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BY COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY

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# DETERMINATION OF TRACE AMOUNTS OF MERCURY IN SOLID SAMPLES USING POROUS GOLD AS A COLLECTOR BY COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY

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## 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 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<sup>1),2)</sup>, soil<sup>3)</sup>, sediment<sup>4),5)</sup>, fishes and shellfishes<sup>6),7)</sup>], 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.

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Pre-treatment is necessary to determine the mercury in solid sample precisely. Wet method that decomposes the sample chemically with sulfuric acid-nitric acid<sup>8)</sup>, nitric acid-potassium permanganate<sup>9)</sup>, nitric acid-hydrogen peroxide<sup>7)</sup> since before, was used. Mercury evaporates easily by heating the sample physically. Drying method that utilized this behavior in recent years, is used widely<sup>10)-11)</sup>. 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.

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

Activated alumina (Nishio kougyou) 30/60 mesh was used.

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

Calcium hydroxide (Nakarai Chemicals) was used.

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

Sodium carbonate (Nakarai Chemicals) was used.

(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.

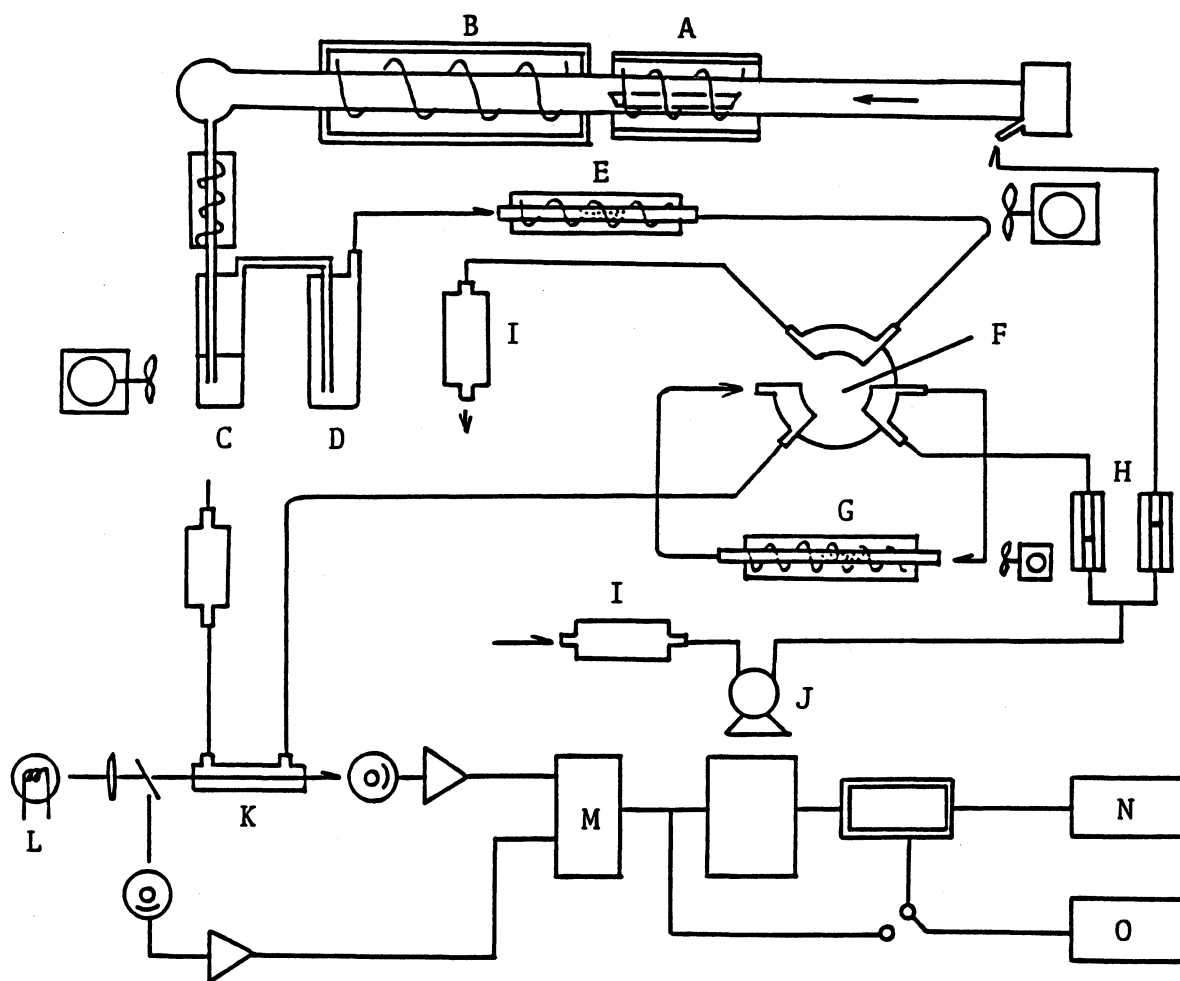


Fig.1 Schematic diagram of apparatus for the determination of mercury in solid sample by cold vapor atomic absorption spectrometry.

A : Heating furnace, B : Oxidizing furnace, C : Washing bottle (Phosphate buffer solution pH 6.86), D : Condenser, E : 1st mercury trapping room, F : Multi-pass-autobulb, G : 2nd mercury trapping room, H : Flow meter, I : Activated charcoal, J : Air pump, K : Absorption cell, L : Hg glow tube, M : Amplifier, N : Printer, O : Recorder

