RMI
ANALYTICAL & TESTING INSTRUMENTS

Základy přípravy vzorku pro ICP OES a ICP MS – rozklady

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Rozklady vzorků – převedení vzorku do roztoku

Rozklady – různý přístup v závislosti na konkrétní situaci

- Anorganická matrice, organická matrice, směsná matrice
- Analytický požadavek – matriční prvky, stopové prvky, vybrané prvky nebo kompletní spektrum prvků
- Analytická koncovka – ICP-OES nebo ICP-MS, způsob dávkování vzorku, atd.
- Počet vzorků za definovaný čas, počet vzorků v sérií
- Velikost navážky/objem – velké navážky (homogenita), malé navážky

Anorganické vzorky

Často se spíše jedná o rozpouštění

- Rozpouštění – různé směsi kyselin, zásady, komplexační činidla

  - otevřené rozklady

  - klasické tlakové rozklady – tlakové autoklávy

  - mikrovlnné rozklady – spíše jen urychlení procesu

- Tavení – převedení na rozpustnou formu

Rozklady vzorků – mineralizace

Mineralizace – částečné nebo úplné odstranění organické matrice vzorku a převedení do roztoku

Solubilizace – převedení do roztoku bez výrazného rozkladu matrice

- **Metody na suché cestě**
- **Metody na mokré cestě**
- **Tavení**

Rozklady na suché cestě

Zpopelnění

- probíhá v otevřené nádobě (křemenný nebo Pt kelímek) za atm. tlaku a vysoké teploty (max. 450-550°C); oxidační agens je vzdušný kyslík → popel → výluh popela
- navážka 1-25 g sušiny
- pomocná činidla: HNO_3, $Mg(NO_3)_2$, K_2SO_4, H_2SO_4
- nevhodné pro stanovení těkavých prvků (Hg)
- při stanovení As, Se, P nutný přídavek $Mg(NO_3)_2$

Rozklady na suché cestě

Zpopelnění – jednotlivé fáze procesu

Fáze procesu	Teplota, čas	Zařízení	Poznámka
1. sušení	<110°C 1-2 h	sušárna nebo program. pec	možnost přídavku pomocného činidla*
2. zuhelnění	<350°C 8-20 h	topná deska nebo program. pec	pomalý nárůst teploty
3. spalování	450-500°C 12-20 h	programovatelná pec	po ukončení možnost přídavku pomocného činidla **
4. vyluhování popela	20-100°C 0,5-1 h	topná deska nebo ultrazvuková lázeň	výsledná koncentrace kyseliny : 0,1-1 M

* zpravidla $Mg(NO_3)_2$

** přídavek HNO_3, odpaření do sucha, žíhání v peci 1-4 h při 450-500°C

Rozklady na mokré cestě – základy/teorie

- Chemical digestion of sample matrix
- Heating accelerates rate of reaction
- Max. temperature in open digestion limited by boiling point of solution
- Pressure build-up in closed vessels permits higher temperatures

Rozklady na mokré cestě – základy/teorie

General procedure

1. Homogenisation of sample
2. Weigh-in of a representative aliquot
3. Addition of digestion reagent
4. Supply of energy (usually heat)

Rozklady na mokré cestě – základy/teorie

Reagents

- Acid (e.g. with HCl, H_2SO_4...)
- Base (e.g. with NaOH, NH_3...)
- Oxidising (e.g. with HNO_3, H_2O_2, $K_2S_2O_8$...)
- Reductive (e.g. with HJ, HBr...)
- Complexing agent (e.g. H_3BO_3...)

Rozklady na mokré cestě – základy/teorie

Nitric Acid

- Oxidizing acid $(CH_2)_x + 2\ HNO_3 \longrightarrow CO_2 + 2\ NO + 2\ H_2O$
- Often in mixtures with H_2O_2 or HCl,HF, H_2SO_4
- Boiling point: 122°C (HNO_3 65%)
- Vapour pressure ~25 bar (at ~225°C)
- Forms soluble nitrates with all elements except:
  Au, Pt, Al, B,Cr, Ti, Zr

Nitric Acid + Hydrogen Peroxide

- Increases oxidation potential $2\ H_2O_2 \longrightarrow 2\ H_2O + O_2$
- Reoxidizes NO to NO_3^-
- Typical mixtures $HNO_3 : H_2O_2 = 4:1$

Rozklady na mokré cestě – základy/teorie

Hydrochloric Acid

- Non oxidizing acid
- Boiling point 84°C (HCl 32%)
- Vapour pressure ~25 bar (at ~205°C)
- forms soluble chlorides with all elements except:
  AgCl, HgCl, TiCl
- Dissolves salts of weak acids (carbonates, phosphates, borates)
- Digestion of Iron-alloys
- Following oxides are insoluble: Al, Be, Cr, Sb, Sn, Si, Ti, Zr

Rozklady na mokré cestě – základy/teorie

Aqua Regia

- HCl : HNO_3 = 3:1
- Forms NOCl 2 NOCl —> 2 NO + Cl_2
- Vapour pressure ~25 bar (at ~200°C)
- Digestion of pricous metals, sulfides
- Use always freshly prepared

Rozklady na mokré cestě – základy/teorie

Hydrofluoric Acid

- Non-oxidizing acid
- Decomposes silicates $SiO_2 + 6\ HF \longrightarrow H_2SiF_6 + 2\ H_2O$
- Excess is necessary to prevent loss of BF_3, SiF_4, GeF_4, SeF_4
- boiling point: 108°C (HF 40%)
- vapour pressure ~25 bar (at ~240°C)
- Mostly used in mixtures with other acids
- Digestion of minerals, ores, soil, rock and pflants
- Complexation required $H_3BO_3 + 4\ HF \longrightarrow HBF_4 + 3\ H_2O$

Rozklady na mokré cestě – základy/teorie

Sulfuric Acid

- Non-oxidizing acid
- Dehydration of organic materials
- Boiling point 340°C (H_2SO_4 98%%)l
- Mostly used in mixtures with other acids
- Digestion of plastics, ores, minerals
- Insoluble sulfates for Ba, Pb, Sr

→ Digestion with HNO_3 / H_2SO_4 (1:1) mixture
→ Carbon in matrix made more readily corridible by dehydration
→ Higher digestion temperatures due to lower vapour pressure of mixture

Rozklady na mokré cestě – základy/teorie

Perchloric Acid

- Strongest oxidizing acid
- Boiling point 203°C ($HClO_4$ 72%%)
- Expolsive decomposition at 245°C!
- Vapour pressure ~25 bar (at ~200°C)
- Mostly used in mixtures with other acids (< 20% in HNO_3)
- Always use digestion temperature < 200°C
- Insoluble $KClO_4$

Explosion Hazard ! Use only in exceptional cases!

Rozklady na mokré cestě – základy/teorie

Digestion temperature

- High digestion temperatures → shorter reaction time

Digestion temperatures are limited by:

- vapour pressure of digestion acids
- temperature resistance of container/vessel materials
- pressure resistance of containers/vessels

Rozklady na mokré cestě – základy/teorie

Open method at reflux

- Max. temperature limited by boiling point of acid mixture
- Allows high weigh-ins
- Quality of digestion not always sufficient
- Loss of volatile elements (e.g. Hg, lead salts)

Closed vessel digestion

- Max. temperature 260-300°C
- Reduced acid consumption
- High quality of digestion
- No Loss of volatile elements (e.g. Hg, lead salts)

→ **Speed-up of digestion process in closed vessel by reaching higher temperatures**

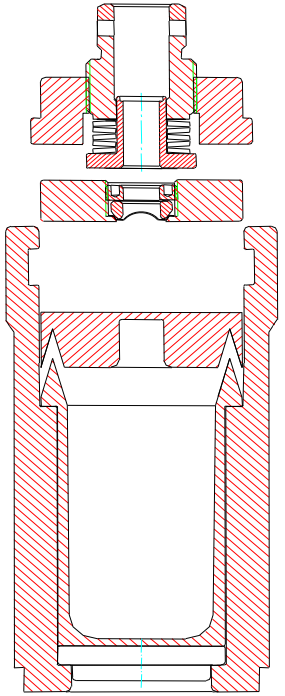
Rozklady na mokré cestě – základy/teorie

Pressure digestion in steel vessels

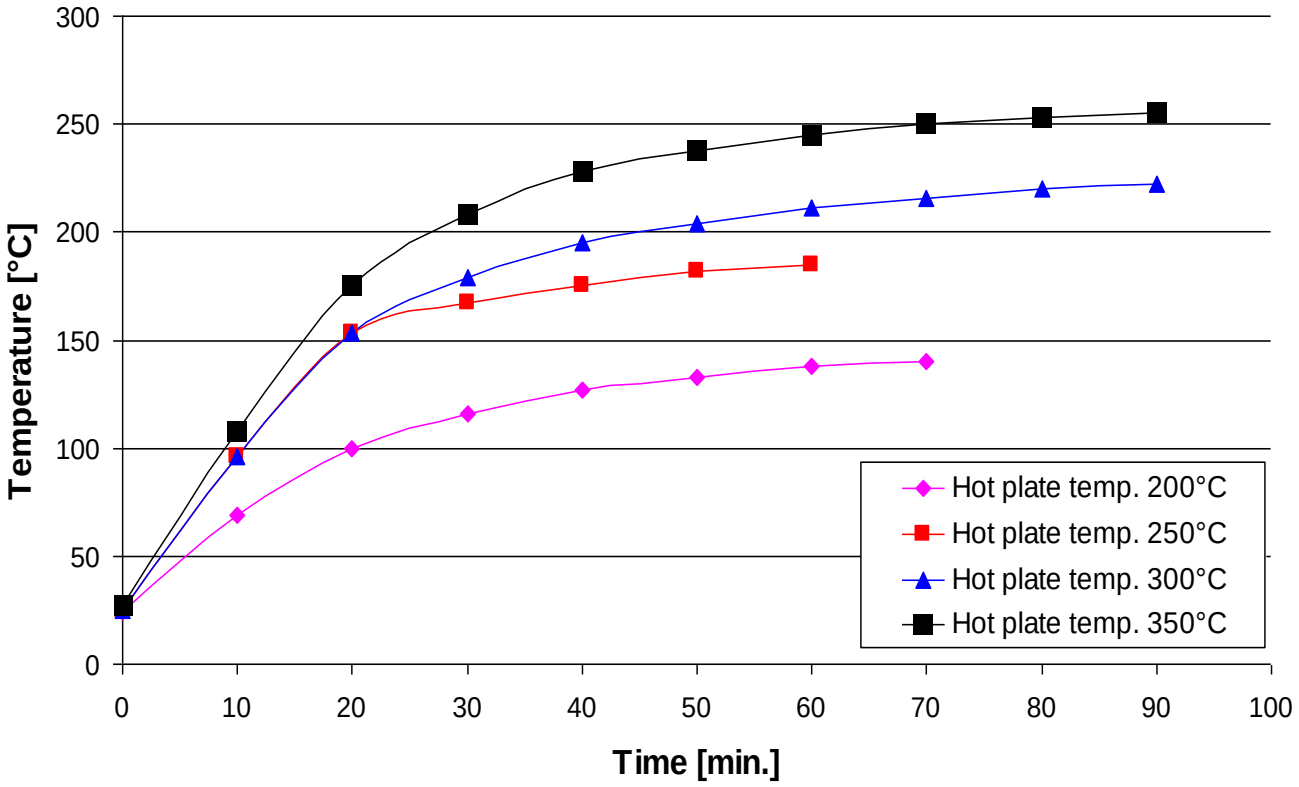
- **Pressure resistance 200 bar**
- Temperature max. 230°C (briefly 260°C)
- Digestion times from about 2 hours to several days
- Free from contamination due to PTFE-TFM lining
- Different internal volumes (25-250 ml) and therefore weigh-in quantities
- Outstanding quality of digestion
- No loss of volatile elements (e.g. Hg, lead salts)
- High degree of safety, easy operation

Rozklady na mokré cestě – základy/teorie

Pressure digestion in steel vessels



Rozklady na mokré cestě – základy/teorie



Rozklady na mokré cestě – základy/teorie

Matrix	Weigh-in	Acid	Temperature	Time
Cellulose/starch	1000 mg	HNO_3	160°C	2h
Flour/grain/leaves	1000 mg	HNO_3/HF	180°C	2h
Tissue/liver	1000 mg	HNO_3	170°C-190°C	2h
Fat/oil	1000 mg	HNO_3 (poss. H_2O_2)	200°C	4h
Plastics	500 mg	HNO_3 /H_2SO_4	200°C	3-4h
Carbon/resin	500 mg	HNO_3	220°C	6h
Ceramics/oxides	500 mg	HF or HCl	230°C	2-8h
Steel	500 mg	HNO_3/HCl	200°C	4h

Digestion Vessel DAB-3 (250 ml)

Rozklady na mokré cestě – základy/teorie

Pressure buildup in closed digestion

Total pressure p

$p = p(CO_2) + p(acid)$

$p(CO_2)$ = partial pressure of CO_2 produced

p(acid) = partial pressure of acid mixture

CO_2 pressure:

- dependent on carbon content of sample and weigh-in

  $p(CO_2)$ = 6.9 * mc [g] * T/V [K/ml]

Example:

V = 30 ml, 0.2 g carbon, 200°C → $p(CO_2)$ = 22 bar

V = 80 ml, 0.2 g carbon, 200°C → $p(CO_2)$ = 8 bar

Rozklady na mokré cestě – základy/teorie

Example (60 ml vessel at 200°C):

- 500 mg carbon develops 930 ml CO_2
  → partial CO_2 pressure of 26 bar

- Acid pressure for HNO_3 at 200°C of approx. 10 bar
  → Total pressure approx. 36 bar (60 ml vessel at 200°C)

Rozklady na mokré cestě – základy/teorie

Pressure build-up in closed digestion

Total pressure p

$p = p(CO_2) + p(acid)$

$p(CO_2)$ = partial pressure of CO_2 produced

p(acid) = partial pressure of axid mixture

Acid pressure:

