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## DETERMINATION OF ULTRATRACE AMOUNTS OF MERCURY IN ATMOSPHERE AND ITS DISTRIBUTION

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### Abstract

Mercury in atmosphere samples was determined by cold vapor atomic absorption spectrometry using porous gold as a collector. The content and distribution of mercury in atmosphere samples taken from various geothermal areas and laboratories in Japan were investigated. Since the existing forms of mercury in atmosphere samples are complex, it is difficult to determine all of the chemical forms. In this research, therefore, metallic mercury vapor was determined. Mercury content of chemical laboratory is high over 10–1000 times than its ambient atmosphere. In geothermal area, there is a high inverse correlation between the content of mercury and the distance from the fumarole. As for this, mercury is discharged into atmosphere as metallic mercury vapor by fumarolic activity.

### Introduction

In recent years, attention has been paid to the mercury content in atmosphere, such as that of the exhaust gas or volcanic gas. As a general rule, mercury is a level of 1–100 ng/m<sup>3</sup> in atmosphere. It is difficult to determine the mercury directly. Therefore, it is necessary to separate and concentrate mercury with some method. The wet method that used sulfuric acid-potassium permanganate conventionally, have been used. This method has the problem that shown in (4) from the following of (1).

- (1) Mercury content in reagents and contamination from laboratory environment.
- (2) Trapping efficiency of mercury is not regular.
- (3) Various organic compounds are given error of positive.
- (4) Because it is wet method, the handling in the open air is bothersome.

The other hand, simple dry method of operation is used widely in comparison with such wet method. Gold wool<sup>1)</sup>, silver wool<sup>2)</sup>, porous silver<sup>3)</sup>, gold coated absorbing agents<sup>4),5)</sup> and activated charcoal<sup>6),7)</sup> are used for trapping agents. Activated charcoal shows fluctuation by maker to blank value of mercury. Also, it is difficult to exclude mercury completely even if activated charcoal is heated. For these reasons, activated charcoal is not practical.

At present, amalgam method that used gold or silver for trapping agents of mercury is

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used widely for the simplicity of operation. Mercury evaporates easily by heating the trapping agents physically. Drying method that utilize this behavior is used widely in recent years. When this method is used, mercury pollution in operation can be small because of the trapping to determination of mercury can be carried out in semi-closed system. In this research, porous gold was used and applied to the determination of ultratrace amounts of metallic mercury vapor in atmosphere.

## Experimental

### *Reagents and Apparatus.*

All reagents were analytical grade of marketing and were prepared in mercury free by heating.

*Porous Gold Agents:* trapping agents of mercury vapor sintered chloroauric acid on the surface of chromosorb and used. This trapping agents is including gold about 11%. This was packed to quartz tube. This trapping agents is possible repetition use over 3,000 times.

*Atomic Absorption Spectrometer Equipment:* the apparatus used Mercury Auto Monitor of Nippon Instruments Corporation (this apparatus was connected to recorder). Schematic diagram of apparatus for determination of mercury is shown in Fig. 1.

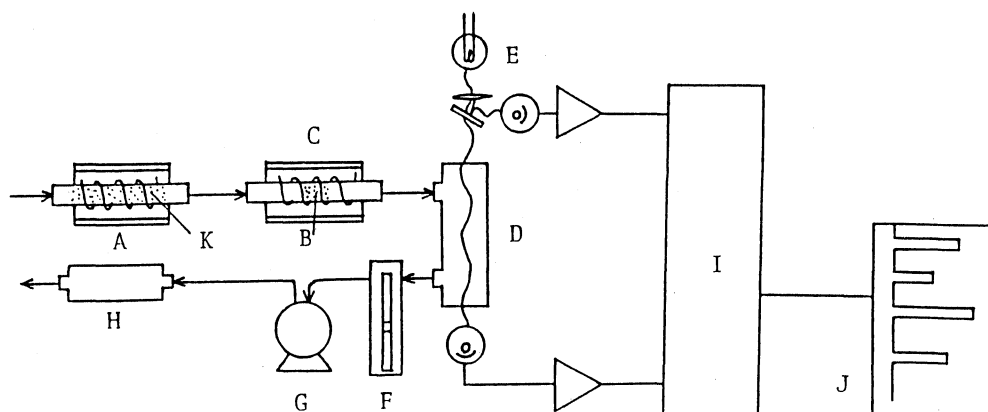


Fig. 1 Schematic diagram of apparatus for the determination of mercury in atmosphere.