## 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

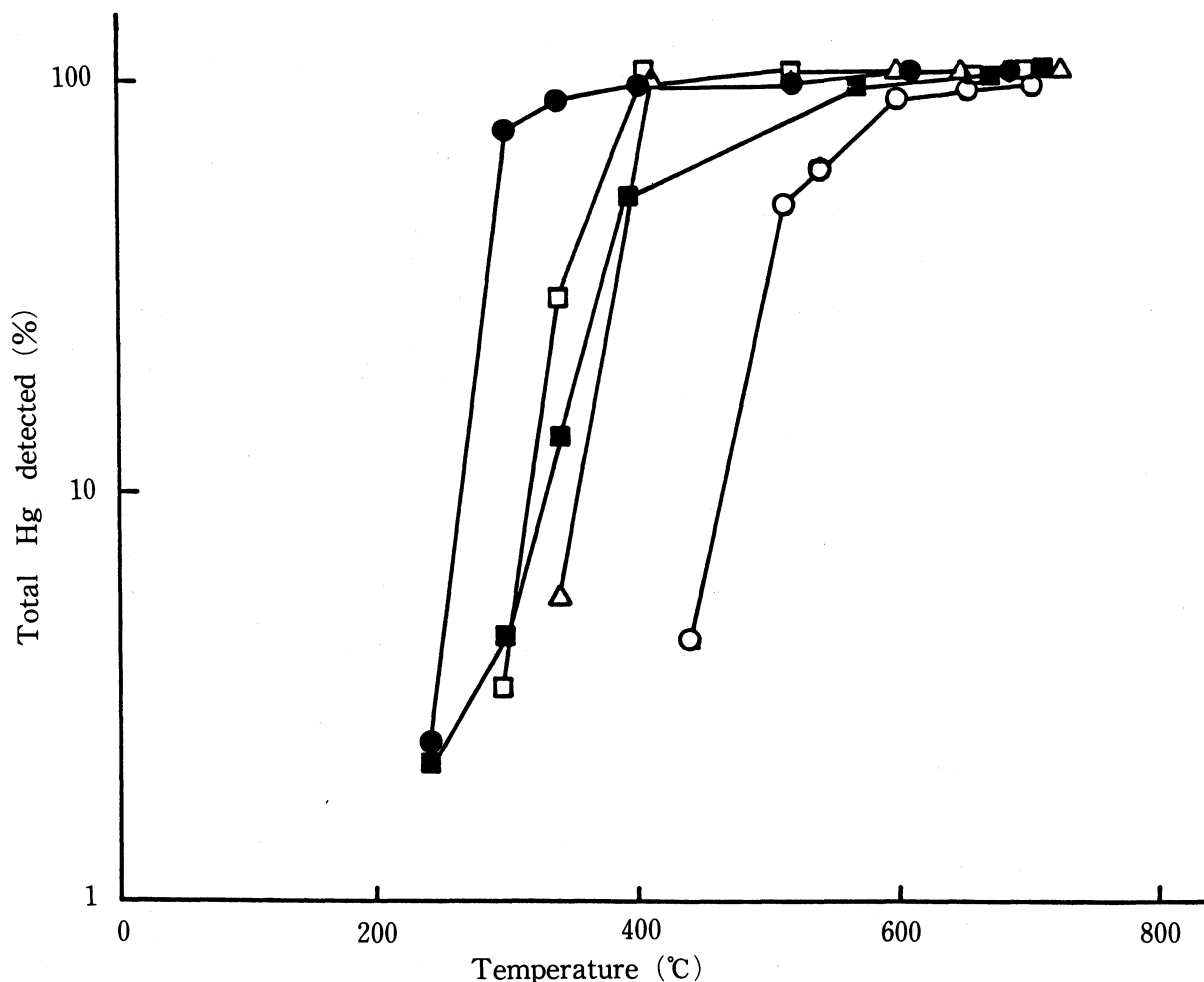


Fig. 2 Effect of temperature on liberation of mercury vapor from the compounds.  
 ○ : HgO, △ : HgS, □ : CH<sub>3</sub>HgCl, ■ : HgCl<sub>2</sub>, ● : C<sub>2</sub>H<sub>5</sub>HgCl  
 Heating time 4 min

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.<sup>12)</sup> 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.

