Some Key Insights into XRF Glass Analysis

By Angela Susak, Dr Bob Brill and Dr Bruce Kaiser

Read carefully insights occur on every page

Chemical Analysis of Roman Glass from Karanis Using X-Ray Fluorescence Spectrometry

A. Susak

Non-destructive X-ray fluorescence spectrometry (XRF) was conducted on 107 glass sherds from the Greco-Roman site of Karanis in Egypt. Principle component analysis was then performed to evaluate the variability of chemical composition among glass recovered from a single trench over three consecutive excavation seasons at Karanis (2006-2008). Knowledge of the chemical composition of the glass corpus at Karanis provides evidence for manufacturing processes, origins, and raw materials employed such as colorants, decolorizers, opacifiers, and fluxing agents. To contribute to the discussion of the origin of the glass material from Karanis, results of this study were compared with similar scientific investigations of glass from other Roman sites. Although prolific amounts of glass has been found at Karanis, whether or not it was a production center is still under debate. The source of manufacturing is crucial in understanding Egypt's role in the industry and trade of glass. This research comprises the beginning of a larger glass study to augment our understanding of glass production, trade, and technology during the late Roman period, as well as the economy and the social demographics of the Karanis settlement.

Introduction

Glass Analysis Utilizing both the UCLA and CMOG Tracers

This analysis was done of glass shards in the field in Jordan by Angela Susak at UCLA and the standards were done by Dr Bob Brill of the Corning Museum of Glass
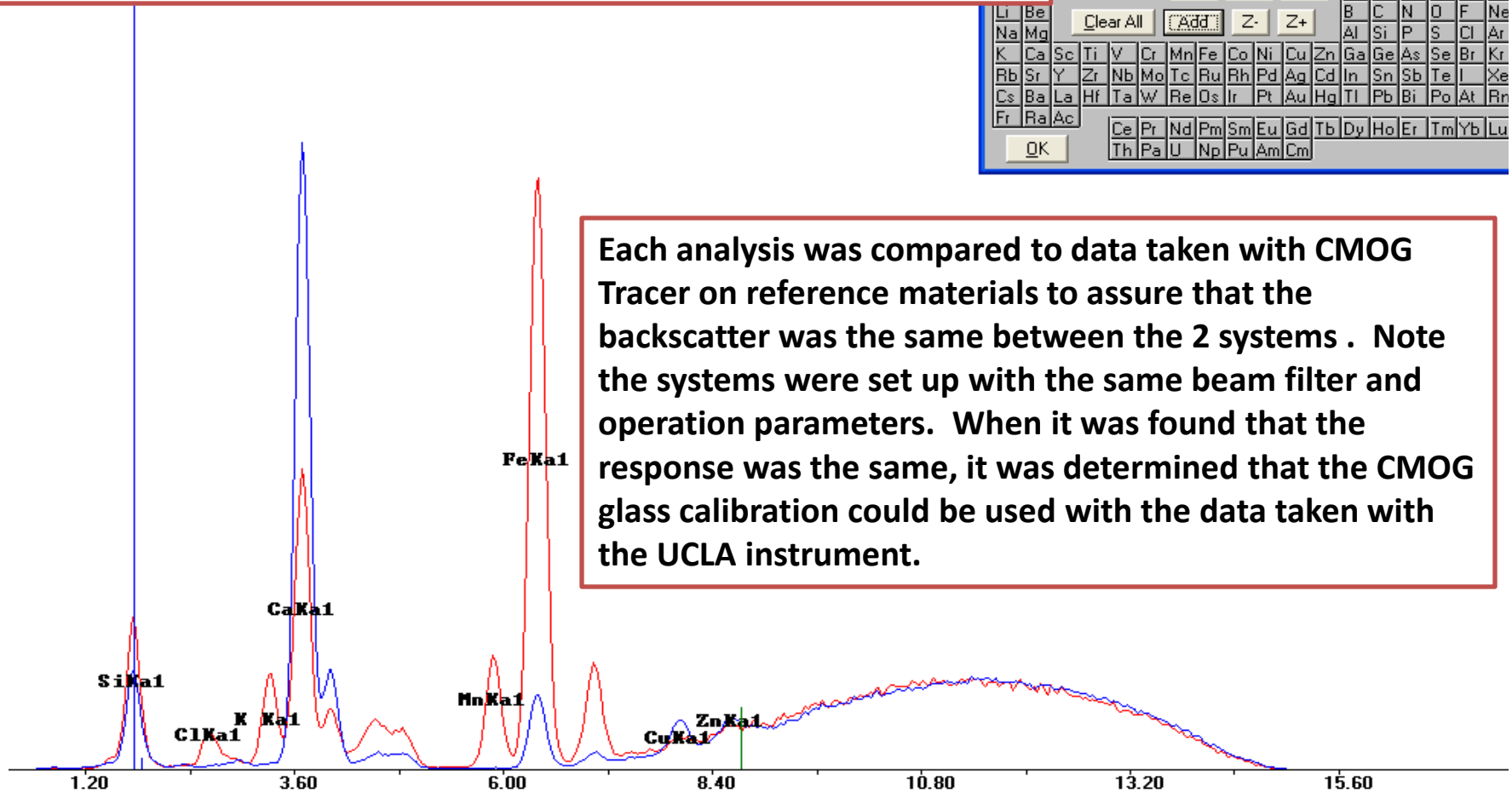
The questions asked were:
1. Does cleaning the shards by sanding alter the analysis?
2. Does it matter if the analysis is done for 180 or 300 seconds?

