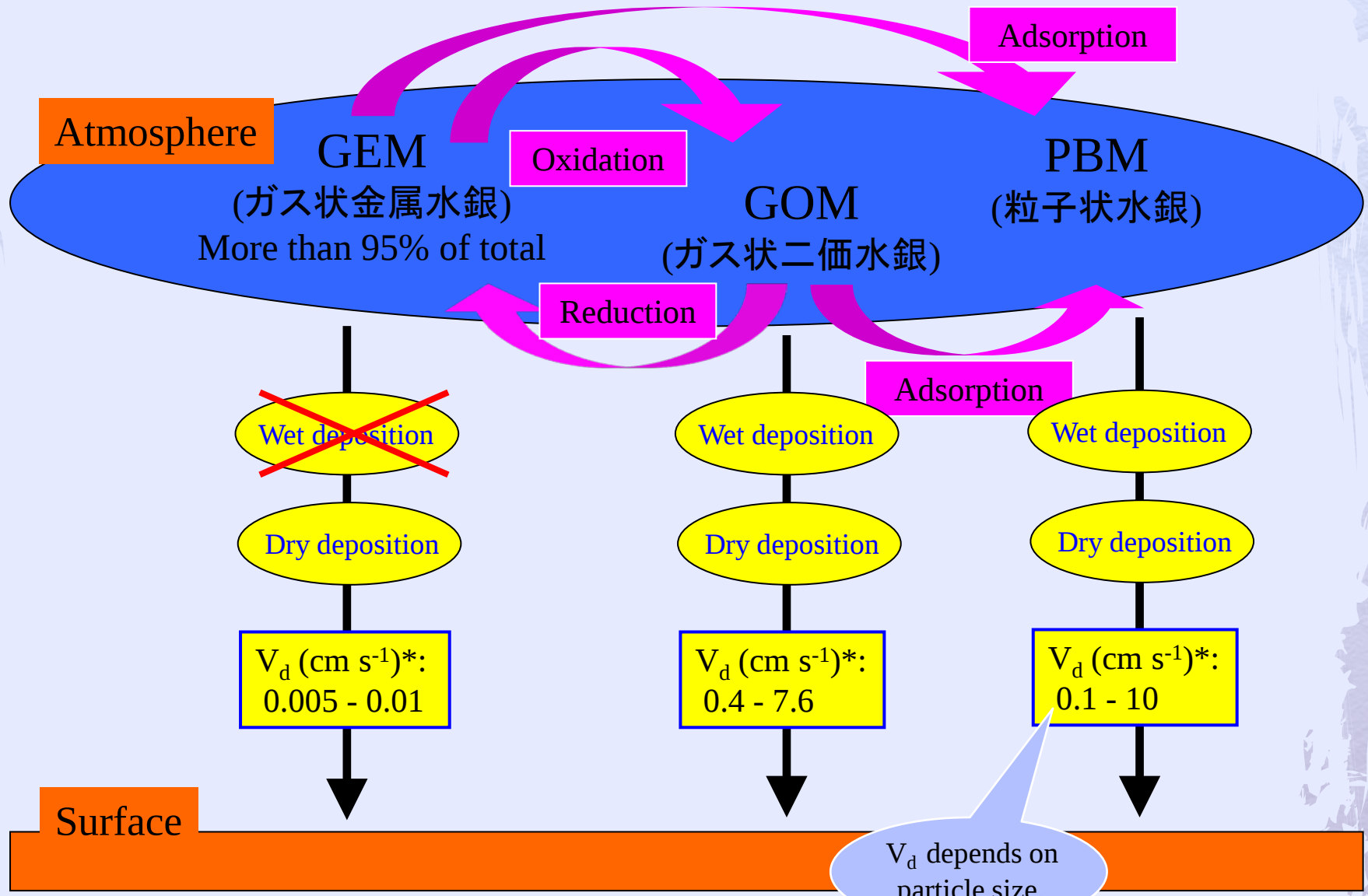


Lecture on atmospheric mercury analysis using MOEJ and NIMD methods

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Senior researcher
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Speciated Hg in atmosphere



* V_d : Dry deposition velocity

Sampling and analysis on atmospheric Hg

MOEJ manual method for TGM

NIMD manual method for GOM and PBM

MOEJ manual method for TGM

Dual gold amalgamation - Thermal desorption - Cold vapor atomic absorption spectrometry (CVAAS)

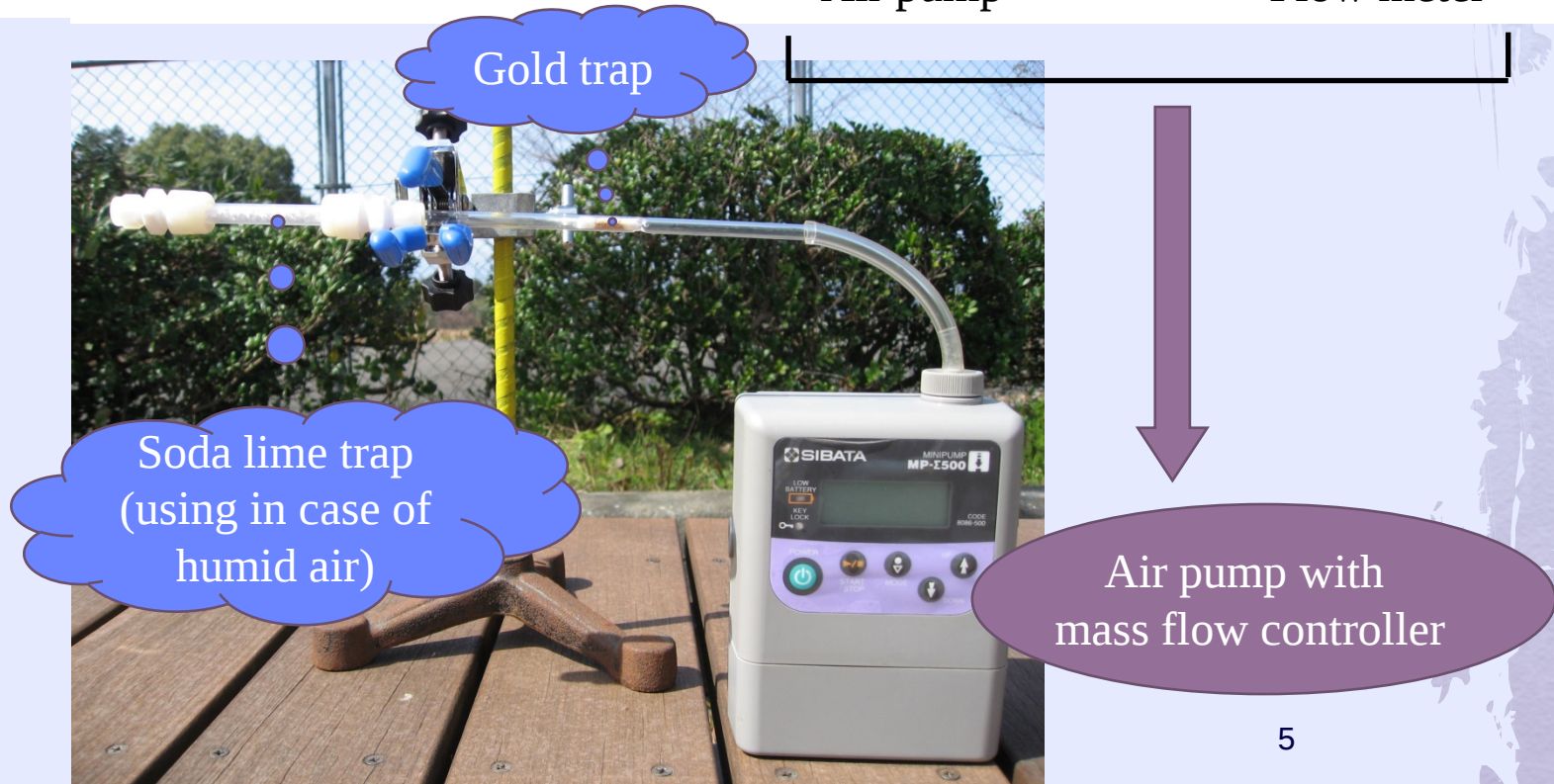
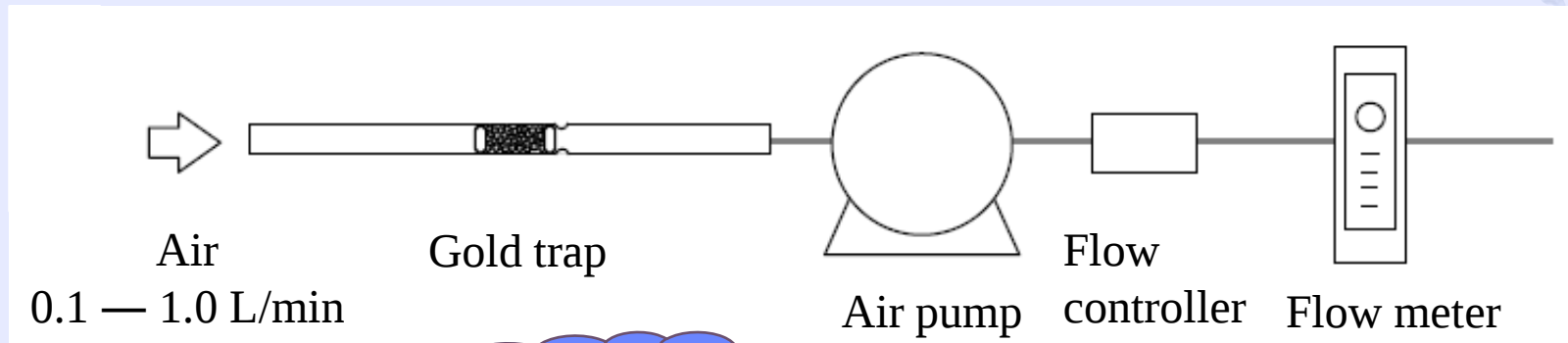
Overview

