Chemical Analysis of Glass and Associated Raw Materials

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1. Introduction

The Analysis and Properties Technical Committee of the SGT (A&P) is dedicated to the chemical analysis and determination of properties of glass and associated raw materials of practical interest to the glass industry. This is achieved through the generation of Certified Reference Materials (CRMs) and the development of methods for analysis to support best practice and quality assurance for suppliers, customers and society.

The production of glass is regulated, in that manufacturers must comply with an ever increasing list of rules and legislation to satisfy the demands of a modern world. Analytical procedures must also ensure that the chemicals used do not constitute a hazard to health. In the United Kingdom, the Control of Substances Hazardous to Health (COSHH) is regulated by the Health and Safety Executive[1]. Therefore there is a requirement to ensure that the glass industry uses procedures which meet or exceed current legislation. Many glassmakers operate on a global basis with quality procedures developed by a central facility and therefore laboratory equipment and analytical methods must comply with a number of national regulatory authorities. Smaller glassmakers may have to meet fewer regulations as they may not have their own analytical laboratory and must rely on others for support. Outsourcing analytical facilities can be problematic with the glassmaker needing proof that a commercial laboratory can deliver reliable analytical data. However, if a laboratory is able to demonstrate that by using an approved standard method for sampling and analysis and it can report results on a CRM within the confidence limits quoted on the certificate, competence is assured.

A frequently encountered problem for many analyses is the general absence of CRMs of direct relevance to a specific industry - the glass industry being no exception. Consequently the SGT A&P committee is working with the Bureau of Analysed Samples Ltd[2] (BAS) to develop a series of CRMs for use across the glass industry to assist glass analysts in their general work programme and to further support the increasing requirement placed upon laboratories to demonstrate compliance / traceability for audit and regulatory purposes. The A&P committee, working with the International Commission on Glass through their technical committee devoted to chemical durability and analysis, ICG/TC2, have assembled a group of cooperating analysts to produce CRMs.

In recent years, the A&P Technical Committee has published a series of methods for the analysis of glassmaking raw materials; sand[3,4], limestone and dolomite[5,6] and soda ash[7]. The latter paper also reviewed the soda ash CRM development and provides general guidance on the overall analytical protocol adopted.

In 2009 ICG/TC2 published a *Handbook of Recommended Analytical Methods*[8] related to various topics, such as the quality of raw materials, the effects of elemental oxidation stages on glass colouration and the quantification and distribution of foreign elements in glass cullet.

2. Analytical techniques

It is recognised that laboratories may use a number of different analytical techniques to fully meet their analytical needs using the facilities at their disposal. The techniques used today include:-
X-ray fluorescence spectrometry (XRF)
Inductively coupled plasma-optical emission spectrometry (ICP-OES)

Ultraviolet-visible spectrometry (UV-VIS)
Atomic absorption spectrometry (AAS)

No attempt is made to specify which technique(s) should be used as it would be invidious to do so; rather this section of the Compendium is offered as a practical guide to assist both the glass-maker and the analyst in selecting a methodology that satisfies both analytical need and budget. Instrumental techniques develop overtime offering improvement in sensitivity whereas wet chemical procedures may change to reflect legislation regarding the use of chemical substances.

2.1 X-ray fluorescence spectrometry

The daily routine to support the management of quality control procedures in a glass works is a team effort. Raw materials and ecology cullet are delivered by suppliers who can prove that they have systems in place to meet agreed customer requirements. Valuable information about melting conditions and furnace operation give insight into the condition of refractory materials in the furnace that may modify the glass composition.

A glass works management system is designed to produce glass with the desired chemical and physical properties for the forming machines to make ware to support the order book. The glass technologist will agree a target composition with batch compositions calculated accordingly. Routine quality control checks are performed to ensure that the glass produced meets the agreed properties. Unlike the steel industry where the molten metal has to be analysed by sampling from the ladle to ensure that the melt meets the required composition, before transfer to the next production stage, analysis of glass is carried out after manufacture.

In a modern glassworks quality assurance for the composition of glass is made by means of regular density determinations. The density of annealed glass can be related to its chemical analysis and so provide valuable information on composition changes. Routine analysis to ensure that the glass produced matches the target composition is performed less frequently, in many instances on a weekly basis.

