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Improved determination of gaseous divalent mercury in ambient air using KCl coated denuders

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Abstract An improved method for the determination of gaseous divalent mercury (GDM) in ambient air using KCl coated denuders has been developed and tested. GDM collected in the KCl coated denuders can be quantitatively desorbed at 450 °C in 10 min. After being completely thermally reduced to Hg⁰ at 900 °C, all mercury released from the denuder is pre-concentrated on the analytical Au trap, and detected by cold vapor atomic fluorescence spectrometry (CVAFS). The absolute detection limit of the method is less than 3 pg. Preliminary data of GDM concentration in ambient air from different sampling stations show that GDM concentrations in the urban air of Göteborg are much higher than in rural air (Rörvik and Sasetta), which indicates the anthropogenic origin of GDM.

1 Introduction

Mercury occurs in various physical and chemical forms in the atmosphere [1, 2]. Most of atmospheric mercury is made up of gaseous Hg compounds, while the remainder is associated with particulate. Although Hg⁰ is the predominant form of gaseous mercury in the atmosphere, a small amount of gaseous divalent mercury (GDM) does exist in the air as well [2]. Normally, it is represented by reactive gaseous mercury (RGM), which is, however, operationally defined and accordingly depends on the Hg^{IIa} in the aqueous phase, defined by Brosset [3]. However, an important aspect of the speciation of mercury in the ambient air is the possibility of emissions of methylated mercury forms, i.e. monomethyl mercury (MMM) and dimethylmercury (DMM). Both species have been shown to be pre-

sented in air at pg m⁻³ levels [4–6]. Even though it makes up only a very small portion of the total mercury concentration in the atmosphere, GDM plays an important role in the biogeochemical cycle of mercury in the environment due to its high solubility in water and easy deposition back to the terrestrial ecosystem by both wet and dry deposition. Recent modelling studies over various spatial scales have shown that even trace amounts of GDM species may control the overall deposition of Hg [7–9]. Therefore, an improved understanding of the speciation of atmospheric Hg is clearly necessary for modelling the fate of atmospheric emissions of Hg.

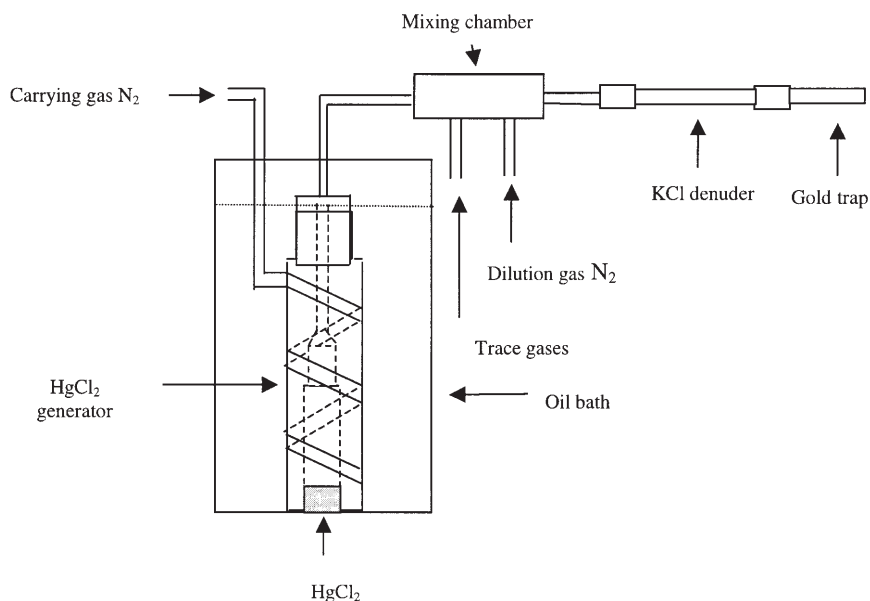
Recently several efforts have been made to develop methods to quantify airborne concentrations of GDM or RGM [10–13]. Brosset [10] tried to determine the concentration of GDM by bubbling air through water solutions. Stratton and Lindberg [11] recently developed a new sampling method for RGM in ambient air with a high flow refluxing mist chamber. Bloom and Prestbo [12] applied cation-exchange membranes for collecting GDM in the air and obtained promising results. In our laboratory, KCl coated denuders have recently been tested and applied for sampling RGM in the air [13]. Later on, a commercial company, Tekran Inc. developed an automated KCl annular denuder system to measure RGM in the ambient air [14].

