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Testing Toys for Lead with a Handheld XRF Analyzer

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Thermo Scientific – Niton Analyzers

Portable Elemental Analysis

Why are we here?

ALTERNATIVE METHODS OF MEASURING LEAD IN PAINT GENERALLY.—

(A) STUDY.—Not later than 1 year after the date of enactment of this Act, the Commission shall complete a study to evaluate the effectiveness, precision, and reliability of x-ray fluorescence technology and other alternative methods for measuring lead in paint or other surface coatings when used on a children's product or furniture article in order to determine compliance with part 1303 of title 16, Code of Federal Regulations, as modified pursuant to this subsection.

CPSIA – Section 101 (f) (4) (B)

CPSIA – Study – Alternative Methods for Lead Paint Testing

Our Recommendations for outputs from the study:

1. Can XRF be "…as effective, precise, and reliable as the methodology used by the Commission for compliance determinations prior to the date of the enactment of this Act,…"?
    1. 90ppm of lead in paint in large amounts of paint
    2. Alternate standard for measurement in units of ug/cm^2

2. How XRF can be used for testing lead in small amounts of paint
    1. Less than 10mg or 1cm^2
    2. Less than 2ug of Pb total
    3. Measured in units of ug/cm^2

3. How XRF can be used for testing lead in bulk materials (plastic, wood, metal)
    1. Measure in units of ppm
    2. Lead limit cascades from 600 ppm to 300 ppm to 100 ppm

CPSIA – Study – Alternative Methods for Lead Paint Testing (2)

4. Adoption of a standardized test method for the testing of lead by XRF:

    1. The Act states, “Nothing in this subsection shall be construed to affect the authority of the Commission or any other person to use alternative methods for detecting lead as a screening method to determine whether further testing or action is needed.”

    2. The CPSC already uses XRF as a screening tool in this way
        1. If the product screens as “non-detect” the inspector moves on to the next item

    3. How can a private company use XRF testing…and be sure that a lead (Pb) non-detect reading on the XRF means “no further testing is needed”
        1. How can private industry use XRF with the same confidence as the CPSC?
        2. Can private industry show sufficient due diligence by via XRF testing?

Current Methods of Testing for Lead in Paint

- The current laboratory based method for testing for lead in paint
  - Scrape the paint from a children's product
  - Mass the sample
  - Digest the paint sample in a known quantity of hot acid solution
  - Measure the lead content solution by ICP or AA spectrometry
  - Calculate the concentration of lead in the paint

- "…as precise, effective, and reliable…"?
- Lab based (ICP) methods are taken to be the "gold standard"
  - While this methodology has its strengths, it also has several weaknesses
- XRF test methods also have weaknesses, which are different than the problems of the ICP/AA based methods

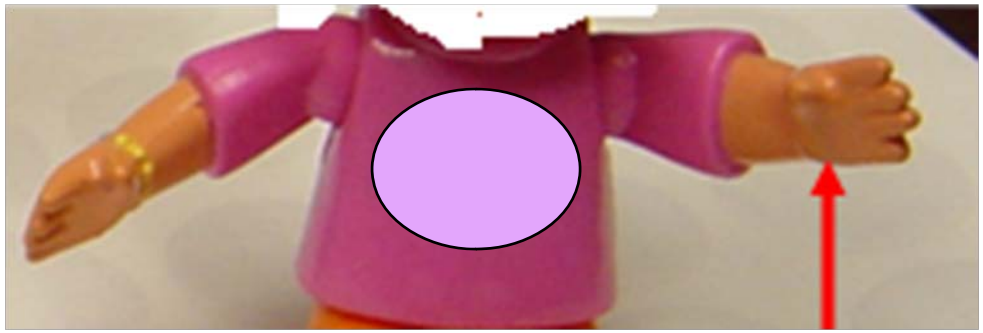
How are these two techniques complimentary to each other?

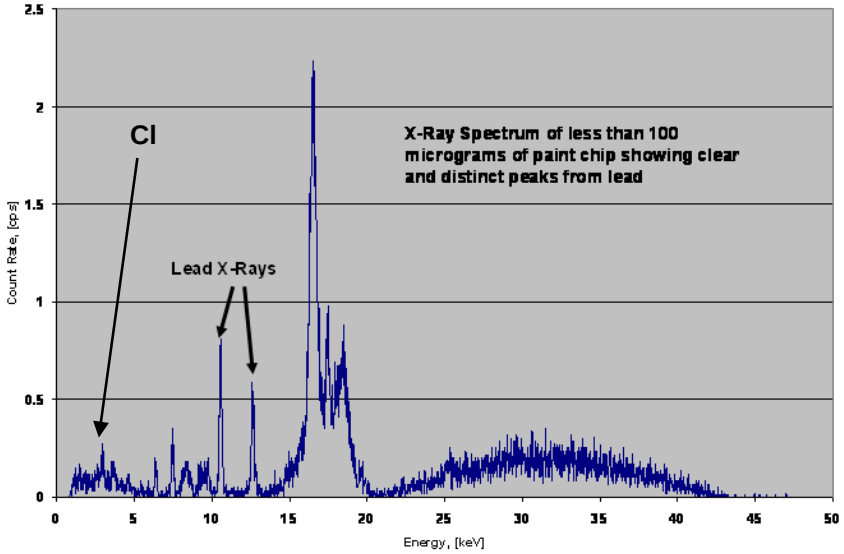
XRF – Test Methods (Myths and Realities)

