CONTINUOUS DETERMINATION OF MERCURY IN AIR BY GOLD AMALGAMATION AND FLAMELESS ATOMIC ABSORPTION

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We have developed an aerial mercury monitoring system whose operating principle is based upon gold amalgamation and flameless atomic absorption. A stable measurement of micro-trace mercury in the air becomes possible by preventing dirt from accumulating in the measuring system and minimizing interference from other gases occupying the same area. As a mercury collecting agent, a Chromosorb P® coated with gold proved to be durable against repeated long-time operation. Absorption of organic gases on the Chromosorb P® can be avoided if the mercury collecting agent is kept heated to 150°C. When measurements were intermittently repeated up to 10 times, the coefficient variation was 3%.

1. Introduction

Fossil fuel, which constitutes the major part of energy consumed today, contains mercury: 0.005 ppm or so in heavy oil, and 0.05 ppm or so in coal. 90% or greater amount of such materials are discharged into atmosphere according to Fujii [1]. It is important to establish a method to continuously measure the concentration of mercury in air.

To collect mercury in air, a wet method using potassium permanganate solution mixed with sulfuric acid has been used. However, mercury contained in the reagent can become the source of mercury when trace mercury measurement takes place [2]. Therefore, recently dry methods have been studied. Some of them employ gold wool, silver wool, or gold-coated absorbent to collect as amalgam, or the activated carbon absorption methods [3].

Most of the measuring systems use flameless atomic absorption; however, Zeeman atomic absorption [4], vacuum ultraviolet atomic absorption [5], detection by quartz piezoelectric sensor [6], and detection by the gold film resistance method [7,8] are also employed.

Most systems have separate units for sample collection and measurement. For ultratrace mercury determination sampled from the atmosphere, increase in the blank test value while the sampling tube is moved from one place to another is a problem. As the atmosphere always changes due to temperature, pressure, and the direction of the wind according to the weather and time of sample collection, the collected mercury volume can show a difference of an order of magnitude within the same day [9].

We have developed an aerial mercury continuous monitoring apparatus [11] which combines a mercury collector [10] using a Chromosorb P® (Gasukuro Kogyo Inc.) specially coated with gold and a measuring unit using a nondispersal type flameless atomic absorption.

We studied the performance of the system especially from interference from organic gases, the influence of water, and the application limit of the mercury-collecting agent.

2. Experimental Apparatus and Method

2.1 General Description of the Apparatus and Method

The apparatus is constructed as shown in Fig. 1. An incorporated computer controls the system to automatically repeat the cyclic operation composed of 1) mercury collection, 2) gas purging, 3)
measurement, and 4) cooling down.

Sample gas is introduced into the mercury collector via an air pump at a constant flow rate of 0.51/min. The sample gas passes a gas washing bottle and a dehumidifying bottle in the scrubber. These bottles are force-cooled by an electronic cooler. Here, the gas is washed in the washing bottle filled with water and dehumidified.

Washing the sample gas in water is very effective to protect the inside of measuring system from contamination that may reduce the sensitivity [12].

When the sample gas passes through the mercury-collecting agent, the mercury is trapped as gold amalgam, and other gases are exhausted outside the system without passing through the absorption cell. When sample collection is completed, valve V₁ is automatically switched to cut off the sample gas. The sample gas remaining in the system is purged by means of the washed and dehumidified air. When this 10-second gas purging is completed, valve V₂ is switched to flow the gas to the absorption cell. After approx. 10 seconds, the mercury-collecting agent is heated so that the atomic mercury becomes free from the gold amalgam and is swiftly led to the absorption cell for measurement by the flameless atomic absorption.

The measured mercury is shown on the digital meter in the unit of 0.001 ng. The value can be recorded by a printer. The measuring range is from 0.001 to 1000 ng. When one cycle of measurement is completed the mercury collection agent is cooled by a fan. When the temperature of the mercury-collecting agent is cooled enough to collect the sample again, valves V₁ and V₂ are reset to start the next measurement.