- Sum of partial pressures of pure acid and water

  $p(acid) = P_{H20} + P_{HCl}$

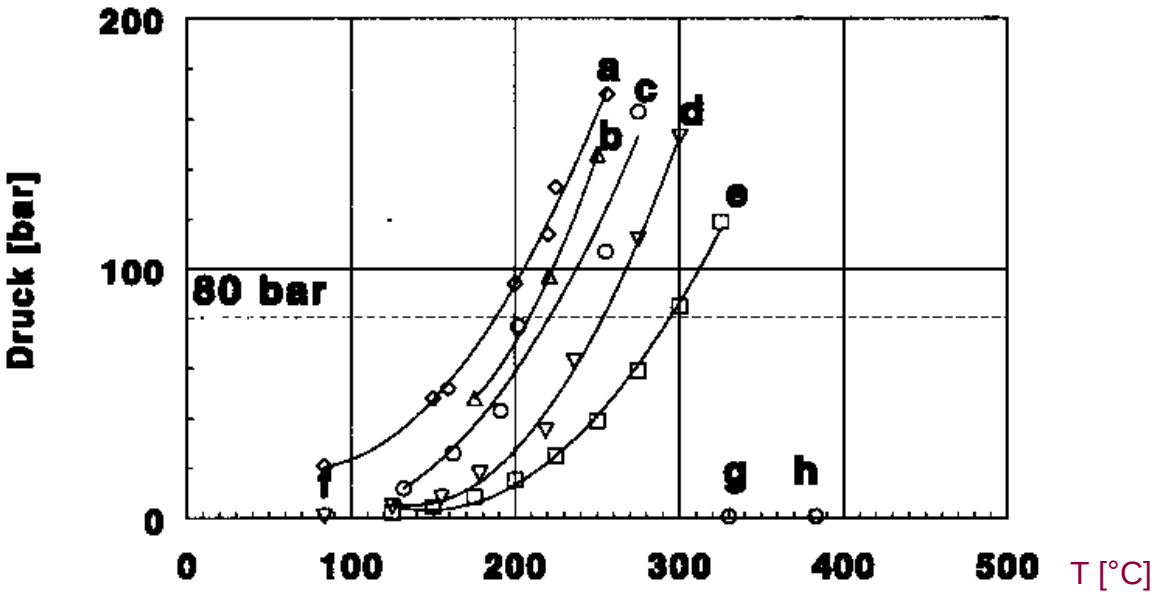
- Characteristic vapour-pressure curves of acid mixtures

- Independent of container volume on condition that acid concentration of solution remains constant

→ **Acid volume must be matched to container/vessel volume**

Rozklady na mokré cestě – základy/teorie

Vapour-pressure curves/graphs of pure acids



a. Aqua regia
b. HCl 36%
c. HNO_3 91%
d. HCl 22.9%
e. Water
f. Boling point HNO_3 100%
g. Boiling point H_2SO_4 100%
h. Boiling point H_3PO_4 96%

(Panholzer, LaborPraxis, Oct. 1994, 32)

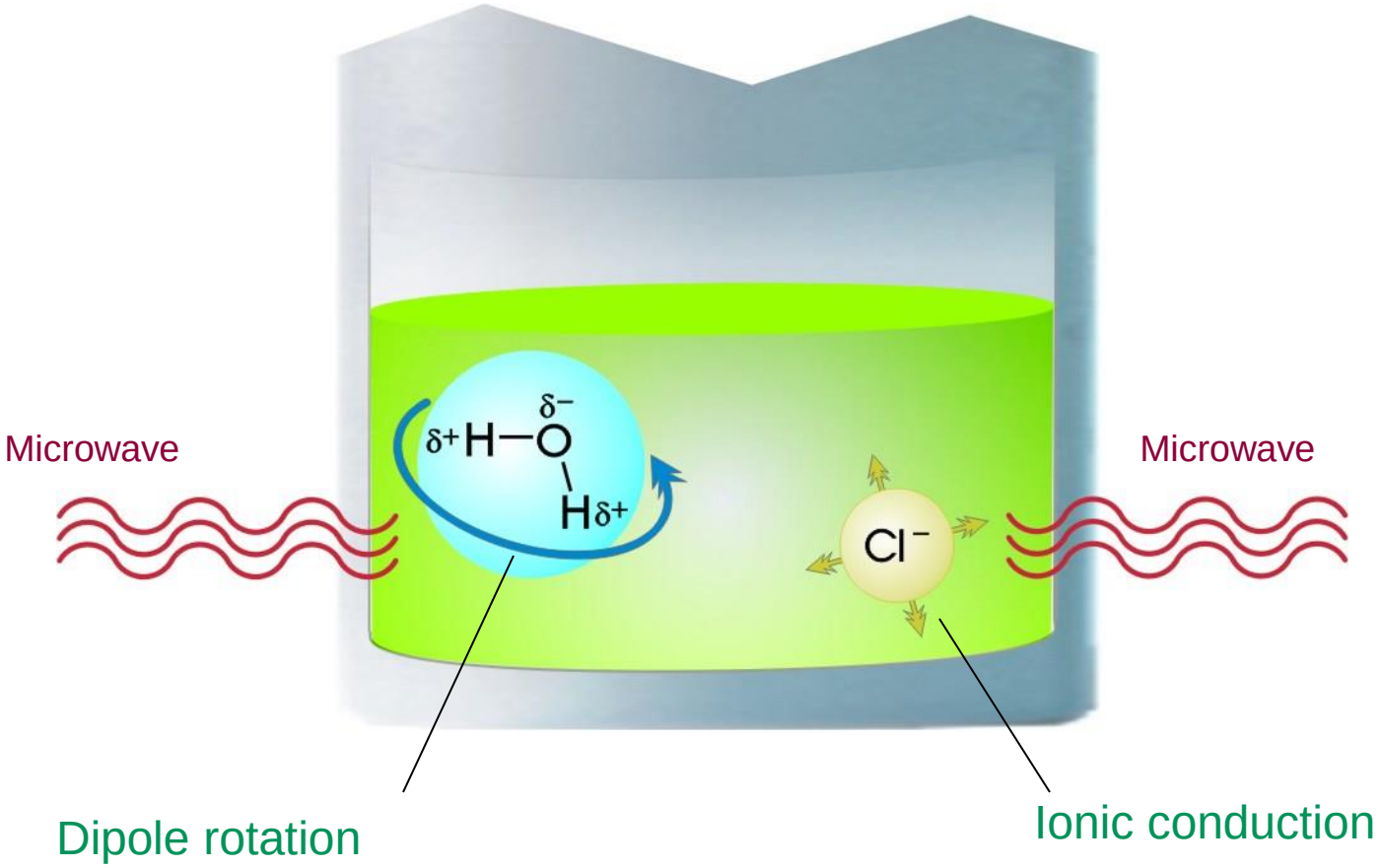
Rozklady na mokré cestě – základy/teorie

Why Microwave Digestion?

- Rapid, direct sample heating
- Rapid, multiple samples thus cost effective
- Closed vessel;
  - reduced blank value
  - higher temperatures are possible
  - improved reproducibility
  - reduced amount of reagent
  - retaining of volatile elements

Rozklady na mokré cestě – základy/teorie

Microwave Heating



Rozklady na mokré cestě – základy/teorie

Microwave Heating

- Dipole Substances and Ions of Acid and Sample contribute to Microwave Heating

→ Blank solutions absorb less microwave energy than sample solutions and reach lower temperatures therefore

→ Sample weight and acid volume has similar influence on termperature

→ Homogeneous microwave distribution necessary for unifom heating of multiple samples

Rozklady na mokré cestě – základy/teorie

Pressure digestion under microwave

- It is primarily the sample that is heated
- Container material (plastic) is only indirectly heated

→ **Relatively high digestion temperatures can be reached for short periods (30-40 minutes)**

Microwave Digestion - Problems and Risks

- Uniform microwave distribution to multiple samples
- Pressure resistance of plastic, microwave transparent vessels
- Monitoring and control of temperature and pressure in microwave field
- Pressure relief mechanism

Rozklady na mokré cestě – základy/teorie

Pressure digestion under microwave

- Pressure resistance dependent on type of container/vessel (40-150 bar)
- Free from contamination through use of PTFE-TFM containers
- Different interior volumes (10-100 ml) and therefore weigh-ins
- Quality of digestion mostly sufficient
- No loss of volatile elements (e.g. Hg, lead salts)
- High throughput of samples due to short digestion times (10-60 mins.)

Rozklady na mokré cestě – základy/teorie

Temperature Control of Exothermic Reactions Control

1. Solution is heated by microwave energy
2. At a certain temperature Activation Energy is provided for spontaneous reaction following:

$$E_{akt} + (CH_2)_x + 2\ HNO_3 \longrightarrow CO_2 + 2\ NO + 2\ H_2O + \text{Energy}$$

Additional Energy is provided, which heats-up solution

3. Microwave power must be reduced to
   - prevent overheating
   - allow cool-down of solution

temperature control for all vessels required for safe digestion

Rozklady na mokré cestě – základy/teorie

Container materials

- PTFE → maximum 260º C
- PTFE-TFM → maximum 260º C
- PFA → maximum 200º C
- Quartz (silica) glass → maximum 1,000º C (theoretically)

Requirements of a modern microwave digestion apparatus

- Digestion temperatures of up to 260°C or higher
- Sample weigh-ins of up to 1,000 mg
- Temperature control in each digestion vessel
- Temperature-controlled, programmed heat-up
- Recording of all temperature profiles
- Optionally: Pressure control in each digestion vessel
  Recording of all pressure profiles

Rozklady vzorků – tavení

- Dlouhodobě „podceňovaný“ způsob přípravy vzorku pro ICP OES
- Velký pokrok s příchodem automatizovaných taviček pro přípravu vzorku
- Moderní tavidla ve vysoké čistotě

Výhody:

- rychlé a snadné převedení do roztoku silikátových materiálů nebo směsných materiálů s vysokým obsahem silikátů
- Ideální pro extrémně rezistentní vzorky – alumina, TiO2
- Ideání pokud chceme analyzovat i obsah Si (nebo Si/Al poměry)

Nevýhody:

- vhodné zejména na oxidické formy vzorku, někdy nutná preoxidace
- zvyšuje se obsah solí – matricově modelované kalibrace
- u stopové analýzy mohou být problémy se slepými pokusy

CLAISSE
THE FIRST AND FINEST IN FUSION®

1955 – Prof. Fernand Claisse at Université Laval

Fusion

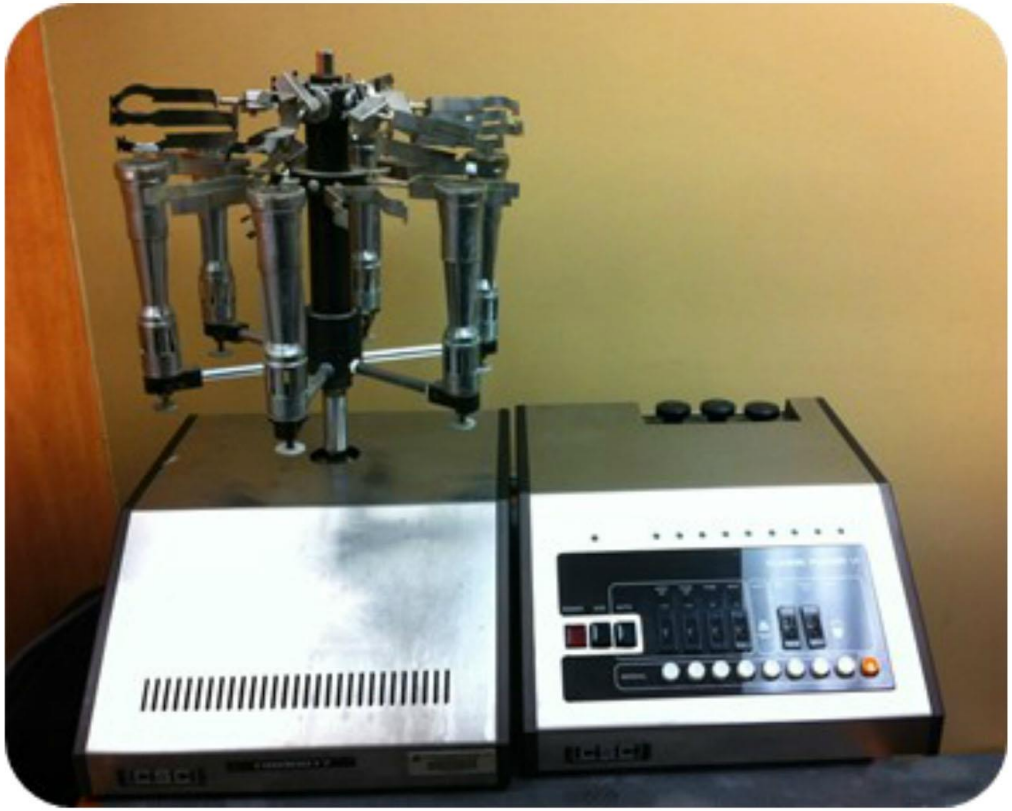
- 1955 - Publishes first work on Fusion Preparation method
- Borate fusions for all oxides
- Removes grain size and mineralogical effects for which there is no other solution

