ELECTRONIC SUPPLEMENTARY INFORMATION

Critical evaluation of quantitative methods for the multi-elemental analysis of ancient glasses using LA-ICP-MS

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Experimental

Quantification strategy: calculations

The quantification strategy was developed during the course of the analysis of glass beads from the University of Aberdeen Museums[39], and follows Longerich *et al.*[1] and Gratuze *et al.*[2]. The ISI method employed in all analysis used the calculation of a response factor (*k*) for each analyte (*e*), determined from each standard reference material (*rm*) and correcting for the mass of sample ablated (represented by the intensity of the signal) for the internal standard, according to the equation:

$$k_e = \frac{(I_{e(rm)}/I_{IS(rm)})\ x\ C_{IS(rm)})}{C_{e(rm)}}$$

where $I_{e(rm)}$ is the intensity of the analyte *e* in the reference material *rm*, $I_{IS(rm)}$ is the intensity of the internal standard *IS* in the reference material and $C_{IS(rm)}$ and $C_{e(rm)}$ are the concentrations of the internal standard and the element in the reference material, respectively. The response factor can be interpreted as the slope of the regression line of a 1-point calibration curve, forced through the origin.

Prior to quantification, average intensities for all analytes measured were standardized with respect to the signal from ^{29}Si, corrected by its concentration in the sample. Because the concentration of the internal standard in the sample is not known, a concentration of 50% SiO_2 is initially arbitrarily chosen. As all of the major and minor components and the majority of trace elements (∑ >99%) are

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measured simultaneously, the sum normalization process[3] will eventually normalize the concentration of each element and elemental oxide to 100%.

Concentrations for each element and elemental oxide are calculated according to the equation:

$$C_{e(sam)} = \frac{I_{e(sam)} / (I_{IS(sam)} / C_{IS(sam)})}{k_e}$$

where $I_{e(sam)}$ is the intensity of the analyte *e* in the sample, $I_{IS(sam)}$ is the intensity of the internal standard *IS* in the sample, and $C_{IS(sam)}$ its estimated concentration in the sample. Response factors from all suitable analytical standards that contained the analyte measured, in an appropriate range of concentration to cover its concentration in the real sample, were employed in the calculations. The quantitative results for each analyte, obtained from each standard independently, were averaged producing equivalent results to the performance of calibration curves. The advantage of using the ISI method is that it allows the selection of individual values that will lead to a more accurate quantification (e.g. deriving from standards where the analyte is contained in a similar concentration), and the direct identification of those response factors which had been affected by fractionation or matrix effects, or heterogeneous distribution of trace elements in the standard. Once quantitative data were obtained, the concentrations of all analytes (major and minor components reported as elemental oxides, and trace elements expressed as elements, all converted to weight percent) were summed up, and sum normalization to 100% according to van Elteren *et al.*[3] was performed.

Results and discussion

Precision: results for individual instrumental set ups

When using the NWR UP213 LA-unit for the analysis of specimens from the University of Aberdeen Museums, the combined standard uncertainty was found to be generally comprised between 1 and 5% and averaging 2.5% for all major and minor components and trace elements, and reaching up to 20 to 50% for volatile elements in low concentration. For the analysis of beads from the NMS the combined standard uncertainty ranged between 4 and 15% (normally averaging around 8%), with higher values for elements close to their LoD, especially those having a low boiling point.

For all beads studied, the analysis yielded very good repeatability in the quantification of individual replicates, characterized by a RSD ranging normally between 0.5 and 5% and averaging around 4%

for major and minor components and trace elements. Individual higher values were measured for specific analytes in particularly heterogeneous glasses (e.g. some opaque glasses), especially in regard to trace elements in extremely low concentration and close to their LoD (such as Be, Cd, W, Au and Bi) and volatile elements (such as Zn, Ag and Sn), for which integration is particularly difficult at low concentrations. Therefore, the data show that the glasses analysed have generally good homogeneity, especially for translucent glasses not subject to micro-heterogeneities given by the presence of individual crystals and pigment clusters dispersed in the matrix. The analysis of standards rendered comparably lower values for analytes in low concentration in respect to the analysis of beads, due to the more homogeneous distribution of trace elements.

