

# 3

## Analytical Methods for the Determination of Lead in the Environment

**Peter C. Hauser**

Department of Chemistry, Analytical Sciences, University of Basel,  
Spitalstrasse 51, CH 4056 Basel, Switzerland  
<peter.hauser@unibas.ch>

ABSTRACT	49
1. INTRODUCTION	49
2. SAMPLING	51
3. SPECTROPHOTOMETRY	53
4. X-RAY FLUORESCENCE	54
5. ELECTROCHEMICAL METHODS	54
6. ATOMIC SPECTROSCOPY	56
7. SPECIATION	57
ABBREVIATIONS	58
REFERENCES	58

**Abstract:** A survey of the methods for the determination of lead in environmental samples is given. These are mainly based on sensitive atomic spectrometry, but alternatives, such as electrochemical and separation methods are also possible. Discussed are also sample preparation and speciation for differentiation between different organometallic forms as well as applications of isotope-selective determinations.

**Keywords:** atomic spectroscopy · electrochemical methods · lead isotopes · test kit · tetraalkyl lead · X-ray fluorescence

### 1. INTRODUCTION

Lead was used widely and continues to be employed for certain applications. The term plumbing derives from its domestic use in piping for water supplies, a

technique which was introduced by the Romans. But even if the actual pipes are not made from lead, the metal may still be present in water service lines of current buildings as part of the solder used for joining of tubings or even in chrome-plated faucets made from brass, which often include a small fraction of lead to render it easier for machining. Lead has also been widely employed as pigment for painting. Red lead,  $\text{Pb}_3\text{O}_4$ , has been in use for rust proofing of iron objects and white lead,  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ , has been used widely especially for the painting of wooden buildings. Chrome yellow,  $\text{PbCrO}_4$ , is the original pigment that lent its characteristic golden yellow color to school buses in the US and Canada and to the post offices in large parts of Europe. The metal is used in roofing and guttering especially to make water proof sealings at corners such as around chimneys. It is being used for applications where its high density is desired, such as in diving weights, sinkers for fishing tackle, and as shot for hunting. It is used for shielding against X-rays and radioactivity. It is present in glazed ceramics and leaded crystal. It is used in lead acid batteries, especially for motor vehicles. It was used extensively in petrol in the form of tetraalkyl lead as anti-knock agent and as part of the solder used in electronic equipment.

On the other hand lead has been found to be highly toxic. The Romans used lead acetate as a kind of artificial sweetener, but its toxic nature has long been established since. Among other problems its effects on the central nervous system of children are most pronounced. It has even been suggested that the crime rate in the US, which peaked in about 1990 and has been falling since, correlates with the peak use of lead in petrol approximately 20 years earlier [1]. While it was already reported in the *New York Times* on April 22, 1925, that the use of lead in petrol is a hazard, the general awareness of lead being an environmental and hygienic problem only dates back to the 1970s when generally environmental issues started to be considered. The loss of the freighter *Cavtat* in the Adriatic Sea in 1974, which carried a large number of barrels containing tetraethyl lead, has been cited as being instrumental in raising the awareness in particular of the environmental hazard of organic lead compounds [2, 3].

The recognition of its toxicity led to a reduction of the use of lead. It is no longer used for water piping or domestic paint. Lead acid batteries are recycled. Leaded petrol was phased-out from the 1970s, even though the initial reason for this was its incompatibility with the catalysts installed in new cars to reduce emission of unburnt hydrocarbons, CO, and  $\text{NO}_x$ . Except for a few isolated countries and some special aviation fuel, lead is now no longer used in petrol. In 2003 the European Union put in force the RoHS (Restriction of Hazardous Substances) directive, which bans the use of lead in solder for commercial electronic equipment. However, its extensive prior use means that lead is still a substantial menace. Old buildings contain lead-based paint and pipings. Soil around domestic buildings and vegetables grown in this soil may therefore show high levels of lead contamination. The wide use also required lead processing factories and smelters, which have now largely been closed down, but airborne pollution caused significant persistent soil contamination over wide areas surrounding these sites. *US Today* identified about 400 such locations in the US [4]. According to the US EPA (Environmental Protection Agency) lead is the most common

