

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

INORGANIC CHEMISTRY DIVISION
COMMISSION ON HIGH TEMPERATURE AND SOLID STATE CHEMISTRY*

QUANTITATIVE ANALYSIS OF A PbO-SiO₂ GLASS BY ELECTRON MICROPROBE

The Results of an IUPAC Collaborative Study
(Technical Report)

Prepared for publication by

J. MATOUSEK¹, V. HULÍNSKY¹, R. METSELAAR² and J. CORISH³

¹Institute of Chemical Technology, Prague, Czech Republic

²Technische Universiteit Eindhoven, Eindhoven, Netherlands

³Trinity College, University of Dublin, Dublin, Ireland

*Membership of the Commission during the period (1985-1995) when this report was prepared was as follows:

Chairman: 1989-95 J. Corish (Ireland); 1985-89 R. Metselaar (Netherlands); *Secretary:* 1991-95 G. M. Rosenblatt (USA); 1987-91 J. Corish (Ireland); 1985-87 P. W. Gilles (USA); *Titular Members:* J. F. Baumard (1985-93; France); H. P. Boehm (1994-95; Germany); J. Corish (1985-89; Ireland); J. D. Drowart (1987-93; Belgium); L. N. Gorokhov (1987-95; USSR); L. V. Gurvich (1985-87; USSR); J. W. Hastie (1987-93; USA); D. Kolar (1994-95; Slovenia); M. H. Lewis (1994-95, UK); M. H. Rand (1985-87; UK); D.-S. Yan (1987-95; China); *Associate Members:* A.-M. Anthony (1985-89; France); G. Balducci (1994-95; Italy); H. P. Boehm (1991-93; Germany); C. Chantillon (1989-95; France); J. B. Clark (1985-91; South Africa); J.-P. Coutures (1985-87; France); J. Drowart (1985-87; Belgium); J. G. Edwards (1987-95; USA); L. N. Gorokhov (1985-87; USSR); J. Hastie (1985-87; USA); H. Hausner (1987-91; Germany); M. G. Hocking (1985-87; UK); L. H. E. Kihlberg (1985-91; Sweden); M. Kizilyalli (1994-95; Turkey); K. Kuomoto (1994-95; Japan); M. H. Lewis (1989-93; UK); J. Matousek (1985-93; Czechoslovakia); H. J. Matzke (1987-93; Germany); R. W. Ohse (1985-87; Germany); G. M. Rosenblatt (1985-91; USA); T. Saito (1989-93; Japan); K. E. Spear (1994-95; USA); M. M. Thackeray (1991-93; South Africa); G. van Tendeloo (1989-93; Belgium); R. J. D. Tilley (1994-95, UK); G. F. Voronin (1989-95; USSR); H. Yanagida (1985-87; Japan). *National Representatives:* M. S. E. El-Sewefy (1985-87; Arab Republic of Egypt); E. J. Baran (1985-91; Argentina); N. E. Walsö de Reça (1994-95; Argentina); P. Etmayer (1986-93; Austria); B. G. Hyde (1987-93; Australia); J. D. Drowart (1994-95; Belgium); O. L. Alves (1991-95; Brazil); D.-S. Yan (1985-87; China); E. Fitzner (1986-93; Germany); F. Solymos (1985-87; Hungary); C. K. Mathews (1994-95; India); A. P. B. Sinha (1985-87; India); G. V. Subba-Rao (1989-93; India); G. De Maria (1985-95; Italy); S. Somiya (1985-87; Japan); C. H. Kim (1989-93; Korea); M. Badri (1985-87; Malaysia); W.-L. Ng (1989-93; Malaysia); K. J. D. MacKenzie (1987-93; New Zealand); F. M. de Abreu da Costa (1991-95; Portugal); F. Hanic (1994-95; Slovakia); M. A. Alario Franco (1987-93; Spain); M. Nygren (1994-95; Sweden); G. Bayer (1985-87; Switzerland); M. Kizilyalli (1987-93; Turkey); K. Spear (1989-93; USA); W. L. Worrell (1985-87; USA); D. Kolar (1987-83; Yugoslavia); M. M. Ristic (1985-87; Yugoslavia).

