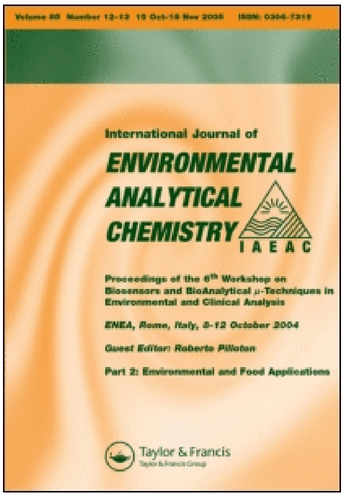

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Application Of The Diffusion Screen Technique To The Determination Of Gaseous Mercury And Mercury (II) Chloride In Flue Gases

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APPLICATION OF THE DIFFUSION SCREEN TECHNIQUE TO THE DETERMINATION OF GASEOUS MERCURY AND MERCURY (II) CHLORIDE IN FLUE GASES

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A technique based on the use of a gold-coated diffusion screen for the collection of gaseous mercury species in flue gases is introduced. Using this technique, collection efficiencies for both metallic mercury and mercury(II)chloride are well above 90% at temperatures up to more than 100°C and at gas flow rates up to 6 l/min. SO_2, NO and H_2O do not have significant effects on the collection efficiency. The method is very convenient considering practical flue gas measurements, because the screen can be used in a compact filter holder suitable for in-stack measurements.

KEY WORDS: Mercury, mercury(II)chloride, flue gas, sampling, diffusion screen.

INTRODUCTION

Atmospheric mercury originates mainly from chloralkali industry, cinnabar and gold mining, waste incineration, fossil fuel combustion, and also from some specific processes such as cement production[1,2]. From the environmental point of view there exists a great need of reliable methods to determine the emissions of gaseous mercury as well as the concentration of mercury in ambient air.

The sampling techniques for gaseous mercury and its compounds known by now are based mostly on liquid absorption or on solid adsorption. Precious metals such as silver and gold are known to act as effective traps for these species in gas flows[3,4]. Conventionally, gold traps used for collection consist of granulated sand or quartz coated with gold. The drawback of these systems is the difficulty to prepare them in a reproducible way. Another disadvantage is the high pressure drop caused by the dense packing of the adsorbent, making it impossible to use high flow rates during the sampling procedure. Additionally, no distinction can be made between vapour phase mercury and particulate mercury unless the collection is preceded by a filter. In this connection it has to be taken into account that the filter material often causes some uncertainty in the results, because part of the gaseous compound may be adsorbed by the filter. On the other hand, the distinction between gas phase mercury and particulate mercury is extremely important in order to reliably determine mercury emissions, to design appropriate control methods for reducing the emissions, and to estimate the dispersion of mercury in the environment.

Recently, the concept of applying a denuder sampling technique to the collection of gaseous metal species was introduced[5,6]. This technique is based on the diffusion and deposition of gas molecules onto a reactive wall coating when passing through a diffusion tube. Due to the large differences in the diffusion coefficients of gaseous and particulate matter, the particles pass through the tube almost completely. This offers the possibility to determine the metal content in the gas phase and in particles separately without any filtration step prior to the sampling of the gaseous fraction. A limitation of the denuder technique is the requirement of a relatively low gas flow rate below about 2 l/min in order to keep the flow laminar (the Reynolds number in the tube should not exceed 2000), and to achieve high collection efficiencies.

Klockow *et al.*[6] used denuders coated with silver for the collection of mercury, while Munthe *et al.*[7] applied denuders coated with gold to the removal of mercury from air. The results obtained with both coatings were highly satisfactory.