KCl coated denuders have been tested to efficiently and selectively collect HgCl₂ in flue gas [27] and both HgCl₂ and methyl mercury chloride in ambient air conditions [13]. Therefore, our KCl coated denuder can also capture methyl mercury, which according to the definition does not belong to the RGM group. In our previous paper [13] a sampling and determination method of RGM in ambient air has been developed and tested, and the mercury collected on the KCl denuders was extracted by 1 mol/L HCl solution, then analyzed for RGM by the method of SnCl₂ reduction and cold vapor atomic fluorescence spectrometry (CVAFS). In that procedure, Hg blanks both from KCl and HCl were found, and the process of blanking the reagents was strenuous and time-consuming. In addition, the desorption and analysis procedure were time-consuming as well.

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Fig. 1 Set-up for generation of the gas phase of HgCl_2



The use of pyrolysis in the determination and fractionation of mercury in samples of soil and sediment has been reported in the literature [15–17]. Wang and co-workers [18] applied pyrolysis (thermal converter) for on-line determination of total Hg in flue gases. Pyrolysis of airborne particulate matter for the determination of total particulate mercury (TPM) has been used by some researchers [19–25], and a new device for sampling and determination of total particulate mercury (TPM) in ambient air that is based on thermal reduction of divalent mercury in particulate has been developed by Lu and co-workers [26]. In this paper, a thermal desorption and reduction method for the determination of GDM in the KCl coated denuders is described.

2 Experimental

2.1 Preparation of KCl coated denuders

Quartz tubes of 6 mm I.D. were cut into 55 cm lengths in order to have a collection efficiency of 99% at a sampling flow rate of 1 L min^{-1} [27]. The denuder coating procedure has been described in a previous paper [13]. After being coated with KCl, both ends of the denuders were cleaned with doubly deionised water (Millipore Milli-Q). The denuders were then preliminarily blanked by heating at $450\text{--}500^\circ\text{C}$ in a tube furnace. The blank of the denuders was tested by using the same procedure as the analysis step described below. The denuders were repeatedly heated until a negligible blank was obtained. Both ends of the prepared denuders were sealed by Parafilm or Teflon stoppers. Denuders that were to be exposed are generally blanked shortly before collection starts.

2.2 Laboratory tests of the thermal desorption efficiency of GDM from denuders

The set-up for the generation of GDM is the same as described by Xiao and co-workers [13] previously. The system was operated at room temperature ($20\text{--}22^\circ\text{C}$). The GDM concentration in the source was determined by use of gold traps. Figure 1 shows the set-up for collecting GDM on the KCl denuders from the source. As a certain amount of Hg^0 does exist in the Hg^{2+} source [13], a gold trap was connected to the downstream of the KCl denuder to collect Hg^0

passing through the denuder. The Hg^0 concentration accounted for about 20% of the source concentration, which seems to rise with increasing the source temperature. The analysis procedure of KCl denuders is illustrated below. The thermal-desorption efficiency of Hg^{2+} from the denuders can be calculated by comparing the Hg^{2+} concentration collected by the Au trap and the KCl denuder. In order to test the thermal-desorption efficiency further, Hg concentrations on newly coated KCl denuders without performing blanking procedures, well blanked denuders and analyzed denuders after collected GDM in the ambient air were determined by using the 1 mol L^{-1} HCl extraction method [13].

