

Supplementary material

Calculation of LOD by GUPIXWIN

LOD (limit of detection or MDL – minimum detection limit) values were calculated using the GUPIXWIN software (see GUPIXWIN manual).

LOD values (in ppm or ng/cm²) are given by the following equation

$LOD = (3\sigma) / (Q * H * Y_{1t} * \epsilon * T)$, where

$\sigma = \text{sqrt}(B)$

B = background area over one FWHM (full width at half maximum) region,

Q = the measured charge in μC ,

H = instrumental constant used in conversion of area to concentration, (in ideal case it is the solid angle),

Y_{1t} = theoretical yield K_{α} , L_{α} or M_{α} X-rays per micro-Coulomb of charge per unit concentration per steradian in the 1 FWHM region centered about the element's principal peak,

ϵ = relative detector efficiency,

T = transmission fraction for the X-rays through any absorber that is present.

Table S1. Elemental concentrations of Corning A archeological reference glass measured by the UTW-SDD and the 3-SDD cluster. Reference values are presented in the left columns of the table. Uncertainty originating from the spectrum fitting (fit error) and detection limits (LOD) are also included.

	CorningA	UTW SDD			3-SDD cluster		
	reference value wt%	conc. wt%	fit err. %	LOD wt%	conc. wt%	fit err. %	LOD wt%
O*	44.710	44.39	2.01	0.1711			
Na	10.610	10.43	0.35	0.0132			
Mg	1.596	1.53	0.69	0.0076			
Al	0.529	0.59	0.96	0.0079			
Si	31.061	31.39	0.09	0.0028			
P	0.035			0.0104			
S	0.056	0.072	4.53	0.0048			
Cl	0.090	0.097	3.01	0.0038	0.084	4.57	0.0016
K	2.381	2.430	0.29	0.0042	2.380	0.62	0.0007
Ca	3.593	3.517	0.23	0.0198	3.458	0.35	0.0088
Ti	0.474	0.511	0.81	0.0072	0.491	0.34	0.0035
V	0.003			0.0131	0.004	10.43	0.0036
Cr	0.002			0.0024	0.001	9.76	0.0003
Mn	0.775	0.774	0.63	0.0021	0.771	0.19	0.0003
Fe	0.763	0.734	0.71	0.0073	0.740	0.18	0.0028
Co	0.134	0.142	2.34	0.0056	0.142	0.3	0.0019
Ni	0.016	0.019	10.01	0.0026	0.014	1.41	0.0006
Cu	0.935	0.937	0.75	0.0011	0.948	0.16	0.0003
CuL		0.882	3.52	0.1621			
Zn	0.035	0.031	8.63	0.0034	0.036	0.71	0.0004
Rb	0.008			0.0096	0.013	4.32	0.0009
Sr	0.085	0.084	12.31	0.0078	0.075	1.3	0.0014
Zr	0.004			0.0300			0.0025
Sn	0.150				0.312	6.86	0.0225
Sb	1.276	1.131	2.91	0.3056	1.408	1.03	0.1994
Ba	0.412	0.380	3.05	0.0832	0.439	0.43	0.0514
Pb	0.067	0.078	9.65	0.0071	0.065	4.93	0.0067
PbM		0.070	20.97	0.0288			

* The O content is calculated from usual oxide forms of elements.

Table S2. Elemental concentrations of NIST SRM610 glass measured by the UTW-SDD and the 3-SDD cluster. Certified and reference* values are presented in the left columns of the table. Uncertainty originating from the spectrum fitting (fit error) and detection limits (LOD) are also included.

