CORNING

# Analysis in an industrial laboratory: technical capabilities and constraints

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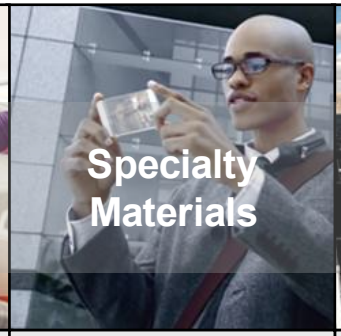
*CS & S - CETC*

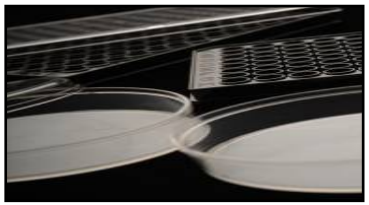
25/11/13, USTV, IPG Paris

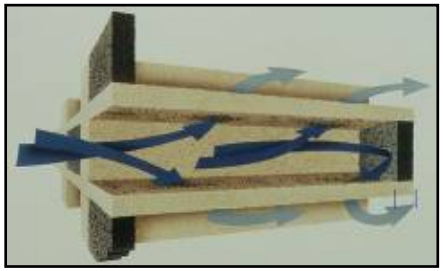
# Corning Market Segments and Additional Operations

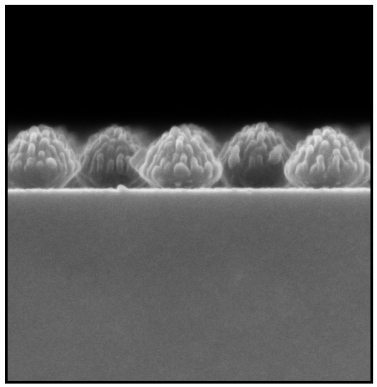
|  |  |  |  |  |  |
|---|---|---|---|---|---|
| • LCD Glass Substrates<br>• Glass Substrates for OLED and high-performance LCD platforms | • Optical Fiber and Cable<br>• Hardware and Equipment<br>– Fiber optic connectivity products | • Emissions Control Products<br>– Light-duty gasoline vehicles<br>– Light-duty and heavy-duty on-road diesel vehicles<br>– Heavy-duty non-road diesel vehicles<br>– Stationary | • Cell Culture and Bioprocess<br>• Assay and High-Throughput Screening<br>• Genomics and Proteomics<br>• General Laboratory Products | • Corning® Gorilla® Glass<br>• Display Optics and Components<br>• Optical Materials<br>– Semiconductor materials<br>– Specialty fiber<br>– Polarcor™<br>• Optics<br>• Aerospace and Defense<br>• Ophthalmic | • Emerging Display Technology<br>• Drug Discovery Technology<br>• New Business Development<br>• Equity Companies<br>– Cormetech, Inc.<br>– Dow Corning Corp.<br>– Eurokera, S.N.C.<br>– Samsung Corning Precision Materials Co., LTD (SCP) |

# CETC - Competencies

- Biochemical sciences
- Systems engineering
- Organic materials and processes
- Thin films and surface science
- Inorganic materials
- Hot glass processes





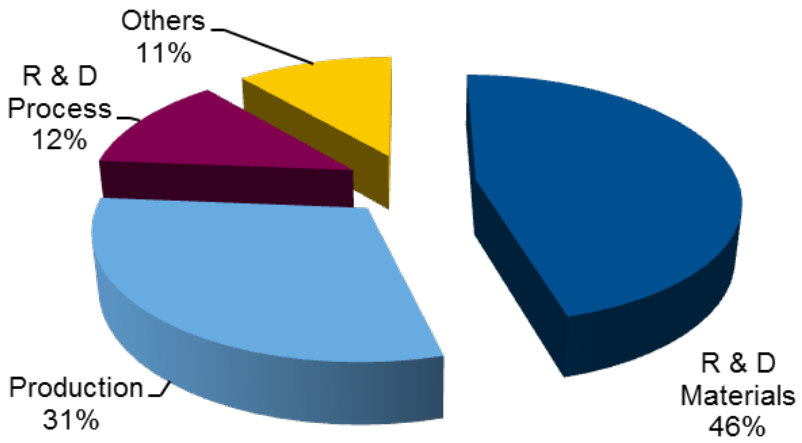



# Characterization Sciences & Services

## **Support:** Research & Development / Manufacturing in Europe

***Competencies :***

- 20 persons
- 70 instruments / pieces of equipment
- 5 services




- Sample preparation, machining and polishing
- Organic chemical analysis
- Micro-characterization, metrology, fractology
- Physical properties measurements / Reliability
- Inorganic chemical & structural analyses

