Development of Methods for the Determination of Reactive Mercury [$Hg(II)_R$] in Natural Fresh Water

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Introduction and Background

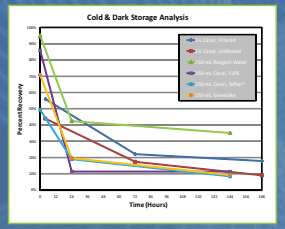
Reactive mercury [$Hg(II)_R$] species are inorganic mercury complexes in the Hg(II) state. $Hg(II)_R$ can easily be reduced to methyl mercury through biotic processes and is considered available for methylation.[1,2] $Hg(II)_R$ is an important species of mercury due to its relationship to methyl mercury; therefore, it is important to develop a robust, accurate, and precise method for measuring $Hg(II)_R$ in fresh water samples.

Currently, $Hg(II)_R$ is measured in fresh water using a variety of operationally-defined procedures, including an acid-labile method developed by Bloom[3] and an unpreserved stannous chloride ($SnCl_2$) reduction method based on the total mercury analysis method EPA 1631e[4]. The study presented here attempts to develop a method that could be used on a routine basis in the laboratory for determination of $Hg(II)_R$ in fresh water samples.

This project looks at two different storage techniques and one alternative test method to develop an accurate analytical method for determination of $Hg(II)_R$ in fresh water samples. For this project reagent water and samples from two Seattle WA locations, the Lake Washington Ship Canal at the Fremont Cut (Canal) and Green Lake (Greenlake), were used. Samples were fortified with ionic mercury ($HgCl_2$) to provide a measurable amount of $Hg(II)_R$. All unpreserved fortified samples were analyzed in triplicate and the recoveries were used to calculate the exact $Hg(II)_R$ spiking levels. Unpreserved samples from both storage techniques were analyzed for $Hg(II)_R$ via CVAFS using pH-neutral reagents. To prevent pH changes, stannous citrate (SnCit) was used in place of $SnCl_2$ to reduce the $Hg(II)_R$ to elemental mercury for pre-concentration without altering the pH of the samples.

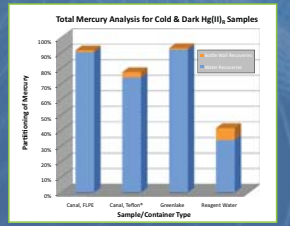
Storage Method #1: Cold and Dark Storage

The first storage technique stored unpreserved samples in a cool, dark place to maintain $Hg(II)_R$ levels. The samples were collected twice, the first time in 2-L fluorinated polyethylene (FLPE) bottles, with sub-aliquots removed, spiked, and analyzed over multiple days. In a second test, samples were collected in individual 250-mL FLPE and Teflon® bottles, spiked, wrapped in aluminum foil, and stored at 0.4 ºC, thus allowing the individual bottles to be removed for analysis without coming in contact with air or light until the actual time of analysis.



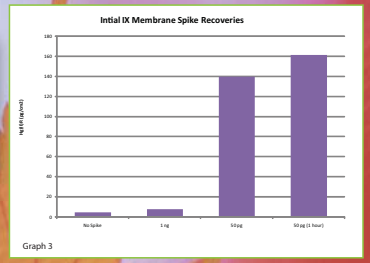
Graph 1 (left): A total mercury analysis of the liquid solution and the bottle wall recoveries for the cold dark storage samples. The combine recoveries are 77-92% of the spike amounts for all samples except reagent water.

Graph 2 (right): The recoveries from spiked 2-L and 250-mL containers of reagent water and natural fresh water over the course of seven days.



Pall I.C.E. 450® Ion-Membrane

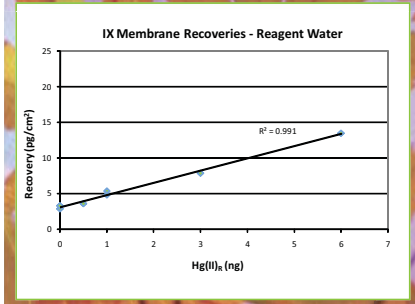
The third part of this study evaluated a completely different analytical method using a Pall I.C.E. 450® Ion-Exchange Membrane[DEM] (IX membrane) which has been shown to collect $Hg(II)_R$ in atmospheric deposition studies.[7] This study looked at aqueous $Hg(II)_R$ spike recoveries in reagent water and natural fresh waters. Measured pieces of IX membrane were put into the unspiked or spiked samples for a variable amount of time before being removed from the water and placed into 50 mL of a 0.02 N BrCl solution for 24 hours. The BrCl solution was analyzed for Hg using CVAFS. Previous work done at Brooks Rand Labs by Andrew Maizel demonstrated the recoveries for extraction technique.[8]



