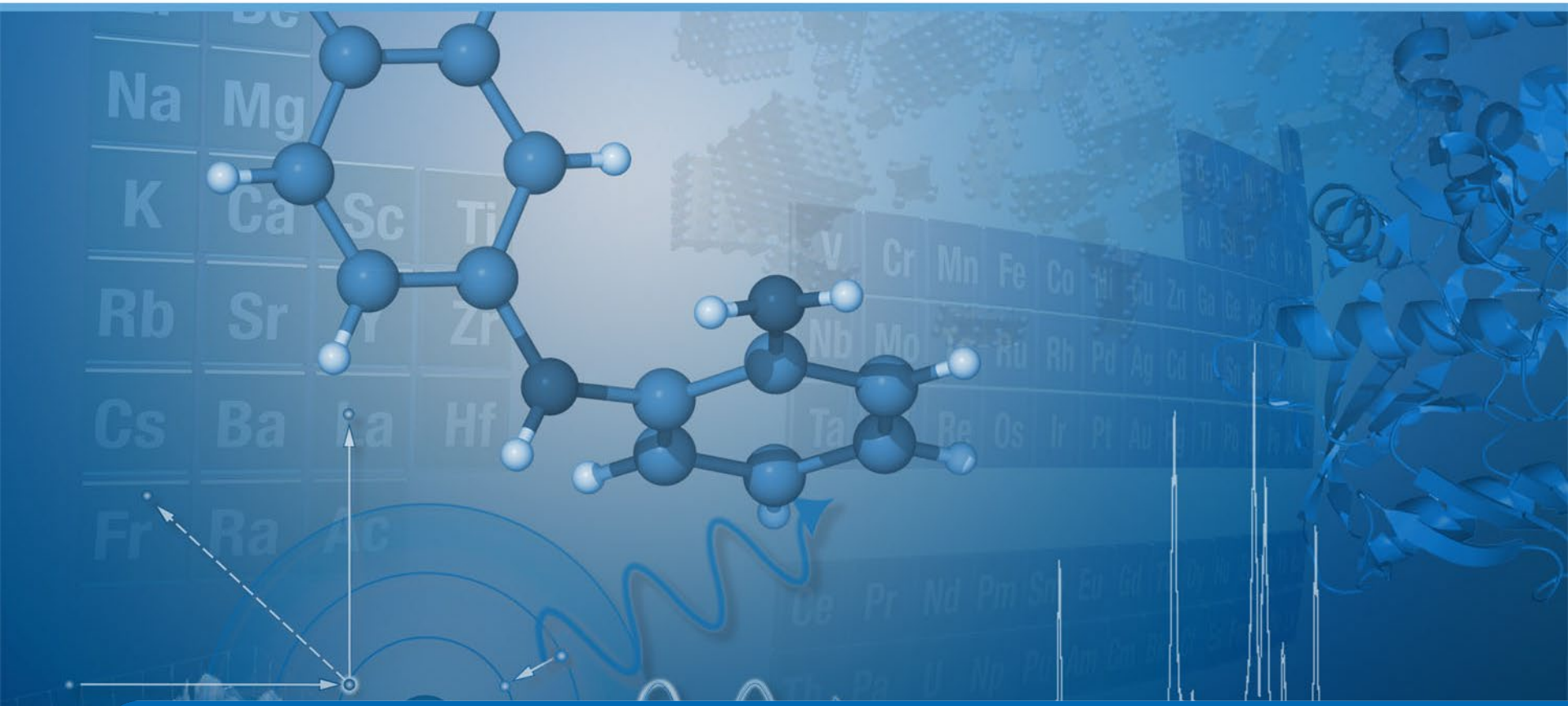
Introduction to Elemental Analysis of Light Elements (CS, ONH) in inorganic materials



Welcome!
Meet your speakers

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Analysis
Bruker
Madison, WI

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Elemental Analysis CS / ONH
Bruker
Karlsruhe, Germany

Audience Poll

Are you currently using any kind of analytical technique to measure light element? (C,S – O,N,H)?

