ICG-TC2

BAM

Federal Institute for Materials Research and Testing and

International Commission on Glass – TC2

Certified Reference Material

BAM-S005A
Multielement Glass for XRF Analysis – Type A

Parameter	Mass fraction	
	Certified value [1] in mg/kg	Uncertainty [2] in mg/kg
Arsenic (III) oxide	132	8
Barium oxide	115	9
Cadmium oxide	62	4
Cerium (IV) oxide	105	6
Chloride	247	33
Cobalt oxide	49.4	2.4
Chromium (III) oxide	15.6	2.4
Copper (II) oxide	112	5
Iron (III) oxide	422	11
Manganese (II) oxide	124	5
Molybdenum (VI) oxide	343	12
Nickel (II) oxide	59.0	2
Lead (II) oxide	202	8
Antimony (III) oxide	132	7
Selenium	19.6	1.7
Tin (IV) oxide	100	7
Sulfur trioxide	1942	85
Strontium oxide	151	7
Titanium (IV) oxide	164	9
Vanadium (V) oxide	350	22
Zinc oxide	203	10
Zirconium (IV) oxide	842	125

1) The certified values are the means of 11-25 series of results (depending on the parameter) obtained by different laboratories. 3 up to 9 different analytical methods were used for the measurement of one parameter. The calibration of the methods applied for determination of element mass fractions were calibrated using pure substances of definite stoichiometry or by solutions prepared from them, thus achieving traceability to SI unit.

2) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor $k = 2$.

Sample description

The CRM consist of a disc of soda lime glass (39 mm diameter and 5 mm thick, with a weight of about 26 g to 30 g) which has been polished at one side. It is. intended to be directly used with X-ray fluorescence spectrometry (XRF) for calibration and determination of the 22 certified trace elements.

Informative values

Not certified informative values were determined by only one of the participating laboratories.

All mass fractions are given in %

Silicon (IV) oxide	71
Sodium oxide	13.7
Calcium oxide	10.5
Magnesium oxide	2.3
Aluminium oxide	1.1
Potassium oxide	0.7

For further information see Certification Report BAM S005-A and BAM S005-B.

Berlin,

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Department I
Analytical Chemistry
Reference Materials

BAM Berlin
Division I.1
Inorganic Chemical Analysis
Reference Materials

Prof. Dr. U. Panne
(Head of Department)

Dr. R. Matschat
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Supply of the reference material by
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Means of the series of measurements for the analytical procedure of one laboratory or of one method in one laboratory (laboratory means)

The results are arranged by increasing values of the laboratory means.
Mass fractions in mg/kg

Note: all measurements for certification (mean values listed above) were carried out at the type B material which comes from the same melt as the type A material and which was certified separately. Because of the different point of time of sample taking from the furnace, both types differ slightly in few mass fractions as demonstrated by statistical tests. Corrections were carried out according to separate measurements at BAM (see Certification Report BAM S005-A and BAM S005-B).

Part 1

Line No.	As_2O_3	BaO	CdO	CeO_2	Cl	CoO	Cr_2O_3	CuO	Fe_2O_3	MnO	MoO_3
1	-	-	47	90	198	39.3	11.4	98	373	105	302
2	-	106	48	92	212	40.3	13.2	99	386	107	315
3	103	106	54	99	234	43.4	13.5	100	394	109	327
4	111	107	55	100	238	43.8	13.5	101	395	110	332
5	119	108	57	101	239	44.5	13.6	103	408	110	332
6	122	108	58	102	250	44.7	14.7	105	411	112	333
7	128	111	59	102	253	46.2	15.0	107	411	113	339
8	131	112	60	104	255	47.2	15.0	107	412	115	344
9	132	113	61	108	270	47.7	15.1	110	412	119	354
10	133	115	63	110	272	49.0	15.3	112	414	120	354
11	135	116	63	112	291	49.2	15.3	113	416	123	355
12	135	117	65	113		49.7	15.4	114	418	124	362
13	142	118	65	113		50.0	15.9	114	423	124	368
14	144	118	66	119		50.8	16.0	114	423	127	385
15	146	118	66	-		51.8	16.2	114	426	128	
16	154	128	66			52.3	16.3	114	436	129	
17	-	129	67			52.7	16.5	114	439	129	
18		-	67			53.0	16.7	116	439	129	
19		-	67			54.0	16.8	116	447	131	
20			68			54.5	16.8	117	448	132	
21			69			54.9	16.9	117	450	132	
22			75			58.3	-	119	454	133	
23						58.8		120	460	136	
24								121	-	145	
25								122		149	
M:	132	115	62	105	247	49.4	15.2	112	422	124	343
s_M:	14	7	7	9	27	5.3	1.5	8	23	12	22

