

Proposal Coversheet

Application Submitted

To: Dr. Arlene Courtney

Program: Ch 462 Experimental Chemistry

Title of Project: Leaching and Analyzing Lead from Ceramic Glazes

Suggested Timeline: Two days

Date Submitted: January 26, 2009

Principle Investigator

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Proposal # 7

Abstract:

Fiesta ware and other antique ceramics were decorated with glazes containing uranium or lead to impart bright colors. Uranium is a radioactive element that decays following a natural decay series to a more stable element, lead. The lead formed from the uranium can be leached from the glazes on these ceramic pieces into the food they hold. The leached lead is ingested by people and is very toxic. Lead affects neurotransmitters, the central nervous system, the cardiovascular system, the kidneys, and other body systems. Estimates say that the average Fiesta ware dish contains about 4.5 grams of lead. It has been found that acidic foods and heat further the process of lead leaching out from the glaze. Western Oregon University owns a Fiesta ware bowl. An experiment is needed to determine the amount of lead that can be leached from the bowl. The amount of lead leached out will be compared to the legal level of 0.005 mg/L of lead set by the Food and Drug Administration (FDA). To leach the lead from the bowl, the standard 24 hour acetic acid leaching procedure carried out at room temperature will be followed, but vinegar will be used in place of acetic acid. Flame Atomic Absorption Spectrometry (AAS) will be used to analyze and determine the concentration of the lead in the leachate. The AAS will have a light source specific to lead, be operated at the maximum absorption frequency for lead (217.0 or 283.3 nm), be capable of instrumental background correction, and use an air-acetylene mixture flame.

Introduction:

Fiesta ware was a popular dinnerware first created during the Great Depression era. This pottery was produced by the Homer Laughlin Company as affordable and attractive dinnerware. Unfortunately, the brightly colored glazes used on Fiesta ware were made from uranium and other materials. Fiesta ware was not the only dinnerware to use uranium in the glaze. Almost every antique dinnerware used harmful chemicals as coloring agents. Estimates have been made indicating that up to fourteen percent by weight of the glaze is uranium (about 4.5 grams per large item). Uranium is a radioactive element that decomposes to a stable element, lead. The lead in the Fiesta ware can leach out of the glazes and into the food they contain. Acidic foods and heating increase the rate of lead leaching.¹

There are three ways in which people are exposed to poisoning from the uranium including being in the vicinity of the object, touching the object, and ingesting the lead leached from the glaze and into the food. The first two methods expose people to beta and gamma rays emitted by the radioactive particles in the uranium. The third method of toxin exposure is by far the most dangerous and concerning since the purpose of the Fiesta ware was to hold food.¹

The uranium in the ceramic glazes undergoes a natural decay series. This means the radioactive uranium is unstable and will transform itself into a more stable element by emitting subatomic particles like alpha and beta particles. Alpha particles consist of two protons and two neutrons ejected from the atom's nucleus. Beta particles are high-energy and high-speed electrons, but less harmful than alpha particles and gamma radiation. Gamma radiation is emitted as a means to release excess energy. The alpha and beta particle emissions account for the transformation of uranium to lead. Uranium always decomposes to a stable isotope of lead.²

People can absorb lead into their bloodstreams through touch, ingestion, or inhalation. Inhalation results in up to 50 percent of absorption of lead while touching lead absorbs less than 1 percent into the bloodstream. Adults absorb less lead through the digestive tract than do children. People with poor health will absorb more lead that has contaminated their food. Lead has been shown to disrupt the function of several neurotransmitters thus affecting the central nervous system and all the bodily functions it controls. Lead poisoning in children can be severe and lead to lowered IQ scores, seizures, coma, and death. Adults with lead poisoning can experience forgetting recently acquired skills, listlessness, trouble with coordination, vomiting, seizures, coma and death. Once the damage has been done, it is hard to reverse. Therefore, it is easier to prevent lead poisoning than to treat it.³

Most modern pieces of ceramic ware that contain small amounts of lead in its glaze will not introduce enough lead into the food to cause concern. The body can handle small doses of lead. Cause for concern arises when the glaze is damaged or the glaze contains a large amount of lead. The Food and Drug Administration (FDA) has set limits on the amount of lead ceramic dishes can safely leach into food. The levels are based on the size of the dish, the type of food it will contain, the temperature of the food, and the frequency of its use. Coffee mugs, for example, have lower allowed leachable lead values because they are used often, hold acidic beverages, and the heat of the liquids they contain speeds up the leaching process.^{3,4}

