Screening for restricted elements using XRF

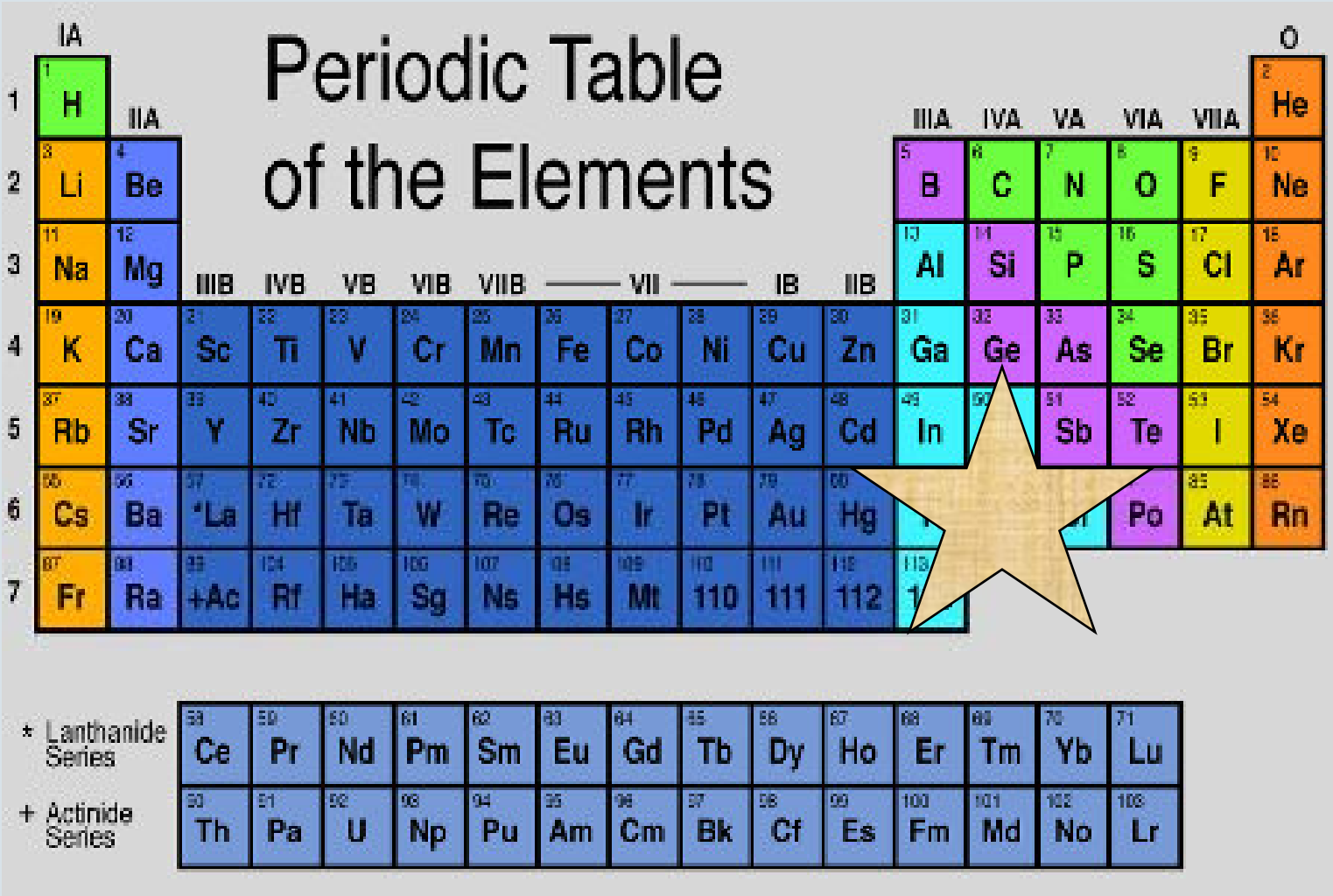
XRF can make our lives safer!

Alexander Seyfarth

Agenda

- Introduction
- Getting the lead out … again
  - Historical perspective
- Analyzing Pd with XRF
  - XRF for paint analysis HUD
  - XRF for restricted elements in food
  - XRF for analysis of consumer product
    - What happens if we screen non homogeneous materials
    - Knowing what to analyze.
- New ASTM materials
- Conclusion

Lead me to Lead



Pb is one of the oldest metals in use

Did lead pipes cause the decline of the roman empire….

- Lead hazards:
  - BIO ACCUMULATION in bones
  - Impact on central nervous system
  - Impact on reproductive organs
  - Kidney and liver failures
  - ADD and Learning deficiencies
  - Delayed mental and physical development
- THE YOUNGER YOU ARE …
  - The more it get's to you!!!

Lead pipe to supply water to the Great Bath at Bath Roman Baths.
The pipe has a folded seam and is thought to have carried water under pressure.

Where do we find lead?

- Consumer product and utility metal
  - Metal pipes (since the Romans)
    - Does not corrode
    - Cheap and mechanically resistant
    - Easy to FORM!
  - Paints, dyes, glazes (for bright vibrant color, high refractive index, pigment)
    - PbO_2 is less expensive than TiO_2
  - PVC as a stabilizer against heat and light
  - Polymers as a stabilizer (light)
  - Alloy in metal (brass has at least 3% lead)
    - Jewelery (luster, weight)

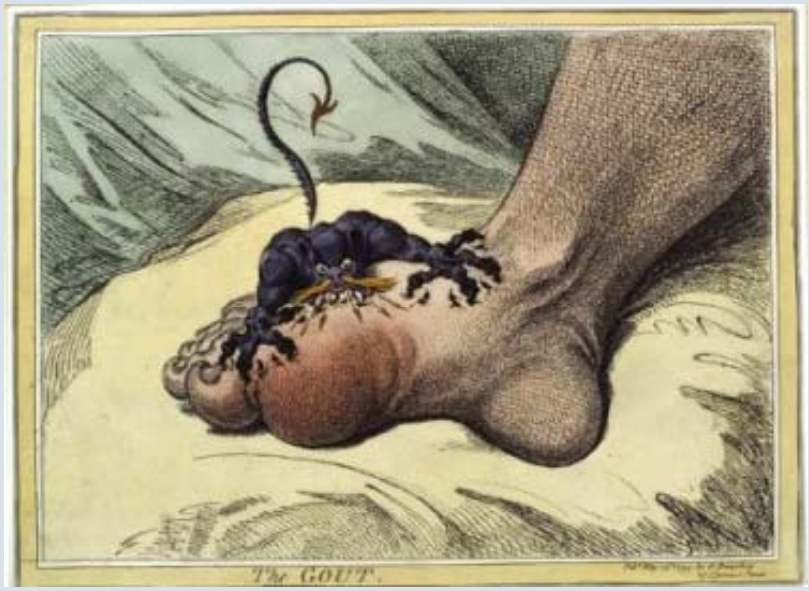
Did the Roman empire fall due to Pb?

- S. Columba Gilfillan proposed a theory for Roman decay in 1965 that involved "poisons esteemed as delicious by the ancient well-to-do." Spoilage was a problem in ancient Rome, and vintners discovered that wine tasted better and lasted longer if it was mixed with a concentrated grape syrup called sapa. The best sapa was boiled in lead pots, allowing lead to leach into the syrup. When sapa was mixed with wine, it sweetened it and also poisoned the microorganisms that cause fermentation and souring. Sapa was also used in fruit and honey drinks, and as a food preservative.
- Josef Eisinger estimated a Roman consuming a liter of wine a day would ingest **about 20 mg of lead per day,** which he said was more than enough to produce chronic lead poisoning.
- A cultural shift at the height of the Roman Empire made it socially acceptable for wives to drink wine, to which Gilfillan attributed a declining birth rate and a low rate of surviving children among the wealthy. Gilfillan hypothesized that the diet of the poor was not so badly poisoned as that of the rich. Although they drank the same water, they lacked the luxuries of cosmetics, lead paint, wine, fruit and honey drinks, or preserved foods.

Effects of lead?
Life in ancient Rome

1979 movie… viewer discretion advised!
http://www.caligulathemovie.com/

- Pb poisoning will cause gout, mental retardation, infertility and ….
- Gout was regarded as the punishment for "indulgence" until the early 1900's



