# Glass characterization

Peggy Georges

Ecole Verre & Optique

USTV, 05-10/10/25

CORNING

# Corning Overview

CORNING

# Information security



CORNING

# At a glance

**>54,000**

employees across 40+ countries

*Excluding Hemlock Semiconductor employees*

**75+**

manufacturing sites

**10**

R&D facilities

Fortune 500 Ranking:

**263**

Core Sales 2024:

**$14.47 billion**

# Unwavering investment in RD&E

Invest about 7–8% of annual sales

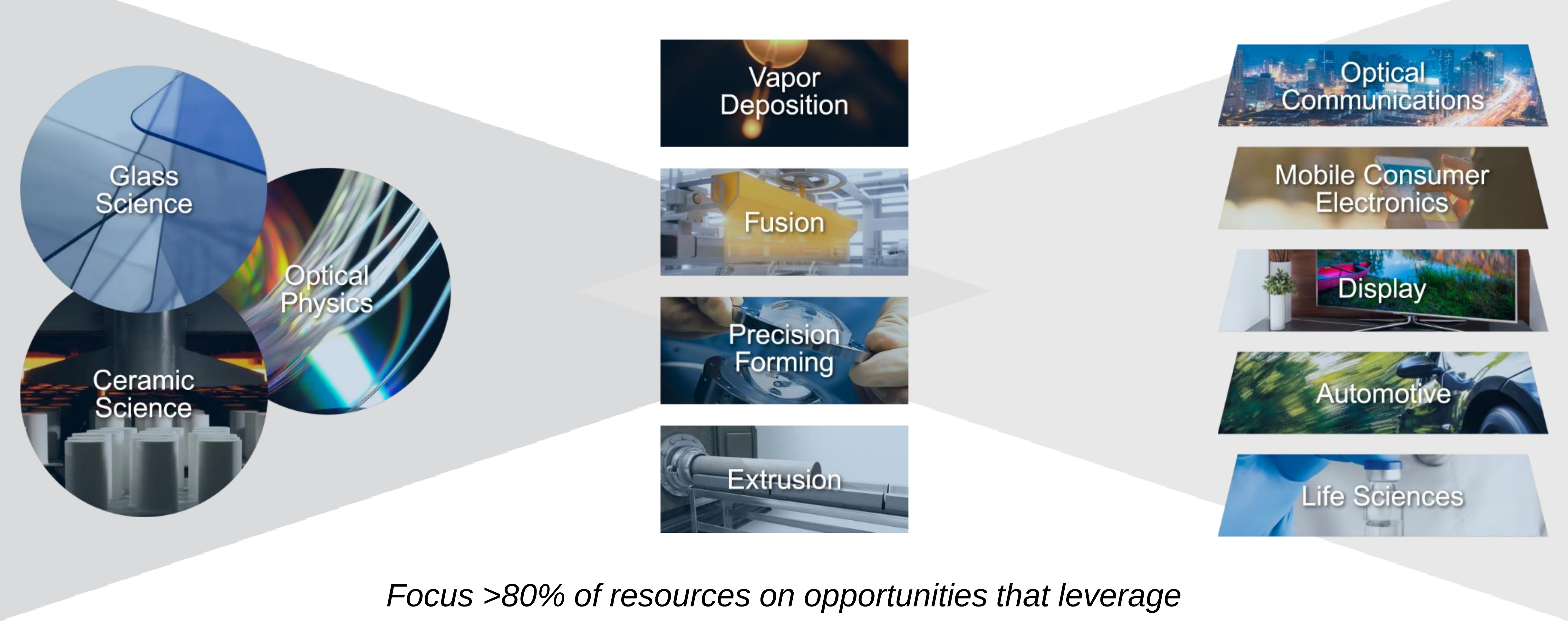
**~$1 billion each year**

# Best-in-the-World Capabilities

**3** Core Technologies

**4** Manufacturing & Engineering Platforms

**5** Market-Access Platforms




*Focus >80% of resources on opportunities that leverage capabilities from at least two of three columns*

# Corning European Technology Center

CORNING

# Global Laboratories

**Corning Scientific Center**
Helsinki, Finland

**Corning European Technology Center**
Fontainebleau, France

**Corning Research Center China**
Shanghai, China

**Sullivan Park Science & Technology Center**
Corning, New York

**Corning Reactor Technology Center**
Changzhou, China

**Corning Research Center India**
Pune, India

**Corning Technology Center Korea**
Asan, Korea

**Corning Research Center Taiwan**
Hsinchu, Taiwan

**Corning Advanced Technology Center**
Taipei, Taiwan

CORNING


Corning European Technology Center
Founded in 1968 in Fontainebleau-Avon, France
172,000 ft² site with 133 well equipped labs
135 permanent employees
Materials and Processes
Research, Development, Engineering,
Transfer to Manufacturing and Commercial support
Strong commitment to
Safety, People
Corning Values

# CETC Organization reflects RD&E nature of our mission

Competencies

**Materials**
20 FTE
- Inorganic
- Organic

**Process**
50 FTE
- Melting, Forming
- Post-processing
- Equipment design
- Meas & Controls

**Product**
9 FTE
- Chemical Eng.
- Heat Management
- Reliability

**Characterization**
24 FTE
- Chemical
- Physical
- Mechanical
- Metrology

Biz. Portfolios

- Opt. Comm.
- MCE
- Display
- Automotive
- Life Science
- EIG, EK & Oth.
- Sustainability
- Futures

