

## Improving a continuous mercury analyzer with circulated carrier gas: Economic and operational advancements

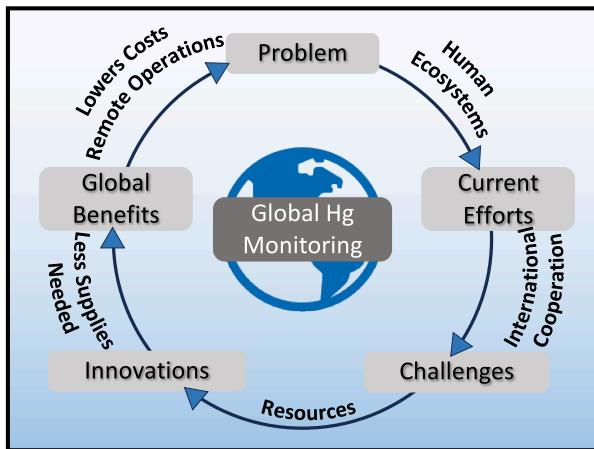
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### HIGHLIGHTS

- Industrial mercury emissions have led to global ecological and health issues, demanding international cooperation and monitoring.
- Traditional Hg analyzers require frequent and costly carrier gas replenishments, limiting their use in remote environments.
- A new Hg analyzer prototype reduces carrier gas usage by 99%, reducing operational costs in isolated locations.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

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### ABSTRACT

Elevated mercury (Hg) emissions since industrialization have created worldwide elevated levels of Hg in environment, causing ecosystem and human health impacts. Addressing these concerns requires across-nation efforts and international cooperation. In cooperation with the United Nations Environment Programme (UNEP), through its implementation of the Minamata Convention (MC), several international and intranational projects have monitored Hg levels in the atmosphere, water, soil and biota for decades. Obviously, these global monitoring projects require substantial resources, such as government funding, human resources, and analytic instruments. Different types of Hg analyzers have been developed and used in these global monitoring projects, however, most of them require inert carrier gas (i.e. Ar, He) supply, especially if detection requires fluorescence spectroscopy. Frequent consumption and replenishment of carrier gas during normal operation incur substantial financial and human resource costs. Therefore, these instruments cannot operate autonomously for long periods of time and require a carrier gas cylinder exchange, a limitation especially in remote regions and on ocean research cruise campaigns where it is challenging to function autonomously for long duration, limiting data collection in these locations. To address this issue, we developed a novel prototype automated Hg analyzer with a new design using a circulated carrier gas system. This development decreases the carrier gas consumption and

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increases the Hg analyzer operation duration, saving up to 99% on carrier gas consumption compared to the widely used Tekran 2537 and NIC AM-6F atmospheric Hg analyzers instruments. By using the circulated carrier gas design, our Hg analyzer only consumes 1 L per week. Overall, this improvement not only saves carrier gas but also enhances the instrument's self-operating capability in remote areas and reduces the financial and human resource costs associated with frequent replacement of the carrier gas.

## 1. Introduction

Elevated mercury (Hg) emissions since the industrial period have become a global concern, as it has triggered widespread ecological and human health issues (AMAP/UNEP, 2018). As Hg can be dispersed globally through atmospheric transport, ocean circulation and river runoff and accumulate into soil, water and biota within a short time scale to elevated levels (Amos et al., 2015; Driscoll et al., 2013), this environmental challenge demands collective actions that go beyond individual countries and economies and requires strong international collaboration (AMAP/UNEP, 2018). Indeed, the United Nations Environment Programme (UNEP) has organized scientists and led international efforts to facilitate the implementation of initiatives and regulations among countries, such as the Minamata Convention (MC).

Under MC, many cooperative efforts have led to the establishment of numerous international and national projects aimed at monitoring Hg levels in various environmental compartments, including the atmosphere, water, soil and biota, thereby, mitigating Hg emissions and releases from human activities. For example, the Global Mercury Observation System (GMOS) (Sprovieri et al., 2013), Global Observation System for Mercury (GOS<sup>4</sup>M) (Pirrone et al., 2022), European Monitoring and Evaluation Programme (EMEP) (EMEP, 2018), Asia Pacific Mercury Monitoring Network (APMMN) (Sheu et al., 2019), Arctic Monitoring and Assessment Programme (AMAP) (Hung et al., 2010) and National Atmospheric Deposition Program (NADP) (Gay et al., 2013) have operated many monitoring sites across Europe, Asia-Pacific, Arctic and North America regions for the long-term and high precision observations and analysis of Hg levels in atmosphere, water, soil and biota. Although these comprehensive monitoring endeavors have provided large coverage datasets, the execution of these extensive monitoring programs demands significant resources, including government funding, skilled specialists, and analytical instruments.