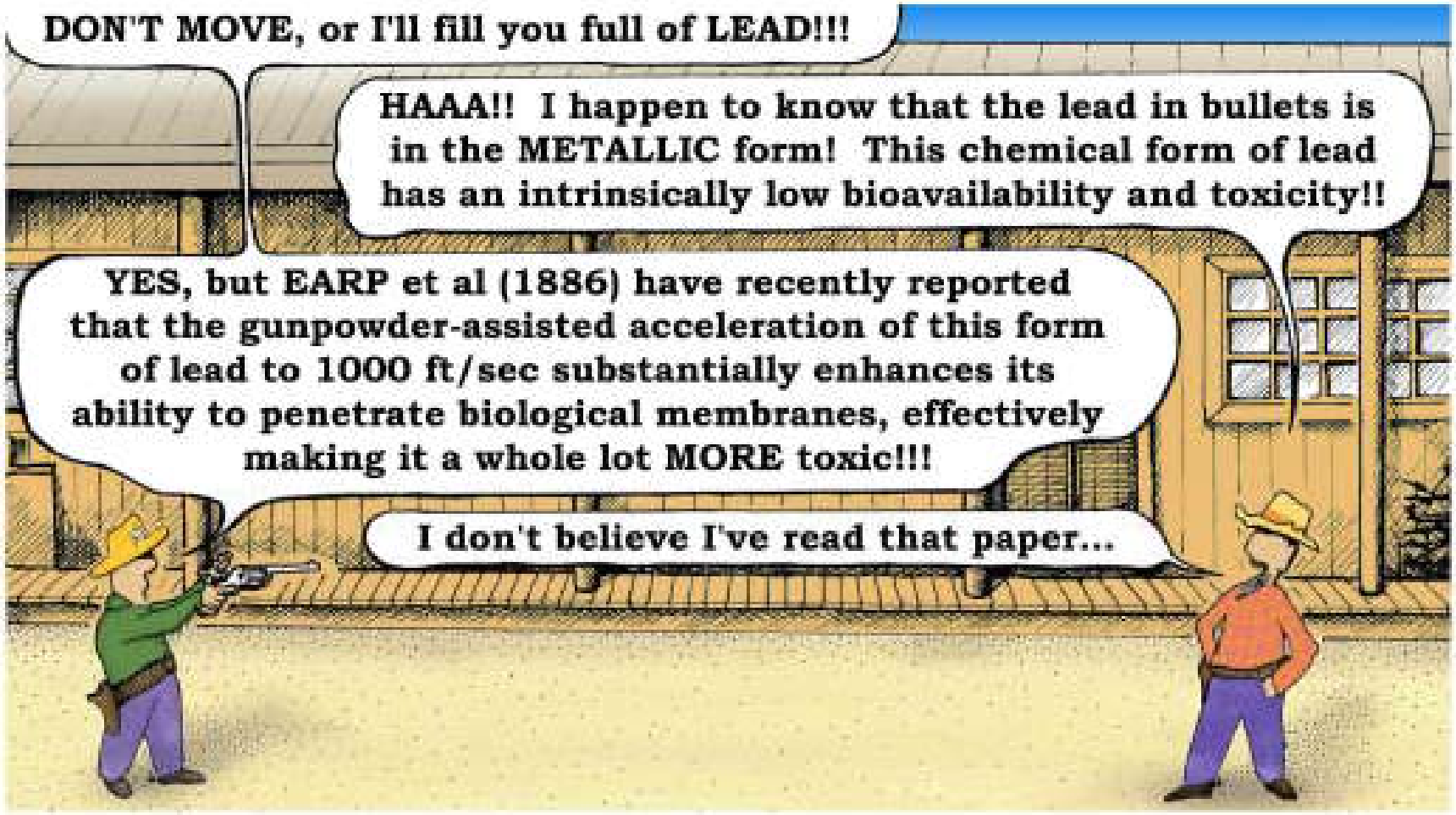
http://en.wikipedia.org/wiki/Gout

1650! Banning Pb in wine… for economic reasons…

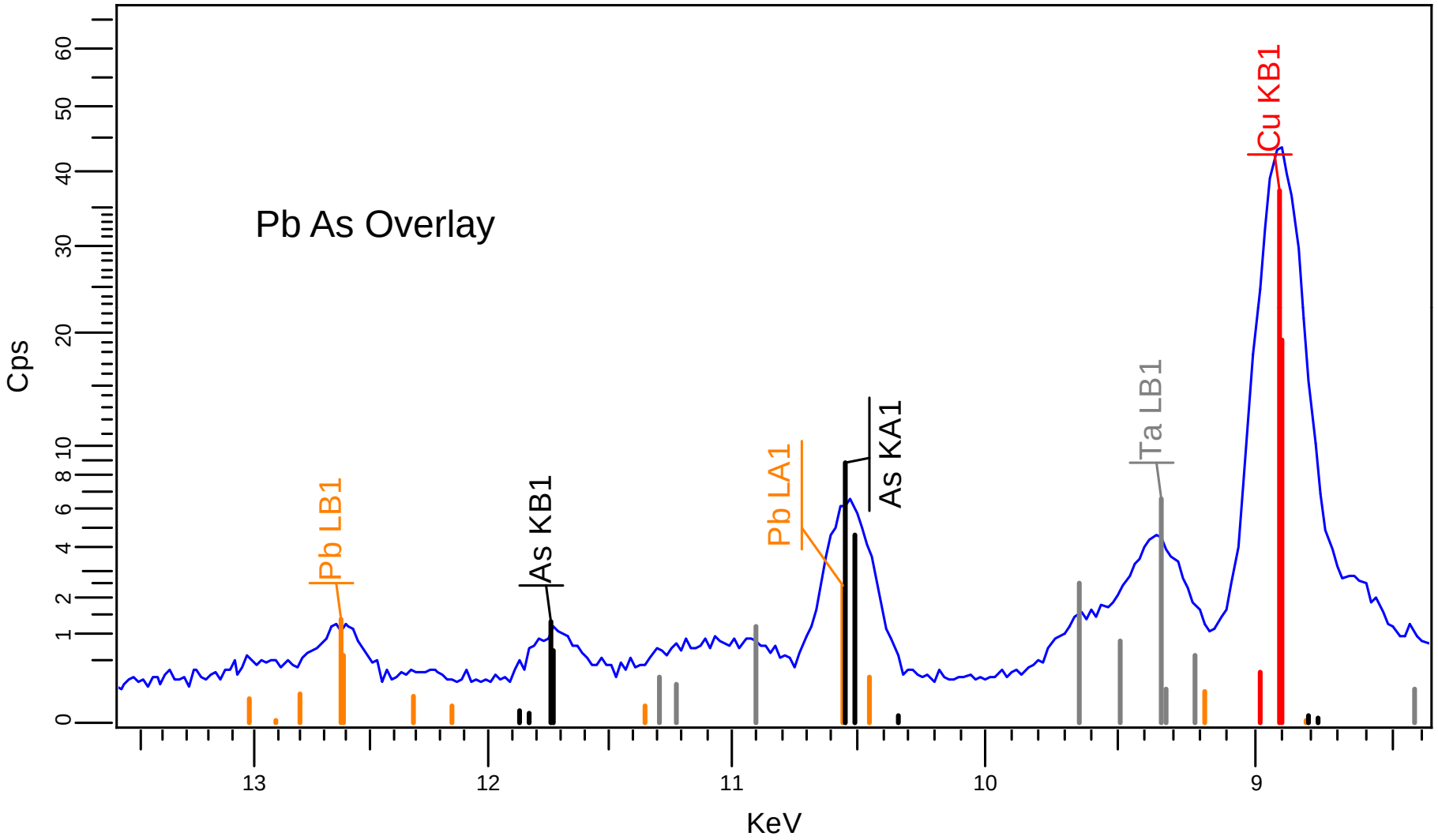
- In the German city of Ulm, during the late 1690's, there was a severe outbreak of colic, an illness characterized by a variety of symptoms, including excruciating abdominal pain. Ulm's official physician noted that at a local monastery the monks who did not drink wine were healthy while those that did developed colic. Upon a detailed investigation he found the culprit to be the agent used to sweeten the wine, litharge, a white oxide of lead. When this concentrated sweetener was added to sour wine it brought it back to life and made it drinkable. The entire region depended upon the wine export as a major source of revenue. If the word spread that the wine from Ulm caused colic then the city's economy was threatened. In 1696, Duke Ludwig issued a decree forbidding the use of lead-based additives in any wine product. **For anyone who violated this decree, the punishment was death!**

http://www.leadpoison.net/general/history.htm

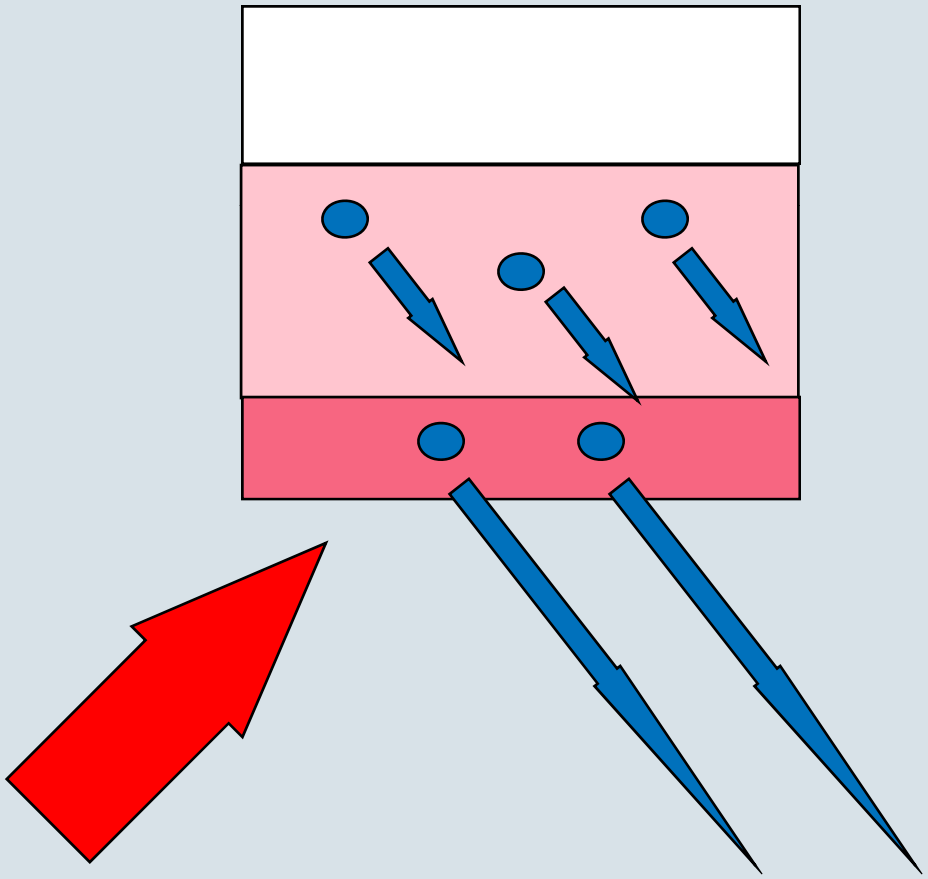
Toxicity of Pb



How to analyze for Pb!

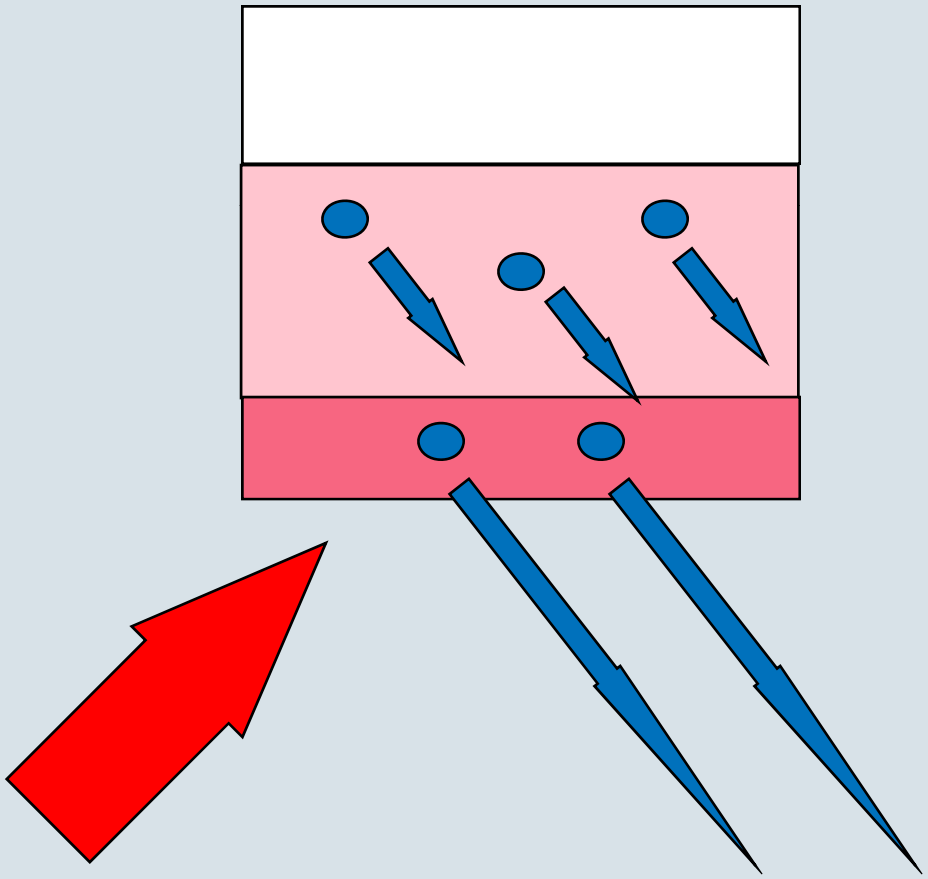


X-ray Fluorescence Analysis "Infinitely Thick Sample"