A: Heating column, B: Mercury trapping room, C: Heater, D: Absorption cell, E: Hg glow tube, F: Flow meter, G: Air pump, H: Activated charcoal, I: Amplifier, J: Recorder, K:  $\text{Na}_2\text{CO}_3$

### *Determination of Ultratrace Amounts of Mercury in Atmosphere by Cold Vapor Atomic Absorption Spectrometry Using Porous Gold as a Collector.*

Porous gold collector and spectrometer of non-dispersion system were combined by Nippon Instruments Corporation. An outline of a device is shown in Fig. 1. This device can repeat a process of (4) automatically from (1), by controller built in equipment.

- (1) Trapping of mercury.
- (2) Gas purge.

(3) Atomic absorption measurement.

(4) Cooling.

Sample gas sucks in limited flow rate with pump (G) only time when it set up. Acidic gas is removed from sample gas with the tube that packed sodium carbonate (K) heated about 100°C first of all. After that, pass sample gas through the quartz tube for limited time. Here mercury is trapped as gold-amalgam. When trapping ends, porous gold collector is heated with heater (C). At this time, evolved mercury vapor passes to quartz absorption cell (D) after limited time and cold vapor atomic absorption of mercury is measured. The result is indicated to digital panel meter with 0.01 ng unit. An outline of procedure of determination of mercury in atmosphere is shown in Fig. 2. The chemical forms of mercury that is determined by this procedure is metallic mercury vapor. Mercury of mist forms traps as gaseous mercury on passing through the electric furnace. A difference is not almost existent to the one that does not pass it with the one that passed the electric furnace as pre-treatment, in this research. Thereupon, metallic mercury vapor was determined.

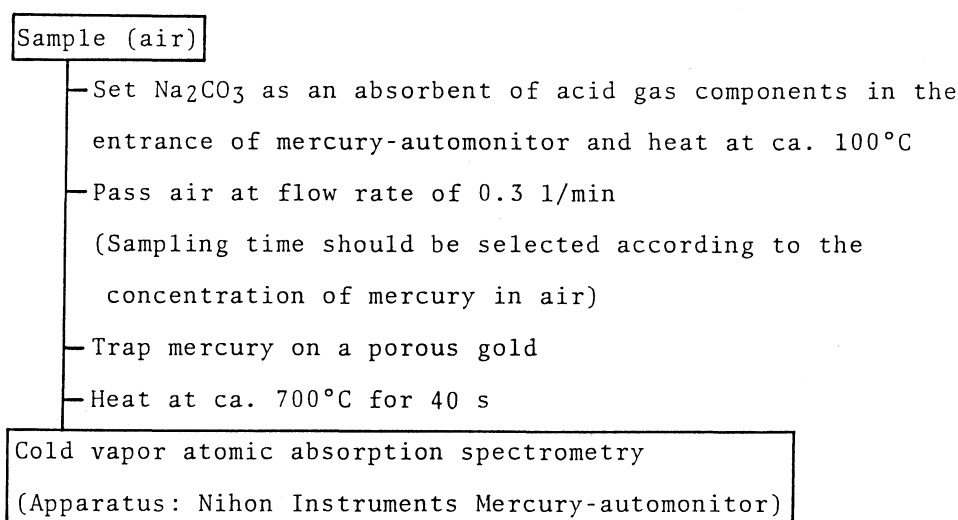


Fig. 2 Analytical procedure of mercury in atmosphere.

#### *Calibration of Mercury Analyzer.*

Mercury vapor is introduced to correct digital value of mercury analyzer precisely by reduction method. Metallic mercury was inserted in polyethylene container that showed in Fig. 3. Takes definite volume of saturated mercury vapor and it infuses to mercury analyzer. It calculates amounts of saturated mercury vapor in gas phase from state equation of saturated mercury vapor pressure and ideal gas of mercury. Saturated mercury vapor amounts  $W$  g that is included in  $l$  ml  $P$  mm Hg, temperature  $T$  (k), it is given as follow.  $W = 3.215 \times 10^{-3} P/T$  (g) Calibration by this method agreed with value by reduction method. Accordingly, saturated mercury vapor method was used to calibration of mercury analyzer in the open air.

