

Application Note: XRF

Analysis of “as-is” Glass Particulates Using μ -beam EDXRF Methods



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Quantitation of glass particulates using the EDAX Orbis XPL μ -beam EDXRF spectrometer

An example of how a micro X-ray beam EDXRF system can be employed for the rapid analysis of glass fragments

Introduction

Micro X-ray beam EDXRF (Energy-Dispersive X-ray Fluorescence) methods can be (and are) used as an alternative technique to EDS-SEM (Energy-Dispersive Spectroscopy – Scanning Electron Microscopy) methods for element mapping and analysis applications. Benefits of μ -beam EDXRF methods include zero damage to the specimen by the primary excitation beam, no need for coating the specimen in order to make it electrically conductive together with improved sensitivity for mid to higher analyte energy lines.

The analysis of “small” particles has always been considered the role of microanalysis X-ray methods using electron beam excitation as in, for example, the Scanning Electron Microscope. The advent of laboratory based μ -beam XRF spectrometers providing high intensity primary beams of $\sim 50\mu\text{m}$ enables them to also be considered for such tasks, with the added benefits associated with XRF techniques.

This paper describes the measurement & calibration procedure employed for glass particulates ranging in size from $100\mu\text{m}$ and above. The calibration procedure is akin to that employed in microanalysis methods i.e. normalisation to 100% oxide for the analyte elements Na, Mg, Al, (Si), S, K, Ca, Ti & Fe. This compensates for absolute intensity variations due to sample irregularities. Whilst the XRF method is also capable of detecting other trace elements e.g. Cr, Cu etc, these were not included in this investigation since they are not typically considered with electron-beam microanalysis techniques.

Overview of sample presentation

The basic components of the EDAX Orbis μ -EDXRF system are illustrated in Figure 1. A micro-focus X-ray tube in conjunction with a “focussing” capillary system provides a high intensity primary X-ray beam consisting of characteristic & Bremsstrahlung tube radiation directed onto a specimen supported on a motor controlled X-Y-Z stage. The metal stage surface is covered with Plexiglas. A close-coupled Si(Li) detector captures the generated specimen spectra and a video camera is used to view the sample and assist in the location of the analysis spot. The environment around the X-ray optical path may be evacuated using a rotary pump to overcome air absorption of lower energy analyte lines (in particular, those for the lower atomic number elements).

Specimens may be mounted directly onto the sample stage. However, if the specimen is too small to intercept the whole of the primary beam &/or insufficiently thick to absorb, in particular, its higher energy components, some of the extraneous/transmitted radiation will be scattered by the low Z stage material in the direction of the detector.

Small particulate samples are best handled by adhering to a plastic film (e.g. adhesive tape) and then mounting the film to a support, which distances the sample from the stage. This simplifies sample handling and reduces X-ray scatter off the stage surface.