CLAISSE
THE FIRST AND FINEST IN FUSION®

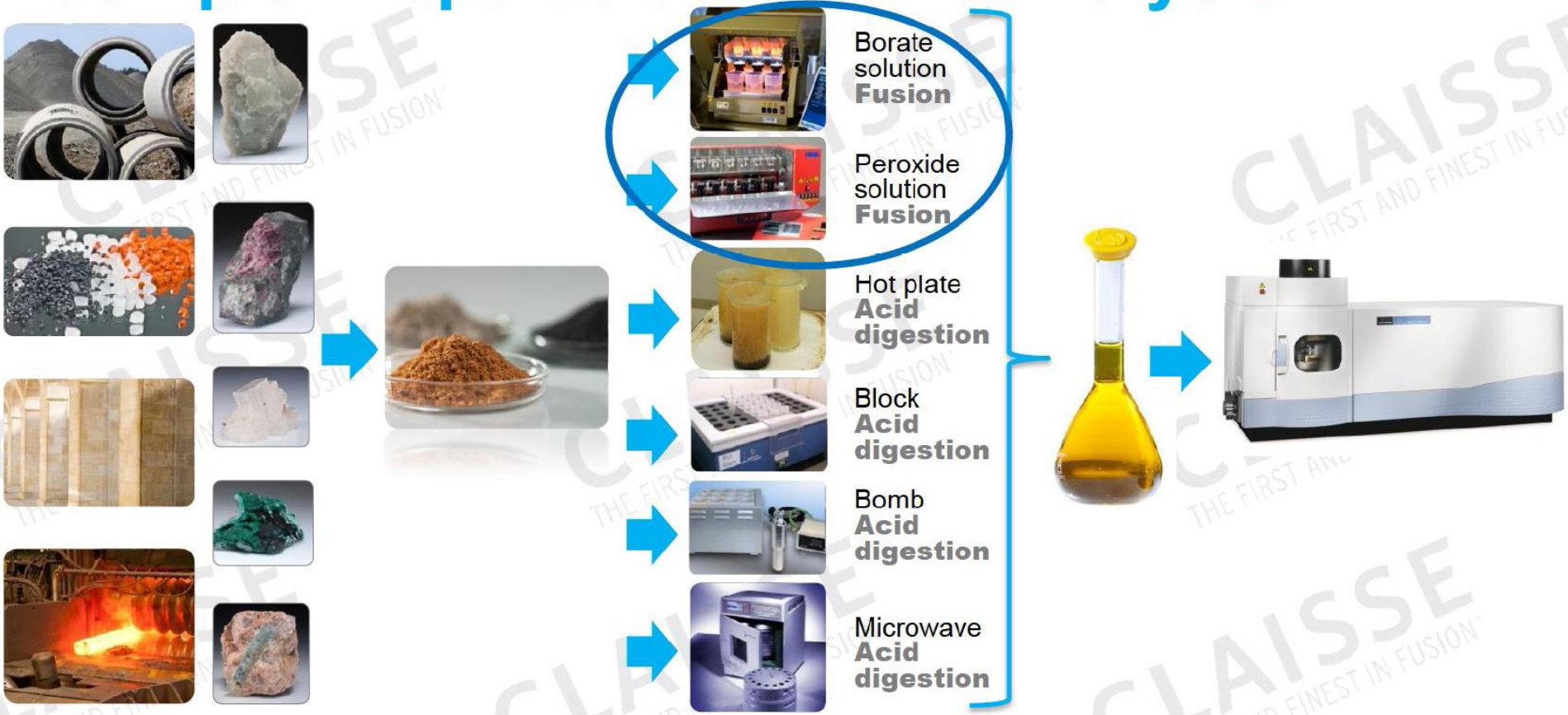
Meeker Burner and Ring Stand

1970's - Fusion Automation

- Claisse Model 6 (6 Position) Gas Fluxer

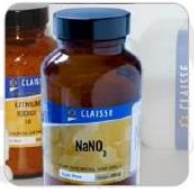


Sample Preparation for ICP Analysis



Sample Preparation by Fusion:
Equipment for ICP Analysis







Borate Fusion

Peroxide Fusion

ELECTRIC

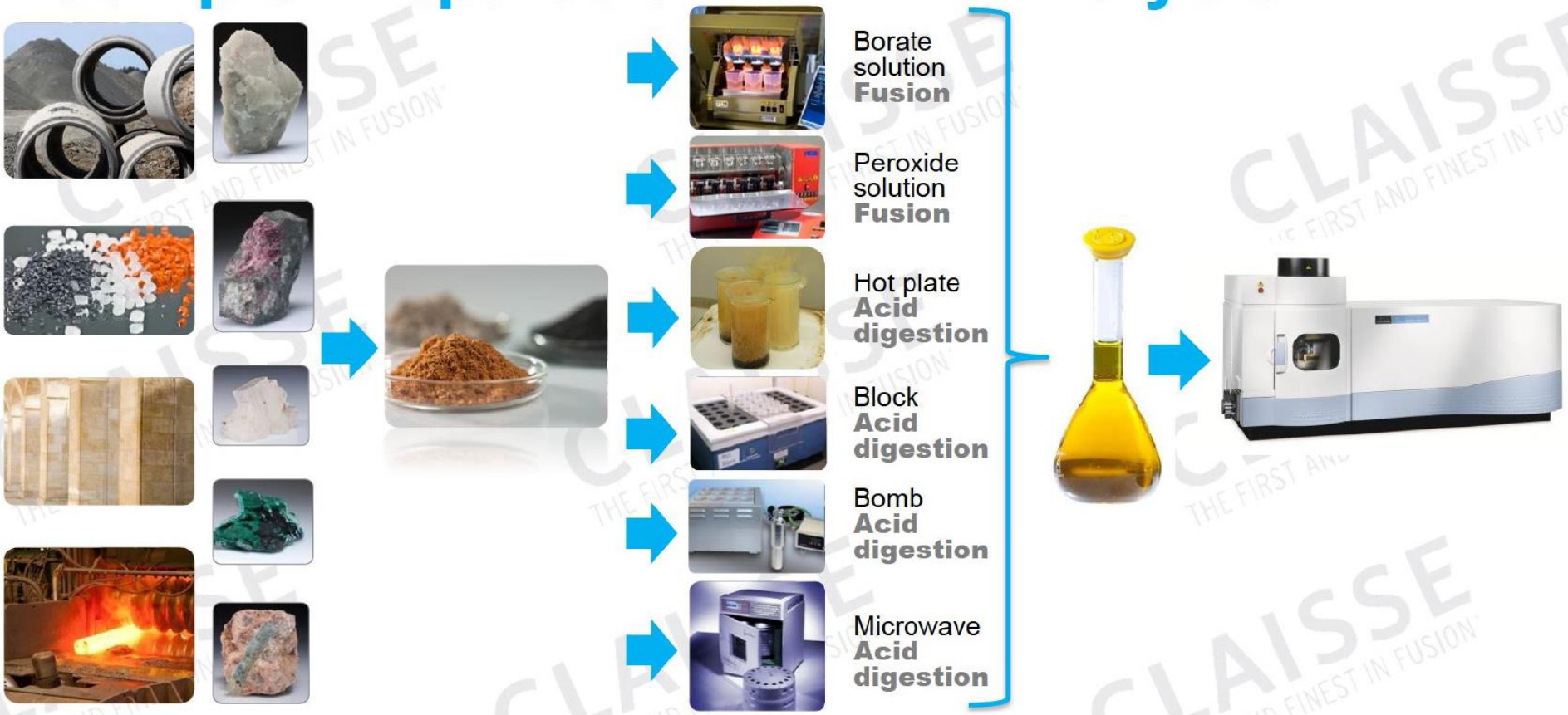
(Borate and Peroxide)

GAS

(Borate)

(Peroxide)

Sample Preparation for ICP Analysis



Typical Solution Fusion Procedure – Step 1

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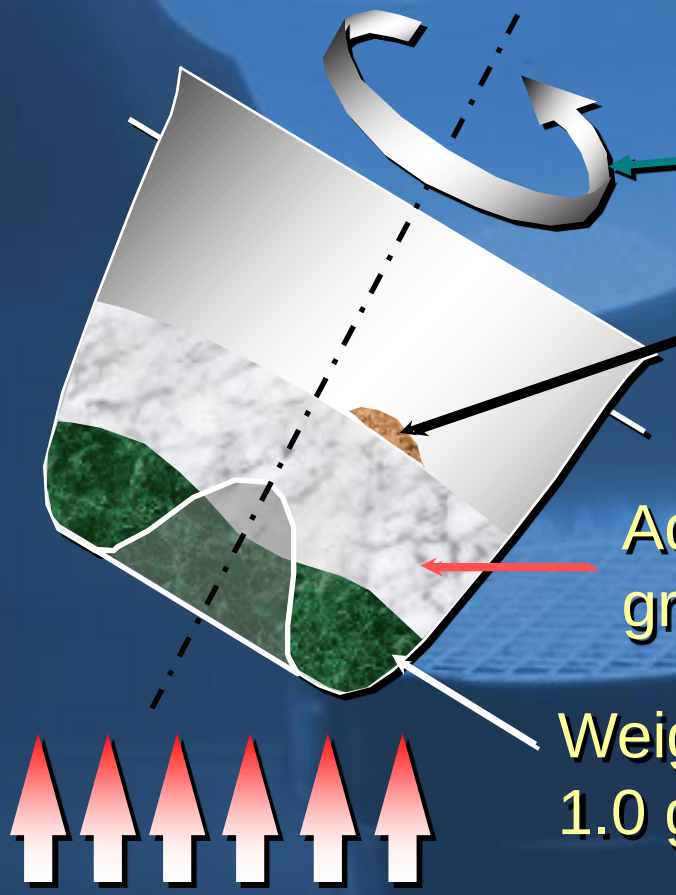


Rotate crucible on incline

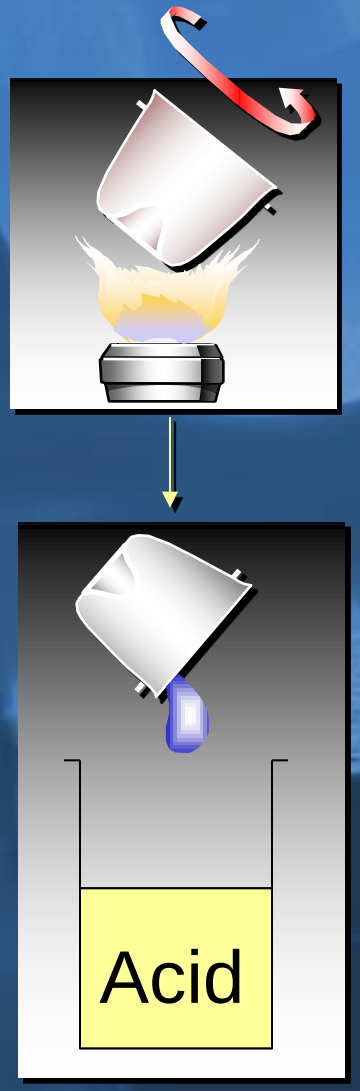
Add 0.20 g iodide or bromide on top

Add 0.15 g sample ground to -200 mesh.

Weigh into crucible 1.0 g LiM borate flux

Heat at 1000°C while agitating

Typical Solution Fusion Procedure – Step 2



Microwave digestion

Alpha-Alumina → Acids : H_3PO_4 and H_2SO_4; Time: 50 min

Tungsten oxide W_2O_5 → Acids : HF and HNO_3; Time: 40 min

Advantages over microwave digestion

Microwave

Al_2O_3:
Acids :H_3PO_4 and H_2SO_4

Time: 50 min

W_2O_5:
Acids : HF and HNO3

Time: 40 min

Fusion

Flux: Lithium metaborate

Time: 10 min

4 to 5x faster

Microwave digestion

(Chromite ore)

Step 1

Acids: H_3PO_4 and H_2SO_4
Time: 60 min

Step 2

Acids: HNO_3 and HF
Time: 35 min

Step 3

Acid: H_3BO_3
Time: 30 min

Time: 2hrs 5 min

5 different acids

Advantages over microwave digestion

CLAISSE

(Chromite ore)

Microwave

Time: 2hrs 5 min

5 different acids

Step 1
Acids: H_3PO_4 and H_2SO_4
Time: 60 min

Step 2
Acids: HNO_3 and HF
Time: 35 min

Step 3
Acid: H_3BO_3
Time: 30 min

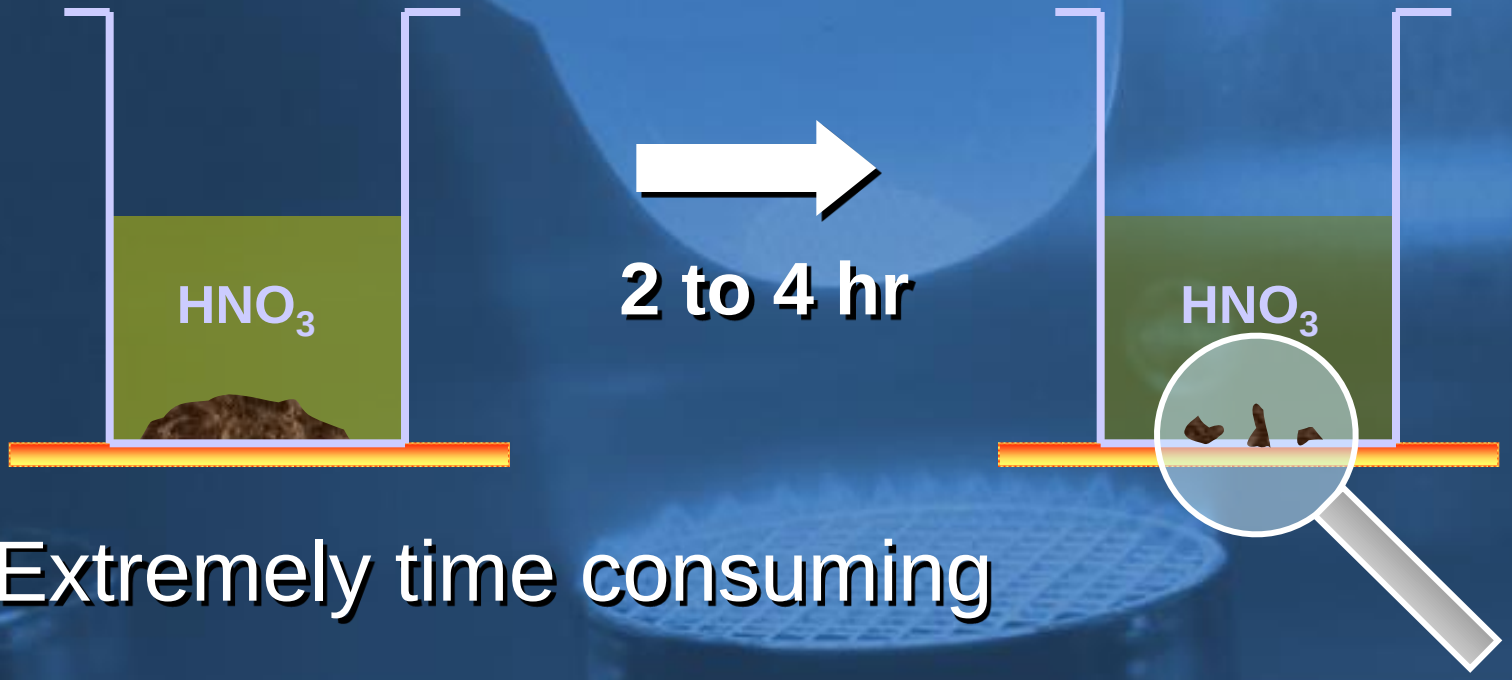
Fusion

Flux: Lithium metaborate

Time: 10 min

12x Faster

Hot plate acid digestion



- Extremely time consuming
- Low or partial dissolution (SiO_2, TiO_2…)

→ Low analytical accuracy

Advantages over hot plate acid digestion

- Complete dissolution of the sample → **High analytical accuracy**
- Easy to use
- Quick dissolution of the sample

→ **Time savings**

Money savings

12 to 20x Faster

Examples of Fusion Solutions

Bauxite

Catalyst

Copper

Ceramics

Peroxide Fusion

Peroxide fusion **transforms powders of pure metals**, **alloys**, **noble metals** and **highly refractory samples into acids solutions**. These solutions are analysed by ICP or AA.

