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Z. Xiao · J. Sommar · S. Wei · O. Lindqvist

Sampling and determination of gas phase divalent mercury in the air using a KCl coated denuder

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Abstract KCl coated denuders were employed for the measurement of divalent mercury (Hg^{2+}) species in the air. Laboratory tests show that gaseous Hg^{2+} can be collected by the denuder with an average efficiency of 98% and elemental Hg will pass through it freely. Hg^{2+} trapped in the denuder can be quantitatively extracted by 1 mol/L HCl and analyzed by the method of $SnCl_2$ reduction-CVAFS determination. Hg^{2+} concentrations of 0.04–0.15 ng m^{-3} corresponding to about 2–9% of the total gaseous mercury in the ambient air were determined at several sampling locations.

1 Introduction

Mercury (Hg) exists in the atmosphere in different physical and chemical forms, which have different characteristics in transport, deposition and influences on ecosystems. Long-distance transportation of mercury, followed by wet and dry deposition, is regarded as the reason for mercury accumulation in fish at harmful levels in remote lakes receiving no direct mercury discharge [1, 2]. A small portion of the total gas phase mercury such as $HgCl_2$, $Hg(OH)_2$, or CH_3HgX ($X = Cl^-$ or OH^-) is of great importance due to their high solubility in water, hence easy deposition back to the environmental surface [3].

Although this importance has been recognized during the last two decades, very limited investigations have been done. This is mainly because the concentration of Hg^{2+} in the air is extremely low and suitable sampling methods are still lacking. Brosset [4] tried to determine the concentration of Hg^{2+} in air by bubbling air through water solutions. Stratton and Lindberg [5] recently described a sampling method for Hg^{2+} in the atmosphere with a high flow refluxing mist chamber. The Hg^{2+} concentration was reported to be 2–8% of the total gas phase mercury (TGM). Cation exchange membranes have recently been applied to sampling of Hg^{2+} in the air and promising results were obtained [6].

Denuder techniques have been successfully used in the measurement of gas phase species in the atmosphere such as ammonia, sulphur dioxide, nitric acid, nitrogen dioxide and chlorinated organic compounds [7–9]. Gold or silver coated denuders have been developed and applied for measurements of particulate and gas phase Hg in the air [10–13]. Larjava [14] introduced a KCl coated denuder for collection of gas phase Hg^{2+} from flue gas at a concentration level of several tenths of mg m^{-3}.

In this paper, the application of KCl coated denuders to sampling and analysis of Hg^{2+} from the atmosphere is described. The collection efficiency of KCl coated denuders for $HgCl_2$ and CH_3HgCl has been tested in the laboratory at a Hg concentration of about 400 ng m^{-3} and at room temperature. Experimental results show that gaseous Hg^{2+} can be quantitatively collected by the denuder, which in turn can be extracted by 1 mol/L HCl solution. The corresponding laboratory test results are presented together with field measurements of Hg^{2+} concentrations in the air using KCl denuders.

2 Experimental

2.1 Preparation of KCl-denuders

Glass tubes of 6 mm i.d. were cut into 55 cm lengths in order to have a collection efficiency larger than 99% at a sampling flow rate of 1 L min^{-1} [14]. They were soaked in $K_2Cr_2O_7$-H_2SO_4 solution overnight, then thoroughly rinsed with deionized water and Milli-Q water and dried in an oven at 120°C. The pre-treated tubes were coated with saturated KCl in methanol solution at a temperature of ca. 50°C. The solutions were sucked into the tubes, which were kept in their vertical positions, and maintained for about 20 min before draining them out. Coated denuders were inspected under the electron-microscope and well-coated denuder surfaces were observed to be covered evenly by tiny crystals of KCl.