inorganic contaminant at polluted sites in the US. Similarly, mining towns are affected, and the pollution of the landscape in such areas has been found to affect not just humans but also wildlife. While organic lead compounds are mobile, and the rise and fall in the use of leaded petrol can also be tracked by determining organic lead compounds in vintage wines [5], inorganic lead is persistent as the predominant Pb(II) species are mostly water-insoluble. In central areas of large cities with a high volume of road traffic many tons of lead were deposited as dust or via rainfall over the years in which leaded petrol was in use. In the US 5 million tons of lead have been spread in this way, and the soil in inner cities like Sydney in Australia are still found to contain up to 1400 mg of lead per kg even though leaded petrol was phased-out more than 20 years ago [6]. Children playing in the grounds of affected properties are at risk. Highly problematic are also the open fire methods employed in some developing countries for recycling electronic waste.

Given the persistent risks from lead pollution, reliable lead analysis is highly important. At the time of writing two cases involving lead analysis were widely reported in the press. Old water piping is still a problem as highlighted by the Flint water crisis in 2015. Flint is a city of about 100,000 inhabitants in Michigan which were exposed to excessive lead levels in the municipal water supply. Controversial analytical results were part of the ensuing scandal. Also in 2015 Nestlé had to recall a large number of packages of instant noodles produced in India due to alleged contamination with lead. The company however, disputed the analytical results presented by the authorities [7]. The on-going interest in lead analysis is also reflected by the high rate of publications in the scientific literature concerning the determination of lead in different kinds of samples or the development of new methods, which numbers about 50 per month (as shown by a keyword search on the Web of Science). Most commonly atomic spectroscopic methods are used, which have the required sensitivity for the often relatively low concentrations to be determined. Alternatives based on electrochemical methods such as polarography, or separation methods such as ion-chromatography, capillary electrophoresis or even gas-chromatography exist, but generally tend to be less sensitive than the atomic spectrometric methods and are therefore not routinely employed. Chemical sensors for lead have also been proposed, but tend to lack sufficient specificity. Environmental samples usually require extensive pretreatment before quantification can take place. Speciation analysis is sometimes needed for environmental studies and special insights can be gained with isotope analysis.

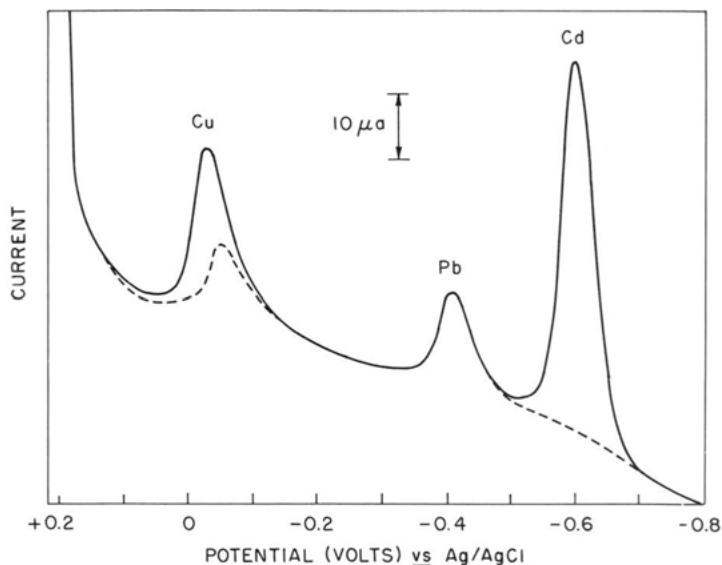
## 2. SAMPLING

The most simple sampling procedure applies of course to the collection of aqueous specimens. These usually only need to be acidified to prevent precipitation as Pb(OH)<sub>2</sub> during storage. If necessary, filtration is carried out with membrane filters, usually with 0.45 µm pore size. When sampling at depths in water bodies is required, this is achieved with special sampling devices that open at desired

levels. For solid samples, e.g., of soils or sediments, care has to be taken to obtain representative samples. As most quantification methods require the sample to be present in liquid form solid samples usually need to be subjected to dissolution or extraction procedures.

