

**Analytical methods for mercury analysis in coal and coal combustion
by-products**

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Abstract

This review deals with the analysis of mercury present in different types of solid, liquid and gaseous samples involved in the coal combustion process, focusing on the specific characteristics of each type of sample and the problems typically associated with these products. The main aim of the paper is to describe the methods that, at the current stage of development, are preferable in each case (*i.e.* the most frequently used in most laboratories and the standard methods). The advantages and disadvantages of each method are discussed with reference to the quality of the results and the uncertainties involved in the evaluation of mercury behaviour during coal combustion processes.

Keywords: *Mercury, mercury analysis, mercury speciation, coal-fired power plants*

Introduction

Coal combustion is the main source of anthropogenic mercury emitted into the environment (UNEP, 2008). In Europe, mercury emissions from stationary combustion facilities represent 53% of the total amount of anthropogenic mercury in the air, whereas in North America they account for 43% (Pirrone et al., 2010). The most recent estimates suggest that fossil fuel combustion produces 45% of the total mercury emitted world-wide from human activity (Pacyna et al., 2010). In light of these data and because: 1) the emission limits of mercury from coal burning power plants have not been universally defined; 2) measures to implement these limits are still under consideration; 3) the role of gas cleaning systems for NO_x, particulates and SO₂ emissions in mercury emissions is still unknown; and 4) research into the development of systems for mercury capture is ongoing (UNEP, 2010a and 2010b), accurate replicable quantification of mercury present in the products involved in coal combustion is of great importance. Accuracy and precision in the analysis of a trace element as toxic as mercury are always essential, but in the case of the main anthropogenic source of this element, are crucial. To record mercury emissions and to develop methods for reducing them it is necessary to determine and identify mercury and its compounds in solid, liquid and gaseous products. Moreover, accurate and precise mercury analyses are the key to obtaining reliable information on emissions and on mass balances. The present review, therefore, discusses those methods that, at the current level of development, are generally preferred by laboratories which work with coal and coal combustion by-products (CCBs), with reference to the quality of the results and the effect that analytical uncertainty has upon the evaluation of contamination.

1.-Mercury analysis: general considerations

As is the case with analytical problems, to obtain reliable data on mercury content it is necessary to follow the appropriate sampling procedure and sample pre-treatment process, to select the appropriate method of measurement, and to validate the results. During these operations, contamination and random loss of the element through volatilization, adsorption, diffusion etc., must be prevented. In the case of mercury, each and every one of these operations is critical and needs to be strictly controlled, because some mercury species are extremely volatile and can easily be adsorbed on and diffuse through the walls of containers and equipment employed.

Before describing how to analyze mercury, it is necessary to review some general features of the mercury compounds. Atmospheric mercury is commonly grouped into three predominant species: elemental mercury (Hg^0), which is the dominant species in the atmosphere; oxidized mercury (Hg^{II}), which is the most reactive; and particulate mercury (Hg_p). In general, oxidized mercury (Hg^{II}) is the predominant form of mercury incorporated in soils (Schuster, 1991). Hg^{II} may be reduced to elemental mercury (Hg^0) or it may become involved in methylation-demethylation cycles, acquiring a methyl group and resulting in methyl mercury (MeHg), which is an especially toxic species (Ayira et al., 2009). Coal combustion and gasification is a source of Hg^0 , Hg^{II} and Hg_p . MeHg is the end product of biochemical reactions, but as it is not present in coal and combustion by-products it is outside the scope of this paper. In the coal combustion process mercury compounds present in the feed materials and by-products are mainly inorganic species which are in solid, liquid, or gas phase. To analyze them, the preparation phase needs to be strictly controlled, because the volatilization of mercury from solid and liquid samples may occur. It may also be necessary to stabilize liquid

samples and solutions obtained from solids in order to prevent their adsorption and diffusion through the containers. It is also important to bear in mind the ability of mercury to amalgamate with metals, and also to be cognizant of the problems arising from memory effects and interferences within the equipment.

1.1.- Volatilization from solid samples during the preparation for analysis

Mercury and its compounds are extremely volatile species. They may be lost during sampling, storage, preparation or analysis, even if the samples are subjected to relatively low temperatures. To our knowledge, no studies have been carried out on mercury evaporation at room temperature from coal. However, some research has been conducted on the possible evaporation of mercury from solid CCBs, including fly ashes and gypsum produced in flue gas desulphurization (FGD) units. These studies were mainly aimed at determining the loss of mercury when CCBs are processed for different industrial applications. For instance, Rubel et al. (2006) found that mercury was thermally stable up to 300 °C in a series of ash samples. However, studies carried out using modified versions of a laboratory test, especially designed for this evaluation and performed over different periods of time (Hassett et al., 2002; Hassett et al., 2004, Heebink and Hassett, 2004 Heebink and Hasset 2005), showed that mercury may be released from the FGD derived gypsum samples studied at temperatures between 150 and 180 °C. These studies also assessed the release of mercury in vapour form at long-term ambient and near-ambient temperatures from six CCB samples, with mercury contents ranging from 0.112 to 0.736 $\mu\text{g g}^{-1}$. Although their results were found to be inconclusive because they varied depending on the experimental conditions, extremely low emissions of mercury from ash samples were observed. The average amount released from all these ashes was of the order of pg of mercury, and there was no clear

evidence that the rate of mercury emitted was related to the total mercury concentration. What is remarkable is that in one series of tests (Heebink and Hassett, 2004) one of the ash samples appears to have absorbed mercury from the environment instead of losing it. The release of mercury from disposed or utilized CCBs requires additional study.

