DETERMINATION OF TRACE AMOUNTS OF MERCURY IN SOLID SAMPLES USING POROUS GOLD AS A COLLECTOR

BY COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY

| 著者 | 鹿児島大学大学院理学研究科 理学専攻 講師
| --- | --- |
| 雑誌名 | 鹿児島大学理学部紀要 ▽ 数学・物理学・化学
| 巻号 | 21
| 号数 | 11
| 別言語のタイトル | 捕集剤として多孔質金を用いた冷原子吸光光度法による固体試料中の微量水銀の定量
<p>| URL | <a href="http://hdl.handle.net/10232/6456">http://hdl.handle.net/10232/6456</a> |</p>
<table>
<thead>
<tr>
<th>著者</th>
<th>高尾 茂男, 木脇 隆寛, 野原 陽之男</th>
</tr>
</thead>
<tbody>
<tr>
<td>別言語のタイトル</td>
<td>捕集剤として多孔質金を用いた冷原子吸光光度法による固体試料中の微量水銀の定量</td>
</tr>
<tr>
<td>正誌名</td>
<td>鹿児島大学理学部紀要 • 数学・物理学・化学</td>
</tr>
<tr>
<td>5巻, 111-120頁</td>
<td></td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10232/00000498">http://hdl.handle.net/10232/00000498</a></td>
</tr>
</tbody>
</table>
DETERMINATION OF TRACE AMOUNTS OF MERCURY IN SOLID SAMPLES USING POROUS GOLD AS A COLLECTOR BY COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY

Hayao Sakamoto*, Takashi Tomiyasu* and Norinobu Yonehara*

(Received September 10, 1988)

Abstract

Analytical method of trace amounts of mercury in solid samples was carefully checked and examined. In the determination of trace amounts of mercury, care is needed to prevent the contamination from reagents and experimental environment. Reagents used were the thing that removed mercury by heating for more than 2 hours at ca. 700-800°C. Apparatus prevented a mercury pollution from experimental environment as semi-closed system. The separation of mercury from solid samples is carried out by heating at ca. 700°C to avoid any contamination of mercury from reagents. Then the mercury evolved is collected by trapping on the porous gold collector. The mercury was determined by cold vapor atomic absorption method by heating. Detection limit of mercury was 0.1 ng. The relative standard deviations in the determination of 5.0 ng mercury was 1.7%. The determination of mercury in some standard reference materials were performed and the satisfactory values of mercury were obtained.

Introduction

In solid samples such as rock, soil, sediment, fishes and shellfishes, their mercury contents are ppb or ppm level. Investigations concerning mercury has been paid attention for the toxicity. There have been many reports concerning the mercury. In this study, we are done fast and precisely determination of trace amounts of mercury in solid samples. Thus it is very difficult to get the precise and reliable results on them by direct measurement, and pre-concentration is therefore needed on the determination of mercury in such samples. In the determination of trace amounts of mercury, care is needed to prevent the contamination from reagents and experimental environment.

* Department of Chemistry, Faculty of Science, Kagoshima University, Kagoshima, 890, Japan.
Pre-treatment is necessary to determine the mercury in solid sample precisely. Wet method that decomposes the sample chemically with sulfuric acid-nitric acid\(^8\), nitric acid-potassium permanganate\(^9\), nitric acid-hydrogen peroxide\(^7\) since before, was used. Mercury evaporates easily by heating the sample physically. Drying method that utilized this behavior in recent years, is used widely\(^{10-11}\). When this method is used, from the occurrence to measurement of mercury vapor even can be carried out in semi-closed system and mercury pollution in operation can be small. It checked in detail about heating temperature, heating time and added reagents in this research, and applied determination of trace amounts of total mercury to solid samples.

**Experimental**

*Reagents and Apparatus*

All reagents were analytical grade of marketing and were prepared in mercury-free water.

- Mercury (II) oxide (Nakarai Chemicals) was used.
- Mercury (II) sulfide (Nakarai Chemicals) was used.
- Methyl mercury (II) chloride (Tokyo Kasei) was used.
- Ethyl mercury (II) chloride (Tokyo Kasei) was used.
- Silicon(IV) oxide (Nakarai Chemicals) was used.
- Activated alumina (Nishio kougyou) 30/60 mesh was used.
- Calcium hydroxide (Nakarai Chemicals) was used.
- Sodium carbonate (Nakarai Chemicals) was used.

(Heating for 2 hours in an electric furnace at ca. 800°C)

(Heating for 2 hours in an electric furnace at ca. 800°C)

(Heating for 2 hours in an electric furnace at ca. 800°C)

(Heating for 2 hours in an electric furnace at ca. 700°C)

Atomic absorption spectrometer equipment: the apparatus used included a Rigaku Mercury SP (this apparatus was connected to an Ohkura recorder). Schematic diagram of apparatus for determination of mercury is shown to Fig. 1.
Determination of trace amounts of mercury in solid samples using porous gold as a collector by cold vapor atomic absorption spectrometry

Fig. 1 Schematic diagram of apparatus for the determination of mercury in solid sample by cold vapor atomic absorption spectrometry.

