



**Study on the Effectiveness, Precision, and Reliability of X-ray
Fluorescence Spectrometry and Other Alternative Methods for
Measuring Lead in Paint**

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Summary:

X-ray fluorescence (XRF) spectrometry has the potential to accurately measure lead content in painted films on children's products at the limits required under the Consumer Product Safety Improvement Act (CPSIA) of 2008, but appropriate standard reference materials (SRMs) and standard analytical methods need to be developed before a complete evaluation or determination is possible. Staff members from the U.S. Consumer Product Safety Commission (CPSC) are working with the National Institute of Standards and Technology (NIST) to develop appropriate SRMs, and with the ASTM International (formerly the American Society of Testing and Materials) to develop appropriate standard test methods.

In contrast to the situation for paint films, the foundations required for XRF analysis of polymers are in place. A consensus standard test method for lead in polymers exists and some appropriate SRMs of leaded polymers are available. With the appropriate test methods and SRMs, XRF spectrometry is suitable in many cases for the determination of lead in polymers. CPSC staff has conducted comparison testing of plastic samples and SRMs by XRF and by using current wet chemical methods and found generally good agreement. XRF produced good results on homogeneous plastic SRMs with certified concentrations as low as 13.6 parts per million (ppm).

Background:

The CPSIA, section 101(f)(4)(A) requires the CPSC to complete a study to evaluate the effectiveness, precision, and reliability of XRF methods and other alternative methods for measuring lead (Pb) in paint or other surface coatings when used on a children's product. This report describes how XRF and another alternative method, Laser Induced Breakdown Spectroscopy (LIBS), could potentially be used to test painted children's products. Standard reference materials and performance based standard methods need to be developed and approved before these analytical techniques could be used to certify that paints on children's products contain less than 0.009% Pb (or 90 mg/kg) as required under CPSIA section 101(f).

Current Test Method:

The current CPSC staff test method¹ for determining total Pb in paint involves removing paint from a product by scraping or using a solvent, dissolving the paint scrapings in nitric acid, and analyzing the acid solution by spectroscopic means such as inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FLAA) or graphite furnace atomic absorption spectrometry (GFAA). These analytical techniques are capable of yielding precise and accurate results and have low enough detection limits to measure Pb in paint at the new limits of 90 mg/kg. Paint powder SRMs such as NIST SRM 2581 (contains 0.45% Pb) and 2582 (contains 0.02% Pb) are available to laboratories to verify performance. The current test method is based on standard test procedures such as ASTM E 1645², ASTM E1613-04³ and Association of

¹ US CPSC. Test Method CPSC-CH-E1003-09 *Standard Operating Procedure for Determining Lead(Pb)in Paint and Other Similar Surface Coatings*, March 2009

² ASTM Standard Practice for Preparation of Dried Paint Samples by Hotplate or Microwave Digestion for Subsequent Lead Analysis 2007

³ ASTM Standard Test Method for Determination of Lead by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Flame Atomic Absorption Spectrometry (FAAS), or Graphite Furnace Atomic Absorption Spectrometry (GFAAS) Techniques

Official Analytical Chemists (AOAC) standard AOAC 974.02⁴. This procedure is time consuming, typically requiring several hours to prepare and analyze samples, and is sample destructive.

XRF Principles:

In XRF analysis, a source of x-rays irradiates a sample. The source can be an x-ray tube or a sealed radioisotope. When a sample is irradiated with x-rays, the source x-rays may undergo either scattering or absorption by the sample atoms. When an atom absorbs the source x-rays, the incident radiation can dislodge electrons from the innermost shells of the atom, creating vacancies. Electrons from outer shells will fill the inner shell vacancy and emit x-ray photons. The energy of the emitted x-ray depends on the difference in energy of the shell with the initial vacancy and the energy of the electron that fills the vacancy. Each atom has specific energy levels, so the emitted radiation is characteristic of that atom. By measuring the energy of the radiation emitted it is possible to identify which elements are present in a sample. By measuring the intensity of the emitted energies it is possible to quantify how much of a particular element is present in a sample.

Types of XRF Instrumentation:

There are a variety of XRF systems in the marketplace with highly varied power levels, filter systems, and analysis algorithms for converting raw data to useful output information. For any analytical equipment and technique, it is critical for the analyst to understand the capabilities, principles and settings of the particular instrument and technique especially with regard to the particular application and sample in question. XRF analyzers are generally classified as being either Energy Dispersive (EDXRF) or Wavelength Dispersive (WDXRF), but there are some additional sub categories within these two systems. This section provides a brief description of the two major types of XRF.

Energy Dispersive X-ray Florescence (EDXRF) - There are a variety of EDXRF spectrometers commercially available. EDXRF spectrometers have a detector that is capable of separating and measuring the different energies of the characteristic radiation emitted from the sample to determine elements present. EDXRF spectrometers include the hand held portable devices used for inspecting paint in homes to determine if lead based paint is present. The U.S. Department of Housing and Urban Development (HUD) has guidelines⁵ for the use of portable EDXRF spectrometers. The x-ray sources for portable hand held EDXRF systems may be low powered (1-2 watts) x-ray tubes or radioisotopes. EDXRF systems also include more advanced laboratory models that have higher power, better resolution, and lower detection limits, but are not portable. High Definition XRF (HDXRF) is a type of EDXRF that utilizes special optics to enhance measurement intensities. CPSC staff currently utilizes portable hand held XRF analyzers, as well as larger EDXRF laboratory models for screening samples for the presence of lead.

Wavelength Dispersive X-ray Fluorescence (WDXRF) - WDXRF spectrometers utilize a system of collimators and diffraction crystals to diffract the x-rays of different wavelengths in different

⁴ Association of Official Analytical Chemists (AOAC) standard AOAC 974.02 (Lead in Paint Test) 1976

⁵ U.S. Department of Housing and Urban Development Guidelines for the Evaluation and Control of Lead Based Paint Hazards in Housing, Chapter 7 Lead Based Paint Inspection

directions. The spectrometers may have a moving detector on a goniometer which measures the intensities of the different wavelengths one at a time or sequentially. Spectrometers can also be equipped with a set of fixed detection systems to allow simultaneous analysis of multiple wavelengths. WDXRF systems are generally slower, more expensive, and require more sample preparation than EDXRF systems, but generally have increased sensitivity and lower detection limits.

Advantages of Using XRF for Paint Analysis:

The main advantages of utilizing XRF over the current digestion/ICP method are:

1. XRF is often non destructive and the paint can be tested *in situ* on the item.
2. Little to no sample preparation is required which greatly reduces the analysis time and cost. Sample times for XRF *in situ* are typically less than 2 minutes. It takes several hours to collect paint scrapings, digest and analyze using the current test method.
3. XRF can be utilized more easily to test small painted areas. It can be difficult to remove enough paint from a small area to quantitatively analyze using the current digestion and ICP method. Small painted areas generally require the compositing of like paints from multiple items of a sample lot to obtain sufficient material for analysis. XRF analyzers equipped with video cameras can be used to analyze spot sizes of a few millimeters.
4. Hand held XRF analyzers are portable, allowing for field-screening of products.

Limitations in Paint Film Analysis:

In situ analysis of paint films on children's products by XRF has the following limitations:

1. XRF instruments do not readily measure lead in thin paint films in mass per mass units such as weight %, mg/kg, or ppm. XRF methods typically report the amount of analyte in a thin layer such as a paint film in mass per unit area, e.g. $\mu\text{g}/\text{cm}^2$ because energetic x-rays are typically measured for a known spatial area and the count rate of x-rays is a function of both mass fraction and thickness of the specimen layer. The source radiation can travel through a thin paint film and into the underlying substrate. For example, if paint films of different film thickness, containing the same lead concentration by weight were analyzed by XRF, the thicker film would yield a higher measurement count rate. Paint film thicknesses on children's products vary considerably, which makes it difficult to quantitatively analyze and compare to calibration standards on a mass per mass unit basis.
2. The source radiation can travel through the paint film into the underlying substrate, leading to a measurement result that has contributions from both. Special care needs to be taken in ascertaining the source of lead in any measurement.
3. XRF is matrix sensitive⁶. Spectral and matrix interferences must be taken into account during analysis, especially from the underlying substrates. X-ray fluorescence measurements are typically particularly susceptible to errors from metal substrates.
4. There are currently no consensus industry standard test methods for quantifying lead in paint films on a mass per mass unit basis.

⁶ The matrix is the local environment of chemical components in a sample, other than the analyte.

Alternative Unit of Measurement

XRF analysis results of lead in paint films are typically expressed in units of mass per area such as milligram or microgram per square centimeter (mg/cm^2) or ($\mu\text{g}/\text{cm}^2$). The only currently available paint film standard reference materials are certified in units of mg/cm^2 , and this is the unit of measurement that HUD recognizes for evaluating lead in household paint using EDXRF. In order to convert a mass per area unit of measurement such as $\mu\text{g}/\text{cm}^2$ to a mass per mass unit of measurement such as mg/kg , the dried paint film thickness and density need to be known. The calculation is as follows:

$$C_{\mu\text{g}/\text{cm}^2} = C_{\text{mg}/\text{kg}} \times D \times T/10000$$

$C_{\mu\text{g}/\text{cm}^2}$ is concentration of lead in the paint in units of micrograms per square centimeter

$C_{\text{mg}/\text{kg}}$ is concentration of lead in the paint (mg/kg)

D is density of the dry paint film in units of grams per centimeter cubed (g/cm^3)

T is thickness of the dry paint film in units of micrometers (μm)

The paint film thickness can be determined non-destructively using ultrasonic gages, but the film thickness is likely to vary throughout the product. The density of the dry paint film can only be determined through labor intensive and destructive means such as scraping all the paint from a known area, collecting the paint scrapings and weighing. The difficulty in determining dry paint film thickness and densities on consumer products limits the use of *in situ* XRF analysis if the allowable lead levels can only be reported on a weight percentage basis as is stated in the CPSIA for paint. A paint film with a density of $1.4 \text{ g}/\text{cm}^3$ that is 50 microns thick and contains 0.009% Pb would have $0.63 \mu\text{g}$ of Pb/cm^2 . Paint films on consumer products that contain 0.009% Pb by weight are likely to have mass per area concentrations in the range of $0.5 - 2 \mu\text{g}/\text{cm}^2$.

Availability of Standard Reference Materials and NIST Collaboration

Standard reference materials should be used to validate any test method. NIST has a series of 6 paint film standard reference materials used mainly for checking the calibration of hand held XRFs when evaluating lead in household paints following HUD guidelines. NIST SRM 2575 has the lowest nominal lead concentration of $0.3 \text{ mg}/\text{cm}^2$ or $300 \mu\text{g}/\text{cm}^2$, other than NIST SRM 2570 at $<0.001 \text{ mg}/\text{cm}^2$ which serves as a blank. Paints containing 0.009% to 0.06% Pb would likely have Pb levels in the range 0.5 to $15 \mu\text{g}/\text{cm}^2$, which is a small fraction of the amount found in NIST SRM 2575. Paint film standards that contain certified levels of Pb closer to the allowable limits of the CPSIA need to be developed to validate *in situ* XRF analysis of paint films on children's products. The paint film standards need to have certified Pb values on a mass per area unit basis (mg/cm^2) as well as a mass per mass unit basis (weight %). The paint films should also be well characterized and certified with respect to dry film thickness and density.

NIST is currently working on developing paint film SRMs that have these characteristics and could be used for calibrating and validating *in situ* XRF analysis of paint films on children's products. CPSC staff is working with NIST in this effort. CPSC staff is also collaborating with NIST in the evaluation of XRF for determining low levels of lead in paint films. Attachment (A) describes some initial work that NIST and CPSC staff have done, using XRF to characterize prototype paint films formulated at CPSC and NIST laboratories. This work was intended to provide information for the following purposes:

1. Produce prototype paint films and measure those films using available XRF tools.
2. Develop the procurement specifications for the materials that will be the new paint film

SRMs for low Pb levels.

3. Provide background information and example analyses in support of CPSC staff efforts to understand the capabilities of current XRF instrumentation.

One important finding in this initial study was that the hand held XRF analyzers that CPSC staff currently uses were not able to detect lead in the paint films that had been spiked with 50 mg/kg (wet paint basis) lead naphthenate and applied to metal substrates. This is of concern since the dried paint films spiked this way had lead concentration similar to the regulatory limits set by the CPSIA. The manufacturer of the instrument has subsequently demonstrated a newer version of the hand held XRF that has an improved type of detector, called a silicon drift detector that was able to detect lead on these same specimens. Other manufacturers also market hand held XRF instruments with silicon drift detectors.

Besides this report, the additional achievements directly resulting from this collaboration include:

1. NIST XRF experts contributed to the public meeting on XRF capabilities that was held by CPSC staff in November 2008.
2. NIST has received a demonstration of new HDXRF technology, and is making arrangements to use an instrument on loan to help qualify candidate SRM films for heterogeneity.
3. CPSC staff's lead in paint test method CPSC-CH-E1003-09 has been further validated by comparison to NIST XRF analyses.
4. NIST is in the process of procuring of paint film SRM candidate materials.

