THE CHALLENGES OF XRF ANALYSIS OF CULTRUAL HERITAGE GLASS OBJECTS

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The Corning Glass Museum has been using XRF and watching its development over the course of about 40 years. Like all other analytical techniques it has its advantages and disadvantage for the analysis of glass objects, artifacts and antiquities. The earlier lab based xrf systems allowed for destructive analysis of shards or of material that had been “prepared“ for analysis by homogenizing the samples. For xrf analysis sampling and homogenization of the sample still is the only way to get fail safe accurate elemental analysis of glass. Unfortunately this technique just cannot be used on most important glass objects because destructive analysis is absolutely not acceptable. With the advent of the x-ray tube hand held system, with laboratory based capabilities, non destructive, non sampling, no effect on the object xrf analysis became possible. But great care must be used when using xrf of any type on unprepared samples. The physics of xrf analysis is dependent on; the inverse square of the distance to the element, exponentially relative to matrix density, exponentially relative to elemental X ray energy emission, exponentially relative to element location in the sample matrix, exponentially relative to beam filtering and energy and X ray beam distribution. Thus, if you do not have perfect sample uniformity, analysis by any xrf system must be treated with great care. For three years Corning glass museum and the scientists at Bruker Elemental have been developing and studying the best methods, techniques, and strengths and weakness of the application of x-ray tube hand held xrf system with laboratory based capabilities to the analysis of a broad array of glass objects at the Corning Glass museum. The results of this study and what can be determined and what cannot be determined because of the limit of the physics will be discussed.

Energy dispersive xrf advantages

1. Non sampling,
2. non destructive “artifact is in exactly the same condition after the analysis as it was before the analysis”,
3. portable,
4. instant semi quant elemental analysis,
5. quantitative if the situation allows, situation is very often misunderstand.

Limitations

1. light elements,
2. surface conditions,
3. sample uniformity,
4. measurement depth,
5. must know standard composition very accurately;
6. calibrations are specific families of glass composition.

Understand the Situation/overcoming the limitations

1. Physics
2. Depth,
3. uniformity,
4. matrix effects,
5. elemental interferences,

Never ever believe numbers unless you know the physics and your sample atom by atom

Answers vary as;

1. **the inverse square of the distance to the element**
2. **Exponentially relative to matrix density**
3. **Exponentially relative to elemental X ray energy emission**
4. **Exponentially relative to element location in the sample matrix**
5. **Exponentially relative to beam filtering and energy**
6. **X ray beam distribution**
7. **Orders of magnitude relative to sample uniformity**

Key families of glasses often encountered

1. **Na_2O: CaO:SiO_2**
2. **K_2O: CaO:SiO_2**
3. **PbO: (Na_2O/K_2O) :SiO_2**
4. **PbO: BaO: SiO_2**
5. **K_2O: SiO_2**

Calibration process

selecting the primary standards and/or Reference glasses typical of the unknown artifacts

1. **must include all elements of interest**
2. **must cover the range of concentrations**
3. **must include elemental combinations typical of unknowns.**
4. **Must know the concentrations accurately**
5. **Must assure that the standards are at least 4 mm thick**
6. **Must assure the standard is very uniform**
7. **Elemental range of calibration 1, 2 or 3**

defining the optimum operating parameters for the measurements, keep in mind what it is you wish to learn by the analysis

Are your Standards the same MATRIX?

Are your samples the same MATRIX as the standards?

Measurements of artifacts

Assure operating conditions are the same as calibration

1. Overlay cal spectra with unknown
2. Same backscatter
3. Maximum concentration
4. All fluorescent peaks are Identified
5. Only then can you trust the quant data

Examples of 2 different matrix glasses
Red in a Ca Silica glass
Blue is a Pb glass

Note backscatter differences!!

