

LEAD AS A TOXIC WATER CONTAMINANT – HEALTH EFFECTS AND METHODS OF ANALYSIS

PANDURANG NARAYAN PATIL ¹

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Abstract. Lead is heavy metal and toxic pollutants and it creates a health problem in both human and animals. Lead comes in drinking-water due to used in plumbing, fittings, solder, pipes, tetraethyl and tetramethyl used as antiknocking in petrol, food processing industries, herbal remedies etc. Children's and pregnant women's are mostly affected due to small concentration of lead in the body. Children's are affected due to exposure of lead in soils and household dust. Young children absorb 4–5 times as much lead as adults. Infants can absorb 50 % of lead through GI tract and men can absorb 10 -15 %; from food, water, dust or soil. Lead is accumulative in various body organs. It affects the central and peripheral nervous system. Various acute disease symptoms are occurs in human body at the blood lead levels of 100– 120 µg/dl in adults and 80–100 µg/dl in children.

It is essential to analyse the water for its lead content time to time. WHO has given a guideline value for lead is 0.01 mg/lit. There are various analytical methods reported for the detection of lead such as, atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS) and the inductively coupled plasma emission spectrometry (ICP).

Keywords: Lead, water contamination, toxic metals, Health effects, Analysis.

1. INTRODUCTION

Lead is a soft, heavy metal available in the form of several stable isotopes ²⁰⁸Pb, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁴Pb. It is soft metal having melting point 327 °C. Guideline value for lead in water is 0.01 mg/litre. Lead is considered one of the environmentally hazardous elements because, along with cadmium, mercury, copper, zinc and chromium it poses a particularly high risk of disturbing the chemical balance in the ecosystem [1].

Heavy metal pollution is and will be a public health problem. Lead, which produces several diseases, is one of the most important and widely distributed pollutants in the environment. It is called environmental priority pollutants. It is therefore important to monitor the levels of lead in environment. Environmental pollution by lead is a worldwide public health problem, exemplified by elevated blood lead levels among people living in the polluted areas [2]. Most lead in drinking-water arises from plumbing in buildings and the remedy consists principally of removing plumbing and fittings containing lead. This requires much time and money, and it is recognized that not all water will meet the guideline immediately.

¹ Bharati Vidyapeeth's College of Engineering, Department of Chemistry, 416013 Kolhapur, Maharashtra, India.
E-mail: pnpatil_chem@rediffmail.com.

Meanwhile, all other practical measures to reduce total exposure to lead, including corrosion control, should be implemented.

Pollution of streams and rivers flowing through agricultural areas where pesticides, fungicides, etc may have been applied, and industrial districts where there may have been metal waste deposits, all these present varied and difficult problems due to drainage into our different water bodies. Effluents discharged into rivers, which may affect aquatic animals like fish, may do so either directly or indirectly [3]. Lead, which produces several diseases, is one of the most toxic elements and has accumulative effect. Lead poisoning has severe adverse health impacts, which particularly affect children [4].

2. LEAD CONTAMINATION IN WATER

Generally lead is used very commonly in the lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors, ammunition, glazes and plastic stabilizers etc [5]. Lead used in the petrol in the form of Tetraethyl and tetramethyl lead as antiknock compounds. Lead comes in drinking-water due to different sources such as, in plumbing fittings and as solder in water distribution systems. Lead pipes may be used in older distribution systems and plumbing [6]. Many countries are restricted on use of tetraethyl and tetramethyl in petrol and lead containing solder in food processing industries. Concentrations in air and food are declining, and intake from drinking-water constitutes a greater proportion of total intake. Lead is rarely present in tap water as a result of its dissolution from natural sources; rather, its presence is primarily from household plumbing systems containing lead in pipes, solder, fittings or the service connections to homes. The amount of lead dissolved from the plumbing system depends on several factors, including pH, temperature, water hardness and standing time of the water etc [7].