Sodium peroxide is typically used, but a wide variety of fluxes can also be used.

These fusions are usually made in **zirconium** (Zr) or **nickel** (Ni) **crucibles**.

Here are the steps of the chemical reactions:

- Oxidation made on the Peroxide Fluxer instrument: $\mathrm{Na_2O_2} + E \xrightarrow{T \geq 460C} \mathrm{Na_2O} + EO$
- Reaction with water in solution: $Na_2O + EO + H_2O \rightarrow 2Na^+_{(aq)} + EO + 2OH^-_{(aq)}$
- Acidification: $EO_{(s)} + 2H^+ \rightarrow H_2O + E^{2+}_{(aq)}$

Peroxide fusion

- https://www.youtube.com/watch?feature=player_detailpage&v=OCji1uEoktk

ICP-OES Application

Peroxide Fusion Solution for the Determination of **Platinum, Palladium** and **Rhodium** in Automotive Catalytic Converters by **ICP Analysis**

Authors: Janice Pitre & Mélanie Bédard | Claisse

Quebec | Canada

METHOD

1 - Sample Preparation by Peroxide Fusion

CLAISSE® PEROXIDE™ FLUXER (Figure 1)

- Zirconium crucibles and covers (Figure 2)
- 0.25 g of ground sample
- 3.0 g of Sodium peroxide flux
- 3.5 minutes of heating at 600°C
- 4.0 minutes of cooling
- Dissolution in a HCl/HNO_3 solution (Figure 3)

FIGURE 1: Claisse® Peroxide™ Fluxer

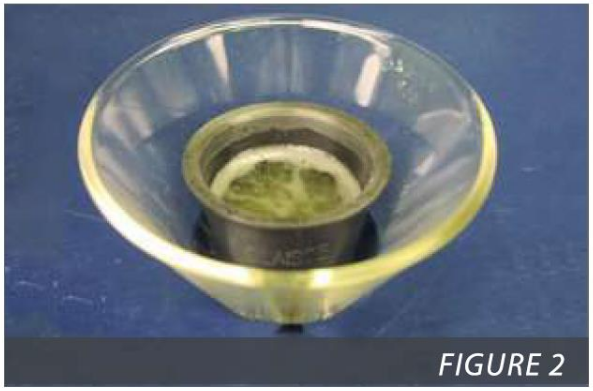


FIGURE 2

FIGURE 3

Benefits of Using Peroxide Fusion

Complete dissolution of samples	Versatile
Fast method - quick turnaround	Simple protocols
Safe (no health risks)	Only dilute acids are required
Very cost-effective - low labor costs	Simple waste management
Repeatable results	Method is not matrix-dependant
Clean method	Uses zirconium crucibles

Benefits of Using Borate Fusion

Only dilute HCl or HNO_3 is used

- No HF, no aquaregia and no $HClO_4$ required
- No large waste quantities
- No endless paperwork to fill for strong acids disposal

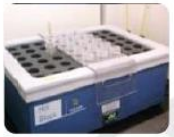
Dissolves within 12 minutes even the most refractory samples such as chromites, zeolites, silica, zircons and titanium oxides

Highly pure fluxes (99,995+%) allow to do some trace analyses

Benefits of Using Borate Fusion

Complete dissolution of even the most refractory samples (Zr, Cr, Si and Al oxides)	Versatile
Fast method - quick turnaround	Simple protocols
Safe (no health risks) - No HF	Only dilute acids are required
Very cost-effective - low labor costs	Simple waste management
Repeatable results	Method is not matrix-dependant
Completely automatic	Possible to identify some trace elements
Clean method	Reusable and recyclable labware
Automatic pouring of fused sample in dilute acid	Ultra high purity fluxes are available (99,995+%)

ICP Sample Preparation Method Comparison



	Hot plate **Acid digestion**	Block **Acid digestion**	Microwave **Acid digestion**	Bomb **Acid digestion**	Peroxide solution **Fusion**	Borate solution **Fusion**
Safe (no use of HF or perchloric acids)					++	++
Complete digestion/ dissolution of refractory samples					++	+
Big batches	++	+	+	+		
Fast throughput			+	+	++	++
Simple protocols					+	++
Temperature monitoring and some control			+	+	++	++
Automatic			+		+	++
Clean			+	+	+	++
Even heat distribution		+			++	++
Cheap	++	+				
Low labor costs			+	+	++	++
Methods are not matrix dependant					++	+

Basics of Sample Preparation by Fusion

Keys to success:

1. Sample oxidation
2. Flux selection
3. Flux / sample ratio
4. Particule size
5. Fusion temperature
6. The quality of the platinumware surface
7. Cooling rate (specific to XRF application)
8. Other special keys for ICP

Keys to success: 1. Sample Oxidation

Sample must be in its oxidized form in order to dissolve in the molten lithium-borate flux.

Three possibilities to develop a fully operational method **:**

1. High temperature ventilated furnace
2. Wet oxidation (HNO_3, LiOH…)
3. Solid dry oxidation on Fluxer

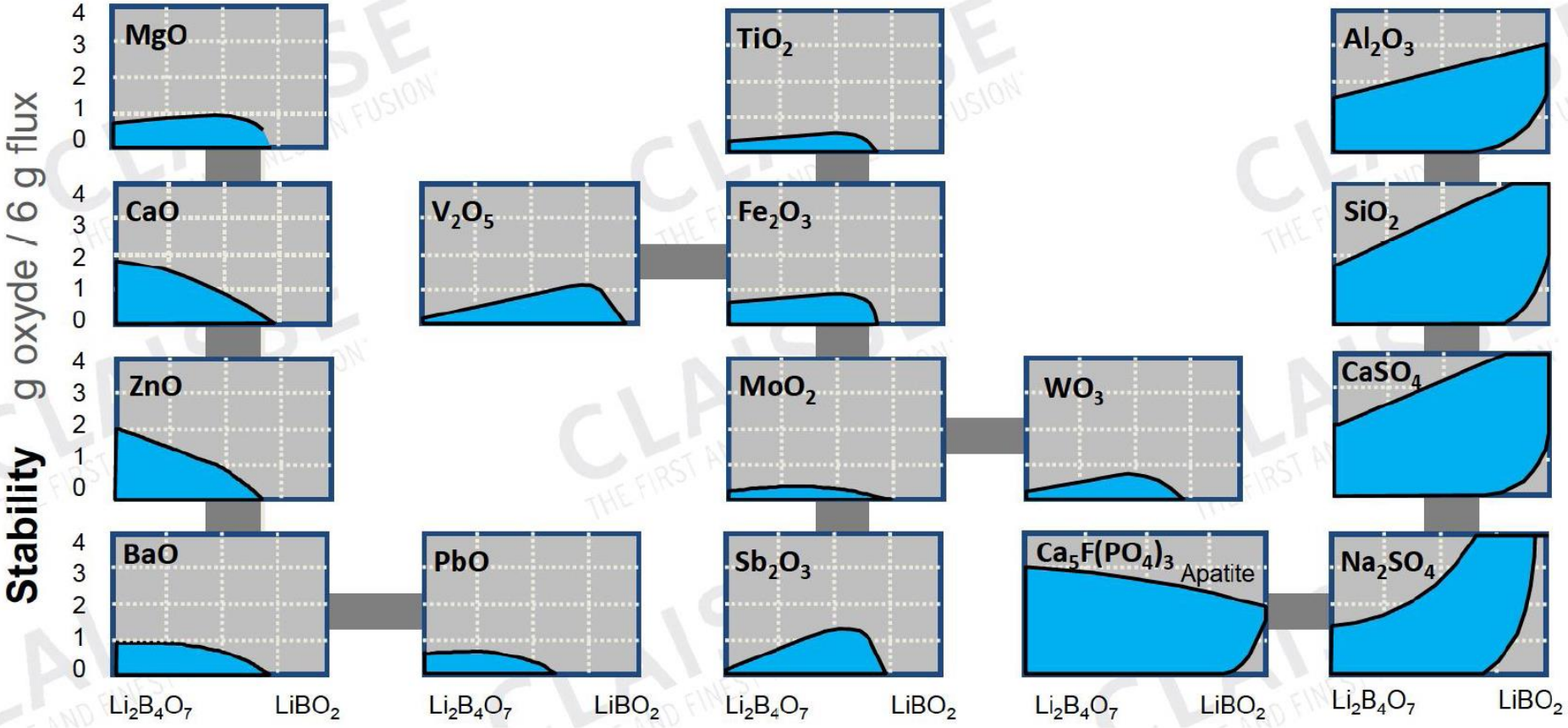
Platinová koroze

- Reakce platiny s dalšími prvky
- Platinové jedy: B, Si, P, S, Zn, As, Sn, Sb, Pb, Bi
- Nad 1 000 ℃ je napadána i oxidy železa a olova
- Nebezpečný je i uhlík, oxid uhelnatý, silná redukční činidla ► vzorek se musí oxidovat

Fusion = Benefits for your Laboratory

But There's More: Successful Fusions!

Keys to success: 2. Flux Selection



Fluxes

Two Main Products:

1. Lithium tetraborate ($Li_2B_4O_7$)
2. Lithium metaborate ($LiBO_2$)

Two Types of Fluxes:

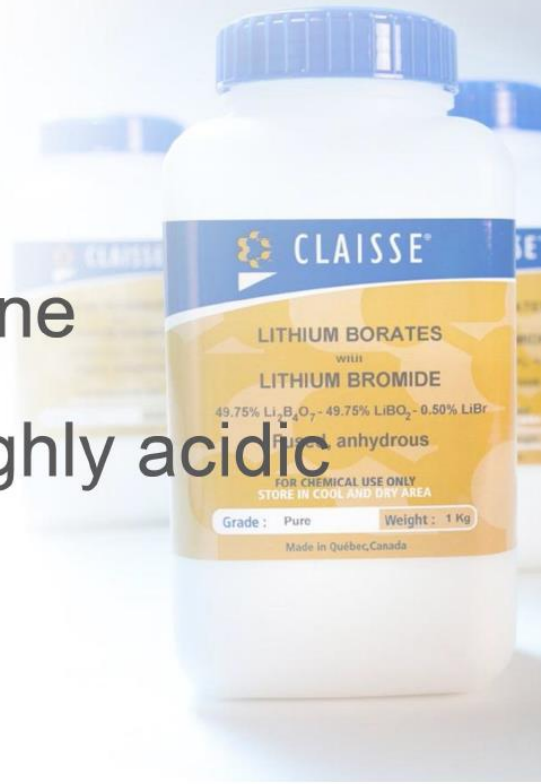
1. Powder
2. Pre-fused

Reminder: Lithium Tetraborate (LiT, $Li_2B_4O_7$)

- Acidic flux
- Melting point: 920°C
- Makes stable glass beads
- Best choice for the fusion of pure alkaline oxides
- Slightly hygroscopic
- Viscous

Reminder: Lithium Metaborate (LiM, $LiBO_2$)

- Basic flux
- Melting point: 849°C
- It will definitely crystallize if fused alone
- It will produce vitreous beads with highly acidic oxides
- Perfect to prepare solutions



Reminder: Mixture of Lithium Borates

- Lowers the melting point
- Higher fluidity = less sticking
- Stable glass beads
- Concentrations vary from 90% LiT / 10% LiM to 20% LiT / 80% LiM

It is the BEST option for most samples.

