



COMPARATIVE ANALYSIS ON METHODS OF EXTRACTION FOR THE DETERMINATION OF LEAD AS A POTENTIALLY TOXIC METAL IN DECORATIVE PAINTS AROUND LAGOS

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ABSTRACT: *Potentially toxic metals (PTMs) are metals of high density that are relatively toxic in the environment, even at low concentrations. Lead as a potentially toxic metal, affects the human body system when it finds its way into it, especially in infants. Lead when absorbed, hinders the formation of haemoglobin and causes a lot of other health disorderliness in humans. The aim of this research project is to access the level of lead in decorative paints on walls of houses around Lagos, Nigeria. Twelve paint samples were collected from walls at different buildings around Lagos, digested, and analyzed using Flame Atomic Absorption Spectrometer. Lead in the paint samples was extracted using three different methods; a mixture of HNO₃ and HClO₄, a mixture of HNO₃ and H₂O₂, dry ashing in a muffle furnace followed by leaching with HNO₃. The analysis was done using flame atomic absorption spectrometer (FAAS), Buck Scientific Model 210 VGP, serial number: 1619. There was no significant difference between the methods of extraction when compared using ANOVA at a 95% confidence level. This means that all three methods are good for extraction of lead in paint chips, although extraction with HNO₃ and HClO₄ showed the highest recovery of 81.93% while that of the dry ashing showed the lowest recovery of 66.70%. It can be conclusively stated that all the paint samples contained significant amounts of lead, although none exceeds the US EPA limit of 90ppm.*

KEYWORDS: Lead, PTMs, Paints, Lagos, Toxic.

INTRODUCTION

Lead is one of the elements in nature. It is usually found in combination with other elements to form different minerals. The mineral called galena is most often mined to produce lead metal (Plumbum) as we recognize it. The sources of Lead in our environment are many. An individual can get Lead poisoning from many sources. Major sources of Lead exposure include Lead in paint, gasoline, water distribution systems, food, and Lead used in hobby activities (Carolyn, 1997).

Lead-based paints and Lead dust in older homes are the main domestic sources of Lead. The effects of this Lead paints and Lead dusts are greater in infants. Millions of homes have peeling or chipping of lead-based paint and high levels of Lead-contaminated dust. A high percentage of these homes have young children living in them. People may be exposed to lead by breathing or swallowing lead or Lead dust. Once it enters the body, Lead can become a health hazard (US EPA, 1986).



Lead affects all organs and systems of the body once absorbed or ingested into the body. Children six years old and below are more susceptible to Lead poisoning. Even low levels of Lead in the blood of children can result in medical incongruities such as; behavior and learning problems, lower IQ and hyperactivity, slowed growth, hearing problems, anemia etc. In rare cases, ingestion of lead can cause seizures, coma and even death (Parkinson *et al.*, 1987).

Lead poisoning through introduction to lead-containing paints is perceived as a noteworthy community wellbeing issue around the world. Due to the immense adverse effect of lead in paints, many countries have banned the use of lead in paints used for interior and exterior decorations. Different countries have various limits for lead in paint, for example, USA: 90ppm, Singapore: 600ppm and, Australia: 1,000 ppm (Kumar and Gottesfeld 2008; US CPSC, 2011). In china, the limit for lead in paints is 90ppm, yet there is no enactment in India and a few Asian and African countries that limit the use of potentially toxic metals in paints used for decorations. This is probably the reason behind the easy accessibility of lead-based paints in the markets of numerous developing nations over the world (Mohanty *et al.*, 2013).

Lead

Lead is an element in the periodic table with chemical symbol Pb. With a natural solid state, it has an atomic number of 82, and located on group 6, period 14 in the periodic table. Pb which is derived from the Latin *Plumbum*, which translates to “plumber”. This indicate the use of lead pipes in ancient Roman plumbing systems. Lead is a bluish-white heavy metallic element. It is found in nature as a metal in the earth’s crust, mined as galena ore (lead sulfide, PbS), (Robert, 1922).

Due to the abundance of lead in nature, its ease of extraction and ease to work with, lead is used in a variety of products including Paint, Solders Pipes, Ceramics, Gasoline, Cosmetics and Batteries. Since 1980, the US federal and state regulatory standards have helped to minimize or eliminate the amount of lead in consumer products and occupational settings. Today, however, the most common sources of lead exposure in the United States are: Lead-based paint in older homes, contaminated soil, Household dust, Drinking water, Lead crystal, Lead-glazed pottery (National Institute of Environmental Health Sciences, 2016).

Sources of Lead

Paint

After the prohibition of leaded petrol in many countries around the world, focus shifted to other sources of lead poisoning in children (Lin *et al.*, 2009). In South Africa, studies shows that even after the phase out of leaded petrol, large number of their young children continue to be at risk of elevated blood lead concentration. According to a research carried out by the Medical Research Council, wall paint samples of some homes were taken for analysis for potentially toxic metals, 20% of these sampled homes had lead-based residential paint (Montgomery and Mathee, 2004).



Dust

Lead dust is the most widely recognized route of exposure to lead. Inside the home, most lead dust originates from paint chipping, sanded or scratched paints especially during renovation of homes. Infants due to their mouthing behavior gets lead dust into their mouth when in such environments. Lead dust may not be obvious to the bare eyes (EPA, 2016).

Soil

Beginning in 1973, the American government began a steady stage down of lead substance in fuel, and by 1996, banned the use of leaded fuel. Be that as it may, lead from auto exhausts blended with soil close to streets and is still there today. Homes close to busy lanes may have elevated amounts of lead on the ground. Today, lead still originates from metal refining, battery production, and different processing plants that utilize lead. Lead gets into the air and after that blends with the soil close to homes, particularly if the house is near one of these sources. Chipping of toxic paint on the outside of structures can likewise blend in with the soil near structures. Lead-based paint blending with soil is an issue amid home rebuilding if specialists are not watchful. Once the soil has lead in it, wind can blend up lead dust, and blow it into homes and yards (Mielkey and Reagan, 1998).

Drinking Water

Lead occasionally occurs unsurprisingly in water supplies like rivers and lakes. Lead gets into drinking water mainly as a result of the corrosion, or wearing away, of materials containing lead in the water supply system, domestic or building plumbings. In 1986, the use of lead solder containing greater than 0.2% lead was banned in the US, and the lead content of faucets, pipes and other plumbing materials was restricted to 8.0%. Older structure may still have plumbing that has the probability to contribute lead to drinking water (Davidson and Rabinowitz, 1992).