Mercury in the atmosphere is collected at a constant flow rate by using the collection tube filled with adsorbent which is composed of diatomaceous earth particles with gold baked on their surface. Mercury in the atmosphere is collected as gold amalgam. During the sampling, the surface of adsorbent may adsorb interfering gas and measured values could be compromised. In order to eliminate the influence of interfering gas, recollect the mercury vapor generated by collection tube attached to the heating furnace into the another collection tube controlled to maintain appropriate temperature.

The collection tube used to re-collect mercury is heated at high temperature, and mercury vapor is led to the absorption detector cell of the atomic absorption spectrometer by carries to determine the quantity of mercury by measuring the atomic absorption at a 253.7 nm wavelength.

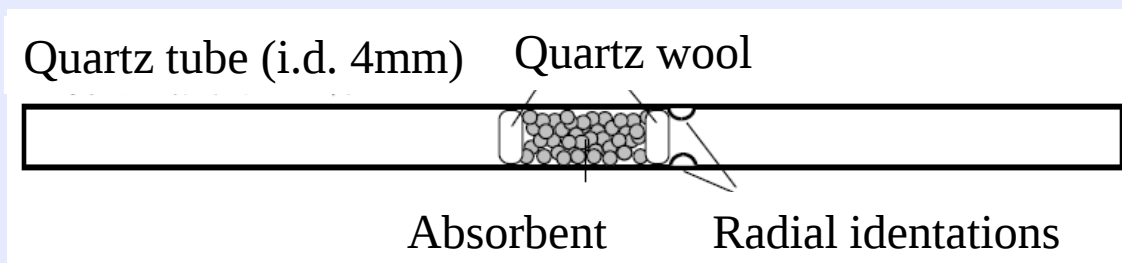
MOEJ manual method for TGM

Sampling equipment



MOEJ manual method for TGM

Hg collection trap



a) Collection trap (Gold trap)

As illustrated in the figure, a collection tube is filled with quartz wool, approximately 80 mg of adsorbent, and again with quartz wool in a quartz glass tube with three radial indentations.

Prior use, the traps is heated at 600°C to remove the residual Hg in the traps.

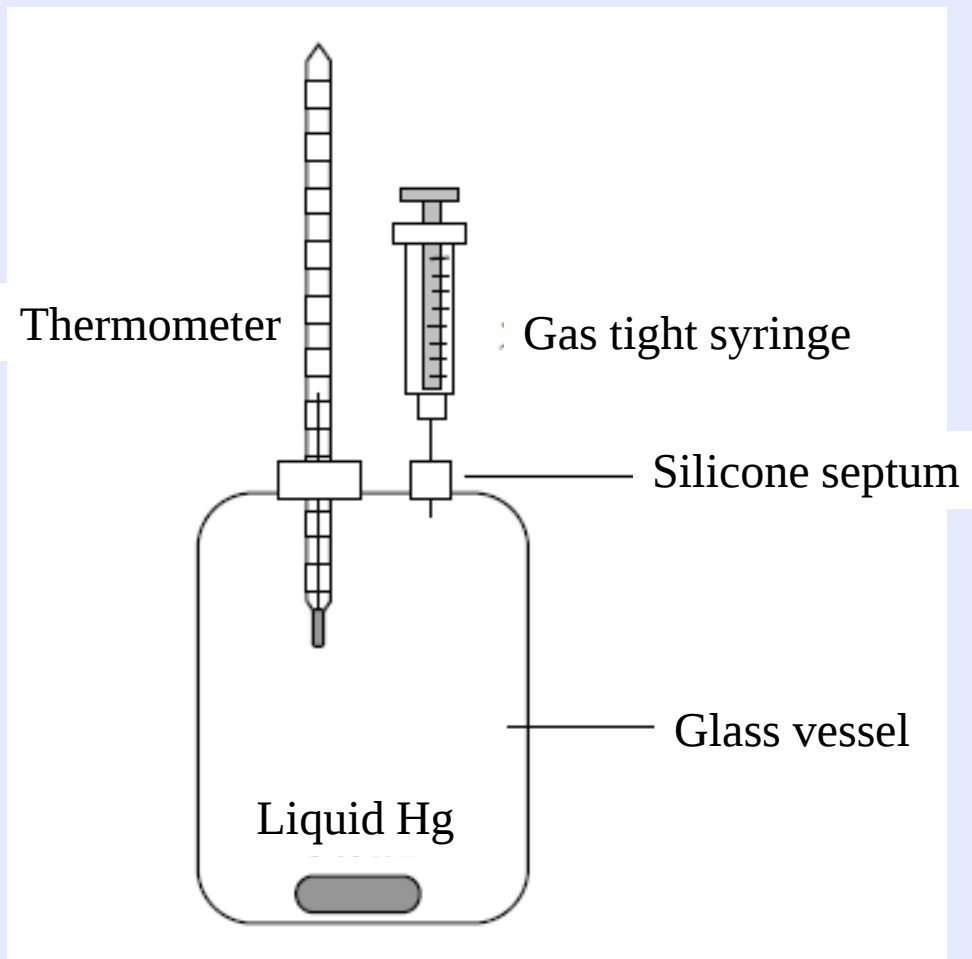
b) Collection tube storage container

Container should be made by glass test tube and be possible to be sealed by butyl stopper. It should be free from mercury contamination during storage.