Fossil fuel combustion; metal mining and smelting; chemical production; wastes incineration; and mercury amalgamation for gold mining are the main human activities which release heavy metals in global environment [8]. Report of Environment Canada & Environmental Protection Service revealed that concentrations of lead in air are mainly depend on use of lead additives in petrol. Canada declined lead concentration steadily from 0.74 $\mu\text{g}/\text{m}^3$ in 1973 to 0.10 $\mu\text{g}/\text{m}^3$ in 1989 [9, 10], reflecting the decrease in the use of lead additives in petrol. An atmospheric emission of lead is decreased since the introduction of legislation restricting its use in fuels. Water has assumed new importance as the largest controllable source of lead exposure in the USA [11]. Lead is present in tap water due to dissolution from natural sources, but primarily from plumbing systems in which the pipes, solder, fittings or service connections to homes contain lead as well as polyvinyl chloride (PVC) pipes also contains lead compounds that result in high lead concentrations in drinking-water. Dissolved Oxygen, chlorides, pH, temperature and acidity of water (plumbo-solvent) are the important factor on which the lead concentration is depends in water [12, 13]. Leaching of lead from soldered joints and brass taps decreases with time [11]. Lead can also be released from old galvanized plumbing that has accumulated lead from lead sources such as plumbing and service connections. The level of lead in drinking water may be reduced by corrosion control Measures by adding lime and the adjustment of the pH and making little bit alkaline [14, 15].

The leaching of lead to potable water from corrosion of lead bearing plumbing materials has been nationwide studied and managed by the Environmental Protection Agency (EPA) lead and copper rule (LCR) [16]. While recent studies by [17] Bellinger et al. and

others [18-20] have heightened concerns regarding low lead exposure on cognitive development of children.

Lead is also present in food, and it is increased when we use water, cooking utensils containing lead and if acidic food stored in lead – ceramic pottery or lead soldered cans. We can reduce the amount of lead by preventing these containers [21]. Lead is also found in lead-glazed ceramics; and food stored in containers painted with lead-based paint may contain significant amounts of lead. One study associated the storing of food in lead-glazed containers with elevated blood lead levels [22].

Free chlorine can dramatically reduce lead solubility relative to waters with chloramine or oxygen as an oxidant. Under at least some circumstances, chloramines can attack brasses and can significantly increase lead leaching. Study of chloraminated versus chlorinated water shows that the use of chloramine versus chlorine increased median lead leaching by about a factor of 10 [23]. In alkaline solutions (pH >13), high concentrations of nitrate break down pure lead passivity and cause pitting. The direct attack of metallic Pb by nitrate was reported [24, 25]. There is also a suggestion that the combination of ammonia and higher nitrate would synergistically drive lead corrosion. Specifically, lead weight loss in the study increased with higher concentrations of ammonia and nitrate in the water [24, 26] Moriber (1974) found that drinking water contaminated by wastes from mines producing cadmium; lead and zinc resulted in ricket-like diseases. The metals laden effluent may flow into a receiving water body.

3. HEALTH ISSUE

Some metals are not biodegradable and their way in food chain through a number of path ways and may accumulate in different organs of human beings or animals ⁴. The metals like cobalt, copper, manganese, zinc, nickel and lead are essential micronutrients at trace level, but are toxic if present in higher concentration [27].

Main area of exposure of lead on small children is soils and household dust, which is ranging from 5 µg/g to 10 mgs per gram in contaminated areas [28-30]. Infants can absorb 50 % of lead through GI tract as compared to men who can absorb 10 -15 %; from food, water, dust or soil [31]. Herbal remedies from India, China, and other parts of Asia may be potential sources of lead exposure. Certain Ayurvedic herbal products manufactured in South Asia were found to be contaminated with lead ranging from 5-37,000 µg/g [32]. Construction workers are having very high risk of lead exposures [33]. Even valves currently used in drinking water supply lines may contain 5-7 percent leaded brass, have been shown to discharge lead into drinking water, and constitute a significant source of lead in the water supply [34].

