As, Hg, and Se Flue Gas Sampling in a Coal-Fired Power Plant and Their Fate during Coal Combustion

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As, Hg, and Se are the most volatile elements in the flue gas from a coal-fired power plant. Significant amounts of these elements cause an undesired direct gaseous emission, which leads to a serious environmental health risk. The main focus of this study is to evaluate the possibility of simultaneous sampling of these volatile elements using an accurate official method for Hg (the most volatile element). A study of As, Hg, and Se emissions from a 1400 MW coal-fired power plant equipped with electrostatic precipitators (ESPs) was carried out for the combustion of a mixture of two types of coal. Simultaneous sampling of coal, bottom ash, fly ash, flue gas, and particles associated with the gas phase has been performed. Flue gas has been sampled by the Ontario Hydro Method Sampling Train, an ASTM method for Hg speciation. This sampling method was tested for As and Se sampling. As and Se determinations have been performed by HG-AAS, and Hg has been determined by CV-AAS. The results were used to examine the following: overall mass balances, relative distribution of these elements in the coal-fired power plant; As, Hg, and Se concentrations in coal and combustion residues; and predominant oxidation state for Hg in flue gas. The mass balances obtained for As, Hg, and Se were satisfactory in all cases; nevertheless, relative enrichment values in fly ash for As and Se were low; therefore, we concluded that As sampling in flue gas can be conducted by application of the Ontario Hydro Method; nevertheless Se released in the gas phase is not completely collected by this sampling train. Application of this sampling method allowed for performance of Hg speciation. The results indicated that Hg(II) was the predominant species in flue gas. It has also been proved that 24%, more than 99.8%, and 90% for As, Hg, and Se in the stack emissions, respectively, were in the gaseous phase.

Introduction

Coal contains most naturally occurring elements, at least in trace concentrations (*1*). The behavior of these elements during combustion depends on their volatility. Volatile elements such as Hg are likely to leave the boiler with the flue gases, whereas most of the nonvolatile elements, such as Mn, will be collected with the fly ash or bottom ash (*2*). As and Se present an intermediate volatility, and they will be emitted to the atmosphere to a large extent (*3*, *4*). However, the real behavior of these elements cannot be predicted in a laboratory, because of the fact that coal combustion is conditioned by high complexity processes, such as combustion temperatures, halogen species concentration (*5*), redox conditions (*6*), and interaction between different species (*7*).

To consider the environmental consequences of these emissions, disposal of accurate sampling methods is needed. At present, several methods for sampling and quantifying As, Hg, and Se in flue gas are used. These methods are classified in two main groups: methods based in solid sorbents and methods that employ impingers with oxidant solutions. The first group is easier to use and safer than the second one. However, salt blocking layer and preference canals formation on the sorbent surface is possible. Furthermore, it is found that the collection efficiency of Hg^0 decreases at an increasing temperature of flue gas (*8*, *9*). Thus, the use of an oxidant solution-based method is recommended. Hg^0 sampling is difficult because it vaporizes easily, even when present in solutions. Also, it diffuses readily through synthetic materials such as PVC or Teflon (*9*). To avoid these problems, metallic Hg has to be converted into a stable form such as Hg(II). Therefore, some aqueous oxidative solutions were tested by Shendikar et al. (*10*) such as 10% H_2O_2, acidified 10% H_2O_2, 0.2 M $(NH_4)_2S_2O_8$, 0.2 M $(NH_4)_2S_2O_8$ + 0.025 M $AgNO_3$, and 1.5% $KMnO_4$ in 10% H_2SO_4. Good collection efficiencies for Hg^0 by using more than one impinger were exclusively obtained by the two last methods. $K_2Cr_2O_7$ (4%) in 4 M HNO_3 solution was tested to sample Hg in flue gas of a coal fired power plant by Meij (*11*). Yokoyama et al. (*12*) employed $KMnO_4/H_2SO_4$ for Hg sampling in a Japanese coal fired power plant. Furthermore, several impinger-based methods have been used for other trace elements sampling, such as As and Se, in emissions of coal fired power plants. Andren et al. (*13*) reported an impinger train consisting of two 10% Na_2CO_3 solutions, and they obtained a Se mass balance of 87%. Aunela-Tapola et al. (*14*) employed bottles containing 38% HNO_3 for the collection of several gaseous elements in two coal fired power plants, obtaining mass balances of 125% and 88% for As and Hg, respectively; no details concerning Se were given.