1.2.-Stability of the liquid samples; adsorption and diffusion through the containers

Loss of mercury from diluted solutions depends on a number of factors and that in a relatively short space of time may amount to more than 90% of all mercury within the sample (Lo and Wail, 1975). Two points must be taken into consideration. One is the possible loss of mercury during storage, and the other the possibility that the solution may be contaminated by adsorption of mercury from the walls of the container or the surrounding atmosphere. The stability of mercury solutions depends on the concentration of the mercury, its mode of occurrence, the composition of the matrix solution, the material from which the container is made, the previous cleaning and pre-treatment of the containers, and, above all, the preservative added or the preservation technique employed. The two mechanisms which are responsible for the loss of mercury from solution are adsorption on to the container walls and volatilization. Hg^{II} can be reduced in the presence of a reducing agent, resulting in Hg^0 that is able to escape from the solution. Moreover, the formation of undetectable forms of mercury, such as highly stable chemical complexes or stable amalgams after the reduction of oxidized mercury, may also occur (Leermakers et al., 1990).

The most popular types of container material are polyethylene, borosilicate glass and Teflon. Polyethylene containers are not suitable for maintaining low concentrations of mercury; glass is more effective (Bothner and Robertson, 1975; Feldman, 1974; Lo and Wail, 1975). The main preservatives that have been used with good results are

acids, oxidizing agents and complexing agents. The use of chemical preservatives appears to be necessary in order to maintain mercury concentrations in diluted aqueous solutions. An oxidant such as dichromate or an auric compound is required in a nitric acid medium (Caroli et al., 1996; Coyne and Collins, 1972; Dobb et al., 1994; Feldman, 1974). In any case, random problems in stabilization protocols are always possible, and it is advisable that diluted mercury solutions be prepared and analyzed as quickly as possible to ensure accurate results.

1.3.-Amalgamation with metals

All metals can form amalgams with mercury, iron and platinum being notable exceptions. Moreover, HgCl_2 is a corrosive species that can also amalgamate with metals, such as aluminium. In order to avoid the loss of analyte through this process, the material used for the analysis of the mercury species needs to be controlled. This includes not only the containers in which samples are stored, but also the other tools and equipment involved in the analysis.

1.4.- Memory effects and interference

The memory effect in an analysis of mercury or another element is a problem that originates when species of that element remain somewhere in the equipment, resulting in a positive bias in the subsequent analyses. Inductively coupled plasma-mass spectrometry (ICP-MS) is an example of a technique that often has a pronounced memory effect from mercury. This is due to retention of the mercury in multiple locations: the sample introduction tubes, the nebulizer and the spray chamber (Woller et al., 1997), as well as the torch itself. Different approaches have been tried with ICP-MS analysis to eliminate mercury memory effects. Allibone et al. (1999) found that by adding gold to samples of water analyzed by ICP-MS, the memory effects decrease, but,

in general, the effectiveness of the procedure depends on the type of sample (Harrington et al., 2004; Moreton and Delves, 1998; Woller et al., 1997).

Interference is a common problem when conducting analyses by cold vapour atomic absorption spectrometry (CVAA). It is due to the presence of a substance that leads to systematic error of a magnitude higher than an established value. The substance that causes the interference distorts the analytical signal, preventing identification of the element or causing an error to occur. In general, interferences depend not only on the analytical method used for the identification or determination, but also on the type of sample. Because each sample has a different composition, the choice of a method that will avoid interferences will depend on the matrix of the sample. A typical example of interference in the analysis of mercury in coal combustion products by (CVAA) is the presence of SO₂ by absorbing light at the wavelength being measured.

2. -Samples from coal combustion processes

The solid samples involved in the coal combustion process are the inputs (the combustible feed and the limestone used in FGD plants) and the outputs or CCBs (bottom ashes, fly ashes, and the gypsum produced in the FGD plants).

The fuel is usually the main source of mercury (Ochoa, et al., 2011). The mercury content of coals all over the world ranges from 0.01 to 1 µg g⁻¹ (Yudovich and Ketris, 2005). In so far as trace elements are concerned, the mode of occurrence of mercury has still not been completely ascertained. It is highly probable that the mercury present in most coals is in the form of sulphide or associated with pyrite. Mercury may also be associated with the organic matter in some cases (Yudovich and Ketris, 2005).

Although data on the mercury content of limestone are relatively scarce, some works have reported values lower than $0.45 \mu\text{g g}^{-1}$ (Johansen and Hawkins, 2003; Senior and Eddings, 2006). In other studies, the mercury content of limestone reached values as high as $1.11 \mu\text{g g}^{-1}$ (Lopez-Anton et al., 2011a), suggesting that this input could be an important source of mercury in some FGD plants and, as a consequence, in FGD by-products. There is also a lack of information on mercury speciation in limestone (Johansen and Hawkins, 2003). No correlation between mercury content and pyritic sulphur has been found in limestone samples. Whereas some limestone samples appeared to contain mercury primarily in the form of HgS, others contained HgSO₄ and HgO (Senior and Eddings, 2006). Fly ashes showed the largest percentage of CCBs. The mercury content of fly ashes may vary considerably, depending not only on the characteristics of the coal but also on the type of combustion system and boiler used, although it generally ranges between 0.02 and $2 \mu\text{g g}^{-1}$ (Hower et al., 2010; Lopez-Anton et al., 2011a). As for the mode of occurrence, mercury can be expected to occur in fly ashes as chlorides, sulphates, associated to the inorganic or carbon particles, or even as elemental mercury (Lopez-Anton et al., 2010).

Bottom ashes or slags have mercury contents that are usually below $0.01 \mu\text{g g}^{-1}$ (Córdoba et al., 2011), very close to the detection limits of methods used for mercury analysis.