## CETC Strategic Vision 2035

- Deliver **impactful technology innovations** (RDE) leveraging our core competencies, capabilities, and strong relationship with Corning businesses and technology community
- Lead key technology innovations for a **sustainable** world
- Serve Corning as a Technology Hub for **European** manufacturing sites, suppliers and customers
- Be the meaningful and exciting place to work that the **best talents** want to join and stay

**HR, Admin & Operations** - 12 FTE

# Glass properties Characterisation

CORNING

# Glass properties

## Example of a data sheet

### Corning 7056 Alkali Borosilicate Glass

| | |
|---|---|
| Color | White |
| Glass Type | Hard Crown |
| Application | Optical, electronic, and Kovar sealing |

### Mechanical Properties

| | Metric | English |
|---|---|---|
| Density | 2.29 g/cm$^3$ | 143 lb/ft$^3$ |
| Young's Modulus | 6.4 x 10$^3$ kg/mm$^2$ | 9.2 x 10$^6$ psi |
| Poisson's Ratio | 0.21 | |
| Shear Modulus | 2.7 x 10$^3$ kg/mm$^2$ | 3.8 x 10$^6$ psi |

### Viscosity

| | | |
|---|---|---|
| Working Point (10$^4$ poise) | 1058 °C | 1936 °F |
| Softening Point (10$^{7.6}$ poise) | 718 °C | 1324 °F |
| Annealing Point (10$^{13}$ poise) | 512 °C | 954 °F |
| Strain Point (10$^{14}$ poise) | 472 °C | 882 °F |

### Thermal

| | | |
|---|---|---|
| Linear Expansion Coefficient (0 - 300 °C) | 51.5 x 10$^{-7}$ / °C | 28.5 x 10$^{-7}$ / °F |
| Linear Expansion Coefficient (25 °C to set point 477 °C) | 54.5 x 10$^{-7}$ / °C | 30.0 x 10$^{-7}$ / °F |

### Optical

Refractive Index

| Line | | λ (nm) | Value |
|---|---|---|---|
| F' | Cadmium | 480.0 | 1.49300 |
| F | Hydrogen | 486.1 | 1.49200 |
| e | Mercury | 546.1 | 1.48900 |
| d | Helium | 587.6 | 1.48640 |
| D | Sodium | 589.3 | 1.48635 |
| C' | Cadmium | 643.8 | 1.48550 |
| C | Hydrogen | 656.3 | 1.48500 |

| | | |
|---|---|---|
| Abbe Number | ve | 65.4 |
| | vd | 65.5 |

### Electrical

| | |
|---|---|
| $Log_{10}$ Volume Resistivity at 250 °C | 10.3 ohm-cm |
| $Log_{10}$ Volume Resistivity at 350 °C | 8.4 ohm-cm |
| Dielectric Constant at 20 °C, 1 MHz | 5.7 |
| Loss Tangent at 20 °C, 1 MHz | 0.27% |

### Transmission

| | |
|---|---|
| Visible | 380 - 780 nm |
| Luminous Transmission Factor (10 mm thickness) | 91% |
| Color- Minimum R Value (T400/T650) 5.5 mm thickness | 0.90 |
| Light Absorption or Beta Value | Maximum 1.5% / cm |

Beta Value = $((1 - r)^2 - T) / ((1 - r)^2 \cdot t)$

r: $((nd - 1) / (nd + 1))^2$

t: length of the sample in cm

T: Average transmission at 450, 507.7, 529.8, 543.7, 550, 555.4, 566.3, 576.9, 587.9, 600.1, 615.2, 639.7, 650 nm

### Coating and Tempering

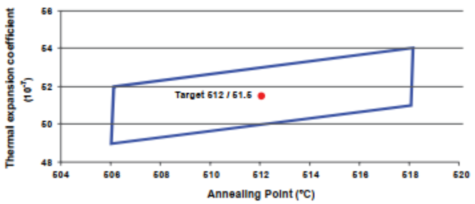
| | |
|---|---|
| Vacuum Coating | YES |
| Chemical Tempering | N/A |
| Air Tempering | N/A |

### Chemical Durability (class)

| | |
|---|---|
| To Water; NF ISO 719 | N/A |
| To Acid; DIN 12-116 | N/A |
| To Alkalis; ISO 695 | N/A |

**7056 Glass Strips Specification**

Annealing Point and Thermal Expansion Coefficient




CORNING

Corning SAS - Specialty Glass
Rue St Laurent - CS 10243 Bagneaux sur Loing
77797 Nemours Cedex - FRANCE

# Glass properties

## Huge range of composition and related properties

### Mechanical

Density, Young modulus, Poisson's ratio, shear modulus...

### Thermal & Rheological Properties

- Thermophysical (CTE, glass viscosity, thermal diffusivity/conductivity…)
- TGA / DSC / Cp

### Optical

Refractive Index, Abbe number, transmittance, color, shadow-scopy, haze determination, bubbles & defects count