In this work, the application of the Ontario Hydro Method Sampling Train, an ASTM method for the speciation of Hg in stacks of coal-fired stationary sources (*15*), for sampling As and Se has been studied. For this purpose, samples were collected from all the relevant input and output coal fired power plant streams: coal, bottom ash, fly ash, flue gas, and particles associated with the gas phase. The microwave acid extraction procedure has been used for solid samples solution. Determination of As and Se concentrations in collected samples has been performed by Hydride Generation-Absorption Atomic Spectroscopy (HG-AAS). Hg has been determined by Cold Vapor-Absorption Atomic Spectroscopy (CV-AAS). Due to using oxidant solutions to As, Hg, and Se sampling from flue gas, the presence of As(V) and Se(VI) is possible. It is known that in the hydride generation process As(V) and Se(VI) show lower sensitivity than As(III) and Se(IV) (*16*). Therefore, As(V) and Se(VI) must be reduced to the trivalent and tetravalent states, respectively, before the hydride generation step. For this purpose, hydroxylamine hydrochloride has been used. Finally, overall mass balances have been performed to determine the efficiency of the Ontario Hydro Method for As and Se sampling.

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TABLE 1. Proximate and Ultimate Analysis of the Burned Mixture of Coals during Sampling

	sampling 1	sampling 2	sampling 3
gross calorific value (Kcal kg coal^{-1})	4.427	2.892	2.785
specific consumption (Kcal kWh^{-1})	2.247	2.347	2.364
moisture (wt %)	28.4	33.5	33.9
ash (wt %)	27.3	22.3	22.8
carbon (wt %)	29.3	29.8	29.1
hydrogen (wt %)	2.41	2.43	2.37
nitrogen (wt %)	0.47	0.35	0.35
sulfur (wt %)	2.07	2.14	2.28
oxygen (wt %)	10.1	9.50	9.18
chlorine mg/kg	45.6	39.8	37.8

TABLE 2. Spectrometer Operating Conditions

	λ (nm)	slit width (nm)	intensity current (mA)
As	193.7	0.7	10
Hg	253.7	0.7	7
Se	196.0	2.0	16

Power Plant Data. *As Pontes* power plant (Northwest of Spain) has four independent pulverized coal power generation units (GI-GIV), each with 350 MW installed capacity and equipped with tangential burners. The stack has four liners, one for each unit, and each liner was sampled independently. The power plant burns a 50%-thermic base mixture of lignite coming from a nearby mine and sub-bituminous coal which is mostly imported from Wyoming (U.S.A.) and Indonesia. Proximate and ultimate analyses of the burned mixture of coals are shown in Table 1. Due to high sulfur concentration in lignite, imported sub-bituminous coal is used to control SO_2 emissions.

Experimental Section

Instrumentation. A MLS 1200 Milestone microwave oven (Sorisole, Italy), programmable for time and microwave power, was used for the element extraction from the samples. A batch mode system Perkin-Elmer MHS-10 hydride generator coupled with a Perkin-Elmer Model 2380 atomic absorption spectrometer equipped with hollow cathode lamps as radiation sources was used for measurements. The peak height measurements mode was used throughout. The spectrometer operating conditions are shown in Table 2.

