Volatile Metal Species in Coal Combustion Flue Gas

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Volatile Metal Species in Coal Combustion Flue Gas

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Metals are released in effluents of most of combustion processes and are under intensive regulations. To improve our knowledge of combustion process and their resulting emission of metal to the atmosphere, we have developed an approach allowing us to distinguish between gaseous and particulate state of the elements emitted. This study was conducted on the emission of volatile metallic species emitted from a coal combustion plant where low/medium volatile coal (high-grade ash) was burnt. The occurrence of volatile metal species emission was investigated by cryofocusing sampling procedure and detection using low-temperature packed-column gas chromatography coupled with inductively coupled plasma−mass spectrometry as multielement detector (LT-GC/ICP−MS). Samples were collected in the stack through the routine heated sampling line of the plant downstream from the electrostatic precipitator. The gaseous samples were trapped with a cryogenic device and analyzed by LT-GC/ICP−MS. During the combustion process, seven volatile metal species were detected: three for Se, one for Sn, two for Hg, and one for Cu. Thermodynamic calculations and experimental metal species spiking experiments suggest that the following volatile metal species are present in the flue gas during the combustion process: $COSe$, $CSSe$, CSe_2, $SeCl_2$, Hg^0, $HgCl_2$, $CuO−CuSO_4$ or $CuSO_4 \cdot H_2O$, and SnO_2 or $SnCl_2$. The quantification of volatile species was compared to results traditionally obtained by standardized impinger-based sampling and analysis techniques recommended for flue gas combustion characterization. Results showed that concentrations obtained with the standard impinger approach are at least 10 times higher than obtained with cryogenic sampling, suggesting the trapping microaerosols in the traditional methods. Total metal concentrations in particles are also reported and discussed.

Introduction

The world's coal reserve is the most abundant fossil energy source. Assuming that the production remains constant, coal mining would continue for at least 250 yr, whereas oil reserves will last for approximately 45 yr, and natural gas will last for 65 yr. Therefore, there is still a continuous strong interest in coal science following the series of papers from the International Conferences on Coal Sciences between 1981 and 1997 (*1*).

The major use of coal is the generation of power through combustion. Coal analyses have demonstrated that several elements (Pb, Hg, As, Cu, Zn, Cd, Se, Sn, Ba, Ce, Cs, Mn, etc.) are presently ubiquitous in the matrix in concentrations less than 0.01 wt % (*2−5*). During the combustion process, coal trace elements are released and redistributed in the bottom ash, the fly ash, and the gaseous phase (*3*). Flue gas is filtered to remove particulate emissions. Most effective electrostatic precipitators or fabric filters usually installed can remove more than 99% of the fly ash, but fine particles of less than 10 μm in diameter as well as all gaseous species are emitted to the atmosphere with the outgoing stack gas (*4*). Studies have demonstrated that, in terms of volatility, these elements can be subdivided into three groups. Hg is an example for the most volatile element; As, Cd, Cu, Pb, Se, and Zn are considered to be semivolatile elements; and Ba, Ce, Cs, and Mn represent the least volatile elements (*3*). In the case of mercury, the coal combustion in electric power plant and industrial utilities is the dominant source in eastern Europe (40% during 1990−1992) (*6*).

The phenomena involved in metal partitioning are important because they determine how and where trace elements are emitted. Linak and Wendt (*5*) reviewed mechanisms governing the fate of trace elements during coal combustion and showed possible routes along which trace metals are partitioned into vapor, submicron, and supermicron particles. Concerning the occurrence of toxic metals in coal combustion systems, the formation of ash and the transformation of mineral matter during combustion have been subject to intensive studies by numerous research groups (*7−10*), whereas only few articles only deal with the characterization of volatile metal compounds in the gas phase. Apart from SO_2, NO, and CO_2, which are highly abundant gaseous components as compared to trace metals or metalloids, only mercury species (*11−14*) have been determined in coal combustion flue gas as a gaseous species. In a critical review, Galbreath and Zygarlicke (*15*) compared different measurement techniques applied for mercury speciation. They stressed that the species determination performed by the described methods (e.g., denuder, sorbent, diffusion screen) is an operational classification rather than a true species identification. They concluded that the main limitation of the described methods is that the chemical forms of the elements are not determined independently from each other. More recently, Laudal et al. (*16*) described a speciation bench-scale experiment where they used a impinger-based mercury sampling technique (e.g., Ontario Hydro Method). They observed that when Cl_2 is present in the sampled flue gas, all impinger-based methods detected and measured a statistically significant amount of Hg^{2+} even though only Hg^0 was added, suggesting no specificity of the technique used and a probable reaction between Cl_2 and Hg^0 to form $HgCl_2$. Additional information on species that interfere with impinger methods can be found elsewhere (*17*).

Furthermore, for standardized techniques used for the collection of particles and gaseous compounds (*18−21*), the use of filtration and chemical absorption in solutions with impinger methods do not allow the discrimination between metal bond to submicron particulate matter passing the factory filters and the genuine gaseous metal species illustrating the weakness of the method (*22*).

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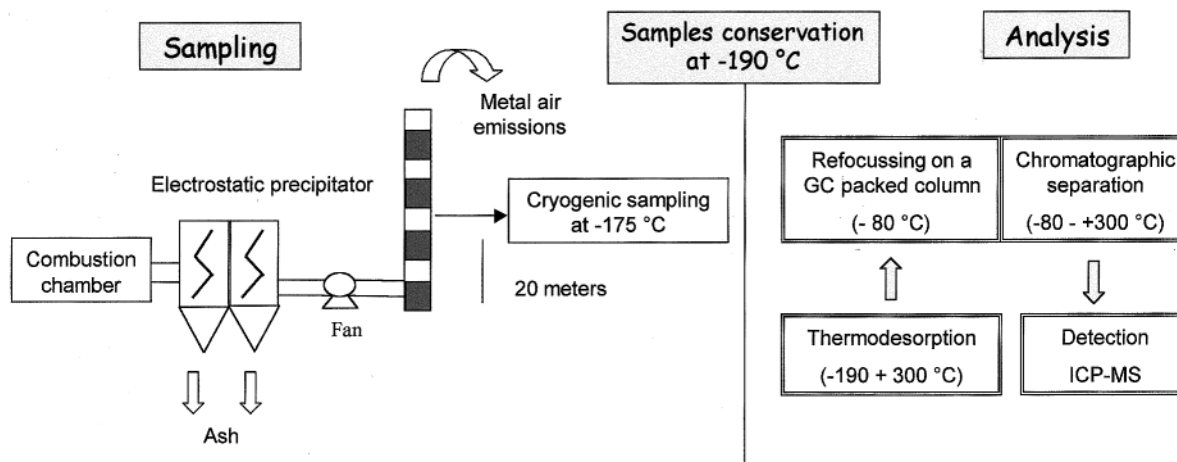
FIGURE 1. Schematic overview of the process unit, sampling, and analysis procedure.

The chemical form of heavy metals in the stack gas depends on the composition and quantity of other compounds present and also on gas temperature and residence time in the flue gas. Trace elements speciation in coal may also have an influence on trace elements redistribution. Recently, Yan et al. (23) demonstrated in a study about selenium fate in coal combustion that the forms of Se spiked in the coal influenced the Se volatility. Thermodynamic calculations can be used to predict chemical forms of volatile compounds during incineration processes. Linak and Wendt (5) used multicomponent equilibrium calculations to estimate vaporization and condensation temperatures for Sb, As, Be, Cd, Cr, Pb, Hg, Ni, and Se compounds in coal combustion flue gas. More recently, calculations were performed that reproduce the transformation of metals during waste incineration (24). It was stated that any mercury present will be volatilized similarly to most of the lead and cadmium, whereas the amounts of volatilized copper and tin strongly depends on the operational conditions, in particular with respect to the sulfur and chlorine concentrations. Under these conditions, the formation of chloride metal species as $HgCl_2$, $SnCl_4$, $PbCl_2$, and $ZnCl_2$ was predicted.

The identification and quantification of individual volatile trace metal species in the gas phase is imperative for addressing questions regarding toxicity, mobility, and atmospheric fate and transport mechanisms since each species has distinctive physical and chemical properties governing their environmental impact. Furthermore, it is important for an effective emission control to distinguish between the different gaseous forms in which metals are released into the atmosphere and the metals bond to particulate matter.