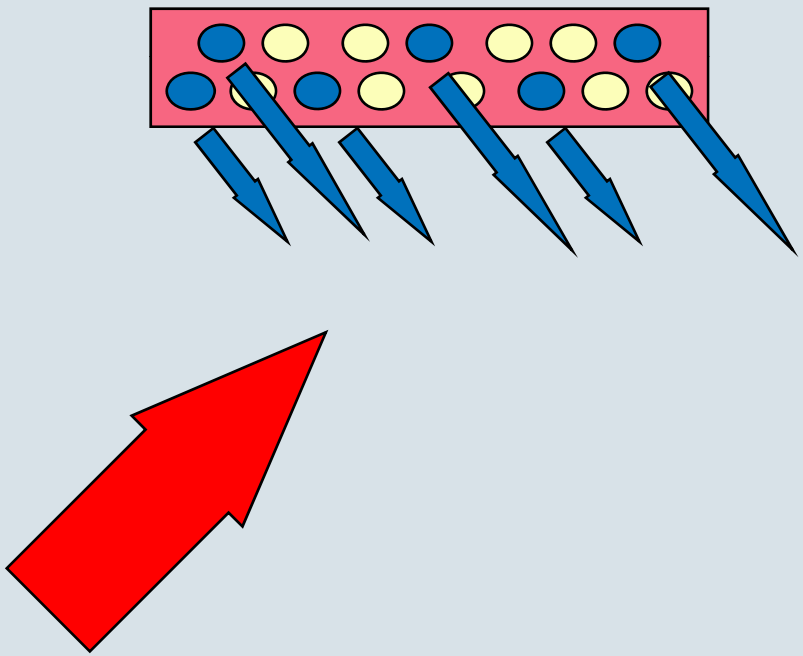
- no excitation of the inner parts of the sample
- an intermediate part can be excited, but the fluorescence radiation is absorbed within the sample
- the detectable fluorescence radiation comes from the parts close to the surface
- the sample thickness has no influence on the intensity
- the sample thickness can <u>not</u> be measured by XRF

X-ray Fluorescence Analysis "Infinitely Thick Sample"



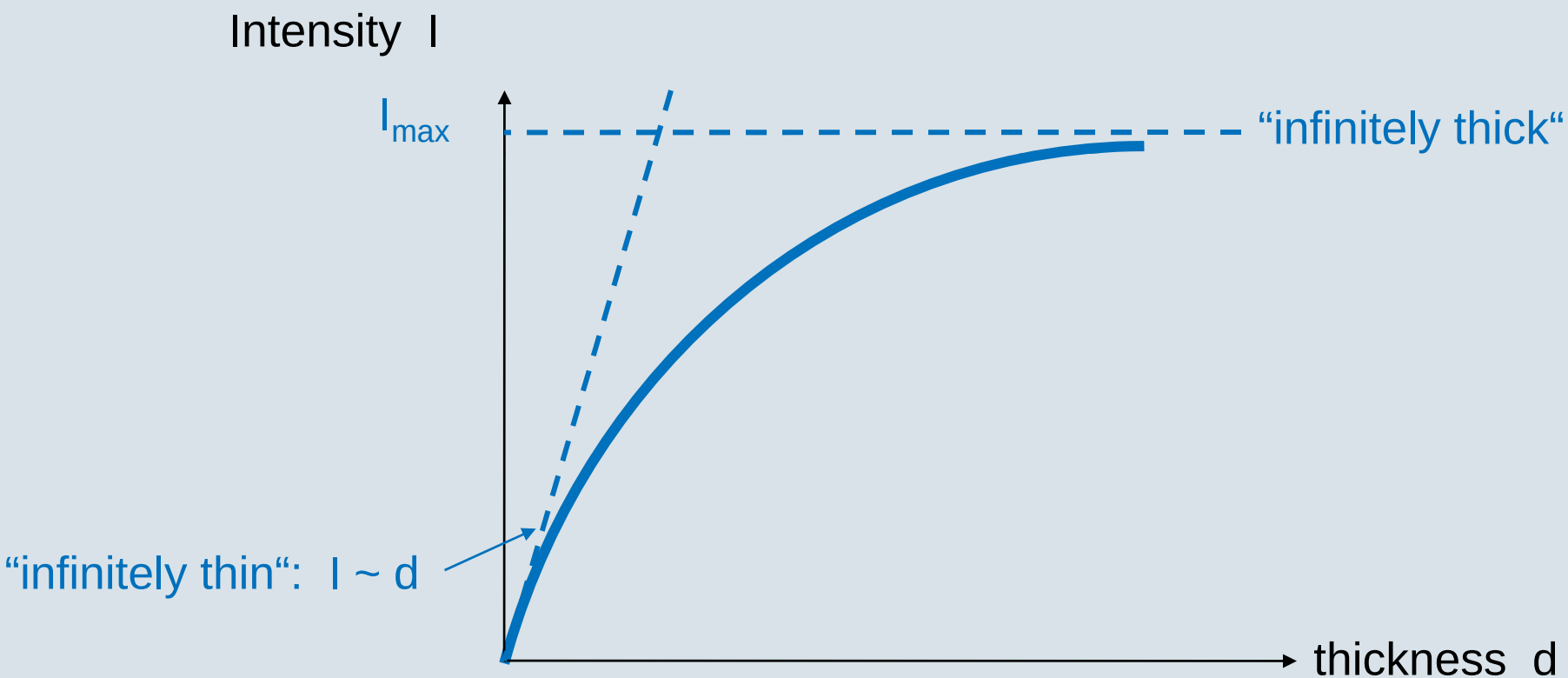
- The concentration is affected by the matrix
- Matrix matching or "defined matrix"

X-ray Fluorescence Analysis "Infinitely Thin Sample"



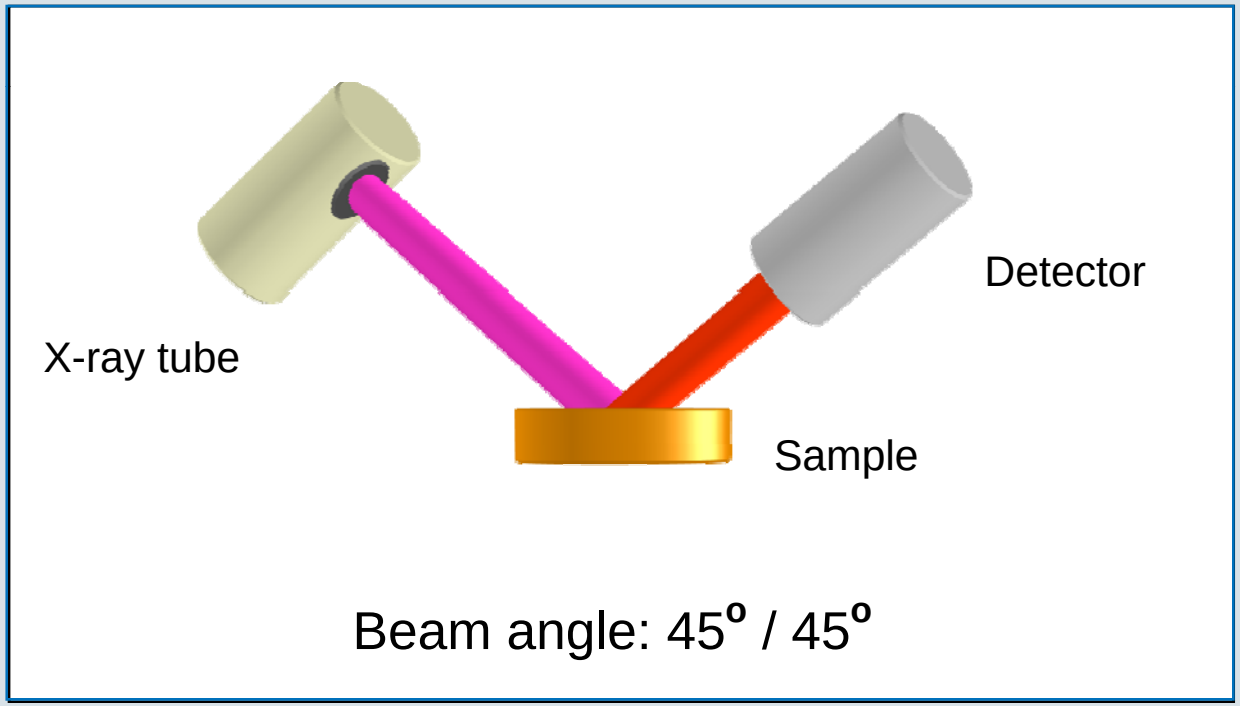
- the absorption of the exciting and the fluorescence radiation can be neglected
- the intensity of a characteristic line is proportional
  - **to the number of atoms of this element per area**
  - **to the mass per area (g/cm²) of this element**
  - **to the thickness (for constant density and composition)**