- Shortcomings of the XRF testing (Myths and Realities):
  - XRF will not easily measure lead in thin dried films of paint in units of ppm
    - Why not use an alternate standard in units of ug/cm^2, which is just as safe for children, which XRF is clearly capable?
  - Direct measurement of heterogeneous samples may give inaccurate results
    - No analytical technique can directly measure a heterogeneous sample
    - All methods have a “homogenizing” or “sample isolation” step
    - The test method for XRF or any other technology must deal with such sample preparation and presentation issues
  - Oversimplification of the XRF methods
    - Viewed to always work as a “point and shoot” analyzer 100% of the time
    - Any analytical technique can be used incorrectly
    - Any SOP can be ignored

Current Methods of Testing for Lead in Paint (1)

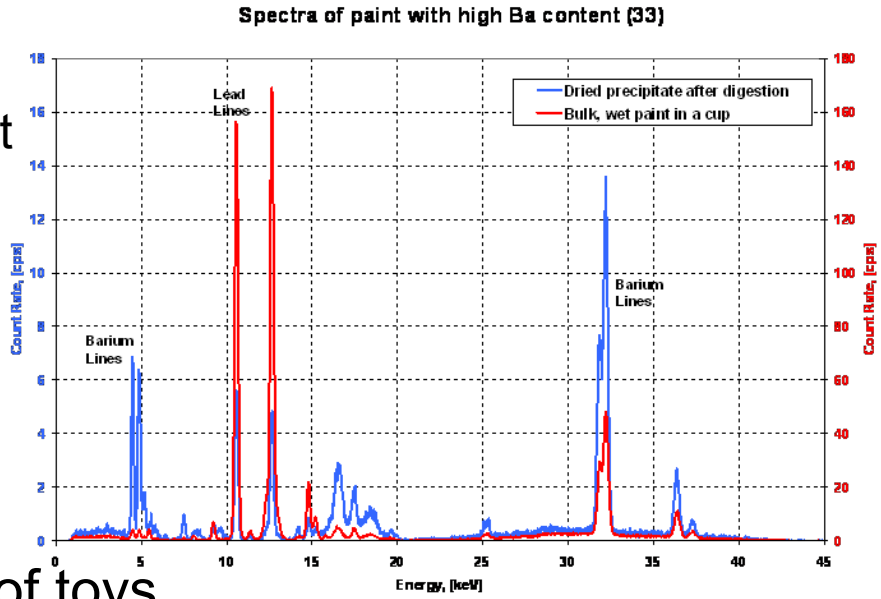
- Just how “effective, precise, and reliable” is the ICP/AA based test method?
  - Problem of sampling, scraping paint with a blade
    - minimum sample of 10 mg from one object or area?
    - problems of blending clean and contaminated paint of the same appearance/color, dilution
    - problem of blending by dilution with substrate





Current Methods of Testing for Lead in Paint (2)

- Problem of incomplete digestion
  - Often, paint does not completely digest in the acid solution
  - The lead reading is artificially low



- Problem of sampling large volumes of toys
  - Prohibitive time for total analysis
    - (sampling, acid digestion, testing)
  - Destructive – 100% inspection is impossible

- 17,000 shipping containers arrive each day, containing 15,000+ different products = 6,205,000 containers/year = 93,075,000 products/year!!!

Edmonson, R.G. Beyond Calculation. August 25, 2003. Journal of Commerce.

Other accepted uses of XRF for lead testing

- The U.S. Environmental Protection Agency adopted XRF technology in the 1990's to screen soil for heavy metals (US EPA Method 6200, part of SW-846), as well as ASTM Practice E 2119-00 for lead in paint and other coatings.
- The U.S. Department of Housing & Urban Development (HUD) has had XRF guidelines for assessing lead-based paint hazards in housing for more than 10 years. (HUD Guidelines, Chapter 7, 1997 revision)
- XRF is approved for testing the amount of lead in gasoline under ASTM D5059-07.
- The electronics industry adopted XRF as a tool for testing electronic and electric products for compliance with the European Union's RoHS Directive (IEC Test Method 62321) that went into effect July 1, 2006. XRF is specifically selected to be a first step of testing, and further confirmatory testing may or may not be performed.

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XRF – Discussion of Analytical Performance

Dichotomy of Units of Measure in Assessing Lead Hazard

- Why are chemical limits usually expressed in units of “mass per unit mass” or PPM?
  - A commonly accepted and intuitive way of expressing fractional content

- XRF is capable of directly measuring in units of PPM in large, thick samples. In thin materials (< 1mm), XRF is capable of giving accurate results in units of “mass per unit area” or mg/cm^2.

- In order to convert mg/cm^2 to PPM, the instrument needs to know the mass of the sample being analyzed. How?
  - Since we already know the area, we just need to know the density and thickness of the thin sample (paint layer), then we can get to mass. Measuring these parameters adds time, cost, and complexity. No value is added in the prevention of toxic poisoning.

It seems that CPSC has authority to address the issue and solve the problem via a rule making approach by establishing the limit for lead in paint in units of $\mu g/cm^2$, based on some toxicological modeling?

Toxicology modeling

How many grams of material in a typical item?

How much surface area on a typical item?

What is the leech rate per gram of material?

The two unique limits should provide the same level of protection

What is the leech rate per unit surface area?

