Application of the quartz crystal microbalance method for measuring mercury in the air of working environments involved to artisanal and small-scale gold mining (ASGM)

Kohji MARUMOTO*, Kazutoshi NODA**, João P. G. PEREIRA***, Marcelo DE OLIVEIRA LIMA++, Iracina M. DE JESUS***, Masumi MARUMOTO****, Hirokatsu AKAGI*****

* Environmental Chemistry Section, National Institute for Minamata Disease (NIMD), 4058-18 Hama, Minamata, Kumamoto 867-0008, Japan
** Environmental Measurement Research Institute, Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki, 305-8569, Japan
*** Environmental Section, Institute Evandro Chagas (IEC), Rodovia BR-316 km 7 s/n - Levilandia - 67030-000, Ananindeua, Para, Basil
**** Toxicologic Pathology Section, National Institute for Minamata Disease (NIMD), 4058-18, Hama, Minamata, Kumamoto 867-0008, Japan
***** International Mercury Laboratory (IML), 426-2 Fukuro, Minamata, Kumamoto 867-0034, Japan

† To whom correspondence should be addressed.

E-mail address: marumoto@nimd.go.jp (K. Marumoto)
Abstract

Artisanal small gold mining (ASGM) is responsible for approximately 40% of the total Hg emissions into the atmosphere worldwide. In developing countries, many people are occupied in ASGM activities. We developed a small, simple Hg measuring device, which detects Hg in the air based on the change of the oscillation frequency of an Au electrode on a quartz crystal microbalance (QCM). This device is called QCM-Hg. We tested the viability of the QCM-Hg in various work settings including a gold mining area and gold shops. In working environments with an airborne Hg concentration of several μg m⁻³, the changing rate of the oscillation frequency for either 2 or 3 min corresponded with the Hg concentrations measured using the conventional method of gold amalgamation and cold vapor atomic absorption spectrometer (CVAAS). The results revealed that the QCM-Hg is a useful device for real-time Hg monitoring in actual working environments involved in ASGM activities and Hg treatment facilities.

Keywords: Mercury, Air, Quartz crystal microbalance, Working environment, Artisanal small gold mining (ASGM), Gold shop
1. **Introduction**

Hg is a toxic element of global concern and is dispersed worldwide, primarily through atmospheric long-range transport. The Minamata Convention came into force in August 2017, and active discussions regarding Hg emission control and environmental risk management of Hg for humans and the natural environment are ongoing.\(^1\) Artisanal and small scale gold mining (ASGM) is responsible for approximately 40% of total Hg emissions into the atmosphere (2,220 tons in 2015).\(^2\) Gold is easily and cheaply extracted from mineral ores and alluvial gold by the use of elemental Hg. In developing countries, many people are occupied in ASGM, including children, despite the hard labor and health risks involved from the Hg vapor. Thus, understanding Hg exposure is an essential issue for the health management of the workers and residents in the vicinity of these mining areas. In addition, the Minamata Convention calls on parties to determine the actual situation of Hg use in industries, including ASGM activities, and reinforce Hg waste management, as well as the health management of workers. However, the situation remains unclear due to the lack of detailed real-time monitoring. A cold vapor atomic absorption spectrometer (CVAAS) and a cold vapor atomic fluorescence spectrometer (CVAFS) are typically used for real-time measurements of Hg in the air. These monitors have high accuracy but are costly and not portable, except for some novel instruments. Thus, a simpler, more cost-effective monitoring device is needed to obtain greater monitoring coverage.

Recently, the quartz crystal microbalance (QCM)\(^3\) has been used for measuring air pollutants such as trichloroethylene,\(^4\) HCl,\(^5\) and aerosol particles,\(^6\) among others, as a simple, real-
Researchers have reported the viability of QCM for measuring Hg in industrial environments, where concentrations are higher than 100 μg m⁻³. When airborne Hg reacts with the surface of the Au electrode of a QCM, the electric resonance oscillation frequency of the electrode changes in proportion to the mass change caused by the Hg adsorption. This device is called a QCM-Hg. It is reported, however, that the lowest observed adverse effect level (LOAEL) for Hg vapor is approximately 15 - 30 μg m⁻³, and WHO Europe established the guideline value for inorganic Hg vapor levels to be maintained at 1 μg m⁻³ as an annual average. Thus, a more sensitive QCM-Hg is needed for managing working environments where Hg is used.