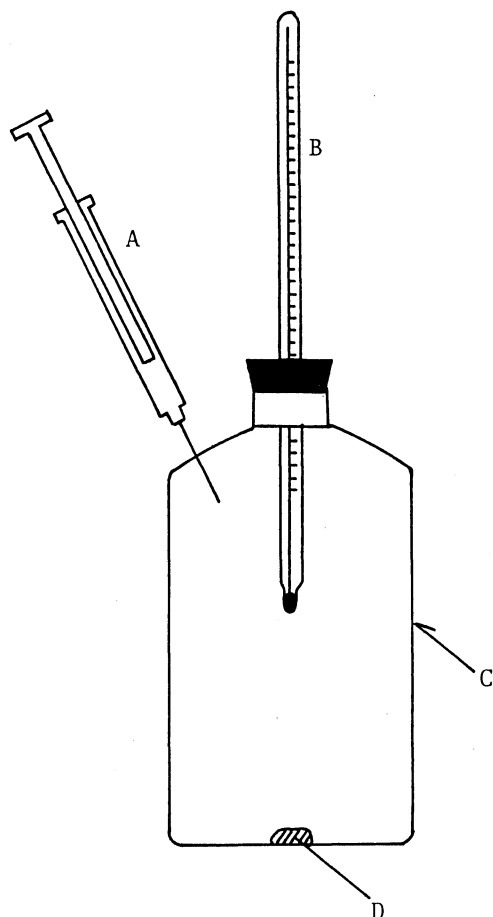


Fig. 3 Apparatus used for mercury vapor generation.  
A: Microsyringe, B: Thermometer, C: Polyethylene  
bottle, D: Mercury drop

## Results and Discussion

### *Determination of Mercury in Atmosphere of Laboratory and Its Ambient Air.*

Samples were collected in Kagoshima University and Chiba University. The results are shown in Table 1. Also, mercury content in atmosphere around Kagoshima University is shown in Table 2. Mercury determination of Table 1 sample was carried out at Japan Environmental Sanitation Center. Mercury content in atmosphere around faculty of science of Kagoshima University is the same level as the value that determined at faculty of science of Chiba University by Oikawa *et al.*. Mercury content of chemical laboratory is over 10–1000 times of ambient air. Also, most of the mercury are metallic mercury vapor. Laboratory that is exposing especially showed high value abnormally. This becomes contaminated factor on the occasion of the determination of ultratrace amounts of mercury. Therefore it pays attention to the control of atmosphere of laboratory that carries out pre-treatment of mercury sufficiently. Also, it needs to try mercury trapping in exhaust gas with activated charcoal and others.

### *Simplicity Concentration of Mercury in Atmosphere and Its Determination.*

Trapping tube (inner diameter:4 mm, length:160 mm) of quartz article that packed

Table 1. Analytical results of mercury in atmosphere of laboratories by Ag trap method<sup>a)</sup>.

Sampling station	Date	Gaseous Hg (ng/m <sup>3</sup> )	Particulate Hg (ng/m <sup>3</sup> )	Total Hg (ng/m <sup>3</sup> )
Chem. Lab. (Anal. Chem. 1)*	Feb. 8-Feb. 9, '76	96.8	0.6	97.4
〃 〃 ( 〃 〃 〃)*	〃 9- 〃 10 〃	51.1	1.1	52.2
〃 〃 ( 〃 〃 2)*	〃 8- 〃 9 〃	141	0.0	141
〃 〃 ( 〃 〃 〃)*	〃 9- 〃 10 〃	72.2	1.0	73.2
〃 〃 (Passage)*	〃 10- 〃	64.7	5.9	70.6
〃 〃 (Phy. Chem.)*	Jul. 8-Jul. 9, '79	4200	—	4200
〃 〃 (Org. Chem.)*	〃 12 〃	3540	—	3540
〃 〃 (Bio. Chem.)*	〃 12 〃	330	—	330
Spectrum Room**	〃 25-Feb.27 〃	35.1	0.4	35.5
Chem. Lab. (Nakagawa)**	〃 27-Mar. 1 〃	21.2	1.0	22.2
Balance Room**	Mar. 1- 〃 2 〃	86.7	—	86.7
〃 〃	〃 3- 〃 5 〃	50.0	—	50.0
Chem. lab. (Student)**	〃 2- 〃 3 〃	50.9	—	50.9
Darkroom**	〃 5 〃	382	—	382
〃 〃	〃 〃 〃	792	—	792

: Faculty of Science of Kagoshima University      a): Oikawa et al. (1976)

\*\* : Faculty of Science of Chiba University

Table 2. Analytical results of mercury in ambient air outside the chemical laboratory (Fac. Sci., Kagoshima Univ.).