# Inorganic chemistry & structural analyses

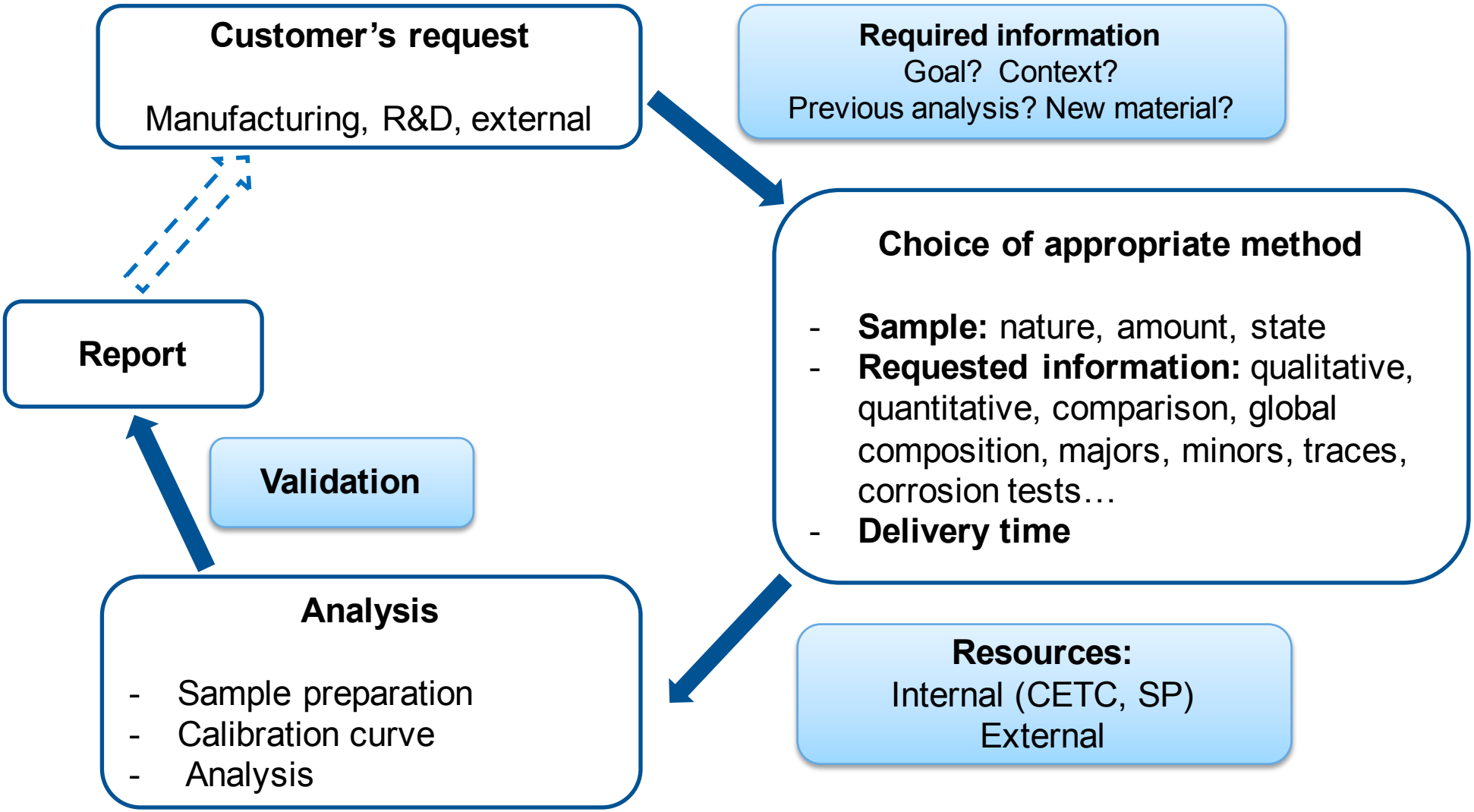
***Team : 4 persons***

***Equipment: a lot …***

- ***Sample preparation***: planetary balls and vibratory disc mills, pellet press, microwave oven, graphite block digestion system …
- ***Chemical analysis***: ICP-OES, ICP-MS, AAS, XRF, LIBS, wet chemistry…
- ***Structural analysis***: Particle size analyzer, XRD

# Inorganic chemical & structural analyses

## Global methodology



# Inorganic chemical & structural analyses

## Choice of appropriate method

**Technique adapted to sample nature and/or researched element**

**Liquid**

**Powder**

**Bulk**

**Expected value in known matrix**
(RM, Production…)

**Non expected value in known matrix**
(contamination, coloration…)

**Non expected value in unknown matrix**
(benchmarking…)

**Qualitative or semi-quantitative analysis:**

- XRF
- ICP-OES

**Quantitative analysis:**

- **XRF**
- **ICP-OES**
- Wet chemistry
- AAS
- ICP-MS
- ***XRD***

# Inorganic chemical & structural analyses

## XRF – X rays fluorescence

### Advantages

- Bulk, powder and liquid analyses
- Relative ease, rapid
- Low cost and fast sample preparation
- High accuracy and stability
- Analysis of elements from B to U from 100% to sub-ppm-level.