Another technique based on diffusion-controlled sampling of the species of interest is the use of a diffusion screen[8]. The theory of the diffusion screen has been developed by Cheng and Yeh[9], and the technique has been applied, e.g., to the selective collection of gaseous and particulate airborne carboxylic acids[10,11]. Based on filtration theory, the theoretical collection efficiency for diffusion screens can be expressed as [9,15].

$$E = 1\text{-}\exp[(-10.8\alpha L D^{2/3})/(\pi(1-\alpha)d_w^{5/3}v^{2/3})] \qquad (1)$$

where α = 1 - screen porosity = $\frac{\text{volume of soild part of screen}}{\text{total volume of screen}}$

d_w = width of the wire

L = depth of the holes

D = diffusion coefficient

v = flow velocity = Q/A_g

Q = volume flow rate

A_g = gas flow cross-sectional area

The calculated efficiency as a function of the depth of the holes for two different flow rates is shown in Figure 1. The following data were used in the calculation: d_w = 100 μm, D = 0.1124 cm^2/s (at room temperature)[7], and the distance between the wires = 63 μm. It can be seen that at 1 l/min a collection efficiency higher than 99% can be obtained choosing

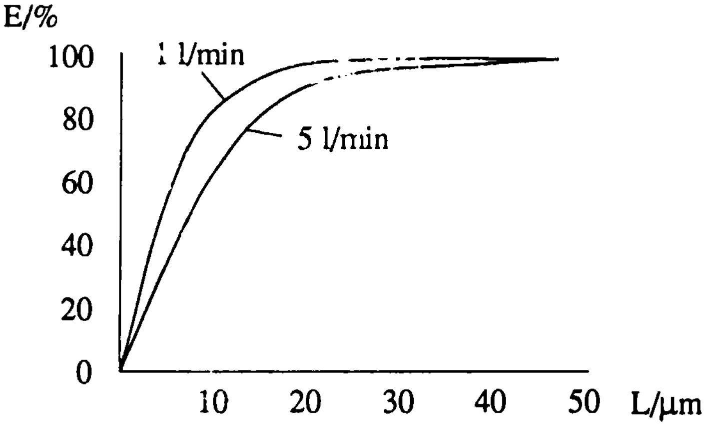

Figure 1 Calculated collection efficiencies for mercury vapour of a diffusion screen (d_w = 100 μm, α = 0,85) as a function of the depth of the screen for two different gas flow rates.

a screen depth as low as 20 μm. In order to reach the same collection efficiency with a tubular denuder, a length of about 60 cm is required[7]. The practical collection efficiency, however, is often lower than the theoretical one, because of an incomplete reaction between the gas atoms or molecules and the coating material, and also because of possible re-entrainment of collected species in the gas flow.

Because the deposition on a diffusion screen may occur not only via diffusion but also via impaction, larger particles (≥ 1 μm diameter) have to be removed with a cyclone or an impactor, placed in front of the screen[10,11,12].

In our previous paper[4] preliminary results on the use of a gold-coated diffusion screen for the determination of gaseous mercury and mercury(II)chloride in a test gas mixture were reported. In the following results of a more detailed study are presented and goals for further research suggested.

EXPERIMENTAL

Generation of test gases

In order to generate test gas mixtures containing gaseous mercury species, a method involving a diffusion cell was applied. This method has been described in more detail elsewhere[4,13]. In the present study test gases containing metallic mercury (from mercury metal, p.a., Merck No. 4403) and mercury(II)chloride (from $HgCl_2$, p.a., Merck No. 4419) were generated. Nitrogen (99.999%, AGA) was used as a dilution and carrier gas. Before the collection experiments were started, the mercury generator was allowed to stabilize at the appropriate temperature with a constant N_2 flow through the cell for approximately one hour. The mercury contents of the test gases were in the order of a few tens of micrograms per m^3 and were determined via collection with an Ag-denuder and $K_2Cr_2O_7/HNO_3$-absorption solution.

When studying the effect of flow rate and the effect of concomitant gases (SO_2, NO, H_2O) on the collection efficiency of the diffusion screen, these additional gases were mixed with the main carrier gas stream in a mixing chamber placed behind the generation cell. Thus the flow rate through the cell and the conditions in the cell were maintained constant in order to assure a constant generation rate of the mercury species. SO_2 and NO were introduced to the mixing chamber as 5000 ppmv mixtures in N_2 (both products of Messer Griesheim). The H_2O content in the test gas was controlled by a thermostated water bath through which part of the dilution gas was passed.

Preparation of diffusion screens

The diffusion screens were prepared from a net made of stainless steel. The mesh size was 63 µm * 63 µm and d_w was 100 µm ($\alpha = 0.85$). From the net round discs of 47 mm diameter were cut, which were then coated with a gold layer of 200 nm thickness by vacuum sputtering.

