Protocol for Bruker XRF Analysis of Non Uniform Material containing or coated with Heavy Metal Poisons

It is generally and physically impossible for xrf analysis to provide one with a quantitative elemental measurement, such as ppm, of various materials that are non uniform in space, material type, density and elemental composition; this includes painted wood, fur, feathers, toys, soil, pottery, basketry, clothing, stuffed animals etc.

But it is possible to detect the presence of heavy metal poisons and to estimate from the **raw** xrf spectrum whether the amount of the poisonous element is significant or trace and whether it is present as a part of the original fabrication of the material or that it was applied later with the intention of preserving the material. What is described here is Protocol for XRF Analysis of Materials for Heavy Metal Poisons; As, Pb, Hg, Cd, Br, Se.

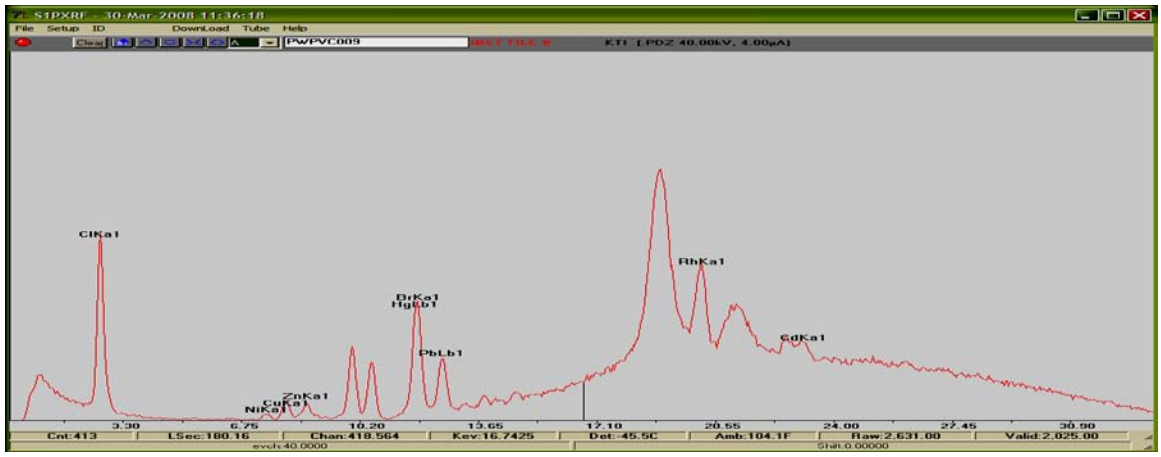
Tracer III SD Operation Conditions for XRF Analysis of materials with Heavy Metal Poisons

The sensitivity to particular elements is a function of the instrument setup, of the element, and of the material but with the settings described below the sensitivity to As, Pb, Hg, Cd, Br, Se in plastics, soils, liquids is typically 1 to 20 ppm if the material is uniform and at least 5 mm thick. What this means, is that when you review the raw spectrum and note that you can barely see the presence of the spectral PATTERN for one of these elements, it means, it might be present in the location that was measured near this level. ***This does not mean the object contains that ppm***. It just means that that element appears to be barely present in that location. It could be simply covered or imbedded in the object at 100 % and you are just barely detecting it through a coating. NOTE THE ENTIRE SPECTRAL PATTERN FOR THAT ELEMENT MUST BE THERE. Then one MUST measure that object or material is SEVERAL locations to determine the extent of that element in that object always looking for at the raw spectrum and the ENTIRE SPECTRAL PATTERN FOR THAT ELEMENT MUST BE THERE.

Parameters for the Measurement of "Poisons" using the Tracer III SD (higher Z elements Hg, Pb, Br, Se, Cd, Br, As:

1. 0.001" Cu, .001" Ti, .012 Al ***(Red Filter)***
2. 40 kV
3. Highest current setting available
4. No vacuum

These settings allow all the x rays from 14 keV to 40 keV to reach the sample thus efficiently exciting the elements Hg, Pb, Se, Cd, Br, As. These are some of the key elements that are of concern for health effects. There is little sensitivity to elements below Fe with these settings. To measure Cr requires a different instrumental set up.



There are five specific steps that one must flow:

1. The Xrf analysis system operation conditions and characteristics must be known:
    a. Beam pattern or profile
    b. X ray beam energy spectrum and intensity
    c. Detection sensitivity for the elemental x ray emissions of interest
2. Measure known uniform reference materials similar in composition to the artifacts to be analyzed with various concentrations of the heavy metal poisons of interest.
3. Measure the materials of interest in several diverse locations, noting material type, position and a general material description including a color photograph of the material noting location of each analysis.
4. Review the all the raw spectrum from a given material over laid in a single plot noting:
    a. Presence or absence of given spectral lines from the elements of interest
    b. The relative intensity of the lines present from location to location on the artifact
    c. The physical appearance of the artifact at the location where spectral lines of interest are present in the spectra
    d. Finally relate the intensities noted that are determined to likely be the Heavy Metal Poisons to the intensity of the peaks of those spectra of known materials and concentrations in step 2.
5. Report observations.

