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Analysis of lead in dust by ICP-MS – Development of a method for estimation of the exposure of children to lead

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Master's Thesis

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Abstract

The aim of this study, which was performed at the ENSP, École Nationale de la Santé Publique, Rennes, France, was to create a protocol for the analysis of lead in house dust using inductively coupled plasma – mass spectrometer (ICP-MS). The reason for this is the possibility of making a risk assessment on site, in this case in the homes of small children.

Lead is a dangerous toxic and in particular to children in the ages of 0-6 years because of their behaviour. They tend to put toys and other items into their mouths along with the dust. It is crucial to keep the amount of lead in the blood on a low level, preferably less than 100 µg/l blood. One way to assess exposure, via all media including dust, is to take blood samples of the children. The other and much more comfortable way is to analyse the house dust. By digesting the dust via leaching, the bioavailable lead can be estimated. It can tell whether or not a dust is dangerous to the child's health.

Nine different dust samples from homes in Rennes and it's surroundings were examined along with two reference materials, SRM 2583 and SRM 2584, with known lead content. Tests showed that nitric acid gives good recoveries compared to the nitrohydrochloric acid (1/3 nitric acid and 2/3 hydrochloric acid) during a mineralisation. And in the choice between a micro-wave and the Digiprep, as a digestion system, the Digiprep has more advantages. The leaching made it obvious that the amount of bioavailable lead is very small compared to the total lead available. Further on, not all lead is bioavailable simply because the lead can be more or less tightly bound in different chemical compounds. This means that a dust rich in lead is not necessarily dangerous to the health. It all depends on how the lead is bound.
The isotopic ratios are very useful in the search of the lead sources. In this case it was used to dismiss sources as being potential lead sources. It was concluded that the samples didn't exhibit lead from plumbing, industry, rainwater, water plants or leaded gasoline. Instead the lead might originate from the ancient mine of Pont-Péan in the south of Rennes.

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1. Introduction

This report represent my master's thesis and is the final part of the study programme in Chemical Engineering at Chalmers University of Technology, Göteborg, Sweden. The master's thesis was carried out at École Nationale de La Santé Publique, ENSP, in Rennes, France. The aim of the work was to create a protocol for the analysis of lead in house dust by using inductively coupled plasma – mass spectrometry (ICP-MS) for the analytical determinations.

Lead is a toxic metal and may give rise to neurological and intellectual problems for children. Effects on the child's IQ have been reported indicating that a child shouldn't be exposed to lead giving rise to concentrations in blood exceeding 100 µg/l blood.

Children, less than two years, tend to put toys and other items in their mouths along with lead-containing dust. This is true in particular for children who live in old houses where the walls have been painted with lead-containing paint and also in houses close to industries emitting/having emitted lead. In those cases the soil and the dust often contains increased amounts of lead and it is therefore interesting to know the content in order to evaluate the health risks on site.

The use of the (ICP-MS) for the analytical determinations, does not only give the opportunity to determine the amount of lead in a sample but also, with the use of the isotopic ratio, the source. Lead has four isotopes and the mass ratio between the isotopes may vary in lead from different sources. However, this ratio is constant and unchangeable no matter what chemical and physical changes the lead goes through and can therefore be used as a fingerprint for the lead in the sample. Usually knowledge of the exposure is obtained from the analysis of blood, but analysis of housedust combined with other information such as dust intake rate and intake from other media (food, water, air) are easier ways. If both the total amount of lead and the bioavailable lead are estimated, then the exposure of the child is determined indirectly.

2. Theory

Lead is a toxic metal that can be found everywhere in the environment. Humans, children in particular, are sensitive to lead. Dust is an important lead source and determination of lead in dust can be used for the estimation of lead exposure.

2.1. Lead's properties and origin

Lead, atomic number 82, is a soft, silver-coloured metal that can be found everywhere in the environment and originates from either natural or anthropogenic sources. It has four naturally occurring isotopes (204, 206, 207, and 208) and the isotopic ratios for different mineral sources vary. The isotopic distribution of lead in the environment is 1.4% of ^{204}Pb, 24.1% of ^{206}Pb, 22.1% of ^{207}Pb and 52.4% of ^{208}Pb.

Even though lead has four valence electrons in its outer shell it looses only two of them readily and therefore the most common oxidation state is +2 and not +4.

Lead is a metal that is very resistant to corrosion but soluble in nitric and sulphuric acid. The solubility of lead salts in water varies depending on the type of salt. Lead sulphide and lead oxides are poorly soluble while the nitrate, chlorate and chloride salts are quite soluble in cold water. Lead forms salts with organic acids like lactic and acetic acids. It also forms stable organic compounds like tetraethyl lead and tetramethyl lead [1].

The level of lead in the earth's crust is about 20 mg/kg. The industrial revolution gave a rise to an increased amount of lead in the environment and even more so around 1920 when the leaded gasoline was introduced. Leaded gasoline is still not banned everywhere in the world, but it is in the developed countries. Lead containing paint was, from the beginning of till the middle of the 20th century, common in homes since it protects against humidity and has great covering abilities [1]. For decades, lead industry has been emitting lead to the atmosphere [1], [2]. Even though law, more or less efficiently, controls the emissions today, the soil in industrial areas is already polluted. Lead in air can be deposited on soil and water and can in this way reach the food chain, drinking water and house dust [1].

Lead from the plumbing system can be dissolved in the drinking water if the water is acidic. Even food contains lead that comes from the soil, the atmosphere, industries nearby and streets [3]. Furthermore lead arsenate insecticides used in orchards release lead to the soil [2].

2.2. Human exposure

In areas where leaded gasoline is banned the major exposure pathways of non-smoking adults are from food and water. Airborne lead can contribute to the exposure depending on use of tobacco, occupation, proximity to motorways, lead smelters and some leisure activities such as pottery [4].

To infants and young children the major potential exposure pathways are food, air, water and dust/soil. Lead in soil and dust in urban areas depends on the age and condition of buildings, the use of lead-based paints, lead in petrol and urban density [4].

The child's age and behaviour as well as the amount of bioavailable lead in the source determine the amount of lead that is taken in [1, 4]. Only 10% of the lead up-take in adults comes from food. For children the rate is 50% from food and 30% via lead absorption from dust. This depends on, among other things, the diet and its deficiency in certain elements. Diets that are deficient in calcium, phosphate, selenium, zinc, iron and vitamin D cause an increase of lead absorption. Blood lead (PbB) is widely used as a measure of body burden and absorbed lead. The distribution of the lead in the body is uneven, with a rapid uptake into blood and soft tissue and a slower redistribution in the bones. Lead's half-life is much shorter in blood and soft tissue (28-36 days) than it is in the skeleton where it can stay for many years. The relative retention of lead in body stores is higher in children than adults. Inorganic lead is not metabolised and is secreted from the body [1, 4].

2.2.1. Toxic effects on humans

Humans, children in particular, are sensitive to lead. Until it reaches the age of about six years the child is subjected to lead through many pathways. The lead can, for instance, be transmitted from the mother to the foetus through the placenta or by the breast milk. Children, less than two years, tend to put toys and other items in their mouth along with lead-containing dust that often originates from wall paint [4, 5]. This is called the hand-to-mouth route [6]. In extreme cases the child has Pica, a syndrome which results in the ingestion of non-food items that may contain high concentrations of lead [4, 5]. Smaller particles adhere readily to a child's hands and are therefore more likely to be ingested. Furthermore a child's breathing zone is closer to the floor level [7].