- Yes
- Somewhat
- Not really
- No

EA of Light Elements (CS, ONH)
Topics

- Introduction
  - Definition of Elemental Analysis
  - History of Elemental Analysis
  - C/S & O/N/H for *inorganic* materials
    - Basic Principles
  - Overview of BAXS CGA Product Line
    - O/N/H (by Inert Gas Fusion)

      → G8 GALILEO / G6 LEONARDO
    - diffusible H (by carrier gas extraction)

      → G4 PHOENIX
    - C/S (by HF-Induction, NDIR-Detection)

      → G4 ICARUS HF

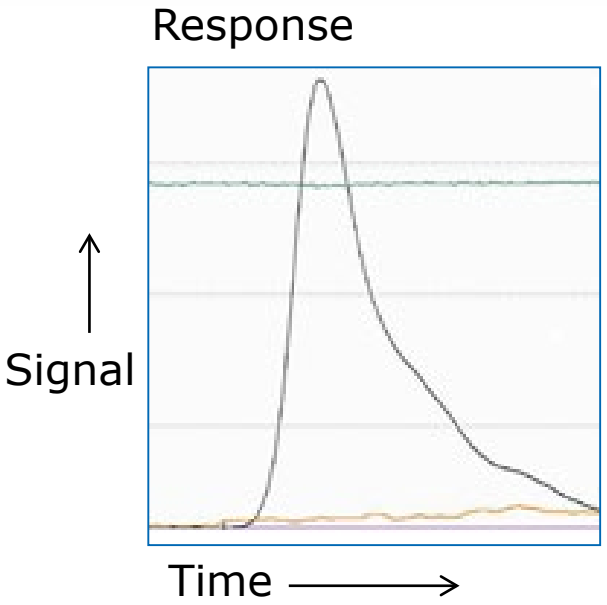
EA of light Elements (CS, ONH)
Definition of Elemental Analysis

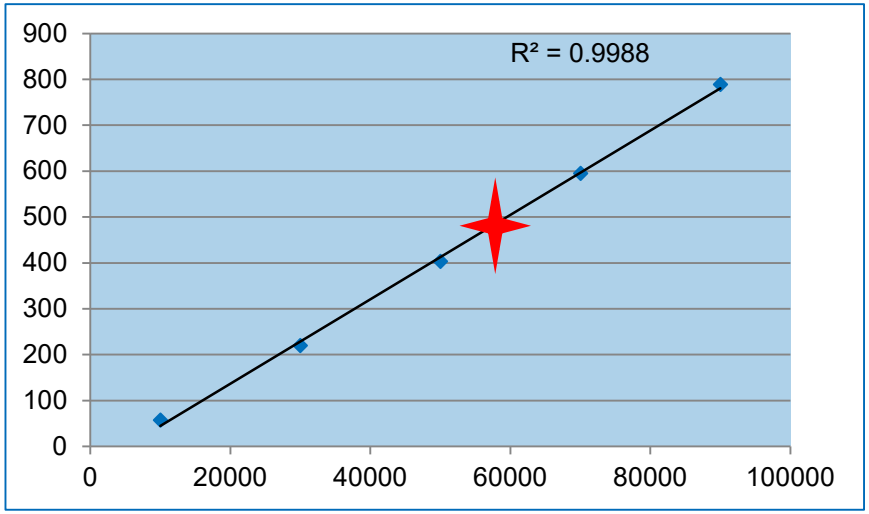
Elemental Analysis: The determination of elemental (and isotopic) composition of a material (major, trace and ultra-trace). Not limited to any specific matrix, target analyte or method.

Qualitative: What elements are present?

Quantitative: How much of those elements are present?

EA of light Elements (CS, ONH)
Definition of Elemental Analysis





Qualitative: What elements are present?

Quantitative: How much of those elements are present?