2.2 Reagents

Mercury Standard Solution: 135.4 mg of guaranteed mercury(II) chloride (nacalai Tesque Corp.) was dissolved by a 0.001% solution of L-cysteine and 0.2% nitric acid to make 1-liter of solution to adjust a 100 ppm mercury standard solution. This solution remains effective for six months when stored in a refrigerator. To obtain a mercury standard solution of a specific concentration, a 100 ppm mercury standard solution was diluted with a 0.001% solution of L-cysteine and 0.2% nitric acid.

Mercury Standard Gas: Several grams of mercury were put into a 1-liter Teflon pot whose outside surface is covered with thermal insulation materials. A thermometer was inserted into the pot. Saturated mercury vapor was used as mercury standard gas.

Gas Washing Solution: Distilled water.

Mercury Collecting Agent: A Chromosorb P® (AW) of 30-60 mesh was sieved to obtain 3 g of 30-40 mesh grains. This then was immersed in a solution made by dissolving 1 g of chloroauric(III) acid tetra hydrate (Nacalai Tesque Corp.), into several milliliters of water. After the water was evaporated, the Chromosorb P® was heated in a tubular furnace for 30 minutes at about 800°C while a stream of air was continuously flowed through the furnace.

2.3 Calibration

When strict calibration was required, vaporized mercury produced by reducing vaporization was introduced from the inlet in Fig. 1. However, as a practical method, a fixed volume of saturated mercury vapor was injected into the inlet with an airtight syringe.

The volume of saturated mercury vapor existing in the gaseous phase can be determined by the equation of mercury's saturated vapor pressure and ideal gas status. The mercury content, wg contained in a volume of 1 ml, can be obtained by the following equation:

\[ W = 3.215 \times 10^{-5} P / T \]

where P is pressure in mmHg, and T is temperature in °K. The calibration using this method agreed with that obtained by the reducing vaporization. Therefore, for calibration of the measuring instruments for outdoor use, the above-mentioned saturated mercury vaporization will be convenient. However, as this calibration system shows a fast response to rising temperatures, but a slow
response to falling temperatures, utmost care should be used to thermally isolate the pot.

3. Results of Experiment and Discussion

3.1 Linearity and Reproducibility Obtained Using, Standard samples

We investigated the linearity in two measuring ranges of 1 ng full scale and 100 ng full scale, as shown in Fig. 2. For the former, saturated mercury vapor is sampled with a 50 µl syringe, and injected into the inlet. For the latter, a reducing vaporization chamber is provided at the inlet to perform the reducing vaporization mercury equivalent to 30, 60, and 90 ng, and draw a calibration curve.

The values in Fig. 2 are the reading (Hg, in ng) of the digital display on the apparatus. As for the reproducibility, 20 µl of mercury vapor (equivalent to 0.188 ng mercury) saturated at 16°C was injected in 10 repetitions, and the relative coefficient variation resulted in 3%.

3.2 Interference from Organic Gases

Most organic gases show absorption outside the ultraviolet region, and absorb mercury's resonant wavelength of 253.7 nm. This meant that it is necessary to separate organic gases and mercury gas when mercury-in-air is determined in an atmosphere both mercury and organic gases are present. Although a majority of organic gases pass through the mercury collecting agent, a certain percent of organic gases can be physically absorbed on the mercury collector, because our system uses the Chromosorb P® especially coated with gold as the mercury collector. When the mercury collector is heated, organic gases are led to the absorption cell together with mercury, causing double peaks that become a problem when attempting to determine trace mercury. 0.5 ml of the saturated vapor of a variety of organic solvents shown in Table 1 was the sampled in a syringe, and 0.1 ml of saturated mercury vapor was also taken into a syringe. Then, both of them were injected into the inlet of the apparatus. The resulting data showed double peaks throughout. The influences in Table 1 were obtained by converting the organic gas peaks to the amount of mercury. Some organic gases showed higher peak values than those of the mercury. To obtain a mercury peak only, we heated the mercury collector to about 150°C. It was found that organic gases dislodge from the mercury collector at relatively low temperatures. When the mercury collector is heated to the said temperature, organic gases pass through the mercury collector. In Fig. 3 the first one of the double peaks (A) is of hexane and the second one is of mercury. As the temperature curve shows, when the mercury collector was pre-

