

# Basic Detection Characteristics of Quartz Crystal Microbalance-based Method of Determination of Mercury

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Mercury (Hg) is a toxic element of global concern, and the Minamata Convention on Mercury came into force in 2017. Intensive discussions on the reduction of Hg emissions and the environmental monitoring of Hg have been undertaken through the United Nations Environment Programme. To reduce the environmental risks posed by Hg, a simple and rapid detection system for Hg in the environment is needed. We developed a simple Hg detection device based on a quartz crystal microbalance (QCM-Hg). It utilizes the direct reaction of Hg and the Au electrode of the quartz crystal element via the phenomenon of Au–Hg amalgamation. In this study, experiments were conducted to examine the new measurement system and to clarify its detection characteristics. The experimental results show a positive relationship between Hg concentration and frequency shift. When the gas flow rate is high and the measurement time is long, the Au–Hg amalgam reaction proceeds more efficiently and the frequency shift increases. On the basis of the calibration curve obtained, it is possible to determine the Hg gas concentration. In the case of  $10 \mu\text{g Hg/m}^3$ , a frequency shift of 4.8 Hz/min is obtained using a 30 MHz quartz crystal element of the surface mount device (SMD). This new detection system enables easy measurement of very low concentrations of Hg. These results revealed that QCM-Hg is a useful Hg measurement system.

## 1. Introduction

The Minamata Convention on Mercury<sup>(1)</sup> for the international management of mercury was adopted in 2013. The Japanese Government implemented the Act on Preventing Environmental Pollution of Mercury, which incorporates measures such as mercury reduction and waste management, and ratified the Minamata Convention on Mercury in 2016.<sup>(2)</sup> The government must manage and monitor sources of mercury emissions and mercury concentrations at waste treatment facilities.

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Japan's mercury emissions are much less than global mercury emissions. Artisanal and small-scale gold mining (ASGM) is a very large source of mercury emissions, accounting for about 37% of the total global mercury emissions.<sup>(3)</sup> The reason for the large mercury emissions from ASGM is that the gold amalgam method is used to extract gold. It is a very inexpensive gold extraction method and can be easily used by anyone. This method is mainly used in mountain and forest areas in Southeast Asia and South America. In addition to environmental pollution, concerns are raised about health hazards to workers owing to mercury exposure.<sup>(4–6)</sup> We do not have much data on health hazards to workers in these areas owing to a lack of detailed surveys. The WHO European Committee recommends that mercury concentrations in the work environment should be less than  $1 \mu\text{g}/\text{m}^3$  (about 0.12 ppb).

There are two methods of determining mercury levels in air:<sup>(7,8)</sup> one is based on the change in the amount of light absorbed, and the other involves the use of a gas detection tube for chemical reactions (detected as a color change) between a chemical substance and mercury.

Instruments used for light absorption measurement are very expensive, and many measuring instruments cannot be used in locations where commercial power supply is not available. On the other hand, gas detection tubes have low detection sensitivity at concentrations indicated in the WHO guidelines.<sup>(9)</sup>

Therefore, there is an urgent need for a simple detection system that is capable of measuring trace concentrations of mercury. To this end, we have developed a quartz crystal microbalance<sup>(10)</sup> (QCM)-based mercury detection system (QCM-Hg) and have been improving it to put it into practical use as a sensor that can be easily used by anyone, anytime, and anywhere.

## 2. Principle of Measurement

The QCM-Hg is based on the conversion of the change in the mass adsorbed on the electrode surface of the quartz crystal into a change in frequency. This principle is commonly used in gas and odor sensors.<sup>(11–18)</sup> Generally, when a QCM is used as a gas sensor, a detection film, on which the target gas is adsorbed, is formed on the electrode surface. This method is based on the gas adsorption and desorption mechanism on a detection film.

The detection method using a quartz crystal element is generally called a QCM method.<sup>(10)</sup> In the mercury detection mechanism of QCM, gold used as the electrode of the QCM reacts directly with mercury in the air. This reaction is called the amalgam reaction or amalgamation. Generally, the electrode of the QCM is gold and can be used for the detection of mercury under as-is conditions. Because of this, the system does not require film forming, making it an affordable system.