### Electrical properties

Resistivity, Dielectric constant, Loss tangent

### Metrology

Dimension, surface roughness

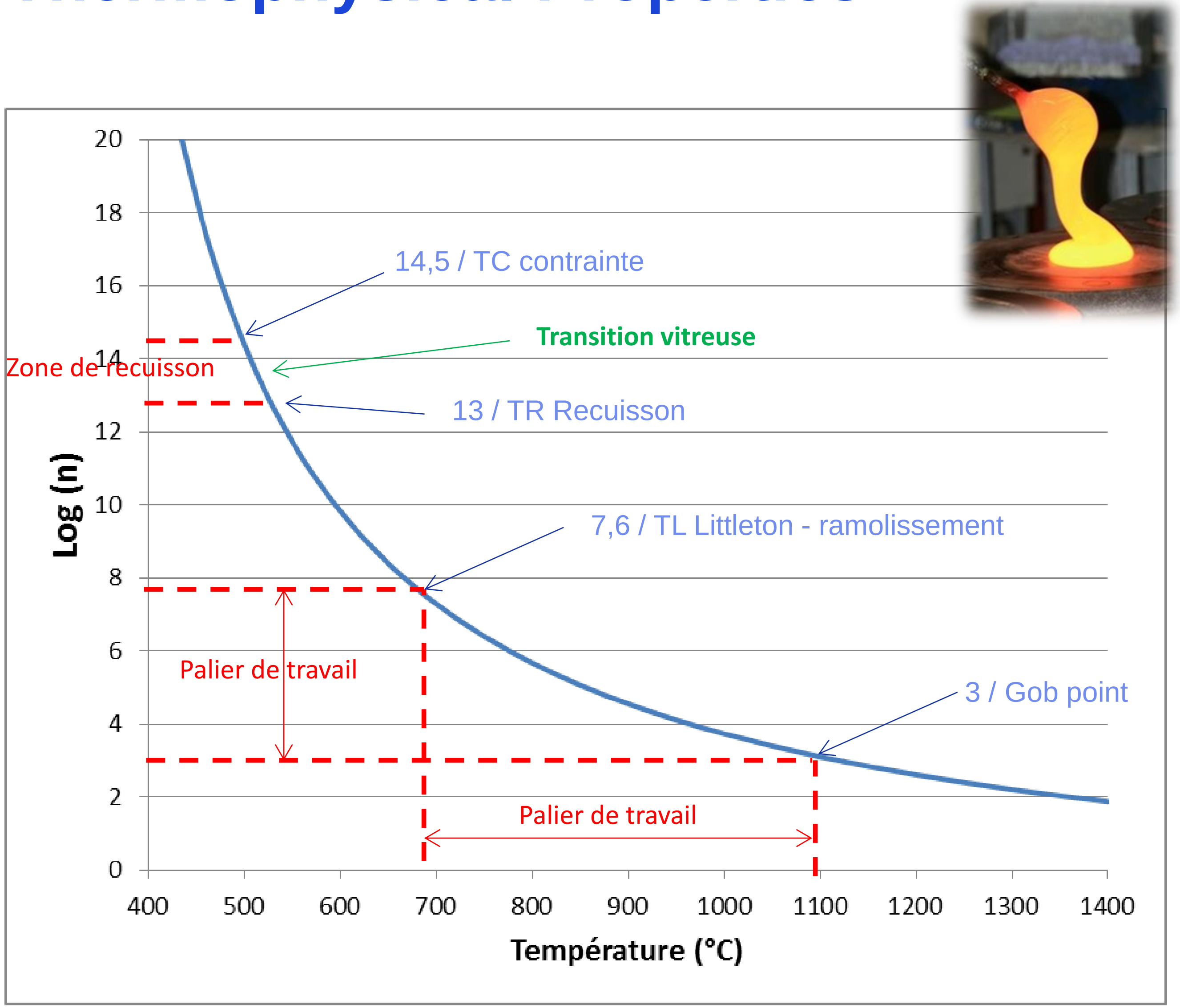
### Chemical properties

Composition, Durability

### Defects characterization

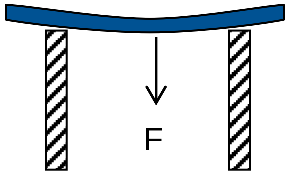
SEM, Raman, µXRF, µXRD…

# Thermophysical Properties

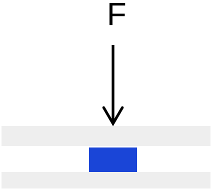



Fiber elongation

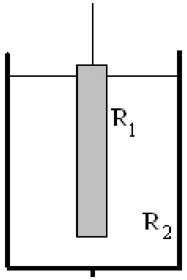

BBV
Beam Bending
Viscosimeter ($10^{12}$-$10^{10}$)



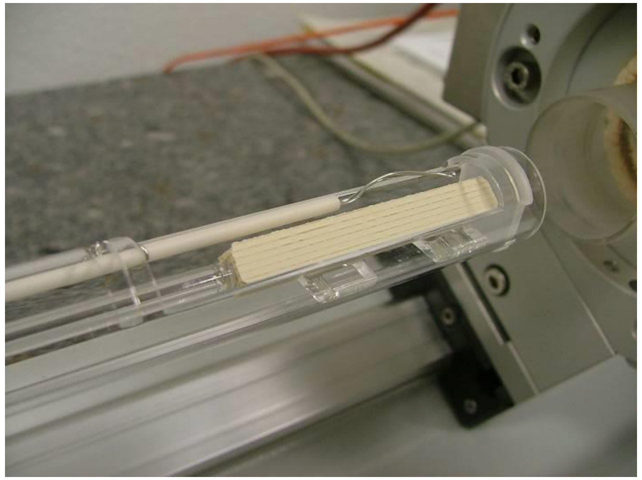

PPV
Parallel Plate Viscosimeter
($10^{9}$-$10^{6}$)




HTV- Rheometer with
coaxial cylinders ($10^{5}$- )



# Thermophysical Properties



## Density

GasPycnometer

## Linear Expansion Coefficient

- 0-300°C
- 25°C to set point

$$\alpha = \frac{1}{L} \times \frac{\Delta L}{\Delta T}$$

Sodalime $9.10^{-6}$ °C$^{-1}$
Fused silica 0,5 .$10^{-6}$ °C$^{-1}$
ULE 0 ± 0,03.$10^{-6}$°C$^{-1}$