A single sample was checked by doing 3 analysis of the clean sample at 180 sec, and at 300 sec. A single analysis was done of the uncleaned material for 300 seconds.

Each analysis was compared to data taken with CMOG Tracer on reference materials to assure that the backscatter was the same between the 2 systems . Note the systems were set up with the same beam filter and operating parameters. When it was found that the response was the same, it was determined that the CMOG glass calibration could be used with the data taken with the UCLA instrument.

Comparing the cleaned and unclean glass

Elements

SiKa1 - 14   ⊙ K   ○ L   ○ M

Clear All   Add   Z-   Z+

Each analysis was compared to data taken with CMOG Tracer on reference materials to assure that the backscatter was the same between the 2 systems . Note the systems were set up with the same beam filter and operation parameters. When it was found that the response was the same, it was determined that the CMOG glass calibration could be used with the data taken with the UCLA instrument.

Over lay of 9450_BB_3_lowKv_vac_300 (RED)/5 NBS 1830 lo (BLUE) This shows the Backscatter from the 2 different systems from 8 keV to 15 keV to be the same. The blue spectra is data taken with the CMOG Tracer of an NBS STD and the red is data taken with the UCLA instrument of a glass shard in Jordan. This implies the physics in the same between the instruments and the calibration from the CMOG instrument will give reasonable results..
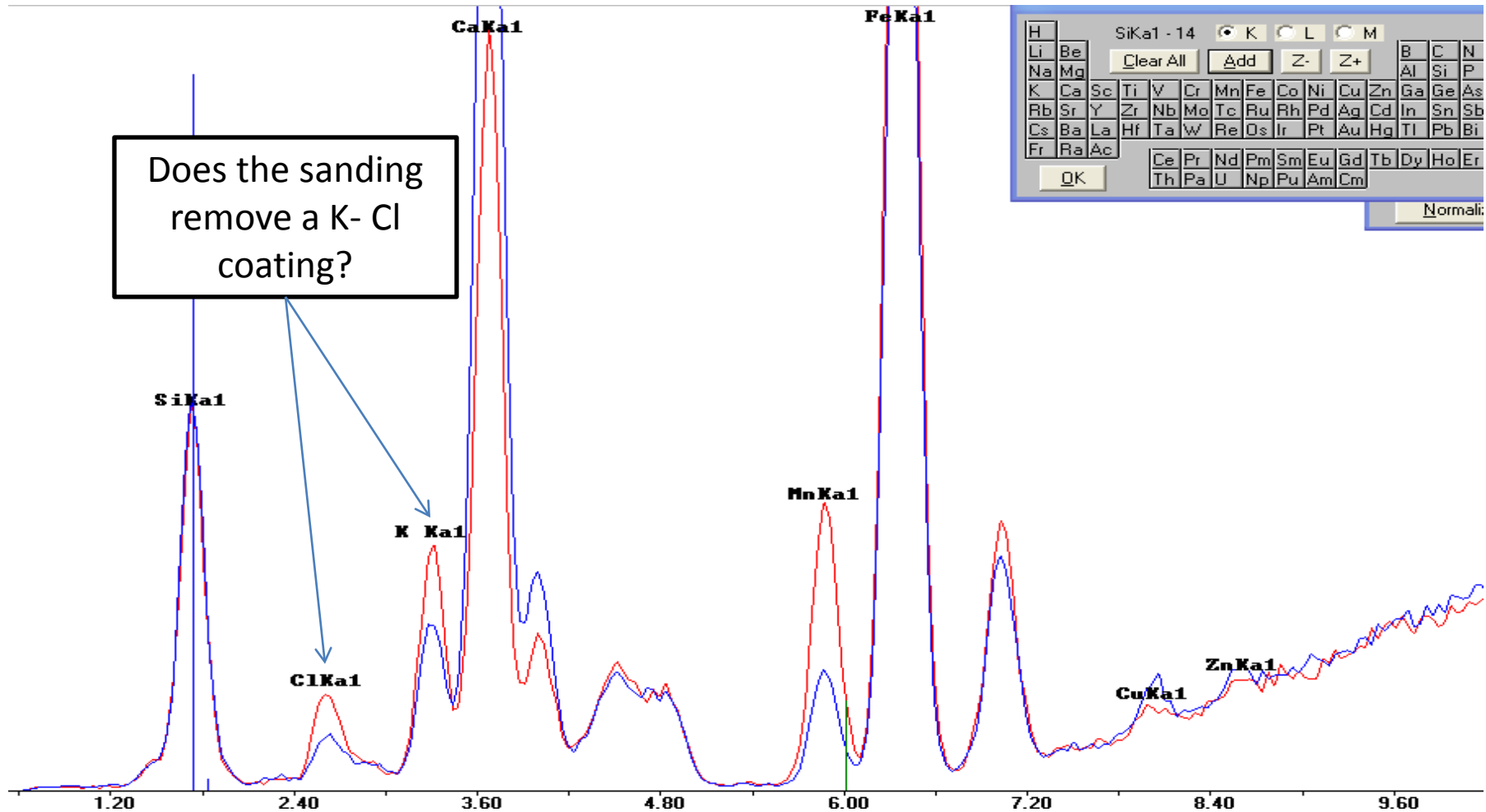
FY08_9450_BB_3_lowKv_vac_300_not_cleaned (RED)
/FY08_9450_BB_3_lowKv_vac_300_trial1_sanded (BLUE): It is interesting that sanding did not change the Si intensity, this means the "dirt" layer contains Si. But sanding did reduce the Cl, K, Mn and Fe. The Ca signal more than doubled when the glass was sanded. This indicates that the coating was composed of the Si, Cl, K, Mn and Fe. Also since Cl is still present after the cleaning and is not normally found in glass, one can suspect that some of the coating remains. This should be kept in mind when looking at ALL the analysis as the depth of analysis when looking at x rays from 1 to 7 keV is very shallow. Look at the plot on the next slide for further insight on this.

