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Literature Review on Determination and Estimation of Lead in Vegetable Food Stuff Grown With Industrial Wastewater By Polarography Techniques

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ABSTRACT: Lead pollution has increasingly become the focus of environmental pollution, which is a great harm to the ecological environment and human health. Strict control of the emission of lead pollutants and accurate monitoring of lead are very important. The lead ion detection technologies are introduced here, including spectrophotometry, electrochemical method, atomic absorption spectrometry, and other detection methods, and the methods' applicability, the advantages, and disadvantages are discussed. The detection limits of voltammetry and atomic absorption spectrometry are as low as 0.1 µg/L, and those of atomic absorption spectrometry are as low as 2 µg/L. The detection limit of photometry is higher (0.01 mg/L), but this method can be achieved in most laboratories. The application of different extraction pretreatment technologies in lead ion detection is introduced. The new technologies develop at home and abroad, such as precious metal nanogold technology, paper microfluidic technology, fluorescence molecular probe technology, spectroscopy, and other emerging technologies in recent years, are reviewed, and the principle and application of various technologies are expounded

KEYWORDS-lead, vegetable food stuff, industrial wastewater, polarography techniques

I. INTRODUCTION

Lead is the most abundant heavy metal in the earth's crust, which has stable chemical properties, excellent ductility, and easy to form alloys with other metals. Lead can absorb X, γ, and other rays, so it is widely used in industry. The universality of lead use also leads to the universality of lead pollution in our environment. It is a toxic heavy metal, and there has been a lot of research on environmental safety. It is a pure toxic, neurotoxic, heavy metal that has no metabolic benefits and is easily absorbed by the human body, especially through the ingestion of contaminated food or water. There has been sufficient evidence to prove that the toxic effect of excessive intake of lead on humans, especially children, is enormous [1]. Even a small amount of lead that enters the environment should be controlled. However, the discharge of three wastes from lead industry, the use of common daily products, such as lead-containing ceramics/ink/cosmetics, automobile exhaust emissions, and the consumption of lead-contaminated food, have all led to the potential safety hazards of unconscious lead intake in our daily life, which threatens people's health. Lead pollution is widespread in our daily life [2,3,4]. Wang et al. [5] found in a comparative survey on food intake and lead exposure of Chinese residents that people are most exposed to lead in beverages, followed by dried beans and dark vegetables. Even if the percentage of lead intake is small, it means that lead accumulates in the body all the time through the food people eat every day. With the improvement of people's requirements for the quality of life, the detection and analysis of lead has been paid more attention.[1,2,3]

Lead is usually absorbed by human body or animals and plants in the form of lead ions, then it reacts with biological macromolecular affinity sites in biological systems, affecting different organs of organisms with acute or chronic toxic effects. The heavy metal lead cannot be degraded by organisms and is extremely difficult to discharge, so it accumulates in living organisms. Simultaneous exposure to two or more heavy metals can also have a cumulative effect. Lead is a neurotoxic substance, which is mainly absorbed through the respiratory tract, digestive tract, and skin, and it is rapidly distributed to organs and tissues of the whole body after entering the blood. Therefore, lead is a toxic heavy metal

that can lead to systemic diseases of the human body, such as central nervous system damage, lung dysfunction, anemia, cardiovascular dysfunction, etc., and even has certain carcinogenicity [6,7]. Most of the lead in the human body is mainly stored in the bone in the form of trilead phosphate, and a small amount is stored in the liver, spleen, brain, and other organs and cells, and maintains a dynamic exchange process with blood at any time. Therefore, blood lead concentration is usually used in medicine to reflect the health hazards of lead in the human body. The blood lead content of the human body is between 0 and 99 μg/L. The median blood lead of male and female in eastern China is 44.00 (29.00–62.16 μg/L) and 37.79 (25.13–54.35 μg/L), respectively [8]. The international level of concern for human lead poisoning is 100 μg/L. When the contamination of lead in soil reaches a certain degree, it will have a large impact on the growth and quality of plants. High concentrations of lead will inhibit the germination of plant seeds and the growth of seedlings, reduce the content of chlorophyll in plant leaves, resulting in the decline of plant photosynthesis, and affect plant growth and fruit yield [9,10,11,12].

