

Proposal Coversheet

Application Submitted

To: Dr. Arlene Courtney

Program: Ch 462 Experimental Chemistry

Title of Project: [Lead Analysis Project]

Suggested Timeline: [Monday lead leaching 24Hours, Tuesday 1-2 hours for conducting experiment]

Date Submitted: [1/26/09]

Principle Investigator

Applicant's Contact Information *Proposal #2*

Abstract:

During the 1930's Uranium was popular component of glazes used for ceramics. The glaze would radioactively decay releasing radiation and lead.¹ This posed a health hazard as the lead would be consumed by anyone eating food off of these plates. A simple leaching test can be conducted to determine if the plate is safe to eat from. The interior of the fiestaware bowl is to sit in a vinegar solution (4% acetic acid) for 24h. A flame atomic absorption spectrometer will be used to analyze the lead content of the acid solution. From here a conclusion can be drawn as to whether or not the bowls are safe to eat from.

¹Experimental Chemistry. Course home page. Dept. of Chemistry

Introduction

In the 1930's Homer Laughlin started to mass produce and mass market simplistic brightly mono colored dinnerware coined Fiestaware.² Uranium oxide was used to prepare the glazes that produced the bright and vibrant colors commonly associated with the Fiestaware line. During this period of time the toxicity of Uranium was not well understood or well known. Through multiple decay processes, Uranium-238 radioactively decomposes to Lead-206 with the release of alpha and beta particles.³ This isotope of lead is stable and will not decay any further. The concern for this decay product is that lead can affect the nervous system, high blood pressure and other effects.

There are three reasons why lead is leached from these plates; the glaze was improperly formulated, the glaze was not properly fired, and/or coloring agents were improperly used.⁴ Leaching of lead due to acidic food is usually exaggerated due to one or more of said reasons. New techniques such as fritting (chemically binding the lead) have largely eliminated leaching concerns. An increase in temperature will cause more lead to be leached from the ceramic.

The Fiestaware in the natural science building is believed to contain lead in the glaze. These bowls were produced in a timeframe when uranium was commonly used in the glazes in ceramics to produce vibrant colors. The objective of this study is to determine the amount of lead leached from the ceramic. The data from this experiment can then be compared to the government accepted standard of lead consumption to determine if these plates are accepted for food serving.

Justification

Consumer safety testing has the potential to save many lives from faulty products and money from lawsuits. From an ethical and economic point of view this should be sufficient reason to conduct this experiment. Lead poisoning has very serious side effects to children and adults and determining the safety of this bowl would be of great importance.^{5,6} Fortunately there is an efficient and economical method for analyzing suspect samples.^{7,8} The method involves soaking the ceramic dish containing lead in a batch of acetic acid 4% solution for 24 hours at about room temperature (20-24 Celsius). A Flame Atomic Absorption Spectromometer (FAAS) can be used to detect lead at very low concentrations. The materials needed for testing can be easily found in the store or are already present in the laboratory. A 4% solution Acetic acid (vinegar) can be easily found in the grocery store or produced from glacial acetic acid. The lab in room 114 is already equipped with the necessary lab ware to conduct the experiment such as a FAAS and beakers. Instructions on conducting this experiment and operating the lab equipment are well documented in literature and can be referenced upon if needed. 5

Budget + timeline

Budget: The most expensive piece of equipment, the FAAS is already provided to us at no cost. Western Oregon University's lab is very well stocked with glassware and chemicals. If the required chemicals are not present they can be ordered with a minor cost incurred.

²Experimental Chemistry. Course home page. Dept. of Chemistry'

³Argonne National Laboratory

⁴Lead Glazes for Ceramic Foodware

⁵Ecole Nationale De La Sante Publique

⁶Karray Academy for Technology

⁷AOAC Official Method 973.32

⁸The Journal of KMITNB

Timeline: This lab can be completely run in one class day as long as the bowl is prepared 24 hours in advance. The group conducting the lead experiment should only take about 45-60 minutes at the most. 15-20 minutes of time will need to be budgeted for preparing the stock solutions. 15-20 minutes of time will need to be budgeted for preparing the calibration curve. The remainder of time will be budgeted for aspirating the lead leach solution. Our group has conducted similar experiments in Instrumental analysis and this experiment should be fairly elementary process. More time can be budgeted if needed.

Literature Review

Procedures from various scientific articles were reviewed to determine a valid method for lead analysis. The Association of Official Agricultural Chemist's (AOAC) official method 973.32 and was chosen as the procedure for analyzing the lead content of solutions. Another method known as ASTM C738 – 94 was reviewed. This procedure was essentially identical to AOAC procedure. Both recommend the same equipment, chemicals and so on.⁹ The other method was chosen due to the fact that a previously reviewed article based its procedures off of the AOAC method.¹⁰

A research group, Tatsuya Seki et al. of Nissan Chemical Industries, was analyzing traces of lead in river-water and seawater by flow Injection Flame Atomic Absorption Spectrometry (FI-FAAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Data was collected using a Shimadzu Model AA-6400F atomic absorption spectrophotometer and a Seiko Instruments SPQ9000 ICP-MS. Data collected by the group indicated that the ICP-MS was far superior in terms of detection ability.¹¹ The group even had to change elution media as the ICP-MS was detecting lead impurities within the reagents. With budget constraints in mind the FAAS is a realistic alternative to the more expensive ICP-MS.

Furthermore AAS is a common technique for detecting metals in the environment such as lead.^{10,11,12} The method of operation is very simplistic. A sample of the solution to be tested is aspirated which is injected into a heat source (C₂H₂/O₂ flame). The flame source is placed between a light source and a detector. The vaporized metal blocks the path of light and the detector records that reduction as absorption. A calibration curve can be formed by aspirating known solutions and the concentration of an unknown sample of metal can be determined.