Dissolution is first attempted in acids and often this is carried out aided by addition of energy in the form of heat or microwaves. The use of hydrofluoric acid is required for samples containing silicates and some minerals need to be subjected to fusion procedures (dissolution in molten salts). Plant material may be decomposed with ashing procedures such as combustion in closed containers to avoid sample loss.

For the determination of organolead compounds solvent extraction is used. Besides the classical operation with separating funnels a number of newer methods which are more easily automated and require less solvents are available. Most notable is solid phase extraction (SPE) which is based on cartridges containing solid lipophilic materials which trap analytes when the aqueous sample is passed through. The species of interest are then flushed from the cartridge with a small amount of organic solvent prior to quantification. Many of the new developments have focussed on miniaturization to allow working with smaller sample volumes (a comprehensive overview on extraction methods for organo-metallic species has been prepared by Moreda-Piñeiro et al. [8]). The extraction procedures do not only separate the analytes from the matrix, but can also be employed to achieve a preconcentration so that the demands on the detection limit of the quantification method is relaxed.



**Figure 1.** Determination of Pb, besides Cu and Cd, in a sample (solid line) and a blank (broken line) by stripping voltammetry, which gave identical results for Pb due to a contamination of the reagents at approximately  $10^{-7}$  M Pb. Reprinted with permission from G. W. Ewing, *J. Chem. Ed.* **1973**, 50, p. A131; copyright 1973, American Chemical Society.

As the concentrations of interest are generally at the trace level, proper sampling procedures are essential in order to prevent contamination. This is particularly important when ambient environmental background levels are to be determined. Sampling from boats may need to be carried out from the bow and against the direction of the wind [9]. Containers made from high density polyethylene are generally used for storage, never glass. These have to be subjected to an acid-based precleaning procedure [9]. High purity acids and other reagents have to be employed. For the most demanding applications so-called “electronic” or “semiconductor” grade acids, which are produced for the semiconductor industry, are required. In the laboratory, samples for trace analysis have to be handled on clean benches (under filtered clean air). In the early days of trace metal analysis these requirements were not fully understood and it has been said that much of the environmental data for lead determined prior to about 1975 is not valid due to contamination [10]. This problem is illustrated in Figure 1.

### 3. SPECTROPHOTOMETRY

Spectrophotometric measurements, i.e., molecular absorption spectrometry, by adding an appropriate color-forming reagent are usually the simplest methods because of the comparatively low cost of the spectrometers. The most common spectrophotometric method employs dithizone as reagent and involves an extraction procedure with an organic solvent in order to achieve selectivity, and quanti-



**Figure 2.** Test kit for lead as sold in hardware shops.

fication at 520 nm [11]. Simple colorimetric test kits, i.e., methods where a color change is observed by the naked eye, are also available. Such a test kit is shown in Figure 2. These are sold at hardware shops primarily to home owners who wish to test their painting for the presence of lead. They are based on sulfide or rhodizonate as color-forming reagents and contain the reagents in liquid form or are based on a self-contained test device in which a tube containing the reagents is crushed to release the reagents onto a cotton bud which is then used to directly sample the suspected surface.

## 4. X-RAY FLUORESCENCE

X-ray fluorescence (XRF) [12] has the significant advantage that no sample preparation is necessary, i.e., it is possible to directly analyze solid samples, such as paint and soil. In X-ray fluorescence element-characteristic X-rays are quantified. Excitation is achieved by irradiation with X-rays, hence the name, but it is also possible to employ the gamma rays of a radioactive isotope source such as  $^{107}\text{Cd}$ . In one possible method of detection based on semiconductors, namely energy dispersive detection, a spectrum is acquired with a multichannel analyzer which bins the signals according to their peak heights. As can be seen in Figure 3, such instruments can be very compact and battery operated. They are more sensitive and reliable than the colorimetric test kits and this type of instrument is therefore in common use by authorities or companies specializing in remediation of homes or other contaminated sites.