### Limitations

- Matrix effects: mass absorption and overlap
- Quantitative program / type of sample
- Need of standards
- Lithium
- X-ray source: Rh

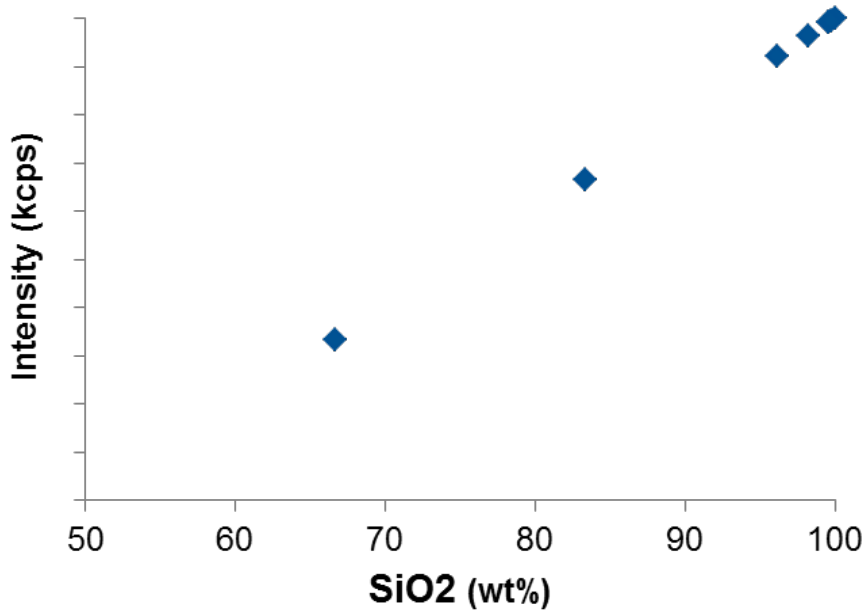
### Applications

- XRF spectrometer in most of industrial lab
- Most widely used methods for analysis of major and traces
- Routine, Semi-quantitative, Comparative analysis

# Inorganic chemical & structural analyses

## XRF – Powder sample

Example : Silica sand
Fused bead
(sample + $Li_2B_4O_7$)




**NF EN ISO 12677, nov. 2011**

**Compositional range**

$SiO_2$: 93-100
$Al_2O_3$: 0,01-2,0
$Na_2O$: 0,05-5
$K_2O$: 0,01-2
MgO: 0,03-0,5
CaO: 0,01-3
$TiO_2$: 0,01-5
$Fe_2O_3$: 0,01-2

**Choice of flux and ratio flux / sample**

- Mix of CRM and high purity chemical products

# Inorganic chemical & structural analyses

## XRF – Powder sample

Silica sand
Alumina
Ba, Ca, Na carbonate
Feldspath
Cordierite

Cu, Ni, Fe, La, Ti, Zr,
Zn, Co, Pb, Sn…
oxides

**Fused bead or pressed pellet**

**Principal components**

**Traces**
$Fe_2O_3$ : 10-500 ppm
CoO, NiO, : 1-100 ppm
S: 50-500 ppm

**Certified Reference Materials (CRM)**

**No CRM available**

**Use of another technique**
(Wet chemistry, ICP..)

# Inorganic chemical & structural analyses

## XRF – Bulk sample

**Glass ceramic (wt %)**

$SiO_2$ : 55-70
$Al_2O_3$ : 15-27
$Li_2O$: 1-5
BaO:0-5
MgO: 0-4
ZnO: 0-4
$TiO_2 + ZrO_2$: 2-5
Others: $Fe_2O_3$, $SnO_2$, $As_2O_3$, CoO, $V_2O_5$…

**Photochromic glass (wt%)**

$SiO_2$ : 40-60
$Al_2O_3$ : 5-10
$B_2O_3$ : 14-20
$Nb_2O_3$: 0-15
$ZrO_2$: 1-12
BaO, $Na_2O$, $TiO_2$, SrO: 0-6
Cl, Br, Ag: 0,1-0,5
CuO, $Sb_2O_3$, $Er_2O_3$, SnO, $La_2O_3$, $Fe_2O_3$: traces

