SHORT COMMUNICATION

**Xinbin Feng · Julia Y. Lu · Yingjie Hao · Cathy Banic
William H. Schroeder**

Evaluation and applications of a gaseous mercuric chloride source

Abstract In this study, a diffusion-type device for generating gaseous mercuric chloride ($HgCl_2$) was systematically evaluated and applied to validate the annular denuder method for sampling gaseous $HgCl_2$ species in a synthetic gas stream. The results show that it takes at least 48 h for the system to reach a steady-state condition after the diffusion cell reaches the temperature set-point and the carrier gas is activated. The primary Hg species from the source was proven to be $HgCl_2$. In the temperature range from –5.00 to 11.80 °C, the Hg emission rates from the source vary from 1.8 to 14.2 pg min^{-1}. It is shown that, under the experimental conditions examined, KCl-coated annular quartz denuders designed for ambient reactive gaseous mercury (RGM) collection could quantitatively collect $HgCl_2$. It is also demonstrated that the impactors used to remove coarse airborne particulate matter could lead to a loss of up to one third of the $HgCl_2$ in the gas stream.

Keywords Gaseous mercuric chloride · Diffusion source · Annular denuder · Mercury speciation · RGM · Atmospheric mercury measurements

Introduction

On the basis of chemical and physical properties, three inorganic mercury species in ambient air can so far be distinguished: gaseous elemental mercury (Hg^0), reactive gaseous mercury (RGM), which mainly consists of gaseous oxidized inorganic mercury (GOIM) species, and particulate Hg (P-Hg) [1]. In the atmosphere under typical envi-

X. Feng · J. Y. Lu (✉) · Y. Hao
Department of Chemistry and Biology, Ryerson University,
350 Victoria Street, Toronto, Ontario M5B 2K3, Canada
e-mail: julialu@ryerson.ca

C. Banic · W. H. Schroeder
Meteorological Service of Canada, Environment Canada,
4905 Dufferin Street, Toronto, Ontario M3H 5T4, Canada

ronmental conditions, Hg^0 is the predominant form with only a few percent of the total present as RGM and/or P-Hg [2]. Nevertheless, air could be enriched with RGM and P-Hg in the vicinity of point sources [3] and in the Arctic troposphere after polar sunrise [4, 5].

The chemical speciation of atmospheric RGM is currently unknown, though it is usually assumed to be $HgCl_2(g)$, $Hg(OH)_2$, or other mercuric halides [6], which have a higher chemical reactivity and water solubility than Hg^0. A recent study [7] also suggested that $Hg(NO_3)_2 \cdot H_2O$ could be a candidate species of RGM, since it has been positively identified as the primary Hg(II) species in certain simulated flue gases. Because of the higher inherent reactivity and water solubility, RGM can be scavenged by both dry and wet deposition more efficiently than Hg^0 and P-Hg, and therefore RGM may, in some cases, dominate the total Hg depositional flux in the ambient air. Techniques for gaseous elemental mercury (GEM) sampling and measurement are now quite mature [2]; methods for RGM sampling, however, are still under development [8]. Currently there are three types of collection methods used for RGM sampling: a multi-stage filter pack method [9], a refluxing mist chamber method [10], and a KCl-coated annular or tubular denuder method [8, 11]. These methods were recently inter-compared on two occasions and a discrepancy among the methods was observed [2, 12]. However, considering the uncertainty associated with these methods, the inter-comparison results suggest that these methods did produce comparable results, though neither of the methods can be considered as a standard method [2, 12]. So far, the annular denuder method has been more widely employed because of the simplicity of its analytical procedure and of the high time-resolution measurement results achieved. Based on the annular denuder technique, an automated RGM sampling unit (Tekran 1130) with a Tekran 2537A mercury vapor detector is commercialized. Definitive and incisive laboratory tests, however, are still needed to evaluate and validate current RGM sampling methods apart from field inter-comparison. Stable and reliable RGM sources are essential to objectively evaluate and validate the current RGM sampling methods.