Note: Where a „ - “ appears in the table it indicates that an outlying value has been detected by a statistical test (see Certification Report BAM S005-A and BAM S005-B) which was withdrawn or omitted after discussion in ICG-TC2 meetings. The line number should not be mistaken for the laboratory code number.
M: Arithmetic mean of the laboratory means
s_M: Standard deviation of the laboratory means
The laboratory means are based on 3 – 6 single values (in most cases 6 single values).

Note: all measurements for certification (mean values listed above) were carried out at the type B material which comes from the same melt as the type A material and which was certified separately. Because of the different point of time of sample taking from the furnace, both types differ slightly in few mass fractions as demonstrated by statistical tests. Corrections were carried out according to separate measurements at BAM (see Certification Report BAM S005-A and BAM S005-B).

Part 2

Line No.	NiO	PbO	Sb_2O_3	Se	SnO_2	SO_3	SrO	TiO_2	V_2O_5	ZnO	ZrO_2
1	51.0	169	105	17.0	-	1834	128	126	279	-	-
2	52.7	175	116	17.4	76	1848	128	134	291	187	-
3	53.5	178.	121	18.7	85	1867	128	155	294	187	760
4	54.3	182	122	18.9	92	1883	132	157	312	188	772
5	55.5	185	123	19.3	94	1927	138	157	326	192	779
6	56.2	189	124	19.4	95	1933	140	157	328	193	792
7	56.3	192	126	19.6	95	1983	141	160	334	195	800
8	58.1	196	128	20.2	101	2001	144	163	335	198	800
9	58.1	197	128	20.6	101	2004	146	164	339	199	810
10	58.3	200	129	20.7	102	2012	148	164	341	199	820
11	58.6	200	132	20.8	103	2061	148	166	347	204	840
12	58.6	201	133	21.2	107		149	166	354	204	842
13	60.0	201	137	21.2	108		151	166	356	200	842
14	61.2	203	138	-	114		154	167	369	205	851
15	61.2	205	138		120		160	173	373	208	856
16	62.1	209	140				162	173	415	208	859
17	62.7	215	148				162	178	434	208	873
18	62.7	215	149				163	184	436	210	875
19	63.3	216	157				165	189		210	903
20	63.4	217					167	-		214	937
21	65.2	220					168			216	972
22	65.2	221					174			218	
23	-	221					175				
24		222									
25											
M:	59.0	202	132	19.6	100	1942	151	163	349	203	842
s_M:	4.1	16	13	1.4	12	76	15	15	46	10	56

Note: Where a „ - “ appears in the table it indicates that an outlying value has been detected by a statistical test (see Certification Report BAM S005-A and BAM S005-B) which was withdrawn or omitted after discussion in ICG-TC2 meetings. The line number should not be mistaken for the laboratory code number.
M: Arithmetic mean of the laboratory means
s_M: Standard deviation of the laboratory means
The laboratory means are based on 3 – 6 single values (in most cases 6 single values).

Analytical methods used for final determination

List of abbreviations

Comb.-IR	Combustion method with infrared detection
ET AAS	Atomic absorption spectrometry with electrothermal atomisation
F AAS	Flame atomic absorption spectrometry
FI-HG AAS	Atomic absorption spectrometry with flow injection hydride generation
GRAV	Gravimetry
HG AAS	Atomic absorption spectrometry with hydride generation
ICP OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ID-TIMS	Isotope dilution mass spectrometry with thermal ionisation
INAA	Instrumental neutron activation analysis
K_0-INAA	K_0- Instrumental neutron activation analysis
MAS	Molecular absorption spectrometry
POT	Titrimetry with potentiometric end point determination
TITR	Titrimetry
XRF	X-ray fluorescence spectrometry