In this study, the gas emitted from the stack of a pulverized-coal combustion plant was investigated. To determine volatile metal species present in the gaseous state, an analytical method based on cryosampling followed by packed-column GC/ICP−MS analysis was applied. This method has initially been used successfully to analyze volatile metal and metalloid compounds in urban atmosphere (25). Similar methods using cryogenic sampling followed by GC/ICP−MS analysis were used for the determination of several volatile organometallic species as well as carbonyls in different matrixes such as landfill and sewage gas, soil air, emission from hot springs, and human breath (26−28). Hydride generation and Purge-and-trap methods followed by cryogenic GC/ICP−MS or GC coupled to atomic fluorescence spectrometry were applied to determine volatile selenium and mercury species in water samples (29). These examples show that the cryosampling procedure enables a universal trapping of species, while low-temperature storage minimizes reaction and degradation of the compounds due

TABLE 1. Flue Gas Operating Conditions[a]

gas velocity (m/s)	9.3
emission flow (wet) (Nm³/h)	1 042 987
emission flow (dry) (Nm³/h)	957 223
gas temp at 20 m (°C)	130
humidity (%)	8.2 (vol)
CO_2 (dry) (%)	11
O_2 (dry) (%)	8
NO_x (mg/Nm³)	503
SO_x (mg/Nm³)	1862

[a] These measurements were done by INERIS.

to kinetic inhibition. The stability of organometallic compounds ($SeMe_2$, Me_2Se_2, Me_4Sn, Et_4Sn, Me_2Hg, Et_2Hg, Me_4Pb, and Et_4Pb) as well as Hg^0 stored cryogenically at temperature below −190 °C has been shown to exceed 3 weeks (29).

Sampling and measurements were performed under extremely difficult conditions due to the flue gas matrix and high water content. This aspect had to be overcome by a complex drying system enabling high drying efficiency. Additionally, high contents of SO_2 and CO_2 were collected, and they interfere with the analysis by GC/ICP−MS. Nevertheless, we could show that the method applied is suited for gaseous metal speciation in emission gas, even under the most difficult conditions.

Materials and Methods

Sampling Site. Gas samples were collected during a 3-h period in the stack of a coal combustion plant. The plant (240 MW) was provided with a pulverized-coal boiler and an electrostatic precipitator (ESP). Previous studies (10) demonstrated that ESP displayed minimal collection efficiency for a range of submicron particles diameter. For each hour, 120 t of coal was mixed with 3 kg of copper oxychloride and was burnt. The copper additive was used to facilitate the boiler cleaning. The emission of major compounds (NO_x, SO_x, CO_x, H_2O, O_2) was measured routinely via a non-isokinetic heated sampling line (120 °C). The sampling point corresponded to a height of 20 m across the stack. The same gas line was used for our sampling procedure.

Figure 1 gives an overview of the coal combustion plant and the sampling location in the chimney. During the sampling period, the conditions of the coal combustion and the emission flow were constant. Table 1 gives the major compound concentrations in the flue gas and the main physical parameters. The coal composition is listed in Table 2 as given by external measurements.

Sampling Procedure. Combustion flue gas samples were collected through the pre-installed heated sampling tube
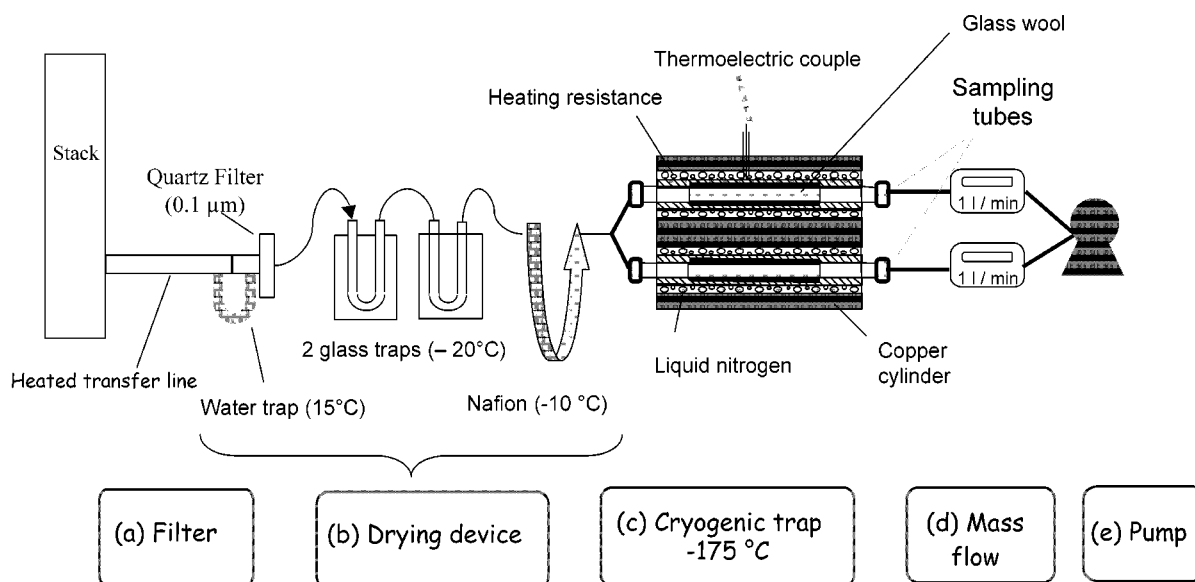
FIGURE 2. Cryogenic air sampling device with its different components: (a) filter, (b) drying device, (c) cryogenic trap (−175 °C), (d) mass flow controller, and (e) pump.

TABLE 2. Elementary and Trace Metal Coal Analysis vs Monitored Isotopes for Cryogenic Sample Analysis Collected in the Flue Gas

elementary coal analysis	(% dry material)	isotope monitored	elementary coal analysis	(% dry material)	isotope monitored
ashes	39.4		S	0.73	^{34}S
C	53.50	^{13}C	N	0.99	
O	3.13		Cl	0.03	^{37}Cl

trace metal analysis	mg/kg (dry coal)	isotope monitored	trace metal analysis	mg/kg (dry coal)	isotope monitored
As	6.3	^{75}As	Mo	1.3	
Ce	7.8		Pd	<1	
Cu	61	^{63}Cu, ^{65}Cu	Tl	<1	^{205}Tl
Zn	57	^{64}Zn, ^{66}Zn, ^{67}Zn	Bi	<1	
Pb	23	^{208}Pb	Ag	<1	
Cd	1.7	^{112}Cd,^{114}Cd	Hg	<1	^{200}Hg, ^{202}Hg
Cr	10	^{52}Cr, ^{54}Cr	Sn	<1	^{118}Sn, ^{120}Sn
Ni	20	^{58}Ni, ^{60}Ni	Se	<1	^{77}Se, ^{78}Se, ^{82}Se
Co	7.5	^{59}Co	Sb	<1	^{121}Sb
V	9	^{51}V	Te	<1	^{125}Te
B	76		Be	<1	
Ba	64		Mn	nd^a	^{55}Mn
Li	12		P	nd	^{31}P
Sr	41				

^{a} nd: not determined.

mentioned above with a laboratory-made air sampler (Figure 2).

Flue gas sampling was performed by cryogenic trapping at −175 °C on silanized glass wool (Supelco, pesticide grade) packed in a glass tube (i.d. 5 mm, length 19 cm). This temperature was shown to be sufficiently low for trapping species with a boiling point as low as −87.5 °C (PH₃), while trapping of O₂ is avoided. Two samples were collected simultaneously. For each sampling tube, the flow was regulated to 1 Nl/min by a mass flow controller (Aalborg). Prior to cryogenic trapping, the gas was filtered and dried as described below. A filtration cartridge (Millipore) equipped with a quartz microfiber filter (Whatman) is used to remove the smallest particles from the gas. The outlet of the filter was connected to a Teflon (PFA) sampling tube (i.d. 8 mm, legth 1 m), which serves as inlet to the air sampler drying system. The gas was dried using different drying systems

connected in series: first, a water trap made of Teflon tubing (length 10 cm, i.d. 8 mm) set at ambient temperature, next two empty U-shaped glass traps held at −20 °C, and finally a semipermeable Nafion membrane dryer tube (length 24 cm, i.d. 2 mm, and o.d. 3 mm; Perma Pure Products, New Jersey) set at −10 °C. The role of temperature and drying efficiency of the Nafion drying system have been reported in the literature (*30*) for ambient temperature and humidified air. In our laboratory conditions with ambient air, for the same levels of humidity (8.2% vol) and using the sampling flows (2 nL/min) operated during the sampling campaign, the dew point of the exhausting air was found to be −10 °C.

After collection, the sampling tubes were placed in a PVC tube, sealed with silicon caps, and stored at least −190 °C in a dry atmosphere cryocontainer (Voyageur 12, L'air Liquide, Paris, France). The sampling lines were made of Teflon and washed with detergent, soaked 1 day in 10% nitric acid, and rinsed with Millipore Milli-Q water (18.2 MΩ.cm). Prior to use, the sampling tubes were cleaned by heating 10 min at 300 °C in a flow of helium.

During the sampling time, variable amounts of gas were collected due to partial clogging of the column. These harsh conditions generated insufficient drying of the extremely humid gas (8.2% vol water content) and trapping of CO₂, which is the most abundant gas under these conditions. The collected volume for each sample varied between 3 and 5 L. Under optimal conditions, eight samples could be collected.