Reagents and Standard Solutions. KCl for analysis (Merck, Darmstad, Germany), KMnO$_4$ purissime (Probus, Barcelona, Spain), 70% HNO$_3$ for analysis (<0.1 μg L^{-1} Hg and <2 μg L^{-1} As) (Baker, Phillipsburg, PA), 96% H$_2$SO$_4$ (<0.01 μg L^{-1} As, <0.0001% heavy metals), and H$_2$O$_2$ for analysis (Panreac, Barcelona, Spain) were employed for As, Hg, and Se flue gas sampling. As(III) chloride, Hg(II) chloride, and Se(VI) chloride stock standard solutions of 1000 mg L^{-1} were used. HNO$_3$ (70%), 38% HCl (<0.01 μg L^{-1} As, 0.0001% Heavy Metals), 51% HF (<0.01 μg L^{-1} As and <0.001 μg L^{-1} Hg) (Baker), and HBO$_3$ (Aldrich, Milwaukee, USA) were used for sample extraction. NaBH$_4$ (Aldrich) dissolved in 0.5% (w/v) NaOH (0.00004% As and 0.0005% Heavy Metals) (Panreac) was used as the reducing solution, and H$_3$NOHCl purissime (Fluka, St. Louis, U.S.A.) was used for As and Se prereducing. These solutions were prepared daily. Whatman GF/A filters were employed particles associated with the gas-phase sampling. NIST-1632b trace elements in coal (bituminous), NIST-1635 trace elements in coal (sub-bituminous), and NIST-1633b trace elements in fly ash (U.S Department of Commerce

National Institute of Standards and Technology, Gaithersburg, MD) were employed to evaluate the accuracy of the analytical method. Acetylene C-26 was used for quartz cell heating for As and Se determination. Argon N-50 purity (99.999%) (Carburos Metálicos, Barcelona, Spain) was used to transfer the vapor to the quartz cell.

Sampling Strategy. In this study, real samples coming from a pulverizing 1400 MW coal-fired power plant have been used. The industrial size of this power plant justifies the limited number of experiments because sampling procedures disturb the usual operation of its power generation units.

Solid Samples. Sampling of solid samples was carried out simultaneously to the sampling of gaseous emissions. The conveyor belt must run continuously during sampling (30 min). The coal, bottom ash, and fly ash masses sampled were 250, 100, and 40 kg, respectively. To collect representative samples, these must be quartered and the particle size reduced until obtaining 500 g of each type of sample. Fly ash came from ESPs.

Gaseous Samples. Although EPA 108 Method and EPA 29 are not adequate methods for mercury speciation, these multielemental sampling trains employ two impingers with H$_2$O in order to collect several elements as As and Se (*17*). Therefore it is predicted that these elements will be captured in aqueous solution of KCl. As, Hg, and Se in flue gas were collected in the sampling stage placed at a height of 215 m in the stack, under isokinetic conditions using the Ontario Hydro Method Sampling Train. Figure 1 shows a scheme of this sampling train. One m^3 of flue gas was sampled for a period of 1 h. The sample is withdrawn from the flue gas stream isokinetically through a filter system, maintained at 120 °C, followed by a series of impingers in an ice bath. Particles associated with the gas phase are collected in a filter placed in a heated area (Figure 1) of the sampling train. Oxidized Hg is collected in impingers containing a chilled aqueous 0.1 M KCl solution. In the other hand, elemental Hg is collected in subsequent impingers (one impinger containing a chilled solution of 5% HNO$_3$ in 10% H$_2$O$_2$ and three impingers containing chilled solutions of 4% KMnO$_4$ in 10% H$_2$SO$_4$). Flue gas sampling conditions are shown in Table 3. At our sampling conditions (sampling temperature 400 K), the major species predicted for As and Se are SeO$_{2(g)}$, H$_2$Se$_{(g)}$, and AsO$_{(g)}$ (*7*) (Cl available is low). Nevertheless the affinities of trace elements to chlorine (to form chlorides) are greatly affected by the possible formation of a large quantity of HCl$_{(g)}$ in the flue gas. Furthermore, there is an influence of the ratio H/Cl on the metal chlorides formation. When this ratio is low, more Cl is available for reaction with As, Hg, and Se. Therefore these results of thermodynamics calculations will be altered in real situations, where gas–solid reactions are kinetically controlled. The Cl-containing components in coal may react with several trace elements before they are transformed into HCl. Thus the amount of HCl in a real flue gas from a coal combustor may be much less than thermodynamically predicted. When Cl content in coal is high, AsCl$_{3(g)}$ and Se$_2$Cl$_{2(g)}$ are the major species predicted for As and Se in flue gas (*7*), and the presence of Cl ions in 0.1 M KCl impinger might have a negative influence in solubility of As and Se chlorides.