Many glassworks do not therefore have facilities on site for the determination of chemical composition. Samples are collected and sent for analysis to the company Technical Centre or an external accredited laboratory. Classical wet chemical determinations are lengthy and therefore expensive. The preferred instrumental method for the determination of chemical composition is XRF.

Like all instrumental techniques for the determination of composition, the method(s) used actually measure some other property related to composition by theory and then convert to the desired value (mass content in % related to the sample dried at 105°C) through these relationships. In an X-ray spectrometer, the sample is bombarded with X-rays to generate characteristic radiation that represents the elements present in the sample. In general terms, the intensity of the characteristic radiation is proportional to the concentration of the element present. The spectrometer is therefore calibrated with samples of known composition, (CRMs) to cover the analytes of interest over appropriate concentration ranges.

The technique is rapid, non-destructive and capable of detecting elements from Boron (B) to Americium (Am) in the periodic table. As the technique is comparative, calibration standards and unknowns should be presented to the spectrometer in the same form. Samples can be analysed in the form of solids, powders and liquids. For glass and related materials the three main sample forms are:-

- solid, polished glass discs

- pressed powder pellets
- fused glass beads

Samples are generally 40 mm in diameter and must be robust to withstand analysis under vacuum.

2.1.1 X-ray theory

X-rays form part of the electromagnetic spectrum which includes radiowaves, microwaves, infrared and visible radiation, gamma rays etc. They occur in the region having wavelengths between 0.01nm and 10nm. Since the process leading to the emission of characteristic X-radiation occurs at the atomic level, the XRF technique is classified an atomic spectrochemical method.

Using Bohr's model of the atom, in which electrons revolve in fixed orbits around a central nucleus, see Figure 1, characteristic radiation can be shown to be generated as a consequence of energy transferences involved in the re-arrangement of orbital electrons following bombardment of an atom in the sample during the excitation process.

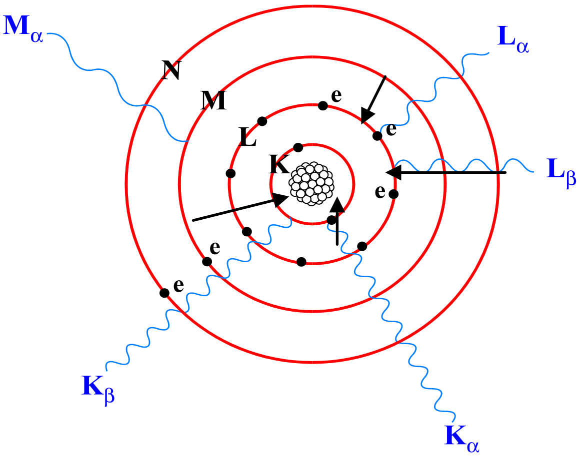

Fig. 1. Schematic diagram of an atom showing energy transfers

Radiation from the excitation source (usually an X-ray tube) will eject electrons from the atom making the atom unstable. A process of transition of electrons then takes place to fill vacancies left by the ejected electrons. Thus, if a K level electron is ejected, the vacancy may be filled by an upper level electron. The transition of an L_3 electron to the K level results in the emission of a photon labelled K-L_3 ($K\alpha_1$ in Siegbahn notation). It is also possible for a K level vacancy to be filled by M level electrons, e.g. K-M_3 ($K\beta_1$).

Similarly, L level vacancies may be filled by other electrons from any outer orbits generating L_3-M_5 ($L\alpha_1$), L_2-M_4 ($L\beta_1$) etc. Each electron transition constitutes an energy loss resulting in the emission of an X-ray photon with an energy equal to the difference between the two energy levels involved, see Figure 2.

