

Article

Challenges in Using Handheld XRFs for In Situ Estimation of Lead Contamination in Buildings

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Abstract: Lead in buildings can be found in certain materials such as paints or can be a result of contamination during the use stage. In situ methods for lead identification can be vital for the proper treatment of hazardous CDW (from repair works or selective demolition). A conventional handheld XRF (HHXRF) spectrometer can be used for this purpose, and this study analysed its reliability. A laboratory experiment was conducted to test different calibrations, and to establish a procedure for the conversion of the HHXRF lead concentrations into lead loadings. Model latex paint with a constant lead content was used on two types of surfaces (plasterboard and concrete). A field study was performed to identify and quantify the lead in paint on masonry walls in a public building. ICP-MS analysis was performed in order to verify the lead content. The coefficients of proportionality in the proposed model depend on various parameters: the contamination type, the layer thickness, the substrate, and the built-in calibrations. Despite the limitations of the HHXRF and the discrepancy of the mean lead loadings from the HHXRF and ICP-MS analysis, the HHXRF can be useful for the identification of lead in paint layers up to 1 mm, with a low limit of detection of the order of 0.01 mg/cm² at worst.

Keywords: lead; contamination; paints; buildings; XRF; in situ measurements; identification; quantification; calibration



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1. Introduction

Lead is one of the heavy metals that can be toxic to humans and environment [1,2]. Lead in buildings might be present in lead-containing materials, such as paints, or as result of contamination during the use stage of industrial buildings [3]. One of the primary sources of lead exposure is activity during the renovation or demolition of buildings, when lead-containing/lead-contaminated materials are scattered and can be swallowed by breathing or oral ingestion or can be released to the air and soil outside the buildings.

Ever since the toxicity of lead (Pb) was identified in the 1970s, it has been limited or prohibited in many countries for use in paints, liquid coatings and other household products. In Europe, the ban was introduced 20 years ago with the European Directive 2002/95/EC [1]. In Bulgaria, this directive was transposed by the Ordinance on hazardous chemical substances and products subject to prohibitions or restrictions on trade and use from 2003 [2]. Later on, the Directive 2002/95/EC was repealed by Directive 2011/65/EU, which restricts the maximum allowed concentration of lead in homogeneous materials to 0.1% by weight [4]. The Bulgarian building stock is quite old (Figure 1), such that the risk from lead-determined hazardous health effects would remain for an unspecified period.

Nowadays, many of the buildings constructed before the discovery of lead-related health risks and the prohibition of lead-containing paints are being renovated (mostly residential and public buildings, due to the energy efficiency requirement) or demolished (especially many industrial buildings), which either results in the release of lead dust or forms contaminated construction and demolition waste (CDW). In both cases, the identification of lead-containing materials prior to construction/deconstruction activities is crucial in order to preserve human health, and to ensure the proper treatment of such waste.

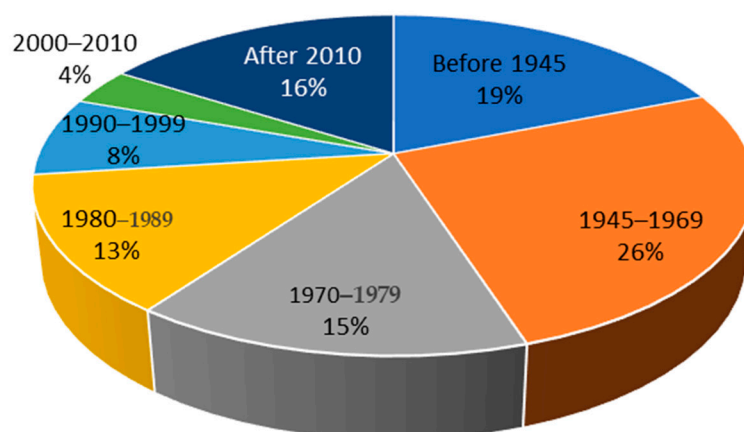


Figure 1. Distribution of Bulgarian building stock (residential and public service buildings) for each period of construction [5].

According to the principles of the Waste Framework Directive [6] and its subsequent amendment [7], the CDW should be treated in a sustainable way, ensuring the efficient use of resources. This means that lead-containing CDW should be collected, processed, transported and stored separately, such that it does not contaminate other waste materials that can be easily reused or recycled (e.g., bricks or concrete) [8].

In this study, the reliability of a handheld XRF (HHXRF) analyser/spectrometer for the identification and quantification of the lead contamination in buildings is discussed, such that it can be used as an assisting technique in pre-demolition audits, selective demolition, and waste management activities (e.g., the collection and disposal of contaminated CDW).

2. Significance of Lead in CDW

2.1. Lead Sources

Apart from historical applications of lead such as metal sheets in damp and water-proofing systems, lead pipes and joints, lead solders on pipes, cables and fittings, prior to the restrictions introduced in 2002–2003, lead was mainly used as an ingredient in paints and primers, as base layers of coatings, as a drying agent, and as a finishing layer for the protection of steel and timber elements [9]. Lead compounds have been widely used for the improvement of the physical properties they provide: durability, UV-resistance, and corrosion protection. These elements determine the anticipated source of Pb in the refurbishment and demolition waste of buildings.