Microwave Acid Extraction for Solid Samples. The microwave acid extraction procedure employed for solid samples has been described by Moreda-Piñeiro et al. (*18*). The amount of coal (0.4 g) (previously dried) or 0.2 g of bottom ash or fly ash was placed into the PTFE bombs; the aqua regia mixture (AR), 6 mL and 2 mL of HCl(c) and HNO$_3$(c), respectively, was added; and the mixture was subjected to microwave energy (Tables 4 and 5). For the analysis of particles associated with the gas phase, a similar procedure was employed for flue gas filter digestion, nevertheless 4 mL
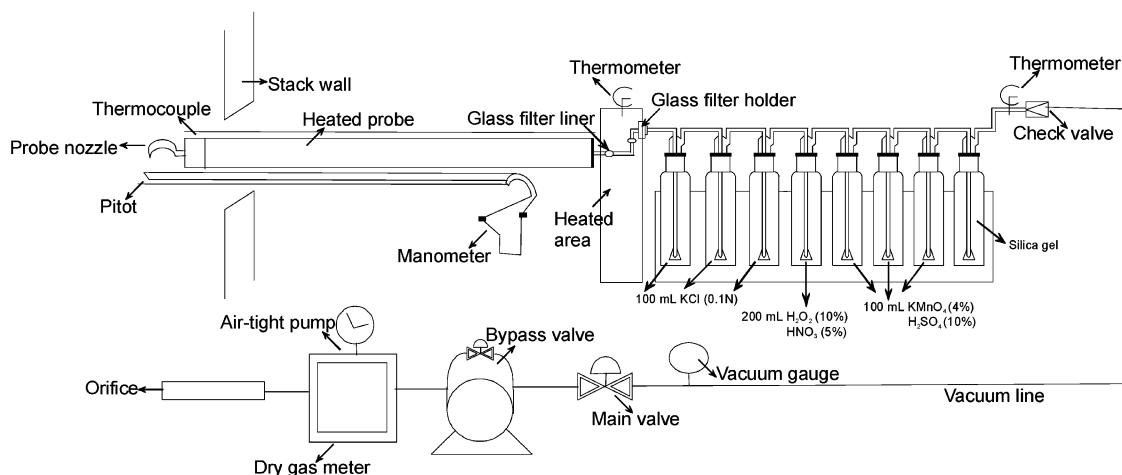
FIGURE 1. The Ontario Hydro Method Sampling Train.

TABLE 3. Flue Gas Sampling Conditions

	sampling 1	sampling 2	sampling 3
volume (m^3)	0.98	1.13	0.90
sampling time (h)	1	1	1
mean temperature (°C)	175	169	169
mean pressure (mmHg)	714	712	712
O$_2$ (%)	8.3	7.4	7.0
date	11/21/01	06/01/01	06/01/01

of HF was added in order to dissolve glass fibers of filters. HBO$_3$ (0.2 g) was added to neutralize the excess of HF. After microwave extraction, the bombs were cooled in a water bath. Then the acid liquid phase was filtered using Whatman No. 40 paper filter (Whatman International Ltd, Maidstone, UK). The solutions were made up to a 25-mL volume, for all types of samples, with ultrapure water, and then they were stored in polyethylene bottles at 4 °C before measurements.

CV/HG-AAS Procedure. Five milliters of impingers solution and 5 mL of acid extract from coal, bottom ash, fly ash, and particles associated with the gas-phase samples, on each case, were placed in the reaction vessels. HCl (3.0 mL, 37% m/v) was added for As and Se determination and 0.7 mL for Hg determination and made up to a 10-mL volume with ultrapure water. To get As(V) and Se(VI) prereducing, 2.5 mL of H$_3$NOHCl (60% w/v) was added to flue gas samples collected in H$_2$O$_2$/HNO$_3$ and KMnO$_4$/H$_2$SO$_4$ impingers. Then, an adequate volume ($\sim$6 mL) of NaBH$_4$ (3% m/v) was added to generate volatile forms of As (H$_3$As), Se (H$_4$Se), and Hg(Hg^0); then they were transferred with argon gas (argon flow rate of 1.1 mL min^{-1}) to the quartz cell. For As and Se determination, the quartz cell was heated with an acetylene/air flame; for Hg determination, a glass wool column was used to dry the cold vapor, avoiding water condensation into the quartz cell. Hydride and cold vapor generation conditions are shown in Table 6. Limits of detection (LOD) and quantification (LOQ) obtained under spectrometer operating conditions are shown in Table 7. Reagents blanks were analyzed obtaining values lower than LOD.