Non-wetting Agents

- Are also called releasing agents
- Are halides (Br, I…)
- Can be added as salt and solution or are already pre-fused with flux or pills
- Affect the tension of the surface
- Decrease the tendency to stick

Basic Concept

You can predict the best choice of flux by using a basic chemical model:

The acidity / alkalinity equilibrium

An **ACIDIC** sample requires an **ALKALINE** flux
and
an **ALKALINE** sample requires an **ACIDIC** flux

Calculating the Acidity Index

$$\text{Acidity index} = \frac{X}{Y} \quad \frac{\text{Oxygen atoms}}{\text{Other atoms}}$$

Lithium tetraborate ($Li_2B_4O_7$ ACIDIC)

$$\text{Acidity index} = \frac{7}{6} = \boxed{1.17}$$

Lithium metaborate ($LiBO_2$ ALKALINE)

$$\text{Acidity index} = \frac{2}{2} = \boxed{1.00}$$

Calculating the Acidity Index of a Mixture

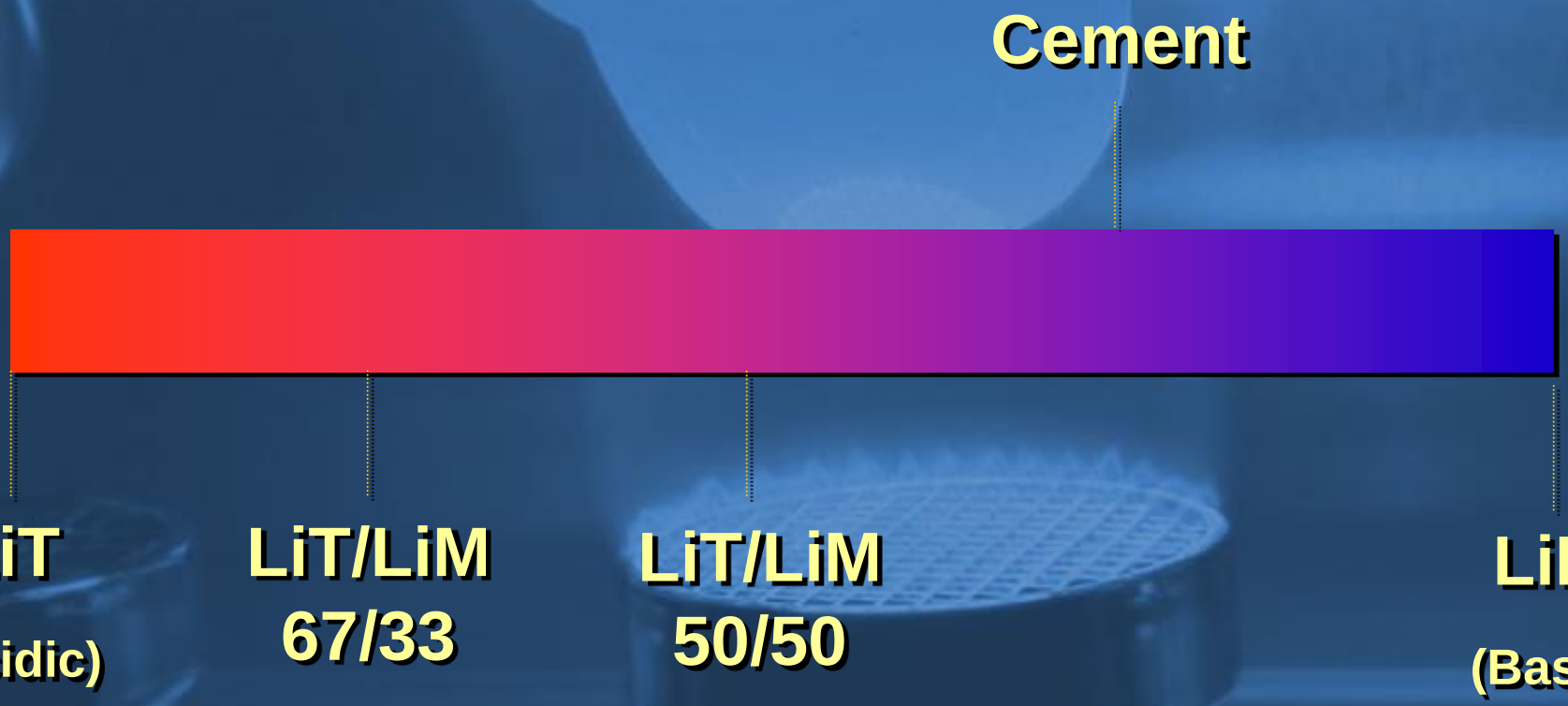
$$\text{Overall acidity index} = \frac{Qty_A \, X \, AI_A + Qty_B \, X \, AI_B}{Qty_{tot}}$$

Flux mix, e.g. 67%LiT / 33%LiM

$$\frac{0.67 \;\; X \; 1.17}{1.0} + \frac{0.33 \;\; X \; 1.00}{1.0} = \boxed{1.11}$$

Important parameters to consider during fusion

1. Flux selection



Examples of How to Calculate the Acidity Index

Calcium oxide (CaO ALKALINE)

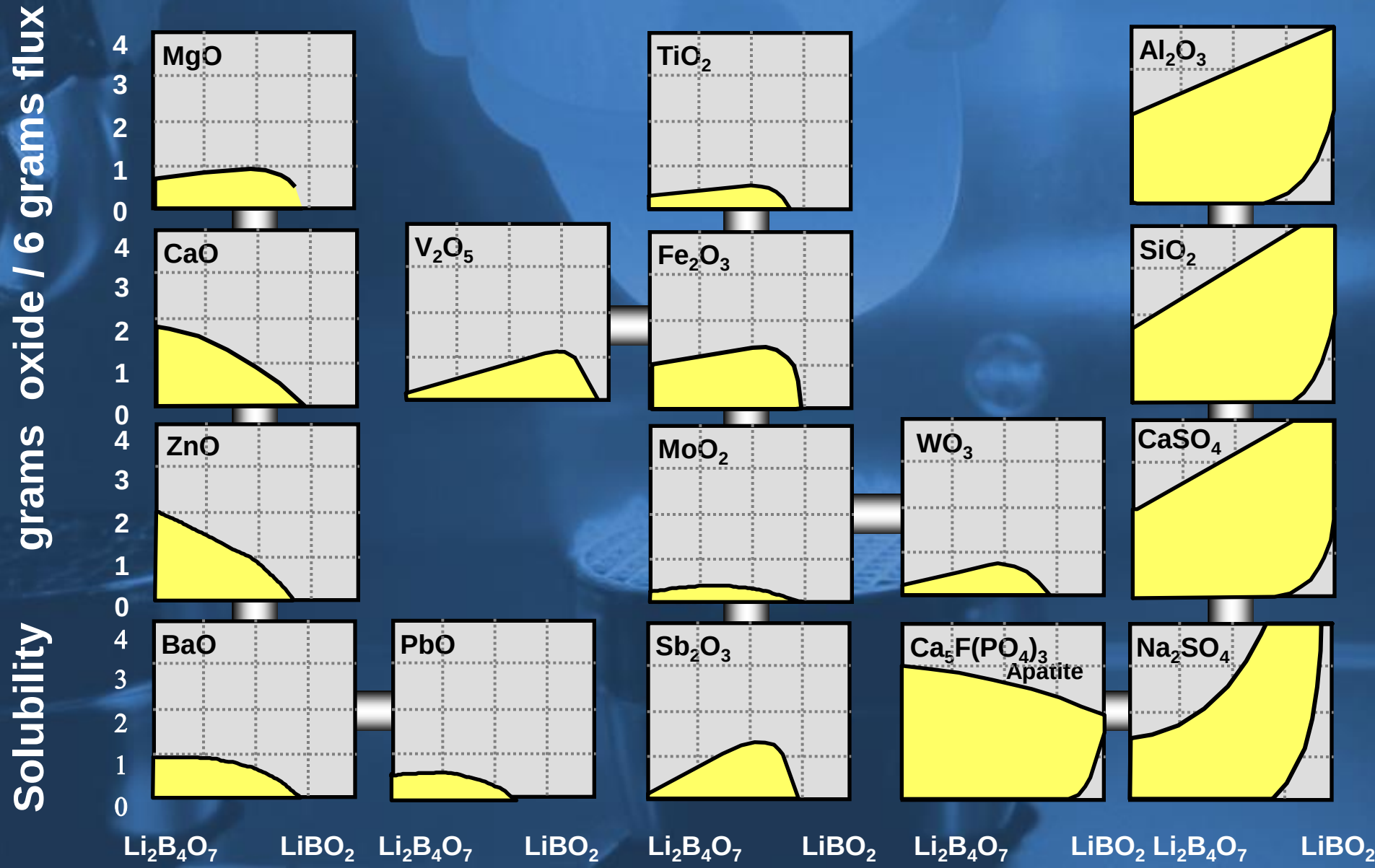
$$\text{Acidity index} = \frac{1}{1} = \boxed{1.00}$$

Iron oxide (Fe_2O_3 ACIDIC)

$$\text{Acidity index} = \frac{3}{2} = \boxed{1.50}$$

Important parameters to consider during fusion

1. Flux selection



Keys to success: 2. Flux Selection

- Optimizes solubility of the sample
- Glass disk stability
- Appropriate melting point
- Better fluidity
  - Accelerates dissolution
  - Better pouring
  - Less sticking on the platinum
  - Retains less bubbles

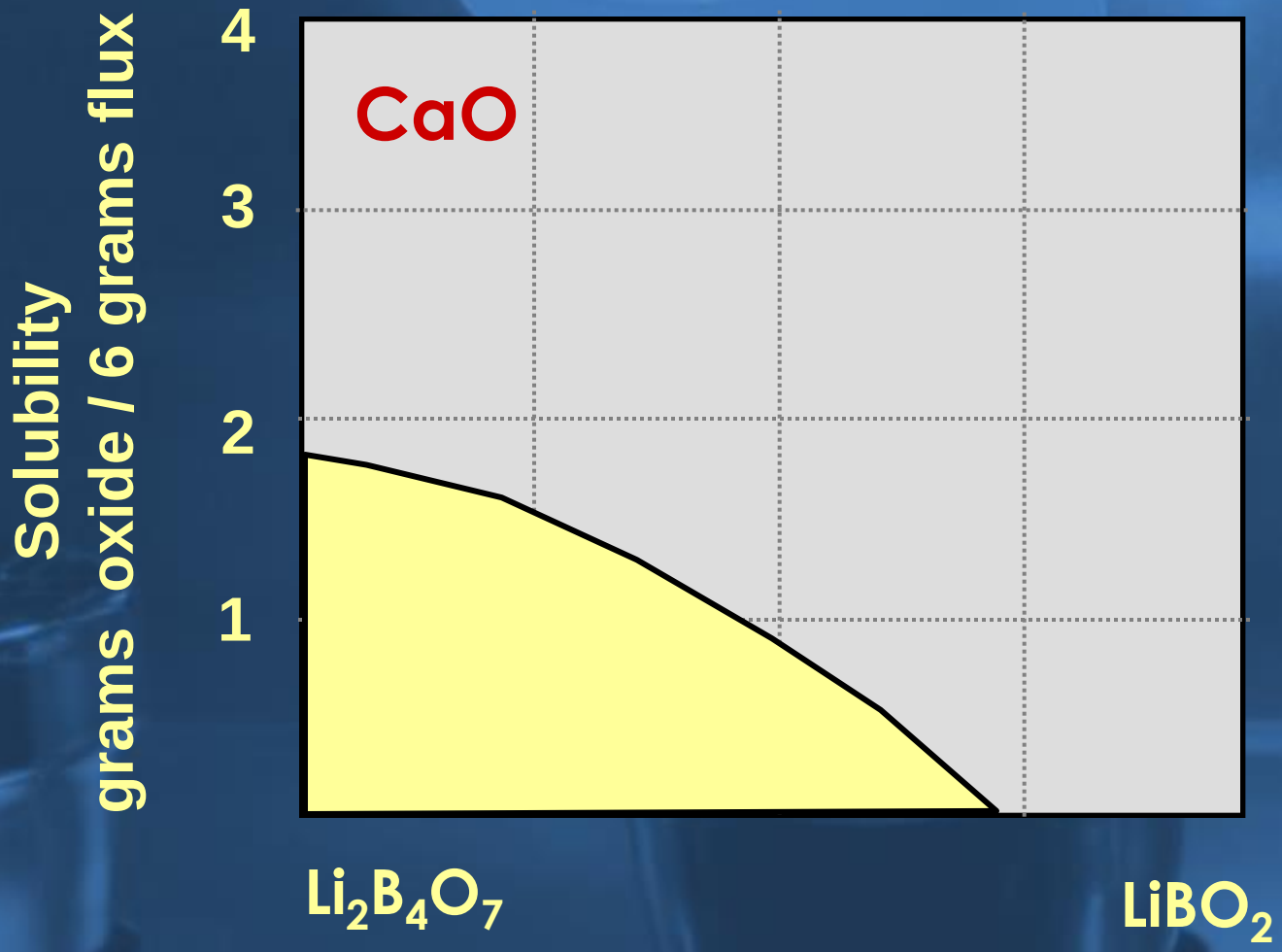
Fe_2O_3 with LiT

Fe_2O_3 with 50/50

Fe_2O_3 with LiM

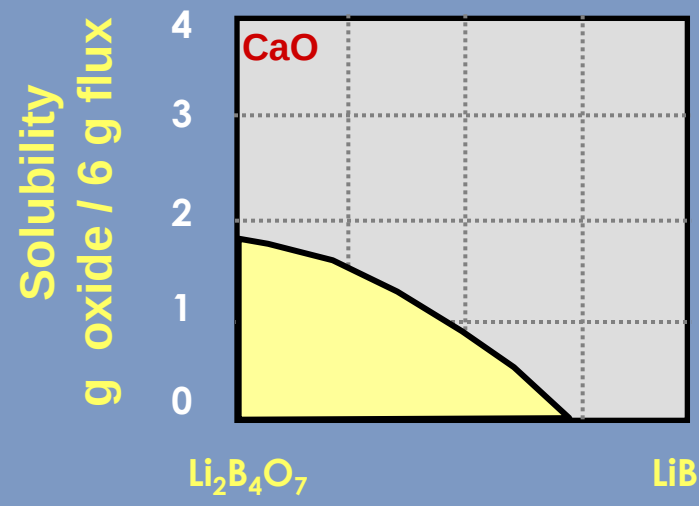
Important parameters to consider during fusion