The sampling system

Each diffusion screen was placed in a filter holder made of stainless steel [diameter of active filtration area 38.5 mm] and connected to the sampling line using Swagelok connectors. The whole sampling system is shown schematically in Figure 2. Two filter holders in series, each one containing one screen, were used. The first filter holder was placed inside a tubular furnace to perform collection experiments at various temperatures (70...180°C). The second holder was always at room temperature to prevent vaporization of collected mercury and thus assure a complete collection of the mercury fraction passing through the first screen. This arrangement was necessary to determine the collection efficiency of one screen at a specific temperature. In the first experiments a denuder, coated with silver, or a liquid absorption unit ($K_2Cr_2O_7/HNO_3$) was placed behind the second screen in order to test, if any mercury passes through the second screen. In all cases no mercury could be detected in the denuder tube or absorption solution. The sampling time varied between 0.5 and 3 h.

Analysis of the mercury content of the screen

After each collection of metallic Hg the diffusion screen was immersed for 30 min in 5 ml of 65% HNO_3 (p.a., 0.0000005% Hg max, Merck No.452). This elution was repeated, and after that the screen was rinsed with ultrapure water, purified in a NANO-pure II System (Barnstead Company), so that the final volume of the sample solution was 70 ml. In the case of $HgCl_2$, the screen was first immersed in water and only after that in HNO_3, in order to prevent the dissolution of the gold coating due to the etching effect of the strong nitric acid solution containing ce^- ions.

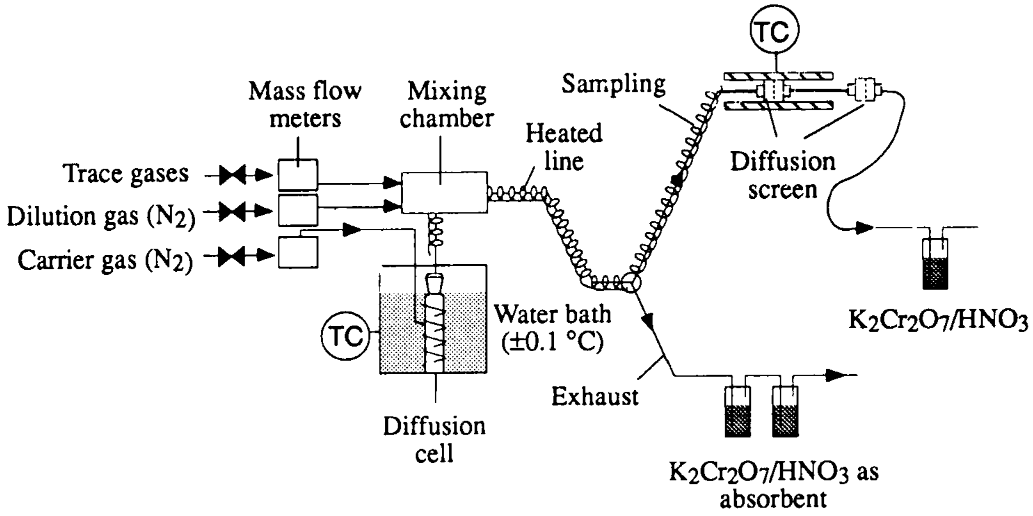

Figure 2 A scheme of the generation and sampling system for mercury species.

The mercury content of the solutions was analysed using a Jerome 511 mercury analyzer. This analyzer is based on the measurement of the change in resistance of a gold plate due to the adsorption of mercury on its surface.

RESULTS

The first experiments with a gold-coated diffusion screen for the collection of mercury gave astonishingly good results. At 86°C and a sampling flow rate of 0.7 l/min the collection efficiency was 99%, when a total amount of 2 μg of mercury was supplied (sampling time approximately 3 h).

As shown in Figure 3, the collection efficiency of a gold-coated diffusion screen with respect to metallic mercury vapour is well above 90% even at a temperature as high as 125°C. (Flow rate of the test gas 0.7 l/min).

