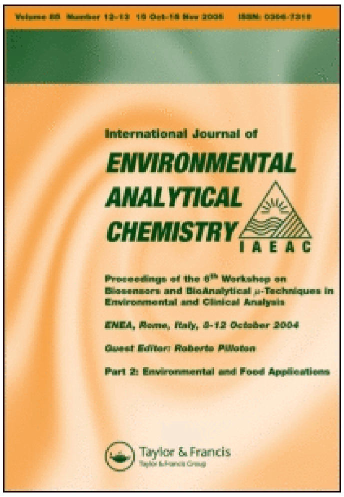

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Measurement and Control of Mercury Species in Flue Gases from Liquid Waste Incineration

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MEASUREMENT AND CONTROL OF MERCURY SPECIES IN FLUE GASES FROM LIQUID WASTE INCINERATION

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New measurement methods have been developed for speciation of mercury and its compounds under flue gas conditions. Total mercury can be collected by a silver denuder or by a gold-coated diffusion screen. Mercury halides can be selectively preconcentrated by a potassium chloride denuder. The use of a microwave-induced plasma source combined with optical emission spectrometry for continuous monitoring of total mercury is investigated.

Incineration of municipal and industrial wastes is the most relevant mercury emission source. Therefore, first experiments have been carried out with solid adsorbents in order to evaluate attempts towards reduction of mercury emissions from such sources.

KEY WORDS: Emission measurement, emission control, mercury, speciation, waste incineration

INTRODUCTION

General

Mercury is, as reported first in 1934 by Stock, a trace component in the entire environment[1]. Catastrophic pollution in Japan at Minamata and Niigata in the 1950s and 1960s initiated numerous investigations into its sources and fate in the environment. It has been stated that mercury emissions from anthropogenic sources have increased during recent decades[2]. As a consequence, stricter emission limits have been assessed — for instance the new emission standard of refuse incineration emissions for mercury and its compounds in Germany is 0.05 mg/m^3 (23.11.1990, 17.BlmSchV). During the last decade many studies on the behaviour, measurement and control of mercury and its compounds under flue gas conditions have been carried out. This paper contributes to these items also, focussing on waste incineration.

Globally, the most important industrial sources of atmospheric mercury are chloralkali industry, cinnabar mining, refuse incineration and electric power generation (fossil fuel combustion)[3,4]. Global atmospheric mercury emissions are estimated to be in the order of 2000–3000 tons/year from anthropogenic sources[3]. In Europe (1979), according to Pacyna[4], 221 tons/year were emitted from coal combustion, 77 tons/year originated from primary non-ferrous metal production, 20 tons/year from refuse incineration and 20 tons/year from industrial applications of metals. As emitted mercury is mainly gaseous, it is transported worldwide through the atmosphere. According to Lindberg[3], precipitation scavenging (wet deposition) seems to be the major removal process of mercury from the atmosphere, and it should have more importance when acidification and airborne oxidant concentrations increase. The global wet deposition of Hg is estimated to be 10^6–10^7 kg/year. Dry deposition rates of Hg are not well known[3].

Mercury behaviour in flue gases

Due to its high volatility, mercury is vaporized easily and thus emitted into the atmosphere after incineration and combustion processes. It vaporizes far below normal combustion temperatures (T_b = 357°C, p = 101,3 kPa). According to thermodynamic equilibrium calculations, it remains totally in the vapour phase even when the flue gases are cooled down to 200°C [5]. Otani et al. have made both, theoretical and practical investigations concerning the behaviour of mercury[6]. According to their results, the fraction of mercury in the particulate phase is well below 1%. Many authors report that mercury appears mostly in the gaseous phase in flue gases emitted into the atmosphere, depending on the control systems used in the process. According to Angenend and Trondt[7], 95% of the input mercury were released from the waste during the combustion, 5% remaining in the bottom ash. About 28% of the fraction released during the combustion was bound to particles, and after the electrostatic precipitator (ESP) and wet flue gas desulphurization unit, 10% of the mercury input were emitted into the atmosphere[7]. In coal-fired power plants equipped with an ESP and wet scrubber (desulphurization), about 70% of the total mercury input in coal was found in the cleaned flue gases[8]. Germani and Zoller[9] have noticed that 98% of the mercury released from coal during pulverized coal combustion was emitted after the ESP.