![Fig. 2](image1)  
**Fig. 2** Calibration of the mercury analyzer.  
(A) Calibration by injection of mercury vapor saturated at 16°C, Blank: 20 µl, 40 µl, 60 µl; (B) Calibration by reductive acretion of HgCl	extsubscript{2} solution, Blank: 30 ng, 60 ng, 90 ng

![Fig. 3](image2)  
**Fig. 3** Double peak caused by organic vapor and its elimination.  
Sample: A mixture of hexane vapor (0.5 ml) and mercury vapor (0.1 ml, 1.89 ng; saturated at 24.4°C); A: Double peak (ghost peak) when mercury collector is not heated at the sampling, B: Single peak when mercury collector is heated at the sampling, C: Temperature control of mercury collector (formation of double peak (A)), D: Temperature control of mercury collector (formation of single peak (B)).
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3.3 The Effect of Washing Gas

In continuous determination of the mercury-in-air, it was observed that the sensitivity is gradually reduced if the introduced sample gas is not washed. However, this problem was solved by washing the gas to be measured. But, as there is a paper suggesting that mercury is soluble in water, we carried out the following experiments. A Teflon sample tube installed outdoors was connected to two measuring units via a Y-tube. Simultaneous sampling was preformed with the two units for 1 hour at a rate of 0.5 l/min, and resultant data from the units were compared. We calculated correlation linearity of the data by the method of least squares and determined that the slope was 1.0123, and correlation coefficient, r, 0.991 (Fig. 4(I)). We repeated the experiment, but this time removing the gas washing bottle from one of the units and calculated the data, determining that the slope was 1.0445, and correlation coefficient, r, 0.971; this showed almost no less of mercury due to gas washing.

3.4 Mercury Holding Capability of the Mercury Collecting Agent

80 mg of mercury collecting agent containing 11 mg of gold was packed in a quartz tube measuring 6 mm φ O.D. and 4 mm φ I.D. Two such tubes were connected in series, and the second tube was heated by a heater jacket. From the inlet of the first tube, mercury gas was injected at a rate of 0.5 l/min. The mercury holding capability of the agent can be determined by measuring the amount of mercury detected by the second tube. A variety of mercury gas had been prepared by heat vaporization on an appropriate amount of standard solutions (1, 10, and 100 ppm). As shown by line A in Fig. 5, if a large volume of mercury gas was applied to the collecting tube at one time, a leak of 1% or so was measured at the holding volume of 2.7 µg. However, the holding capacity could be extended to 5 µg without a leak when mercury gas was applied in a series of less volumes, e.g. 100 ng at a time. To measure a high mercury concentration when this measuring system is applied to stack gas monitoring, it is desirable to maintain a large mercury holding capacity for the mercury collector. We improved the mercury holding capability of the mercury collecting agent up to 10 µg by tripling the amount of gold coating per unit weight and increasing the amount of mercury collector agent to 100 mg (containing 32 mg of gold), as shown by line B in Fig. 5.

<table>
<thead>
<tr>
<th>Organic solvent</th>
<th>Concentration (%)</th>
<th>Influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>48.8</td>
<td>++</td>
</tr>
<tr>
<td>Ethanol</td>
<td>9.1</td>
<td>+</td>
</tr>
<tr>
<td>MIBK</td>
<td>30.0</td>
<td>+</td>
</tr>
<tr>
<td>Benzene</td>
<td>26.7</td>
<td>+</td>
</tr>
<tr>
<td>Pyridine</td>
<td>5.4</td>
<td>+++</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>7.7</td>
<td>+++</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>64.5</td>
<td>++</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>9.0</td>
<td>+++</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>29.6</td>
<td>+</td>
</tr>
<tr>
<td>Hexane</td>
<td>47.4</td>
<td>+</td>
</tr>
<tr>
<td>Isoamyle alcohol</td>
<td>1.1</td>
<td>+</td>
</tr>
</tbody>
</table>

Table 1 Influence of organic solvent vapor on the response of mercury collector.

*Organic solvent vapor-saturated air (5 ml, 20°C) was analyzed. The concentration was calculated by Antoine's formula. The ghost peak caused by organic solvent vapor was regarded as mercury. +: 0 ~ 0.1 ng, ++: 0.1 ~ 1.0 ng, + +: > 1.0 ng.