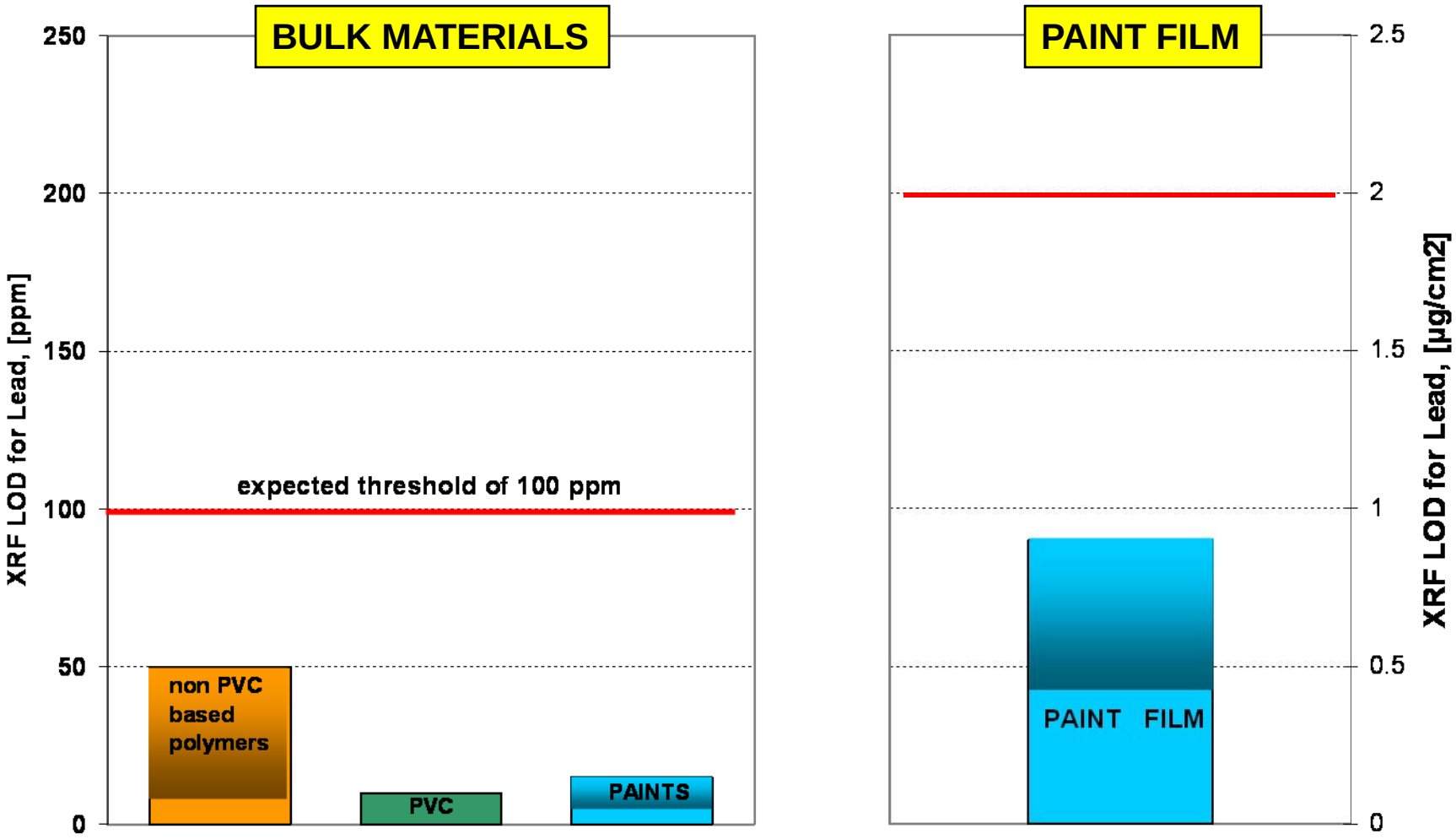
Set safe limit in PPM

Set safe limit in μμg/cm^2

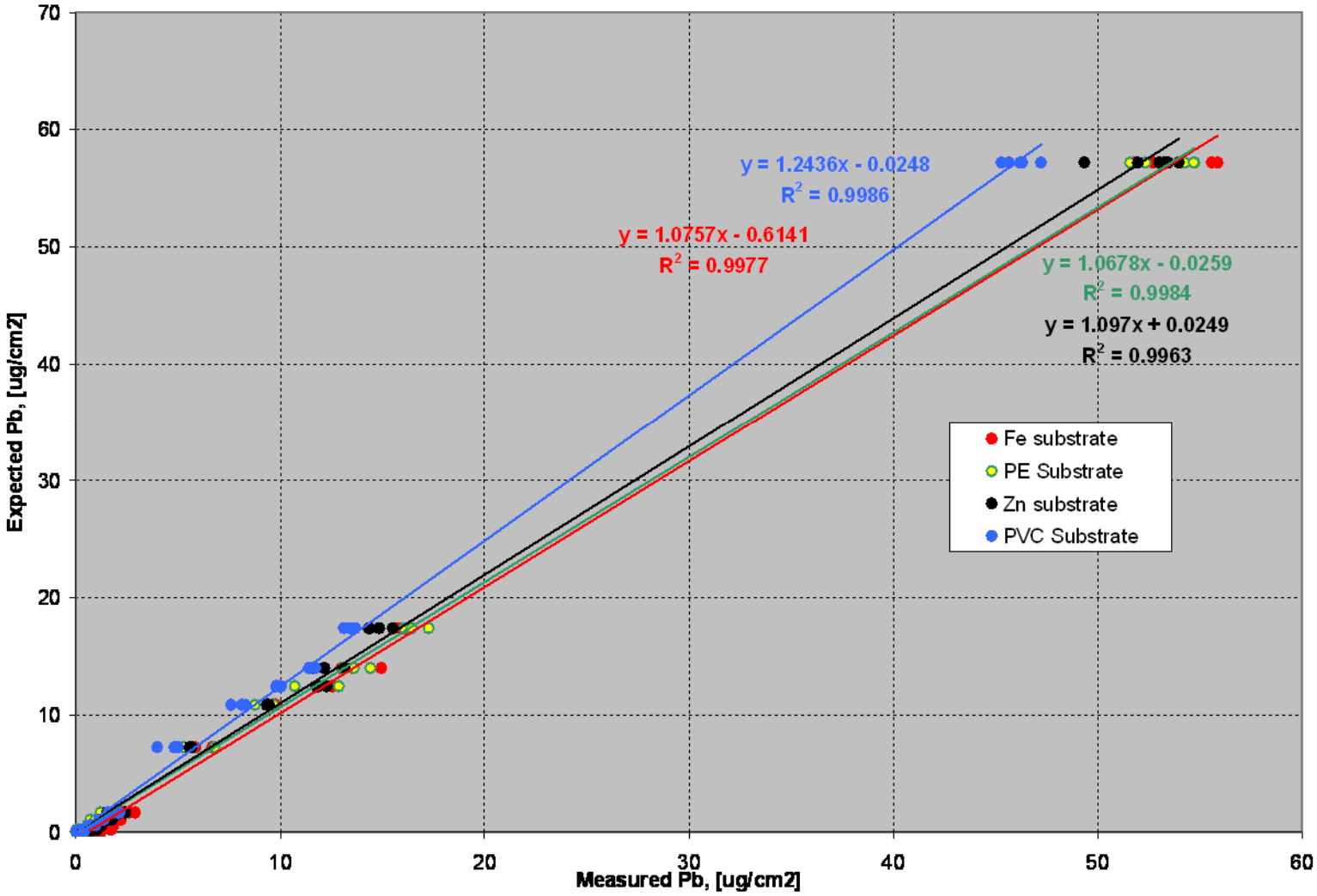
XRF advantages

- XRF tests must be legally compliant in order to prove due diligence in a court of law.
- Limit in PPM is OK for bulk materials
- Limit in $\mu g/cm^2$ needed for thin layers of coatings (paint)
- Advantages of allowing for XRF as quantitative screening tool:
  - Testing becomes faster (seconds compared to days)
  - Testing becomes non-destructive (test actual toys not samples)
  - A greater volume of product is tested (cast wider net/catch problems)
- The more items (homes/toys/jewelry) that get screened, the safer we all will be!