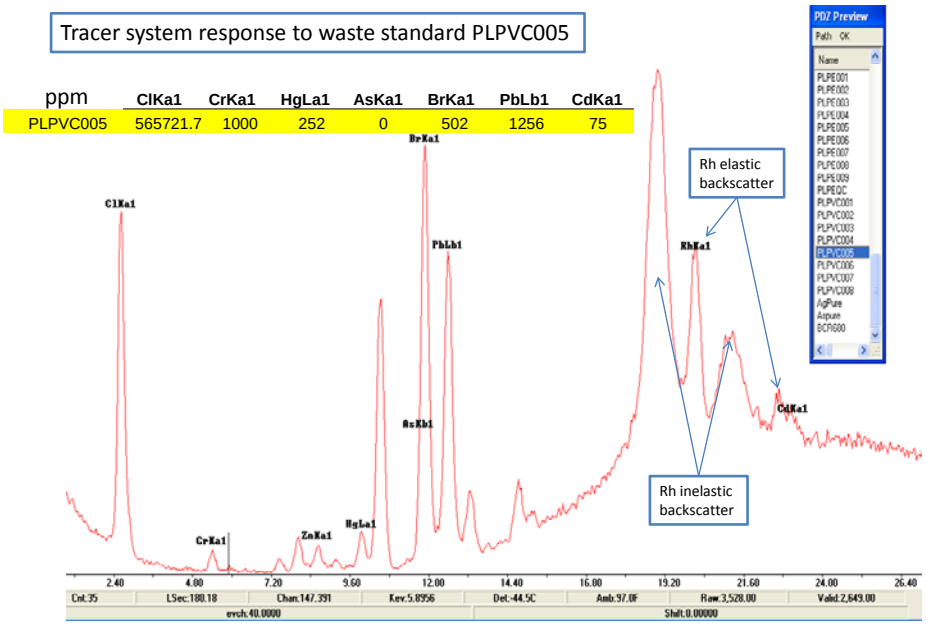
As a general note, the elements of interest in heavy metal poisons are As, Pb, Se, Cd, Hg and Br. All of these elements can be part of the artifact's composition or original fabrication process. In particular note Vermillion, which is a naturally occurring red pigment, is composed of Hg and S. Pb occurs often in paint and glass and is found in almost all materials that predate 1975 in trace amounts because of the use of leaded gas in cars over the years. Arsenic occurs in green pigments, as a natural constituent of glass and in Cu alloys as a trace element. Bromine occurs in some natural materials as part of the natural make up.

Once these elements are detected to determine whether they are natural or applied one must analyze the artifact in several diverse locations and use the detailed knowledge of the artifact's original make up to determine its source.

X ray beam energy spectrum and intensity:

Detection sensitivity for the elemental x ray emissions of interest:

Note that the Rh inelastic peak can be used as a relative gauge of the amount of an element in the beam path. Elemental peaks that go above Rh K inelastic back scatter are well above trace and should be considered as a very purposeful content in the artifact. Those that the elemental spectral patterns can barely be seen are either at ppm levels or are present behind a layer of material. Below is a typical spectrum of a standard that can be used to compare to analysis of unknown materials.



Concentration of typical waste standards made in PVC is shown below. Spectra of Ref material samples can be used as visual references for measurement of unknown materials. Like the one above.

	ClKa1	CrKa1	HgLa1	AsKa1	BrKa1	PbLb1	CdKa1
PLPVC001	567472.4	0	0	0	0	0	0
PLPVC002	566776.1	51	101	0	51	999	25
PLPVC003	566243.8	753	51	0	1009	251	101
PLPVC004	566230.2	1251	507	0	251	50	130
PLPVC005	565721.7	1000	252	0	502	1256	75
PLPVC006	565467.5	651	815	0	1289	768	10
PLPVC007	566276.7	255	997	0	750	100	5
PLPVC008	566797.1	501	35	0	104	500	50
PLPVC009	566257.4	100	1267	0	274	350	150
PowPVC001	567472.4	0	0	0	0	0	0
PowPVC002	566768.2	51	99	0	50	1016	25
PowPVC003	566238.1	749	50	0	1026	250	100
PowPVC004	566222.8	1251	517	0	258	49	127
PowPVC005	565703.6	1000	262	0	518	1262	75
PowPVC006	565564.5	643	734	0	1221	754	10
PowPVC007	566259.7	263	998	0	771	100	5
PowPVC008	566771	522	34	0	103	528	49
PowPVC009	566193.9	100	1265	0	273	465	150
PWPVC10	564554.6	643	734	1779.784	1221	754	10
PWPVC11	564580.6	500	503	3042.825	500	500	50
PVC01A	567472.4	0	0	0	0	0	0
PVCL07A	566564.4	400	200	0	500	400	100
PVCH06A	564803	1001	1101	0	1101	1201	300