Availability of Standard Test Methods

ASTM International Committee F40 on Declarable Substances is currently developing a proposed new standard, WK21957, Test Method for Identification and Quantification of Lead in Paint and Other Coatings Using Energy Dispersive X-ray Spectrometry (EDXRF). ASTM F40 also started a work item for developing a standard for lead in paint analysis using HDXRF. CPSC staff is collaborating with ASTM in these efforts.

Possible Use of XRF as a Screening Tool

In situ quantitative lead analysis of paint films on a mass per mass unit basis using portable XRFs may not be acceptable until suitable SRMs and analytical methods are developed and validated. It may still be possible to use in-situ XRF as a screening tool. Criteria need to be developed to certify the XRF analyzer used is capable of detecting 0.009% lead in paint films on common toy substrates such as plastic, wood, steel, zinc, and aluminum, with dry film thicknesses and densities in the lower ranges of expected values found for children's products. Standard test methods need to be developed to address pass/fail criteria, and circumstances where confirmatory analysis using other techniques such as those outlined in CPSC-CH-E1003-09 need to be performed. Paint film SRMs containing lead levels in the 0.009% to 0.06% range need to be developed to calibrate and certify XRF analyzer capabilities.

***Ex situ* XRF Analysis**

Quantitative analysis of lead in paint on a mass per mass unit basis is possible using *ex situ* XRF techniques in which the paint is removed from the product and analyzed by an XRF spectrometer as a homogeneous sample. *Ex situ* XRF analysis is more time consuming than *in situ* analysis due to required sample preparation steps which include removing the paint from the product and grinding paint scrapings to a fine powder. *Ex situ* XRF analysis is destructive to samples. The US Environmental Protection Agency (EPA) Method 6200⁷ could be used to provide guidance to develop *ex situ* XRF test methods. Paint powder SRMs such as NIST SRM 2581 (contains 0.45% Pb) and 2582 (contains 0.02% Pb) are available to laboratories to verify performance.

Laser Induced Breakdown Spectroscopy

LIBS is a type of atomic emission spectroscopy like ICP-OES. LIBS involves use of a high power laser as the excitation source. A laser is focused on a sample surface, and a small amount of mass (in the nanogram range) is ejected by various thermal and non thermal processes. The ablated mass interacts with the laser pulse and becomes a highly excited plasma. LIBS systems analyze the spectral plasma emission allowing both quantitative and qualitative analysis. Operating conditions of a LIBS system can be adjusted to limit the depth of sample surface ablation which allows only analysis of the paint or surface coating and not the underlying substrate. A LIBS system may be able to determine concentrations of lead in paint on a mass per mass unit basis provided adequate reference materials are available to serve as calibration standards, but variations in paint matrices may pose challenges for this emerging technology. The types of lead in paint film SRMs under development by NIST for XRF methods would also be needed to validate methods and equipment for LIBS analysis.

Future Evaluation

As noted above, CPSC staff will continue to work with NIST in the development of low level lead paint SRMs, and with ASTM F40 in the development of standard test methods for determining lead in paint films by XRF. When the low level lead in paint SRMs become available, CPSC staff will work with NIST and ASTM to participate in an interlaboratory study of the effectiveness, precision, and reliability of XRF methods and other alternative methods for measuring lead in paint.

XRF Analysis of Plastics

Quantitative analysis of homogeneous plastic or polymeric materials for Pb content using XRF technologies is possible at this time. Recognized consensus standard test methods such as ASTM F2617-08⁸ exist. Some lead containing polymeric reference materials from both metrology institutes and commercial sources exist such as ERM[®]-EC680k and EC681k⁹. CPSC staff has recognized the applicability of XRF for determining lead in polymeric materials in

⁷ US EPA Method 6200 *Field Portable X-Ray Fluorescence Spectrometry For The Determination Of Elemental Concentrations in Soil and Sediment*

⁸ ASTM Test Method F2617-08 *Identification and Quantification of Chromium, Bromine, Cadmium, Mercury, and Lead in Polymeric Material Using Energy Dispersive X-ray Spectrometry*

⁹ European Reference Material, produced and certified under Institute for Reference Material and Measurements (IRMM)

CPSC-CH-E1002-08¹⁰. Components could be analyzed intact without any sample modification if they have suitable surface characteristics, geometry and homogeneity. Compton scatter, or incoherent scatter of the x-ray tube lines can be utilized to account for different types of plastics. Compton scatter occurs when x-rays from the x-ray tube or target strike atoms in the sample without promoting any fluorescence, and energy is lost in the collision. The amount of Compton scatter that occurs gets proportionately smaller as the average atomic number of the sample gets larger. Polyvinyl chloride (PVC) would have less Compton scatter than polyethylene. Rayleigh scatter or coherent scatter of the x-ray tube lines can be utilized to account for irregular shaped samples or samples smaller than the x-ray beam area. Rayleigh scatter occurs when x-rays from the x-ray tube or target strike atoms in the sample without promoting fluorescence, and energy is not lost in the collision. The amount of Rayleigh scatter will decrease as the area of the sample exposed to the x-ray beam decreases. Destructive sample preparation techniques such as milling and compression molding may still be required for certain components to create a uniform sample for testing, or may be necessary in instances when higher degrees of precision and accuracy are needed.

CPSC staff has developed various data comparing XRF and microwave digestion followed by ICP-OES analysis. Table 1 compares XRF and ICP-OES measurements of reference materials. Table 2 shows the repeatability (standard deviation) calculated for 10 measurements on plastic reference materials using the portable XRF spectrometer. Table 3 compares XRF screening results obtained on samples to ICP-OES results. The XRF measurements were done on intact sample components. No special sample preparation techniques such as milling or compression molding were used prior to XRF analysis. XRF results are typically within $\pm 30\%$ of ICP-OES results. Table 4 compares XRF results obtained on cryomilled samples to ICP-OES results. The XRF results on the powders of the cryomilled samples were within $\pm 15\%$ of ICP-OES results. If additional sample preparation techniques such as compression molding of the powder to create a more uniform surface had been done, XRF results would likely have been in even closer agreement with ICP-OES results.

These findings suggest that XRF technology can probably be used to accurately measure lead in plastics relative to regulatory limits under the proper conditions. Section IIB of the CPSC staff test method for determining total lead in non-metal children's products¹¹ provides guidance on how XRF could be utilized to analyze for lead in plastic components of children's products and criteria for which additional testing may be required. CPSC staff has concluded that analysis using wet chemical procedures outlined in sections IIA of the CPSC staff test method needs to be done on any samples with lead results determined by XRF to be greater than 200mg/kg before certifying the item meets the Pb requirements of the CPSIA.

Duke University Medical Center did a study comparing testing for lead in plastics by XRF and traditional acid digestion followed by GFAAS analysis¹². Results of that study were comparable to results found by CPSC staff.

¹⁰ US CPSC. *Test Method CPSC-CH-E1002-08 Standard Operating Procedure for Determining Total Lead (Pb) in Non-Metal Children's Products*, Feb 1 2009

¹¹ US CPSC. *Test Method CPSC-CH-E1002-08 Standard Operating Procedure for Determining Total Lead (Pb) in Non-Metal Children's Products*, Feb 1 2009

¹² *Comparison of testing of plastics for lead by x-ray fluorescence and traditional nitric acid digestion/GFAA after muffle furnace combustion*, Nov 8, 2008, Danielle Cappellini, B.Sc., MHA and Woodhall Stopford, MD, MSPH

Conclusion:

The ability of XRF to be used to accurately measure lead content in painted films on children's products at the limits required under the CPSIA is currently limited due to the unavailability of SRMs and standard analytical methods. CPSC staff will continue to study the feasibility of using XRF technology for analyzing painted films on children's products as SRMs and standard analytical methods become available.

XRF technology is suitable in many cases for the accurate determination of lead in plastics provided appropriate test methods are followed, with the use of appropriate SRMs.

Table 1. XRF and ICP-OES Analysis Results of Certified Reference Materials

Reference Material	Type of Plastic	Certified Lead Quantity Pb mg/kg	**Digestion and ICP Analysis Pb mg/kg	***XRF Analysis Pb mg/kg
ERM® - EC680K	Granulated Low Density Polyethylene	13.6±0.5	12.0±0.6	13.1±2.0
ERM® - EC681K	Granulated Low Density Polyethylene	98±6	98.5±7.3	91.5±5.8
*PL(PVC)3-1E(P)-2	Milled Polyvinyl Chloride Powder	300 ±12	303.6±4.8	331.9±13.0
*PL(PVC)3-1E(P)-3	Milled Polyvinyl Chloride Powder	604 ± 24	614.3±28.8	669.1±22.8

*PL(PVC)3-1E(P)-2 and 1E(P)-3 were made and certified by Analytical Services, Inc

** Represents the mean and standard deviation of at least ten replicates except for ERM® -EC680K for which only 3 replicate measurements have been performed.

*** Represents the mean and standard deviation of ten replicates. Measurements were done for a minimum of 30 seconds using ThermoNiton model XLT portable XRF

Table 2. Replicate XRF Data for Plastic Reference Materials

Replicate	ERM-EC680K Pellets		ERM-EC680K Disk		ERM-EC681K Pellets		ERM-EC681K Disk		PL(PVC)1-1E(P)-1 powder		PL(PVC)1-1E(P)-2 powder		PL(PVC)1-1E(P)-3 powder		*PVC-L-03A Disk		*PVC-H-02A Disk	
	Pb ppm	±2σ	Pb ppm	±2σ	Pb ppm	±2σ	Pb ppm	±2σ	Pb ppm	±2σ	Pb ppm	±2σ	Pb ppm	±2σ	Pb ppm	±2σ	Pb ppm	±2σ
1	11	5	17	5	88	11	111	12	123	23	331	37	683	51	403	40	1197	70
2	11	5	12	5	87	11	111	12	122	23	332	36	630	50	436	41	1098	67
3	10	5	11	4	95	12	101	11	121	22	313	36	695	52	423	41	1212	72
4	13	5	10	4	93	11	115	12	109	22	329	36	676	50	401	40	1168	70
5	13	5	14	5	90	11	111	12	109	22	316	37	652	50	397	39	1229	73
6	15	5	14	5	86	11	110	11	115	23	331	37	634	50	399	39	1279	74
7	16	5	17	5	100	11	109	11	120	22	351	38	679	51	395	39	1131	68
8	15	5	13	5	100	11	122	12	104	22	331	38	674	51	391	40	1154	69
9	14	5	10	4	93	12	117	12	119	23	355	38	693	51	410	40	1136	69
10	13	5	16	5	83	12	109	12	98	21	330	36	675	51	438	41	1163	69
avg	13.1		13.4		91.5		111.6		114		331.9		669.1		409.3		1176.7	
stdev	2.0		2.7		5.8		5.6		8.6		13.0		22.8		17.1		53.3	
RSD (%)	15.0		20.0		6.3		5.0		7.5		3.9		3.4		4.2		4.5	
Certified Value	13.6±0.5		13.6±0.5		98±6		98±6		100±4		300±12		604±24		400*		1200*	

*PVC disks are distributed by Analytical Reference Materials International Corporation. The disks are not certified reference materials. Similar disks from the same vendor are supplied with the ThermoNiton XRF to be used to verify instrument performance.

±2σ= reported confidence interval for each reading based on a calculated +/-2 standard deviations of the stability of the count rate. Each measurement was done for 30 seconds.