EA of light Elements (CS, ONH)
Definitions

- **Organic Analysis:** is the combustion of light elements in organic matrices in one single analysis

- **Inorganic Analysis**: is the combustion of light elements in inorganic matrices that require the Carbon and Sulfur to be measured with Combustion, and the Oxygen, Nitrogen, and Hydrogen to be measured with the Fusion Gas Analysis technique.

EA of light Elements (CS, ONH)
Definitions

- **Combustion Gas Analysis**: Uses oxygen as a carrier gas, a high frequency furnace, a combustion occurs, and dedicated detectors for **carbon and sulfur.**

- **Fusion Gas Analysis**: Sample is fused in the absence of Oxygen, but uses inert carrier gas and dedicated detectors for **Oxygen, Hydrogen, and Nitrogen.**

EA of light Elements (CS, ONH)
History of Elemental Analysis

- Elemental Analysis in the 18th and 19th Century

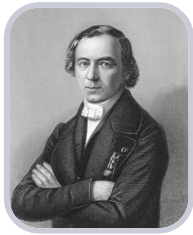
  Qualitative & quantitative determination of the elements
  Carbon, Hydrogen (as main constituents of all organic matter) as well as so called "hetero atoms":
  Nitrogen, Oxygen, Sulfur rarely also Phosphorous and Chlorine in organic molecules

  Goals
  - Molecular mass determination
  - Presence of O, N, S, Cl in unknown compounds
  - Empirical formula determination (molar ratios) of a compound
  - Molecular formula (combining m. mass & empirical formula)