For the impinger systems, standardized sampling techniques were used (*18*−*20*) and collected for both particles and gaseous compounds. Standardized sampling techniques impose an isokinetically particle collection and to have a sampling probe position across the stack. After a coarse preliminary filtration stage (GORE-TEX membrane, expanded poly(tetrafluoroethylene) fiber fabric, 0.35 mm thick, air filtration efficiency >99.5% for 0.3 μm particle diameter according to the NFX-44013 procedure (*31*) and >99.99% for 0.1 μm particle diameter according to Gore & Associates air filtration efficiency test), the flue gas was aspired through the impinger solutions to collect the remaining submicron particles and gaseous compounds. A standard solution of HNO₃ + K₂Cr₂O₇ was used for gaseous mercury absorption and a solution of HNO₃ + H₂O₂ for all other metallic compounds. Two sampling series were done in parallel to the sampling performed cryogenically. For each series, the gas was aspired with a flow rate of 2 L/min during 1.5 h.
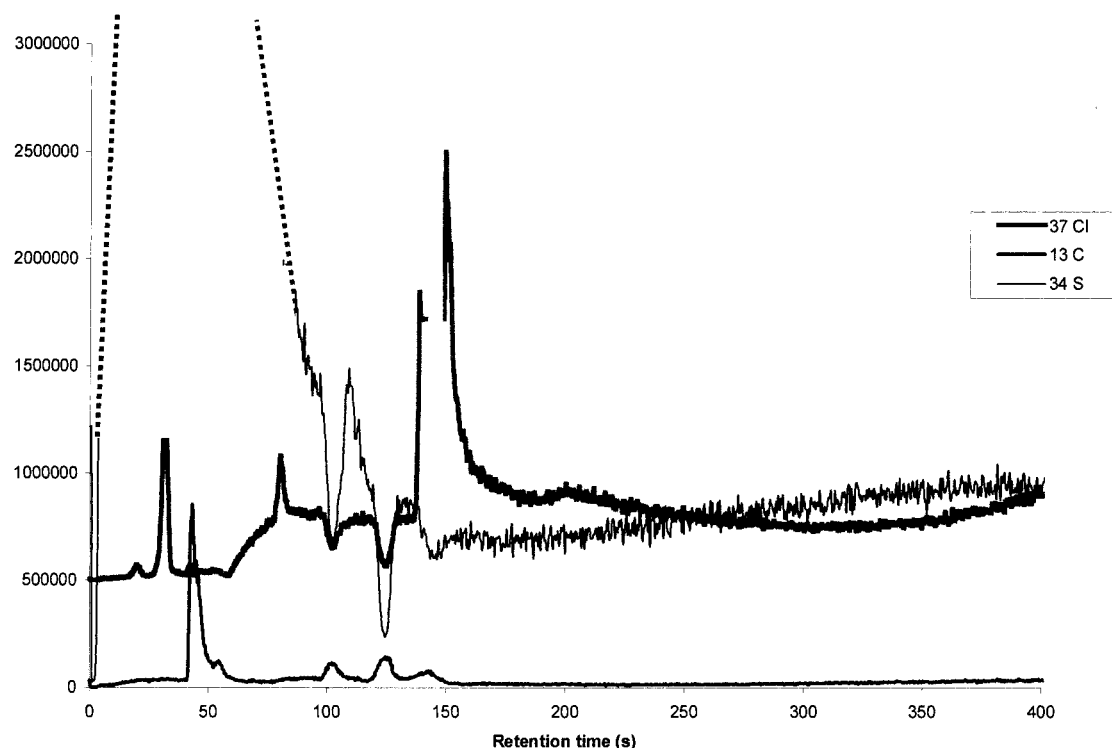
FIGURE 3. Typical chromatogram of the major compounds present in the flue gas; S, C, and Cl corresponding to the *m/z* 34, 13, and 37 mass monitored.

Analytical Procedure. (a) Cryogenic Samples Analysis. The overall sampling and analytical sequence is summarize in Figure 1. The analytical procedure includes thermodesorption of the cryogenically trapped samples, refocusing, subsequent separation on a packed GC column, and final detection using an ICP−MS as an element selective detector. A detailed description of the entire procedure follows below.

Desorption and Chromatography. For analysis, sample tubes are removed from the cryocontainer, placed in a stainless steel tube with heating facility, and connected to the carrier gas line (helium, 100 mL/min) and the packed column (length 320 mm, i.d. 8 mm), which is half-filled with Chromosorb WHP (60/80 mesh, 10% SP 2100, Supelco). Thermal desorption of the sample is performed by heating the sampling tube to +300 °C in about 5 min; the liberated species are transported to the packed column and refocused at −80 °C. The refocusing temperature is maintained by immersing the column in a bath of acetone/liquid nitrogen. Usually, the analytes are refocused in the packed column at −196 °C (liquid nitrogen). Since cryogenic sampling was performed at −175 °C, the major gaseous compounds contained in the flue gas (CO_2, SO_2) were also trapped during sampling due to their boiling point (−78 and −10 °C, respectively) together with the trace compounds. Thus, these species are also desorbed and refocused on the packed column at −196 °C together with the analytes. As the column is heated, these compounds are released as well and transported into the plasma of the ICP−MS. The extremely high amount of SO_2 and CO_2 eluting from the column severely disturbs the plasma leading to its extinction. To avoid these problems (high concentration of CO_2 and SO_2), samples were refocused at −80 °C on the GC column. Figure 3 displays the chromatogram of matrix compounds containing carbon, sulfur, and chlorine. It is evident that, even by refocusing at −80 °C, high amounts of these matrix compounds are trapped in the packed GC column as can be recorded by the detector saturation for S and Cl. After this refocusing stage was adopted, sample analysis could be performed. Similar sampling and analysis of volatile organometallic compounds

using cryosampling and refocusing at −80 °C indicates that a trapping efficiency of more than 90% can be assumed for compounds with a boiling point higher than +40 °C (*32*). We can therefore assume that, under these conditions, carbonyl compounds such as $Ni(CO)_4$ (bp 42.5 °C) if present would not be totally lost during analysis.

The trapping efficiency was assessed for nonpolar organometallic substances to be 0.1% for SnH_4 (bp −52 °C), 87% for Me_2SnH_2 (bp +35 °C), and 100% for *n*-$BuSnH_3$ (bp +100 °C) (*33*). In our studies, a trapping efficiency of less than 2% was found for PH_3 (bp −87.5 °C) and Hg^0 (bp 357 °C) after refocusing at −80 °C (*34*).

After the cooling bath was removed, the chromatographic column was heated to 250 °C in 3 min using a Thermocoax wire, while a constant helium carrier gas flow of 100 mL/min was applied. The species eluted are transferred to the ICP−MS through a heated Teflon line (120 °C) connected to the ICP torch by a Teflon mixing piece.

