Measuring gas phase mercury emissions from industrial effluents

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Measuring Gas Phase Mercury Emissions from Industrial Effluents

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1 Introduction

A number of hazardous and toxic gaseous species are emitted into the atmosphere from a large variety of industrial-scale processes. Of the trace metal species that have been identified in industrial gaseous emissions, mercury and its compounds (expressed as mercury or Hg) has received the most attention due to the perceived health and environmental risks associated with its release into the atmosphere. Hg emitted from industrial sources is therefore now recognized as a major concern by governments and environmental bodies worldwide.

Anthropogenic emissions have resulted in global atmospheric Hg deposition rates approximately three times higher than in pre-industrial times, with increases of 2 to 10 times in and around the most industrialized regions [1]. According to the United States Environmental Protection Agency (US-EPA), in its *Mercury Study Report to Congress* [2] in 1997, the amount of mercury released into the atmosphere from human activities in 1995 was between 50 and 75 percent of the total yearly release (including natural, anthropogenic, and oceanic emissions) of 5,500 Mg. The most common estimates for anthropogenic Hg emissions to the atmosphere range between 2,000 to 2,900 Mg per year; China is widely cited as the largest anthropogenic emitter, being responsible for approximately a quarter of global emissions with ~690 Mg in 2003 [3]. While there are comprehensive Hg emission inventories regarding industrial processes for many countries, significant gaps still remain within the data. Additional uncertainties remain about how far mercury may travel from its respective emission source, and thus its impacts on the surrounding environment cannot be fully quantified.

The continuous monitoring and controlling of these emissions is an important factor in increasing the sustainability of many industrial processes worldwide. Globally, Hg emissions have been decreasing; more than 11% reduction has been observed between the year 2000 (2,190 Mg) and 2005 (1,930 Mg) levels [4, 5]. Although it is expected that Hg emissions from industrial sources in the year 2020 will be reduced to $\pm 20\%$ of year 2000 levels [4], others [6] estimate an increase of ~25% on 2005 levels will occur if no further action is taken to reduce emissions globally. Such increases, when based merely on loss of IQ (Intelligence Quotient), is expected to have an annual cost of ~US\$3.7 billion (2005 dollars) in 2020 [6]. The ability to rapidly detect Hg emissions over a range of industrial processes will significantly assist various industries to comply with new and future Hg emission guidelines. Furthermore, it will provide a better understanding of the causes and effects of how different process operating conditions influence Hg emissions rates from the many different types of industrial sources worldwide.

1.1 Mercury Emissions from Industry

Historically, mercury has been used for a variety of diverse applications which range from batteries, thermometers and electrical switches to liquid mirrors for telescopes. Currently, mercury is primarily used in some specialized electrical, lighting and electronic devices and in the manufacture of some industrial chemicals, and thus is a valuable commercial commodity. In industrial situations mercury can enter into the environment through its improper disposal (e.g. landfill or incineration) or via its direct release into the atmosphere from stationary industrial sources that use combustion and high temperature processes, such as those found in coal-fire combustion processes for power generation and within the mining and mineral refining sectors.

Given the efforts of the US-EPA to regulate Hg emissions from industrial sources over the past few decades [7-10], it is foreseeable that new air emissions standards for coal- and oil-fired power utilities operating in the US will force the utilities to comply with tougher monitoring and emissions regulations [11]. Thereafter it is highly anticipated that other industries contributing to the total amount of mercury emitted to the atmosphere are also likely to be subjected to similar regulations, in much the same way as the cement industry in European countries are currently facing [12]. Since the year 2000, for example, continuous monitoring of Hg emission in cement kilns in Germany has become mandatory [13] with Hg emission limits of 50 and 30 $\mu\text{g}/\text{m}^3$ for half-hourly and daily averages, respectively [12].

In order to understand the significance of the issue, much effort has been dedicated to identifying which industries are the predominant emitters, as well as trying to understand the mercury cycle within each industrial process, so as to limit Hg emissions into the atmosphere. Typically the main industrial processes which emit Hg into the atmosphere can be broken down into the following categories:

- Combustion of coal, oil, municipal waste and natural gas.
- Mining and refining processes (e.g. smelting, refining of minerals and hydrocarbons).
- Some chemical and manufacturing processes (e.g. caustic soda and cement production).

Apart from industries which fall into the categories above, environmental contamination occurring from the dental/medical community and landfill are also known causes. However, in comparison the associated Hg emissions are much lower than those of large industrial sources. Similarly it should be noted that open biomass burning, which is not always considered anthropogenic, can also be an important source of Hg emissions in certain parts of the world [14-17].

The first global emission inventories were compiled by Pacyna et al. [18, 19] and Pirrone et al. [20], with more recent mercury emission inventories compiled in [4, 21, 22]. It has been estimated that 7,527 Mg of Hg was emitted worldwide in the year 2010, which includes the primary emissions and re-emissions of already deposited mercury and natural sources [21, 23]. Approximately 2,320 Mg is said to be emitted from anthropogenic sources where the major global sources are from fossil-fuel fired utilities (810 Mg), gold mining (400 Mg) non-ferrous metals manufacturing (310 Mg) cement production (236 Mg) and caustic soda production (163 Mg) [21]. Future estimates of Hg emissions up until the year 2020 in Europe and 2050 globally have been projected by Pacyna et al. [24] and Streets et al. [25] (and references therein), respectively. Streets et al. [25] also lists a number of studies covering Hg emissions from particular regions and countries as well as a breakdown of emissions for each industry.

Figure 1 shows some of the major Hg emission contributions from different regions of the world. It may be deduced that most of the regional emission rates are decreasing with time, with the exception of China, Australia and the US. Although there is a lack of data available for developing countries and countries with economies in transition (such as India and China), it can be observed that China experienced an increase in Hg emissions up until the year 2003. This was partially due to the coal combustion and non-ferrous metals smelting sectors increasing from 3-4.2 % every year (up to 2003), which comprises ~80% of China's total Hg emission sources [3]. This is of major concern as it is estimated that China represented over 26% of global anthropogenic Hg emissions in the same year [21]. Unfortunately a lack of data exists for the 4 years before 2010 (data for 2005 was taken from an United Nations Environmental Program (UNEP) report [5] and can be identified by the marked arrows). Similarly, India lacks anthropogenic Hg emissions data, however it is estimated that India's anthropogenic emissions decreased from 321 Mg in the year 2000 to 253 Mg in 2004 [21]. The main sources are reported to be coal combustion (52%) and waste disposal via incineration (32%). The reduction in India's Hg emission is attributed to conversion of over 86% of its chlor-alkali caustic soda processes to mercury free membrane cell technology; however emissions from coal-fired power plants and municipal solid incineration increased by ~20% and 40% over the same period, respectively.

Figure 1: Hg emission contributors around the world. Extracted from various sources for each region: Europe(27) [26], Canada [27], USA [28], China 1995-2003 [3], India 2000 and 2004 [29], China and India 2005 [5], Australia [30], and South Africa [31].

In comparison to developing and economically transitioning countries, it is easier to predict the major Hg emission sources for countries such as the US, Canada, Australia and most of Europe, where emission inventories are well developed and readily available to the general public from national pollutant inventory websites [26-28, 30]. The increased emissions in Australia observed in Figure 1 are due to mining comprising one of the most significant sectors that contributed to Australia's gross domestic product, increasing from 4.5% in 1994 to 8% in 2007 (www.abs.gov.au). Subsequently over 40.6% of the total Hg emitted from Australia in the year 2009 originated from the non-ferrous metal sector. Similar information is also available for European countries, with the average Hg emission for Europe-27 (excluding Iceland, Liechtenstein, Greece, Luxembourg and Turkey due to a lack of data) representing 3% of the total emissions in 2004 (97.9 Mg). Further decreases, spurred by regulations restricting the use of mercury and the progressive closure of mercury emitting industries, has lead to 2% reductions in 2008 in Europe (87.4 Mg). The overall reduction in Hg emissions in the past decade is more evident when comparing the detailed technical background report presented to UNEP, which covers Hg emissions and sources from each country around the globe for the year 2005 [5], with other studies reporting Hg emissions for years prior to 2005. For example, comparing the data from UNEP report with that of Mukherjee et al. [29] it is observed that India cut its total Hg emissions in 2005 to nearly half of its 2000 emission levels.

In order to improve Hg inventory data, the US-EPA is pursuing bilateral programs with China and India on air quality, promoting best management practices to reduce environmental Hg releases and to encourage Hg emission monitoring and data management/inventory collections [9, 32]. Limited information is also available for anthropogenic Hg emissions from African countries. However, it is widely regarded that most of the Hg emissions originates from mining and small scale artisanal gold mining activities [21]. South Africa is of particular interest [33] due to its rapid industrial growth, resulting in ferrous metal production and power generation accounting for ~81% of its emissions sources [21] at an estimated 40.2 Mg in 2004 [23]. Interestingly, out of the top 10 anthropogenic emitting countries, the first three (China, India and US) are responsible for nearly 60% of total Hg emissions globally in 2005, while the bottom three (Australia, Republic of Korea and Columbia) emitted less than 5% of the total global emissions [5]. Additionally, new data available on the Hg content of Australian coal has reduced Hg emission estimates by 240 Mg (~10% of global emissions) from Australian anthropogenic sources [34], placing it below Brazil on the 2005 top 10 list of countries having the highest anthropogenic Hg emissions [5]. Brazil, the 6th highest emitter for 2005, is estimated to emit over 45% of its mercury from gold production [5]; although it has the second largest coal reserve in South America [35] it only emits 5.7 Mg of Hg from coal-fired power plant sources annually [29]. Sources of data regarding natural emissions, which are omitted from Figure 1, can be found in [5, 21, 23, 36] and references therein.

1.1.1 Thermal Power and Industrial Boilers

The largest contributing category of Hg emissions from stationary industrial sources into the atmosphere is widely recognized to be fossil fuel-fired thermal power plants and large industrial boilers. Although relatively large volumes of oil and natural gas are burned each year for power or steam generation, Hg emission from oil and natural gas combustion represents a minor contribution compared to that emitted from coal combustion [21]. Thus, in comparison to other fossil fuels, mercury emissions into the atmosphere from coal-fired combustion is found to be significantly higher [37]. Depending on the grade and origin of coal, trace amounts of mercury can vary substantially from 0.02 to 0.25 ppm with an average content of 0.09 ppm [38]. Although coal does not contain a high concentration of mercury, due to the large quantity of coal consumed and large number of coal-fired power stations worldwide it is estimated that ~878 Mg of Hg was emitted into the atmosphere from fossil fuel combustion for power and heating purposes in 2005 [5], which represents approximately 45% of all anthropogenic mercury emissions worldwide for that year. Additionally, mercury is released from coal gasification processes and when coal is burned for heating and cooking purposes, which is prevalent in rural areas in countries such as China [39] and South Africa [33].