As in the case of fly ash, the mercury content of gypsum varies depending on the characteristics of the power plant, the nature of the coal burned and the performance of the FGD plant. All of these variables may modify the distribution of the mercury retained in the FGD plant between the water and gypsum, and also its speciation. The

concentration of mercury in the gypsum by-products in the samples analyzed to date has ranged from <0.01 to $0.2 \mu\text{g g}^{-1}$ (Rallo, et al., 2010a; Schroeder and Kairies, 2005).

In addition to the solid samples, it is necessary to analyze the mercury content of the waters involved in the combustion process, such as the water used for preparing the limestone slurry and the water filtered from the gypsum slurry in FGD plants. The mercury content of the gases in the stack also needs to be controlled, and in some cases the air around the power plant needs to be analyzed. In the case of the flue gases, small amounts of SO_2 , H_2O and NO_x may be present, producing interferences in some of the methods used for mercury analysis. For this reason, the equipment and methods need to be carefully selected and controlled.

3. -Analytical methods for the determination and speciation of mercury

When using any of the analytical methods described in the following sections, the simultaneous determination of certified reference materials (CRMs) is imperative to ensure the quality of the data. Currently, CRMs for different matrices are commercially available from several organizations, including the IAEA (International Atomic Energy Agency, Analytical Quality Control Services), NIST (National Institute of Standards and Technology, Office of Standard Reference Materials, USA) and NRCC (National Research Council of Canada).

3.1. Solid and liquid samples

A number of methods for the mercury analysis of solid samples have been developed (Bettinelli et al., 1999; Long and Kelly, 2002; Río-Segade and Bendicho, 1999), and reviews on these analytical methods have already been published.

The collection of solid samples needs to be carried out following a standard method (such as ASTM D 2013), to obtain a representative sample for analysis. The preparation of the samples does not pose a problem when the method used allows the direct analysis of mercury in the solid sample. However, analytical methods that require the mercury to be in solution must be considered carefully. It should be remembered that coal is a heterogeneous material composed of organic and mineral matter, and the dissolution of mercury from such a product involves the oxidation of the organic matter and the dissolution of the minerals. In most cases organic matter may be eliminated using either wet or dry methods. The dry methods (ashing), even at low temperatures, are not feasible for an element of such high volatility as mercury. Wet methods (Pollock, 1975) need to be performed inside a closed vessel at high or low pressures, in order to avoid any loss of mercury (Bettinelli et al., 1987; Park et al., 2006; Wu et al., 1996).

Among the most common techniques employed today by laboratories for trace element analysis in coal, ICP-MS is the most common, and it is used for mercury analysis due to its excellent sensitivity (theoretically between 1 and 10 pg ml⁻¹) (Allibone et al., 1999; Bettinelli et al., 1987; Wilbur, 1999; Wu et al., 1996). However, as already mentioned, this method may pose several problems in relation to the volatility of mercury compounds and the memory effects that, to some extent, restrict its use. For this reason, the conventional methods of measuring total mercury, including neutron activation analysis (NAA), CVAAS and cold vapour atomic fluorescence spectroscopy (CVAFS) are more common.

NAA should not strictly speaking be considered a conventional method due to its high cost (resulting from the need for a nuclear reactor and an expensive counting

apparatus), and the strict safety requirements for handling radioactive materials. However, this technique is employed by several key laboratories. In NAA, thermal neutrons are irradiated in a nuclear reactor and the gamma radiation from the ^{197}Hg generated is measured by means of comparative quantification with the standard sample. This method allows a non-destructive analysis in which the sample is analyzed directly without the need for any pre-treatment. Its main advantage is that it is very precise and sensitive (Blanchard and Robertson, 1997; Dams, 1992; Olmez, et al., 1993; Olmez et al., 1995).

Cold-vapour (CV) methods use reducing agents, such as SnCl_2 or NaBH_4 , to convert the ionic Hg^{II} in solution into Hg^0 in gas phase. The liberated $\text{Hg}^0(\text{g})$ is introduced into the absorption cell of an atomic absorption or fluorescence spectrometer where it is detected (Morita, 1995; Price, 1979; Robinson, 1996; Slavin, 1978; Ure, 1975). CV techniques are much more sensitive than conventional flame atomic absorption spectrometry, reaching mercury detection limits as low as $0.01\text{-}0.2 \text{ ng ml}^{-1}$ (Doering et al., 2000; Mniszek, 1996). The standard CVAAS procedures have been revised and discussed by Pavlish et al. (2003), including Swedish Standard SS 02 84 23, US EPA Method 303F (1980), US EPA Method 245.1 and 245.2 (1983), and US EPA 7470 and 7471(1988). The standard procedures based on CVAFS include the US EPA Methods 245.7, 1631 and 7474 and ISO 17852.

The main standard methods used for mercury analysis in coals are: i) ASTM D3684 Bomb Combustion CVAAS; ii) ASTM D6414 Acid Extraction CVAAS iii) ASTM D6414 Wet Oxidation CVAAS; iv) ASTM D6722-01 Direct Combustion Analysis v) US EPA 7471A Acid Extraction CVAAS; and vi) ISO 15237 Bomb Combustion CVAAS. All of them involve detection of mercury by CVAAS, the

differences being in the method of organic matter oxidation and mercury dissolution. In the ASTM D3684 and ISO 15237 methods, mercury in coal is determined by combusting a weighed sample in an oxygen bomb with diluted nitric acid. In the case of ASTM D6414, and US EPA 7471 the mercury present in coal and CCBs is dissolved by heating the sample in a mixture of acids, which may also contain a catalyst, inside a closed digestion vessel. The acid solutions produced are transferred to a vessel where the mercury is reduced to elemental mercury. In ASTM D6722-01 the sample of coal or CCBs is thermally and chemically decomposed and oxidized in a furnace.