Young children absorb 4–5 times as much lead as adults, and the biological half-life may be considerably longer in children than in adults. Lead is a general toxicant that accumulates in the skeleton. Infants, children up to 6 years of age and pregnant women are most susceptible to its adverse health effects. Inhibition of the activity of d-aminolaevulinic dehydratase in children has been observed at blood lead levels as low as 5mg/dl, although adverse effects are not associated with its inhibition at this level. Lead also interferes with calcium metabolism, both directly and by interfering with vitamin D metabolism. Gastrointestinal absorption of lead is decreased by increasing intake of magnesium, phosphate, alcohol and dietary fats [35, 36]. Lead is toxic to both the central and peripheral nervous systems, inducing subencephalopathic neurological, renal system, vascular system

and behavioral effects [37]. There is electrophysiological evidence of effects on the nervous system in children with blood lead levels well below 30mg/dl.

These are the some systems of the lead toxicity [38]:

- a. *Hypertension*
- b. *Hyper-reflexa*
- c. *Tremors*
- d. *Upper extremity weakness*
- e. *Decreased nerve conduction velocity*
- f. *Gingival lead lines*
- g. *Buccal lead staining*
- h. *Papilledema*

In children's:

- a. *Growth failure*
- b. *Language delay*
- c. *Hyperactivity*
- d. *Increased intracranial pressure*
- e. *Abdominal pain*

Children are far more susceptible to lead neurotoxicity than adults because they absorb a higher fraction of bioavailable lead and have a developing system of cell differentiation and growth that is more vulnerable to inhibition and damage [37]. USEPA perform a population-based study, children who lived in a home that had undergone some type of renovation, repair, or remodeling work in the prior year were at 1.3 times greater risk of having an elevated blood lead level than children not exposed to such activities [39]. Lead exposure mainly through two routes such as, respiratory and gastrointestinal tract (GI) and gastrointestinal absorption depends on nutritional status and age of human [40, 41].

Lead is stored in one of two compartments in the bone – the exchangeable pool at the bone surface and the non-exchangeable pool deeper in cortical bone. Lead present in exchangeable pool can easily enter in to plasma but from non-exchangeable pool it move to the surface of the bone when bone is actively being resorbed. A study revealed that approximately 40-70 percent of blood lead in adults comes from bone lead [42]. Lead is stored in soft tissues such as liver (largest repository 33%), kidney cortex, medulla, pancreas, ovary, prostate, adrenal gland, brain, testis, heart, skeletal muscle etc [43]. Lead (PbBs 20-29 ug/dL) also correlates with significance increase circulatory and cardiovascular mortality [44].

Children absorbs more lead contained in food as compared to adults, it is estimated around 30 % from soil and dust [45,41]. Absorption is increased when the dietary intakes of iron or calcium and phosphorus are low [46-48]. Red blood cell are the principal vehicle for the transport of lead from the intestine to the various body tissues [49] where in lead is bound primarily to haemoglobin and has a special affinity for the beta, delta and, in particular, fetal gamma chains [50]. Lead is absorbed in a soft tissue pool, consisting of the blood, liver, lungs, spleen, kidneys and bone marrow, which is rapidly turned over, and in a more slowly turned over skeletal pool.

Lead having signs of acute intoxication, including dullness, restlessness, irritability, poor attention span, headaches, muscle tremor, abdominal cramps, kidney damage, hallucinations, loss of memory and encephalopathy, occur at blood lead levels of 100– 120 µg/dl in adults and 80–100 µg/dl in children. Signs of chronic lead toxicity, including tiredness, sleeplessness, irritability, headaches, joint pain and gastrointestinal symptoms, may appear in adults at blood lead levels of 50–80 µg/dl.

Renal disease has long been associated with lead poisoning; however, chronic nephropathy in adults and children has not been detected below blood lead levels of 40 µg/dl [51, 52]. Damage to the kidneys includes acute proximal tubular dysfunction and is

characterized by the appearance of prominent inclusion bodies of a lead– protein complex in the proximal tubular epithelial cells at blood lead concentrations of 40–80 $\mu\text{g}/\text{dl}$ [53]. There are indications of increased hypertension at blood lead levels greater than 37 $\mu\text{g}/\text{dl}$ [54].