In the case of $HgCl_2$ (see Figure 4) the collection efficiency at 125°C was approximately 90%, i.e. slightly lower than in the case of metallic mercury. However, at 106°C it was as high as 96%, which shows that the method is well suitable also for the collection of mercury(II)chloride at relatively high temperatures, well above the dew points usually found in flue gases with respect to water.

The effect of the gas flow rate on the collection efficiency of the diffusion screen was tested in the range 0.7–10 l/min (temperature 106°C). The results (Figure 5) indicate that the collection efficiency is above 90% when the flow rate is equal or below 5 l/min. Even in the range 5–10 l/min the collection efficiency remains better than 80%. These results are in good agreement with the ones obtained by Schilling[10].

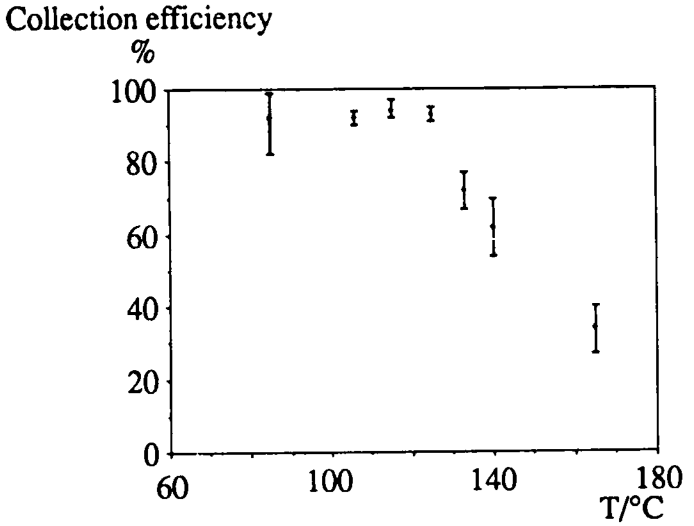

Figure 3 The effect of temperature on the collection efficiency of metallic mercury using a gold-coated diffusion screen; carrier gas N_2, flow rate 0.7 l/min.

The addition of SO_2, H_2O and NO in rather high concentrations had no significant effect on the collection of metallic mercury, as shown by the results given in Tables 1–3.

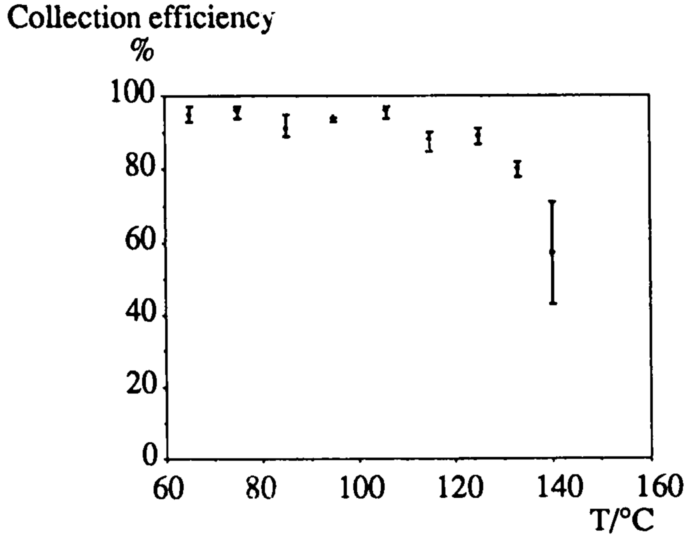

Figure 4 The effect of temperature on the collection efficiency of mercury(II)chloride using a gold-coated diffusion screen; carrier gas N_2, flow rate 0.7 l/min.