Mercury is vaporized during coal combustion processes, where some of the mercury condenses on the ash and the rest passes into the stack gas. It is widely recognized that there has been a substantial reduction in Hg emissions from coal burning facilities over the last few decades due to the industry's continued adoption of air pollution control devices (APCD) and other associated mercury removal technologies, which has been shown to remove upwards of 90 percent of Hg in an economically sustainable manner. A bill presented to the US senate in 2010 for the clean air act amendments (CAAA) introduces further legislation requiring coal-fired power plants to cut mercury emissions by 90 percent across the US by the year 2015 by utilizing the maximum available control technology (MACT) [10]. The total mercury (Hg^T) in the coal-derived flue gas can be broken down into three forms: elemental (Hg^0), oxidized (Hg^{2+}) and particle-bound mercury (Hg^P) [40]. Electrostatic precipitators (ESPs), fabric filters (FF), baghouses and flue gas desulfurization (FGD) processes are efficient in removing Hg^{2+} and Hg^P species, however they are not suitable for removing Hg^0 . The most widely used process for removing Hg^0 is based on activated carbon injection. Due to the high complexity and the large composition variability of streams in plants located in different regions of the world, there has been a strong push to understand how different chemicals affect the removal efficiencies for each of the different removal technologies. The lifetime of the three different forms of Hg is also significantly different. In the case of Hg^0 , a lifetime of anywhere between 6 months to 2 years in the atmosphere has been reported [41, 42], whereas Hg^{2+} and Hg^P species are reported to have an atmospheric lifetime of only a few days and tend to be deposited on nearby land and vegetation. However, the overall environmental impact of Hg^{2+} and Hg^P is marginal in comparison to Hg^0 emissions, since Hg^{2+} and Hg^P are relatively easy to remove from flue gases by FGD equipment and FF/ESPs, respectively [40].

Given that Hg^0 vapor has a low affinity for oxygen, is chemically inert, has very low water solubility (49.4×10^{-6} g/l at 20°C), high volatility (vapor pressure of 0.180 Pa at 20°C) and is extremely mobile, it is thought to be the most abundant form of mercury, representing 90-99% of the total mercury in the atmosphere. Galbreath et al. [43] reported that the Hg^T concentration in coal combustion flue gas range from 5 to $50 \mu\text{g}/\text{m}^3$, with variations in the concentrations of Hg^0 , Hg^{2+} and Hg^P dependent on combustion conditions, coal composition and flue gas quench rate. There have been Hg^T concentrations as high as $10 \text{ mg}/\text{m}^3$ reported [44], however this could be due to the use of low quality coal or an untreated stream. During combustion, mercury is liberated from coal as Hg^0 . However as the flue gas cools some of the Hg^0 is oxidized, presumably to mercury(II) chloride (HgCl_2) [40] because of the large excess of chlorine present in some coal ores. Other compounds within the stream such as SO_2 , NO_x , CO , O_2 , oxidized calcium, chlorine and fly ash particles are also known to significantly influence the transformation of mercury between its elemental, ionic and particulate forms within various stages throughout a coal-fired combustion process. For instance, the concentration of Hg^0 is generally much higher than Hg^{2+} , however when Cl_2 , NO_x and SO_2 concentrations increase within the stream it has been shown that the percentage of Hg^{2+} typically increases proportionally [45]. Similar findings by other studies have found that Hg reacts with Cl_2 , HCl , NO_2 and O_2 but not with NH_3 , N_2O or H_2S , which indicates that Hg could be oxidized by a number of different routes [46, 47], thus demonstrating the complex chemistry of Hg within coal-fired combustion processes. Additionally, it has also been shown that 100 ppm of SO_2

in flue gas at 150°C can reduce the capture rate of mercury from 90% to 40%. This effect was largely reversed when this gas mixture also contained 100 ppm of HCl [48]. It should be noted that gas desulphurization equipment, which is based on the same technology that is used to remove other pollutants such as NH₃, NO_x, SO₂, etc. via selective catalytic reactors (SCRs) and wet scrubbers, can be adapted to efficiently remove Hg²⁺ from coal-fire combustion streams. However adsorption based collection processes (typically carbon based) are still needed due to the higher quantities of Hg⁰ in the flue gas, which is substantially harder to collect [37].

1.1.2 Waste Incineration

Waste incinerators (municipal, industrial, hazardous, medical, sewage sludge, etc) and human crematoria are also recognized as major sources that emit Hg into the atmosphere. Similarly, combustion processes that use either natural gas or oil are also known sources of mercury emissions, however to a far lower extent. In the case of municipal waste combustors (MWCs) the levels of mercury can be ten to one hundred times higher than those of coal-fired combustion processes. Additionally, as the flue gases typically also have far higher chlorine content, ESP, FF and FGD systems can be used more effectively [49].

Although incineration is a very efficient means of reducing municipal and hazardous waste, if not properly treated emissions of particulate matter and other heavy metals besides Hg can have adverse affects on human health and the ecosystem [50]. In many countries, including China, incineration is increasingly replacing landfill as the preferred waste management strategy [51, 52]. As atmospheric Hg emissions from incinerators are highly dependent on the original mercury content of the waste being incinerated, it is possible to effectively limit or prevent Hg emissions by removing mercury loaded waste from the source feed. Additionally, emission regulations imposed on incineration facilities to undergo air pollution control processes have been implemented. However, due to the different national regulations and technology implementations, unsurprisingly Hg emission standards vary from 0.05-0.08 mg/m³ for Europe and the United States to up to 0.2 mg/m³ for China [52]. Overall, medical waste incineration is reported to be the fourth largest contributor of Hg to the global environment [53].

Recently, Kim et al. [54] compiled a list of anthropogenic Hg emission sources in Korea for the year 2007. Although the list is limited to Korean emissions, it highlights the high contribution of anthropogenic Hg emissions from incineration in comparison to coal-fired power stations and various other sources. It was estimated that 17% of Hg emissions came from various types of incineration compared to 26% being released from coal-fired power plants [54]. In general, emission from incinerators have decreased due to the use of efficient Hg removal systems and the progressive decommissioning of high polluting facilities governed by better environmental management practices. Such practices were presumably spurred by the US-EPA ruling between 1995 and 1997 that all municipal and medical incinerators cut their emissions by 90 to 94% in the US [7]. Mercury reductions have been achieved by the implementation of direct injection of activated carbon or sodium sulfide, wet or dry scrubbing, and the use of activated carbon beds [38]. The effectiveness of these techniques is due to mercury being present primarily in the soluble Hg²⁺ form. In contrast, thermal power plant flue gas contains lower concentrations of total mercury; however they have larger proportions of Hg⁰ (non-soluble) than Hg²⁺ species. Additionally, thermal power plants have significantly larger volumes of stack gas than municipal or hazardous waste incineration plants.

1.1.3 Cement Manufacturing

In the case of cement manufacturing, Hg emissions emanate from the cement kiln exhaust gas, which is generated from a combination of the pyroprocessing of the raw materials and the fuel combustion process used to raise part of the kiln to temperatures of ~1480°C [55]. Hg emissions from the latter are the major contributing source for the cement manufacturing process. It is estimated that to produce each tonne of clinker (cement) 3 to 6 GJ of fuel is required, depending on the raw materials and the process used. Primarily, cement is manufactured by heating mixtures of limestone, shale, clay or sand with other materials in a long rotary kiln to produce a powdered mixture of calcium, silicon, alumina, ferric and magnesium oxides that is then suitable for mixing with water to form a hydrated solid. Most cement kilns consume large quantities of coal and petroleum coke as the primary fuel feed, and to a lesser extent natural gas, oil and/or alternative fuels, such as solid waste and tyre-derived fuels [55, 56]. Mercury emission issues from cement

plants arise mostly from those plants that burn hazardous waste in their cement kilns [49]. Although the majority of cement plants do not use waste as their primary source of fuel, there is a large number of facilities that consider burning waste to be a viable alternative fuel and thus may choose to change their fuel feeds in the future. Additionally, selected waste and by-products containing useful minerals such as calcium, silica, alumina, and iron can be used as raw materials in the kiln, replacing raw materials such as clay, shale and limestone. For example, sewage sludge has a low but significant calorific value, though it burns to give ash containing minerals useful in the clinker matrix. This sometimes leads to confusion when categorizing waste materials either as an alternative fuel or as raw materials. Both dry and wet process kilns can be designed to utilize waste fuel, which in effect can subsidize their running costs by not only reducing raw material needs but also by providing additional waste disposal service to other industries. As well as raw material changes, other common methods for Hg reduction processes used by the cement industry are dust removal, wet scrubbing, mercury roasting systems, dry sorbent injection and dry and semi-dry scrubbing. These processes have been covered in detail in [57].

The high temperature calcination process of the raw materials (limestone, clay minerals and potentially waste byproducts) can lead to the release of gas, dust and fly ash that is rich in volatile heavy metals (i.e. thallium, cadmium etc.) other than mercury. These elements are often found in trace quantities in minerals such as pyrite, galena and zinc blends, and also need to be captured prior to the gas escaping through the kiln exhaust. Additionally, due to the inherent recycling of Hg between the hot and cold end of a kiln, and also from the re-injection of Hg-containing cement kiln dust into the kiln, it is difficult to quantitatively measure the distribution of Hg within a kiln [49]. It has been shown that the process can comprise of many mercury cycles which are strongly dependent on the operating conditions and kiln processes used. In a recent study [56], it was not only found that the cycling process causes a significant enrichment of Hg inside the kiln, but also observed that the efficiency of Hg removal was strongly related to the dust removal efficiency. This is one of the reasons that dust control devices such as electrostatic precipitators and bag-filters are used in many industries [58], with bag filters shown to be very efficient at removing all mercury species [56]. However in a dry kiln process the cycling of Hg tends to occur at the point between the pre-heater and the exhaust exit, where it can condense and partially re-adsorb on the raw materials entering the kiln. In the case of a wet kiln process, the gases cool to ~200°C or less at the kiln exhaust, where Hg can oxidize and/or re-condense back on the raw materials only to be re-vaporized in the middle of the kiln after the solids dry and begin calcining. Therefore the recycling loop is potentially larger than what would occur in dry kiln process.

It can take a long time for mercury to reach a steady state within the kiln due to large temperature gradients and the actual recycling of Hg species, making it difficult to accurately mass balance the mercury entering the kiln and that being removed by air pollutant control devices (APCDs). Attempts to model the Hg cycle within a cement kiln have been used to predict its distribution within the kiln, with the intent that the models might be used in conjunction with control technologies to minimize Hg emissions [49]. A better understanding of the Hg cycle in individual parts of the process, especially in the coal mill, the pre-heater (cyclones), the cooling tower and filters would also promote better design of Hg control technologies as well as increase production yields [56]. Such improvements are especially encouraged by the National Emission Standards for Hazardous Air Pollutants (NESHAP) implemented by US-EPA in 2010 to regulate Hg emissions from cement-manufacturing industries [59-61]. The standard requires the installation of Hg emissions control technology on ~163 kilns in 35 states, requiring each kiln to control its Hg emission concentration to less than 12 µg/m³ for existing facilities and 4 µg/m³ for new facilities [13]. These rules are estimated by US-EPA to cost the industry up to \$950 million annually in 2013, with an estimated 10% of the plants in the US being shut down as they will not be able to meet the Hg control costs to comply with the regulations [60, 61].