ICP−MS Parameters. To evaluate the occurrence of possible volatile metal species present in the flue gas, 31 isotopes representing 14 elements were monitored simultaneously by appropriately adjusting the sweeping conditions of the mass spectrometer. The following isotopes were selected according to earlier report on trace element partitioning during coal combustion (*35*) and the occurrence of trace elements in coal, which are also likely to be transformed into volatile species (*3*): [13]C,[31]P, [34]S, [37]Cl, [55]Mn, [51]V, [52]Cr, [54]Cr, [58]Ni, [59]Co, [60]Ni, [63]Cu, [65]Cu, [64]Zn, [66]Zn, [67]Zn, [75]As,[77]Se, [78]Se, [82]Se, [112]Cd,[114]Cd, [118]Sn, [120]Sn,[121]Sb, [124]Xe, [125]Te, [200]Hg, [202]Hg, [205]Tl, and [208]Pb (Table 2). Xenon was introduced continuously and used for plasma parameter optimization. The operating parameters were selected according to our routine conditions used for the analysis of volatile species (nebulizer gas flow, 0.95 L/min; cooling gas flow, 15 L/min; auxiliary gas flow, 0.8 L/min; power, 1250 W; dwell time per mass, 10 ms resulting in a time resolution of 430 ms between data points for one isotope). An additional flow of O_2 was required to avoid carbon deposition on the cones of the mass spectrometer. A complete description for the gas flow optimization (He, O_2, Xe) in dry
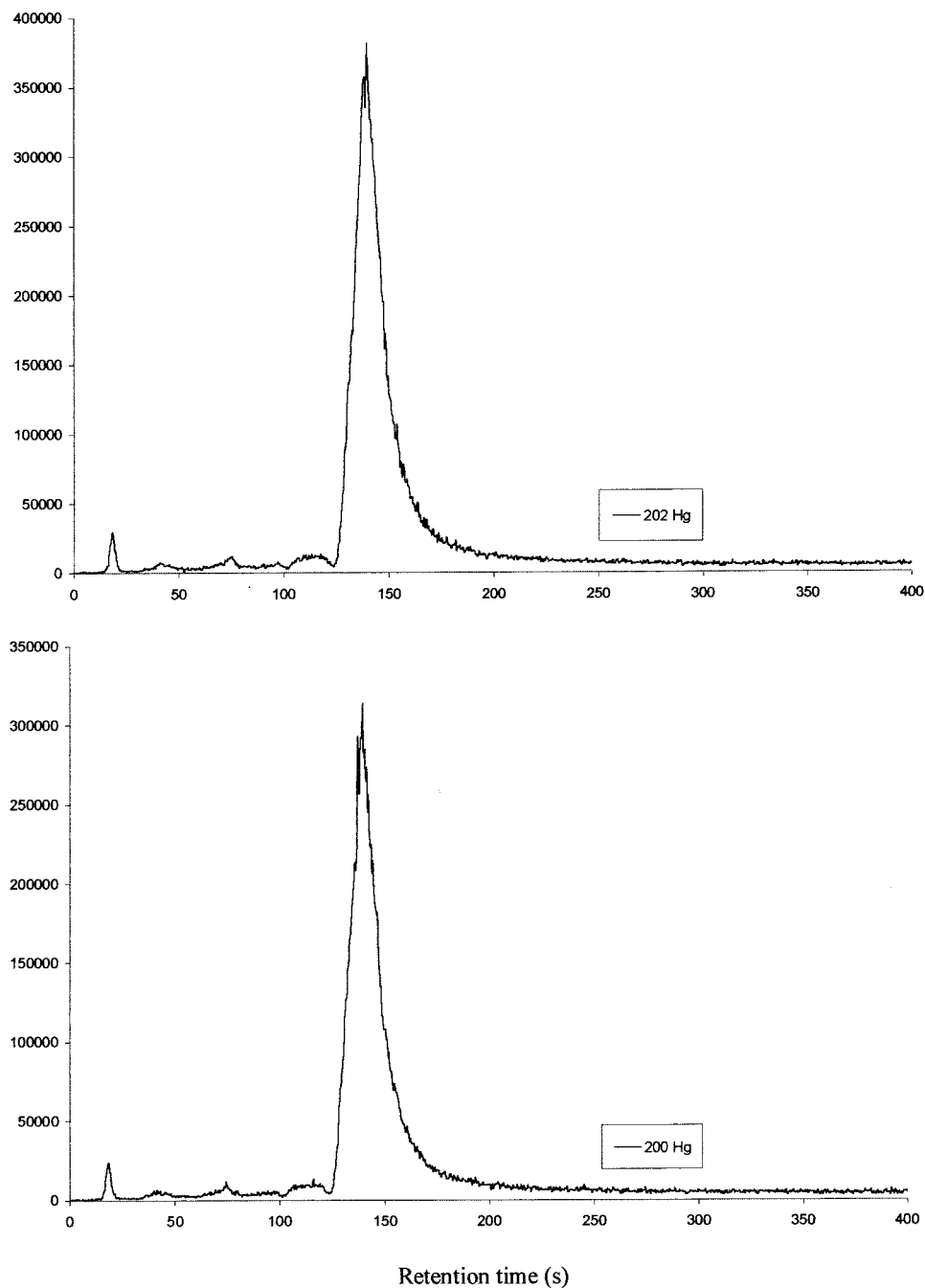
FIGURE 4. Typical chromatogram obtained for volatile mercury species detected in the flue gas (m/z 200 and 202 were monitored). The isotopic ratio measurements obtained are 202/200 Hg = 1.25 (Hg1) and 202/200Hg = 1.27 (Hg2).

plasma conditions for the analysis of volatile metal species was described elsewhere (*36*).

Isotopic Pattern. To assess and confirm the presence of a species containing an element, the isotopic ratios were determined on at least two isotopes of this element and were compared with the natural isotopic ratio. According to previous experiments (*25*), an agreement of 95% was considered to be satisfactory. Under our analytical conditions, the precision of the isotopic ratio is affected by the short dwell time acquisition mode (10 ms) and by the fast GC transient signal. Furthermore, potential interfering molecular ion signals were also monitored simultaneously in order to detect and correct for interference (as, for example, in the case of $^{75}As^+$, which is interfered by $^{40}Ar^{35}Cl^+$).

Volatile Metal Species Identification. Species identification is based on the chromatographic retention time together with the confirmation of the isobaric signature of the metal for the considered peak. To confirm the identity of the compound, the retention time of the species of interest is tested against a pure standard substance. In general, a linear relation between the boiling point of volatile organometallic standards (Me_2Se_2, Me_2Se, Me_4Pb, Et_4Pb, Me_4Sn, Et_4Sn) and the experimental retention time can be obtained (*26*, *29*). The equation obtained from the above analytical conditions is described by

$$bp = 1.79rt - 46.5 \qquad (1)$$

with bp = boiling point (°C) and rt = retention time (s). Despite of the differences of physicochemical properties of the compounds investigated (relationship established for organometallic compounds), we have used it to derive boiling
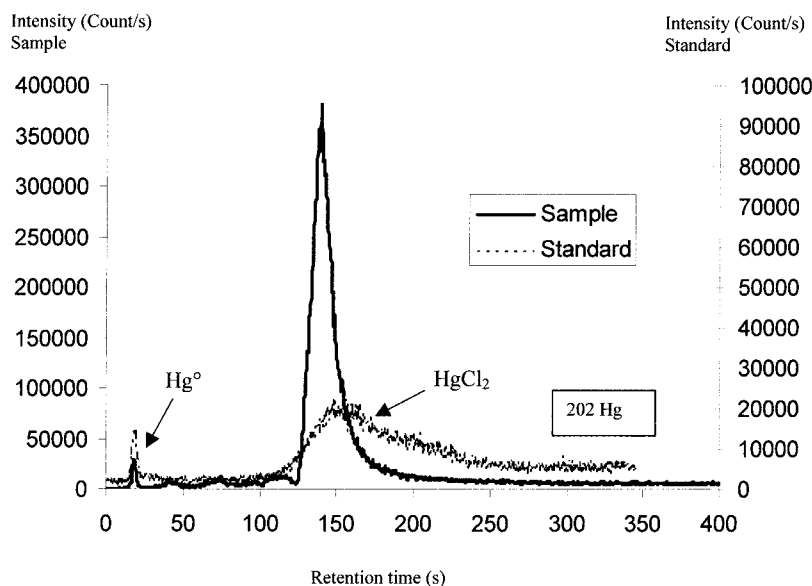
FIGURE 5. Chromatogram obtained for standard volatile mercury species injection in the laboratory (Hg^0 and HgCl$_2$) and compared to a real sample chromatogram.

points of unknown species. The boiling point estimated then can be used to compare it to literature data of element species (*37−40*). If the boiling points suggested match that of a possible species that can also be found and is available as pure standard, the retention behavior is then checked experimentally. Finally, we also rely on information derived from literature about the characterization of trace element emissions from combustion systems. These data suggest the occurrence of different species during the combustion by equilibrium calculations.

Volatile Metal Species Quantification. Quantification of the analytes is performed by external calibration, i.e., injections of known amounts of volatile standards directly into the chromatographic column. The species detected have been assumed to be inorganic species (see later in the text). Ideally, quantification is carried out with the respective species. Between the few volatile metallic standards available on the market, we selected those which contain the element of interest. We assumed that, in the plasma, atomization and ionization of different organometallic species would be independent of its bounding states and therefore considered that the response of inorganic and organometallic compounds would be comparable. For selenium, Me$_2$Se (99%, Strem) was used. For tin, Me$_4$Sn (99%, Strem) was selected. Volatile mercury species were quantified by injecting Hg^0 vapor from the headspace of a vial containing pure Hg^0 (99.99%, Strem). For copper, no volatile element species was available, thus no quantification attempt was performed.

Measurements of blank sampling columns that reflect possible contamination during column preparation and storage did not show any detectable amounts of tin, selenium, or copper, whereas elemental mercury was found in the negligible amount of less than 10 pg. In these conditions, the detection limits calculated for 5-L sampling volume were 0.6 ng/m^3 for Hg^0, 0.02 ng/m^3 for tetraalkyltin species, and 0.1 ng/m^3 for alkylselenide species (all concentrations are expressed with respect to the metal content). The reproducibility (RSD) for repeated analyses concerning the overall analytical method was determined to be better than 20% for volatile lead species collected in urban air (*25*).

(b) Particles and Absorption Solution Analysis. The samples collected on the filter and in impinger solutions were analyzed by traditional ICP−MS methods used routinely at INERIS (XP-X43051 method; *19*). The solid aerosols were digested with microwave procedures.