Republication or reproduction of this report or its storage and/or dissemination by electronic means is permitted without the need for formal IUPAC permission on condition that an acknowledgement, with full reference to the source along with use of the copyright symbol ©, the name IUPAC and the year of publication are prominently visible. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

Quantitative analysis of a PbO–SiO₂ glass by electron microprobe (Technical Report)

Synopsis: A standard glass sample denoted by the National Institute of Standards and Technology as K-456 was analyzed by an international collaborative team. The results of quantitative determinations of the two oxide glass components, PbO and SiO₂, are compared and the deviations from the standard values are calculated. Methods of preparation, conditions of quantitative determination and procedures used for the evaluation of the results are also summarized.

INTRODUCTION

Quantitative determination of the composition of lead glasses by means of electron probe microanalysis (EPMA) appears to be relatively difficult especially if they contain a large amount of Pb. In addition to the uncertainties caused by specimen preparation and by the choice of parameters of the measurements, the selection of standards and the correction methods used for the evaluation of the results have considerable influence. A glass sample consisting of PbO and SiO₂ was chosen to compare and verify procedures used in a number of laboratories dealing with analysis of glasses by means of electron microprobe. This study follows the paper describing results of electron probe microanalysis of a multicomponent glass obtained by an international collaborative team and published previously [1].

GLASS SAMPLE CHARACTERIZATION

A standard specimen K-456, supplied by the National Institute of Standards and Technology (NIST), Washington, D.C., USA was used [2]. The certified composition of the glass in wt% was as follows:

| | |
|-----|--------------|
| Pb: | 65.67 ± 0.26 |
| Si: | 13.37 ± 0.24 |

The oxygen value (20.35 wt%) was calculated from the stoichiometry of the oxides and was not certified. For the purpose of this study the following oxide contents, again in wt % were calculated according to the stoichiometric relations:

| | |
|--------------------|--------------|
| PbO: | 70.74 ± 0.28 |
| SiO ₂ : | 28.62 ± 0.51 |

These values of the oxide contents have been used as the basis for all calculations presented in this paper. The uncertainties assigned to the composition are the 2-sigma values. The glass sample was specifically fabricated for use in microanalytical techniques such as electron probe microanalysis.

The samples were sent to the participants on the project (these are listed in Appendix 1) in the form of small rods. The participants were asked to perform quantitative analysis using an electron microprobe but with the procedures and conditions chosen by themselves.

SPECIMEN PREPARATION OF GLASS SAMPLE

The procedures used by the participants to prepare the glass surface for analysis are summarized in Table 1. The aim of surface treatment i.e., to achieve a smooth and clean glass surface covered by an electrically conductive layer, was fulfilled by the participants using a variety of methods. All the procedures used involved the same elementary steps, i.e., embedding of the sample followed by surface preparation including grinding, polishing, cleaning and coating with carbon. In principle, no new or special methods were reported by the participants. In comparison with the procedures described previously, the main differences appeared to be in the polishing processes in which diamond pastes were preferably used. As will be evident later the variety of specimen preparation methods used did not have an impact on the accuracy of the results.

Table 1 Specimen Preparation

| Lab. No. | Embedding | Grinding | Polishing | Cleaning | Carbon Coating |
|----------|--------------------------------------|-----------------------|------------------------------------|------------------|-----------------|
| 1 | not specified | | | | |
| 2 | mounted between two pieces of glass | hand by SiC | hand polishing by CeO ₂ | - | judged visually |
| 3 | polyester resin | not specified | | acetone | not specified |
| 4 | epoxy resin | grinding disc | diamond paste | alcohol | c 20 - 30 nm |
| 5 | epoxy resin | hand by SiC | diamond paste | warm water, soap | c 25 nm |
| 6 | sealing wax | corundum powders | diamond paste | water, alcohol | c 30 nm |
| 7 | epoxy resin | Sic powders | diamond paste corundum slurry | - | c 25 nm |
| 8 | mounted by Ag paste on brass support | hand by SiC | hand by CeO ₂ | - | c 20 nm |
| 9 | fixed by Ag paste on brass support | not specified | | | c 30 nm |
| 10 | bakelite hot pressing | diamond grinding disc | pressed CeO ₂ disc | acetone | ~ c 20 nm |

EQUIPMENT AND EXPERIMENTAL CONDITIONS OF ANALYSIS

Different types of electron microprobe equipment were used for the quantitative analysis of the K-456 glass sample: these are listed in Table 2. Most of the measurements were made using the wavelength dispersive system (WDS) although energy dispersive systems (EDS) were used in two cases. The accelerating voltage applied varied between 10 and 30 kV and the corresponding absorbed current values differed significantly from 10 to 50 nA. Very low currents 0.25 and 1.6 nA, respectively, were used with the EDS technique. The electron beam diameter varied from 0.2 to 50 μm . In one case the beam was scanned over a raster covering an area of 20 x 20 μm .