Severe intoxication reveals itself by neurological means. The child becomes slower, it hallucinates, it looses its memory, it becomes irritable and nervous as well as it gets headaches, stomach-aches and shaking. These symptoms appear at a PbB higher than 800 µg/l blood. A child subjected to low lead intoxication may show great tiredness, sleeping disabilities, irritability, headaches, joints and gastrointestinal pains. Kidney and bone damage can also occur. The lead gives rise to anaemia by the inhibition of the haemoglobin synthesis and also the destruction of the red blood cells. Further, it interferes with the activities of several important enzymes that are important for the haeme synthesis [4, 8].
A child shouldn't be exposed to lead giving rise to a concentration in blood exceeding 100 µg/l [3].

Adults, as well, can be affected by lead and suffer from headaches, high blood-pressure, digestive problems, memory and concentration problems, mood changes, sleeping disorders and muscles and joint pain. If a pregnant woman gets exposed the foetus can develop abnormally. Miscarriages and stillbirths are common among female workers exposed to high lead levels [1, 7-8].

As mentioned above, children suffer the most from exposure to lead and it is difficult to determine the source of exposition because lead is an ubiquitous pollutant [9].One way is, though, through the analysis of dust by ICP-MS which gives the isotopic ratios.

2.3. House dust

The dust's composition varies greatly in a home as well as between different homes, across seasons and among locations in a country. It consists of fibrous and non-fibrous components in different quantities e.g. the kitchen is often the room with the least amount of fibres. Many of the major components in dust are the same in all of the rooms. Particles smaller than 75 µm mostly contain crumbs, hair, soil, starch, plant parts, skin, insect parts and pollen [10].

2.3.1. The dust particle size

A big part of house dust consists of fine particles that are considered to be the most biologically significant for the hand-to-mouth route in childhood lead poisoning [9]. Simply because particles of small size, 10-100 µm, stick more readily to children's hands [6, 11-13]. Further on, most research indicates that the amount of lead is in general concentrated in the fine particles and that the absorption of lead in the body is inversely related to the particle-size. The smaller the particle (it has to be less than 250 µm) the more efficiently it is absorbed [3, 12-13]. The lead is, though, not always enriched in the fine fraction, mining or industry can give lead-enriched coarse particles. This means that the lead-source has great importance [3].

2.3.2. Sources of lead in dust

House dust can contain numerous types of lead compounds that vary from house to house and from region to region. Factors deciding the lead concentration in house dust are:

- soil and area of exposed soil
- the age of the house, house material and the presence of deteriorated or damaged paint
- distance to roads, type of road and street dust (This is still true despite the ban of leaded gasoline in the year 2000 in France)
- renovation, remodelling and abatement
- distance to commercial garages and smelting/mining operations
- dust-fall rates and suspended particles in-doors
- carpet wear and the presence of a fireplace
- some parental occupations and hobbies like pottery [9, 13]

2.3.3. Isotopic ratios

Lead is one of the most common anthropogenic contaminants in an ecosystem and the lead concentration alone cannot provide enough information about the anthropogenic contamination since a great deal of lead originates from natural processes. Studies have shown that stable lead isotopes can be used to trace the sources of lead pollution because the isotopic distribution remains unaffected by physical and/or chemical processes. The lead ores display isotopic signatures that depend on the original composition and the age of the ore bodies [14]. Thus, the lead measurements in soil, water, paint and dust can be compared to the isotopic ratios of lead in human tissue and thereby tell whether the lead in a sample comes from wall paint, gasole, mining or smelting etc. Lead has four stable isotopes of masses 204, 206, 207 and 208. The isotopic distribution of lead in the environment is 1,4% of ^{204}Pb, 24,1% of ^{206}Pb, 22,1% of ^{207}Pb and 52,4% of ^{208}Pb. Mined lead contains radiogenic lead isotopes of 206, 207 and 208 that are created from the decay of uranium and thorium [5, 15-17]. The 204 is the only isotope that is not produced by radioactive decay and is considered to be a measure of the original lead present after the condensation of the solar system. In the ICP-MS there are often interferences of ^{204}Pb and ^{204}Hg. Environmental scientists tend to use ^{208}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb or ^{208}Pb/^{206}Pb vs. ^{206}Pb/^{207}Pb as isotopic ratios since they have a better analytical precision than the others [14] and they are also the ones that give most information.

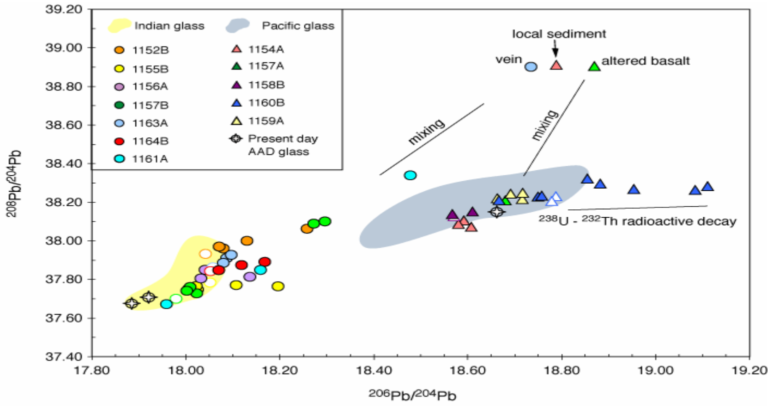

Fig. 1 Example of isotopic ratios [19]

In general, the higher the amount of lead, the lower the isotopic ratios indicating that the lead is anthropogenic [18].

2.4. Sampling and Analysis

The analysis requires a certain quantity of collected dust in order to give a proper image of the exposition. The dust, which can be collected by many different means, needs to undergo digestion before it can be analysed in the ICP-MS.

2.4.1. Collecting dust

In the selection of a device for the dust collection one or both of the two following design options ought to be fulfilled:

1. the device used should as much as possible mimic the hand’s ability to pick up and retain the particles

2. the device should pick up all or a reproducible amount of the dust in a certain area.

It is easier to find a sampler that collects dust from a smooth surface than from a textured surface simply because it is more difficult to get an even contact between the device and a textured surface [10].

The lead is measured as either lead loading; micrograms lead per square centimetres of surface, or as lead concentration in the collected dust, micrograms of lead per gram dust [10, 20]. The wipe must then be weighed before and after sampling.
There are several dust-sampling methods, but the most used are the wipe method and the vacuum method [9, 13]. Some researchers have used a paintbrush and a plastic-scoop, while others have collected the dust in ordinary vacuum cleaner bags [15, 20].

2.4.1.1. Wipe methods

- The Vostal method: Paper-towels moistened with 20% denatured alcohol are used to wipe a pre-determined uncarpeted area. The intensity and the time of the rubbing are carefully controlled. It has been determined that the first wipe collects ¾ of the lead available. No paint-flakes were allowed in the sample because it was considered that the children don’t ingest paint-flakes. Using this method the bioavailable lead was measured [13, 21-22].

- The Farfel method: The surface was wiped back and forth twice in each direction and this was repeated after folding of the towelette in half. The same surfaces were wiped up to ten times in order to state the sampling efficiency. Here paint-chips were sampled as well [13, 21].

- The HUD (U.S. Department of Housing and Urban Development sampler) has used towelettes pre-moistened with detergent in a fixed number of passes to wipe up the dust in a defined area. The detergent may affect the collection efficiency by solubilizing more dust than does water by its own. Being very easy and cheap it is a widely used method in the assessment of lead loading [8, 10, 13, 24].