We therefore developed a QCM-Hg that can measure relatively low concentrations of Hg (around 1 μg m⁻³), through a clean manufacturing technique of the Au electrode in the QCM-Hg. In addition, there is the possibility that this device become widely used in the future because the cost of this device is approximately 1,000 USD, 20 times lower than the cost of conventional Hg monitors. In the laboratory experiments using a standard Hg gas at a given concentration under the condition which the temperature was controlled, we found that (1) the shift of the oscillation frequency (Δf shift) is strongly correlated with the airborne Hg concentration, ranging from 1 to 100 μg m⁻³ for a 10 min observation; (2) the Δf shift is also positively correlated with a sampling flow rate under constant Hg concentration; and (3) the air temperature dependence affecting the Δf shift is approximately 0.3 Hz/°C between 10 and 40 °C.

In this study, we tested the viability of the QCM-Hg as a simple, cost effective screening method for airborne Hg in actual working environments, including a gold mining area and gold...
shops, in comparison to the measurements obtained using conventional methods of gold amalgamation and CVAAS. In addition, long term monitoring (more than 10 min) which is dependent on the airborne Hg concentration and the usage of the QCM-Hg as a real-time monitor are investigated for practical applications.

2. Methods

2.1 Principals of Hg measurement using a QCM-Hg

Generally, the electrode of the QCM is made of Au and can be used for Hg detection under as-is conditions. A QCM-Hg is a simple, small monitoring device which utilize a QCM through a technique involving airborne Hg reacting directly with the surface of an Au electrode in a quartz oscillator. The phenomenon relies on the amalgamation of Hg and Au. In QCM-Hg, the frequency decreases in proportion to the increase in mass due to the substance adsorbed on the electrode surface. The mass sensitivity is calculated from the Sauerbrey’s equation 3, as shown below (1).

\[ \Delta f = -2 \frac{F_0^2 \Delta M}{A (\rho \mu)^{1/2}} \]  

Here, \( F_0 \) is the fundamental frequency (Hz), \( \Delta M \) is the change in the mass of the deposited matter (g), \( A \) is the electrode area (cm\(^2\)), \( \rho \) is the crystal density (g/cm\(^3\)), and \( \mu \) is the elastic modulus (g/cm\(^2\)) of the crystal. Typically, the mass sensitivity of AT-cut, 9 MHz QCM is approximately 1 (ng/cm\(^2\) Hz). We used a 20 MHz (\( F_0 \), AT-cut) element for a higher sensitivity.
The element thickness of this quartz crystal Au electrode is 230 nm/side and the area of the Au electrode is 3.14 mm² (Piezo Parts Co., Ltd.). When using this 20MHz element, the sensitivity is approximately 5 times higher than when using the 9 MHz element. Therefore, the mass sensitivity of the 20 MHz element used in this study is approximately 0.2 ng/cm² Hz.

Figure 1 shows the QCM-Hg measuring system and Au electrode with a resonance frequency of 20 MHz. The air, including the Hg vapor, is pulled into the inlet of the system at a flow rate of 0.1 L min⁻¹ using a suction pump with a mass flow controller (Model 220-1000TC; SKC Inc.). A soda lime column and a hydrophobic Teflon® air filter with a 0.45 μm pore size are installed at the air inlet to exclude the influence of moisture and airborne particulate matter. The detection limit of another QCM detection system (F₀= 30 MHz, AT-cut) as a reference was less than 1 μg m⁻³ for an observation time of 10 min. The data on the oscillation frequency and the meteorological parameters including air temperature, relative humidity, and air pressure were recorded at every 10 s intervals during the operation.

2.2 Hg measurement using a conventional method

Airborne Hg concentrations in a gold mining area and gold shops were measured using a conventional Hg monitor based on a CVAAS (EMP-2Hi or EMP-2 Gold⁺; Nippon Instruments Corporation Co., Ltd.). The EMP-2Hi is a continuous CVAAS monitor without a gold amalgamation trap unit system. The detection limit of this monitor is 10 μg m⁻³, and the measurable upper limit is 9,990 μg m⁻³. Conversely, the EMP-2 Gold⁺ has a gold amalgamation trap unit system, and its detection limit is less than 0.025 μg m⁻³, derived by multiplying 3 times
the standard deviation of the field blank (0.013 ± 0.003 ng, N=5), and an air volume of 0.4 L (0.8 L) in the case of 1 min (2 min) of sampling with a flow rate of 0.4 L min⁻¹. The EMP-2Hi and the EMP-2 Gold⁺ were calibrated prior to measurements using a continuous standard Hg gas generator (MGA-1; Nippon Instruments Corporation Co., Ltd.) and the manual Hg injections from a standard Hg gas box (MB-1; Nippon Instruments Corporation Co., Ltd.). Using the EMP-2 Gold⁺, Hg amounts were calculated using the primary calibration curve, which is related to absorbance. When the Hg amount exceeded 4 ng, however, the calibration curve became non-linear and higher amounts of Hg were calculated using the cubic calibration curve (Figure 2).

