

# DETERMINATION OF MERCURY (Hg) IN WATER BY HAND-HELD, PORTABLE COLD VAPOR ATOMIC FLUORESCENCE SPECTROMETRY

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## BACKGROUND

Water is the most abundant compound on the Earth's surface, covering 71% of its surface area.<sup>[1]</sup> It is a vital component for all known forms of life and is the aquatic habitat for thousands of species of microalgae, fish and shellfish.<sup>[2]</sup> With the presence of running water in our buildings, school yards, and outdoor fountains, it may be easy for people to believe that all water we encounter in our daily lives is abundant and usable. The fact is only 2.5% of the Earth's water is freshwater, and only a small percentage of that is both usable and easily accessible.<sup>[3]</sup> Due to the precious and fixed reserves of water at our disposal, it is vital to protect our water resources from contaminants that harm all forms of life if consumed. One of the hazardous pollutants that will render water unusable is mercury. This toxic element readily disperses in water and accumulate in watersheds, where it is then absorbed by plants and consumed by animals.<sup>[4]</sup> Because of bio-accumulation of mercury in the food chain, and its toxicity in minute concentrations, the EPA has included mercury in its regulation plan through the Clean Water Act.<sup>[5][6]</sup> In 1968, Hatch et. al. published a method using atomic absorption spectroscopy to detect mercury (Hg) at the sub microgram quantities.<sup>[7]</sup> This analytical technique, along with gold film sensing, has been the leading methods for mercury detection, but atomic absorption has drawbacks in the presence of hydrocarbons, since these molecules also absorb at the wavelength of detection used by Hg.<sup>[8]</sup> In 1964, Winefordner, et. al. first described atomic fluorescence as a useful analytical method for analyzing chemical materials.<sup>[9]</sup> However, until recently it has not been widely used for investigation of chemical species. For mercury detection, this method proves more useful than atomic absorption since it reduces the possibility of signaling from other chemical compounds. This is due to the different fluorescing wavelength of elemental mercury compared to other compounds. Traditionally atomic fluorescence analyzers have been available as large, stationary instruments designed for laboratory conditions. Recently Arizona Instrument LLC successfully produced a hand-held, portable atomic fluorescence based analyzer used for detecting mercury in air. In the present paper, this instrument was used to measure mercury concentrations in water, using a method adapted from EPA method 1631, Revision E.<sup>[10]</sup> This experiment eliminated the requirement of a gold trap, giving it a more robust application, both by portability to work stations and by optimized testing procedures.