In some specific cases a large amount of mercury has been found in particles. Bergström[10] has reported results of pilot-plant tests when burning waste. In some experiments, 91% of the total mercury could be removed with the dust in the fabric filter when additional fly ash was injected into the exhaust gas before the filter. When lime was added, no similar effect could be observed[10]. It is obvious, that mercury can be attached to the particles, but only when the fly ash concentration and especially the carbon content of the ash is relatively high[11]. It can be stated, that there is still a lack of knowledge on mercury behaviour under flue gas conditions. Mercury can be adsorbed by particles, but the adsorption is strongly dependent on the flue gas conditions, particularly on the unburnt carbon content in fly ash particles. The conditions which favour the adsorption of mercury on the particles and thus the easy removal of it are most probably difficult to match with optimal combustion conditions.

Measurement and control of mercury

Because of the predominant occurence of mercury in the gaseous form, its measurement in flue gases appears to be easier than its control. Conventionally, strongly oxidizing absorption solutions such as nitric acid/peroxydisulphate solutions[12] and acidic permanganate solutions[13] are used for the collection of mercury. Potassium dichromate/strong nitric acid solution has also been introduced as a very efficient collection medium[14]. Its disadvantage is its high toxicity.

Solid adsorbents, especially activated carbon, have been introduced for efficient mercury collection under flue gas conditions[8,15]. With activated carbon complete adsorption of mercury(II)chloride can be achieved, even at temperatures up to 200°C. Metallic mercury is only partially adsorbed at these temperatures. However, when using iodized activated carbon, metallic mercury can be efficiently collected at 180°C, most probably due to the formation of Hg_2I_2 [15]. Amalgamation of mercury with precious metals such as silver and gold has also been used as a means for mercury collection [13, 16 ... 19].

It is very important to distinguish between the different mercury compounds because of their different behaviour in flue gases. For example, mercury(II)chloride condenses rather easily, but metallic mercury does not have this tendency[15]. The possibility for mercury speciation has been introduced by Metzger and Braun[15]. First mercury(II)chloride is collected with ion exchange material (Dowex), and then an iodized activated carbon scrubber collects metallic mercury passed through the ion exchange resin. By using the denuder technique[30] it is also possible to separate these two forms of mercury[19]. This approach towards speciation based on diffusion controlled deposition is discussed later in this paper.

For monitoring of mercury under flue gas conditions only a few techniques are available. One possibility is to use the cold-vapour technique (AAS) combined with continuously operating mercury reduction (with flue gas condensate) [20]. Another approach is differential optical absorption spectroscopy (DOAS), which however can only be applied to the measurement of metallic mercury[20].

In this work optical emission spectrometry (OES) combined with a plasma source has been investigated as a possibility for the monitoring of volatile metals in emissions. OES is a widely used analytical tool for element determinations in the laboratory. Inductively coupled plasma optical emission spectrometry (ICP-OES) has been used for the real-time detection of metals in ambient air and flue gases[21,22]. Microwave-induced plasmas (MIP) started to gain significance after Beenakker[23] introduced an TM_{010}-type resonant cavity in 1976. Another means to support a microwave-induced plasma is the "surfatron"[24]. Both devices are capable of sustaining noble gas (Ar or He) discharges at atmospheric pressure, at moderate power and with low support gas consumption. Microwave-induced plasmas are very efficient excitation sources for volatile elements like mercury, zinc, sulphur and halogens. However, they are limited with regard to sample introduction and thermal energy[25]. Dry aerosols and especially vapours can easily be introduced into the MIP. Deutsch and Hieftje[26] have described a nitrogen plasma (MINDAP) sustained at moderate power (500 W) in a Beenakker cavity. This offers an interesting possibility concerning direct flue gas introduction into the plasma and continuous monitoring of harmful heavy metals and metalloids present. It is challenging to investigate the possibilities for applying the MIP techniques, which are much cheaper than ICP-OES, to the continuous monitoring of volatile metals with direct sample introduction into the discharge. In the following, preliminary laboratory results of the analysis of Hg-vapour test gases with a MIP-OES system will be presented.

