Simple mercury determination using enclosed quartz cell with cold vapour-atomic absorption spectrometry

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COMMUNICATION

Simple mercury determination using enclosed quartz cell with cold vapour-atomic absorption spectrometry

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A simple method for determining total inorganic mercury (Hg) in solution using an enclosed quartz cell applying cold vapour-atomic absorption spectrometry (CV-AAS) can reduce sample volume, reductant, and cost compared with those of official methods. The Hg determination under the optimised conditions achieves precision similar to that of conventional CV-AAS.

Mercury (Hg) is a highly toxic element found in the environment both naturally and due to having been artificially introduced[1,2]. In the global material flow (MF) of Hg, the emission is 7060 to 9930 tons per year, 24 to 34% of which is artificial emission[1]. In recent years, the sources of Hg-MF, including products, processes, storage, industries, exports, and imports, have been strictly controlled and regulated due to the approval of the Minamata Convention on Mercury in October 2013[3]. Based on the treaty conclusion, simple handling, low Hg sample consumption, and easy installation for improving the sophistication of the Hg-MF control is required worldwide. In general, Hg concentration is determined using four types of methods, based on the combination of Hg vaporisation, such as heating or reduction, and measurement methods, such as atomic fluorescence spectroscopy (AFS) or atomic absorption spectroscopy (AAS)[4-7]. Of these techniques, the redacting vaporisation method is suitable for the determination of Hg solution samples in the low concentration range, and commonly uses open T-shaped quartz cells. Specifically, it requires: (1) a Hg sample volume of approximately 10–20 mL for each analysis, (2) a gas cylinder for sending Hg vapour, and (3) parallel-established local ventilation. Therefore, a simple Hg determination using an enclosed quartz cell (EQC) with cold vapour-AAS (CV-AAS) was developed to achieve the low consumption of Hg samples, low initial cost, and easy analytical procedures, without a gas cylinder or local ventilation system, thereby enhancing the availability of Hg determination worldwide. Several instruments, reagents, and methods used in this research are summarised within the 'Experimental' section in the supplementary material. The stages of this method, including Hg sample collection, storage, reduction, vaporisation, and determination were completed only in an EQC. For the vaporisation method of Hg, the addition of a reductant to the Hg sample under an open

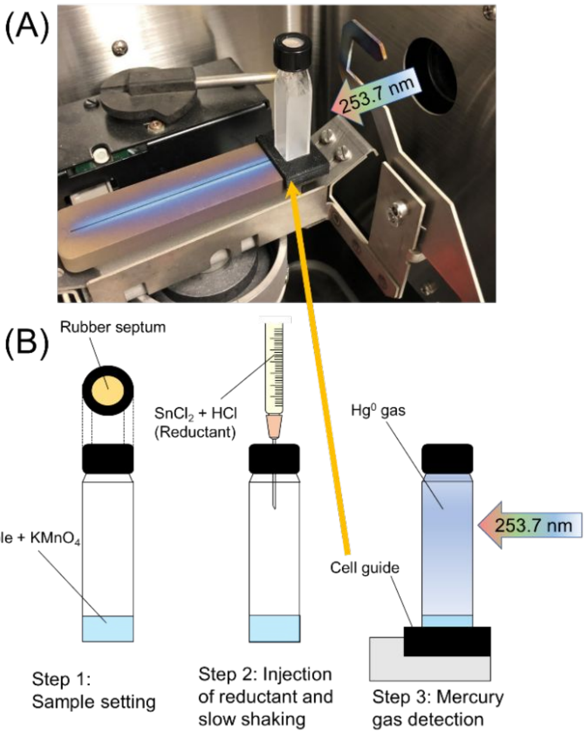

Fig. 1 (A) Photograph of EQC with CV-AAS. (B) Analytical procedure of EQC-CV-AAS.

