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QUANTITATIVE ANALYSIS OF A MULTICOMPONENT SILICATE GLASS BY ELECTRON MICROPROBE

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Abstract - A standard glass sample denoted by the National Institute of Standards and Technology as K-412 was analyzed using electron microprobe by an international collaborative team. The results of quantitative determination of the oxide glass components are compared and the deviations from the standard values are calculated. Also methods of glass surface treatment, conditions of quantitative determination and procedures used for evaluation of results are summarized.

INTRODUCTION

Determination of the composition of glasses using electron microprobe appears to be one of the methods most used in both research and in the glass industry. Despite the common use of this method there are still some uncertainties in the reproducibility and accuracy of the measurements. Those are caused by :

i) relative complexity of glass surface preparation,
ii) influence of voltage, electron beam diameter, time of counting and other parameters of the analysis,
iii) standards and methods used to convert X-ray intensities into concentration values.

Therefore, it is of great interest to compare conditions of measurement, reproducibility and accuracy of measurements in some laboratories dealing with glass analysis (ref. 1,2).

GLASS SAMPLE CHARACTERIZATION

A standard probe K-412 supplied by the National Institute of Standards and Technology, Washington D.C.(USA) was used (ref. 3). The certified composition of the glass was as follows (in wt %):

45.35 ± 0.2 SiO_2
19.33 ± 0.2 MgO
15.25 ± 0.2 CaO
9.27 ± 0.2 Al_2O_3
9.96 ± 0.2 FeO

The uncertainty of ∓ 0.2 wt % assigned to the certified values is the 2-sigma value. This composition made it possible to compare the results of analytical measurements on the relatively stable glass containing very common oxides.

The samples were sent to the participants on the project (see Appendix) in the form of a small stick. The participants were asked to make quantitative analysis of the glass sample using an electron microprobe and procedures and conditions chosen by themselves.

SURFACE TREATMENT OF GLASS SAMPLES

Procedures used by the participants to prepare the glass surface for analysis are briefly summarized in the Table 1. Most of the authors fixed the glass sample by embedding in epoxy resin. Only in one case was the sample stuck using a carbon paste on a carbon block. Various procedures were used for grinding. Grinding powders, papers and discs made it possible to prepare glass surfaces with a roughness 5 µm. Not all authors stated how the grinding procedure was performed and which roughness of the surface was obtained.

In one case the fracture surface of the glass sample was used without any grinding and polishing. Cerium oxide in the form of a disk or a paste was used preferably to polish glass surface. Also alumina powder and diamond pastes were used in some cases. After cleaning of the glass surface with alcohol or water a thin carbon layer was sputtered on the sample. The thickness of the layer was 20-50 nm.

TABLE 1. Glass sample preparation

	embedding	grinding	polishing	cleaning	carbon coating
1.	epoxy resin	grinding machine	polishing diamond pastes	alcohol	C 20-30 nm
2.	sticking by a carbon paste on a carbon block	-	-	-	C 40 nm
3.	hot pressing using fenol resin	grinding diamond discs (30-5 µm)	polishing disc (CeO_2)	alcohol	C 25-30 nm
4.	epoxy resin	grinding discs (30-5 µm)	polishing disc (CeO_2)	alcohol acetone	C 30-50 nm
5.	epoxy	SiC on glass	polishing diamond pastes	warm water, soap	C 25 nm
6.	resin and wax	corundum powder (20-7 µm)	CeO_2-paste	water, alcohol	C 30 nm
7.	epoxy resin	SiC-papers-800	0.3 um alumina + MgO	-	C 25 nm
8.	epoxy resin	grinding paper 200-600	alumina powder 1 um-0.3 µm	distilled water freon	C 20 nm
9.	brass block, carbon paste	SiC-1000	CeO_2-powder	?	C 30 nm
10.	sticking by a Ag paste on a carbon block	-	-	-	C 30 nm

EQUIPMENT AND EXPERIMENTAL CONDITIONS OF ANALYSIS

Different types of electron microprobe equipment were used for quantitative analysis of the K-412 glass samples (see Table 2). All equipment used was essentially based on the wavelength dispersive system (WDS) although an energy dispersive system (EDS) was alternatively used in some cases.