MOEJ manual method for TGM

Hg standard



Overview of mercury vapor calibration device



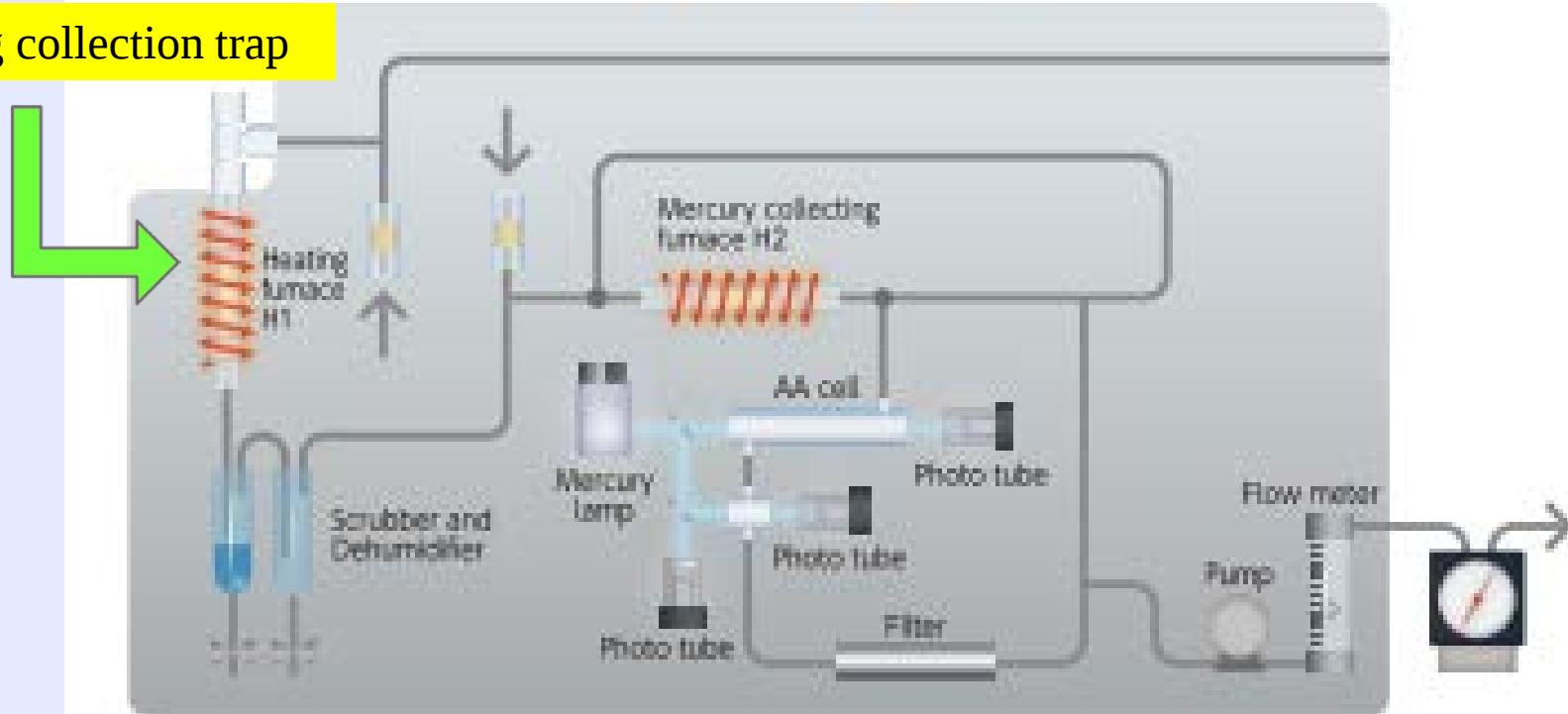
MOEJ manual method for TGM or GEM

Hg measurement

Dual gold amalgamation - CVAAS

WA-5A (Atomic Absorption System)

Hg collection trap



Dual gold amalgamation - CVAAS or CVAFS with auto sample tube changer (30 positions) produced by Nippon Instruments Corporation

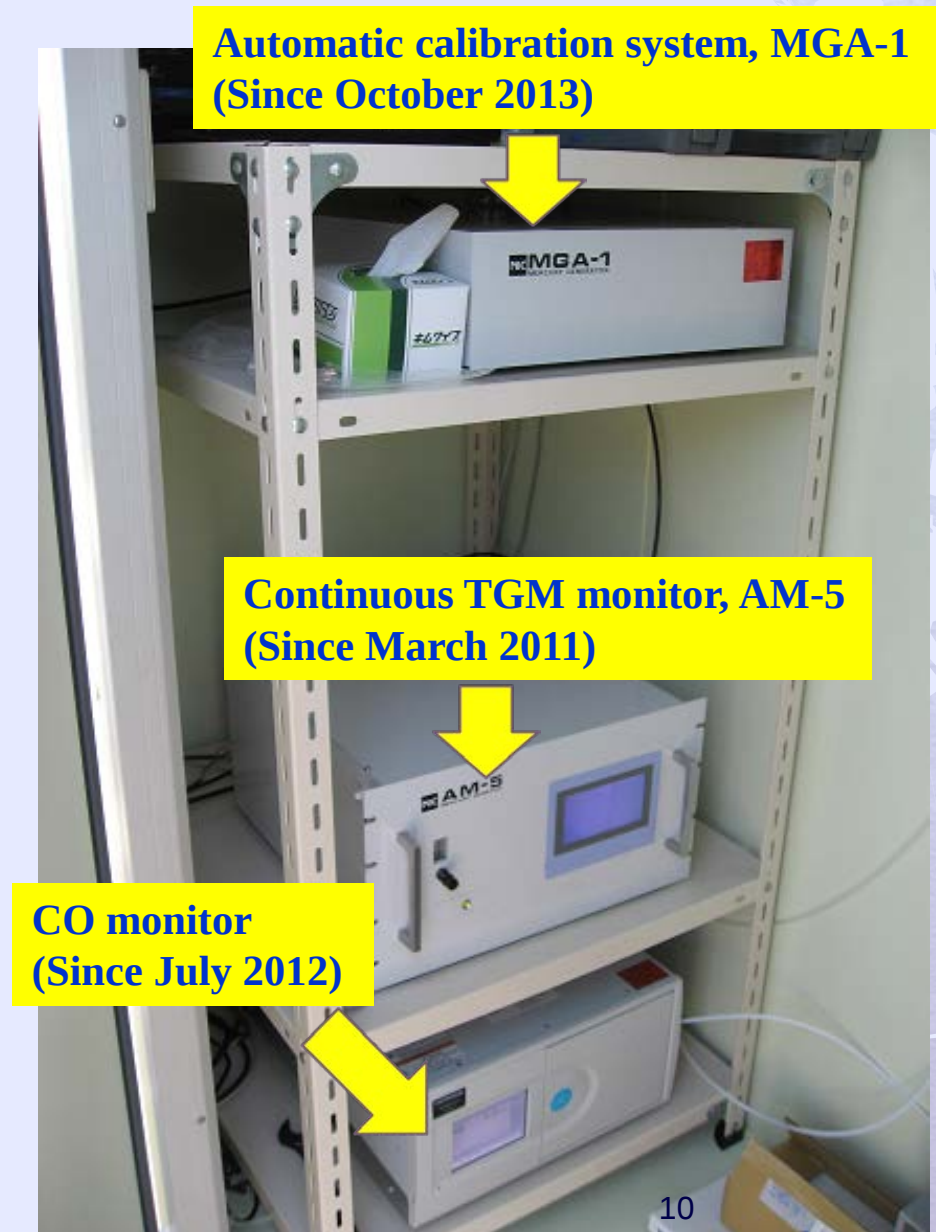


Gold trap

Minamata Station (Continuous TGM monitor)

Total gaseous Hg (TGM) is measured at 15 minutes intervals using a continuous TGM monitor (AM-5, Nippon Instruments Corporation) since June, 2011. The monitor is manually calibrated once a week using a standard gas of Hg(0). In addition, since October 2013, Automatic calibration system has been installed and the calibration is carried out every 24 hours.