The influence of surface roughness of the tube on coating and Hg collecting efficiency was also investigated by using HF of different concentrations (5–20%) and different etching times (5–20

Z. Xiao (✉) · J. Sommar · S. Wei · O. Lindqvist
Department of Inorganic Chemistry,
Chalmers University of Technology and University of Göteborg,
S-412 96, Göteborg, Sweden

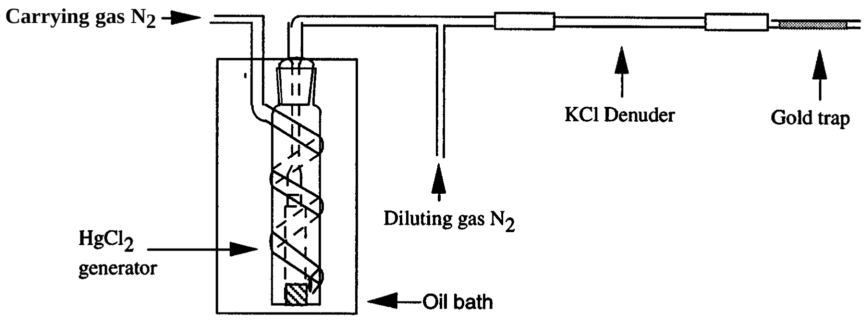

Fig. 1 Set-up for testing the collection efficiency of the KCl denuder for Hg^{2+}

min). It was found that there are no differences concerning the collection efficiency for Hg^{2+} between tubes with and without HF treatment. Therefore, the HF treatment was abandoned since it might make it more difficult to extract Hg^{2+} from the denuder by HCl solution before analysis.

2.2 Laboratory tests of denuder efficiencies for Hg^{2+} and Hg^0

The efficiency of the denuder for collecting Hg^0 was studied by an automatic mercury analyzer of type GARDIS-1A [15], which is essentially an AAS with in-built double gold traps for preconcentrating and analyzing Hg. The efficiency of the KCl denuder for the collection of Hg^0 was estimated by delivering a certain amount of gaseous Hg either directly into the inlet of the GARDIS-1A instrument, or via the KCl denuder.

Figure 1 illustrates the system for testing the collection efficiency of KCl denuders for Hg^{2+}. Several grams of solid $HgCl_2$ were placed into a diffusion cell. The Hg^{2+} concentration in the system depends on temperature and the flow rates of carrying and diluting gases. A detailed description of a gaseous Hg^{2+} generating system has previously been given by Larjava [14] and Wang et al [16].

The collection efficiency of Hg^{2+} on the denuder was then calculated based on these experiments, with and without KCl between the Hg^{2+} source and gold trap. Mercury trapped in the denuder was extracted by 10 mL of 1 mol L^{-1} HCl (super-grade) and analyzed by $SnCl_2$ reduction and the CVAFS determination procedure. This technique was used both for the laboratory tests of the denuder efficiency and field measurements of Hg^{2+} in the air.

2.3 Field sampling sites and sampling set-up

Two lines were set up for simultaneous sampling of Hg from air, as illustrated in Fig. 2, one for collecting gaseous Hg^{2+} species using a KCl denuder and the other for conventional sampling of total gaseous Hg [11].

Sampling was performed at four sites. The first site Brottkärr is located on the Swedish west coast, approximately 15 km SW of the city of Göteborg. The samples were collected at a height of 3 m above the ground. The total gaseous mercury concentration was determined on a 10 min basis with the GARDIS-1A mercury analyzer, usually on a background level of less than 2 ng m^{-3}. The second site is located outside the building of the Chemical Department, Chalmers University of Technology in the centre of Göteborg. The total gaseous Hg concentration was about 2 ng m^{-3}, measured at several occasions. The third site of St. Jörgen is about 20 km from the center of Göteborg, where a combustion simulator was under operation and sometimes Hg was delivered into the system for research purposes. The fourth site, Mace Head, is situated on the west coast of Ireland, approximately 80 km west of the city of Galway. Sampling was performed along with an international intercalibration for Hg measurements. 12 groups joined this exercise during September 11–15, 1995 [17].