Results and Discussion

Qualitative Results on Species Determination. Analysis of the cryosamples was performed by the procedure described above. The fast scanning possibility of the mass detector allowed us to provide evidence of the absence of volatile species of the following elements: P, Mn, V, Cr, Ni, Co, Cd, Tl, Pb, As, Zn, and Te. Conversely, gaseous Hg, Se, Sn, and Cu species were detected.

Detection Limit. The detection limit estimation of undetected elements and of Cu are explained as follow. The detection limits of Hg, Se, and Sn were calculated using different volatile metallic standards (see before Volatile Metal Quantification section), and detection limit of P, As, and Pb could have been calculated using PH$_3$ and AsH$_3$ gas standard and alkyllead species. Under these conditions, the detection limits will correspond respectively for P, As, and Pb to 3, 0.15, and 0.01 ng/m^3 for 5-L sampling volume. Nevertheless because of the lack of available volatile standards, we can only provide an estimation of the detection limit in the range of nanograms per cubic meters for the following elements: Cu, Mn, V, Cr, Ni, Co, Cd, Tl, Zn, and Te.

Chromatograms of Hg, Se, Sn, and Cu volatile species are displayed in Figures 4−8. At least two volatile species of mercury, three for selenium, one for tin, and one for copper are present in the flue gas.

Plasma Stability And Isobaric Interference. Matrix compounds containing Cl, C, and S have also been detected during sample analysis (Figure 3). The sample matrix may induce changes in the analyte signal intensity and affect the entire mass range by modifying the plasma ionization zone and the ion extraction efficiency particularly for the light elements (*41*) (space charge effect). The signal obtained for the adjacent masses of the detected element and other monitored masses (i.e., m/z 31, 51, 52, 54, 55, 59, 60, 64, 66, 67, 125, 205, and 208) are reported in Figure 9. A plasma disturbance affecting the whole mass range is indeed not observed as can be seen on the stable and low background on, for example, m/z 31, 51, 55, 59, 125, 205, and 208 (Figure 9). During the same run, the signal of the internal standard xenon did not show a significant change during elution of the compounds except for a peak at the retention time of tin, which corresponds to a tin isotope (^{124}Sn) and again reflects the natural isotope ratio for tin.
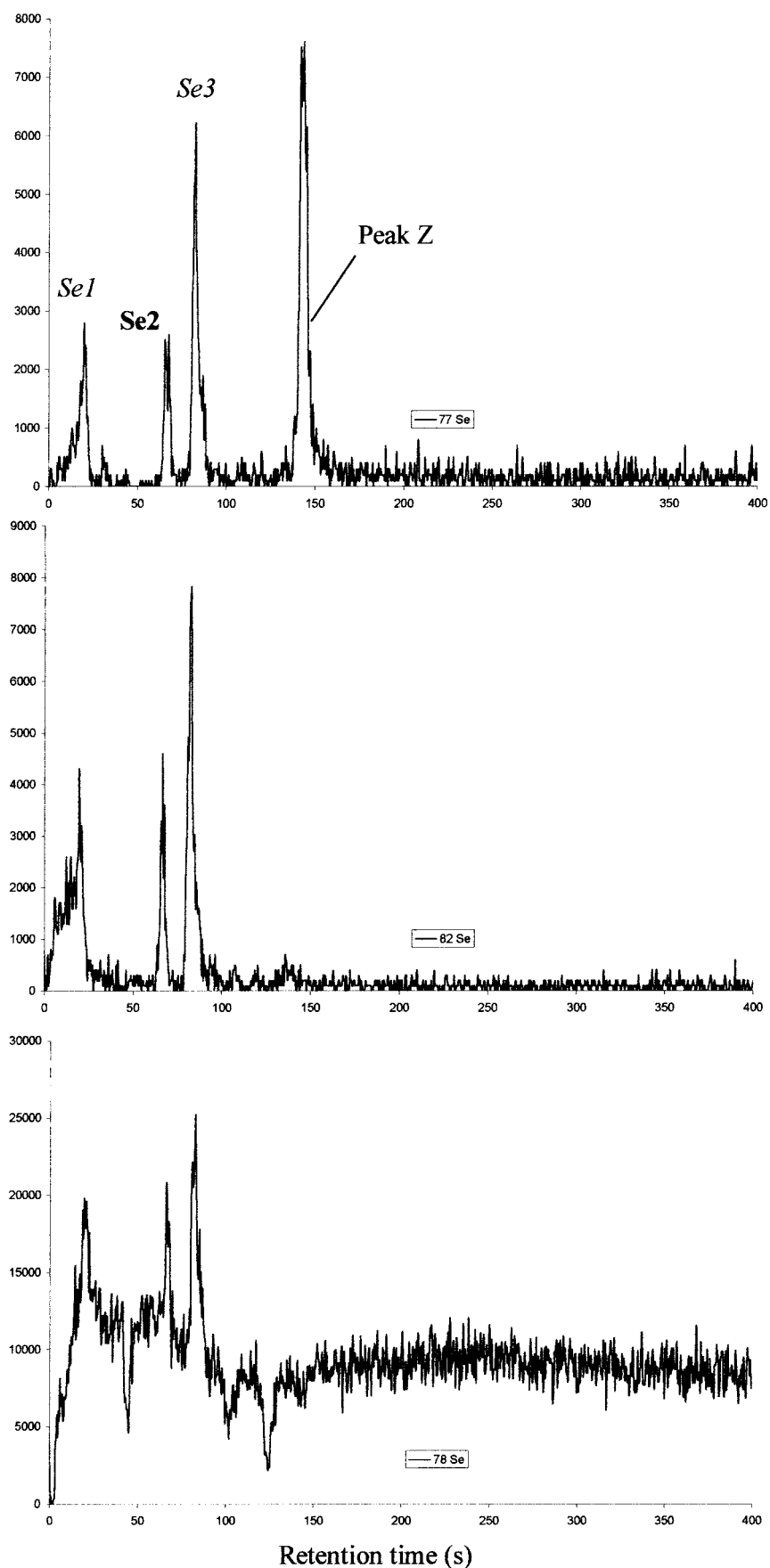
FIGURE 6. Typical chromatogram obtained for volatile selenium species detected in the flue gas. The channels m/z 77, 78, and 82 were monitored. The isotopic ratio measurements obtained are 82/77 Se = 1.44 (Se1), 82/77 Se = 1.32 (Se2), and 82/77 Se = 1.31 (Se3).
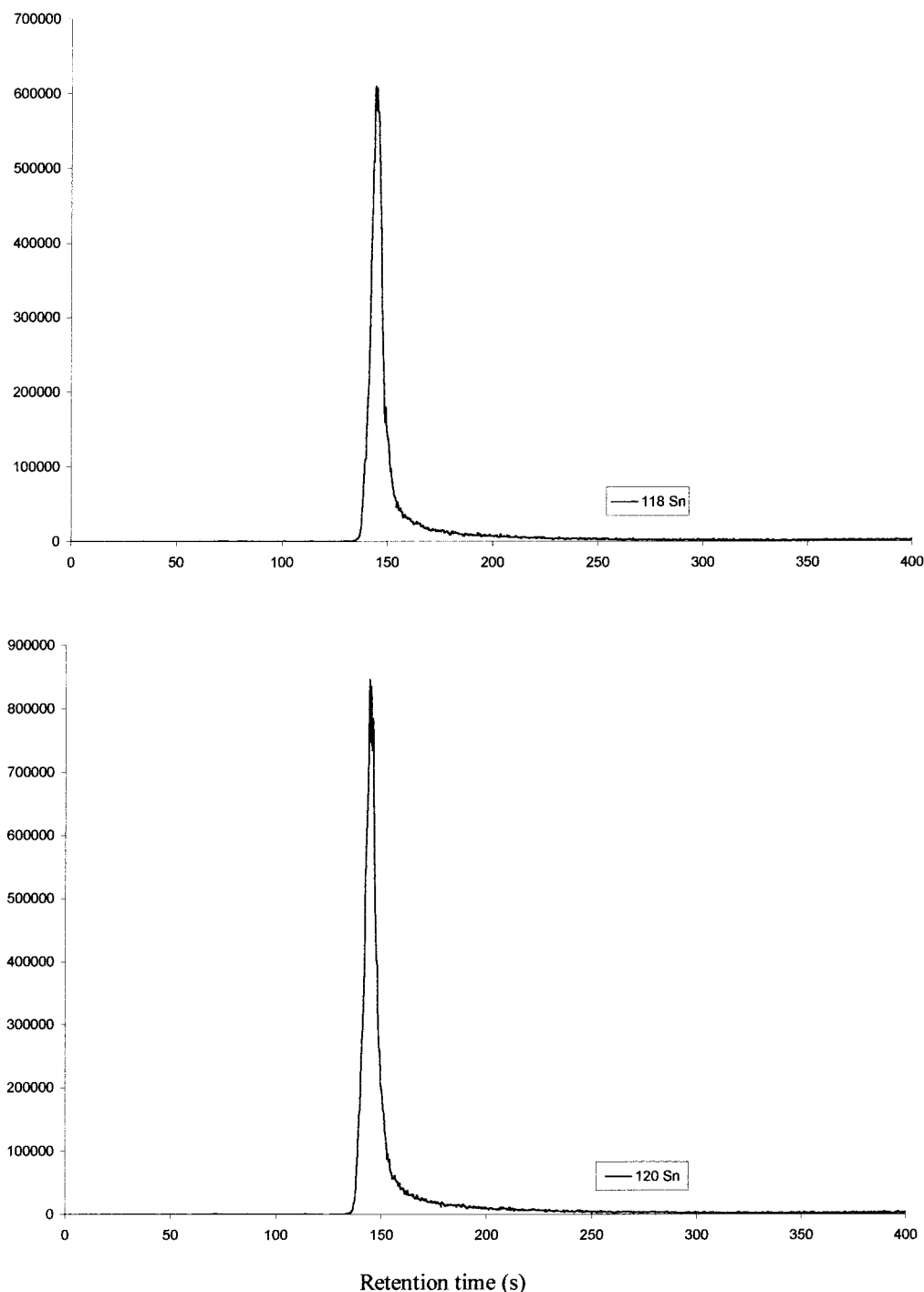
FIGURE 7. Typical chromatogram obtained for volatile selenium species. The channels m/z 63 and 65 were monitored. The isotopic ratio measurement obtained are 63/65 Cu = 2.38 (Cu1).