Measurements performed by sampling the specimens with the GeoLas LA-unit were subject to the combined standard uncertainty normally ranging between 2 and 6%, and always better than 10% for all analytes, with the exception of those in concentrations very close to the LoD.

Spot ablation using the NWR UP193HE LA-unit yielded values ranging between 8 and 15%. Lower values (between 4 and 7%) were calculated for CMG standards, while the ablation of NIST 600 series glasses rendered values comparable to those of the real samples in most cases. The use of lines yielded comparable signal intensity, with no statistically important increase in the number of cps measured. Increased noise on the signal and lower precision as reported by Smith *et al.*[22] for 213 nm lasers were not observed in this study, where the combined standard uncertainty is comparable to (or lower than) that obtained during the ablation of spots. The effect observed by Smith *et al.*[22], leading to more pronounced matrix effects and a possible increase in elemental fractionation, was attributed to the production of a constant supply of larger particles entering the plasma, when scanning across the surface of the sample rather than using spot ablation. Shorter wavelengths however, were proven to produce smaller particles[4-6], and 193 nm lasers such as those used in analysis performed here may be free of this effect.

References

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Supplementary Tables

Table S1. Concentration of major and minor components and trace elements in the measurement of NIST RSM 612, as measured with the different instrumental set-ups. The table reports repeatability (RSD) and accuracy (Δ%). Compositions are quoted in weight % (oxide) for major and minor components, and in mg kg^{-1} (element) for trace elements.

		University of Aberdeen						***Ghent University***				
		New Wave Research, UP213[a]			**New Wave Research, UP213[b]**			**Microlas Lasersystem GmbH, GeoLas**			**New Wave Research, UP193HE**	
Analyte	**Accepted values**	**Average *n=9***	**RSD**	**Δ%**	**Average *n=19***	**RSD**	**Δ%**	**Average *n=3***	**RSD**	**Δ%**	**Measured**	**Δ%**
						[w/o]						
SiO_2	71.9	72.2	1.9	1.4	72.8	1.0	1.3	72.0	0.45	0.3	72.5	0.9
Na_2O	14.0	14.6	7.1	6.8	13.6	3.9	3.9	14.0	1.9	1.6	13.3	5
CaO	11.9	11.1	4.6	7.7	11.2	3.7	6.0	11.6	0.3	2.6	11.7	1.6
Al_2O_3	2.11	1.93	2.9	9.3	2.07	3.7	3.3	2.06	0.93	2.4	2.06	2.5
MgO	0.013	0.010	12	32	0.01	8.1	14	0.012	3.4	9.3	0.01	25
K_2O	0.008	0.017	130	39	0.02	60	53	0.008	15	13	0.02	60
PbO	0.004	0.005	27	26	0.005	12	9.2	0.005	2.0	8.0	0.004	8.9
						[mg kg^{-1}]						
Li	42.0	42.3	11	6.3	37.1	7.6	14	36.8	2.4	14	40.1	4.8
Be	38.0	38.3	0.76	0.28	39.0	8.0	6.6	38.1	5.0	4.0	39.5	3.9
B	35.0	33.8	8.0	7.0	41.3	53	16	34.9	0.9	0.64	72.9	52
P	51.0	72.1	28	25	73.4	24	28	219	9.5	77	337	85
S	377	n.d.			935	114	49	645	34	36	1149	67
Cl	131	879	14	85	695	27	80	502	7.5	74	1044	87
Ti	44.0	41.4	6.5	8.0	41.7	17	15	46.3	8.2	7.8	43.5	1.1

[a] Laser in loan from ESI, New Wave Research, used for the method development and the first part of the study.
[b] Second instrumental set-up, used for the remaining part of the study; the laser was a different, recently refurbished device.