4. GUIDELINE DEVELOPMENT

WHO *International Standards for Drinking-water*, in 1958 has recommended a maximum allowable concentration of lead was 0.1 mg/litre, based on health concerns. This value was lowered to 0.05 mg/litre in the 1963. The tentative upper concentration limit was increased to 0.1mg/liter in the 1971 International Standards. In the first edition of the *Guidelines for Drinking-water Quality*, published in 1984, a health-based guideline value of 0.05 mg/liter was recommended [7].

The 1993 Guidelines proposed a health-based guideline value of 0.01 mg/liter, using the PTWI established by JECFA for infants and children, on the basis of that lead is a cumulative poison and that there should be no accumulation of body burden of lead. The Guidelines also recognized that lead is exceptional, in that most lead in drinking-water arises from plumbing, and the remedy consists principally of removing plumbing and fittings containing lead [7].

5. METHODS OF ANALYSIS

Analysis of various trace and heavy metals present in water is very important and essential. Numerous analytical methods are available for the determination. Analytical chemistry has very important role for detection of various trace and heavy metals present in the environment such as air, water, soil and biological samples. Trace metal ions have important roles in a wide spectrum of life functions. As a result, the determination of trace metal ions is becoming very important due to interest in environmental sampling [55]. Some of the trace metals are essential micronutrients for organisms and plants. However, they are toxic at higher levels.

Many of the analytical methods used for environmental samples are the methods approved by federal agencies and organizations such as EPA and the National Institute for Occupational Safety and Health (NIOSH). Some methods are those that are approved by groups such as the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA). Additionally, analytical methods are included that modify previously used methods to obtain lower detection limits and/or to improve accuracy and precision.

5.1. CONSIDERATIONS FOR METHOD SELECTION

Several factors should be considered when selecting an analytical method for the determination of lead in environmental samples. Method selection will greatly depend on the purpose for the measurement and the circumstances surrounding the analytical investigation. Important parameters that must be clearly defined before a method is selected include:

- the limit of detection required;
- the accuracy and precision needed;
- the turnaround time desired;
- the number of samples to be analysed;
- the need/possibility to perform analysis at the point of care;
- the need to confirm the environmental source of exposure (through isotopic analysis);
- any regulatory or legal issues surrounding the measurement.

5.2. ANALYSIS OF LEAD IN WATER

Some trace metals are not biodegradable and they accumulate in different body organs of human and animals, there for determination of trace metal concentration in natural water has increasing attention [111]. Several analytical techniques such as atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), polarographic analysis and inductively coupled plasma mass spectrometry (ICP-MS) are available for the determination of lead with sufficient sensitivity for most of applications. The most common analytical methods for the lead trace determination are the flame atomic absorption spectrometry (FAAS) [56, 57] the electrothermal atomic absorption spectrometry (ETAAS) [58-60] and the inductively coupled plasma emission spectrometry (ICP).

Water can be analyzed for both particulate and dissolved (organic) lead. Particulate lead collected on a filter is usually wet ashed prior to analysis. GFAAS and AAS methods for particulate lead showed that the GFAAS technique is about 100 times more sensitive than the latter, although both offer relatively good accuracy and precision [61]. ICP/MS has been used to determine lead in water. Chelation and / or extraction can also be used to recover lead from aqueous matrices [62].

GC/AAS has been used to determine organic lead, present as various alkyl lead species, in water. Sample preparation for organic lead analysis was either by organic solvent extraction⁶³ or purge-and-trap. Sensitivity was in the ppb to ppt range and reliability was similar for all three methods. Total lead can be determined by digesting samples with acid and analyzing by either AAS or the more sensitive GFAAS according to EPA 1986c.