The kidneys, cardiovascular system, and the nervous system are the most susceptible to lead poisoning. The maximum legal levels of lead in water is just under 0.015 mg/L defined by the Environmental Protection Agency (EPA) and 0.01 mg/L as defined by the World Health Organization (WHO). The maximum legal level of lead in food set by the FDA is 0.005 mg/L.⁴

Western Oregon University has obtained ownership of a Fiesta ware bowl. Previous use of a Geiger counter has confirmed its radioactivity. The radioactivity indicates uranium is present in the glaze. Since uranium is present, its decomposition product, lead, should be present as well. It must be determined if the amount of lead leached from the glaze is higher than the maximum legal limits. The lead will be leached from the glaze using vinegar and analyzed using flame atomic absorption spectrometry (AAS). Analysis will determine if the bowl is safe for food use by determining the amount of lead leached out and comparing this value to the legal limits.

Justification:

The goal of this experiment is to leach lead from a Fiesta ware bowl and determine its concentration. The experiment should use an acidic liquid like vinegar to successfully leach the lead from the bowl. The standard experiment uses 4 percent acetic acid to leach the lead from the glaze but vinegar is comparable, readily available, and cheaper. The entire experiment takes a little more than a day to complete. Analyzing the leached lead with flame AAS using standard solutions of known lead concentrations and controls will determine the concentration of the leached lead. Comparison of this value to the legally set values will qualify the bowl as safe or unsafe for use with foods.

The flame AAS instrument is the most reliable method to analyze lead content although inductive coupled plasma mass spectrometry (ICP-MS) has also been used. AAS is versatile and sensitive enough for most purposes. The AAS method of analysis will measure the resonance absorption of the lead atoms. The frequencies of this resonance are known to be 217.0 and 283.3 nm and reproduced by a cathode lamp used to induce the resonance. Using the AAS along with standards and controls will result in a 1-5 percent accuracy.⁵ Previous work has proven

successful in leaching lead from Fiesta ware and other antique ceramics with acetic acid and analyzing the concentration with AAS.

An AAS instrument is available in the lab already so it will be the analysis method of choice. Since the equipment is already available, the only cost for the experiment will be the vinegar to leach the lead. Discovering the amount of lead leached from this ceramic bowl will help to notify those owning similar ceramic pieces about the dangers of its improper use. This will help prevent some future lead poisoning.

Literature Review:

Lynch and his colleagues studied ceramic ware that had been decorated with glaze composed of lead oxide and other materials. They focused their efforts on the benefit of the Hispanic society from their experiment since Hispanic families are traditionally more likely to use ceramic cookware to prepare and serve food. They discovered that increased food volumes, fluid temperatures, cooking times, and food acidity all contributed to the amount of lead leached from the glaze and into the food. From their research, they found that around 84 percent of tested ceramics yielded leached lead levels exceeding the Mexican standard of 7 mg/L.⁶

They performed the standard 24-hour acetic acid assay to leach lead from the sample ceramic containers. The FDA action level for large ceramic bowls is 1.0 µg/mL. From the tested samples, 52 percent were found to exceed the FDA action level. However, there is some controversy surrounding this result. The measured amount of lead leached from the container using acetic acid does not accurately assess the risk posed to people from ingesting food prepared in these vessels. The risk depends on the type of food cooked in the vessel, the pH of that food, and the portion size of the food consumed. However, they also tested several types of food that may be cooked in these containers. They found that acidic foods like tomatoes would

cause concern and result in elevated blood lead levels but basic foods like beans would not. All tested vessels had been previously used, so the values obtained in their experiment were under-representations of the initial lead levels possibly leached from the glaze. Therefore, the danger of using these ceramic vessels was greater when they were new. Also, the food they tested was only cooked in the vessels for five minutes. A longer cooking time would have leached more lead into the food.⁶