In view of the harmfulness and destructiveness of heavy metal lead ions to the environment, it is of great practical value and scientific significance to use effective technology to remove heavy metal lead from the environment. At present, many methods have been used to remove heavy metal ions in sewage, such as precipitation method, adsorption, electrochemical methods, etc. [13,14,15] Among them, the adsorption method is the most commonly used method and is considered to be one of the most promising methods because of its advantages of simple design, low cost, high efficiency, and easy operation [16,17,18]. Since lead is ubiquitous in our living environment, it is essential to detect lead ions in order to effectively avoid or reduce lead intake. How to quickly and accurately detect the content of lead ion in aqueous solution is a topic actively explored by relevant industry personnel, which is of great significance for people to avoid significant economic losses in agricultural planting and maintain personal health.

II. DISCUSSION

A rapid, precise procedure is described for the determination of lead in food and feed products with electrothermal atomic absorption spectrophotometry. Samples were mineralized in a microwave acid digestion bomb in the presence of nitric acid and vanadium pentoxide. Lead concentrations were determined directly from digested samples. The detection limit was 0.04 ng/mL. Accuracy and precision were checked against National Institute of Standards and Technology standard reference material. The analytical method was tested with 51 food and feed crops from Mediterranean zones in Spain and found to be suitable for these products. Lead concentrations in samples ranged from not detectable to 2.695 micrograms/g (fresh weight). By means of atomic absorption spectrophotometry, the authors determined the lead content in vegetable, fruit and soil samples from the environments of a lead-smelting plant. The lead values obtained were some 10- to 100-fold higher than those found normally. The mean lead content in vegetables varied from 2 to 150 p.p.m. in dry matter; that in fruits, from 4 to 35 p.p.m. Lead concentrations ranging from 575 to 2900 p.p.m. were detected in the soil samples. The mean lead content in the atmosphere was between 0.62 and 0.95 mug/m3 (maximum value 12 mug/m3). From these data it was calculated that the total resorption of lead from vegetables, fruits, potatoes and air varied from 0.04 to 0.49 mg/day[4,5,6] in the territory under investigation. To protect the population against increased intake of lead, it is recommended to abandon individual and commercial vegetable and fruit growing, especially leaf vegetables. Since the contamination of the soil persists for generations, the authors discuss its replacement by non-contaminated surface soil.

Lead has long been recognized as a hazardous metal to fish and other wildlife (1). For humans, lead is a neurotoxic metallic element that can be absorbed by the body primarily through the lungs and stomach. Lead poisoning occurs when repeated exposure to a lead-containing environment happens so that lead is slowly accumulated in bones and tissues.

III. RESULTS

Exposure to high concentrations of lead can cause serious health problems, including nervous system dysfunction of fetuses and infants, hemotoxic effects, reproductive dysfunction, gastrointestinal tract

alterations, nephropathies, and Alzheimer's disease. Lead poisoning is related to anemia, because the activity of heme synthetic enzymes can be inhibited by lead ions (2). Lead is also a risk factor for hypertension in women (3). If lead poisoning is left untreated, it may damage kidneys, the nervous system, and the brain. Because of the possibility of permanent impairment, lead poisoning is particularly dangerous during infant development and for children under 7 years of age, who can absorb 50% of lead ingested, compared with adults who only absorb 10% of it (4). In 1985, the Centers for Disease Control defined childhood lead poisoning as blood lead levels >25 µg/L or 25 ppb. This definition has been revised down to 10 ppb based on new scientific evidence and observations that show children with lead levels as low as 10 ppb have decreased intelligence and slower neurological development (5).

As a metal that has been widely used in industry for many years, lead is omnipresent in the environment—either from natural resources or from pollutants. In the United States, the average lead background level in soil is 7– 40 ppm (5–7). The maximum allowable lead level in food is 2 ppm (6). In agricultural products, food, raw dietary supplements, and pharmaceutical materials, lead usually exists at levels <1 ppm. To determine lead at ppm or sub-ppm levels, some analytical instruments with high-sensitivity detection capabilities are available, including inductively coupled plasma mass spectroscopy (ICP-MS) and graphite furnace atomic absorption spectroscopy (GFAAS) (8–13). Ion chromatography also has been used for lead determination; however, its sensitivity is not as good as that of ICP-MS and GFAAS (14–15).