9Lead Glazes for Ceramic Foodware

10The Journal of KMITNB

11Seki T.; Hirano Y.; Oguma K. On-line Preconcentration and Determination of Traces of Lead in River-water and Seawater by Flow Injection-Flame Atomic Absorption Spectrometry and ICP-Mass Spectrometry JSAC

12Atomic Absorption Spectroscopy

Method

A modified version of the AOAC method for detecting lead is disclosed here.⁸

B. Apparatus

- (a) Atomic absorption spectrometer.--Equipped with light sources specific for lead (hollow cathode), instrumental background correction, and a 4-in (102 mm) single slot or boiling burner head. Digital concentration readout may be used. Use air-acetylene flame, instrumental background correction, and operating conditions recommended by instrument manufacturer. Measure Pb at 217nm or 283.3 nm.
- (b) Laboratory beakers, flasks, stirring rods.--Use chemically resistant plastic, borosilicate glass, quartz, or Teflon. Clean by rinsing with dilute nitric (1 + 10) acid followed by copious quantities of water. Fiestaware bowl.

C. Reagents

- (a) Acetic acid. 4%. Mix glacial acetic acid and H₂O (1 + 24). Since this experiment is simulating the safety of using foodtype products in the bowl, vinegar (4% acetic acid) will be used instead
- (b) Detergent wash. Use detergent designed for washing household dishes by hand. Mix with lukewarm tap water according to product instructions.
- (c) Lead standard solutions.--(1) Stock solution. 1000ug/mL. Dissolve 1.5985 g Pb(NO₃) in 4% acetic acid and dilute to 1L with same solution. Commercially prepared stock solution may be used.
- (2) Working solutions. Dilute 0.0, 1.0, 2.0, 3.0, 5.0, and 10.0 mL stock solution to 1 L with 4% acetic acid (0, 1, 2, 3, 5, and 10 ug/mL).

D. Extraction

Take a method control through entire procedure, using a laboratory beaker with dimensions similar to ware being tested.

Cleanse Fiestaware bowl using detergent wash. Rinse with tap H₂O followed by distilled H₂O, and dry. Fill the bowl with 4% acetic acid to within 6-7mm of overflowing.

Measure distance along surface of bowl, not vertical distance. Record volume of acid used. Prevent evaporation by covering each unit with an inverted glass or plastic Petri dish or laboratory beaker. Cover bowl to prevent interaction with light. After 24 h leach, stir leach solution and remove a portion by pipetting into clean container.

Calculation.—Calculate ug/mL in test and independent check solutions by comparing absorbance of test and check solutions to absorbance of working standards and multiplying by dilution factor. Calculate ug/mL released from test units by subtraction.

$$\text{Ug/mL released} = (A * B) - C$$

Where A = ug/mL found in test leach solution; B = dilution factor (volume of diluted solution/volume of aliquot diluted); and C = concentration found in the method control solution. For each unit report Pb released in ug/mL, leach volume of test unit in mL, depth of test unit mm, and type of test unit.

⁸AOAC Official Method 973.32

References:

¹Argonne National Laboratory/EVS, *Natural Decay Series: Uranium, Radium and Thorium* [Electronic Version], <http://www.ead.anl.gov/pub/doc/natural-decay-series.pdf> August 2005, Human Health Fact Sheet.

²Lehman, L. R. *Lead Glazes for Ceramic Foodware*, First edition, The international Lead Management Center, 2002, 1-7, 10-11, 127
<http://www.ilmc.org/Publications/ILMCFinalCombo8-02B.pdf> (last accessed 1/12/09)

³Disyawongs, G.; Mukprasert A. *The Journal of KMITNB* [Online Version] Jan-Mar. 2005, Vol. 15, No. 1, 34-38 <http://www.kmutnb-journal.net/journal/252910255019030.pdf> (last accessed 1/12/09)

⁴Seki T.; Hirano Y.; Oguma K. On-line Preconcentration and Determination of Traces of Lead in River-water and Seawater by Flow Injection-Flame Atomic Absorption Spectrometry and ICP-Mass Spectrometry *JSAC* [Online Version] March 2002, Vol. 18,

⁵Karim H., *Analysis of lead in dust by ICP-MS-Development of a method for estimation of the exposure of children to lead*, Ecole Nationale De La Sante Publique [Online Version] March 2005, Pg. 2-3,7,11 (last accessed 1/12/09)

⁶Mansour Mohammed E., Lead Traffic Air Pollution, Karray Academy for Technology, pg. 5-7 (last accessed 1/12/09) <http://www.ses-sudan.org/english/conferences/Environment/2/Mohammed%20Eltayeb%20Mansour.pdf>

⁷The Determination of Hazardous Substances According to RoHS and WEEE directives Pg. 3

⁸Lead and Cadmium in Cookware. In *Official Methods of Analysis of AOAC International*; P. AOAC International: Gaithersburg, MD, 1998; Ch 9 6-6a

⁹Guihua Ma, Georgina Wilson Gonzalez, *Environmental Sampling & Monitoring Primer* (accessed 1/12/09),
<http://www.cee.vt.edu/ewr/environmental/teach/smprimer/aa/aa.html>

¹⁰Atomic Absorption Spectroscopy (accessed 1/12/09),
<http://www.gmu.edu/departments/SRIF/tutorial/aas/aas.htm>

¹¹Courtney, Arlene. *Experimental Chemistry*. Course home page. Dept. of Chemistry, Western Oregon University. 23 Jan. 2009 <<http://www.wou.edu/las/physci/ch462/proposal.htm>>.