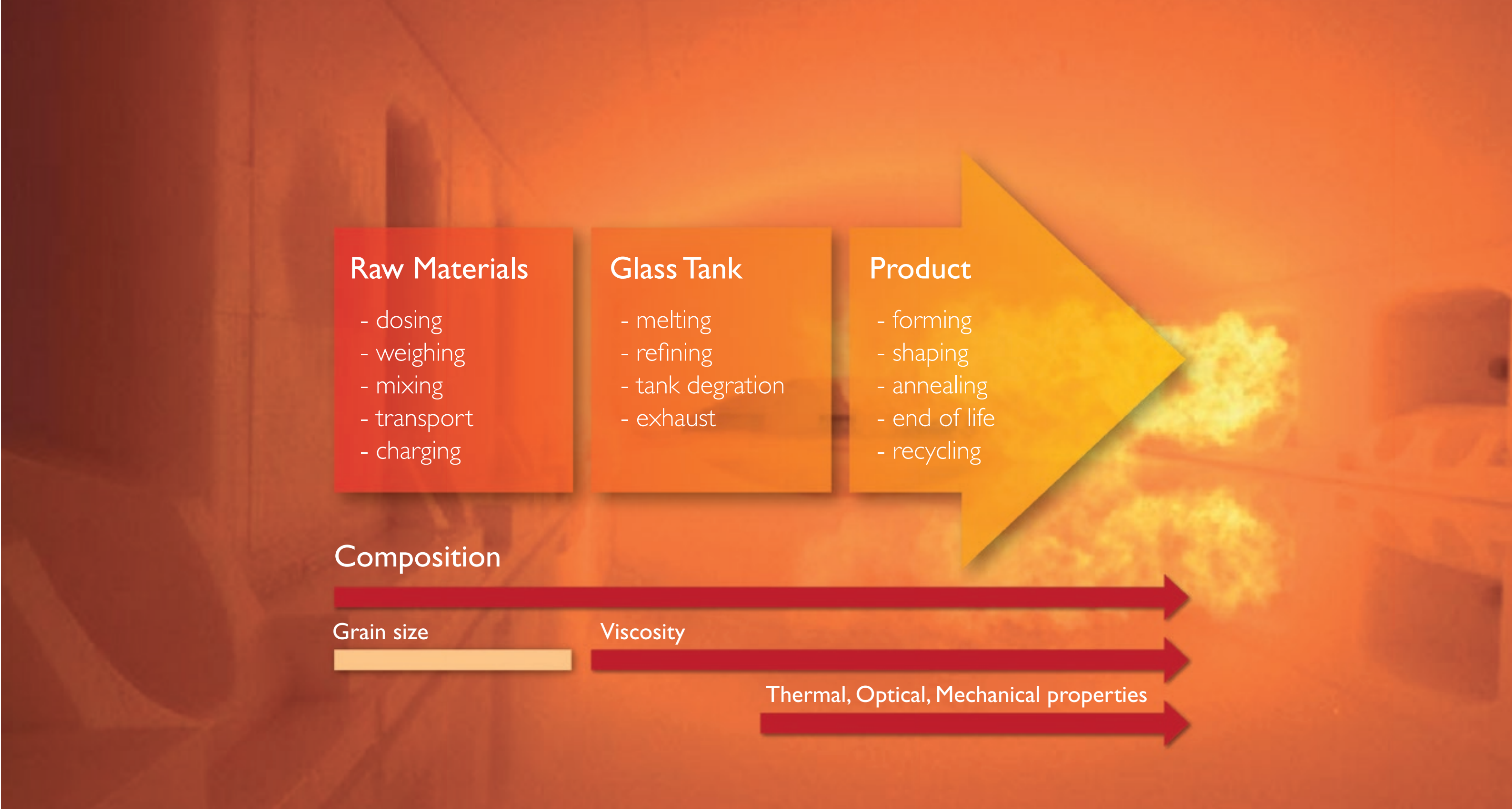


Raw Materials

- dosing
- weighing
- mixing
- transport
- charging

Glass Tank

- melting
- refining
- tank degration
- exhaust

Product

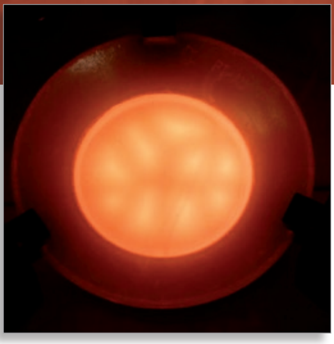
- forming
- shaping
- annealing
- end of life
- recycling