In certain cases, however, due to the specific use of some industrial buildings, lead can be found in other materials as well (in concrete to a depth up to 5 cm, or in timber structures). A possible indirect source of Pb dust can originate from the emissions from coal burning (in power plants or industrial facilities with intensive firing processes such as cement production plants, smelters, etc.) [10–13].

In older roads, tunnels, bridges and infrastructure, lead contamination may appear from car exhaust gases from leaded petrol fuels used in the past. Though the use of lead in petrol has been restricted for a long time, the risk from accumulated lead dust on roofs and walls remains; such risk is also observed near petrol processing facilities [9]. Lead-containing fine particles can also be transported by air currents to neighbouring districts

and might be deposited as lead-contaminated dust in the cavities of buildings and in surrounding soils.

2.2. Health and Environmental Effects

Lead, similarly to mercury, is toxic both to humans and to ecosystems. It is important to know that Pb does not decompose, so even after migrating from one location to another, the total amount of lead is unchanged [14]. This underlines the importance of necessary precautions and measures to restrict the exposure to lead-containing sources. The mechanisms by which lead enters the human body are inhalation, ingestion and absorption. Ingestion and absorption are related to eating vegetables grown in contaminated soils and petrol-processing facilities, which are outside the scope of this study. Regarding construction or demolition activities, workers and people in the neighbourhood can inhale Pb dust and fumes, most of which are absorbed or stored in bones and teeth and can later be released into the bloodstream upon the deficiency of certain nutrients to other organs, i.e., the brain, liver and kidneys [14]. Young children, pregnant women and babies, as well as people working with lead-containing compounds, are the most vulnerable [15].

Beside its human toxicity, Pb is hazardous for animals and plants. Increased levels of lead can influence not only the health and mortality rate of species per se but also can lead to the extinction of species because of low nutrients in the environment. Lead can affect plant growth, soil organisms, and productivity [9]. These effects typically occur as a cumulative consequence as the ecosystem balance is broken and the nutrient production and migration are changed.

Lead in materials does not pose a risk if the element or layer is intact and no flakes or dust are released. The significant hazard occurs when the materials deteriorate and begin to detach or break down. This situation is often observed with old paints in buildings, on all substrates (timber, metal, renders, concrete). In such cases it is important for the paint to be removed with the respective protection for workers and people in the environment (residents, passengers, etc.). During the removal of old paints, power sanders and blow torches are often used; this generates lead dust and fumes [9]. Dust, in turn, can deposit on furniture or other surfaces in the premises, and can disperse the contamination. In case the paint waste is allowed to be mixed with other CDW, e.g., concrete intended for backfilling, it can further contaminate the soil at the site.

It also must be considered that the amounts of heavy metals in construction materials, which could be transferred to CDW, can increase by accumulation through dust absorption.

Furthermore, the distribution of Pb dust can go beyond the site in the surrounding areas [16] and can deposit on sidewalks and streets [17].

Some remediation measures can be used to reduce the solubility and leaching capacity of heavy metals (including Pb) in soils and CDW debris, e.g., the addition of lime, the use of immobilization agents (phosphates, nano-iron), or the use of elution agents (glyphosate) and washing to extract the Pb compounds [10], but in practice this is too costly, and the predominant disposal method of lead-contaminated waste is landfilling in special landfills where the pollution to soil, ground water or air is eliminated by technical measures.

2.3. Challenges in Lead Identification in Buildings and CDW

The broad aspects in which lead can pose a significant toxicological issue require the proper handling and treatment of CDW. In order to ensure safe waste management, proper audits of buildings (e.g., following [18]) allowing the identification of lead-containing materials and waste—and the characterization of the waste—are necessary. This audit requires the application of rapid, innovative methods and approaches that can be used in situ because the conventional waste characterization procedures—requiring sampling and analysis in a laboratory (e.g., acc. to [19])—are time and resource consuming. The problem is amplified by specific issues in regards with the buildings and CDW, such as the sampling procedures, the number of samples, and how representative they are for the whole amount.

A promising method that can be used for the immediate identification of lead contaminations in buildings is the HHXRF analyser. A multitude of measurements can be performed on building elements, and contaminated/lead-containing spots can be discovered and mapped before the formation of lead-containing waste. This allows the undertaking of proper measures for the protection of operational health and safety during repair and demolition works, the prevention of the contamination of non-hazardous CDW with lead dust, and the separate collection of lead-containing waste.

Similar studies have been performed by [20–22] and are oriented mostly towards the identification and assessment of the amount of Pb in paints on building elements. The conclusions from these surveys, however, are contradictory in terms of the identified amounts because the use of HHXRF is associated with many challenges.