- The LWW (Lioy-Weisel-Wainman) sampler was designed for the measurement of lead loading, dust loading and also lead concentration. The pressure applied to the wipe is controlled in order to give a more standardised measurement. The applied pressure is limited and the moistened filter paper is fastened to a smooth solid block and therefore the LLW sampler collects less than the HUD from an uneven surface [9-10, 15, 24].

- Pre-weighed wipe methods: The cotton gauze or the filter papers are weighed prior to and after the wiping. The filters may be accompanied by unused filter papers since daily humidity differences can affect the filter weights. There are nevertheless losses of sampling media during the sampling and laboratory handling process. Some researchers have used self-adhesive labels that were pressed on the surface of interest [13].

- Dislodgeable dust methods: This method collects the dust that the child most likely comes in contact with. Either the bare-hand-press method or the roller method does the collectionning. In the bare-hand-press method the sampling technician presses a hand on a specified area with a certain pre-determined pressure. In the roller method the wipe sampling material is wrapped on a roller and the roller is then passed over a carpet with a certain pressure [13].

- Dust fall methods: The lead suspended in air is sampled in plates that are placed in out-of-the-way places for periods of about one month. From these plates the dust fall- and lead fall rates can be estimated. This makes it possible to establish the lead deposition on toys and food surfaces and the lead inhalation exposure as well [13].

Studies have been made to compare the different wipe materials and it was found that on smooth surfaces a recovery of 80-95% was obtained. On plywood, on the other hand, the recoveries dropped to less than 43% and the adhesives performed better than the wipes [9, 13].

2.4.1.2. Vacuum methods

There are several vacuum methods that are more or less the same, but the one that has been used the most is the dust vacuum method, the DVM method. This sampler was designed to collect particles of sizes less than 250 µm [6, 10, 13, 22]. Even ordinary vacuum-cleaners have been used.

One of the problems encountered is that not all of the dust can be recovered from the bag and therefore much of the fine dust is lost [25]. Another problem is that the dust in the vacuum-bags is a dust that differs from real dust. In a vacuum cleaner an artificial dust is created since the small particles stick to fibres and larger dust-particles due to oils (existing in the air) and electrostatic forces generated during the vacuum-process [13]. But at the same time rugs and carpets can function as reservoirs of house dust lead and by repeated vacuuming a lot of leaded dust can be collected. The amount obtained by wiping is less [9].

2.4.2. Digestion

The measurements of lead in a sample require its liberation from the organic matter [26]. That is, the sample needs to be digested. The digestion can be carried out using either a dry or a wet method. In the dry method the organic matter is calcinated at about 500 °C. Samples containing lots of organic matter can end up with great losses by volatilisation of the lead. The wet method, using different acids, is much more common. Some research is based on measurements of total lead and others on leached lead. The leached lead has more resemblance to lead absorbed in the body by ingestion and is called bioavailable lead. Thus, lead can be digested in many different ways depending on what is asked for.

2.4.2.1. Acid mineralisation

The aim of the acid digestion is to liberate the lead from the solid matrix of silica and put it in solution. The sample is digested on a hot plate or in a microwave oven. Different acids such as, hydrochloric acid (HCl), nitric acid (HNO_3), hydrofluoric acid (HF), perchloric acid ($HClO_4$) and sulphuric acid (H_2SO_4) can be used either alone or in different combinations. In some cases hydrogen peroxide is used [6, 15, 20, 25]. In the use of sulphuric acid evaporation of the acid is recommended because the diluted acid causes polyatomic ion interferences and degradation of the nickel sampler cones in the ICP-MS. Samples rich in sulphur may lead to interferences in digestion procedures where sulphuric acid is not used [27].

2.4.2.2. Acid leaching

The dust samples are soaked in dilute acid, usually hydrochloric acid (HCl), at room temperature for a specific time. This procedure liberates less lead than does the acid mineralisation and it gives the bioavailable lead. The bioavailable lead is the lead that is most likely absorbed in the stomach. There is, though, no common agreement yet on how to measure the lead that is ingested and then absorbed by the body. The absorption of lead is complex and not completely understood since several factors such as the lead particle-size, the chemical form of lead, the person's diet and the age of the exposed person play important roles [13].

Acid mineralisation procedures give total lead recoveries near 100% while leaching is less consistent [13].

2.5. Instrumental analysis

The analysis of the samples can be carried out by the use of several different instrumental methods e.g. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), the Graphite Furnace Atomic Absorption Spectrophotometry (FAAS) and the Energy Dispersive X-ray Fluorescence (XRF). Thermal Ionisation Mass Spectrometry (TIMS) and the Inductively Coupled Plasma Mass Spectrometer (ICP-MS) which are the only methods that give the isotopic ratios [28].

2.5.1. ICP-MS

The ICP-MS is a powerful apparatus which allows the detection of trace and ultra trace elements. It has a plasma, consisting of ions, electrons and neutral particles that atomises and ionises the elements in a sample at an elevated temperature of about 6700 °C [29].

A radio frequency (RF) signal is fed into a tightly wound and water-cooled coil where it generates an intense magnetic field. In the middle of the coil a glass or a quartz torch that creates the plasma is found. The plasma is formed in the argon gas by a spark from 1 Tesla unit that ionises some of the argon atoms. The liberated cations and electrons are accelerated towards the magnetic field. Inelastic collisions between the charged particles (cations and electrons) and neutral argon atoms give rise to a stable plasma with high temperature. Equilibrium of the concentrations of the electrons, cations and argon atoms is reached shortly after and is maintained as long as the magnetic field exists and the supply of argon gas is constant [29].

The design of the torch is such that it allows the sample to be injected directly into the centre of the plasma. The sample, in the form of a fine aerosol, collides with the free electrons, the argon cations and the neutral argon atoms in the plasma and the molecules in the sample are

rapidly broken down into charged atoms of M^+ and a couple of M^{2+}. Some of these will recombine to create stable and metastable components e.g. MAr^+, MO^+.
A set of special metal cones (nickel for example) and ion-focusing elements extract the charged atoms from the plasma which works at atmospheric pressure into the mass analyser that operates at a much lower pressure of $1*10^{-7}$ mbar. Behind the cone is a space called the expansion chamber where the pressure is 1-1.5 mbar. When the jet of gases passes, the speed of sound is exceeded and a conical chock wave is created. This is ended at a mach disk as the gases slow down. Another cone, named the skimmer cone, terminates the expansion chamber. The mass spectrometer that is situated behind the skimmer cone is held at a pressure of less than $2*10^{-7}$ mbar. When the ions have passed the skimmer cone they are at first accelerated by a high voltage potential gradient and then they pass through a series of focus lenses directly into the mass analyser [29].