One of the major missions in the monitoring of Hg levels is determining the atmospheric Hg species, especially elemental Hg (Hg<sup>0</sup>), the dominant atmospheric form, which necessitates the design and utilization of a high-resolution automatic Hg analyzer. Most of these Hg analyzers have been built based on the principle of determining the elemental Hg concentration in air using atomic fluorescence spectroscopy with the need for a continuous supply of carrier gas (i.e. N<sub>2</sub>, Ar, He) (Feng et al., 2000; Fitzgerald and Gill, 1979), while there are some types of Hg analyzers that don't require carrier gas supplies (e.g., envea UT-3000). This need for carrier gas poses logistical and financial challenges, as it not only involves the consumption of the gas but also requires its regular replenishment to maintain the operation of the Hg analyzer. Therefore, the demand for carrier gas becomes a particular burden in the context of long-term monitoring projects in remote locations or places with limited resources. For example, many of the monitoring sites are located in remote (e.g., islands, rural fields or in deep forests) (Zhou et al., 2023), or inaccessible areas (e.g., mountains, glaciers, permafrost) (Swartzendruber et al., 2006), or conducted as part of cruise campaigns (He and Mason, 2021; Mason et al., 2017), or during aircraft campaigns (Lyman and Jaffe, 2012; Swartzendruber et al., 2009a). Some monitoring sites are located in developing and underdeveloped countries (e.g., Algeria, Indonesia) which are not able to manufacture pressurized inert gas cylinders or have limited access to Ar or He, and this causes extra costs to import supplies from abroad, given the limited funds from governments and international organizations (Pirrone et al., 2022). Such monitoring locations can face heightened

challenges due to difficulties in ensuring a steady supply of the necessary consumables, including carrier gases. Passive samplers are one mechanism to overcome these sampling issues, but these devices cannot currently collect Hg data at high resolution (Naccarato et al., 2021). Overall, reliance on instruments with high consumption of carrier gas largely hampers the automatic monitoring level of Hg in remote locations at high resolution, by restricting their operational duration and the scope of data collection on Hg pollution.

To address this limitation, a new design of Hg analyzer is urgently needed to improve the extent of automatic monitoring by lowering carrier gas consumption and decreasing the financial and human resource requirements. There has been the development of passive air samplers for Hg, which can save costs on deployment and maintenance. However, the limitations of passive sampler are apparent: 1) lower sensitivity and specificity; 2) they are influenced by environmental conditions (e.g., wind speed, humidity, temperature, etc.); 3) the longer time required for obtaining a detectable Hg signal; 4) their difficult *in situ* calibration; and 5) the inability to capture rapid changes in the Hg levels (Huang et al., 2014). Therefore, the high-resolution active Hg sampler still has substantial advantages for atmospheric Hg monitoring in most cases as it provides important information about diurnal and other short-term variations that can enhance understanding of Hg sources. In this study, we describe a simple and robust prototype automatic Mercury Analyzer with Circulated carrier gas (MAC), which is newly developed, calibrated and tested in the laboratory. This MAC uses carrier gas to flush the entire sampling system at the beginning of a session, then the carrier gas is trapped within the system's gas loop for repeated use. During the circulation, carrier gas passes through a Hg scrubber (activated carbon trap) which can remove remnant Hg<sup>0</sup> vapor from the recirculating gas. The whole circulation of carrier gas during sample analysis follows its passage after the scrubber through soda-lime trap pretreatment, the dual gold trap operational (A/B) section used for continuous measurement, and the cold vapor atomic fluorescence spectrometry (CVAFS) detector. Air sampling occurs with a diaphragm pump, and the airflow is monitored with a mass flow controller (MFS) in the system's sampling train. Carbon traps remove Hg from air for calibration and blanking operation of the instrument providing Hg-free air ("zero air"). This MAC is derivative to the commercial Hg analyzers, such as Tekran 2537 and NIC AM-6F, for automatically and continuously determining Hg<sup>0</sup> concentration in the atmosphere. It has a low detection limitation (DL) of 0.2 ng/m<sup>3</sup> and, surprisingly, low carrier gas consumption of ~1 L/week, compared to Tekran 2537X at ~700 L/week and NIC AM-6F at ~250 L/week. The successful laboratory test with this MAC indicates it can maintain high time resolution (5–10 min), and high precision (<5% relative variation during 12 h) comparable to the other automated samplers, but with low carrier gas consumption. Despite its advantage of low gas use, this prototype MAC demonstrates that there is gradual increase of the relative variation between consecutive samples (>5%) after the carrier gas has been circulated for more than 12 h, which could be due to the buildup of external air components in the system loop, such as diatomic molecules (i.e. N<sub>2</sub>, O<sub>2</sub>) that can quench the fluorescence, raise the baseline of the CVAFS detector and increase the noise signal. Therefore, there is more work necessary to address this problem for the future researcher to allow for longer use of the circulated carrier gas. However, we present the information here to allow the Hg community to benefit from this prototype MAC for current and future cost-effective and long-term Hg monitoring projects.

## 2. Materials and methods

### 2.1. Experimental apparatus

The design diagram of the MAC is shown in [Fig. 1](#) and the basic principle is similar to the commercial Hg analyzers, such as Tekran 2537X and NIC AM-6F, with the ability for continuous atmospheric Hg monitoring however, equipped with innovated circulated carrier gas system. Therefore, the biggest difference of this MAC operating principle and working logic is that once the instrument in the running mode, the carrier gas that has been introduced into the system is contained in the gas lane and recirculated.