Pioneers of Elemental Analysis

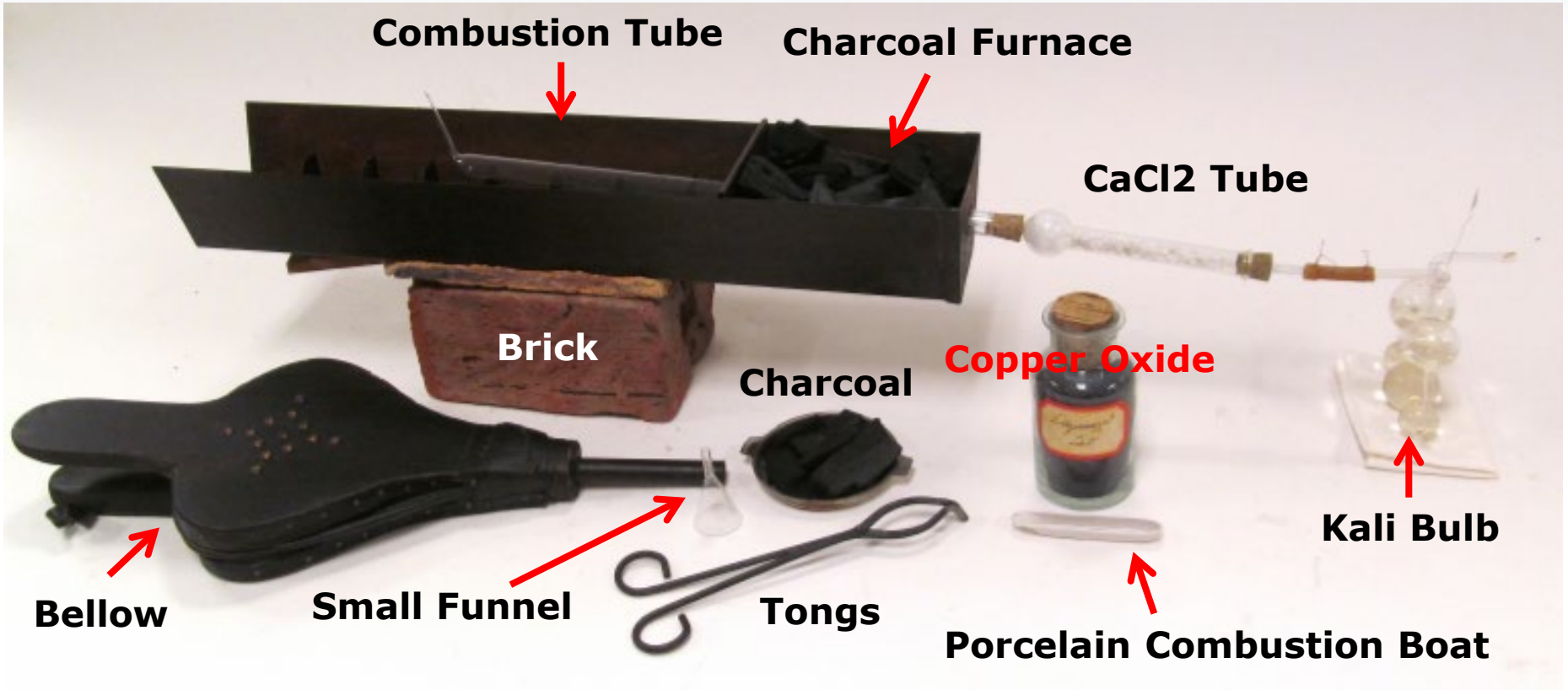

Justus von Liebig
(~1866)


Johan Kjeldahl
(~1883)


Jean-Baptiste Dumas
(~1833)


Fritz Pregl
(1923: Noble Price)

EA of light Elements (CS, ONH)
History of Elemental Analysis



The basic principle
Light element analysis in inorganic solids

- Weighing of dry solid sample

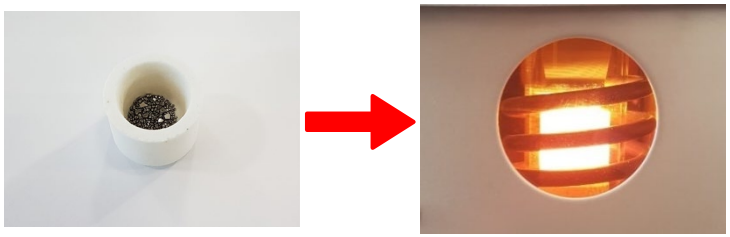

Turnings

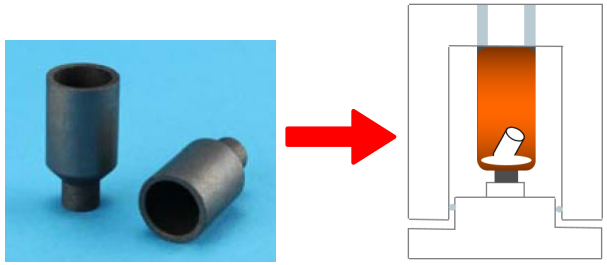

Billets


Bars


Powders

- The sample is placed in a crucible and then heated HF-Induction furnace (C/S) or Electrode furnace (O/N/H)

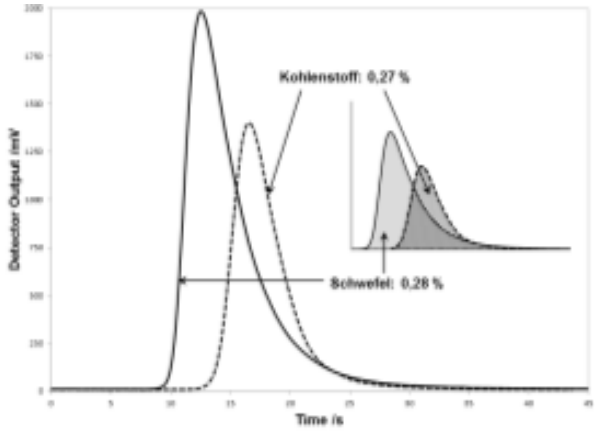

Combustion


Fusion

EA of light Elements (CS, ONH)
Gas Release and Detection

- The elements: C, S, N, O, H are released from the sample in a stable gaseous form (= molecules) and transported by the carrier gas stream to detectors for quantification. Eventually disturbing by-product are removed upfront