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5. **Exponentially relative to beam filtering and energy**
6. **X ray beam distribution**
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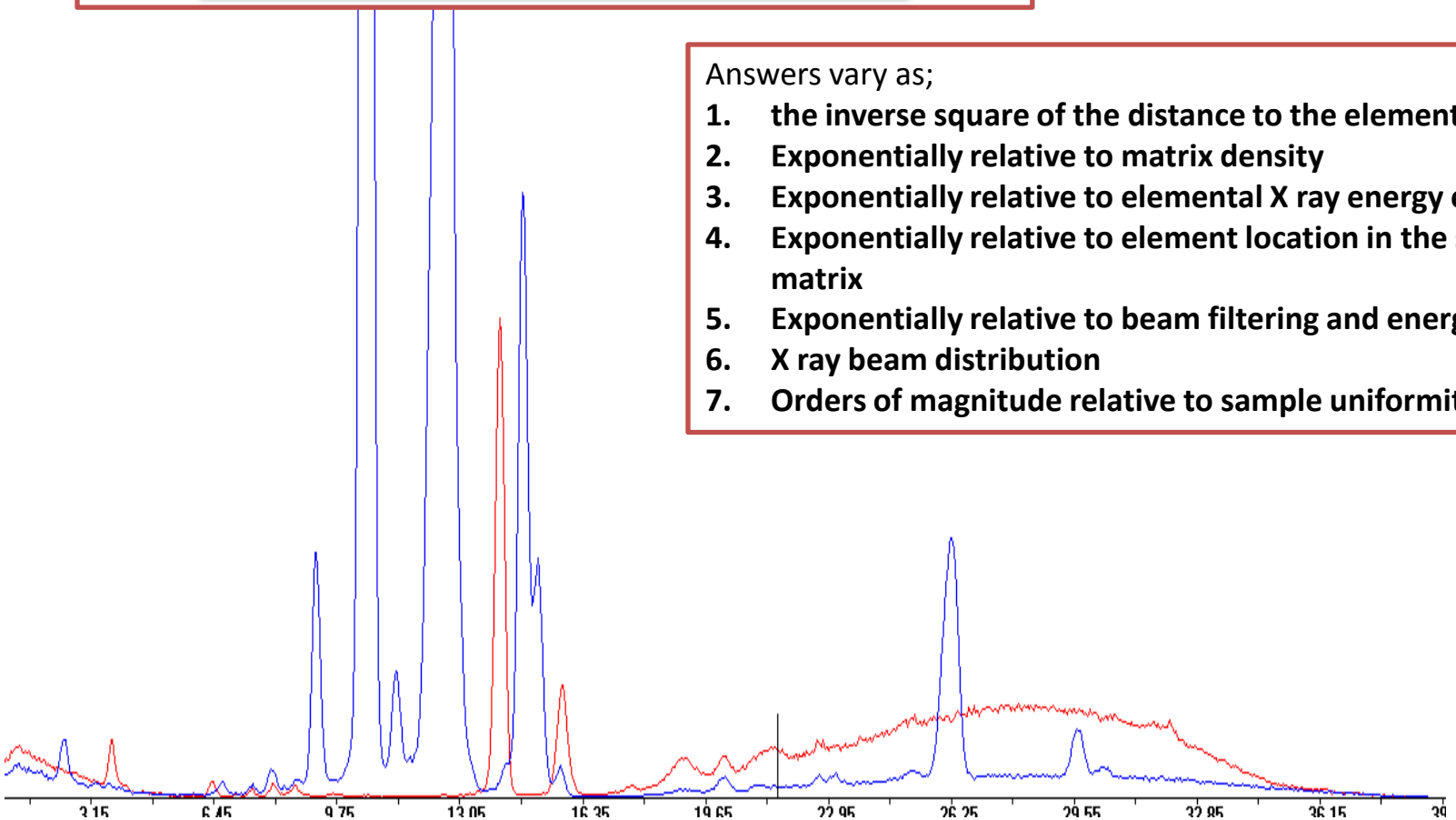
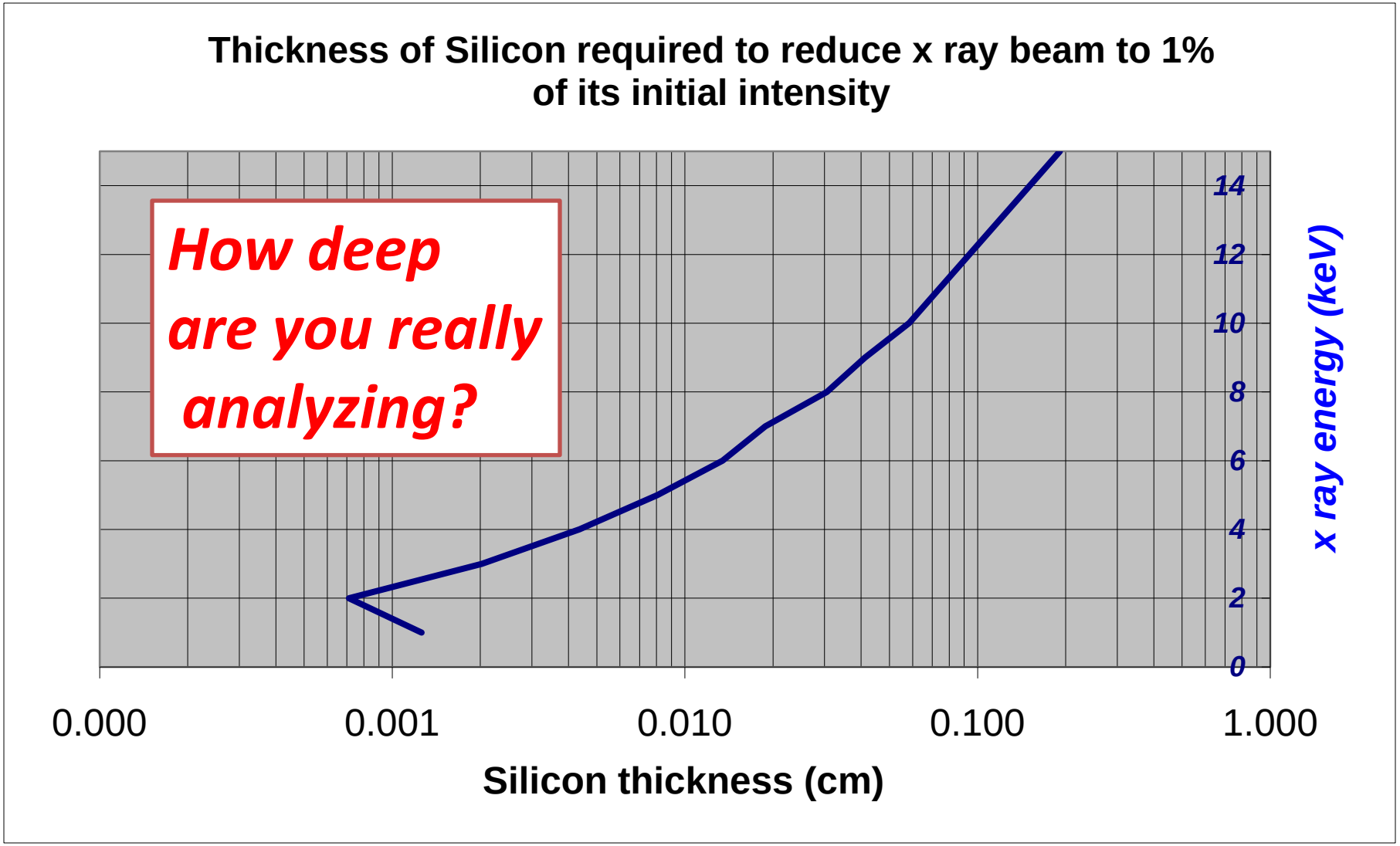
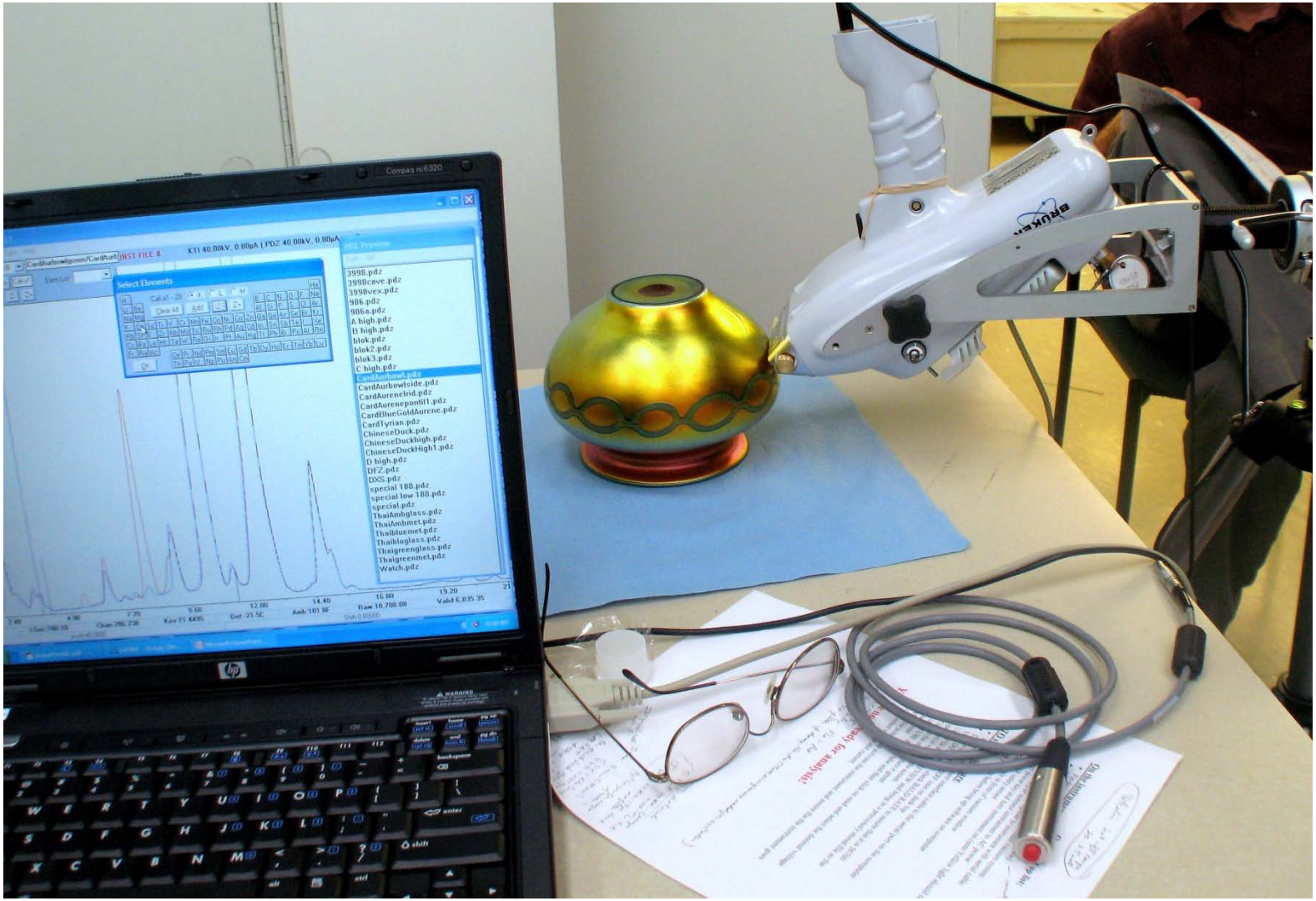