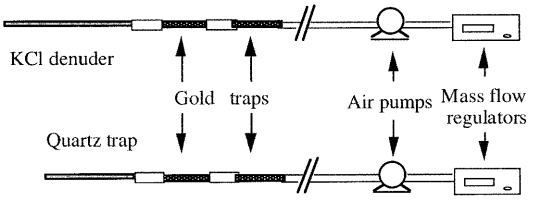

Fig. 2 Experimental set-up for sampling different Hg species from air

3 Results and discussions

3.1 Efficiency of the KCl denuder for Hg^0

The corresponding test results are summarized in Table 1. The non-100% efficiency in this Table was interpreted as a system error from the temperature variation of the Hg^0 source, the accuracy of syringe reading, the instrument stability and the operating error of the operator. In order to verify this, gold traps were used to sample before and after the KCl denuder. Hg collected by the gold traps was analyzed by CVAFS with an integrator for peak area recording. A digital syringe (Hamilton® model 1700) was used for Hg delivery. The median peak areas obtained from gold traps before and after the denuder are 2.26×10^6 ($n = 18$) and 2.26×10^6 ($n = 10$), respectively, when the same volume of gaseous Hg^0 was repeatedly intro-

Table 1 Breakthrough of Hg^0 through the KCl denuder

Experiment data	Hg loaded into denuder (pg)	Hg found after denuder (pg)	Breakthrough[a] (%)
950301	279.1	267.5	95.8
	274.4	265.4	96.7
	268.3	266.4	99.3
950325	357.5	355.2	99.4
	363.4	364.6	100.3
	355.4	351.4	98.9
950411	260.9	262.8	100.7
	265.5	260.8	98.2
	267.7	265.8	99.3
		Average	98.7 ± 1.5 ($n = 9$)

[a] Hg found after the denuder divided by Hg load into the denuder

duced into the test system. This means that elemental Hg simply passes through the denuder without being adsorbed, which agrees well with Larjava's [14] experimental results conducted at higher concentrations of mercury (several tenths of μg m^{-3} level).

3.2 Efficiency of the KCl denuder for gas phase Hg^{2+}

The efficiencies of the KCl denuder for collecting both inorganic and organic Hg^{2+} species were tested by using $HgCl_2$ and CH_3HgCl as sources.

3.2.1 Efficiency for inorganic Hg^{2+}, $HgCl_2$

The concentration of the source was determined, prior to each set of efficiency tests, by use of gold traps. Afterwards, the KCl denuder was connected to the system, and Hg that passed through the denuder was collected by gold traps, cf. Fig. 1. The experimental results are summarized in Table 2 with the number of measurements given in parenthesis. It can be seen from Table 2 that under the experimental conditions, the source concentrations of gaseous Hg^{2+} (in the form of $HgCl_2$) used in the investigation were 544.4 ± 40.8 ($n = 71$) ng m^{-3}, which was influenced by the variation of room temperature and pre-conditioning time for carrying and diluting gases through the system. Generally, it takes at least 5–6 h to reach a stabilized concentration due to the fact that Hg^{2+} adsorbs on all surfaces available [14]. Collection efficiency tests were only started after such an equilibrium state of the source had been reached.

The average apparent collection efficiency of denuders for Hg^{2+} varied from 74% to 94%, which is not satisfactory to meet the requirements for a quantitative field work. One possibility may be the inherent properties of the denuders, i.e. the variation of efficiency depends on the coating quality; another may be that a small portion of Hg^0 is present in the Hg^{2+} source, which was formed continuously in the system [16]. It can be seen from Table 2 that the breakthroughs among different denuders were very close to each other during each set of experiments conducted at the same day, corresponding to lower standard deviations (1.1–10.8 ng m^{-3}), while they were quite different among different sets of experiments performed on different days, resulting in from 3 to 39 times higher standard deviation (38.6 ng m^{-3}) for the gross mean value. This seems to favour the second possibility.