Results and Discussion

Temperature for Evaporation of Mercury.

An existing form of mercury in solid sample is complicated. It is small that the chemical form is known. Little information is available about the temperature necessary for the liberation of mercury from solid samples. Representative inorganic and organic mercury compounds were heated in electric furnace. Effect of temperature on liberation of mercury vapor from the compounds was checked. The mercury vapor that evolved by heating trapped to sulfuric acid-potassium permanganate solution or porous gold collector. It checked about evaporation
temperature of various mercury compounds by heating. The result is shown in Fig. 2. A mercury compound that is difficult to dissolve to water dilutes with

calcium hydrate or silicon oxide powder that removed mercury and is used.

According to Fig. 2, mercury(II) oxide, mercury(II) sulfide, methyl mercury chloride and ethyl mercury chloride are showing that mercury can be removed quantitatively by heating the standard mercury compounds at ca. 600°C over for 4 minutes.

Wakita et. al. heated neutron activated rock sample like a stage. And the relation between evaporation and temperature of mercury be being checked. This is agreeing in all of our experiment result.

**Effect of Heating Time.**
Silicon(IV) oxide or activated alumina that removed mercury is added in porcelain boat. A mercury standard solution is added to activated alumina in porcelain boat by using digital pipet. After that, cover is done with a mixture of calcium hydroxide and sodium carbonate (volume 1:1). And it heats about 400°C for 3 minutes in the 1st and then 700°C for 4 minutes in the 2nd. The air flow (0.5 l/min) that removed mercury with activated charcoal during that interval, is poured. The relation between heating time and discharged mercury at ca. 700°C is shown to Fig. 3. Mercury is determined by atomic absorption method. The mercury is discharged completely for the most part by heating of 4 minutes at ca. 700°C as a result.

Fig.3 Effect of heating time on the amalgamation of mercury vapor released from the mercury standard covered by the 1:1 mixture of Ca(OH)₂ and Na₂CO₃. Hg : 5 ng, Air flow rate : 0.5 l/min, Heating temperature : ca. 700°C.

Ventilation Volume at the Time of the Amalgamation.
Making the heating temperature at ca. 700°C, heating time was set up in 4
minutes. Mercury 5 ng was added in porcelain boat and then was inserted to a mercury vapor occurrence device. Air flow is changed into 0.2-1.0 1/min. The relation of amalgamation and ventilation volume is shown in Fig. 4. A constant value was obtained with air ventilation volume 0.4-0.8 1/min.

![Graph showing the effect of air flow rate on the determination of mercury.](image)

Fig. 4 Effect of air flow rate on the determination of mercury.
(The sample is the same as that used in the experiment shown in Fig. 3)
Hg : 5 ng, Heating temperature : ca. 700°C.

**Addition Reagents**

When added an addition reagents than only a solid sample can mask a coexistence substance. Thereupon, a solid standard sample is taken to porcelain boat and cover is done with a mixture of calcium hydroxide and sodium carbonate. The result that checked about an addition reagents shows to Table 1. From Table 1 difference of mercury content by a difference of addition reagents is not eliminating a part of sample. Thereupon, addition reagents chose for the purpose of causing acidic gas absorption that the removal of mercury is easy. In this research,
Determination of trace amounts of mercury in solid samples using porous gold as a collector by cold vapor atomic absorption spectrometry.

calcium hydroxide and sodium carbonate (volume 1 : 1) were used.

Table 1 Effect of added reagents on mercury recovery.

<table>
<thead>
<tr>
<th>Added reagent</th>
<th>JG-1 Hg (µg/kg)</th>
<th>River sediment Hg (µg/kg)</th>
<th>Pepperbush Hg (µg/kg)</th>
<th>Sasa 78-1 Hg (µg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)₂</td>
<td>13.6 (3)</td>
<td>1050 (3)</td>
<td>53.5 (5)</td>
<td>74.7 (5)</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>13.4 (3)</td>
<td>1100 (3)</td>
<td>54.8 (5)</td>
<td>82.8 (5)</td>
</tr>
<tr>
<td>Ca(OH)₂ + Na₂CO₃</td>
<td>14.9 (5)</td>
<td>1030 (5)</td>
<td>56.2 (5)</td>
<td>82.0 (5)</td>
</tr>
<tr>
<td>Ca(OH)₂ + Na₂CO₃ + Al₂O₃</td>
<td>14.9 (5)</td>
<td>1080 (5)</td>
<td>56.6 (5)</td>
<td>86.6 (5)</td>
</tr>
</tbody>
</table>

Reference value 14 1100 ± 500 53-57.6 77-190

( ): Number of repetition

Sample (0.01-0.5 g) (Porcelain boat)

- Add ca. 2g of a mixture of Ca(OH)₂ and Na₂CO₃
- Heat at ca. 400°C for 3 min and next 700°C for 6 min by passing mercury free air at flow rate of 0.5 l/min
- Trap mercury on a porous gold
- Heat at ca. 700°C for 1 min
- Pass mercury free air at flow rate of 0.3 l/min

Cold vapor atomic absorption spectrometry

(Apparatus: Rigaku Mercury SP)

Fig. 5 Analytical procedure of mercury in solid sample.
Determination of Trace Amounts of Mercury in Solid Sample by Heating Vaporization-Cold Vapor Atomic Absorption Spectrometry.