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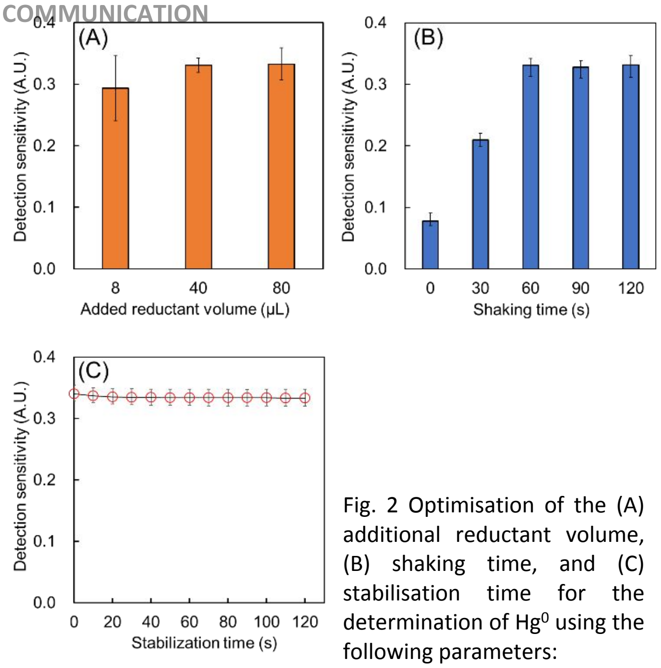

Fig. 2 Optimisation of the (A) additional reductant volume, (B) shaking time, and (C) stabilisation time for the determination of Hg^0 using the following parameters:
(A) Hg sample volume: 400 μL, Hg concentration: 200 μg/L, shaking time: 60 s, stabilisation time after setting the cell: 60 s; (B) and (C) added volume of the reductant: 40 μL, while all other conditions were the same as in (A).
A.U.: absorption unit

system and subsequent mixing of these solutions to reduce Hg in a closed system have been reported in previous studies[8,9]. However, mixing these under the open system carries a risk of analytical error due to leakage of the Hg^0 gas.

Based on the above points, the concept in this study is to complete all process steps under a closed system, which has not previously been reported. As shown in Fig. 1 (A), the developed EQC-CV-AAS method can be applied directly to the existing AAS system using a polylactic resin cell guide printed by a three-dimensional printer (da Vinci mini Maker 3D Printer, Taiwan). In this method, a commercially available quartz cell with a 10 mm path length and a rubber septum cap was used. The analytical procedure of the three steps in our method are shown in Fig. 1 (B). In step 1, a mixture of Hg sample with 50 mg/L $KMnO_4$ solution and 1.5 w/w% HNO_3 was inserted into the EQC and closed with a cap and a rubber septum. In step 2, a reductant (mixture of 10 w/w% $SnCl_2{\cdot}2H_2O$ and 10 w/w% HCl) was injected to vaporise the Hg followed by shaking at a slow pace for 60 s to prevent the solution from attaching to the light path wall of the cell, as shown in Fig. S1 (A). In step 3, vaporised Hg^0 gas that filled the EQC was determined using a basic flameless AAS system with a Hg electrodeless discharge lamp (253.7 nm). The detailed AAS conditions are summarised in Table S1.

To optimise the EQC-CV-AAS procedure, the Hg sample volume in step 1, reductant injection volume and shaking time in step 2, and the stabilisation time for the determination in step 3 were studied.

In step 1, sample volumes of 200–800 μL were studied. As shown in Fig. S1 (B), the quartz cell had a square pillar shape with an active height of approximately 32.0 mm, while the diameter of the incident light used in the AAS system was 10 mm. The detection sensitivity was increased by increasing the sample volume while the liquid levels accounting for the surface tension were increased as follows; 4.0-10 mm (200-800 μL). However, increasing the sample volume led to a larger standard error. This was because increasing the sample volume increases the potential risk of attaching the solution to the light pass of the cell wall by shaking the sample and reductant. Therefore, based on the above factors, the optimised sample volume was 400 μL, considering both minimisation of sample volume and increase of the detection sensitivity.

In step 2, reductant injection volumes of 8–80 μL were studied. As shown in Fig. 2 (A), similar detection sensitivities were obtained for reductant additions of 40 and 80 μL, while the variability for 8 μL was higher than for both 40 and 80 μL. Based on the above optimisation, 40 μL was selected as the optimal reductant addition volume, considering the adequate reducing capacity of Hg, as determined through this study. After the addition of the reductant, the shaking time was varied from 0 to 120 s. For shaking between 60 and 120 s, similar variabilities and detection sensitivities were obtained, while lower sensitivities were obtained at both 0 and 30 s owing to the incomplete reduction with shorter mixing time, as shown in Fig. 2 (B). Based on the data obtained above, our research group selected a shaking time of 60 s after reductant addition for this study.