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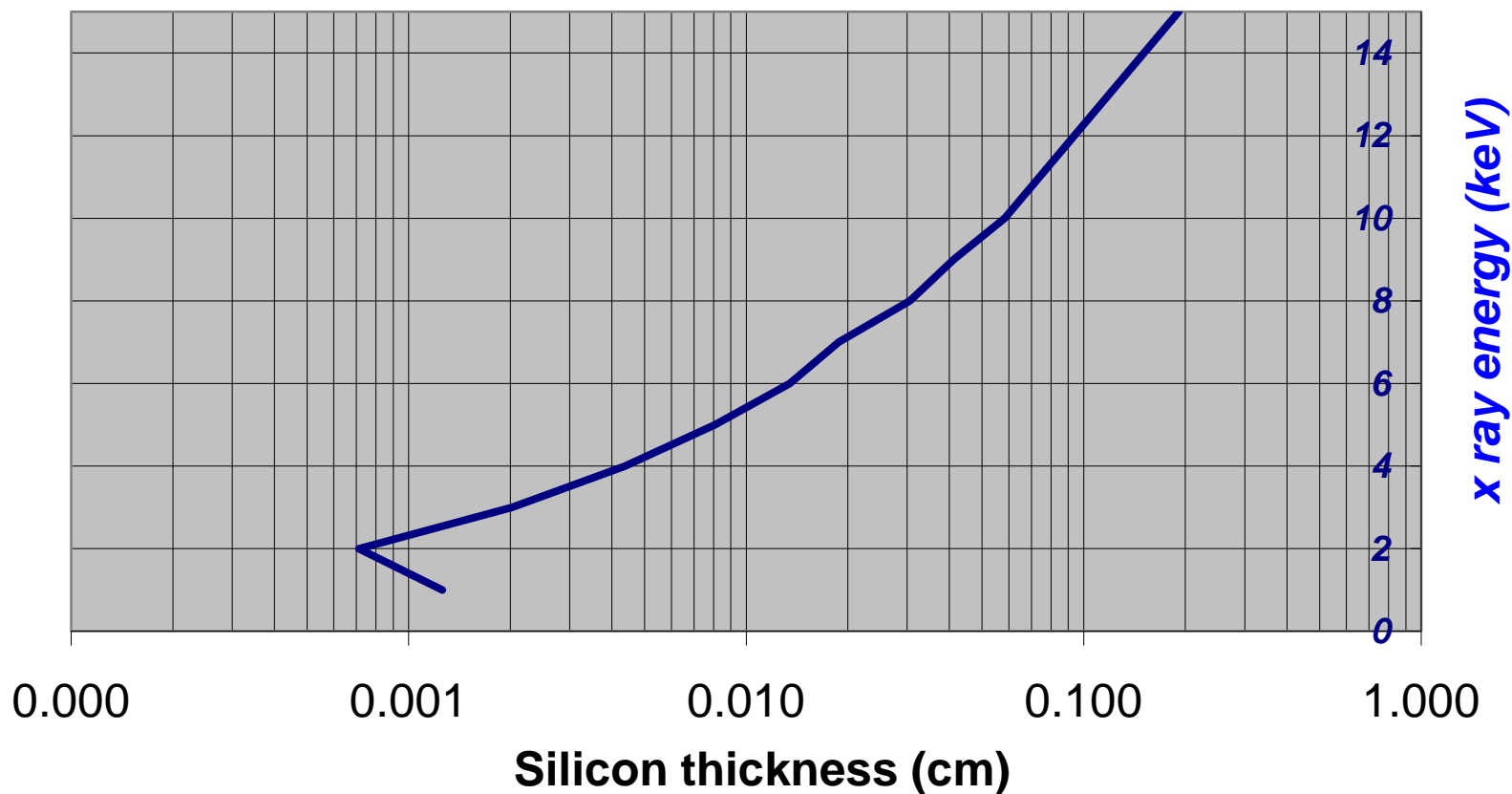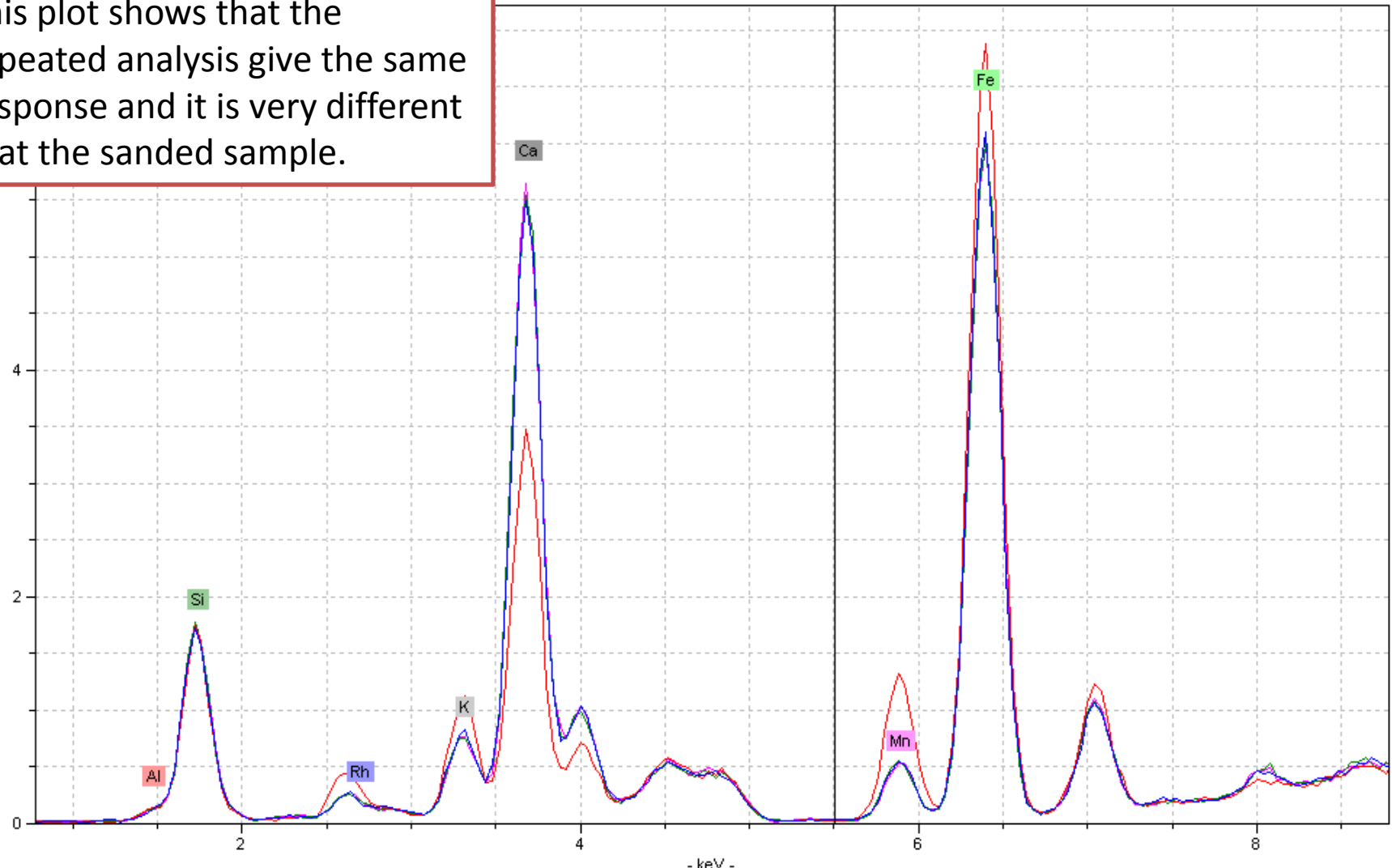