X-ray Fluorescence Analysis
Influence of Sample Thickness



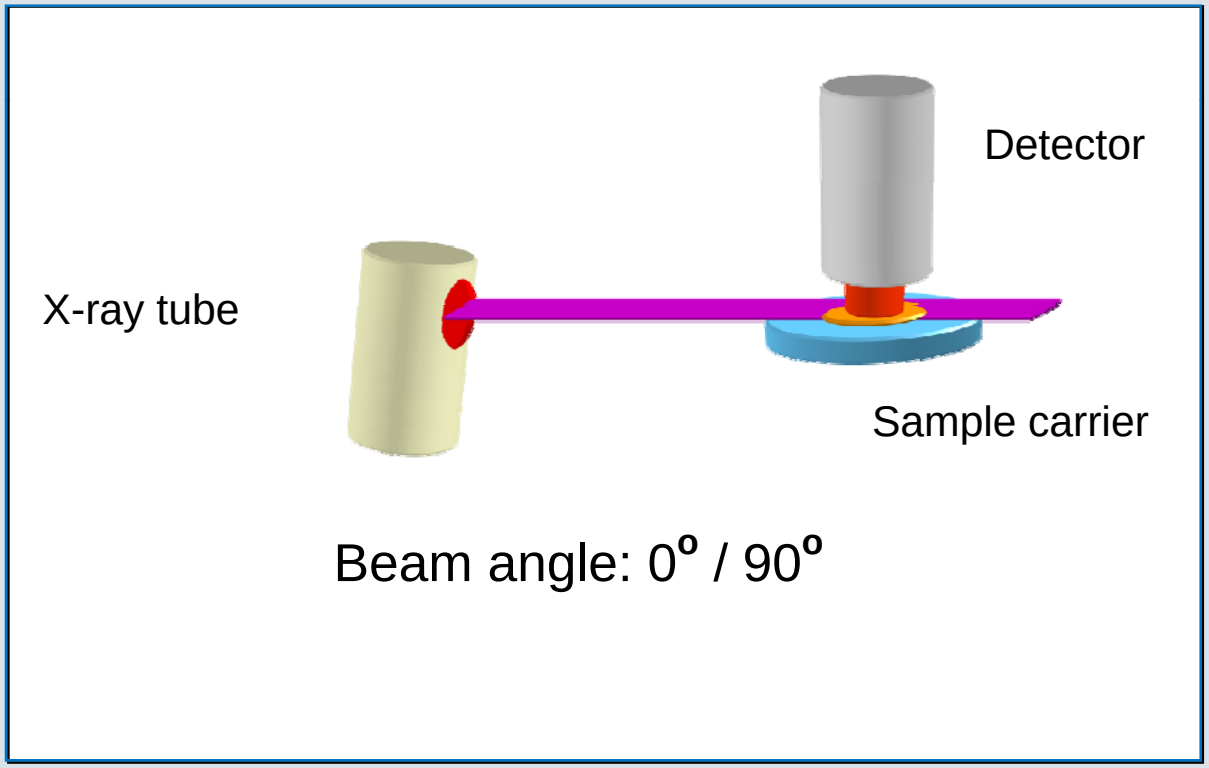
Principles of X-ray fluorescence spectroscopy

„Common“ XRF-optics



Principles of total reflection X-ray fluorescence spectroscopy

Total reflection X-ray fluorescence spectroscopy



Trace Elements in Food & Beverages
Lead in Rum

History

During the late 1690's, there was a severe outbreak of colic in Germany. The Duke issued a decree forbidding the use of lead-based additives in any wine product.

Sample

- Rum, 18 years old

The competition

- Flow-injection hydride-generation atomic absorption spectrometer with flame-quartz atomizer (FI-HG-AAS)
- S2 PICOFOX TXRF spectrometer

Source: Latif Elçia, Zikri Arslanb & Julian F. Tyson (2009):
Determination of lead in wine and rum samples by flow injection-hydride generation-atomic absorption spectrometry,
Journal of Hazardous Materials, Volume 162, Issues 2-3,

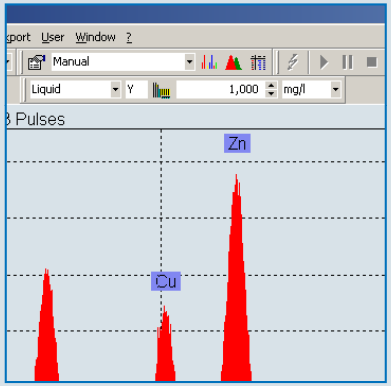
Sample Preparation
Liquid Samples

You'll need just a few steps for the preparation of liquid samples




- Fill sample in micro tube
- Add internal standard
- Homogenize
- Pipette on carrier

Sample Preparation
Final Steps



- Dry by heat / vacuum
  - Load the instrument
    - Start data aquisition

Trace Elements in Food & Beverages
Rum

	TXRF	FI HG AAS
Sample preparation	1. addition of Ga standard to 1 ml rum 2. 10 µl sample on quartz carrier	1. acidification of 170 µl rum to 0.30 Vol-% HCl, 2. addition of 3% solution of oxidant $K_3Fe(CN)_6$ in HCl 3. Neutralisation with $NaBH_4$ formation of lead hydride (PbH_4)
Measurement	1000 s measurement time	1. calibration 2. measurement

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Measurement	1000 s measurement time	1. calibration 2. measurement
Recovery Standard deviation Detection limits*	96.5 % 2 % 0.56 ppb wide linear range	error margin 4.6 % < 12 % 0.16 ppb restricted linear range up to 8 ppb
Remarks	simultaneous detection of other harmful metals	

*) current limit values for wine according to european legislation = 200 ppb

Pb started it all (with XRF)

- First general XRF use was for Pb in paint:
- Paints containing more than 1 mg/cm2 Pb needed to be removed
- Systems usually have LLD 0.05 mg / cm2 Pb
  - Map-4/LPA-1 using Co Isotope source and CdTe detector (around since 1997)
  - Niton “brick”
  - InnovX LBP4000 HUD: tube based system
- XRF is the preferred method due to portability and immediate response

CPSIA 2008 Consumer Product Safety Improvement Act

- Became law August 14, 2008 –passed in response to massive recalls in 2007
- Restricts Lead and Phthalates in children's products
  - Covers all consumer products for a child under 12
  - Major expansion from Toys (Pb in paint restricted)
- Lead Levels - bulk
  - 600 ppm February 10, 2009
  - 300 ppm August 14, 2009
  - 100 ppm August 14, 2011 – if technologically feasible

2007 Existing Standards DIN EN 71-3

- Toy safety standard for EU
  - Section 3 details maximum migration limits for certain elements based on HCl extraction

Element	Sb	As	Ba	Cd	Cr	Pb	Hg	Se
Toy material	60	25	1000	75	60	90	60	500
Art/Clay	60	25	250	50	25	90	25	500
Rel % correction	60%	60%	30%	30%	30%	30%	50%	60%

2007 Existing Standards
ASTM F963-07e1

ASTM F963 - 07e1 Standard Consumer Safety Specification for Toy Safety

- Includes
  - 16 CFR 1303 Ban of Lead-Containing Paint and Certain Consumer Products Bearing Lead Containing Paint
- Includes
  - EN71-3 Extractable elements list
- CPSIA 2008 “makes” ASTM F963-07
  - Several sections excluded

Extractable vs.Total content

- EN71-3 and ASTM F963-07 specify extractable levels of toxic metals
  - Extractable imply the amount dissolved in a solution simulating gastric fluids and in many cases is much lower than total
- CPSIA 2008 refers to total levels of toxic materials
  - Total levels are the total measurable levels regardless of how they are bound in the product.
  - Toxic material may or may not be bio avaliable
  - CPSIA decided measurement of total has no measurement issues

CPSIA 2008
Lead in Paint and Coatings

- Effective August 14, 2008
  - Lead in paint and coatings must be less than 600 ppm
- Effective August 14, 2009
  - Lead in paint and coatings must be less than 90 ppm
- Method for screening lead in small painted areas
  - XRF may be relied on to determine lead is less than 2 micrograms in an area of less than 1 cm^2 or 10 milligrams

CPSIA 2008
Alternative Method for Measuring Lead

- Not later than 1 year after the date of this Act the CPSC shall complete a study to evaluate the effectiveness, precision and reliability of XRF and other techniques to measure lead in paint used on children's products

- If the CPSC determines that XRF is as effective, precise and reliable as current methodology, they may issue regulations governing the use of such method(s)

CPSIA 2008 Exclusions

- Excludes inaccessible components (e.g. electronics boards)
  - Shielding by paint is not deemed inaccessible

- Excluded Materials (proposed Dec 2008):
  - Precious gemstones
  - Certain semiprecious gemstones
  - Wood
  - Natural fibers – cotton, silk, wool, linen
  - Other natural materials – coral, amber feathers
  - Only for untreated and unadulterated by the addition of materials of chemicals

KIDS toys…

- Example from CBS (Canada)

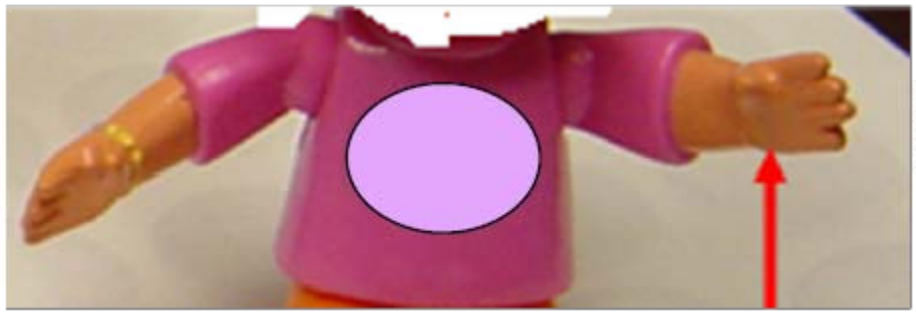
Barbie Lipstick Red	— 1.37 PPM
Barbie Lipstick Orange	— 1.80 PPM
Barbie Candy	— 2.86 PPM
Checkers by Encore Sales	— 4.12 PPM
Steve by Blues Clues	— 5.53 PPM
Furby Knapsack	— 7.12 PPM
Britney Spears Doll Suit	— 19.36 PPM
Bevy's Babes Jewellery Fish Key Chain	— **165.37 PPM**
Pencils by Stravina	— **289.86 PPM**
Bevy's Babes Jewellery Candy Necklace	— **88954.38 PPM**
Bevy's Babes Jewellery Heart Necklace	— **80287.77 PPM**

CPSC Testing Method

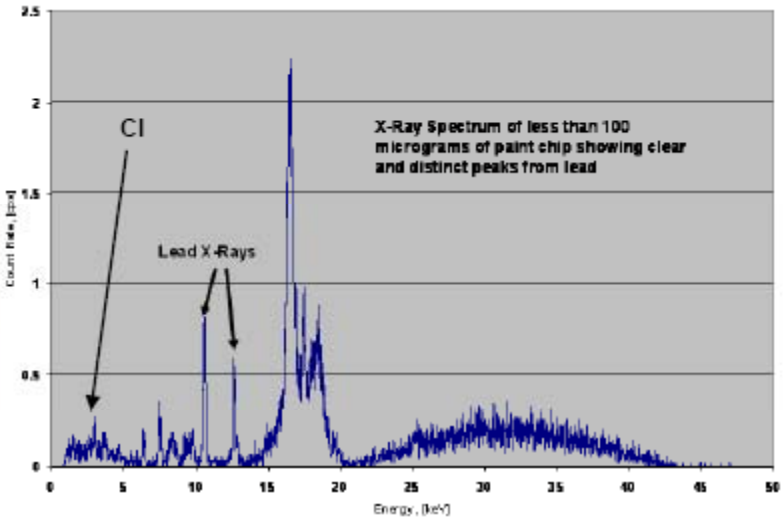
- CPSC Testing Laboratory Chemistry Division LSC developed and audited SOP's for paint and jewelry:
  - Paint (based on AOAC 974.02)
    - Sampling of up to 20 mg
    - Digestion by nitric acid of the paint (ASTM E1645)
    - ICP or AAS (ASTM E 1613) TXRF in approval process
    - HH XRF is allowed as SCREENING to help sampling
  - Jewelry (CPSC-CH-E1001-08)
    - Sampling
    - Hot block or microwave digestion with aqua regia
    - ICP or AAS (ASTM E 1613) TXRF

Are the "Wet/ICP" methods perfect?