2.3 Sampling sites and sampling set-up

The sampling set-up is illustrated in Fig. 2. The denuder kept in a vertical position to prevent deposition of particles on the KCl layer was heated by heating tapes up to a temperature of 20 to 30°C above

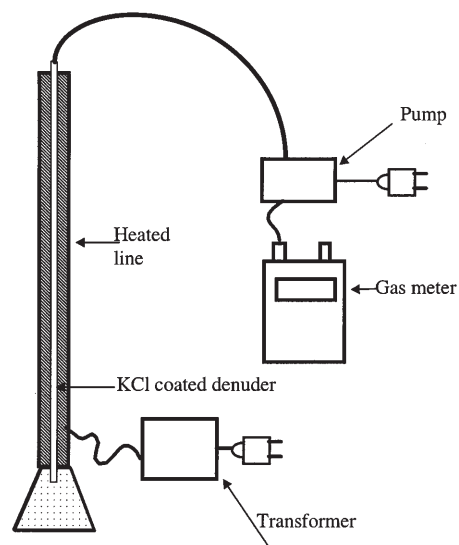


Fig. 2 Sampling set-up for gaseous divalent mercury in the ambient air

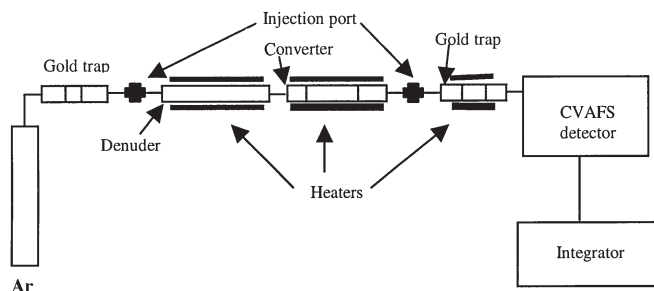


Fig. 3 Experimental set-up for the analysis of divalent gaseous mercury

the ambient air temperature in order to prevent condensation of water vapor on the inner surface of the denuder. As long as no water condensed on the KCl coated surface, even if the humidity level of the air was very high, the sampling efficiency of the system does not decrease. Usually about 1–1.5 m³ samples were collected in the KCl denuder with a flow of 0.7–1 L min⁻¹.

Sampling was performed at 3 sites. The first site was located outside the building of the Chemical department, Chalmers University of Technology and Göteborg University in the center of Göteborg, Sweden. The total gaseous mercury concentration was about 2 ng/m³. The second site was situated in Sassetta, approximately 100 km south of Pisa, Italy. Sampling was performed along with an international intercalibration campaign of atmospheric mercury speciation and measurement supported by Mercury Over Europe (MOE) and Mediterranean Atmospheric Mercury Cycling (MAMCS) projects. The campaign was held from 27 June to 7 July 1998 and involved 8 laboratories. The average total gaseous mercury concentration was about 2.0 ng m⁻³ during the campaign. The third site, Rörvik, which is 35 km SW of Göteborg, was one of the sampling stations of the MOE projects. The total gaseous mercury concentration was in the range 1.5–2.0 ng m⁻³.

2.4 Determination

The experimental set-up for the determination of GDM in the denuders is shown in Fig. 3. During sample analysis, the sample denuder was heated externally to 450 °C for 10 min using nickel-chromium alloy resistance heating wire. The released Hg species were carried by a stream of argon at a flow rate of 200 mL min⁻¹ into a thermal converter that consisted of a quartz tube containing smashed quartz chips. The converter was heated up to 900 °C by an external nickel-chromium alloy resistance heating wire. The converter reduced all mercury compounds to the elemental form [18, 29], which in turn was preconcentrated on the analytical gold trap downstream. The Hg trapped in the analytical Au trap was thermally desorbed at 500 °C and detected by a CVAFS. Calibration of the analytical system was achieved by injecting of known volumes of air saturated with Hg⁰ vapor.

2.5 Reproducibility tests of the method

Triplicate samplings in parallel were performed at two sites. One site was at Sassetta, Tuscany, approximately 100 km south of Pisa, Italy [28]. Sampling was conducted along with the field inter-comparison campaign which took place from June 27 to July 3, 1998. The other site was in the laboratory of a pilot-scale flue gas simulator at S:t Jörgen about 20 km from the center of Göteborg. The tests were performed when both Hg⁰ and HgCl₂ were injected into the flue gas duct for an intercomparison of the methods of speciation of mercury in flue gases.