## 5. ELECTROCHEMICAL METHODS

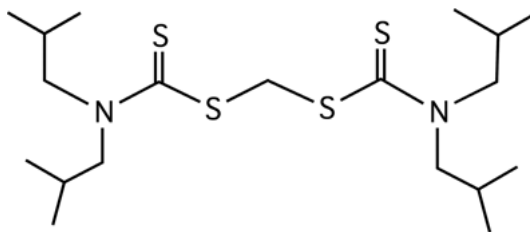
Several electrochemical methods are available [13], of which polarography has been the most commonly employed technique. This is based on the use of a mercury electrode on which the dissolved analyte ion is reduced. The resulting current is proportional to the concentration. Anodic stripping voltammetry is a technique derived from polarography in which the analyte is first deposited in the metallic form by reduction, followed by re-dissolution by oxidation. The first step leads to an effective preconcentration and the current is measured in the second step. Impressive limits of detection (LOD) in the ppt range are possible employing comparatively simple and inexpensive instruments. Such high sensitivity is otherwise only possible with the much more complex and costly atomic spectroscopic instruments as discussed below. Mercury has generally been employed as electrode material, as the kinetic hindrance of the reduction of water on this metal allows the reduction of heavy metals at negative potentials at which otherwise hydrogen evolution would interfere. Furthermore, the renewal of the electrode surface is readily possible, simply by letting a drop of the liquid metal flow from a capillary. However, due to the toxicity of mercury the method is loosing popularity. The Minamata convention on the ban of the use of mercury



**Figure 3.** A portable XRF analyzer employed for soil testing. Reprinted with permission; copyright Thermo Fisher Scientific.

signed in 2013 by 128 countries still permits its use in the laboratory, but the use of mercury in polarography has already been banned in Sweden. For this reason alternatives have been extensively researched in recent years. In particular bare or bismuth-coated screen printed carbon electrodes provide a simple replacement. These electrodes can be produced cheaply, so that single use is possible, and are commercially available from several small producers, but have not been adopted widely.

Also possible is the determination of lead ions in solution by potentiometry with ion-selective electrodes. These are either based on crystalline membranes made from pressed PbS or on membranes of plasticized PVC containing an ionophore. Such electrodes have LODs of about  $10^{-6}$  M and are a simple and inexpensive. A special feature of potentiometry with ion-selective electrodes is the fact that only free, but not complexed, lead ions are measured. Careful attention



**Figure 4.** S,S'-Methylenebis(N,N-diisobutyldithiocarbamate), an ionophore for lead employed in ion selective electrodes.

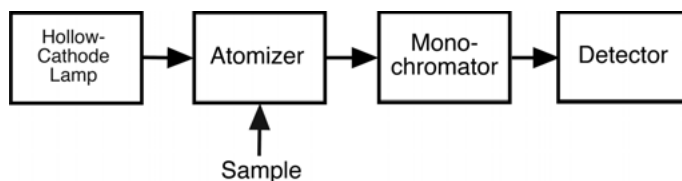
has to be paid to their selectivity, as for example  $\text{Cd}^{2+}$  is a significant interferent for crystalline membrane-based electrodes. Typical applications are the analysis of plating baths. A commercially available ionophore which selectively binds  $\text{Pb}^{2+}$  in PVC-based membranes, and thus leads to the creation of an electrode potential in dependence on the lead concentration in the sample solution, is shown in Figure 4.