1.1.4 Mining and Refining Processes

The process of mining and refining minerals, metals and fossil fuels contributes significantly to anthropogenic Hg emissions into both the atmosphere and the localized surrounding environment. The production of zinc, copper, lead, iron, alumina, gold, silver and mercury are the major causes. Although there are uncertainties between the emission data provided by each country, it is estimated that China followed by Australia are the largest emitters of Hg from industrial ore processing activities. Other regions of interest are South America and Africa. In 2003, China's

emissions from zinc, copper and lead smelters alone were estimated to be between 203 and 275 Mg [3, 62], which is equivalent to approximately 39% of China's total emission for that year. Typically, processes that require ore-roasting can release significant Hg emissions. Such processes are used for the extraction of Hg from cinnabar ore or other sulfide containing minerals, such as corderoite and livingstonite. The Hg is extracted by heating the ore and condensing the vapor to liquid mercury, which is then sold for use in other industrial processes or products. Roughly half of all Hg mined globally in history has been used to mine gold and silver, although the annual production of Hg peaked during the 20th century as a result of increased industrial use [1]. Interestingly, the increase in demand for compact fluorescent bulbs has encouraged the re-opening of some old cinnabar mines to obtain the Hg required for compact fluorescent bulb manufacture in China. Unfortunately such sites, as well as other abandoned Hg mine processing sites, often contain hazardous waste piles of roasted cinnabar calcines, which are recognized source of ecological damage.

Ore roasting, which is generally the first step in refining iron, zinc or lead, is another significant process that can result in Hg emissions into the atmosphere. The purpose of the roasting process at high temperatures ($>1000^{\circ}\text{C}$) is to remove moisture and volatile impurities such as Hg from the ore before the roasted ore is coke-fired (smelted) and refined by one of a number of electrolysis techniques. In the case of iron and steel manufacturing, the ore is generally roasted prior to it being chemically reduced in blast furnaces to form pig iron. The addition of coal to the blast furnace during the coking process also contributes to Hg emissions, where the mercury from the coal mixes with the additional Hg impurities in the ore. Mercury emission inventories indicate that a significant quantity of mercury (45.4 Mg) was emitted globally in 2005 by pig iron and steel production [5]. Zinc and lead refining make up an even more significant portion of the emissions resulting from non-ferrous metal smelting activities worldwide. In China alone, 115-187.6 and 70.7 Mg out of the total 320 Mg for non-ferrous metal smelting activities were emitted for zinc and lead refining activities respectively in 2003 [3]. In fact, over 100 mg/m^3 of Hg has been estimated to escape in the flue gas generated from smelting processes due to sulfide-rich ores that can contain between 100 to 300 mg of Hg for every kilo of ore [63]. This clearly indicates that the environment surrounding a zinc plant would contain significantly higher levels of Hg deposits when compared to a large thermal power plant. Emissions for ore-roasting copper pyrites to extract copper are also known to release significant quantities of Hg, however these quantities are much lower when compared to emissions from zinc and lead refining processes. Reductions in emissions from copper processes are also partly due to advances in smelter technologies which now limit ore-roasting requirements.

In the context of alumina refineries, trace quantities of Hg have been found in emissions from various sources, in particular oxalate kilns, digestion, calciners, and other minor sources such as liquor burners and boilers. Depending on the origin of the bauxite ore, the mercury content can range from between 50 mg [64] to 431 mg [65] per tonne of bauxite. During the refinery process much effort is made to capture the Hg before it is emitted into the environment, however measurable quantities of Hg are still emitted for every metric tonne of alumina produced [66]. Often these emissions can be controlled or significantly reduced by using effective gaskets and seals to contain mercury within the process stream; however, Hg build-up within a chemical refining process can occur which is not dissimilar to the Hg cycling issues that occur within a larger cement kiln process. For instance, during the extraction process of alumina from bauxite (via the Bayer process), the concentration of Hg^0 in the vapor phase reaches steady state, typically ranging from below 0.1 to 32 mg/m^3 within different stages of the process [66]. This is largely due to the cyclic nature of the Bayer process, which recycles a highly caustic liquor stream through a variety of processes ranging from digestion, evaporation and calcination processes that operate at a range of different temperatures between 20 and 200°C . In contrast to industries such as coal-fired utilities and municipal waste incinerators, which emit all three forms of Hg (i.e. Hg^0 , Hg^{2+} and Hg^{P}), data collected from the Bayer process shows that Hg emissions are predominantly in the elemental form [66]. Approximately 2.9 Mg of Hg^0 is estimated to have been emitted by Australian alumina refineries in a one year period spanning 2006-2007 [30]. Although these emissions are less significant than those emitted by the zinc or lead refining processes, a large alumina refinery would emit higher quantities of mercury into the atmosphere than a comparable stream (flow rate) from a coal-fired power plant.

Emission concerns from both small and large scale gold mining operations are also categorized as significant industrial emitters. In the case of small scale mining operations, gold is extracted using mercury to amalgamate with very small gold particles in the ore, thus separating the gold from the ore. Thereafter the amalgamated particles are heated to boil off the mercury. This process is very effective in extracting the gold, however is hazardous due to the toxicity of Hg vapor which must be reclaimed in an effective and safe manner. Many illegal mining operations dispose of the mercury improperly or allow significant quantities to escape. Unfortunately due to its illegal nature, precise data on Hg emissions from small scale operations employing amalgamation technology are subject to large uncertainties [3]. In regards to large scale gold mining operations, amalgamation technology has been gradually phased out. However, it is estimated that artisanal and small scale gold mining releases between 640 to 1350 Mg of mercury per annum into the environment (rivers, lakes, soil, etc.), with estimated 300 to 400 Mg contributing to atmospheric emissions [67]. Gold mining conducted in the Amazon region has been reported to contribute 10% of Brazil's annual Hg emission total [5], which mainly resulting from small-scale gold mining processes [68].

Mining and extraction of fossil fuels such as natural gas, oil and coal are other major sources from which significant Hg emissions can occur. As one would assume, Hg is only one of a number of harmful substances that are present in small concentrations in these reserves. The natural occurrence of As, Cd, Cr, F, Pb, Se and Hg within coal leads to their emission into the atmosphere when unwanted solid waste piles undergo spontaneous combustion during the coal mining process. Spontaneous combustion of such piles may be a source of serious environmental pollution in countries such as China, which are credited as the largest coal producer in the world [69]. Similarly, in the process of extracting natural gas, the removal of many naturally occurring contaminants such as mercury, CO₂, H₂S, NH₃, thiols and other sulfide containing compounds is required. The refining process not only reduces emissions by the end-user but also increases the production and transportation efficiencies of the natural gas. However, the removal of Hg at the extraction/refining site can lead to pollution of the localized surrounding environment, thus Hg emission control technologies are used by most large facilities. A study conducted in Croatia found that very high Hg concentrations between 0.2 to 2.5 mg/m³ were measured in extracted natural gas [70], which lead to the Hg contamination of the soils around gas processing equipment with Hg concentrations of 0.32 to 40 mg/kg. In the same study the authors reported that atmospheric testing 54 km away from the processing plant detected an average Hg concentration of 6 ng/m³. Anomalies of up to 90 ng/m³ were observed during these measurements, indicating that bursts of Hg vapor also travel vast distances away from the plants. The levels of Hg in the atmosphere were shown to increase with decreasing distance from the process plant, where levels of 120 ng/m³ were detected at a distance of 6.8 km [70].

1.1.5 Chemical Manufacture and Other Industrial Processes

The manufacture of chemicals such as chlorine and sodium hydroxide (caustic soda), which utilize mercury within their processes, have historically been the largest Hg emitters from the chemical manufacturing sector. In a chlor-alkali plant using mercury cell technology, elemental liquid mercury is used to form a cathode electrode in an electrolysis process to produce chlorine and sodium hydroxide from sodium chloride brine. A mercury cell consists of two major parts: an electrolyzer and a decomposer. In the electrolyzer section, sodium chloride is passed along the mercury cathode where the sodium forms an amalgam with the mercury, thus releasing the chloride ions as chlorine gas. In the decomposer, the amalgam is used to produce hydrogen (H₂) gas and sodium hydroxide (NaOH), thus converting the amalgam back into Hg⁰ so the process can be repeated. The process is essentially enclosed and recycles the Hg that is used to amalgamate and to provide a transportation mechanism for sodium ions within the mercury cell, however unintentional losses are unavoidable. Although much of the industry has converted to mercury free processes which use mercury free ion-exchange membranes or diaphragm cell technologies [71], it is estimated that approximately 100 mercury cell plants still operate worldwide, with mercury cell plants accounting for 43% of capacity in Europe in 2006. Other significant producers of chlorine and caustic soda that use Hg within their processes are based in India and the Middle East [29]. Interestingly, a study conducted on human exposure to Hg in the vicinity of an Italian chlor-alkali plant concluded that the plant operation posed no health effects above the product of anthropogenic and natural sources of Hg present in the Mediterranean, therefore indicating that the mercury cell chlor-alkali plant itself did not pose an additional risk to human health [72]. However, the authors estimate that 14% of emitted gaseous Hg is deposited within 5 km from its

source, with the remaining 86% being dispersed and transported further away where it is supposedly added to the natural atmospheric Hg cycle.

Similarly, it is well known that forest fires are an important pathway for mercury that has previously deposited on soil and vegetation to exchange between the biosphere and atmosphere [73]. A study of a mixed vegetation fire in the southern Cape Peninsula in Africa suggests biomass burning accounts for 12-28% of annual global total gaseous Hg emissions [73, 74]. Comparable findings have also been expressed in the US, where it is estimated that fires emit the equivalent of almost 30% of the total US anthropogenic Hg emissions, which is equivalent to the emissions from coal-fired power plants [75]. Emissions from landfill sites are also known to contribute to atmospheric Hg emissions, however a lack of data exists for this source. It has been speculated that the entire waste mass of a landfill site can act as a significant Hg emission source and that much of the Hg present is in the elemental form, which is primarily from broken light bulbs and contaminated plumbing [76-81].

Although the use of mercury has decreased significantly in the last decade, mercury is still an important material that is used in the manufacturing of products for both commercial and residential use. For example, batteries and fluorescent lamps contribute significantly towards Hg emissions when discarded at the end of their usable lifetime. A survey conducted by Chang et al. [82] to investigate the fate and management of mercury-containing fluorescent, ultraviolet and high pressure mercury lamps in Taiwan showed that 886 kg of Hg was used in the year 2004 for these applications. Fortunately, a reduction in the use of mercury with time is partly due to the use of alternative materials used in products that traditionally use mercury in their manufacture [83]. In the case of alkaline batteries, environmental regulations restricting the use of mercury as a corrosion inhibitor for the zinc cathode has significantly reduced Hg emission issues from discarded batteries. Such regulations were passed in the US and Europe in the 1990s and have also made the recycling of the batteries (which now employ plastic insulators) easier, as well as give the newer batteries more than twice the capacity of the same size Hg containing batteries [84]. Similarly, the use of alcohols in thermometers and mercury substitutes in other industrial and consumer items has also led to a reduction of Hg emissions into the environment. However, these reductions have been counterbalanced by the increased demand for fluorescent lamps and PVC, which has resulted in an increase in mercury utilization in China due to import restrictions [62, 85, 86]. Other industrial emission sources of mercury and its compounds are glass manufacturing, the wood paper-pulp industry and the chemical manufacture of chemicals such as acetaldehyde [66]; however, such sources generally result in the release of mercury in its ionic form via aqueous emissions.