Analyte	Line number	Analytical method used
As_2O_3	3	F AAS
	7	FI-HG AAS
	5, 9, 16	HG AAS
	12	ICP-MS
	(1), (2),4, 6, 8, 13, 15, (17)	ICP OES
	10	INAA
	11	K_0-INAA
	14	MAS
BaO	17	ET AAS
	(18), (19)	F AAS
	2	K_0-INAA
	14	ICP-MS
	(1), 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 15, 16	ICP OES
	11	XRF
CdO	3, 13	ET AAS
	2, 8, 10, 15, 18, 20	F AAS
	19	K_0-INAA
	17, 21	ICP-MS
	1, 4, 5, 6, 7, 9, 11, 12, 14, 16, 22	ICP OES
CeO_2	6	K_0-INAA
	12	ICP-MS
	1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 13, 14, (15)	ICP OES
Cl	9	K_0-INAA
	8	MAS
	1, 2, 3, 4, 5, 6, 7, 10, 11,	POT
CoO	10, 20	ET AAS
	5, 8, 15, 16, 23	F AAS
	19	INAA
	13	K_0-INAA
	21, 22	ICP-MS
	1, 2, 3, 4, 6, 7, 9, 11, 12, 17, 18	ICP OES
	14	MAS

Cr_2O_3	12, 19	ET AAS
	3, 4, 6	F AAS
	15	INAA
	9	K_0-INAA
	11	ICP-MS
	1, 2, 5, 7, 8, 10, 13, 14, 16, 20, 21, (22)	ICP OES
	17	ID-TIMS
	18	MAS
CuO	6, 11	ET AAS
	4, 14, 17, 18, 19, 22	F AAS
	20	ICP-MS
	1, 2, 3, 5, 7, 8, 9, 10, 12, 13, 15, 16, 23, 25	ICP OES
	21	ID-TIMS
	24	MAS
Fe_2O_3	16	ET AAS
	9, 11, 13, 15, 17, 19	F AAS
	6	K_0-INAA
	1, 2, 3, 4, 10, 12, 14, 18, 20, 21, 22, 23, (24)	ICP OES
	5, 7, 8	MAS
MnO	10	ET AAS
	2, 9, 16, 20, 21, 23, 25	F AAS
	17	K_0-INAA
	22	ICP-MS
	1, 3, 4, 5, 7, 8, 11, 12, 13, 14, 18, 19, 24	ICP OES
	6	MAS
	15	XRF
MoO_3	7	F AAS
	5	K_0-INAA
	11, 14	ICP-MS
	1, 2, 3, 4, 6, 8, 9, 10, 12, 13	ICP OES
NiO	11, 21	ET AAS
	1, 9, 12, 15, 18, 22	F AAS
	14	ICP-MS
	2, 3, 5, 6, 7, 8, 10, 13, 16, 17, 19, 20, (23)	ICP OES
	4	MAS
PbO	11, 21	ET AAS
	6, 8, 12, 14, 20, 22, 24	F AAS
	18	ICP-MS
	1, 2, 3, 4, 5, 7, 9, 10, 13, 15, 16, 23	ICP OES
	17	ID-TIMS
	19	XRF
Sb_2O_3	12	ET AAS
	1, 4, 7	F AAS
	17, 15	FI-HG AAS
	14, 16	HG AAS
	11	INAA
	9	K_0-INAA
	18	ICP-MS
	2, 3, 5, 6, 8, 10, 13, 19	ICP OES
Se	7	ET AAS
	2, 4, 5	FI-HG AAS
	8, 10	HG AAS
	9	INAA
	12	K_0-INAA
	3	ICP-MS
	1, 6, 11, 13, (14)	ICP OES