Dry lime injection into flue gases is a very efficient method (efficiency even higher than 99%) for the control of hydrochloric acid emissions released during waste incineration. It is a relatively cheap method and can be carried out under normal flue gas conditions without additional cooling. Dry lime also absorbs SO_2, but for an efficient reaction high temperatures (1000°C) are required. The adsorption behaviour of mercury at dry lime is not well known, and thus this question was the subject of more thorough investigations.

Lime is normally injected into the exhaust gas before it reaches the fabric filter and is then collected by the filter. It forms a cake with fly-ash particles and reacts with the components to be removed. A practical laboratory test system was built to simulate this situation.

EXPERIMENTAL

Generation of test gases

In order to develop measurement and control devices for mercury and other metal species in flue gases, proper test gas sources are required. To generate the most important mercury species appearing in flue gases, mercury(II)chloride and metallic mercury, the diffusion principle was employed. The complete generation system is presented in Figure 1. A diffusion cell, made of borosilicate glass, permits a dynamic generation of known and constant concentrations of mercury and its compounds in various test atmospheres. The test gas concentrations can be varied over a wide range just by changing the dimensions of the capillary and the generation temperature. They can be calculated theoretically by employing the dimensions of the capillary, the generation temperature, the carrier gas flow and the diffusion coefficient of the analyte[27]. However, it is better to calibrate the system and to keep the carrier gas flow through the diffusion cell always constant because of the non-ideal behaviour of the diffusion rate[28]. The cell is placed into a temperature-controlled water (or oil) bath (± 0.1 °C), and the flow rates of the purified carrier gases (argon, helium or nitrogen) passing through it are controlled by calibrated mass flow meters. The generation rates were obtained by taking samples with absorber solutions ($K_2Cr_2O_7/HNO_3$) contained in two sequential wash bottles, and by analyzing these solutions with cold-vapor AAS.

The primary test gas can be mixed with trace gases like H_2O, HCl, NO and SO_2 in order to obtain real flue gas conditions. The same system has been used also for the continuous monitoring tests (MIP-OES) and for the mercury adsorption experiments.