2 Standardized Methods for Measuring Mercury

Several standardized methods exist for measuring mercury from industrial emission sources or process streams. The first step involves collecting a representative sample of the flue gas either by a sampling train or a dry sorbent trap technique. Once a representative sample is collected, quantification analyses of the sample train or sorbent bed/s are performed via a spectroscopic technique, which can be based on either photometry, fluorescence or mass spectroscopy [87, 88]. These can include atomic absorption spectroscopy (AAS), atomic fluorescence spectrometry (AFS), UV differential optical absorption spectroscopy (DOAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) techniques [89]. However, AAS and AFS based methods are generally preferred as both have been approved by the US-EPA to perform measurements from industrial point sources [90-93]. Although AFS has superior sensitivity and detection limits to AAS, due to the requirements of most industrial applications and the quenching of the fluorescence signal by nitrogen and oxygen being more frequent in the AFS systems, AAS based systems are more common [94].

Both AAS and AFS instruments are susceptible to cross-interference by other gases within the many industrial process streams, such as SO₂, NO₂, H₂O, O₃ and carbonyl containing volatile organic compounds (VOCs) such as benzene, toluene and acetone. These gas species absorb the same wavelength as mercury (253.7nm) and can therefore produce misleading results [93, 95-97]. In order to overcome the presence of such gases, gold traps or cold vapor (CV) methods are sometimes used in conjunction with the AAS and AFS systems (referred to as CV-AAS or CV-AFS)

for determine lower concentrations of Hg. Gold traps involve having a collection material (i.e. gold-coated sand and quartz wool, gold or silver foil, iodized carbon or other activated carbon) to trap and enrich the Hg prior to the detection step [89, 98] and allows direct determination of Hg without an atomizer unit [89]. Mercury vapor is amalgamated with the sorbent material and later released via heating in an argon carrier gas for detection. This allows the ventilation of interfering substances from the gas stream before measurement.

Overall both the sample train and dry sorbent methods have been shown to provide accurate data when used by experienced operators following strict protocols to collect the flue gas sample. However the difficulty in measuring mercury arises from issues such as low Hg concentrations, simultaneous existence of speciated forms of Hg (i.e. Hg^0 , Hg^{2+} and Hg^{P}), complex flue gas chemistry, high temperatures, particulate loading and mercury reactivity (i.e. inter-conversion between Hg^0 and Hg^{2+}) within the flue gas samples. Owing to these complexities, a number of standard sampling and measurement protocols have been developed that utilize either sampling train or dry sorbent traps to capture the mercury content for different industrial stream conditions [99].

2.1 Sampling Train Methods

Several sampling train methods exist that are normally used to capture Hg vapor from stationary anthropogenic sources. All the sample train methods described below use isokinetic sampling, with particulate filters attached to the sample nozzle to pass the sample gas through a train of glass impingers containing various chemical agents to collect the mercury. The particulate filters are used to collect the fly ash and Hg^{P} content in the stream prior to the sample train, which can be analyzed separately. Each of the methods has its own advantages and limitations depending on conditions such as the flue gas matrix and whether total or speciated mercury needs to be measured in the collected gas sample. Generally, the purpose of the various liquids used in the sample train impingers is to separate and pre-concentrate the different species of mercury from the filtered gas sample. The first method that was introduced by the US-EPA for capturing Hg from stationary sources in response to the addition of mercury to the 1990 clean air act amendments (CAAA) was EPA method 29 [99].

2.1.1 EPA Method 29

EPA method 29 (also known as the multi-metals sampling train method) was first introduced as a draft method in 1992 for the determination of metals and/or particulate emissions from stationary sources. It was originally designed to monitor the emission of metals such as Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, P, Se, Ag, Tl, and Zn [100], however its use for Hg speciation analysis was also investigated due to researchers presuming the physical and chemical properties of Hg [101, 102]. As a result, the metals Hg, Cd and Pb were also added in the 1994 proposal prior to it being approved by EPA [99]. By 1996, a review of the available mercury measurement methods indicated that the EPA method 29 is the most widely used method for determining Hg in flue gas [41].

The method comprises of 7 impingers, the first of which is left empty. The second and third impingers are identical, containing 10% hydrogen peroxide (H_2O_2) and 5% nitric acid (HNO_3) in 100 mL of water. These are followed by another empty impinger and then two identical impingers containing 4% potassium permanganate (KMnO_4) and 10% sulfuric acid (H_2SO_4) in water. The final impinger contains silica gel to collect moisture from the sampled gas in order to prevent damage to the dry-gas meter and pump downstream. The stack gas is withdrawn isokinetically and enters the probe/nozzle through a heated filter to collect the particulates, which are used to determine the Hg^{P} content. Additionally, the purpose of the probe is to remove reactive particles which can either oxidize Hg^0 or reduce Hg^{2+} and bias the results. The acidic H_2O_2 solutions are used to capture any Hg^{2+} , while the KMnO_4 containing impingers capture Hg^0 . For each measurement, the sampling is performed for a continuous 2 to 3 hour period in order to obtain a representative sample, as well as to ensure that a detectable concentration of Hg is captured within the solutions. At the end of the capture process, the filters, impingers and lines are rinsed and all the solutions are sent for analysis. Typically the Hg content is analyzed using CV-AAS.

Using the same principles as EPA method 29, a comparable European standard (EN 14385, which is also a multi-element method) was adapted to measure Hg from stationary emission sources

using a side stream sampling technique (EN 13211) [103]. Similarly, another European standard for mercury monitoring in industrial gases is the VDI 3868 method [13, 104]. However, in 1997 Laudal and colleagues [105] published their research findings concerning the speciation ability of EPA method 29, which were conducted at the North Dakota Energy & Environmental Center (EERC) and were supported by Electric Power Research Institute (EPRI) and the U.S. Department of Energy (DOE). It was found that the EPA method 29 was not able to detect speciated mercury properly in coal-combustion flue gas. This shortcoming of the method was due to Hg^0 being captured with Hg^{2+} in the H_2O_2 containing impingers, which resulted in a bias or measurement error.

2.1.1.1 Ontario Hydro Method

While the Hg speciation issues faced in EPA method 29 were being investigated, the Ontario Hydro (OH) method was developed in 1994 by Ontario Hydro Technologies [106]. Subsequently, in 2005 the US-EPA identified the OH method (also known as the ASTM D6784-02 standard) as the means to measure Hg^0 , Hg^{2+} , Hg^{P} and Hg^{T} from coal-fired stationary sources [101, 107]. The method is a modification of EPA method 29 with the only difference being the number and content of the impingers [108]. In the 8-impinger OH method, the first acidified peroxide solution of EPA method 29 is replaced by three impingers of 1 M potassium chloride (KCl) dissolved in deionized water for a more selective capture of Hg^{2+} . The purpose of these impingers is to eliminate some of the complications that occur during the preparation of the peroxide solution for analysis and avoid the interference of SO_2 that was shown to exist in the bench-scale studies of EPA method 29 [105]. The fourth impinger contains 10% H_2O_2 and 5% HNO_3 solution, while the following three impingers contain 4% KMnO_4 and 10% H_2SO_4 . The H_2O_2 impinger was specifically added for flue gas containing SO_2 , which if not captured in the trap would otherwise react with the KMnO_4 and neutralize it, affecting the capture efficiency of Hg^0 and resulting in a measurement error. The final impinger contains silica gel to remove moisture from the sampled gas prior to the pump and dry-gas meter.

The OH method is able to measure speciated Hg while minimizing the possible interference by SO_2 from the flue gas in CV-AAS measurements [109]. However, pilot-scale testing undertaken by EERC verified early test results by other researchers showing that mercury is actually lost from some of the solutions in the first three KCl traps. To counter this, either acidified permanganate, dichromate or acidified peroxide solution needs to be added to the KCl solution immediately following sampling. Furthermore, Cl_2 and different ratios of NO/NO_2 (in the presence of fly ash) have also been shown to have a significant effect on Hg speciation as measured by the OH method. This is because Cl_2 reacts with Hg to form HgCl_2 while the fly ash can catalyze Hg^0 to Hg^{2+} in the presence of NO/NO_2 [110]. Additionally, the study showed that HCl appeared to have little influence on Hg speciation at concentrations and temperatures typically found at the outlet of ESPs and baghouses of a coal-fired process stream. This method has also been compared with the European standard reference method for determining Hg in exhaust gases from ducts or chimneys. The average bias between EN 13211 and the OH method was 2.9%, indicating that the bias between the two methods is not statistically significant [111].

2.1.1.2 Tris-Buffer Method

The Tris-Buffer sampling train method, developed by Radian International (now URS), is another modification of EPA method 29 designed to measure speciated Hg in industrial flue gas. For this method, the contents of the nitric acid/peroxide impingers in EPA method 29 are replaced with a 1M tris(hydroxymethyl) aminomethane buffer solution. Ethylene di(tetraamine) or EDTA is added to the Tris-Buffer solution as a complexing agent to retain HgCl_2 [99]. The purpose of the buffer is to remove the SO_2 and Hg^{2+} without removing Hg^0 [108], however, a negative aspect of this method is that the solution must be at a pH of 6 or above for it to be effective [99]. Bench-scale experiments conducted at EERC [105] have shown that sampling and measuring speciated mercury at a baghouse inlet using different Hg sampling methods showed similar results for the Tris-Buffer and OH methods. Interestingly, it was found that more than 30% of the spiked Hg^0 was measured as Hg^{2+} in the EPA method 29 while nearly 100% was measured using both the OH and Tris-Buffer methods. Further bench-scale testing of the different types of coal showed that the difference in speciation between the different sample train methods was affected by the particulate and total Hg concentrations in the flue gas generated by firing different types of coals. Furthermore, mercury recovery from the tris solution has proven to be difficult, as the addition of

HNO₃ and H₂O₂ to preserve the mercury in solution results in evolution of CO₂ and therefore requires great care to be exercised in order to prevent the loss of Hg-containing tris solution. Based on the pilot- and bench-scale tests conducted at the EERC, the OH method was shown to better speciate Hg over the Tris-Buffer method and EPA method 29 [110].