Air

Lead can be present in outdoor and indoor air. Lead in outdoor air comes mainly from industrial sources (e.g., smelters, waste incinerators, utilities, and lead-acid battery manufacturers). Wind-blown soil and road dust also may contain naturally occurring lead as well as lead from industrial sources, deteriorated paint, and the combustion of leaded gasoline and aviation fuel. Sources of lead in indoor air include outdoor air, suspended dust, and some hobbies (e.g., making stained glass objects using lead solder, shooting using lead bullets at indoor firing ranges) (EPA, 2016).

Folk Medicines, Ayurvedics and Cosmetics

Some folk medicines contain lead. They often are imported from the Middle East, Southeast Asia, India, the Dominican Republic, or Mexico. Two samples are Greta and Azarcon. Azarcon is a bright orange powder also known as Maria Luisa, Rueda, Alarcon, and Coral. Greta is a yellow powder. They are used to treat an upset stomach. Pay-loo-ah also contains lead. It is a red powder used to treat a rash or a fever. Other folk medicines that contain lead include Bala (or Bala Goli), Golf, Ghasard, and Kandu. Some cosmetics such as Kohl (Alkohol) and Surma also contain lead.



Ayurveda is a traditional form of medicine practiced in India and other eastern Asian countries. Ayurvedic medications may contain herbs, minerals, metals, or animal products. These medicines may come in both standardized and non-standardized formulations. Ayurvedic medications are typically imported into the United States by both practitioners and followers of Ayurvedic medicine (Gunturu *et al.*, 2011).

Children's Jewelry and Toys

Lead has been found in inexpensive children's jewelry sold in vending machines and large volume discount. It has also been found in old or antique toys passed down generations and in inexpensive metal amulets worn for good luck or protection (Nebraska DHHS, 2013).

Workplace and Hobbies

Level of lead exposures were evaluated for workers at a battery reclamation factory in Alabama. The evaluation was done on the factory workers and their families with comparison with families in the neighbourhood. It was noticed that the workers' blood levels and that of their children had increased significantly over a period of 2 years when compared with their neighbours'. The lead contamination on surfaces such as armrests were much more significant as compared to the neighbours' (Gittleman *et al.*, 1994).

Lead-Glazed Ceramics, Leaded Crystal, Pewter

Lead may get into foods or liquids that have been stored in ceramics, pottery, china, or crystal with lead in it (Block, 2006).

Imported Food in Cans

Canned and non-canned food beverages purchased in Nigeria were analyzed for lead and cadmium using AAS. 79.3% of the non-canned beverages indicated lead levels above the US EPA's maximum contaminant level of 0.015 mg/L, while all (i.e. 100%) of the canned beverages had lead levels that were greater than the maximum contaminant limit (Maduabuchi *et al.*, 2006).

Firearms with Lead Bullets

Wildlife that is killed using lead ammunitions could serve as a means of lead contamination to the human consumers. This is based on studies showing rise in the blood lead concentration in subsistence hunter populations in the US. Fluoroscopy scanning of some carcasses of wildlife animals shot by hunters with lead-core, copper-jacketed bullets showed metal fragments in 80% of total number of samples scanned. Majority of these fragments were identified using ICP-AES as lead. Isotope ratios of the lead in meat matched that in the bullets and differed from that in the bone (Hunt *et al.*, 2009).

Some Other Common Sources of Lead

Batteries, radiators for autos and trucks, and a few shades of ink likewise contain lead (EPA 2016).



Effects of Lead

Effects of Lead on Soil

Lead accumulates in the soil, especially those with high level of organics (US EPA, 1986). This accumulated lead is leached into lower levels of the soil where it could be held for quite a long time. Atmospheric lead in the soil will keep moving into lower organisms in the soil and grazing food chains, until a balance is achieved. From the study of lead chemistry in the soil, the US EPA suggested that the uneven circulation of lead in the biological systems can displace several metals the binding sites on the organic matter. Lead in soil may turn out to be even more soluble thereby being easily accessible for intake by plants (US EPA, 1986).

Effects of Lead on Plants

Plants on the land have the tendency to absorb and retain lead from the soil through their roots. The uptake of lead from the soil can be reduced by the calcium and phosphorus of the soil. A few types of plants could accumulate lead in high concentrations (UNEP, WHO, and ILO, 1991). Lead contamination in plants coat the pores of the leaves that are meant to aid photosynthesis and decreases the measure of light getting to the plant. The coating of the leaves pore results in other adverse effect than hindrance to photosynthesis, e.g., restraining breath. Some studies show that lead can influence populace hereditary qualities. All these impacts have been observed in disconnected cells of hydroponically developed plants e.g., the lead levels experienced by plants close to smelters and road sides. Lead in the atmosphere can be up-taken by the plants through the soil. The type and level of lead accumulating are to an extent determined by the condition of development of the vegetation. There will be vigorous development during the spring period and low developments during fall and winter (Greene, 1993).

Effects of Lead on Micro-organisms

It has been found that lead at the roadside which sometimes gets as much as 10,000- 40,000 ppm dry weight in concentration, can eliminate whole populations of bacteria and fungi on leaf surfaces and in the soil. The microorganism populations may be replaced but, with less efficient ones at decomposing organic matter. It is noteworthy that microorganisms can make lead soluble enough to be up-taken by plants. This is done by bacteria that exudes organic acids that lower the pH in the vicinity of the plant root (EPA, 1986).

Effects of Lead on Animals

Lead affects almost every organ and system of the body. Children 6 years and below exhibit the greatest effects of lead poisoning. This include behavioral and learning problem, lower IQ and hyperactivity, slowed growth, hearing problems, anemia and sometimes, coma or death. Lead poisoning is usually more difficult to tackle when the infants grow above 2 years. Lead could be stored in the one over a long period of time along with calcium of the bone. Lead affects the fetus of a pregnant mother by developing in the fetus' bone like calcium or bypassing the placenta barrier. This leads to reduced growth of fetus, or premature birth. Adults exposed to lead can suffer from cardiovascular effects, increased blood pressure among many other ailments (Carpenter, 2001).