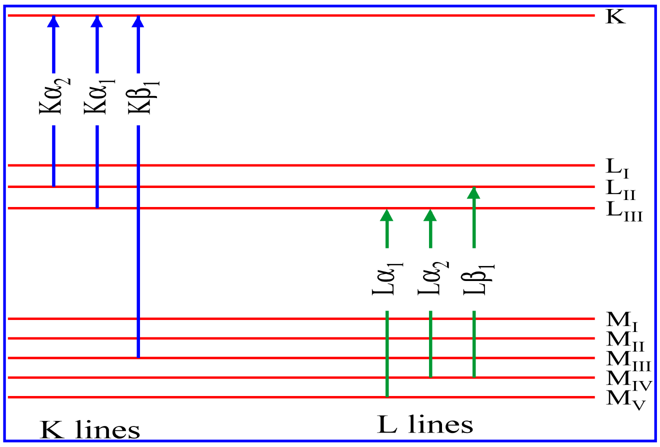

Fig. 2 Schematic showing origin of characteristic X-ray spectra

In general, the K spectrum is more intense than the L spectrum and so for reasons of sensitivity and precision, K lines are preferred for X-ray fluorescence analysis. However, for the larger atoms (Z>~55) the excitation potential for the K spectrum may be too high to achieve optimum excitation and so mostly L lines are used. As a rough guide, K spectra are used in the determination of elements from Z = 5 - 53 (B-I) and L spectra for Z = 55 - 92 (Cs-U). For the elements with Z from 37 (Rb) to about 60 (Nd) either the K or the L spectrum can be used successfully, and the choice often depends on the nature of the sample (solid, liquid, fusion) and other elements present (spectral interferences).

When the incident beam (wavelength λ) penetrates the sample and generates the characteristic radiation, the characteristic photons (wavelength $\lambda_{(Z)}$, original intensity I_0) travel through the sample to reach the surface with a reduced intensity I. Due to this absorption in the sample there is only a finite depth (d) from which the X-rays will pass to the sample surface. This depth is called "the critical depth" and generates 99.9% of the measured intensity for that wavelength. Critical depths therefore depend on the analyte of interest and the material as shown by the examples in Table 1.

Material	Mg Kα	Cr Kα	Sn Kα
Pb	0.6	4	50
Fe	0.9	30	260
SiO_2	7	100	8 mm
$Li_2B_4O_7$	12	800	4.1 cm

Table 1. Critical depth in µm

It follows that a sample will produce a polychromatic beam of characteristic radiation that must be dispersed to allow measurement of individual wavelengths. Radiation from a sample passes through a collimator on to an analysing crystal at an angle θ where the beam is diffracted in accordance with Bragg's Law,

$$n\lambda = 2d.\sin\theta$$

where d is the interplanar spacing of the crystalline material.

The diffracted beam then enters a detector.

2.1.2 Spectrometer configuration

An X-ray spectrometer provides a safe means for the excitation of a sample, the dispersion and detection of the characteristic radiation with a computer to assist in the conversion of intensities to meaningful concentration data. X-ray spectrometers may be divided into two main categories depending on the fundamentals of the detection system; wavelength dispersive (WDXRF) and energy dispersive (EDXRF). WDXRF employs diffraction by a dispersive system (crystal or multilayer) to separate the characteristic radiation emitted from the sample. In contrast EDXRF spectrometers use the proportional characteristics of a photon detector to separate the characteristic photons emerging from the sample in terms of their energies. As there is a simple relationship between wavelength and energy, these techniques provide the same basic type of information. The two configurations differ mostly in their general sensitivities and the way in which data are collected and presented. In general, a WDXRF system is about an order of magnitude more sensitive than an EDXRF spectrometer. However, an EDXRF spectrometer measures all elements within its range at the same time, whereas a WDXRF system identifies only elements for which it is programmed using appropriate dispersive devices. Further comprehensive information may be found in Margui and Van Grieken[9], *X-ay fluorescence spectrometry and related techniques.*

The most common radiation sources are X-ray tubes. However, other sources may be used to irradiate the sample including radioisotopes, synchrotron radiation and particle beams. Within the glass industry WDXRF is commonly used. A typical spectrometer may have a Rh X-ray tube, up to 8 analysing crystals and 3 detectors for the analysis of glass, raw materials and refractories. The analytes of interest are measured sequentially in application specific programmes often with analysis times of a few minutes. The optical path of a wavelength dispersive system, as shown in Figure 3, is designed to accommodate the analytes of interest for glass and related applications.