## Thermal Conductivity / ability to conduct heat

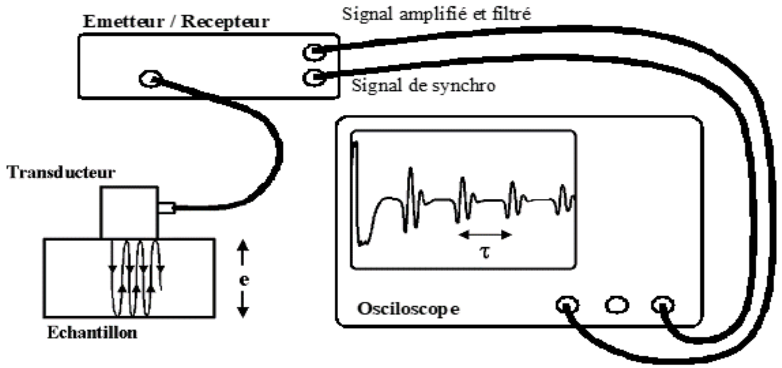
Rate at which heat energy is transferred through the material when there is a temperature gradient

$$\lambda(T) = \rho(T).\, c_p(T).\, \alpha(T)$$

Heat pulse or Laser flash methods => diffusivity α(T)

DSC => $c_p$

# Mechanical Properties
## *Young Modulus (E), Poisson's Ratio (V), Shear Modulus (G)*




Measuring the propagation speed of ultrasonic waves through the material

Need of density and thickness of the sample

Longitudinal waves (compressional waves ($V_L$))

- Particles vibrate in the direction of wave propagation
- Provide information about the material's elastic behavior under compression

Transverse waves (or shear waves, ( $V_T$ ))

- Particles vibrate perpendicular to the direction of wave propagation.
- These waves are related to the shear behavior of the material.

$$G = \rho . V_T^2$$

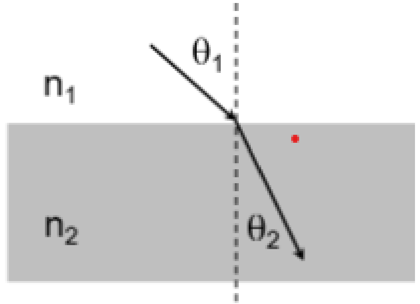
$$E = \rho \cdot \frac{3V_L^2 - 4V_T^2}{\left(\frac{V_L}{V_T}\right)^2 - 1}$$

$$\nu = \frac{E}{2G} - 1$$

# Optical Properties – Refractive Index and Abbe Number
## *in the middle range of the visible spectrum*

- Support to glass composition exploration and screening.
- Values used to establish specs for new products and validate production quality control.
- Dispersion curves for bulk materials and films are commonly used for optical modeling and product design.
- Dependent on the wavelength (i.e. frequency) of light

$$n_1 \sin\theta_1 = n_2 \sin\theta_2$$




Methods

- Refractometer (critical angle)
- Immersion (Becke line)
- Reflexion & Transmission
- Interferometry
- Spectrometry

***Nombre d'Abbe***

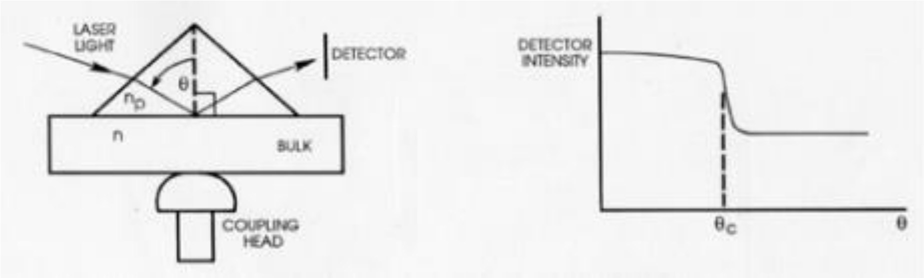
$$V_d = \frac{(n_D - 1)}{(n_F - n_C)}$$

*Raie D Sodium à 589,3 nm*
*Raie F Hydrogène à 486,1 nm*
*Raie C Hydrogène à 656,3 nm*

# Optical Properties – METRICON
## *Critical Angle Prims Coupling*

- RI / birefringence of bulk materials
- RI & thickness of thin films
- Loss of optical waveguides

### Principle

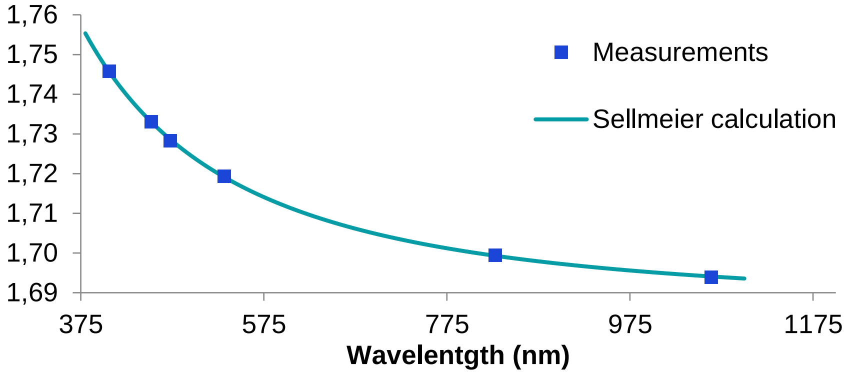



### Advantages

- Cover a broad wavelength range 405-1550 nm and refractive index range (1.0- ~2,7)
- High precision: up to ±.0002
- Speed: quick and reproductible measurement
- Versatility: wide range of materials including solids, thin films and certain liquids