Episodes of Lead Poisoning

Lead Poisoning in China

More than 1,300 children were poisoned by a year-old manganese factory in central China, it was reported in August 2009, by the state media. The exposure of mass lead contamination in Wenping Township, Hunan province, was the second case in many weeks.

Blood samples of children living nearby showed that 60% to 70% had unhealthy levels of lead in their blood. The authorities closed the factory instantly and detained two executives on suspicion of "causing severe environment pollution" (Reuters 2009).

Lead Poisoning in Niger State, Nigeria

In 2009, the death of 28 people, mainly children, was reported as a result of lead poisoning incidents in Angwan Maijero and Angwan Karo Madaka Districts of Rafi Local Government Area of Niger State, Nigeria. The cases of lead poisoning purportedly resulted from activities of informal miners in Angwan Maijero and Angwan Karo, Madaka districts, Rafi LGA, Niger State (Dooyema *et al.*, 2011).

Lead Poisoning Crisis in Zamfara State, Northern Nigeria

In March 2010, Doctors without Borders/Médecins Sans Frontières (MSF) was alerted to a high number of child fatalities in Zamfara State, Northern Nigeria—an estimated 400 children died. Laboratory testing later confirmed high levels of lead in the blood of the surviving children. MSF was a central player in treating lead poisoning in Zamfara State, and in responding to the acute phase of this emergency. The mortality rate has been controlled, but patients with lead poisoning will require significant long-term treatment and follow-up. The root cause of the lead poisoning crisis was unsafe mining and ore processing (Lo *et al.*, 2012).

Methods of Determination of Lead In Paint

There are three main approaches for determining the lead content in paint:

- 1) In situ determination of Lead content in paint using chemical test kit.
- 2) Measurement using a portable X-ray fluorescence (XRF) device.
- 3) Analytical method involving sampling, digestion and determination using FAAS, GFAAS, ICP-AES, ICP-MS, NAA.

These approaches are briefly described below;

Chemical Test Kit

Lead present in paints above a concentration more than 0.5% by weight can be detected using a chemical test kit. This kit detects lead by a chemical reaction that brings about a colour change. Chemical test kits are relatively inexpensive and easy to use. There are various types of test kit available. One type uses a sodium, sulfide or sodium rhodizonate solution that may be applied to the paint chip, Lead is indicated if the solutions turns to the appropriate colour. The other type uses a swab that is rubbed onto a paint surface and color change indicates the presence of lead (Schmehl *et al.*, 1999).



The EPA does not recommend the chemical test kit method for certain reasons such as, possibility of false readings, does not tell the quantity of lead present in the paint, and it's quite difficult to read when testing dark colours (USDA Forest Service, 1996).

Advantages--The chemical spot testing method is quick, easy, and inexpensive. Test kits can be purchased directly from the manufacturer, distributor, or hardware store. Testing can be done at your convenience and you get the results right away (Cole, 1999).

Disadvantages--The chemical test does not tell you how much lead is present. Sometimes the test indicates lead is present when it is not (a false positive) and other times indicates lead is not present when it is (a false negative). The chemical samples only test the exposed layers, not the underlying layers that may be more likely to contain lead (Ashley *et al.*, 2010).

Portable X-Ray Fluorescence (XRF) Device

The Portable X-ray fluorescence device using high energy radiation (gamma rays) to measure the amount of lead on a painted surface. This is done by exposing the surface to the radiation, which causes lead to emit x-rays at a characteristic frequency. The intensity of the rays is measured by the instrument's detector and converted to a number (usually in mg/cm³) that represents the quantity of the lead present per unit area. Operators of this machine requires special training to prevent radiation exposure (Beckley and Groenier, 2008).

Advantages--The XRF instrument can tell immediately if the paint has lead in it and how much lead is present. Testing does not damage the painted surface. It is the best method when many surfaces or buildings are being tested (Wilson, 2009).

Disadvantages--XRF measurements have a larger margin of error than laboratory analysis of paint chips. XRF instruments should not be used to test highly curved or intricate surfaces because of safety concerns, poor reliability of the results, and the inability to determine the exact surface area. Laboratory analysis of paint chip samples is recommended when irregular surfaces are being examined or when an inconclusive measurement is taken. An inconclusive measurement is a reading within the tolerance zone of the XRF machine around the established lead limit of 1.0 milligram of lead per square centimeter of a painted surface. For example, if an XRF instrument had a tolerance zone of +/- 0.2 mg/cm², the inconclusive range would be between 0.8 mg/cm² and 1.2 mg/cm². A reading of 0.9 mg/cm² would require that a paint chip sample be analyzed to verify the results (Üstün, 2009).

Analytical Method

In analytical method of determination of lead, paint samples are taken from the source to the lab for analysis. The paint samples could be in dried form (paint chips) or wet unused paint samples. The paint samples can be tested for lead using atomic absorption spectrophotometry (AAS), inductively coupled plasma Mass Spectrometer (ICP-MS), Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES), Neutron Activation Analysis (NAA), Ion Chromatography (IC).

The samples need to be pre-processed prior to the analysis. For the measurement of total lead, an acid digestion method is usually implored, but for the measurement of soluble lead (i.e. the lead that could be absorbed if ingested by an infant), an acid extraction process is adopted. A minimum quantity of about 300mg is usually needed to conduct an analysis, although this is



determined by the sample preparation method, method of analysis, and the concentration of lead in the sample.

For a proper sampling process, it is recommended that; all layers of paint are collected as the older paints are more likely to contain high level of lead; the underlying material is avoided as much as possible to avoid erroneous results; distorted wall surfaces are repaired to avoid escape of lead dust into the atmosphere; the location of each sample is recorded. The actual lab analysis can be conducted using techniques such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), and inductively coupled plasma atomic emission spectrometry (ICP-AES), Inductively coupled Plasma Mass Spectrometry (ICP-MS), (WHO 2011).

Advantages

This method is considered the most accurate method as long as paint sample contains all layers of paint and do not include substrate material.

Disadvantages

The method takes several days to several weeks to obtain a result, depending on the lab and method adopted. The wall surface must be distorted and repaired.

The following sections briefly describe the instrumental techniques usually used.

