

# Field Evaluation of Mercury Vapor Analytical Methods: Comparison of the “Double Amalgam Method” and ISO 17733

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**Abstract:** In this study, a gold amalgam method called the “Double amalgam method” was compared with the ISO 17733 method for mercury vapor analysis method. In terms of sensitivity and ease of operation, the amalgamation method is superior to the oxidation method. Two parallel samplings were carried out in this research at a button battery factory, where the mercury vapor level in the air was about 0.001 mg/m<sup>3</sup> and at a fluorescent lamp factory, where the mercury vapor level was about 0.015 mg/m<sup>3</sup>. In the both cases, the measured values of the two showed good agreement with each other. As these two workplaces represent typical mercury levels in industries today, the double amalgam method is applicable to working environment measurement.

**Key words:** Mercury, Mercury vapor, Workplace air, Gold amalgam, Double amalgam, Hopcalite®, ISO 17733

The hazards of mercury exposure have been well known since early times. Recently, mercury is also a suspected of being an endocrine disrupter<sup>1</sup>). Environmental mercury concentrations in workplace air and/or personal exposure to airborne mercury are measured to prevent undue occupational exposure to mercury. The regulated values of mercury vapor in the workplace are 0.025 mg/m<sup>3</sup> (Ministry of Health, Labour and Welfare, Japan) and 0.01 mg/m<sup>3</sup> (OSHA, USA). As the Japanese regulation level was reviewed from 0.05 mg/m<sup>3</sup> to 0.025 mg/m<sup>3</sup> in 2004, more sensitive mercury vapor analytical methods are needed for work environment control.

There are two types of sampling and analysis methods for mercury vapor. One method is oxidation based mercury collection with cold vapor atomic absorption spec-

troscopy (CV-AAS). Oxidation method is widely used for industrial hygiene. In Japan a liquid collection method using permanganate oxidation has been adopted as the official assessment method<sup>2</sup>), while an air-oxidation method using a Hopcalite® based catalyst adsorbent tube is widely used in the U. S. and Europe<sup>3, 4</sup>). The latter method has become the international standard method, known as ISO17733<sup>5</sup>).

The other mercury sampling and analysis method is based on amalgamation. Mercury vapor is trapped onto gold or silver containing absorbent as metal-mercury alloy (amalgam). The mercury is thermally desorbed and introduced into CV-AAS. This amalgamation based analysis is also widely used as a sensitive method for mercury vapor measurement<sup>6–9</sup>). A method using a preheated second mercury trap, which captures mercury vapor and passes it through interfering substances such as volatile organic compounds, is called the “Double amalgam method”. At second step of the “Double amalgam method”, the mercury trap is heated up to at 700 °C to

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desorb mercury vapor for CV-AAS measurement. The double amalgam method was adopted as the Japanese official method for mercury vapor measurement in the environment air analysis<sup>9)</sup>.

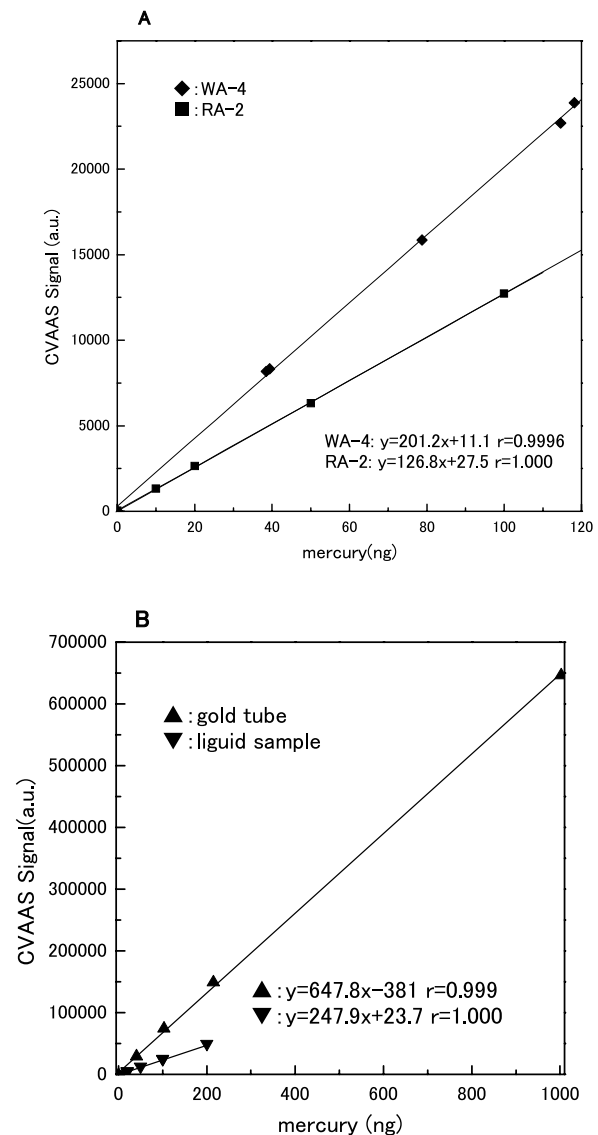
In terms of sensitivity and ease of operation, amalgamation method is superior to oxidation method. In this study, we performed parallel measurements of the ISO 17733 method and the double amalgam method at the two fields to introduce double amalgam method for work environment measurement.