Monitoring of Carbon monoxide (CO), which is an indicator (TGM/CO) of influences on long range transported Hg from Asian continent, are operated from July, 2012 to the present.



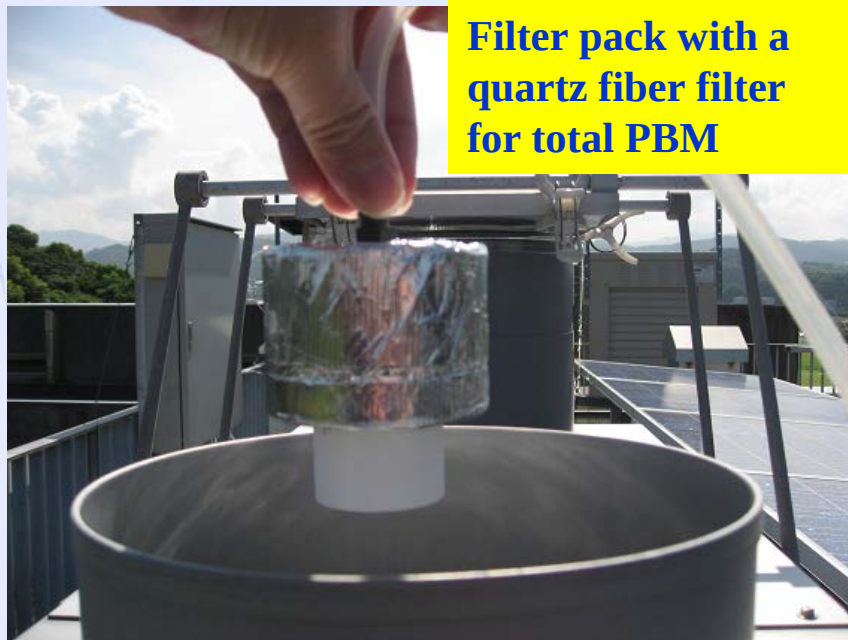
Manual sampling system for Speciated Hg)

Gaseous elemental Hg(GEM), gaseous oxidized Hg (GOM) and particle bound Hg (PBM) are sampled using a manually operated offline sampling system at about 12 hour intervals in 6 days a month. The sampling was carried out during the period from January 2011 to December 2013.

After sampling, these Hg species are measured by CVAFS or CVAAS following thermal desorption. The detection limits (3σ) of GEM, GOM and PBM are 0.3 ng/m^3 , 0.6 pg/m^3 and 1.7 pg/m^3 , respectively.



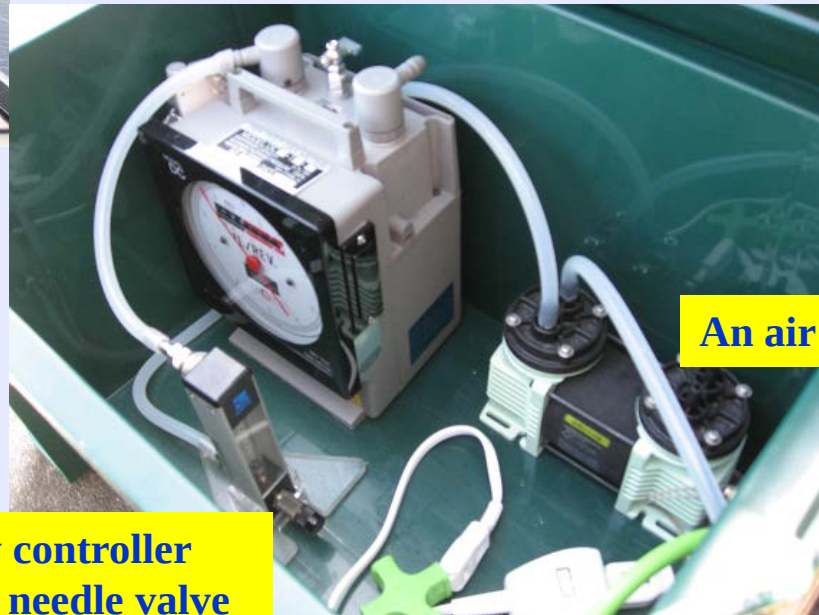
Manual sampling system for total PBM



Filter pack with a quartz fiber filter for total PBM

Total PBM has been sampled on a quartz fiber filter for a week using a two or four stage filter pack. The flow rate is 3 – 4 L/min. (Air volume for a sample is approximately 30 m³)

A dry integrating gas meter



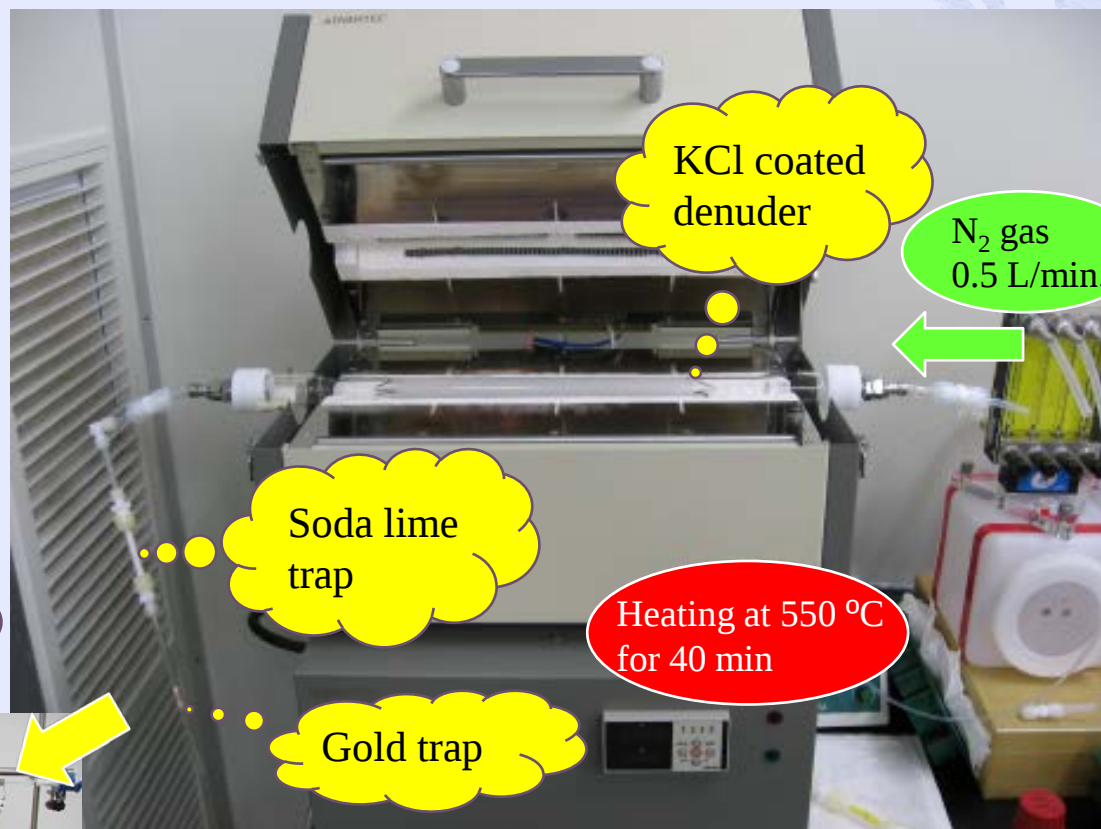
An air pump

The detection limits (3σ) of total PBM is approximately 2 pg/m³, calculated from three times the standard deviation of replicate measurements of a blank filter setting up on a subsequent stage of the sample filter stage

A flow controller with a needle valve

Analysis for GOM

Thermal desorption -
dual gold amalgamation -
CVAFS



Nichrome wire

Soda lime
trap

Gold trap

Heating at 550 °C
for 40 min

N₂ gas
0.5 L/min.