2.3 Study site information

In the Tapajós River basin in the Brazilian Amazon, which is one of the most active regions for ASGM globally, Hg use and consequential Hg pollution are ongoing. Thus, we selected Itaituba city located in the middle of the Tapajós River basin as our study area. Since the 1980s, Itaituba city is one of the most famous cities in the Au trade. Nowadays, approximately 60 gold shops exist in the city and transact with ASGM workers, called Garimpeiros. In these shops, the Hg-Au amalgam received from ASGM workers is burned and the Hg is removed in the form of a vapor to obtain Au with of a high degree of purity. Many researchers have studied Hg pollution involving workers in both ASGM sites and in gold shops in and around this city. In this study, we tested the QCM-Hg system at 10 gold shops in October 2018 and 7 gold shops in November 2019. In addition, we selected a gold mining area in the Cachoeira do Piriá located 200 km east of Belém, the provincial capital of the Pará State,
since this region has been studied by our colleagues previously.\textsuperscript{19} In this mining area, mineral ores including Au are mined from 80 m below the ground and the Au in the ore is extracted using the Hg amalgamation method.

3. Results and Discussion

3.1 Application for gold shops

Figure 3 shows the time series of the $\Delta f$ shifts and relevant meteorological parameters such as air temperature, relative humidity, and air pressure in the gold shop (Shop No.8) observed in 2018. The QCM-Hg was measured in Hg-free air for approximately 5 mins at the start and end of the observation by inserting the gold amalgamation trap at the air inlet. During these periods, air pressure dropped, and the $\Delta f$ shift variation was small. In gold shops, the installation of a fume hood to exhaust the indoor air is a legal requirement in order to operate the business. Therefore, almost all of the shops had relatively low concentrations (from 1 to 5 $\mu g \text{ m}^{-3}$) of indoor Hg. In addition, the airborne Hg concentrations were lower in open dooried shops than in shops with closed doors and small spaces. Several gold shops with closed doors had extremely high Hg concentrations, which exceed the LOAEL (15 - 35 $\mu g \text{ m}^{-3}$),\textsuperscript{20} despite normal conditions. As shown in Figure 3, the $\Delta f$ shifts and the rate of change were raised when the Hg and Au amalgam was burned for Au purification. In this time, the airborne Hg concentrations also increased (Figure 4). Notably, the $\Delta f$ rate of changes (Hz/min) were calculated at 10 s intervals using the data from the reading at the time when it dated back 1, 2, 3.
and 5 mins to the current reading. The “SLOPE” function of Microsoft® Excel was used for the
calculation. The results are shown in Figure 4 along with the variation of the airborne Hg
concentrations in Shop No.8 observed in 2018. The Δf rate of change using 1 min of data
showed a large fluctuation which is most likely due to the influence of the pulsation from the
suction pump. On the other hand, an increasing time lag was observed when using the data for a
period longer than 3 min. From the data measured at the 10 gold shops in 2018, the Δf rates of
change using either 2 or 3 mins of data had strong correlations with airborne Hg concentrations.
However, the regression lines obtained from the data in 2018 exhibited a slightly wide range of
error. A previous study \(^1\) revealed that the installation distance between the Au electrode and the
inlet of the QCM-Hg unit was significantly influenced as a result of the Δf shift. In 2019, the
QCM-Hg measurement was carried out by ensuring that the electrode-to-inlet distance was
within 2 mm. Figure 5 shows the relationship between the airborne Hg concentrations and the
Δf rates of change on the basis of the slope calculation from 2 mins of the data measured at the
7 gold shops in 2019. The range of the error (95% confidence interval) of the regression lines
was reduced to 3.0 % in 2019 compared to 4.0% in 2018. Using the regression line and the
simple calculating program proposed above, we can roughly monitor the real-time
concentrations of airborne Hg from the Δf rate of change.