- **Sampling is the crux and weak point**
  - How do you sample the "paint" on a toy?
  - Pink area was sampled and found to contain no lead, whereas the "hand" contained measurable lead.



Pb



Are the "Wet/ICP" methods perfect?

- Problem of sample acquisition
  - Sample is obtained by scraping paint off substrate
  - Sampling is very tedious and time consuming
- Problem of incomplete digestion
  - Often paint does not completely digest
  - This leads to low readings of lead
- Problem of sampling large volumes of toys
  - Prohibitive time for total analysis (sampling, digestion and testing)
  - Destructive testing – 100% inspection is impossible

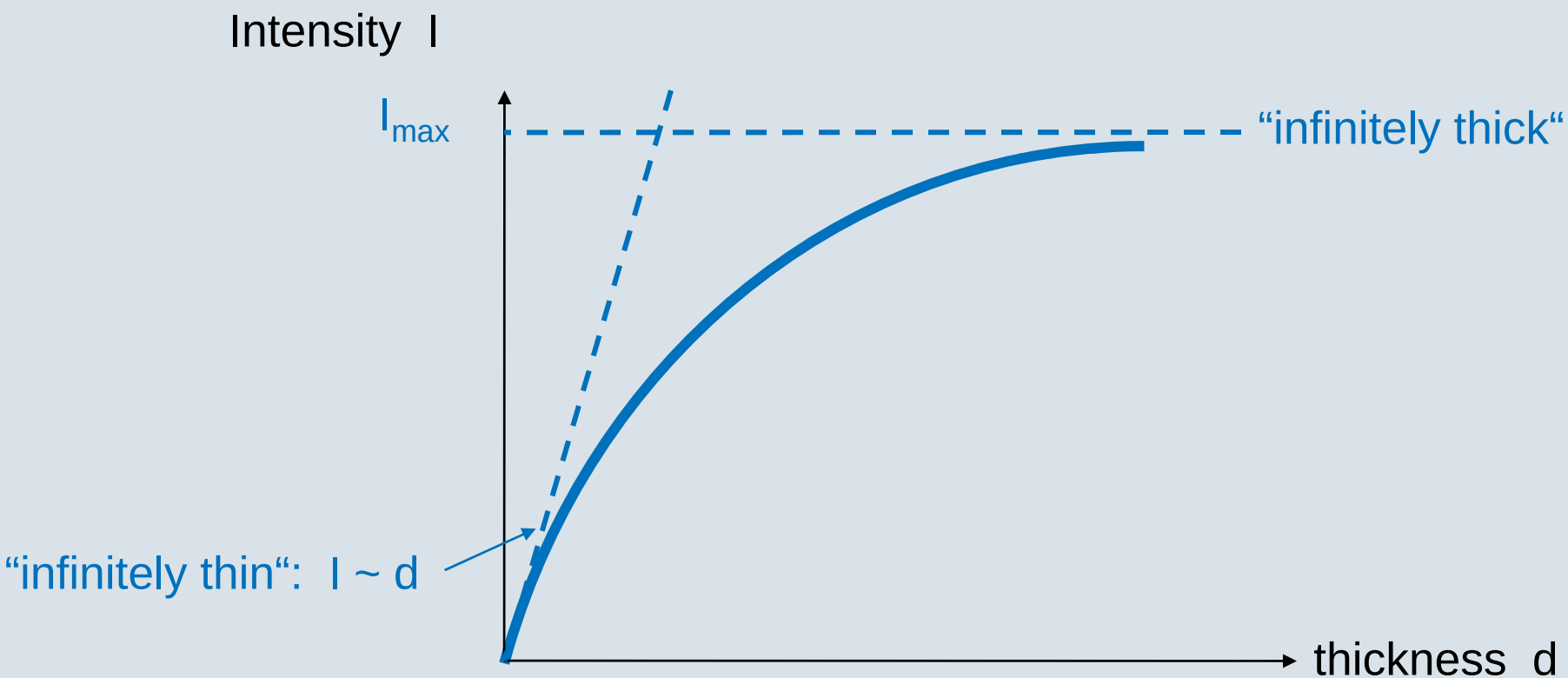
XRF As Alternative?

- Method is non-destructive
- Method is fast (10-60 sec measurement times)
- Results for homogeneous materials is equivalent
- Results for coatings is given in micrograms/cm^2
- Screening is appropriate
  - No lead detected will pass
  - High lead will fail
  - Intermediate values need further testing
- Can be used continuously during production to audit products

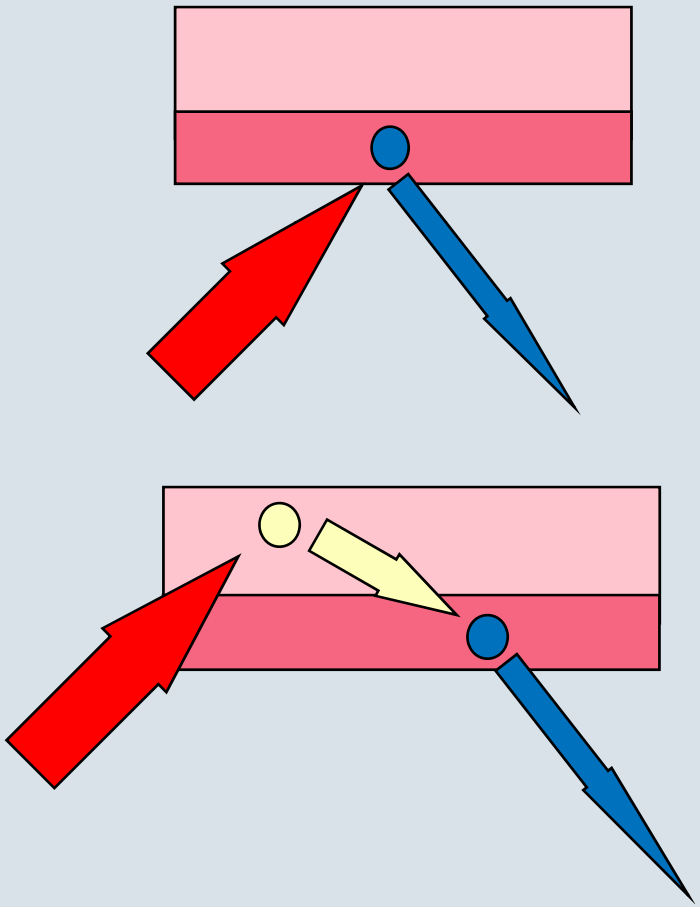
What about XRF and CPSIA 2008

- No problem to use in homogeneous substrate samples
  - Quantitative Analysis is possible
  - Use ASTM F2716 Heavy metals in Polymers
  - Mobile HH XRF for nondestructive use
  - Lab based XRF destructive with sample prep
  - All can report total lead which can be referenced to CRM's in existence (specialized calibration per matrix or Universal calibrations)
    - E.g. polymers, glass, metal etc.
  - Good for infinitely thick samples
- TXRF is suitable for analysis of undigested samples as well as digested samples instead of ICP/OES!

X-ray Fluorescence Analysis
Influence of Sample Thickness

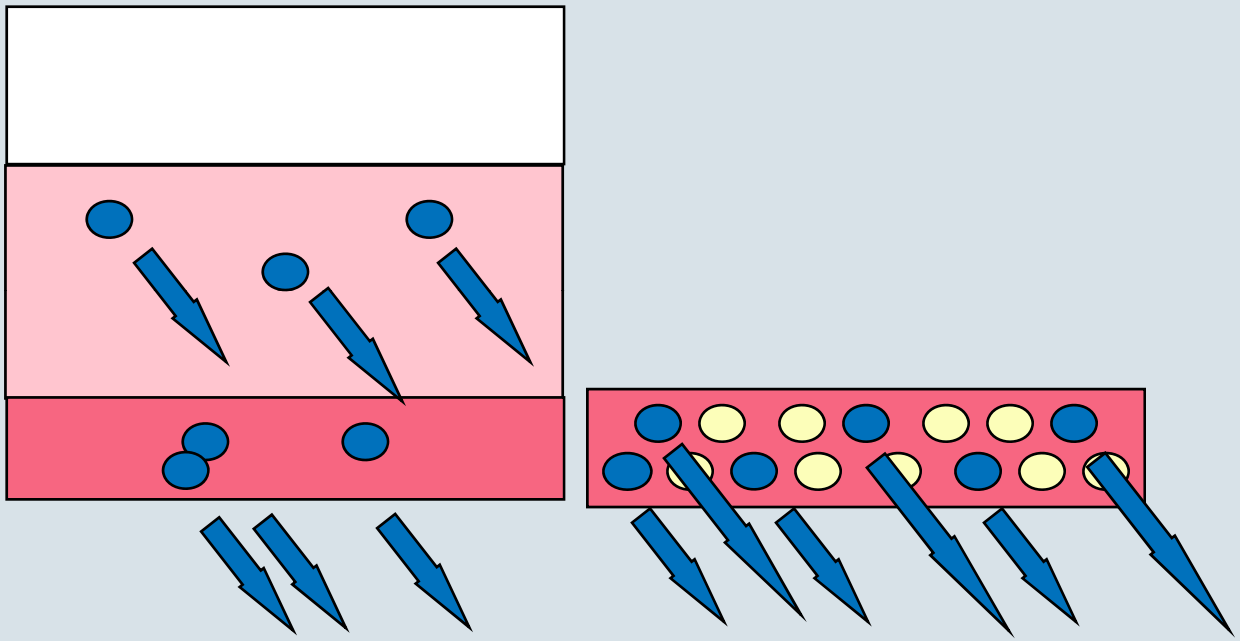


X-ray Fluorescence Analysis
Thin Layers



- a thin layer on a substrate can be determined in the same way as a thin sample
- possible difference:
  secondary excitation (enhancement) by an element in the substrate

Homogeneous thick and thin samples
No problem for XRF!