CVAFS detector with
gold amalgamation

Analysis for PBM(1)

Thermal desorption - gold amalgamation – CVAAS (MA2000, NIC)



No additional gas is needed.



However, two additional agents (Activated aluminum and alkaline powder) are needed.

Analysis for PBM (2)



Prior to analysis, sample ceramic boats and two additional agents should be heated at 750°C overnight.



Hg standard solution and two kind of standard reference materials (SRM) are measured.

Standard solution: $\text{Hg}(\text{NO}_3)$ in cysteine
SRM: NIST SRM1633b (Coal fly ash)
CRM SO-2 (Soil)*

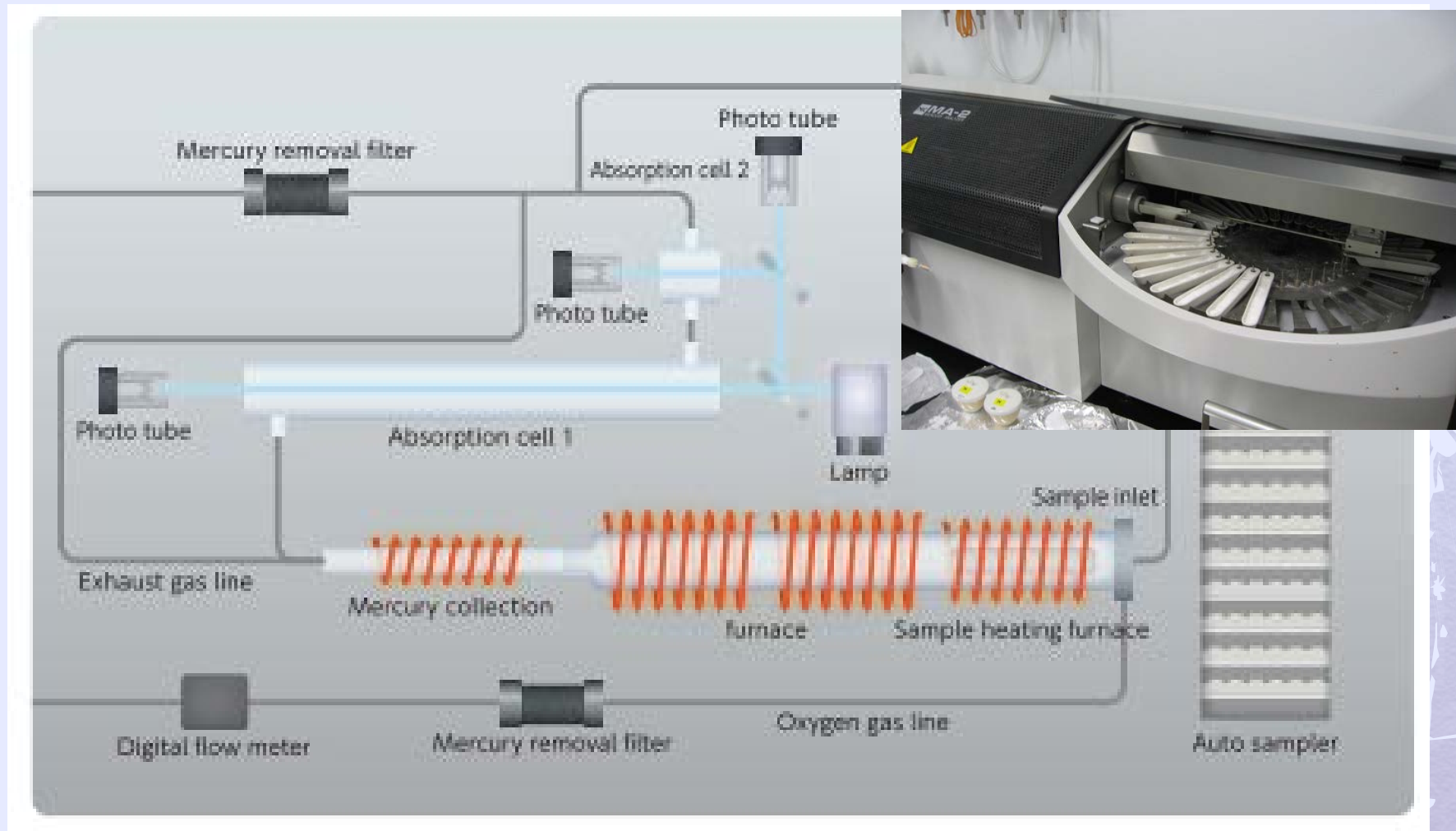
* This material was provided by Canadian Certified Reference Materials Project



Slit a filter sample including PBM using a scissor and set it in the ceramic boats with two additional agents.

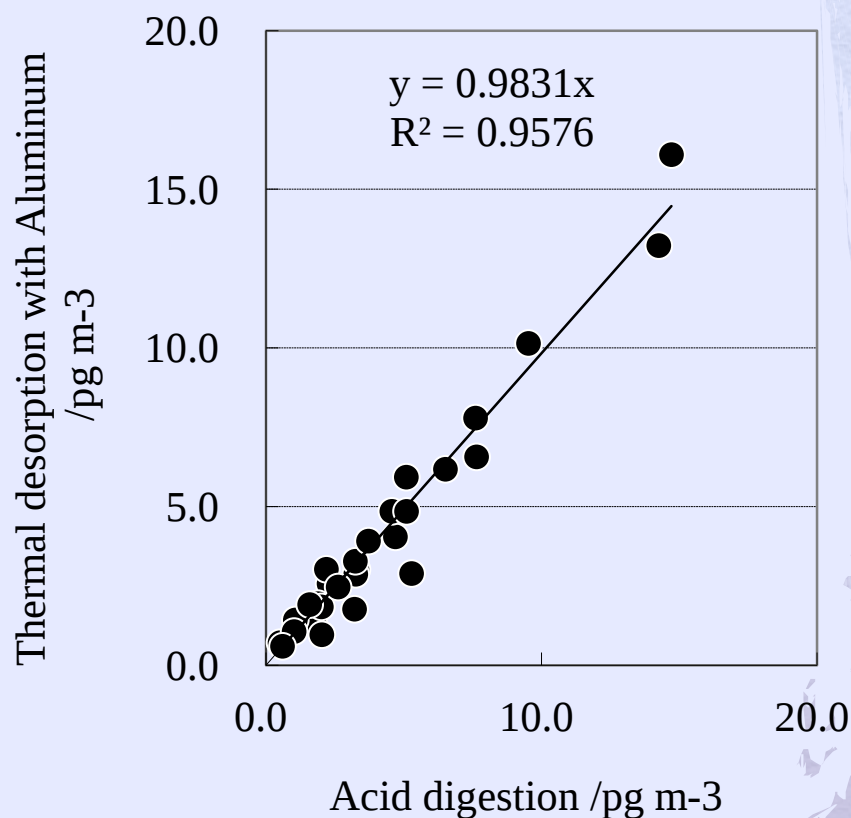
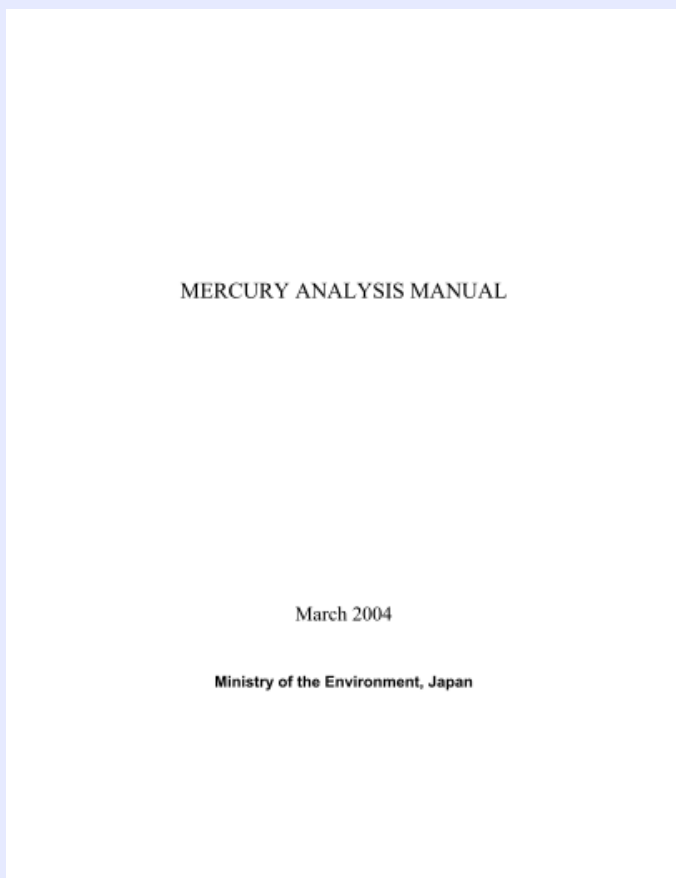
Analysis for PBM (3)

