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Lead Detection in Water

Using Hydroxyapatite and Atomic Absorption

Nicolas Cantarero

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Hydroxyapatite is a mineral that is very inexpensive, easily made, and binds well to lead. In this procedure its application will be paired with Flame Atomic Absorption Spectroscopy (Flame AA) to detect lead concentrations in water to ppb levels. While ppb concentrations of lead are too dilute to produce a response from the Flame AA by using Hydroxyapatite to concentrate lead molecules from a larger volume and dissolving the Hydroxyapatite into a smaller volume it may be able to produce a response. The method could provide an inexpensive, efficient, and accurate way to detect lead concentrations to the ppb level in water.

Introduction:

Lead is a commonly used metal that is found in everything from car batteries and radiation shielding, to pipes and solder. Lead was discovered in 3500 B.C. but wasn't used extensively until silver from lead ore was discovered in 2500 B.C. The Greeks and Romans were the first to use lead on a massive scale using an average of 60,000 tons of lead per year for 400 years (Nriagu 43-44). The reasons for leads prolific use are: durability and corrosion resistance, it expands with water and does not burst by free-thaw cycle, easily reparable, easy to make, lead pipes do not rust, lead is easily found and mined, highly malleable, easy to smelt, and cheap (Nriagu 1-2). It was formerly used extensively in paint, gasoline, and plumbing but has since been discontinued because of lead poisoning. Lead is highly toxic to humans if ingested; it is a potent neurotoxin that accumulates in tissues and bone and causes many adverse health effects. The Environmental Protection Agency (EPA) has labeled lead a harmful contaminant and set standards for allowable concentration levels in foods, water, paint, and air (particulate matter).

The greatest exposure to lead is from ingestion via swallowing or breathing. Lead is not commonly found in point sources of water (streams, lakes, rivers, ground water) but leaches into the water from corroded pipes and plumbing materials, especially in houses built before 1986; homes built before then are more likely to have all lead pipes and fixtures (Lead in Drinking Water, EPA). Since the Safe Drinking Water Act was passed in 1974, drinking water has been closely monitored for trace levels of metals and other contaminants. In 1986 Congress restricted the use of lead pipes and other lead plumbing materials in drinking water system (Consumer Factsheet on Lead, EPA). The

EPA has set a maximum contaminant level (MCL or action level) of 15 parts-per-billion (ppb) and a maximum contaminant goal level (MCGL) of 0 ppb for lead (Lead in Drinking Water, EPA). Because of this it is very important that methods used for detecting lead be able to detect in the ppb range.

Lead has a very long residence time in the human body and accumulates in the bones. Lead is absorbed into the red blood cells and plasma where it is then redistributed to the bones and soft tissues. From there it is slowly excreted and as a biological half-life of approximately 10 years (Yantasee 1684). Associated short-term exposure health risks include: interference with red blood cell chemistry, delays in normal physical and mental development in babies and young children, slight deficits in the attention span, hearing, and learning abilities of children, and slight increases in the blood pressure of some adults. The long-term exposure health risks include all of the short-term health risks as well as: stroke and kidney disease; cancer. (Consumer Factsheet)

The annual drinking water quality report of Lincoln from 2008 gave an average of 4.09 ppb for the city of Lincoln, well below the 15 ppb MCL. (Annual Drinking Water Quality Report) Being that this is a city wide average, there are places which have lower concentrations of lead and others that could contain concentrations much higher than 5 ppb. Houses built after the lead ban came into effect have little chance of lead water contamination but many houses in older communities still have their original lead plumbing which could be a major source of lead contamination.

For my project I attempted to develop a method for lead detection to ppb levels using Hydroxyapatite (HA) and Flame Atomic Absorption Spectroscopy (Flame AA). Hydroxyapatite is a naturally occurring mineral ($Ca_5 (PO_4)_6(OH)_2$) that makes up

approximately 70% of our bones. Hydroxyapatite readily binds with lead (one of the reasons that lead accumulates in bones in the human body) creating lead apatite. It has many medical and dental applications including synthetic bone and teeth development. Its crystal structure, high surface area, and affinity to lead make it bind strongly. The Flame AA does not have the detection limit to be able to acquire a response from lead at low ppb levels. In order to be able to detect lead to such low detection limits the Hydroxyapatite was used to concentrate the lead to higher levels which the Flame AA will be able to detect. Essentially, using the HA to bind to the dissolved lead and concentrate water samples with lead to a concentration range that is within the scope of the Flame AA.

