A study on the stability of Mercury (Hg) in water for proficiency testing in Thailand

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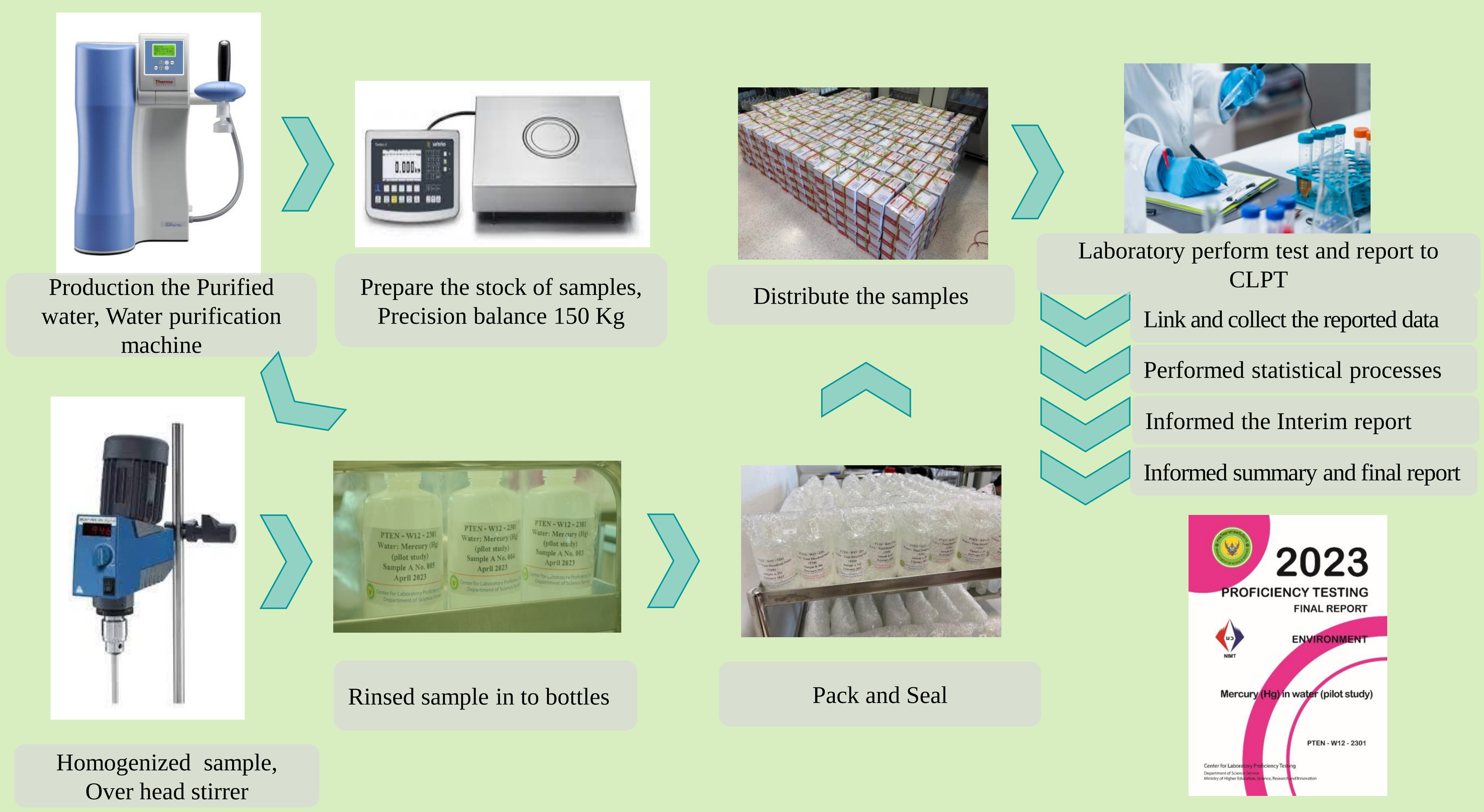
Mercury (Hg) is a naturally-occurring chemical element that is found in air, water and soil. It is released into the environment in various way such as volcanoes, the weathering of rocks and human activity. It is generally accepted that mercury is one of the most challenging elements for analysis. The stability is poor unless mercury is preserved in a proper preservative agent. The loss of mercury tends to occur at low-level mercury analysis. **This study was to improve the stability of mercury (Hg) in water for proficiency testing (PT) in Thailand.** Low concentration of mercury was studied in accordance with the national regulatory limit (1 µg/L, 1ppb) in drinking water. Two preservative agents (HCl and BrCl) were chosen to prepare two different kinds of preserved water for PT samples. The assigned value (x_{pt}) and measurement uncertainty ($U(x_{pt})$) were given by National Institute of Metrology (Thailand). The reference values for sample A and B were 0.900 ± 0.070 and 0.109 ± 0.040 µg/L, respectively. The performance of laboratory was accessed using z and En scores according to ISO/IEC 13528 **The results suggested that both HCl and BrCl preservatives were appropriate for mercury preservation in water.** Two types of preserved water contained in polyethylene bottle provided the stability enough for this proficiency testing, $\leq 0.3\sigma_{pt}$. 97 laboratories participated in the proficiency testing programme. The performance of laboratories were accessed. The results showed that successful participation (|z-score| $\leq$ 2.0) was about 77.3% (preserved water: HCl) and 67.7% (preserved water: BrCl). For long-term stability test, HCl offered more stability in PE bottle at 60 days of storage. HCl may give more benefit for PT sample preparation in terms of chemical supply, waste management and safety for preparation in mass production (> 100 L) due to the oxidation property of BrCl.