Since it is generally assumed to be the primary RGM species present in ambient air, only $HgCl_2$ has so far been used in constructing RGM sources. Three types of $HgCl_2$ source have been utilized: permeation source [13], diffusion source [14], and hydrocarbon solution source [15]. The permeation source operated at 50 °C, and solid $HgCl_2$ in the permeation cell (Teflon) was purged with an inert gas, and a portion of this sample stream was mixed with laboratory air to provide working concentrations of $HgCl_2$ in the range of approximately 500–3,000 pg Hg m^{-3}. Since high temperature is used for the permeation cell, all tubing and connections were wrapped with heating tape to minimize deposition of $HgCl_2$ to the walls. Transformation of $HgCl_2$ to other mercury forms (e.g., Hg^0), however, may occur during the permeation process. Although diffusion-type sources have been used in flue gas studies [14] and in ambient air studies [16], these sources, to the best of our knowledge, have not been systematically evaluated.

Materials and methods

Gaseous $HgCl_2$ source setup, evaluation, and validation

A diffusion-type device for generating gaseous $HgCl_2$ was described by Wang et al. [14] but the operational conditions in this study were modified. The temperature of the device was controlled in the range of –5.00 to 11.80 °C using a circulating liquid bath. Because the source temperature is set at values below the room temperature ($\approx$20 °C), it is not necessary to wrap heating tapes to heat all tubing and connections to prevent and minimize $HgCl_2$ deposition to the walls. The flow rate of the carrier gas (N_2) was controlled at 500 mL min^{-1} using a mass flow controller. To determine the time required to reach an equilibrium condition, the temperature of the $HgCl_2$ source was set and as soon as the source was flushed with dry N_2 immediately after reaching the temperature set-point, the mercury emitted from the source was monitored continuously by collecting the mercury onto a gold trap for 10 to 15 min. The mercury collected on the gold trap was measured by double-stage amalgamation coupled with atomic fluorescence spectrometry (AFS) detection. The mercury emission rates were then calculated.

To verify if there is any Hg^0 emitted from the $HgCl_2$ source, an impinger containing a 0.06 M HCl solution was connected to the $HgCl_2$ source. The impinger was wrapped with aluminum foil to prevent light from penetrating, since Hg^{2+} in aqueous solution could be photo-reduced to Hg^0. Mercury concentrations before and after the impinger were determined by collecting Hg onto gold traps and analyzing by dual stage amalgamation coupled with AFS detection. A soda lime trap is connected between the impinger and the gold trap to remove any microdroplets generated from the impinger. If there is any Hg^0 emitted from the source, it will pass through the impinger and will be collected on the gold trap connected after the impinger, while $HgCl_2$ emitted from the source will be trapped in the solution.

Evaluation of annular denuders for sampling gaseous $HgCl_2$

Information regarding preparation of KCl-coated annular denuders was offered by Landis et al. [8]. The annular denuders used in this study were manufactured by URG Corporation (USA). The denuder is designed to have a sampling flow rate of 10 L min^{-1} at ambient air conditions and an impactor is attached to the inlet of the denuder to remove particles greater than 2.5 μm [8], because these particles will deposit on the KCl coating surface and then deteriorate collection efficiency of RGM by the denuders. Particles smaller than 2.5 μm flow through the denuder because of the laminar conditions maintained under the proper flow-rate conditions.

A 9.5 L min^{-1} N_2 dilution gas from a pressurized cylinder was added to a mixing chamber to obtain 10 L min^{-1} flow rate that is desired for denuder sampling.

To test the collection efficiency, two denuders were connected in series, and then exposed to the $HgCl_2$ source for 10 to 15 min at 10 L min^{-1} flow rate. To evaluate the effect of the impactors (URG Corporation, USA) on collection of $HgCl_2$ onto denuders, two groups of experiments were conducted. In one group of experiments, an impactor was connected at the inlet of the denuder. Three impactors tested can be categorized into two types: one with a glass impaction surface (impactor C), and two with stainless steel impaction surfaces (impactors X and Y). Meanwhile, denuders without impactors were used for comparison. Denuders with and without an impactor were connected to the $HgCl_2$ source alternately at 10 L min^{-1} for 10 min. The $HgCl_2$ collected on the denuders was thermally decomposed, at 525 °C in a tube furnace (Lindberg Blue, USA), into an Hg-free air stream and subsequently analyzed as Hg^0 using a Tekran 2537A mercury vapor analyzer.