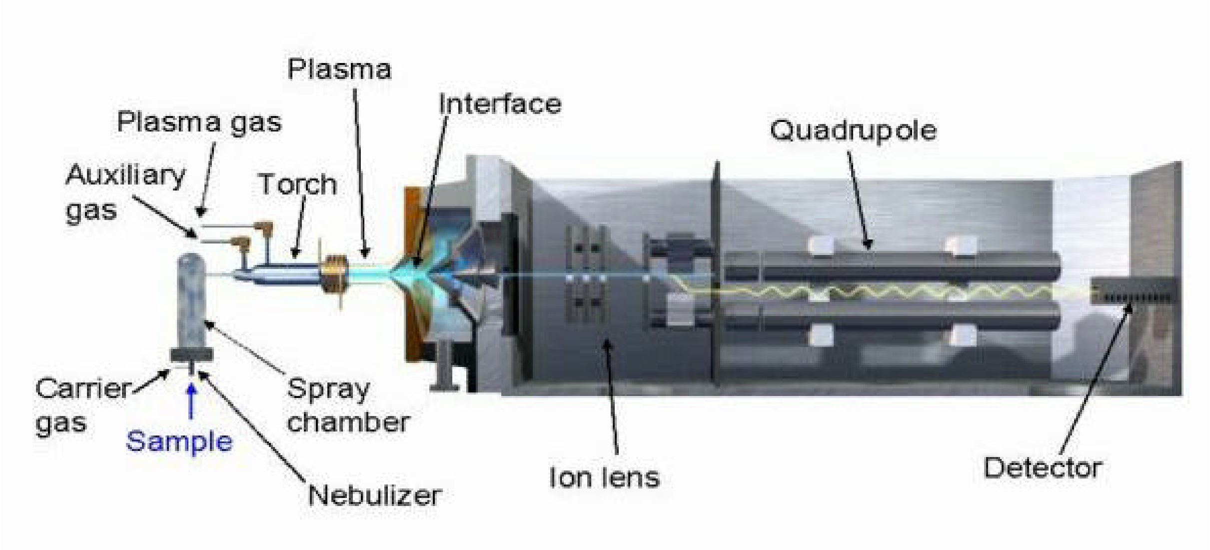

Fig. 2 The ICP-MS block diagram [30]

The quadrupole mass analyser is made up of four cylindrical rods which are subjected to both RF (Radio Frequency) and DC (Direct Current) electric fields. The ions start to oscillate in both the X and Y planes when they enter the quadrupole and depending on whether it is the alternating component (RF) or the direct component (DC) in the electric field that is exceeding the ions will have different destinations. Ions with low mass number (m/e) are thrown out and don’t reach the detector when the RF component is exceeding the DC. This makes it possible to have an effective low mass filter. The reverse is true when the DC exceeds the RF and the ions with high m/e become unstable creating an effective high mass filter.
In the quadrupole a combination of the two is produced with the X plane acting as a low mass filter and the Y plane as the high mass filter. A careful matching of the fields makes it possible to let only ions of a particular mass pass through. The quadrupole mass analyser is very fast and efficient [29].

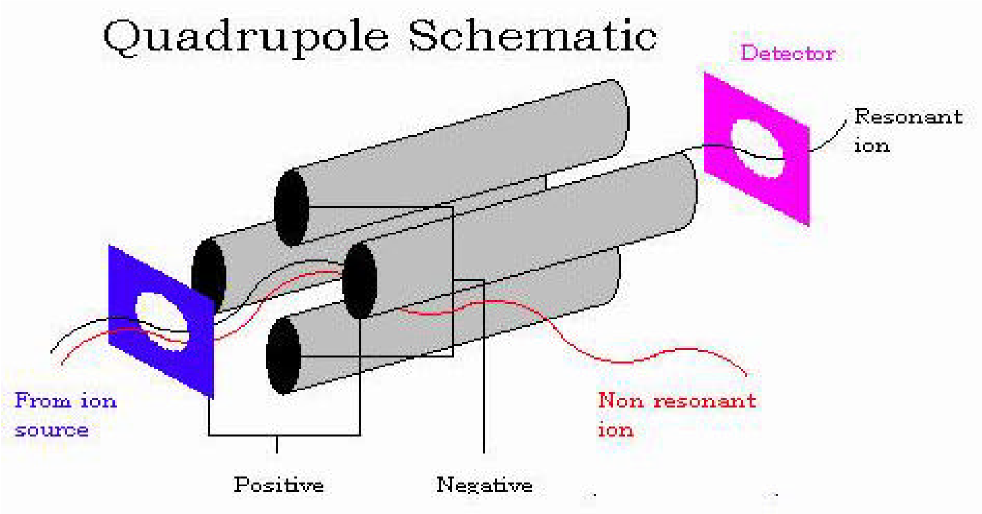

Fig. 3 The quadrupole mass analyser [29]

The quadrupole ICP-MS can work at an effective mass resolution of 3-400 which means that ions with masses M and M+1 can be resolved if M is less than 300. This results in a peak of less than 1 mass unit. Thus, the quadrupole mass analyser can differentiate between the isotopes of a single element or between one element and another of a differing mass. Since there aren’t any magnetic fields in the quadrupole ICP-MS it can go from mass to mass with great precision resulting in “peak hopping”, where only a single point of data is acquired at the top of the peak of each element [29].

The elimination of Ar-based molecular interferences can be done in two ways. The first and more ancient method is the use of cold or cool plasma which is achieved by lowering the RF power. This reduces the amount of Ar^+ ions in the plasma. In newer models of the ICP-MS, on the other hand, an octopole reaction system containing simple gases like hydrogen and helium are found. These gases prevent interferences since they don’t react and create new cluster ions. This passive cell only requires selection of gas type and flow rate and this needn’t be based on a pre-analyte basis. In the cell, where hydrogen is used, polyatomic ions of the same mass and the same kinetic energy as monatomic analyte ions suffer much more collision due to larger cross section. The interfering ions are thereby rejected whereas the analyte ions enter the quadropole. For elements having several polyatomic species contributing to the background helium is preferred. The octopole reaction system even solves the problem of high background noise caused by high-energy photons in the detector by eliminating them together with the polyatomic molecules [17, 29].

The response of the mass spectrometer is in counts per seconds and directly proportional to the concentration of the element in the sample. The system is therefore easily calibrated by the use of external standards at different concentrations. A sample that enters the mass spectrometer under the same conditions as the standards will result in a count rate fitted to the calibration graph and give the concentration of each and every element in the sample.
It is important to ensure identical conditions for each sample. Factors that may change the conditions are

- variations in plasma ionisation efficiency
- clogging or erosion of cone apertures
- different matrix or matrix concentrations in the samples leading to matrix suppression

- changes in laboratory temperature or humidity resulting in recombination of elements into molecules
- molecules that can be formed by the elements in the sample can interfere with other elements.

These problems are all corrected for by external calibration, internal standards, and spiked samples. In the external calibration a series, containing all of the elements that will be analysed for, is prepared. The different concentrations are supposed to cover the range of the concentration of the analyte in the sample. If the sample falls outside the range it is diluted and run again so that it falls within.
Internal standards, consisting of elements that are known to be missing in the sample, are added to all samples and standards. The concentration is known so that any variation in the signal's intensity can be corrected to the known concentration. The same correction is applied to the other elements and in this way the correct concentration can be calculated.
Spiked samples mean that a duplicate of a sample is prepared containing a known spike of every standardised element. This is used for difficult matrixes and can give the recovery efficiency of each element so that discrepancies can be discovered and investigated. An example of this is the interference of ^{204}Hg with ^{204}Pb resulting in a higher concentration than it should be. Switching to higher resolution can tell whether or not it is an interference [29, 31].

3. Material and Methods

The different digestion methods were carried out on nine different vacuum bags from homes in Rennes and its surroundings. Standard dust samples (SRM 2583 and SRM 2584, bought from Techlab, France) with certified lead contents of 85.9 ± 7.2 µg/g and 9761 ± 67 µg/g respectively were analysed in order to determine the efficiency of the digestions. The dust is collected from households, cleaning services, motels and hostels in North Carolina, Maryland, Ohio, Wisconsin, Montana and New Jersey in USA.

3.1. Characterisation of the dust

The contents of the vacuum bags were sorted out and the larger debris were thrown away. The dust was then sieved with two plastic sieves, one of 2 mm and the other of 250 µm [See Appendix A]. The aim was to get a dust consisting of particles of a size that is known to stick readily to hands. Homogenisation of the dust by use of an agate mortar was abandoned when it turned out that the dust was too volatile. The samples therefore have to be considered as unhomogen. To avoid contamination, all of the pre-treatment and treatment of the dust had to be carried out in materials that don't emit Pb. In this case plastics were used.