Introduction

Mercury is released into the environment in various ways such as volcanoes, the weathering of rocks and human activity. It is one of the persistent organic pollutants (POPs) and found in inorganic forms. The determination of mercury in various water contents is gaining more importance particularly in drinking water because it affects the human health directly. In the determination of mercury, there were so many challenges to overcome. The United State Environmental Protection Agency (USEPA) also reviewed and approved some methods for the determination such as Method 245.1 (ICP-MS), Method 245.2 (ACVT), Method 245.7 and Method 1631 (CV-AFS) [1]. The conduct of mercury species was to investigate the effects of acidified and bottle type on the holding time. Mercury may lost to the bottle walls in some cases. The wall loss mechanism has been described by Bloom (1994) and Jenifer et al. (2004). It is generally accepted that mercury is one of the most challenging elements for analysis. The stability is poor unless mercury is preserved in a proper preservative agent. The loss of mercury tends to occur at low-level mercury analysis. This study was to improve the stability of mercury (Hg) in water for proficiency testing (PT) in Thailand.

PT Process



Scheme 1. The preparation process of PT samples.

Low concentration of mercury was studied in accordance with the national regulatory limit (1 µg/L, 1ppb) in drinking water. Two preservative agents (HCl and BrCl) were chosen to prepare two different kinds of preserved water for PT samples. Samples were contained in PE bottle. After distribution period (10 days), all bottles were stored in refrigerator (4 - 8 °C) for long term stability study. The assigned value (x_{pt}) and measurement uncertainty ($U(x_{pt})$) were given by National Institute of Metrology (Thailand). The reference values for sample A and B were 0.900 ± 0.070 and 1.090 ± 0.040 µg/L, respectively. The target standard deviations (σ_{pt}), 30 % CV were used for proficiency assessment. The participants' performance is evaluated z - score. The performance of laboratory was accessed using z and En scores according to ISO/IEC 13528.

Sample A: Preserved with HCl, the appearance is clear colorless solution.

Sample B: Preserved with BrCl the appearance is clear light yellow solution.

Figure 1: Characteristic of PT sample with two preservative agents

Result and Discussion

Homogeneity and stability of PT samples

Two types of preserved water had different appearances (Figure 1). **The homogeneity assessment** and **stability assessment** of the sample was performed in accordance with ISO/IEC 13528. Statistical analysis showed that samples were stable throughout laboratory proficiency testing periods. **These results suggested** that both HCl and BrCl preservatives were appropriate for mercury preservation in water.

Proficiency results

97 laboratories participated in the proficiency testing programme. The summary of statistic were shown in Table 1. Details of analytical methods and instruments are shown in figure 2. Normal distribution occurred in both samples (Figure 3). The performance of laboratories was accessed, results shown in Table 2.

