



# Precision of Elemental Analysis Measurements of Glass by $\mu$ -XRF and the Impact on Forensic Comparisons

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## ABSTRACT

Many forensic laboratories are performing elemental analysis on glass samples as an additional comparison criterion to traditional analyses (e.g., color, thickness, fluorescence, density, and refractive index). Major, minor, and trace elements present in the glass can provide increased discrimination of the samples over previously employed analysis schemes when using a sensitive method for elemental analysis. This study was designed in part to specifically examine the precision or reproducibility of measurements of elemental concentrations in glass samples by micro X-Ray Fluorescence Spectrometry ( $\mu$ -XRF) and to determine how that precision impacts the forensic comparison of glass samples. While accuracy is an important consideration in any analytical technique, for the purposes of typical forensic comparisons between questioned and known samples, precision is more critical.

## MATERIALS AND METHODS

An inter-laboratory study was conducted in 2009 by the Elemental Analysis Working Group (EAWG) which was coordinated by the International Forensic Research Institute (IFRI) at Florida International University via a grant from the National Institute of Justice (NIJ). Two standard reference glasses (FGS1 and FGS 2) were analyzed by seven participating laboratories using  $\mu$ -XRF. FGS1 and FGS2 are float glass standards designed to resemble float glass composition (see Table 1) and were produced as a joint research project between Schott Glass AG (Germany) and the Bundeskriminalamt (BKA). Each laboratory performed seven replicate analyses on full thickness fragments of FGS1 and FGS2.

	Mg	K	Ca	Ti	Fe	Sr	Zr
FGS1	23900	920	60600	69	580	57	49
FGS2	23400	4600	59300	326	2600	253	223

Table 1: Reported concentrations of elements in FGS1 and FGS2, mg/kg

## INSTRUMENTAL SETUP

A variety of instrument configurations were used. Each laboratory was directed to use their own instrumental parameters normally employed by their laboratory for glass analysis (see Table 2).

Lab ID	A	B	C	D	E	F	G
Instrument	EDAX Eagle III	EDAX Eagle II	EDAX Eagle III	Phillips XL30-IXRF	EDAX Eagle III	EDAX Eagle III	EDAX Eagle II
Dead Time (%)	35	45	35	35-40	35-20	18-22	Average
Beam Size (mm)	114	300	100	100	210	100	50
Beam Energy (kV)	40	40	50	45	45	50	38
Time Constant ( $\mu$ s)	17	17	35	2	17	35	17
Acquisition Time (Lsec)	1500	1200	1200	1200	1200	1800	600
Beam Type	Poly	Mono	Mono	Poly	Poly	Mono	Poly
Tube Material	Rh	Rh	Rh	Mo	Rh	Rh	Rh

Table 2: Instrument configurations as reported by participating laboratories A-G.

## RESULTS

The laboratories reported data for detected elements with atomic number greater than ten, including at least Na, Mg, Al, Si, K, Ca, Ti, Fe, Sr, and Zr. A normalization of the data versus the standard reference material NIST SRM 1831 (National Institute of Standards and Technology, Gaithersburg, MD) was then conducted. The normalization allowed for direct comparisons of laboratories with different instrument configurations and elemental responses and helped to minimize relative inter-laboratory differences. Results were reported based upon semi-quantitative analysis using elemental intensity ratios, a common technique within the forensic community for sample comparisons. The following ratios were used for evaluation: **Ca/Mg, Ca/Ti, Ca/Fe, Sr/Zr, Fe/Zr, and Ca/K**.

Fe provided the best precision, even at the lower FGS1 concentration (see Figure 1 below). Mg presented some problems possibly due to lower sensitivity with some instrument systems or variation in auto-integration algorithms in the low energy portion of the spectrum. Ti demonstrated some of the worst performing precision data at the lower FGS1 concentrations, most likely due to resolution issues with the adjacent large Ca K $\beta$  peak and a sloping background continuum resulting in auto-integration variations in some systems (see Figure 1 below). Zr performed similarly to Ti at the lower FGS1 concentrations.