Flame Atomic Absorption Spectrometry (FAAS)

Atomic absorption spectrometry (AAS) depends on the way that free atoms assimilate light at normal wavelengths for the component of interest: 283.3 nm as for ground-state atoms of lead. The measure of light absorbed can be related directly to the analyte concentration in a given sample. To perform an AAS measurement, the lead-containing test sample should first be prepared by the instrument in order to create ground-state molecules as a vapor within the light path of the instrument, a procedure known as atomization. FAAS utilizes an air–acetylene or a nitrous oxide–acetylene–air laminar flame to atomize lead at temperatures up to 2600 °C.

FAAS detection limits are moderate, yet adequate for generally cases. As immediate sample aspiration is required, at least around 5 ml of the digest is required for aspiration and estimation of a steady signal. FAAS estimations are liable to some obstruction from light dispersing and molecular absorption by matrix parts, which can be remedied by different methodologies. FAAS gadgets, which require some lab skills to use, are generally accessible with or without autosamplers. The initial instrument expense is moderately low, and consumables, for example, acetylene gas, are generally cheap. Support needs are generally low, and test throughput can be a few samples for every moment (Dakashev *et al.*, 2012).

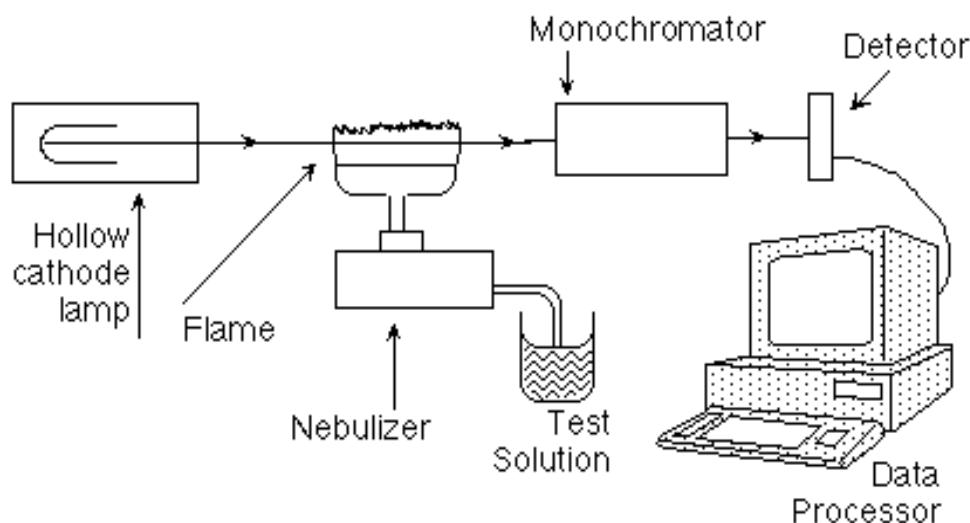


Figure 1: Schematic diagram of flame atomic absorption spectrophotometer

Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

GFAAS is an AAS method that makes use of an electrically heated graphite tube to vaporize and atomize the analyte at temperatures up to 3000 °C before it is detected. GFAAS instruments give low detection limits and require just little process volumes (around 20 µl). The light scattering interference and molecular absorption by matrix components can be sufficiently redressed utilizing different methodologies, including the utilization of matrix modifiers. GFAAS gadgets must be operated by research facility specialists.

GFAAS gadgets are generally accessible and require autosamplers to expand accuracy and throughput. Introductory instrument expense is moderate, and upkeep and consumable expenses are significant. Test throughput is roughly one sample each 2 to 3 minutes (Meeravali *et al.*, 1997).

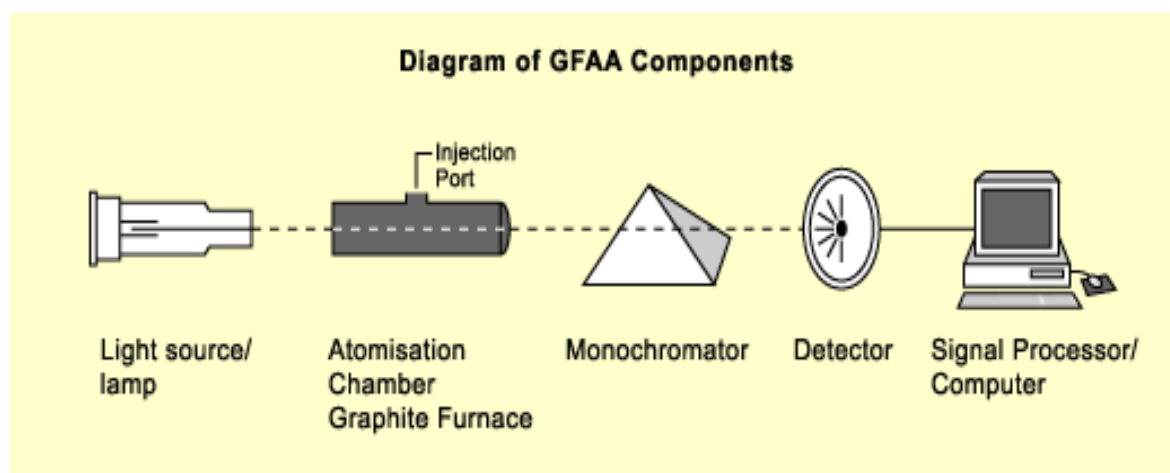


Figure 2: Schematic diagram of graphite furnace atomic absorption spectrophotometer

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

ICP-AES utilizes an inductively coupled plasma (a high temperature ionized gas made out of electrons and positively charged particles) source to separate the samples into its constituent atoms or particles. Under these high-energy conditions, lead (in the same way as other different components) radiates light at characteristics wavelengths. The measure of light discharged can be measured and associated to the concentration of lead in the sample. ICP-AES instruments offer the advantage of having the capacity to determine several components at the same time.

Detection limit for lead is average, yet at the same time adequate to quantify lead precisely in paint at normally observed concentrations. Test volume prerequisites are moderate. Some spectral impedances are regular, yet can be rectified. ICP-AES instruments must be operated by prepared research center staff. The initial instrument expense is high, yet the major consumable is just argon gas. Upkeep expenses are generally high as a result of the complicated outline of ICP-AES instruments. Test throughput is intermediate, commonly around one sample for each minute (Greenfield 1983).