2.1.2 EPA Method 101

EPA method 101 was developed for the determination of particulate and gaseous Hg emissions from sources like chlor-alkali plants, where the gas sample is mostly comprised of air [112]. Isokinetic sampling is performed to collect the Hg emissions in 0.1 M acidic iodine monochloride (ICl) solution in the first three identical impingers of this 4-impinger method. The final impinger contains 200 g of silica gel and removes moisture from the gas sample. Interference during sample collection is known to occur for gases containing sulfur dioxide (SO₂), which reduces the ICl and prematurely depletes the solution. Following sampling, the ICl needs to be completely removed as concentrations greater than 10⁻⁴ M will inhibit the reduction of the Hg (II) ion in the aeration cell of the analytical instrument. This is an extra pre-treatment step but necessary to accurately perform the final Hg measurement step [112].

2.1.3 EPA Method 101A

EPA method 101A is designed for the determination of total gaseous and particulate Hg in the flue gas emissions from sewage sludge incinerators [113]. The method only measures Hg^T but it can be of special interest to sources that need to measure both Hg and Mn emissions. Mercury emissions are withdrawn isokinetically from the source and are collected in first three identical impingers containing 4% KMnO₄ and 10% H₂SO₄ in water. These impingers are designated for Hg⁰ capture, whereas the first oxidizing impinger in the OH method is the fourth impinger in this method. The Hg collected (in its mercuric form) is reduced to Hg⁰. Thereafter the solutions are aerated into an optical cell and measured by AAS. In this method, interferences can occur for an industrial gas stream containing excessive oxidizable organic matter, which prematurely depletes the KMnO₄ solution and thereby prevents further collection of Hg. Unlike the OH method, interference from SO₂ is possible in this method when analyzing the impinger solutions with AAS [109, 114].

2.2 Dry Sorbent Methods

Generally speaking, solid sorbent materials are more suitable for flue gas sampling than sample train methods because of their greater stability and easier handling. For this reason, various solid sorbent methods have also been developed for Hg vapor determination in industrial flue gases over the last two decades [115].

2.2.1 Certification Procedures

There are two main solid sorbent based reference methods recognized by the US-EPA that are designed to certify if another method is working properly [116]. These are the Appendix K method and EPA method 30B.

2.2.1.1 Appendix K Method

The Code of Federal Regulations (CFR), Title 40, Part 75, Appendix K is a quality assurance and operating procedure that must be met in order for the US-EPA to consider a sorbent type valid for the measurement of mercury from a stack gas [117]. The method encompasses sorbents that are based on iodated charcoal or other suitable reagents and generally refers to a performance based sorbent trap method; however, Appendix K is not an actual method in itself. Appendix K requires that the flue gas be drawn in-situ through a pair of traps, each containing a series of three sorbent trap sections. Each section of each sorbent trap is then sent for analysis following a sampling period of approximately 3-7 days. In order for any method to be valid, the relative deviation between the two traps must result in ≤10% for a Hg concentration of ≥ 1 μg. Furthermore, the first section of a trap must capture the majority of the captured mercury, limiting the second section to contain no more than 5% of the Hg^T being reported. The traps are analyzed either by wet chemistry or thermal desorption/combustion methods that employ absorption or fluorescence spectroscopic analysis, respectively. This method has been reported to suffer issues with

sampling, recovery and analytical procedures related to both the sampling time and acid gas (e.g. SO_x, NO_x and HCl) concentrations contained in some flue gases [55].

2.2.1.2 EPA method 30B

EPA Method 30B is a reference method for measuring Hg^T emissions from coal-fired combustion sources using a solid carbon based sorbent trap that employs sampling and extractive or thermal analytical techniques. This method is only intended for use under relatively low particulate conditions (e.g. sampling after all APCDs) [118]. The method is designed to measure Hg^T concentrations in flue gas and is not designed to measure speciated Hg. EPA method 30B differs from Appendix K in that it is a two-section rather than three-section trap and that the sampling time is limited to only 2 hours or less. Results from previous studies have shown that EPA Method 30B can produce results similar to the OH method with relative accuracy ≤ 20% [55, 119].

2.2.2 MESA Method

The mercury speciation adsorption (MESA) sampling method employs a series of heated (90–100°C) solid phase adsorbent traps to selectively capture and separate mercury species [120]. Flue gas is first withdrawn through heated quartz tubing containing quartz wool to remove particulate matter. Immediately following the quartz wool is the first sorbent containing a mixture of potassium hydroxide, calcium oxide and potassium chloride, which is designed to capture HgCl₂ and methyl mercury (Hg²⁺). The second sorbent is iodine-impregnated activated carbon that collects Hg⁰. Total Hg is determined by summation of the different species. In the laboratory, CV-AFS is used to measure the collected Hg from the solid sorbents following appropriate sample digestion and preparation processes [120]. The MESA method has been previously evaluated for species stability, matrix effects, breakthrough, artifacts and precision in coal combustion flue gas at the inlet of pollution control devices. Comparison of the MESA method with other methods (such as EPA method 29 and EPA method 101A) has shown MESA to be precise and in agreement in determining Hg⁰, Hg²⁺ and Hg^T. Additionally, the MESA method is capable of mercury speciation for flue gas streams containing Cl₂, which is not always possible with the OH method [121]. Compared to EPA method 29, MESA is reported to have a lower detection limit, a much simplified sample collection process and requires less sampling time. However, research conducted at EERC showed that the MESA method did not measure speciated mercury correctly when used in flue gas containing ~600 ppm NO_x and 1500 ppm SO₂ [105]. The major limitation of the MESA method is the non-quantitative collection of particulate material (Hg^P). These gas constituents were found to induce an overestimation of Hg²⁺ fraction when using the MESA method and EPA method 29, however this was not the case with the OH and Tris-Buffer methods.

2.2.3 MIT Method

The MIT method was developed by the Massachusetts Institute of Technology (MIT) for the collection of atmospheric vapor phase Hg using activated charcoal sorbents. Sampling is conducted by passing the flue gas through two activated charcoal based sorbents connected in series and then analyzing the traps using instrumental neutron activation analysis (INAA) to determine the total Hg collected [122]. The sorbent traps are maintained at 100–120°C to prevent moisture condensation. The method is used to conduct Hg^T measurements and therefore is of little use for applications of flue gas in coal-fired and cement type plants where Hg speciation and measurement is necessary as part of the US-EPA regulations. Previous studies that compared the MIT method with EPA method 29, 101A, MESA and HEST (discussed below) showed a reasonably good agreement among the Hg^T measurements for the different methods [123], indicating that the MIT method can be used to confirm Hg^T measurements.

2.2.4 HEST Method

The hazardous element sampling train (HEST) method was developed by Chester Environmental and uses an in-stack filter probe to draw gas samples isokinetically through a pack of three filters arranged in series [123, 124]. The first filter is made of quartz or Teflon and is used for particulate collection. The second and third filters are carbon impregnated filters designed to adsorb gas phase Hg⁰. Following the sample collection, the filters are analyzed by non-destructive energy dispersive x-ray fluorescence (XRF) and result in the determination of total Hg in the gas sample. This method was tested in an industrial coal combustion site along with EPA method 29 and the dry sorbent MESA method. The correlation between the three methods was found to be excellent,

despite the Hg^{T} concentration within the industrial stream fluctuating by an order of magnitude over the 3 day sampling period [124]. The HEST method is able to differentiate between the different speciated forms of Hg and can be used by most Hg emitting industries where speciation is required, with sampling intervals as short as 10 minutes. It is claimed that this method can measure Hg and all other elemental hazardous air pollutants in the US-EPA's hazardous air pollutants (HAPs) list (except beryllium) with a detection limit that is an order of magnitude better than that of EPA method 29. A comparison of the HEST method EPA method 101A at a municipal incinerator showed agreement between the averages (within 4%), proving the method effective in characterizing elemental HAPs emissions [124].

2.2.5 FAMS Method

The flue gas absorption mercury speciation (FAMS) method is based on different solid sorbents that are selective towards the different species of Hg and is therefore able to separate and quantify Hg^0 , Hg^{2+} and Hg^{P} from emissions in flue gas streams [125]. A 100 mL volume of the flue gas is drawn through the heated (95 ± 5 °C) FAMS sorbent train for sampling. The traps are then leak-tested prior to removing from the sampling train, capping and shipping to an analytical laboratory. The method requires no exposed glassware, on-site solution preparation, rinses, clogging filters or hazardous materials. Testing is normally completed within a few days with minimal disruption of plant operations. The US-EPA conducted several comparison tests of the FAMS method with the OH method at the EERC in 2001. It was concluded that the FAMS method was valid for the determination of Hg^{T} , Hg^{P} , Hg^{2+} and Hg^0 concentrations in flue gas matrices and was equivalent to the OH method [126]. Frontier Geosciences (now Frontier Global Sciences), the developer of FAMS as well as Appendix K and EPA method 30B, has compared FAMS with the OH method using over 8 years of data collected from emissions in flue gas, where they concluded that the FAMS method is a faster, more reliable and cost effective alternative [125]. Others also report the method to be highly precise (repeatable results), sensitivity (for low Hg concentrations) and accurate, making it a viable method for measuring speciated Hg in industrial flue gas [126].

2.2.6 FMSS Method

The flue gas mercury sorbent speciation (FMSS) method consists of two lots of dual dry sorbent traps placed in series, which are used to speciate Hg from the flue gas stream. The method relies on a semi-isokinetic sample from a flue gas duct through a particulate filter and a heated solid sorbent sample train. The filter and the sorbent train are analyzed to determine the different species of Hg. The first trap contains dry KCl-coated quartz chips used to capture Hg^{2+} followed by the second trap containing tri-iodine-impregnated activated carbon to capture elemental Hg from the flue gas stream. The entire sample train is sent to a laboratory for analysis using CV-AFS following a vigorous chemical treatment process. The analysis of Hg^{P} in the fly ash is done by thermal desorption at 800°C using CV-AFS. This method was developed by Frontier Geosciences and validated at the EERC according to a modified EPA method 301 [102]. The FMSS showed good agreement with the OH method and its accuracy was better than $\pm 20\%$ for all species for the range of conditions in the validation study tests [102]. It is one of the two solid sorbent methods validated by the US-EPA; the second method is the QSEM method, which does not measure speciated Hg and is used only to determine Hg^{T} [101].

2.2.7 QSEM Method

Following many years of research since 1990 and the development of solid sorbent trap methods for capturing mercury, Frontier Geosciences together with ADA Environmental Solutions and the Electric Power Research Institute (EPRI) developed the Quicksilver Emissions Monitor (QSEM) method, otherwise known as the draft EPA method 324 [101]. After undergoing various validation tests, the US-EPA published the dry sorbent trap sampling method as draft method 324 in 2004 and the method is now in extensive use for Hg measurements in low-dust coal-fired plants and other stationary source applications [127]. QSEM is a non-isokinetic test method that samples flue gas while minimizing particulate capture, and provides Hg^{T} emissions measurements. The sampling and trap analysis methods are similar to the FMSS method except that the solid sorbents used are specially treated forms of activated carbon. The method can be used over periods of time ranging from 30 minutes to several days with detection limits of an order of magnitude lower than the OH method. The method is relatively simple, can be used for long term Hg emissions

evaluation under various process conditions with minimal effort and can be conducted in self-sustained (unmanned) mode with periodic changeover of the sample traps [127].

