for fly ash, which makes an overall comparison slightly difficult. On the basis of the ranges shown in Table 3, the scattering of the values seems better (i.e. smaller) than in the case of the fly ash sample. This is due to the fact that one laboratory that had reported evidently erroneous results for the fly ash sample did not take part in the analysis of the coal sample. The relative standard deviations for Al, Cr, Cu, Mn, V and Zn were below 10%, while for As, Cd, Co, Hg, Ni and Pb they were higher than 10%. For Hg, a high value of 72% was obtained. In the intercomparison reported by Ondov *et al.*[1], atomic spectroscopic analysis of Cr, Mn, Ni and V resulted in the highest relative standard deviation for Cr, i.e. a different behaviour from the one in our intercomparison was observed.

No laboratory using atomic spectroscopic methods reported values that systematically differed from the others (see Table 4.3). The results obtained by means of XRF were systematically lower (except for Al and V) than the medians and the mean values of the laboratory results. This is probably due to the higher detection limit of XRF compared to atomic spectroscopic techniques. NAA also seemed to suffer from the low concentrations. The agreement of values obtained by means of different atomic spectroscopic methods shows that the digestion methods used have probably been efficient enough. No significant difference was observed between microwave digestion and digestion in an open vessel under heating (see Table 6.2), although in the latter case a loss of easily volatile elements might have occurred. HF was used by all laboratories (see Table 1) in the digestion of the coal sample (except for Hg determination), which confirmed that all the silicate-based constituents were dissolved.

In the case of Hg, only two results were reported, and different digestion methods were employed (see Table 7). This made any comparison of the digestion methods impossible. Unfortunately, mercury was not determined after digestion in an open vessel. Therefore, the suitability of open vessel digestion for all types of trace elements cannot be evaluated well enough.

It is worth mentioning that the coal sample was not ashed by any laboratory before digestion in a microwave vessel or in an open container, although ashing is recommended, for instance, in ASTM standard D 3683–78, Standard Test Method for Trace Elements in Coal and Coke Ash by Atomic Absorption.

FGD product (sample E)

The trace element concentrations in the by-product from flue gas desulphurisation were lower than in the fly ash (C) and coal (D) samples, which is reflected by higher relative standard deviations than the ones obtained for samples C and D (see Table 3). For Mn the relative standard deviation was below 10%, and for Al it was below 20%, but for As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Se, Tl, V and Zn the deviations were higher than 20%.

Because of the low concentrations, XRF and NAA were not suitable for the analysis of this sample. No significant differences were observed between the results obtained using different atomic spectroscopic methods (see Table 4.4). The use of HGAAS resulted in a low value for As as observed also in the analysis of the coal sample. The results of CVAAS analysis (Table 5) were characterized by a high relative standard deviation, but the digestion may have had a strong influence on this.

The test-tube digestion employed by one laboratory seemed to give a poor yield (see Table 6.3) for a few metals (Cr, Pb, Tl, V). It is, however, difficult to conclude, whether this is because of the digestion or because of difficulties in the ICP-MS analysis. The results of samples A, C and D indicate that Cr, Pb, Tl and V can be reliably analyzed using ICP-MS. One possible source of error is the use of HF in the digestion: in the presence of Ca insoluble CaF_2 may be formed, causing an incomplete dissolution of the sample.

In the Hg analysis, non-pressurized digestion resulted in a lower value than pressurized digestion (see Table 7).

CONCLUSIONS

Of the analytical techniques used, ETAAS and ICP-MS seemed to be the best techniques considering the whole range of samples in this intercomparison. Although the use of these techniques most often requires digestion of the sample, their sensitivity made them best suited to trace element analysis of samples from a coal-fired power plant.

Microwave digestion was widely used for solid samples, but digestion at room temperature was also successfully applied. Microwave digestion is rapid and relatively safe. However, the composition of the acid mixture used in the digestion seemed to be more decisive than the method of heating.

It was surprising that the standard deviations for element concentrations in the HNO_3 sample were in many cases higher than for concentrations in the fly ash sample. Considering samples with very low trace element concentrations (i.e FGD product and in some cases also coal), the standard deviations were higher than for the HNO_3 and the fly ash samples.

On the basis of a comparison with other interlaboratory studies reported in the literature it can be concluded that the relative standard deviations obtained in this intercomparison were of the same order of magnitude as those reported by Abraham *et al.*[3] and Abraham and Schlums[13]. Also the standard deviations obtained using atomic spectroscopic methods in the study reported by Ondov *et al.*[1] were about the same as in this study. On the other hand, smaller relative standard deviations were obtained in the intercomparison reported by Griepink and Wilkinson[18], and also in the NAA intercomparison reported by Ondov[1].

Of the elements considered, Co, Ni and Pb (also Se and Tl, but they were analyzed by only few laboratories) showed the smallest relative standard deviations in the liquid HNO_3 sample, while Al, Cu, Mn, Ni, V and Zn showed the smallest relative standard deviation in solid samples on average. Regarding all the samples, Al, Cu, Mn and Ni seemed to be the easiest to determine with reasonable accuracy. The results for Hg showed the highest relative standard deviations. However, because of the low number of laboratory results reported for Hg, the values calculated for the standard deviations must be regarded as slightly uncertain. Satisfactory agreement between Hg results obtained using CVAAS and those obtained using a Au-film Hg analyzer was observed.

As indicated above, the number of analytical results reported for Be, Hg, Se and Tl were surprisingly low. Considering the importance of Be, Hg, Se and Tl, more analytical facilities should be available.

The results of this intercomparison suggest that further development of analytical methods for trace elements in power plant samples is urgently required.

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