### Limitations

- Contact required
- Only for transparent or semi-transparent materials
- Expensive equipment

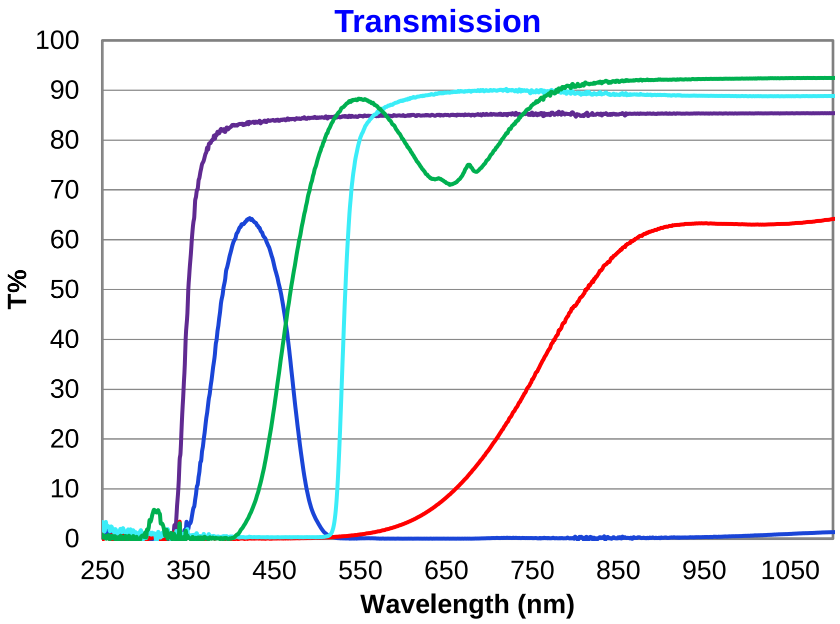


# Optical Properties

## UV-Vis-NIR Spectrophotometry & FTIR spectrometry

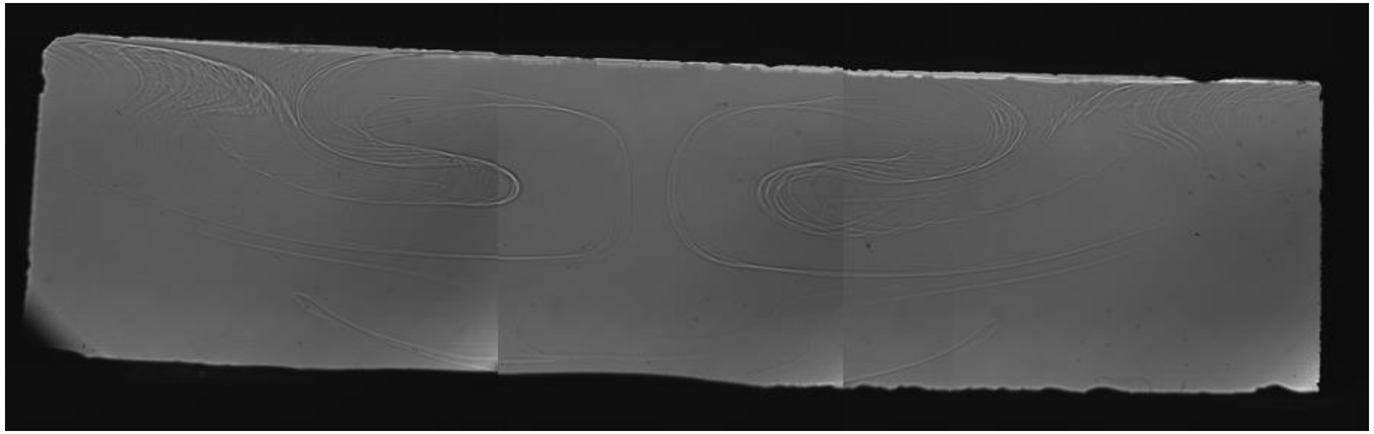
- Non-destructive technique to characterize light transmission, reflection, absorption or scatter of materials as a function of the wavelength
- Optical performance control
- Color, yellow index
- Haze

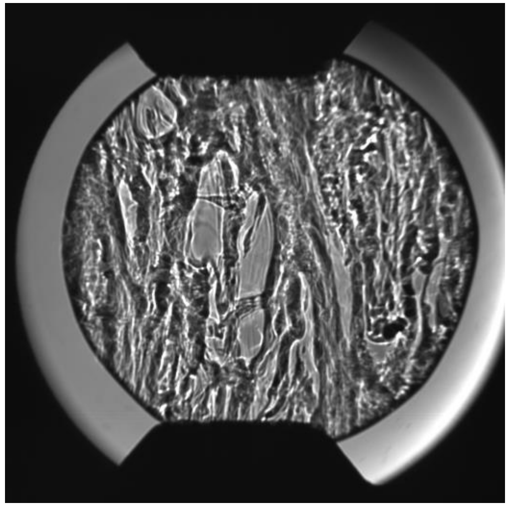
- Material identification (FTIR)