- Detection Principles: IR-absorption (NDIR), Thermal Conductivity (TC) or Mass Spectrometry (MS)



EA of Light Elements (CS, ONH)
Typical Applications of C/S, O/N/H/Ar


Foundry


Casting


Welding


Automotive


Cement


Limestone, Lime & Dolomite


Ores & Minerals


Copper production


Al and Mg

CS/ONH Analysis
Technical Overview

Inert Gas Fusion, MS

O N H dH Ar

O N H

dH

Combustion

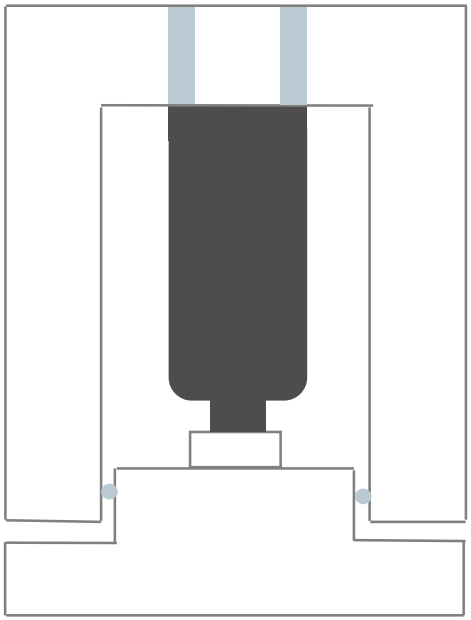
C S

G8 GALILEO & G6 LEONARDO

ONH Analysis by inert gas fusion

G8 GALILEO & G6 LEONARDO

How are the gases released from the sample?



Inert gas fusion analysis

1. Graphite crucible is compressed between two electrodes.

G8 GALILEO & G6 LEONARDO

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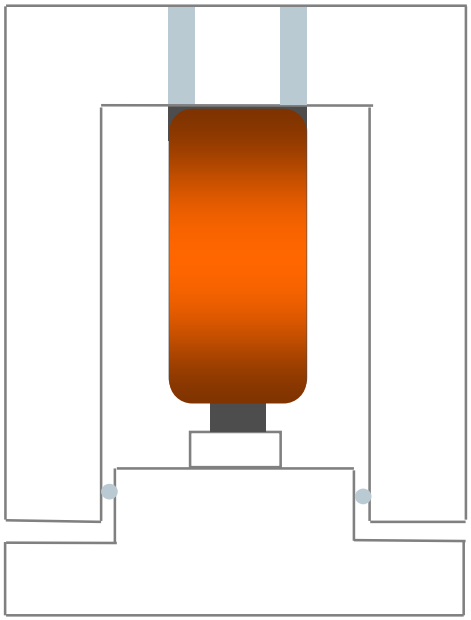

Inert gas fusion analysis

1. Graphite crucible is compressed between two electrodes.
2. Potential is applied across the two electrodes causing heating at the point of greatest resistance (crucible) – up to 3,000°C.

G8 GALILEO & G6 LEONARDO

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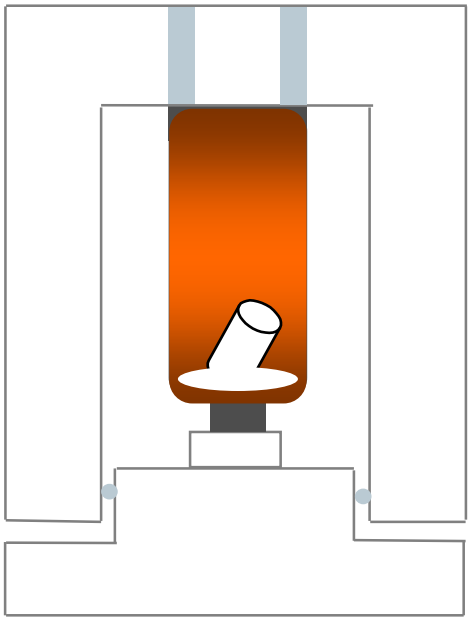

