Analysis of glass by X-ray fluorescence with the ARL OPTIM'X WDXRF spectrometer

Keywords
ARL OPTIM'X, glass, WDXRF, X-ray fluorescence

ARL OPTIM'X XRF spectrometer

Introduction

The simplest form of glass is the single component fused silica (SiO_2). However it is both difficult to process and expensive. To reduce these difficulties, some other oxides are added imparting specific properties to the resultant glass.

Most of glasses are composed of about 70% silica, which is a glass former, soda as a flux in the form of carbonate and sulfate (about 14%), and lime as a stabilizer in the form of limestone (about 10%). Other types of oxides like alumina or magnesia improve the physical characteristics of glass, particularly the resistance to atmospheric conditions.

In-depth coloring is obtained by incorporation of various metallic oxides: oxides of chromium, iron, manganese or copper.

Instrumentation

A Thermo Scientific™ ARL™ OPTIM'X WDXRF Spectrometer is used to derive limits of detection and precision for the analysis of glasses. The ARL OPTIM'X spectrometer is a wavelength dispersive system that provides superior resolution and light elements capability. It is fitted with an air-cooled Rh end-window tube with thin Be window (0.075 mm) and has a maximum power of 50 Watts. Thanks to close coupling between the X-ray tube anode and the sample the performance of the ARL OPTIM'X spectrometer is equivalent to a 200 W conventional WDXRF instrument. The instrument can be equipped with the unique Thermo Scientific™ SmartGonio™ Goniometer, a series of monochromators, or both Table 1 shows limits of detection for various elements in soda-lime glasses prepared as pressed powders.

Table 1. Analytical parameters and limits of detection for various oxides/element in soda-lime glass (100 sec. counting time).

Oxide element	Line	Crystal	Detector	LoD (ppm)
Na_2O	$K\alpha_{1,2}$	AX06	FPC	100
MgO	$K\alpha_{1,2}$	AX06	FPC	60
Al_2O_3	$K\alpha_{1,2}$	PET	FPC	47
SiO_2	$K\alpha_{1,2}$	PET	FPC	N.R.
P_2O_5	$K\alpha_{1,2}$	PET	FPC	48
SO_3	$K\alpha_{1,2}$	PET	FPC	23
Cl	$K\alpha_{1,2}$	PET	FPC	24
K_2O	$K\alpha_{1,2}$	LiF200	FPC	14
CaO	$K\alpha_{1,2}$	LiF220	FPC	12
TiO_2	$K\alpha_{1,2}$	LiF200	FPC	12
Cr_2O_3	$K\alpha_{1,2}$	LiF200	FPC	9
MnO	$K\alpha_{1,2}$	LiF200	FPC	9
Fe_2O_3	$K\alpha_{1,2}$	LiF200	FPC	9
ZnO	$K\alpha_{1,2}$	LiF200	FPC	3.6
SrO	$K\alpha_{1,2}$	LiF200	FPC	2.4
ZrO_2	$K\alpha_{1,2}$	LiF220	FPC	1.8
BaO	$L\beta_1$	LiF200	FPC	51
PbO	$L\beta_1$	LiF220	FPC	9

N.R. = LoD is not relevant for major elements

FPC = flow proportional counter

SC = scintillation counter

Excitation conditions: 40 kV / 1.25 mA

Collimator: 0.29°

Calibration and limits of detection

A series of pressed glass samples have been measured on an ARL OPTIM'X spectrometer. Calibration curves have been derived by relating intensities for each oxide (or element) to concentrations in the standard samples. X-ray fluorescence measures elements, but the results can be related directly to the oxide forms of these elements when only one single form is present in the sample. Using the calibration curves, limits of detection are determined using the SmartGonio goniometer for the most common oxides/elements found in soda-lime glasses (Table 1). The recommended crystals for glass application are AX06, PET, and LiF200.

Precision tests

Precision tests have been carried out by analyzing repeatedly the same pressed pellet sample for eleven consecutive analyses. Eighteen oxide/elements are determined using a counting time of 36 seconds per analytical line. The results are summarized below for two different glass samples (Tables 2 and 3). In the case when precision should be improved for some elements this counting time could be increased. Doubling the counting time would improve the precision by a factor of about 1.4 (square root of 2).

Conclusion

All limits of detection obtained show that the ARL OPTIM'X spectrometer can deliver adequate analysis results, notably for bottle glass application. Repeatability of analysis is excellent for major and minor elements even for Na2O and MgO. Longer counting time may be used in case elements present below 100 ppm need to be controlled precisely. These results show that the ARL OPTIM'X spectrometer is well suited to produce precision results for the determination of the main oxides and the coloring agents
in glasses.

Table 2. Repeatability for the analysis of the major and minor oxides in Sample A at 36 seconds per oxide/element.