XRF analysers determine the chemical composition of a sample (including the presence of contaminants) by measuring the fluorescent (secondary) photons emitted from the sample when it is irradiated by an X-ray or γ -ray source. The thickness of the layer under study depends on the energy of the exiting spectral line. For this reason, the World Health Organisation (WHO) recommends the use of devices with built-in γ -ray isotope sources of radioactivity that are capable of the excitation of K-characterisation lines in the spectrum of Pb [23], while for most HHXRF spectrometers with X-ray tubes the maximal energy of excitation is about 50 kV and can excite only the L-characterisation lines of the Pb. Devices with built-in isotopes can measure the content of heavy metals at deeper levels, but they are subjected to special regime of storage, transportation and use [24], and cannot be widely used.

High-definition HHXRF is another technique, using the Pb $L\alpha$ ($L\alpha_1 = 10.55$ keV) spectral line [25,26], which is delivered by a conventional X-ray tube. The X-ray spot is applied to a certain layer with a constant thickness. It is applicable in paint lead control, but this novel method is still quite expensive due to the additional X-ray optics and the small number of manufacturers.

Therefore, many teams use conventional HHXRF for the investigation of lead contamination prior to demolition works.

The conventional HHXRF device optics impose certain limitations. Figure 2 represents the optical scheme of a conventional HHXRF: D is the device detector, and X-ray is the source tube. In the focal plane (FP), which is determined by the device frame, both the X-ray tube and the detector spots overlap. However, at a deeper level, moving away from the FP, due to the angle α between both optical axes, a significant offset between their apertures could be observed. In the P1 plane, which is far enough from the FP, both the emitting and receiving apertures are totally displaced, and the device is not capable of registering a useful signal from this plane.

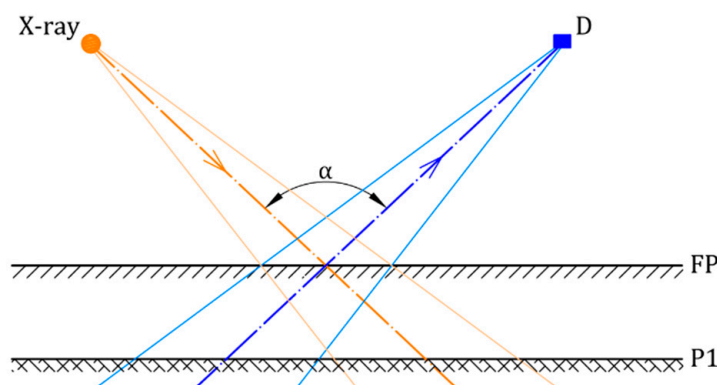


Figure 2. General scheme of the XRF analysis technique.

The last but not least limitation derives from the fact that conventional HHXRF devices are usually sold with integrated calibrations which are appropriate for certain measurements only, e.g., measuring heavy metals in soil or in polymeric paints.

Therefore, despite the tempting application of HHXRF for the identification and quantitative assessment of lead in buildings, a series of investigations are needed to determine the limits within which the measurements are reliable.

3. Materials and Methods

3.1. Concept Description

The lead content in paint can be expressed as a mass concentration (expressed as a percentage, ppm, or mg/kg), or as the mass of lead per unit area (e.g., of painted surface), also known as lead loading, expressed for example in mg/cm². The mass concentration is used for legally binding controls on the production, import, sale and use of lead paint, and most regulatory standards refer to the total amount of lead in the dried paint film. The same mass concentration limits are used to determine whether Pb-containing waste is hazardous or not. However, the last approach might be misleading in the case of CDW management—depending on the type and thickness of the paint substrate (e.g., only the paint layer, plaster with paint, or a whole painted wall), the measured Pb concentration in CDW will vary in a significant range, because there are different lead contents (if any) in each layer—paint, plaster, and the uncontaminated substrate. For the purposes of pre-demolition audit and selective demolition, and to assess the risk from lead-containing dust during repair works, the lead loading should be estimated using, for example, the guidelines of the WHO, for which the recommended units are mg/cm² [23].

A laboratory experiment was conducted in order to test the different calibrations' impacts and to establish a procedure for converting the HHXRF-measured lead concentrations into lead loadings. Model latex paint with a constant lead content was used on two types of surfaces (plasterboard and concrete tile), and the lead loading was calculated from the lead concentration in the paint, the painted area, and the paint quantity.

A field study was performed to assess the reliability of a HHXRF analyser for the identification of the presence of lead in paint on masonry walls in a public building (constructed in the 1940s), and to correctly determine the lead content. The building is in a process of renovation, but it has suffered many previous interventions as well. No data on the paint composition were available.