In order to test if some Hg^0 exists in the $HgCl_2$ source, a bubbler containing 1 mol L^{-1} HCl solution was inserted between KCl denuder and gold traps (cf. Fig. 1). The gas phase Hg^{2+} should mainly be collected on the KCl denuder and the portion of Hg^{2+} which passed through the denuder should be trapped in the HCl solution. The Hg^0, however, if it exists, should pass through double traps of the KCl denuder and the HCl solution and finally be collected on the gold trap. The portion of Hg^0 dissolved in the HCl solution is negligible, due to its low solubility and the continuously gas purging through the system at a flow rate of 1 L min^{-1}. Therefore, what was collected on the gold trap in this sampling train should be Hg^0. Hg trapped on the gold trap was analyzed and the results are listed in Table 3. The Hg^0 in the Hg^{2+} sources varied from 30 to 100 ng m^{-3}, accounting for 5.3 to 18.9% of the source concentration, which seems to rise with increasing source temperature. An average value of 6.8% was obtained with source temperature between 20 and 21°C.

Taking this factor into consideration, the actual collection efficiency of the denuder for the absorption of Hg^{2+}

Table 2 Collection efficiencies of the KCl denuder for inorganic $HgCl_2$ (g)

Experiment data	Source temp. (°C)	Hg source conc. A (ng m^{-3})	Hg found after denuder B (ng m^{-3})	App. col. eff.[a] (%)	Act. col. eff.[b] (%)
950404	21.0	597.8 ± 23.4 (5)	34.5 ± 9.3 (7)	94.2	100
950405	20.0	563.3 ± 48.6 (6)	35.9 ± 9.1 (5)	93.6	100
950412	20.0	560.3 ± 43.8 (10)	46.2 ± 8.2 (12)	91.7	98.6
950420	20.5	535.5 ± 27.6 (10)	51.6 ± 5.6 (8)	90.4	97.2
950421	21.0	536.7 ± 40.2 (8)	47.2 ± 2.6 (3)	91.2	98.0
950512	21.5	508.9 ± 19.0 (8)	–	–	–
950621	21.0	513.9 ± 25.4 (5)	64.8 ± 10.4 (6)	87.4	95.2
950630	22.5	528.7 ± 39.3 (9)	34.2 ± 7.5 (6)	93.5	100
950711	23.0	567.6 ± 23.2 (6)	109.2 ± 10.8 (8)	80.8	99.5
950802	24.5	532.5 ± 6.2 (4)	138.3 ± 1.1 (10)	74.0	93.5
Average		544.4 ± 40.8 (71)	67.9 ± 38.6 (66)	87.5	98.0

[a] Apparent collection efficiency (%) = 1-(B/A) × 100
[b] Actual collection efficiency, see text below for explanation

Table 3 Hg^0 found from the $HgCl_2$ source

Experiment data	Source temp. °C	Hg source conc. (ng m^{-3})	Hg on gold trap (ng m^{-3})	HCl blank[a] (ng m^{-3})	Hg^0/Hg^{2+} (%)[b]
950412	20.0	560.3 ± 43.8 (10)	34.1 ± 3.5 (3)	4.1 ± 2.1 (3)	5.35
950418	21.0	544.4	59.5 ± 1.4 (5)	7.2 ± 1.4 (3)	9.6
950420	20.5	535.5 ± 27.6 (10)	33.5 ± 2.3 (5)	4.1 ± 2.1 (3)	5.5
950802	24.5	532.5 ± 6.2 (4)	110.9 ± 10.8 (5)	7.1 ± 1.4 (3)	19.5

[a] Hg^0 collected in gas phase by gold trap when Hg free gas was driven through the HCl solution bubbler
[b] The HCl blank was subtracted

Table 4 Collection efficiencies of the KCl denuder for organic Hg^{2+}

Experiment data	Source temp. °C	Hg source conc. (ng m^{-3})	Hg found after denuder (ng m^{-3})	Act. eff. (%)
950907	20.0	795.6 ± 52.3 (8)	45.8 ± 7.7 (6)	94.2
950911	20.0	286.9 ± 37.0 (10)	11.8 ± 5.3 (9)	95.9
950922	20.0	343.0 ± 27.6 (5)	22.9 ± 5.6 (5)	93.3

Table 5 Recovery of Hg^{2+} from the KCl denuders by HCl extraction and CVAFS analysis