Date	Hg (ng/m <sup>3</sup> )	Remarks
Apr. 16. '79	210	ca. 1 m from Chem. Lab.
〃 17 〃	90	〃 〃
〃 18 〃	60	〃 〃
〃 19 〃	60	〃 〃
〃 20 〃	60	〃 〃
〃 23 〃	60	〃 〃
〃 24 〃	110	〃 〃
〃 26 〃	70	〃 〃
〃 27 〃	80	〃 〃
May 1 〃	20	ca. 10 m 〃
〃 2 〃	50	〃 〃
〃 14 〃	20	〃 〃
〃 15 〃	30	〃 〃
〃 16 〃	60	〃 〃
〃 17 〃	40	〃 〃
〃 18 〃	30	〃 〃

porous gold agents in this research, was prepared. While mercury free nitrogen gas pass through, the trapping tube is heated in electric furnace about 700°C. And then, mercury in porous gold agents is removed. After that, cap of polyethylene is attached to trapping tube and prevents mercury contamination with vinyl tape wrap it up. This preparative trapping tube is done opening in field and connects to mini pump of battery style. The device is

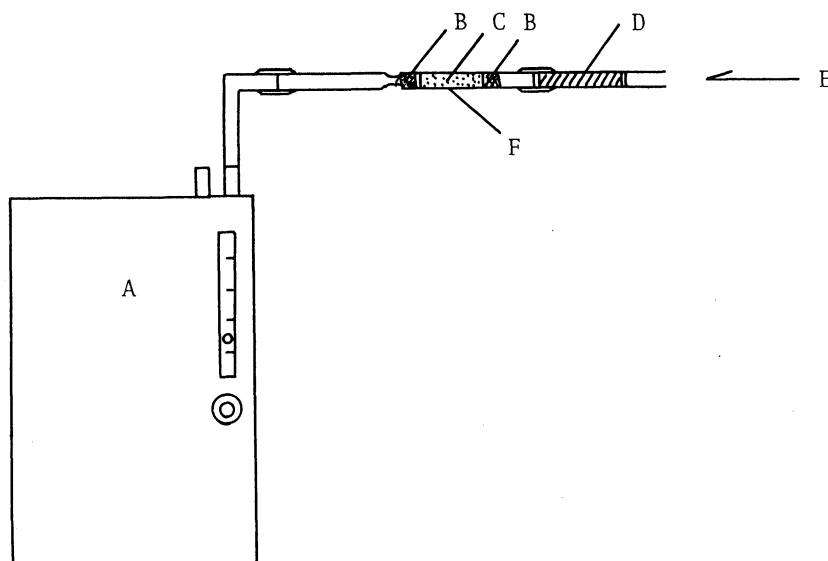


Fig. 4 Apparatus used for measuring mercury concentration in atmosphere.

A: Mini pump, B: Quartz wool, C: Porous gold, D: Anhydrous sodium carbonate, E: Air inlet, F: Quartz tube

shown in Fig. 4. Air sample is sucked limited time at flow rate of 0.3 l/min. Ventilated air volume calculate from flow rate and suction time. This trapping tube is heated in electric furnace about 700°C and mercury vapor is evolved. After that, the mercury vapor is determined by cold vapor atomic absorption spectrometry.

Anhydrous sodium carbonate is packed to an entrance of trapping tube in the case that influence of volcanic gas is. The decrease in disturbance of water vapor and acidic gas are done. The mercury of volcanic area of Usu of Hokkaido, Kirishima of Kagoshima, Ebino of Miyazaki and the others were determined. The results are shown in Table 3. Also, Fig. 5 shows the relationship between mercury content and distance from the fumarole. As may be apparent this figure, the content of mercury sharply decrease with the distance between the sampling position and the fumarole. Accordingly mercury is discharged into atmosphere by fumarolic activity. Also, chemical forms of mercury discharged is metallic mercury vapor. If greatly, such simplicity mercury collector is set down simultaneously in environmental atmosphere, it is able to utilize in a nonexistent place of the power supply. However, a help is necessary and it is not able to recommend for the determination of long period.