Some researchers claim that the most promising methods for determining mercury in coal are ASTM D3684, ASTM D6414 and ASTM D6722-01 (Sondreal, et al., 2000). Most of these methods can also be used for mercury analysis in materials other than coal. However, gypsum and limestone samples are usually analyzed by means of the US EPA Method 1631 (Kairies et al., 2006). In this method, after digestion of the samples, the total mercury is determined by oxidizing it to Hg^{II} with BrCl . The sample is then reduced with $\text{NH}_2\text{OH}\cdot\text{HCl}$ to destroy the free halogens, and further reduced with SnCl_2 to convert Hg^{II} to Hg^0 . The Hg^0 is taken out of the solution either by purging it with nitrogen, helium, argon or by vapour/liquid separation. The Hg^0 is collected in a gold trap and then desorbed into an inert gas stream that channels the mercury into the detection cell of a CVAFS.

The main disadvantage of these methods is that the mercury must be present in a solution and for this reason the use of automatic mercury analyzers (AMA) that allow direct analysis of the solid or liquid sample is the preferred method. These analyses are based on the CV technique which has already been mentioned (ASTM D6722-01). The sample preparation consists simply of weighing it, thereby minimizing contamination

and errors introduced during the sample preparation of digestive methods (Costley et al., 2000; Richaud et al., 1998). The mercury evaporates from the solid after combustion and decomposition of the sample in an oven, where reduction to elemental mercury also takes place. The mercury in the gas phase is transported to an amalgamator containing gold, retained, and then evaporated and detected as $\text{Hg}^0(\text{g})$. The advantages of this technique are that it can be performed in equipment that is relatively well shielded so as to avoid the loss of mercury, and detection limits as low as 0.01 ng can be attained.

The quality of the results obtained by using AMA (254 Mercury Analyzer (LECO)), has been assessed in a study by Lopez-Anton et al. 2006, using standard samples (two coals and a fly ash). Precise results, statistically indistinguishable from the certificate or reference values, were obtained in the two types of samples (Table 1). The average values of 10 determinations performed by the same operator were compared with the reference or certificate values. The RSD% was less than 10% for the fly ash and close to 5% for the coals (Table 1). These results suggest that the method, in addition to being fast, simple and relatively free of interferences, provides statistically accurate and precise results. There are several types of equipment available on the market, based on the same principle as the US EPA method 7473, 2007. These include the DMA-80 Direct Mercury Analyzer (MILESTONE), the AMA 254 Mercury Analyzer (LECO), the Hydra-C Mercury Analyzer (Teledyne Leeman Labs), and the RA-915+ Mercury Analyzer equipped with the pyrolyzer PYRO-915.

Table 2 provides a comparison of the different techniques that are most frequently used for mercury analysis; ICP-MS, AMA, CVAFS, CVAAS and NAA. The samples analyzed were two reference materials prepared in the laboratory by impregnating a commercial activated carbon with mercury. Impregnation was

performed in order to obtain samples with a wide range of mercury concentrations; 1 and 10 g g⁻¹. The average value of all the analyses was taken as the reference value. In all cases, the relative standard deviations from the result obtained for one of the methods were found to be lower than 10% of the reference value. The results obtained using the solid sample methods (AMA and NAA) were similar. In general the lowest values were detected by the methods that require dissolution (CVAFS and CVAAS), with the exception of the ICP-MS method, where, apparently, the loss of mercury through volatilization during the preparation was balanced by memory effects.

Identification of mercury species in coal, ashes, and solid products involved in combustion and gas cleaning systems is also a matter of concern from the environmental and research point of view. Mercury speciation in solid samples from coal combustion and their expected concentrations is of great interest, but it is a difficult problem to resolve. X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) are techniques that have been used to identify the speciation and binding of mercury on a variety of materials employed as sorbents for mercury capture in coal combustion processes (Huggins et al., 1999, Huggins et al., 2003; Laumb et al., 2004; Olson et al., 2005, Hutson et al., 2007). However, the use of these techniques to characterize the surface of coals and fly ashes is no easy task, due to the low concentration of mercury in most samples. Mercury analysis by XPS has the added disadvantage of spectral interferences from silicon, which is present in some of these materials (Laumb et al., 2004).

Another method employed for mercury speciation in solid samples is thermally induced desorption. The mercury thermo-desorption technique has been used since 1904 (Aston and Riley, 1972; Henry et al., 1972; Koksoy et al., 1967; Lidums 1972), but only