Results and discussion

$HgCl_2$ source evaluation and validation

Emission rates

As can be seen from Fig. 1, at the source temperature of 5.00 °C a stable Hg emission rate was obtained after the system was flushed with N_2 for two days. The results obtained under other temperature conditions show that an equilibrium condition can be reached when the system was run for about 48 h. After reaching equilibrium conditions, the mercury sources generate emission rates of 1.8–14.2 pg min^{-1} with standard deviations ranging from 0.3 to 2.0 pg min^{-1} in the temperature range of –5.00 to 11.80 °C, as can be seen from Table 1.

Identification of the mercury species generated from the $HgCl_2$ source

The results in Table 2 show that almost all of mercury emitted from the source was trapped in the impinger, sug-
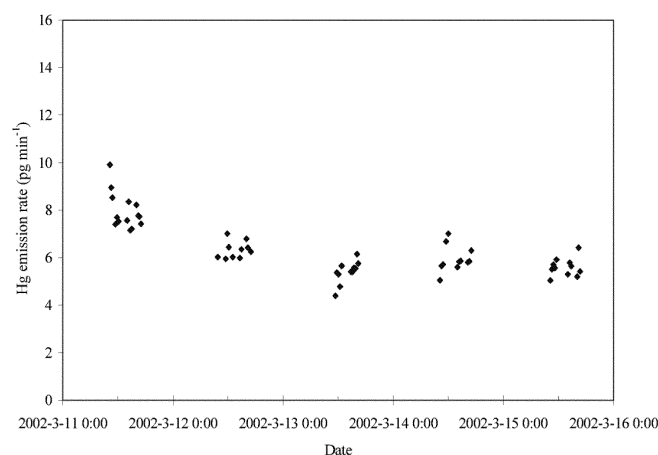

Fig. 1 The temporal trend of mercury emission rate from the $HgCl_2$ source at 5.00 °C (the temperature was set to 5.00 °C and the carrier gas was turned on in the morning of March 11, 2002)

Table 1 Mercury emission rates from the diffusion source at equilibrium conditions

No	Experiment date	Temperature of the source (°C)	HgCl2 emission rate (pg min^{-1}) Average±SD	n
1	Jan 18–29, 2002	11.80	14.2±2.0[a]	28
2	March 05–08, 2002	11.80	13.6±1.4	17
3	March 13–15, 2002	5.00	5.6±0.5	33
4	March 19–22, 2002	5.00	5.3±0.6	28
5	March 27–28, 2002	11.50	12.5±2.0	27
6	April 02–04, 2002	11.50	11.8 ±1.4	44
7	April 22–25, 2002	0.00	2.4±0.4	39
8	April 15–17, 2002	–5.00	1.8±0.3	51

[a]Emission rate of the source was determined using KCl-coated denuders

Table 2 Comparison between $HgCl_2$ emission rates from the source, before and after impinger containing a 0.06 M HCl solution (temperature of the source is 11.50 °C; the carrier gas flow rate is 500 mL min^{-1})

Sample number	1	2	3	4	5	Average	SD
Emission rate from the source before the impinger (pg min^{-1})	12.6	10.8	13.9	11.4	12.4	12.2	1.20
Emission rate from the source after the impinger (pg min^{-1})	0.23	0.13	0.2	0.61	0.63	0.36	0.24
Percentage breakthrough from the impinger (%)	1.8	1.2	1.4	5.3	5.1	2.9	1.84

gesting that $HgCl_2$ is the major mercury species emitted from the source. Theoretically, the amount of mercury penetrating the impinger represents Hg^0, as $HgCl_2$ will be trapped by the solution in the impinger and the soda lime trap will certainly capture any microdroplets which may contain $HgCl_2$. Although previous studies [16] showed that, on average, about 6.8% (from 5.3–18.9%) of the mercury emitted from their $HgCl_2$ sources was in the form of Hg^0, and the percentage seemed to rise with increase of the source temperature, since the amounts of mercury measured after the impinger in this study are small (an average of 2.9%) and are within the experimental uncertainty

at 11.5 °C from our experiment, it is reasonable to believe that under our experimental conditions (from –5.00 to 11.80 °C) the predominant, if not the only, mercury species from the diffusion source is $HgCl_2$.