For some of the isotopes displayed, we observed some peaks that were attributed to molecular interference. Indeed, molecular ions might be formed from different types of compounds such as radicals from gases in the plasma. Polyatomic ions give strong signals in the mass range up to 80 atomic mass units and may hamper the determination of light elements as a result of spectral interference. At higher masses, doubly charged ions can occur that may interfere with the light elements (*42*). For each element, these interference can easily be evidenced by comparing the isotopic ratio measured to the theoretical one. This approach is effective for the recognition of spectral interference. For all the Hg, Se, Sn, and Cu species detected, natural and experimental isotopic ratios gave a good agreement (Table

3). However on m/z 52 and 54 signals, Cr peaks (Figure 9) cannot be considered as volatile chromium species but are attributed to carbon and nitrogen molecular ion interference with different combinations such as $^{40}Ar^{12}C^+$ and $^{40}Ar^{14}N^+$. Peaks on Zn (m/z 67) and Ni (m/z 60) isotopes were observed (Figure 9) too but do not show the correct isotope distribution of these elements. Thus, as described for Cr, these peaks were not considered as Ni or Zn species.

Species Identification. To propose molecular formulation of the compounds identified, we used in combination the equilibrium calculations results found in the literature and an experimental approach using the linear relation (bp vs rt) and by injecting the volatile standard compounds when available. This approach was used for the molecular formula
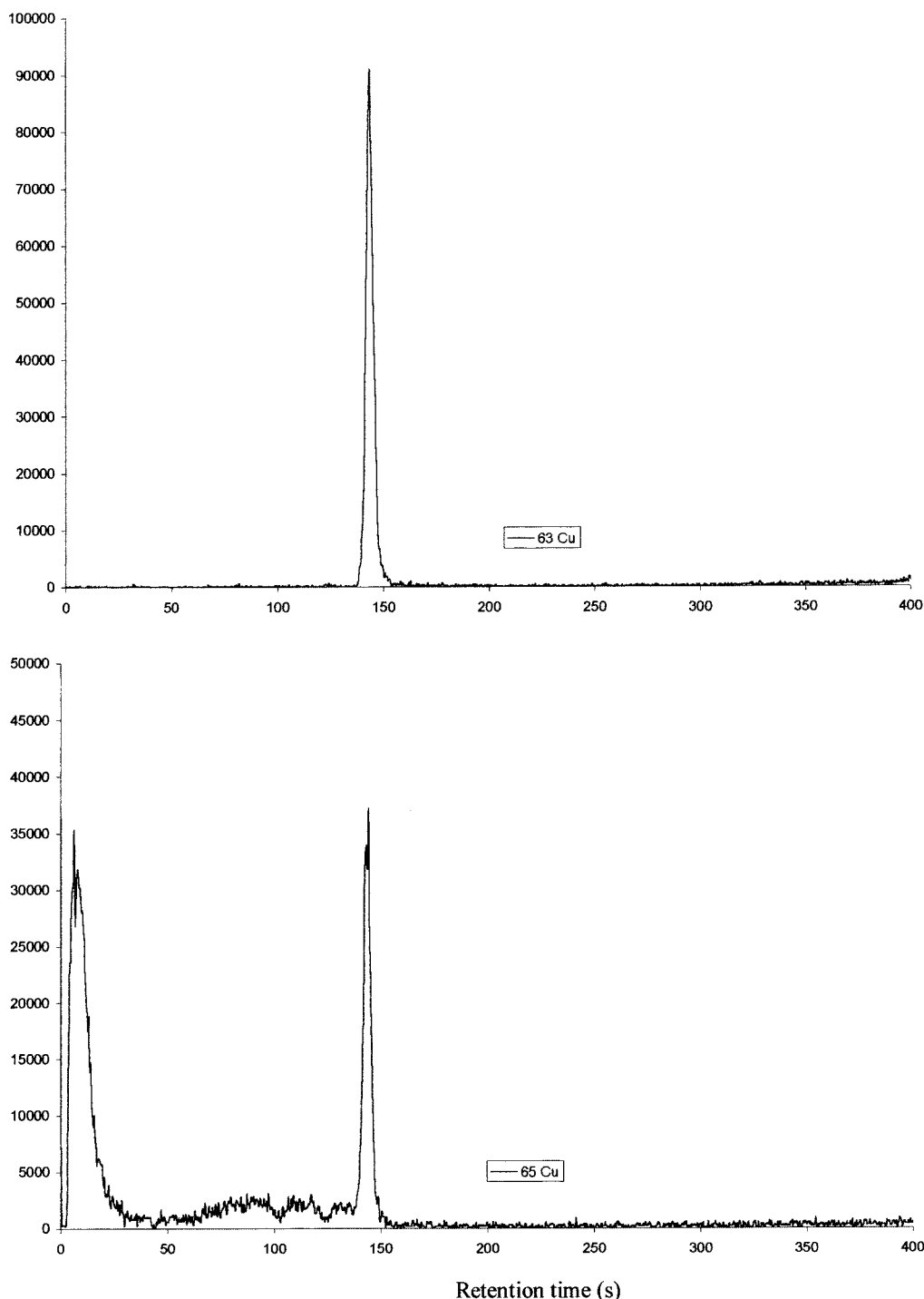
FIGURE 8. Typical chromatogram obtained for volatile tin species in the flue gas. The channels m/z 118 and 120 were monitored. The isotopic ratio measurement obtained are 120/118 Sn = 1.35 (Sn1).

determination of mercury, selenium, copper, and tin species. Table 4 gives the calculated boiling point for each species obtained.

Mercury Species. Figure 4 represents the chromatograms obtained for the mass m/z 202 and 200. Comparison of natural and experimental isotopic ratios confirms the presence of two mercury species (Hg1 and Hg2) in the flue gas (Table 3).

Three oxidation states of Hg, elemental (Hg^0), mercurous (Hg_2^{2+}), and mercuric (Hg^{2+}) must be considered in speciation analysis. Mercurous compounds have been found to be unstable in flue gas and under atmospheric conditions (*15*). So Hg_2Cl_2 is very unlikely to be present in the coal emission