Composition

Grain size

Viscosity

Thermal, Optical, Mechanical properties



Glass Analysis

- Fast and accurate
- Materials expertise
- Fully equipped analysis lab
- Application knowledge

Glass is a valued base material for many products, ranging from optical fibres to light bulbs. The reason for this universal usage can be found in its outstanding physical-chemical properties. MiPlaza Material Analysis lab supports glass development, production and recycling with a wide variety of analytical tools and a substantial expertise in glass.

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Large portfolio of analytical techniques

Glass analysis comprises a vast number of analytical techniques, allowing for the characterization of glass from raw starting material to end products. Each step in the glass product creation process requires its own set of characterization techniques, as indicated in the front page diagram. MiPlaza Material Analysis lab offers a large portfolio of analytical techniques for glass characterization as presented in Table 2. Below, compositional analysis as well as the most important physical characterization techniques will be discussed in more detail.

Composition

Compositional knowledge is relevant throughout the entire life cycle of glass: inspection of incoming raw materials, regular production control, root-cause analysis dealing with glass faults and melting tank degradation.
MiPlaza Material Analysis lab offers a complete portfolio for compositional analysis:X-Ray Fluorescence (XRF) provides accurate and precise multi-element information in the desired concentration range at relatively low costs. For the lighter elements (<F, Li, ..) additional techniques, e.g. Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) should be used. Boron, an excellent neutron absorber, can be analysed with Neutron Transmission Analysis (NTA).
Depending on the sample, additional gravimetrical measurements are occasionally relevant: LOD (loss on drying) and LOI (loss on ignition) are used to determine the amounts of water and carbonates, organic components and crystal water, respectively.

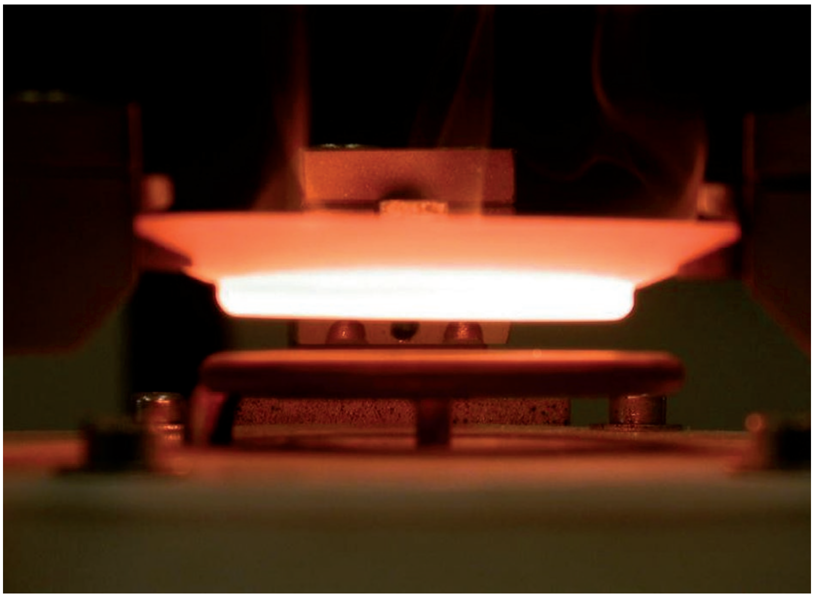


Fig. 1: High frequency fusion fluxer for the preparation of fused glass beads.