*Relation between the Mercury Contents in Atmosphere and Volcanic Activity in Sakurajima Volcano.*

Mercury is rich in volatility with a metal of low boiling point. Even if mercury becomes compound, it is easy to be reduced and decompose by heating and becomes metallic mercury vapor. Accordingly mercury is mainly discharged with metallic mercury vapor forms of simple substance from fumarole. Therefore, mercury is also one of the element that is capable of catching variation of volcanic activity. There are Siegel<sup>8)-10)</sup> and Nakagawa<sup>11),12)</sup>

Table 3. Mercury content in ambient air around volcanic area(1).

No.	Sampling location	Date	Hg(ng/m <sup>3</sup> )	Remarks
1	Azuma-itsusaikyo (Fuk.)	Sept. 23. '79	4.6	
2	" "	" " "	4.4	
3	" "	" " "	1.7	
4	" "	Oct. 10. "	3.5	
5	" "	" " "	2.3	
6	" "	" " "	18	
7	" "	" " "	6.0	
8	" "	" " "	4.8	
9	" "	" " "	5.2	
10	" "	" " "	5.3	
11	" "	" " "	174	
12	Maruo (Kag.)	Oct. 23. "	5.0	
13	Shiratoriwōyama (Miyaz.)	Nov. 2. "	16.1	ca. 1 m from a fumarole
14	" "	" " "	124	" "
15	" "	" " "	106	" "
16	" "	" " "	108	" "
17	" "	" " "	601	" "
18	" "	" " "	1.7	ca. 300 m
19	" "	" " "	4.0	ca. 200 m
20	" "	" " "	8.3	" "
21	" "	" " "	8.3	" "
22	Motomura (Kag.)	Oct. 10. '80	19	
23	Shintake ( " )	" " "	210	ca. 1 m from fissure
24	" ( " )	" 11. "	43	5 m
25	" ( " )	" " "	58	15 m
26	" ( " )	" " "	97	" "
27	Shiratori-onsen (Miyaz.)	Feb. 12. '81	38.8	
28	Ebinokōgen (Miyaz.)	" " "	16.7	
29	Iwōdani (Kag.)	" " "	44.0	
30	Kirishimasō (Kag.)	Mar. 13. "	13.1	
31	Yunono (Kag.)	Mar. 13. '81	1080	ca. 1 m from a fumarole
32	Usu (Ginnuma) (Hok.)	Nov. 13. '82	9.7	150 m
33	" ( " ) ( " )	" " "	9.5	" "
34	" ( Kakōnai ) ( " )	" " "	17.2	10 m
35	" ( " ) ( " )	" " "	53.9	" "
36	" ( Gairin ) ( " )	" 14. "	6.6	700 m
37	Tōya (Suimeisou) ( " )	" " "	4.6	
38	Osorezan (Aom.)	" 15. "	36.2	
39	Unagi onsen (Kag.)	Dec. 18. "	2.9	
40	Noboribetsu (Hok.)	Oct. 25. '83	67.5	
41	Tōya (Suimeisou) (Hok.)	Oct. 26. '83	3.4	
42	Usu (Kakōnai) (Hok.)	" " "	7.4	ca. 50 m from a fumarole
43	" ( " ) (Hok.)	" " "	7.8	100 m
44	" ( " ) (Hok.)	" " "	63.0	10 m
45	" ( " ) (Hok.)	" " "	2620	1 m
46	" ( " ) (Hok.)	" " "	1010	" "
47	" ( " ) (Hok.)	" " "	10300	0 m
48	Unagi onsen (Kag.)	Nov. 2. "	3.6	
49	" " (Kag.)	" " "	5.0	



Table 3. Mercury content in ambient air around volcanic area(2).