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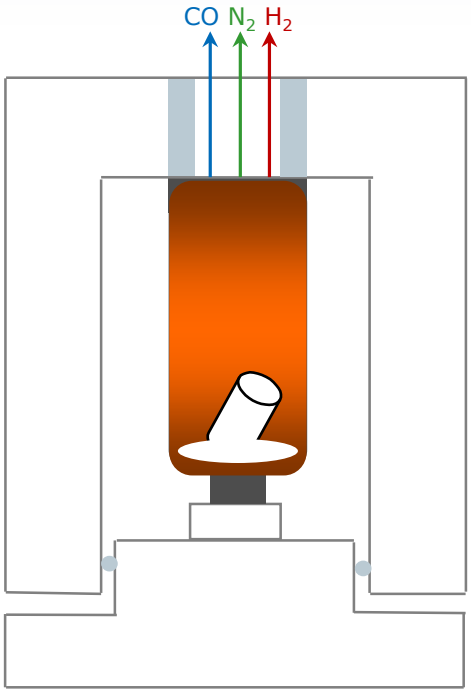
3. Sample dropped into the hot crucible fuses (melts) and releases forms of oxygen, nitrogen, hydrogen and also argon.

G8 GALILEO & G6 LEONARDO
How are the gases released from the sample?



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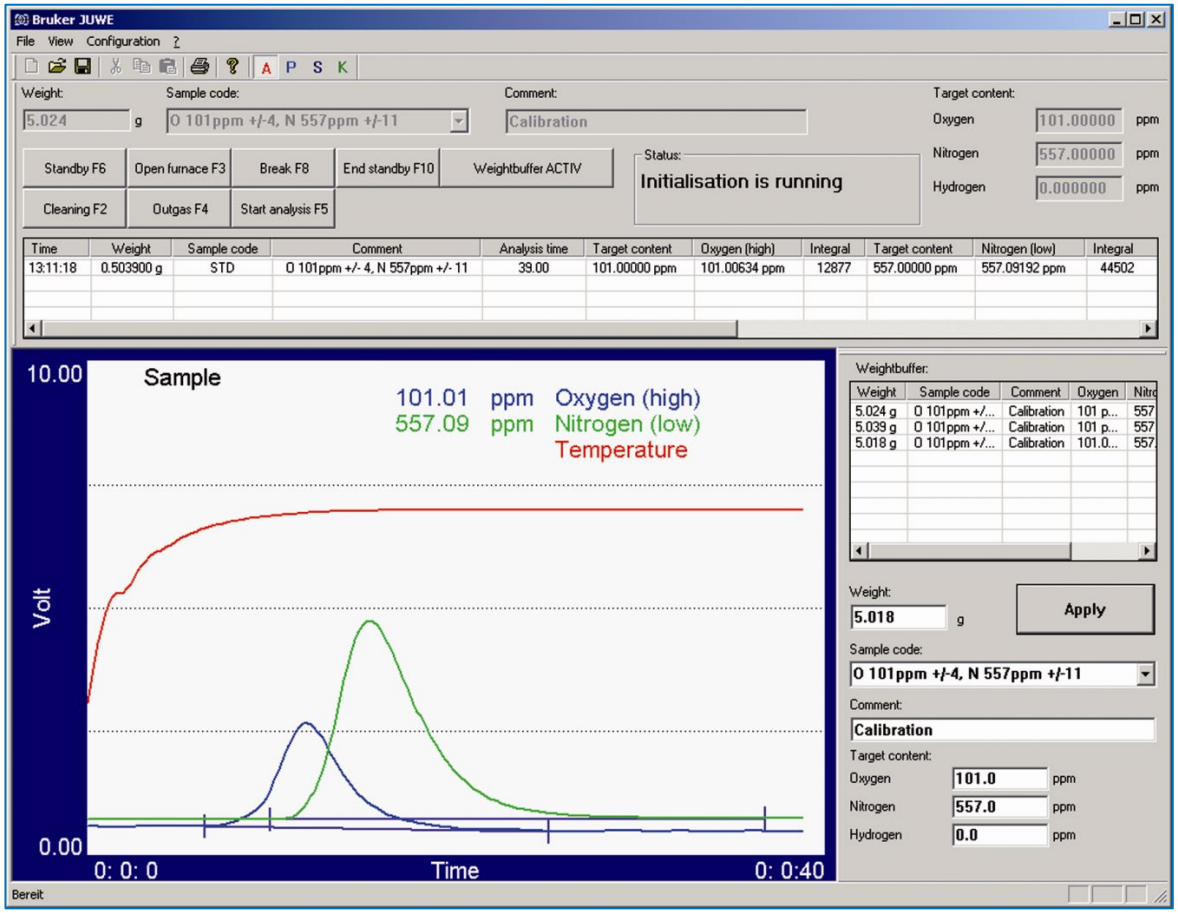
3. Sample dropped into the hot crucible fuses (melts) and releases forms of oxygen, nitrogen, hydrogen and also argon.
4. Oxygen reacts with C from crucible to CO, N and H are released as N_2 and H_2 from the sample and are swept by carrier gas to detection system.