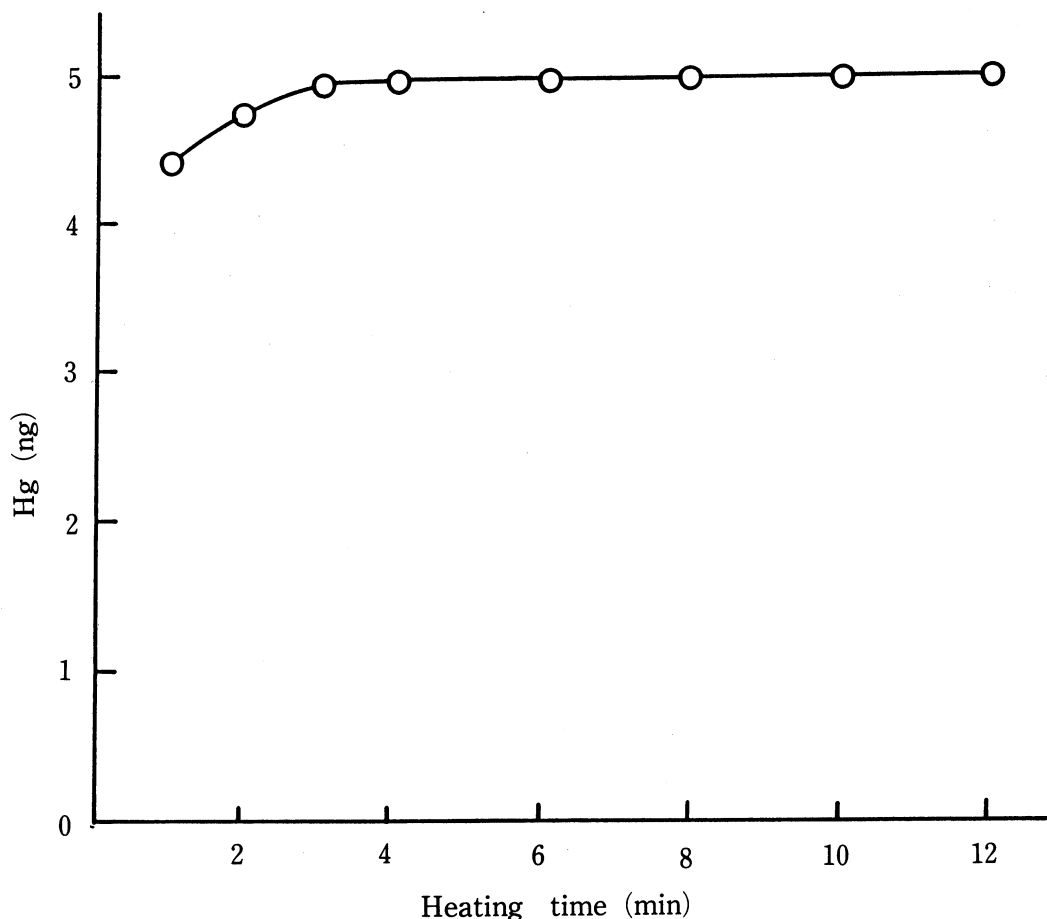


Fig.3 Effect of heating time on the amalgamation of mercury vapor released from the mercury standard covered by the 1 : 1 mixture of  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$ .  
Hg : 5 ng, Air flow rate : 0.5 l/min, Heating temperature : ca. 700°C.

*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 l/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 l/min.