TABLE 2. Equipments and experimental conditions

	type of equipment	principle of operation	voltage (kV)	intensity (nA)	electron beam diameter (µm)
1.	JCXA-733	WDS-aut.	15	20	10
2.	JXA-50A	EDS, Kevex 7000	15	0.3	area of 13 x 13
3.	JXA-5	WDS	10,15,20	13-18	5
4.	JXA-733	WDS	10,20	7-70	10
5.	Camebac Micro	WDS-aut.	15	18	5
6.	JCXA-733	WDS-aut.	15	50	20
7.	JCXA-733	WDS-aut.	15,20	30	20
8.	JCXA-733	WDS-aut.	15	17.1	10
9.	SHIMADZU SM-7	WDS	15	10	50
10.	ARL SEMQ	WDS-aut. EDS-Kevex 7000	20	9-WDS 3-EDS	0.5

WDS.... wavelength dispersive system
EDS.... energy dispersive system

TABLE 3. Intensity measurements and calculation of omposition

	time of counting /s/	number of measurements	correction method	type of correction programme
1.	20	40	ZAF	individual
2.	300 (EDS)	6	ZAF	MACK V KEVEX
3.	10	10	ZAF	modification of COR-SONDAX
4.	100	5	ZAF	modification of COR-SONDAX
5.	10	15	ZAF	CORREX from CAMEBAX
6.	5	3	BA, ZAF	ALBEE-JCXA-733
7.	10	5	BA, ZAF	JEOL-ZAF
8.	38 (Si) 30 (others)	200	ZAF	Duncumb and Jones version 12F from TRACOR
9.	20	5	BA	individual
10.	40 (Al,Fe) WDS 48 (Mg,Si,Ca) 100, 200 EDS	10	ZAF	COLBY MAGIC IV,V

ZAF ...... atomic number absorption and fluorescence correction
BA .... BENCE-ALBEE (semiempirical method)

The accelerating voltage applied varied between 10 and 20 kV but the value of 15 kV was used preferably. The corresponding absorbed current values differed significantly from about 10 to 70 nA. Extremely low values (0.3 and 3 nA respectively) were used with EDS method.

The electron beam diameter varied from 0.5 μm to 50 μm. In one case a scanning procedure was used and the scanned area was 13 x 15 μm .

In addition to the parameters summarized in the previous table the time and number of measurements together with correction methods and types of correction programmes were also compared (see Table 3).

Counting times varied between 5 and 300 seconds with the highest values pertaining to the EDS measurements. The maximum value observed in WDS measurements amounted to 100 s.
The number of the measurements reported by participants differed significantly from 3 to 200. The value of this parameter clearly depends on the availability of an automation system.

All results of the measurements were evaluated by a correction programme. Different types of correction programmes were used but the ZAF correction method clearly predominated.

STANDARDS AND MONOCHROMATORS

Simple oxides were used as standard materials for quantitative determination of MgO , SiO_2, Al_2O_3 and Fe_2O_3. Also some multicomponent standards were applied (chromite, kaersutite, pyrope, albite, jadeite, olivine, wollastonite and silicate glass) in some cases.

Three main crystals were used in the measurements: TAP (thallium acid phthalate) for Mg, Si, Al, PET (pentaerythrite) for Ca and Fe and LiF for Fe predominantly. The K lines were employed for Mg, Al, Si, Ca and Fe determination.

RESULTS

The results of the K-412 glass sample analyses are summarized in Table 4 which includes values of the oxide content in wt.% together with standard deviations as they were measured and calculated by the participants. Also the certified composition according to the NIST certificate is shown in that table. The deviations between values determined by the participants and corresponding NIST values are shown in Table 5.

TABLE 4. Results of quantitative analysis of the K-412 sample

	$MgO \pm$ wt %	% rel.	$Al_2O_3 \pm$ wt %	% rel.	$SiO_2 \pm$ wt %	% rel.	$CaO \pm$ wt %	% rel.	$FeO \pm$ wt %	% rel.	wt %
1.	19.44	0.8	9.42	1.5	45.54	0.7	15.26	1.0	10.39	1.1	99.92
2.	17.7	5.0	8.8	3.4	46.1	1.3	17.00	4.0	10.4	4.8	100.00
3. 10 kV	19.47		9.10		45.87		14.96		9.74		99.14
15 kV	19.44	2.8	8.94	2.1	44.84	0.4	14.90	0.4	9.60	1.0	97.72
20 kV	19.29		8.77		44.38		15.85		9.47		97.76
4. 10 kV	19.83	0.8	9.38	1.0	46.76	0.9	14.87	0.2	9.50	0.9	100.34
20 kV	19.66	0.9	9.26	1.2	46.30	0.7	15.00	0.5	9.80	0.5	99.62
5.	19.8	1.0	9.70	0.8	45.20	0.4	14.90	0.9	10.5	1.2	100.1
6. ZAF	20.10	1.2	9.22	1.4	45.84	1.0	14.74	1.7	10.42	3.0	100.34
BA	20.32	0.7	9.24	0.7	45.85	0.4	14.48	0.4	10.37	1.4	100.27
7. ZAF	19.11	0.3	9.87	0.7	45.92	0.6	14.94	0.5	10.17	1.0	100.01
BA	19.23	0.3	9.41	0.7	45.80	0.6	14.90	0.5	9.84	1.0	99.19
8.	19.11	0.7	8.7	0.6	45.52	0.3	15.08	0.5	10.78	1.4	99.19
9.	19.97	0.1	9.2	0.2	45.19	0.1	15.40	0.1	9.25	3.3	99.01
10. WDS	20.1	0.7	8.9	2.8	46.4	1.0	14.8	1.0	9.8	1.0	100.00
EDS	19.54	1.2	9.67	2.0	46.3	0.5	14.92	1.0	9.45	2.3	99.88
K-412 (NIST certificate value)	19.33	0.5	9.27	1.0	45.35	0.2	15.25	0.6	9.96	1.0	99.16