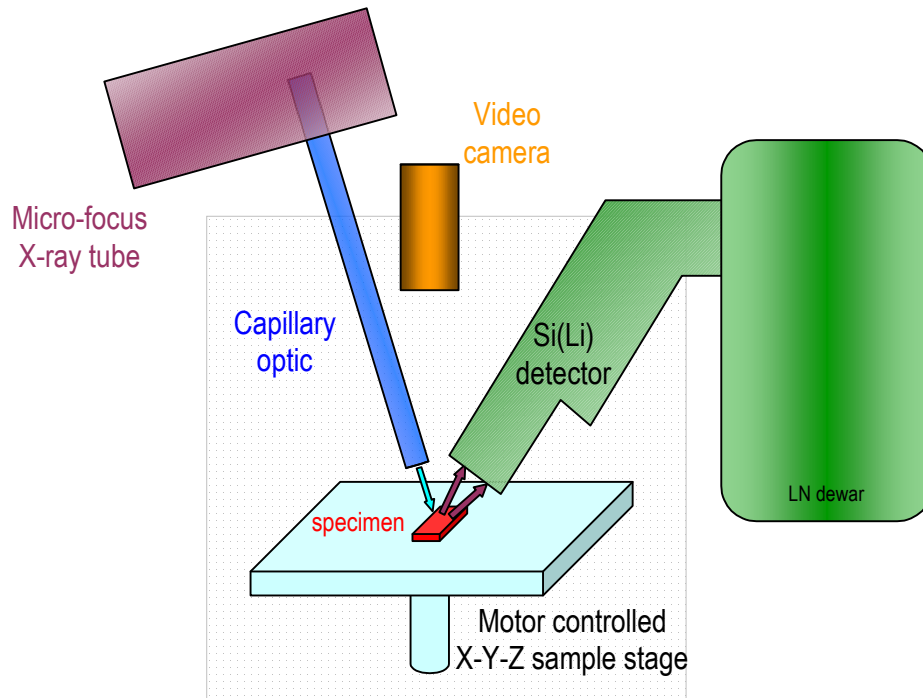


Figure 1. Schematic of major components within a μ -beam EDXRF spectrometer.

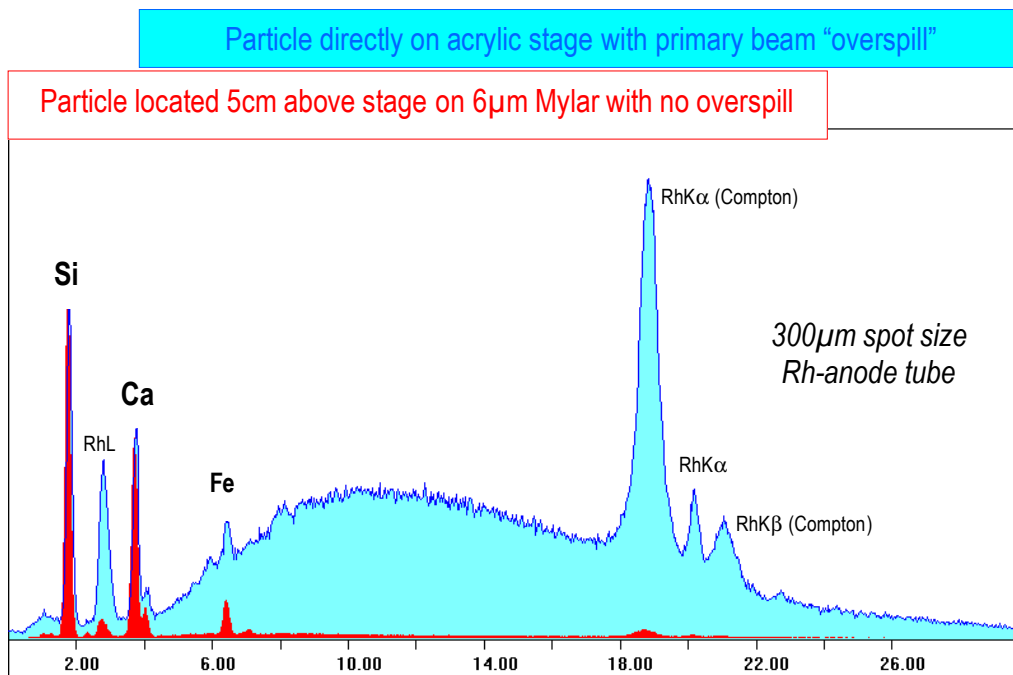


Figure 2. Illustrating the effect of "small" sample presentation method on analyte line signal/noise ratio.

Results obtained for two extremes of specimen presentation, e.g. on & off the stage and with & without overspill, are illustrated in Figure 2. Here spectra from two fragments of the same glass matrix are shown, one for a sample placed directly on the acrylic stage with primary beam overspill and the other without overspill supported approximately 5cm above the stage. In the case of the sample supported away from the stage, there is a substantial increase in signal to noise due to the reduction of X-ray scatter, which leads to background. Whilst this example is for a 300 μm primary beam diameter incident upon a 100 \times 50 μm specimen on the stage, a similar scenario exists for the higher energy components of the tube spectrum that are transmitted **through** a thin specimen only to be scattered by the underlying support.

The sample presentation method adopted for this investigation strove to emulate the minimal support mass situation and provide a multiple sample capability. The sample support system was simply the insert taken from a box of ninety-six (8 \times 12) 200 μl Aerosol Barrier Tips. Overall dimensions were (W:D:H) 120:85:40mm which conveniently provided a platform of 5mm apertures regularly arrayed at 9mm intervals. Mylar film was affixed to the top of this support using an acetone-based liquid adhesive (UHU). A thin diluted layer of the same adhesive was used to position the glass particulates. Figure 3 illustrates the method used.

