THE CHALLENGES OF XRF ANALYSIS OF CULTURAL HERITAGE GLASS OBJECTS

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key insight, support, and analysis from by Dr. Bob Brill, Research Scientist Emeritus of The Corning Museum of Glass".

BRUKER 50 years of innovation

Energy dispersive xrf Advantages and limitations
Non sampling, non destructive "artifact is in exactly the same condition after the analysis as it was before the analysis", portable, instant semi quant elemental analysis, quantitative if the situation allows, situation is very often misunderstand. Limitations light elements, surface conditions, sample uniformity, measurement depth, must know standard composition very accurately; calibrations are specific families of glass composition.

Understand the Situation/overcoming the limitations

Physics
Depth, uniformity, matrix effects, elemental interferences,
Some key families of glasses often encountered
• Na_2O: CaO:$SiO2$
• $K2O$: CaO:$SiO2$
• PbO: ($Na2O/K2O$) :$SiO2$
• PbO: BaO: $SiO2$
• $K2O$: $SiO2$

Calibration process
• selecting the primary standards and/or Reference glasses
  1. typical of the unknown artifacts
  2. must include all elements of interest
  3. must cover the range of concentrations
  4. must include elemental combinations typical of unknowns.
  5. Must know the concentrations accurately
  6. Must assure that the standards are at least 4 mm thick
  7. Must assure the standard is very uniform
  8. 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
• measurement process
  1. placing of sample
  2. operating parameters
  3. time (the longer the better
  4. select surface
• calibration process
Calibration RESULTS
• PLOT OF ACTUAL fit
• Table of actual versus given
Measurements of artifacts
• Assure operating condition are the same as calibration
• Overlay cal spectra with unknown
  1. Same backscatter
  2. Maximum concentration
  3. All fluorescent peaks are Identified
  4. Only then can you trust the quant data
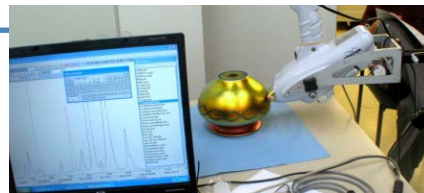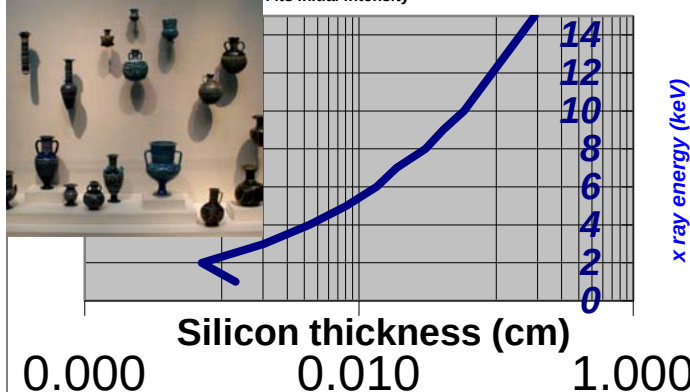
The Corning Museum of Glass has been using XRF and watching its development over the course of about 40 years. Like all other analytical techniques it has its advantages and disadvantage for the analysis of glass objects, artifacts and antiquities. The earlier lab based xrf systems allowed for destructive 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 The Corning Museum of Glass 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.
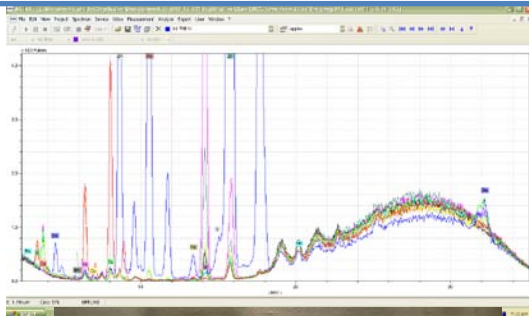
How deep are you really analyzing?

Thickness of Silicon required to reduce x ray beam to 1% of its initial intensity

x ray energy (keV): 14 12 10 8 6 4 2 0

Silicon thickness (cm)
0.000   0.010   1.000

Are your Standards the same MATRIX?

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?