Table 1 Collection efficiencies of the KCl denuders for gaseous inorganic HgCl₂

Experiment date	Hg loaded into the first denuder (pg)	Hg loaded into the second denuder (pg)	Breakthrough ^a (%)	Collection efficiency ^b (%)
980518	650.6	30.4	4.7	95.5
	312.4	10.1	3.2	96.9
	1256.7	44.9	3.7	96.6
Average (n = 3)				96.3 ± 0.7

^aBreakthrough (%) = Hg loaded into the second denuder/Hg loaded into the first denuder × 100; ^bcollection efficiency (%) = Hg loaded into the first denuder/(Hg loaded on the first denuder + Hg loaded on the second denuder) × 100

3 Results and discussion

3.1 Adsorption efficiency of the KCl denuders for GDM

In our previous paper [13], the adsorption efficiency of KCl denuders for GDM was tested by comparing GDM concentrations recovered by both KCl denuders and gold traps from the Hg source. The results showed that when the Hg load on one KCl denuder is less than 30 ng, which is more than enough for sampling GDM in the ambient air, the collecting efficiency of the denuder for GDM was 95–100% [13]. In these studies, we tested the collection efficiency of the KCl denuders for GDM further by connecting two KCl denuders in series to the Hg source. It was found out that the amount of Hg trapped in the second KCl denuder made up less than 5% of that in the first KCl denuder (Table 1) and that the average collection efficiency of KCl denuders for GDM was 96.3%, which agreed well with the results of the previous tests [13].

3.2 Determination of temperature and heating time for the thermal desorption of GDM from the KCl coated denuders

In order to find out a suitable temperature for the thermal desorption of GDM trapped in the KCl denuders, different temperatures from 200 °C to 600 °C were tested. First of all, newly prepared KCl denuders were heated to 200 °C for a certain time (10 to 30 min) by using nickel-chromium alloy resistance heating wire; the Hg desorbed from the denuders was thermally reduced to Hg⁰ by the converter and then trapped on the analytical gold trap. The Hg trapped in the analytical Au trap was thermally desorbed at 500 °C and detected by a CVAFS. The above procedures were repeated until very low and stable blanks were obtained. The temperature of the thermal desorption of the denuders was then increased to a higher value. At temperatures between 200 °C and 400 °C, by increasing temperature, more mercury was desorbed from the denuders. However, above 450 °C, an increase of temperature did not lead to any more desorption of mercury from the denuders. Obviously,

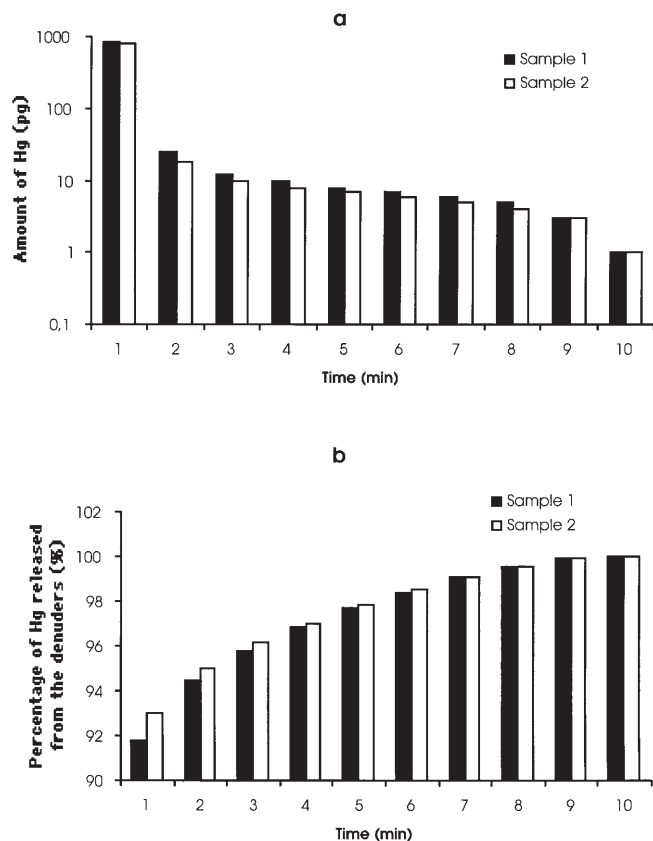


Fig. 4 Behavior of Hg released from the denuders during 10 min heating period. **a.** Amount of Hg released from the denuders in each minute; **b.** accumulation percentage of Hg released from the denuders with increasing heating time