When the concentrations are high, lead may also be determined by the electrochemical method of electrogravimetry, in which the amount of lead deposited from the sample is determined by weighing, or the related technique of coulometry, where the charge required for complete electrolysis of the lead contained in the sample is determined. Both techniques are relatively time-consuming, and in the case of electrogravimetry it entails significant manual labor, but have the advantage of higher accuracy and precision than other methods.

## 6. ATOMIC SPECTROSCOPY

Despite their comparatively high cost, most commonly used in practice are the atomic spectroscopic methods. These techniques have very good sensitivity, are robust and are much less prone to interference than most other methods. Atomic absorption spectrometry (AAS) instruments (see Figure 5) are based on absorbance measurements on the free and neutral atoms in the gas phase. The method relies on hollow cathode lamps as light sources, which contain the same metal as the analyte in order to produce matching wavelengths, so that a high reliability is assured. Monochromators are still required to suppress unwanted wavelengths. Most commonly the atomizer consists of a flame into which the samples are introduced as an aerosol. These instruments are widely available. Limits of detection of about 10 ppb are obtained with this method [12]. Lower detection limits of about 0.05 ppb are possible by the more elaborate graphite furnace atomizer, where a small aliquot of the sample is heated electrothermally [12]. A further atomizer variant is the hydride generation technique suitable for elements which form volatile hydrides when sodium borohydride is added to the sample. This is a relatively simple method in that the gaseous hydrides are simply atomized in a resistively heated quartz tube and which generally gives very good





**Figure 5.** Principle of atomic absorption spectrometry.

detection limits. However the sensitivity of this method for lead, while better than with the most widely used flame AAS, is relatively poor compared to other hydride forming elements such as arsenic [13] with a reported limit of detection for lead of 0.1 ppb [14].

Also common in laboratories for trace analysis of metals are spectrometers employing an inductively coupled plasma (ICP) into which the samples are also introduced as aerosol. These are available in two variants, either based on optical emission spectrometry (ICP-OES) or on mass spectrometry (ICP-MS). The latter is possible as at the high temperature of the plasma (up to about 10,000 °C) the analyte species are not only converted to free elements, but also ionized. These instruments are more expensive in capital outlay and running costs than the AAS instruments, in particular the ICP-MS, but have the advantage of multi-element analysis, in case other analytes besides lead are to be determined. The detection limit for lead obtained with the ICP-OES of about 4 ppm [12] is relatively modest, but with 0.02 ppb excellent for the ICP-MS.

## 7. SPECIATION

Speciation analysis, i.e., the distinction and quantification of different forms of lead, is important for lead-containing organometallic species. This mainly concerns studies of the environmental fate of the tetraalkyl lead compounds that used to be added to petrol, which was a highly important topic 20–25 years ago but is obviously less relevant now. The main compound which used to be added to petrol was tetraethyl lead, but tetramethyl, and mixed ethyl-methyl compounds were also employed [15]. Their degradation products include singly or doubly charged species such as  $\text{Et}_3\text{Pb}^+$  and  $\text{Et}_2\text{Pb}^{2+}$ . The speciation of the neutral and charged compounds is generally based on a so-called hyphenated method which combines separation by gas chromatography with sensitive quantification by one of the atomic spectroscopic methods. To allow the separation by gas chromatography the ionic compounds are rendered neutral and volatile by propylation or butylation, rather than methylation or ethylation, to still allow the distinction of all possible species. Hydrogenation is not suitable for this purpose as the dialkyl lead species reportedly do not form hydrides [16].