Table 2 Equipment and Experimental Conditions used in the Analyses

| Lab. No. | Instrument | Operational Principle | Voltage (kV) | Absorbed current (nA) | Electron beam diameter (μm) |
|----------|-----------------|-----------------------|--------------|-----------------------|--|
| 1 | not specified | | | | |
| 2 | SEM JEOL JM 810 | EDS TN 5500 | 20 | 0.25 | area of 20 x 20 |
| 3 | JEOL JXA-733 | WDS | 10 | 40 | 10 |
| 4 | JEOL JXA-733 | WDS | 15-30 | 15-20 | 10 |
| 5 | Camebax Micro | WDS | 20 | 28 | 5 |
| 6 | JEOL JCX-733 | WDS | 25 | 50 | 3 |
| 7 | JEOL JCX-733 | WDS | 20 | 30 | 50 |
| 8 | SHIMADZU SM-7 | WDS | 15 | 12 | 50 |
| 9 | ARL SEMQ | WDS | 20 | 10 | 0.2 |
| | | EDS - KEVEX 7000 | 15 | 1.6 | 0.2 |
| 10 | JEOL JXA-5 | WDS | 20 | 15 | 5 |

WDS . . . wavelength dispersive system

EDS . . . energy dispersive system

Table 3 Details of regime of measurements and of the correction methods

| Lab. No. | Counting time (s) | Number of measurements | Correction method | type of correction programme |
|----------|------------------------|------------------------|-----------------------|--|
| 1 | not specified | | | |
| 2 | 200 (EDS) | 10 | ZAF | TRACOR NOTHERN (COLBY MAGIC IV) |
| 3 | 10 | 3 | ZAF | ZAF-SONDAX |
| 4 | 20 | 24 | ZAF | individual |
| 5 | 10 | 5 | ZAF | PMA 87 (individual) |
| 6 | 5 | 3 | ZAF | JEOL-ZAF |
| 7 | 5 | 20 | ZAF | JEOL-ZAF |
| 8 | 10 | 5 | ZAF | individual ZAF |
| 9 | 300 (EDS) 100 (WDS) | 5 10 | ZAF (EDS) BA (WDS) | COLBY MAGIC V (ZAF) SEMQ QUANT (BA) |
| 10 | 100 | 3 | ZAF | ZAF-SONDAX |

ZAF. . . . atomic number, absorption, and fluorescence correction

BA. . . . Bence-Albee correction method

In addition to the experimental parameters and conditions summarized in Tables 1 and 2 the times and number of measurements together with correction methods and types of correction programmes used are detailed in Table 3. Counting times varied between 5 and 300 s with the highest values pertaining to the EDS measurements. Times of between 5 to 20 s were chosen for the WDS measurements. The number of repetitions of the measurements differed from 3 to 24.

The results of the measurements were all corrected. Different types of correction programmes were used but the ZAF correction method was utilized in all cases with one exception. The correction methods can be specified as follows:

- atomic number "Z" correction according to the Duncumb and Reed method [3];
- absorption correction according to the Philibert method modified by Heinrich usually with mass absorption coefficient after Heinrich [4]; and
- a fluorescence correction according to the Reed method [5].

STANDARDS AND MONOCHROMATORS

The standards and crystals used by the participating laboratories are summarized in Table 4. Synthetic or natural pure compounds with well-defined chemical composition were most often applied as standards. Some of the participants preferred synthetic glasses or a combination of both of these types of materials. Three main crystals were used in the measurements: TAP (thallium acid phthalate) and PET (pentaerythrite) both for Si and Pb determination. In the case of Pb the use of an LiF crystal was also reported. The K_{α} line was employed for Si and M_{α} and L_{α} lines Pb detection.