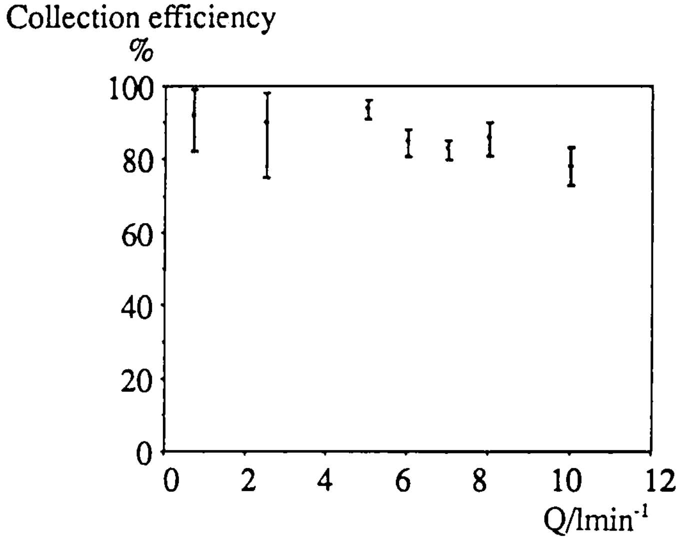

Figure 5 The effect of the flow rate of the test gas on the collection efficiency of metallic mercury using a gold-coated diffusion screen; carrier gas N_2, temperature 106°C.

DISCUSSION

The results reported above show, that the diffusion screen technique is very promising for the determination of gaseous mercury and mercury(II)chloride under flue gas conditions. Compared, e.g., to the use of activated carbon as an adsorbent, the gold-coated diffusion screen can be used for the sampling of mercury at much higher temperatures. This result together with the fact, that no significant decrease in the collection efficiency is observed even at sampling flow rates higher than 5 l/min, makes the diffusion screen technique superior to other methods known so far. Additionally, the negligible influence SO_2, H_2O and NO have on the collection efficiency, is very important for measurements in flue gases.

Considering the practical applicability of the proposed technique, the following features are worth mentioning: The physical appearance and size of the sampling system are very convenient, because a compact filter holder suitable to carry 47 mm plane filters can be used.

Table 1 The influence of different concentrations of SO_2 on the collection efficiency of mercury using a gold-coated diffusion screen; collection temperature 86–106°C, flow rate of the test gas 1–4 l/min.

SO_2 concentration	*collection efficiency*
0	95%
100 ppmv	93%
1000 ppmv	96%

Table 2 The influence of different concentrations of H_2O on the collection efficiency of mercury using a gold-coated diffusion screen; temperature 86–106°C, flow rate of the test gas 1.5–4 l/min.

H_2O concentration	*collection efficiency*
0	95%
30 g/m^3	89%
60 g/m^3	91%

The filter holder containing the diffusion screen can easily be placed inside the stack. Consequently, no change in the state of the gas mixture occurs because of the sampling procedure. One additional advantage is the fact, that no glass parts are necessary, which makes the system safe and easy to handle. A restriction of the technique is, that bigger particles in the sample gas have to be removed by a pre-separator[12].

In the denuder method introduced by Klockow *et al.*[6], the coating of the silver denuders was dissolved after the collection, and the solution was analysed. Due to the high standard potential of silver, its presence made the reduction of Hg^{2+}-ions difficult and thus complicated the analysis. This is why a method, in which no precious metals are present in the solution to be analysed, is preferable. The use of gold is more practical, because mercury can be dissolved from its surface without any significant dissolution of the substrate. While the preparation of gold denuders is rather slow and laborious[7], gold-coated diffusion screens can be prepared relatively easily applying sputtering or vaporization techniques. Thus the use of gold-coated diffusion screens makes the whole collection and determination procedure much more simple.

In order to determine the amount of Hg collected on a screen, it is also possible to heat the screen and to release the mercury vapour directly into the analyzer. In this case possible reactions between gold and steel at high temperatures (> 500°C) have to be considered[14]. Relevant investigations are presently carried out.

For speciation of mercury, the additional use of more selective collectors is required, since gold acts as a collector for all mercury species (both inorganic and organic, see, e.g., Ref. 3). An example of how mercury species can be selectively collected by different types of denuders has been given previously[6,13].

Further experiments on the use of diffusion screens in flue gas measurements are being carried out. By now it has been observed, that mercury concentrations of 0.5 µg/m^3 can be easily determined under flue gas conditions using sampling times of 0.5 h.

Table 3 The influence of different concentrations of NO on the collection efficiency of mercury using a gold-coated diffusion screen; temperature 106°C, flow rate of the test gas 4 l/min.

NO concentration	*collection efficiency*
0	95%
100 ppmv	96%
1000 ppmv	92%

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