Using a non-dedicated system without exact calibration for our purposes would not be appropriate to quantify the lead content. The lead concentration measured by the HHXRF tool (HHXRF readings in ppm) is fictitious, i.e., it cannot be considered exact. A correction coefficient was proposed to recalculate the readings from the HHXRF into lead loadings. According to the conclusions of [27], the intensity of a certain lead spectral line usually measured like the registered count of photons by the detector per second (CPS) can be expressed as:

$$I_{Pb} = [C_{Pb} \times K / \mu_{Pb}] [1 - \exp(-\mu_{Pb} \times \rho \times d)] \quad (1)$$

where C_{Pb} is the lead concentration in a homogeneous sample (i.e., the mass fraction of the lead), ρ in g/cm³ is the sample density, and d in cm is the sample thickness. The factor K is a constant depending on the various properties of the spectrometer, such as the spectrometer geometry, its voltage, the current, and the excitation probability for this certain line under the given conditions. μ_{Pb} in cm²/g is a mass absorption coefficient quantifying the mass fraction of the other elements in the sample. This coefficient varies for the different characteristic lines, having a higher value for the $K\alpha$ series than the $L\alpha$ series, for example. For a sample with a layer thickness $d \rightarrow \infty$, the exponential part of (1) can be neglected, as it is close to 0, and the process can be described with:

$$I_{Pb} = [C_{Pb} \times K / \mu_{Pb}] \quad (2)$$

This is the usual way to calculate the concentration from the fluorescent yield through the factory calibrations.

A critical layer thickness is defined as a thickness delivering 90% of the signal for a certain line [27]. A sample with a thickness exceeding the critical one is considered infinitely thick, and is to be described with (2).

Contemporary interior paints are polymeric. Their critical layer thickness for the lead spectral line at 10.55 keV (Pb L α 1) [28,29] is around 5–10 mm, i.e., no layer is infinitely thick from an analytical point of view. On the other hand, for a very thin layer ($d \rightarrow 0$), Taylor's theorem for the first derivative could be used to simplify (1) to

$$I_{Pb} = C_{Pb} \times K \times \rho \times d \quad (3)$$

or

$$m_{pb}/S = I_{Pb}/K \quad (4)$$

where m_{pb}/S (m_{pb} in g is the mass of the lead, and S in cm^2 is the area) represents the lead loading according to the World Health Organization [23]. Therefore, if we consider a very thin layer where the Pb spectral line absorption in the paint can be ignored, the lead loading is proportional to the intensity measured by the HHXRF.

Usually, HHXRF systems determine the concentrations in infinitely thick samples by means of built-in calibrations based on (2), for example for the determination of the concentration of lead in soils. When measuring the lead content in a paint layer with a certain thickness (not infinite, but defined), it is very important to take into account the different densities of the paint and the soil. However, even when the measurements are performed with inappropriate calibration, the measured concentrations are still proportional to the real intensity of the spectral line. The HHXRF system readings of these concentrations, called "fictitious", could be recalculated as an intensity in terms of (2), and could be used in (3) to calculate the lead loading:

$$m_{pb}/S = C_{Pbf}/(K \times \mu_{Pbf}/K_f) \quad (5)$$

The index f signifies the fictitious values, giving the fictitious concentration C_{Pbf} based on the measured intensity. The concentration C_{Pbf} is not related to the real lead concentration in the paint whatsoever, and is to be perceived only as a reading with factor $1/(\mu_{Pbf}/K_f)$. Both coefficients μ_{Pbf} and K_f have meanings as per (1), but are related to the matrix used in calibration, e.g., soil (so, a "fictitious" matrix), while the coefficient K is related to the real material being investigated (i.e., paint).

It has to be mentioned that due to the angle between the tube and the detector (Figure 2), increasing d would saturate the measured intensity similarly to the situation described by (1).

3.2. Handheld XRF Tool Measurements

3.2.1. Instrumentation

The measurements were carried out with a portable X-ray BRUKER AXS fluorescent spectrometer (HHXRF) S1 TITAN 600 equipped with a 50 kV high-voltage source, an Rh X-ray tube and a Silicon Drift Detector (SDD). The X-ray tube's spot size is 8 mm. The S1 TITAN integrated calibrations allow the measurement of heavy metals in light, medium and heavy polymers and soils. It is not possible to precisely estimate the angle between the tube and the detector, and for this reason the distance between the diaphragms of the X-ray tube and the SDD was measured as 7 mm.

3.2.2. Laboratory Experiment

The wall-models were prepared by consecutive application on concrete and plaster-board substrates of up to nine Pb-containing latex layers. For this purpose, lead acetate trihydrate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3(\text{H}_2\text{O})$) with a purity of 99% was dissolved in 100 mL water and mixed with the latex, such that the latter dissolved paint contains 5.7% Pb. After applying each paint layer, the wall models were dried for 15 minutes at 70 °C in a ventilated oven. The weight of the remaining paint was measured, such that the quantity of the lead in each paint layer could be calculated. The layer's thickness was measured with a caliper with precision 0.1 mm. In this case, the lead loading is proportional to the thickness of the paint.

Correlation coefficients between the lead concentration and lead loading for four types of factory calibrations were found.

3.2.3. In-Situ Measurements

The HHXRF measurements were performed on the existing walls in a public building at 14 randomly chosen spots with dimensions 155 × 155 mm. Seven measurements in each spot were performed. Afterwards, the whole amount of paint from each spot was scratched out. Very often, a thin layer from the plaster underneath was removed together with the paint layer. The sample mass was measured with a precision of 0.005 g. Then, the materials were ground with a laboratory mill to prepare the samples for elemental chemical analysis performed by an ICP-MS system.