RESULTS

The results of the K-456 glass sample analyses are summarized in Table 5 which includes values of the oxide contents in wt% together with standard deviations as they were measured and calculated by the participants. The certified composition given in the NIST certificate is also shown. The deviations between values determined by the participants and the corresponding NIST values are shown in Table 6.

Table 4 Standards and monochromators used in the measurements

| Lab. No. | Standards | Monochromators |
|----------|--|---|
| | PbO | SiO ₂ |
| 1 | not specified | |
| 2 | crocoite PbCrO ₄ glass (21.8 PbO) | quartz EDS-TRACOR NORTHERN Si - K _α , PbM _α |
| 3 | PbSe | SiO ₂ TAP-SiK _α , PET - PbM _α |
| 4 | anglesite(PbSO ₄) galenite (PbS) | glass K-412 diopside TAP-SiK _α , LiF - PbL _α |
| 5 | PbMoO ₄ | not specified TAP-SiK _α , PET - PbM _α |
| 6 | PbMoO ₄ | SiO ₂ TAP-Si , LiF - Pb |
| 7 | PbSe | quartz PET-SiK _α , PET - PbL _α LiF - PbL _α |
| 8 | multicomponent lead glass (59.06 PbO) | quartz PET-SiK _α , PET - PbM _α |
| 9 | two glasses: 1. 72.8 PbO, 13.2 Al ₂ O ₃ , 13.6 SiO ₂ 2. 49.7 MO, 7.4 Al ₂ O ₃ , 42.4 SiO ₂ | ADP-SiK _α , EDT - PbM _α |
| 10 | 1) PbSe 2) Pb-glass (0.5 Pb, 0.2 Si, 0.3 O - wt%) | quartz Pb-glass RAP-SiK _α , PET - PbM _α |

Table 5 Results of quantitative analysis of the K-456 sample: all values are in wt %

| Lab No. | SiO ₂ | | | PbO | | | Total | Remarks |
|-----------------------------------|------------------|---|------|-------|---|------|--------|-------------------------|
| 1 | 29.35 | ± | 0.22 | 71.20 | ± | 0.22 | 100.55 | |
| 2 | 30.15 | ± | 0.54 | 72.38 | ± | 0.02 | 102.54 | quartz, crocoite |
| | 30.02 | ± | 0.56 | 72.72 | ± | 1.56 | 102.73 | glass (standards) |
| 3 | 30.56 | ± | 1.1 | 70.53 | ± | 2.4 | 101.09 | |
| 4 | 28.21 | ± | 0.22 | 71.77 | ± | 0.57 | 99.98 | |
| 5 | 28.30 | ± | 0.2 | 71.60 | ± | 1.08 | 99.9 | |
| 6 | 28.78 | ± | 0.6 | 71.09 | ± | 0.93 | 99.87 | |
| 7 | 27.47 | ± | 0.66 | 72.86 | ± | 0.56 | 100.33 | |
| 8 | 29.51 | ± | 0.4 | 70.46 | ± | 0.37 | 99.97 | |
| 9 | 28.83 | ± | 0.5 | 71.12 | ± | 0.45 | 99.95 | EDS |
| | 28.90 | ± | 0.4 | 71.10 | ± | 0.60 | 100.00 | WDS |
| 10 | 28.30 | ± | 1.3 | 71.84 | ± | 1.4 | 100.14 | PbSe, SiO ₂ |
| | 27.27 | ± | 1.3 | 71.91 | ± | 1.4 | 99.18 | Pb-glass (standards) |
| K-456 (NIST certificate value) | | | | | | | | |
| | 28.62 | ± | 0.51 | 70.74 | ± | 0.28 | 99.36 | |
| Mean value of participant results | | | | | | | | |
| | 28.90 | ± | 1.00 | 71.58 | ± | 0.76 | 100.48 | |

Table 6 Absolute values of the deviations from the NIST certificate values in wt% for SiO₂ and PbO as measured by each laboratory

| Lab. No. | SiO ₂ | PbO |
|----------|------------------|-------|
| 1 | 0.73 | 0.46 |
| 2 | 1.53 | 1.64 |
| | 1.4 | 1.98 |
| 3 | 1.94 | -0.21 |
| 4 | -1.41 | 1.03 |
| 5 | -0.32 | 0.86 |
| 6 | 0.16 | 0.35 |
| 7 | -1.15 | 2.12 |
| 8 | 0.89 | -0.28 |
| 9 | 0.21 | 0.38 |
| | 0.28 | 0.36 |
| 10 | -0.32 | 1.10 |
| | -1.35 | 1.17 |

SiO₂ determination

Most of the results are within the limits defined by the NIST values and corresponding standard deviations (see Tables 5 and 6). The highest deviation from the standard value was 1.94 wt% and appeared to result from a measurement made at a very low accelerating voltage of 10 kV.