2.3 Limitations

It is apparent from the existence of well established analytical instruments that measurement of Hg is not the main issue; the main challenge lies in sampling for speciated Hg from a complex flue gas without manipulating the gas matrix prior to measurement [128]. In fact, the precision of the method used to sample the different species of Hg is influenced by flue gas concentration and source type as well as procedural and equipment variables. Strict adherence to the chosen method/procedures is therefore necessary to reduce these effects. Several sampling train methods, such as EPA methods 29 and 101A and the Tris-Buffer and OH methods mentioned above, are approved by the US-EPA, however results from the OH method (for example) can take several days to turn around if off-site analytic analysis is used. Many of the dry sorbents that use adsorption, amalgamation, diffusion and/or ion exchange processes to capture Hg must be transported to a laboratory for pre-conditioning before analysis is undertaken. As these methods are designed to be used after APCD and particulate control devices, the use of these methods with a filter in a high-dust situation such as the inlet to the ESP or baghouse can bias speciated Hg concentrations. This is particularly true when reactive particulate matter is present, which is known to bias Hg^{2+} and/or Hg^0 concentrations [99]. In trying to overcome these limitations, the methods can potentially have the drawbacks of increased expense, lack of real- or long-term data or emission variation data, a requirement for complex sample trains with hazardous chemicals or sorbent processes, and are manual and difficult to apply in practice over the long term [105, 129, 130]. These limitations makes the sorbent methods inadequate for use in Hg emissions control loop feedback systems [99]. Hence, there is a need for rapid, on-line continuous emission monitors that are capable of accurately speciating Hg in a variety of different types of industrial flue gas stream environments. Such a system, which would benefit both legislators and plant operators alike, would allow plant operators to make informed decisions concerning their control technology requirements and provide them with feedback for advanced process control technologies [128].

3 Mercury Continuous Emission Monitors (CEMs)

Although the methods described in the previous section are capable of determining total and speciated mercury concentrations in industrial streams, real-time data collection can only be obtained using portable emission analyzers or continuous emission monitoring (CEM) systems. Environmental bodies in the US, Canada, Europe and others are working towards the development of regulations requiring industries such as cement, waste incineration and coal-fired power utilities to monitor their Hg emissions on a continuous basis. Recently the monitoring and reporting program outlined in the 2010 Clean Air Act Amendments (CAAA) bill submitted to the US Congress requires the operation, reporting, and certification of CEM systems to accurately measure the quantity of mercury that is emitted by electric coal and steam utilities in the US. This bill, if passed, will be the first clear step in requiring US cement, coal-fired electric and steam utilities to continuously monitor, verify and publicly report on their Hg emission levels [10, 57]. Some states in the US and other countries are taking steps to meet the future regulations before such policies are finalized. Massachusetts is incorporating Hg CEMs and sorbent trap protocols into their Hg rule requiring coal-fired utilities to continuously monitor Hg emissions [131]. Similarly, in Germany it is reported that over 34 cement kilns have Hg CEMs currently installed and that all waste incineration plants are required to continuously monitor total Hg emissions [13]. Although CEM systems are often bulky and costly to purchase and install, they offer a variety of benefits over manual chemical emission measuring techniques, such as [99]:

- Real-time measurement capabilities,
- Immediate evaluation and feedback for mercury control strategies,
- Greater understanding of process variability and identification of 'spike' emissions,
- The potential to be less costly than current manual chemical methods,
- Availability of significantly larger data sets, and
- Greater public assurance that industries are complying with emission reduction targets.

However, based on the current state of the art technologies, mercury CEMs are not without challenges, particularly in terms of on-going maintenance, the collection of particle-free yet representative gas samples, the presence of interfering gases and large fluctuations in the low concentrations of Hg to be measured (generally below 10 $\mu\text{g}/\text{m}^3$) [129, 132]. A detailed report prepared for the US-EPA in 2006 compares several well known commercially available CEMs for their suitability in a 550 MW coal-fire power utility [133]. It was reported that source characteristics can have a significant effect on a CEM's performance and that the sample transfer and conditioning of the stack gas can be a major issue. Moreover, the challenges with the tested CEMs were found to be more mechanical or physical rather than chemical, and thus the analytical component of the systems were not generally found to contribute to the measurement problems. The report recommended that a CEM system should have a proven track record under the site-specific conditions as well as be customized to the site/source and operated on-site for six months as a requisite to demonstrate its capability to perform reliably and accurately as part of a performance warranty agreement with the manufacturer [133].

3.1 Commercially Available CEMs

Currently, Hg CEMs are primarily based on well-established analytical components such as CV-AAS, CV-AFS or ZAAS [99]. Systems are also being developed based on atomic emission spectroscopy (AES) [134] and laser based technologies [135]. Additionally, in some cases, portable Hg analyzers employ solid-state chemical microsensor technologies which work on mercury amalgamation and/or chemi-adsorption principles (see next section). CEMs come in several forms, each working slightly differently. Apart from the different detector mechanisms, they can be categorized as either extractive or in-situ [44]. Extractive systems are usually located in a central position and may have several switchable gas feeds to sense mercury levels from multiple locations, whereas in-situ systems are mounted on the duct of a given stack stream. A typical on-line Hg CEM comprises several different key components that integrate to accurately and reliably measure Hg emissions from industrial flue gas. At the heart of the system is the main Hg analyzer (AAS, AFS, etc.), which may or may not employ a pre-concentrator based on gold amalgamation. Other important parts can include the isokinetic sampling probe, particulate removal system, and the sample conditioning and the sample transfer lines that are required to transfer a representative flue gas sample to the Hg analyzer. In addition, some CEMs require a calibration source for Hg^0 vapor in order to obtain a calibration span. This can be achieved either by an internal permeation device, an external calibrated source or by introducing a known quantity of mercury. A list of the major commercially available Hg CEM systems and industry used analyzers/monitors is provided in Table 1, where the website for each vendor is provided with separate references for research papers that have utilized the analyzer (if applicable). Additionally, several of the listed CEMs have been extensively tested in industrial streams, either within the US-EPA Environmental Technology Verification (ETV) program [131, 136, 137], US-EPA programs [133], the European based TÜV Rheinland (www.tuv.com) certification program or independent researchers [44, 70, 130].

The US-EPA created the ETV program in 1995, which develops test protocols and verifies the performance of innovative technologies that have the potential to improve the protection of human health and environment [138]. The ETV program is a voluntary program designed to provide credible performance information to purchasers, reducing risk to financial investors in the technology. Similarly, the European based TÜV Rheinland certification provider has also tested and certified some commercially available Hg CEMs by manufactures such as Seefelder, Sick, Durag, Opsi and Semtech for waste incinerators in Europe [44]. The latter has been certified by TÜV Rheinland for the determination of compliance with the German legal limit of 50 $\mu\text{g}/\text{Nm}^3$ for total Hg emissions from waste incinerators [102]. However, Tekran and Thermo Scientific systems are typically purchased by utilities within the US [116]. Researchers are also supported by institutes and government environmental bodies (i.e. the US-EPA, DOE, EPRI, etc.) to conduct on-site tests of commercially available and prototype Hg CEMs in order to build confidence in their future usage [70, 130]. Of late, in the absence of a definitive regulatory legislation, the US-EPA has re-proposed that newly installed CEMs should at least meet the performance specification 12A (PS-12A) [139, 140], which is a test procedure requiring a CEM to:

- Be capable of measuring Hg^T (excluding Hg^P),
- Include an automatic sampling system and a diluents (CO_2) monitor,
- Measure relative accuracy, measurement errors and drift using specified procedures,

- Be installed according to standardized procedures,
- Follow measurement and data analysis procedures, and
- Follow procedures for comparing the data with a certified reference method.

In order to meet PS-12A, the CEM must contain a filter to remove particulates (e.g. fly ash) and condition any Hg^{2+} content in the flue gas by reducing it to Hg^0 prior to measuring the total Hg content of the stream. It is also proposed that once the CEM has been properly installed, five tests should be conducted to certify the instrument. These five tests are referred to as the 40 CFR Part 75 mercury monitoring provisions, Appendices A and B [117] and include a 7-day drift test, a cycle time test, a system linearity and integrity check and a relative accuracy test audit (RATA). The basic requirements for a RATA are that a minimum of nine valid paired reference method sorbent traps (either by the OH method, EPA method 29, 30A or 30B) be taken and compared to the Hg CEM data taken over the same time. The two results should be compared and the relative accuracy calculated [116, 141].

Table 1: A list of commercially available gas phase Hg analyzers/equipment and CEMs predominantly targeted towards industrial use. The company websites are provided as well as some references to applicable research papers that have used the analyzer.

Vendor/Product	Analysis Method	Range	Comment / References
Ohio Lumex www.ohiolumex.com			
<i>EVT</i> Appendix K – RP-M324	Dry Sorbent – ZAAS	1–100,000 ng	Appendix K Trap Mercury Analyzer, RATA approved
<i>EVT</i> RA-915+	ZAAS	2–500 ng/m ³	Hg ⁰ [97, 99, 130, 142-144]
RA-915 Light	ZAAS	0.1–100 µg/m ³	Hg ⁰ [145, 146]
IRM-915	ZAAS	0.5–1000 µg/dscm	Hg ^T or Hg ⁰ by TC CEM, RATA approved
RA-915 MiniCEM 2x	ZAAS	0.1–200 µg/m ³	Hg ^T by TC CEM, OH replacement
RA-82	AAS	50–99999 ng/m ³	Portable field-use analyzer
Thermo Electron Corporation www.thermoscientific.com			
Model 80i	AFS	0–50 µg/m ³	used in Freedom system
<i>EVT</i> Mercury Freedom System	AFS	3–9 µg/m ³ Verified	Hg ^S by TC/SD CEM, meets PS-12A [133]
Clean Air Engineering www.cleanair.com/Services/MercuryMonitoring			
MET-80	Dry Sorbent analysis by AAS		PS-12A, RATA Tested
Nippon Instruments Corporation www.hg-nic.com/e_index			
WA-4	AAS	0.01–1000 ng	For use in nonferrous refining
<i>EVT</i> AM-2 /3	AAS	5–25 µg/m ³	Hg ^S by TC/WC [130]
AM-4	AAS	0.001–1000 ng	
AMG-1	AAS		CEM for use in LNG & LPG
MA-3000	AAS	0.002–25,000 ng	Hg ⁰ or Hg ^T
EMP-1A/B	AAS	0.001–5.0 mg/m ³	Hg ⁰ Portable monitor [147]
EM-5	AAS	0.001–2.0 mg/m ³	Hg ⁰ workplace monitor
<i>ETV</i> DM-5	AAS	5–25 µg/m ³	Hg ^S by WC/TC, CEM [99, 130, 143]
<i>ETV</i> DM-6 /6P	AAS	0.1–1000 µg/m ³	Hg ^T by TC, CEM for coal [99]
DM-6B /A /MS1A	AAS	0.1–1000 µg/m ³	Hg ^S by WC/TC, CEM [99]
DM-6D	AAS	0.1–50 µg/m ³	Hg ^S by DS, CEM [133]
RA series	AAS	Used for liquid based measurements (ppt-ppm)	
PM-2	AAS	0.001–100 ng	Portable workplace monitor
TM-series	AAS	0.01–99.99 mg	For fluorescent tube industry
Tekran, Inc. www.tekran.com			
<i>EVT</i> 3300	AFS	Up to 0.001 µg/m ³ resolution	Hg ^S by SD/TC CEM (RATA), for coal-fire, waste [99, 133]