	reference		UTW SDD			3-SDD cluster		
	conc. ppm wt%	unc.	conc. ppm wt%	fit err. %	LOD ppm	conc. ppm wt%	fit err. %	LOD ppm
O	48.20%		49.50%	1.6	3559.5			
Na	9.95%		9.60%	0.4	112.8			
Mg			352	17.2	81			
Al	1.10%		1.18%	0.6	77			
Si	32.50%		31.50%	0.1	7.2			
S			794	3.9	50.2			
Cl			505	4.9	36.3	379	8.1	16.8
K	461**		561	5.4	46.4	827	2.5	21.8
Ca	8.20%		8.38%	0.1	33.6	8.36%	0.3	10.1
Ti	437**		524	3.3	23.5	530	1.0	9.1
V			469	4.4	33.3	461	0.9	12.1
Cr	415	29	595	5.7	39.8	492	0.7	7.9
Mn	457	55	376	5.3	28.3	507	0.7	9.9
Fe	458	9	481	4.2	29.4	520	0.5	11.8
Co	390**		453	5.0	32.2	596	0.8	9.7
Ni	459	4	463	5.4	35.1	286	1.5	22.4
Cu	444*		410	6.5	37.4	422	0.7	12.8
Zn	433**					534	0.5	6.6
Ga						427	0.6	8
Ge						456	0.6	6.4
As	340	20				323	1.1	10.8
Se	115.2	3.2				115	2.4	7.6
Rb	425.7	0.8				406	1.3	8
Sr	515.5	0.5				497	1.2	7.2
Y						407	1.7	13.6
Zr						401	2.1	17.8
Nb						437	2.5	16.7
Mo						344	3.4	17.7
Cs						629	4.4	10.2
Ba	453	37				407	4.2	79.1
La						368	4.3	27.3
Ce						512	2.0	39.1
Pr						666	1.6	48.5
Nd						609	1.5	21.7
Sm						574	1.5	22.4
Eu						393	3.0	71.7
Gd						432	2.4	27
Tb						463	2.0	38.4
Tm						500	2.4	42.1
Yb						399	3.7	113.1
Lu						318	3.1	69.3
Hf						499	1.6	38.7
W						521	2.0	31.9
Pb						424	2.3	56.4
Bi						365	2.5	25.4
Th	457	1.2				426	3.4	38.8
U	461	1.1				381	3.5	30.7

Table S3. Calculated elemental concentrations of Corning A glass (measured by the UTW-SDD) using 3 different methods in GUPIXWIN. 1) fix matrix solution: the matrix is known a priori, and is given to the software before running the calculation, collected charge was calculated from the measurement time and beam current measurement before and after the irradiation. 2) iterated matrix solution: concentration of all measured components – including O - were evaluated and normalized to 100%. 3) iterated matrix solution using the common oxide forms of elements: concentrations of oxide forms of all measured components were evaluated and normalized to 100%. Reference values are presented in the left columns of the table. Uncertainty the fit errors are also included.

	reference	fix matrix solution		iterated matrix solution		iterated matrix solution with oxide formula	
	conc. wt%	conc wt%	fit err %	conc wt%	fit err %	conc wt%	fit err %
O	44.710	45.926	2.56	44.388	2.01		
Na	10.610	10.232	0.34	10.429	0.35	10.577	0.36
Mg	1.596	1.503	0.66	1.530	0.69	1.540	0.69
Al	0.529	0.588	0.96	0.590	0.96	0.590	0.96
Si	31.061	30.283	0.10	31.391	0.09	31.364	0.09
P	0.035	0.034	16.04	0.008	64.90	0.044	14.04
S	0.056	0.071	4.17	0.072	4.53	0.072	4.51
Cl	0.090	0.102	2.64	0.097	3.01	0.097	3.00
K	2.381	2.414	0.29	2.430	0.29	2.405	0.29
Ca	3.593	3.482	0.27	3.517	0.23	3.482	0.23
Ti	0.474	0.493	0.85	0.511	0.81	0.505	0.81
Cr	0.002	0.017	9.02	0.019	8.86	0.019	8.92
Mn	0.775	0.743	0.61	0.774	0.63	0.766	0.63
Fe	0.763	0.707	0.68	0.734	0.71	0.728	0.71
Co	0.134	0.137	2.27	0.142	2.34	0.141	2.34
Ni	0.016	0.020	9.29	0.019	10.01	0.019	10.00
Cu	0.935	0.919	0.73	0.937	0.75	0.928	0.75
CuL		<i>0.880</i>	<i>3.30</i>	<i>0.832</i>	<i>3.52</i>	<i>0.937</i>	<i>3.14</i>
Zn	0.035	0.031	8.44	0.031	8.63	0.031	8.68
Sb	1.276	1.094	2.57	1.131	2.91	1.124	2.91
Ba	0.412	0.366	3.06	0.380	3.05	0.377	3.04
Pb	0.067	0.077	9.59	0.078	9.65	0.076	9.82
Pb M		<i>0.076</i>	<i>18.99</i>	<i>0.070</i>	<i>20.97</i>	<i>0.068</i>	<i>21.42</i>

Figure S1. PIXE spectra of aerosol samples collected on PTFE (2 μm pore size) and nucleopore polycarbonate (0.4 μm pore size) filters recorded by the UTW SDD detector.