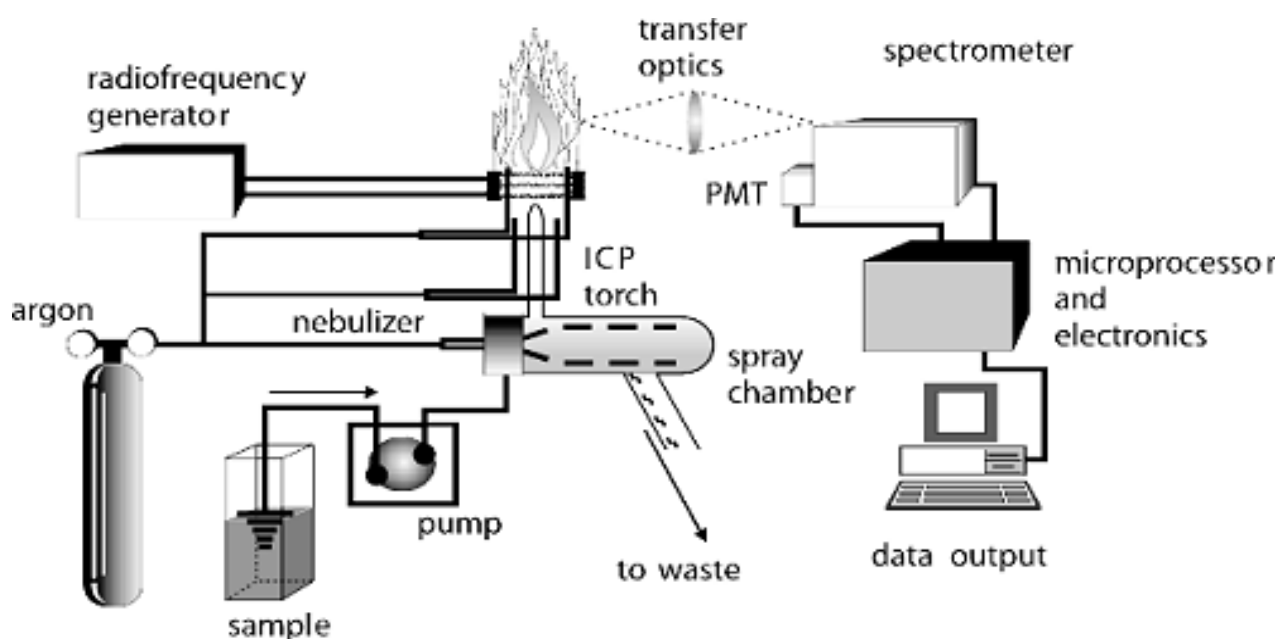


Figure 3: Schematic diagram of inductively coupled plasma atomic emission spectrometer

Important Aspects of Laboratory Practice

In analytical chemistry, even the most complex and precise gear will give inaccurate results if samples have not been suitably gathered and handled, if the hardware has not been utilized effectively or if analytical protocols have not been adopted. Two concerns connected with estimations of lead in paint are unrecognized pollution and deficient QA. These issues are worthy of note.



Aim and Objectives of Research Project

Aim

This research project is aimed at determining the various lead content of different paint chip samples gotten at different locations around Lagos. At the completion of this project, we expect to be able to state affirmatively that paint samples in Lagos, Nigeria contains significant amount of lead (or not) which may be extracted using $\text{HNO}_3/\text{H}_2\text{O}_2$, $\text{HNO}_3/\text{HClO}_4$, or dry ashing.

Objectives of Research Project

The following are the objectives of the research project:

- To determine the lead content of 12 different samples of paint
- To extracted the lead contents of these paints using three different methods; $\text{HNO}_3/\text{H}_2\text{O}_2$, $\text{HNO}_3/\text{HClO}_4$, and dry ashing.
- To compare and contrast the three methods of metal extraction from paint samples.

LITERATURE REVIEW

Due to the hazardous effect of lead on the human race especially infants, and the ecosystem in general, many researches have been conducted by concerned individuals and corporate organizations.

The George Foundation chose 24 paint samples from six paint companies obtained in stores in Bangalore and Chennai. Of the 24 samples taken for analysis, 17 contained lead concentrations surpassing 0.5% lead by weight, 13 had lead concentrations surpassing 1% lead and 5 surpassed 10% lead. On the premise of a two coat paint thickness, the XRF method of determination of paint lead stacking surpassed 1 mg/cm² in five of the samples. The lower Pb concentration paints are the white, blue and chestnut red paints, while all together of expanding Pb concentrations were the green, red, orange and the yellow paints (Alphen, 1999). Yellow paints indicated most noteworthy lead levels when contrasted with others. Yellow paint colors contained up to 200,000 ppm of lead. Yellow-based paints (green and brown) had the following most noteworthy measure of lead. The red paints likewise surpassed the given standard of 1.0 mg/cm² (Clark *et al.*, 2005).

Nineteen samples of privately produced paints acquired from the Nigerian market were taken for analysis of lead in February 2005. The level of lead in the paints ranged from 17.5 µg/g to 515.9 µg/g with mean standard deviation of ±62.2, while the median was 25.1µg/g. It was reasoned that paints sold in Nigeria contain a significant amount of lead with expanded danger of introduction to kids, for whom domestic sources of lead poisoning is more critical than introduction through leaded petrol (Adebamowo *et al.*, 2006).

From an aggregate of 80 paint samples acquired from China, India, and Malaysia – 66% of new paint samples were found to contain 5000 ppm or a greater amount of lead, the US definition of toxic paint in existing homes, and 78% contained 600 ppm or more, the utmost for new paints.



Conversely, the practically identical levels in an adjacent developed nation, Singapore, were 0% and 9%. An examination of lead levels in paints of the same brands acquired in various nations demonstrated that a few brands had lead-based paints in one of the nations and paints meeting US limits in another; another had no lead paint accessible in all nations where samples were gotten. A few brands of paint sold in two or more nations had leaded paint in one nation and low-lead paints in the nation that had an administrative limit. They additionally reported that 100 percent (n=17) of paint samples from India had more than 600 ppm of lead concentration while 82% samples had more than 5000 ppm of lead (Clark, *et al.*, 2006).