2537A 1135 / 1130	AFS	0.0001–10 µg/m ³	Hg ⁰ using SD [16, 130, 143] Particulate and Speciation unit for Hg ⁰ and Hg ²⁺
<i>Seefeldler Messtechnik</i>		www.seefeldler-messtechnik.com/english.html	
HG-Monitor 3000	AAS	0.1–2000 µg/m ³	Work place monitor
Hg-Mat 2	AAS	0–75 µg/m ³	Extractive CEM [143]
<i>PS Analytical</i>		www.psanalytical.com	
PSA 10.525	AFS	0.001–2500 µg/m ³	Hg ^S by D/WC CEM for use in LNG & LPG or waste or coal [99, 130, 143, 148, 149]
<i>EVT</i> Sir Galahad			
Sir Galahad II			
PSA 10.670	AFS		Hg ^S by WC CEM for use in LNG & LPG and Petrochemical industry [128]
PSA 10.665			
PSA 10.680			
PSA 10.210	AAS		Hg monitor for chlor-alkali plant
<i>Apogee Scientific</i>		www.apogee-sci.com	
Quick Silver Inertial Separation System			Sampling probe [150]
<i>Opsis</i>		www.opsis.se	
AR602 / Z/600	DOAS*	0–150 µg/m ³	Hg ⁰ [143]
<i>EVT</i> HG200	AAS	0.5–1000 µg/m ³	Hg ^S by SD/TC [99, 130, 133]
<i>Apex Instruments</i>		www.apexinst.com	
<i>EVT</i> XC-6000EPC			Hg ^S Sorbent trap system for combustion sources
XC-30B			Hg ^T Sorbent trap system for coal-fired sources
<i>Arizona Instrument</i>		www.azic.com	
Jerome 431-X /XE	RGFS#	3–999 µg/m ³	Portable field-use sensor [147]
Jerome J405	RGFS	0.5–999 µg/m ³	Portable field-use sensor
Jerome 471	AAS	0.03–250 µg/m ³	Portable field-use analyzer[147]
<i>Sick UPA GmbH</i>		www.sick.com	
<i>TüV</i> MERCEM	AAS	0–100 µg/m ³	Hg ^T by WC CEM [99, 130, 143]
<i>Semtech Metallurgy AB</i>		www.semtech.se	
<i>TüV</i> Hg 2010	ZAAS	0.3–160 µg/m ³	Hg ^T by WC CEM for waste, coal-fire and refining processes [99, 130, 143]
<i>Durag Inc.</i>		www.durag.com	
<i>TüV</i> HM-1400 TR	AAS	0–45 µg/m ³	Hg ^T by TC CEM [99, 130, 133, 143]
<i>Aldora/EcoChem Analytics</i>		www.ecochem.biz	
Hg-MK II	AAS	0–50 µg/m ³	Hg ^T by TC CEM [99, 130]
<i>Envimetrics</i>		www.envimetrics.com	
<i>EVT</i> Argus-Hg 1000	AES	0–200 µg/m ³	Hg ^T by TC CEM for coal, cement, waste etc. [99]
<i>ST2 Technologies</i>			
<i>TüV</i> SM-3	AAS	0–500 µg/m ³	Hg ^S by TC [99, 130]
<i>Mercury Instruments Corporation USA</i>		www.mercury-instrumentsusa.com	
3000 IP	AAS	0.1–2000 µg/m ³	Hg ⁰ Portable monitor [147, 151]
VM 3000	AAS	0–2000 µg/m ³	Hg ⁰ Portable monitor [152]
UT 3000	AAS	0.1–10000 ng/m ³	Hg ⁰ for Use in LNG & LPG
MMS	AAS	0.01–2000 µg/m ³	Multi-channel CEM
MMS-NG	AAS	0.001–2000µg/m ³	Multi-channel CEM for LNG
<i>Genesis Laboratory Systems</i>		www.genlabsystems.com/mercury	
Hg253	AAS	0.001–10 mg/m ³	Hg ⁰ Portable monitor [147]
Process Sentinel	AAS	0.0001 mg/m ³	Hg ^S by, TC CEM [130, 133]
		detection limit	
Sky Sentinel	AAS		Hg ^S by TC CEM
MultiMatrix	AAS	<5pg to 6 mg/m ³	Hg ^S by TC CEM

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Hg^S = reports speciated mercury

Hg^T = reports total mercury

Hg⁰ = reports elemental mercury

*DOAS = UV Differential Optical Absorption Spectroscopy

#RGFS = Resistive Gold Film Sensor

^{EVT} Evaluated under EPA ETV Program [136, 137]

^{TüV} Evaluated by TÜV Rheinland (www.tuv.com)

D/WC = Dry/Wet Chemistry conversion

TC = Thermal Catalytic conversion

SD = Sample Dilution

3.2 Optical and Solid-State Chemical Sensors

A significant amount of work has focused on developing alternative optical and solid-state Hg sensors. Generally solid-state Hg sensors work on mercury amalgamation or chemi-sorption principles between Hg and a selective layer material which overlays a micro-machined transducer platform. Alternatively, optical based sensors work on reflectivity or absorption principles. Work spanning the last few decades has seen the use of Au thin-films as a selective material in conjunction with reflectivity, resistivity or mass based sensor platforms within the research and development community. However, recently selective layers based on palladium, palladium chloride, nanostructured gold and polymeric composite based materials have also been investigated in order to improve both the selectivity and sensitivity characteristics of the developed sensors for Hg sensing applications. The main motivation behind the development of such sensors is their low cost and robust nature in comparison to current analytical techniques (AAS, AFS, etc.). Although much of the developed sensors are initially targeted towards hand-held or portable mercury analyzers, there is an ongoing trend of microsensors based on resistive, acoustic and optical transducer platforms finding their way into commercial products.

3.2.1 Chemi-resistive Sensors

Chemi-resistive based sensors, which are also sometimes referred to as conductometric sensors, work by measuring small resistance changes upon the interaction of a chemical (analyte) with the material (sensitive layer) deposited on the transducer. McNerney et al. [155] was the first to propose Au thin-film based conductometric sensors for Hg sensing applications in 1972, and one year later a prototype sensor was developed which claimed to detect 0.05 ng of Hg [156]. The sensor determined the concentration of Hg based on the resistivity change of the Au electrode upon the Hg-Au adsorption/amalgamation process. Presently, the commercially available Jerome 431-X mercury analyzer by Arizona Instruments is based on the same principles. The change in resistance of the Au film is thought to be due to an increase in scattering of conduction electrons at the Au film once Hg is adsorbed on the surface. Models have been developed to understand the effect of Au film thickness on the sensitivity of these types of transducers in order to optimize the Hg sensor performance [157]. Resistive based Hg sensors are typically made by well established microelectronic fabrication processes, thus they are small sized, have low power consumption and are highly durable, making them highly suitable for small handheld devices that detect Hg vapor concentrations in indoor Hg spills (e.g. dental clinics) [158]. However, it has been reported that such sensors have a high cross-sensitivity towards ammonia and acetylene along with many other interferant chemicals, thus limiting their use. Furthermore, Arizona Instruments have also commercialized a H₂S sensor (model 631-X) which is based upon the same principle. That is, H₂S exposure also induces a measurable resistance change in the Au film, which indicates that H₂S and Hg interactions could be indistinguishable and thus may present significant cross-sensitivity issues [155, 159, 160]. The sensors are also reported to have a minor cross-sensitivity towards other gases such as CH₄, SO₂ and CO that are present in coal-fired and cement plant flue gas.

Materials other than gold have also been studied by NASA to develop an electronic nose (array of conductometric sensors) for Hg detection in air [161]. These materials include polymer-carbon black composite films with amines in the polymer structure, gold islands on polymer films and sintered PdCl₂ films [162, 163]. Additionally, other work has involved the use of hexadecanethiol self assembled monolayers (SAMs) which have been successful in repelling some interferant gases such as sulfuric compounds and humidity, yet simultaneously permit the interaction of Hg with the underlining Au film to induce a signal [164]. However other studies have indicated that Hg

adsorption on Au substrates with alkanethiol SAMs induces reorientation and reorganization of the alkanethiols [165, 166], thus resulting in the formation of Hg nanoparticles at the surface [167]. This is believed to make the sensor unstable when exposed to Hg containing environments, and thus the development of such surfaces and chemical filter layers is ongoing.

3.2.2 Acoustic Sensors

Acoustic based sensors, which are also sometimes referred to as resonant or gravimetric sensors, operate by detecting minute changes of mass at the active surface(s) of the device. Additionally, some varieties are also sensitive to changes in sheet conductivity of the sensitive layer, and thus can also be used to measure very small changes in conductivity at the surface [168]. Acoustic based sensors have been widely studied for Hg sensing applications [169-174]. Bristow [175] first demonstrated the use of quartz crystal microbalance (QCM) for Hg vapor sensing in 1972, which was based on the adsorption/amalgamation of Hg on the QCM Au thin-film electrodes. Other investigators followed, further demonstrating QCM use for Hg vapor sensing applications [176-183]. Recent studies by the authors have also been undertaken to better understand Hg interaction with Au films [184, 185], where modified and nanostructured Au surfaces were studied for potential use as Hg sensors in alumina refinery streams [186-188]. Similarly, research conducted by other groups has also demonstrated various other types of gravimetric devices for Hg vapor sensing applications. These devices include surface acoustic wave (SAW) sensors [189-191], magnetoelastic sensors [192] and piezoelectric microcantilevers [193-195]. SAW based sensors have been identified as possible transducer platforms for Hg CEMs [132, 143] due to their superior sensitivity (they are approximately 100 times more sensitive than QCM based sensors). Although SAW sensors have yet to be commercialized, a comparison of SAW sensors with a Semtech Hg 2000 and a PS Analytical Sir Galahad mercury CEM is provided in [132]. The report shows that the tested SAW sensors have potential to be made into a relatively low cost portable analyzer even though preconditioning and preconcentration subsystems were needed to deal with interferant gases present in the tested streams. Microcantilever based sensors, which employ similar microcantilevers to those used in atomic force microscopy (AFM), have also shown promising results, although they suffer the same cross-sensitivity issues due to their use of Au sensitive layers [196, 197].