Table 1 Summary Statistics for assessment laboratories performance

Summary statistics	Sample A	Sample B
Number of results	93	94
Assigned value (xpt), µg/L	0.900	1.090
Standard deviation for proficiency assessment (σpt), µg/L	0.270	0.327
Robust standard deviation (s*), µg/L	0.326	0.576
Homogeneity	passed	passed
Stability	passed	passed

Table 2 Summary of z – scores performance of participants

z - score	Sample A: HCl	Sample B: BrCl
	Percentage	Percentage
$\lvert z \rvert \leq 2.0$	77.3	67.7
$2.0 < \lvert z \rvert < 3.0$	7.2	12.5
$\lvert z \rvert \geq 3.0$	15.5	19.8

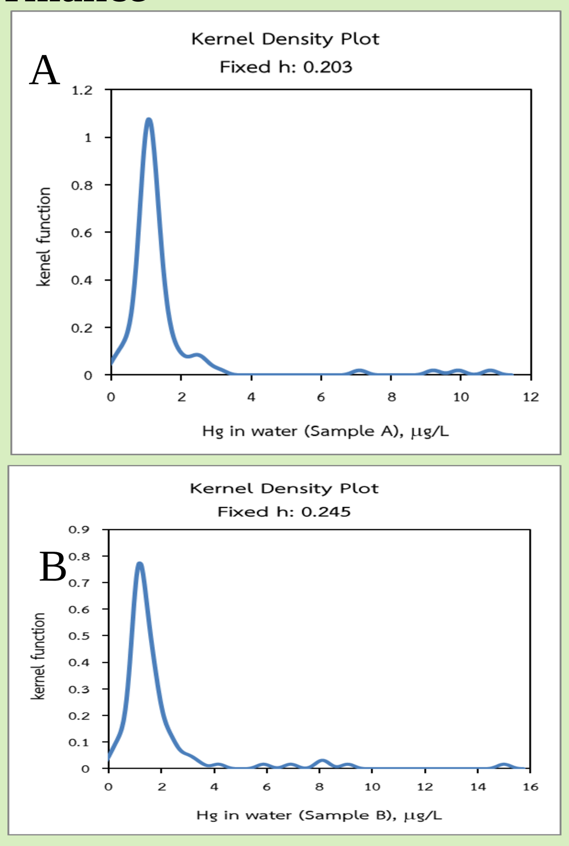


Figure 3: Kernel density plot
Shown the distributed of sample A: HCl and B: BrCl.

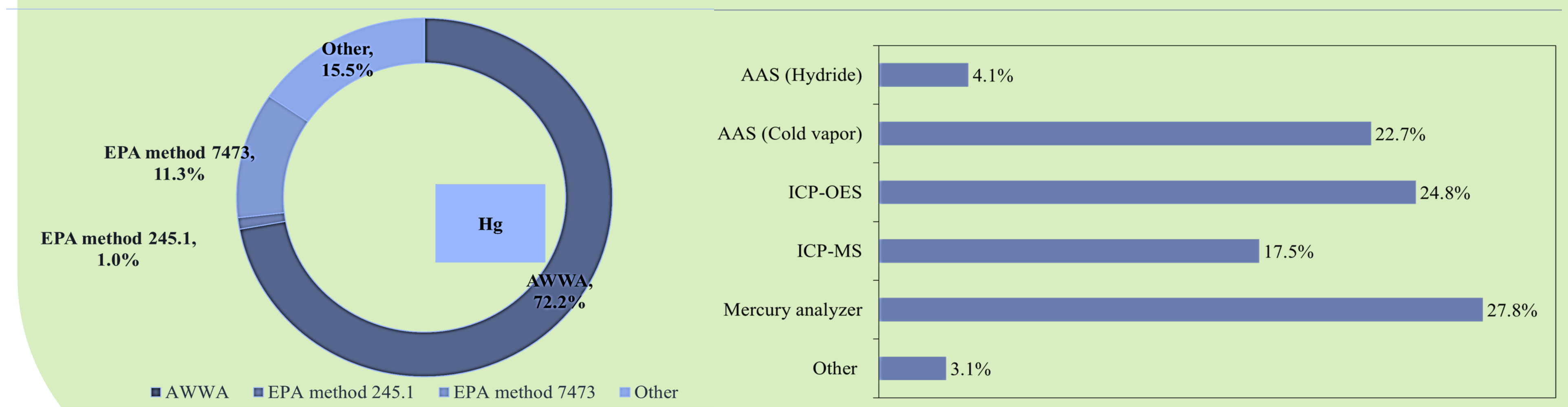


Figure 2: The details of analytical methods and instrument used in proficiency testing

Long term Stability

For long term stability properties, the amounts of mercury were measured and compared with the general average of measurements at 0, 30 and 60 days of storage. Sample B (BrCl) has a significant difference in concentration at 60 days of storage, > 0.3σpt. The concentration of mercury in sample A and sample B has diffed down from 0 day about - 0.061 µg/L and - 0.135 µg/L at 60 days, respectively **(Figure 4)**.