Schematic diagram of direct thermal desorption mercury analyzer



Analysis for PBM (4)

PBM on filter samples can be measured by acid digestion method using HNO_3 , HClO_4 and H_2SO_4 (Mercury analysis Manual, 2004)

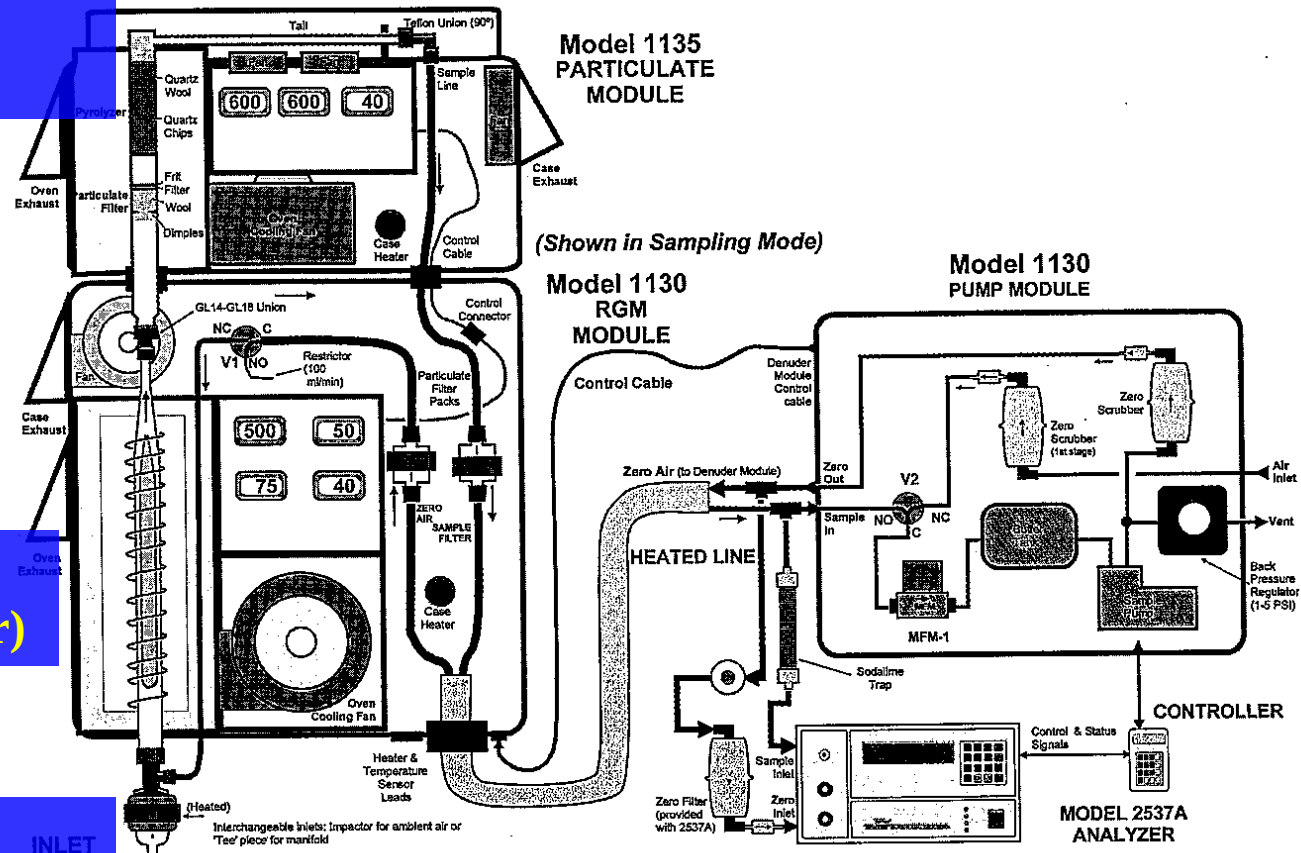


Continuous monitor for speciated Hg (Tekran Inc.)