Generally, a QCM measurement system, including the QCM-Hg system, is susceptible to
influences from the temperature and humidity as the Δf shifts. We have already confirmed that
Δf shift increases by 0.3 Hz when the temperature rises by 1 Celsius degree for the observation
time of 10 mins. In addition, the $\Delta f$ shift also increases when the relative humidity rises. There is no data on the longer-term influences from the temperature and relative humidity. However, the air temperature and relative humidity in the majority of the gold shops was stable due to air conditioner control; during the QCM-Hg measurements, the temperature variations in each gold shop were within a maximum of 3 °C and the $\Delta f$ shifts caused by the temperature variation only were estimated at less than 1 Hz. As the soda lime column and the hydrophobic Teflon® filter were always used for the QCM-Hg measurements, the relative humidity during the measurements were relatively low (less than 70%) and variations in each shop were also small within 10%, except for Shop No.13 (17.3%). Additionally, in open field and a gold shop with no air conditioner, there is a possibility that the influences from the temperature and relative humidity tend to be partly offset because the temperature may be inversely proportional to relative humidity. Although influences on $\Delta f$ shifts and the $\Delta f$ rate of change due to the variations of the temperature and relative humidity can be large in the case of the low Hg concentrations, the calculated Hg concentrations by the QCM-Hg should be in alignment with actual concentrations despite of the different conditions. The $\Delta f$ rates of change, however, began to decrease after a measurement time of 20 min even when more than 70 - 80 $\mu$g m$^{-3}$ of the airborne Hg concentrations were kept going. This indicates that after this time period, the Hg absorption on the surface of the Au electrode is approaching saturation and subsequently the rate of the alloying reaction between Hg and the Au electrode can vary. Therefore, the measurable duration of the QCM-Hg depends on an airborne Hg concentration.
3.2 Application for gold mining area

In the gold mining area at Cachoeira do Piriá, the mean airborne Hg concentration was 4.6 ± 0.76 μg m⁻³ (N=4) in the workplace, where fine ore particles, including Au, are accreted onto the metallic plate covered by elemental Hg under a water flow. This process is carried out almost daily. Thereafter, the metallic plate with the Hg and Au amalgam was burned, and the amalgam was whittled away from the metallic plate and collected in a large bowl. In that time, the airborne Hg concentrations increased, albeit temporarily, reaching the upper limit of the Hg monitor, EMP-2Hi (9,990 μg m⁻³). In addition, the Δf shift of the QCM-Hg increased to more than 1,000 Hz for 1.67 min before it reached a plateau, indicating that the saturation point of the QCM-Hg had been reached. During this time, the Hg concentration was roughly estimated to be 3,030 ± 260 μg m⁻³, calculated from the calibration curve on the basis of the Δf rate of change. It is possible that the rate of Hg adsorption on an Au electrode is largely different under conditions of extremely high Hg concentrations as it is closer to the level of saturation. From the Sauerbrey’s equation, it is estimated that approximately 70 ng of Hg was adsorbed on the electrode surface of the QCM-Hg (f₀: 20MHz) under this estimated Hg concentration. Assuming that the actual Hg concentration was 10,000 μg/m³ or more, the theoretically adsorbed Hg amount on the electrode surface would be 200 ng or more. However, the measured Hg amount in the Au element of the QCM-Hg was only 120 ng, indicating that airborne Hg was no longer absorbed on the Au surface for the whole period of time. Although the estimated Hg concentrations calculated from the results of the Δf rate of change are lower than the actual
concentrations obtained by the conventional Hg monitor, this response of the QCM-Hg provides information on the upper limit of measurement when extremely high Hg concentrations are detected.

The concentrations at the surrounding sites at several dozen meters from the workplace were averaged at $0.28 \pm 0.23 \, \mu g \, m^{-3}$, ranging from 0.061 to 1.14 $\mu g \, m^{-3}$ (N=27). These values were less than one-tenth of those recorded at the workplace, but much higher than the concentrations in the background air ($0.001 - 0.002 \, \mu g \, m^{-3}$).