In order to characterise the dust, the humidity of the samples was determined. This was done by heating of the pre-weighed samples in an oven (Firelabo) at 105 °C for a couple of hours. The sample weight was registered (Sartorius MCI) until it was constant. The amount of organic and inorganic matter was also determined by heating in an oven (Nabertherm N11) at 550 °C overnight.

3.2. Digestion

As mentioned before, the lead has to be liberated from its matrix in the dust and this can be done in many ways. Several protocols were carried out in order to find the ultimate procedure that can function readily at the LERES (Laboratoire d'Étude et du Recherche en Environnement et Santé) laboratory.

3.2.1. Acid mineralisation

The acid mineralisation is much more powerful than the acid leaching and therefore it liberates a larger amount of lead.

3.2.1.1. The LERES protocol

The objective of this protocol, which is used for digestion of soil, sludge and sediments, is mineralisation by use of a blend of hydrochloric acid (36%) and nitric acid (69%) of a specific ratio. The solution contains 2/3 hydrochloric acid and 1/3 nitric acid and is called nitrohydrochloric acid [For further information about the procedure see Appendix B]. Some distilled water (Millipore 18.2MΩ) was used to slow down the vigorous reaction that occurs between the dust and the acid when the acid is added. During the digestion large quantities of vapour and gas are generated [32].

According to the protocol the mineralisation is carried out in a micro-wave (Milestone MLS 12000 Mega, Rotor HPR 300/10) where the samples are subjected to micro-waves, but there are other means as well. In the Digiprep MS (SCP Science) digestion system the samples are digested by heating with a graphite heating block. [33].

The efficiency of the nitrohydrochloric acid compared to that of only nitric acid was studied.

3.2.2. Acid leaching

The acid leaching shows the bioavailability of an element and can be considered to mimic the actual uptake in the body.

3.2.2.1. The acid soluble protocol

To make the leaching as realistic as possible the hydrochloric acid (36%) has a pH that slightly resembles to that in the stomach. Furthermore, the agitation is carried out in a bath of 37 °C, just as it is in the body, using a heating plate (Brewer) [See Appendix C].

3.2.2.2. The INRA protocol

This protocol, which is carried out on non-treated dust samples shows the bioavailability in plants [See Appendix D]. It is actually the movements of metals in soil that are studied. The solutions attack the sample in different ways:

1. Distilled water
   This extraction frees the lead that is weakly bonded and gives an image of what is easily absorbed by the plants. The amount released is very low.

2. $Ca(NO_3)_2$
   The neutral salt of $Ca(NO_3)_2 \cdot 4H_2O$ makes an exchange of cations with other more soluble elements, in this case lead.

3. EDTA-ammonia, pH 7
   The EDTA-solution is made from a potassium magnesium salt, $C_{10}H_{12}K_2MgN_2O_8$ which is dissolved in ammonia (25%). The EDTA-solution extracts the exchangeable metals in the soil and dust. A complex is formed with the organic matter, the iron-oxides and the carbons.

4. Acetic acid
   The acids solubilise soluble elements, carbons, sulphuric elements, hydroxides, and oxides. Elements that belong to the alumino-silicate are either slightly or not soluble at all.

3.3. Analysis

The samples were analysed with an Atomic Absorption Spectrophotometer (Varian, SpetrA A-640Z) in order to give an idea of the size of the lead contents in the samples before the analysis in the ICP-MS.

3.3.1. ICP-MS

The ICP-MS in the laboratory is an Agilent 7500c octopole reaction system ICP-MS. The octopole reaction system, also called the collision cell, minimises the interferences and therefore there is no need for a cold plasma. Before the analysis of the samples an optimisation of the lead analysis in the ICP-MS had to be carried out. This was done with the lead in hydrochloric acid without any collision gas (the standard mode) in the octopole reaction system. It made it possible to determine which elements that can be analysed for in the presence of Cl^- ions [See Appendix E for the adjustments of the instrument]. In this case we were mainly interested in Pb but Cd, As, Ni, Zn, Cu, Mn and Fe could also be analysed for. Each and every element is analysed in a mode that minimises the interferences with Cl^-. See Table 1.

Element	*Mode (1 = H_2, 2 = He, 3 = standard)*
Pb	3
Cd	3
As	2
Ni	2
Zn	2
Cu	2
Mn	2
Fe	1

Table 1. Operation mode in the ICP-MS

In order to ascertain the same operation conditions both an external calibration series and an internal standard were used. The calibration series was made in different acids depending on what had been used as digestion acid in the mineralisation of the samples. Some of the samples had to be diluted since they fell out of the range of the calibration series which was between 1 and 50 µg/l. The limit of detection is 1.5 µg/g and the limit of quantification 5 µg/g. Since the ICP-MS is sensitive to acid concentrations exceeding 5% all of the samples and standard solutions had to be made at an acidity of 0.5%. If not it would have lead to incrusts on the cones and thereby less sensibility in the detection of the elements.

4. Results and Discussion

Lead intoxication is a serious problem, in particular for small children. Usually the knowledge of the exposure is held by blood sampling, but analysis of the housedust may be an easier way.

4.1. Characterisation of the dust

The samples were dried in an oven at 105 °C in order to determine the humidity. The mineral and organic content was obtained by burning of the samples in an oven at 550 °C.

Samples	*Humidity (%)*	*Mineral content (%)*	*Organic content (%)*
A	4	54	42
B	4	59	37
C	3	55	42
D	4	56	40
E	3	64	33
F	3	69	28
G	6	24	70
H	2	57	42
I	2	65	33
SRM 2583	5	61	34
SRM 2584	4	56	40

Table 2. Characterisation of the dust.

The samples had very low humidity but their content of minerals and organic material differed for one sample only. Sample G has an extremely low mineral content compared to the others.

4.2. Acid digestion

The samples that were analysed came from bags of vacuum cleaners, simply because we needed large amounts of dust to analyse in the search for the optimal acid and the optimal mineralisation method. This dust doesn't really give the right image of a household dust and in the request of accurate lead contamination it is preferable to choose a wipe-method or a specialised vacuum cleaner, like the ones mentioned in section 2.4.1.2. The standard dust samples (SRM 2583 and SRM 2584) with known lead contents according to certificates, were very important in the optimisation. They were first analysed with AAS and then with the ICP-MS. Even though the two instruments function differently they gave the same results.

4.2.1. Acid mineralisation

The mineralisation gives the total lead in the dust.

4.2.1.1. The choice of acid for mineralisation

Different acids used for mineralisation of dust samples are described in literature [6, 15, 20, 25]. Some acids are very strong and have to be used cautiously. Our goal was to find an acid that is not only efficient but also easy to use. In the laboratory of the ENSP, a mineralisation protocol with nitrohydrochloric acid (1/3 nitric acid and 2/3 hydrochloric acid) is already in use. The ultimate choice would be nitric acid alone, simply because it would facilitate the work in the laboratory if dust analysis becomes routine. We digested the standard samples SRM 2583 and SRM 2584 with nitrohydrochloric acid and nitric acid, respectively in order to determine which acid is the most efficient. Both the micro-wave and the Digiprep were used.