recently has it been revived as an important tool in the study of mercury speciation in solid matrices, such as CCBs (Lee et al., 2009; Li et al., 2007; Milobowski et al., 2001; Rallo et al., 2010a; Rallo et al., 2010b). This technique is attractive because different species of mercury can be desorbed over different ranges of temperatures. To define these temperatures, a number of pure mercury compounds (HgCl_2 , HgS , HgSO_4 , HgO , Hg_2Cl_2 , Hg_2SO_4 , HgBr_2) were tested to determine their specific thermograms and obtain a set of “fingerprints” that would serve as a standard of comparison for the profiles resulting from desorption of the CCBs (Milobowski et al., 2001; Lopez-Anton et al., 2010). The temperature rate of the mercury species were arranged in increasing order as follows $\text{HgBr}_2 < \text{HgCl}_2 < \text{Hg}_2\text{Cl}_2 < \text{HgS}(\text{black}) < \text{Hg}_2\text{SO}_4 < \text{HgS}(\text{red}) < \text{HgO} < \text{HgSO}_4$ (Lopez-Anton et al., 2010; Milobowski et al., 2001). In a study of samples obtained from wet FGD processes it was found that the samples showed two thermal decomposition curves (Lopez-Anton et al., 2010). In the case of the first curve it was difficult to tell whether it corresponded to HgS or HgO , whereas the second clearly corresponded to HgSO_4 . Lee et al. (2009) tested five standard mercury compounds (Hg_2Cl_2 , HgCl_2 , HgO , HgS and HgSO_4), to compare their thermal evolution profiles and to identify the mercury species present in gypsum and wallboard products. Out of these standards, Hg_2Cl_2 and HgCl_2 corresponded to the signals observed in the profiles of the samples. This method was also used to identify the mercury species present in fly ashes of different origins that had been used as mercury sorbents in different atmospheres (Lopez-Anton et al., 2011b). The Hg compounds present in a fly ash from a fluidized bed combustion plant after it had been used as a sorbent in an atmosphere of elemental mercury in N_2 and in a simulated flue gas from coal combustion were found to be mainly HgCl_2 and HgSO_4 . The Hg species present in two fly ashes from pulverized coal combustion plants was HgCl_2 , although the presence of Hg^0 could not be ruled out, and HgS was the species

formed when the ashes were used as a Hg sorbent in a typical coal gasification atmosphere. Finally, HgCl₂ was the only Hg compound identified in the fly ashes after a sorption experiment in which HgCl₂ (g) was used in all the atmospheres evaluated.

3.2 - Gases

The analysis of mercury in gases may be performed by a number of different procedures, some of which allow mercury speciation. It has already been mentioned that, in coal combustion processes, mercury can be found as elemental or oxidized mercury, which affect its degree of removal, atmospheric fate, impact on health and other risks. As a consequence, it is very important to determine the different mercury species in the gas phase. As shown below, there are several ways to sample and analyse mercury in gases. One way is to use a trapping medium, which may be a solution or a train of solutions and a solid or a train of solids that are subsequently analyzed. The other is to use commercially available mercury instruments specially recommended for field measurement. These are devices that allow the simultaneous sampling and analysis of mercury species.

In the early 1990s the Electric Power Research Institute (EPRI) and the U.S. Department of Energy (DOE) initiated very extensive air-toxic characterization programs for electric utilities. These programs included the emission of mercury species. Because there was no validated method for sampling mercury species separately, the U.S. EPA Method 29 and the Bloom method, developed by Brooks Rand (hereafter referred to as the MESA method), were used. The results of these tests showed that, in certain conditions, Method 29 is unable to speciate mercury properly. The US EPA Method 29 allows multi-metal measurements using two sets of impingers to capture mercury in the gas phase. The first set of impingers consists of HNO₃/H₂O₂

while the second set consists of KMnO_4 . Method 29 was not designed to speciate mercury, and it has been suggested that only oxidized mercury is captured by the $\text{HNO}_3/\text{H}_2\text{O}_2$ impingers, while the remaining mercury (elemental mercury) is captured in the KMnO_4 impingers. The advantages and disadvantages of the impinger method for flue gas mercury determination (e.g. Method 29 and Method 101A) have been discussed elsewhere (Meij, 1991). In general, the main disadvantages of the impinger method are its cost, the hazards involved in the transport of the chemicals, the large volume of sample needed to overcome the high mercury blanks, SO_2 interference, and the loss of mercury through the container walls. These disadvantages and the need for mercury speciation prompted the development of the other methods, such as the MESA method (Bloom et al., 1993; Prestbo and Bloom, 1995). The MESA method, designed to speciate flue gas mercury, follows a similar approach to Method 29 except that it uses a different means of capture. This method employs solid sorbent traps consisting of soda lime and iodated carbon to capture oxidized and elemental mercury, respectively. The MESA method is greatly affected by the interaction between SO_2 and NO_x in the flue gas, as a result of which the ionic mercury fraction is overestimated (Laudal, et al., 1996b). There were also doubts as to the ability of the MESA method to speciate mercury in flue gas from coal combustion (Chu and Porcella, 1995). After extensive reviews and evaluations (Laudal, et al., 1996a; Laudal, et al., 1997a; Laudal, et al. 1997b), the Ontario Hydro (OH) method has been established as the accepted wet-chemical method for measuring total and speciated mercury (ASTM D6784-02). Laboratory and field validations have revealed relative standard deviations of $\sim 10\%$ (Laudal, 1999). Using this method, three forms of mercury are measured: i) Hg_p , that is separated by filtration; ii) gaseous Hg^{II} , which is collected in potassium chloride impingers, and iii) gaseous Hg^0 that is oxidized and collected in nitric acid/peroxide and

acidified permanganate solutions. Well-trained personnel are required to use this method, and several restraints must be applied to stabilize the solutions and prevent sample contamination (Sondreal et al., 2000; Sun, et al., 2003). Other methods under development, such as the Solid Ontario Hydro (SOH), use solid reagent cartridges instead of liquid impingers. The results indicate good agreement with the wet OH method for Hg^0 and Hg^{II} , but particulate mercury cannot be measured (Prestbo and Laudal, 2000). There are a number of commercial sorbent traps which are simple to use and offer precision and accuracy (Laudal, 2006), but SOH, like the OH method, is not designed for continuous sampling. Most sorbent traps are able to measure total mercury, even if some traps employ multiple sorbents to determine mercury speciation. The U.S. EPA Method 30B is a procedure designed to measure total vapour-phase mercury emissions from coal-fired combustion sources using sorbent trap sampling and an extractive or thermal analytical technique. This method is only intended for use if the presence of particulates is low.