Run	Na_2O (%)	MgO (%)	Al_2O_3 (%)	SO_2 (%)	K_2O (%)	CaO (%)	Fe_2O_3 (%)	SO_3 (ppm)	TiO_2 (ppm)	P_2O_5 (ppm)	Cl (ppm)	Cr_2O_3 (ppm)	MnO (ppm)	As_2O_3 (ppm)	SrO (ppm)	ZrO_2 (ppm)	BaO (ppm)	PbO (ppm)
Run 1	13.98	0.185	1.79	72.59	0.588	10.85	0.330	582	579	166.9	113.4	93.6	48.4	101.6	127.4	209.1	454	228
Run 2	13.93	0.193	1.81	72.60	0.582	10.82	0.333	640	563	146.3	129.5	91.4	44.7	101.5	124.8	204.6	393	219
Run 3	13.97	0.177	1.80	72.64	0.588	10.82	0.330	608	563	193.3	111.2	91.1	43.8	95.9	127.1	207.0	362	198
Run 4	14.01	0.178	1.80	72.64	0.588	10.87	0.330	645	581	199.2	104.6	96.2	29.9	103.8	127.0	205.4	376	235
Run 5	13.95	0.182	1.80	72.60	0.588	10.83	0.329	576	564	158.1	111.8	94.6	41.8	103.2	127.7	204.7	385	228
Run 6	13.94	0.177	1.81	72.61	0.589	10.82	0.329	573	569	171.3	107.9	85.2	49.5	95.0	123.6	203.8	355	195
Run 7	13.86	0.185	1.80	72.64	0.588	10.83	0.330	658	569	203.6	113.4	88.9	40.3	99.6	125.0	205.4	434	234
Run 8	13.92	0.186	1.81	72.59	0.585	10.84	0.331	652	566	190.4	135.6	94.5	44.7	96.8	129.5	203.4	315	207
Run 9	13.94	0.184	1.81	72.63	0.591	10.82	0.334	651	579	150.7	110.1	88.6	43.1	99.2	129.1	206.2	401	221
Run 10	13.98	0.183	1.80	72.63	0.586	10.87	0.332	617	526	255.0	104.0	83.6	41.9	99.2	125.8	206.2	402	215
Run 11	13.95	0.188	1.78	72.62	0.588	10.83	0.330	619	561	218.3	97.9	80.6	38.9	97.7	128.8	203.1	430	198
Avg.	**13.95**	**0.183**	**1.80**	**72.62**	**0.587**	**10.84**	**0.331**	**620**	**565**	**186.6**	**112.7**	**89.9**	**42.4**	**100.5**	**126.0**	**205.4**	**392**	**216**
Std. Dev.	**0.04**	**0.005**	**0.01**	**0.02**	**0.002**	**0.02**	**0.0015**	**32**	**15**	**32.5**	**11**	**5**	**5.2**	**5.7**	**1.4**	**1.8**	**40**	**15**

Table 3. Repeatability for the analysis of the major and minor oxides in Sample B at 36 seconds per oxide/element

Run	Na_2O (%)	MgO (%)	Al_2O_3 (%)	SiO_2 (%)	K_2O (%)	CaO (%)	Fe_2O_3 (ppm)	SO_2 (ppm)	TiO_2 (ppm)	P_2O_5 (ppm)	Cl (ppm)	Cr_2O_3 (ppm)	MnO (ppm)	As_2O_3 (ppm)	SrO (ppm)	ZrO_2 (ppm)	BaO (ppm)	PbO (ppm)
Run 1	13.35	0.180	1.67	73.07	0.556	10.77	773	0.177	556	884	100.7	63.4	9.3	118.2	122.4	227.2	884	896
Run 2	13.33	0.180	1.68	73.08	0.564	10.76	758	0.181	568	961	111.2	65.9	3.9	112.0	122.2	226.1	961	914
Run 3	13.28	0.186	1.67	73.08	0.554	10.81	790	0.180	555	925	115.7	64.7	18.2	115.6	119.9	225.3	925	911
Run 4	13.28	0.185	1.66	73.11	0.559	10.83	768	0.186	587	891	103.5	74.7	8.7	105.6	126.5	225.1	891	900
Run 5	13.35	0.181	1.67	73.05	0.554	10.79	764	0.181	595	949	99.3	63.6	12.3	106.8	124.6	226.2	949	905
Run 6	13.32	0.172	1.67	73.11	0.566	10.89	767	0.182	541	960	114.6	59.3	14.7	115.2	125.5	225.5	960	904
Run 7	13.33	0.185	1.67	73.06	0.555	10.78	759	0.185	570	961	111.2	66.9	9.3	101.5	124.7	227.1	961	910
Run 8	13.26	0.185	1.69	73.04	0.554	10.78	772	0.183	565	918	95.2	66.8	9.3	101.0	124.7	227.4	918	920
Run 9	13.33	0.180	1.64	73.11	0.561	10.82	776	0.183	554	917	101.5	64.1	9.3	109.6	124.6	222.9	917	913
Run 10	13.30	0.193	1.68	73.08	0.556	10.80	764	0.181	573	981	100.8	64.4	10.0	103.4	123.0	226.6	981	912
Run 11	13.31	0.184	1.66	73.06	0.561	10.78	785	0.182	566	951	109.0	70.8	13.8	106.9	122.1	227.7	951	876
Avg.	**13.31**	**0.183**	**1.67**	**73.08**	**0.558**	**10.80**	**770**	**0.183**	**567**	**936**	**105.8**	**65.8**	**9.7**	**109.9**	**123.8**	**226.1**	**936**	**906**
Std. Dev.	**0.03**	**0.01**	**0.01**	**0.03**	**0.004**	**0.02**	**10**	**0.003**	**15**	**31**	**7.2**	**4.3**	**4.9**	**5.4**	**2.2**	**1.4**	**31**	**12**