4. Conclusion

In the gold shops, the airborne Hg concentrations measured by the conventional Hg monitor ranged from approximately 1 $\mu g \, m^{-3}$ to more than 100 $\mu g \, m^{-3}$. The concentrations increased when the Hg-Au amalgam was burned to obtain the high-grade Au ingot. The $\Delta f$ rate of change of the QCM-Hg also changed, corresponding to the increased Hg concentrations at this time. For real-time monitoring of airborne Hg concentrations, the $\Delta f$ rate of change is continuously calculated using data during the period from the time going back either 2 min or 3 min to the current time, minimizing time lag. However, the measurable duration of the QCM-Hg depends on the airborne Hg concentration. In a gold mining area, extremely high Hg concentrations of more than 9,990 $\mu g \, m^{-3}$ were observed when Hg-Au amalgam on the metallic Hg plate was burned and collected by scraping the plate. During this time, the $\Delta f$ of the QCM-Hg rapidly changed and reached a plateau in a few minutes. This phenomenon indicates the reaction between the Au surface of the
QCM-Hg and Hg vapor is saturated due to the exposure of extremely high Hg concentrations over a short period. These results revealed that the QCM-Hg is a simpler, lower cost, real time Hg monitoring device that is useful in work settings where airborne Hg concentrations range from approximately 1 μg m\(^{-3}\) to 100 μg m\(^{-3}\). It should be noted, however, that the measurable duration depends on the airborne Hg concentration in working environments. In addition, this device has potential for use as a warning system, wherein an alarm sounds when a rapid increase in the Δf rate of change is detected. Further performance tests on the long-term influences from environmental factors, such as temperature and relative humidity, and the interference of other gases are required for practical use of the QCM-Hg as a real-time area monitor. In the future, it could be utilized as a personal Hg exposure monitor through the development of a long-term operation period of at least 8 hours and a smart wearable design.

Acknowledgement

We would like to thank M. Yurisawa for the interpretation and coordination during the field survey. In addition, we are grateful to S. Onitsuka, A. Morimoto and F. Hashimoto in NIMD for their assistance with the Hg analysis. This study was financially supported by the Environment Research and Technology Development Fund (JPMEERF20175004) of the Environmental Restoration and Conservation Agency in Japan.
References

1. United Nations Environmental Programme. Minamata Convention on Mercury. http://www.mercuryconvention.org/ (Accessed by 20 April 2020).

2. United Nations Environmental Programme, Chemicals and Health Branch. “Global Mercury Assessment 2018”, 2019, United Nations Environmental Programme.

3. G.H. Sauerbrey, Zeitschrift fur Physik 1959, 155(2) 206-222. (in German) https://doi.org/10.1007/BF01337937

4. K. Noda, H. Aizawa, S. Kurosawa, Sens. Mater. 2008, 20(4) 179-189.

5. M. Matsuguchi, Y. Kadowaki, K. Noda, R. Nakagawa, Sens. Actua. B: Chem. 2007, 120(2) 462-466.

6. M. Chen, F. J. Romay, L. Li, A. Naqwi, V. A. Marple, Aero. Sci. Technol. 2016, 50(9) 971-983.

7. Y. M. Sabri, S. J. Ippolito, J. Tardio, V. Bansal, A. P. Mullane, S. K. Bhargava, Sci. Rep. 2014, 4: 6741, DOI: 10.1038/srep06741.

8. K. M. M. Kabir, S. J. Ippolito, G. I. Matthews, S. Bee Abd Hamid, Y. M. Sabri, S. K. Bhargava, J. Sens. 2015, Article ID 727432, 7 pages, DOI: 10.1155/2015/727432.

9. WHO regional office for Europe, “Air Quality guidelines – Second edition – Chapter 6.9 Mercury”, 2000, Copenhagen, Denmark.

10. K. Noda, K. Marumoto, H. Aizawa, K. Tanida and T. Watanabe, Proceeding paper of the 33th SENSOR SYMPOSIUM (IEE Japan), 2016, SS33-24pm3-D-7 (in Japanese).
11. K. Noda, H. Aizawa, K. Marumoto, Proceeding of 2019 IEEE International Symposium on Olfaction and Electric Nose (ISOEN) 2019, 10.1109/ISOEN.2019.18972252.

12. K. Noda, H. Aizawa, K. Marumoto, Sens. Mater., 2020, 32(6), 2159-2166.

13. H. Akagi, Y. Kinjo, F. J. P. Branches, M. Harada, O. Malm, W. C. Pfeiffer, H. Kato, Environ. Sci. 1994, 3(1) 25-32.

14. H. Akagi, O. Malm, F. J. P. Branches, Y. Kinjo, Y. Kashima, J. R. D. Guimaraes, R. B. Oliveira, K. Haraguchi, W. C. Pfeiffer, Y. Takizawa, H. Kato, Water, Air, Soil Pollut. 1995, 80 85-94.