The gold amalgam based absorbent was a packed gold-cromosorb tube supplied by Nihon Instruments Corporation (NIC, Tokyo, Japan, catalog code: M160A). Two air oxidation catalyst absorbent tubes for ISO 17733 were supplied by SKC (Eighty Four, PA, USA, catalog code 227-17-1A and 227-17-3A). Both tubes (227-17-1A and 227-17-3A) contain a Hopcalite<sup>®</sup> based absorbent called "Anasorb C300". The 227-17-1A tubes contain 200 mg of Anasorb C300 per tube and 227-17-3A tubes contain 500 mg of Anasorb C300 per tube, respectively. All air samples were collected using flow stabilizing pumps (Airchek 2000<sup>®</sup>, SKC or Pocket pump<sup>®</sup>, SKC).

In the present study, three types of CV-AAS based mercury analyzers were used: air sample analyzer (WA-4, NIC), aqueous sample analyzer (RA-2, NIC), and a multi-purpose mercury analyzer (SP-3D, NIC). WA-4 is composed a programmed thermal desorption unit with a second mercury trap and CV-AAS. RA-2 has a bubbler and CV-AAS. SP-3D has both functions of WA-4 and RA-2 and the double amalgam based thermal desorption unit and bubbler are exchangeable. SP-3D has the same performance and better usability than WA-4 and RA-2. In latter experiment of this study SP-3D was used instead of WA-4 and RA-2.

Figure 1 shows the calibration curves of CV-AAS in WA-4, RA-2 and SP-3D. Saturated mercury vapor was taken by gas-tight syringe and applied into WA-4 or SP-3D as a standard for the double amalgam method. Standard solution of mercury for atomic absorption spectrometry was used for RA-2 or SP-3D as the standard for ISO 17733. The calibration curves of CV-AAS were linear ranging from 0.01 to 1000 ng of mercury. The range was wide enough for work environment measurement. The variation of the background level of mercury in the 227-17-3A tubes was 5.0 ng ( $n = 5$ ) for the tubes used. The lower determination limit of ISO 17733 was set at 50 ng/tube ( $10\sigma$ ) in this study.

After air sampling, M160 tubes were put into glass tube containers one by one, and immediately sealed by butyl rubber stoppers. They were carried to our laboratory and analyzed 22 d after in the case of a field (*field A*) and 12 months after in the case of the other field (*field B*). It is recommended by the manufacturer to analyze the gold



**Fig. 1. Calibration curves of the CV-AAS instruments used in the experiments.**

A: The calibration curves of measurements of field A samples.  $\blacklozenge$ : Calibration curve of the WA-4 mercury vapor analyzer. The mercury vapor standards were generated by a standard mercury box which was containing saturated mercury vapor.  $\blacksquare$ : Calibration curve of the RA-4 liquid sample mercury analyzer for ISO 17733. The mercury vapor standards were generated by reductive vaporization by tin chloride. B: The calibration curves of SP-3D used for measurements of field B samples.  $\blacktriangle$ : Calibration curve for the double amalgam method.  $\blacktriangledown$ : Calibration curve for ISO 17733.

amalgam tube within 6 months of sampling.