Another study on lead levels of paints (5 colours) produced in Nigeria, the lead was measured by fire nuclear ingestion spectroscopy. It was found that 96% of the paints had higher than prescribed levels of lead. The lead level of paints ranged from 84.8 to 50,000 ppm, with a mean of 14,500 ppm and median of 15,800 ppm. The fundamental determinant of lead levels was the shade of the paint. The study concluded that attempts should be made to evaluate the presence of high lead levels in existing houses and if identified, mediation programs for eliminating danger of exposure ought to be created notwithstanding, measures to expand mindfulness and authorized directions prompting the disposal of lead-based residential paint (Adebamowo, 2007).

A review of the lead concentrations in paint samples gathered from residences situated in arbitrarily chosen Johannesburg rural areas was led by the South African Medical Research Council. Of the 239 homes incorporated into the overview, 20% had paint lead concentrations > 5,000 $\mu\text{g/g}$ (the U.S. reference level). Paint with high lead levels was found in old and also recently constructed residences (Montgomery and Mathee 2005).

Paint samples bought from Johannesburg and Cape Town stores were analyzed for lead content. No lead was found in water-based or white shades of enamel paint. Disturbingly, high lead concentrations (up to 189,000 $\mu\text{g/g}$) were measured in samples of pigmented enamel paints. A sum of 83% samples of pigmented lacquer paints were toxic. High lead concentrations were found in prominent and also lesser-known brands of lacquer paint, and just 2 out of 25 samples of lead-based paint showed notices of the high lead content. Additionally high lead concentrations (up to 145,000 $\mu\text{g/g}$) were found in paint expelled from general infant toys, (for example, building hinders) that were obtained from 7 noteworthy toy, grocery store, and stationery chain stores and flea and craft markets. High lead levels were found in privately produced and imported toys (Mathee *et al.*, 2007).

A study on lead in paints in India led by Toxics Link and entitled "Brush with Toxics" concentrated on various sorts of paints. Lead substance was observed to be high up to 140,000 ppm in numerous oil based enamel paints. Concentrations of lead in 83.87 % of the lacquer paint samples were observed to be more than 1000 ppm and 61.3% of samples had more than 5000 ppm. The shade of the paint was identified with lead content. While yellow and orange hued paints had the most noteworthy concentrations of lead, black and white demonstrated the least concentrations (Kumar, 2007).



METHODOLOGY

Although various methodologies were adopted for the sample preparation stage, the method adopted for the analysis of lead in paint chips is the Flame Atomic Absorption Spectrometry (FAAS). The approaches used for the sample preparation include;

- i. Metal extraction with Conc. Nitric acid (HNO_3) and Perchloric acid (HClO_4).
- ii. Metal extraction with Conc. Nitric acid (HNO_3) and Hydrogen peroxide (H_2O_2).
- iii. Metal extraction by dry ashing and leaching with Conc. Nitric acid (HNO_3).

Sampling and Sample Preparation

12 paint chip samples were collected from different buildings around Lagos. The buildings included homes, schools, and workplaces. Each sample were divided into three parts in order to implement the three methods intended. For each method used, a duplicate digest was made. The apparatus used were acid-washed using dilute Nitric acid. This is to ensure any traces of metal is eliminated to avoid erroneous results during analysis.

Extraction with Conc. HNO_3 and HClO_4

0.5g of each samples were weighed into a 50ml beakers, 7.5ml of nitric acid and 2.5ml of perchloric acid were added to each of them. The resulting mixtures were heated for about 10mins on a hotplate at temperature of about 140°C . The mixtures were heated until the paint chips form a milk-like solution with the acids. About 2ml of nitric acid is added to further digest any sample that does not seem digested when acid is almost completely evaporated. The digesting mixtures are covered with watch glasses to prevent sputtering of acid on the hotplate or cross-contamination of samples (Ranasinghe *et al*, 2016).

The digests are cooled for some minutes, sieved into sample bottles to form clear solutions of extract and are taken for AAS analysis.

Extraction with conc. HNO_3 and H_2O_2

Again, 0.5g of each samples were weighed into a 50ml beakers, 7.5ml of nitric acid and 2.5ml of Hydrogen peroxide were added to each of them. The resulting mixtures were heated for about 10minutes on a hotplate at temperature of about 140°C . The mixtures were heated until the paint chips form a milk-like solution with the acids. About 2ml of nitric acid is added to wash sputtered paint particles back into the beakers and further digested. The digests are cooled for some minutes and sieved into 25ml standard flasks to form clear analyte solutions and transfer into sample bottles. This process was repeated to obtain duplicate samples. The solutions are then taken for AAS analysis (Scalera and Remmers, 1993).

Extraction by Dry Ashing and Leaching with Conc. HNO_3

0.5g of each samples were weighed into ceramic crucibles and heated at 315°C in a muffle furnace for 8hours. At the end of 8hours, the ashed samples were brought out and cooled for a moment. The ashed samples were then transferred into 50ml beakers where they were digested using conc. HNO_3 for about 5minutes. The acidic mixtures were then sieved into 25ml standard



flasks and made up with water to the mark. The clear solution of analytes obtained were transferred into acid-washed bottles to take for analysis (Scalera and Remmers, 1993).

Recovery Studies of Lead Using Spiked Samples

0.5 g of 2 samples were weighed in duplicate into 4 separate beakers and 1.5 ml of liquid lead was added to each of the beakers. 0.5 g of a third sample was weighed in duplicate into 2 separate crucibles and again, 1.5 ml of lead was added to each of them. Two of these sample mixtures in beakers were digested using the HNO₃/ HClO₄ method, the other two were digested using the HNO₃/ H₂O₂ method. The two sample mixtures in the crucibles were also ashed in the muffle furnace at 315 °C and digested with HNO₃. These samples were all sieved and made up to the 25ml mark of a standard flask. They were then taken for analysis along with the rest of the samples.

RESULTS AND DISCUSSIONS

Comparison of Results

The series of tables below show a comparison between the quantities of lead extracted from the 12 samples using HNO₃ and HClO₄; HNO₃ and H₂O₂; HNO₃ subsequent to Dry ashing. The quantity of lead contained in various samples according to their colours can also be observed from the tables.