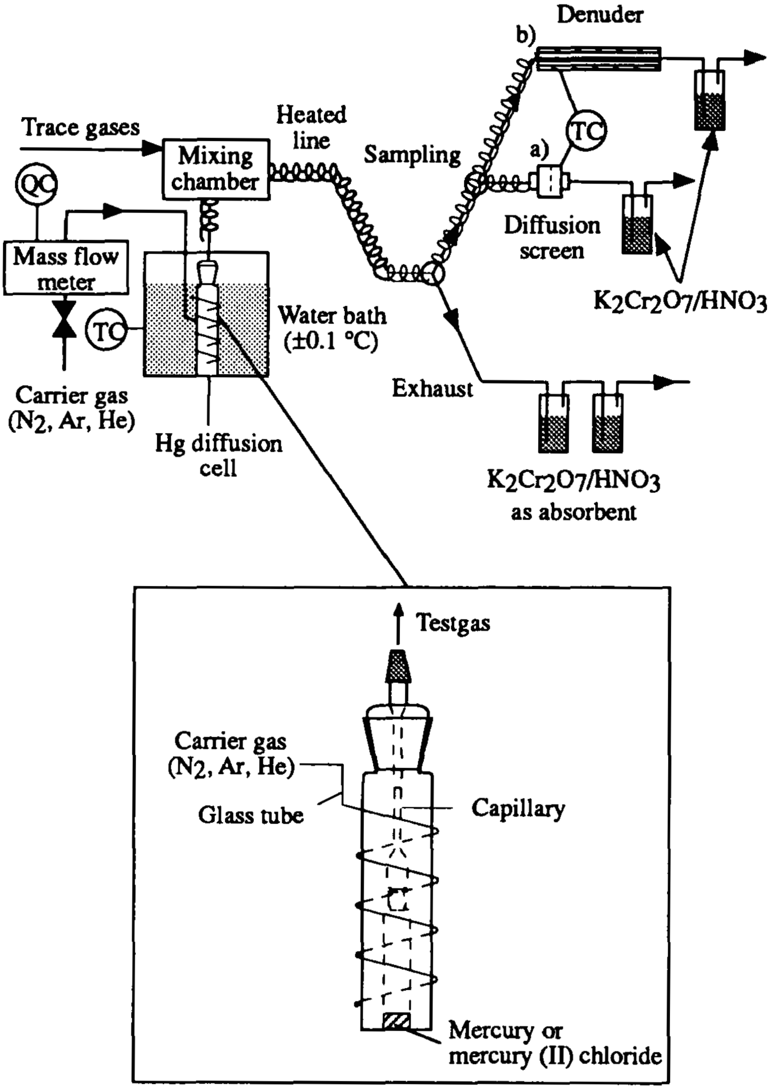


Figure 1 Test gas-generation and sampling system for mercury species; a scheme of the diffusion cell enlarged.

The dependence of the generation rate on the diffusion cell temperature is presented in Table 1. The reproducibility is better than 6% (95% statistical significance).

Speciation of mercury compounds

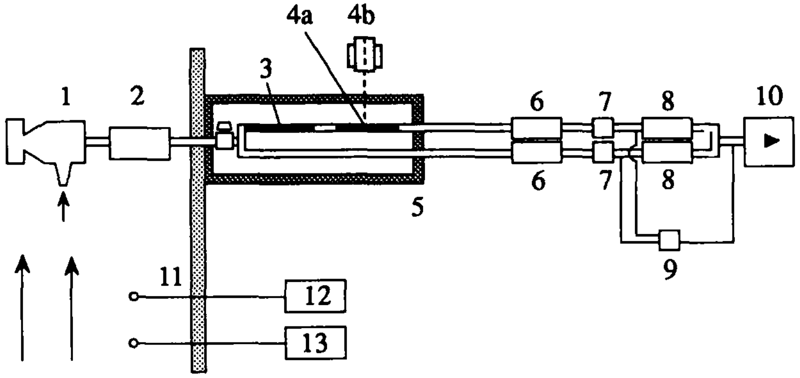
For speciation and collection of mercury compounds in flue gases a denuder sampling technique has been developed (Figure 2). A small cyclone is used for the removal of large

Table 1 Generation rate of Hg as a function of temperature. Carrier gas flow rate 30 l/h; capillary diam. 1.8 mm; capillary length 20 mm.

Generation temperature *K*	Diffusion rate ng/s
343	0,56
363	2,0
383	9,5
403	32

particles ($D_{p,ae} > 2$ μm). Smaller particles ($D_{p,ae} < 2$ μm) may be collected with a quartz filter. In the diffusion collector (two denuders in series in a temperature-controlled oven) a denuder coated with KCl is located in front of a denuder coated with silver. In some experiments the latter was replaced by a diffusion screen[29,30] coated with gold (see below). Usually denuders are placed upstream of filters in order to avoid interaction of gaseous matter with the filter material prior to diffusion controlled deposition[19,30]. However, in case of very high particle concentrations in the stack gas — e.g. at sampling sites located in front of the stack gas filtration unit — a sampling train as shown in Figure 2 has been found to be more suitable. This is particularly true when diffusion screens are used for collection of metal vapours, because fractions of the μm size range of particulate matter may be deposited on the screen also[30,36], such leading to erroneous results.

For analysis the denuders and screens were treated with nitric acid to dissolve the



1 cyclone
2 filter
3 1. diffusion collector (KCl-denuder)
4 2. diffusion collector (Ag-denuder or Au-screen)
5 oven
6 drying
7 filter
8 critical orifice
9 pressure measurement
10 pump
11 pitot tube
12 micromanometer
13 temperature measurement

Figure 2 Diffusion sampling system for mercury species; dimensions of denuder tubes: 50 cm length, 6 mm i.d.; sampling flow rates: up to 1 l/min for denuder tubes, up to 5 l/min for diffusion screen.