In step 3, the stabilisation time for the Hg determination after setting the cell with a cell guide to the AAS system was studied from 0 to 120 s. As shown in Fig. 2 (C), it was nearly stable 30 s after setting the cell; an optimal stabilisation time of 60 s was selected for the determination of Hg^0 in this study.

From the optimised results, the analytical conditions were set to: a Hg sample volume of 400 μL, injected reductant volume of 40 μL, shaking time of 60 s, and a stabilisation time of 60 s.

Optimised EQC-CV-AAS was compared to the conventional CV-AAS adopted based on the official method (JIS K 0102, ISO 12846). These data are summarised in Table S2[10,11].

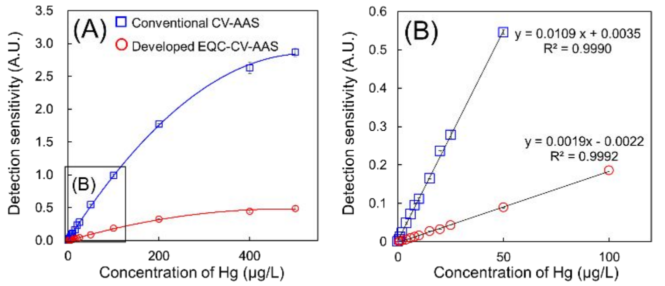

Fig. 3 Comparison between the linearity ranges of conventional CV-AAS and developed EQC-CV-AAS calibration curves using a Hg sample volume of 400 μL and a 60 s stabilisation time for analysis after setting the cell.

The required sample and reductant volume of the developed EQC-CV-AAS are 1/25-50 and 1/62.5, respectively, of conventional CV-AAS. Additionally, a gas cylinder for sending Hg vapour and a local ventilation system were required for CV-AAS, but not for EQC-CV-AAS.

Regarding the linearity range of the calibration curve, the highest linearity was obtained at 0.50–50 μg/L (R^2 = 0.9990) when using CV-AAS compared to 0.50–100 μg/L (R^2 = 0.9992) using EQC-CV-AAS, as shown in Fig. 3. In addition, linearities (R^2) were maintained at 0.9948 and 0.9962 under CV-AAS and EQC-CV-AAS, respectively, until 200 μg/L, while both linearities decreased dramatically from 400 μg/L (CV-AAS: R^2 = 0.9713, EQC-CV-AAS: R^2 = 0.9545).

The limit of detection (LOD) and limit of quantitation (LOQ) obtained using EQC-CV-AAS were 0.442 and 1.46 μg/L, respectively, while LOD and LOQ obtained using CV-AAS were 0.0360 and 0.118 μg/L, respectively. Conversely, the relative standard deviation (RSD) values (n = 5) of the developed EQC-CV-AAS, and conventional CV-AAS were 4.10% and 0.600%, and 3.65% and 0.720%, respectively, at 10 and 50 μg/L. Based on the above comparison between the developed and conventional methods, similar values were obtained for the RSD, while the LOD and LOQ of the developed method were approximately 12 times higher than those of the conventional method. This is because of the different quartz cell lengths of the developed (10 mm) and conventional (122 mm) methods, based on the Beer–Lambert law. The analytical performance data, including the linearity range of the calibration curve and its correlation coefficient (R^2), RSD, LOD, and LOQ, are summarised in Table S3.

The optimised EQC-CV-AAS and conventional CV-AAS were applied to the monitoring of Hg concentrations of extracted solutions from certified reference materials for Hg (0.0032 w/w% as $Hg(NO_3)_2$) in soils (JSAC 0463) and the river water sample with the artificially added Hg standard (2–50 μg/L). Generally, total concentration of Hg in solid samples such as soil and sediment are monitored by using thermal desorption (TD) method for the Hg vaporisation with AAS (TD-AAS) used for detection[12,13]. The advantages of this method are easy operation, possibility of the direct analysis of solid sample and lower working range (0.05–600 ng), whereas the disadvantages are requiring the individual apparatus integrated with AAS, heating block and gold trap for Hg and high implementation cost compared with the developed CV system.