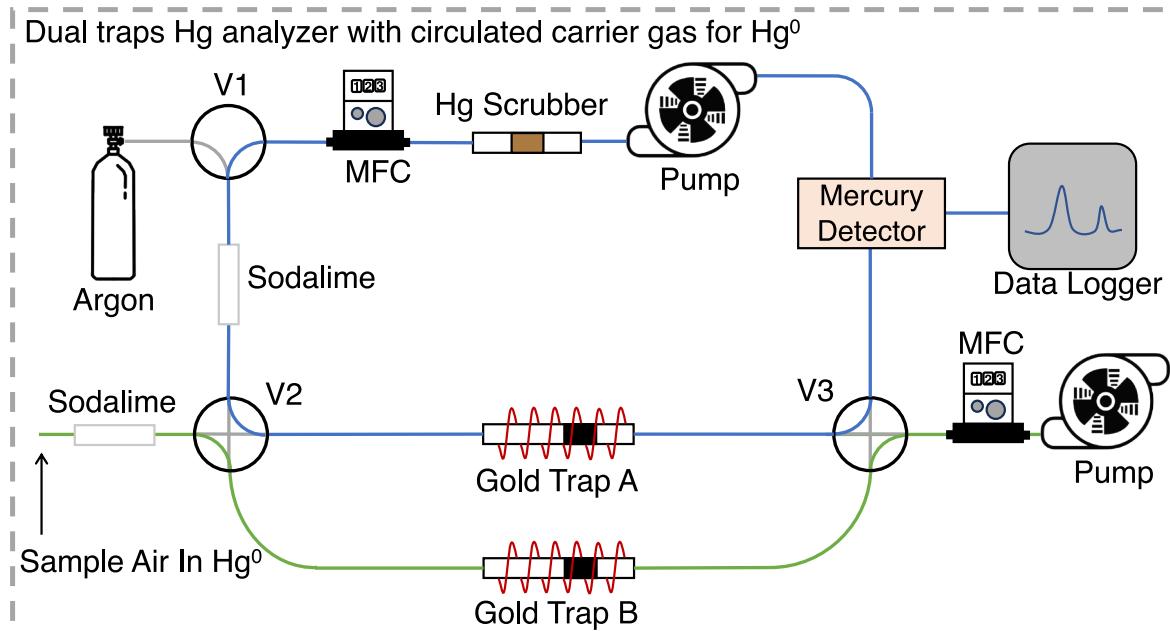
Detailed setup parts and operations of this MAC are as follows. The carrier gas for this MAC is argon (UHP, Airgas Inc.), which is the most common carrier gas for the CVAFS detector. Before the MAC is set into the running mode, the carrier gas is introduced into the inner circulation loop of the gas lane at  $\sim 5$  psi, which then passes through the soda lime trap (4–8 mesh, Alfa Aesar; 10 cm length, 1/4 in. OD) for removing the water vapor, a gold trap (gold-coated borosilicate glass beads, Brooks Rand; 10 cm length, 1/4 in. OD quartz tube), the CVAFS detector (Tekran Inc.), and then to the Hg scrubber where  $\text{Hg}^0$  is permanently removed from the carrier gas. The voltage information from the CVAFS and the peak area is recorded and integrated using a PeakSimple chromatography data system (model 333, SRI Instruments Inc.). The analysis step takes 2 min from the start of the thermal desorption to the peak integration. Then, the entire cycle then finishes and the gold trap B remains in the circulated loop lane until the gold trap A completes the sampling and the next cycle starts. The carrier gas is circulated in the loop lane until the baseline of the CVAFS starts to drift (after 12 h or longer if more variability is tolerated by the analyst), then new carrier gas can be flushed into the system to replace it. The MAC setting and analytical parameters are summarized in [Table 1](#). The sampling step and analysis step are controlled by a programmable script which mainly commands the solenoid valves (V1, V2 and V3) in the circulated loop lane, and the heating coil and cooling fan for the gold traps (A and B). All tubing and connectors are Teflon with 1/4 in. OD (Cole Parmer Inc.), unless elsewhere stated. And the total length of Teflon tubing used in this MAC is about 1 m, which results in the volume of the circulated loop lane for carrier gas of  $\sim 0.03$  L.

While in the running mode, during an entire adsorption-desorption cycles, the two gold traps (A and B) are always working separately – one is in the sampling lane while the other one is in the circulated loop lane for analysis. For example, when gold trap A is in the circulated loop lane and gold trap B is in the sampling lane, the sampling air with  $\text{Hg}^0$  will be drawn through the soda lime trap for removing the water vapor and then  $\text{Hg}^0$  will be absorbed by the gold trap B according to the amalgamation process. The sampling flow rate used here is 1 L/min, which can be adjusted between 0.5 and 2 L/min. The sampling time is 10 min in this study, which can also be changed based on the ambient  $\text{Hg}^0$  level. As the MAC's DL is 0.2 ng/m<sup>3</sup>, a longer sampling time can enhance the ability for Hg detection. Once the sampling is finished