at 450 °C all Hg species existed inside the KCl crystals of the denuders, therefore, are thermally desorbed, and if there are any GDM species trapped on the surface of KCl crystals of the denuders during sampling period, they will certainly be thermally desorbed from the denuders as well. Studies show [14] that some of the GDM species such as HgCl_2 are thermally reduced to Hg^0 at this temperature. For these reasons, we set the temperature for the thermal desorption of Hg from the denuders during the analysis of the field denuders to 450 °C.

Two well-blanked denuders were connected to the Hg source. After collecting about 900 pg of Hg, the denuders were analyzed by the method described above with a heat-

ing time of 1 min. The analytical procedures were repeated 10 times. Figure 4 gives the amount and percentage of Hg released during each heating period. From this figure, it can be seen that more than 90% of mercury trapped in the denuders can be thermally desorbed during the first minute of the heating period at the temperature of 450 °C, and moreover that with a 10 min heating time all mercury trapped on the denuders can efficiently be desorbed. According to the results of this experiment, we chose 10 min as the heating time during the analysis of the field denuders.

3.3 Efficiency of the thermal desorption of GDM from KCl coated denuders

The Hg concentration from the source was determined prior to each set of efficiency tests, by using gold traps. Afterwards, the KCl denuder was connected to the system, and Hg passed through the denuder was collected by a gold trap, cf. Fig. 1. The experimental results are summarized in Table 2. From this table, it can be seen that the thermal desorption efficiencies of GDM from the denuders at the temperature of 450 °C and with a heating time of 10 min varied from 94.5% to 107.1%.

The blanks of KCl coated denuders (newly coated KCl denuders without performing blanking procedures, well blanked denuders and analyzed denuders after collected GDM in the ambient air) were determined by using the 1 mol L^{-1} HCl extraction method [13]. Table 3 shows the average blanks of the three different kinds of denuders. Usually, the newly coated KCl denuders contain very high Hg blanks, which mainly come from the reagents such as KCl and methanol. The heating procedure will dramatically decrease the Hg blank in the KCl coated denuders. Moreover, from Table 2 it can be seen that the heating procedure during the analysis of the field denuders will desorb all mercury species trapped on the denuders.

3.4 Results of reproducibility test

Table 4 shows the reproducibility test results at the two sites. At Sasseta, the sampling volume was around 0.4–0.5 m^3 due to the low capacity of the pumps, and the total amount of GDM trapped on the denuders was around or less than 10 pg, which was quite close to or only slightly

Table 2 Thermal desorption efficiencies of the KCl denuders for gaseous inorganic HgCl_2

Experiment data	Source temperature (°C)	Hg conc. on denuders (ng m^{-3})	Hg source conc. (ng m^{-3})	Hg^0 concentration in source (ng m^{-3})	Desorption eff. (%)
980414	21	197.0 ± 16.8 (3)	263.2 ± 18.2 (4)	54.8 ± 8.1 (3)	94.5
980415	20	183.1 ± 33.5 (3)	229.9 ± 6.8 (4)	44.5 ± 18.9 (3)	98.8
980416	22	274.9 ± 27.4 (3)	375.6 ± 64.2 (7)	101.2 ± 19.2 (3)	100.2
980427	22	–	400.1 ± 92.2 (12)	–	–
980512 ^a	22	1245.9 ± 324.6 (4)	1579.6 ± 105.8 (3)	384.3 ± 29.5 (4)	104.2
980513 ^a	22	1135.8 ± 17.2 (4)	1340.6 ± 38.4 (3)	280.1 ± 19.7 (4)	107.1