Samples	*Lead content according to certificate (µg/g)*	*Lead content determined after mineralisation (µg/g)*	*RSD (%)*	*Amount of obtained lead in percentage of available lead (%)*
SRM 2583	85.9	75	1.1 (n=6)	87
SRM 2584	9761	8780	5.4 (n=5)	90

Table 3. Mineralisation with nitrohydrochloric acid according to the guidelines of the LERES protocol. Number of trials = n.

Samples	*Lead content according to certificate (µg/g)*	*Lead content determined after mineralisation (µg/g)*	*RSD (%)*	*Amount of obtained lead in percentage of available lead (%)*
SRM 2583	85.9	83	7.5 (n=6)	97
SRM 2584	9761	9170	0.02 (n=6)	94

Table 4. Mineralisation with nitric acid according to the guidelines of the LERES protocol. Number of trials = n.

In Tables 3 and 4 it is shown that the recovery was higher when nitric acid was used than when nitrohydrochloric acid was used and indicates that nitric acid is more efficient for mineralisation of these samples.

4.2.1.2. The choice of mineralisation method

The second thing to do, was to choose the mineralisation method. In the laboratory, two options are available, in form of a microwave and the Digiprep. The microwave is used on a regular basis since it is efficient and powerful. The Digiprep is newer, allows multiple mineralisation and is designed to be used with the ICP-MS. Tests were carried out on samples digested with nitric using both methods to compare their performances. The origin of the samples (A-I) is described in 4.2.1.3.

Samples	*Microwave (µg/g)*	*RSD (%) (n=3)*	*Digiprep (µg/g)*	*RSD (%) (n=3)*
A	7780	8.1	5440	11.8
B	19.4	14.0	19.6	9.5
C	25.2	10.2	21.1	6.4
D	613	8.6	565	8.0
E	48.4	10.6	39.9	6.0
F	459	5.2	477	11.9
G	72.8	16.8	83.2	4.2
H	64.6	11.6	59.1	27.4
I	82.6	17.4	59.5	16.1
SRM 2583	75.6	5.1	74.5	6.8
SRM 2584	9110	-	8440	5.7

Table 5. Mineralisation of the samples using the microwave and the Digiprep method.

The comparison doesn't show that there is a systematic difference between the two methods. See Table 5. The Digiprep will be chosen, though, because it is very straightforward and useful. The amounts of lead in the samples are almost the same with fairly low relative standard deviations except for sample H. This can be an indicator of the inhomogenity of this sample.

4.2.1.2.1. Optimisation of the mineralisation in the Digiprep
As mentioned earlier, the Digiprep allows multiple mineralisation which is ideal in a laboratory. The method is slow though, using a graphite block. The rise in temperature is carried out in two steps. In the first step the temperature climbs to 60 °C during 30 minutes and it is kept there for another 30 minutes. The second temperature at 95 °C is reached within 20 minutes and kept for 90 minutes. It is very important that the mineralisation tubes (made of polyethylene) containing the dust and the acids, don't go dry. This means that the volume of the acid is crucial and the sensor detecting the temperature in the blank must be covered during the heating process, otherwise the graphite block might heat too much and the tubes go dry. If the tubes go dry they might melt and the samples are lost [See Appendix F].

4.2.1.3. Our samples

The nine samples studied (A-I) came from different houses in the centre of Rennes and from houses located in the countryside north of Rennes [See Appendix G]. One house is very old, dating from the 18th century, and others like the Bio-house that is constructed of bio-material only, are much more recent.

Samples	*Proximity and direction from the city of Rennes*	*Proximity to roads (km)*	*Year of house construction*
A	City of Rennes	0.4-0.5	1930
B	15 km north of Rennes	2	1999 (A Bio-house)
C	40 km north of Rennes	No roads	1869
D	City of Rennes	0.1	1930
E	30 km north of Rennes	4	1950
F	City of Rennes	0.2	~1930
G	City of Rennes	0.001	1900
H	16 km north of Rennes	30	1992
I	22 km north-west of Rennes	0.05	~1700

Table 6. Origin of the dust samples.

Some houses contain more lead than other and in general the houses situated in the centre of Rennes have the highest concentrations. See Table 7.

Samples	*Lead content obtained by mineralisation (µg/g)*	*RSD % (n=6)*
A	6790	14.0
B	24.5	20.0
C	33.9	4.6
D	515	12.8
E	51.7	25.2
F	478	9.9
G	65.4	3.7
H	61.0	4.1
I	62	9.2

Table 7. Lead content after mineralisation of samples A-I using the Digiprep method.

Samples A, D and F are from a house and apartments that date from the 1930's and are situated close to main roads. This means that, even though the ban of leaded gasoline was introduced in the year 2000 here in France and a decrease in the lead concentration in soil has been noted, the soil still contain a lot of lead. Besides, some old cars need the lead to function and therefore the owners add it to the gasoline themselves. All three homes have been renovated recently but there is perhaps still some leaded paint on the walls e.g. behind the radiators. Sample A that lies in the south-east part of Rennes could be affected by the ancient lead mine in Pont-Péan. This mine was shut down in 1903 and the soil around it was treated in the 1980's, nevertheless the soil contains large amounts of lead [34]. Other sources can be car tyres, car batteries and plumbing. Sample G, with its low lead content is an exception, since it is also situated in the centre of Rennes. This lead might originate from traffic.
Samples B and E show high relative standard deviations, but the corresponding concentrations are close to the detection limit of the ICP-MS. The detection limit for sample B, for example, is approximately 15 (µg/g), while the quantification limit is close to 50 (µg/g). The closer the actual limit is to the detection limit the higher the RSD, meaning that the sample falls out of the standard calibration graph. Sample B from the Bio-house and sample C from the house at the countryside far from any roads exhibit the lowest concentrations. Further on, those samples, along with samples H and I, come from houses situated on siltstone, which is known to contain very little lead. In sample E the lead content is fairly low and it can probably be attributed to traffic or to the fact that the ancient wolfram mine of Montbelleux lies there. Lead might have been released together with the minerals and metals.

4.2.2. Acid leaching

The bioavailability obtained by leaching is a very important indicator in the risk assessment.

4.2.2.1. The acid soluble protocol

The acid soluble protocol gives an idea of just how much of the total lead in dust that is actually bioavailable. The lead can be in many different shapes and forms that are more or less bioavailable. The determination of the bioavailability is a very useful tool in the risk assessment.

The total lead that is achieved from the mineralisation of sample A, SRM 2583 and SRM 2584 compared to the bioavailable lead expressed in percent is showed in Table 8. In the literature the amount of bioavailable lead in soil/dust is determined to on average 30% [35]. Compared to our samples this is very high. According to the test-results sample A contains a lot of lead of which only a very small amount is bioavailable. The same can be said for standard sample SRM 2583 and SRM 2584. In the standard sample SRM 2583, on the other hand, 7.4% is bioavailable. This indicates that a house can contain a lot of lead in varying forms but it is not certain that it constitutes a great danger to a child's health. Another important thing, is that each and every person has a different digestion meaning that some persons are more susceptible than others. So these tests give an average that is less specific.

Samples	*Total lead after mineralisation (µg/g)*	*Bioavailable lead after leaching (µg/g)*	*Amount of bioavailable lead in percentage of the total lead (%)*
A	6790	5	0.07
SRM 2583	83	6	7.2
SRM 2584	8860	45	0.5

Table 8. The bioavailable lead expressed as percentage of the total lead.

4.2.2.2. The INRA protocol

The INRA protocol describes a leaching method as well, but it is the leaching that occurs in plants and is quite different from the leaching in the human body.

Sample	*Total lead after mineralisation (µg/g)*	*Bioavailable lead after leaching (µg/g)*	*Amount of bioavailable lead in percentage of the total lead (%)*
A	6790	1120	16.5

Table 9. Lead concentrations in samples using the INRA protocol.