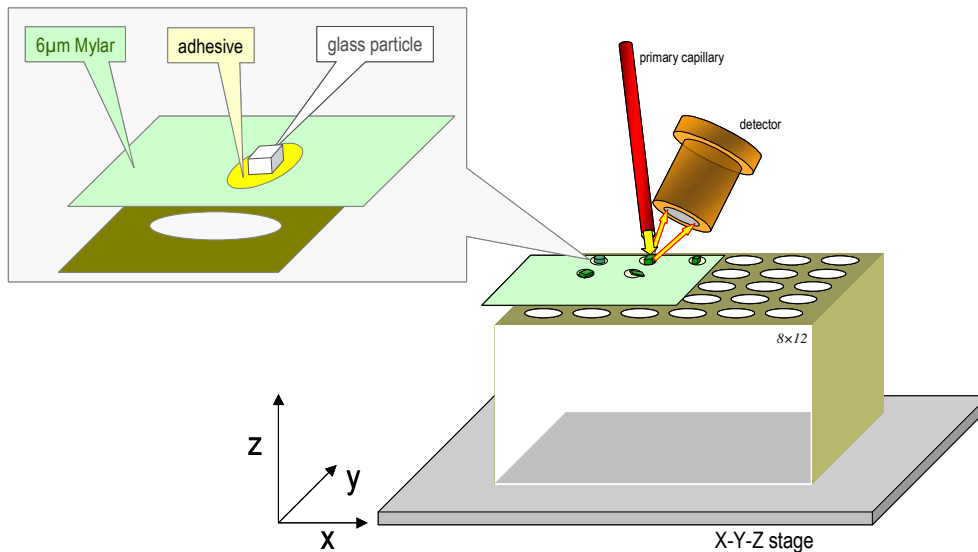


Figure 3. “Elevated” sample presentation method adopted for small particle analysis.

The specimens used for establishing a calibration were commercially available certified materials available in fragmented form. Of course, it is essential to ensure that the analysis surfaces are clean, uncontaminated, and inclusion-free. Figure 4 shows typical specimens used in the calibration process. A central marker indicates the nominal analysis area.

Measurement & data reduction parameters

The EDAX Orbis XPL spectrometer was used to collect data in the following configuration:

- Rh anode X-ray tube (operated at 20 kV, 400 μA)
- Monolithic poly-capillary
- LN₂ cooled Si(Li) detector
- Measuring time = 500 live seconds

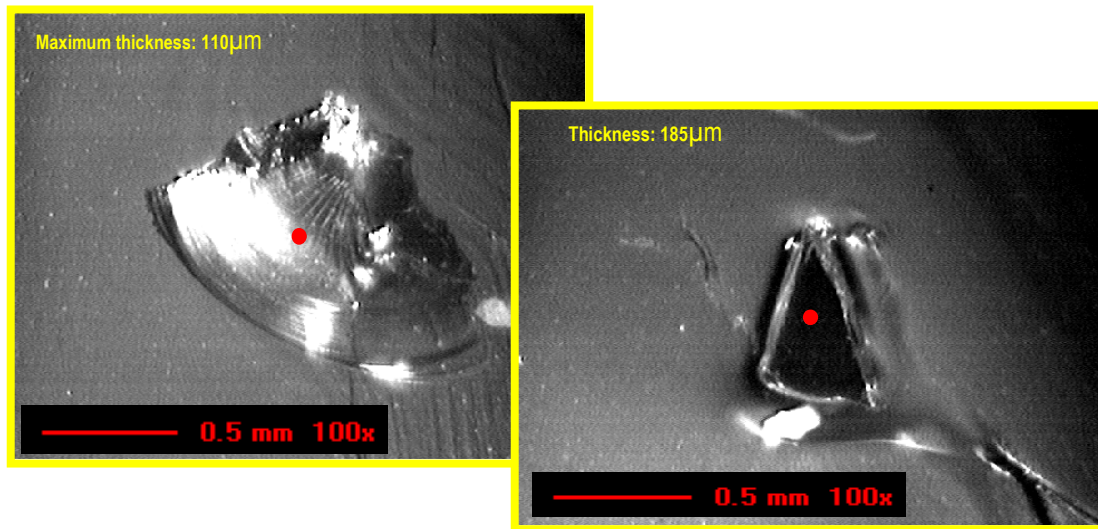


Figure 4. Typical specimen configurations used in calibration process.