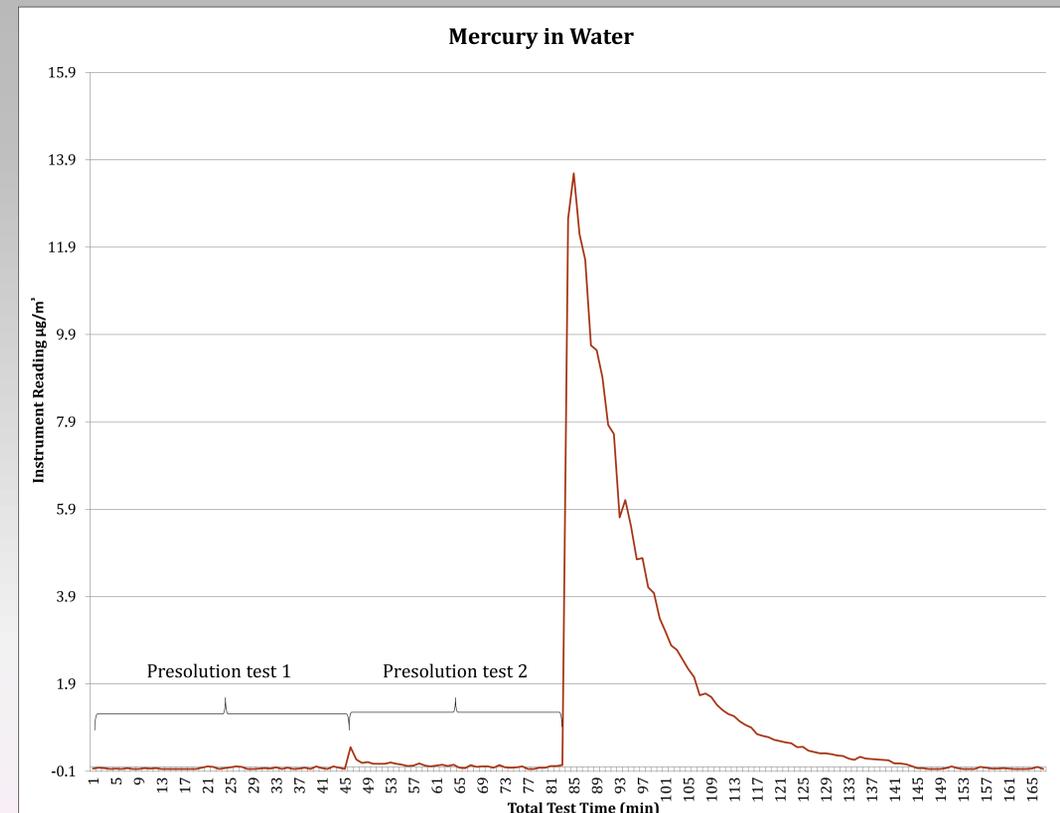
## EXPERIMENTAL

200mL of ultra-pure H<sub>2</sub>O was poured into a vacuum flask. The flask was placed on a Barnstead Thermolyne Super-Nuova stir plate set at 300rpm. The J505 was set to auto sample, sampling once every minute for a minimum of 10 minutes. Results were recorded in the instrument using the site name "Presolution Test 1." Once the presolution test 1 was finished 1mL of the SnCl<sub>2</sub> solution was added to the 200mL of ultra-pure water (UP H<sub>2</sub>O) and the instrument sampled for a minimum of 10 minutes. The Jerome® J505 was in auto sample mode and sampling occurred every minute. Results were recorded in the instrument using the site name "Presolution Test 2." To ensure that the HgCl<sub>2</sub> solution did not provide a signal 5.0mL of the 0.1ppm solution was tested in duplicate without SnCl<sub>2</sub> present. No signal was observed. The Hg was reduced and a signal was measured. Presolution 2 can be made with either SnCl<sub>2</sub> or HgCl<sub>2</sub> in dissolved in UP H<sub>2</sub>O. Hg water testing – At the conclusion of all the pretest checks various known concentrations of mercury were introduced. Individual testing was conducted at a concentration of 0.1 ppm, the following volumes were added to 200mL of UP H<sub>2</sub>O: 0.1mL (0.1ppm), 0.2mL, 0.3mL, 0.4mL, 0.5mL, 1mL, 2mL, 3mL, and 4mL. Each volume was introduced into the testing apparatus using a 1mL Tuberkulin syringe with an 18 gauge 1.5" needle. Testing was conducted for a minimum of 1 hour with the instrument in auto sample mode, sampling every minute. Test results were recorded as Hg in H<sub>2</sub>O. Instrument zero check - Once the Hg testing was completed the instrument was removed from the testing apparatus and fitted with an activated carbon filter and sampled for a minimum of 10 minutes, in auto sample mode, sampling every minute. This was to ensure the instrument would read below 0.10µg·m<sup>-3</sup> and the reaction chamber inside the instrument was free of any mercury. Test results were recorded in the instrument using the site name "post test zero."

## RESULTS

Standard result comparison	
Expected Value	Measured Value
0.01	0.010
	0.011
0.02	0.020
	0.018
0.03	0.033
	0.034
0.04	0.039
	0.038
0.05	0.048
	0.054
0.1	0.102
	0.108
0.2	0.196
	0.200
0.3	0.290
	0.309
0.4	0.421
	0.430

Standard test values for known concentrations of 0.430µg that the signal measured was Hg and not the solution containing SnCl<sub>2</sub> and Ultra-Pure H<sub>2</sub>O, the data was plotted.



The graph is from a 0.2µg test and is a typical output from the instrument's analysis. For this experiment the pretest

## CALCULATIONS

The Hg concentration was calculated using the following formula:

$$\sum_{t=1}^{t=ism} Adj. \text{ sample measurments } dt * \frac{1m^3}{1000L} * \text{measured flow } \frac{L}{min}.$$

Where  $t=1$  is the time of the first sample and  $t=ism$  is the time that the last sample measurement was taken. The volume conversion must be done due to the Jerome® J505 providing results as µg·m<sup>-3</sup>. The calculated values were then compared with the expected values determined by the following calculation:

$$ppm \stackrel{def}{=} \frac{mg}{kg}$$

Therefore:

$$\frac{\mu g \text{ Hg}}{kg} = \frac{mg}{kg} * \frac{kg}{L} * \frac{L}{1000mL} * \frac{1000\mu g}{mg} * \text{injection volume}$$

## CONCLUSION

The Jerome® J505 hand held atomic fluorescence spectrophotometer can effectively measure elemental mercury in water by measuring the headspace above contaminated water without using a gold film trap. The portability allows for use outside of the lab, providing results as samples are drawn. Additionally, signal strength showed that the instrument effectively detects 10ng of Hg in 200mL of UP H<sub>2</sub>O. Further testing is still to be done to determine the lower detection limit of the instrument, as well as testing optimization that would reduce testing and throughput time.

## REFERENCES

- "The world fact book." [https://www.cia.gov/library/publications/the-world-factbook/geos/xx.html#Geo\\_CIA](https://www.cia.gov/library/publications/the-world-factbook/geos/xx.html#Geo_CIA). July 2013
- "International Decade for Action 'Water for Life' 2005-2015." <http://www.un.org/waterforlifedecade/background.shtml> United Nations. July 2013
- Cleek, P.H., ed. (1993). *Water in Crisis: A Guide to the World's Freshwater Resources*. Oxford University Press. p. 13, Table 2.1 "Water reserves on the earth".
- da Silva, DG, Portugal, LA, Serra, AM, Ferreira, SLG, Cerdá, V (2012). "Determination of mercury in rice by MSFA and cold vapour atomic fluorescence spectrometry". *Food Chemistry* 137 (1-4): 159-63.
- "Mercury in the Food Chain." <http://www.ec.gc.ca/mercure-mercury/default.asp?lang=en&n=d721ac1f-1>. Government of Canada. July 2013
- "Total Maximum Daily Loads." <http://www.epa.gov/agriculture/lcwa.html#Total%20Maximum%20Daily%20Limits>. EPA. March 2013
- Hatch et. al. "Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry." *Anal. Chem.* 1968 (40) 2085-2087
- Wang, G et. al. "Surface-enhanced Raman Scattering in nanoliter droplets: towards sensitivity of detection of Mercury (II) ions." *Analytical and Bioanalytical Chemistry*. Aug 2009 394(7) 1827-1832.
- Winefordner JD, Vickers, TJ. "Atomic Fluorescence Spectroscopy by Means of Analysis." *Anal. Chem.* 1964 36(1) 161-165.
- Ure, AM. "The determination of mercury by non-flame atomic absorption and fluorescence spectrometry: A review." *Analitica Chimica Acta*. May 1975; 76(1) 1-26
- Dodd, JN et. al. "Letter to the Editor: The modulation of resonance fluorescence excited by pulsed light." *Proceedings of Phys. Soc.* 1964. 84(1)176-178.
- "Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry." Aug. 2002. EPA-821-R-02-19