No.	Sampling location	Date	Hg(ng/m <sup>3</sup> )	Remarks
50	Usu (Kakōnai) (Hok.)	Jun. 24. '85	244	ca. 5 m from a fumarole
51	〃 ( 〃 ) (Hok.)	〃 〃 〃	259	〃 〃
52	〃 ( 〃 ) ( 〃 )	〃 〃 〃	67.1	〃 〃
53	〃 ( 〃 ) ( 〃 )	〃 〃 〃	109	〃 〃
54	〃 ( 〃 ) ( 〃 )	〃 〃 〃	7500	0 m 〃
55	〃 ( Gairin ) ( 〃 )	〃 25. 〃	6.3	700 m 〃
56	〃 ( Ginnuma ) ( 〃 )	〃 〃 〃	56.2	150 m 〃
57	Tokachidake ( 〃 )	〃 26. 〃	19.0	50 m 〃
58	Usu (Gairin) ( 〃 )	〃 27. 〃	4.6	700 m 〃
59	〃 ( 〃 ) ( 〃 )	〃 〃 〃	6.5	700 m 〃
60	〃 ( Ginnuma ) ( 〃 )	〃 〃 〃	15.7	150 m 〃
61	Tōya (Kohantei) (Hok.)	〃 〃 〃	5.3	

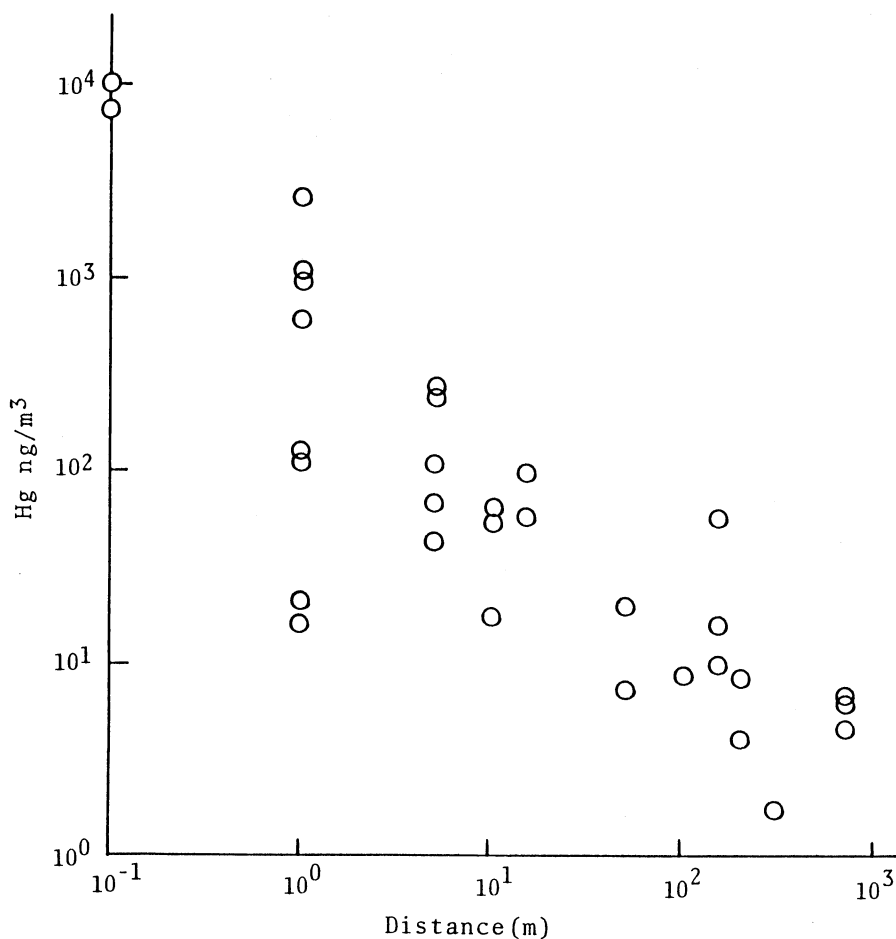


Fig. 5 Relation between mercury content and the distance from the fumarole in ambient air around volcanic area.

report about the point. Also, there are Koga<sup>13-15)</sup> and Akeno<sup>16)</sup> report as geochemical geothermal prospecting method that made mercury indicative element. However, continued research of mercury in Sakurajima volcano is hardly carried out. Oikawa *et al.*<sup>17)</sup> carried out the investigation of mercury in environmental atmosphere of every place in Japan. It is reporting that mercury content in atmosphere of volcanic area is high. The one that source of supply of the mercury in atmosphere is discharged from volcanic crater. A thing by evaporation from ground surface and artificial combustion are not able to be disregarded. Mercury that is discharged from a crater is influenced wind direction, wind velocity, other weather conditions and configuration of the ground in many cases. Mercury analyzer is established in every direction, to determine the mercury of volcanic origin. It is desirable that mercury determines simultaneously. However, wind direction was thought from each circumstances. Mainly sampling station settled at Harutayama and Kurokami Observatory of Kyoto University.