Viscosity

Viscosity is one of the most important parameters for glass processing. Therefore, it is important to know the viscosity-temperature relation and its characteristic viscosity points (e.g. strain point, working point, melting point), see Figure 2.
Measuring the viscosity is straightforward: a force is applied on the glass sample, the resulting velocity gradient is measured and the viscosity is calculated.

Viscosity data can be fitted by the Vogel-Fulcher-Tamman (VFT) equation:
Log η = A + B/(T-C) Where T is the temperature, A, B and C are fitting constants and η is the dynamic viscosity.
In practice, no single method is capable of measuring the full dynamic range of viscosities and/or the entire temperature range. To fully cover this range three methods are available (Figure 3).

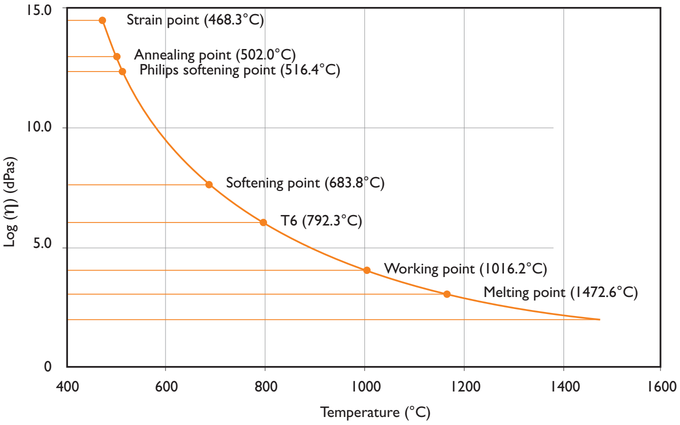
- The fibre elongation method is used for the high viscosity range.
- The beam-bending method, equipped with a high temperature furnace, has been proven to be of great value in measuring viscosities of quartz glasses in the middle region.
- A rotation method is applied for the low viscosity range.

The precision is better than 2 °C and the accuracy is tuned with appropriate reference materials. In order to realize accurate and precise results, the temperature gradients in the sample are kept as small as possible.

Thermal expansion behaviour and stress

Often glass parts have to be joined with other glasses or even completely different materials to form the final product. It is of great importance that the thermal expansion behaviour of the materials involved are well matched. Thermal expansion coefficients

Fig. 2: Viscosity(η) vs T curve of a general purpose soda glass.



Principles of XRF

When a beam of X-rays is directed onto the bulk of a specimen, secondary or fluorescent radiation is emitted by the elements present in the specimen.The wavelength of this radiation is characteristic for the elements and each element has a relatively small number of fluorescence lines.The intensity of the fluorescence lines is related to the concentration of the elements and thus can be used for quantification purposes. Generally, quantification is performed with well known reference materials.

A typical example: glass recycling

Recently, recycling of glass has become an important topic for glass production. The chemical composition of large cullet batches (i.e. batches of waste glass for recycling) can be determined with XRF. This is a typical example where sampling is the decisive parameter for the relevancy of the final result. Table 1 shows the final result of four independent samplings on a large cullet batch. These results demonstrate that the average composition and its "homogeneity" can be determined by XRF extremely well.

	avg Weight %	rsd (%)
Na_2O	6.80	0.6
MgO	1.19	3.2
Al_2O_3	3.00	1.7
SIO_2	56.5	0.4
K2O	7.23	0.4
CaO	2.34	2.1
TiO_2	0.16	6.1
Fe_2O_3	0.080	2.3
ZnO	0.21	3.9
SrO	3.1	6.0
ZrO2	0.64	8.1
Sb_2O_3	0.31	1.6
CeO_2	0.14	8.2
BaO	4.3	4.5
PbO	14.1	3.8

Table 1: Average cullet batch (recycling glass) composition of four independent samples analysed by XRF. In the second column the relative standard deviation is presented.

