Flame Atomic Absorption Work by H. M. Brinson and James McDowell Report by H. M. Brinson

EXECUTIVE SUMMARY

In order to determine the concentration of lead in a solution, the technique of flame atomic absorption was employed. An AA-6300 Shimadzu Flame Atomic Absorption Spectrophotometer was used, as well as an ACS-6100 auto-sampler. The flame was fed with acetylene and air, and the chosen emission line was 283.3 nm. By creating a calibration curve from standard solutions of Milli Q water and a stock solution of 20 ppm of lead, the lead concentration of eight unknown samples was calculated. Six of the eight samples (all four water samples, Licorice A/F, and Kava Kava) were below the limit of detection. The other two samples produced calculable concentrations. American Skullcap had a concentration of 1.683 ppm and Clove Buds had a concentration of 1.600 ppm.

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INTRODUCTION/BACKGROUND

Though there is not a coherent and well accepted definition, heavy metals are generally individual metals and metal compounds that have an adverse effect on a person's health, as described by the Occupational Safety and Health Administration (OSHA).¹ The difficulty inherent in heavy metals is the fact that many of them are necessary for living organisms to survive, but only in certain concentrations. Should too much accumulate in a system, serious damage can occur. Consider lead, for example. According to lead's MSDS sheet, should lead be absorbed through skin, inhaled, or ingested, damage to the blood, kidneys, and central nervous system can result.² This hazard makes regulation of lead's concentration in industrial settings and food content vitally important to the general population.³ To that end, it is imperative that a simple, cheap method be used to determine the presence of lead at fairly low concentrations.

One of the simplest methods currently in use today is flame atomic absorbance spectroscopy. This technique is based on the principle that each ground state metal absorbs light at a specific wavelength.⁴ Once the specific wavelength needed is determined, in this case 283.3 nm, the solutions are ionized by passing it through a flame. The ions are then subjected to light at the precise wavelength and the amount of light that is absorbed can be detected. However, this technique is not only simple because of the hardware used. The mathematical relationships behind the technique are also highly simplistic. Absorbance and concentration are directly related through the equation $A = \epsilon bc.^5$ As the concentration of the heavy metal increases, the amount of absorbance recorded increases as well.

However, flame atomic absorbance spectroscopy is only useful with the use of a calibration curve. Absorbance in and of itself is not an absolute term and therefore must be calibrated if it is to be of any use. Calibration curves are not difficult to construct. By supplying

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a known linear equation relating concentration and absorbance (see Graph 1), any other absorbances that fall into the range of the curve can be calculated.

According to lead's MSDS sheet, it is classified as a group 3 compound by the American Conference of Governmental Industrial Hygienists (ACGIH).² This classification means that lead is known to be a carcinogen to animals but has an unknown relevance to humans. According to OSHA's website, the common symptoms of acute lead poisoning are the following: loss of appetite, nausea, vomiting, stomach cramps, constipation, difficulty in sleeping, fatigue, moodiness, headache, joint or muscle aches, anemia, decreased sexual drive, and can result in death. The symptoms of chronic overexposure are severe damage to the blood-forming, nervous, urinary, and reproductive systems.⁶

EXPERIMENTAL

First, seven standard solutions were diluted with Milli Q water from a 20 ppm of lead stock solution. With a concentration range of 0 - 5 ppm, these solutions were used to make a calibration curve. Next, eight samples were gathered for lead testing. Of the eight, four were water samples gathered from around the laboratory building. One was taken from the hall's water fountain; one was taken from the sink in the ladies' bathroom; one was taken from a sink in the laboratory; and one was taken from the sink in the men's bathroom. The remaining four unknowns tested were Licorice A/F (starting material: 1.2035 g/50 mL of 5% Nitric acid/95% water), American Skullcap (starting material: 1.1362 g), Kava Kava (starting material: 0.984 g), and Clove Buds (starting material: 1.0331 g). These four samples were microwave digested in 5 mL of nitric acid before being diluted to 50 mL with Milli Q water.

Once the 15 solutions were ready, the flame atomic spectrophotometer was started. In this experiment, an AA-6300 Shimadzu Flame Atomic Absorption Spectrophotometer was used,

in conjunction with an ASC-6100 auto-sampler. The flame was fed by acetylene and air, and the light source was a hollow cathode filled with neon gas. Each of the 15 solutions were loaded into the auto-sampler and tested at an emission line of 283.3 nm. The first seven solutions were used to construct a calibration curve while the other eight were tested to determine their lead concentration.