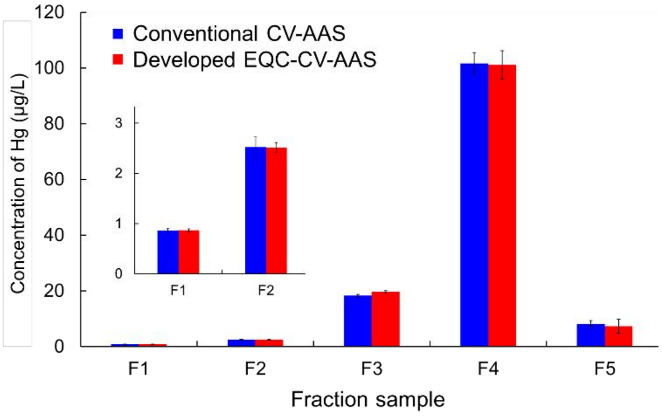

Fig. 4 Analysis of the five extractants (F1–F5) from certified reference materials for Hg in soils based on the Bloom extraction method.

Meanwhile, the Hg in liquid samples such as the soil extraction sample, river water and industrial wastewater are generally vaporised by using the conventional CV method with AAS[14,15] or AFS[16]. The advantage/disadvantage of the conventional CV and developed CV methods are provided in the previous section on page 1, and the analytical comparison of real samples is provided below.

In the case of the application to the soil extraction sample, Hg was extracted using a sequential extraction procedure reported by Bloom et al., which was developed for Hg in soil[17,18]. The extraction method includes five fractions (Fraction 1 (F1): deionised water, F2: 0.01 M HCl/0.1 M CH_3COOH, F3: 1 M KOH, F4: 12 M HNO_3, F5: aqua regia). The detailed extraction procedure is explained in the experimental section in the supplementary material. The monitored values of F1–F5 using the developed and conventional methods are compared in Fig. 4. The errors in Hg concentrations in the fractions measured by the developed and conventional methods were 0% in F1, 0.5% in F2, 5% in F3, 0.1% in F4, and 0.2% in F5. Accordingly, the Hg concentrations determined using EQC-CV-AAS agreed excellently with those by the conventional technique without being affected by the extractant of each fraction. The recovery rates of the conventional (100.9 %) and developed methods (99.6 %) were calculated using the standard addition method by spiking the 2 μg/L Hg standard in F4 of the extracted sample.

Meanwhile, river water sample was analysed using the developed and conventional CV-AAS method, and from this analysis, concentration of Hg was under the detection limit of the developed and conventional CV-AAS. Therefore, several concentrations (2–50 μg/L) of the Hg standard samples were added and compared between the analytical values of the developed and conventional CV-AAS methods. As shown in Fig. S2, the developed CV-AAS method ranged from 95.0 to 104.2 % of the recovery ration, whereas the conventional CV-AAS method ranged from 96.5 to 104.1 % of the recovery ratio.

Conclusions

In this research, a simple determination of Hg using EQC-CV-AAS was developed. The advantages of using this method are as follows: (1) reduction of the required Hg sample (1/25-50) and reagent (1/62.5) volume compared to those of the conventional CV-AAS, (2) no requirement for a gas cylinder for sending Hg vapour, (3) no requirement for a local ventilation system, and (4) easy adaptation to the existing AAS system. In addition, the optimised EQC-CV-AAS was compared to the conventional CV-AAS to demonstrate the usefulness of our method both in terms of the analytical performance as well as its application to monitoring extracted samples from the certified reference materials for Hg in soils and Hg standard added river water samples. As a result, similar analytical performances for the linear range of the calibration curve and for RSD were achieved, while the LOD and LOQ of the developed method were approximately 12 times higher than those of the conventional method because of the quartz cell length. From the above-mentioned benefits, the developed

EQC-CV-AAS method has the potential to replace the conventional CV-AAS method to monitor Hg as a simple determination method.

In the future research, different types or shapes of enclosed quartz cells with long light paths will be applied to this system to improve the detection sensitivity.

Conflicts of interest

There are no conflicts to declare.

Author Contributions

Daisuke Kozaki: Conceptualisation, Funding Acquisition, Project Administration, Supervision. Masanobu Mori: Supervision. Shinichi Hamasaki: Formal Analysis, Methodology. Tomotaka Doi: Formal Analysis, Methodology. Souma Tanihata: Conceptualisation, Resources. Atushi Yamamoto: Conceptualisation, Validation. Takeshi Takahashi: Investigation. Koutarou Sakamoto: Investigation. Shigeto Funado: Investigation.

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