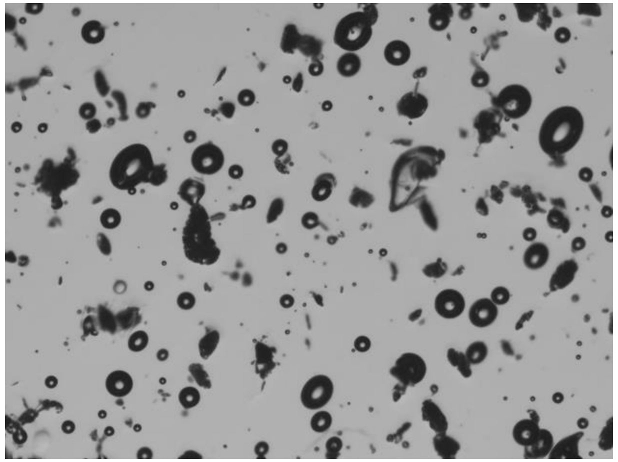


# Optical Properties
## Glass defects

- Shadowscopy
- Bubbles count
- Defects count and characterization



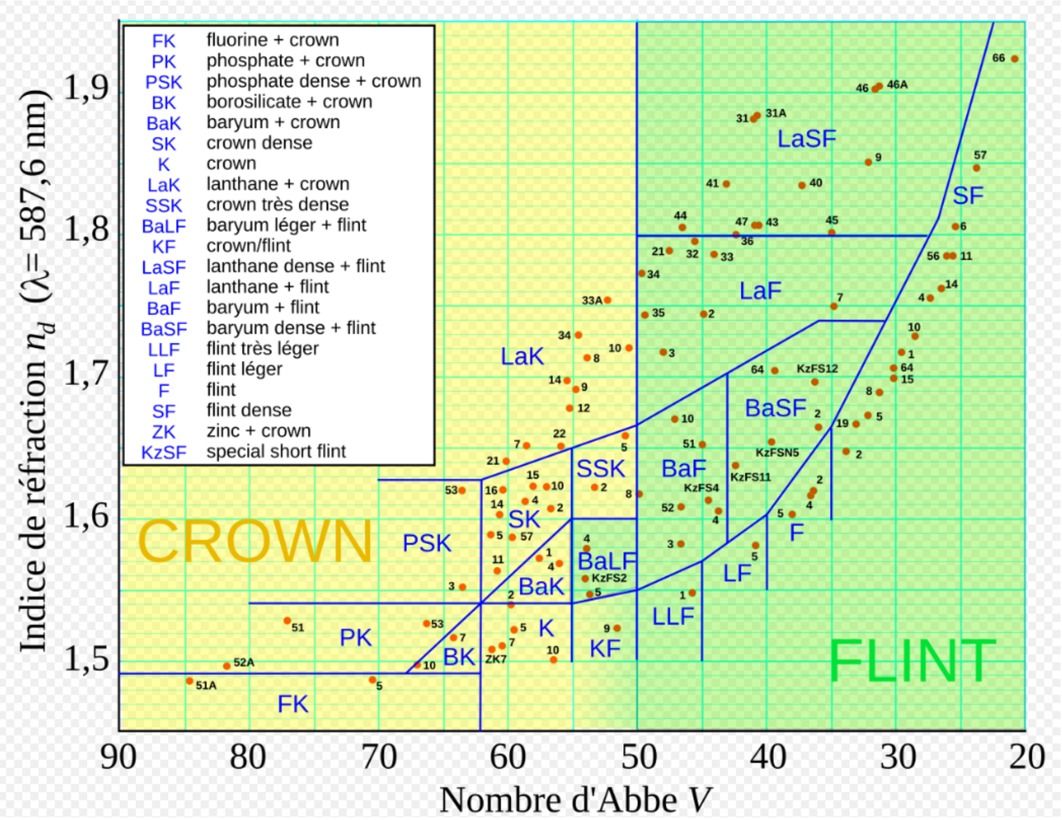




Metrology

- Shape and dimension control

# Composition




Wide variety of glass, with very different compositions

Control, standard creation, benchmark

The choice of the method depends on:

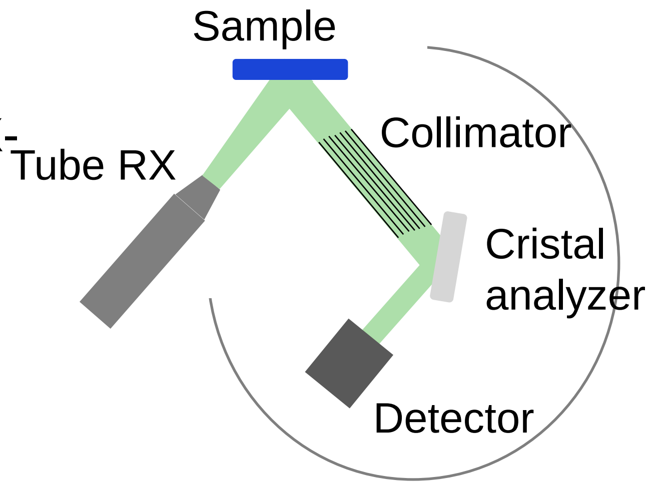
- Sample shape: bulk, fragments (cullet) powder
- Quantity of material available and its homogeneity
- Matrix
- Elements being analyzed and their level (major, minor, trace)
- Need: production control, unknown sample, new composition / quantitative, qualitative or semi-quantitative analysis
- Frequency of the measurement and the timeframe

Methods:

- X-ray fluorescence (wavelength or energy dispersive), µXRF, Handheld..
- Wet chemistry (complexometry, colorimetry, pH)
- Spectrometry (AA, ICP-OES, ICP-MS)

# Composition – XRF Principle

Emission of characteristic "secondary" (or fluorescent) X-rays from a material (solid or liquid) that has been excited by being bombarded with high-energy X-rays