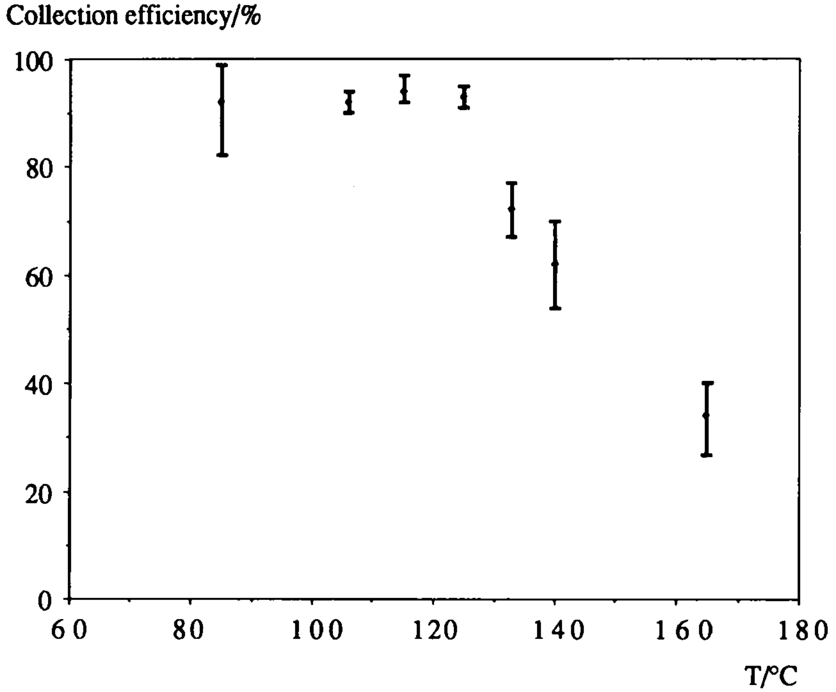


Figure 3 Efficiency of metallic mercury collection as a function of temperature using a gold-coated diffusion screen.

collected mercury. The solutions were analyzed by using a Jerome 511 mercury analyzer, which is based on the change in resistance of a gold plate due to adsorption of mercury on its surface.

The KCl-denuder efficiently collects $HgCl_2$-vapour. Collection efficiencies have been well above 90% for $HgCl_2$ and about 0% for Hg^0 in laboratory experiments at temperatures below 110°C. The Ag-denuder efficiently collects both, metallic and oxidized mercury, and is thus a suitable collector for total mercury[19].

Another mercury collection method, based on the use of a gold-coated diffusion screen, has also been developed and tested in the laboratory. A fine mesh screen made of stainless steel (wire diameter 100 μm, distance between the wires 63 μm) was first cut into a round disc (diam. 47 mm) and then coated with metallic gold, sputtered or vaporized in vacuum. A commercial filter holder made of stainless steel was used as a screen holder, making the collector easily applicable to normal stack conditions. The dependence of the diffusion screen collection efficiency for metallic mercury on the temperature is presented in Figure 3. It can be seen that the collection efficiency is well above 90% at temperatures up to 125°C. This is a much higher temperature than those at which most of the other known mercury collectors operate. In the case of $HgCl_2$, the collection efficiency was above 90% at temperatures up to 115°C. It was also observed that it is possible to operate with flow rates up to 5–6 l/min, which are much higher than the ones applicable for tubular denuders. This agrees well with the results obtained by Schilling[29,30], who used diffusion screens with alkaline coatings for collection of airborne carboxylic acids.

The influence of water vapour and sulphur dioxide, the main potential interferences in

Table 2 Instrumental parameters for the MIP-OES system.

MIP	- water-cooled TM_{010} resonant cavity (Beenakker, modified by van Dalen et al. /32/) - water-cooled Surfatron /24/ - Suprasil quartz tubes with inner and outer diameters: i.d. 1 mm, o.d. 5 mm or i.d. 2 mm, o.d. 6 mm or i.d. 4 mm, o.d. 6 mm
Microwave generator	- AF, GMW 24–301 DR 300 W at 2.45 GHz
Monochromator	- Czerny-Turner monochromator, holographic grating: 58 mm × 58 mm, constant 1/1800 mm; entrance slit width: 20 μm, exit slit width: 20 μm
Photomultiplier	- 9789 QA

flue gases, on the collection efficiency of metallic mercury was also tested. With water vapour concentrations below 60 g/m^3 and SO_2-concentrations below 1000 ppmv no collection efficiency reduction could be observed.

Investigations with MIP-OES

The microwave discharges were sustained at atmospheric pressure in a Beenakker cavity and in a surfatron, respectively. One-filament (1-F) and three-filament (3-F) argon plasmas, as described by Kollotzek et al.[31], were used. The metallic mercury test gases, produced as described above, were introduced continuously into the MIP discharge.