Table 3. ICP Analysis and XRF Screening Results of Compliance Samples

Sample No.	Item	Digestion and ICP Analysis Pb mg/kg	XRF Analysis Pb mg/kg
09-304-6136	Tires	1080-1230	1210-1540
09-304-6139		130-170	170-190
09-304-6140-02	Tires	834	1180
09-304-6140-03	Tires	2621	3680
09-304-6142	Big tire	238-250	290
09-304-6142	Small tire	630-690	710-760
09-304-6145		1540-1590	1958-2138
09-304-6146-03		1860	2560±130
09-304-6146-04		1340	1873±115
09-304-6147		2170	2605
09-304-6148		1500-1800	1500-2000
09-304-6308	Green forceps	450-460	390-500
09-304-6309	Green scissors	400-490	450-490
09-304-6310	Green farm sign	740-880	700-850
09-304-6460	Yellow belt	2600-2770	2860-3870
09-304-6567	Basketball	21070-22640	29800-32700
09-304-6567	Football	6610-6780	11100-11500
09-304-6567-06-1		731	970
09-304-6567-06-2		161	177
09-304-6567-07-1		65	288
09-304-6567-07-2		932	752
09-304-6568-05	Penguin	1110	1797
09-304-6568-05	Dolphin	780	1202
09-304-6568-05	Shark	750	927
09-304-6568-05	Walrus	640	834
09-304-6568-08	Penguin	700	1038
09-304-6568-08	Dolphin	700	981
09-304-6568-08	Shark	750	968
09-304-6568-08	Walrus	660	917
09-304-6625	Monkey	1440	1314-1415
09-304-6626	Monkey	1380-1420	1298-1570
09-304-6627-03	Monkey	2050	2380-2495
09-304-6627-04	Monkey	60	<LOD
09-304-6643	Black	330-340	470-490
09-304-6643	Red	340-370	440-500
09-304-6635	Arm and leg	850	970-1050
09-304-6644	Black nut	90-110	80-120
09-304-6645-03	Nut	315	385
09-304-6645-03	Long screw	81	88
09-304-6645-03	Short screw	87	99
09-304-6645-07	Nut	74	113
09-304-6646-05	Nut	235	297

Table 3 Continued			
Sample No.	Item	Digestion and ICP Analysis Pb mg/kg	XRF Analysis Pb mg/kg
09-304-6646-05	Screw	94	97
09-304-6646-07	Screw	75	80
09-304-6647-03	Screw	73	77
09-304-6647-03	Nut	142	147
09-304-6647-05	Nut	135	166
09-304-6647-05	Screw	93	80
09-304-6655	Hard hat	132-154	155-176
09-304-6655	Buckle	102-196	121-258
09-304-6656	Necklace	332-365	113-440
09-304-6557	Chrome covered plastic	330-440	320-480
09-304-6558	Chrome covered plastic	500-520	505-545
09-304-6675	Horse and dog	1090-1470	1540-1730
09-304-6685	Green vinyl patch	2890-2910	2930
09-304-6691	Blue cat	720-750	810-830
09-810-8387	Buttons	5048-5410	3900-4400
09-810-8389	Buttons	3922-4052	2800-2900
09-810-8390	Buttons	3662-3967	2500-2600
09-810-8391	Buttons	2882-3024	2227±56
09-810-8392	Buttons	2943-2993	2250±56
09-810-8393	Buttons	2922-3018	2072±53
09-810-8394	Buttons	2913-2924	2236±56
09-810-8395	Buttons	2517-2645	1726±46
09-810-8396	Buttons	1529-1546	1128±40
09-810-8397	Buttons	2603-2858	1828±49
09-810-8398	Buttons	3938-4314	3128±72
09-810-8438	Buttons	2900-3100	1450-1750
09-810-8439	Buttons	2900-3100	1400-1650
09-810-8440	Buttons	2700-3030	3000-3300
09-810-8441	Buttons	2980	3000-3400
09-810-8442	Buttons	3020-3150	3040-3202
09-810-8443	Buttons	3080-3130	3100-3300
09-810-8444	Buttons	4808-4966	5100-5500
09-810-8445	Buttons	4122-4176	4300-4850
09-810-8446	Buttons	4662-5321	5400-5500
09-840-6769		206-213	230-350
09-840-9775		1160-2240	1467-3094

Table 4. ICP and XRF Analysis of Milled Plastic Samples

XRF	Standards			Samples							
	PL(PVC)1-1E(P)-1	PL(PVC)1-1E(P)-2	PL(PVC)1-1E(P)-3	PVC	NON-PVC	PVC	NON-PVC	PVC	PVC	PVC	PVC
replicate	PL(PVC)1-1E(P)-1	PL(PVC)1-1E(P)-2	PL(PVC)1-1E(P)-3	6265-02GL	6789CB	6265-02P	6263Y	6265-01P	6265-01S	6788cow	6788zebra
1	108	308	712	901	418	587	548	791	262	1407	1539
2	116	306	664	927	406	610	525	772	237	1366	1524
3	97	318	701	874	395	593	558	784	275	1351	1619
4	109	309	643	833	383	598	534	738	266	1407	1560
5	111	284	602	817	381	590	526	766	276	1338	1464
6	120	319	663	896	377	532	536	798	275	1354	1542
7	116	324	686	968	361	629	543	757	266	1381	1523
8	113	265	650	856	392	621	517	715	300	1389	1449
9	132	320	655	861	373	568	542	756	262	1358	1498
10	106	335	662	803	398	574	533	813	262	1330	1574
11	102	344	693								
12	106	308	705								
13	137	334	695								
14	129	342	660								
15	132	331	655								
16	129	325	629								
17	120	358	718								
18	114	344	650								
19	129	335	658								
20	124	320	714								
mean	117.5	321.45	670.75	873.6	388.4	590.2	536.2	769	268.1	1368.1	1529.2
std	11.3	21.5	31.0	50.9	16.8	28.0	12.1	29.2	15.9	27.0	50.6
Adjusted Mean *	105.6	290.7	607.8	791.9		534.6		696.9	242.3	1240.7	1386.9
ICP											
replicate				6265-02GL	6789CB	6265-02P	6263Y	6265-01P	6265-01S	6788cow	6788zebra
1	***	**	**	707	402	551	542	703	244	1262	1408
2				670	399	560	544	767	232	1292	1473
3				706	412	512	543	690	233	1074	1347
4					378					1198	1347
5					388					1176	1341
mean	100±4	303.6	614.3	694.3	395.8	541.0	543.0	720.0	236.3	1200.4	1383.2
std		4.8	28.8	21.1	13.1	25.5	1.0	41.2	6.7	84.8	57.2

*Adjusted mean determined using PVC standards with manufacturer certified values as calibration standards.

** These standards routinely run as control standards for lead analysis in polymer materials. The mean and standard deviation values determined from all analyses performed to date which exceed 20 replicates.

*** The value represents the certified value and uncertainty reported by manufacturer.

U.S. Department of Commerce
National Institute of Standards and Technology
Chemical Science and Technology Laboratory
Analytical Chemistry Division
Gaithersburg, MD 20899

REPORT OF ANALYSIS

March 20, 2009

*This report
has already
been released*

Submitted to: S. A. Wise, Chief
Analytical Chemistry Division

Title: Investigation of the use of X-Ray Fluorescence Spectrometry for
Determinations of Lead in Paint

Authors: J. L. Molloy, D. Cobb and J. R. Sieber

Constituents: Pb

Methods: Wavelength Dispersive X-Ray Fluorescence Spectrometry (WDXRF),
Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF), and
Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES)

Copies to: ACD DocuShare Intranet, J. Recht (CPSC)

Background: The NIST is assisting the Consumer Products Safety Commission with their efforts to investigate the use of XRF for determinations of Pb in paints. The CPSC has the authority to regulate the sales of children's products under the recently enacted Consumer Products Safety Improvement Act (CPSIA) of 2008. This act of Congress also gives CPSC the task of reporting on the efficacy of XRF for measuring the Pb contents of said products. The Inorganic Chemical Metrology Group (ICMG) of NIST volunteered to assist Dr. Joel Recht of CPSC and his staff by developing new Standard Reference Materials for Pb in paint. This task requires NIST XRF experts to learn about the formulation and application of paint and about the use of XRF to quantitatively determine the amount of Pb.

Dr. Molloy and Mr. Cobb have created paint films with guidance from J. Chin of the Materials and Construction Research Division of the Building and Fire Research Laboratory. These paint films consist of household latex paint spiked with either PbCO_3 or lead naphthenate. The goals were to learn how to apply thin films using a draw-down bar and to learn how to use WDXRF in the ICMG lab and handheld XRF using the CPSC instrument. Results for comparisons were available from an inductively coupled plasma optical emission spectrometry (ICPOES) instrument in the CPSC Gaithersburg laboratory. The information and experience gained from this effort will be applied to the design of new paint film SRMs by NIST and to the investigation of the performance of XRF instruments and software that are commercially available to

government agencies, testing labs, manufacturers of children's products and retailers of those products.

This report covers the XRF analyses performed at NIST using a wavelength dispersive spectrometer (WDXRF). The NIST WDXRF instrument is typical of those available today. It provides high resolution measurement capability coupled with high sensitivity for three key spectral lines of Pb: $L_{3-4,5}$ ($L\alpha_{1,2}$), L_{2-3} ($L\beta_1$), and L_{2-3} ($M\alpha_{1,2}$). The L-series lines are commonly used by portable and bench-top spectrometers for measurements of Pb. Some commercial instruments also use Pb K- $L_{2,3}$ ($K\alpha_{1,2}$) lines that cannot be accessed by the NIST WDXRF spectrometer due to their high energies. To the knowledge of the authors, the M-series lines are not used in handheld instruments due to their low energies, the low sensitivity afforded by using these lines, and the inherent surface specificity of measurements of low energy X rays. It is that surface specificity that is attractive in this investigation because it is desired to develop a method for quantifying the Pb mass fractions of thin paint layers. The CPSIA stipulates that Pb content of paint be assessed in units of "parts per million" which is taken to mean the SI units of mg/kg (or $\mu\text{g/g}$).

XRF methods typically report the amount of an analyte in a thin layer as mass per unit area, e.g. $\mu\text{g}/\text{cm}^2$, because energetic X rays are typically measured and the count rate of X rays is a function of both mass fraction and thickness of the specimen layer. Conversion between mass fraction and mass per unit area requires knowledge of the density of the layer (or layers) and the distribution of the Pb within the layer (or layers). By measuring two or more different X-ray lines for Pb, it is possible to derive some information about the layer thickness and the distribution of Pb in the specimen. This effort is aided by measurements of scattered primary radiation, viz. from the instrument's X-ray source, usually a tube source. By using the M-series lines, in addition to the L-series lines, it may be possible to determine the mass fraction of Pb directly at the same time as the mass per unit area is obtained. Because the derivations may require the information, attempts will be made to measure the thickness of the film and bulk density of dried paint.

Equipment: The following equipment was used to prepare paint films, cut specimens, and measure the specimens.

Draw-Down Bar: The bar was obtained on loan from CPSC. It is approx. 16 cm wide and constructed of aluminum alloy. Adjustments of bar height are made using two micrometers to move the bar attached under spring tension.

Hole Saw: Disks of polymethylmethacrylate (PMMA) were cut using a hole saw attachment for a drill press located in the 839 shop in building 227.

Pan Balance: NIST Mettler¹ PE1600 located in building 227, room A330, capacity 1600 g with lowest increment of 0.01 g.

¹Certain commercial equipment, instrumentation, or materials are identified in this poster to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Pan Balance: CPSC Mettler Toledo PG-503S, capacity 510 g with lowest increment of 0.001 g.

Semi-micro Balance: Sartorius MC 210 S located in building 227, room A330. The balance is maintained according to TP839.01-110.

Micrometer: Manual micrometer English units model manufactured by Scherr-Tumico, St. James, MN, USA. Currently, this micrometer is not calibrated using a traceable reference material.

Ultrasonic thickness gage: Positector model 200B manufactured by DeFelsko for determining polymer coating thicknesses nondestructively with a precision of $\pm 2 \mu\text{m}$. Attached probe sends out an ultrasonic pulse which is reflected by the substrate material. Assuming a polymer film, the speed of the pulse is known and the time for the reflected echo is measured to determine the thickness of a polymer layer.

Hydraulic Press: Two presses were used to prepare specimens. For high-precision preparation of specimens, a SPEC model 3630 automated press was employed. For pressing requiring more careful or slower application of lower pressures, a Beckman model OO press was used. In both machines, pressing was done using standard dies and die pellets constructed of steel in diameters of 31 mm and 13 mm.

Head-Over-Heels spinning apparatus: Manufactured by VOOR'T LABO in Belgium for mixing the contents of small bottles by rotating the bottle perpendicular to its axis of cylindrical symmetry.

Oven: Lindberg/Blue M Box Furnace model BF51842PBFMC located in building 227, room A330. Oven was set to 55 °C for curing paint samples before they were cut into subsamples for analysis.

Mixer: SPEX Industries mixer/mill catalog number 8000 located in building 227, room A344. This was used to mix paint samples for 5 minutes immediately before application to substrates.

Portable XRF Spectrometer: ThermoNITON model XL1, property of CPSC. The instrument is an EDXRF spectrometer, and it was calibrated by the manufacturer. Details of the calibration and calculations are not available.

WDXRF Spectrometer: PANalytical model PW2404 located in building 227, room A326. The spectrometer is maintained according to the manufacturer's specifications. The spectrometer performs to the manufacturing specifications for stability as demonstrated on a periodic basis. The spectrometer is equipped with a Rh anode, end-window tube capable of operation at up to 4 kW with a maximum potential of 60 kV or a maximum current of 125 mA. The calibration of this spectrometer is performed in accordance with TP-839.01-023.

Chemicals and Materials: The following chemicals were used in the preparation of specimens and calibrants for the experiments described in this report.

Latex Paint: Valspar brand, interior semi-gloss, white acrylic latex household paint. Ingredients listed on label are water, acrylic latex, titanium dioxide, ethylene glycol, and crystalline silica.

Lead Carbonate: Spectrum, ACS reagent grade powder.

Lead naphthenate: Alfa Aesar, lot number D205013, nominal concentration in 61 % mineral spirits, 24 % as Pb, formula: $\text{Pb}(\text{C}_{11}\text{H}_{17}\text{O}_2)_2$. Calculations show that the uncertainty in the mass fraction of mineral spirits must be 2 %.

Plastic sheet: Several different plastics in sheet form were used as substrates for paint films, as backing material for specimens, as blank specimens, and as calibrants.