The results show that there is difference between the bioavailability in the body and the bioavailability in a plant. This depends not only of the different chemical processes in the body and the plant, but also the temperature, different minerals in the soil etc. According to our results it can be concluded that the plants absorb much more than does the body.

4.3. Isotopic ratios

According to the literature, scientist prefer to use $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{207}Pb$ as isotopic ratios since they have a better analytical precision than the others. Nevertheless some important information may be lost if $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ aren't used [14]. The ^{204}Pb is in minority with only 1.4% in the environment and there are often interferences with ^{204}Hg that can reduce the accuracy.

The dust samples were compared to isotopic ratios obtained from the literature on lead from different sources in France.

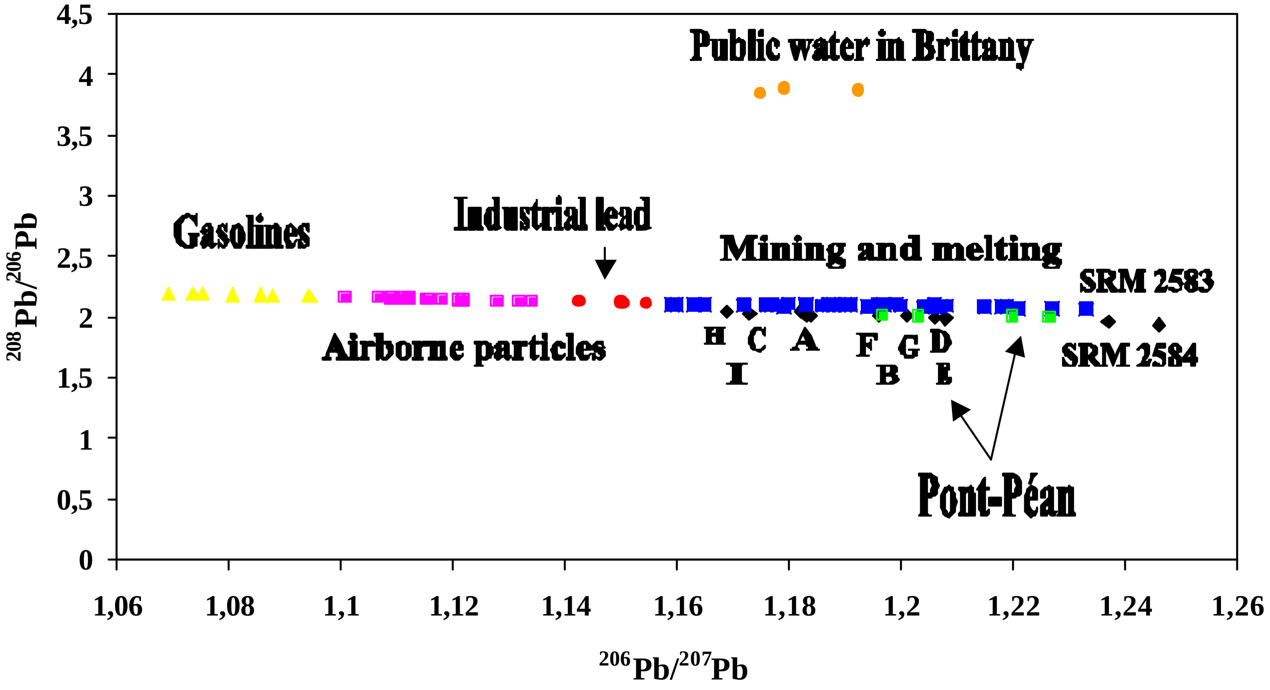

Fig. 4 $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{207}Pb$ in dust samples A-I together with SRM 2583 and SRM 2584 compared to ratios obtained from public water samples in Brittany, soil samples from Pont-Péan and the literature on mining, smelting, gasoline and industries [18, 36] .

As can be seen in Fig. 4, our dust samples are situated far from the public water samples in Brittany indicating that the lead in the dust isn't the same as the lead in the plumbing. With the leaded gasoline being banned in France, there doesn't really seem to be much left in the environment. The leaded gasoline might therefore be considered as no longer being a big threat to the environment in France. The households that were investigated are all of them situated in areas remote from lead industries and industrial lead can be excluded as a source. The airborne particles are also from regions that are far away and it seems more likely that the lead in our samples originates from the mine of Pont-Péan that is situated in the south of Rennes. The standard reference samples, SRM 2583 and SRM 2584, are farther away from the other samples which is understandable considering their origin in the USA.

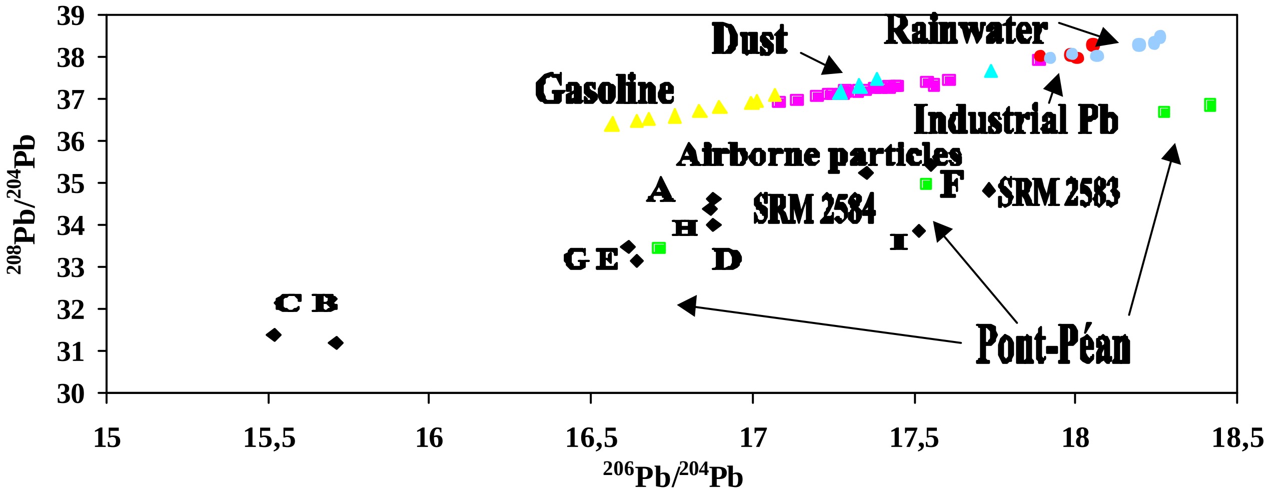

Fig. 5 ^{208}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb compared to ratios from gasoline, industries, water treatment, rainwater and dust [14, 18].

The ^{208}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb gives a result that differs from the one given in ^{208}Pb/^{206}Pb vs. ^{206}Pb/^{207}Pb. The samples are coupled together in pairs, which is logic for samples A and D since they came from areas that are close. But the others are mixed without any consideration to the geographic location. This means that the lead found in each home has an origin that isn't contributed to the location. Once again it can be concluded that some of the lead in our samples comes from Pont-Péan, but not all of it. In order to draw proper conclusions of these samples origin, we need more information about the surrounding areas.

5. Conclusions and Recommendations

The aim of this study was to create a protocol [See appendix F] for the analysis of lead in house dust using inductively coupled plasma – mass spectrometry (ICP-MS) for the analytical determinations. The reason for this is the possibility of making a risk assessment on site, in this case in the homes of small children.