- For homogeneous thick or “thin” samples XRF will be able to report data…
- For thin samples ug/cm2 are used (based on physics!)

What about XRF and CPSIA 2008

- How can ug/cm2 be related to PPM (mg/kg)
  - NOT DIRECTLY!
  - Need to know layer thickness and density to convert
- Can we use small spot screening rule?

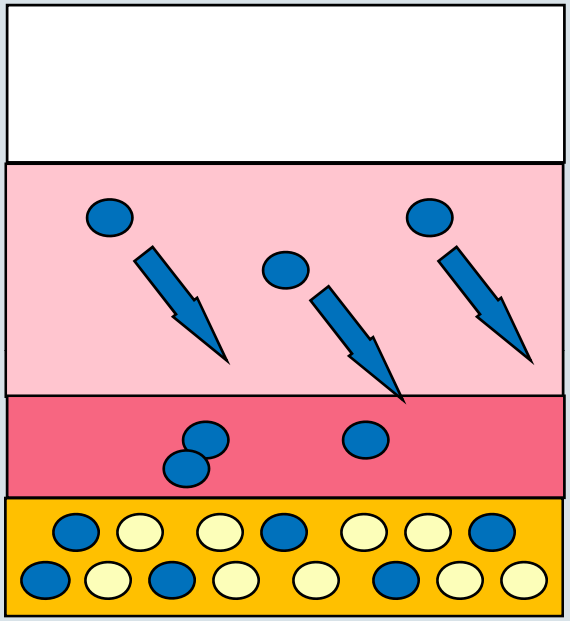
  Small Areas:
  - 2 micrograms/square centimeter Pb max
  - 2 micrograms/10 milligrams or less

    with conservative "thin sample" setting

ASTM F40 Methods for Pb

- ASTM F40 – Restricted Materials
- ASTM F2617 – Heavy Metals in homogeneous polymers
- Work Item 21957 –
  - Quantify layers in micrograms/cm^2
  - Screen layers against the 2 microgram/cm^2 limit
  - Participants are welcome

The real sample!



- Multilayer samples
- Can we get a real reading with XRF here?
- Screening is appropriate here

CPSC view on XRF (1)

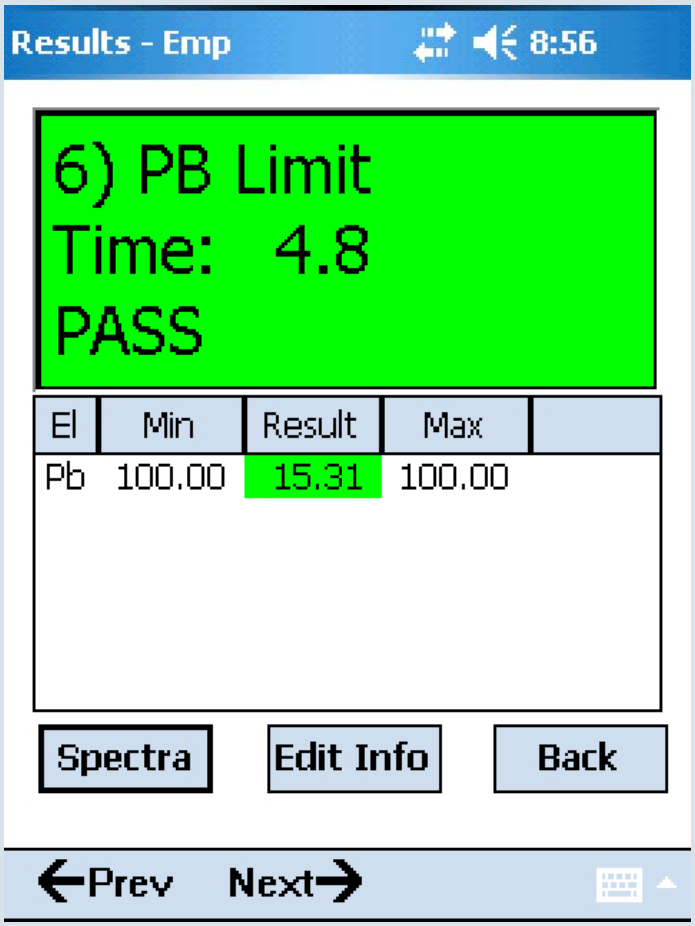
- XRF can be used as a screening tool for lead in paint, but requires an understanding of it's limitations and how it relates to a painted surface. Conservative approach is to use THIN sample mode with dedicated calibration.
  - CONSERVATIVE!
  - SCREENING!
  - LOWER sample volume!
  - INFORMED USE!
  - "destructive sample prep (scraping) = quantification
    - ED WD XRF or even TXRF!

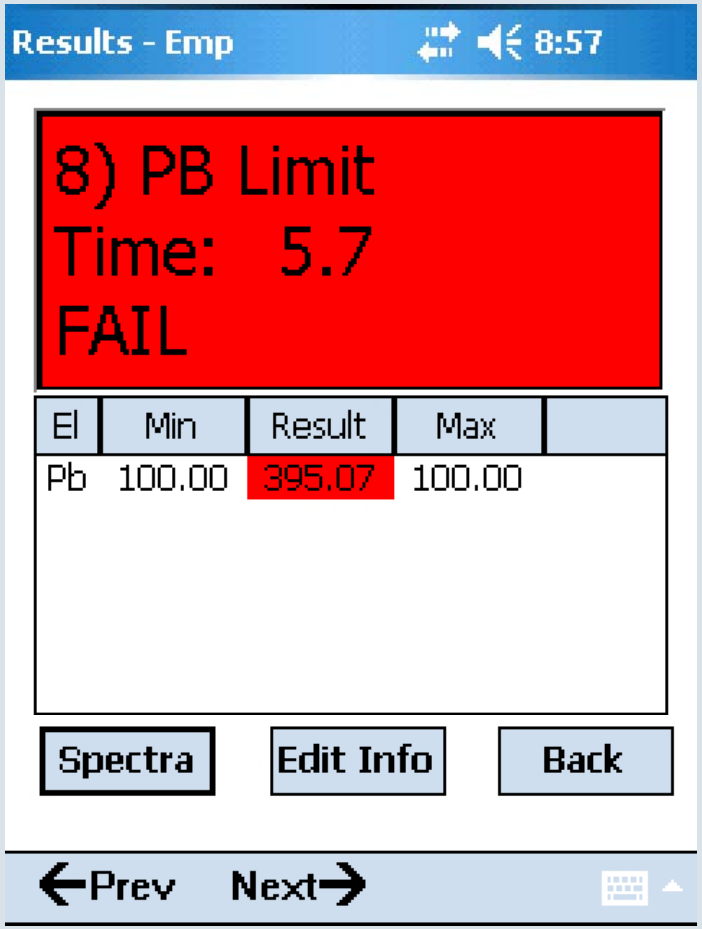
What tool to use, when?

- Inspection especially for sampling
  - HH XRF
  - Examples to follow
- Quantitative check
  - KNOWN sample to select the correct mode
  - Thin sample mode (remove paint)
  - Bulk sample mode (raw material)
  - Defined coating (thru ML software)
  - TXRF -> Thin sample with internal standard as PPM!

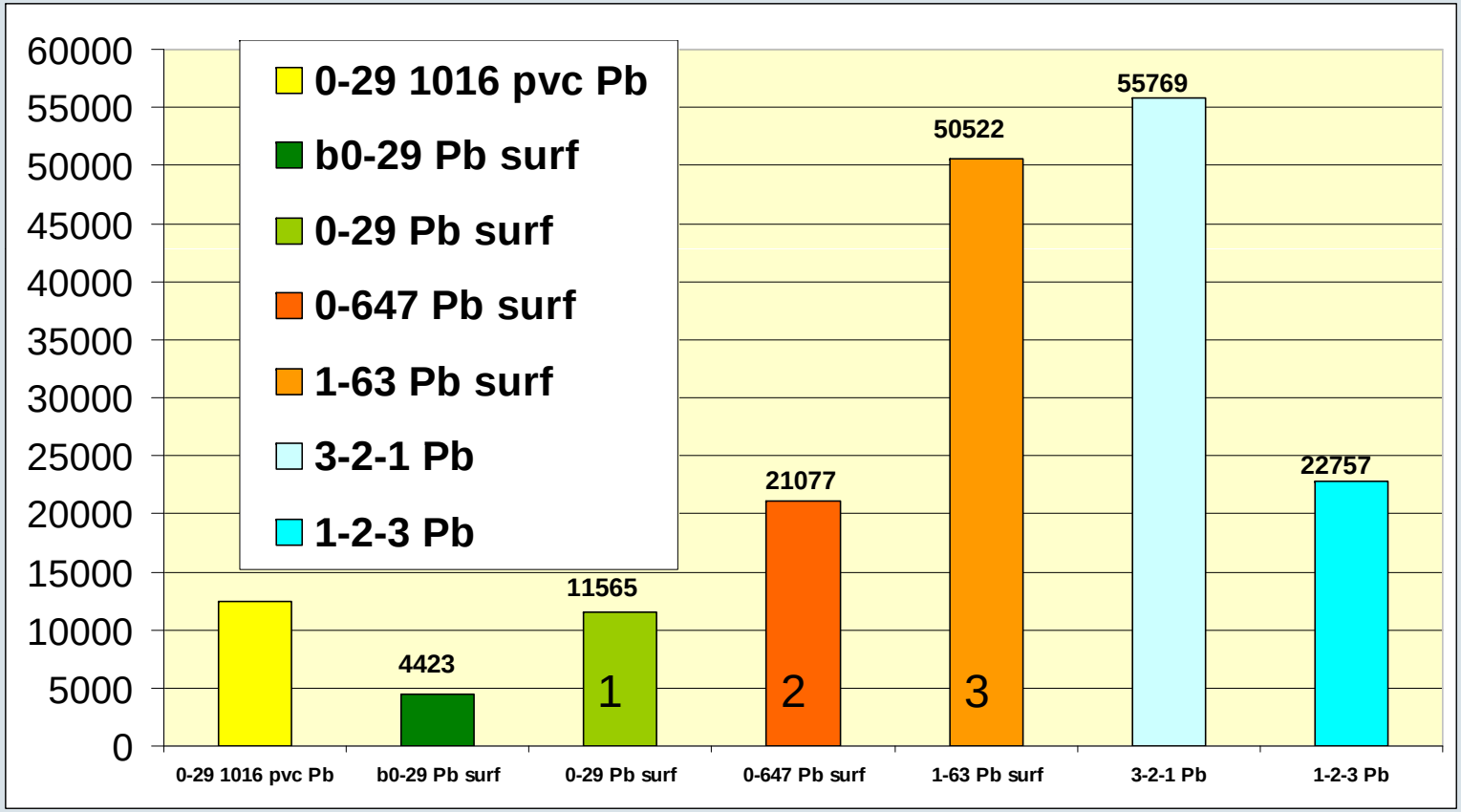
Application of XRF Screening

Application of XRF Screening





Understanding the distribution of the element of interest is vital to quantification!