Exp. data	Source temp. °C	Hg source concen. (ng m^{-3})	Hg found after denuder (ng m^{-3})	Hg retained in denuder[a] (pg)	Hg recovered from denuder (pg)	Recovery efficiency (%)[b]
950630	22.5	528.7 ± 39.3 (9)	34.2 ± 7.5 (6)	495.0 (6)	500.0 ± 68.2 (5)	101.2 ± 13.8 (5)
950711	23.0	567.6 ± 23.2 (6)	109.2 ± 10.8 (8)	458.0 (8)	444.0 ± 40.0 (9)	97.0 ± 8.6 (9)
950802	24.5	532.5 ± 6.2 (4)	138.3 ± 1.4 (10)	394.0 (10)	380.0 ± 65.6 (9)	96.4 ± 16.7 (9)

[a] Hg retained in denuder = (Hg source) - (Hg found after denuder)

[b] Recovery efficiency (%) = (Hg recovered from denuder) ÷ (Hg retained in denuder) × 100

was corrected, and is listed in the last column of Table 2. If the same value, 6.8%, could be applied to all the experiments performed with source temperature between 20 and 21°C and 18.9% to those experiments conducted at temperature higher than 23°C, the actual collection efficiency of the KCl denuder for Hg^{2+} can be estimated to be 95–100%.

3.2.2 *Efficiency for organic Hg^{2+}, CH_3HgCl*

The same method was used to test the efficiency of the denuder for the collection of organic Hg^{2+} species using CH_3HgCl solution as a source, since this compound has been reported to exist in the atmosphere. The average efficiency was around 94%, which is a little lower than for inorganic Hg^{2+} species. Once again, Hg^0 forms in the CH_3HgCl solution. The contribution of Hg^0 has been subtracted from that of the Hg source; therefore the last column of Table 4 gives the actual collection efficiency of the KCl denuder for organic Hg^{2+}.

The mechanism of retention of Hg^{2+} on the denuder has not been studied in this investigation. It is probably due to the interaction of divalent Hg molecules with chloride ions on the surface, an effect no doubt related to the rather high affinity of divalent Hg for halide ions [18].

3.3 Extraction and analysis of Hg^{2+} collected on the KCl denuder

Effective recovery and analysis of the collected Hg from the denuder is an important step for its practical use. In addition, direct measurements of Hg trapped in the denuder would further confirm its collection efficiency. A mass balance approach was adopted for this investigation and the results obtained are listed in Table 5. The recoveries of Hg from the denuder by the HCl extraction method were calculated to be 98.2 ± 13.0% (n = 23), which implies that the KCl denuder can be used for sampling and determining Hg^{2+} species in the air with good accuracy.

At the beginning of this study, high method blanks were noticed, about 70–80 pg per denuder. These mainly result from the HCl extraction solutions which contain less than 1 ppb Hg according to the manufacture. Following the method of Lou [19] who purified HCl of pro analysis grade with $SnCl_2$ and H_2O_2 addition and aeration; the 1mol L^{-1} HCl contains less than 1 ppt Hg after treatment. The method blank varies between 20–40 pg and as low as 15 pg can be obtained if care is taken to avoid every possible contamination. The absolute detection limit based on 3σ of the method blank has been determined to be less than 10 pg (47.27 ± 2.23 pg, n = 18), when dual analysis of 9 pieces of the denuder blank was performed.

3.4 Capacity of the KCl denuder for the absorption of Hg^{2+}

The capacity of the KCl denuder for the absorption of Hg^{2+} is another interesting parameter concerning its practical use. A newly made KCl-denuder was connected to the Hg^{2+} source and gold traps were used to collect Hg at flow rate of 1 L min^{-1} after the denuder in a time interval of 20 min continuously. The results are illustrated in Fig. 3, which shows that the efficiency decreases with the total Hg load. If efficiencies of 95% or higher are required, the