- Polymethylmethacrylate (PMMA) - molecular formula $\text{C}_5\text{H}_8\text{O}_2$. Thick sheets (~ 6.5 mm) were used as the substrate for drawn films of household latex paint.
- Polyester - molecular formula $\text{C}_{10}\text{H}_8\text{O}_4$. The NIST paint film SRMs and commercial films of Pb metal are supported on polyester sheets.
- Acrylonitrile butadiene styrene copolymer - commonly known as ABS, several CRMs from Japan are composed of ABS.
- Polyethylene - low density polyethylene (LDPE) was used as the matrix for some calibrants custom made at NIST and containing Pb ethylhexanoate (see calibrants section).
- Polypropylene - several reference materials from PR China were used as calibrants.

Steel sheet: Galvanized, low alloy steel was used for the deposition of paint layers and as an absorber behind the Pb metal films on polyester. The sheet steel has a thick Zn coating from galvanizing. Pieces of SRM 1768 High-Purity Iron were used behind the SRM 2570 paint films before the sheet steel became available. Lead was not detected in either the steel or the iron.

Aluminum sheet: Aluminum alloy sheet containing 2 % Mg by mass was used for the deposition of paint layers and as an absorber behind the SRM paint films and the Pb metal films on polyester.

Calibrants: Calibrants consisted of SRM paint films, SRM powdered paint, SRM natural matrix materials, CRM polymers from the National Metrology Institute of Japan (NMIJ), and metal films on polymer substrates.

NIST SRM paint films: SRM 2579, set of four Pb paint films and one blank lacquer film on polyester sheets; NIST SRM 2579a, set of five Pb paint films and one blank lacquer film on polyester sheets; and NIST SRM 2576, one Pb paint film and one blank lacquer film on polyester sheets.

NIST SRM paint powders: SRM 2581 nominal 0.5 % Pb in paint, SRM 2582 nominal 0.02 % Pb in paint, SRM 2586 Pb paint in soil, and SRM 2587 Pb paint in soil.

NIST natural materials: SRM 1566a oyster tissue, SRM 1575 pine needles, and SRM 2583 household dust.

NMIJ CRMs: CRM 8105a and CRM 8106a Cd, Cr, and Pb in ABS resin. These materials are 30 mm diameter disks of approximately 2 mm thickness.

Metal films: Three reference materials were custom-made by Micromatter Inc., WA, USA. All are Pb metal deposited on 6.3 μm thick polyester sheets using an evaporative process and gravimetry. The three materials were designed to simulate coatings containing Pb in the range of 20 $\mu\text{g}/\text{cm}^2$ to 300 $\mu\text{g}/\text{cm}^2$.

Sampling Details: Each type of material was prepared in a different manner as described below.

Paint Film SRMs: One unit of each SRM composition was cut to provide either a square or a circle that covered the 17 mm diameter opening of a sample holder for the WDXRF spectrometer.

Powdered Paint and Natural Matrix SRMs: The powders were prepared as briquettes by pressing to 20 tons in a steel die. Briquettes of SRM 2581 and SRM 2582 were prepared from 0.5 g with no support to give thickness of approximately 300 μm . SRMs 1566a, 1575, 2583, 2586, and 2587 were prepared from 6 g in Al support caps to create briquettes of about 3 mm thickness.

Laboratory Prepared Paint Films: Four paints containing low levels of lead compounds were prepared at the CPSC laboratory on Nov 10, 2008 using white latex paint, lead carbonate, and lead naphthenate. The lead compound was added to a clean, tared bottle and weighed. Paint was then added to the bottle and weighed. Weighing measurements were conducted on the Mettler Toledo PG-503S balance. A magnetic stirring bar was placed in each bottle and the bottles were capped and the paint solutions were stirred for 2 hours. The bottles were then placed in a Head-Over-Heels spinning apparatus and spun at 75 rpm for 6 h. Table 1 lists the mass of the lead compounds and paint for each mixture, and the calculated Pb concentrations in wet paint. The rightmost column is the estimated combined standard uncertainty, u , of [Pb] based on uncertainty of weighing and the uncertainty of the Pb mass fraction in each compound.

The paint was applied to clean substrates as follows. The drawdown bar was washed with paint thinner to ensure the working surface was clean of dried paint. The height of the bar was set using micrometer screws. 2 mL to 3 mL of paint were poured on one end of the substrate. The drawdown bar was passed over the pool of wet paint and substrate, creating a wet film. Excess paint was drawn past the end of the substrate and the substrate was removed to air dry for 1 d. The sample was then allowed to cure for 5 d in an oven at 55 °C. Finally, subsamples were cut from the substrate using machine tools in the Division 839 shop.

Film thickness was determined using the ultrasonic depth gage detailed earlier. Film density was determined using the thicknesses obtained in conjunction with the mass of dried films peeled off substrates. The paint films peeled free of metal substrates leaving no visible residue. The density values obtained for peeled paint films were used for densities of paints applied to PMMA substrates at the same Pb concentrations. Paint was more difficult to remove from PMMA

substrates without accidental removal of the substrate itself or destruction of the film, so paint density was assumed to be relatively unchanged for a given Pb concentration. This contributed to some uncertainty in the paint film density values for PMMA samples.

Summary of Analytical Methods: Three test methods were used or developed by NIST and CPSC researchers. All NIST XRF analyses were performed using the PW2404 wavelength-dispersive spectrometer. The spectrometer is equipped with multiple masks for selecting the area of the specimen to be measured, multiple collimator for optimizing the resolution of secondary X-rays from the specimen, multiple crystals and diffracting structures for optimizing resolution and sensitivity, three detectors for optimizing sensitivity and selectivity. Measurement conditions were chosen to maximize sensitivity, minimize counting statistical uncertainty (CSE), and minimize spectral interferences.

Pb L-Series Lines: Typical spectrometers designed specifically for Pb measurements are optimized for measuring the Pb L-series and Pb K-series characteristic lines. The excitation of K-series lines requires primary source energy in excess of 90 keV. This is not possible with the PW2404 spectrometer. Excitation of the L-series lines requires source energy in excess of 16 keV, which is possible. No known portable or benchtop spectrometers for Pb analyses utilize the Pb M-series X-ray lines. These lines are low energy (2.3 keV to 2.5 keV), and are of lower inherent sensitivity because they are absorbed strongly by air and their fluorescence yields are lower than those for K-series and L-series lines.

The PW2404 spectrometer is well-equipped for excitation and measurement of L-series and M-series lines of Pb because it has a Rh anode X-ray tube. Rh K-series X rays are well suited for causing fluorescence of Pb L-series X-rays, and Rh L-series X rays are well suited for causing fluorescence of Pb M-series lines. In addition, the Rh K-series lines are measured for use as internal references in a manner similar to an internal standard, but without the need to spike something into each specimen.

Measurement conditions were established for Pb $L_{\alpha_{1,2}}$, Pb L_{β_1} , one background location on each side of each peak, Rh K- $L_{2,3}$ ($K\alpha_{1,2}$) Rayleigh peak, and Rh $K\alpha_{1,2}$ Compton peak. Peak locations were chosen from scans of both high concentration and low concentration specimens. To the extent possible, the measurement condition settings were kept constant for all of these measurements. See Table 2 for the measurement conditions.

Medium resolution collimation was used to resolve the spectral interferences from the L-series peaks and background locations. For the Pb $L_{\alpha_{1,2}}$ peak, significant interferences include Bi L-series lines at the high energy tail of the Pb peak and Ba K-M lines (3rd order diffraction) near the low energy tail of the Pb peak. These Ba lines are of little consequence because 3rd order diffraction yields very low intensity. Selection of the background measurement angles is complicated by Sr K-L lines on the high energy side of the Pb peak and Rh K-M lines (2nd order) on the low energy side. The potential background interferences are far enough from the Pb peak to cause no significant problems. For the Pb L_{β_1} , the only significant, potential interferences are with background location selection. Se $K\alpha_{1,2}$ lines are on the high energy side of the Pb peak and Rh $K\alpha_{1,2}$ (2nd order) lines are on the low energy side. For this work, the high energy

background angle was chosen near to the Se lines because additional, more likely interferences exist at higher angles.

Background measurement is complicated by the wide variety of specimen compositions and by the requirement for low detection limits for the measurement process. Both Pb peaks require two background measurements bracketing the Pb peak because the background slopes either upward in count rate or downward with increasing goniometer angle. The direction of slope and rate of change with angle depend on the matrix composition of the specimen, including the substrate beneath the coating layer(s). Background counting times must be high to maximize the detection limits. Targets for detection limits were set to 5 mg/kg to 10 mg/kg. Again, condition settings are given in Table 2. Background count rates must also be minimized to improve detection limits. The choice of medium collimation reduces background at the expense of sensitivity, but sensitivity is more than adequate using the L-series lines. Background can also be reduced by careful selection of the discriminator setting for pulse height selection.

Pb M-Series Lines: The Pb M-series lines require a different set of measurement conditions. For the X-ray tube, low voltage (25 kV) and high current (125 mA) are optimum because those settings create a strong set of Rh L-series lines from the anode. These Rh lines enhance fluorescence of the Pb M-series lines. The Pb line being measured is Pb $L_{2,3}$ ($M\alpha_{1,2}$). The most important spectral interference is the S $K\alpha_{1,2}$ peak that partly overlaps the Pb $M\alpha_{1,2}$ peak on its low energy tail when the mass fraction of S is high. Because there are other interfering lines on the high energy side of the Pb peak, a single background angle must be chosen far enough below the S peak energy that the tail of a strong S peak will not interfere with background measurement. In this case, the background angle is $10^\circ 20'$ greater than the Pb peak angle.

Measurement Geometry: The area of measurement was chosen to be approximately the same as the typical area viewed by a handheld spectrometer. A channel mask of 17 mm inner diameter was chosen to measure all specimens. Inside the PW2404 spectrometer, the X-ray tube illuminates the specimen and its holder over a diameter of approximately 45 mm from an angle of 45° below the horizontal surface of the specimen. A set of masks are positioned to intercept the secondary X rays at an angle 90° from the axis of the X-ray tube and 45° from the horizontal surface of the specimen. Because the X rays are collected from a take-off angle of 45° with respect to the surface of a sample, the effective escape depth of measured X rays must be considered in that same direction. This works to the advantage of the analyst when measuring thin specimens because the thickness of the layer must be divided by the cosine of 45° to estimate the thickness in the viewing direction. For the Pb $M\alpha_{1,2}$ X rays, the thickness of paint that attenuates 100 % of the X rays is approximately 112 μm [1]. This is called "infinite thickness" because no X rays can pass completely through the material. When the viewing angle is 45° from the surface, a layer 80 μm thick appears to be infinitely thick for that energy of X rays. Under conditions of infinite thickness, the count rate is a function of mass fraction only.

Measurement Time: Measurement times were calculated by the SuperQ software on the basis of data collected by scanning low concentration specimens and choosing the required detection limit, in this case 10 mg/kg because the method must be capable of quantifying 90 mg/kg Pb. Again, see Table 2 for the calculated times.

Calibrations: Quantitative calibrations were based on the general algorithm shown in Equation 1. Detailed listings of the parameters for the analytes are stored in the PANalytical SuperQ software in calibration file *lead_films* and in the Excel spreadsheet *leadfilm.xls*.

$$C_i = D_i + E_i R_i + F_i R_i^2 \quad (1)$$

where C_i = the concentration of analyte i in mass fraction or mass per unit area,

D_i = the intercept,

E_i = the coefficient of the linear term,

R_i = the measured count rate for the analyte

F_i = the coefficient of the quadratic term

It is well known that the relationship between measured count rate and specimen mass per unit area is nonlinear when the specimen thickness is less than the infinite thickness for the X-ray energy and the material composition. Typical correction could be applied to account for varying amounts of scattered X-rays from substrate materials. However, plotting instrument response versus concentration gave virtually identical results regardless of the substrate used. This is observed by the similar instrument responses for all substrates shown in Figure 1 and Figure 2. Furthermore in the region of interest (Figure 1b and Figure 2b), the calibration for all three substrates could be assumed to be linear.

It is possible to prepare a number of calibration curves for determinations of either mass per unit area of Pb or mass fraction of Pb. First, the discussion will cover the Pb L-series lines used for determinations of mass per unit area. Second, the discussion will turn to using the Pb M α line for determinations of mass fraction Pb in a layer.

Pb L-Series Lines:

All six curves were fit to data measured from paint film SRMs 2570 through 2579a, excluding SRM 2571, SRM 2576, and SRM 2579 Level I. The SRMs were excluded because the curves are not linear above 2000 $\mu\text{g Pb/cm}^2$ and it seemed appropriate to use standards which were within a similar concentration regime as the samples measured. Reference materials from Micromatter prepared by evaporation of Pb metal onto polyester sheet were also included because there are no available paint films having less than 290 $\mu\text{g Pb/cm}^2$. Figure 1a and Figure 2a both show a polynomial fit using all the standards, while Figure 1b and Figure 2b use linear fits additionally excluding SRM 2572, SRM 2573, and SRM 2579 Levels II and III. The intercepts of all curves in Figure 1b and Figure 2b were set equal to the intercepts obtained by fitting just the data from the Micromatter and blank SRM specimens. The reason for locking the intercept is that XRF data is heteroscedastic. During the regression to fit a curve, the lowest concentration points should be weighted more heavily than the higher points. However, it is quite difficult to perform weighted regressions using Microsoft Excel. It is much simpler to force the curve through a fixed origin. For both Figures, one of the three curves in each Figure is data measured from specimens with plastic disks behind them, another with aluminum sheet

placed behind the specimens, and a third with steel disks behind the specimens. Count rates are virtually identical for all three substrates, suggesting that no correction for scattered X-rays from the substrate is necessary.