RESULTS

In order to determine the concentrations in the unknown samples, a calibration curve was first constructed. Table 1 shows the concentrations tested and the corresponding absorbance.

Table 1: Calibration Curve Data		
Concentration (ppm)	Absorbance	
0	0.005	
0.025	0.007	
0.05	0.008	
0.1	0.007	
0.3	0.014	
1.0	0.035	
5.0	0.126	

This was used in Graph1 to determine the linear relationship between concentration and absorbance. The equation of the line was then used to determine the concentration in the eight unknown samples.



Using this, Table 2 was constructed from data obtained during the experiment and calculations obtained from Graph 1.

Table 2: Experimental Data		
Solution Tested	Absorbance	Concentration (ppm)
Water Fountain	Below LOD*	
Girl's Bathroom	Below LOD	
Laboratory Sink	Below LOD	
Boy's Bathroom	Below LOD	
Licorice A/F	Below LOD	
American Skullcap	0.047	1.683
Kava Kava	Below LOD	
Clove Buds	0.045	1.600
*Limit of Detection		

As the table shows, most of the solutions' lead concentration was too low to detect, much less quantify.

Below is a sample calculation used to determine the lead concentration in an unknown, in this case, American Skullcap.

Y = 0.024X + 0.007

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$$Y = 0.047$$

$$X = \frac{Y - 0.007}{0.024} \text{ ppm}$$

$$X = \frac{0.047 - 0.007}{0.024} \text{ ppm}$$

$$X = 1.683 \text{ ppm}$$

DISCUSSION

As recorded in Table 2, most of the solutions tested did not have a detectable amount of lead present to determine concentration, which is as close to zero as analytical chemistry can reach. The limit of detection is defined to be $LOD = 3\sigma$, or three times the standard deviation of the blank. At minimum, the analyte's signal must be three times the instrument's noise in order to say there is something present. On the other hand, the limit of quantification is the minimum value needed to accurately determine how much of the analyte is present. The limit of quantification is defined to be $LOQ = 10\sigma$, or ten times the standard deviation of the blank. The difference between the detection limit and the quantification limit is rather simple. The limit of detection can give a false negative (ie, say there is no analyte) nearly half of the time, whereas the limit of quantification has a highly minimal chance of producing a false negative.⁷

During the course of this experiment, an exact limit of detection was not calculated. In previous tests, such attempts not only greatly complicated matters, but also distorted the instrument's readings and threw off the entire data collected. So, for the purposes of this experiment, anything said to be below or above the LOD is far enough removed for such an assumption to be made.

In Graph 1, the coefficient of determination, R^2 , has a value of $R^2 = 0.997$. The purpose of the coefficient of determination is to determine how well a model fits the available data. For calibration curves, the model was a linear trendline. The closer the R^2 value is to 1, the better the

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fit. In this case, the calibration curve is an excellent predictor of concentration (given the concentration is within the boundaries of the curve).

In the four water samples, it is expected that concentration would be below the LOD. The water in this country goes through a highly complicated and thorough cleaning process, in part to remove any heavy metals in the drinking water. In the remaining unknown solutions, only two produced detectable absorbance signals, resulting in concentrations of 1.6 and 1.683 ppm, well within the range of the limit of quantification.

One of the largest sources of error in this experiment would result from memory effects. The presence of analyte within the mechanisms of the instrument between testing solutions can be problematic when attempting to determine the concentration of analyte present in a slew of solutions. The primary method used to reduce any memory effect was to rinse thoroughly the auto-sampler. Even though this only occurred between the standard solutions and the unknown, when the data is considered, it is clear that there was no great memory effect present in this experiment. The calibration curve has a rather high coefficient of determination, indicating precision in the employed method. The calibration curve was also completed by testing the solutions with the lowest concentration to the highest. Any lead accumulation during the calibration curve samples would be of a greatly lesser concentration than the solution actively being tested, resulting in a minimal memory effect. The unknown solutions tested, most of the samples were below the LOD, which would not occur if there was build up of lead in the instrument. Not only that, but there was a "blank" solution between the two samples with a higher concentration. Again, the Kava Kava sample would not read "blank" should a serious memory effect be taking place.

CONCLUSION

Flame atomic absorption spectroscopy is one of the easiest methods used to determine heavy metal concentrations in solution. Of the eight unknowns tested, only the American Skullcap and Clove Buds produced calculable concentrations, at 1.683 and 1.600 ppm respectively; the rest were below the limit of detection.

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