3.2.4. Data Processing

An average value of HHXRF measurements for each wall spot was calculated. No data were excluded in order to assess the impact of the paint's heterogeneity.

For the data treatment, and to establish the relationships (linear and exponential regressions) illustrated in Figures 3 and 4, the optimum package of Gnu Octave V4.4.1. software [30] was used.

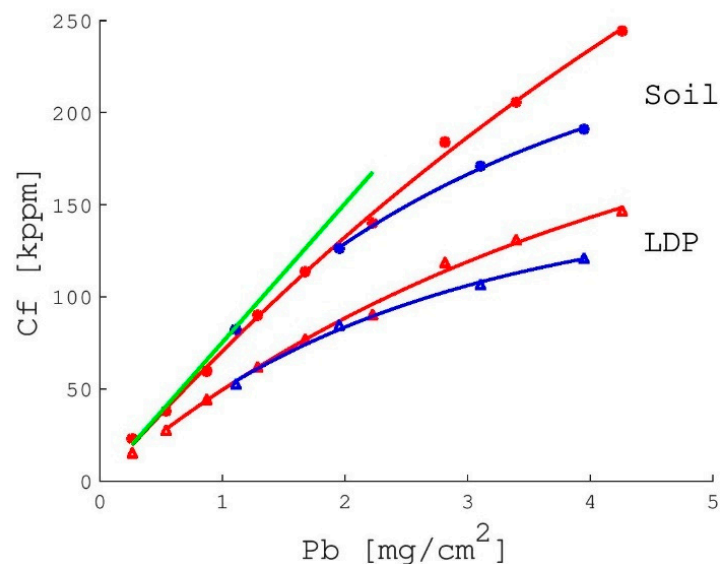


Figure 3. Data from the latex measurements with built-in calibrations for soil (●) and low-density polymers (▲) on plasterboard (red) and concrete (blue) substrates. The green line is a tangent for soil calibration at point 0.

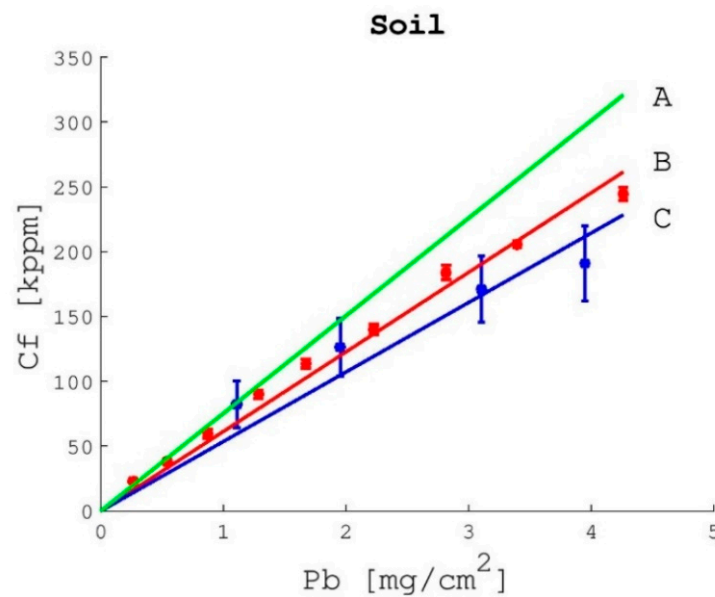


Figure 4. Linear fit $F = a \times x$ of the data from the intensity measurements with the soil calibration (A: tangent at 0 of the exponential relationship; B: linear approximation in the case of a plasterboard substrate; C: linear approximation in the case of a concrete substrate).

The least square exponential fitting was made by means of the following exponential function:

$$F = a \times (1 - \exp(x/b)) \quad (6)$$

where (a, b) and (x, F) are the parameters of the fit and variables, respectively.

A linear relationship of the following type was used:

$$F = a \times x \quad (7)$$

where a is the parameter of the fit, and (x, F) are the variables.

3.3. ICP-MS System Measurements

Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most promising destructive analytical techniques for the quantitative determination of chemical elements.

The high-temperature ionization source (ICP) ensures the ionization of all of the elements with ionization potential lower than 15.6 eV. A high population of ions of the trace elements is achieved, which is the reason for the low detection limits (pg/g), thus allowing small amount of samples (mg) to be analyzed. Besides this, the method is characterized with a dynamic range of 6–7 orders of magnitude, high sensitivity and selectivity, and precision below 1% relative standard deviation (RSD).

3.3.1. Reagents and Sample Preparation

Samples of mass 12–14 g were prepared by the preliminary crushing and homogenisation of sampled paints, taken from each location where the lead content was measured in situ by HHXRF.