Looking at this plot one can determine that the Si x rays (1.74keV) can only come from a depth of about .0007 cm (.00028") and the Fe x rays (6.4 keV) can come from a depth from a depth of about .015 cm (.006")

Clearly one is very sensitive to the surface of the glass!! And assuming the surface analysis accurately defines the bulk must be done with great caution.

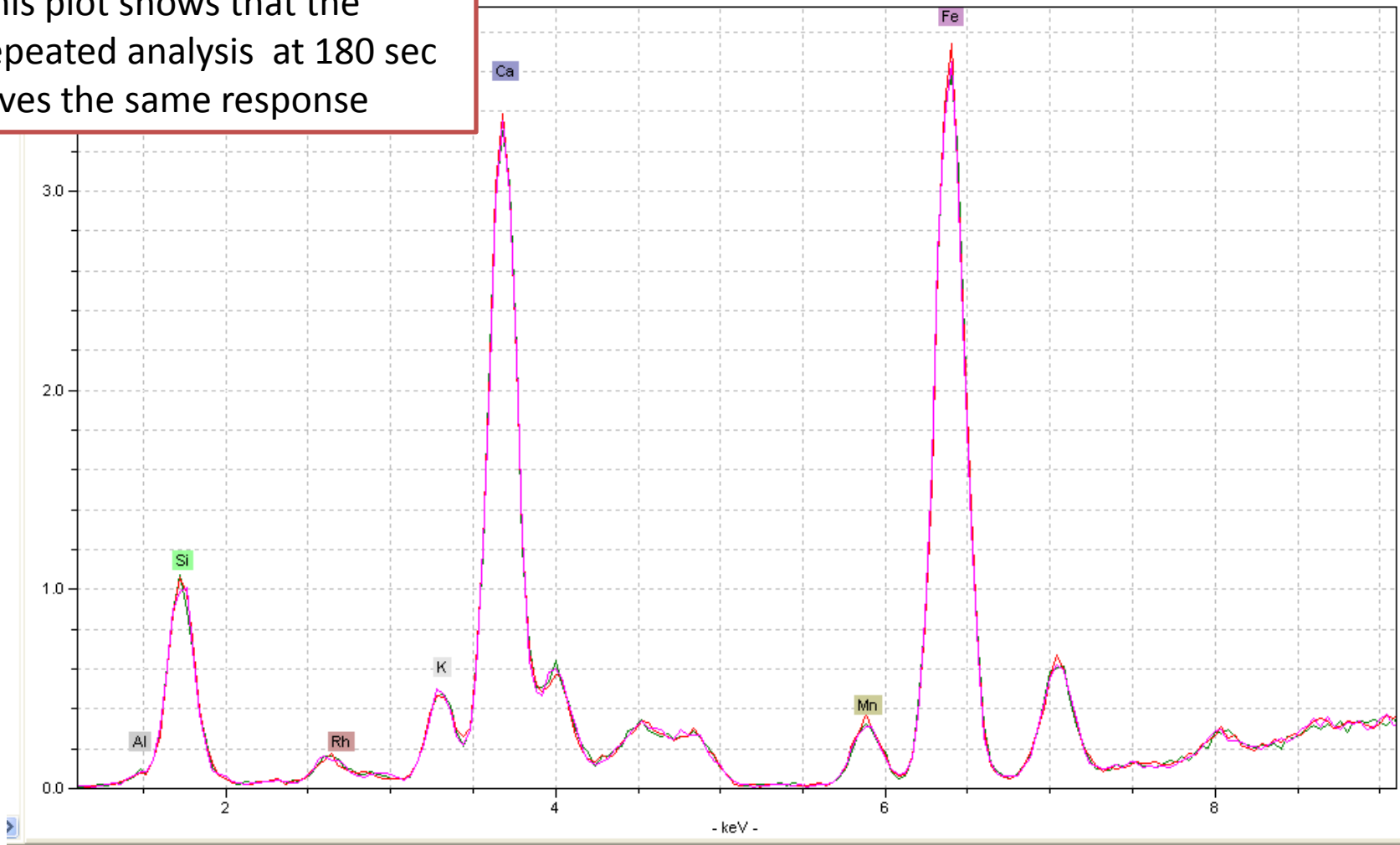FY08_9450_BB_3_lowKv_vac_180_trial2_sanded@121209_12583