## 3. Method of Testing

We conducted tests to determine the basic detection mechanism of the QCM-Hg. The QCM used is of the surface-mount device (SMD) (NX3225SA; Nihon Dempa Kogyo Co., Ltd.) type. A SMD-type QCM is commonly used mainly in communications devices and is readily

available. Owing to its small size, the detection device was mounted on a substrate for ease of handling. The fundamental oscillation frequency of the SMD-type QCM is 30 MHz. Since the detection device is small, the detection part is capped with a flow cell for an efficient reaction of the mercury in the air with the gold electrode of the QCM (Fig. 1).

Figure 2 shows the test setup. A thermostatic chamber was used to maintain a constant temperature (SH-220; ESPEC Corp.). Gaseous mercury (Hg gas) at a given concentration and the QCM surface were kept at the same temperature. To produce the Hg gas used in the test, a trace amount of Hg (a few micrograms) was injected into a vaporization bottle and vaporized by supplying gas at a constant flow rate. Artificial air ( $N_2 + O_2$ ) and nitrogen as the reference gas were used in the test. There was no significant difference in results between the artificial air and nitrogen. A given amount of Hg gas was injected into a sample bag, diluted with the reference gas, and used as a sample gas for the test. The concentration of mercury was determined by measuring the concentration of the Hg gas using a mercury survey meter EMP-2 from Nippon Instruments Corporation (NIC).

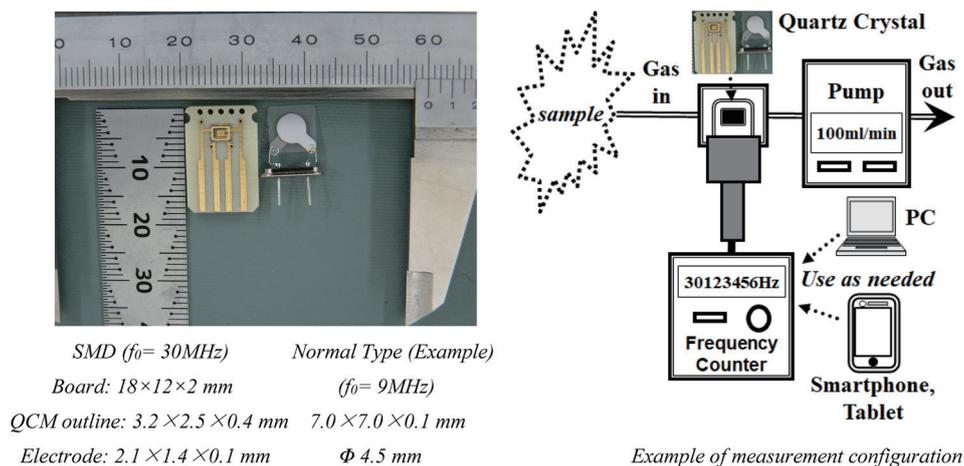


Fig. 1. (Color online) SMD-type QCM and example of QCM system

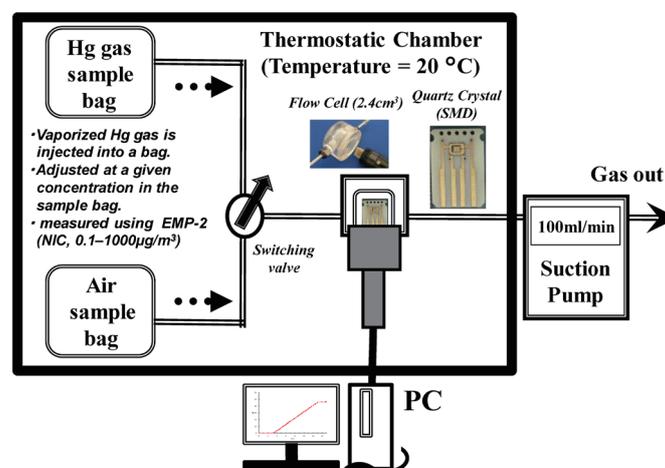


Fig. 2. (Color online) Test setup.

First, we conducted two tests: a test to determine the concentration range of mercury that can be detected and a test to investigate the response characteristics of this method. In the test of response characteristics, the artificial air or nitrogen was injected at a constant flow rate into the flow cell containing the quartz crystal element, and the change in oscillation frequency was observed. When mercury-free air is supplied to the microbalance, no reaction occurs; therefore, there is no change in the frequency. Then, the reference gas was changed with a sample gas containing a given concentration of Hg gas. The oscillation frequency of the QCM decreases as the concentration of mercury changes. The quantities of change in frequency were measured and recorded on the PC. The reaction between the gold on the electrode and mercury is irreversible. When the supply of Hg gas is stopped and the Hg gas is changed again with the artificial mercury-free air or nitrogen, the frequency of the QCM stops to decrease and remains unchanged.