One way to determine the lead content in a house is to take blood samples of the children. Usually knowledge of the exposure is obtained from the analysis of blood, but analysis of housedust combined with other information such as dust intake rate and intake from other media (food, water, air) are easier ways. If both the total amount of lead and the bioavailable lead are estimated, then the exposure of the child is determined indirectly. This can indicate whether or not a dust is dangerous to the child's health.

Tests showed that mineralisation with nitric acid gives better or just as good recoveries as when nitrohydrochloric acid (1/3 nitric acid and 2/3 hydrochloric acid) is used. In the choice between the micro-wave and the Digiprep, as a digestion system, the Digiprep method has more advantages. The Digiprep is straightforward, allows multiple mineralisation and is designed to be used with the ICP-MS.

Homes in the centre of Rennes exhibit the highest lead content, while the Bio-house and the houses in the countryside exhibit the least. The majority of the old houses, where leaded paint could be found, are renovated. Nevertheless, there can be old paint underneath the new coat that might emit lead. Behind or beneath radiators, some old paint may be left and that can fall into the dust. Another source is the ancient lead mine in Pont-Péan that might still contribute with lead emissions to the environment. In the north of Rennes there is an old wolfram-mine that was shut down in the 1960's and the soil in its surroundings might be interesting to analyse. This would give a source that our samples can be compared to.

Our results from the leaching-tests, which were very different from the amounts in the literature, made it obvious that the amount of bioavailable lead is very small compared to the total amount of lead. It seems as if only a minor part of the lead is bioavailable, which can be explained in terms of chemical compounds. The lead can, thus, be more or less tightly bound or integrated in a chemical compound. This means that a dust rich in lead is not necessarily rich in bioavailable lead. If both the total lead and the bioavailable lead is estimated there is perhaps no need to subject the child to blood samples.

The isotopic ratios are a good tool if enough data is available. In our case, we need much more information about the surrounding areas. Nevertheless the information that we have can give us a hint of what might contribute to our lead content. It seems as if the lead mine in Pont-Péan emits a great deal even if it was shut down in the beginning of the 20th century.

These tests should be conducted again but without the use of bags from ordinary vacuum cleaners because of their tendency to give an artificial dust. A wipe-method or a specialised vacuum might give another result.
Another thing that can be interesting to know is whether or not dust contain other elements like cadmium, arsenic etc. This can be done easily using the ICP-MS.

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Appendix A

Pre-treatment of the dust

1. Sort out the dust in the bag. Remove small objects such as toys, pins, small sticks etc.
2. Sieve the sample to a size less than 250 µm.
3. Homogenise with a mortar.
4. Dry the sample in an oven at 105 °C until the weight of the sample is constant.

Appendix B

LERES Protocol - Mineralisation in a micro-wave

Nitric and hydrochloric acid – nitrohydrochloric acid

1. Weigh ~ 1 g of the dust in a Teflon-beaker.
2. Dissolve with some de-ionised water.
3. Add 5 ml HCl-36% and 2.5 ml HNO_3-69% in a 25 ml vial.
4. Add de-ionised water to the mark.
5. Place the samples in the carousel and start the microwave. Milestone MLS 12000 Mega. Rotor HPR 300/10.
6. Put the carousel in the microwave.
7. When the mineralisation is over, filter the samples [37].

Nitric acid

1. Weigh ~ 1 g of the dust in a Teflon-beaker.
2. Dissolve with some de-ionised water.
3. Add 7.5 ml HNO_3-69% in a 25 ml vial.
4. Add de-ionised water to the mark.
5. Place the samples in the carousel and start the microwave. Milestone MLS 12000 Mega. Rotor HPR 300/10.
6. Put the carousel in the microwave.
7. When the mineralisation is over, filter the samples.

Appendix C

The Acid soluble protocol

1. Weigh 100-200 mg sieved dust
2. Add 25 ml 0.07 mol/l HCl, pH 1
3. Agitate the solution in a water-bath of 37 °C for one hour.
4. Filtrate the sample [38].

Appendix D

The INRA protocol

The INRA protocol examines the mobility of the lead in plants in order to establish the bioavailability. The sample is subjected to four different manipulations.

Distilled water

1. Weigh 10 g sieved dust in a plastic bottle.
2. Add 50 ml distilled water and agitate the solution for two hours in room temperature.
3. Filtrate the solution and add 1 ml of HNO_3 (14 N).
4. Store the solution at 4 °C prior to analysis [39].

$Ca(NO_3)_2$ in different concentrations

1. The same dust-sample as in the preceding step is put in a 50 ml solution of calcium nitrate of two different concentrations 0.1 N and 0.05 N.
2. The solution is agitated for two hours at 20 °C.
3. Filtrate the sample and add 1 ml of HNO_3 (14 N).
4. Store the solution at 4 °C prior to analysis [39].

EDTA-NH_4, pH 7

1. 5 g of the same dust-sample as in the preceding step is put in a 50 ml solution of EDTA.
2. Agitate for one hour.
3. Filtrate the solution and store at 4 °C [39].

Acetic acid

1. 5 g of the same dust-sample as in the preceding step is mixed with 200 ml of 0.43 mol/l acetic acid.
2. The sample is agitated for 16 hours at 20 °C.
3. Filtrate the solution and store at 4 °C [39].

Appendix E

Tuning parameters

Plasma conditions

Plasma gas (Argon): 15 l/min
RF Power: 1500 W
RF matching: 1.64 V
Sample depth: 7 mm
Torch-H: -0.4 mm
Torch-V: -0.2 mm

Carrier gas: 0.75 l/min
Make-up gas: 0.3 l/min } Nebulasator Micro-flow
Optional gas: -
Peripump 1: 0.1 rps (0.4 ml/min)
Peripump 2: -
S/C Temp: 2 °C

Ions lenses

Extract: 3.6 V
Einzel 1, 3: -115 V
Einzel 2: 20 V
Cell entrance: -33 V
Cell exit: -20 V
Plate bias: -50 V

Octopole parameters

OctP RF: 190 V
OctP bias: -7 V

Q-pole parameters

AMU gain: 128
AMU offset: 125
Axis gain: 1.0004
Axis offset: -0.14
QP bias: -3 V

Detector parameters

Discriminator: 8 mV
Analog HV: 1670 V
Pulse HV: 1200 V

Reaction cell

Reaction mode: Off
H_2 gas: 0 ml/min
He gas: -
Optional gas: -

The parameters in *italics* are fixed and they are changed only in case of problems in the adjustment of the instrument. The others are changed during the optimisation.

Appendix F

Mineralisation of dust in the Digiprep using nitric acid

Mineralisation

1. Weigh ~ 0.1 g of the dust in the tubes.

2. Dissolve with 1 ml de-ionised water.

3. Add 7.5 ml HNO_3-69% to the sample. Shake!

4. Place the samples in the Digiprep and start the programme.

    30 minutes to reach 60 °C
    Keep it at 60 °C for 30 minutes

    20 minutes to reach 95 °C
    Keep it at 95 °C at 90 minutes

5. Let the tubes cool down to room-temperature.

Filtration

1. Wash the filter:
    1. Moisten the filter with de-ionised water.
    2. Wash the filter with 7.5 ml HNO_3 in a vial of 50 ml. Adjust with de-ionised water.
    3. Rinse the filter with 50 ml de-ionised water.

2. Filter the samples directly in the plastic vials of 100 ml. Adjust to the limit with de-ionised water.

3. Before analysis in the ICP-MS the sample needs a dilution of 1/2.

Appendix G

Ille et Vilaine, Bretagne, France. Scale (1:2330)