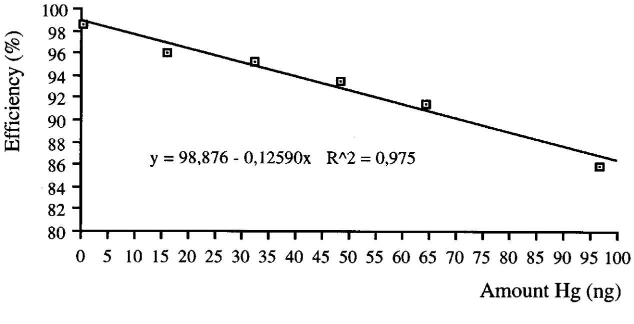

Fig. 3 Collection capacity of the KCl denuder for Hg^{2+} species

Table 6 Concentration (ng m^{-3}) of Hg^{2+} in the air measured at different sampling sites

Date	Hg$_{(TGM)}$	Hg$^{2+\ a}$	Hg^{2+}/Hg$_{(TGM)}$ (%)
Brottkärr, outside Göteborg			
950812	1.89	0.11	5.8
950815	1.96	0.08	4.0
Chalmers, Göteborg			
950830	2.43	0.14	5.8
950903	1.94	0.11	5.7
950902	1.61	0.15	9.3
Mace Head, Ireland			
950911	2.50	0.093	3.7
950912	2.43	0.078	3.2
950913	2.43	0.041	1.7
950915	2.50	0.090	3.6
St. Jörgen, Göteborg, only Hg^{2+} were measured			
960613		0.096 ± 0.008 ($n = 4$)[b]	
960614		0.021 ± 0.004 ($n = 4$)[b]	
960615		0.019 ± 0.004 ($n = 4$)[c]	

[a] Hg collected by KCl denuder
[b] inside the simulator building
[c] outside the building

maximum Hg load on one denuder should be less than 30 ng which is more than enough for sampling Hg^{2+} in the atmosphere.

3.5 Application of the KCl denuder to sampling and analysis of gas phase Hg^{2+} species in the atmosphere

Sampling duration was about 24 h at an air flow rate of 1 L min^{-1}, which was controlled by a mass flow regulator (cf. Fig. 2). Part of the results are summarized in Table 6. At the two sampling sites of Brottkärr and Chalmers around the city of Göteborg, the concentrations of TGM were in the range of 1.6–2.4 ng m^{-3}. The concentrations of Hg^{2+} varied between 0.08 and 0.15 ng m^{-3}, accounting for about 2–9% of the TGM, respectively. At the sampling site in Ireland, the concentration of TGM was higher than that found in Sweden, while the concentration of Hg^{2+} was apparently lower, only accounting for 2–4% of the TGM. These values agree well with those reported by Stratton and Lindberg [5] (2–8%). At the sampling site of St. Jörgen, no TGM was measured, the purpose here was to see the reproducibility of the method. Two parallel sampling lines were run with dual analysis and the variations were around 10–20%.

4 Conclusions

The KCl denuder can quantitatively collect Hg^{2+} from the air while retaining no elemental Hg. The Hg species trapped on the denuder surface can be eluted by 1 mol L^{-1} HCl solution with recovery efficiencies larger than 98%, which makes it possible to apply the denuder for sampling and analysis of Hg^{2+} in the air. Hg^{2+} concentrations measured at different chosen sites vary from 0.04 to 0.15 ng m^{-3}, corresponding to about 2–9% of the total gaseous mercury in the atmosphere. The absolute detection limit is estimated to be less than 10 pg, based on 3σ of the method blanks.

The KCl denuder method reported here has some advantages:

a). The whole sampling and analysis procedures are relatively easy.

b). The possibility of sampling artefacts of Hg^{2+} formation through oxidation of Hg^0 or dissolution of co-sampled particulate Hg is kept low due to the working principle of the denuder of gaseous-molecule-only, compared to solution absorption and filter-based sampling methods.

c). In combination with a GC-column separation procedure, the KCl denuder method may be useful for sampling and analysis of other forms of Hg^{2+} species in the air, for example CH$_3$HgCl, with longer sampling times and an adequate solution for the elution of Hg from the denuder surface.

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