1. Flux selection

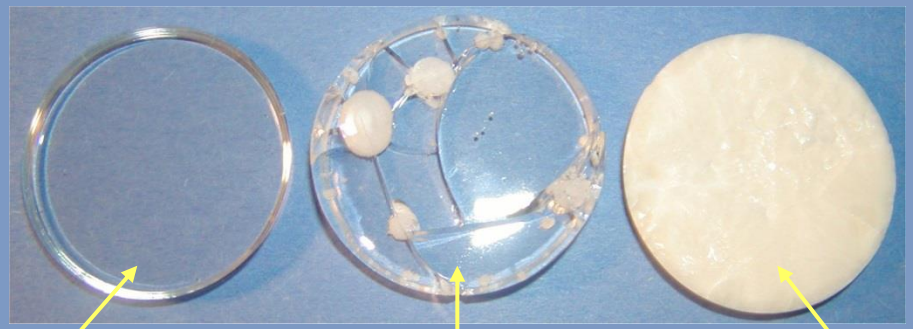


Important parameters to consider during fusion

1. Flux selection



$$CaCO_{3(s)} \xrightarrow[825\ ^oC]{\Delta T\uparrow} CaO_{(s)} + CO_{2(g)}$$



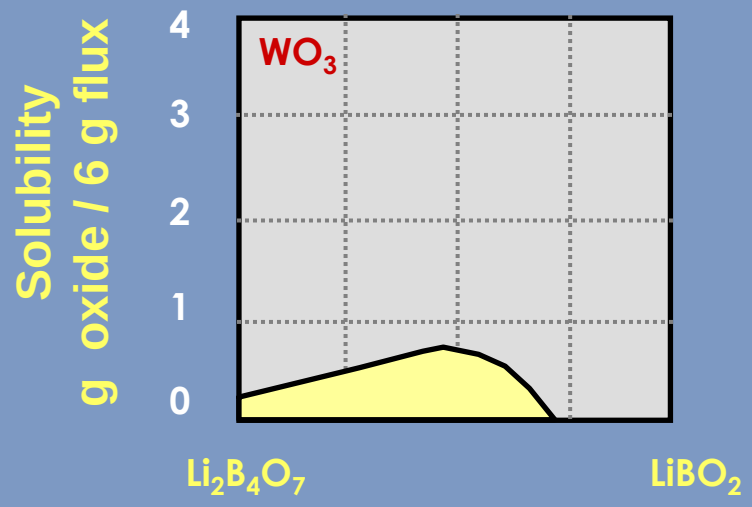
$CaCO_3$ with LiT

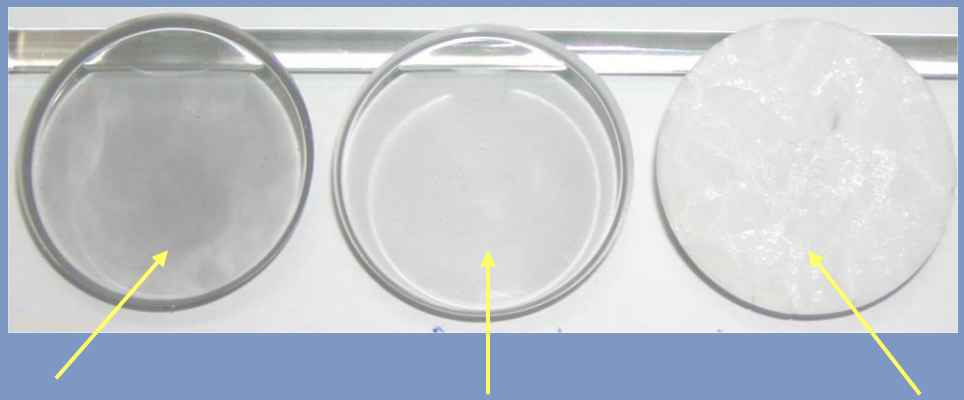
$CaCO_3$ with 50/50

$CaCO_3$ with LiM

Important parameters to consider during fusion

1. Flux selection





WO_3 with LiT

WO_3 with 50/50

WO_3 with LiM

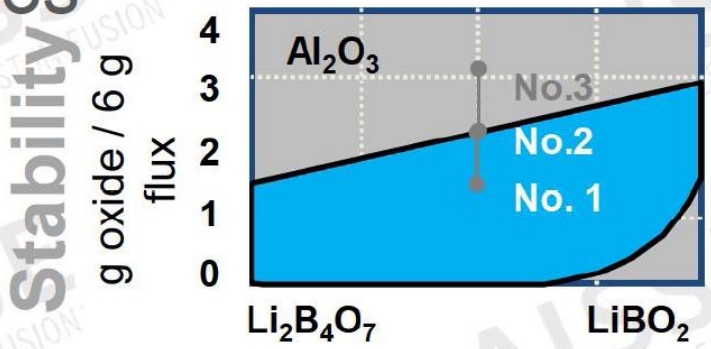
We Recommend

Cement	→	67/33 or 50/50
Ceramic	→	50/50 to 35/65
Catalyst	→	67/33 to 35/65
Limestone	→	67/33
Iron ore	→	50/50
Alumina	→	35/65

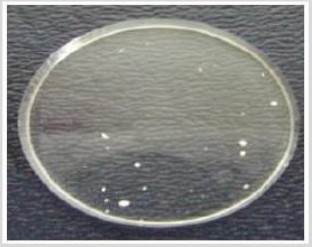
Keys to success: 3. Flux / Sample Ratio

Same sample but different ratios

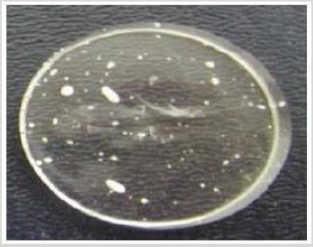
SAMPLE:	1.0 - 3.0 g
FLUX:	6.0 g



1 g Al_2O_3



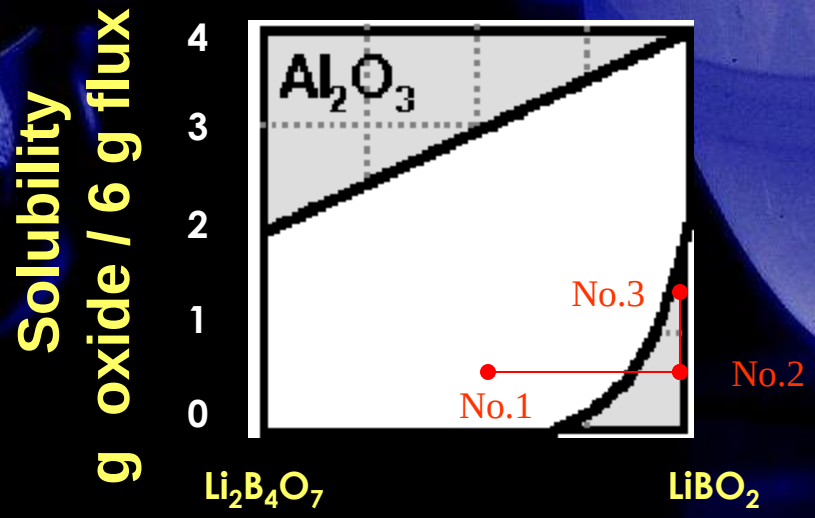
2 g Al_2O_3



3 g Al_2O_3

2. The sample/flux ratio

Example of an alumina fusion



Mix composition

No.1 Sample : 0.5 g
Flux (50/50): 6.0 g

No.2 Sample : 0.5 g
Flux (LiM): 6.0 g

No.3 Sample : 1.5 g
Flux (LiM): 6.0 g

Results :

No.1 No.2 No.3

It is inadvisable to use a ratio lower than 20/80 of LiT/LiM

2. The sample/flux ratio

Saturated glass disk

Undissolved particles

Over-saturated particles

Glass disks made from cement samples

Keys to success: 4. Particule Size

Smaller particles are easier to oxidize and are dissolved faster

Coarser than 100µm

Incomplete oxidation + Cracking

Finer than 100µm

Complete oxidation and dissolution

Keys to success: 5. Fusion Temperature

Melting and dissolving are two different phenomena:

In a fusion context, the flux must MELT before the sample can DISSOLVE into the molten flux

Importance of fusion temperature

HIGH temperature (>1050°C)

- Loss of volatile elements (Na & SO_3) and non-wetting agent
- Loss of flux by volatilization
- Platinum deterioration

LOW temperature (<1050°C)

- Negligible loss of material
- Higher accuracy
- Retention of SO_3 & Na

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A thermogravimetric analysis study of volatilization of flux mixtures used in XRF sample preparation†

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This paper deals with the thermal behaviour occurring during the formation of lithium borate glasses. Thermogravimetric analysis and differential scanning calorimetry were employed to identify reactions occurring during fusion in pure flux mixtures. The conditions around the identified reactions were reproduced in a muffle furnace to obtain larger quantities of material for further investigation using spectroscopic techniques. It was shown that above 1050 °C lithium borate fluxes volatilize, which could lead to inaccurate analytical results.

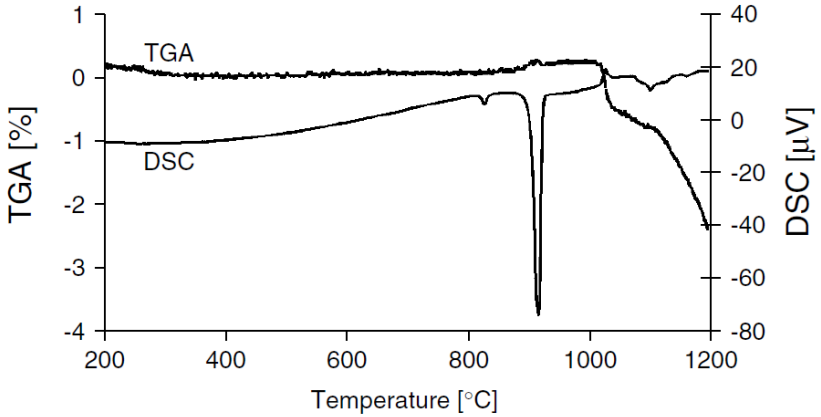


Figure 1. TGA and DSC curves for lithium tetraborate: source A.

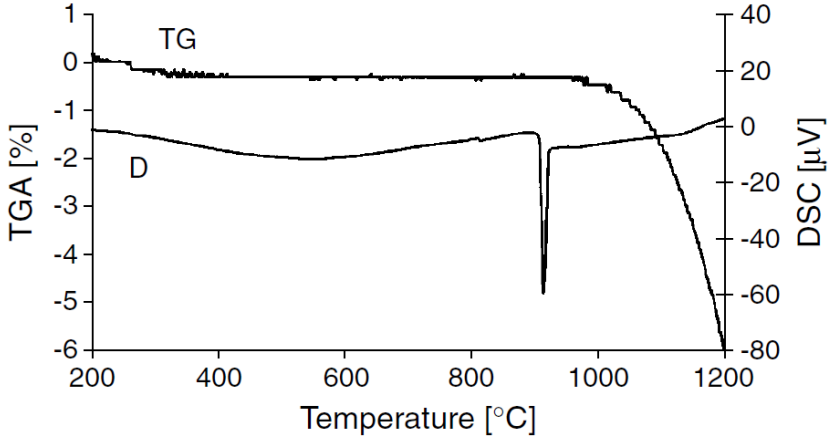


Figure 2. TGA and DSC curves for lithium tetraborate: source B.

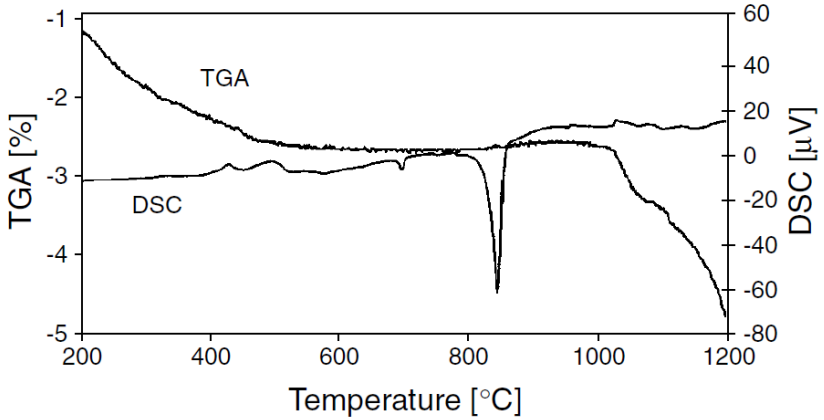


Figure 4. TGA and DSC curves for lithium metaborate: source A.

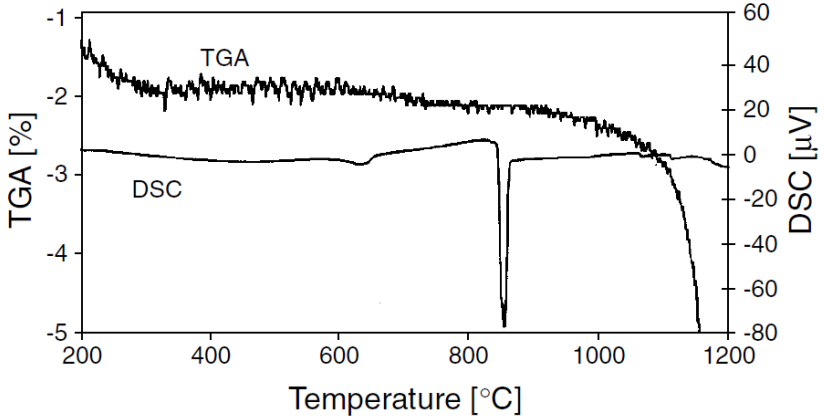


Figure 5. TGA and DSC curves for lithium metaborate: source B.

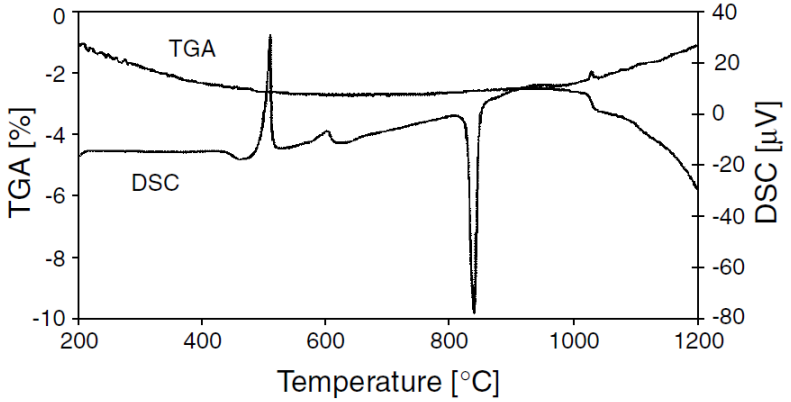


Figure 7. TGA and DSC curves for 20%$Li_2B_4O_7$–80%$LiBO_2$: source A.