SnO_2	9, 10	ET AAS
	11	F AAS
	8	K_0-INAA
	12, 13	ICP-MS
	(1), 2, 3, 4, 5, 6, 7, 14, 15	ICP OES
SO_3	1, 3, 5, 11	Comb.-IR
	10	GRAV
	2, 4, 6, 7, 9	ICP OES
	8	TITR
SrO	22	ET AAS
	2, 3, 8, 17, 18, 23	F AAS
	19	K_0-INAA
	7	ICP-MS
	1, 4, 5, 6, 9, 10, 11, 12, 13, 14, 15, 20, 21	ICP OES
	16	XRF
TiO_2	1, 4, 7, 8, 9, 10, 11, 12, 13, 16, 18, 19, (20)	ICP OES
	2, 3, 5, 6, 15, 17	MAS
	14	XRF
V_2O_5	16	F AAS
	14	K_0-INAA
	10	ICP-MS
	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 15, 17, 18	ICP OES
	13	XRF
ZnO	(1), 11, 15, 17, 18, 19	F AAS
	12	INAA
	8	K_0-INAA
	5	ICP-MS
	2, 3, 4, 6, 7, 9, 10, 13, 14, 16, 20, 21	ICP OES
	22	XRF
ZrO_2	8	INAA
	10	K_0-INAA
	20	ICP-MS
	(1), (2), 3, 4, 5, 7, 9, 11, 12, 13, 15, 16, 19, 21	ICP OES
	6, 14, 18	MAS
	17	XRF

Note: Line numbers in parenthesis refer to values not used in the calculation of the certified value.

Participating laboratories

Allocation and preparation of the material

- The material was melted, sampled and the discs were mechanically shaped by Stazione Sperimentale del Vetro, Murano – Venice (Italy).
- The material for the certification was crushed by Stazione Sperimentale del Vetro, Murano – Venice (Italy).
- The sample discs were wrapped and packed by BAM, Federal Institute for Materials Research and Testing, Berlin (Germany).

Homogeneity testing

- All measurements and statistical evaluations were carried out by BAM.

Certification analysis

- The samples for certification analysis were distributed by Stazione Sperimentale del Vetro, Murano – Venice (Italy).
- The interlaboratory comparison was organized by BAM.

Participating laboratories in the interlaboratory comparison for certification (arranged alphabetically)

BAM, Federal Institute for Materials Research and Testing
- Laboratory: Activation Analysis; Gas Analysis
- Laboratory: Isotope Dilution and Nuclear Fuel Analysis
- Project group: Quality Assurance and Metrological Aspects in Production of High Tech Reference materials

Corning Europe Inc. SA CERF, Avon (France)
Corning Inc., Corning (USA)
CRITT Matériaux LNE EST, Schiltingheim Cedex (France)
Forschungsinstitut für anorganische Werkstoffe – Glas/Keramik GmbH, Höhr-Grenzhausen (Germany)
Fraunhofer-Institut für Silikatforschung, Würzburg (Germany)
Glasforskningsinstitutet (GLAFO), Växjö (Sweden)
Glass Institute, Hradec Králové (Czech Republic)
Glaverbel Mecaniver SA, Jumet (Belgium)
INISMa (Institut National Interuniversitaire des silicates sols et Matériaux), Mons (Belgium)
ISOVER Saint-Gobain CRIR, Rantigni (France)
"Jožef Stefan" Institute, Ljubljana (Slovenia)
NSG Techno-Research Company, Itami-city, Hyougo (Japan)
Pilkington European Technical Centre, Group Analytical Services, Lancashire (Great Britain)
Saint-Gobain Glass Deutschland, Forschung und Entwicklung Bauglas (FEB), Herzogenrath (Germany)
Saint-Gobain Recherche, Aubervilliers Cedex (France)
Schott Glass Technologies Inc., R&D-Technical Services, Duryea (USA)
Schott Glas, Mainz (Germany)
Stazione Sperimentale del Vetro, Murano-Venice (Italy)
TU Bergakademie Freiberg – Institut für Silikattechnik, Freiberg (Germany)
Turkiye Şişe ve Cam Fabrikalari A.Ş., Glass Research Center, Topkapi-Istanbul (Turkey)

Determination of informative values

- The informative values were determined by
  Stazione Sperimentale del Vetro, Murano – Venice (Italy).