$HgCl_2$ source applications

Efficiency of KCl-coated denuders for collecting gaseous $HgCl_2$

The results from the $HgCl_2$ collecting efficiency tests are listed in Table 3. Generally almost all $HgCl_2$ emitted from the source was collected on the first denuder. It can be clearly seen that all the denuders except D3 had a collection efficiency of more that 95%. After being recoated with KCl, a good collecting efficiency (95.6%) was also obtained for D3 (+D2). The average collection efficiency for all the denuders employed in the test was computed to be 98.0±1.8%, which agrees with the collecting efficiency test results performed on tubular denuders [16]. Our results highlight that annular denuders with appropriate KCl coating can quantitatively collect $HgCl_2$ species in a dry nitrogen gas stream at a sampling flow rate of 10 L min^{-1}.

Effect of impactor on $HgCl_2$ collection

The percentage losses of $HgCl_2$ with an in-line impactor were computed and listed in Table 4. There was no significant difference among the impactors with two different types of impaction surfaces. It is obvious that the denuders downstream of an impactor collected less mercury than the ones without an impactor, suggesting that the impactor either itself sorbs or leads to the loss of gaseous $HgCl_2$. Generally, with an impactor, around one third of $HgCl_2$ emitted from the source was lost under our experimental conditions. The concentration of $HgCl_2$ in the test gas stream was around 1,400 pg m^{-3}, which is much higher than those under normal ambient air concentrations; therefore, it is not advisable to simply apply our results to ambient air sampling conditions. During mercury depletion events (MDEs) in the Arctic after polar sunrise, however, RGM concentrations can reach levels approaching 1,000 pg m^{-3} [5]. The effect from the impactor can be significant and should be considered under these conditions.

Table 3 The efficiency of KCl-coated denuders for collecting gaseous $HgCl_2$

Sample No	Sampling Date	Denuder No[a]	Hg in the first denuder (pg)	Hg in second denuder (pg)	Collecting efficiency (%)
1	2002–1-21	D11+D2	172.8	0.0	100
2	2002–1-21	D13+D5	106.5	1.1	99
3	2002–1-21	D3+D11	100.3	21.8	82.1
4	2002–1-22	D5+D13	119.7	3.3	97.3
5	2002–1-22	D2+D3	127.4	4.4	96.6
6	2002–1-22	D7+D11	128.6	0.4	99.7
7	2002–1-22	D3+D2	116.7	5.4	95.6
Average[b]					98.0±1.8

[a]First denuder No + second denuder No

[b]Without sample 3, as after being recoated D3 gives a high collecting efficiency as shown in sample 7

Table 4 Comparison of HgCl$_2$ collected on the denuders with and without an impactor (sampling time was 10 min and the sampling flow rate was 10 L min^{-1})

	With an impactor[a]				Without impactor
	X	Y	C	Overall	
Average (pg)[a]	94.7±4.3	100.0±8.7	101.5±12.9	99.3±9.7	147.1±11.1
Number of test	3	3	5	11	12
HgCl$_2$ loss (%)	35.6	32.0	31.0	32.5	

[a]Impactor X and Y have a stainless steel impaction surface, and impactor C has a glass impaction surface
[b]Average±SD (standard deviation)

Conclusions

The diffusion-type HgCl$_2$ source tested in this study has the following advantages: (1) stability; (2) capability of generating gaseous HgCl$_2$ at different emission rates; and (3) capability of maintaining the source temperature lower than that of the sampling device, so that condensation/loss of gaseous HgCl$_2$ to the tubing wall can be minimized. Our HgCl$_2$ device is being modified toward improving its heat conductivity to reduce the equilibration time and its ruggedness to suit field applications. Further experiments are needed to test, under ambient air conditions, the efficiency and the potential negative effect of impactors on HgCl$_2$ collection by KCl-coated denuders.

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