#### *Continuous Determination of Mercury in Atmosphere*

Mercury auto analyzer was used for the mercury determination of long period. We carried out the determination of mercury content in Sakurajima volcano atmosphere at Harutayama Observatory of Kyoto University. Table 4 shows monthly average of mercury content and one month interval highest value (2 hours interval). Monthly average of mercury content is 13–22 ng/m<sup>3</sup> that February, 1980 is eliminated. Next, the mercury in atmosphere was determined with 2 hours interval, January 13, 1980 at Harutayama. The results are shown in Fig. 6. These results are influenced considerably wind direction, wind velocity, other meteorological conditions and topography. How to revise them is important factor.

Table 4. Mercury content in ambient air around Sakurajima Volcano from May in 1979 to February in 1980.

Locality	Month	Hg (ng/m <sup>3</sup> ) (Monthly average)		Maximum value within the month
Kurokami	May,	1979	13	60(May, 19), 60(May. 22)
"	Jun.	"	15	78(Jun. 6)
"	Jul.,	"	13	32(Jul. 3)
Harutayama	Sept.,	"	17	66(Sept. 26), 90(Sept. 27)
"	Oct.,	"	22	56(Oct. 1), 58(Oct. 30)
"	Nov.,	"	18	60(Nov. 4), 52(Nov. 11) 53(Nov. 18), 51(Nov. 30)
"	Dec.,	"	17	68(Dec. 8), 113(Dec. 12) 50(Dec. 27)
"	Jan.,	1980	20	648(Jan. 12), 139(Jan. 13)
"	Feb.	"	3	13(Feb. 17)

#### *Controversial Point in Automatic Determination of Mercury in Atmosphere Used Porous Gold Agents.*

Air sample is ventilated to porous gold agents and metallic mercury vapor is condensed as gold amalgam. After that, the mercury is determined by cold vapor atomic absorption

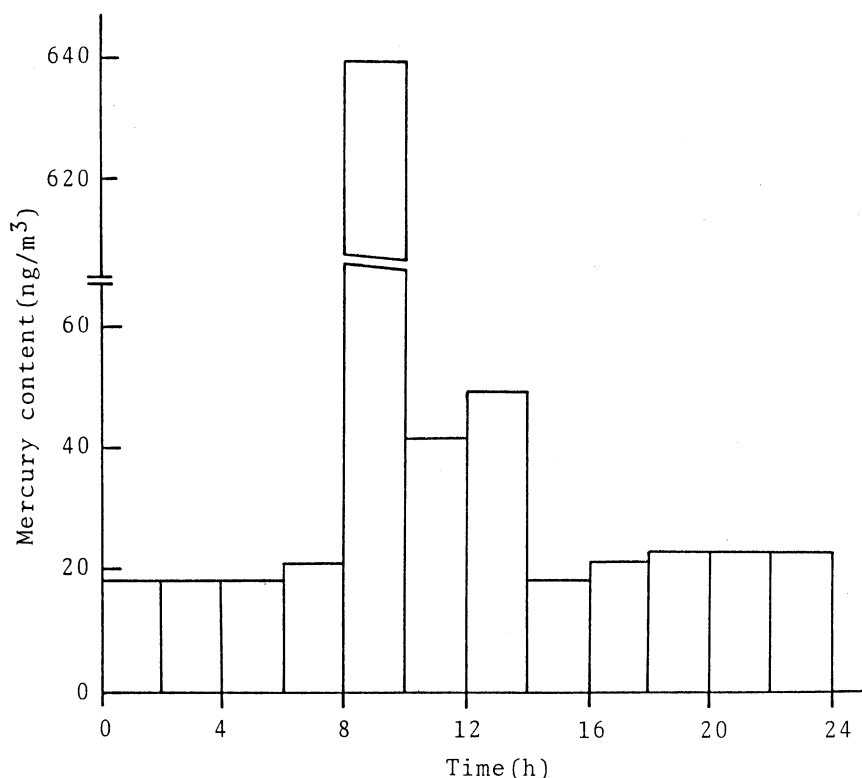


Fig. 6 Variation of mercury content in air with time at Harutayama. Date: Jan.13, 1980, Wind direction: SE, Wind velocity:9 m/sec

spectrometry. When the mercury in atmosphere of volcanic area is determined by using this device, there is the problem as follows:

- 1) It is a problem of the minute volcanic ejecta that floated.
- 2) It is a problem of water vapor.
- 3) It is a problem of background value.