How XRF Analytical Performance pairs with Regulations



Analytical Performance – paint films

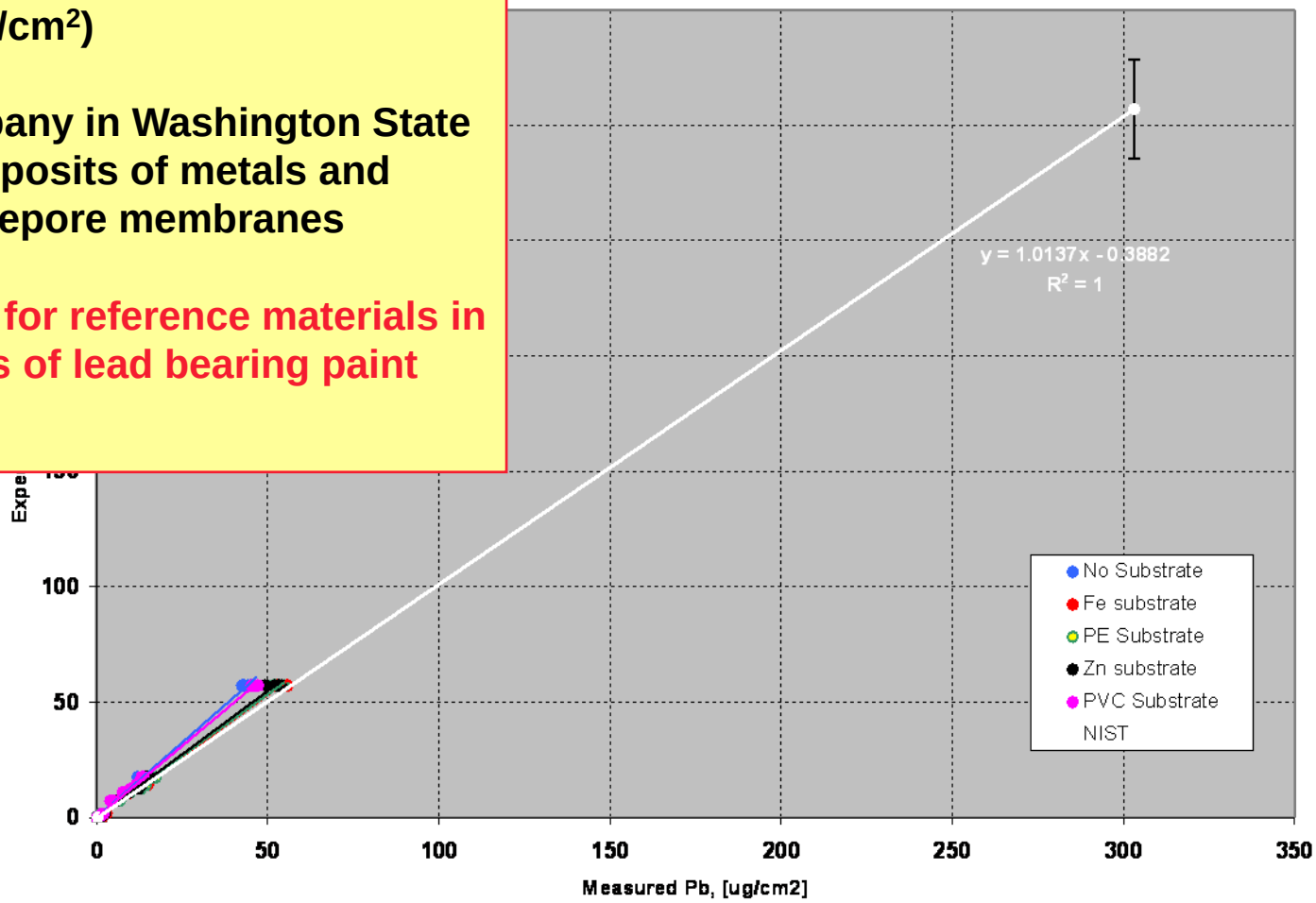


Calibration, Reference Samples for paint films

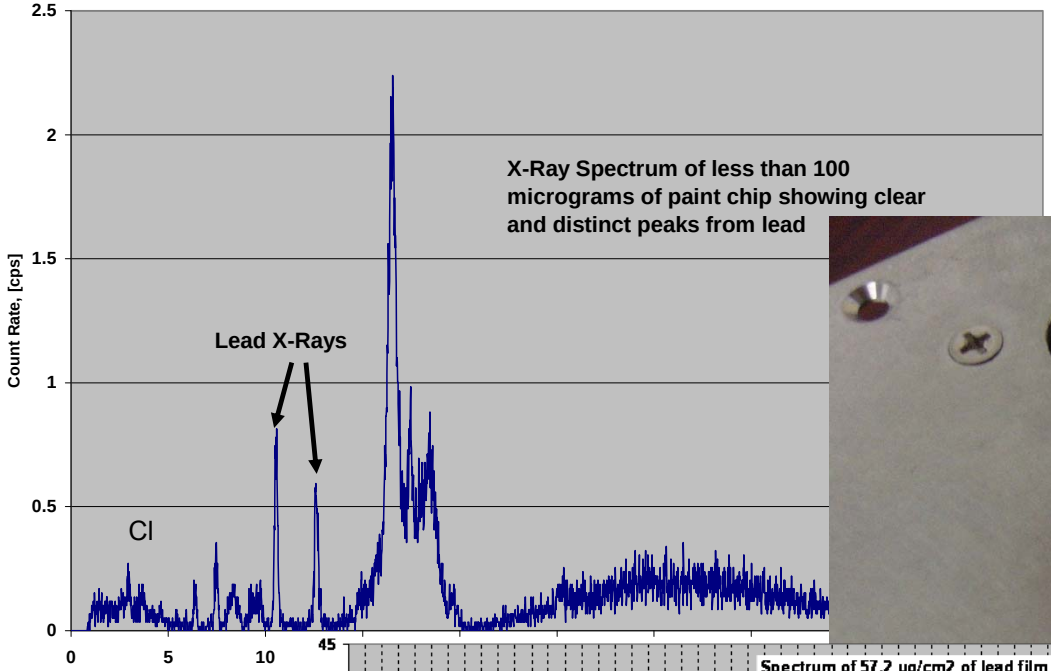
At present there is only one CRM, NIST SRM 2575 and it is not quite adequate (0.307 ± 0.021 mg/cm^2)