Methods:

Firstly the Hydroxyapatite must be synthesized, I based my Hydroxyapatite synthesis found in "Science and Medical Applications of Hydroxyapatite" by Hideki Aoki (Aoki 11-13). Once the Hydroxyapatite is synthesized it was filtered, collected, and dried. A 15 ppb lead standard was made using 1000 mg/L stock lead solution. A lead calibration curve was made ranging from .1 ppm to 2 ppm and run on the Flame AA, see graph 1. Glass columns were packed with 0.5-1.0 grams of Hydroxyapatite and 15 ppb lead standard solution was put through the column. Sample 1 was packed with 1 g of very fine Hydroxyapatite and 500 mL of 15 ppb lead standard was run through the column, afterwards 1 mL of concentrated Nitric acid was run through the column and diluted to 10 mL with deionized water (10% nitric acid). The columns for Samples 2-4 were also packed with 1g of Hydroxyapatite but were first sieved. 500 mL of 15 ppb lead

standard was run through the column for sample 2 and it was eluted with 1 mL of concentrated nitric acid and diluted to 10 mL with deionized water. Sample 3 was prepared just as sample 2 but 2 mL of concentrated nitric acid was used to collect the lead and it was diluted to 20 mL with deionized water. For sample 4 only 333 mL of 15 ppb lead standard was run through the column (calculated amount to give a signal in the middle of the standard curve) and 1 mL of nitric acid was used to collect the lead and it was diluted to 10 mL with deionized water. For samples 5 and 6 the columns and Hydroxyapatite were pre-washed with 10 mL of 10% nitric acid and then 300 mL of 15 ppb lead standard was run through the column. The column for sample 5 was packed with 0.5 g of Hydroxyapatite and the column for sample 6 was packed with 1.0 g of Hydroxyapatite, both columns were eluted with 10 mL of 10% Nitric acid.

Four blanks were also prepared to evaluate contamination from reagents. Blank 1 the column was packed with 1.0 g of Hydroxyapatite and 500 mL of deionized water was run through the column and then eluted with 1 mL of concentrated nitric acid and diluted to 10 mL with deionized water. Blank 2 was packed with 0.5 grams of Hydroxyapatite and 500 mL of deionized water was run through the column and then eluted with 1 mL of concentrated nitric acid and diluted to 10 mL with deionized water. For blank 3 the column was packed with 1.0g of Hydroxyapatite and 333 mL of deionized water was run through the column and then eluted with 1 mL of concentrated nitric acid and diluted to 10 mL with deionized water. Blank 4 was composed of just 10% nitric acid.

The samples and blanks were then run on the Flame AA and the resulting signal was used to calculate the concentration of lead in the sample using the standard curve. The Flame AA had a laminar flow burner and an air-acetylene flame with a lead hollow

cathode lamp set to 283.3 nm. Finally, dilutions were factored in and a final

concentration for the sample was calculated.

Results:

The responses for blanks 1-4 are as follows: 0.022, 0.019, 0.023, and 0; see table

1. The responses for samples 1-6 are as follows: 0.032, 0.025, 0.028, 0.033, 0.004, and

0.009, see table 2. The signals were then entered into the equation for the best fit line

from the lead standard curve (see graph 1) and the following concentrations were

calculated for samples 1-6 (ppm): 2.66, 2.08, 2.33, 2.74, 0.325, and 0.742; see table 2.

Then the various dilution factors were calculated in and the final concentrations for

samples 1-6 (ppb): 53.2, 41.5, 93, 82.8, 10.8, and 24.7; see table 2. Finally the blanks

were factored in and the final calculated values for samples 1-6 (ppb): 16.5, 4.83, 19.7,

24.8, 10.8, and 24.7; see table 3.

Conclusion:

Based on the results the pre-treated Hydroxyapatite with nitric acid would be the

most effective. Conditioning the Hydroxyapatite with 10% nitric acid reduces some of

the background interference and by running more samples the exact amount of

Hydroxyapatite needed could be determined, while 0.5 g Hydroxyapatite wasn't enough

to collect all the lead and 1g had too much interference a value somewhere in between

might work. While the very fine Hydroxyapatite from sample 1 yielded good results

most likely to its high surface area it is not practical because it took several hours for the

entire sample to run through the column. Using the 10% nitric acid to collect the lead

also reduced the background noise as opposed to using the concentrated nitric acid and diluting it afterwards which dissolved all the Hydroxyapatite in the column and the 1% nitric acid which was not strong enough to remove the lead from the Hydroxyapatite. Many of the calculated concentrations were scattered from the true value of 15 ppb for the samples, this could have been caused by potential contamination or user error during preparation. Future research could look into determining the optimal amount of Hydroxyapatite to pack into the column, crystal size and surface area of Hydroxyapatite, and different elution methods.

This procedure is a plausible method for lead detection and with more research could be fine tuned to offer a sensitive and accurate means of lead detection in water. It offers a relatively simple method, low estimated per sample cost and doesn't require expensive instrumentation like an ICP-MS. Acquisition of a Flame AA, maintenance, labor, and reagent costs would place this method at around 5 dollars per sample while for an ICP-MS it would be around 10 dollars per sample. Samples can be prepared and run very quickly, the materials and equipment are readily available, and the skill of the operator required make this an attractive method for lead detection.