G8 GALILEO ONH:
Measuring Signals and Evaluation



Analysis Screen

- Input of sample weight by direct transfer from the balance
- Weight buffer
- Graphical display of signal data
- Display of the results of last five analysis

G8 GALILEO
Features

Watercooled electrode furnace (up to 3000dC)
with pyrometer (range 900-2400dC)
and dust trap

ONH G8 Galileo (IGF)
ppm to %, mass dependent

Infrared furnace for dH
(up to 900dC)

Chemicals to remove interfering elements

Mass spectrometer
higher sensitivity
Ar and H analysis

Automation possible: autocleaner,
crucible changer, sample loader

G6 LEONARDO
ON/OH/O/N/H

- The G6 LEOANRDO is a more economical system than the G8 GALILEO
  - Configuration can be either: ON/OH/O/H/N
  - The Software platform (FUSION.ELEMENTS) is same software framework as Bruker's OES, EDX, and Benchtop WDX spectrometer
  - The G6 also doesn't have automation for cleaning or crucible changing, this means less moving parts

G6 LEONARDO vs. G8 GALILEO
A Comparison

NDIR Infrared detector for CO detection	✓	✓
Thermal conductivity detector for N_2 or H_2 detection	✓	✓
New lower electrode insert	✓	✓
New dust trap	✓	✓
Open/Close furnace	Electronic	Pneumatic
Multi element configuration	ON, OH	ON, OH, NH & ONH
Software	FusionElements	GA Client
Gas calibration	–	✓
Autosampler	–	✓
Crucible changer	–	✓
Automatic cleaning	–	✓
Mass spectrometer	–	✓
Diffusible hydrogen analysis	–	✓
Automatic gas switching	–	✓
Reagent tubes	Large tubes (G4 Icarus)	Small tubes

G8 GALILEO or G6 LEONARDO O/N/H

Inert Gas Fusion Principle : Approvals

Conforms to ASTM :

E-1019

Determination of C/S/N/O in Steel and in Iron, Nickel and Cobalt Alloys

E-1587-94

Determination of C/S/N/O in refined Nickel

E-1937 & E-1409

Determination of N & O in Titanium and its Alloys

E-1569

Determination of O in Tantalum

E-1806 (ISO 14284)