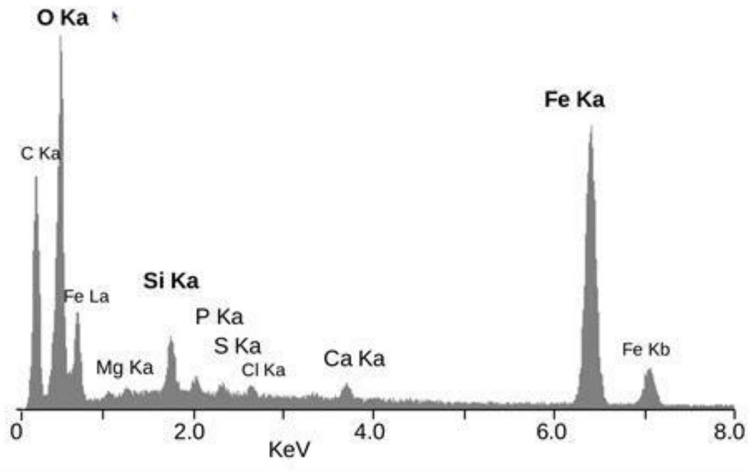

Energy Dispersive- XRF: the detector converts each photon into an electrical pulse proportional to its energy.

Wavelength Dispersive XRF: the emitted photons diffract on a crystal of known and stable dimensions, which separates them.

The emitted spectrum is characteristic of the sample's composition

Energy/Wavelength ↔ Element

Intensity ↔ Concentration




Elemental range: Be – U

LLD: 0.1 ppm – 100%

# Composition – XRF – Samples prep and type of analysis

| Sample | Solid | Powder | | *Liquid* |
|---|---|---|---|---|
| | | **Fused bead** | **Pressed pellet** | |
| |  |  |  | |
| **Preparation** | Cutting<br>Polishing | Milling if needed<br>+ flux | Milling if needed<br>+ wax | *Liquid container* |
| **Applications** | Glass<br>Glass ceramic<br>Metal | Mineral samples<br>Raw material<br>Cullet | | *Liquid*<br>*Oil* |
| **Advantages** | Rapid sample prep | Homogeneity<br>No grains effect | No volatilization | |
| **Disadvantages** | Semi-quantitative or need of bulk standard | Volatile elements | Grains effect | *Atmosphere*<br>*Helium* |

## Qualitative or semiquantitative analysis

- Based on internal system calibration
- Full scan (from B)
- Good approximation of the compo
- Ideal for unknown sample or for comparison
- Analyst experience required (interferences)

## Quantitative analysis

- Calibration using dedicated standards
- Routine analysis
- Repeatability
- Simultaneous analysis of major and trace elements

# Composition – XRF Systems

**WDXRF**

Sequential or simultaneous analysis (fixed positions) / Be – U

High resolution and low detection limits (light elements)

Tube power ranging from 400 to 4000 W (50 kV)

Robust analysis

High throughput (multi-position sample changer)

**Systems**

Benchtop

Spectrometer

**EDXRF**

Simultaneous analysis / Na –U

Less resolution compensated by simultaneous analysis

Tube from 4 to 50 W (50kV)

Instrument small and compact

Minimal maintenance

No need for fluids (water, air, gas)

**Systems**

Benchtop

Portable System (HHXRF)

µXRF (poly-capillary optics / beam from 100 to 30 µm)

# Composition – Wet Chemistry & Spectroscopy

When XRF isn't enough

- Trace elements
- Standard creation
- Benchmark

Necessary to use wet chemistry methods

Choice based on the nature of the sample and the target element

**Gravimetry**: Quantification of Lead or Barium

**UV-Visible Colorimetry:** Based on the properties of certain ions to form colored complexes with organic reagents (e.g., quantification of Boron, $Fe^{2+}$)

**Selective Electrodes:** Quantification of Fluoride

**Spectroscopic Analyses**

First step, milling and dissolution of the sample…



# Sample Dissolution

## Opened system

| | Advantages | Disadvantages |
|---|---|---|
| **”Cold”**<br>RT | - Rapid<br>- No loss of volatile elements (B, As, Sb…) | - Inefficient on refractory materials<br>- High detection limit for impurities |
| **“Hot"**<br>Heating plate, Heating bloc, Infra red radiator | - Efficient for some refractory materials<br>- Matrix simplification for traces | - Loss of volatile elements |
| **Voie sèche**<br>Fusion alcaline | - Efficient for refractory materials (flux decreases $T_{fusion}$)<br>- Preliminary step to halogenide analysis | - Matrix with high level of alkalis<br>- Flux impurities<br>- High detection limits |