The signal and background intensities were measured axially (end-on). The Hg I 253.6 nm line was used as analytical line. Further information on the test device is listed in Table 2.

Beenakker resonator

A one-filament discharge was obtained in a 1 mm i.d. (inner diameter) quartz tube, which gave a more stable plasma than a 2 mm i.d. tube. The argon discharge was stable at gas flows of 20–120 l/h and at microwave powers of 50–150 W. The radial intensity profiles of the line and background signals and especially the signal/background ratios obtained show a fair analytical response for mercury at a power of 100 W and continuous analyte introduction of 25 μg Hg/m^3 (Figure 4a). It can be seen that the optimal viewing zone is not in the centre of the plasma.

A three-filament argon MIP was obtained by attaching a chuck of brass with three jaws to the TM_{010} cavity[31]. The three plasma filaments were fixed with these jaws, and the discharge could be sustained in a 4 mm i.d. tube at a power of 100 W and gas flow rates of 30–90 l/h. At higher powers the filaments were unstable. The line and background signals as well as the signal/background ratios are shown in Figure 4b. The optimal observation zone is at the edge of the plasma. Besides argon, also helium was used as a working gas. It was necessary to start the MIP discharge with argon and then to change gradually to helium. The radial intensity profiles of the line and background were found to be similar to the profiles obtained with the 1-F argon plasma. The noise of both, line and background signals, was 2 – 4 times higher than in the case of argon. In the power range below 300 W the

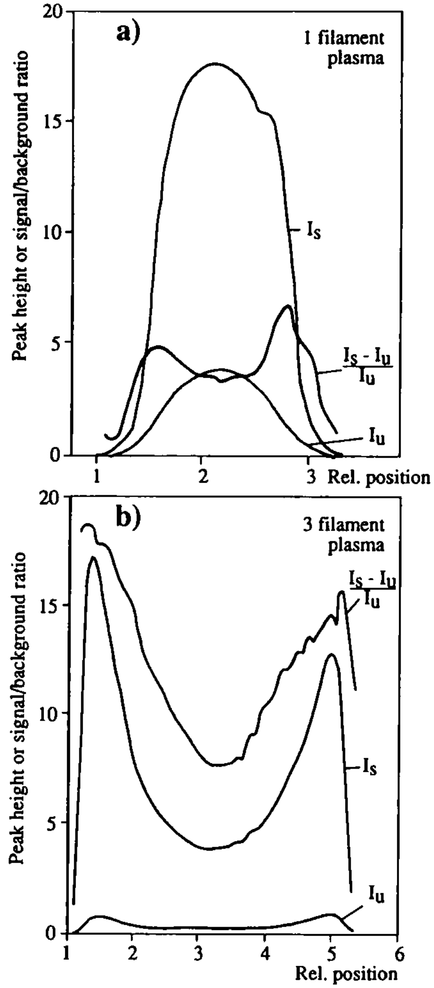


Figure 4a Signal and background intensities (I_s and I_u) and signal/background ratios of MIP-OES when measuring a mercury concentration of 25 μg/m^3 with a one-filament plasma in a Beenakker resonator. Applied power 100 W; flow rate 35 l/h; inner tube diam. 1 mm. **Figure 4b** Signal and background intensities ($I_s$and I_u) and signal/background ratios of MIP-OES when measuring a mercury concentration of 25 μg/m^3 with a three-filament plasma in a Beenakker resonator. Applied power 75 W; flow rate 35 l/h; inner tube diam. 4 mm.

operation of an MIP in nitrogen was not yet successful, which might be related to an unsuitable i.d. of the resonator[33]. However, higher power will be applied to obtain nitrogen discharges in further investigations.

Surfatron

In the first phase, the tuning performance of the surfatron used was determined for argon,

Table 3 Detection limits for mercury using MIP-OES.