collection, the role of two gold traps will be swapped by switching the flow paths as controlled by the solenoid valve V2 and V3. Then the gold trap A is in the sampling lane for the next cycle of sampling, and the gold trap B is in the circulated loop lane which is ready for analysis. The carrier gas is circulated in the loop lane at 60 ml/min and is controlled by the MFC. The analysis of gold trap B relies on thermal desorption at 500 °C for 30 s using the nichrome resistance wire coil, wrapped around the trap. The argon carries the desorbed  $\text{Hg}^0$  from gold trap B to the CVAFS commercial detector (Tekran Inc.) and then to the Hg scrubber where  $\text{Hg}^0$  is permanently removed from the carrier gas. The voltage information from the CVAFS and the peak area is recorded and integrated using a PeakSimple chromatography data system (model 333, SRI Instruments Inc.). The analysis step takes 2 min from the start of the thermal desorption to the peak integration. Then, the entire cycle then finishes and the gold trap B remains in the circulated loop lane until the gold trap A completes the sampling and the next cycle starts. The carrier gas is circulated in the loop lane until the baseline of the CVAFS starts to drift (after 12 h or longer if more variability is tolerated by the analyst), then new carrier gas can be flushed into the system to replace it. The MAC setting and analytical parameters are summarized in [Table 1](#). The sampling step and analysis step are controlled by a programmable script which mainly commands the solenoid valves (V1, V2 and V3) in the circulated loop lane, and the heating coil and cooling fan for the gold traps (A and B). All tubing and connectors are Teflon with 1/4 in. OD (Cole Parmer Inc.), unless elsewhere stated. And the total length of Teflon tubing used in this MAC is about 1 m, which results in the volume of the circulated loop lane for carrier gas of  $\sim 0.03$  L.

### 2.2. Peak integration

The fluorescence signal from the CVAFS is amplified 100 times and recorded at 10 Hz by the PeakSimple data-logger. Ideally, the CVAFS would detect a symmetric Gaussian-shaped peak. However, peaks often appear asymmetric with a long tail, complicating peak identification and area integration. To address this, we developed an algorithm with two main steps: 1) identifying the peak start and end points by fitting the signal to a log-normal distribution, and 2) integrating the area between these points. The signal typically emerges at a fixed retention time,



**Fig. 1.** Schematic diagram of the prototype automatic Hg analyzer with circulated carrier gas (MAC) showing the main sampling and analytic steps, including dual gold traps, mass flow controllers (MFC), diaphragm pumps, soda lime tubes, Hg scrubber, solenoid valves, cold vapor atomic fluorescence spectrometry (CVAFS) and data logger. The system allows the continuous measurement of atmospheric  $\text{Hg}^0$  at 10-min time resolution with circulated carrier gas.

**Table 1**

Settings of automatic Hg analyzer with circulated carrier gas and analytical parameters used and validated in this study.

Sampling lane	
Sampling flow rate	1 ± 0.1 L/min (by mass flow controller)
Drying tube	Soda lime (5.0 g, 4–8 mesh)
Sample trap	Gold borosilicate glass beads (1 g)
Sampling duration	10 min
Circulation loop lane	
Carrier gas	Argon (UHP)
Carrier gas loading	5 psi
Circulation flow rate	60 ± 2 ml/min (by mass flow controller)
Residence time	30 s
Heating temperature	500 ± 50 °C (30 s)
Hg scrubber	Activated carbon (3 g)
Retention time of Hg <sup>0</sup>	50 s
Analysis duration	2 min
Detector and data logger	
Detector	CVAFS (Tekran 2500)
Data logger	PeakSimple (Model 333)
Peak integration	LabVIEW or other software
Valve controller	Arduino UNO

approximately 50 s after heating the nichrome wire coil, and exhibits a right-skewed distribution, similar to a log-normal distribution. The fitting equation used is:

$$f(t) = \frac{1}{t\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln t - \mu)^2}{2\sigma^2}\right)$$

where  $t$  is time,  $\sigma$  represents the peak width and  $\mu$  is the mode time. [Fig. S1](#) illustrates a typical peak and its fit. Post-fit, the curve helps pinpoint peak start and end points. The start is marked by an increase over seven consecutive time points exceeding a 20 mV interval, and the end by a decrease over five points below a 15 mV interval. The right skew of the peak necessitates more stringent criteria for start point identification. The baselines at the start and end are calculated using the ten preceding and succeeding signals, respectively. The area is then computed as:

$$\text{Area} = \sum_{t_{sr}}^{t_{end}} \text{signal}(t) - \frac{(b_{sr} + b_{end})(t_{end} - t_{sr})}{2}$$

where  $\text{signal}(t)$  is the recorded millivoltage at each time point,  $t_{sr}$  and  $t_{end}$  are the start and end time point,  $b_{sr}$  and  $b_{end}$  are the respective baseline values. With this algorithm, the peak area of each component can be calculated by the program. Also, there are some other algorithms of peak area integration, which could be used as an alternative ([Ambrose, 2017](#); [Swartzendruber et al., 2009b](#)).