V	39.0	39.1	4.7	3.7	36.4	5.0	8.1	37.8	1.9	3.1	37.3	4.7
Cr	36.0	34.0	10	9.0	34.3	8.9	7.9	37.0	5.5	4.5	35.0	2.8
Mn	38.0	35.6	6.3	7.1	39.3	6.1	5.5	39.2	1.6	3.0	39.7	4.4
Fe	51.0	171	81	58	141	85	45	72.6	13	29	161	68
Co	35.0	35.6	4.7	4.2	37.6	4.6	6.8	37.2	0.78	5.9	35.8	2.2
Ni	38.8	38.3	6.5	5.3	41.0	3.6	5.4	40.2	0.78	3.4	38.0	2.2
Cu	37.0	35.2	13	11	42.1	11	11.6	38.9	3.8	4.9	37.2	0.6
Zn	38.0	30.9	12	24	41.0	17	13	38.5	12	9.6	33.6	13
Ga	36.0	35.9	1.3	0.92	n.d.			n.d.			n.d.	
As	37.0	36.8	1.4	1.0	41.2	16	12	37.5	9.0	7.5	37.1	0.4
Rb	31.4	33.6	9.9	11	33.5	6.5	6.9	33.3	2.8	5.8	31.2	0.6
Sr	78.4	73.3	12	8.9	77.5	7.5	5.8	79.3	2.0	1.9	80.0	2
Y	38.0	n.d.			38.8	8.6	6.5	37.7	3.4	2.4	36.8	3.3
Zr	38.0	35.4	16	13	37.7	8.1	5.9	39.7	3.7	4.1	38.3	0.8
Ag	22.0	34.0	20	33	28.7	11	25	25.1	4.2	12	23.6	6.8
Cd	28.3	n.d.			31.9	29	18	30.2	8.3	7.9	26.9	5.1
Sn	38.0	45.1	18	18	39.5	8.4	5.8	38.6	1.4	1.5	43.0	12
Sb	38.0	38.8	16	12	41.9	9.4	9.5	38.5	7.1	5.7	37.5	1.4
Ba	39.7	47.5	14	19	48.7	7.1	18	50.2	6.7	21	45.4	13
La	35.8	n.d.			36.4	6.2	4.0	37.7	3.8	4.9	36.6	2.0
Ce	38.7	38.5	1.4	0.99	38.6	6.2	4.3	40.0	2.7	3.1	38.9	0.67
Pr	37.2	n.d.			37.2	5.6	3.8	37.9	2.5	2.5	37.1	0.35
Nd	35.9	35.7	1.4	1.0	36.1	6.9	4.8	36.5	2.2	2.2	35.2	1.8
W	40.0	n.d.			39.9	12	9.2	41.3	1.2	3.2	39.9	0.11
Au	5.10	4.66	1.9	0.78	5.43	17	14	4.89	5.4	4.6	4.69	8.8
Bi	30.0	30.7	16	3.7	34.4	14	14	32.0	4.2	6.1	32.4	7.3
Th	37.8	n.d.			38.4	13	8.4	39.0	4.5	4.6	37.3	1.4
U	37.4	37.3	1.3	0.91	37.3	17	13	38.8	3.2	3.6	37.1	0.8

<LoD = Below limits of detection; n.d. = not determined

Table S2. Concentration of major and minor components and trace elements in the measurement of NIST RSM 610 and 614, as measured with the different instrumental set-ups. The table reports repeatability (RSD) and accuracy (Δ%). Compositions are quoted in weight % (oxide) for major and minor components, and in mg kg^{-1} (element) for trace elements.