Results and Discussion

Optimization of Operating Conditions. *Acid Microwave Extraction Analytical Recovery.* Acid extraction induced by microwave energy was used in order to extract the trace metal content in the solid samples studied. The reference materials NIST-1632b (bituminous) and NIST-1635 (sub-bituminous) trace elements in coal and NIST-1633b trace elements in fly ash were analyzed in order to assess the accuracy of the employed method; in Table 8 accuracy values are shown.

Adequate analytical recoveries (98%) for coal and fly ash reference materials by using aqua regia were obtained for As. Similar analytical recovery (105%) was achieved for Se. For Hg, adequate analytical recovery was achieved (70% and 95% for coal and fly ash, respectively). It must be taken into account that the Hg analytical recoveries were calculated using an information Hg value (a value given by NIST as additional information but not certified) offered by the NIST-1632b coal reference material. Thus, it may be assumed that there are no As, Hg, and Se losses during extraction procedure. Acid microwave extraction procedure blanks were made obtaining values lower than LOD.

Chlorine Concentrations and its Relative Distribution. Chlorine is a very volatile species at power plant conditions, and it is assumed that it will be emitted mainly in the gas phase (*19*). Cl concentrations found in coal can be considered low (*20−23*). In this study, volatility found for Cl is in agreement with the literature (*24−26*). In Tables 9 and 10 concentrations and mass balance for this element are shown, respectively. The enrichment factor was not included due to its high volatility.

As, Hg, and Se Concentrations in Coal, Bottom Ash, Fly Ash, Flue Gas, and Particles Associated with the Gas Phase. As, Hg, and Se concentrations found in the different samples studied are shown in Table 9, and the range of concentrations of each element is given with the mean value ($N = 3$). As and Hg concentrations in coal are in agreement with the ranges of concentration reported by several authors (*1, 24*), whereas Se concentrations found are larger in all cases. On the other hand, concentrations of these elements in coal combustion products of this power plant are in agreement with values reported by López-Vilariño et al. (*27*).

As, Hg, Se, and Cl Mass Balances. To evaluate efficiency of the Ontario Hydro Method Sampling Train for As, Hg, and Se sampling in flue gas of a coal fired power plant, mass balances were calculated. For this reason, a comparison was established for each compound as follows

$$Cc \times Fc = Cs \times Fs + Ca \times Fa + Cg \times Fg \qquad (1)$$

where Cc, Cs, Ca, and Cg represent the concentration, expressed in μg kg^{-1} or μg m^{-3}, of each compound in coal, bottom ash, fly ash, and flue gas, respectively. Fc, Fs, Fa, and Fg are the input/output rates for each element in coal, bottom ash, fly ash, and flue gas, respectively. These rates are expressed in kg kgcoal^{-1}, except for Fg, which is expressed in m^3 kgcoal^{-1}.

$$Fs = \% \text{ mineral residue} \times 0.15$$

$$Fa = \% \text{ mineral residue} \times 0.85$$

TABLE 4. Microwave-Acid Extraction Program

samples	acid mixture	microwave program
coal fly ash bottom ash	aqua Regia (AR)	5 min (300 W) → 3 min (650 W) → 3 min (450 W) → → 3 min (0 W)
particles associated with the gas phase (filter)	aqua regia + HF (AR + HF)	5 min (300 W) → 3 min (650 W) → 3 min (450 W) → → 3 min (0 W) bombs were cooled, 1 g of boric acid was added 3 min (450 W) → 3 min (0 W)