15. J. J. B. Nevado, R. C. R. Martin-Doimeadios, F. J. G. Bernardo, M. J. Moreno, A. M. Herculano, J. L. M. Do Nascimento, M. E. Crespo-Lopez, Environ. Int. 2010, 36(6) 593-608.

16. J. S. Marinho, M. De Oliveira Lima, E. C. De Oliveira Santos, I. M. De Jesus, M.C. N. Pinheiro, C. N. Alves, R. C. S. Muller, BioMed Res. Int. 2014, Article ID 945963, DOI: 10.1155/2014/945963.

17. L. S. N. Dos Santos, R. C. S. Müller, J. E. De S Sarkis, C. N. Alves, E. Da S Barbo, E. De O Santos, M. H. Da S Bentes, Sci. Tot. Environ. 2000, 261 1-8.

18. R. M. S. Santa Rosa, R. C. S. Müller, C. N. Alves, J. E. De S Sarkis, M. H. Da S Bentes, E. Da S Barbo, E. S. De Oliveira, Sci. Tot. Environ. 2000, 261 169-176.

19. T. C. De Souza, J. R. Dos Anjos, Environ. Sci. 2003, 10(2) 091-098.

20. WHO, “International Programme on Chemical Safety (IPCS) Environmental Criteria 118: Inorganic Mercury”, 1991.

21. F. Sprovieri, N. Pirrone, M. Bencardino, F. D'Amorel, F. Carbone, S. Cinnirella, V. Mannarino,
M. Landis, R. Ebinghaus, A. Weigelt, E.-G. Brunken, C. Labuschagne, L. Martin, J. Munthe,

I. Wangberg, P. Artaxo, F. Morais, H. Barbosa, J. Brito, W. Cairns, C. Barbante, M. Dieguez,

P. E. Garcia, A. Dommergue, H. Angot, O. Magand, H. Skov, M. Horvat, J. Kotnik, K. A.

Read, L. M. Neves, B. M. Gawlik, F. Sena, N. Mashyanov, V. Obolkin, D. Wip, X. B. Feng,

H. Zhang, X. Fu, R. Ramachandran, D. Cossa, J. Knoery, N. Marusczak, M. Nerentorp, C.

Norstrom, *Atmos. Chem. Phys.* **2016**, 16, 11915-11935.
Figure Captions

Figure 1 Photograph of an QCM-Hg system

Figure 2 An example of the calibration curve using Hg standard gas obtained by the conventional CVAAS monitor with a gold amalgamation trap unit system (EMP-2 Gold™; Nippon Instruments Corporation Co., Ltd.)

Figure 3 Time series of the Δf shift and meteorological parameters such as air temperature, relative humidity and air pressure observed at Shop No.8 in October 2018.

Figure 4 The time series of the Δf rate of change calculated at 10 s intervals using the data from the reading at the time dated back 1, 2, 3 and 5 min to the reading at the current time. Concentrations of airborne Hg measured by the EMP-2 Gold™ are also shown in this figure.

Figure 5 Relationship between the Δf rate of change over 2 mins and airborne Hg concentrations at the 7 gold shops observed in November 2019.
Fig. 1

QCM-Hg

Sensor for meteorological parameters

Air Pump

0.45μm Filter

Soda lime column

Air inlet

Au electrode of a QCM-Hg

($f_0 = 20$ MHz, AT-cut)
Fig. 2

\[ Y = (3 \times 10^{-3})x^3 - (4.6 \times 10^{-3})x^2 + 0.267x \]

\( r = 0.9999 \)
Fig. 3

---

**Analytical Sciences**

Advance Publication by J-STAGE
Received May 25, 2020; Accepted August 13, 2020;
Published online on August 21, 2020
DOI: 10.2116/analsci.20P178
Fig. 4

![Graph showing Air Hg (ng/m³) and Rate of Δf change (Hz/min)]

- Air Hg (ng/m³) → Δf 1min → Δf 2min → Δf 3min → Δf 5min
Fig. 5

![Graph showing the relationship between Air Hg concentration (μg/m³) and the Rate of δf change (Hz/min) for different shops. The equation Y = 0.204X with r² = 0.991, P < 0.001 is indicated on the graph. Different symbols represent different shops: Shop No. 2 (square), Shop No. 3 (diamond), Shop No. 6 (triangle), Shop No. 8 (cross), Shop No. 12 (circle), Shop No. 13 (black circle), and Shop No. 15 (square).]