Mercury continuous emission monitors (Hg CEMs) are relatively new technologies. They work in a way similar to continuous monitors of other gaseous compounds already operating in power plants. When continuous mercury monitoring is used for mercury speciation problems may arise in conjunction with the quantitative transport of the mercury species from the stack to the mercury detector. Several Hg CEMs are commercially available (Bergan et al., 1999), some of which have been designed as adaptations of those already used in waste incinerators. However, measuring coal-derived flue gases is more difficult, due to the low mercury concentrations (below $10 \mu\text{g m}^{-3}$) and the presence of fine particulates and gaseous acids, such as HCl, SO_2 , and NO_x , that can interfere with the measurements (Laudal et al., 2000). Although Hg CEMs detect only Hg^0 , they can be implemented to measure

total mercury by using a conversion system which reduces the oxidised mercury to elemental mercury. The amount of oxidised mercury can be calculated by difference. The particulate-bound mercury is typically filtered out. This may be important for high particulate-emitting sources (e.g., sources with minimal particulate matter (PM) control), or in cases where the mercury measurements are conducted upstream of PM control devices. As a result, in most commercially available CEMs the total amount of mercury measured is, in fact, total gaseous mercury (TGM). Therefore, the possibility of sampling and analyzing the filtered particles to measure Hg_p should be a viable procedure.

The options available for the reduction of Hg^{II} can be divided into two groups: i) wet conversion using a liquid reducing agent (e.g., stannous chloride); and ii) dry conversion methods (with high temperature catalysts or thermal reduction units to reduce oxidised mercury). The first option is the most established, but wet chemicals are typically corrosive, require frequent renewal and produce hazardous wastes (Laudal et al., 2004; Ryan and Kilgroe, 2001).

The most frequently used methods of differentiating between the Hg CEMs are based on the mercury measurement detection principle: CVAAS, CVAFS, in-situ ultraviolet differential optical absorption spectroscopy (UVDOAS) and atomic emission spectrometry (AES). As with the detection equipment used for mercury analysis in solids, most of the commercially available Hg CEMs are based on CVAAS or CVAFS.

Several Hg CEM devices are available on the market, the chief characteristics of which are outlined below. The *Sir Galahad II* (PS Analytical Ltd., 2011) is an automated continuous emission monitor for elemental mercury and total vapour-phase mercury (TGM). It consists of a mercury speciation module and an enclosed cabinet

which houses an amalgamation atomic fluorescence mercury detector, a stream selector module and a mercury calibration source. The speciation module converts oxidized mercury in the sample gas to elemental mercury by means of a proprietary aqueous reagent, thereby allowing Hg^0 and TGM to be detected separately. The *Ohio Lumex RA-915+* (Lumex Ltd., 2011) uses catalytic pyrolysis to decompose oxidized mercury to Hg^0 , which is detected by CVAAS equipped with Zeeman high-frequency polarization background correction. The Lumex CEM is a two-channel instrument, in which one mercury detector operates with the catalytic pyrolyzer and the other without. It is therefore able to provide simultaneous and continuous readings of total and elemental mercury, respectively. The *Tekran 2537* (Tekran Instruments Corporation, 2011) samples the gas and traps mercury vapour inside a cartridge containing an ultra-pure gold adsorbent. The amalgamated mercury is thermally desorbed and detected using CVAAS. A dual cartridge design allows alternate sampling and desorption, thereby permitting the continuous measurement of the mercury stream. Furthermore, it is designed to be insensitive to the presence of SO_2 , NO_x , CO_2 , HCl and other common combustion by-products. The Tekran system also allows simultaneous measurement of Hg^0 , gaseous Hg^{II} and particulate matter (Keeler, et al., 2009). Several round robin studies have reported reliable data via this system (Landis et al., 2002; Munthe et al., 2001), although problems have been observed for speciation in the presence of ozone (Lyman, et al., 2010). The *AM-2* (Nippon Instruments Corporation, 2011) is another example of a Hg^0 pre-concentration and detection system. In this device a flow of sample is drawn through a distilled water scrubbing trap, where oxidized mercury species are removed before reaching a dehumidifier. The sample then passes through a gold amalgamation trap, which collects and concentrates the Hg^0 . This detection system is a CVAAS. In the *DM-6/DM-6P* system (Nippon Instruments Corporation, 2011) a

solid reducing agent is used to reduce Hg^{II} to Hg^0 by passing the gas through a catalyst bed. After exiting the catalyst, the sample is cooled and then filtered by means of a membrane filter before being transported to the CVAAS detector. The *MS-1/DM-5* (Nippon Instruments Corporation, 2011) monitors Hg^0 and Hg^{II} continuously in gases from the stack, using a speciation unit and two CVAAS detectors, one for Hg^0 , the other for Hg^{II} . The *Semtech 2010* (Semtech Metallurgy AB, Lund, Sweden, 2011) is essentially a portable Zeeman-modulated CVAAS that is able to monitor Hg^0 continuously. The Zeeman-effect background correction system, which combines a modulated magnetic field and a mercury lamp, minimizes interferences from SO_2 , hydrocarbons, and fine particulates. Semtech offers a wet-chemistry conversion system to reduce Hg^{II} to Hg^0 . However, the conversion system only works if there is no SO_2 present in the sample gas. The *Opsis HG200* (Opsis AB Furulund, Sweden, 2011) contains a dual gold amalgamation trap followed by a dual beam CVAAS. This system measures the total mercury, reducing the vapour phase Hg^{II} to Hg^0 by means of a dry thermocatalytic converter. The detection limit, which is 0.5 ng m^{-3} without the trap, reaches 0.05 ng m^{-3} with dual amalgamation. The *MERCEM* (SICK MAIHAK GmbH, Germany, 2011) is also based on gold trap amalgamation and CVAAS and uses SnCl_2 reduction to convert Hg^{II} to Hg^0 . The measurement range is $0\text{-}45 \text{ } \mu\text{g m}^{-3}$ and the detection limit is $<1.5 \text{ } \mu\text{g m}^{-3}$. In the *HM 1400TR* device (DURAG, Inc., US, 2011) the gas is sampled by direct extraction and transferred to a dry thermo-reactor for the conversion of Hg^{II} to Hg^0 . Continuous monitoring is based on the principle of CVAAS as detected by a UV Photometer. The dual beam arrangement allowed by a reference cell eliminates any background interference due to SO_2 absorption. The detection limit is $0.05 \text{ } \mu\text{g m}^{-3}$. The *Argus-Hg 1000* (EnviroMetrics, 2011) measures total mercury with the aid of a catalytic converter which reduces molecular forms of mercury. The mercury is