TABLE 5. Acid Extraction Conditions

sample	mass (g)	mixture acid	volume (mL)	final volume (mL)
coal	0.4	AR	6 mL HCl + 2 mL HNO$_3$ + 1 mL H$_2$O	25
bottom ash	0.2	AR	6 mL HCl + 2 mL HNO$_3$ + 1 mL H$_2$O	25
fly ash	0.2	AR	6 mL HCl + 2 mL HNO$_3$ + 1 mL H$_2$O	25
particle associated to gas phase	filter	AR + HF	6 mL HCl + 2 mL HNO$_3$ + 4 mL HF + 1 mL H$_2$O	25

TABLE 6. Hydride/Cold Vapor Generation Conditions

	vol. HCl (mL)	acetylene/ air	concn HCl (M)	vol. NaBH$_4$ (mL)	concn NaBH$_4$/% (w/v)	Ar flow rate (mL min^{-1})
As	3	0.5	3.1	6	1.5	1.1
Hg	2		2.1	6	1.5	1.1
Se	3	0.5	3.1	6	1.5	1.1

TABLE 7. LOD and LOQ Relative to Mass Sample Obtained for As, Hg, and Se ($N = 3$)

	coal (mg kg^{-1})		bottom ash (mg kg^{-1})		fly ash (mg kg^{-1})		flue gas (μg m^{-3})		particles associated with the gas phase (μg m^{-3})	
	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ
As	0.10	0.35	0.20	0.67	0.17	0.60	0.42	1.4	0.07	0.23
Hg	0.014	0.050	0.040	0.13	0.026	0.090	0.245	0.810	0.030	0.10
Se	0.13	0.43	0.25	0.83	0.19	0.63	0.39	1.3	0.04	0.13

In these equations it is assumed that 15% of the mineral residues generated in coal combustion is present in bottom ash form and 85% in fly ash form. These values are calculated from coal power plant historical data.

On the other hand

$$Cc \times Fc = \mu g \text{ of element in coal by kg of burned coal}$$

$$Cs \times Fs = \\ \mu g \text{ of element in bottom ash by kg of burned coal}$$

$$Ca \times Fa = \mu g \text{ of element in fly ash by kg of burned coal}$$

Finally, Fg can be calculated by the following multiplication: Fg is the total gas emission value (m^3 kg coal^{-1}). Then

$$Cg \times Fg = \\ \mu g \text{ of element in flue gas by kg of burned coal}$$

Once all factors of eq 1 were known, As, Hg, Se, and Cl mass balances were calculated for coal, bottom ash, fly ash, and flue gas. Particles associated with the gas phase were included in As, Hg, and Se flue gas mass balances.

The mass balances are shown in Table 10. Acceptable results were obtained; the values of these were 67%, 113%, and 68% for As, Hg, and Se, respectively ($N = 3$).

These results improve earlier studies. Yokoyama et al. (12) reported values of 138% for adjustments of Hg mass

balances in a Japanese coal fired power plant, employing KMnO$_4$/H$_2$SO$_4$ for Hg sampling. Senior et al. (28) studied several coals by Neutron Activation Analysis, obtaining mass balances of 29% for As and 190% for Se in American coals.

Relative Distribution of As, Hg, and Se in the Power Plant. During coal combustion, trace elements bound in coal are distributed into bottom ash, fly ash, and flue gas. They are broadly classified into three groups depending on their partitioning behavior during coal combustion (1): Class I: They are readily incorporated into the bottom ash. In this group Mn and U are included. Class II: Poorly incorporated into bottom ash, they are concentrated in the fly ash. In this group As, B, Cd, Pb, Sb, Se, and Zn are included. Class III: They remain essentially in the gas phase. In this group Hg is included.

Results are in agreement with this study. Hg is more volatile than As and Se, and, therefore, the proportion of this element in the gas phase is larger (76.5%, 1.2%, and 3.7%, respectively). As and Se are mainly condensed in fly ash (97.7% and 90.3%, respectively).