The light blue bars show the analysis of the same 2 NIST thin film paint standards on a thin sheet of cardboard. Simply reversing the order changes the intensity measured by about 2.5 times. The analysis of these three standards separately(1,2 and 3) gives 83164, 50% higher than the samples measured together

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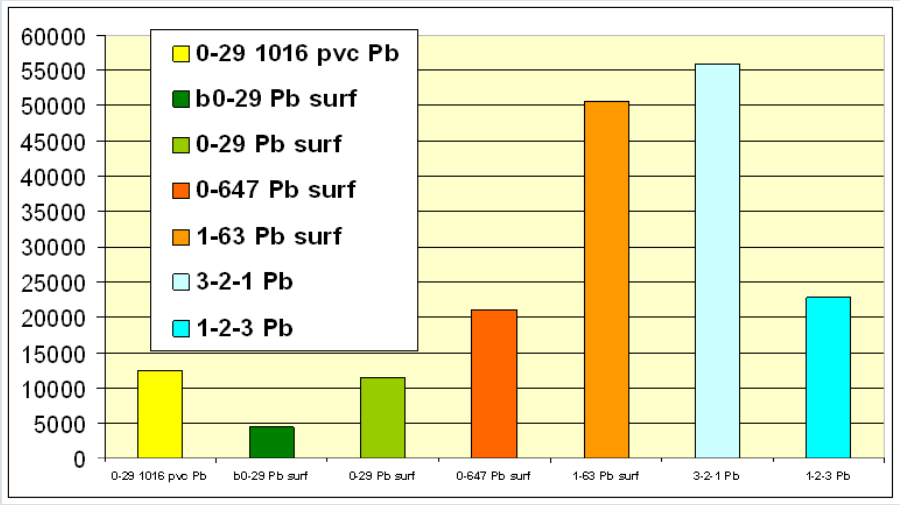
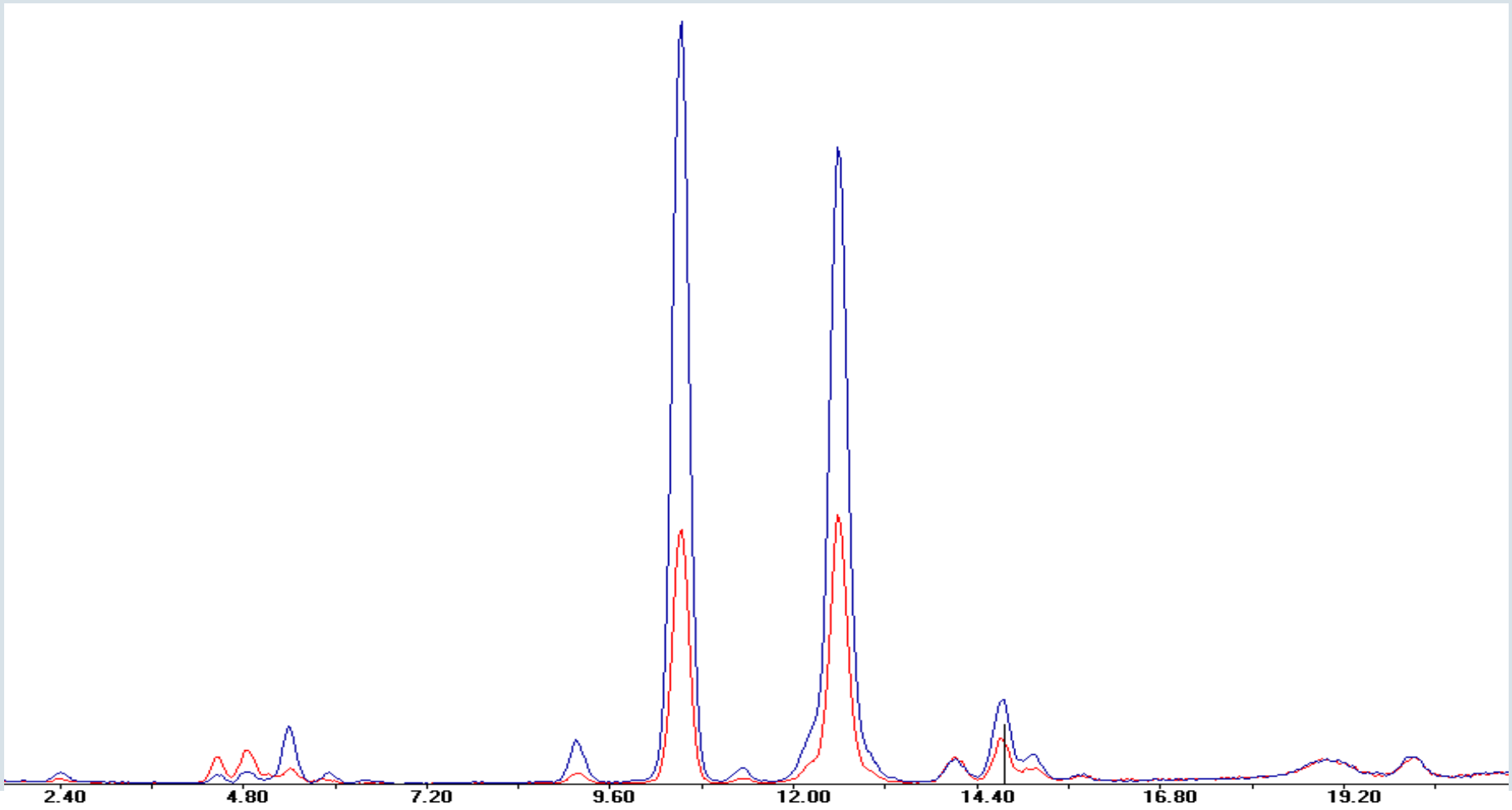
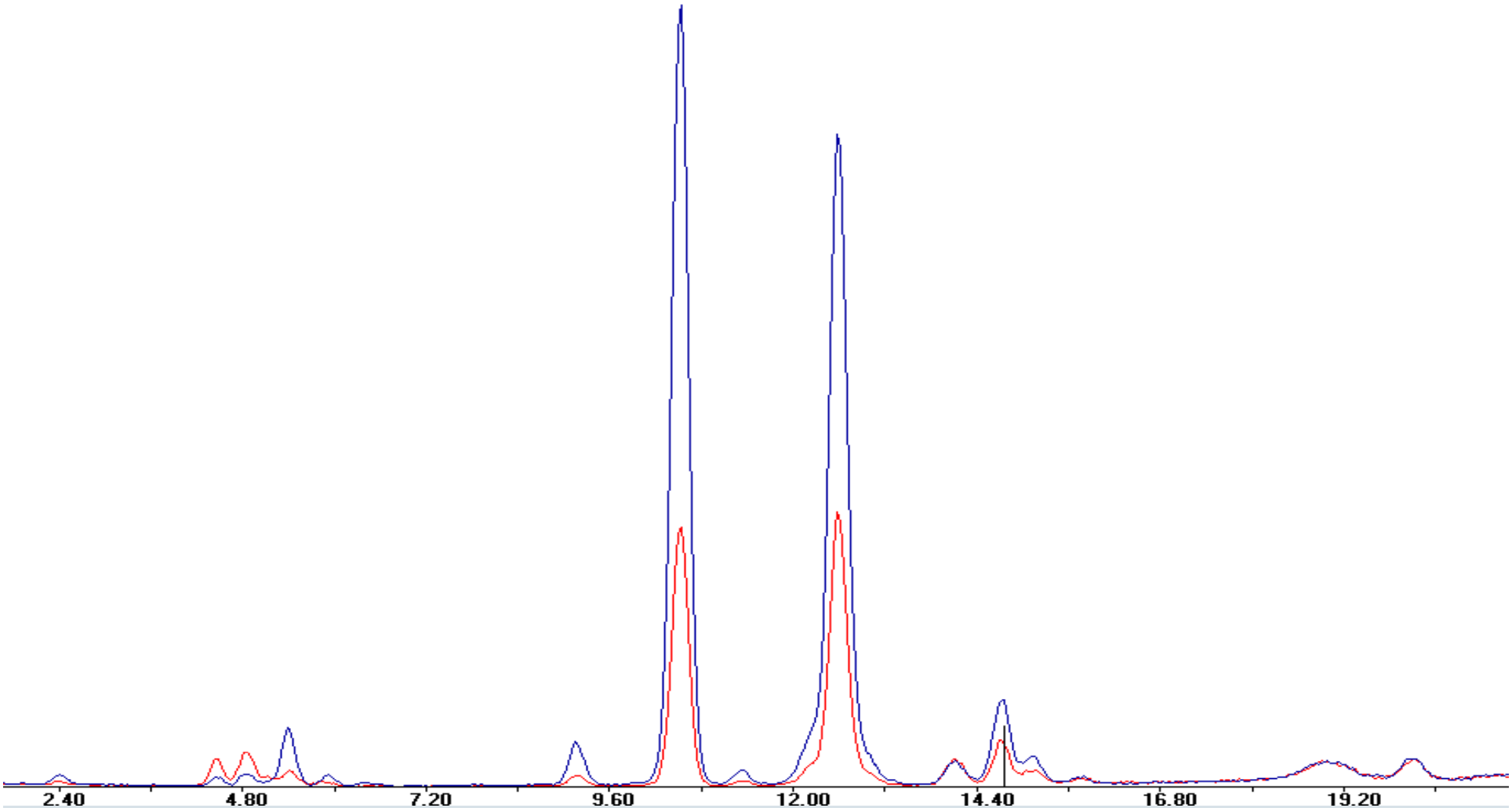


Over laying of 1-2-3 and 3-2-1 shows clearly the x ray scattering is the same but the intensity of the all the Pb lines are very different. Note the shift in the ratio of the 2 major lead L lines indicating that the major source of the Pb lead x rays come from below the surface of the sample.