Also, a trouble of a device is many when it determines continuously without staff actually. 1) of a problem of floating matters solves if filter is set up in the circuit. However, loading is caused while it is long and flow rate changes. When porous gold agents absorbs water vapor, mercury determination interferes. If dehumidification is attempted by using electronic cooling system, this problem is solved.

A value in atmosphere that a problem of a background value parted distantly from volcano is not necessarily a background value. Zero correction need to be done by using air or other gas that mercury is removed completely. This outside, there are return of circuit after power breakdown and decrease of sensitivity for long period of automatic mercury determination.

### Conclusion

In this research, mercury in atmosphere of laboratory and geothermal area was

determined by cold vapor atomic absorption spectrometry using porous gold collector (tube of quartz article is packed porous gold agents).

In comparison of mercury content of atmosphere of chemical laboratory to ambient air, chemical laboratory is high over 10–1000 times than ambient air. A prudent attention is necessary to control of laboratory that aims at the analysis of ultratrace amounts of mercury especially. The result of high reliability is not obtained by the contamination from laboratory atmosphere when there is not treatment carefully.

Mercury content is increasing to approach to fumarole in atmosphere of geothermal area. As for this, mercury is discharged into atmosphere by fumarolic activity. It is discharged with forms of metallic mercury that makes gold amalgam as the chemical forms.

We have determined the mercury that dispersed in atmosphere from crater of summit in definite point. Relation to volcanic activity was checked. The result receives an influence by wind direction, wind velocity, temperature and other meteorological conditions. How to revise them is important factor. Also, problem of suspended material and drop of sensitivity of apparatus must be solved for the mercury determination of long period.

### References

- 1) Z. Yoshida and K. Motojima, *Anal. Chim. Acta*, **106**, p 405–410 (1979).
- 2) S. J. Long, D. R. Scott and R. J. Thompson, *Anal. Chem.*, **45**, p 2227–2233 (1973).
- 3) K. Imaeda, K. Ohsawa and M. Wako, *Bunseki Kagaku*, **26**, p 651–655 (1977).
- 4) D. H. Anderson, J. H. Evans, J. J. Murphy and W. W. White, *Anal. Chem.*, **43**, p 1511–1512 (1971).
- 5) K. Imaeda and K. Ohsawa, *Bunseki Kagaku*, **28**, p 239–244 (1979).
- 6) F. P. Scaringelli, J. C. Puzak, B. I. Bennett and R. L. Denny, *Anal. Chem.*, **46**, p 278–283 (1974).
- 7) H. Nakamachi, K. Okamoto and I. Kusumi, *Bunseki Kagaku*, **23**, p 10–15 (1974).
- 8) B. Z. Siegel, S. M. Siegel and F. Thorarinsson, *Nature*, **241**, p 526 (1973).
- 9) S. M. Siegel and B. Z. Siegel, *Environ. Sci. Technol.*, **9**, p 473–474 (1975).
- 10) B. Z. Siegel and S. M. Siegel, *Environ. Sci. Technol.*, **12**, p 1036–1039 (1978).
- 11) R. Nakagawa, *Nippon Kagaku Kaishi*, **1984**, p 709–715 (1984).
- 12) R. Nakagawa, *Nippon Kagaku Kaishi*, **1985**, p 703–708 (1985).
- 13) A. Koga and T. Noda, *Chinetsu*, **12**, p 21–28 (1975).
- 14) A. Koga, *Butsuritansa*, **29**, p 72–82 (1976).
- 15) A. Koga and T. Noda, *Chinetsu*, **14**, p 9–14 (1977).
- 16) T. Akeno, *Chinetsu*, **19**, p 5–20 (1982).
- 17) K. Oikawa, Y. Kawabe, Y. Takizawa, M. Kamada, R. Nakagawa and Y. Ohyagi, *Nippon Kougishi*, **23**, p 659–663 (1976).