### 2.3. Laboratory validation

The solid phase adsorbent for Hg<sup>0</sup> used in the MAC is the commercial gold-coated borosilicate glass beads, which has a high and stable efficiency with no breakthrough issue and has been widely used in many previous studies ([Mason and Fitzgerald, 1990](#); [Tseng et al., 2003](#)). The gold traps are baked at 500 °C for 2 h to remove the potential Hg contamination after assembled from the beads. Similarly, to prevent the potential Hg interference, all Teflon tubing and connectors are soaked with 10% hydrochloride acid (HCl), rinsed with deionized water, and dried in the clean lab under the hood. The following assembling and testing of the entire setup are also performed in the clean lab.

The retention time of the Hg<sup>0</sup> peak in the MAC is determined by injecting Hg<sup>0</sup> vapor directly into the system. The Hg<sup>0</sup> vapor is obtained from the Tekran 2505 calibration unit with a temperature set at 20.0 °C. A fixed volume glass syringe (Hamilton Comp.) is used to draw the Hg<sup>0</sup> vapor from the headspace. The retention time for Hg<sup>0</sup> is 50 s after the heating of nichrome resistance wire coil. The DL, determined as three

times of the standard deviation of multiple analysis of a known amount of Hg<sup>0</sup> vapor, is 2.0 pg for the MAC. According to the sampling duration of 10 min at 1 L/min, the DL for the atmospheric Hg<sup>0</sup> is 0.2 ng/m<sup>3</sup>. The calibration of the MAC is performed before the actual measurement by injecting 5, 10 and 15 µL of the Hg<sup>0</sup> vapor at 20 °C. The calibration curve is found to be linear and have a small variation (<10% relative variation). And both pre- and post-calibrations (before and after MAC has been running for 12 h) agree well as shown by the linear relationship ( $R^2 = 0.91$ ,  $p < 0.001^{***}$ ; [Fig. 2a](#)). In addition, a low system blank (<0.1 ng/m<sup>3</sup>) is achieved by keeping the MAC running under the circulated carrier gas without the sampling steps on the gold traps A and B.

### 2.4. Field measurement

After the blank test and calibration of the MAC, simulated field measurements were performed by measuring air with a known Hg<sup>0</sup> concentration to evaluate the MAC's accuracy and stability. To do this, we co-located a Tekran 2537B and our MAC, and drew the indoor ambient air into the Tekran 2537B and the MAC at the same time with the same flow rate of 1L/min. The air Hg<sup>0</sup> concentration measured by the Tekran 2537B was treated as a reference and used to assess the MAC's performance. The two instruments were left running for a few days. The MAC was run with the circulated carrier gas without refresh for 6, 12, 24 and 36 h. Meanwhile, several calibrations were performed after the circulated carrier gas had been used for 6, 12, 24 and 36 h. During the field measurement, the ambient air Hg<sup>0</sup> concentration was relatively stable around  $1.31 \pm 0.07$  ng/m<sup>3</sup>. Thereafter, the MAC's accuracy and stability was demonstrated by comparing its output with Tekran 2537B ([Fig. 2b](#)).

## 3. Results and discussion

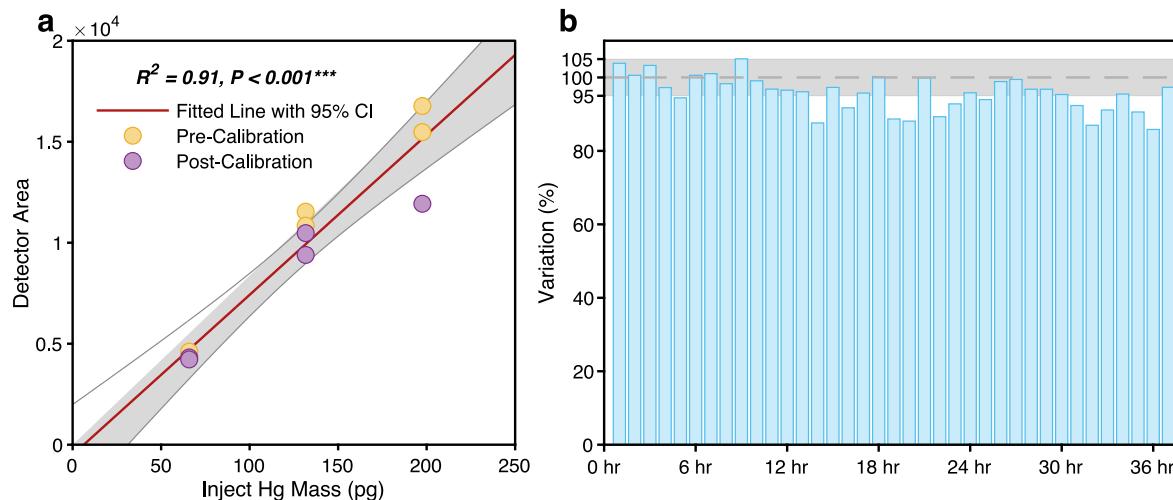
### 3.1. Validation of the MAC

The absorption efficiency of the gold trap used in the MAC was quantified as  $100 \pm 1\%$  by injecting the Hg<sup>0</sup> vapor. And there were no breakthrough issues found during our test, which means the gold traps had a high and stable efficiency for Hg<sup>0</sup>. The retention time for Hg<sup>0</sup> was determined to occur about 50 s after the heating coil is turned on. The retention time can be changed by adjusting the carrier gas flow rate in the circulation loop lane. In this MAC, a good carrier gas flow rate is determined at 60 ml/min, as a higher flow rate or a lower flow rate caused a shorter retention time with a narrow peak shape or a longer retention time with a wide peak shape, respectively. These two conditions were not optimum for the peak integration process ([Temmerman et al., 1990](#)). According to the total volume of the circulation loop lane, the residence time of the carrier gas is about 30 s.