Fig. 4 Correlation of analyzed values obtained by two independent sets of mercury analyzer. I: Operated in normal mode; I: Gas scrubber of apparatus A was removed.
3.5 Degradation of Mercury Collector Agent

We built an experimental device to repeat heat/air-cool cycles of the mercury-collecting agent at approx. 8-minute intervals and performed an operation over 40 days (or approx. 7400 times). On the 7th and 10th days, and at 5-day intervals thereafter, we injected mercury gas into the measuring units to trace the recovery of the mercury. The data showed values of 98-105% against the initial values, and degradation of the mercury collector agent was not found. However, there is a report [12] stating that decreased mercury collection capability was observed when, instead of simple heat/cool cycles, 12 absorption/desorption cycles of a large amount of mercury were performed. Therefore, we additionally ran 20 absorption/desorption cycles with the mercury-collecting agent to collect the amount of 3 µg, which is close to its holdable limit. In the first and the last cycles in the series of runs, we connected a mercury collector tube in series, similar to that used in 3-4, to the outlet of the mercury collecting agent tube to measure a leak. The resultant data were 1.5% and 0.96%, respectively, and no decreased collection efficiency was observed.

3.6 Measurement of Mercury in Environmental Air

We installed a Teflon sampling tube outside the 4th-floor window of the Company's factory in Takatsuki, Osaka to measure the amount of mercury in the environmental air for several days. Measurements were run at a flow rate of 0.51/min at 60-minute intervals. As seen in Fig. 6, the values ranged from 3.77 to 17.87 ng/m^3 depending upon the time and date. Mean value was 5.86 ng/m^3 and coefficient variation was 2.34 ng/m^3.

Simultaneously we also collected data on sulfur dioxide, nitrogen dioxide, and meteorological data to study their contribution to the mercury volumes detected, and found a meaningful correlation with the data for sulfur dioxide and nitrogen dioxide. This correlation agreed with the works by Kobayashi et al. [14], and Matsumoto et al. [15] that suggest the amount of mercury in environmental air is influenced by the generating sources.

3.7 Example of printout

4. Conclusion

We developed a continuous mercury-in-air monitor that is based on the gold amalgamation and flameless atomic absorption principle. For stable and continuous measurement of trace mercury, it was necessary to satisfy the following conditions: 1) wash and dehumidify sample gas,
2) avoid absorption of the sample gas by organic gases, ensuring that sample gas is not introduced inside the measuring system, 3) use dehumidified clean air as a carrier gas for the absorption cell, 4) preheat the mercury collecting agent to 150°C, and 5) be able to detect amounts of mercury as low as 0.01 ng.

With our system it became possible to determine the variation of mercury-in-environmental air on an hourly basis as well as a daily basis, which had been impossible with a conventional batch mode system. Elimination of interference from organic gases in the mercury collecting agent made it possible to apply our system to the determination of trace mercury in gas from common smoke stacks.

References

Continuous determination of mercury in air by gold amalgamation and flameless atomic absorption. Koji Tanida, Munehiro Hoshino (Nippon Instruments Corporation, Osaka Factory, 14-8, Akaoji-cho, Takatsuki-shi, Osaka).

Aerial mercury was determined by using a newly constructed, flow-type mercury analyzer. The sample gas was led to a scrubber and washed with water. The gas stream, after dehydration, was then introduced to the mercury collector maintained at 150°C, where mercury collected on porous silicate particles (Chromosorb P) by gold amalgamation. The lower collecting temperature caused an adsorption of organic materials to the collector and gave rise to ghost peak in the subsequent mercury detection. The temperature of collector was then raised to 700°C, and the mercury released was determined by flameless atomic absorption method. The capacity of collector did not change after 7400 repeated uses. The retention of the collector was able to extend up to 10 µg by increasing the quantity of gold coated on the collector. The coefficient of variation in the determination of 0.19 ng mercury (20 µl of mercury vapor-saturated air, 16°C) was 3.0%. The concentration of mercury in the environmental air varied between (3.77 ~ 17.9) ng/m³.

Key word phrases
Continuous determination of mercury in air; gold amalgamation; flameless atomic absorption; interference of organic vapor in mercury determination.

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