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

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Introduction

Water is the most abundant compound on the Earth's surface, covering 71% of its surface area.^[1] 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.^[2] 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.^[3] Because of 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.^[4] 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.^{[5][6]}

In 1968, Hatch et. al. published a method using atomic absorption spectroscopy to detect mercury (Hg) at the sub microgram quantities.^[7] 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.^[8] In 1964, Winefordner, et. al. first described atomic fluorescence as a useful analytical method for analyzing chemical materials.^[9] 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.^[10] 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

Reagents

All solutions and standards were prepared using deionized water (dH₂O) filtered through three mix beds. Water was monitored using the Signet 9900 transmitter and had a resistance greater than 17MΩ-cm. Ion mix beds were provided by GE Pure solutions. All reagents were analytical grade and HCl solutions were prepared using standard dilution methods.

Stannous chloride – 20.0g of SnCl₂·2H₂O was added to 10.0mL of concentrated HCl. The stannous chloride dissolved for 2 hours before being added to 100.0mL of dH₂O. The solution was purged overnight with N₂ gas at a flow rate of 500mL·min⁻¹. The solution was then bottled in a brown glass bottle.

Bromine Chloride – In an Erlenmeyer flask, 5.40g of KBr was added to 500mL of conc. HCl and allowed to dissolve for 2 hours. 7.60g of KBrO₃ was slowly added to the solution. The solution was stirred for 1 hour and corked.

Standards

A 10,000ppm stock standard was prepared using 13.59g Alfa Aesar 99.5% pure HgCl₂ to 500mL of dH₂O. 5.0mL of BrCl was added, and the solution was diluted to the mark in 1000mL of dH₂O using a volumetric flask.

Secondary standard was prepared by adding 10mL of the stock standard to 500mL of dH₂O in a volumetric flask. 5mL of BrCl was then added, and the solution was diluted to the mark using dH₂O in a 1000mL volumetric flask. This was labeled as "secondary standard – 100ppm."

Working standard A was prepared by adding 10mL of the secondary standard to 500mL of dH₂O in a volumetric flask. 5mL of BrCl was then added, and the solution was diluted to the mark using dH₂O in a 1000mL volumetric flask. This was labeled as "Working standard A – 1ppm."

Working standard B was prepared by adding 1mL of the secondary standard to 500mL of dH₂O in a volumetric flask. 5mL of BrCl was then added, and the solution was diluted to the mark using dH₂O in a 1000mL volumetric flask. This was labeled as "Working standard B – 0.1ppm."

The 0.1ppm working solution was stored in a 1000mL volumetric flask that was corked. The concentration was no longer accurate after 1 month, and had to be remade.



Apparatus

A 500mL Büchner flask was used for testing. The side hose barb was fitted with 24" of tubing, and at the end of the tubing an activated carbon filter was attached to ensure no mercury in the air was entering and being measured. The top of the flask was fitted with a #7 rubber stopper with a hole in it. The hole had a 12" glass tube inserted, followed by 36" of Tygon tubing. This tubing was inserted into the Jerome® J505 for mercury measurement. Once the solution was poured into the Büchner flask approximately 3" of head space was between the glass tube and the solution level. A picture of the setup is below.



Image 1. Apparatus and instrument setup.

Standard Testing

Pretest checks – Prior to testing, the Jerome® J505 atomic fluorescence mercury analyzer was checked weekly using the Arizona Instrument LLC calibration procedure (not the recommended year calibration period) from Arizona Instrument, to ensure it was measuring mercury concentrations accurately. Once the instrument was vetted, it was fitted with an activated charcoal filter and allowed to sample for a minimum of 10 minutes in auto sample mode, sampling once every minute, to ensure the instrument was able to read less than $0.10\mu\text{g}\cdot\text{m}^{-3}$ consistently. This was recorded as the pretest zero.

After the instrument was qualified, the instrument was connected to the testing apparatus with no solutions introduced. The instrument was then allowed to sample for a minimum of 10 minutes in auto sample mode, sampling once every minute, to ensure the instrument was able to read less than $0.10\mu\text{g}\cdot\text{m}^{-3}$ consistently. This was recorded as Glass Test.