#### 4. Test Results and Discussion

First, we investigated the response of the QCM to mercury. Figure 3 shows the response characteristics in a test run. In this test run, gas was supplied at a rate of 100 ml/min. Each measurement was carried out for 10 min at this flow rate, and the quantities of change in frequency during this period were obtained. Sample gas (1000 ml) was blown onto the electrode surface of the QCM. The test results showed that the quantities of change in frequency increase linearly at a constant rate.

Then, we obtained the maximum frequency change ( $\Delta f$ ) at several concentrations of mercury. The results showed that the change in frequency is proportional to the concentration of mercury. From the test results, we obtained a calibration curve on the basis of the change in frequency (Fig. 4). The following is an approximation formula for the calibration curve under the test conditions.

$$y = 1.883x \quad (1)$$

Here,  $y$  is the Hg concentration ( $\mu\text{g}/\text{m}^3$ ) and  $x$  is the frequency change (Hz/min).

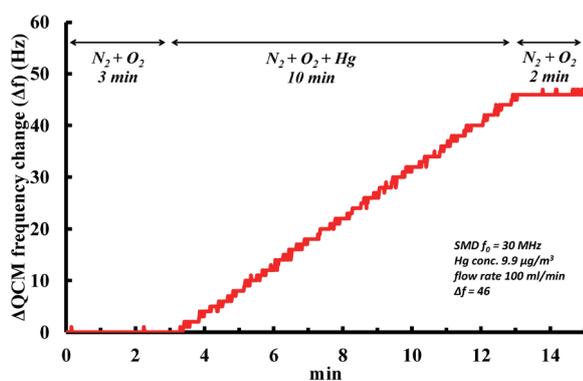


Fig. 3. (Color online) Response characteristic in test run.

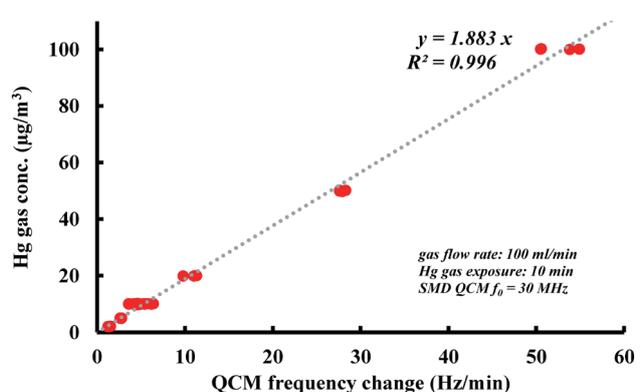


Fig. 4. (Color online) Calibration curve.

Under these test conditions, the change in frequency is proportional to the concentration of Hg. This means that on the basis of the calibration curve, the quantities of change in frequency can be converted into Hg concentration. A sensitivity of  $5 \text{ Hz}/\mu\text{g}/\text{m}^3$  (Hg gas exposure 10 min) was determined from the calibration curve. The above results show that under these test conditions, the mercury level of  $1 \mu\text{g}/\text{m}^3$  (about 0.12 ppb) in the work environment indicated in the WHO guidelines can be measured.

Second, we conducted a test to investigate the relationship between the quantities of change in frequency and the flow rate (Fig. 5). The test showed that the quantities of change in frequency increase with increasing flow rate. However, the rate of change does not increase much at a flow rate of 250 ml/min or higher. The flow velocity at the exit of the pipe (inner diameter, 2 mm) is about 0.5 m/s at a flow rate of 100 ml/min, about 1.3 m/s at a flow rate of 250 ml/min, and about 2.6 m/s at a flow rate of 500 ml/min. The test results indicate that in the amalgam reaction between Hg and the gold electrode, the amount of unreacted Hg increases and electrode  $\Delta f$  against flow rate decreases when the flow velocity of the Hg gas coming into contact with the gold is above the mercury amalgam reaction velocity.