Table 4. 1: Extraction using HNO₃ and HClO₄

Sample Code	1 st Digestion (ppm)	2 nd Digestion (ppm)	1 st Digest (µg/g)	2 nd Digest (µg/g)	Mean (µg/g)	Standard Deviation
L3P	0.46	0.36	23	18	20.5	3.535534
L4P	0.21	0.23	10.5	11.5	11	0.707107
L6P	5.55	5.5	277.5	275	276.25	1.767767
L8P	0.49	0.47	24.5	23.5	24	0.707107
L10P	0.49	0.5	24.5	25	24.75	0.353553
L11P	4.11	4.13	205.5	206.5	206	0.707107
L12P	4.54	4.51	227	225.5	226.25	1.06066
L14P	2.39	2.44	119.5	122	120.75	1.767767
L15P	46.76	46.42	2338	2321	2329.5	12.02082
L19P	0.96	0.92	48	46	47	1.414214
L23P	1.31	1.36	65.5	68	66.75	1.767767
L24P	64.29	64.15	3214.5	3207.5	3211	4.949747

Table 4.1 above shows the quantity of lead obtained from the 12 samples of dry wall paint chips using an acid mixture of HNO₃ and HClO₄ in the ratio 3:1, vol/vol. Sample L24P showed highest lead concentration with mean value of 3211 µg/g ± 4.9497.

Table 4. 2: Extraction using HNO₃ and H₂O₂

Sample Code	1 st Digestion (ppm)	2 nd Digestion (ppm)	1 ST Digest (µg/g)	2 nd Digest (µg/g)	Mean (µg/g)	Standard Deviation
L3H	0.31	0.34	15.5	17	16.25	1.06066
L4H	0.38	0.4	19	20	19.5	0.707107
L6H	6.72	6.69	336	334.5	335.25	1.06066
L8H	0.39	0.29	19.5	14.5	17	3.535534
L10H	0.37	0.39	18.5	19.5	19	0.707107
L11H	3.64	3.61	182	180.5	181.25	1.06066
L12H	4.59	4.5	229.5	225	227.25	3.181981
L14H	2.28	2.31	114	115.5	114.75	1.06066
L15H	47.5	48.1	2375	2405	2390	21.2132
L19H	0.54	0.57	27	28.5	27.75	1.06066
L23H	0.49	0.51	24.5	25.5	25	0.707107
L24H	67.8	67.6	3390	3380	3385	7.071068

Table 4.2 above shows the quantity of lead extracted from the 12 samples of dry wall paint chips using a mixture of HNO₃ and H₂O₂ in ratio 3:1 vol/ vol. once again, it is observed that sample L24 has the highest lead content in it from this extraction method.

Table 4.3: Extraction Using Dry Ashing Method.

Sample Code	1 st Digestion (ppm)	2 nd Digestion (ppm)	1 ST Digest (µg/g)	2 nd Digest (µg/g)	Mean (µg/g)	Standard Deviation
L3D	0.39	0.4	19.5	20	19.75	0.353553
L4D	0.4	0.42	20	21	20.5	0.707107
L6D	7.82	7.8	391	390	390.5	0.707107
L8D	0.32	0.23	16	11.5	6.375	3.181981
L10D	0.69	0.73	34.5	36.5	35.5	1.414214
L11D	2.56	2.51	128	125.5	126.75	1.767767
L12D	2.91	2.86	145.5	143	144.25	1.767767
L14D	1.68	1.66	84	83	83.5	0.707107
L15D	30.4	30.3	1520	1515	1517.5	3.535534
L19D	0.59	0.6	29.5	30	29.75	0.353553
L23D	0.68	0.69	34	34.5	34.25	0.353553
L24D	59.8	59.1	2990	2955	2972.5	24.74874

Table 4.3 above shows the quantity of lead extracted from the 12 samples of dry wall paint chips by ashing the samples in a muffle furnace at 315 °C for 8 hours each. The samples were



thus extracted with conc. HNO_3 . Sample L24 had the highest concentration of lead from this method of extraction too, with a value of $2,972.5\mu\text{g/g}$.

Table 4. 4: Comparison of Digestion Methods

Sample	Paint type	Colour	HNO_3 and $\text{HClO}_4(\mu\text{g/g})$	HNO_3 and $\text{H}_2\text{O}_2(\mu\text{g/g})$	Dry Ashing method ($\mu\text{g/g}$)
L3	Water paint	GREY	20.5 ± 3.5355	16.25 ± 1.0607	19.75 ± 0.3536
L4	Water paint	PEACH	11 ± 0.7071	19.5 ± 0.7071	20.5 ± 0.7071
L6	Water paint	GREY	276.25 ± 1.7678	335.25 ± 1.0607	390.5 ± 0.7071
L8	Water paint	CREAM	24 ± 0.7071	17 ± 3.5355	6.375 ± 3.1820
L10	Water paint	WHITE	24.75 ± 0.3536	19 ± 0.7071	35.5 ± 1.4142
L11	Water paint	CREAM	206 ± 0.7071	181.25 ± 1.0607	126.75 ± 1.7678
L12	Water paint	WHITE	226.25 ± 1.0607	227.25 ± 3.1819	144.25 ± 1.7678
L14	Water paint	GREY	120.75 ± 1.7678	114.75 ± 1.0607	83.5 ± 0.7071
L15	Water paint	BLUE	2329.5 ± 12.0208	2390 ± 21.2132	1517.5 ± 3.5355
L19	Water paint	GREY	47 ± 1.4142	27.75 ± 1.0607	29.75 ± 0.3536
L23	Water paint	CREAM	66.75 ± 1.7678	25 ± 0.7071	34.25 ± 0.3536
L24	Water paint	PEACH	3211 ± 4.9497	3385 ± 7.0711	2972.5 ± 24.7487

From the table of comparison of the three methods above, it is observed that the extraction method using HNO_3 and HClO_4 recorded highest lead recovery in six, out of twelve samples. The other two methods showed three highest lead recovery each. It is also noticed that of all the different colours of paint analyzed, the peach coloured paint (sample L24) contained the highest amount of lead, followed by the blue colour paint (sample L15).

Calibration Curve and Regression Analysis

The calibration curve uses an empirical equation to express the response function of the instrument used (AAS in this case) to the concentration of a specific analyte (lead in this case) in the sample matrix. It creates an equation that relates the absorbance (A) with the analyte concentration (C). According to Fig. 1 below, the equation is linear with all points falling in line. This implies that through the process of the experiment, minimal error was encountered and interference effects from other components in the matrix is negligible.