pre-concentrated by an absorbent which is thermally desorbed, and is analyzed by exciting the sample using a patented microwave plasma source. The emissions are then detected by a low-resolution ultraviolet spectrometer. The *Thermo Electron Mercury Freedom System* (Thermo Electron Corporation, 2011) is able to measure Hg^0 , Hg^{II} and TGM. An advanced CVAFS design provides continuous sample measurement, with no additional gases or pre-concentration required and virtually no interference from SO_2 . Detection limits as low as 1.0 ng m^{-3} allow high sample dilution (100:1) and minimize moisture, heat and interfering pollutants. In the *Mercury Stack Gas Monitor SM-3* (Mercury Instruments, 2011) forms of mercury such as HgCl_2 , HgO , HgS and particulate mercury are detected as well as elemental mercury. In this system, the thermo-catalytic reduction of ionic and bound mercury takes place. The gas is then fed into the mercury detector where the mercury is measured by means of CVAAS. The *VM-3000 Mercury Vapor Monitor* (Mercury Instruments, 2011) measures Hg^0 by means of AAS, and does not require an amalgamation step or any expensive carrier gases. The *UT-3000 Mercury Vapour Monitor* (Mercury Instruments, 2011) combines a GoldTrap amalgamation module with a CVAA detector.

To render Hg CEMs eligible for regulatory compliance assurance, their performance needs to have been demonstrated as reliable. During the last 10 years the US Environmental Protection Agency (U.S. Environmental Protection Agency, 2001a, 2001b, 2003a, 2003b, 2003c, 2003c, 2003e, 2007a, 2007b), has undertaken a verification program to evaluate Hg CEMs at full-scale pilot sites using the Hg CEMs commercially available in the US, and has compared the results with the OH method. The most significant results of the verification campaign are presented in Table 3. Although this is not indicated in Table 3, the results show that almost all the lower readings correspond to the CEMs (U.S. Environmental Protection Agency, 2001a,

2001b, 2003a, 2003b, 2003c, 2003c, 2003e, 2007a, 2007b). However, good correlations with the OH method were obtained ($r^2 = 0.839-0.989$) in all cases (Table 3), with the exception of the Lumex CEM. The lack of good correlation in that case was due to the loss of mercury in the inlet systems and the low pyrolyzer temperatures in several of the tests conducted with the Lumex CEM. This device was relatively new when the verification programme was carried out (2011), and during the verification test modifications were introduced by the Lumex staff. From these results it can be concluded that, in general, CEM systems offer a reliable alternative to the OH method for mercury measurement in industrial applications, with the added advantages that they are simple to use and that measurements can be made on line.

4. An example of the evaluation and control of mercury in coal power plants

In order to provide an approximation of the results that can be obtained in a study of mercury behaviour in a power plant, an example of the application of these methods to a real problem (i.e. that of mass balances in power plants) is presented. In this study, the uncertainty of the results of the analysis for all the products involved in the running of the power plant was calculated and the confidence limits of the results that can be expected from the analytical results are presented. The methods used to carry out this evaluation are among the most commonly used. To determine the amount of mercury in coal and CCBs, direct combustion analysis (ASTM D6722-01) performed using the different instruments previously described is the main procedure. Acid extraction or wet oxidation/CVAA (ASTM D6414-01) for other solid and liquid samples is also a widely used procedure. In addition, the Ontario Hydro method (ASTM D6784-02) is the standard method for the analysis of mercury species in a gas stream. All these methods were used for the analysis of mercury in the products involved in coal

combustion in two pulverized power plants, one of which was equipped with a flue gas desulphurization (FGD) system. Table 4 shows the mercury contents along with the degree of uncertainty for the analysis of these products. The results and uncertainty were calculated according to the ASTM D6722-01 method for solid (coal, bottom ash, fly ash, and gypsum) and liquid (water) samples because it was possible to analyze these samples directly using an automatic mercury analyzer and they fell within the appropriate range of concentration for this method. The results and uncertainty for the particulate matter were determined using the ASTM D6414-01 method after acid digestion in a microwave oven. With the OH method an acceptable degree of uncertainty is <11% for mercury concentrations in a gas phase of $>3 \mu\text{g m}^{-3}$ and <34% for mercury concentrations in a gas phase of $<3 \mu\text{g m}^{-3}$. In the gas analyses presented in Table 4, the confidence limits were of this order in both cases. For the rest of the samples, solids and liquids, the limits of confidence in the analysis of solid samples are of the same order. Consequently, if the percentage of products found in each power plant after combustion are examined (% out values in Table 4), the highest degree of uncertainty associated with the analytical procedure corresponds to the analysis of the samples with the highest proportion of mercury. In the case of the power plant without an FGD unit this was the analysis of the gases, whereas in the power plant with an FGD system this was the analysis of the gypsum samples