Third, we conducted a test to investigate the relationship between the quantities of change in frequency and the measurement time. The test showed that the quantities of change in frequency increase with increasing measurement time. The detection sensitivity increases with increasing fundamental oscillation frequency. However, as with the flow rate, there may be a critical point for the detection efficiency.

This detection system uses the amalgam reaction between Hg and the gold electrode and has high selectivity to the target gas. This indicates that owing to the lack of an organic detection film, gases other than gaseous mercury are less easily adsorbed on the gold electrode surface. Our previous test results show that an unmodified electrode (without a detection film formed) is less affected by substances other than water, trimethylamine, and sulfur-based substances.<sup>(19–21)</sup> Even when volatile organic chemicals (VOCs) are present, the Hg-gold electrode reaction is irreversible and unique at room temperature, indicating that the amalgam reaction is less affected by VOCs. Therefore, the effect of substances other than mercury can be eliminated by

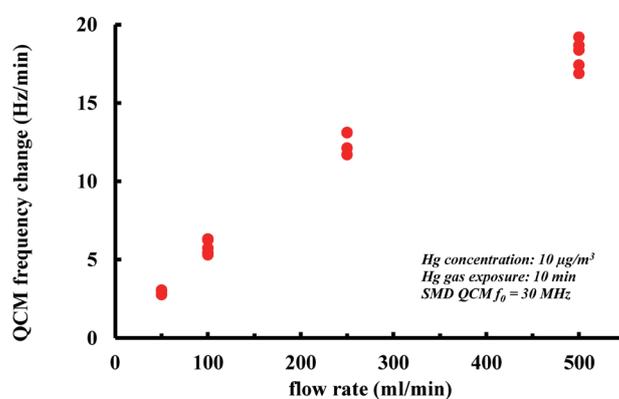


Fig. 5. (Color online) Relationship between quantities of change in frequency and measurement time.

continuing to supply only air or a non-Hg-containing gas to the QCM. Measurements carried out for an extended period may cause the adsorption of substances other than mercury, which are then immobilized on the surface of the quartz crystal element. The measurements were carried out for less than 1 h, indicating that immobilization is less likely to occur. However, we will further develop the system such that the personal exposure monitoring for mercury is possible for an extended period (about 8 h); to this end, we need to investigate the effect of mobilization and take measures to eliminate this effect. The amalgam reaction may be affected, particularly by suspended particulate matter (SPM) such as PM<sub>2.5</sub>. Since a disposable membrane filter (e.g., ADVANTEC's DISMIC-25AS with a pore size of 0.2  $\mu\text{m}$ ) is used in EMP-2, which is a commercially available mercury survey meter, it is less affected by SPM. This indicates that these effects may be reduced by using such a filter.

Generally, a QCM measurement system is susceptible to temperature and humidity as frequency change ( $\Delta f$ ). The QCM-Hg is the same, too. This QCM-Hg is promising for about 10–15 min per measurement. In a normal measurement environment, rapid changes in temperature and/or humidity are unlikely to occur in a short time, so this QCM-Hg does not consider their influence.

However, corrections ( $\Delta f$ ) of the QCM-Hg must be performed as needed. In that case, corrections ( $\Delta f$ ) of the QCM-Hg can be performed by measuring the frequency change again under the same temperature and/or humidity condition as those for the artificial air (mercury-free) measurement. The above results show that a system using a surface-mount-type QCM (30 MHz) has sufficient capability to detect mercury at concentrations below 1  $\mu\text{g}/\text{m}^3$ .

## 5. Conclusions

We have evaluated the basic characteristics of a QCM-based mercury detection system. The detection method used in this system is based on the reaction (amalgam reaction) between the gold electrode of a QCM and mercury and converts the change in the mass on the electrode surface into a change in frequency.

The following are the test results:

- (1) There is a proportional relationship between the Hg concentration and the change in oscillation frequency.
- (2) With higher measurement flow rates and longer measurement times, the reaction is promoted and the quantities of change in frequency increase. Also, the quantities of change in oscillation frequency do not increase much compared with the increase in the flow rate.
- (3) The detection system needs to be optimized by using a measurement unit (a flow cell).

These results show that with the QCM-based mercury detection method combined with optimal measurement conditions, we can detect Hg at a concentration of about 1  $\mu\text{g}/\text{m}^3$ , at which its detection has been possible only with commercially available analysis systems. Moreover, we can detect mercury concentrations below 1  $\mu\text{g}/\text{m}^3$ .

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