The calibration of the MAC is performed by injecting known amounts of Hg<sup>0</sup> vapor. We have performed the pre- and post-calibration before and after the MAC has been running for 12 h. The calibration result showed in [Fig. 2a](#) indicates a good linear relationship ( $R^2 = 0.91$ ,  $p < 0.001^{***}$ ) between the injected Hg<sup>0</sup> vapor mass and the signal peak area of the CVAFS detector, which is also used to convert the peak area to Hg mass as a factor in our calculation. The estimated DL for atmospheric Hg<sup>0</sup> with the MAC is 0.2 ng/m<sup>3</sup>, which is comparable to the commercial Hg analyzers, such as Tekran 2537 and NIC AM-6F.

### 3.2. Field measurement

The MAC and Tekran 2537B were deployed to measure the indoor ambient air Hg<sup>0</sup> level. Both instruments sampled the same air at the same temperature and flow rate. The only difference was the MAC used the circulated carrier gas, while the Tekran 2537B continuously consumed the carrier gas. We used the air Hg<sup>0</sup> concentration measured by the Tekran 2537B as a reference to assess the MAC's performance. Throughout the field measurement, the indoor ambient air Hg<sup>0</sup>



**Fig. 2.** (A) The pre- and post-calibration of the prototype automatic Hg analyzer with circulated carrier gas system (MAC) at the start (yellow cycle) and end (purple cycle) of running. The fitted linear relationship with 95% confidence level area (red line; grey area) are denoted between the injected Hg mass and the signal peak area ( $R^2 = 0.91$ ,  $p < 0.001^{***}$ ). (b) The relative variation of continuous measurements of the MAC for each hour from 0 to 36 h represented by the blue bar. The horizontal grey area shows the  $\pm 5\%$  relative variation.

concentration measured by Tekran 2537B was quite stable about  $1.31 \pm 0.07 \text{ ng/m}^3$ . This stable air Hg<sup>0</sup> concentration was suitable for our instruments' performance comparison. After both instruments had been running for a few days, we observed an increase of the systematic variation of the MAC, especially after it has been running for 12 h and longer (Fig. 2b). Within the first 12 h, the calculated variation of the MAC is within  $100 \pm 5\%$ , suggesting that the accuracy and stability of the MAC is comparable to the Tekran 2537B's measurement. The air Hg<sup>0</sup> concentration measured by MAC is about  $1.27 \pm 0.06 \text{ ng/m}^3$ , which is comparable to the air Hg<sup>0</sup> concentration measured by Tekran 2537B. However, after 12 h, the variation of MAC becomes larger and some data points were out of range of 95–105%, suggesting that there is a decline of the MAC's accuracy and stability. As shown in Table S1, the variation of MAC drops below the 95% value at around 13 h, and then becomes more frequently below 95% until the end of field measurements. For the later field measurements, we have tried a new Hg scrubber with more active carbon loading to examine if this could help with the stability of the measurement. However, using a new Hg scrubber (activated carbon trap) with a larger loading of activated carbon did not solve the problem of an increase in the MAC's variation, suggesting that the MAC's accuracy and stability starts to decrease after using the same carrier gas for 12 h. We suggest that the reason, causing the increased variability during our measurement, is that air components, such as N<sub>2</sub> and O<sub>2</sub>, gradually build up inside the circulation loop due to their entrapment when the solenoid valves V2 and V3 switch between the gold trap A and B. N<sub>2</sub> and O<sub>2</sub> are diatomic molecules, which can quench the fluorescence, raise the baseline of the CVAFS detector and increase the noise signal (Bloom and Fitzgerald, 1988). Therefore, after the air components gradually build up in the closed loop, the raised baseline begins to interfere with the peak integration process. So, with the current version of the MAC, we would recommend refreshing the circulated loop with clean carrier gas every 12 h. Overall, the MAC showed its ability to measure the atmospheric Hg<sup>0</sup> concentration with high time-resolution and high precision with the extremely low consumption of the carrier gas, which is about 1 L/week (estimated based on total inner Teflon tubing volume), very low compared to the Tekran 2537X as  $\sim 700$  L/week and NIC AM-6F as  $\sim 250$  L/week.