5. Conclusions

The analysis of the products and by-products involved in the processes of energy production from coal (coal, ashes, limestone, gypsum, water and gases) is an indispensable tool for controlling and preventing environmental problems that may be

initiated by emissions of mercury compounds. The characteristics of mercury compounds are such that, whatever the analytical method used, the strictest precautions need to be taken to prevent the loss of, and contamination by, mercury species during the analytical procedure. Once this has been achieved, the analysis of the total mercury species in solid and liquid products offers no problem. User-friendly equipment that meets the standards for analysis of total mercury in solid and liquid products is readily available. The analysis of mercury in the flue gas of combustion plants is more difficult. Although equipment for the analysis of gas samples can be found on the market, it is not always free of interferences.

However, unarguably the biggest problem related with mercury analysis, both in general and with coal and coal combustion by-products in particular, is that of identifying the species of mercury present in the samples. This is where there is a need for further analytical development.

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Table 1.-Results obtained from the analysis of mercury using AMA equipment

	SARM19 (coal)	SARM20 (coal)	1633b (fly ash)
n	10	10	10
ref./cert ($\mu\text{g g}^{-1}$ Hg)	0.2	0.25	0.14
x ($\mu\text{g g}^{-1}$ Hg)	0.23	0.25	0.15
SD	0.010	0.013	0.014
RSD %	4.3	5.2	9.3

Table 2. Comparison of mercury analyses obtained by different techniques (average values of two replicates)

	Reference ($\mu\text{g g}^{-1}$)	ICP-MS $\mu\text{g g}^{-1}$	AMA $\mu\text{g g}^{-1}$	CVAFS $\mu\text{g g}^{-1}$	CVAAS $\mu\text{g g}^{-1}$	NAA $\mu\text{g g}^{-1}$
CA1	1.15	1.22	1.21	1.07	1.05	1.20
CA10	11.5	12.4	10.9	10.6	11.2	11.1

CA 1 and CA 2 are synthetic samples prepared from impregnation of an activated carbon with mercury.

Table 3. Results from the Quality Assurance (QA) study carried out through verification testing (U.S. Environmental Protection Agency, 2001, 2003, 2007).

Hg CEM	Industrial facility	Date	Relative Accuracy (%)	Precision (%)	Correlation ¹ (r ²)	Response time
Argus Hg-1000	Tennessee Toxic Substances Control Act Incinerator (TSCAI)	September 2003	76.5-55.5	10.1-22.1	0.839-0.976	7 min
DM-6/DM-6P	Tennessee Toxic Substances Control Act Incinerator (TSCAI)	September 2003	20.3	9.1-10.9	0.953	2 min
MS-1/DM-5	Tennessee Toxic Substances Control Act Incinerator (TSCAI)	September 2003	Hg ⁰ : 10.1 Hg ²⁺ : 78.6 Hg _T : 11.2	9.2-17.3	Hg ⁰ : 0.989 Hg ²⁺ : 0.985 Hg _T : 0.9879	3 min
Opsis Hg 200	Tennessee Toxic Substances Control Act Incinerator (TSCAI)	September 2003	63.1-76.3	12.5-43.4	0.935	5 min
Sir Galahad II	Tennessee Toxic Substances Control Act Incinerator (TSCAI)	September 2003	Hg ⁰ : 54.7 Hg _T : 59.8-42.8	8.9-15.9	Hg ⁰ : 0.948 Hg _T : 0.875	5-6 min
AM-2	Rotary Kiln Incinerator Simulator	August 2001	Hg ⁰ : 14-23	10-15	Hg ⁰ : 0.878	13 min
Lumex	Rotary Kiln Incinerator Simulator	August 2001	Hg ⁰ : 50.2-107 Hg ²⁺ : 99-69.4 Hg _T : 58.2-71.0	10-15	Hg ⁰ : 0.052 Hg ²⁺ : 0.631 Hg _T : 0.621	20-150 s
Tekran 3300	R. M. Schahfer Generating Station	February 2007	Hg ⁰ : 27.8-15.4 Hg _T : 28.7-18.5	4.7-6.9	Hg ⁰ : 0.735 Hg ²⁺ : 0.098 Hg _T : 0.805	7.5-10 min
Thermo	R. M. Schahfer Generating Station	February 2007	16.4	2.6-7.2	—	3-4 min

¹. Correlation with Ontario Hydro method

Table 4. Precision of the test methods according to ASTM D 6722-01, ASTM D6414-01 and ASTM D6784-02 norms for determining mercury in solids, liquids, particulate matter (PM), water and gases in two pulverized coal combustion (PCC) plants with and without flue gas desulphurization units (FGD).

	In		Out											
	Coal		Bottom ash		Fly ash		Gypsum		PM		Gas		Water	
	$\mu\text{g g}^{-1}$	%	$\mu\text{g g}^{-1}$	%	$\mu\text{g g}^{-1}$	%	$\mu\text{g g}^{-1}$	%	$\mu\text{g m}^{-3}$	%	$\mu\text{g m}^{-3}$	%	$\mu\text{g ml}^{-1}$	%
PCC	0.06±0.02	100	0.017±0.009	0.31	0.24±0.04	39.5	---	---	0.03±0.02	0.47	3.3±0.4	59.7	---	---
PCC-FGD	0.09±0.02	100	---	---	0.05±0.02	14.8	0.12±0.03	50.7	---	---	2.1 ±0.8	25.4	0.04±0.02	8.4