Carrier gas	*Carrier gas flow l/h*	*Plasma form*	*Detection limit µg/m³*	
			TM₀₁₀	*Surfatron*
Ar	35	1-F	0,8	1,4
Ar	35	3-F	0,3	-
He	50	Diffuse	0,6	0,7

helium and nitrogen. The performance depends on the position of coupler and plunger as well as on the gap [34]. Without taking these facts into account, the ignition of even argon is impossible. Up to now the analytical investigations have been confined to argon and helium MIPs. Both discharges were sustained in a 2 mm i.d. quartz tube. Optimum stability of an 1-F argon plasma was obtained at a gas flow of 20 – 80 l/h and a microwave power of 75 – 140 W. At higher power the reflected power became too high. Optimum tuning conditions were achieved when the quartz tube protruded 2 – 3 cm out of the resonator. The line and background intensity ratios for Hg were similar to those obtained with the 1-F Ar-plasma produced in a TM $_{010}$ cavity. For He, gas flows of 20 – 200 l/h and a microwave power of 75 – 150 W were suitable. In contrast to the TM$_{010}$ cavity, the He discharge could be ignited directly.

The detection limits for mercury vapour were determined with both, TM$_{010}$ cavity and surfatron (Table 3). The most sensitive configuration was the 3-F argon plasma with the TM$_{010}$ resonator. A mercury concentration of 0.3µg/m^3 could be measured, which is totally sufficient with respect to emission measurements. Quimby et al.[35] have obtained detection limits below 0.1µg/m^3 in investigations in which they used a Beenakker cavity as a detector for gas chromatography.

Mercury emission control investigations employing solid adsorption

In order to investigate the adsorption of mercury(II)chloride on solid adsorbents, the test system shown schematically in Figure 5 was used. A nitrogen stream containing a controlled amount of mercury(II)chloride, generated in a diffusion cell, was passed through a thin adsorbent layer (thickness about 10 mm, mass 0.3 – 1 g) at different controlled temperatures. The generation rate of $HgCl_2$ in these experiments was in the range 40 – 400 ng min^{-1}. A membrane pump maintained a pressure of 32 – 80 kPa in the whole system. The fraction of $HgCl_2$ which passed through the adsorption filter was reduced in a $NaBH_4$/NaOH solution to metallic mercury or alternately absorbed at 4 minute intervals in $K_2S_2O_8/HNO_3$ solution and then reduced with $SnCl_2$. The determination of mercury was carried out with cold-vapour AAS. The breakthrough experiment was concluded, when the amount of mercury determined behind the adsorption filter equaled the amount of mercury generated in the cell.

The first experiments with the laboratory system for solid adsorption were carried out in a nitrogen atmosphere to investigate the adsorption behaviour of $HgCl_2$ with two commercial lime products (specific surface 12.5 and 36.1 m^2/g BET) in the temperature range of 373 –

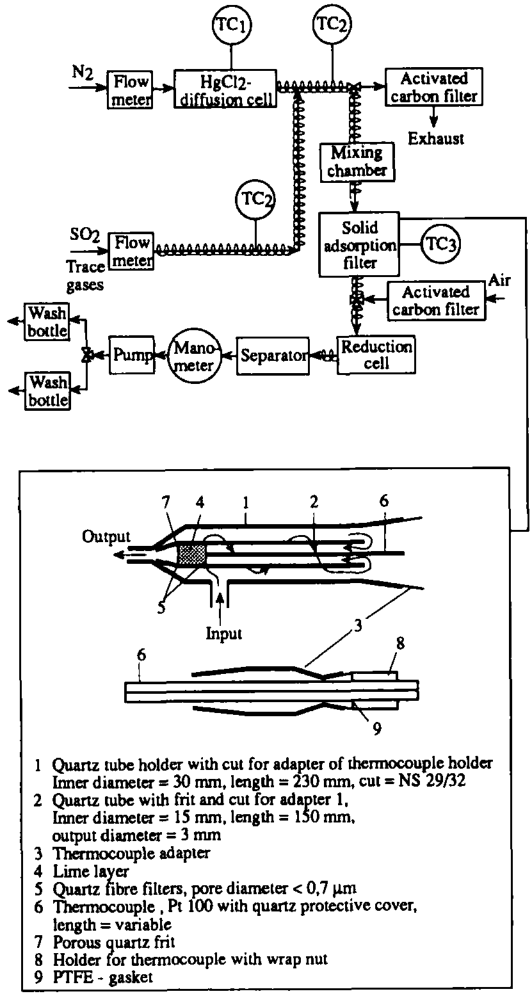


Figure 5 Laboratory test system for solid adsorption experiments; a scheme of the solid adsorption filter enlarged.