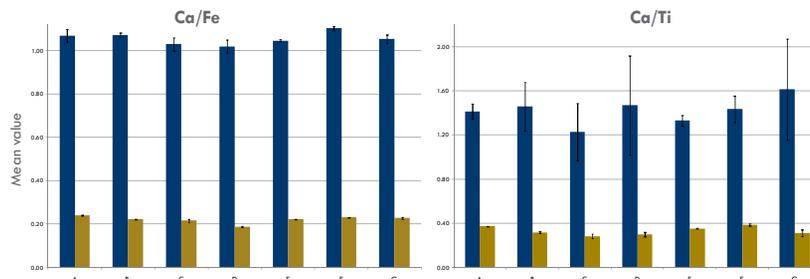


Figure 1(a) (left): Mean ratio data for Ca/Fe for FGS1 (blue) and FGS2 (gold) for participating labs; Figure 1(b) (right): Mean ratio data for Ca/Ti for FGS1 (blue) and FGS2 (gold) for participating labs; Error bars represent  $\pm 1$  SD for the seven replicate analyses performed by each lab for each sample

## DISCUSSION

The majority of the RSDs for the given element ratios were less than 10%, with exceptions noted previously. Most RSDs ranged from 2-7% for both FGS1 and FGS2, with better precision in the FGS2 glass, as expected due to the generally higher element concentrations. This interlaboratory exercise led to subsequent improvements in analytical methodology by the participant laboratories.

FGS1	% Relative Standard Deviation						
	A	B	C	D	E	F	G
Ca/Mg	2.01	0.98	5.74	62.06	1.17	2.62	4.03
Ca/Ti	4.66	15.08	21.13	30.83	3.68	8.37	28.70
Ca/Fe	2.97	1.00	2.52	2.79	0.47	1.13	2.12
Sr/Zr	9.03	11.48	6.77	13.05	7.31	5.82	47.45
Fe/Zr	20.99	5.44	5.57	10.54	5.58	5.13	53.03
Ca/K	3.58	6.04	6.89	29.14	2.54	2.17	2.26

FGS2	% Relative Standard Deviation						
	A	B	C	D	E	F	G
Ca/Mg	1.68	0.88	4.44	40.02	1.66	1.64	4.87
Ca/Ti	0.88	2.72	6.25	7.61	1.13	2.09	10.51
Ca/Fe	0.95	0.64	3.13	1.72	0.44	0.45	1.73
Sr/Zr	2.14	3.08	14.79	7.37	2.47	2.34	9.69
Fe/Zr	5.07	7.83	39.76	7.51	2.37	5.24	21.11
Ca/K	0.71	1.94	0.75	6.99	0.44	1.11	0.70

## SIGNIFICANCE OF STUDY

Four interlaboratory tests were also administered to each participating laboratory. Each test consisted of samples designed to simulate glass transfer evidence. Participants were asked to analyze the "questioned" and "known" samples utilizing the parameters normally employed by their laboratories and indicate whether the samples were distinguishable or indistinguishable based upon their elemental composition. Samples consisted of both full thickness fragments as well as small broken fragments and were chosen based upon similarities between their physical and optical properties. The samples were designed to represent "worst-case scenarios" that may be encountered in casework exhibiting very small chemical differences between samples from different sources.

The  $\mu$ -XRF participants were able to correctly associate or determine differences in nearly all of the submitted samples utilizing the match criteria from their laboratories. In two instances some users were unable to distinguish two samples that were produced in the same plant two weeks and 3 months apart. It should be noted that, although the elemental profiles of these two samples were very similar, these samples could be distinguished by other elemental analysis methods (LA-ICP-MS), in part by using Ba as the discriminator. Ba is not an element typically used as a discriminator in flat glass sample analysis via  $\mu$ -XRF due to its low concentration and low resolution with other surrounding energy lines. Additional samples produced from the same plant one month apart were able to be correctly distinguished by the  $\mu$ -XRF users. The use of other match criteria, in addition to those typically used by the individual labs, was also able to assist in correctly discriminating some of the samples.

This data indicates that the reported RSDs are an acceptable range for elemental analysis of glass samples utilizing  $\mu$ -XRF. The performance of the technique was tested utilizing casework type samples and results indicate that  $\mu$ -XRF performs well for elemental analysis comparisons of forensic glass samples.

## ACKNOWLEDGEMENTS / REFERENCES

<sup>2</sup>Florida International University, Miami; <sup>3</sup>Federal Bureau of Investigation (CFRSU), Quantico, Virginia; <sup>4</sup>Johnson County Crime Laboratory, Kansas; <sup>5</sup>Florida Department of Law Enforcement, Orlando; <sup>6</sup>US Army Criminal Investigation Laboratory; <sup>7</sup>Michigan State Police, Grand Rapids, Michigan; <sup>8</sup>Miami Dade Police Department; <sup>9</sup>Microtrace, LLC

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