Micromatter Company in Washington State makes thin film deposits of metals and their salts on Nuclepore membranes

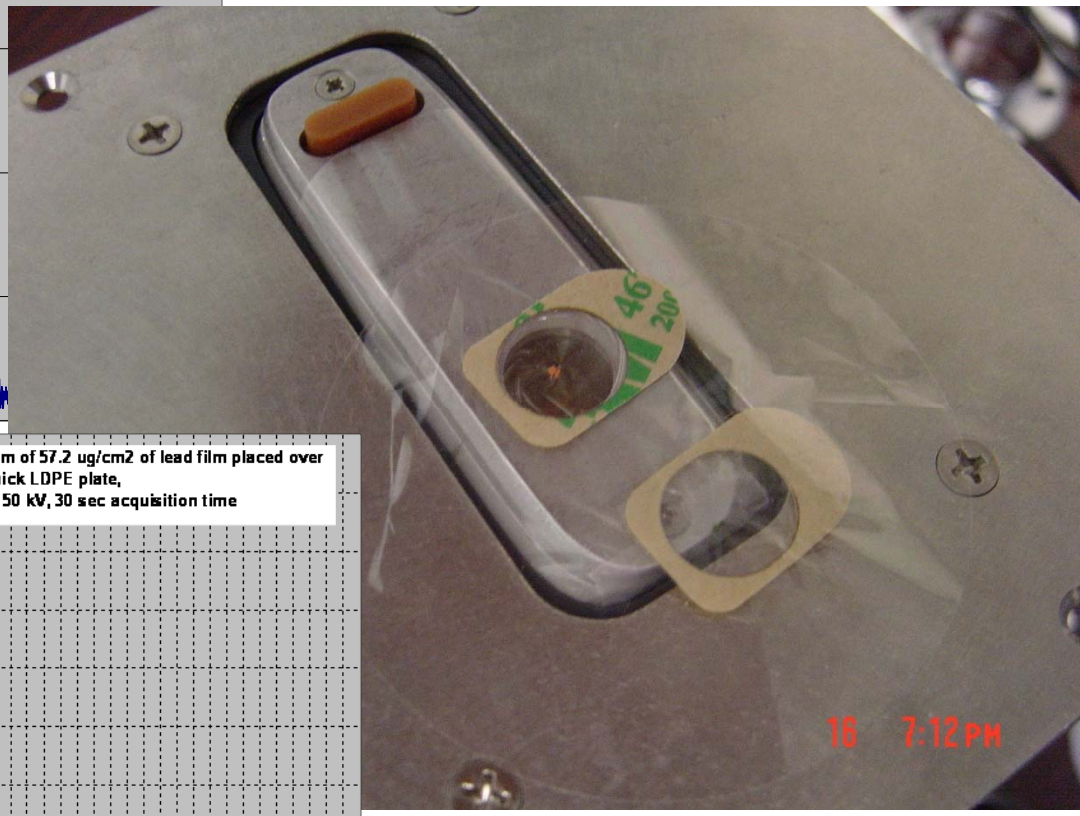
There is dire need for reference materials in a form of thin films of lead bearing paint