Instructions for use

Area of application

The main area of application is checking the trueness of results of the determination and calibrating the determination of the certified analytes in soda-lime glass using direct sampling methods in combination with XRF. The direct use of the polished disc is preferred compared to XRF analysis by sample preparation in terms of crushing the glass and incorporating it into a pressed pellet with wax or fusing it with a flux (such as lithium tetraborate, $Li_2B_4O_7$) and casting the melt into a disc. The uncertainties given in the certificate are only valid in case of direct XRF analysis of flat glass samples. The polished disc guarantees very stable reference measurements over a very long period of time, at least several years. In contrast, pressed pellets and fused discs have the disadvantages that the measured samples are not stable over time and that their surface cannot be refreshed in a simple way. Such samples have to be re-prepared from time to time, whereas the polished disc needs only to be re-polished occasionally, as outlined below. One important point is, that the CRM sample can be used to improve the results of semi-quantitative procedures by providing a one reliable point of calibration for each certified analyte.

Recommendations for correct sampling and sample preparation

Before first using the CRM it is recommended to abrade the surface to be measured using, for example, aqueous slurry of Al_2O_3 powder on a flat surface. The latter might be a glass plate covered

with the polishing slurry (for grinding and polishing manually), or the surface of the active part of a lapping machine. The surface of the sample is then polished, either manually or in a polishing machine, with polishing compounds of decreasing particle size. The final polishing with, for example, 1 µm diamond or ceria powder suspension leaves a mirror-like polished surface.
Note: ceria based polishing compounds should not be used if the intention is to determine cerium in the glass.

From time to time, depending on the frequency of use, the sample again has to be polished slightly by hand or in a polishing machine with the finest particle size polishing compound. In this way, a very thin surface layer is removed that contains absorbed atmospheric pollution, degradation products from X-ray irradiation and any surface corrosion layer of the glass itself. According to our experience no statistically significant shift occurs in the X-ray measurements over a period of about 4 weeks. However, the optimum interval between re-polishing procedures depends on the storage conditions of the sample.

Recommendations for correct storage

The sample should be stored in a dust-free and dry environment avoiding contamination and moisture (desiccator).

Possible line interferences

When using the CRM for XRF analysis it has to be taken into account that spectral overlapping may occur for some spectral lines and that the low thickness of the sample disc can influence the results.
No spectral interferences were observed for the Kα-lines of Ba, Ce, Co, Cu, Fe, Mn, Ni, Se, Sn, Sr and Zn.
If the thickness of the sample is too low, use the Ba-Lα or Ce-Lβ instead of K-lines of Ba and Ce, respectively.
The following table shows interferences which have been observed and possibilities to overcome these interferences.

Observed spectral interferences and their handling

Interfered element		Interfering element		What to do?
Element	Line	Element	Line	
As	Kα	Pb	Lα	Use the not interfered As-Kβ line
Cl	Kα	Mo	L	Interfering line with very low intensity, interference in CRM sample not relevant
Cr	Kα	V	Kβ	The intensity of Cr-Kβ line is too low, interference has to be corrected
Mo	Kα	Zr	Kβ	Use the not interfered Mo-Kβ line; a filter has to be used if a Rh tube is applied
Pb	Lα	As	Kα	Use the not interfered Pb-Lβ line
S	Kα	Mo	L	Interfering line with very low intensity, interference in CRM sample not relevant
Ti	Kα	Ba	L	Interfering line with very low intensity, interference in CRM sample not relevant
V	Kα	Ba	L	Interfering line with very low intensity, interference in CRM sample not relevant
Zr	Kα	Sr	Kβ	Interference has to be corrected
Zr	Kβ	Mo	Kα	Interference has to be corrected

Safety guidelines

1. The handling of the material does not require more safety precautions than the handling of any other glass material.
2. First aid measures
   In case of contamination of the eyes by dust (which may arise during dry polishing), rinse thoroughly with water with the eyelids held open. If product is swallowed, induce vomiting and consult a physician.
3. Handling
   Avoid formation and deposition of dust when polishing. Avoid braking of the sample.
4. Disposal considerations
   Unused material: reuse if possible.
   Or: may be disposed of in controlled landfills provided local regulations are respected.

Expiration of certification

Providing correct handling and storage of the material, this certification is valid within the specified uncertainty limits for ten years from the date of purchase. It is not excluded that the certified parameters will remain valid after this period.