A different form of speciation analysis is the differentiation between isotopes of lead. This can be achieved by inorganic mass-spectrometry such as ICP-MS. The use of laser ablation ICP-MS or SIMS (secondary ion mass spectrometry)

allows the analysis of small amounts of solid materials. In these methods tiny amounts of sample are vaporized either with high energy laser pulses or by sputtering with an ion beam. Lead has 4 stable isotopes, namely  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$ . The latter three are the products of the radioactive decay of  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$ , respectively. This means that different sources of lead have different isotopic compositions, which allows the determination of the source of lead samples. A possible application of this is the verification of paintings of the old masters based on the analysis of the white pigment consisting of white lead [17]. Lead isotope analysis is also important in the dating of geological specimens, in the so-called uranium-lead dating method. Due to the long half-lives of the parent elements the determination of the isotopic ratios of the precursor element and the product allows the dating of rocks up to 100s of millions of years old. Often the mineral zircon is employed for this purpose as in its crystallization lead is strongly excluded while uranium is admitted into its crystal structure. Thus, it usually does not contain any naturally occurring lead, but only that produced by the radioactive decay. The determination of both, the ratio of  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{207}\text{Pb}/^{235}\text{U}$ , allows a verification of an absence of contamination or loss of either of lead or uranium as both measurements should give identical results.

## ABBREVIATIONS

AAS	atomic absorption spectrometry or spectrometer
EPA	Environmental Protection Agency
ICP	inductively-coupled plasma spectrometry or spectrometer
LOD	limit of detection
MS	mass spectrometry or spectrometer
OES	optical emission spectroscopy or spectrometer
PVC	poly(vinyl chloride)
RoHS	restriction of hazardous substances
SIMS	secondary ion mass spectrometry
SPE	solid phase extraction
XRF	X-ray fluorescence

## REFERENCES

1. R. Nevin, *Environm. Res.* **2007**, *104*, 315–336.
2. G. Tiravanti, G. Boari, *Environm. Sci. Tech.* **1979**, *13*, 849.
3. M. Branica, Z. Konrad, *Lead in the Marine Environment: Proceedings of the International Experts Discussion on Lead Occurrence, Fate and Pollution in the Marine Environment, Rovinj, Yugoslavia, 18–22 October 1977*, Pergamon, Oxford, 1980.
4. <http://content.usatoday.com/news/nation/smelting-lead-contamination>, accessed on April 26, 2016.
5. R. Lobinski, C. Witte, F. C. Adams, P. L. Teissedre, J. C. Cabanis, C. F. Boutron, *Nature* **1994**, *370*, 24.

6. <http://www.abc.net.au/catalyst/stories/4174798.htm>, accessed on April 26, 2016.
7. <http://www.nestle.com/ask-nestle/maggi-noodles-india-msg-lead-ban-recall>, accessed on April 26, 2016.
8. A. Moreda-Piñeiro, J. Moreda-Piñeiro, P. Bermejo-Barrera, in *Speciation Studies in Soil, Sediment and Environmental Samples*, Ed. S. Bakirdere, CRC Press, Boca Raton, 2014.
9. T. R. Crompton, *Determination of Metals in Natural Waters, Sediments, and Soils*, Elsevier, Amsterdam, 2015.
10. G. Benoit, *Environm. Sci. Tech.* **1994**, 28, 1987–1991.
11. R. Lobinski, Z. Marczenko, *Spectrochemical Trace Analysis For Metals And Metalloids*, Elsevier, Amsterdam, 1996.
12. R. Jenkins, *X-Ray Fluorescence Spectrometry*, Wiley, New York, 1999.
13. J. A. Plambeck, *Electroanalytical Techniques, Basic Principles and Applications*, Wiley, New York, 1982.
14. J. W. Robinson, *Atomic Spectroscopy*, Marcel Dekker, New York, 1996.
15. B. Welz, M. Sperling, *Atomabsorptionsspektrometrie*, Wiley-VCH, Weinheim, 1997.
16. K. C. Thompson, D. R. Thomerson, *The Analyst* **1974**, 99, 595–601.
17. R. Lobinski, W. M. R. Dirks, J. Szpunar-Lobinska, F. C. Adams, *Anal. Chim. Acta* **1994**, 286, 381–390.
18. J. Szpunar, R. Lobinski, *Hyphenated Techniques in Speciation Analysis*, The Royal Society of Chemistry, Cambridge, 2003.
19. G. Fortunato, A. Ritter, D. Fabian, *The Analyst* **2005**, 130, 898–906.