		Ghent University								
		Microlas Lasersystem GmbH, GeoLas		**New Wave Research, UP193HE**			**Microlas Lasersystem GmbH, GeoLas**		**New Wave Research, UP193HE**	
Analyte	**NIST610 Accepted**	**Measured**	**Δ%**	**Measured**	**Δ%**	**NIST614 Accepted**	**Measured**	**Δ%**	**Measured**	**Δ%**
					[w/o]					
SiO_2	70.0	71.0	1.4	71.5	2.1	72.3	72.2	0.1	72.6	0.4
Na_2O	13.4	13.7	2.6	13.2	1.5	13.6	13.7	1.0	13.4	1.2
CaO	11.5	11.7	2.0	11.7	1.5	11.9	11.6	1.3	11.7	1.7
Al_2O_3	2.04	2.04	0.14	2.05	0.6	1.99	2.11	5.7	2.05	2.8
MgO	0.077	0.079	2.9	0.080	3.1	0.006	0.008	28	0.005	13
K_2O	0.059	0.055	6.9	0.063	7.8	0.004	0.004	11	0.020	82
PbO	0.049	0.052	5.9	0.045	10	0.0003	0.0003	8.7	0.0004	32
					[mg kg^{-1}]					
Li	485	452	7.3	468	3.7	1.60	2.11	24	<LoD	
Be	466	452	3.2	472	1.3	0.670	0.75	11	0.64	4.9
B	356	336	6.0	370	3.9	1.40	6.47	78	53.6	98
P	343	487	30	711	52	13.0	213	94	262	95
S	693	574	21	956	28	306	327	6.3	1231	75
Cl	438	617	29	1166	62	92.0	536	83	<LoD	
Ti	434	470	7.7	445	2.5	0.855	<LoD		8.31	90
V	442	452	2.1	432	2.4	1.00	0.99	1.3	2.09	52
Cr	405	363	12	406	0.25	1.80	6.53	72	<LoD	
Mn	485	466	4.2	469	3.4	1.40	1.55	9.7	1.73	19

Fe	458	632	28	524	26	19.0	47.4	60	127	85
Co	405	432	6.2	430	5.9	0.850	2.36	64	0.74	15
Ni	459	464	1.1	456	0.58	1.00	1.56	36	<LoD	
Cu	430	442	2.6	441	2.5	1.37	2.44	44	1.8	24
Zn	456	433	5.2	425	7.4	2.50	2.39	4.4	2.64	5.6
Ga	-	n.d.		n.d.		-	n.d.		n.d.	
As	317	335	5.3	334	4.9	0.660	0.703	6.1	<LoD	
Rb	426	444	4.0	437	2.6	0.855	0.884	3.2	0.953	10
Sr	516	531	2.9	538	4.1	0.760	46.6	98	46.6	98
Y	450	457	1.6	473	4.8	0.750	0.787	4.7	0.742	1.0
Zr	440	464	5.1	474	7.1	0.840	0.898	6.5	0.814	3.2
Ag	239	294	19	284	16	0.420	0.487	134	0.409	2.6
Cd	259	282	8.1	271	4.4	0.580	1.35	57	0.588	1.3
Sn	396	433	8.6	507	22	1.60	1.85	13	1.76	9.4
Sb	369	415	11	455	19	0.780	0.87	9.9	0.885	12
Ba	435	536	19	529	18	3.20	3.41	6.1	3.62	12
La	457	447	2.2	457	0.08	0.720	0.743	3.1	0.708	1.7
Ce	448	459	2.4	468	4.3	0.810	0.802	1.0	0.775	4.6
Pr	430	438	1.8	447	3.7	0.760	0.765	0.61	0.736	3.2
Nd	431	429	0.5	439	1.9	0.740	0.761	2.8	0.742	0.3
W	445	463	3.8	479	7.1	0.880	0.843	4.3	0.821	7.1
Au	23.0	24.2	4.9	25.0	8.0	0.450	0.488	7.7	0.454	1.0
Bi	358	351	2.2	383	6.4	0.580	0.666	13	0.614	5.5
Th	457	453	0.9	472	3.1	0.748	0.780	4.1	0.738	1.4
U	462	452	2.0	469	1.6	0.823	0.853	3.6	0.819	0.48

Table S3. Concentration of major and minor components and trace elements in the measurement of Corning Museum of Glass standard D, as measured with the different instrumental set-ups. The table reports repeatability (RSD) and accuracy (Δ%). Compositions are quoted in weight % (oxide) for major and minor components, and in mg kg^{-1} (element) for trace elements.