Following the solution free glass testing, the apparatus and instrument were moved to the fume hood and 200mL of ultra-pure H_2O was poured into the Büchner flask. With a 1" teflon coated stir bar, 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_2 solution was added, using a 1.0mL Teburculin syringe with an 18 gauge 1.5" needle, to the 200mL of ultra-pure water (UP H_2O) 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_2 solution did not provide a signal 5.0mL of the 0.1ppm solution was tested in duplicate without SnCl_2 present. No signal was observed from either the SnCl_2 or the HgCl_2 solutions. The Hg was reduced and a signal was measured. Presolution 2 can be made with either SnCl_2 or HgCl_2 in dissolved in UP H_2O .

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_2O : 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 Tuberculins 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_2O .

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 $0.10\mu\text{g}\cdot\text{m}^{-3}$ 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."

Glassware Cleaning

Once all testing was complete and the instrument was disconnected from the testing apparatus, the stir bar was removed and placed in a small beaker, and the solution was emptied into a large glass jar marked "Acid Waste." The glassware and stir bar used were rinsed twice with 100mL of 12M HCl. The first rinse was from a collection of 12M HCl used in previous rinses, and the second was from unused reagent grade HCl. The glass was then rinsed twice with 100mL of dH_2O . Each rinse was poured into the acid waste disposal jar. The glass was then washed with liquid detergent and dH_2O , rinsed with acetone, and placed on the drying rack for 1 hour. It was then



transported to a convection oven and heated at 150°C for a minimum of 1 hour.

Results and Discussion

Standard Testing

First, the signal from the last 10 samples from the presolution 2 testing was averaged, and this average was removed from signal provided from the mercury testing. The Hg concentration was calculated using the following formula:

$$\sum_{t=1}^{t=10} Adj. sample measurements dt * \frac{1m^3}{1000L} * measured flow \frac{L}{min.}$$

Where $t=1$ is the time of the first sample and $t=10$ is the time that the last sample measurement was taken. The volume conversion must be done due to the Jerome[®] J505 providing results as $\mu g \cdot m^{-3}$. The flow was measured using an Aalborg calibrated flow meter by attaching it to the front of the instrument and taking a sample. The calculated values were then compared with the expected values determined by the following calculation:

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

Therefore:

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

This converts ppm into the total mass of Hg present in the solution and results in the following table:

0.1ppm	
Injection Volume	μg Hg
1.0mL	0.1
2.0mL	0.2
3.0mL	0.3
4.0mL	0.4

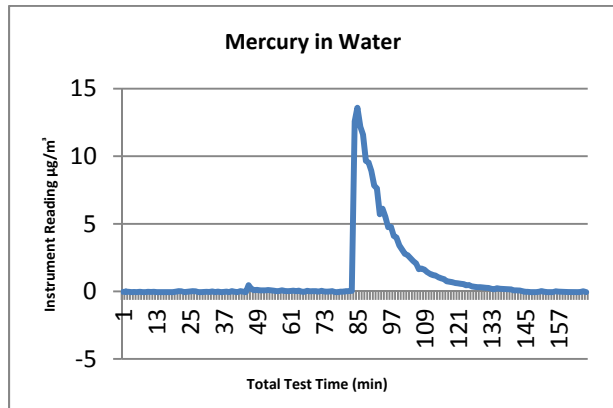
Table 1. Conversion of sample size to theoretical μg Hg

Comparing the expected result to the measured result yielded:

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

Table 2. Standard test values for known concentrations
To ensure that the signal measured was Hg and not the solution containing SnCl₂ and Ultra-Pure H₂O, the data was plotted.

Once the testing was complete it was downloaded to a USB memory stick as a text file. The data was transferred to an excel file where the calculations were done and a graph of the testing was generated.



Graph1. Real time measurement of Hg Concentration from the Jerome® J505

Graph 1 is from a 0.2µg test and is a typical output from the instrument's analysis. For this experiment the pretest checks were conducted from minutes 1 through 83. At minute 84 the Hg water testing began, using 2.0mL of 0.1ppm Hg solution. From minutes 84 to 144 the instrument sampled the headspace above the solution. Removing the gas in the headspace also removed the Hg from the air above the solution, causing more Hg to evolve out of solution as it attempted to achieve equilibrium. The signal decay seen in the graph closely resembles an exponential distribution. At minute 145 the instrument zero check was started, ending at minute 164.

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 H₂O. 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.

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