Comparisons of specimens can be made by calculating the ratio of the Pb $L\alpha$ and $L\beta$ net count rates because the Pb $L\beta$ X rays are more penetrating than the $L\alpha$ X rays. The ratio of the Pb L lines count rates may provide a clue about whether Pb is present in the layer, the substrate, or both. For example, a plastic toy with a blue coating gave a result 50 % greater for the net $L\beta$ count rate than for the net $L\alpha$ count rate. It was found that the plastic contained at least as much Pb as the coating did. This example is in contrast to Figures 1 and 2 where the Pb containing standards on Pb-free substrates gave higher count rates for Pb $L\alpha$ X rays than Pb $L\beta$ X rays. In either case, it is critical to have some knowledge of the paint layer thickness so that a determination can be made regarding the substrate's role in calibration. A layer may be thin enough that its effects on the primary radiation are negligible compared to those of the substrate. These effects as well as the mass absorption coefficients are typically included in a calibration model of an X-ray spectrometer intended for determinations of coating thickness. A brief, informative discussion may be found in a recently published book on portable X-ray spectrometers [2].

When specimens are less than infinitely thick with respect to the distances traveled by the measured X rays in the matrix, it is common to correct for the effect by calculating the ratio of the analyte count rate to the count rate of an internal reference line such as the scattered, primary Rh radiation from the X-ray tube. However, this approach only works when the thin specimens have no supporting substrate or when all have the exact same substrate composition. For the paint films prepared for these experiments, the substrates absorb the primary X rays to very different extents. Steel absorbs Rh X rays more strongly than aluminum and much more strongly than PMMA. Therefore, the count rates of Rh radiation can be used as an indicator of the nature of the substrate beneath the paint layer(s). However, the scattered radiation cannot be used to correct for the thickness of the paint layer unless all substrates are the same composition and thickness among all specimens and calibration standards.

Pb M-Series Lines: Figure 3 is a calibration curve for Pb $M\alpha_{1,2}$ data from what are essentially bulk specimens of powdered paint and natural material SRMs. That is, the briquettes of these SRMs are more than thick enough to be infinitely thick for Pb $M\alpha_{1,2}$ X rays. The curve does not include data from paint film SRMs for two reasons. There are no mass fraction values available for the paint films, and the protective polymer film on each SRM sheet absorbs > 85 % of Pb $M\alpha_{1,2}$ X rays. If any products have a protective, Pb-free layer applied to their surface, it would not be possible to obtain accurate results using the Pb M-series lines.

Figure 3 is used to illustrate the behavior of Pb $M\alpha_{1,2}$ X rays as the quantity of Pb increases in a thin specimen. This curve represents data measured for the Micromatter reference materials. The horizontal axis is the mass of Pb (μg) estimated to be present in the measured area of each film. The shape of the curve illustrates the response as the number of Pb atoms in a thin layer is increased. However, the curve cannot be compared to measurements of coatings because Pb atoms in a coating are surrounded by a polymer matrix that strongly absorbs low energy X rays

such as $Pb M\alpha_{1,2}$. A fully successful calibration using measurements of $Pb M\alpha_{1,2}$ must include the effects of the matrix in which the Pb atoms reside as well as the effects of layers that are less than infinitely thick for $Pb M\alpha_{1,2}$.

Mass fraction results given in the report were determined using the calibration in Figure 4. This was done in spite of the fact that some of the specimens were not infinitely thick for Pb M-series X rays ($<80 \mu\text{m}$) because the research was designed to show trends and to illustrate the numerous complications of XRF analyses of thin specimens. Later in the report, the calculated results are compared to ICPOES results obtained at CPSC for the purpose of testing the limitations of XRF analyses using Pb M-series lines. It was never a goal to obtain high accuracy results in this manner.

Results for Lead in Latex Paint Films: Determinations of mass fraction and mass per unit area were performed on the paint films prepared at NIST using latex paint spiked with $PbCO_3$ or lead naphthenate. The results are collected in a series of tables, Table 3 through Table 6, one for each substrate type, plus one for the repeatability measurement results. Summaries of the results are shown in Figure 5 through Figure 7. For comparison to CPSC ICPOES results in the Figures, thickness measurements from Table 7 were used in conjunction with a measured average paint film density of 1.4 g/cm^3 to convert from mg/kg to $\mu\text{g/cm}^2$.

Table 3 and Figure 5 show the results obtained for paint applied to a PMMA substrate. All paint films were applied with the drawdown bar set to 25 mils ($640 \mu\text{m}$). Sample identifiers starting with 1 and 2 were spiked with $PbCO_3$, while 3 and 4 denote spiking with lead naphthenate. The "A" and "B" identifiers indicate agitation of the container of paint before use, with "A" samples agitated for 5 minutes and "B" samples not being agitated. The agitation did not appear to have a significant effect. The linear calibrations shown in Figure 1b and Figure 2b were used for value assignment for the $Pb L\alpha$ and $Pb L\beta$ lines while the calibrations from Figure 4 was used for value assignments using the $M\alpha$ line.

It is evident from looking at Table 3 that similar results are obtained for Handheld XRF and WDXRF measurements for the paint films on PMMA. Comparison to ICPOES also shows similar results in Figure 5. The error bars shown in Figure 5 are only indicative of the standard deviation of the samples, with the "A" and "B" samples combined for each concentration. It is also important to note that while the Handheld XRF and WDXRF results are for the same samples, ICPOES results are for different samples from the same drawdown, and may have different concentrations due to the method of preparation.

Table 4 and Table 5 give the results for analysis of paint films on metal substrates. In this case the film thicknesses were varied. The lead naphthenate spiked paint used for the application to PMMA was used. The $PbCO_3$ was not used in the interest of limiting the number of samples and because the lead naphthenate spiked paint showed better reproducibility with different digestion types for ICPOES.

The most significant item in this collection of data is that the Handheld XRF instrument was not able to detect Pb on either of the substrates spiked with 50 mg/kg lead naphthenate. This is a

concern as the dried paint films at this level would have a concentration similar to the regulatory limits set by the CPSIA. Figure 6 and Figure 7 summarize the results for paint films on Steel and Aluminum respectively. For both substrates, the results for WDXRF and ICPOES are similar at the lower concentration level (Figure 6a and Figure 7a), and higher concentration levels (Figure 6b and Figure 7b).

The results of using the Pb M line are shown in Figure 8 and 9. It is evident that the lower concentration (50 mg/kg) Pb containing paint films show agreement with the ICPOES analysis. However, at higher Pb concentrations the two techniques do not agree. One probable explanation is that during drying, the Pb is partitioning into the topmost regions of the paint films. The Pb M X rays are indicative of the Pb concentration near the surface while the ICPOES results give a result where any depth heterogeneity is eliminated by sample preparation. While this is a possible explanation, it does not seem as likely as a calibration problem. Because most of the paint films are still less than infinite thickness (80 μm), depth heterogeneity should not play a significant role. It is more probable that other interferences such as matrix effects are causing the WDXRF measurements to be erroneously high. Further study using fundamental parameters and taking into account mass absorption coefficients would be expected to yield more accurate results.

Repeatability of Using Different Spectrometers: The repeatability standard deviation was calculated for 10 measurements of a single location on a single specimen of Pb-spiked paint on each of the three substrates used. The test was done with the PW2404 spectrometer and with the ThermoNITON handheld spectrometer. The results are provided in Table 6 where the individual results (for the L β line) are listed along with the mean for each sample, the standard deviation of the 10 results, and the relative standard deviation (RSD). Only two different samples within the same drawdown were measured by ICPOES, once with each digestion procedure, and do not represent an attempt to determine repeatability.

It is clear that the WDXRF spectrometer provided more repeatable measurements, and there are several reasons why this was expected. The WDXRF spectrometer has much greater sensitivity resulting in higher count rates. Counting times were optimized for low detection limits, which in turn, results in lower counting statistical uncertainty according to Poisson statistics. The handheld spectrometer is configured for fast analyses of 30 s or 60 s. Its software can be set to choose a longer time when a low count rate is encountered. However, the count rates are typically very low and relative counting uncertainty is $> 1\%$ and possibly $> 5\%$. By comparison, WDXRF relative counting uncertainty is typically $< 1\%$. An additional source of variance in the use of the handheld unit is movement of the instrument and analyst possibly resulting in small changes to measurement angle and location on the specimen. In contrast, the WDXRF spectrometer loaded the specimen and measured it repeatedly before unloading it. The only noted change was damage to the paint surface in the form of roughness due to apparent outgassing in the heated vacuum chamber.

The repeatability measurements were also made on one sample of Pb-free paint film, sample A3. Table 6 shows results from the WDXRF measurements of a "blank" sample, but not from other techniques. The handheld spectrometer reported a 'less than' value when no Pb X rays were

counted. In two minutes measuring time, the reported value is $< 0.7 \mu\text{g Pb/cm}^2$. The WDXRF results for mass per unit area are positive values, but they are less than the limit of quantification and near the detection limit for each Pb line. While the RSD values for 10 measurements of the blank and lower concentration standards were high (14% - 51%), the WDXRF was able to measure the amount of Pb present while the handheld spectrometer was not able to give any data.

Sample Homogeneity: The largest contributor to uncertainty of the amount of Pb in a given paint film was the variance of the deposition of Pb across a substrate within a single drawdown. While it can be observed that the drawdown to drawdown variability is not high from looking at the "A" and "B" samples on PMMA, the variability of samples within a given drawdown can be quite significant. Examples of this would include samples 3-15-1 in Table 4 and samples 3-25-1 through 4 in Table 5. Such variation could be caused by uneven dispersal of the paint pool on the substrate before the drawdown bar is passed over it. Additionally if the drying surface was not completely level, or the substrate not completely flat, paint dispersal during drying could have become uneven. Variability of the dried paint film thickness is also evident from Table 7, with variability of the film thickness ranging from 30 % to 60 % for a given wet film thickness.

Conclusions: The following statements can be made about determinations of Pb in paint and similar layered coatings based on the information in this report and the studies that lead to the accumulation of said information.

1. This exercise was designed and carried out for the purpose of self education of the authors because they began the project with minimal experience with paint films and needed to be able to specify and obtain candidate materials for new SRMs within approximately six months.
2. WDXRF spectrometers have the resolution and sensitivity to determine Pb in layers and substrates at mass fractions and mass per unit area values below the levels accessible with the handheld instrument evaluated.
3. XRF calibrations are easily established for mass per unit area using available materials, i.e. deposited Pb metal films and NIST SRM 2570 series paint films on various substrates. The responses are linear for mass per unit area in the region of interest, and sensitivity is not affected significantly when the substrate is changed.
4. The handheld XRF instrument tested in this exercise has limited sensitivity and is programmed to do the job rapidly. It was unable to report mass per unit area values low enough for the CPSC regulation. Without knowledge of how to override the programming, it is impossible to test the true capabilities of the instrument.
5. The ICPOES test method used by CPSC can be used to obtain mass per unit area results comparable to those obtained using WDXRF. The results from the handheld instrument are similar, but of lower precision partly as a result of the instrument's programming.
6. To compare XRF and ICPOES results, it is necessary to obtain the thickness and density of the layer being tested. In this work, the results appear to be useful, but the limits could not be determined relative to the new regulations for Pb in/on children's products.
7. The Pb $M\alpha$ line may be useful for direct determination of the mass fraction of Pb in a paint layer. The measured count rate of this X-ray line is subject to matrix effects from other constituents of the layer. Correction of matrix effects was not included in this study as is

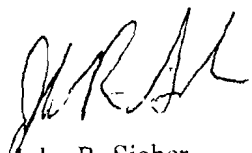
easily seen in the scatter of points in Figure 4 and disagreement between techniques in Figure 9. In addition, it is expected that many coatings on children's products are much thinner than the infinite thickness for Pb M-series X rays in paint and similar materials.

8. Even with a low level of experience, it was possible to prepare useful paint film samples using the drawdown technique. However, it is obvious that additional measures must be taken if a uniform paint film thickness is desired. In many cases, the paint layer thickness varied at least 30% over the course of only a single drawdown. While additional variance was not observed between samples from multiple drawdowns (in the case of PMMA), the need to measure Pb in terms of mass fraction requires much tighter control of the paint layer thickness.
9. The levels of Pb within single drawdowns were not homogeneous. This appears to be a separate issue from the uniformity of layer thickness as unpredictable Pb concentrations were observed independent of the emission line used for calibration. It is not obvious if this heterogeneity was a result of incomplete mixing/dissolution of the Pb in the paint or a result of uncontrolled variables during the drying process.

References: Project data and document files are stored on the Docushare ACD intranet. The data are stored in Excel spreadsheets: "leadfilm.xls" for the original data. Raw data and locations of subsamples upon each drawdown samples are located in lab notebook #839803 pgs 101-125.