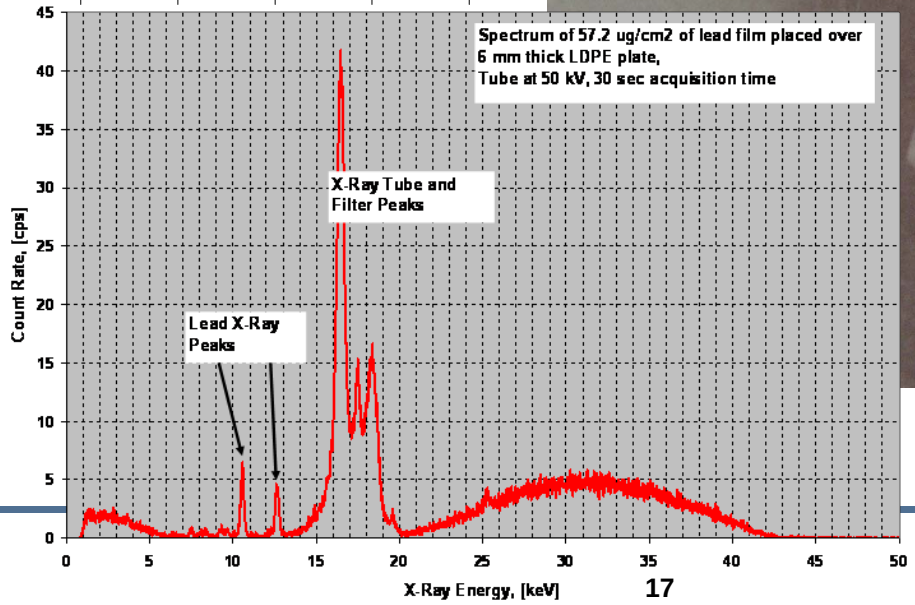


Direct XRF analysis of a tiny paint chip – an alternative method

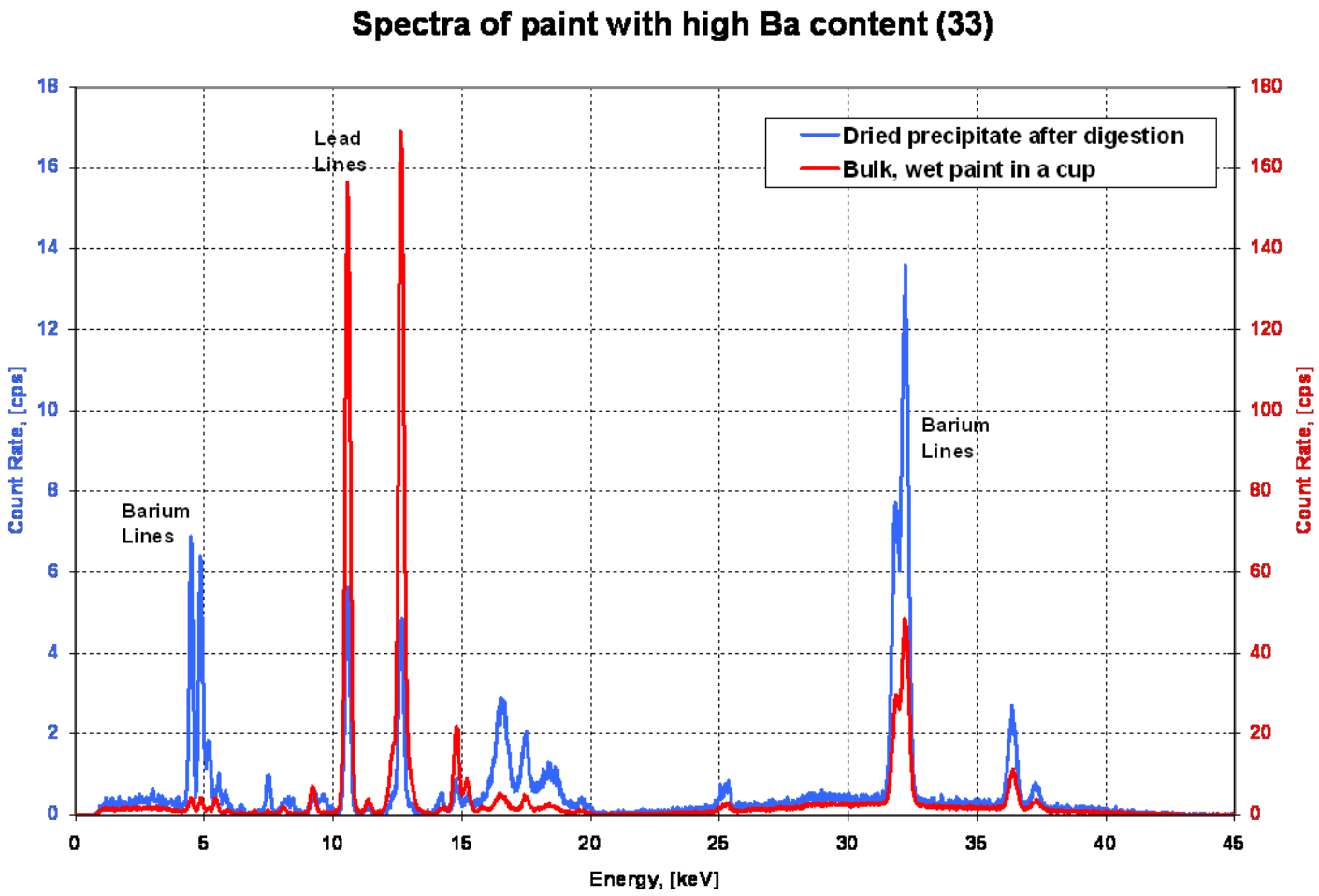


By comparing two spectra we can estimate lead content in chip of paint to be on the order of 5% (or 5 micrograms)!!!