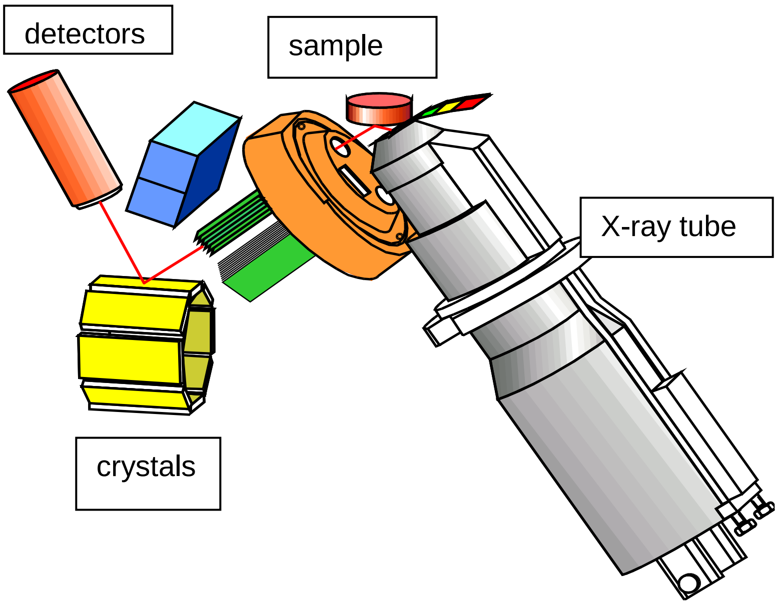

Fig. 3. Schematic diagram of spectrometer optics for a sequential wavelength dispersive system

2.1.3 Sample preparation

Solid glass discs form an ideal sample for XRF analysis, if a flat surface can be presented to the X-ray beam. In the container industry, it may be possible to core drill a 40 mm diameter disc from the punt or a flat sided bottle. The surface must then be ground and polished to satisfy the requirements for analysis of low atomic number elements such as Na where the critical depth is just a few micrometers.

Many products, however, cannot meet this criterion and further preparation is needed. Glass may be ground to a fine powder (75μm) and pressed into a pellet before analysis. Compacted powders may be a cause for concern; the grinding medium must be selected to avoid contamination of the sample from analytes that are in the glass or those giving rise to interference effects. Spectrometers used for the routine analysis of powders suffer from vacuum problems, again a cause for concern in the analysis of low atomic number elements where the longer wavelength radiation is vacuum sensitive.

An alternative approach, adopted in many laboratories, is to fuse the powdered glass with a flux such as lithium tetraborate, $Li_2B_4O_7$ in order to present a 40 mm fused bead for analysis. This sample preparation method has the added advantage in that synthetic calibration standards can be used to augment the certified reference materials (CRMs) required for calibration.

2.1.4 Calibration

Reference materials are used for the calibration of measuring equipment and the evaluation or validation of measurement procedures. They provide a powerful means of quality assurance for the scientific and technical community and enable the transfer of values of measurement between laboratories and also between supplier and customer partnerships.

The International Organisation for Standardisation (ISO) has produced a series of guidelines to demonstrate objectively that reference materials are produced in accordance with the requirements of the ISO 9000 series [10]. The Society of Glass Technology, through the work of the A&P Technical Committee has produced a series of CRMs of interest to the glass community.

• SGT 4	fluoride opal
• SGT 6	soda-lime-silica
• SGT 7	soda-lime-silica
• SGT 8	lead oxide-potassium oxide-silica
• SGT 10	amber soda-lime-silica container
• SGT 11	green soda-lime-silica container
• Standard sand 8	

Only SGT 10 & 11 satisfy the requirements of the ISO guidelines, whereas those produced earlier satisfied less stringent requirements. As previously mentioned, the Bureau of Analysed Samples Ltd working in partnership with SGT, produce powdered CRMs for the calibration of systems to analyse glass making raw materials.