- [1] web applet: "X-ray Interactions with Matter" http://henke.lbl.gov/optical_constants/ accessed December 2008. Based upon: B.L. Henke, E.M. Gullikson, and J.C. Davis. *X-ray interactions: photoabsorption, scattering, transmission, and reflection at E = 50-30000 eV, Z = 1-92*, Atomic Data and Nuclear Data Tables Vol. 54 (no.2), 181-342 (1993).
- [2] Potts, Philip J. and Margret West. *Portable X-ray Fluorescence Spectrometry*RSC Publishing, Cambridge, UK. (2008).
- [3] TP-839.01-023 XRF Calibration Procedures
- [4] PANalytical SuperQ software version 3.0, Almelo, The Netherlands.

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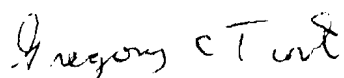
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Table 1. Quantities of ingredients in latex paint

Bottle	Compound	Compound (mg)	Paint (g)	Pb from Compound (mg)	[Pb] (mg/kg)	μ_{Pb} (mg/kg)
1	Lead Carbonate	43	299.8	33	111	2
2	Lead Carbonate	87	335.7	67	201	2
3	Lead Naphthenate	63	299.4	14	48	2
4	Lead Naphthenate	140	169.0	32.2	191	8

Table 2: Measurement conditions for PW2404

General conditions				Quantitative conditions			
Vacuum lock time (s):	4	Measure in decreasing energy order:		Yes			
Delay time (s):	4			Spinner on: Yes			
Analysis medium:	Vacuum			Calibration: lead films			
Collimator mask (mm):	17			Calibration update: <None>			

Quantitative program										Offsets				
Channel	Type	Line	X-tal	Collimator	Detector	Tube filter	kV	mA	Angle (°2 θ)	Bg1 (°2 θ)	Bg2 (°2 θ)	PHD LL UL	Att	PSC
Pb1	Gonio	M α	Ge 111-C	300 μ m	Flow	None	25	48	107.9946	10.0		32 70	No	Yes
Pb	Gonio	L α	LiF 200	300 μ m	Scint.	None	60	20	33.8726	-1.8	2.5	20 80	No	Yes
Pb2	Gonio	L β ₁	LiF 200	300 μ m	Scint	None	55	22	28.1886	-2.4	2.5	20 80	No	Yes
Rh2	Gonio	K α -C	LiF 200	100 μ m	Scint	None	60	20	18.3194			30 70	No	Yes
Rh1	Gonio	K α	LiF 200	100 μ m	Scint	None	60	20	17.4440			25 70	No	Yes

Channel	Time (s)	CSE (%)	Bg Factor	Bg const (kcps)	Bg of channel	Bg Method
Pb1	110					Fixed factors
Pb1Bg1	90		1.0000			
Pb	110					Fixed factors
PbBg1	16		0.5814			
PbBg2	10		0.4186			
Pb2	110					Fixed factors
Pb2Bg1	20		0.5102			
Pb2Bg2	16		0.4898			
Rh2	60					None
Rh1	60					None

Notes:

- Gonio = Goniometer
- Offsets = degrees from peak to measure background
- PHD = Pulse Height Discriminators
- Att. = Attenuator
- PSC = Pulse Shift Correction
- Ge 111-C = Ge crystal, 111 cut Curved
- LiF 200 = Lithium fluoride, 200 cut
- K α -C = Compton scatter peak from K α line
- CSE = Counting Statistical Error

Table 3: Results of analysis of paint films on PMMA substrate

Sample Name	Pb spiked into wet paint mg/kg	Form of Pb added	Handheld XRF $\mu\text{g}/\text{cm}^2$	WDXRF			ICPOES mg/kg
				Pb L α	Pb L β	Pb M α	
				$\mu\text{g}/\text{cm}^2$	$\mu\text{g}/\text{cm}^2$	mg/kg	
1A1	100	PbCO ₃	1.9	3.1	2.6	119	150
1A2	100	PbCO ₃	1.1	2.4	1.8	126	160
1A3	100	PbCO ₃	2.0	2.5	1.9	124	
1B1	100	PbCO ₃	1.9	2.2	1.3	87.0	120
1B2	100	PbCO ₃	1.1	2.1	1.1	85.9	100
1B3	100	PbCO ₃	2.0	2.3	1.4	67.4	
1B4	100	PbCO ₃	1.3	2.5	1.7	109	
2A1	200	PbCO ₃	3.9	4.6	4.0	303	260
2A2	200	PbCO ₃	4.5	4.7	4.0	288	290
2A3	200	PbCO ₃	2.3	4.0	3.7	313	
2A4	200	PbCO ₃	3.2	4.5	4.0	370	
2B1	200	PbCO ₃	3.8	4.5	3.8	316	280
2B2	200	PbCO ₃	3.9	4.3	3.8	311	280
2B3	200	PbCO ₃	2.9	4.5	3.9	310	
2B4	200	PbCO ₃	3.1	4.3	3.7	337	
3A1	50	Lead Naphthenate	1.4	2.1	1.5	107	120
3A2	50	Lead Naphthenate	1.2	2.0	1.4	121	120
3A3	50	Lead Naphthenate	1.2	2.1	1.4	115	
3B1	50	Lead Naphthenate	1.5	2.2	1.5	101	120
3B2	50	Lead Naphthenate	1.8	2.3	1.2	106	110
3B3	50	Lead Naphthenate	1.6	2.4	1.4	99.0	
4A1	200	Lead Naphthenate	9.8	8.6	8.5	591	460
4A2	200	Lead Naphthenate	8.6	8.2	8.0	581	440
4A3	200	Lead Naphthenate	9.5	8.2	8.1	578	
4B1	200	Lead Naphthenate	8.1	8.1	8.1	589	470
4B2	200	Lead Naphthenate	8.2	7.8	7.9	595.3	520
4B3	200	Lead Naphthenate	7.8	8.8	8.6	590	
4B4	200	Lead Naphthenate	7.7	8.0	7.8	584	

Table 4: Results of analysis of paint films on Steel substrate

Sample Name	Wet Film Thickness	Handheld XRF	WDXRF			ICPOES
	μm		Pb L α	Pb L β	Pb M α	
		$\mu\text{g}/\text{cm}^2$	$\mu\text{g}/\text{cm}^2$	$\mu\text{g}/\text{cm}^2$	mg/kg	mg/kg
3-10-1	250	-	0.8	1.0	112	128
3-10-2	250	-	0.8	0.9	119	103
3-10-3	250	-	0.8	0.9	95.4	116
3-10-4	250	-	0.6	0.7	101	111
3-15-1	380	-	1.1	1.2	244	150
3-15-2	380	-	0.8	1.0	109	124
3-15-4	380	-	0.9	1.0	106	113
3-15-5	380	-	0.9	1.0	104	117
3-15-6	380	-	0.8	0.9	108	
3-25-1	640	-	1.2	1.6	95.4	121
3-25-2	640	-	1.4	1.6	101	120
3-25-3	640	-	0.4	0.5	111	112
3-25-4	640	-	0.4	0.6	108	112
3-25-5	640					110
3-25-6	640					115
4-10-1	250	1.9	2.7	2.8	653	531
4-10-2	250	3.1	3.5	3.7	797	426
4-10-3	250	3.5	2.6	2.9	666	480
4-10-4	250	3.5	3.5	3.7	876	490
4-10-5	250	3.1	2.9	2.9	691	
4-15-1	380	5.1	4.4	4.8	625	484
4-15-2	380	4.3	4.6	4.9	579	464
4-15-3	380	3.9	4.4	4.7	618	468
4-15-4	380	4.6	4.4	4.9	629	469
4-25-1	640	5.7	5.3	5.8	605	491
4-25-2	640	6.4	6.2	6.8	630	474
4-25-3	640	8.3	7.5	8.4	646	455
4-25-4	640	8.7	7.6	8.7	612	445

Table 5: Results of analysis of paint films on Aluminum substrate

Sample Name	Wet Film Thickness	Handheld XRF	WDXRF			ICPOES
			Pb L α	Pb L β	Pb M α	
	μm	$\mu\text{g}/\text{cm}^2$	$\mu\text{g}/\text{cm}^2$	$\mu\text{g}/\text{cm}^2$	mg/kg	mg/kg
3-10-1	250	-	0.5	0.7	104	123
3-10-2	250	-	0.7	0.7	121	129
3-10-3	250	-	0.9	0.8	106	113
3-10-4	250	-	0.7	0.7	111	156
3-15-1	380	-	1.0	1.1	112	137
3-15-2	380	-	1.2	1.3	108	133
3-15-3	380	-	1.1	1.3	125	122
3-15-4	380	-	0.8	0.7	123	123
3-25-1	640	-	0.4	0.5	138	121
3-25-2	640	-	2.5	2.7	584	124
3-25-3	640	-	0.9	1.0	315	115
3-25-4	640	-	1.1	1.2	193	115
4-10-1	250	2.6	3.5	3.6	639	490
4-10-2	250	2.4	2.8	3.0	630	499
4-10-3	250	3.3	3.7	3.9	630	493
4-10-4	250	2.6	3.2	3.5	664	459
4-15-1	380	3.9	5.9	6.1	872	381
4-15-2	380	4.3	4.9	5.2	860	487
4-15-3	380	4.2	4.8	5.0	753	601
4-15-4	380	5.1	5.6	5.8	733	469
4-25-1	640	6.8	6.9	7.5	613	524
4-25-2	640	6.4	4.1	4.3	607	502
4-25-3	640	7.0	6.4	7.0	632	469
4-25-4	640	7.3	7.5	8.4	604	452

Table 6: Repeatability for measurements made on paint standards using PW2404 WDXRF and ThermoNiton XL T handheld XRF

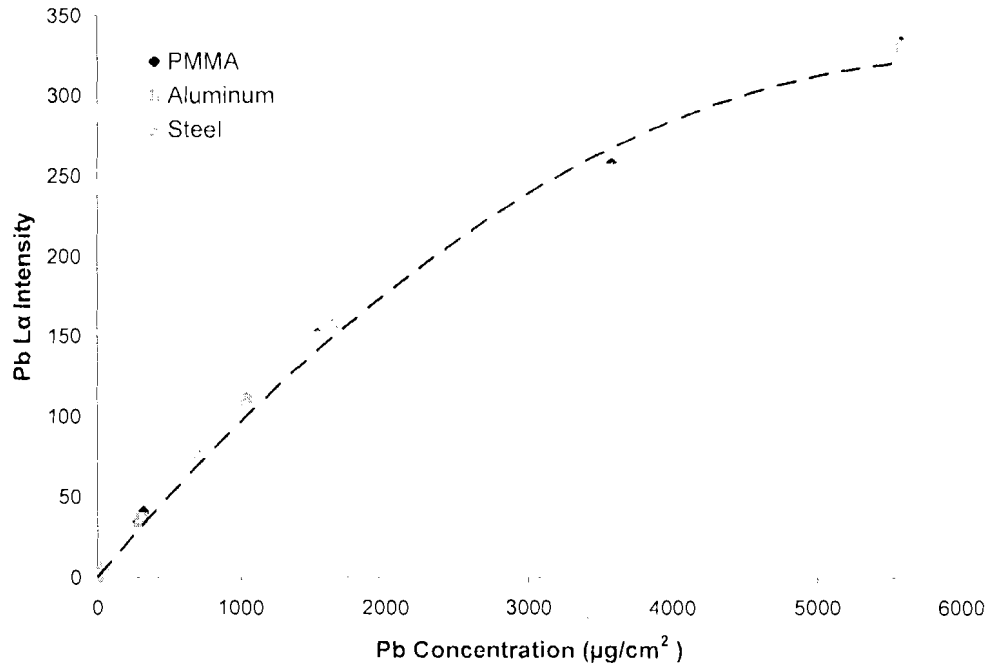
Substrate	Handheld	Handheld	WDXRF	WDXRF	WDXRF	WDXRF	WDXRF	WDXRF
	PMMA	Aluminum	PMMA	PMMA	Aluminum	Aluminum	Steel	Steel
Sample Name	4A1	4-25-1	A3	4A1	3-25-1	3-10-3	3-10-2	4-25-2
	9.8	6.8	-0.1	0.8	0.5	0.9	6.8	8.5
	9.1	7.0	-0.2	1.0	0.4	0.8	6.9	8.5
	9.0	6.6	-0.2	1.1	0.4	0.9	6.9	8.2
	8.4	8.0	-0.5	0.9	0.4	0.9	6.8	8.7
	8.1	6.4	-0.3	1.0	0.4	1.1	6.9	8.6
	9.2	7.4	-0.3	0.9	0.5	1.0	6.9	8.7
	8.8	6.0	-0.2	1.0	0.4	1.0	6.9	8.5
	9.3	7.3	0.0	0.9	0.5	0.9	6.9	8.6
	7.7	7.7	-0.4	0.9	0.6	0.9	6.9	8.6
	8.9	6.4	-0.2	1.0	0.4	0.9	6.9	8.4
\bar{X}	8.8	7.0	-0.24	1.0	0.5	0.9	6.9	8.5
s	0.6	0.6	0.12	0.1	0.06	0.1	0.1	0.1
RSD (%)	6.8	8.6	-51	7.9	14	7.7	0.73	1.7