A number of laboratory methods are available to determine blood lead concentrations [64-66]. Four different ISO standard methods can be used for the determination of low levels of lead in drinking water such as,

i. Inductively coupled plasma mass spectrometry (ICP-MS) [67, 68] – This method should be able to reach a limit of detection of 0.1-0.2 $\mu\text{g/l}$ depending on the mass selected for detection.

ii. Atomic absorption spectrometry using graphite furnace (GF-AAS) [69] – In order to check whether spectral and non-spectral interferences influenced the analytical result the analysis can be repeated by adding chemical modifiers to the sample including blanks and calibration standards. The method should be able to reach a limit of detection of 1 $\mu\text{g/l}$.

iii. Inductively coupled plasma atomic emission spectrometry (ICP-AES) [70] –

This method has a typical limit of detection of 2-5 $\mu\text{g/l}$ and may only be used if the laboratory can show that a limit of detection of 1 $\mu\text{g/l}$ can be achieved.

iv. Flame atomic absorption spectrometry (FAAS) – This method is not state-of-the-art – This method describes 3 methods of which method third method may be used if the laboratory can show that a limit of detection of 1 $\mu\text{g/l}$ can be achieved. The method is based on the chelation of lead with hexamethylene ammonium-hexamethylenedithiocarbamate, extraction by a mixture of diisopropylketon and xylene and analysis by flame atomic absorption spectrometry. The range of determination is typically 2-200 $\mu\text{g/l}$.

5.2.1. Flame atomic absorption spectrometry (FAAS)

Flame atomic absorption spectrometry is by far the most widely employed technique for determination of lead in the water samples [71, 72] but this is less sensitive for the direct determination of lead with previous separation and preconcentration. Lead is determined by atomic absorption spectrophotometry in conjunction with a graphite furnace containing a graphite platform [73]. A sample is placed on the graphite platform, and a matrix modifier is added. The sample is then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal produced during atomization is recorded and compared with standards [74].

The lead content was determined in water and in muscle, gill and liver tissue of *Catla catla* by using a graphite furnace atomic absorption spectrometry [75]. Atomic absorption spectrometry and anodic stripping voltammetry methods are most frequently used for determining of lead less than 1 $\mu\text{g/l}$ in environmental and biological materials [76]. Lead has been determined along with iron, manganese and zinc in sea water samples by Atomic Absorption Spectrometry after Preconcentration with Chromosorb 105. A solid phase extraction procedure based a column technique for preconcentration of lead, iron, manganese and zinc from water samples was developed. The analyte ions as its diethyldithiocarbamate complex were retained on a column of Chromosorb 105 from buffered sample solution. Then they were eluted with acetone [77].

Solid phase extraction is one of widely used technique for the separation-preconcentration of trace elements carried out by using sorbents including activated carbon [78], chromosorb 102 [79-81], ambersorb resins [81, 82]. The simultaneous determination of trace levels of Cd(II) and Pb(II) in fresh water was determined by precipitate notation with hydrated iron(III) oxide and iron(III) tetramethylenedithiocarbamate. Electrothermal atomic absorption spectrometry (ETAAS) was used as an instrumental method for a quantitative determination [83].

Various methods for the determination of lead and tin have been developed, such as atomic absorption spectrometry, high performance liquid chromatography, inductively coupled plasma-mass spectrometry⁴ and neutron activation analysis. Also, there are some reports on voltammetric determination of lead and tin. These methods are very sensitive and nanomolar concentrations of these species can be determined. In spite of their high sensitivity, these methods suffer from low selectivity. The oxidation potentials of tin and lead are very close to each other, and their voltammograms are highly overlapped. Therefore, simultaneous determination of these species is not possible by common electroanalytical methods.

Lead and cadmium can be determined by flame atomic absorption spectrometry (FAAS) [84], but literature dealing with precipitate flotation separation in combination with ETAAS is scanty.

Modified Solid phase extraction was developed for the pre-concentration and determination of trace amount of lead in water resources. Lead was reacted with ammonium

pyrrolidinedithiocarbamate (APDC) to make a complex. The complex was then collected in a column packed with surfactant-coated alumina [85]. Determination of lead and cadmium by flame atomic absorption spectrometry (FAAS), but literature dealing with precipitate flotation separation in combination with ETAAS is scanty [84,83].