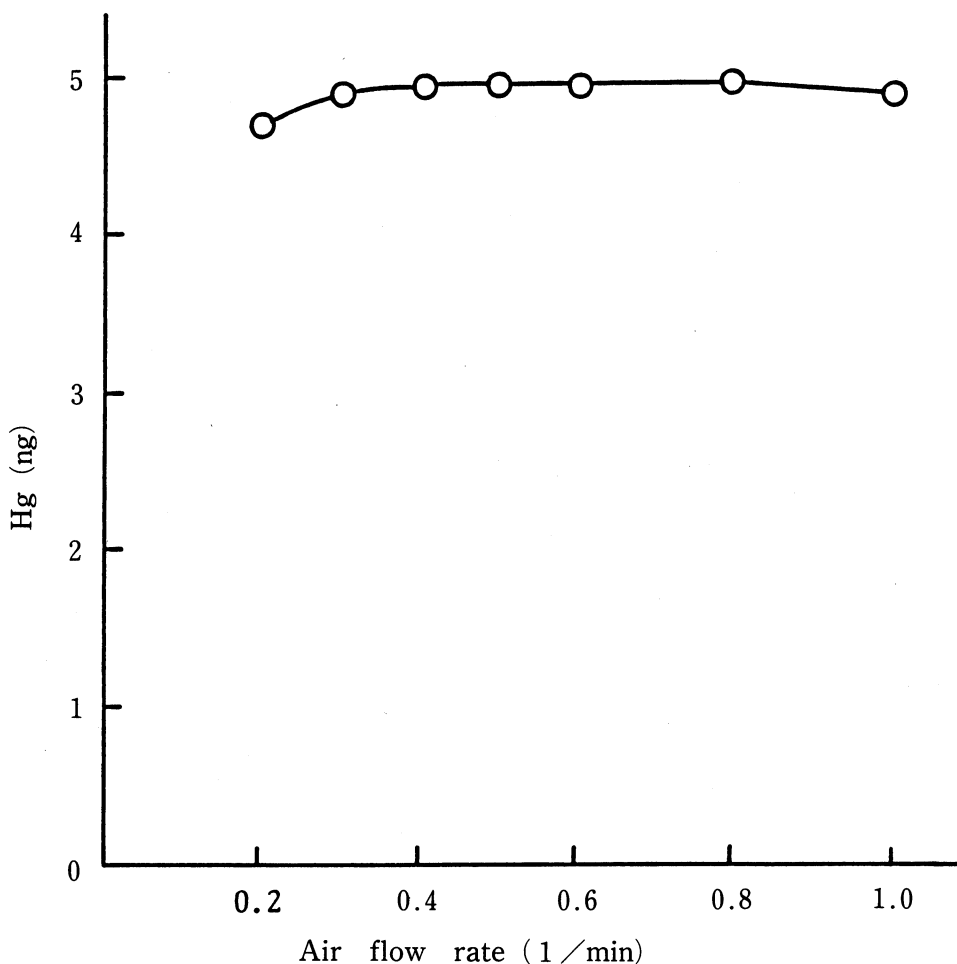


Fig.4 Effect of air flow rate on the determination of mercury.  
[The sample is the same as that used in the experiment shown in Fig.3]  
Hg : 5 ng, Heating temperature : ca. 700°C.

#### *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,



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

Table 1 Effect of added reagents on mercury recovery.