flue gas. Galbreath and Zygarlicke (*15*) indicated with thermodynamic predictions related to temperature and flue gas composition would yield $Hg^0(g)$, $HgCl_2(g)$, and $HgO(g,s)$ as the predominant forms. According to their prediction, HgO would be in the gaseous phase at temperatures higher than 700 °C. It is therefore not likely to be present in the emission gas at 120 °C in our prevailing conditions. For the Hg^0 and $HgCl_2$ species, Linak and Wendt (*10*) have shown that these species have a similar vapor pressure with regards to temperature relation and therefore a high vapor pressure under elevated combustion temperature or even at ambient temperature. Therefore, these compounds are expected to
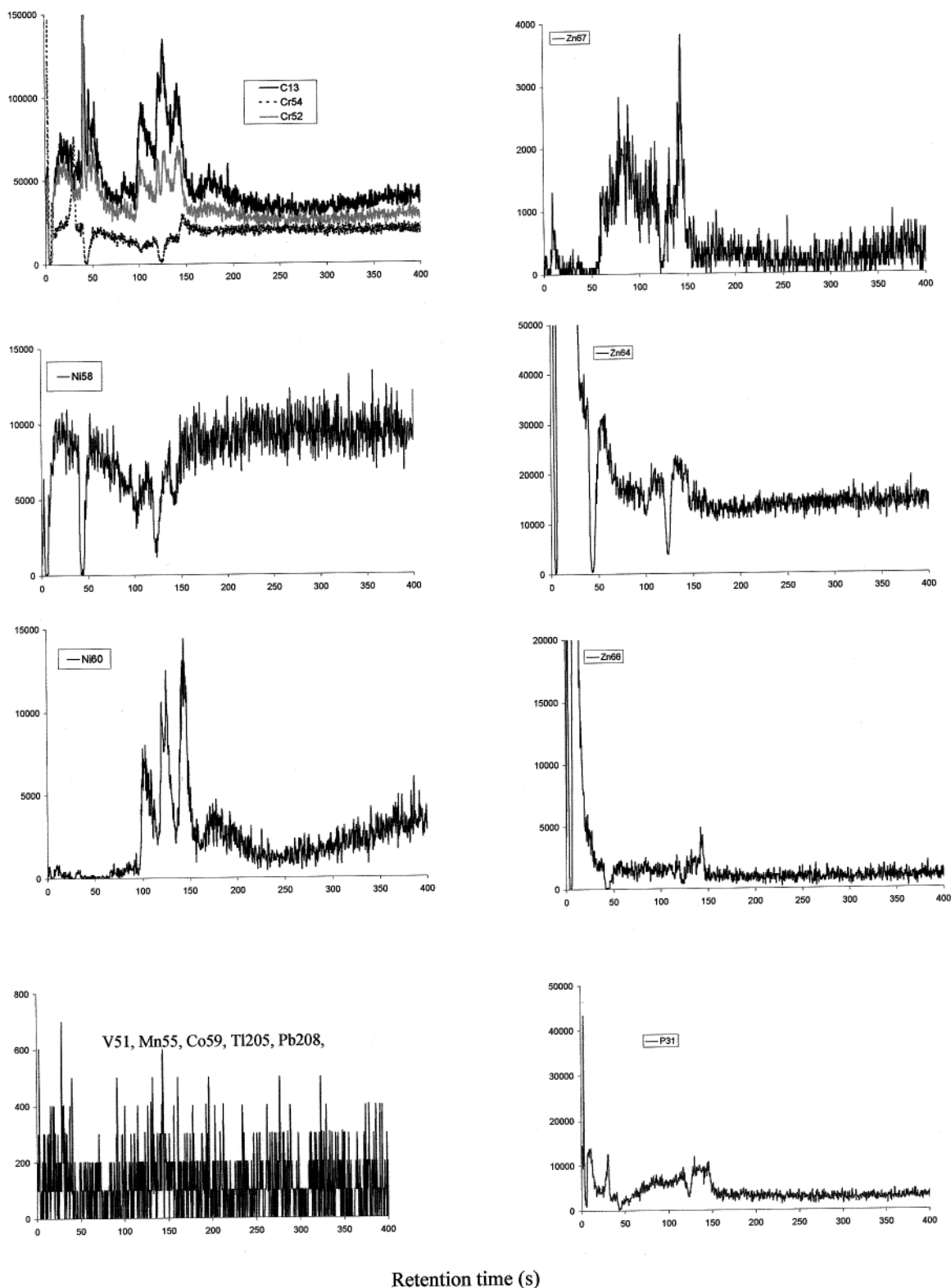
FIGURE 9. Typical chromatograms obtained for the following masses on the same sample to check for any spurious peaks or plasma instability (*m/z* 31, 51, 52, 54, 55, 58, 60, 64, 66, 67, 125, 205, and 208).

be easily vaporized. Recently, Galbreath and Zygarlicke (*43*) reported that the mercury in the coal is initially transformed to Hg^0 in the high-temperature combustion environment; next, mercury chlorination (i.e., $HgCl_2$ formation) is assumed to be the dominant mercury transformation mechanism. Furthermore, the presence of $HgCl_2$ as been also mentioned since it has been demonstrated that electrostatic precipitators cannot remove $HgCl_2$ (*15*). Therefore, we would assume that

these species (Hg1 and Hg2) would be Hg^0 and $HgCl_2$, respectively.

To confirm this hypothesis (the occurrence of Hg1 as Hg^0), we used the comparative of retention time after direct injection of 100 μL of Hg^0 vapor into the chromatographic system and obtained comparable retention times. For the experimental identification of Hg2, we mentioned previously that Hg^0 and $HgCl_2$ have a similar vapor pressure and thus

TABLE 3. Natural and Calculated Isotopic Ratio Comparison for Mercury, Selenium, Tin, and Copper Volatile Species Detected in the Flue Gas

	species	calcd isotopic ratio ($\pm 1\sigma$)[a]	natural isotopic ratio
$^{202}Hg/^{200}Hg$	Hg1	1.25 ± 0.03[b]	1.29
	Hg2	1.27 ± 0.02	
$^{82}Se/^{77}Se$	Se1	1.44 ± 0.26[b]	1.21
	Se2	1.32 ± 0.15	
	Se3	1.31 ± 0.10	
$^{63}Cu/^{65}Cu$	Cu1	2.38 ± 0.16	2.23
$^{120}Sn/^{118}Sn$	Sn1	1.35 ± 0.02	1.37
$^{120}Sn/^{124}Sn$	Sn1	5.41 ± 0.21	5.53
$^{112}Sn/^{114}Sn$	Sn1	1.39 ± 0.05	1.49

[a] Standard deviation calculated on 8 samples unless noted otherwise.
[b] Standard deviation calculated on 4 samples.

probably similar chromatographic behavior. To check this assumption, 30 μL of HgCl$_2$ vapor was injected from the headspace of a vial containing pure HgCl$_2$ (99.99%, Merck) held at ambient temperature. Under these experimental conditions, we then obtained a peak with similar retention time as obtained for Hg2, thus Hg2 may be attributed to HgCl$_2$ (Figure 5). We therefore considered that Hg^0 and HgCl$_2$ were present in the flue gas.

It is worthwhile noticing in Table 4 that Hg^0 does not follow the conditions of the equation given by retention time/boiling point relation. This fact can be related to its high vapor pressure and its low interaction with the chromatographic phase, eluting them far too early. The same effect can be assumed for HgCl$_2$, explaining the earlier elution than expected by the species' boiling point.

Selenium Species. Figure 6 represents the chromatograms obtained for the m/z 77, 78, and 82 ions. Three selenium species (Se1, Se2, and Se3) are detected and confirmed by comparison of the isotopic ratios (Table 3). The selenium isotope on m/z 77 can be interfered by the polyatomic ion $^{40}Ar^{37}Cl^+$. The peak quoted Z in Figure 6 with a retention time of 140 s is only observed on m/z 77 and could be attributed to $^{40}Ar^{37}Cl^+$ polyatomic interference since at the same retention time a peak was detected on m/z 75, which could correspond to $^{40}Ar^{35}Cl^+$. Thus, we cannot ascribe this peak to a selenium species but probably to a chlorine interference.

Selenium occurs in five different oxidation states: -2, 0, $+2$, $+4$, and $+6$. SeO$_2$ and Se^0 are the thermodynamically stable selenium species in flue gas (44). It has also been mentioned that at low temperature (less than 150 °C), SO$_2$ could act as a reducing agent to form elemental Se^0 from SeO$_2$ (45, 44) (highly volatile compound present in the vapor phase). Yan et al. (46) identified Se^0 and SeO$_2$ as the dominant Se species in the particulate phase using X-ray photoelectron

spectroscopy. We therefore assumed that none of the selenium species Se1, Se2, or Se3 could correspond to SeO$_2$ or Se^0.

According to the linear relation (bp vs rt), the calculated boiling point for Se1 is -14 ± 7 °C. Carbon oxyselenide (COSe) has a boiling point of -21.5 °C and hence could be related to Se1 (Table 4). Feldmann (32) demonstrated that neutral metal carbonyls show the same separation characteristics as neutral methylated species, using a similar analytical setup with identical support for the chromatographic separation. Thermodynamic calculations (46), showed that H$_2$Se could be present in the flue gas below 230 °C. However in our analytical conditions, the H$_2$Se (bp -42 °C) trapping efficiency at -80 °C should have been about 0.1% (see Cryogenic Sample Analysis section), and its boiling point does not also match with the one predicted for Se1 (Table 4). So we do not think that H$_2$Se could be related to Se1.