The composite construction of variable curvature filaments in monolithic poly-capillaries in conjunction with the energy dependence of critical angles for the reflected primary X-ray beams results in energy dependant beam diameters. A nominal diameter of $50\mu\text{m}$ (FWHM) for $\text{FeK}\alpha$ (6.4keV) would equate to something between 80 to $100\mu\text{m}$ (FWHM) at around 1.0keV (i.e. in the Na-Si element range).

The calibration standards were presented for analysis in the manner indicated in Figure 3. Spectral data was collected from two locations on each standard with, in two cases, duplicate specimens also being used. Each analysis point (i.e. the X-Y-Z stage co-ordinates) was pre-programmed for automated data collection. Repeat measurements (up to 15, not necessarily all in the same location) were also made on two standards in order to assess analytical repeatability.

For the fractured surfaces of glass fragments, absolute intensity data typically show inconsistencies due to the irregular specimen topography. Hence, an intensity ratio method was employed here. Net intensities were determined for the K-series analyte lines of Na, Mg, Al, Si, S, K Ca, and Ti & Fe using manually selected background points. Net intensity data was then ratioed to the Si intensity (also known as “internal ratio” method). Calibration curves of the form, [analyte oxide wt% / Si oxide wt%] versus [analyte intensity / Si intensity] were generated normalising the total wt% of each calibration standard to 100wt%. Normalisation allows for the absolute wt% of all input elements including Si to be calculated. For the glass types considered in this study, this may represent a 0.5% relative error in the worst case as the typical total wt% for the standard oxides was 99.8wt% with just one being 99.5wt%. Such a procedure does mean that it is assumed that there are no other significant elements present in the “unknown” samples to be subsequently analysed. The benefits of this method are illustrated in Figure 5 for the absolute and ratioed Ca intensity data. The ratioed Ca intensity data shows far less scatter than the absolute data.

Trace components such as Cr, Mn, Sr, and Ba etc are ignored in this instance, as per SEM/EDS methods for such materials, purely for comparative purposes. It does not necessarily imply that the analysis of such elements is not possible with μ -EDXRF methods. Figure 6 compares spectra obtained for a glass material using SEM/EDS & Orbis μ -EDXRF methods, which illustrates their relative excitation efficiency differences (reference to the $\text{SiK}\alpha$ line). XRF data shows improved peak to background at the $\text{SK}\alpha$ line and higher.

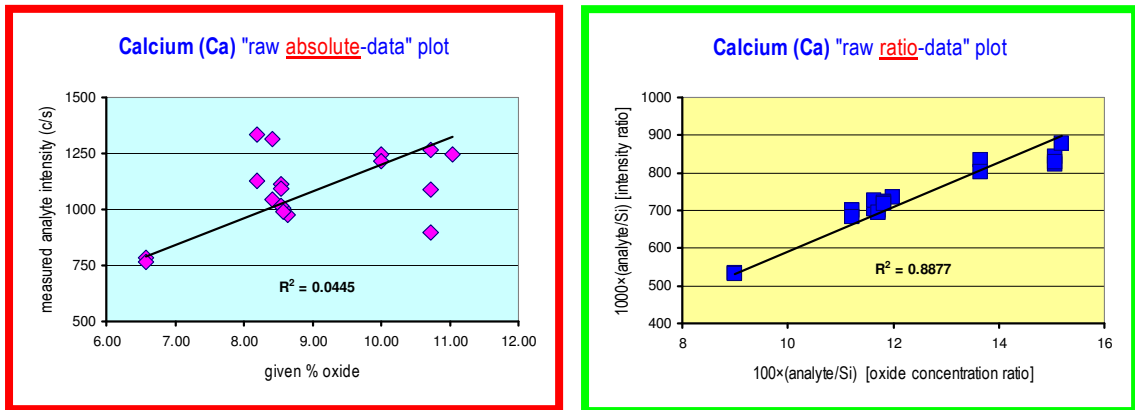


Figure 5. Showing benefits of using “internal ratio” data compared to “absolute” for minimising inconsistencies due to irregular sample topography (data for Ca).