Added reagent	JG-1 Hg ( $\mu\text{g}/\text{kg}$ )	River sediment Hg ( $\mu\text{g}/\text{kg}$ )	Pepperbush Hg ( $\mu\text{g}/\text{kg}$ )	Sasa 78-1 Hg ( $\mu\text{g}/\text{kg}$ )
Ca(OH) <sub>2</sub>	13.6 (3)	1050 (3)	53.5 (5)	74.7 (5)
Na <sub>2</sub> CO <sub>3</sub>	13.4 (3)	1100 (3)	54.8 (5)	82.8 (5)
Ca(OH) <sub>2</sub> + Na <sub>2</sub> CO <sub>3</sub>	14.9 (5)	1030 (5)	56.2 (5)	82.0 (5)
Ca(OH) <sub>2</sub> + Na <sub>2</sub> CO <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub>	14.9 (5)	1080 (5)	56.6 (5)	86.6 (5)
Reference value	14	1100 $\pm$ 500	53-57.6	77-190

( ): Number of repetition

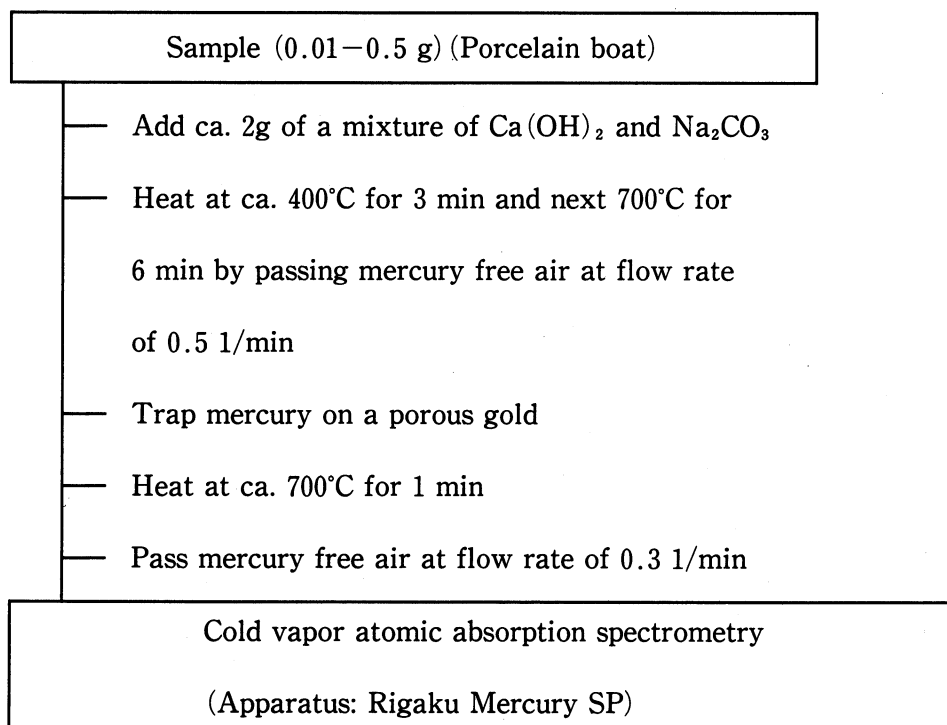


Fig.5 Analytical procedure of mercury in solid sample.