3.2.3 Reflective Sensors

In 1990, Butler et al. reported that the reflective properties of Au thin-films undergo detectable changes following their exposure to Hg [198]. The group used this property to demonstrate the measurement of various concentrations of mercury vapor in air. The method involved exposing Hg vapor to an optically thin Au film evaporated onto the cleaved end of a multimode optical fiber and simultaneously measuring the amount of light reflected back through the fiber. Similar sensing methods were also demonstrated by Morris et al. [199]. In this case various Hg vapor concentrations were exposed to Au nanoparticles of either 3, 5, 12 and 22 nm size where the resultant blue shift of their surface plasmon resonance (SPR) was monitored, thus demonstrating a novel "litmus" film for Hg vapor. In the same year, the group also demonstrated Hg sensing in air by SPR spectroscopy using Au, Ag and Au-Ag thin films, showing that a gold-coated Ag film offers greater chemical stability than a pure Ag film and slightly higher sensitivity than a pure Au film [200, 201]. No literature is available on further development of these devices for an industrial type application, thus presumably it is still in the development stage. The simplicity of these devices and the small detection limit in the ppb range are quite exceptional. However, other researchers have later demonstrated that Au [202] and Ag [203] based surfaces are also sensitive to the adsorption of other small gas molecules such as SO₂, CO, H₂S, He, H₂, C₃H₈ and other species commonly found in Hg emitting industries. Therefore, presumably such a sensor platform would require a separate filtering step for accurate Hg quantification in industrial gas streams.

3.2.4 Emerging Technologies

In addition to the above mentioned technologies, several new and different competing technologies have also been developed in the last decade to sense Hg within industrial processes. An example is the newly developed differential absorption lidar (DIAL) technique that uses a dye laser system [204]. Having been trialed by various chlor-alkali plants in Europe to measure elemental Hg vapor [205], it was found that the system needed frequent servicing due to its fast degrading gain medium [206]. Similarly, in 2007, Toth et al. [207] reported the ability to identify and measure Hg by

prompt gamma emission, generated by bombardment with neutrons. The method is typically used to sense Hg in parts per billion (ppb) concentration ranges in the gaseous phase. Other methods with low detection limits also include laser induced fluorescence (LIF) based sensors, which utilize Au thin-films to measure gaseous Hg⁰ in several gas matrixes [208]. In this case Hg is measured by exciting either by 1-photon LIF or 2-photon LIF and subsequently detecting the fluorescent light with an appropriate photomultiplier tube. However, the presence of nitrogen and some other gases can decrease the signal to noise ratio. Similarly, Magnuson et al. [135] have also reported an in-situ measurement of Hg vapor from a laboratory scale coal-combustor and flow reactor using a diode-laser-based ultraviolet absorption sensor. The sensor detection limits was reported to be 0.3 ppb and it is said that the method eliminates the need for pre-treatment by using a narrow bandwidth source with absorption spectroscopy. However, by using a wide laser-wavelength scan range the off-resonant baseline was established accurately on both sides of the mercury absorption spectral feature. This is reported to allow for discrimination between Hg absorption and attenuation by other species or particles [135], thus resulting in the ability to selectively measure Hg in the flue gas. However, the method is not yet validated and needs to be compared with an accepted method for measuring Hg concentrations, such as the Ontario Hydro method.

3.3 Limitations

Initially, the majority of CEMs were originally developed for measuring Hg emissions from waste incinerators. However their application for use in coal-fired combustion processes has not been without significant challenges. This is primarily due to the lower concentrations of Hg present within coal-fired combustion flue gas and the presence of acid gases such as HCl, SO₂ and NO_x that require some form of pretreatment or conversion to avoid interference issues in the analyzer [44]. Although several test programs have shown that some systems are capable of measuring mercury from coal-fired combustion streams to within 20% of wet chemistry or dry sorbent methods, several challenges still exist [102, 133].

The main challenge facing Hg CEM manufacturers is providing a “clean” sample gas to the mercury analyzer. This includes the heated sample lines and particulate removal subsystems that filter the stream before the sample is transported to the analyzer [99]. There are now commercially available filters that are being developed to overcome such issues [150]. Additionally, the majority of commercially available Hg CEMs are based on CV-AAS or CV-AFS due to CV attachment making the instrument more selective towards mercury. Furthermore, with the addition of a gold amalgamation trap it is possible to condition the stream by separating the Hg content from the interferant gas species before the mercury is measured in the AAS or AFS analyzer using the 253.7 nm detection band. This has the added benefit of decreasing the detection limit of the instrument by preconcentrating the mercury on a gold surface and using argon to carry the mercury to an analyzer after being thermally desorbed from the gold trap in an inert carrier gas. However, several challenges are associated with the gold traps technique when applied to industrial streams. Due to gold not being sufficiently selective enough to mercury, its use cannot always guarantee the elimination of interferant gases. Other gases present in industrial streams, such as thiols, sulfides, alcohols, HCl, NO_x, ammonia and humidity are well known to interact with gold, which results in erroneous mercury measurements [132, 164, 209-216]. Additionally, as conventional traps use Au coated granulated sand or quartz, during the high temperature heating/release cycle of Hg from the trap there is the possibility of distillation of the gold. This can lead to condensation of small amounts of Au on the cooler parts of the system, introducing unmonitored collection sites for Hg that can result in systematic error [98]. Moreover, thermodynamic and hydrodynamic problems may occur while releasing Hg from the Au traps for analysis [217]. Another disadvantage of Au traps is the large pressure drop caused by the densely packed Au coated adsorbent, making it harder to use high flow rates during sampling procedure. To overcome this limitation, denuder techniques have been proposed, where reactive wall coatings are used to trap the Hg in the flue gas [218, 219]. However, as this procedure is known to work best with laminar flows for optimum adsorption, it may be incompatible with the new mercury monitoring regulations that require isokinetic sampling (using a fixed flow rate and velocity). Furthermore, obstacles with the spectroscopy part of the AAS and AFS measurement techniques present their own issues, including the occurrence of undesired photochemical reactions, collision quenching and spurious scattered incident light, the loss or oxidation of Hg via adsorption or catalysis on solid surfaces, and small temperature fluctuations that cause small changes in the output intensity of the UV source, thus leading to errors [220, 221].

Other methods of sample preconditioning are not without their limitations, such as those that use either wet chemistry or thermal catalytic reduction methods. Typically these preconditioning systems are used in CEM installations requiring mercury speciation capabilities. Although wet chemistry preconditioning systems are mostly used for research applications, it has been reported that they have worked well in plants burning either lignite or subbituminous coal [99], however the large amounts of chemicals generally result in large amounts of waste generation (up to 8 litres per day) [99]. Also, wet chemistry preconditioning systems are not always guaranteed to work with streams containing high concentrations of SO_2 or SO_3 . Similarly, in the case of thermal catalytic reduction systems, the expense and maintenance of the catalyst materials may become an issue as they need to be frequently regenerated and/or replaced at semi-regular intervals. Another popular method for sample preconditioning involves diluting the sample gas at or near the sample probe and then either using a wet or thermal catalyst preconditioning system. This makes the sample easier to transport and condition within the CEM system, however due to the dilution process resulting in low mercury concentrations, a CV-AFS analyzer may need to be used over a CV-AAS based system. Given the fact that each system configuration is subject to a variety of limitations, at this time there does not appear to be one instrument or measurement technology that will work best in all applications. Several manufactures and bodies such as the EERC have been working on further developing pretreatment systems for Hg CEMs. One such solution is outlined in a report prepared by Laudal for the US Department of Energy [132], which uses a solid alkali-based sorbent to remove acid gases such as HCl and SO_2 , and a stannous chloride solution to convert Hg^{2+} to Hg^0 . Therefore speciation data could be provided by the CEM by difference measurements.

There also exists a real need for the development of solid-state transducer platforms if they are to be viable competitors to the already well-established spectroscopic techniques used for Hg vapor measurements in industrial applications. Research and development by various scientific groups is underway into these platforms, as their advantages such as their overall small size, ease of use, ability to be used as continuous online sensors, low cost and low power consumption far outweigh their limitations. In a similar case to most spectroscopic techniques, their most critical disadvantage is their lack of selectivity to Hg in the presence of other interferant gases such as H_2S and SO_2 . Similarly, other contaminants present in industrial streams (such as thiols, alcohols, ammonia and humidity) have also been known to readily provide cross-interference issues [164, 209-216]. However, developments in nanotechnology and the use of composite materials are being pursued in order to both increase the sensitivity and selectivity of many solid-state transducer platforms. Furthermore, the use of integrated filter layers, surface modifying agents and Hg sorbent traps could also be potential solutions. Overall, it is generally recognized that the well established microsensor based technologies are less sensitive than the currently employed spectroscopic techniques [89, 164, 222]. However, microsensor platforms are cheap due predominantly to their easy fabrication in batch quantities, thus making them thousands of dollars less than competing spectroscopic analyzers [223, 224]. Although such sensors are far from reaching the stage of working as an online CEM in coal-fired or cement industry type flue gases, the race in developing both optical and solid-state Hg sensors for such applications is ongoing.

4 Future Outlook

The ill effects of Hg on health and the environment are well documented, yet there is a lack of reliable, robust, cheap and accurate online Hg vapor sensors for monitoring emissions from industrial sources. Although much progress has been achieved in the last few decades, techniques developed so far are not yet mature, signifying that more research and development efforts are required. The current commercially available Hg CEMs and analyzers all have similar drawbacks, centering largely on their lack of a reliable transport method for the sample representing the flue gas stack, Hg selectivity, susceptibility towards interferant gas species and their ability to deal with particulate matter present within industrial process streams. Additionally, the economic cost associated with installing and maintaining a CEM is another limiting factor. Given that Hg emission control is rapidly moving up the political agenda, it is inevitable that once the technology matures, industries operating in Western countries will be required to install and report their Hg emissions to the public on a regular basis. Recently, 140 countries began to negotiate a UNEP global treaty on mercury that is expected to be signed in 2013 [225]. The treaty is aimed at addressing the need to

reduce the utilization and trade of mercury related products, the reduction of atmospheric emissions of mercury and enhancing national inventories of Hg emissions worldwide [226]. The US-EPA has also approved an Information Collection Request requiring all US power plants with coal- or oil-fired electric generating units to submit their Hg emission data so that it can be used in the development of future air toxics emissions standards [11]. In the meantime, it is intended that the new air toxics emissions standard for coal- and oil-fired electric power plants under the Clean Air Act (Section 112) will be implemented by March 2011, and finalized by November 2011. Such a ruling would require coal-fired power plants to achieve mercury removal efficiencies of up to 90%, thus there is an urgent need to install mercury control technologies such as wet or dry scrubbers and particulate control devices. It is estimated that by 2013, suppliers of abatement chemicals and catalyst control technologies will service a market of US\$500 million a year or more [227]. Although at first the immediate target markets are in the US, in the coming decade a McIlvaine online article, "Mercury Air Reduction Markets", forecasts a US\$2 billion per year market for equipment and consumables to measure and remove mercury from stack gases for the cement, utility boilers and industrial boiler sectors [228]. Given that Europe and Asia will most likely follow or adapt US regulations and that Chinese cement and power plants emit four times more mercury than US plants, markets outside the US are predicted to grow substantially in the coming decades. The combination of stringent regulations and industrial growth is prompting the need for Hg CEM developments [229, 230] capable of integrating with Hg removal systems to ensure the environmental sustainability of Hg emitting industries worldwide.

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