As and Se Relative Enrichment Factor (R.E.). The relative enrichment factor expresses the element behavior, during coal combustion, in the different streams of the coal power plant. Generally, volatile elements tend to condense in fly ash, producing an enrichment of these elements in this power plant stream. Therefore, elements of class II have a R.E.(fly ash) > 1. On the contrary, elements of class I tend to condense in bottom ash due to these elements from highly refractory compounds. In this case R.E.(bottom ash) > 1. Meij et al. (26) established an expression for R.E.

$$R.E.(\text{fly ash}) = [(Cza)/(Czc)] \times \% \text{ mineral residue in coal} \tag{2}$$

$$R.E.(\text{bottom ash}) = [(Czs)/(Czc)] \times \\ \% \text{ mineral residue in coal} \tag{3}$$

$$z = \text{As or Se}$$

where Cza is the concentration of z in fly ash, Czs is the concentration of z in bottom ash, and Czc is the concentration of z in coal.

As and Se enrichment factors in fly ash and bottom ash are shown in Table 11. R.E. for fly ash is larger than R.E. for bottom ash. It is due to the high affinity of these elements for the smallest particles (fly ash) (12, 27); furthermore, a phenomenon of vaporization-condensation may be considered. However, in this study fly ash relative enrichment for As and Se was <1 in all cases. This fact could be due to

TABLE 8. Accuracy of Method Obtained for Different Reference Materials (*N* = 11)

| | NIST-1635 coal (sub-bituminous) | | NIST-1632b (bituminous coal) | | NIST-1633b (fly ash) | |
	certified value (mg kg^{-1})	found value (mg kg^{-1})	certified value (mg kg^{-1})	found value (mg kg^{-1})	certified value (mg kg^{-1})	found value (mg kg^{-1})
As	0.42 ± 0.01	0.41 ± 0.01	*a*	*b*	136.2 ± 2.6	137.4 ± 5.0
Hg	*a*	*b*	0.10*c*	0.07 ± 0.01	0.141 ± 0.019	0.134 ± 0.01
Se	*b*	*b*	1.29 ± 0.11	1.20 ± 0.1	10.26 ± 0.17	10.37 ± 0.2

a No−certified value. *b* Not determined. *c* Information value.

TABLE 9. As, Hg, Se, and Cl Concentrations in Coal and Its Combustion Products

	coal (mg kg^{-1})	bottom ash (mg kg^{-1})	fly ash (mg kg^{-1})	flue gas (μg m^{-3})	particle associated to gas phase (μg m^{-3})
As	43.9−47.6 45.7	7.1−12.1 10.4	145.4−218.0 169.6	16.2−20.9 18.4	45.4−56.9 53.0
Hg	0.15−0.17 0.16	<LOD	0.07−0.09 0.08	19.1−21.8 20.5	<LOD
Se	10.8−12.3 11.5	3.3−9.7 7.6	32.4−37.9 36.1	47.5−68.7 58.5	4.5−7.4 5.5
Cl	37.8−45.6 41.1	20.9−32.6 23.0	16.8−28.0 24.9	4.8−11.5 6.8	*a*

a Not analyzed.

TABLE 10. As, Hg, Se, and Cl Mass Balances

		bottom ash % total	fly ash % total	flue gas % total	mass balance %
As	sample 1	0.5	97.6	1.9	79.1
	sample 2	1.4	97.6	1.0	64.4
	sample 3	1.4	97.9	0.7	60.2
Hg	sample 1	0.1	21.8	78.1	115.0
	sample 2	0.3	19.4	80.3	113.2
	sample 3	0.4	28.4	71.2	112.9
Se	sample 1	9.8	87.2	3.0	66.8
	sample 2	4.1	91.8	4.1	72.6
	sample 3	4.2	91.9	3.9	63.4
Cl	sample 1	*a*	*a*	*a*	*a*
	sample 2	*a*	*a*	*a*	*a*
	sample 3	2	13	85	109

a Needed data not available.

TABLE 11. As and Se Relative Enrichment Factor in Bottom Ash and Fly Ash

		sample 1	sample 2	sample 3
As	R.E. bottom ash	0.03	0.06	0.06
	R.E. fly ash	0.90	0.74	0.68
Se	R.E. bottom ash	0.07	0.20	0.17
	R.E. fly ash	0.68	0.78	0.69

little error estimation on the As and Se concentrations in the different types of samples analyzed. The high number of factors involved on the mass balances originate that the summation of these little deviations on the As and Se concentrations may give error estimations around 15%.