Suprapur chemicals and double deionised water (MilliQ) were used for the preparation of all of the solutions. For the sample preparation, HNO_3 (65%), HCl (37%), HF (48%), and HClO_4 (68%) from Fisher Chemicals, of TraceMetal Grade, were used. The paint samples were mechanically shaken and homogenized immediately before being weighed. The determination of the total element concentration with ICP-MS was performed after acid digestion by open vessel [31] or microwave-assisted digestion [32] in an $\text{HF}/\text{HNO}_3/\text{HCl}$ acid mixture. The sample digestion in the present study was performed as follows: paint samples of between 0.1 and 0.2 g (three parallel tests of each sample) were placed in Teflon

vessels, and 5.0 mL HNO₃ was added. The samples were subjected to heating for 20 min at 50 °C on a sand bath to remove any organic solvents present. After this predigestion step, 10.0 mL HCl and 10.0 mL HF were added, and the digestion was continued until the acid mixture was evaporated to 1–2 mL. Due to the incomplete digestion of the samples, 5 mL HClO₄ was added, and the samples were heated to reduce the volume to 1–2 mL, followed by the addition of 5 mL HNO₃ and heating. Once the samples were completely digested and transparent, they were evaporated to about 1 mL. The digested solutions were then diluted to 50 mL with double deionized water. Prior the ICP-MS measurement, an additional dilution of 1 mL to 10 mL was performed. The reagent blanks were prepared using the same reagents in equal quantities according to the sample preparation procedure described above.

Working standard solutions of Pb were prepared from single-element calibration solutions (Merck) with initial concentrations of 1000 mg/L by appropriate dilution in 0.1% HNO₃. The calibration standard solutions were in the concentration range from 1 to 1000 µg/L.

3.3.2. Instrumentation

The analysis of the samples was carried out using a Perkin Elmer SCIEX DRC-e ICP-MS system with a crossflow nebulizer. The spectrometer was optimized (RF 1100W, gas flow rate 0.85 L min⁻¹, lens voltage 7.5 V) to provide minimal values of the ratios CeO⁺/Ce⁺ and Ba²⁺/Ba⁺. External calibration by standard solution was performed for ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb. The calibration coefficients for all of the calibration curves were at least 0.99. The accuracy was evaluated by the standard addition method.

4. Results and Discussion

4.1. Relationship between the Calculated Lead Loading and HHXRF Measured Lead Concentration of the Model Samples

The lead loading related to the measured lead fictitious concentration is presented in Figure 3. The total paint thickness was about 1 mm. The curves corresponding to different calibrations which were used (soil and low-density (LD) polymers) were fitted with an exponential function like (6). The derivatives of the functions at point 0 (i.e., the ratio a/b of the fit function (6)) were determined and are given in Table 1 (column A-line). The measurements made with Medium- (MD) and High-Density (HD) Polymer calibrations are close to the presented curves; for this reason, their curves are not plotted. All of the curves were similar, and significant differences due to overcorrection from the various calibrations were not observed.

Table 1. Coefficients of the linear regression and R-square values for four types of calibrations and two types of substrate.

Calibration Type	Derivative of the Exponential Fit at 0 [cm ² /g]	Plasterboard [cm ² /g]	R ²	Concrete [cm ² /g]	R ²
	A-line	B-line		C-line	
Soil	75.33	61.30	0.98	53.60	0.84
HD Polymers	61.74	47.05	0.97	44.85	0.92
MD Polymers	64.26	39.38	0.89	34.40	0.61
LD Polymers	55.38	38.87	0.95	34.11	0.72

The measured fictitious concentrations (C_f) in the case of a concrete substrate compared to those on the plasterboard substrate start to decrease after several layers. It might be assumed that with increase of the number of paint layers up to a certain critical thickness, the intensities would be substantially different. The lead from the first layer of the paint partially diffuses in the substrate, transferring part of the lead loading, which in the case of

the plasterboard can be registered in a way similar to the lead in the paint. The situation in the concrete is quite different due to its higher density (approximately 2200 kg/m³ versus 1000 kg/m³ for plasterboard) and its mass absorption coefficient, participating in (1).

It should be mentioned that direct painting over rough and absorbing surfaces like concrete is not economically justified and thus not likely to happen in practice, but it illustrates the limits of the proposed model. Part of the lead paint could be hidden in the substrate.

From the data presented in Figure 3, it is clear that linear approximation (7) with a derivative in zero would be correct for up to four layers. In order to describe thicker layers, it is better to find other coefficients which give a better approximation for all of the present points.

For Figure 4, only points measured with soil calibration are plotted, and are fitted with the linear relationship (7) for both plasterboard and concrete substrates. The standard deviation in measurements is also presented.

The corresponding coefficients of these linear relationships (7) for the two types of substrates and all of the calibrations used in our study are presented in Table 1; the relevant fit quality R² is given as well. It appears that for both plasterboard and concrete, the coefficients based on calibrations for soils and HD polymers can be successfully used for the estimation of the lead loading. For a concrete substrate, the calibration for MD and LD polymers does not allow precise estimation—the values of R² correspond to the relatively low quality of the linear fits.