PbO determination

The results are again in satisfactory agreement with the standard NIST values, although in the majority of cases the differences between the determined values and the NIST standard exceed the certified standard deviations. Practically all deviations shown in Table 6 are positive values with the only two negative values being within the limits defined by NIST. A systematic shift to a higher concentration of PbO was found compared to the NIST specification in the mean value calculated from the results of all the participants (see Table 5). More detailed data would be needed before it would be possible to judge if the correction programmes are responsible for this systematic error.

It is clear that similar results have been obtained from the different equipment, procedures and experimental conditions used by the participants in this study. It is also evident that the nature of the standards used for PbO determination (selenides, sulphates, chromites, molybdenates, binary and multicomponent lead silicate glasses) does not seem to have a significant effect on the accuracy and reproducibility of the measurements. The variety of chemical compositions of the standards indicates relatively broad variation (0.8 - 1.2) in the values of the correction coefficients. Nevertheless, even the largest corrections seem to lead to satisfactory results. One of the participants reported the drift of monochromators as a possible additional source of scatter in the results (Pb - 2.1%, Si - 0.9%). A drift influence might be expected particularly when a PET monochromator is used.

In the previous report [1] Si, Mg, Ca, Al and Fe concentrations were determined in a K-412 NIST standard. The results reported in that work were in good agreement with the certified values and no systematic departures were observed. Thus the case of lead in the present study is unique in that a systematic shift has been found with 84.6% of the results showing more positive values.

CONCLUSION

Quantitative analyses of a K-456 standard glass supplied and certified by NIST using electron microprobe techniques has been carried out by an international collaborative team. The analytical results are in good agreement with the certified values thus confirming the reliability and accuracy of the work in laboratories participating in the project.

Comparable results have been achieved using different types of equipment. Also the nature and composition of the standards employed do not appear to have any significant effect on the accuracy and reproducibility of the results. Correction procedures used by the participants are suitable to convert intensities into concentrations correctly for all kind of standards. However, systematic errors were found in the case of analysis for lead and suggest that a more detailed examination of the correction procedures is necessary.

Acknowledgements: The authors are most grateful for the voluntary work undertaken by the participants in this project. The encouragement and assistance of members of the Commission on High Temperatures and Solid State Chemistry is also very much appreciated.

REFERENCES

1. J. Matousek, V. Hulinky, R. Metselaar and J. Corish, *Pure and Appl. Chem.* **62** 1187, (1990)
2. R.C. Paule and J. Mandel, *J. Res. Nat. Bur. Stds.* **87**, 377 (1982)
3. P. Duncumb and S.J.B.Reed, *Tube Inv. Res. Lab., Tech. Report* 221, Cambridge (1967)
4. K.F.J.Heinrich, *NBS Technical Note* 521 (1969)
5. S.J.B.Reed, *Brit. J. Appl. Phys.*, **16**, 913 (1965)

APPENDIX: LIST OF THE PARTICIPANTS

| | |
|----------------|--|
| Afonin V.P. | Winogradow Institute of Geochemistry, Irkutsk, (Russia) |
| Hulinky V. | Institute of Chemical Technology, Prague, (Czeck Rep.) |
| Jurek K. | Institute of Physics, Cz. Akad. of Sciences, Prague, (Czeck Rep). |
| Lavrentev J.G. | Institute of Geology and Geophysics, Novosibirsk, (Russia) |
| Li Xiang Ting | Institute of Ceramics, Acad. Sinica, Shanghai, (People's Republic of China) |
| Müller H | Schott Glaswerke, Mainz, (Germany) |
| Spaulding R.F. | Corning Glass Works, Corning, (USA) |
| Nagy G. | Laboratory for Geochemistry Research, Budapest, (Hungary) |
| Wada M. | Nippon Electric Glass, Otsu, (Japan) |
| Wilde P.M. | Central Institute of Inorganic Chemistry, Berlin, (Germany) |