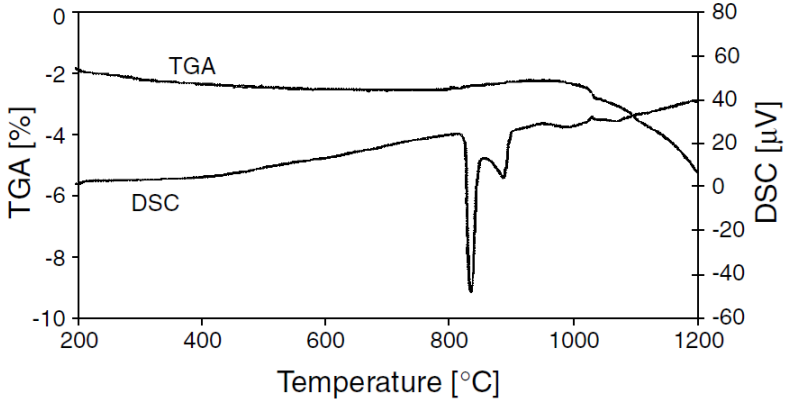


Figure 8. TGA and DSC curves for 66%$Li_2B_4O_7$–34%$LiBO_2$: source A.

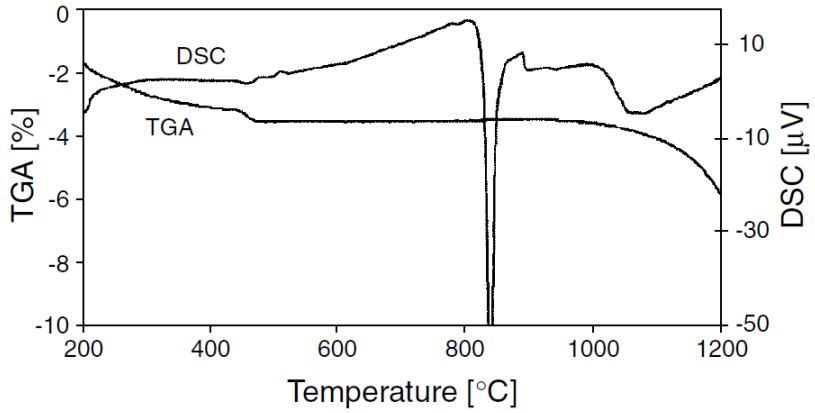


Figure 10. TGA and DSC curves for 35%$Li_2B_4O_7$–65%$LiBO_2$: source D.

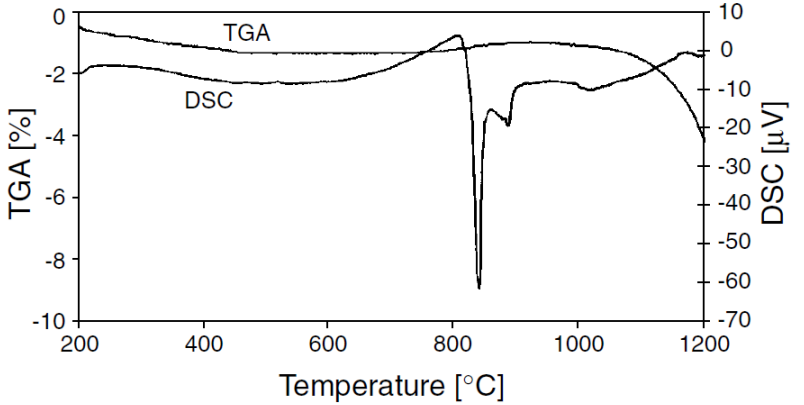


Figure 11. TGA and DSC curves for 57%$Li_2B_4O_7$–43%$LiBO_2$: source D.

3. The fusion temperature

HIGH Temp. >1100°C :

- loss of non-wetting agent results in sticking in molds and crucibles, and cracking of beads
- loss of flux by volatilization results in low reproducibility, low accuracy, *saves only 2 min* in the fusion process
- variable loss of alkali elements by volatilization from samples causes non-systematic errors

LOW Temp. <1000°C:

- no loss of matter except highly volatile elements
- retention of SO_3 sulfur
- best accuracy
- disks can be remelted (standards)

5. The undissolved particles

Problem: Undissolved particles can initiate crystallization.

Solution: -Change the flux

- Increase the fusion time
- Use an oxidizer

The glass disk looks like a spoke wheel

Slag sample

5. The undissolved particles

Problem: Fused beads with dark clouds.

Cause: - Presence of carbon

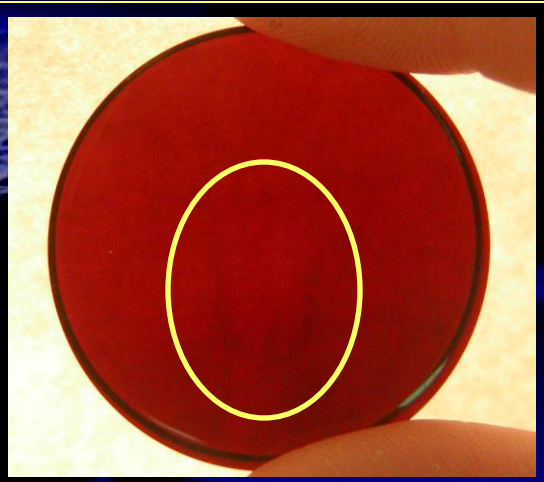
- Presence of sub-oxidized compounds such as Fe^{2+}.

Implication : Decrease of reproducibility.

Solution:

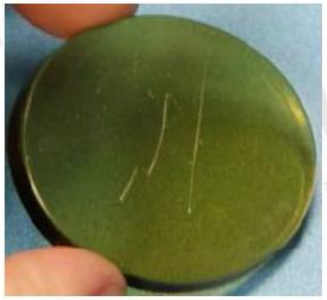
- The use of an oxidizer will assure the transformation of the compound to its maximum oxidation state.
- Another solution would be to ameliorate the crucible agitation.

Slag sample



Iron ore sample

Keys to success: 6. The Quality of the Platinumware Surface



Influences the distance travelled by the X-rays

Affects: elemental intensities

Sticking on the platinum crucible wall

Affects: Affects melt homogeneity and fusion success rate

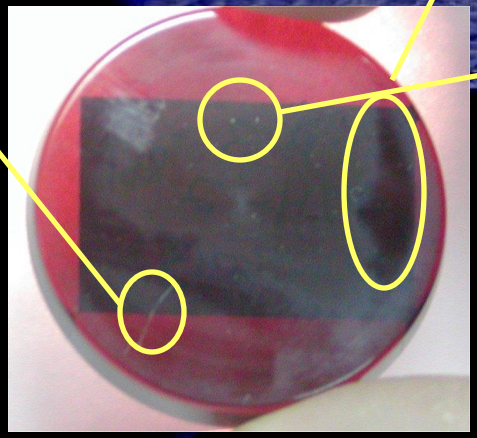
7. The quality of the mould surface

Examples of surface damage

Scratches

Tarnished spots

Pitting



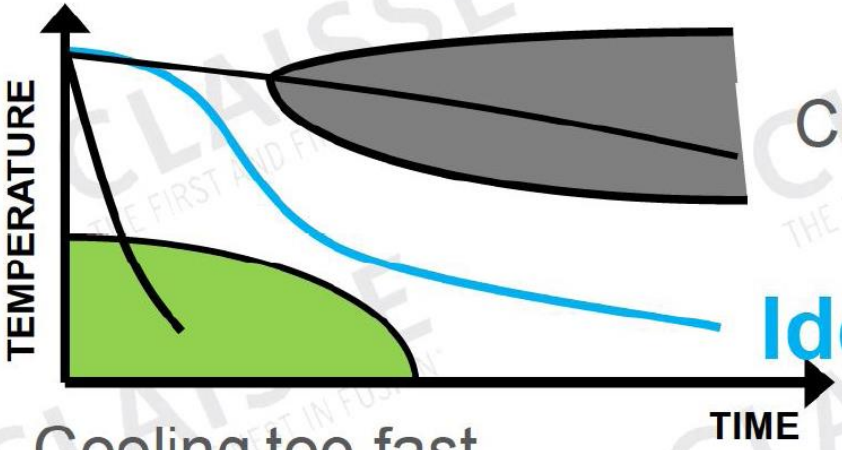
Glass disk made from an iron ore sample

Important parameters to consider during fusion

7. Quality of the mould surface

%CaO	%CaO	%CaO
64.07	63.62	63.22
64.22	63.72	63.05
64.18	63.72	63.05
63.96	63.58	63.15
64.07	63.50	63.42
64.18	63.54	63.16
64.11	63.74	63.17
64.16	63.43	63.14
64.04	63.59	63.19
Average 64.11	63.60	63.17
Std 0.08	0.11	0.11
RSD% 0.13	0.17	0.17

Keys to success: 7. Cooling Rate (Glass Disk) Specific to XRF Application



Cooling too slow

Ideal cooling rate

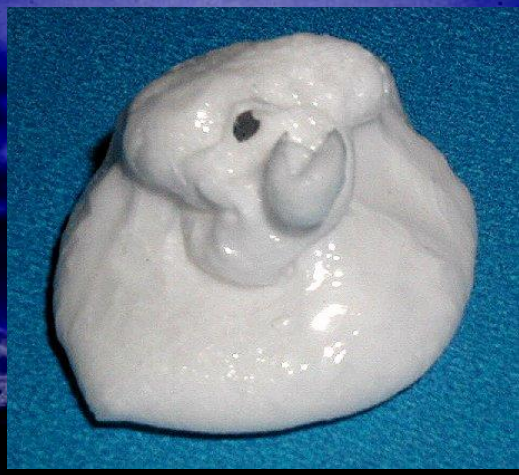
Cooling too fast

8. The influence of the mold temperature

Problem : Volcano-disk

Causes : If the platinum mold is too cold at the moment of pouring, the melt will instantaneously solidify yielding to crystallization and a huge volcano effect.

Solution : Increase the mold temperature



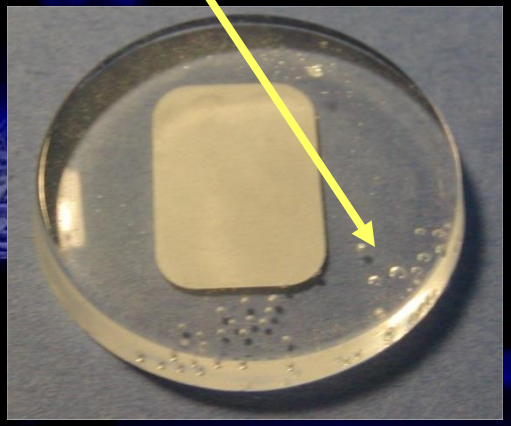
8. The influence of the mold temperature

Problem : Bubbles at the mold surface

Causes : If the platinum mold is hot at the moment of pouring, the non-wetting agent will volatilize

Solution : Decrease the mold temperature.

Bubbles



9. Others...

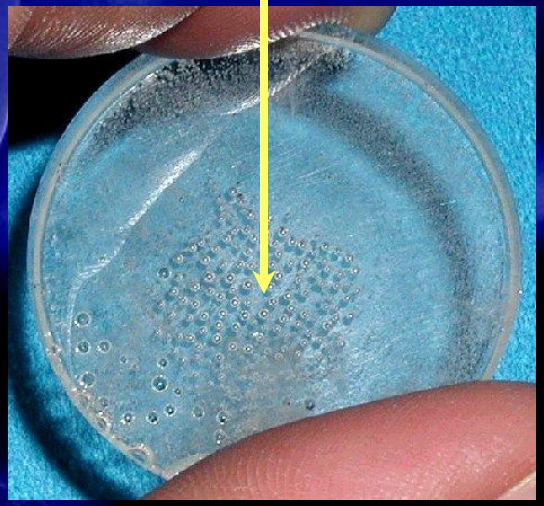
Problem : Cloud of bubbles well distributed in the bead.

Causes : If a sample is not fully dehydrated or contains elements that decompose and volatilize during fusion (e.g..: $CaCO_3$), bubbles are produced and retain in the glass disk.

Solution : -Calcinate the sample prior the fusion

-Place the sample above the flux in the crucible and heat slowly at the beginning of fusion.