On the other hand, R.E. (fly ash) for Se < 1 was referenced in the literature (*29*), and this fact is attributed to the releasing of Se in the gas phase is around 20−30% (*20−34*). In our study, Se released in the gas phase (Table 11) is 4%. Thus, we can conclude that Se in flue gas is not efficiently collected using the Ontario Hydro Method Sampling Train. Neverthe-less, the percentage of As released in our study (1%) is in agreement with the literature (*27, 30−34*). An explanation of these results could be the low solubility of Se species (H$_2$Se

TABLE 12. Hg Speciation in Flue Gas

	sample 1	sample 2	sample 3
% Hg(II)	60.9	64.0	58.3
% Hg^0	39.1	36.0	41.7

and SeO$_2$) in KCl solution (polar solution). This effect is attenuate for AsO due to its higher solubility at these conditions. When Cl content in coal is high, AsCl$_3$ and SeCl$_2$ are the major species predicted, and the presence of Cl ion in KCl impingers prevents a good collection of these spe-cies. Thus we conclude that the Ontario Hydro Method Sampling Train can be an adequate method for As sampling when the ratio H/Cl is high (Cl content in coal is low) because at these conditions the major species for As and Se are not chlorides. In this study, chlorine content in coal can be considered low (*35−37*), and As and Se chlorides formation is very limited.

Hg Speciation in Flue Gas. One of the well-known characteristics of Hg(II) is that, unlike metallic Hg, it is easily soluble in water and even more so in KCl solution. The differences between the two-Hg species in terms of their solubility can be used as a basis for effective speciation. The Ontario Hydro Method application allows studying Hg speciation in flue gas. The different oxidation states from As and Se have similar solubility. However, Hg(II) will be captured in KCl impingers, while Hg^0 will be captured in H$_2$O$_2$/HNO$_3$−KMnO$_4$/H$_2$SO$_4$ impingers by oxidation to Hg(II). Chloride concentration (∼0.04 wt %) found in burned coal is low according to values reported by Carpi (*5*) (0.11% was considered a low concentration of chlorine by this author). Results of Hg speciation are shown in Table 12; particles-bound Hg was not included because it means less than 0.02% of the total emitted Hg. Hg(II) is the predominant Hg species in flue gas (∼60%). At flue gas sampling temperature (∼400 K), thermodynamic equilibrium predicts that the major species for this element under these oxidizing conditions is HgCl$_{2(g)}$ (*7*). Nevertheless Senior et al. (*19*) concluded that the assumption of equilibrium for mercury species in coal combustion flue gas is not valid. Consequently, the ratio Hg(II)/Hg^0 is highly variable de-pending on the coal combustion conditions (*38, 39*). Hg(II) proportion found in the present study can be considered high taking into account the low concentration of chlorine in coal. Nevertheless, many other parameters (temperature, % oxidant species in flue gas, etc.) must be considered in order to understand the behavior of Hg in a coal fired power plant.

As, Hg, and Se in Particles Associated with the Gas Phase. Despite the high efficiency of electrostatic precipitators to removal particles, a small portion of this comes to stack, mainly smallest particles (<0.3 μm) (*40*). These particles act as a condensation nucleus for several elements such as As, Hg, and Se. Hg is more volatile than As and Se; thus, a larger proportion of this metal is released in the gas phase than As or Se. Yokoyama et al. (*12*) reported that more than 99.5% of the Hg in the stack emissions were in gaseous form, and

the proportion in particles form was extremely low, Miller et al. (*41*) reported that Hg is completely volatilized during the combustion of coal, and Kaakinen et al. (*42*) found that about 90% of the Hg in a pulverized coal furnace appears as vapor in the flue gas. Andren et al. (*13*) reported that 93% of the Se emitted in flue gas of a coal-fired power plant existed in the gas phase. Results found in the present study are in agreement with relative volatility of these elements; >99.8% of the Hg in stack leaves it in the gas phase. Ninety percent and 24% of Se and As in stack, respectively, leave it in the gas phase too. These results were calculated from values reported in Table 9.

Acknowledgments

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