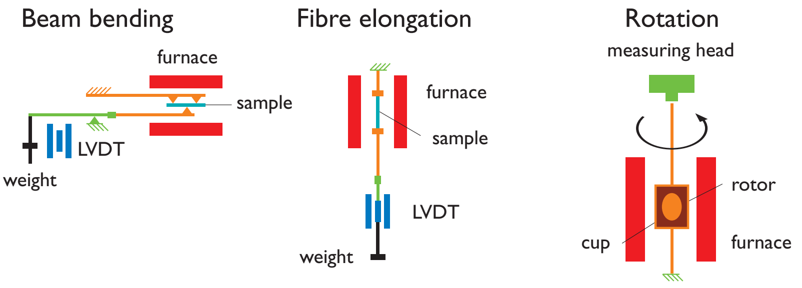


Fig. 3: Measuring principles of the three complementary methods for viscosity analysis

can be accurately measured using a double quartz dilatometer. This set-up measures the elongation of a sample as a function of temperature. An example of the resulting expansion coefficient as a function of temperature is shown in Figure 4.
In addition, stress in glass can be measured using the so-called strain slab method; the sample and a standard glass are sealed. A difference in thermal expansion between the two glasses will yield stress in the seal region. The stress can be quantified by measuring an optical birefringe effect with a polarisation microscope.

Electrical resistance

In some applications the specific electrical resistance of the glass below the transformation temperature is important. In high voltage applications, for example, a high electric resistivity is required to realize low leakage currents. The relation between the specific resistance (ρ) and the temperature (T, °C) can be described with the Rasch-Hinrichsen equation:
$Log(\rho) = A + B/(T + 273.15)$ where A and B are the fitting constants. An example is shown in Figure 5. Specific resistances can be measured in the range of $10^5 – 10^{12}$ Ω.cm with high precision and accuracy

Optical Properties

In many applications the optical properties of glass are important.
Transmission and reflection properties of glass and finished products can be measured over the entire UV-VIS-NIR-IR wavelength region (200 - 16000 nm).
For instance, transmission measurements can be used to determine $Fe2^+$/ $Fe3^+$ ratios in coloured glass and water (β-OH) determinations in quartz.

Fig. 4: The expansion coefficient as a function of T of a soda glass.

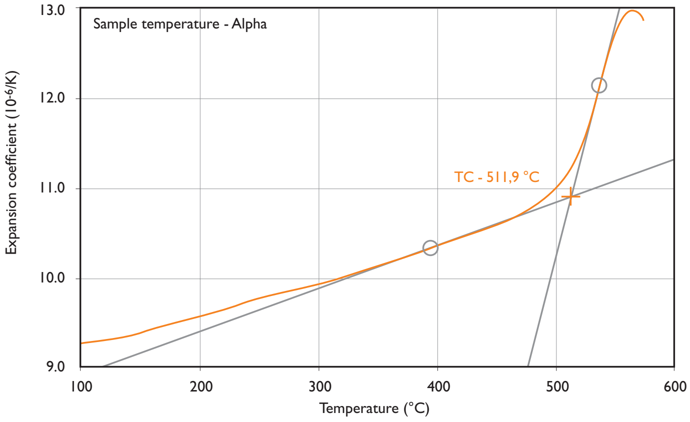
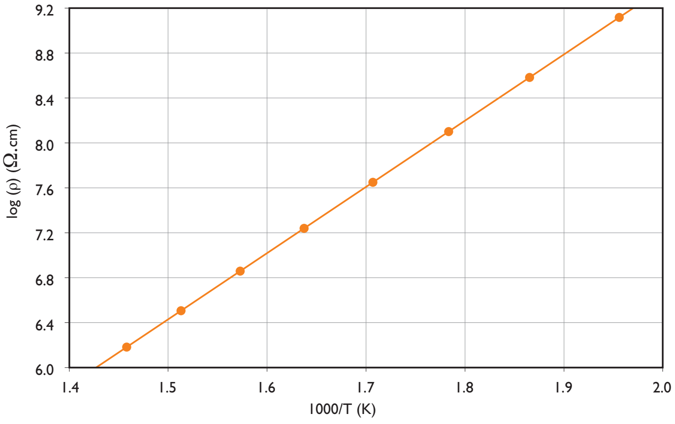


Fig. 5: The specific resistance (ρ) as a function of T of a screen display reference glass.