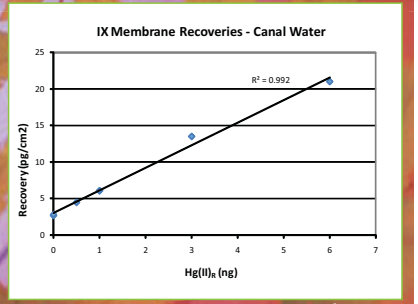
Graph 3

Graph 3: The reagent water in contact with the IX membranes showed spike recoveries of on average 45.3% of the initial spike with excellent comparison to the initial spike level. This analysis showed that IX membranes could recover aqueous $Hg(II)_R$, but that a calibration coefficient would be needed. This analysis used 10 mL of liquid with 130.6 cm^2 of IX membrane.

Initial work with the IX membranes showed a need for a calibration coefficient. Graphs 4a and 4b describe the development of this coefficient; the results indicate the coefficient may vary by sample characteristics. The analyses used 50 mL of liquid with 40 cm^2 of IX membrane.



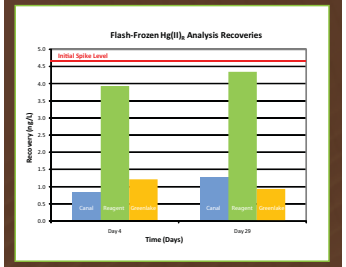
Graph 4a: The reagent water calibration consistently showed 4-9% of the initial spike and had an r2 value of 0.9919 between the $Hg(II)R$ spike value and the sample results.



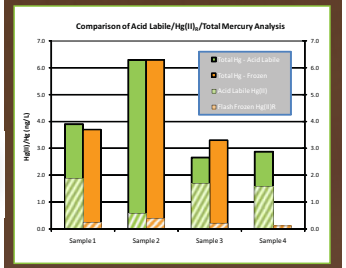
Graph 4b: The fresh water calibration showed 12-14% of the initial spike with an r^2 value of 0.9929 between the $Hg(II)_R$ spike value and the sample results.

Storage Method #2: Flash Freezing

The second storage technique was to flash-freeze the samples in the field, or, in the case of spiked samples, immediately after spiking. The samples were defrosted under nitrogen in a darkened glove box.



Graph 5: An analysis of flash-frozen, spiked samples performed 4 and 29 days after the initial spike was added and the samples were flash-frozen. Samples were in individual 250-mL bottles stored in a freezer before analysis.



Graph 6: Results for $Hg(II)_R$ in 4 samples analyzed by the acid-labile method and the flash-frozen method. Subsequently, the remaining sample was oxidized in the original sample bottles and analyzed for total mercury.

Conclusion

The two storage and preservation techniques for $Hg(II)_R$ did not provide consistent, accurate data. Neither technique could be used with confidence for the determination of definitive concentrations of reactive mercury in fresh water samples. The results from the IX membrane study suggest a strong possibility of calculating the initial reactive mercury levels, but would require more research.

Cold & Dark Storage

- $Hg(II)_R$ showed low, unstable recoveries in reagent and natural water samples.
- Total mercury analysis offered good recoveries of the initial spikes, indicating $Hg(II)_R$ shifted species in solution.

Flash-Freezing

- Recoveries from $Hg(II)_R$ spikes were low, but stable over time.
- Flash-frozen recoveries varied by sample type based on unknown sample characteristics.
- Results were lower for flash-frozen analysis than acid-labile analysis; samples used for this analysis were not spiked so initial reactive mercury levels are unknown.

IX Membrane

- The analysis showed good relationships between initial spike levels and recoveries.
- The calibration coefficient calculated based on spike recoveries varies by sample characteristics.
- More research is needed to develop a robust method.

Next Steps

Future work would continue to look at unpreserved samples because preservation techniques, including acidification, flash-freezing, and cold storage have been shown to alter relative levels of reactive mercury. One goal may be to find a method of analysis in the field to reduce the species shift that occurs during transportation to the laboratory. The difficulty working with this species of mercury is the highly reactive nature, which causes quick alterations in the relative levels of reactive species of mercury species in aqueous fresh water samples.

References

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