For the species Se2 and Se3, some compounds could be suggested according to the calculated boiling point and volatile selenium compounds listed in the literature (37–40). The boiling points of CSSe, CSe$_2$, Se$_2$Cl$_2$, and SeOCl$_2$ (85.6, 125.5, 130, and 177 °C, respectively) are the closest related to the estimated boiling points of Se2 and Se3 (Table 3). From all these possible compounds, only SeOCl$_2$ and Se$_2$Cl$_2$ were currently available on the market. Then, to identify the unknown species experimentally, 5 μL from the headspace of a vial set at ambient temperature containing pure Se$_2$Cl$_2$ and SeOCl$_2$ (99.9%, Strem) was directly injected into the ICP–MS nebulizer gas. This resulted in elevated selenium isotope levels, indicating that volatile Se species were present. However, repetition of this experiment using the cryofocusing trapping procedure on the packed column did not give any selenium peaks. So we may assume that neither Se$_2$Cl$_2$ nor SeOCl$_2$ can be attributed to the unidentified species found in the stack gas. SeCl$_2$ was also observed in the gaseous phase as a product of dissociation of SeCl$_4$ (38, 39) and suggested as dominant species below 230 °C (46), but neither data on its physical properties (e.g., boiling point, vapor pressure) nor any SeCl$_2$ standard could be found to check the possible occurrence of this species in the collected samples. In summary, based on the overall facts described previously, we could then assume that the selenium species formulation of Se1, Se2, and Se3 could be assigned respectively as COSe, CSSe, CSe$_2$, or SeCl$_2$.

Tin and Copper Species. Figures 7 and 8 present respectively the chromatograms for the tin isotopes 118 and 120 and for the copper isotopes 63 and 65. Only one tin (Sn1) and one copper (Cu1) species were detected. The agreement between natural and experimental isotopic ratios were good and are reported in Table 3.

According to the calculated boiling points and volatile copper or tin compounds referenced in the literature, no chemical structure can be suggested. Copper and tin com-

TABLE 4. Mercury, Selenium, Tin, and Copper Volatile Species Estimated Boiling Points and Concentration Range in the Flue Gas

compd (Figures 4–7)	retention time (s) ($\pm 1\sigma$)	calcd boiling point (°C)	amt range trapped in each sample (ng)	concn range (ng/Nm³)	no. of species occurrence	molecular formula identification	boiling point[a] (°C)	melting point[a] (°C)
Se1	18 ± 3	−14 ± 7	0.03−0.19	6−38	4	COSe	−21.9	−122
Se2	67 ± 5	73 ± 10	0.04−0.18	8−37	8	CSSe	85.6	−75.2
Se3	83 ± 5	102 ± 9	0.08−0.18	16−38	8	CSe$_2$	125	−45.5
Cu1	135 ± 16	195 ± 28	nd[b]	nd	8	CuSO$_4$H$_2$O	na[c]	na
						CuO−CuSO$_4$	na	na
Sn1	133 ± 16	191 ± 29	0.05−0.70	10−140	8	SnO$_2$	na	1630
						SnCl$_2$	623	247
Hg1	17 ± 2	−16 ± 4	0.15−0.37	30−73	4	Hg^0	357	−38.9
Hg2	132 ± 6	190 ± 11	1.6−9.35	320−1870	8	HgCl$_2$	304	277

[a] See refs 37 and 40. [b] nd, not determined. [c] na, not available.

pounds have the same retention time, but a mixed compound Cu−Sn should not be volatile at 120 °C. Thermodynamic behavior of metal chlorides and sulfates under the conditions of incineration furnaces was described by Verhults et al. (*24*). They showed that at about 100 °C under reducing conditions and in the presence of sulfur, $SnCl_4$, $SnCl_2$, and SnO_2 are the predominant gaseous tin species. For the copper compound, the formation of complex oxides at about 100 °C ($CuSO_4 \cdot H_2O$, $CuO-CuSO_4$) could be discussed. Besides, during the combustion studied, copper oxychloride ($CuCl_2$, $2CuO$, $4H_2O$) was added to the coal during combustion (see the earlier sampling section). We therefore checked experimentally that Cu1 did not correspond to copper oxychloride by heating some copper oxychloride (Rhône Poulenc) at 120 °C in a closed vial directly connected to the ICP−MS. Under these conditions, no copper compound was evolved. However, copper oxychloride might be decomposed during the combustion processes and transformed into a volatile copper species.

To identify the volatile tin species, an experiment similar to the identification attempt for selenium species was performed. Here, pure $SnCl_4$ (99.9%, Merck) was used. By direct injection into the ICP−MS, $SnCl_4$ was found to be volatile in this conditions, but after cryofocusing and chromatography, no peak was detected. So we suppose that $SnCl_4$ cannot be attributed to the unidentified tin species found in the stack gas. On the basis of the experimental result and thermodynamic predictions, we suggest that the copper and tin species (Cu1 and Sn1) detected could be respectively assigned as $CuSO_4 \cdot H_2O$ or $CuO-CuSO_4$ and SnO_2 or $SnCl_2$.

Quantitation. Quantitation when possible was carried out by external calibration with organometallic standards with respect to the determined peak areas (see Volatile Metal Species Quantification in Analytical Procedure section). Some critical points during sampling and analysis have to be stressed:

(a) The organometallic standards used to evaluate the concentration of the compounds found do not match the species found in the stack gas. A strict quantification should have been done with the species found in the samples. However, using ICP−MS as detector, we can consider that all the species of a given metal show the same behavior during the detection, as all species will be destroyed in the plasma, and the ionization yield should be determined by the metal in question only. Refocusing of the samples was performed at −80 °C, thus some species (e.g., Hg^0) might be partially lost, as explained above.

(b) The collected volume changed between 3 and 5 L for each sample due to clogging of the sampling columns (see Sampling section). The gas flow meters used in this setup showed only the actual flow for each sample. The collected volume was determined by taking the sampling time, resulting in slight uncertainties on the exact sample volume collected.

(c) It is well-known that the use of a membrane Nafion dryer leads to partial loss of polar organic substances, i.e., organic acids or alcohols (Perma Pure Products, technical note). For organometallic species, we checked this by injecting organometallic standards compounds in a T-piece connected to the air sampler. The results showed no significant loss of species compared to analysis without the Nafion dryer in line. Similar experiments using the water glass trap held at −20 °C (*36*) were done and led to the same conclusion. Nevertheless, some of the species found in the stack gas might show different behavior than the nonpolar organometallic species we tested.

(d) The filtration cartridge and the collected particulate matter may probably captured portions of the volatile metal species.

TABLE 5. Total Metal Concentrations of Different Elements in Particles and Gaseous Phase in Flue Gas from Standardized Sampling Techniques

element	total gaseous metal concn range (μg/Nm^3) from absorption solutions	total metal particulate concn range (μg/Nm^3)
Cd	7−20	<1
Hg	11−24	<0.06
Tl	<1	<1
As	3−4	43−80
Se	4−10	<0.5
Te	19−23	<1
Sb	52−71	2−7
Cr[a]	250−279	22−33
Co	10−11	8−12
Cu	52−65	36−51
Sn	33−41	1−4
Mn	15−24	96−141
Ni	35−38	24−34
Pb	129−557	37−52
V	4	75−118
Zn[a]	1400−1587	411−648

[a] Elements for which blank problems were detected.

(e) On the contrary, it can be considered that some ultrafine particles will also become trap in the glass wool of the cryogenic trap. During the thermal desorption step, the volatilization of some species condensed on the particles could occur. This could generate a positive bias in the determination of volatile metal species in the gas phase. However, if this process occurs, this will only probably affect the species quantification assuming that these condensed species will most likely be also present in the gaseous state in the flue gas. The estimated amount trapped in the samples and the concentration range for each species detected in the flue gas are given in Table 4.

Comparison with the Standardized Techniques. The quantitation results obtained from the standardized sampling techniques used for both particles and gaseous phase were compared with the results obtained with the cryogenic method. These results are displayed in Table 5. For gaseous phase sampling results, the data clearly show a large discrepancy between those obtained by cryosampling and those obtained with the impinger solutions. The elements Zn, As, Pb, Cr, Cd, Cu, Sn, Hg, Sb, Tl, Mn, Co, Ni, V, Te and Se were detected in the impinger solutions whereas only Hg, Se, Sn, and Cu were found with the cryosampling method. The concentration levels of Hg, Sn, and Se are respectively about 10, 60, and 30 times higher in the impinger solutions as compared to the levels obtained with the cryogenic sampling method (Tables 4 and 5). These results are not surprising since we assume that the analytes collected in the impingers concern both gaseous and submicron particles issued from the combustion. Experiments have indeed demonstrated (*5*) that ultrafine aerosols can be formed in the post-flame combustion zone. Their diameter distribution ranges between 0.03 and 0.07 μm. These ultrafine particles would then pass the filter and be dissolved in the impinger solution and account for the differences observed between "true volatile" species (cryogenically trapped) as compared to the traditionally referenced as "volatile" ones when using the standard impinger sampling approaches. The largest volatile element concentrations (impinger solutions) as compared to particulate element concentrations (Table 5) enhance this last hypothesis.

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