**Principal components, minors**
Batched composition

**Specific elements**
(coloring, fining, photo responsive…)

**RoHS**

**Contamination**

**No CRM available**

**Very low content**
or
**Very high accuracy**
(300 +/- 5 ppm)
**on interfered element** (V/Ti)

**Case of Li, Rh ?**

# Inorganic chemical & structural analyses

## XRF – Bulk sample

### How can we do?

**Grinding and fused bead?**
→ Additional step

**Use of another technique to quantify ?**
Needs :
→ the appropriate technique
→ the preparation method
→ a control / quality sample

**AAS**
→ Li, K, Na

***(LIBS)***

**ICP-OES**

**Wet chemistry**

**Internal standards**

→ Plant production (target)

→ R & D (global program)

# Inorganic chemical & structural analyses

## XRF – Bulk sample

**Glass ceramic (wt %)**

$SiO_2$ : 55-70
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$Li_2O$: 1-5
BaO:0-5
MgO: 0-4
ZnO: 0-4
$TiO_2 + ZrO_2$: 2-5
$Fe_2O_3$, $Sb_2O_3$, $As_2O_3$...

**Plant production**

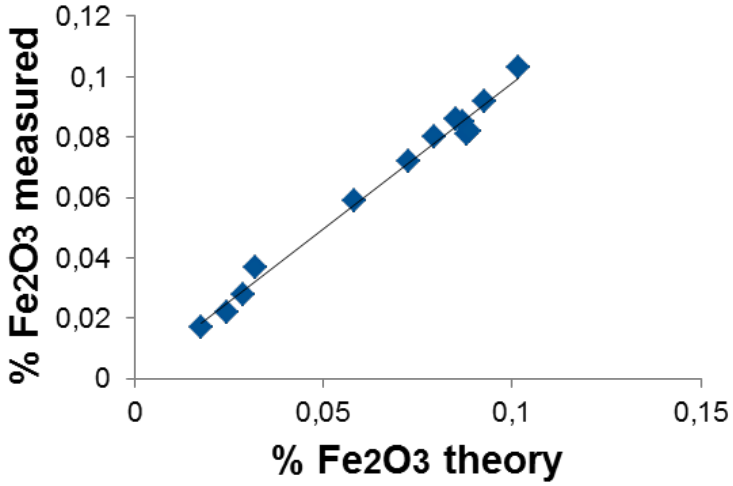
**Target / Program / Sample**

→ 1 standard

**R & D**

**Global program**

→ Narrow compositional range



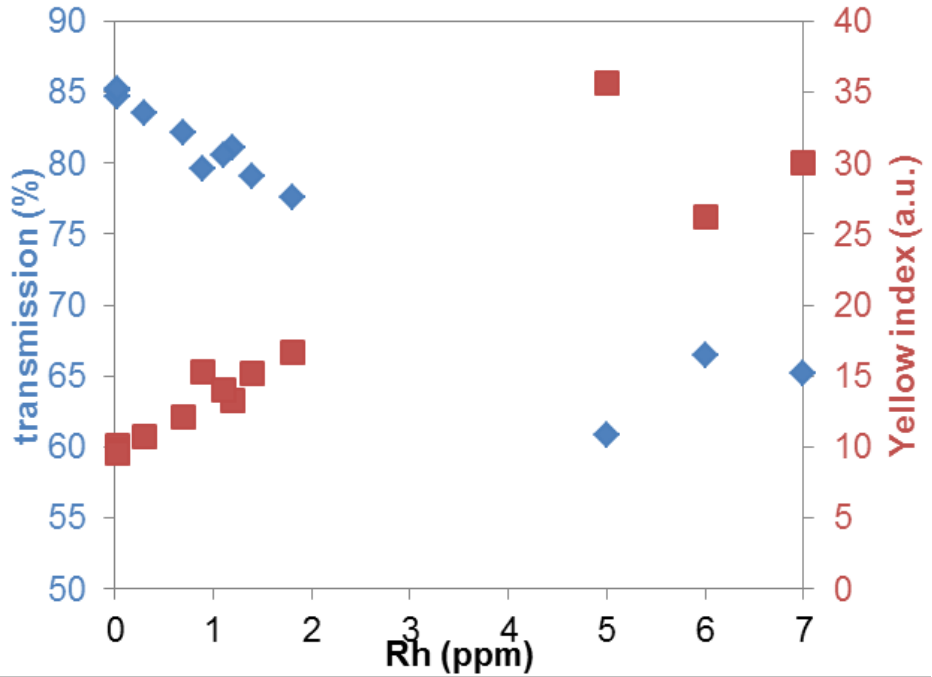

Influence of BaO content on $Fe_2O_3$ content

➢ **Need new data, ICP analysis**
(various Fe2O3 contents for low and high BaO level)