^a The dimension of the diffusion cell inside the mercury source was changed

Table 3 Hg blanks of the newly prepared, well thermally blanked and analyzed denuders determined by using the 1 mol L⁻¹ HCl extraction method (Xiao et al. 1997)

Denuder type	Blanks (pg)	Sample numbers
Newly coated denuders	45.0 ± 20.0	10
Well blanked denuders	3.1 ± 1.5	5
Analyzed denuders	2.3 ± 1.0	3

Table 4 Reproducibility test results at Sasseta and S:t Jörgen

Sampling Site	Date	Average (pg m ⁻³)	RSD (%)
Sasseta, Tuscany, Italy	28–29/06/98	20	20
	29–30/06/98	10	30
	30/06–01/07/98	23	25
	01–02/07/98	22	11
	02–03/07/98	15	30
In the Laboratory at S:t Jörgen	14/10/98	8.51 ^a	5.5
	15/10/98	21.3 ^a	4.1
	26/10/98	2.14 ^a	1.2
	27/10/98	10.1 ^a	3.4

^a: the unit is ng m⁻³

higher than the detection limit of the CVAFS available at the sampling site. This is the reason why the RSD were so high at this sampling site. At the laboratory of the S:t Jörgen pilot scale flue gas simulator, the GDM concentrations were up to the ng m⁻³ level. Tests show that the reproducibility of the method is very good, and the RSD is usually less than 5.5%.

Our method was compared with other methods (KCl coated annular denuder method and mist chamber method) during the intercomparison campaign at Sasseta. Owing to the scarce data set, it was very difficult to rank the different methods. However, it can be concluded that they generally produced relatively similar results with a variability up to 30–40%. The complete data set including total gaseous mercury (TGM) and particulate Hg data will be published elsewhere [28].

3.5 Field measurement results

At the initial stage of the development of the method the thermal converter (Fig. 3) was not used during the determination of GDM, and two peaks were occasionally observed, especially when a relatively long sampling time was used. This double-peak phenomenon was rather similar to that observed by Lu and co-workers [26]. The first peak was judged to be not a mercury peak [30]. After the application of the thermal converter, the double-peak phenomenon disappeared. One of the possible explanations is that some volatile or semi-volatile organic compounds trapped in the denuder will be released during the heating of the denuder and deposit on the surface of gold trap. When the gold trap is heated, these compounds interfering with the analysis of mercury, evaporate at a temperature

Table 5 GDM measurement results at different sampling sites

Site	Date	Sample number	Concentration (pg m ⁻³)
Chalmers, Göteborg	09/04/98–28/05/98	10	45.5 ± 34.6 ^b
Sasseta	27/06/98–07/07/98	14 ^a	18.0 ± 7.7 ^b
Rörvik	23/11/98–06/12/98	14	24.4 ± 13.2 ^b
Rörvik	15/02/99–28/02/99	13	14.6 ± 11.4 ^b
Rörvik	03/05/99–15/05/99	14	25.2 ± 25.6 ^b

^a: include duplicate and triplicate sampling results;

^b: average value ± standard deviations

lower than that required to liberate Hg⁰ from its amalgamated state, resulting in the first peak [30]. However, at 900 °C, these compounds will certainly be decomposed and no interference will occur afterwards.

Table 5 lists the ambient air concentrations of GDM determined using the method in our laboratory. Obviously GDM concentrations in the urban air of Göteborg are elevated compared to rural sites (Rörvik and Sassetta), which indicates the anthropogenic origin of GDM. A detailed discussion of GDM results from these sampling stations will be described in another paper [31].

4 Conclusions

KCl coated denuders can quantitatively collect GDM in ambient air and the thermal desorption method developed in this paper can quantitatively desorb and thermally reduce GDM trapped on the denuder surface, which makes it possible to apply the KCl denuder for sampling and analysis of GDM in ambient air. Based on 3σ of the method blanks, the absolute detection limit of this method is estimated to be less than 3 pg, which is much less than that of the previous acid leaching and SnCl₂ reduction method [13]. The advantages of the method are: a) the total cost of the method is quite low; b) the analytical procedures are very easy and time-saving; c) the denuders can be repeatedly used for at least one month.

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