From the result that was expressed above, the operation procedure is shown in Fig. 5. According to this method, a reagent blank value is produced remarkable small. As for Fig. 6 mercury shows calibration curve from 0 to 10 ng. If this method is used to determination of mercury in solid samples such as rock, sediments, animals and plants, it is possible small the contamination from reagents, appliance and experimental environment. Also, one sample can be done a determination in about 15 minutes. Determination limit is 0.1 ng as the absolute quantity of mercury. This method were repeated by using mercury of 5.0 ng of 5 times. Then, a standard deviation percent was 1.7%.
Determination of trace amounts of mercury in solid samples using porous gold as a collector by cold vapor atomic absorption spectrometry

**Intercalibration of Mercury Using a Standard Reference Materials.**

The determination of mercury was achieved according to the method described in Fig. 5. We used standard reference materials that was prepared in the interior or outside. Analytical results are tabulated in Table 2. The method shown in Fig. 5 is possible sufficient satisfactory from the results of intercalibration analysis.

**Table 2.** Mercury content in standard solid samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>This work Hg(μg/kg)</th>
<th>Ref. value Hg(μg/kg)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>JG-1 (GEOLOGICAL SURVEY OF JAPAN)</td>
<td>14.9</td>
<td>14</td>
<td>1)</td>
</tr>
<tr>
<td>JB-1 (GEOLOGICAL SURVEY OF JAPAN)</td>
<td>21.5</td>
<td>30</td>
<td>1)</td>
</tr>
<tr>
<td>River sediment (NBS-SRM 1645)</td>
<td>1080</td>
<td>1100 ± 500</td>
<td>1)</td>
</tr>
<tr>
<td>Bovine liver (NBS-SRM 1577)</td>
<td>16.4</td>
<td>16 ± 2</td>
<td>1)</td>
</tr>
<tr>
<td>Shark paste (FUWA LABORATORY OF TOKYO VIN.)</td>
<td>340</td>
<td>330</td>
<td>1)</td>
</tr>
<tr>
<td>Maanago pellet (FISHERIS EXPERIMENT STATION OF KAGOSHIMA PRE.)</td>
<td>1220 (990, 1080, 1300, 1420, 1630)</td>
<td></td>
<td>1)</td>
</tr>
<tr>
<td>Pepperbush (NIES-SRM No1)</td>
<td>56.6</td>
<td>(53, 57.6)</td>
<td>2)</td>
</tr>
<tr>
<td>Sasa 77-1 (MATSUO LABORATORY OF YAMAGATA VIN.)</td>
<td>72.8</td>
<td>(53, 77)</td>
<td>2)</td>
</tr>
<tr>
<td>Pond sediment (NIES-SRM No2)</td>
<td>1240 (1300, 1330, 1380, 1420, 1460)</td>
<td></td>
<td>3)</td>
</tr>
<tr>
<td>Chlorella (NIES-SRM No3)</td>
<td>4.8</td>
<td></td>
<td>4)</td>
</tr>
<tr>
<td>Freeze-dried serum (NIES-SRM No4)</td>
<td>2.3</td>
<td></td>
<td>1)</td>
</tr>
<tr>
<td>Human hair (NIES-SRM No5)</td>
<td>4490</td>
<td>4400 ± 400</td>
<td>4)</td>
</tr>
<tr>
<td>Mussel (NIES-SRM No6)</td>
<td>3.7</td>
<td>5.0</td>
<td>4)</td>
</tr>
</tbody>
</table>

1) Air dry basis, 2) Dried for 10 days over silicagel desiccator, 3) 6h dry basis at 110°C, 4) 4h dry basis at 85°C.
Conclusion

Mercury is used for a thermometer, manometer and contact of apparatus in chemical laboratory. Accordingly, chemical laboratory is always contaminated with mercury. Also, it needs to pay attention to an appliance and distilled water. Then apparatus made semi-closed system that opens only at the time of the taking in and out of sample. It needs to prepare a standard reference materials that an analytical value corresponds to various solid samples. It assumed that it causes reliability to analytical value had to analyze a such standard reference materials and solid samples. The determination of mercury in some standard reference materials were performed and the satisfactory values of mercury were obtained using this experimental systems.

References