Lehman writes that lead containing glazes are not dangerous if made and used properly. Glazes that are not made properly, used properly, or fired properly will leach lead in higher levels than that allowed by legal guidelines. He also confirms that the greatest success in leaching lead from glazes is with acidic media like that used in the standard acetic acid procedure carried out at room temperature. Passing the test requires the acetic acid to contain 0.5 to 2 parts per million (mg/L) of lead or less. This value, however, depends on the shape and size of the ceramic piece.⁷

Tatsuya and colleagues studied lead levels in river and sea water using the same methods as used when analyzing lead leached from ceramic dishes. AAS is the best method to detect trace amounts of lead. It is the most reliable and most commonly used method of analysis.⁸

Disyawongs and Mukpresert found that leaching lead from the ceramic dinnerware with the acid at an elevated temperature for a shorter duration produced 1 to 8 times more lead content in the acid than the standard experiments. The AAS analysis of the lead followed AOAC procedures. They also found that the use of more oil in cooking also results in more lead leached from the item.⁹

Methods:

The standard method of using acid to leach the lead from the ceramic piece as described by the AOAC will be used followed by analysis with flame atomic absorption spectroscopy.

The bowl should be properly prepared before the extraction of lead begins. A detergent designed for washing household dishes by hand and lukewarm water will be used to clean the bowl following instructions on the detergent's label. The bowl will be rinsed with tap water to remove any soap residue and then rinsed again with distilled water to remove any lingering surface contaminants. Vinegar will be added to the bowl and the volume added recorded. The same volume of vinegar will be added to a similar sized lab beaker as a control sample. Evaporation of the vinegar will be prevented by covering the test containers. The vinegar will be left to sit in the bowl and beaker for 24 hours at room temperature. Then the vinegar will be stirred and samples taken by pipetting into smaller, clean beakers.¹⁰

It would be most desirable to have several dishes to test; however, there is access to only one bowl. Several different samples taken from different areas of the bowl would need to be analyzed. Since the bowl needs to remain intact, the leach solution will need to be sampled at least three times to obtain an average measurement of leached lead.

A standard lead stock solution of a known concentration of 1000 $\mu\text{g}/\text{mL}$ should be prepared using lead nitrate (PbNO_3) and vinegar. Using the stock solution, working solutions will be made to obtain data for a calibration curve. The working solutions will consist of 0.0, 1.0, 2.0, 3.0, 5.0, and 10.0 mL of stock solution diluted to 1 L with vinegar to make the known concentrations 0, 1, 2, 3, 5, and 10 $\mu\text{g}/\text{mL}$, respectively. In addition, an independent stock solution should be made from a different source of PbNO_3 with a lead concentration of 5 $\mu\text{g}/\text{mL}$.¹⁰

The atomic absorption spectrometer used will be equipped with a light source specific for lead, instrumental background correction capabilities, a 4 inch single slot or Boling burner head, and will use an air-acetylene mixture flame. The instrument will be optimized for maximum signal using a lead lamp and collecting data at a wavelength of 217.0 or 283.3 nm. The background correction and flow rates of the fuel will be set to those specifications recommended by the manufacturer. The AAS will be used to measure the absorbance of the leach solution, the working standards, and the independent check solution. The zero point will be checked between solutions with the control in order to verify the correct preparation of the standard and working solutions. If the concentration of the independent check solution does not match its known concentration to within 5 percent, new standards and independent check solutions should be prepared with a different source of lead and retested. Leach solutions containing more than 10 µg/mL of lead will need to be diluted with vinegar in order to get a more accurate result.¹⁰

The absorbance data from the working solutions will be used to create a calibration curve. This curve will help calculate the concentration of lead from the sampled leach solution. The final amount of leached lead from the bowl can be calculated from the following equation:

$$\mu\text{g/mL released from the bowl} = (A \times B) - C$$

where A is the µg/mL of lead found in the test leach solution, B is the dilution factor (volume of diluted solution divided by volume aliquot diluted), and C is the concentration of lead found in the control sample. The concentration of the lead leached from the bowl will be compared to the FDA standard set at 0.005 mg/L.¹⁰

Budget and Timeline:

The materials needed for this experiment are already available in the lab except the vinegar. The vinegar can be bought at a local grocery store for less than ten dollars. The

experiment will take a little over a day to complete. The vinegar must sit in the bowl for 24 hours and then it should take a maximum of 2-3 hours to complete the analysis.

References:

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