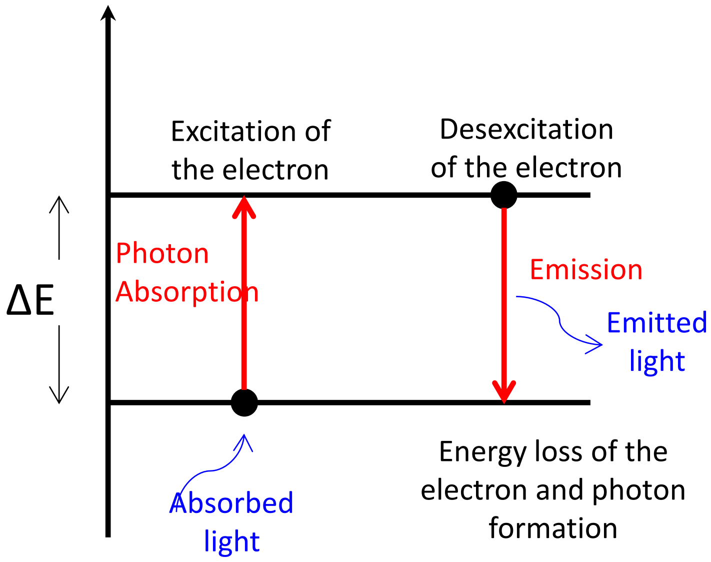
# Sample Dissolution

## Closed system

| | Advantages | Disadvantages |
|---|---|---|
| **Heating bloc** | - Gentle and thorough heating of the tubes (**T < $T_{boiling}$ acids**)<br>- Limited external contamination<br>- Trace detection<br>- Limited loss due to volatilization | - Long duration (up to 4 days) |
| **Microwaves** | - **T > $T_{boiling}$ acids**<br>- Up to 220°C Under light pressure<br>- Limited external contamination<br>- No loss due to volatilization<br>- Cycle duration < 45 min | - Limited cycle duration<br>- Washing (Teflon tube) |
| **Digestion bomb** | - **T > $T_{boiling}$ acids**<br>- Limited external contamination<br>- No loss due to volatilization<br>- Pressure-resistant material | - Maintenance (corrosion)<br>- Risk of metallic contamination |

# Atomic Absorption Spectroscopy

## Principle




**Atomizer:** converts the sample into free atoms usually by heating

- Flame atomization (air-acetylene or nitrous oxide acetylene)
- Graphite furnace atomization (higher sensitivity and detection of trace elements

**Light source:** A Hollow Cathode Lamp (HCL) specific to the element being analyzed emits light at a wavelength corresponding to that element

**Monochromator**: isolates the specific wavelength of light absorbed by the element being analyzed

**Detector**: measures the intensity of light after it passes through the sample. The reduction in light intensity is proportional to the concentration of the element

$$A = log\left(\frac{I_0}{I_t}\right) = k.\varepsilon.I.C$$

### Advantages

⇒ High Sensitivity
⇒ Specificity
⇒ Ease of use
⇒ Cost-effective

### Disadvantages

⇒ Single-element analysis
⇒ Matrix effects
⇒ Detection limits
⇒ Throughput

# Inductively Coupled Plasma Spectroscopy

| | | |
|---|---|---|
| **Sample** | **Liquid** | **Solid** |
| **Nebulization** | Vaporization chamber | LASER ablation |

**Plasma**

Generated by passing an inert gas (Ar) through a high-frequency electromagnetic field

Plasma serves as energy source to excite atoms and ions in the sample

**Detection**

**Optical (ICP-OES)**
Light emission at characteristic wavelengths
Mono or polychromator

**Mass spectrometry (ICP-MS)**
Positively charged ions
Separation and detection based on their mass-to-charge (m/z) ratio using a mass analyzer

# Comparison

## Based on similar methods

- Expected range of composition
- Calibration, line selection, calibration curve
- Blank and Quality samples

## Advantages

- All materials after dissolution
- Calibration using mono or multi-element solutions
- Semi-quantitative programs
- All elements except halogens
- Simultaneous analysis

## Disadvantages

- Sample dissolution
- Detection limit
- Error in accuracy for major elements

| | AAS | ICP-OES | ICP-MS |
|---|---|---|---|
| Sensitivity | High | High sensitivity (ppm/ppb levels) | Ultra-sensitive (ppt/ppq levels) |
| Detection limit | Suitable for trace | Suitable for trace and major elements | Suitable for trace elements |
| Isotopic analysis | | No | Yes |
| Analysis | Single-element | Simultaneous | Simultaneous |
| Cost | $ | $$ | $$$ |
| Speed | Slow | Fast | Fast |

# Chemical Durability

## Key factors affecting chemical durability

- Glass composition: High silica content => highly resistant to chemical attack, $Na_2O$ can reduce durability, making the glass more susceptible to water attack, $Al_2O_3$ or $B_2O_3$ can enhance durability
- pH of the environment
- Temperature
- Surface treatment

## Applications requiring High Chemical Durability

- Laboratory glassware
- Optical components
- Pharmaceutical packaging
- Chemical processing equipment

# Chemical Durability – Technical Glasses

| | Standard | Conditions | Materials | CRM | Comments |
|---|---|---|---|---|---|
| **Hydrolytic** | ISO 719<br>DIN 52296 | $H_2O$, 98°C<br>1 H<br>HCl titration<br>or Na by FAAS | Grains<br>Flat glass | No | Alkali free glass? |
| **Acid** | DIN 12116<br>ISO 1776 | Boiling HCl<br>6H<br>mass loss<br>HCl, 100°C<br>3H<br>Na, K by FAAS | Glass<br>Glass- ceramic | No | Huge amount of acid/base used / how to reduce the waste?<br>Representative of all type of glass?<br>Interest of having a CRM ? |
| **Base** | ISO 695 | Boiling $Na_2CO_3$ + NaOH solution<br>3 H<br>mass loss | Glass<br>Glass- ceramic | No | |

# Chemical Durability – Optical Glasses

| Standard | Conditions |
|---|---|
| ISO 8424 | pH 0,3 ($HNO_3$) or 4,6 (buffer)<br>25°C<br>10 min up to100 H<br>Weight loss |
| ISO 10629 | NaOH<br>50°C<br>15 min up to16 H<br>Weight loss |
| ISO 9689 | Tripolyphosphate<br>50°C<br>Weight loss |
| *ISO WD 13384* | *Water vapor saturated atm*<br>*T alternate between 40 and 50°C*<br>*30 H*<br>*Haze detection* |

CORNING