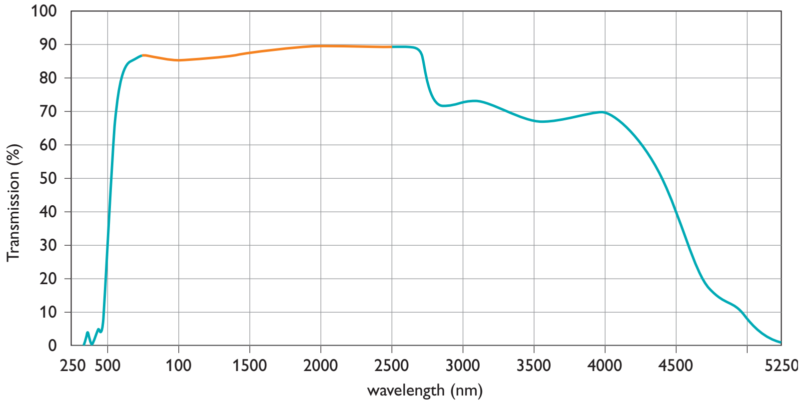


Fig. 6: The transmission as a function of wavelength of an amber coloured glass.

Table 2: Portfolio of analytical techniques for glass offered by MiPlaza.

Composition	
Glass,(raw) materials	XRF, ICP-AES, ICP-MS
Toxic compounds (As, Pb, Sb, Cd, Ni, Co)	XRF, ICP-AES, ICP-MS
Homogeneity (glass, batch, mixer efficiency)	XRF
Free water content	LOD: Loss on drying
Carbonates, organic components, crystal water	LOI: Loss on ignition
Surface analysis	XPS/ESCA
Iron content & valency: Fe(II)/Fe(III)	XRF, UV
Water (β-OH) in quartz	IR
Cullet (recycling glass)	XRF
Physical properties	
Optical properties	Transmission, Reflection (UV/VIS/NIR/IR)
Refractive properties	Abbe Refractometry Pulfrich Refractometry Ellipsometry
Thermal properties	Dilatometry Stress Glass/glass
Glass forming/shaping	Fibre Elongation Viscometry Beam Bending Viscometry Rotation Viscometry
Glass faults (Schlieren, Knots, Stones)	XRF / SEM / XRD
Particle size	Air Jet Sieve (45 – 5600 μm) Laser diffractometry (0.02-2000 μm)
Glass joining	Thermal Expansion (Dilatometry, Stress)
Various	
Analysis of dust in exhaust filters	XRF
Melting tank refractories	XRF, XRD
Identification of fragments, splinters in e.g. food	XRF

Philips Innovation labs
Material Analysis lab
offers a full range of analytical methods and expertise to support both research and manufacturing, serving customers by taking an integral, solution-oriented approach.

World-class expertise – working for you

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Precision and accuracy

The quality of the analytical result is reflected in its precision and its accuracy:

- Precision is the variance of the final result and is affected by analytical equipment, sample preparation and sampling. Because of their high quality and stability the *analytical equipment* used has a small contribution to the overall variance of the final result. Adequate *sample preparation* is the next key factor for successful analysis. For example for XRF analysis the final result of sample preparation should be a flawless fused bead (with or without the use of a fluxing agent like borate). For the preparation of these fused beads we use a fully programmable high frequency fusion fluxer with accurate temperature control (Figure 1). The last prime factor for a good result is *sampling*. Although taking a representative sample can sometimes be laborious and may require a statistical approach, it should be stressed that having minimized all other sources of variance, sampling will determine the significance of the final result.
- Adequate accuracy is realized by careful calibration with appropriate reference materials and standards.

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