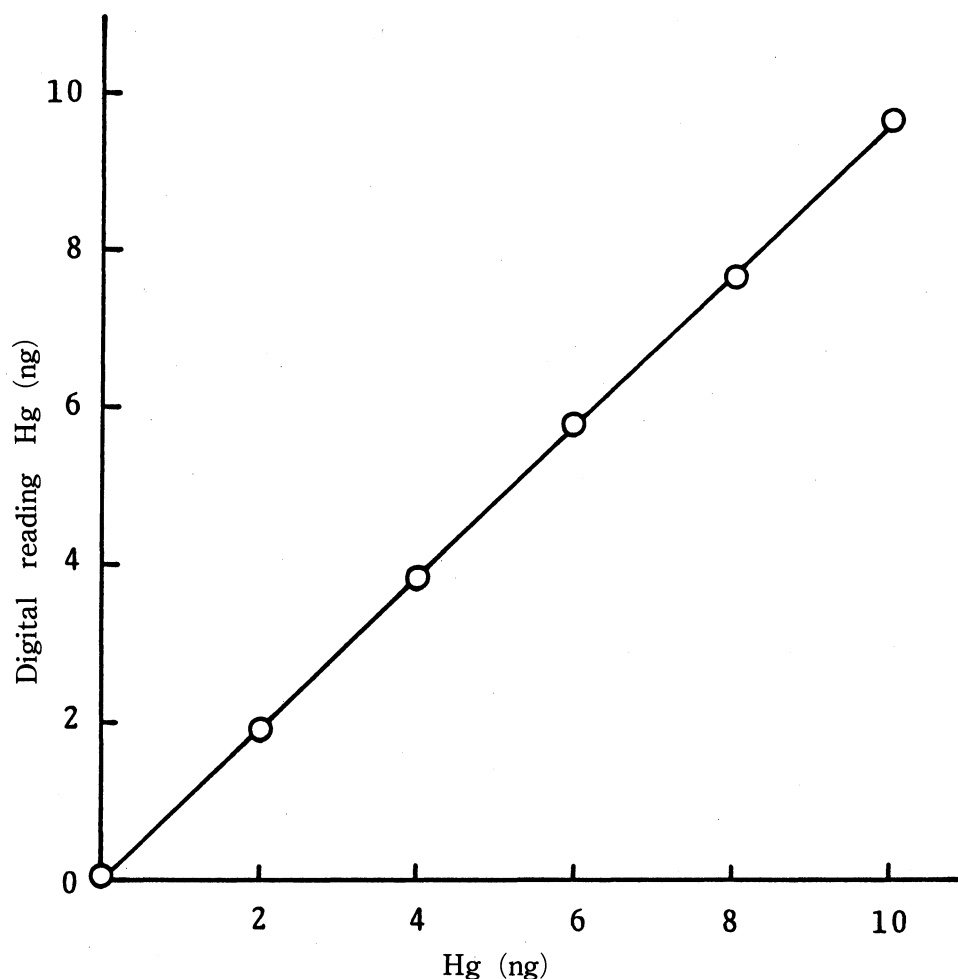


Fig.6 Calibration curve for the determination of mercury in solid samples.

*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%.

*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 were prepared in the interior or outside. Analytical results are tabulated in Table 2. The method shown in Fig. 5 is possibly sufficiently satisfactory from the results of intercalibration analysis.

Table 2 Mercury content in standard solid samples.

Sample	This work Hg ( $\mu\text{g}/\text{kg}$ )	Ref. value Hg ( $\mu\text{g}/\text{kg}$ )	Remarks
JG-1 (GEOLOGICAL SURVEY OF JAPAN)	14.9	14	1)
JB-1 (GEOLOGICAL SURVEY OF JAPAN)	21.5	30	1)
River sediment (NBS-SRM 1645)	1080	$1100 \pm 500$	1)
Bovine liver (NBS-SRM 1577)	16.4	$16 \pm 2$	1)
Shark paste (FUWA LABORATORY OF TOKYOU VINV.)	340	330	1)
Maanago pellet (FISHERIES EXPERIMENT STATION OF KAGOSHIMA PRE.)	1220	(990, 1080, 1300, 1420, 1630)	1)
Pepperbush (NIES-SRM No.1)	56.6	(53, 57.6)	2)
Sasa 77-1 (MATSUO LABORATORY OF YAMAGATA VINV.)	72.8	(53, 77)	2)
Pond sediment (NIES-SRM No.2)	1240	(1300, 1330, 1380, 1420, 1460)	3)
Chlorella (NIES-SRM No.3)	4.8		4)
Freeze-dried serum (NIES-SRM No.4)	2.3		1)
Human hair (NIES-SRM No.5)	4490	$4400 \pm 400$	4)
Mussel (NIES-SRM No.6)	3.7	5.0	4)

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. And then apparatus made semi-closed system that opens only at the time of the taking in and out of sample. It needs to prepared 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.

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