Although their sensitivities make ICP-MS and GFAAS the methods of choice for lead analysis, they are very expensive. For example, a typical ICP-MS instrument ranges in price from $250,000 to $750,000, and daily operational cost can be more than $1000. In addition, because only a small amount of sample solution can be introduced into the instrument, both ICP-MS and GFAAS require a very clean working environment, which adds maintenance cost to operate the instruments, especially an ICP-MS. Therefore, many analytical laboratories cannot afford an ICP-MS. Moreover, for laboratories in which lead analysis is not a routine task, it is not economically worthwhile to own a GFAAS instrument, even though it is less expensive (more than $20,000). Those laboratories prefer sending their samples to other laboratories for lead determination, even though sending samples to an outside laboratory costs money and time.[7,8,9]

To analyze low-level lead quickly, simply, and less expensively, a few analytical methods for lead determination have been developed in the past 10 years. Di Nezio et al. have reported a preconcentration technique involving flow injection spectrophotometry to detect lead in natural water samples (16). Other examples include a dibromo-p-methylsulfonazo spectrophotometric method to detect lead in biological samples, a resonance Rayleigh scattering method to detect lead in tap-water samples, and a fluorescent method to detect lead in soft drinks (17–19). However, these methods have their shortcomings: either they could only be used for water or liquid samples, or their detection limits were too high, or they were not tolerant of other common metal ions.

The method reported in this article is based on the complex formation of lead with dithizone or diphenylthiocarbazone. Although dithizone has been used for lead analysis for more than half a century, limited research has been conducted on the sample digestion and few studies have been conducted on reagent recycling (20–23).

Application of this complex reagent is very limited. A colorimetric method based on a lead-dithizone complex is the procedure recommended for lead analysis according to the US Pharmacopeia (24). Unfortunately, this method can be used only for simple samples and has serious shortcomings. For instance, the method is invalid for samples containing lead at levels <5 ppm. The shortcomings of the USP method include:

- It is not suitable for salts of alkali earth elements because a heavy precipitation is formed during the sample digestion process

- For many samples the digestion process is extremely time-consuming—it can take several hours or even days
- Detection limit is too high for almost all common samples
- The method generates too much waste of dithizone chloroform solution, which is both environmentally and economically unacceptable.

We discuss a practical UV–vis spectrophotometric method for measuring trace amounts of lead (e.g., <1 ppm). The method is applicable to all organic and inorganic samples and eliminates all the shortcomings mentioned for the USP method. It is simple, economical (<$2/sample), reliable, and versatile for any type of sample. The procedure has been validated by standard addition method and a ICP-MS method. Its sensitivity is at sub-ppm levels, similar as those of ICP-MS and GFAAS. Using this method, lead in pharmaceutical, agricultural, food, and raw dietary supplement samples have been determined.[10,11,12]

Experiment

Materials and instruments. The following materials were used: lead stock standard solution, 1000 ppm (analytical grade); chloroform (HPLC grade); dithizone (diphenylthiocarbazone, p.a. grade); diethyldithiocarbamic acid sodium salt (p.a. grade); hydroxylamine hydrochloride (p.a. grade); ammonium hydroxide (ACS reagent grade); nitric acid (ACS reagent grade); hydrogen peroxide 35% (p.a. grade); and sulfuric acid (p.a. grade), which were all purchased from Acros (Morris Plains, NJ). Citric acid (reagent grade) and potassium cyanide (reagent grade) were from Sigma-Aldrich Chemical, Co. (St. Louis, MO). Deionized (DI) water was from a reverse osmosis system at Culligan (Missoula, MT). All other chemicals, including hydrochloric acid, ethanol, phenol red, thymol blue, and so forth, either reagent or better grades, were obtained from Fisher Scientific (Denver, CO). 1% HNO_3, 1% HCl, and 3 N HCl were prepared by mixing appropriate amount of DI water and the concentrate HNO_3 and HCl, respectively. All samples were either obtained from the Department of Quality Assurance of Nutritional Laboratories International Inc. (Missoula, MT) or purchased locally. The instrument was a Cary 50 Bio UV–vis spectrophotometer from Varian (Walnut Creek, CA).