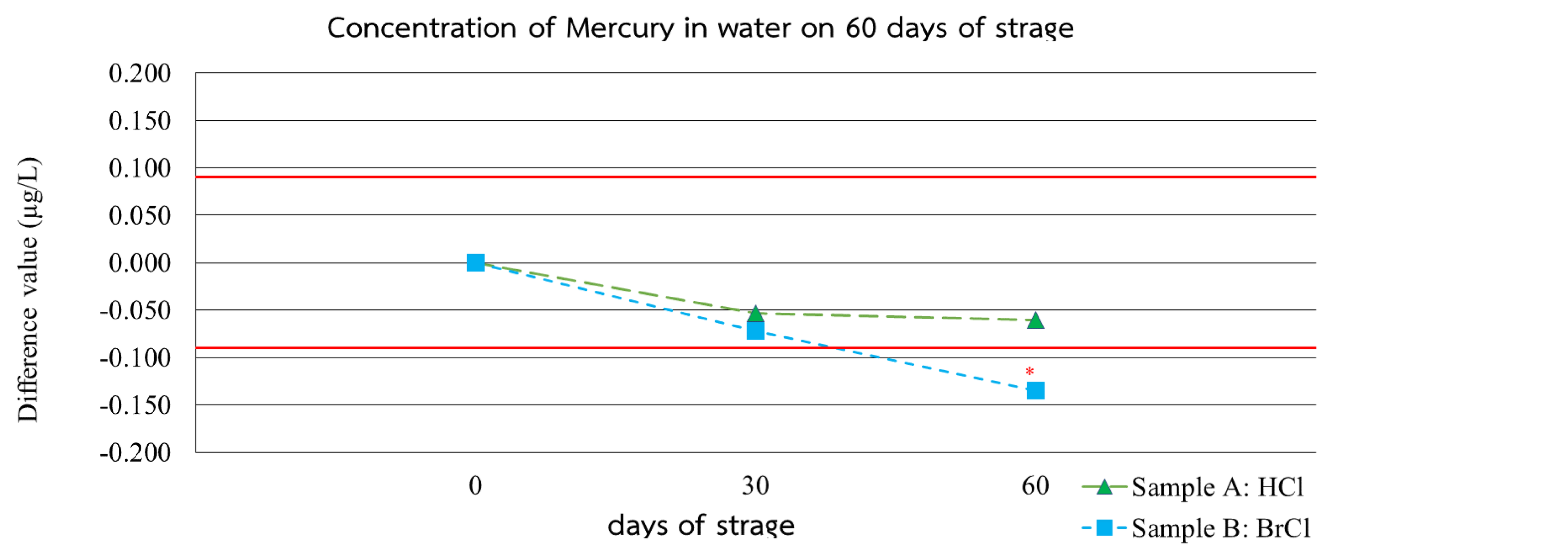


Figure 4: Long terms stability of preserved water
* Represent the difference, > 0.3σpt.

Conclusion

HCl and BrCl preservatives were appropriate for mercury preservation in water. HCl offered more stability in the PE bottle at 60 days of storage at 4 - 8 °C. The transportation has not affected the samples. Two types of preserved water were stable throughout laboratory proficiency testing periods. HCl may give more benefit for PT sample preparation in terms of chemical supply, waste management and safety for preparation in mass production (> 100 L) due to the oxidation property of BrCl. In addition, the mechanism of BrCl preserved water is to oxidize mercury ions to Hg(II). Before testing, the neutralization was to release natural mercury in BrCl-preserved water. The increase in the preparation step leads to higher tolerances in testing unless laboratories perform reagent/method blank to compensate for the discrepancy.

References

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