483 K. Lime with a specific surface of 36.1 m^2/g is normally used for the removal of hydrochloric acid and sulphur dioxide from waste incineration flue gases. For comparison, this lime was also mixed with activated carbon (carbon content in lime 1% w/w, specific surface of carbon 600 m^2/g BET) to investigate its influence on the adsorption capacity.

The capacity curves are presented in Figure 6. It can be seen that both lime products have quite poor adsorption properties and that the capacity depends on the specific surface area. The capacity is greatly increased when the lime/activated carbon mixture is used. This mixture seems to be an effective adsorbent for the removal of mercury(II)chloride from incinerator flue gases at elevated temperatures. Further experiments are necessary to investigate the influence of HCl, SO_2, NO, and water vapour. Also experiments under real flue gas conditions have to be carried out.

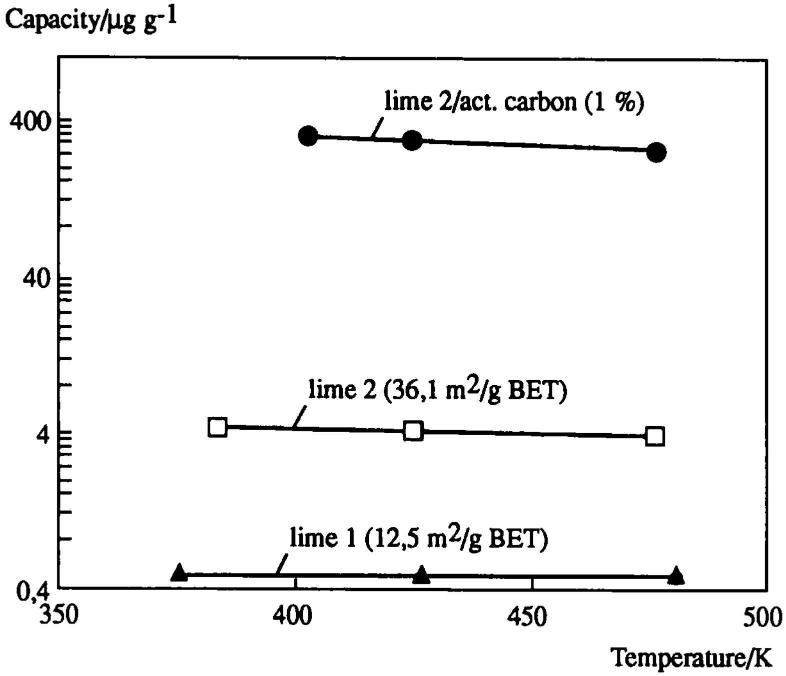


Figure 6 Adsorption capacities for the adsorption of $HgCl_2$ on lime and on a mixture of lime and activated carbon.

CONCLUSIONS

Test systems for the investigation of measurement and control methods for mercury species occuring in waste incineration flue gases are described in this paper. Mercury can be generated using a temperature-controlled diffusion cell. Speciation of metallic mercury and mercury(II)chloride, which are the main species under flue gas conditions, can be carried out by using a KCl- and a Ag-denuder in series. The Ag-denuder can be substituted by a novel diffusion screen collector coated with gold. The Au-screen is small, easy to handle and has a very good sampling efficiency for mercury compounds up to 120°C, even when water vapour and sulphur dioxide are present.

Microwave induced plasma emission spectrometry (MIP-OES) is investigated as a possible method for the continuous monitoring of mercury species. The first laboratory experiments have shown, that it should be possible to measure continuously mercury concentrations down to O.3 $\mu g/m^3$ with a MIP-OES system. The method is under development.

First experiments towards investigation of solid adsorption of mercury halides were carried out with two lime products and a lime/activated carbon mixture. Both lime products were rather poor sorbents at elevated temperatures. However, efficient removal of mercury(II)chloride appears to be possible if a small amount of activated carbon is added to the lime. The optimal ratio of lime and activated carbon as well as the influence of other flue gas constituents on Hg(II) adsorption will be further studied.

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