Reagent preparations. First, we diluted the 1000 ppm of lead stock solution with 1% HNO_3 to 1.0 ppm. Then a 0.003% dithizone extraction solution was made as follows: 30 mg dithizone were dissolved in 1000 mL of chloroform, and 5 mL of ethanol were added as a stabilizer. The solution was stored in a refrigerator. Each time before use, we washed a suitable volume of the dithizone solution with half of its volume of 1% HCl. After washing, the aqueous phase was discarded. We prepared a 0.001% standard dithizone solution by dissolving 10 mg of dithizone in 1000 mL of chloroform and storing it in a refrigerator.

To prepare the 30% ammonium citrate solution, we dissolved 60 g of citric acid in approximately 100 mL of DI water. Two drops of 0.1% phenol red in ethanol were added, and the pH was adjusted with ammonium hydroxide until the indicator turned from yellow to pink. Any lead present in the citric acid was removed by extracting the solution with 10 mL of 0.003% dithizone extraction solution. The extraction was repeated until the dithizone solution did not change color. The citrate solution was then diulted to 200 mL.

To prepare the 2% ammonium cyanide solution, we dissolved 2 g of potassium cyanide in 15 mL of ammonium hydroxide, then diluted it with DI water to 100 mL. For the 5% potassium cyanide solution, we dissolved 25 g of potassium cyanide in sufficient water to make 100 mL. We removed lead from this solution by repeated extracting with 10 mL of 0.003% dithizone extraction solution until the dithizone solution did not change color. We removed any remaining dithizone from the aqueous solution by extracting with 10 mL of chloroform and repeated this process three times. We then diluted the cyanide solution with DI water to 500 mL.[13,14,15]

To prepare the 20% hydroxylamine hydrochloride solution, we dissolved 20 g of hydroxylamine hydrochloride in sufficient DI water to make ~60 mL. Five drops of 0.1% thymol blue in the ethanol solution were added, and the pH was adjusted with ammonium hydroxide until a yellow color appeared. We added and dissolved 0.4 g sodium diethyldithiocarbamate, and allowed it to stand for 5 min. The solution was extracted five times with successive 10 mL of chloroform. Drop by drop, we added 3 N hydrochloric acid until the solution became pink, and then diluted it to 100 mL with DI water.

All reagent solutions were kept in a refrigerator and were stable for at least four weeks

Analytical procedure. In a weak alkaline solution, dithizone can form a stable complex with lead in a 2:1 ratio . This complex has a maximum absorbance at 520 nm .To obtain reliable results, the key step was to quantitatively dissolve and then isolate lead from the sample matrix. The optimized and validated analytical procedure follows.

Step 1. Into a 250-mL beaker, weigh an appropriate amount of samples containing ≤25 μg of lead, such as 1–2 g of inorganic sample, 5 g of a mixture sample of inorganic and organic, or 10 g of organic sample. Add 10 mL of 1:1 H_2SO_4 (1:1 of H_2SO_4–H_2O, v/v) and a few glass beads into the beaker. Cover the beaker with a piece of watching glass and heat the beaker on a hot plate until the sample becomes brown or dark brown.

Figure 2: Spectrophotometric scans of a blank dithizone solution (blue), 1 Î¼g/5 mL (red) and 4 Î¼g/5 mL (purple) of lead-dithizone solutions.

Step 2. Drop by drop carefully add H_2O_2 (35%), until the organic materials are completely destroyed, which is indicated by the solution becoming clear. For mineral-containing samples, some white residue will remain.

Step 3. For some samples of mixed organic and inorganic materials, H_2SO_4–H_2O_2 may not be able to destroy the organic components completely. In this case, alternatively adding H_2O_2 and HNO_3 could speed the digestion. Wait for evolution of SO_3 smoke before switching solvents.