**PBM sampling
(Quartz filter)**

**GOM sampling
(Annular denuder)**

**Air Inlet
(PBM >2.5 is trapped
on quartz frit)**

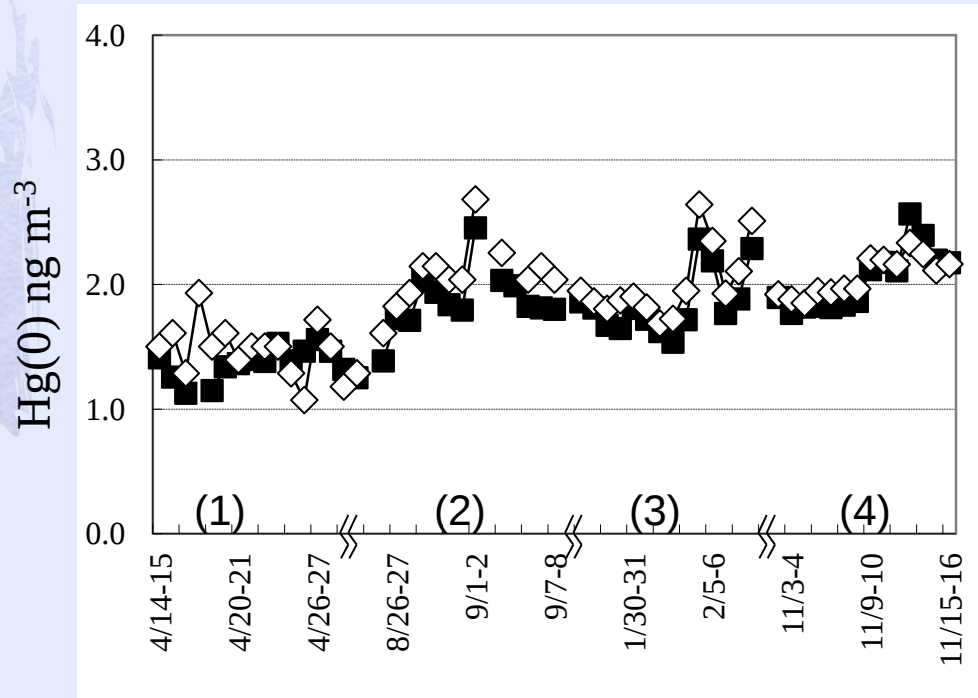


**Continuous Hg monitor
(Model 2537A)**

Comparison of GEM(TGM) measurement values

■ Tekran Hg Analyzer

◇ MOEJ Manual Method*

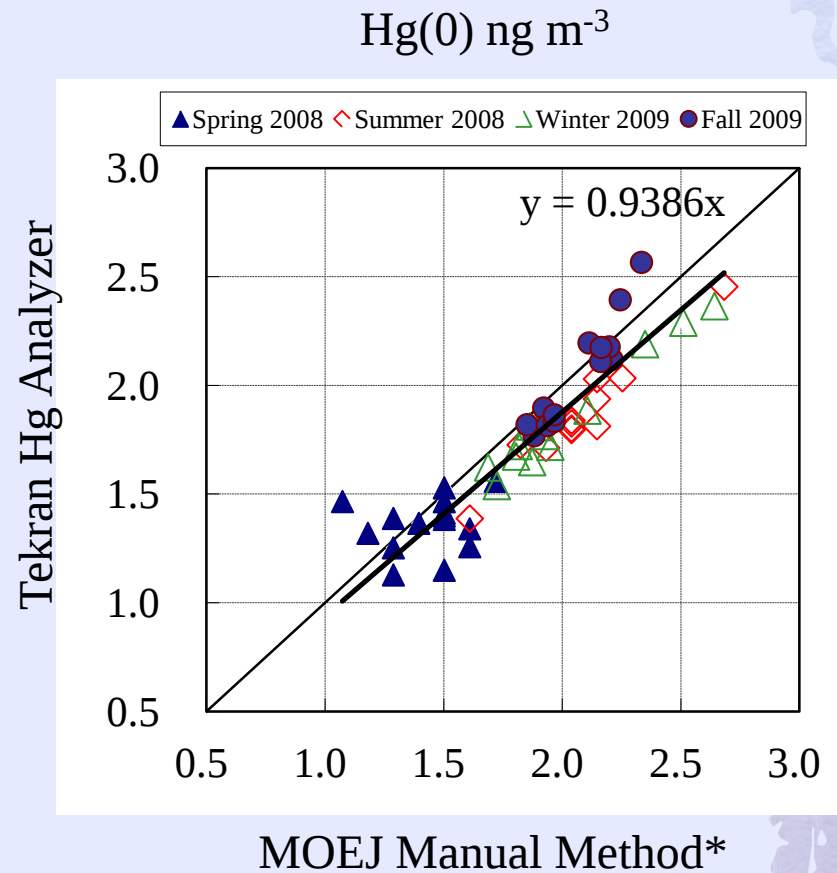


(1) Spring: 14 -30 Apr. 2008

(2) Summer: 25 Aug. - 8 Sep. 2008

(3) Winter: 26 Jan. - 8 Feb. 2009

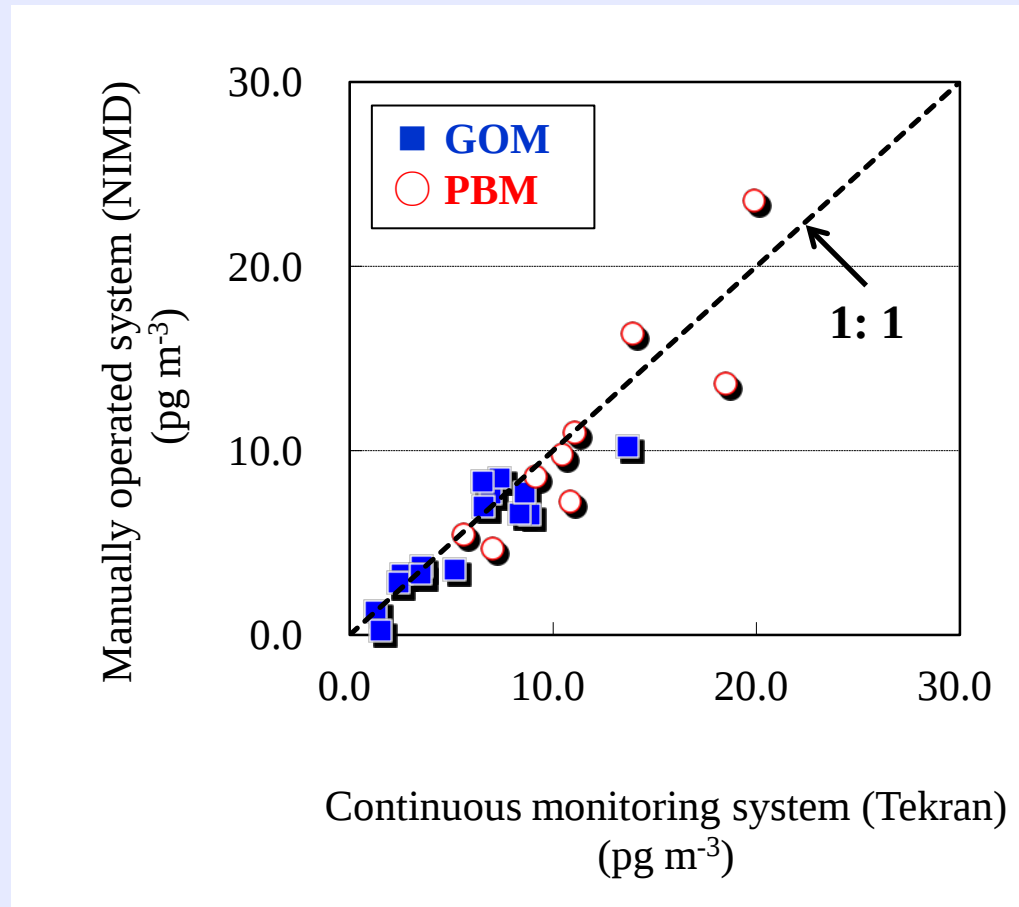
(4) Fall: 2 Nov. – 16 Nov. 2009



* Install soda lime trap just before gold cartridge

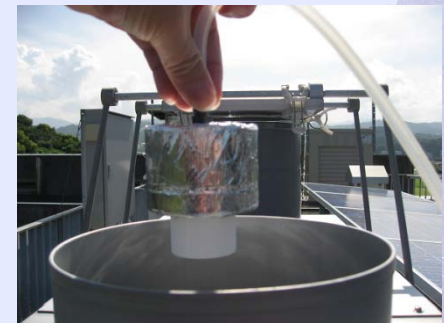
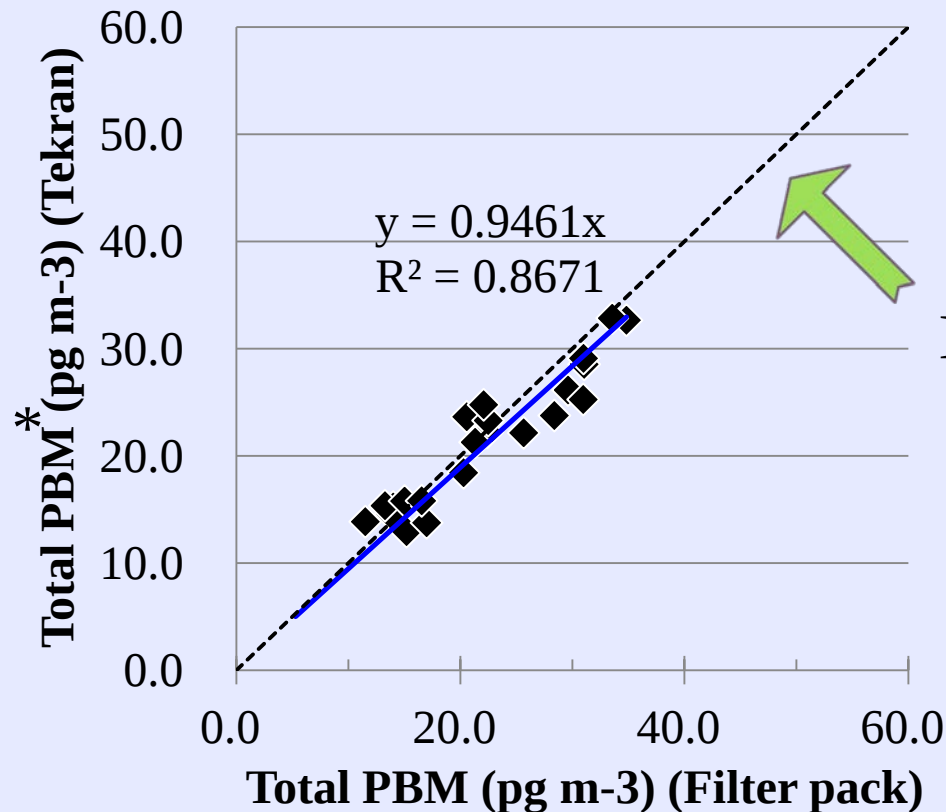
The data was provided by Ministry of the Environment, Japan (MOEJ)