Cloud of bubbles

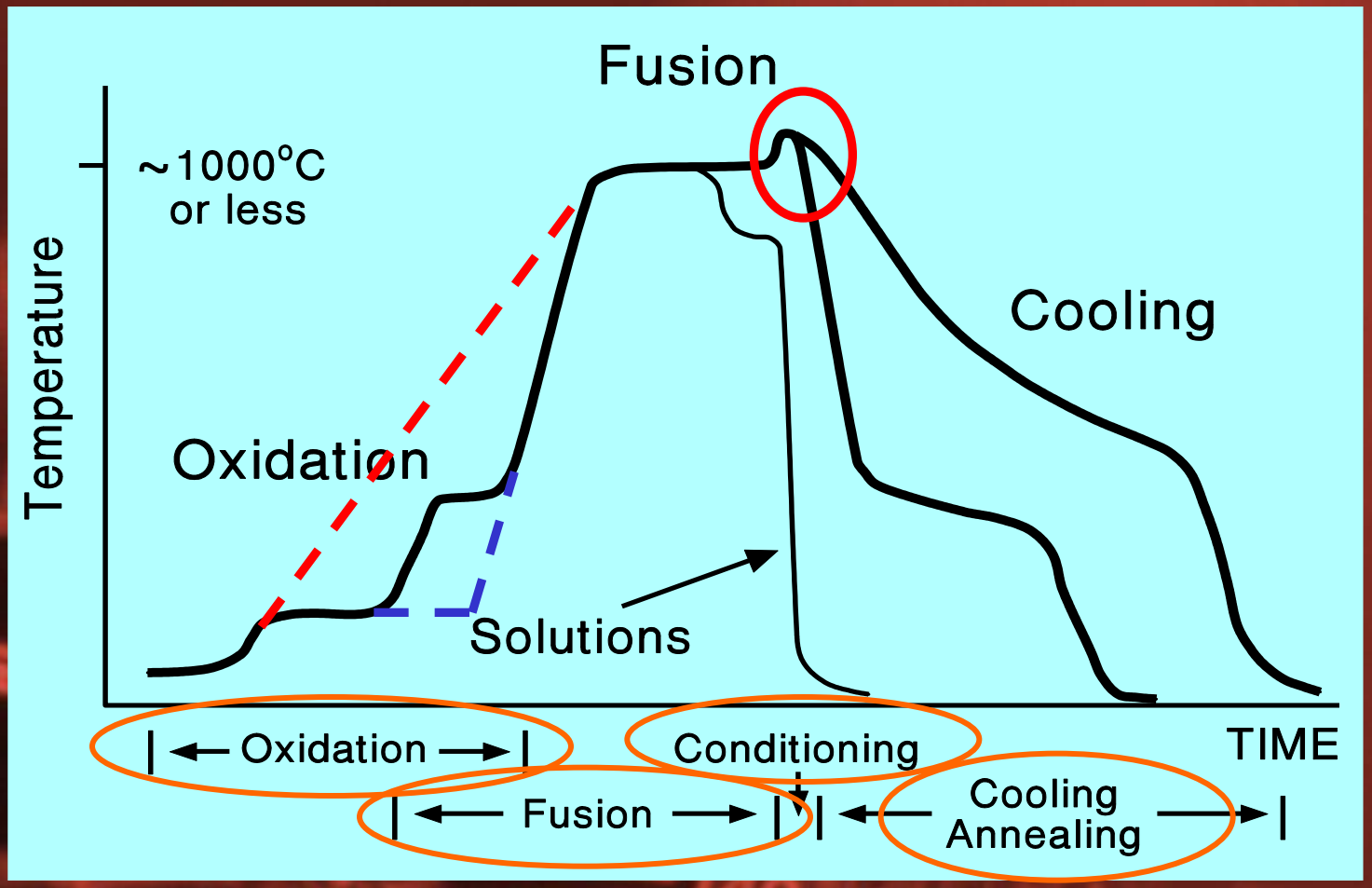


Glass disk bearing many bubbles on its surface

Keys to success: 8. Other Special Keys for ICP Analysis

- TDS must be lower than 1 % on an optical ICP and lower than 0,2 % on an ICPMS– Dilution is necessary
- Reduction of the sample residence time in the plasma
- Use a high energy plasma to avoid deposits on the ICP-OES torch
- Increasing the argon flow rate
- Decreasing the sample flow rate
- Selection of proper sample introduction components:
  - Cyclonic spray chamber
  - Meinhard nebulizer

Fusion basics



Conclusion

- Sample preparation by fusion is a fast and reliable method
- Many different samples can be processed with a single sample preparation method
- Automated method leads to repeatable and precise results
- Possible use of synthetic or pure oxides for calibration

Sample Preparation by Fusion Allows a Quick ROI

- Facilitate routine analysis
- Increase analysis throughput
- Improve the quality of results
- Save time and ressources
- Save money

Fluxes

Two Main Products:

1. Lithium tetraborate ($Li_2B_4O_7$)
2. Lithium metaborate ($LiBO_2$)

Two Types of Fluxes:

1. Powder
2. Pre-fused

Powder Flux

- Fluffy
- Low density (0.3 to 0.5 g/cm^3)
- Segregation possible when LiT and LiM are mixed
- More hygroscopic
- Lower cost

Pre-fused Flux (Fused Vitreous Beads)

- Uniform glass beads
- High density (1,4 g/cm^3)
- No segregation, uniform mixture
- Anhydrous, non-hygroscopic
- Available with NWA (non-wetting agent)
- Stable over time

It is the best option for sample preparation by fusion.

Purity

- Pure: 99,98%
- Ultra pure: 99,995+%

Fusion = Benefits for your Laboratory

But There's More: Successful Fusions!

Fusion = Benefits for your Laboratory

But There's More: Successful Fusions!

LeNeo® Claisse Fluxer®

- Quick return on investment (ROI)
- High performance single position:
- Resistance electric heating
- Safe (fully automated)
- Simple to use

All in a Single Fusion Instrument!

+

Glass disks: XRF

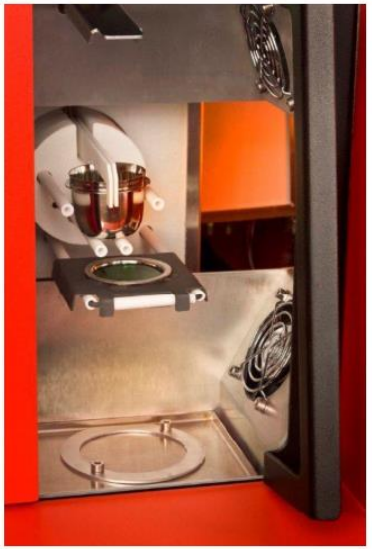
Solutions (borate): ICP

Solutions (peroxide): ICP

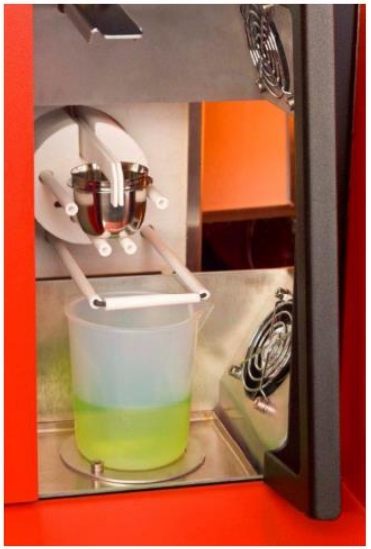
Three Different Preparation Modes

Benefits:

- Lower operational cost
  (three instruments in one)
- Easy to use



Glass disks:
XRF



Solutions
(borate): **ICP**

Solutions
(peroxide): **ICP**

LeNeo Video

- https://www.youtube.com/watch?feature=player_embedded&v=mZm1rONx6sk

Ready to Use Right Out of the Box!

- Easy installation – Quick ROI
- Small and compact

Height	52 cm (20.5 in.)
Depth	55 cm (22 in.)
Width	55 cm (22 in.)
Weight	36 kg (80 lb.)

- Electric

Voltage	208-240 V	230 VAC
Current	20 A	20 A
Frequency	50/60 Hz	50 Hz

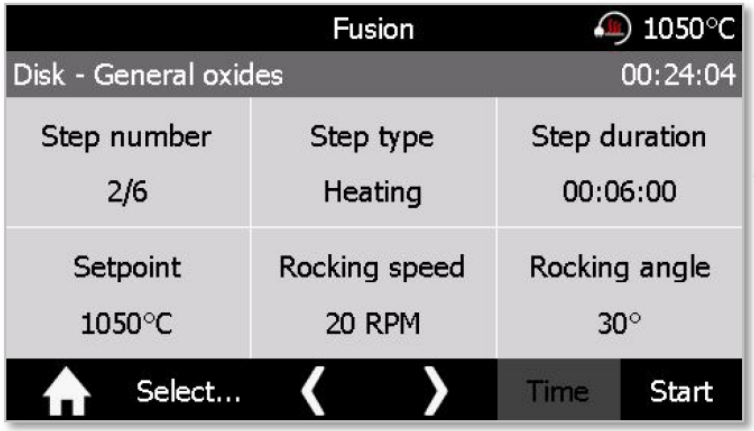
Benefits: Low cost of ownership and quick ROI

Ready to Use Right Out of the Box!

- Intuitive touch screen interface (android/iOS feel)
- The temperature is displayed at any moment during the fusion cycle
- Easy monitoring of the fusion cycle progression (display of remaining time or fusion step progression)
- **Benefit: Ease of use**

Real time temperature

Remaining time



Progression of the fusion process

CLAISSE
THE FIRST AND FINEST IN FUSION®

LE neo FLUXER®

High Analytical Performances

- Mining and geological samples
- Cosmetics, pharmaceutical and environmental samples
- Cement, lime, limestone, carbonates, clay
- Pure metals, non-ferrous alloys, silicon carbide
- Chromite, cobaltite, dolomite, ilmenite, rutile, molybdenite
- Refractories, silica, silicates, glass, ceramics
- Potash, phosphates, fertilizers
- Polymers, pigments
- Steel, ferroalloys, slags
- Coal, ashes
- Hematite, magnetite, iron ores
- Rare earth elements
- Bauxite, alumina
- Autocatalysts, zeolites
- Noble metals
- Sulfides, fluorides

High Analytical Performances: Fusion Programs

The user can choose among ten preset fusion programs:

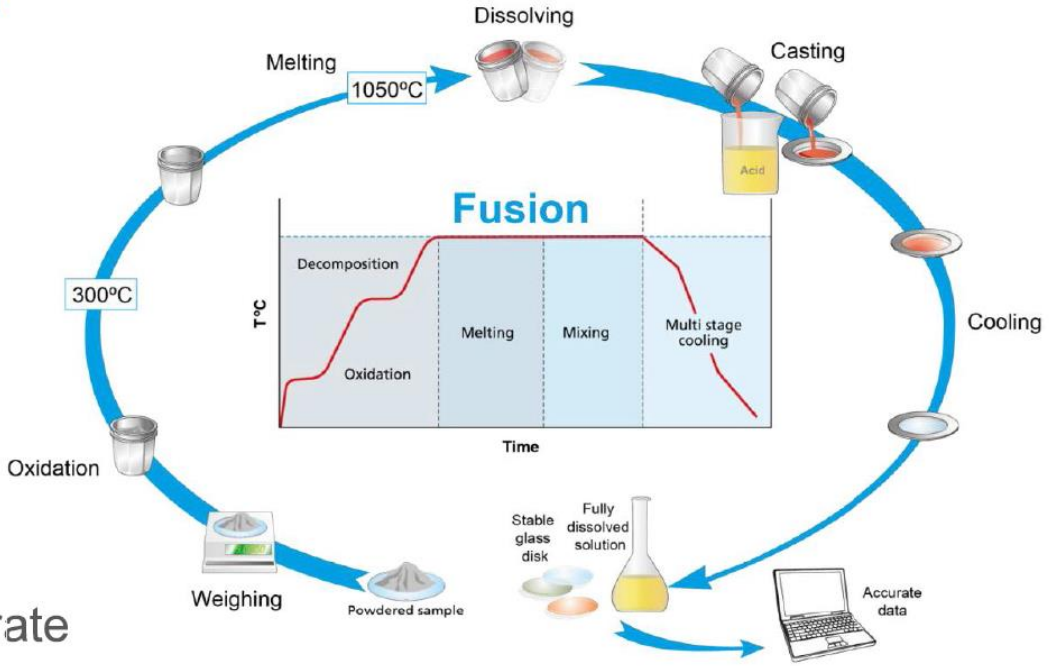
- Glass disks: Cement and raw materials, high refractory materials, volatile elements, etc.
- Borate solutions
- Peroxide fusions

Or the user can create his own fusion program:

- 8 GB compact flash memory storage

High Analytical Performances: Adaptable Fusion Parameters

- Time
- Temperature
- Agitation speed
- Agitation angle
- Cooling fan speed
- Four different pouring modes (on/off vibration and crucible position after pouring)
- Controlled or maximum heating rate

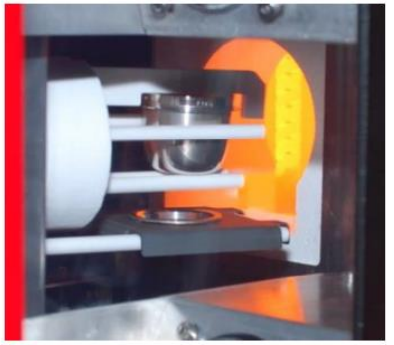


Benefits: High fusion success rate and quick ROI

Additional Features:

- Pre-heat timer
- Heat shut-off timer
- Temperature monitoring
  - 1 x Thermocouple inside heating chamber
  - 1 x Thermocouple between the refractory layers

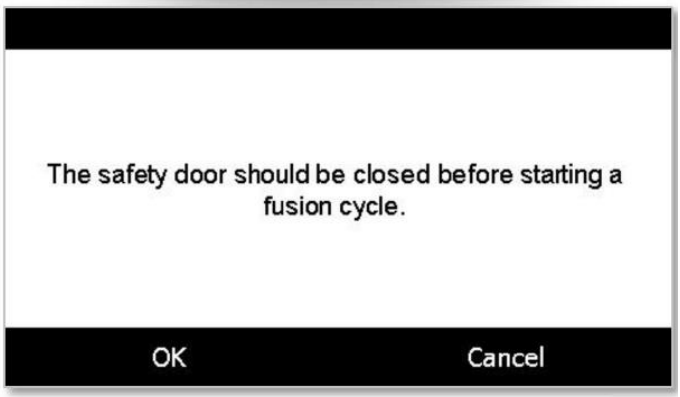
Benefit: Productivity and quick ROI



Safe Operation

- Fully automated pouring:
  - No manipulations of hot vessels
  - No direct exposure to heat
  - Reproducible
  - Operates without any supervision
- Safety door

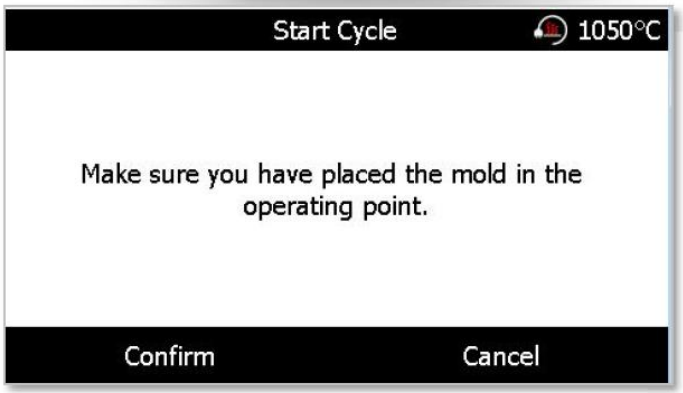
Benefit: Operator security



Safe Operation

- Emergency stop button
- Mold installation confirmation by the user
- Three secured access levels
  (to be granted according to the operator's skills):
  - Method selection and Start/Stop
  - Method development / heating and pouring modes
  - Service

Benefits: Operator security



Designed for your needs

- Customer's autonomy regarding routine maintenance
- Quick and easy replacement of:
  - Heating elements
  - Refractory plates
  - Alumina rods

Benefit: Low cost of ownership, low downtime and quick ROI