Step 4. For alkaline earth-salt samples such as dicalcium phosphate, H_2SO_4 should be avoided for digestion because it can form heavy precipitation with the metal ions and make the lead separation impossible. For these types of samples, neat nitric acid is sufficient.

Step 5. After sample digestion, let the solution cool to room temperature. Wash the beaker with approximately 10 mL of DI water. Heat the solution again until SO_3 smoke is evolved. Repeat the washing and heating one more time to remove any residual H_2O_2. If H_2O_2 is not completely removed, it will fail the lead extraction separation.

Step 6. Add 10 mL of DI water to the sample beaker and stir to dissolve any water-soluble salt. Add 5 mL of 30% ammonium citrate solution, 2 mL of 20% hydroxylamine hydrochloride solution, and mix well. (Note: For alkaline earth-salt samples, do not add the 10 mL of DI water, instead add 20 mL of 30% ammonium citrate and 2 mL of 20% hydroxylamine hydrochloride solution, and mix well.)

Step 7. Add two drops of 0.1% phenol red in ethanol. Carefully adjust the pH with ammonium hydroxide until the solution changes colors from pink to yellow then back to pink again. Cool the solution to room temperature. Completely transfer the sample to a 125-mL separatory funnel for liquid–liquid extraction of the lead.

Step 8. Into the separatory funnel containing the sample solution, add 2 mL of 5% potassium cyanide solution and 5 mL of 0.003% dithizone extraction solution. Shake the separatory funnel for ~30 s, carefully releasing pressure from time to time. Drain the bottom dithizone phase to a 60-mL separatory funnel containing 20 mL of 1% HCl, which is used for back extraction of lead.

Repeat the extraction three more times. Collect all the dithizone phases in the 60-mL separatory funnel. The original aqueous sample solution should be collected in a specific container for waste treatment.[16,17,18]

Step 9. Shake the 60-mL separator funnel for 45 s to back-extract lead to the acidic aqueous phase. Drain the dithizone phase into a beaker containing 20 mL of DI water to recycle the dithizone solution.

Step 10. In the 60-mL separatory funnel, add 4 mL of 2% ammonium cyanide and 5 mL of 0.001% standard dithizone solution. Shake the separatory funnel for 45 s. Drain the dithizone solution into a 10-mL of centrifuge tube for the spectrophotometric determination of lead.

Step 11. To construct the standard calibration curve, extract lead standard solutions containing 0.0, 1.0, 5.0, 10.0, and 25 µg of lead in the same way as described in steps 6–10. Using chloroform as a reference, measure the absorbances of the solutions at 520 nm. Create a calibration curve from the measured results. The R^2 value should be .0.990.

Step 12. Measure the absorbance of the samples at 520 nm. Calculate the lead concentration based on the standard calibration curve obtained at Step 11.

For quality assurance, we performed triplicate analyses for all samples.

Results and discussion

Method validation. The method was validated using two means: standard addition or method recovery and comparison with an accepted ICP-MS method.

Method recovery results. Two samples with nondetectable lead were specifically chosen for lead recovery testing. These samples were spiked with 0.5 –3.0 µg of lead, and triplicate analyses were performed in the same manner as for the regular samples. Table I lists the lead recovery test results. In these tests, 10 g of dried hotdog bun powder and 2 g of green tea extract were used.[19,20,21]

IV. CONCLUSION

This method was used in our quality control laboratory for several months with various samples and proved to be reliable for the determination of trace amounts of lead in all samples. From sample digestion to interfering element masking and to dithizone chloroform solution recycling, each step has been optimized. For certain mixture samples of organic ingredients and minerals, repeated treatment with H_2SO_4–H_2O_2 and H_2SO_4–HNO_3 is very effective and could reduce the digestion time dramatically. For the determination of ppm levels of lead in salts of alkaline earth metals, sulfuric acid should be avoided and an extra amount of citrate reagent should be used to prevent the precipitation. Recycling the dithizone solution can not only reduce the consumption of chloroform but also maximally lower the overall cost. This method is very rugged and could be used for routine analysis of trace amounts of lead as well as for the validation of other instrumental methods such as ICP-MS or GFAA.[22,23,24]

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