TABLE 5. Absolute value of deviations from NIST certificate values in wt %

		MgO	Al_2O_3	SiO_2	CaO	FeO
1.		+ 0.11	+ 0.15	+ 0.16	+ 0.01	+ 0.33
2.		- 1.63	- 0.47	+ 0.75	+ 1.75	+ 0.44
3.	10 kV	+ 0.14	- 0.17	+ 0.52	- 0.39	- 0.32
	15 kV	+ 0.11	- 0.33	- 0.51	- 0.35	- 0.36
	20 kV	- 0.04	- 0.50	+ 0.03	+ 0.60	- 0.49
4.	10 kV	+ 0.5	+ 0.11	+ 1.41	- 0.38	- 0.46
	20 kV	+ 0.33	+ 0.01	+ 0.85	- 0.35	- 0.46
5.		+ 0.47	+ 0.43	- 0.15	- 0.35	+ 0.54
6.	ZAF	+ 0.77	- 0.05	+ 0.49	- 0.5	+ 0.46
	BA	+ 0.97	- 0.03	+ 0.5	- 0.77	+ 0.41
7.	ZAF	- 0.22	+ 0.6	+ 0.57	- 0.31	+ 0.31
	BA	- 0.1	+ 0.14	+ 0.45	- 0.35	- 0.12
8.		- 0.32	- 0.57	+ 0.17	+ 0.17	- 0.82
9.		+ 0.64	- 0.07	- 0.16	+ 0.15	- 0.71
10.	WDS	+ 0.77	- 0.37	+ 1.05	- 0.45	- 0.16
	EDS	+ 0.31	+ 0.40	+ 0.95	- 0.33	- 0.51

The results can be summarized as follows :

MgO determination

Most of the results are within the limits defined by NIST value and corresponding standard deviation (see Table 4). The highest deviation from the standard value amounts to 1.63 rel.%. Deviations from the standard value decreased if the voltage was raised from 10 to 20 kV. The accuracy of the determination does not depend significantly on the principle of the measurements (WDS, EDS) or on the type of correction programme (ZAF, BA). A more systematic study has to be done to verify this conclusion.

Al_2O_3 and SiO_2 determination

Deviations from the certified standard value are in all cases comparable with the standard NIST deviation value. The analytical results show that the accuracy of the measurements is comparable with the results of other oxides. The deviations from the certified value are probably also caused by the drift of monochromator caused by its mechanical and thermal instability. Charging effects can also contribute to a certain lateral defocusation of the spectrometer.

CaO determination

The results are in satisfactory agreement with the standard NIST value (see Table 4) although in some cases the difference between determined value and NIST standard exceeds the certified standard deviation.

FeO determination

The analytical results are in a good agreement with the standard value (see Table 4). Deviations exceed in some cases slightly the certified NIST standard deviation. Quantitative determination of FeO in the multicomponent silicate glass thus seems to be quite reliable.

The reasonable agreement of the analytical results of all glass components indicates that the different procedures and conditions used by the participants do not have a pronounced effect on the accuracy and reproducibility of the measurements. As had to be expected the error of the measurements on a fracture surface are much larger than on polished surfaces.

CONCLUSION

Quantitative analysis of the K-412 glass standard glass using the electron microprobe was carried out by an international collaborative team. The analytical results are in good agreement with the certified values confirming the reliability and accuracy of the work in laboratories participating on the project.

The results show that comparable results can be achieved using different types of equipment with good standards even when procedures and conditions applied are not quite identical.

Values of oxide content obtained in different laboratories were usually within the relative standard deviations certified for the standard K-412 glass. The accuracy of the measurements is affected by the quality of the glass surface, a good polishing procedure is essential.

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