After air sampling, the Anasorb C300 tubes were covered at both ends by attached caps, sealed and brought back to the laboratory. They were carried to laboratory and analyzed 22 d later in the case of *field A* and 21 months after in the case of *field B*.

**Table 1. Mercury concentration of workplace air in Field A and B**

| Sampling ID(sampling time)      | Anasorb C300<br>(ISO 17733)        |               | M160A (double amalgam method)      |               |
|---------------------------------|------------------------------------|---------------|------------------------------------|---------------|
|                                 | conc. ( $\mu\text{g}/\text{m}^3$ ) | Hg /tube (ng) | conc. ( $\mu\text{g}/\text{m}^3$ ) | Hg /tube (ng) |
| <i>Field A</i>                  |                                    |               |                                    |               |
| A (3.5 h) mean value n=2        | 1.14                               | 48            | 0.990                              | 20.79         |
| B (15 min)                      | 0.736*                             | 22.1          | 0.795                              | 11.92         |
| C (15 min)                      | 0.756*                             | 22.7          | 0.954                              | 14.31         |
| D (15 min)                      | 0.654*                             | 19.6          | 0.924                              | 13.85         |
| E (30 min)                      | 1.010                              | 60.6          | 1.002                              | 30.06         |
| F (30 min)                      | 0.931                              | 55.9          | 1.031                              | 30.93         |
| G (30 min)                      | 0.792*                             | 47.5          | 0.865                              | 25.96         |
| <i>Field B</i>                  |                                    |               |                                    |               |
| H (300 min) mean value n=4 (sd) | 15.1(8)                            | 892(50)       | 17.0(0.28)                         | 981(18)       |

\*:smaller than lower determination limit.

*Field A* is located in the Tohoku-area of Japan, and is a factory which makes battery cells for wristwatches. Mercury is used as a zinc amalgam in the production line. All samples were taken at a fixed sampling position, which was 1 m from the zinc amalgam packing machine at 1 m height above the floor. Both long term and short term sampling was performed. The sampling time for long term sampling (*sample ID: A*) was 210 min; the sampling volumes were 42 L for Anasorb C300, and 21 L for M160A respectively. The sampling times for short term sampling were 15 min (*ID: B, C, D*) and 30 min (*ID: E, F, G*); the sampling volumes were 30 L (15 min) and 60 L (30 min) for Anasorb C300, or 15 L (15 min) and 30 L (30 min) for M160A. For short term sampling, 227-17-3A (500 mg) tubes were used with a high sampling rate (2 L/min). For all other sampling, 227-17-1A (200 mg) tubes were used. The amount of mercury in the M160A tubes was measured by the WA-4 and the amount of mercury in the Anasorb C300 tubes was measured by RA-4 liquid sample mercury analyzer.

*Field B* is a factory in Korea which produces fluorescent lights. All samples were statically sampled close to a mercury injecting machine which injected mercury into 130 cm length lamps. A simultaneous sampling of four 227-17-1A tubes and four M160A tubes was performed. The sampling time was 300 min and the sampling volume was 300 L for both types of tube. The amounts of mercury in both types of tube were measured by the SP-3D.

The results of observed mercury concentrations in the air and the mercury quantities in each tube are shown in Table 1. Because the mercury concentration in *field A* was very low, mercury quantities in the 15-min sampling tubes (*ID: B, C, D*) and one 30-min sampling tube (*ID:*

*G*) were below the determination limit of ISO 17733. However, the mercury concentrations both methods showed good agreement. The double amalgam method had sufficient enough sensitivity and no interference. While the quantities of mercury in the tubes sampled at *field B* were near the upper determination limit of the double amalgam method, the double amalgam method gave the same results as those determined by ISO 17733. The samples measured at *field B* were analyzed after a storage period longer than the manufacturer's recommendation. However, both results showed good agreement and the travel blank tubes did not show any contamination. It seems possible to store these tubes for fairly long times at room temperature without loss or contamination.

The two fields measured in this study are typical of factories using mercury, while the mercury levels were different. The double amalgam method for mercury analysis is applicable to the measurement of mercury concentrations in workplace air.

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