Table 7: Paint film thickness measurements on different substrates

	Wet paint thickness (μm)	Average thickness after drying (μm)	Standard deviation of thickness (μm)
Plastic	640	104	30
Aluminum	250	35	10
	380	58	15
	640	103	29
Steel	250	49	10
	380	54	12
	640	89	53

Figure 1: Calibration curves using Pb L α line for three different substrates for a) all standards used and b) the concentration region of interest

a)



b)

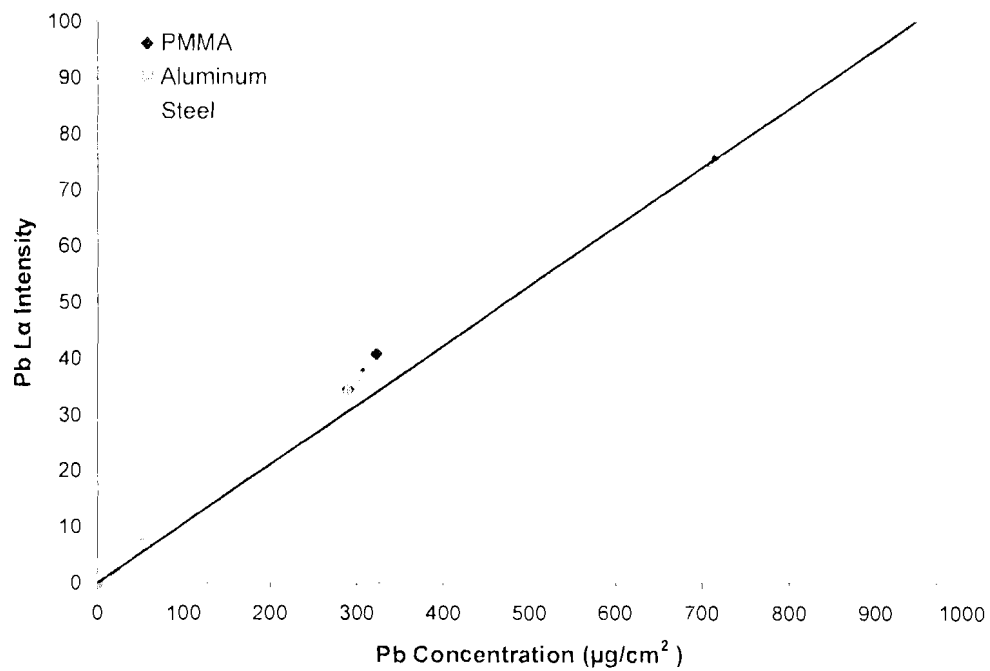
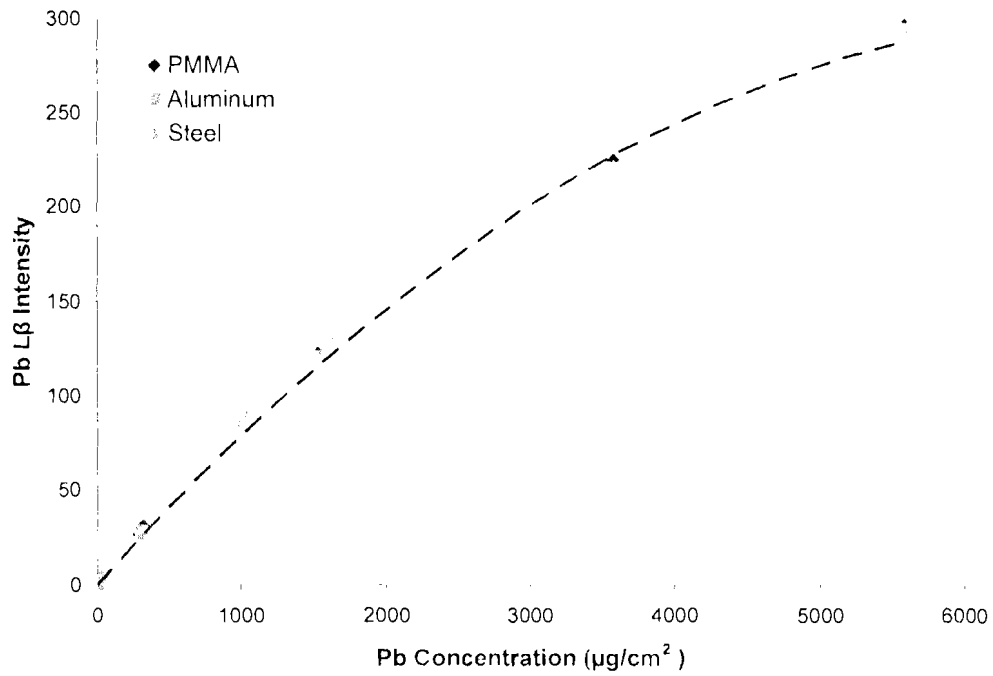


Figure 2: Calibration curves using Pb I, β line for three different substrates for a) all standards used and b) the concentration region of interest

a)



b)

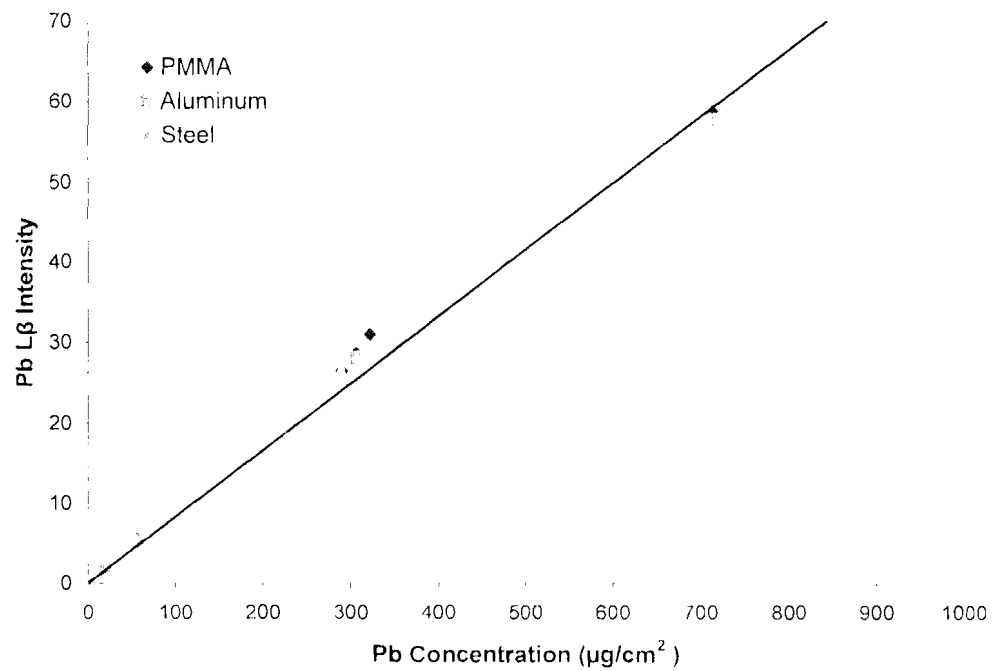


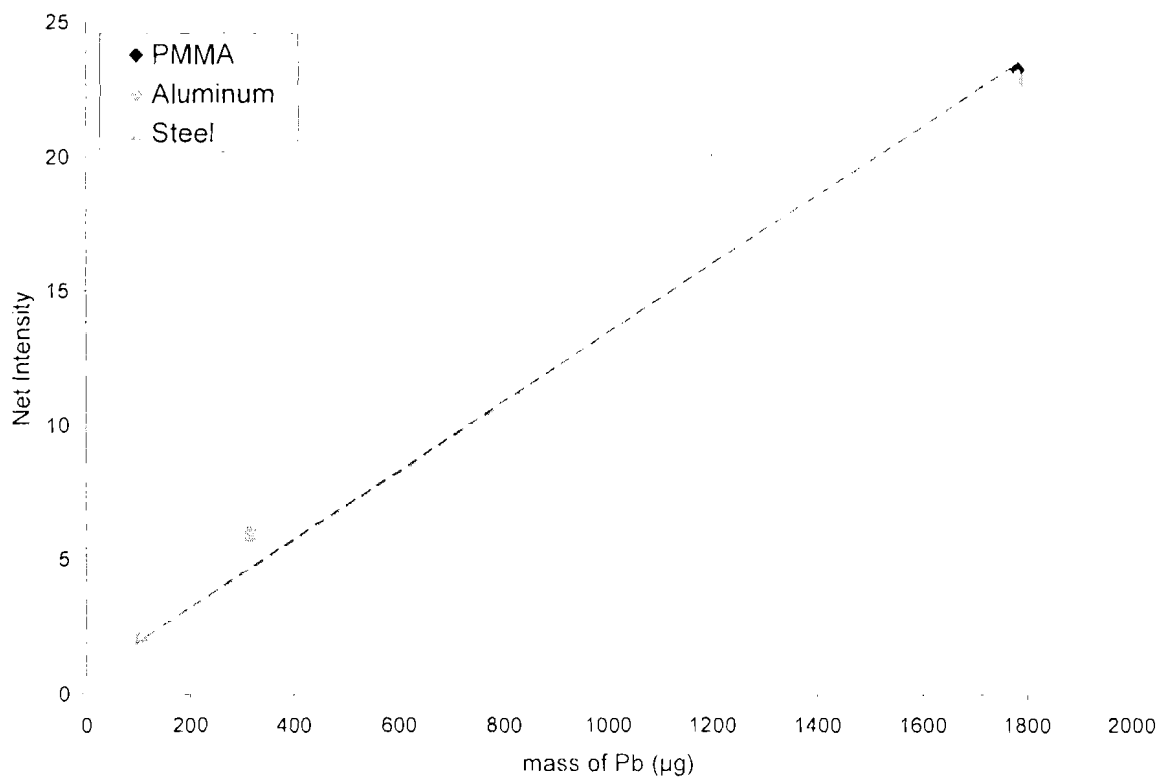
Figure 3: Pb mass using Pb M α emission line for Micromatter reference materials

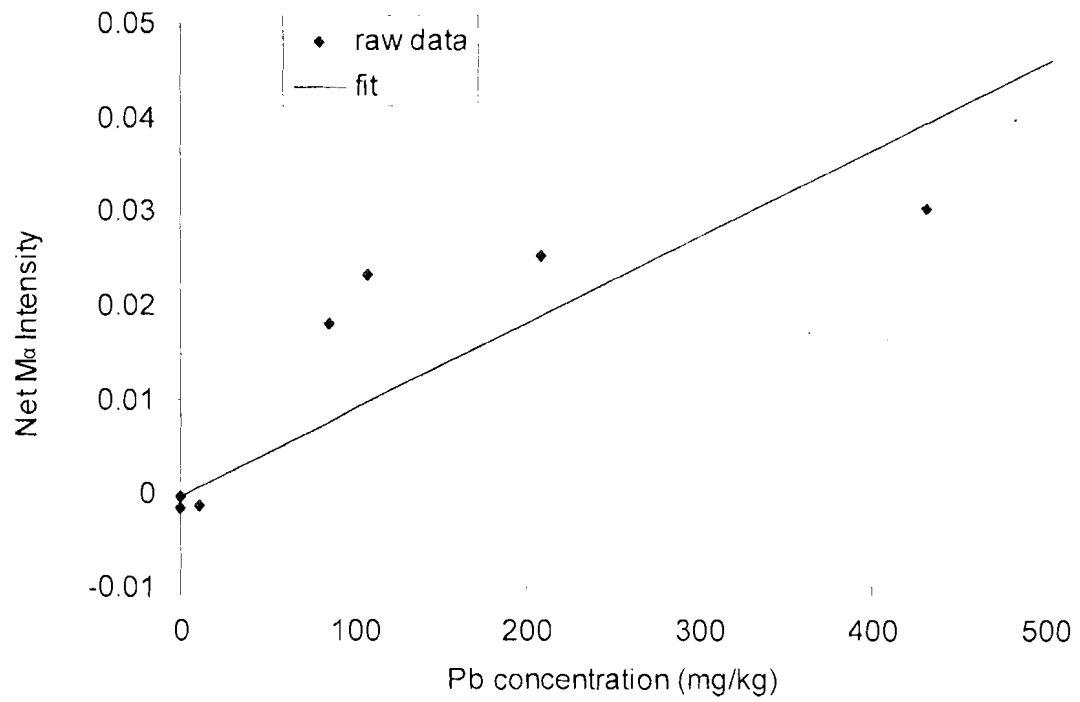
Figure 4: Pb concentration using Pb $M\alpha$ emission line