5.2.2. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) methods

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is used to determine metals and some nonmetals in solution. This method is a consolidation of existing methods for water, wastewater, and solid wastes [61, 28, 86, 87]. The determination of Fe(III), Pb(II), and Ni(II) by flame atomic absorption spectrometry (FAAS) after preconcentrating on a column containing *Aspergillus niger* loaded on silica gel 60 (Biosorbent) is described [88].

Separation and/or preconcentration of trace metals by adsorption on microorganisms loaded on a support material have been widely used [82, 89, 91]. The use of microorganisms as biosorbents for metals has become a good alternative to the other preconcentration methods because of higher recovery, economical advantages, simplicity and environmental protection. In general, microorganisms have the ability to selectively adsorb a specific element without preconcentrating the matrix [92].

In natural water and biological samples their level is low and previous steps of separation and preconcentration are usually required. For this purpose, many separation/preconcentration procedures for trace metal ions such as liquid-liquid extraction [93], cloud-point extraction [94, 95], liquid membrane [63] and solidphase extraction [82, 96-98] have been widely used.

5.2.3. Anodic Stripping Voltametry (ASV)

An additional advantage of ASV over flame atomic absorption spectrophotometry (FAAS), electrothermal atomic absorption spectrophotometry (ETAAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) or inductively coupled plasma-mass spectrometry (ICP-MS), is the simplicity of the instrumentation, which is relatively inexpensive, requires low electrical power and low maintenance, and is portable as well as suitable for automation [99].

ASV is one of the most sensitive, convenient, and cost effective analytical methods for detection and determination of metal ion contaminants, such as lead, in all sources of water. ASV is used to analyze simultaneously very low levels of several metals such as Pb, Cu, Cd and Zn. ASV can detect levels in the range of part-per-million (ppm) or even part-per-billion (ppb) (i.e., $\sim 10^{-10}$ M) (Lab manual). An adsorptive differential pulse stripping method for the simultaneous determination of lead and tin is proposed. The procedure involves an adsorptive accumulation of lead and tin on a hanging mercury drop electrode (HMDE), followed by oxidation of adsorbed lead and tin by voltammetric scan using differential pulse modulation [100]. Determination of lead (II) in water and edible oil samples, using Differential Pulse Adsorptive Stripping Voltammetry (DPAdSV) technique [101].

5.2.4. Cloud Point Extraction technique

Cloud point extraction and atomic spectrometry have been successfully employed for several elements in different matrices and it is an interesting alternative when a complex matrix has to be analyzed [102-104]. Cloud point extraction (CPE) has been used for the preconcentration of lead, after the formation of a complex with 2-(5-bromo-2-pyridylazo)-5-

(diethylamino)-phenol (5-Br-PADAP), and later analysis by graphite furnace atomic absorption spectrometry (GFAAS) using octylphenoxypolyethoxyethanol (TritonX-114) as surfactant [105].

Lead can be determined by cloud point extraction and complex formation with PAN (1-(2-pyridylazo)-2-naphthol) followed by flame atomic absorption spectrometry method. The analyte is quantitatively extracted to the phase rich in the nonionic surfactant Triton X-114 [106]. The cloud point extraction has also been used to pre-concentrate trace metals based on the formation of chelates in the surfactant aggregate. Detection of trace contaminants in water by spectroscopy of micro glow discharges that operate in air using two liquid electrodes (i.e., both the anode and cathode are liquid). A liquid electrode spectral emission chip (LEd-SpEC) has been developed to perform this function [107].

6. CONCLUSIONS

The above review concludes that it is necessary and essential to test the water for its use for any purpose. Especially when you are using water for drinking purpose it must be free from heavy metals lead which is very harmful for the childrens and pregnant womens. Nowadays various water testing laboratories are available, we can explore the facility for analysis of water. We have to try to avoid the lead containing material as a food and water containers. With the most care, we can avoid various diseases which will cause due to lead in drinking water.

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