FY08_9450_BB_3_lowKv_vac_180_trial3_sanded@121209_12583

FY08_9450_BB_3_lowKv_vac_180_trial1_sanded@121209_12583

This plot shows that the repeated analysis at 180 sec gives the same response

Concentration Analysis using
(Lo E CMOG Glass Cal 9 20 2009)

The numbers in the tables below are the result of the CMOG Lo E calibration and are in 0xide weight percent.

The numbers in the tables below are the result of the CMOG Lo E calibration and are in 0xide weight percent. They are of the sanded sample taken at 180 and 300 sec

300 Sec	FY08_9450_BB_3_lowKv_vac_300_trial3_sanded	FY08_9450_BB_3_lowKv_vac_300_trial2_sanded	FY08_9450_BB_3_lowKv_vac_300_trial1_sanded	AVE 300	Std dev 300
Al	1.79	1.78	1.64	1.74	0.08
Si	88.92	89.58	88.93	89.14	0.38
K	1.85	1.76	1.81	1.80	0.05
Ca	7.15	7.17	7.28	7.20	0.07
Mn	0.12	0.12	0.12	0.12	0.00
Fe	1.09	1.07	1.08	1.08	0.01

180 Sec	FY08_9450_BB_3_lowKv_vac_180_trial3_sanded	FY08_9450_BB_3_lowKv_vac_180_trial2_sanded	FY08_9450_BB_3_lowKv_vac_180_trial1_sanded	AVE 180	Std dev 180
Al	1.85	1.92	1.81	1.86	0.05
Si	89.47	89.47	89.06	89.33	0.24
K	1.83	1.73	1.75	1.77	0.05
Ca	7.19	6.93	6.97	7.03	0.14
Mn	0.11	0.12	0.11	0.11	0.00
Fe	1.08	1.02	1.04	1.05	0.03

Summary of previous data

The numbers in the tables below are the result of the CMOG Lo E calibration and are in 0xide weight percent. They are of the sanded sample taken at 180 and 300 sec and the non sanded sample

	AVE 300	Std dev 300	AVE 180	Std dev 180		FY08_9450_BB_3_lowKv _vac_300_not_cleaned
Al	1.74	0.084	1.86	0.053	Al	1.53
Si	89.14	0.375	89.33	0.237	Si	90.41
K	1.80	0.047	1.77	0.050	K	2.69
Ca	7.20	0.074	7.03	0.138	Ca	4.54
Mn	0.12	0.002	0.11	0.002	Mn	0.30
Fe	1.08	0.009	1.05	0.030	Fe	1.24

SUM	101.08		101.15				100.71

The fact that the sum of the oxide content is about 100 % indicates that all other elements if present are in ppm. The fact that the sum is slightly more than 100 % is a result of the error in each element concentration analysis, which is summed because of the addition. It also is likely due to a small bias from one Tracer to the other.

Conculsions

Summary:
1. 300 and 180 sec are the same statistically
2. Washing(sanding) verses not washing (sanding) shows a big shift occurs in elemental surface concentration. This shows that the xrf analysis of glass looking at Al, Si, Cl, K, Ca, Mn and Fe is very much a surface analysis.
3. Chlorine appears to be present in both the clean and non cleaned spectra. It was not present in the CMOG calibration so no values are present in the quant numbers for Cl, high lighting the need to always carefully look at the raw xrf spectrum.
4. Does sanding remove a K Cl coating along with Fe and Mn?