• BCS-CRM 376/1	potash feldspar
• BCS-CRM 512	dolomite
• BCS-CRM 513	limestone
• BCS-CRM 526	soda ash

•	BCS-CRM 313/2	high purity silica
•	BCS-CRM 516	standard glass sand
•	BCS-CRM 528	standard glass sand
•	BCS-CRM 531	low iron sand

The quality of a calibration is dependent upon the uncertainty of the reference used (calibration masses, analytical materials or reagents, CRMs etc.) and the fitness for purpose of the particular reference material for the method concerned. This uncertainty of calibration should be compared with the negotiated tolerances for the analytes of interest as agreed with the customer. Calibration does not, however, make an inaccurate method valid.

A measurement process may be assessed in a number of ways. In a laboratory, a check of precision may be obtained by comparison with a CRM. The limit of precision being expressed in terms of standard deviation and the trueness required in terms of bias of the result. The performance characteristics of the measurement process may be assessed through an interlaboratory programme. Accreditation schemes also operate whereby an independent assessment is made to enable a laboratory to satisfy its customers of the quality of the performance characteristics of the measurement process.

The differences between laboratories can be seen in the detail results published for SGT 10.

Table 2 SGT 10 AMBER SODA-LIME-SILICA CONTAINER GLASS

Laboratory means expressed as oxides
Mass content in % related to the dried (105 Celsius) sample

Method	SiO_2	Al_2O_3	Fe_2O_3	**CaO**	**MgO**	**BaO**	Na_2O	K_2O	TiO_2	SO_3	Cr_2O_3
1		1.67	0.31*4*	10.80	1.82	0.020	12.16	0.37	0.093	0.05	0.017
1		1.60	0.32*5*	10.81	1.82	0.023	12.15	0.34	0.100	0.06	0.017
1	72.52	1.67	0.33*7*		1.82			0.36			
1		1.55	0.32*7*	10.66	1.81		12.26	0.35	0.093		
2	72.69	1.63	0.32*8*	10.66	1.82		12.24	0.35	0.097	0.05	0.024
1	72.72	1.64	0.32*3*	10.63	1.81	0.020	12.22	0.35	0.096	0.04	0.022
1	72.76	1.63	0.30*8*	10.59	1.79	0.021	12.19	0.35	0.098		0.020
1		1.59	0.34		1.82	0.020		0.35	0.095	0.06	0.021
1	72.70	1.57	0.31*5*	10.60		0.021	12.20	0.34	0.098	0.04	0.020
2	72.68	1.63	0.32*8*	10.65	1.81		12.22	0.35	0.100	0.05	0.018
^{M}M	72.68	1.62	0.32*5*	10.68	1.81	0.021	12.20	0.35	0.097	0.050	0.020
^{s}M	0.082	0.040	0.01*0*	0.084	0.009	0.001	0.039	0.009	0.003	0.008	0.002

^{M}M: Mean of the laboratory means ^{S}M: Standard deviation of the laboratory means
The laboratories mean values have been examined statistically to eliminate outlying values.

Method *1* refers to fusion in borate flux.

Method *2* refers to the use of polished glass discs.

The results are reported as the total for each analyte expressed as the oxide e.g. total iron as Fe_2O_3. The mean of laboratory means is assumed to be the best estimate available and used as the certified value. The standard deviation of the laboratory means, ${}^{s}M$, is also published. The certified values on the certificate are presented as a separate table (see table 3) of the certified values with half-width confidence intervals expressed as C(95%)+ and C(95%)-.

Table 3 Certified Values

SGT 10 AMBER SODA-LIME-SILICA CONTAINER GLASS

Mass content in %

	SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**BaO**	**Na_2o**	**K_2O**	**TiO_2**	**SO_3**	**Cr_2O_3**
${}^{M}M$	**72.7-**	**1.62**	**0.325**	**10.7-**	**1.81**	**0.02-**	**12.2-**	**0.35**	**0.097**	**0.05-**	**0.020**
C(95%)+	**72.72**	**1.644**	**0.332**	**10.75**	**1.820**	**0.022**	**12.23**	**0.357**	**0.099**	**0.058**	**0.022**
C(95%)-	**72.64**	**1.587**	**0.317**	**10.61**	**1.807**	**0.020**	**12.17**	**0.344**	**0.095**	**0.043**	**0.018**

The half-width confidence interval is calculated according to ISO guide 35 1989(E)- section 8:4:4

When a laboratory, using these reference materials, finds a difference within the 95% confidence limits quoted on the certificate, the result may be considered accurate and traceable to the fundamental scale. An unacceptable difference would highlight errors in the laboratory analytical procedure. Sample preparation and calibration procedures are the most critical steps.