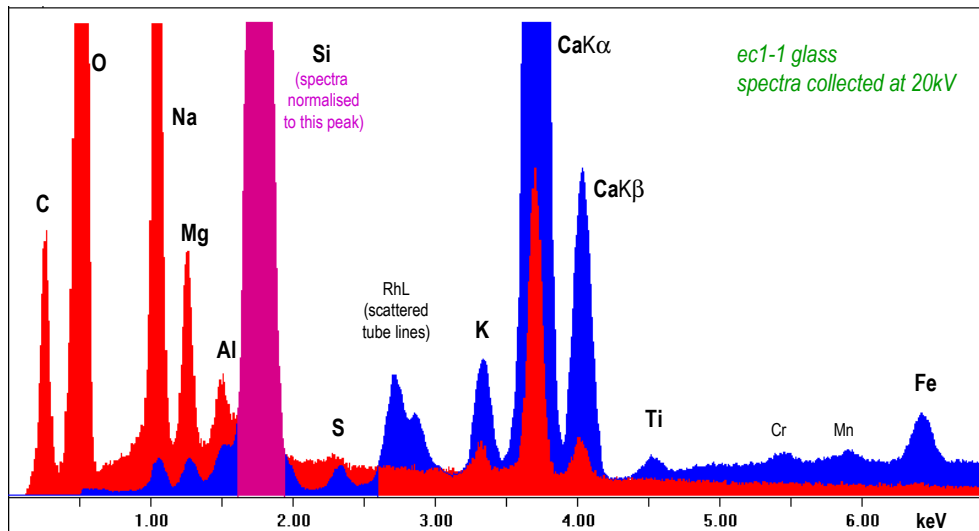


Figure 6. Comparing X-ray spectra collected on a glass sample when using SEM/EDS (red) and μ -EDXRF (blue) excitation methods.

Empirical calibration coefficients were determined, using the modified Lucas-Tooth & Pyne algorithm in EDAX COMB32 S/W, for the relationships between “normalised” concentration ratios versus intensity ratios for all the analyte lines. Si data is always unity. When measuring an unknown, the measured intensity ratios are converted into equivalent concentration ratios via the calibration curves. The sum of the concentration ratios (T) is employed along with the normalization of the total wt% to 100% in order to calculate the individual analyte wt%'s in the following conventional manner.

Consider a five-element matrix containing analyte elements **a**, **b**, **c**, **d** & **e** with corresponding wt% concentrations of *A*, *B*, *C*, *D* & *E*. Given a set of calibration standards, it is possible to construct calibration curves with ratioed intensity as the input and ratioed wt% as the output for 4 of the 5 elements with the 5th element being equal to unity. With the calibration curves, measurement of an appropriate unknown (i.e. the same five-element matrix of a different composition) yields 4 individual wt% ratios $A/D \equiv A'$; $B/D \equiv B'$; $C/D \equiv C'$; $E/D \equiv E'$ assuming that **d** is the nominated internal reference element. This yields the following expression:

$$A/D + B/D + C/D + D/D + E/D = T \quad \text{eqn (1)}$$

where T is the "total" of the concentration ratios.

Each individual wt% ratio and, therefore, the total, T, are known quantities from the measured unknown. Since the total wt% is normalised to 100wt%, (i.e. $A+B+C+D+E=100\text{wt}\%$), it follows from eqn (1) that:

$$100/D = T \quad \text{eqn (2)}$$

Eqn (2) gives the solution for the individual wt%, D. The remaining individual absolute wt%'s can be put in terms of T as follows:

$$A = D [A/D] = (100/T) * [A/D] = (100/T) * A' \quad \text{eqn (3)}$$

Where A' is the measured wt% ratio from the calibration curve for element **a**

The use of internal intensity ratios for such a calibration procedure does anticipate there being no significant critical-depth situations over the analyte energy range covered that could detrimentally influence such ratios. If the specimen thickness exceeds ~100µm, little problem will be experienced for the element range considered here.

