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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, making up 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 can be readily dispersed in water and can 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, have 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 than 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 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 Ionics Pure solutions. All reagents were analytical grade and HCl solutions were prepared using standard dilution methods.

Stannous chloride – 20.0g of $SnCl_2 \cdot 2H_2O$ was added to 10.0mL of concentrated HCl. The stannous chloride dissolved for 2 hours before being added to 100.0mL of dH_2O. The solution was purged overnight with N_2 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 HCl and allowed to dissolve for 2 hours. 7.60g of $KBrO_3$ 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 $HgCl_2$ to 500mL of dH_2O. 5.0mL of BrCl was added, and the solution was diluted to the mark in 1000mL of dH_2O using a volumetric flask.

Secondary standard was prepared by adding 10mL of the stock standard to 500mL of dH_2O in a volumetric flask. 5mL of BrCl was then added, and the solution was diluted to the mark using dH_2O in a 1000mL volumetric flask. This was labeled as "secondary standard – 100ppm."

Working standard A was prepared by adding 10mL of the stock standard to 500mL of dH_2O in a volumetric flask. 5mL of BrCl was then added, and the solution was diluted to the mark using dH_2O in a 1000mL volumetric flask. This was labeled as "Working standard A – 1ppm."

Working standard B was prepared by adding 10mL of the working standard A to 500mL of dH_2O in a volumetric flask. 5mL of BrCl was then added, and the solution was diluted to the mark using dH_2O in a 1000mL volumetric flask. This was labeled as "Working standard B – 0.1ppm."

Standard Testing

Pretest checks – Prior to testing, the Jerome® J505 Atomic fluorescent mercury analyzer was checked weekly using the Arizona Instrument LLC calibration procedure, to

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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 0.10µg·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 0.10µg·m^{-3} consistently. This was recorded as Glass Test.

Following the solution free glass testing, the apparatus and instrument was moved to the fume hood and 200mL of ultra-pure H_2O was poured into the 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 as Presolution Test 1.

Once the presolution test 1 was finished 1mL of the $SnCl_2$ solution was added to the 200mL of ultra-pure 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 as 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. 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.

Standard 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 Tuberculin 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.

Following testing 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^{-3} and the reaction chamber inside the instrument was free of any mercury. Test results were recorded as posttest 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 soap 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.

Apparatus

A 500mL Buchner 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 Buchner 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.

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:

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

Where *t=1* is the time of the first sample and *t=lsm* 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^{-3}. 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
5.0mL	0.5

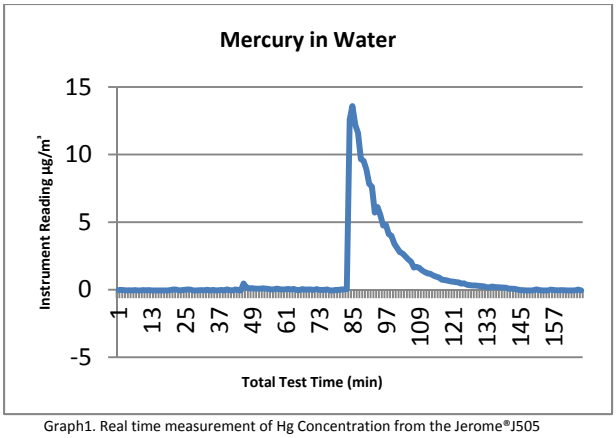
Table 1. Conversion of sample size to theoretical µg Hg

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 $SnCl_2$ and Ultra-Pure H_2O, the data was plotted.



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

From the graph, the pretest sequence was conducted from minutes 1 through 83. At minute 84 2.0mL of 0.1ppm Hg

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solution was added to the Buchner flask causing a response from the instrument. From minutes 84 to 144 the instrument sampled the headspace above the solution. This reduces the Hg concentration in the air above the solution, causing more Hg to evolve out of solution. The signal decay seen in the graph closely resembles an exponential distribution. At minute 145 the J505 was removed from the apparatus, and fitted with an activated carbon filter.

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 concentrations at 10ng/m^3. 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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