### 3.3. Future improvements

This paper provides a straightforward description of the instrument design, development, validation and field testing. To our knowledge,

this new developed prototype Hg analyzer with a circulated carrier gas system provides a prototype that consumes the lowest carrier gas amount among all commercially available Hg analyzers and could provide the basis for the next generation of the Hg analyzer. This type of low carrier gas consumption provides a substantial opportunity for more extensive future Hg monitoring at remote places and also in countries and regions with limited carrier gas supply. Despite its development, there are still some potential improvements, specifically in terms of the stability period, which undoubtedly can be improved in the future. For example, we propose that the circulated loop can gradually build up components from the air which interfere with the CVAFS detection. This could be avoided by shortening the distance between the solenoid valves V2 and V3. Also, a fast pre-flush with the carrier gas through the sampling trap prior to switching could help during the switch between the gold trap A and B. Another issue that would improve the instrument is that we haven't added the auto-calibration function to the MAC, so currently, it still needs manual injection of Hg<sup>0</sup> vapor for the calibration process. These issues can be fixed or improved in the next version of the instrument.

There is also the potential for decreasing the gas use by other instruments. We suggest that a similar approach could be used for improving our dimethylmercury auto-analyzer (He et al., 2022) with this circulated carrier gas system to improve its ability for the field campaigns (Fig. S2). In addition, for instruments, such as the Tekran 2700 and 2600, and the Brooks Rand instruments developed for measuring dissolved methylmercury (MeHg) and total Hg in water, it would also be possible to develop analyzers with this circulated carrier gas system. However, the MeHg and THg analyzers are still under design, with a prototype schematic diagram shown in Fig. S3. To sum up, this prototype of new air Hg analyzer configuration and its contribution to the Hg research community can not only save carrier gas and be more economical, but also enhance the instrument's self-operating capability in remote areas with limited carrier gas supply, eliminating the need to consider the financial and human resource costs associated with frequent replacement of the carrier gas.

## 4. Conclusions

The development and deployment of the MAC represents a significant advance in atmospheric Hg monitoring technology. This study highlights the MAC's capability to conduct high-resolution, high-precision measurements of atmospheric Hg with minimal carrier gas

consumption – an innovation that stands in contrast to traditional methods which require significant amounts of carrier gas. The MAC's innovative design, which enables the recirculation of carrier gas within the system, has demonstrated its potential to reduce operational costs and logistical challenges, particularly in remote or resource-limited environments and conditions. Despite its advantages, the study also acknowledges the MAC's limitations, such as the accumulation of air components in the circulation loop, which can affect measurement accuracy over extended periods. Addressing these challenges through design improvements, such as optimizing the solenoid valve positions and integrating an auto-calibration function, will be crucial for enhancing the MAC's performance and reliability.

Looking ahead, the principles demonstrated by the MAC offer promising avenues for adapting similar technologies in other environmental monitoring instruments. Such advancements could revolutionize field campaigns, particularly in regions where resources are scarce, by reducing the frequency of carrier gas replenishment and thereby supporting more sustainable and extensive monitoring programs. This prototype not only paves the way for more efficient and cost-effective environmental monitoring but also exemplifies the type of innovative thinking necessary to tackle global environmental challenges. As we continue to refine and expand upon this prototype, it is expected that future iterations will provide even greater benefits to the global community engaged in monitoring and mitigating the impacts of Hg pollution.

#### CRediT authorship contribution statement

**Yipeng He:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Robert P. Mason:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2024.120785>.