Results

Summary of calibration results for glass particulates									
sample name	OXIDE of:								
	Na	Mg	Al	Si	S	K	Ca	Ti	Fe
Given %									
cl621	12.75	0.27	2.76	71.19	0.13	2.01	10.72	0.13	0.04
cl622	13.75	3.95	0.13	72.33	0.13	0.04	8.41	0.42	0.84
cl624	13.45	4.04	0.14	72.17	0.18	0.03	8.54	0.02	1.43
sgt5	15.73	2.76	1.13	73.09	0.21	0.42	6.58	0.03	0.04
sgt6	14.69	0.05	1.70	73.25	0.20	0.05	10.00	0.02	0.03
sgt7	13.91	0.14	1.50	72.70	0.19	0.43	11.04	0.04	0.04
srm1830	13.77	3.91	0.12	73.19	0.26	0.04	8.57	0.01	0.12
srm1831	13.32	3.51	1.21	73.08	0.25	0.33	8.20	0.02	0.09
<i>Given concentrations re-adjusted to total 100wt%</i>									
Calculated %									
cl621	12.76	0.26	2.74	71.22	0.12	2.00	10.74	0.13	0.03
cl622	13.68	4.03	0.12	72.22	0.14	0.04	8.51	0.42	0.84
cl624	13.47	3.98	0.14	72.22	0.18	0.03	8.54	0.02	1.43
sgt5	15.70	2.76	1.09	73.09	0.22	0.43	6.61	0.05	0.05
sgt6	14.72	0.06	1.67	73.21	0.20	0.03	10.07	0.01	0.03
sgt7	13.84	0.11	1.51	72.88	0.22	0.44	10.92	0.04	0.05
srm1830	13.82	3.89	0.12	73.21	0.25	0.04	8.53	0.01	0.12
srm1831	13.32	3.55	1.28	73.04	0.25	0.33	8.12	0.02	0.09
typical σ (abs)	0.060	0.075	0.047	0.073	0.016	0.015	0.066	0.007	0.007

Figure 7. Summary of calibration sample concentrations together with computed results.

Calibration-standard concentrations together with results are summarised in tabular form in Figure 7 and graphically presented in Figure 8.