Bruker AXS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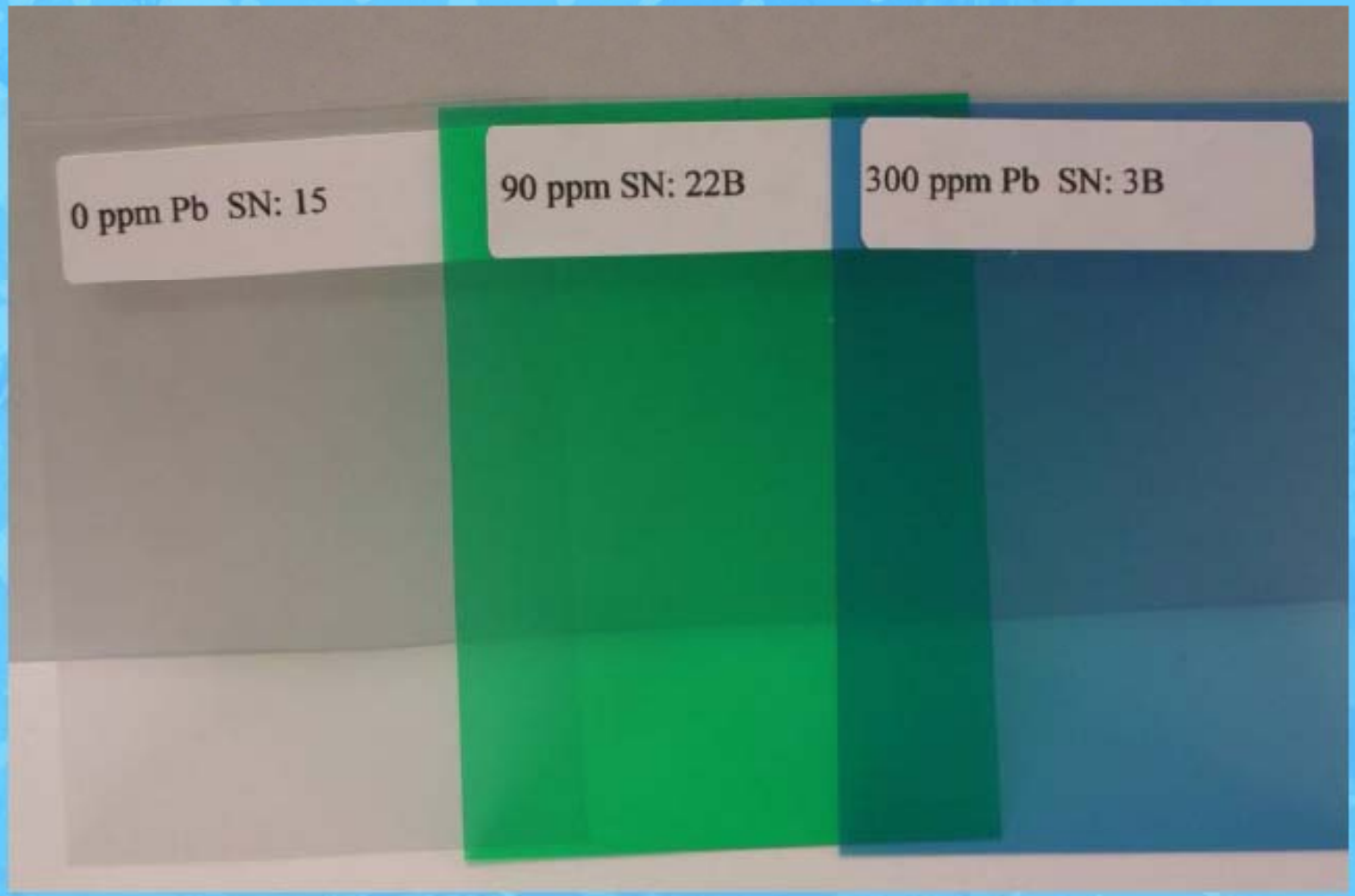
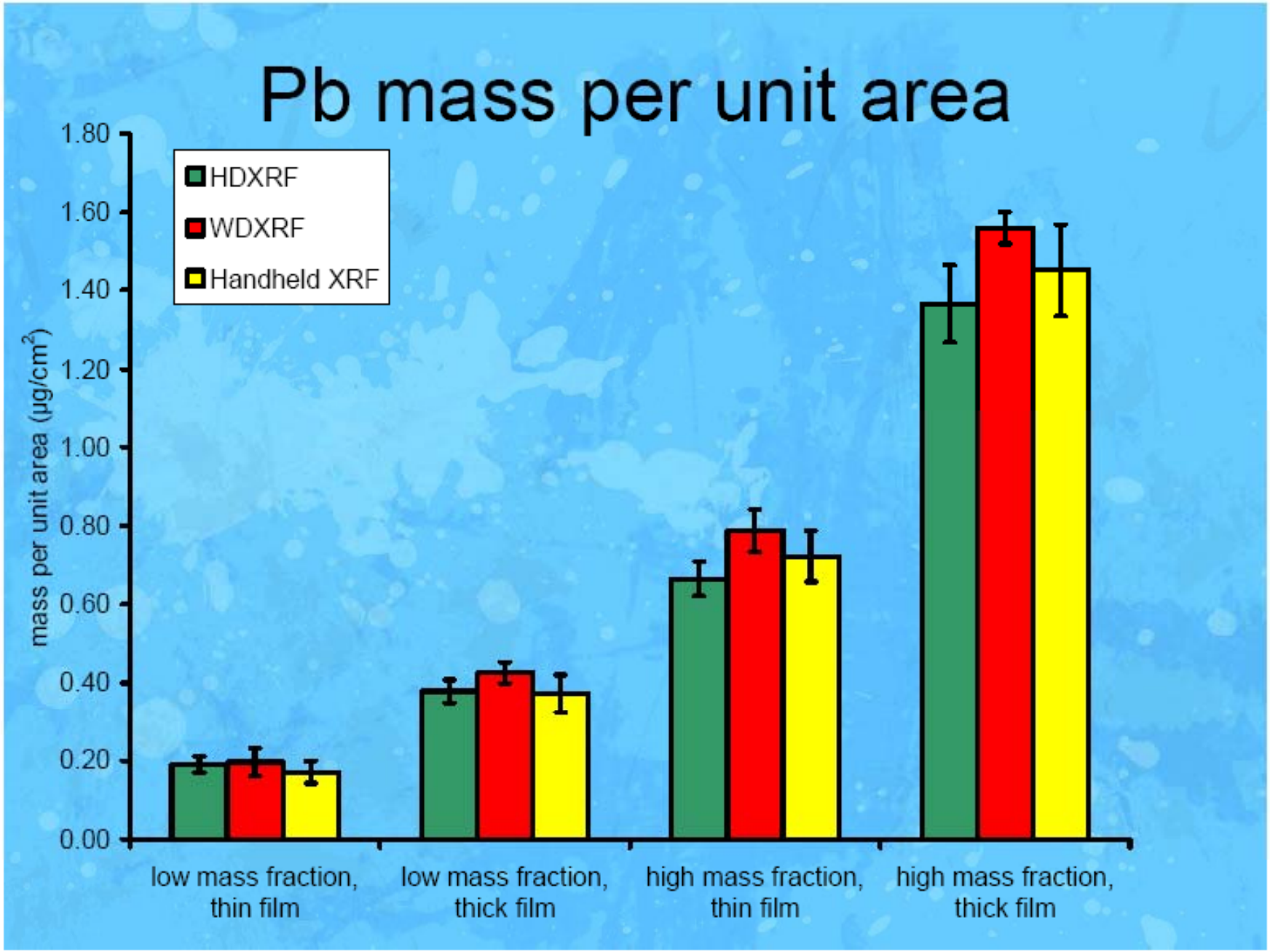
4.80
7.20
9.60
12.00
14.40
16.80
19.20

Paint prototypes



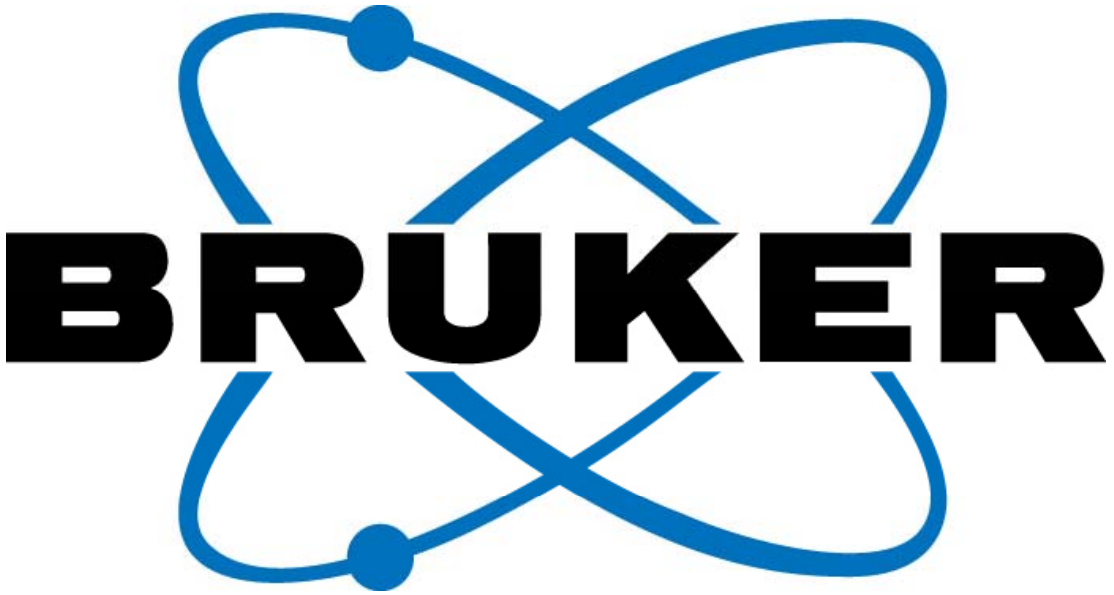
Courtesy John Mollov NIST 2010 PITTCON2010



Courtesv John Mollov NIST 2010 PITTCON2010

CPSC Summary and to do

- 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 µg/cm**2**. (eliminating substrate)!



www.bruker-axs.com