#### References

- AMAP/UNEP, 2018. Technical Background Report to the Global Mercury Assessment 2018. Arctic Monitoring and Assessment Programme. Oslo, Norway/UNEP Chemicals Branch Geneva, Switzerland.
- Ambrose, J., 2017. Improved methods for signal processing in measurements of elemental mercury vapor by tekan A 2537A and 2537B instruments. *Atmospheric Measurement Techniques Discussions* 1–17.
- Amos, H.M., Sonke, J.E., Obrist, D., Robins, N., Hagan, N., Horowitz, H.M., Mason, R.P., Witt, M., Hedgecock, I.M., Corbitt, E.S., Sunderland, E.M., 2015. Observational and modeling constraints on global anthropogenic enrichment of mercury. *Environ. Sci. Technol.* 49, 4036–4047.
- Bloom, N., Fitzgerald, W.F., 1988. Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold-vapour atomic fluorescence detection. *Anal. Chim. Acta* 208, 151–161.
- Driscoll, C.T., Mason, R.P., Chan, H.M., Jacob, D.J., Pirrone, N., 2013. Mercury as a global pollutant: sources, pathways, and effects. *Environ. Sci. Technol.* 47, 4967–4983.
- EMEP, 2018. European Monitoring and Evaluation Programme.
- Feng, X., Sommar, J., Abul-Milh, M., Hong, B., Strömborg, D., Lindqvist, O., 2000. Modified on-line monitoring of total gaseous mercury in flue gases using Semtech® Hg 2000 analyzer. *Fresen. J. Anal. Chem.* 368, 528–533.
- Fitzgerald, W.F., Gill, G.A., 1979. Subnanogram determination of mercury by two-stage gold amalgamation and gas phase detection applied to atmospheric analysis. *Anal. Chem.* 51, 1714–1720.
- Gay, D.A., Schmeltz, D., Prestbo, E., Olson, M., Sharac, T., Tordon, R., 2013. The Atmospheric Mercury Network: measurement and initial examination of an ongoing atmospheric mercury record across North America. *Atmos. Chem. Phys.* 13, 11339–11349.
- He, Y., Mason, R.P., 2021. Comparison of reactive gaseous mercury measured by KCl-coated denuders and cation exchange membranes during the Pacific GEOTRACES GP15 expedition. *Atmos. Environ.* 244, 117973.
- He, Y., Shi, X., Huffman, W.W., Lamborg, C.H., Mason, R.P., 2022. Description of a dimethylmercury automatic analyzer for the high-resolution measurement of dissolved gaseous mercury species in surface ocean waters. *Environ. Sci. Technol.* 56, 13076–13084.
- Huang, J., Lyman, S.N., Hartman, J.S., Gustin, M.S., 2014. A review of passive sampling systems for ambient air mercury measurements. *Environ. Sci. J. Integr. Environ. Res.: Process. Impacts* 16, 374–392.
- Hung, H., Kallenborn, R., Breivik, K., Su, Y., Brorström-Lundén, E., Olafsdottir, K., Thorlacius, J.M., Leppänen, S., Bossi, R., Skov, H., Mano, S., Patton, G.W., Stern, G., Sverko, E., Fellin, P., 2010. Atmospheric monitoring of organic pollutants in the arctic under the arctic monitoring and assessment Programme (AMAP): 1993–2006. *Sci. Total Environ.* 408, 2854–2873.
- Lyman, S.N., Jaffe, D.A., 2012. Formation and fate of oxidized mercury in the upper troposphere and lower stratosphere. *Nat. Geosci.* 5, 114–117.
- Mason, R.P., Fitzgerald, W.F., 1990. Alkylmercury species in the equatorial Pacific. *Nature* 347, 457–459.
- Mason, R.P., Hammerschmidt, C.R., Lamborg, C.H., Bowman, K.L., Swarr, G.J., Shelley, R.U., 2017. The air-sea exchange of mercury in the low latitude Pacific and Atlantic Oceans. *Deep Sea Res. Oceanogr. Res. Pap.* 122, 17–28.
- Naccarato, A., Tassone, A., Martino, M., Moretti, S., Macagnano, A., Zampetti, E., Papa, P., Avossa, J., Pirrone, N., Nerentorp, M., Munthe, J., Wängberg, I., Stupple, G. W., Mitchell, C.P.J., Martin, A.R., Steffen, A., Babi, D., Prestbo, E.M., Sprovieri, F., Wania, F., 2021. A field intercomparison of three passive air samplers for gaseous mercury in ambient air. *Atmos. Meas. Tech.* 14, 3657–3672.
- Pirrone, N., Cinnirella, S., Sprovieri, F., Hedgecock, I.M., D'Amore, F., Bencardino, M., De Simone, F., 2022. The global observation system for mercury (GOS 4 M). *Earth Observation Applications and Global Policy Frameworks* 177–186.
- Sheu, G.-R., Gay, D.A., Schmeltz, D., Olson, M., Chang, S.-C., Lin, D.-W., Nguyen, L.S.P., 2019. A new monitoring effort for Asia: the Asia pacific mercury monitoring Network (APMMN). *Atmosphere* 10, 481.
- Sprovieri, F., Gratz, L.E., Pirrone, N., 2013. Development of a ground-based atmospheric monitoring Network for the global mercury observation system (GMOS). *E3S Web of Conferences* 1, 17007.
- Swartzendruber, P.C., Jaffe, D.A., Finley, B., 2009a. Development and first results of an aircraft-based, high time resolution technique for gaseous elemental and reactive (oxidized) gaseous mercury. *Environ. Sci. Technol.* 43, 7484–7489.
- Swartzendruber, P.C., Jaffe, D.A., Finley, B., 2009b. Improved fluorescence peak integration in the Tekran 2537 for applications with sub-optimal sample loadings. *Atmos. Environ.* 43, 3648–3651.
- Swartzendruber, P.C., Jaffe, D.A., Prestbo, E.M., Weiss-Penzias, P., Selin, N.E., Park, R., Jacob, D.J., Strode, S., Jaeglé, L., 2006. Observations of reactive gaseous mercury in the free troposphere at the Mount Bachelor Observatory. *J. Geophys. Res. Atmos.* 111.
- Temmerman, E., Vandecasteele, C., Vermeir, G., Leyman, R., Dams, R., 1990. Sensitive determination of gaseous mercury in air by cold vapour atomic fluorescence spectrometry after amalgamation. *Anal. Chim. Acta* 236, 371–376.
- Tseng, C.M., Balcom, P.H., Lamborg, C.H., Fitzgerald, W.F., 2003. Dissolved elemental mercury investigations in long island sound using on-line Au amalgamation-flow injection analysis. *Environ. Sci. Technol.* 37, 1183–1188.
- Zhou, J., Bollen, S.W., Roy, E.M., Hollinger, D.Y., Wang, T., Lee, J.T., Obrist, D., 2023. Comparing ecosystem gaseous elemental mercury fluxes over a deciduous and coniferous forest. *Nat. Commun.* 14, 2722.