		University of Aberdeen						*Ghent University*			
		New Wave Research, UP213[a]			New Wave Research, UP213[b]			Microlas Lasersystem GmbH, GeoLas		New Wave Research, UP193HE	
Analyte	**Accepted values**	**Average *n=8***	**RSD**	**Δ%**	**Average *n=4***	**RSD**	**Δ%**	**Measured**	**Δ%**	**Measured**	**Δ%**
SiO_2	55.2	56.8	2.1	3.0	56.7	1.5	2.6	56.5	2.3	56.8	2.8
Na_2O	1.20	1.28	3.6	6.3	1.42	3.0	16	1.00	20	1.32	8.9
CaO	14.8	15.1	3.6	3.2	15.1	2.9	3.0	15.4	3.7	15.7	5.9
Al_2O_3	5.30	5.74	3.3	7.6	5.46	3.0	2.8	5.47	3.0	5.49	3.4
MgO	3.94	4.26	7.1	7.3	4.19	2.5	5.8	3.70	6.6	4.04	2.4
K_2O	11.3	11.4	3.0	2.1	11.6	2.0	3.8	13.3	15	11.3	0.1
PbO	0.48	0.29	8.3	67	0.28	10	71	0.21	124	0.24	102
						[mg kg^{-1}]					
Li	23.2	24.8	5.9	6.5	26.8	5.8	13	26.8	13	31.1	25
Be	-	<LoD			0.045	64		<LoD		0.045	
B	311	327	10	7.4	284	19	14	321	3.3	320	3.0
P	17150	18570	4.8	7.5	18331	4.8	6.3	14259	20	18124	5.4
S	-	n.d.			742	53	28	760		937	28
Cl	4000	2390	27	75	2404	15	69	1617	150	2098	91
Ti	2278	2166	6.2	6.9	2340	2.7	2.9	2376	4.1	2299	0.92
V	84.0	88.8	6.2	6.2	99.2	2.5	15	97.7	14	96.6	13
Cr	17.1	17.6	8.3	6.7	17.9	3.3	4.2	21.1	19	18.4	6.9

[a] Laser in loan from ESI, New Wave Research, used for the method development and the first part of the study.
[b] Second instrumental set-up, used for the remaining part of the study; the laser was a different, recently refurbished device.

Mn	4260	4700	6.7	9.0	4312	2.1	1.7	4256	0.1	4538	6.1
Fe	4042	4225	4.1	4.9	4191	0.6	3.5	4062	0.5	4047	0.1
Co	157	163	5.0	3.9	163	1.4	3.2	154	2.0	156	0.78
Ni	393	425	7.2	7.3	400	2.2	2.4	396	0.82	395	0.61
Cu	3036	3387	11	11	2980	3.9	3.5	3007	0.94	3090	1.8
Zn	803	855	4.8	6.5	811	3.1	2.6	895	10	828	3.0
Ga	-	184	73		n.d.			n.d.		n.d.	
As	-	264	14		357	13		270		268	
Rb	45.7	41.9	5.6	9.5	47.9	3.6	4.4	45.4	0.65	45.6	0.2
Sr	507	535	5.6	6.2	519	4.5	3.2	509	0.30	540	6.0
Y	-	n.d.			0.28	8.0		0.353		0.263	
Zr	92.5	96.3	2.8	3.9	96.1	4.5	4.0	95.5	3.1	89.3	3.6
Ag	46.6	46.7	6.1	5.2	40.6	4.5	15	36.0	29	34.6	35
Cd	-	n.d.			0.32	22		0.346		0.202	
Sn	788	818	6.5	5.8	798	4.1	2.5	698	13	854	7.8
Sb	8103	8488	6.1	5.0	8351	1.4	3.0	7270	11	8362	3.1
Ba	4568	3942	12	17	3684	3.5	24	3307	38	3433	33
La	-	n.d.			0.49	10		0.493		0.531	
Ce	-	0.25	22		0.32	8.2		0.285		0.292	
Pr	-	n.d.			<LoD			0.0240		0.0190	
Nd	-	0.12	23		<LoD			0.102		0.0940	
W	-	n.d.			<LoD			0.0960		<LoD	
Au	-	<LoD			0.12	113		<LoD		0.0570	
Bi	22.4	11.8	35	100	13.0	13	75	11.5	95	12.4	81
Th	-	n.d.			0.73	9.4		0.687		0.651	
U	-	0.15	30		0.18	13		0.170		0.173	