2.2 Wet Chemistry

2.2.1 Inductively coupled plasma-optical emission spectrometry

In this technique atoms or ions in a sample are excited to a higher energy state by inductively coupled plasma and as they return to their low energy state the ions or atoms release their energy in the form of light. The wavelengths of this emitted light are specific to the elements that comprise the sample presented to the plasma. The amount of light emitted by the excited atoms or ions is proportional to their concentration in the sample.
The emitted light is dispersed into individual wavelengths by a grating within the spectrometer to reach a detector. The plasma is formed in a torch through which flows an easily ionised gas such as argon. The torch is placed within the coils of a high frequency generator to induce plasma with high electron density and temperature (10,000 ºK) and this energy is used in the excitation-emission of the sample. Solution samples are introduced into the plasma in an atomized state through the narrow tube in the centre of the torch.

The high temperature plasma will decompose samples to excite the majority of atoms in the periodic table offering a simultaneous multi-element technique for the quantitative analysis of liquids. ICP-OES also offers

- Wide linear region of analytical curve
- Few chemical or ionization interferences
- High sensitivity (low limit of detection for majority of elements is 10 ppb or lower)

2.2.1.1 Calibration

Calibrations may be established to encompass the required concentration range for the analytes of interest, using the standard solutions, in accordance with the manufacturer’s instructions. Several repeat measurements should be made on the standard solutions and on a blank solution. The mean and standard deviation are then calculated and the calibration lines established. The calibration should be validated using a selection of CRMs.

The ICP-OES spectrometer should be standardized each time it is used with appropriate standard solutions and CRMs. The concentration of the unknown may be calculated as follows:

$$\text{Concentration (mg/g)} = \frac{\text{Volume of flask (ml) x ICP reading (mg/l)}}{\text{Sample Weight (g) x1000}}$$

2.2.2 UV-VIS spectrometry

The interaction of electromagnetic radiation with solids, liquids or gases produces various effects, such as absorbance, reflectance or scattering. UV-VIS spectroscopy exclusively investigates the interaction of radiation with matter in the ultraviolet and visible range. When atoms or molecules absorb electromagnetic radiation they are transformed from a ground state into an energetically excited state. Energy of a specific wavelength is absorbed in this process. The various molecular states have a relatively broad energy range in comparison with atoms. Rotation and vibration of a molecule can be stimulated in the infrared range. The absorbance of defined packets of energy (quanta) by the valence electrons is observed in the range of visible and ultraviolet light. The energy of these quanta can be specified as the wavelength of the radiation. The shorter the wavelength, the greater the energy of the quanta. The location of the absorbance points and the relative magnitudes of absorbance can be determined with UV-VIS spectrophotometers.

If a light beam of intensity Io penetrates a medium of thickness d, the light beam is attenuated by the absorbance properties of the sample apart from reflectance and scattering losses. The exiting light beam (transmittance) now has the intensity I.

Transmission

$$T = \frac{I}{Io} \quad \text{or} \quad \%T = \frac{I}{Io}.100\%$$

In contrast to the transmittance, the absorbance of a solution therefore increases with increasing attenuation of the light beam.

Absorbance

$$A = -\log_{10} T = 1g(\frac{Io}{I})$$

Absorbance of organic molecules in the UV-VIS range is often caused by colour bearing species.

2.2.3 Atomic Absorption Spectrometry

In this technique a solution is aspirated into a flame through which a beam of ultraviolet light at a specific wavelength is passed. The concentration of the analyte of interest is proportional to absorption of the UV light measured by the detector. Solutions should be aspirated into the flame in accordance with the manufacturer’s instructions and the sample response compared against a calibration curve covering the concentration range of interest.

2.2.4 Other wet chemistry

Other classical wet chemistry techniques may also be used, although these require experienced analysts working in a specially equipped laboratory. The appended documents give full details for the requisite reagents, stock solutions and laboratory protocols for the analysis of glassmaking sands, limestone, dolomite and soda ash.

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