Can XRF be "…as effective, precise, and reliable…" as ICP?



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Testing of Bulk Materials

Test Method IEC 62321 and others

Titre
IEC 62321 Ed.1: Electrotechnical products – Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers)

Title
IEC/PAS 62596 Ed.1: Electrotechnical products – Guideline for the sampling procedure for the determination of restricted substances

Designation: F 2617 – 08

Standard Test Method for
Identification and Quantification of Chromium, Bromine, Cadmium, Mercury, and Lead in Polymeric Material Using Energy Dispersive X-ray Spectrometry[1]

Screening with XRF as per IEC 62321

- **Definition of Screening as found in IEC62321/PAS**

Screening

It is an analytical procedure to determine the presence or absence of substances or compounds in the representative part or section of a product, relative to the value or values accepted as the criterion for this decision. If the screening method produces values that are not conclusive, then additional analysis or other follow-up actions may be necessary to make a final presence/absence decision.

RoHS Performance for Polymers

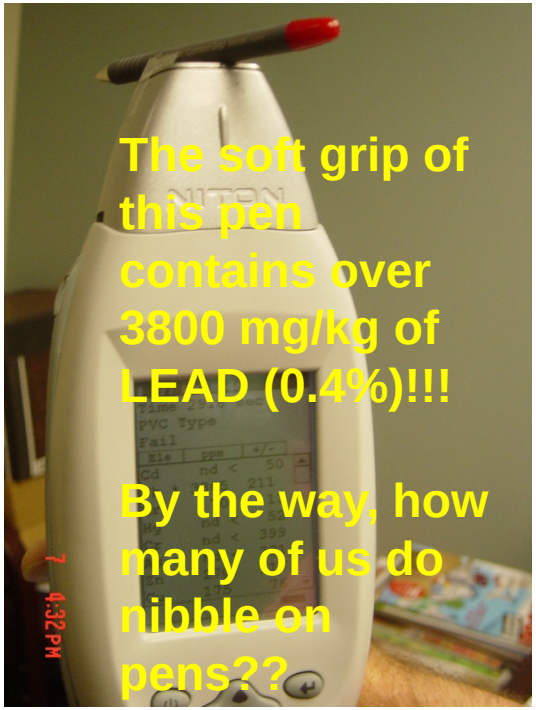
Plastics Samples

Normal Spot (8mm)

	XL3t-700 8mm			
	PE blank	PE+2%Sb	PE+5%Br	PVC
Element	LOD, ppm	LOD, ppm	LOD, ppm	LOD, ppm
Cd	15	30	40	20
Pb	4	10	55	10
Hg	6	18	35	22
Br	3	5	N/A	8
Cr	20	20	25	40
Cl	400	500	750	N/A
Note:	**120 main 60 low**			

Small Spot (3mm)

	XL3t-700 3mm			
	PE blank	PE+2%Sb	PE+5%Br	PVC
Element	LOD, ppm	LOD, ppm	LOD, ppm	LOD, ppm
Cd	20	30	40	30
Pb	7	15	60	20
Hg	12	20	35	60
Br	5	7	N/A	20
Cr	25	30	35	75
Cl	500	500	750	N/A
Note:	**120 main 60 low**			



More Results for “Plastics”

Product	Cadmium	Lead	Mercury	Bromine	Chromium
White PVC binder	<150	65 ± 9	<9	<4	<60
Blue PVC Binder	660 ± 70	<11	<8	<4	<50
Green PVC binder	370 ± 60	1200 ± 40	<7	<4	50 ± 20
Grey PVC binder	900 ± 60	300 ± 20	<9	450 ± 20	<40
Pen	<36	3827 ± 155	<40	64 ± 10	<280
Stapler	<49	174 ± 16	<8	<3	<91
Desk trim	<88	(1.77 ± 0.1)%	<125	65 ± 37	<600

Results are in [mg/kg] *(ppm)* unless noted otherwise

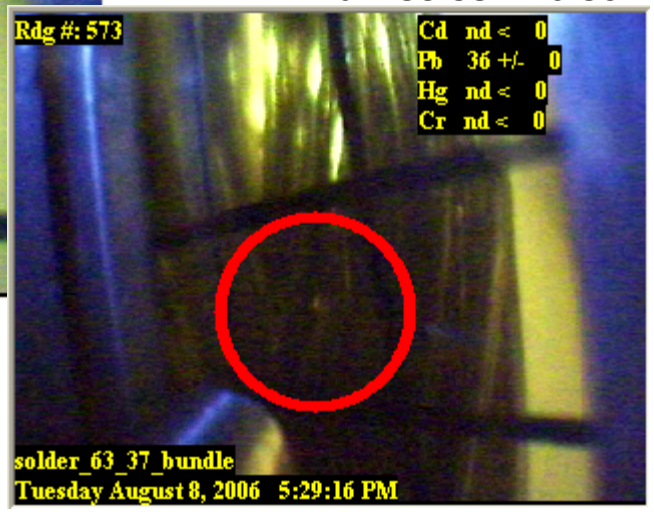
Alloys – Solder wire

Solder wire of nominal composition 63Sn/37Pb was analyzed for 60 sec.