Graph 1
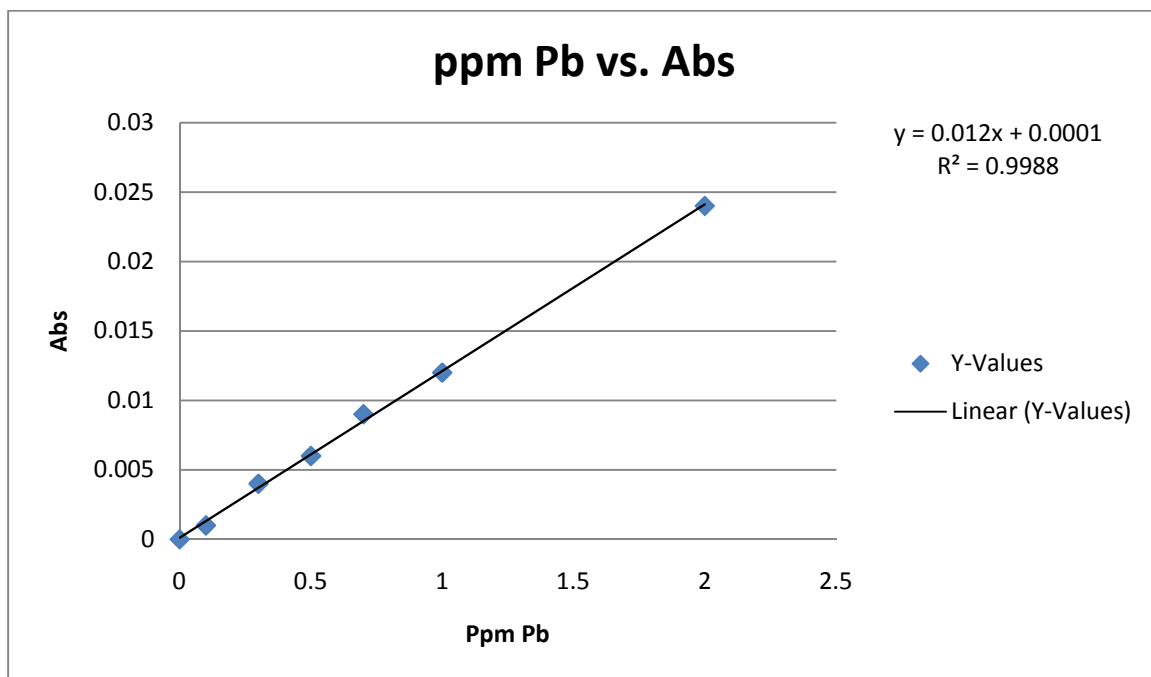
Lead standard curve run on the Flame AA with a concentration range of .1ppm to 2ppm.

Table 1: Flame AA signal for Blanks

Blank Number	Flame AA Signal
1	0.022
2	0.019
3	0.023
4	0

Table 2: Sample response and calculated values

Sample Number	Flame AA Signal	Ppm	Ppb
1	0.032	2.66	53.2
2	0.025	2.08	41.5
3	0.028	2.33	93
4	0.033	2.74	82.3
5	0.004	0.325	10.8
6	0.009	0.742	24.7

Table 3: Sample response and blank corrected values

Sample Number	Flame AA Signal	Ppm	Ppb
1	0.032	0.825	16.5
2	0.025	0.242	4.83
3	0.028	0.492	19.7
4	0.033	0.825	24.8

5	0.004	0.325	10.8
6	0.009	0.742	24.7

<p style="text-align: center;"><u>Works Cited</u></p>

"Annual Drinking Water Quality Report for 2008." *Lincoln.ne.gov*. Lincoln Water
      System, Apr. 2009. Web. 7 Aug. 2009.
      <http://lancaster.ne.gov/CITY/pworks/water/wtrqual/pdf/water08.pdf>.

Aoki, Hideki. <u>Science and Medical Applications of Hydroxyapatite</u>. Tokyo: Takayama P
      System Center Co., 1991. 11-13.

<u>Consumer Factsheet on: Lead</u>. 28 Feb. 2006. Environmental Protection Agency. 21 Mar.
      2008. <http://www.epa.gov/safewater/dwh/c-ioc/lead.html>

<u>Lead in Drinking Water</u>. 24 Aug. 2006. Environmental Protection Agency. 21 Mar.
      2008. <http://www.epa.gov/safewater/dwh/c-ioc/lead.html>

Nriagu, Jerome. "Historical Perspective on the Contamination of Food and Beverages
      with Lead" <u>Dietary and Environmental Lead: Human Health Effects</u>. Ed. Kathryn R.
      Mahaffey. Amesterdam, Netherlands: Elsevier Science Publishers B.V. (Biomedical
      Division), 1985. 1-36

Yantasee, Wassana, Yuehe Lin, Kitiya Hongsirikarn, Glen E. Fryxell, Raymond
      Addleman, and Charles Timchalk. "Electrochemical Sensors for the Detection of
      Lead and Other Toxic Heavy Metals: the Next Generation of Personal Exposure
      Biomonitors." <u>Environmental Health Perspectives</u> 115.12 (2007): 1683-1690.
      <u>American Chemical Society</u>. Love Library. 4 Apr. 2008.