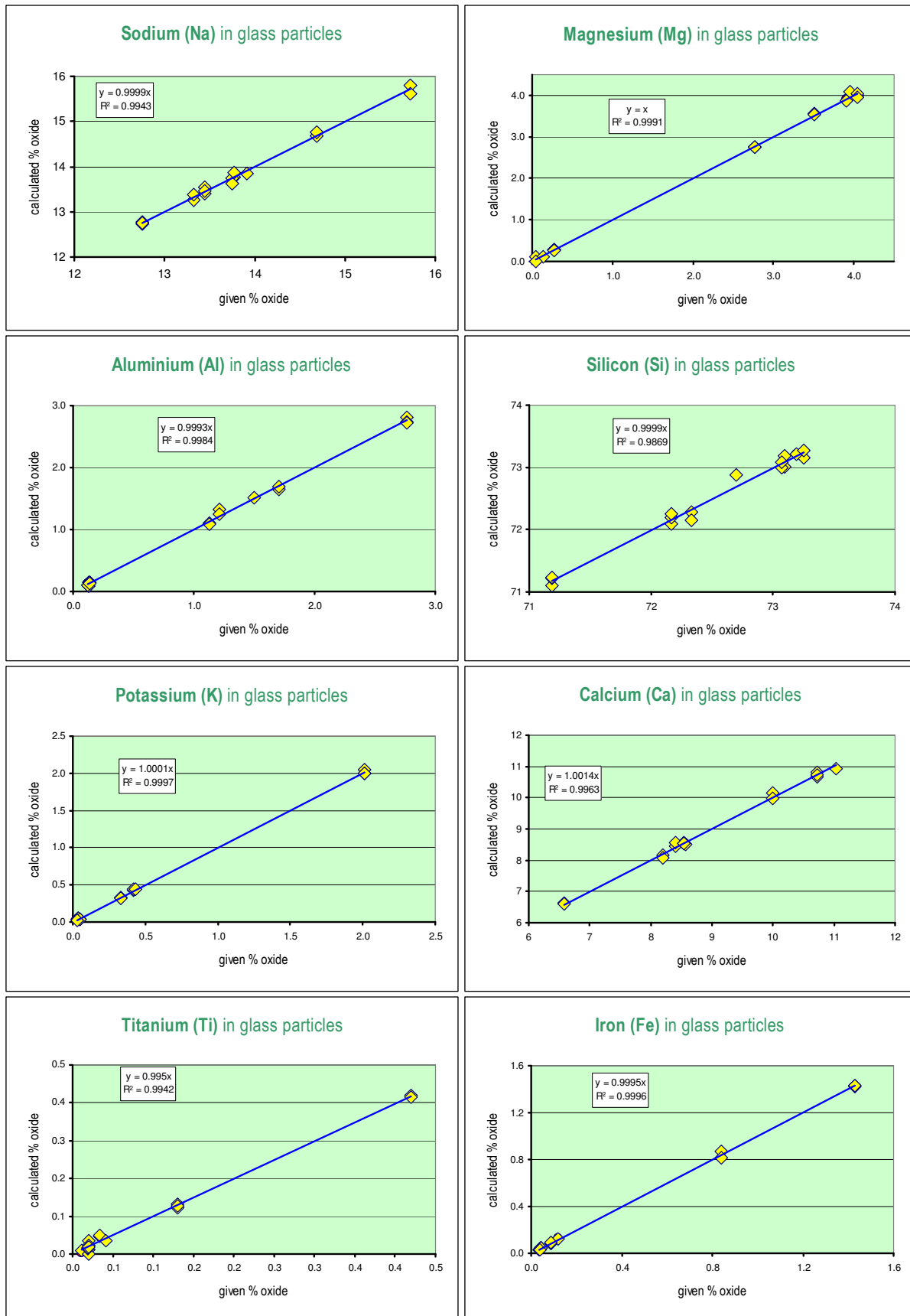


Figure 8. Graphical summary of calibration lines obtained using glass particulates.

Measurement repeatabilities were determined using repeat measurements on examples of two standard materials. The repeat measurement locations were not the same as those used for calibration purposes. The results, shown in Figure 9, represent the repeatabilities obtained for 15 measurements overall per standard type. The “total” RSD represents the overall repeatability of the procedure, i.e. the RSD of the sum of the individual wt% ratios, T, in eqn (1).

Glass particle measurement/analysis reproducibility										
15 measurements		Element oxide								
standard		Na	Mg	Al	Si	S	K	Ca	Ti	Fe
cl624	given wt.% oxide	13.45	4.04	0.14	72.17	0.18	0.03	8.54	0.02	1.43
	calculated	13.46	4.01	0.15	72.17	0.17	0.03	8.56	0.02	1.43
	std dev (abs wt.%)**	0.074	0.075	0.032	0.018	0.003	0.007	0.066	0.007	0.013
	total rsd				0.03					
cl621	given wt.% oxide	12.75	0.27	2.76	71.19	0.13	2.01	10.72	0.13*	0.04
	calculated	12.75	0.27	2.75	71.19	0.13	2.00	10.75	0.13	0.03
	std dev (abs wt.%)**	0.041	0.035	0.037	0.019	0.012	0.020	0.066	0.005	0.002
	total rsd				0.03					
*0.12% BaO+ 0.01% TiO2		**combination of stationary repeats, two different samples								

Figure 9. Measurement repeatability.

Computed Lower Limits of Detection (LLD) expressed as wt% oxide are shown in Figure 10 for the measurement time of 500Lsecs used for the investigation together with those predicted for a 100Lsec time (typical assumed measurement time). The expression used for this calculation was $LLD = (3/sensitivity) \times [\text{sqrt}(\text{background}/\text{time})]$.

elem oxide	LLD (wt.%)	
	100sec	500sec
Na	0.59	0.27
Mg	0.22	0.10
S	0.015	0.007
K	0.011	0.005
Ca	0.009	0.004
Ti	0.008	0.003
Fe	0.005	0.002

Figure 10. Computed detection limits.

Summary

The validity of the method for the analysis of irregularly configured glass particulates (for the specified element list) is clearly demonstrated.

For this method, specimen preparation is minimal and rapid where it is merely necessary to ensure that the surface presented for measurement is clean &/or contaminant-free. Repeat measurements at different locations on the analysed surface or different examples of the same material have been shown to be reproducible within the limits shown in Figure 9 (an overall relative standard deviation of 0.03%).

The system configuration employed for this investigation included a poly-capillary optic with a nominal “focus” beam size of 50µm. Optics having beam diameters down to 20µm (FWHM @ MoK α energy) are now available enabling even smaller samples to be studied with no beam overspill. However, critical depth situations should not be forgotten and where less emphasis need be placed on the Fe result; a specimen thickness of 40µm would suffice.