Comparison of GOM and PBM measurement values



Results on simultaneous monitoring using a continuous online monitoring system (Tekran system, horizontal axis) and a manually-operated sampling system (vertical axis)

Comparison between total PBM (FP method) and Tekran analyzer (weekly average $\text{PBM}_{<2.5}$ plus $\text{PBM}_{>2.5}$ obtained by the analysis of Hg in impactor frits)



* Mean PHg(<2.5) calculated from Tekran data + Hg in impactor frits (>2.5)

Estimation on PBM dry deposition

$$\text{Dry deposition} = V_d * C$$

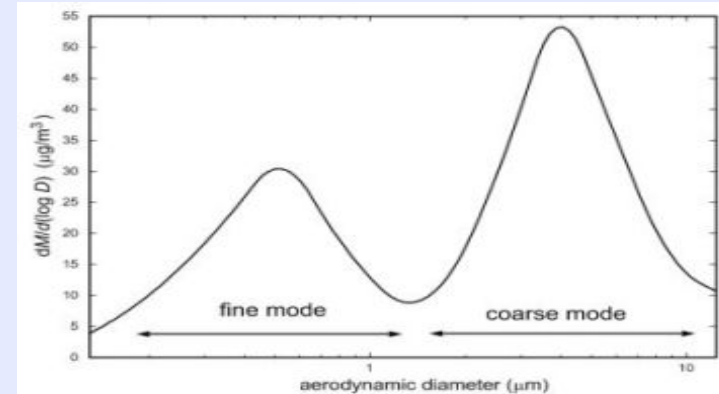
V_d : Dry deposition velocity

C : Atmospheric concentration

$$V_d = V_{st} + V_i$$

V_{st} : Stokes settling velocity

V_i : Inertial deposition velocity by turbulence



Coarse particles

Fine particles

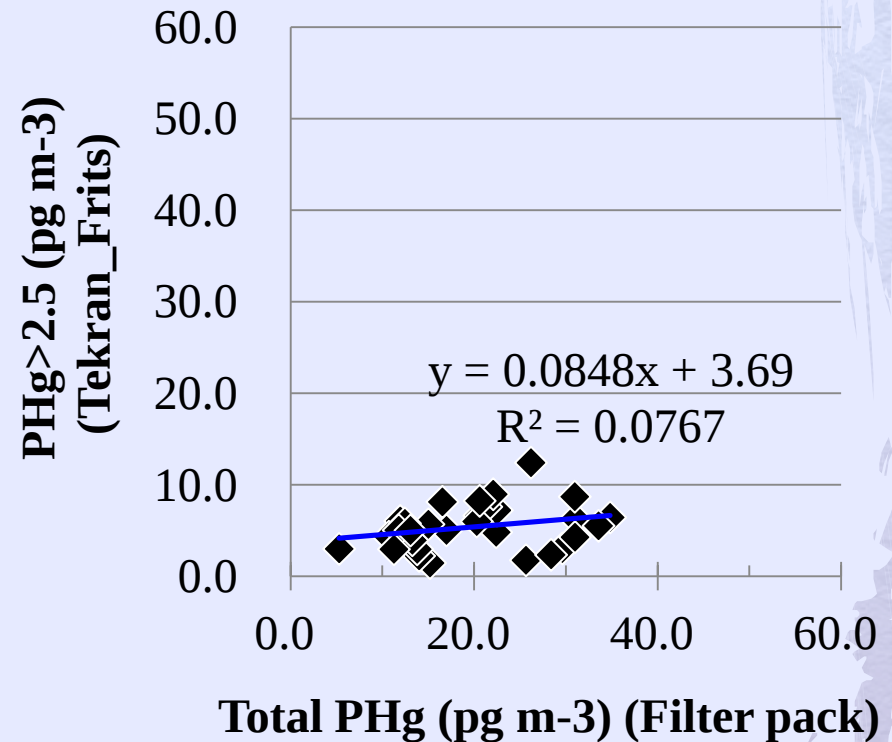
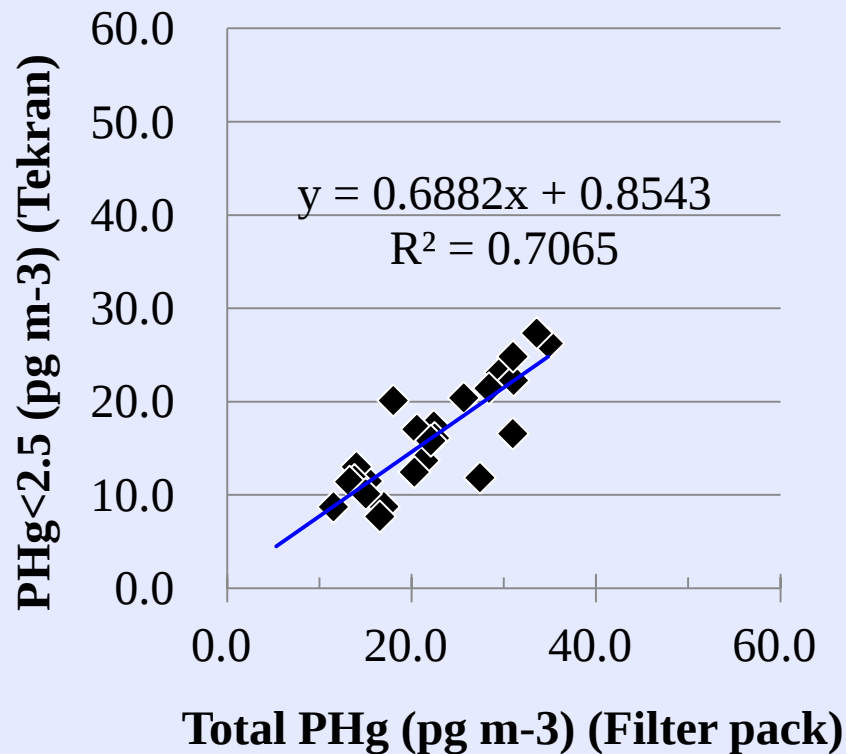
Representative particle size (µm)	V_d (cm s ⁻¹)
10	2
5	0.15
2.5	0.02
1	0.01

100 times

10 times

PBM in coarse particle greatly contributes to dry deposition of total PBM.

Relationships between total PBM and fine $\text{PBM}_{<2.5}$ (Left) and coarse $\text{PBM}_{>2.5}$ (Right), obtained at Fukuoka site





Guest room



Kitchen

Welcome to Minamata !