The three approximation line coefficients can be applied in different cases. The first line (A), coming from the tangent at zero point is appropriate for the situation where the lead loading is spread on the surface of the paint (when a lead-free paint is polluted from external sources). The second line (B) applies to the case in which the densities of the paint and its substrate are similar. The third line (C) is applicable when the lead is absorbed partially by the substrate, and is thus undetectable (e.g., lead-containing paint on a concrete substrate). These three coefficients express the limitations of this model for the estimation of the lead loading.

4.2. Comparison for the Lead Content in the Building Walls' Paint, as Determined by HHXRF Tool Measurements and by ICP-MS Analysis

The HHXRF measurements were performed according to the methodology in Section 3.2.3. The calculated XRF-based Pb loading (XRF L in µg/cm²) is obtained from HHXRF readings (C_{Pbf} in ppm) as follows:

$$\text{XRF L} = C_{\text{Pbf}}/B \quad (8)$$

where B is the B-line slope coefficient which is presented in Table 1 for soil calibration (B = 61.3 cm²/g).

The calculated XRF-based Pb concentration (XRF C in ppm) is obtained as follows:

$$\text{XRF C} = \text{XRF L} \times S/m \quad (9)$$

where S is the surface of the sample in cm², and is constant for all of the samples; m is the total mass of the sample in g. The total mass includes the mass of the paint (all of the paint layers) scratched from the surface S and the mass of the lead-free plaster attached to the paint particles.

The calculated ICP-based Pb loading (ICP MS L in µg/cm²) is obtained as follows:

$$\text{ICP MS L} = \text{ICP MS C} \times m/S \quad (10)$$

where ICP MS C is measured as the ICP MS Pb concentration in ppm, and m and S are the same as in (9).

The data from the ICP-MS and XRF measurements on lead content of building walls paint are summarised in Table 2.

Table 2. Data for the lead content in the building walls' paint.

Parameter	Unit	Min Value	Max Value	Average Value	Standard Deviation
XRF readings (C_{Pbf})	ppm	1460	2720	1957	386
ICP MS measured Pb-concentration (ICP-MS C)	ppm	455	2298	1213	564
Calculated XRF based Pb-loading (XRF L)	$\mu\text{g}/\text{cm}^2$	23.8	44.3	31.9	6.28
Calculated ICP-MS based Pb-loading (ICP-MS L)	$\mu\text{g}/\text{cm}^2$	46.2	105.3	70.7	19.3
Calculated XRF-based Pb concentration (XRF C)	ppm	301	787	527	146

The results emphasize the peculiarities in lead contamination evaluation:

- (1) Heterogeneity: Although the individual in situ XRF measurements were taken in the premises of a building with the same wall structure and painted with the same paint, the difference between the maximum and minimum values of the fictitious concentration C_{Pbf} (ppm) is almost double.
- (2) Influence of sampling: A very precise analytical method such as ICP-MS amplifies the heterogeneity, and the difference between the maximum and minimum value on Pb concentration is fivefold.
- (3) There are necessary corrections for the XRF readings in order to take into consideration the calibration, the substrate type and the parameters (geometry, excitation energy) of the HHXRF spectrometer—the average value of 1957 ppm for Pb concentration (fictitious) is almost four times higher than the limit as per the REACH regulation (500 ppm) [33]; thus, the paint waste can be characterized as quite hazardous and toxic. When recalculated based on correlation coefficients which have been established during the laboratory study, the average value (527 ppm) is barely above the REACH limit. However, taking into consideration the recommendations of the WHO [34] that the total lead content in paint should be no more than 90 ppm by weight of the dried paint film, the calculated concentration is quite high, too.
- (4) The results for lead loading calculated on the basis of HHXRF measurements in situ and the ICP-MS testing of samples differ, but are of the same magnitude; therefore, the determination of lead loading when lead-contaminated areas of buildings are to be mapped, and especially when the paint film is damaged and lead-containing flakes and dust are generated, can be assessed as convenient.

All of the mean results from the 14 different measured fields (measurement spots) are presented in Figure 5. The small red rectangle at the middle shows the average values determined by the two methods for all of the points. The observed standard deviations of the mean ICP-MS C and XRF C values are represented by the bigger red rectangle. As mentioned in 5.1. in regards with the values in Table 1, the type of lead pollution (surface pollution on the paint or the presence of lead hidden in a heavy substrate) can impact the calculated XRF L results. Thus, if another linear regression coefficient corresponding to the type of lead pollution is applied, different values of XRF C will be calculated. For example, if the coefficient $53.60 \text{ cm}^2/\text{g}$ —corresponding to a concrete substrate and soil calibration—is used, the right border of the confidence interval for XRF C expands to the blue vertical line. When the lead content originates from external sources (i.e., it is not included in the paint), it would be more appropriate to apply the coefficient $75.33 \text{ cm}^2/\text{g}$, corresponding to exponential fit. In that case, the left border of the confidence interval for XRF C would shift to the green vertical line.