Sn = 63.85 ± 1.67
Pb = 34.58 ± 0.59

Sn = 64.62 ± 1.28
Pb = 34.79 ± 0.43

Sn = 63.57 ± 1.05
Pb = 35.58 ± 0.36



	Al	Fe	Sn
Element	LOD, ppm	LOD, ppm	LOD, ppm
Cd	16	57	400
Pb	18	60	120
Hg	25	130	185
Cr	160	150	500
Br	20	30	100
Note:	**60 main 60 low**		

Alloys – Solder wire -2

- As little as 1 mg of solder can be analyzed reliably – testing of a single solder joint is feasible

Sn = 59.53 ± 2.94
Pb = 37.11 ± 1.06

Mass = 1.1 mg

Sn = 60.27 ± 2.56
Pb = 38.89 ± 0.95

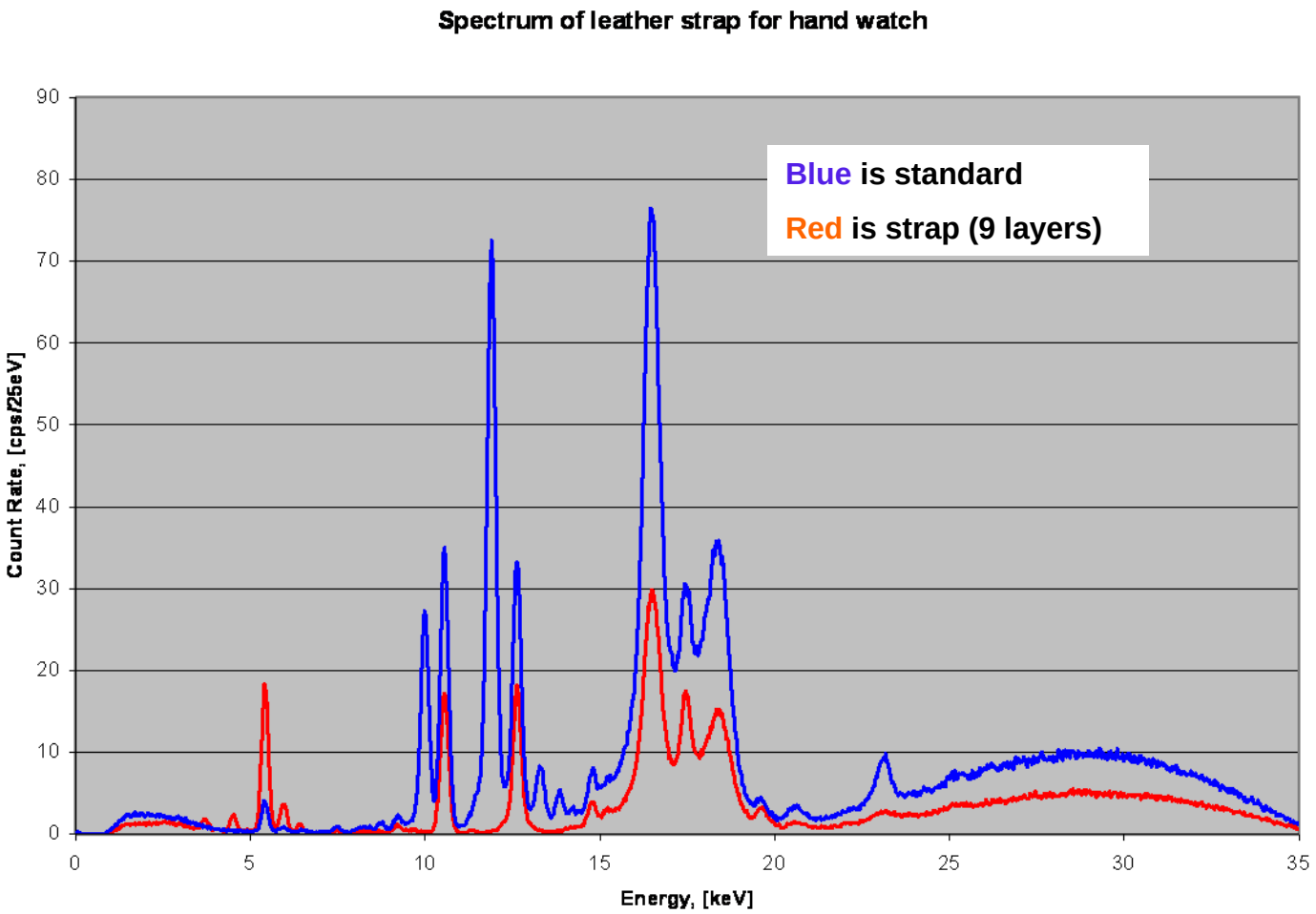
Mass = 2.3 mg

Real Life Examples - Lab Misses Lead

Summary

- Customer is a watch maker. This occurrence involved a leather watch strap (from China) purported to contain 263ppm Pb by the laboratory (As per attached report, not shown here)
- Niton Analyzer measured Pb at 1659 +/- 49 when testing the strap as a single strip and 1491 +/- 32 when testing the strap after being cut up and 9 layers tested (ppm after 120 sec tests). The customer tested the plastic reference sample (Pb = 997 +/- 40) and the Niton Analyzer was reporting 989 +/- 18.
- We have inspected the normalized spectra from the 3 readings and advised the customer to stand by the data.
- Customer did not believe the Niton result until a second laboratory test returned 1117.8 ppm Pb. The lab's ICP had broken down that day but the engineer had believed all was OK!!!!

Example - Lab Misses Lead



Conclusions

- Can XRF be "…as effective, precise, and reliable as the methodology used by the Commission for compliance determinations prior to the date of the enactment of this Act,…"?
  - ICP and XRF each have advantages and weaknesses
    - Lab Methods based on ICP are not "the gold standard"
  - We need certified reference materials for paint and bulk samples to validate each method against objective standards
  - For dry paint films, we should have a toxicologically equivalent lead limit in units of $\mu g/cm^2$.
  - A fair study will show that XRF is suitable for conformity testing!

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Healthier

Cleaner

Safer

Mr. Bob Wopperer – Director of Business Development – Portable XRF

Dr. Stan Piorek – Principal Scientist - Portable XRF

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