# Inorganic chemical & structural analyses

## XRF – Bulk sample

### Process contamination




**XRF: impossible**

**ICP-OES ?**

→ good digestion method

→ instrumental limit

1 ppm (glass) <= > 5 µg/l (solution)

→ Need low LD and high accuracy

➢ **ICP-MS**

# Inorganic chemical & structural analyses

## To summarize…

**Standard analyses**

- Raw material (PSD, specification validations…)
- Glass composition (production control)
- Durability tests (standardized)

**Non standard analyses**

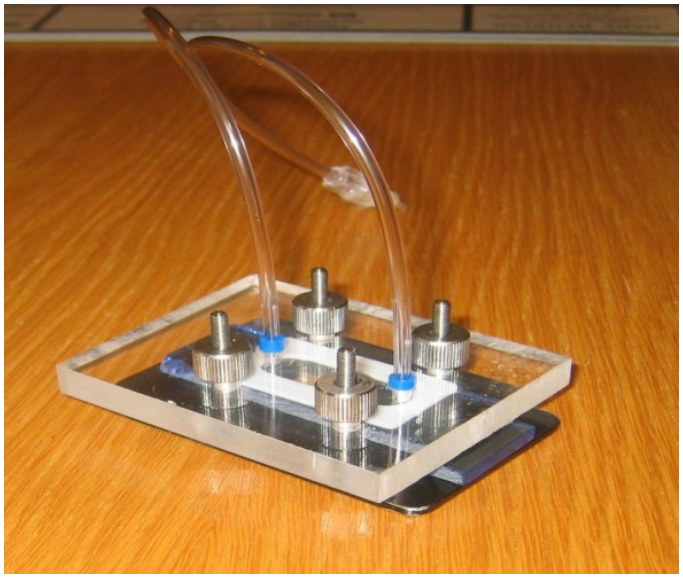
- **New method or adaptation of an existing one**: new product, new specifications, new element, extension of range composition…
- **Standard validation, benchmarking:** new glass, glass ceramic, enamel
- **Use of a unusual technique** SAC, corrosion tests, LIBS…
- **Need of expertise**: Rietveld refinment, XRD

- Orientation to an external lab…

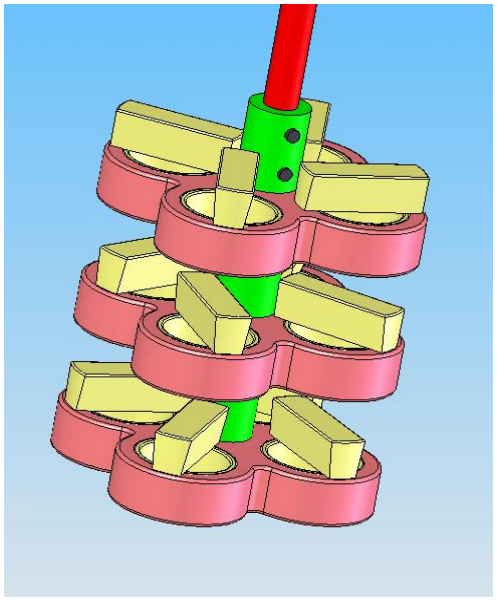
**Problem solving**

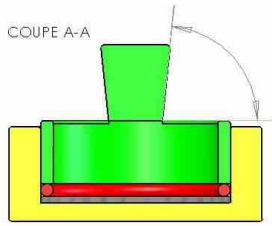
# Inorganic chemistry & structural analyses

## Examples of unusual techniques

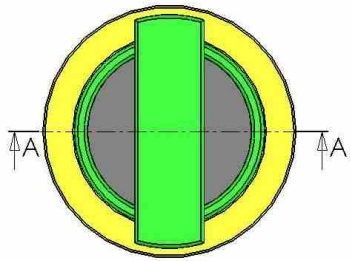


Surface Ablation Cell (SAC)






Corrosion tests



# Inorganic chemistry & structural analyses

## Conclusions

- Need of lower detection limit and more important accuracy…
- **Method validation:** efficiency of dissolution, comparison between 2 different techniques
- **Lack of standards:** CRM, round robin (internal or external)
- **Delivery time:** rapid response

- And when quantification is OK, what about the redox state?

# Thanks for your attention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7:20