Thickness of Silicon required to reduce x ray beam to 1% of its initial intensity
How deep are you really analyzing?
14
12
10
8
6
4
2
0
x ray energy (keV)
0.000
0.001
0.010
0.100
1.000
Silicon thickness (cm)


Compaq nc6320
Select Elements
3998.pdz
3998cavc.pdz
3998vex.pdz
906.pdz
906a.pdz
A high.pdz
B high.pdz
blok.pdz
blok2.pdz
blok3.pdz
C high.pdz
CardAurbowl.pdz
CardAurbowlside.pdz
CardAurenelrid.pdz
CardAurenepnbit1.pdz
CardBlueGoldAurene.pdz
CardTyrian.pdz
ChineseDuck.pdz
ChineseDuckhigh.pdz
ChineseDuckHigh1.pdz
D high.pdz
DFZ.pdz
DXS.pdz
special 180.pdz
special low 180.pdz
special.pdz
ThaiAmbglass.pdz
ThaiAmbmet.pdz
Thaibluemet.pdz
Thaibluglass.pdz
Thaigreenglass.pdz
Thaigreenmet.pdz
Watch.pdz
BRUKER

Are you sure your unknown is:

1.uniform,

2.the same matrix,

3.the same concentration range

4.does not contain elements not in your calibration?

Not one of the glasses pictured
In this presentation meet the requirement s for ppm analysis with xrf analyzed with xrf!

But

many things can be learn from the raw xrf spectrum !
Do you know what?

The Blaschkas

Leopold Blaschka

Rudolf Blaschka

This exhibition is about two men, Leopold and Rudolf Blaschka, and the glass models that made them famous. Leopold Blaschka was born in what is now the Czech Republic in 1822, and he died in 1895. His son, Rudolf, was born in 1857 and died in 1939. Most of their models fall into two clearly defined groups: invertebrate animals (which have no backbone) and plants, the focus of the exhibition.

Leopold made his first botanical models in 1860, but he soon abandoned them to concentrate on invertebrates. He began to create models of invertebrates in 1863 and, assisted by his son from 1876, he continued to make them until 1890. At the invitation of Harvard University, Leopold, with Rudolf's assistance, returned to making botanical models in 1886. After his father's death, Rudolf continued to produce botanical models for the next 40 years.

Leopold Blaschka (1822–1895)
When his ship was becalmed during a transatlantic voyage in 1853, Leopold passed the time observing jellyfish and other small marine animals. He was captivated by their transparent, glasslike appearance. Ten years later, the director of the natural history museum in Dresden, Germany, persuaded Leopold to create glass models of similar sea creatures for display in his galleries.

Rudolf Blaschka (1857–1939)
Rudolf became his father's only assistant in or shortly before 1878. Until Leopold's death in 1895, Rudolf helped to produce models of marine invertebrates, as well as botanical specimens for Harvard University. After 1895, he worked alone to continue supplying Harvard with models of plants.

Leopold made this wry comment on his and Rudolf's ability:

"The only way to become a glass modeler of skill . . . is to get a good great-grandfather who loved glass; then he is to have a son with like tastes. . . . He in turn will have a son [Leopold] who must . . . be passionately fond of glass. You [Rudolf], as his son, can then try your hand, and it is your own fault if you do not succeed!"