Figure 5: Results of analysis of paint film on PMMA

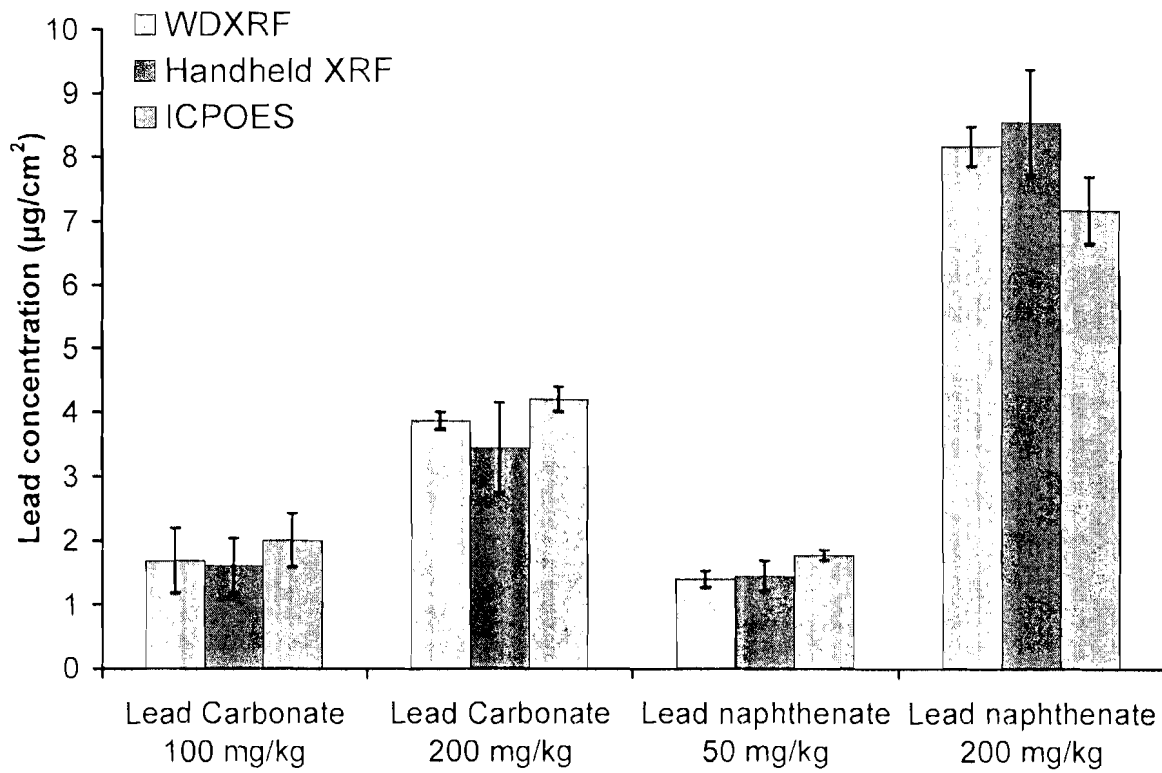
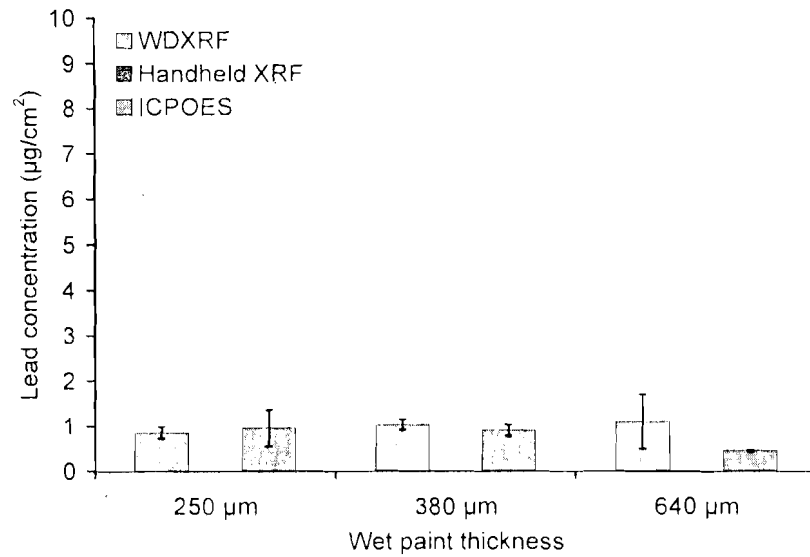


Figure 6: Results of analysis of paint film on Steel for a) 50 mg/kg spiked into wet paint and b) 200 mg/kg spiked into wet paint

a)



b)

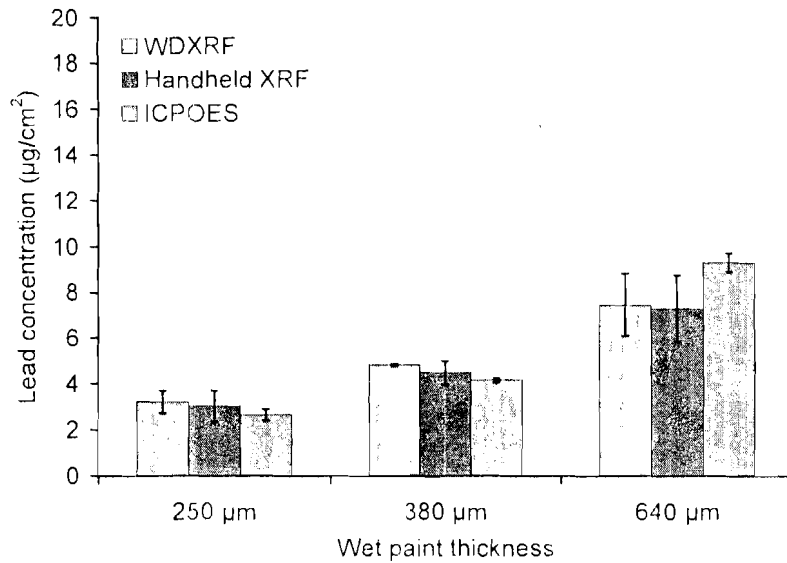
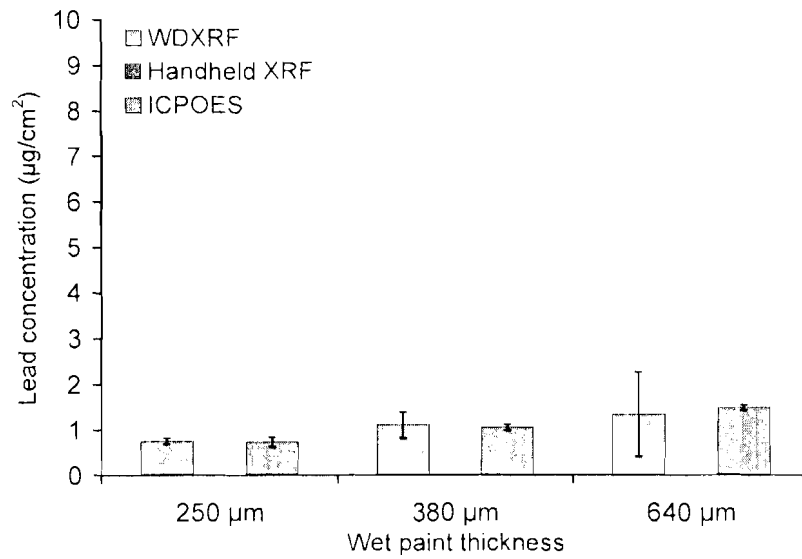


Figure 7: Results of analysis of paint film on Aluminum for a) 50 mg/kg spiked into wet paint and b) 200 mg/kg spiked into wet paint

a)



b)

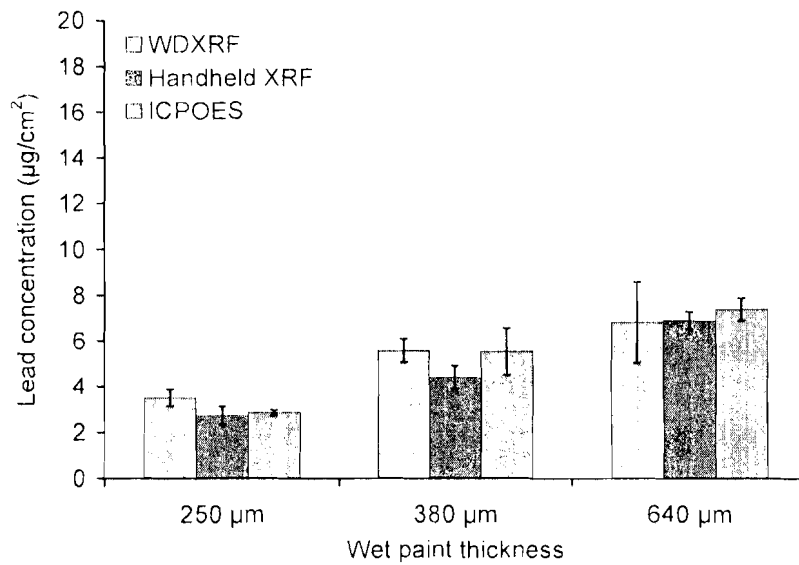


Figure 8: Results of analysis of paint film on PMMA using Pb M X rays

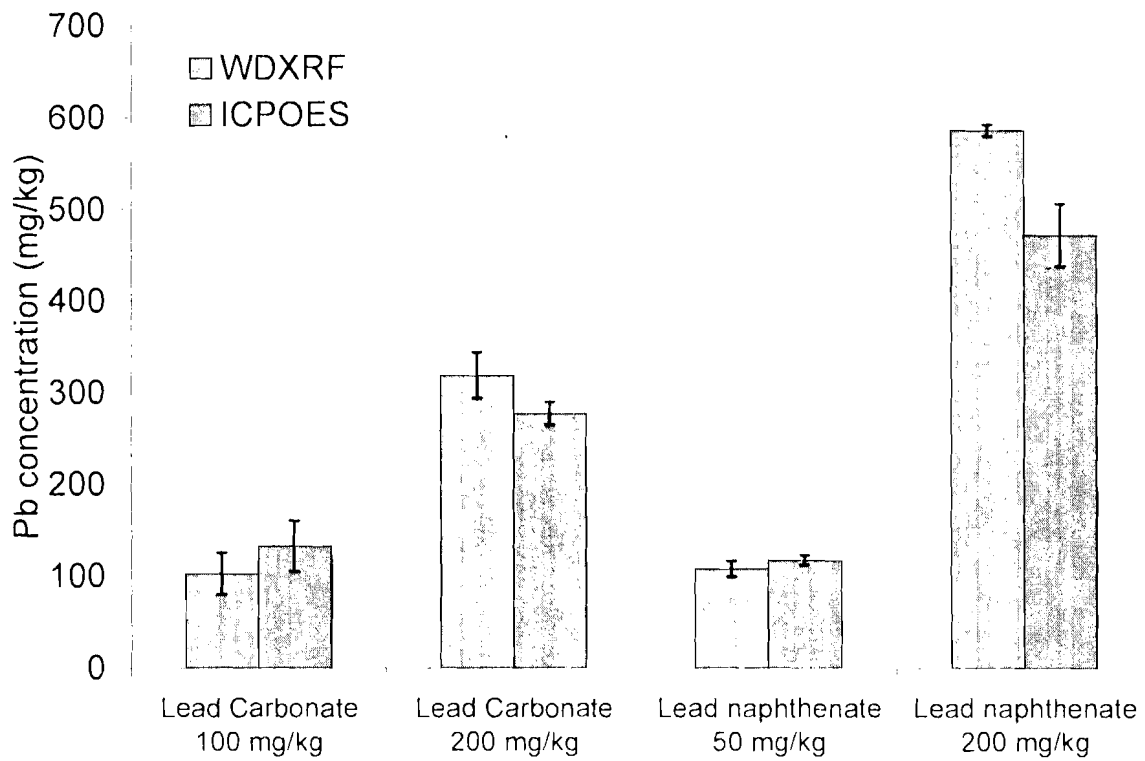
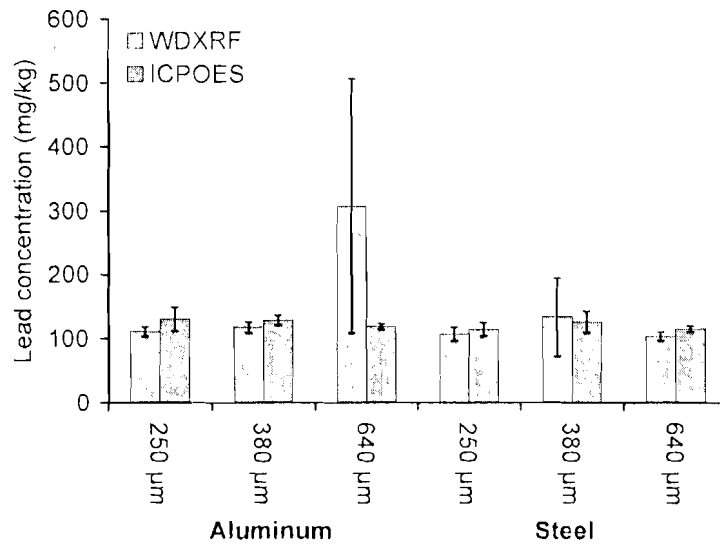


Figure 9: Results of using Pb M X rays for analysis of paint on Aluminum and Steel for a) 50 mg/kg lead naphthenate and b) 200 mg/kg lead naphthenate

a)



b)