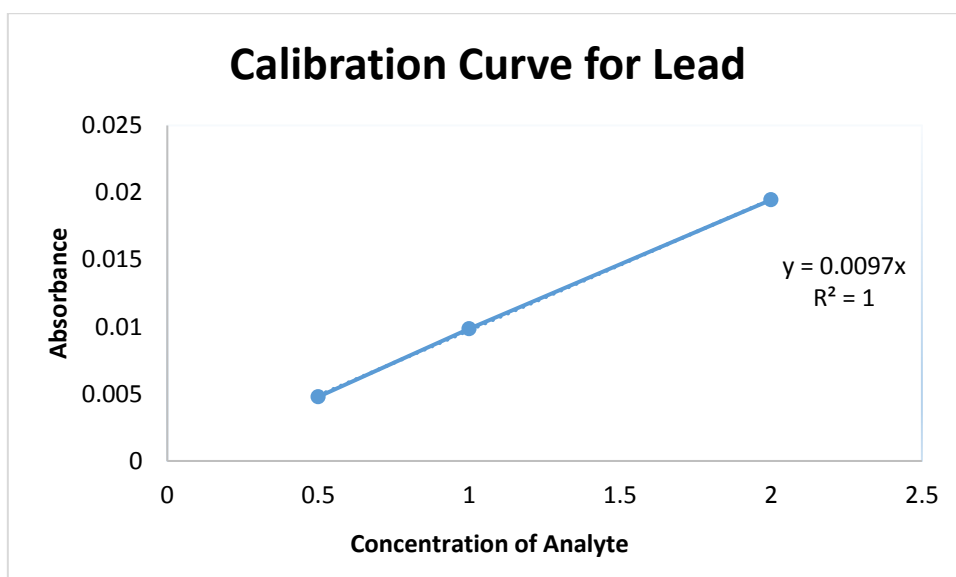


Figure 4: Calibration Curve

Percentage Recovery Analysis

The percentage recovery analysis was conducted in order to detect which of the three methods of digestion was most effective. From the bar chart above, it is noticed that the recovery using the combination of HNO₃ and HClO₄ had the highest percentage. This simply means that the aforementioned method was the most effective one of all three extraction methods adopted.

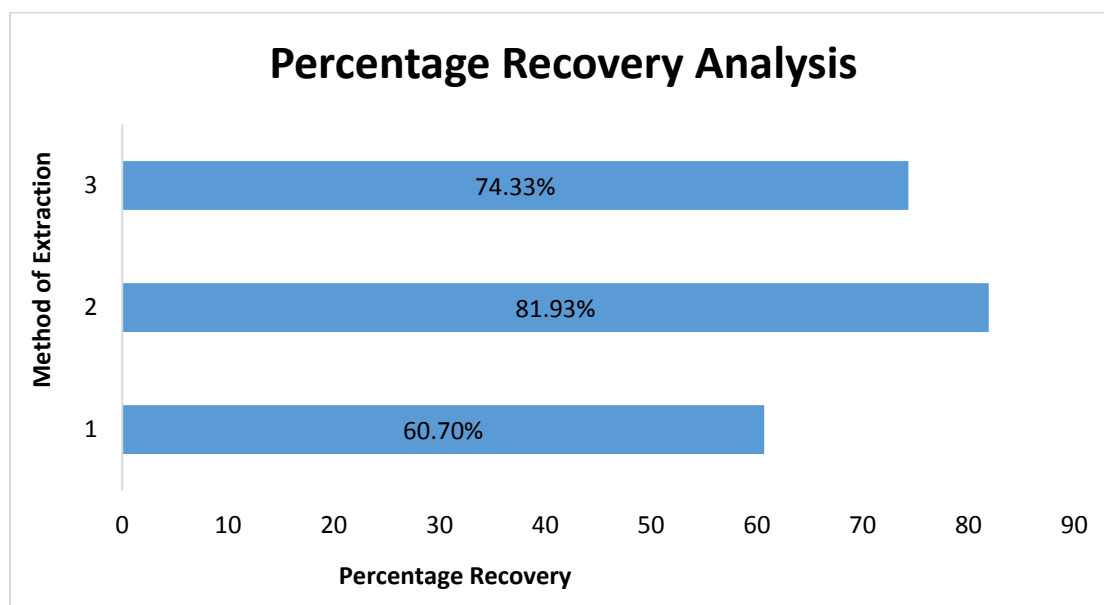


Figure 5: Bar Chart showing Percentage Recovery from various Extraction method

Legend of Bar Chart:

- 1: Extraction using HNO₃/ H₂O₂
- 2: Extraction using HNO₃/ HClO₄
- 3: Dry Ashing



Statistical Comparison on Methods of Extraction Of Lead Using Anova

From the table of comparison using Analysis of variance below, the p-value is greater than 0.05, hence we can state that the population mean of the 3 methods are equal. That is, there is no significant difference between the three methods used.

Table 4. 5: ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	92558.88108	2	46279.44054	0.043831536	0.957170808	3.284917651
Within Groups	34842984.86	33	1055848.026			
Total	34935543.74	35				

CONCLUSION AND RECOMMENDATIONS

Conclusion

In the progress of this research project, three different methods of extraction were adopted and compared. Although, there was no significant difference between these methods according to ANOVA at 95% confidence level, extraction using HNO₃ and HClO₄ proved to be the best method with a percentage recovery of 81.93%. Extraction with dry ashing had the lowest percentage recovery; 66.70%.

All paint chips samples obtained and analyzed had lead contents less than 90ppm- the US limit. Sample L24, a peach-colored paint showed highest lead content of 3211 µg/g. The blue sample L15 showed high paint concentrations of 2329µg/g too.

However, adequate caution has to be exercised when dealing with perchloric acid. This acid has a very high tendency to ignite once temperature is starts to climb above ambient temperature.

Recommendations

Lead in high concentrations poses great risk to the wellbeing of the entire human race, hence the public has to be adequately enlightened on the hazards attached to it. Replacement should be made for its uses. Lead in paints may be replaced with injection moldable “Ecomass” high gravity compounds. Eco-friendly and injection moldable, these thermoplastic composites achieve the density of lead without any toxic concerns.

More research work to encourage Green chemistry should also be encouraged in the paint industry.



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