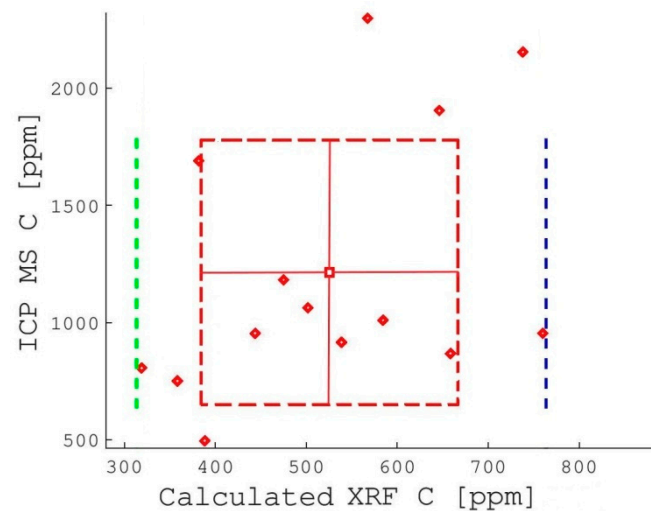


Figure 5. Comparison for the lead content in wall paint, obtained by in situ measurements and ICP-MS tested samples.

Although there is a significant discrepancy between the averages found by the two methods for lead quantification (ICP-MS and HHXRF), their confidence intervals overlap; therefore, the results of both methods can be assessed as compatible.

5. Conclusions

This paper demonstrates that the widely used HHXR with an X-ray tube has constructive limitations for the in situ measurement of lead contamination on building surfaces. These limitations can be summarized as follows:

- (1) There is a wide angle between the source of the X-rays and the detector of the radiation results in the shallow focus of the device.
- (2) The technology uses excitation voltages up to 40–55 kV, which are not enough to excite the K spectral lines of lead, i.e., the use of lines with a higher mass absorption coefficient is necessary.

It was shown that, at a small thickness of the contaminated layer, the lead loading of the building surfaces under study is proportional to the intensity of the registered photons of the L-lines of Pb. The intensity in general is not accessible as information on the display of the HHXRF analyzer; instead, it was suggested that the fictitious concentration should be measured with some of the built-in factory calibrations. It was proven that these readings are also proportional to the lead loadings.

Correlation coefficients were found in laboratory-tested samples from contaminated surfaces that allow the calculation of lead loading from measurements with several built-in calibrations. It was shown that:

- (1) Paint layers with a thickness of up to 0.3 mm can be considered very thin from an analytical point of view, and the coefficient of proportionality can be found between the registered signal and the lead loading. It is estimated that the surface lead contaminations, which might be present due to the use of the premises, do not exceed this thickness.
- (2) For thicker layers, but with a thickness under 1 mm (contamination due to the application of lead-containing paints) another coefficient of proportionality can be found (smaller than the first case) which better describes the results for the lead loading.
- (3) A denser substrate with a coarser absorbing surface can also impact the results. In this case, part of the lead loading can remain hidden, and cannot be registered by the HHXRF device.

The ignorance of the spectral line absorption in paint in the proposed simplified model, the type of contamination, and the substrate can influence the in-situ measurements; this is expressed as uncertainty in the coefficient of proportionality. This can lead to the substantial discrepancy (demonstrated twice) of the results for lead content in the paints samples measured with ICP-MS and the calculated values for lead loading from the HHXRF in situ readings. The heterogeneity of building surfaces and sampling from paint in polluted areas might significantly influence the results from very precise analytical methods. It must be noted that, despite the large discrepancy of the mean values, the confidence intervals of the two methods partially overlap. A correlation between both methods was found, confirming that HHXRF tools can be used as an assisting technique in pre-demolition audits, selective demolition plans, and CDW management activities, e.g., collection, treatment and disposal.

In conclusion, the conventional HHXRF can be useful for the identification of Pb contaminations in up to a 1 mm layer of building coatings, and for the rough quantification of pollution (our device demonstrates a low limit of detection of 0.01 mg/cm² at worst). In the case where an exact match of the value of the pollution is sought, a coefficient of proportionality must be found, based on the reference method for each specific room. Such an approach would help to accurately map the polluted areas.

The proposed methodology allows the conversion of lead concentration from HHXRF readings into lead loadings, and can probably be used in other research with similar HHXRF tools.

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Abbreviations

CDW	Construction and Demolition Waste
EC	European Community
EU	European Union
FP	Focal Plane
HD	High-density (polymers)
HHXRF	Handheld XRF (analyser)
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-MS C	ICP-MS-Measured Pb-Concentration
ICP-MS L	Calculated ICP-MS based Pb-loading
MD	Medium-density (polymers)
LD	Low-density (polymers)
ppm	parts per million

Pb	Lead
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (regulation)
RSD	Relative Standard Deviation
SDD	Silicon Drift Detector
UV	Ultraviolet
WHO	World Health Organisation
XRF	X-ray Fluorescence
XRF C	Calculated XRF-based Pb Concentration
XRF L	Calculated ICP-based Pb Loading

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