Refers to sampling of metal

G8 GALILEO
Determination of Hydrogen

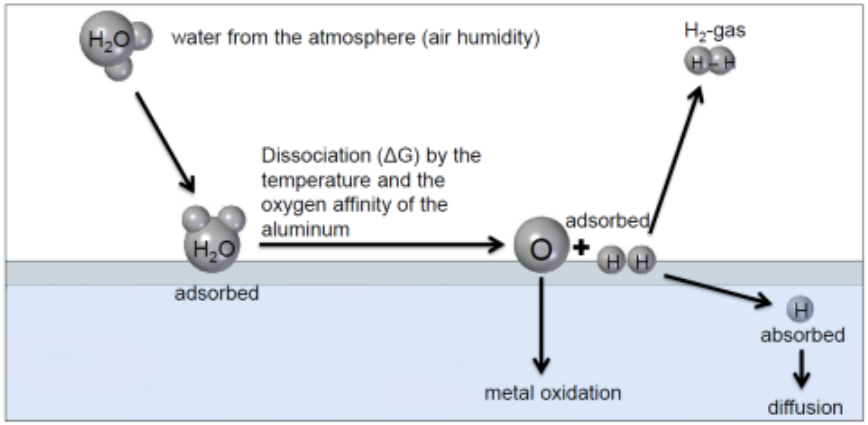
G8 GALILEO with electrode furnace, external infrared heated furnace and quadrupole mass spectrometer

G8 GALILEO offers:

- Determination of total hydrogen by melt extraction in a graphite crucible in the electrode furnace
- Determination of residual and total hydrogen by application of temperature programs for the electrode furnace
- Determination of diffusible hydrogen by hot extraction in the external infrared furnace
- Coupling of a mass spectrometer for detection of ultra-low hydrogen concentrations (thermal desorption mass spectroscopy)

G4 PHOENIX
Diffusible Hydrogen Analysis

- Diffusible Hydrogen responsible for material failure in high strength steel and other metals:
  - Hydrogen diffuses through the material and is absorbed into so-called “traps” (voids, pores, grain boundaries, micro-cracks, substituted atoms)
  - Recombination of H atoms into H_2 molecules → expansion, embrittlement
  - **Extremely important for automotive, aerospace, and welding!**

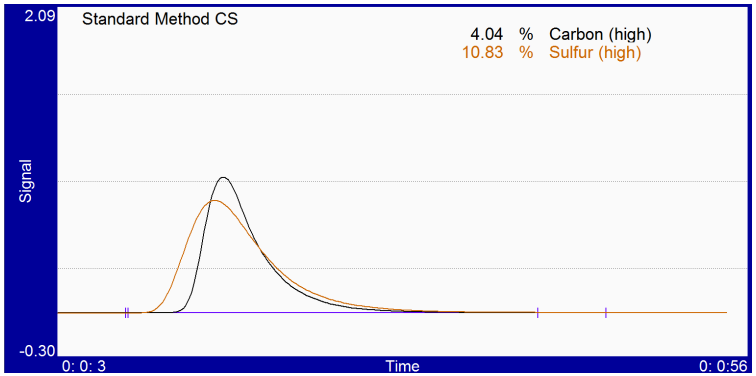


G4 ICARUS Series 2
Combustion Gas Analysis (CGA)

G4 ICARUS Series 2
Method Benefits

Combustion Analysis by HF-induction is:

- Volumetric method: Entire sample mass is analyzed
  - Also applicable to difficult samples with uneven distribution of elements (e.g. C in grey cast iron)
- Provides high precision and accuracy
- Fast: Analysis in ~ 60s
- Applicable over the full concentration range
  (from sub-ppm to 100%, by varying sample mass)
- Flexible in sample type, mass and form
  (powder, pieces, chips, drillings, etc.)
- Easy to operate



... if everything is designed the right way

G4 ICARUS Series 2
A dirty affair…

The dark side of combustion

- Not only oxidation of C and S, but also of sample and accelerator

⇒ can create fine dust

- Fine dust can act as a column to retard or retain analyte delivery to the detectors dependent on amount and type of dust.
- Production of spraying particles and liquid metal splatters due to vigorous combustion

⇒ can damage quartz combustion tube

$$\{M\} + n\ O_2 \xrightarrow{\Delta} MO_{2n}$$

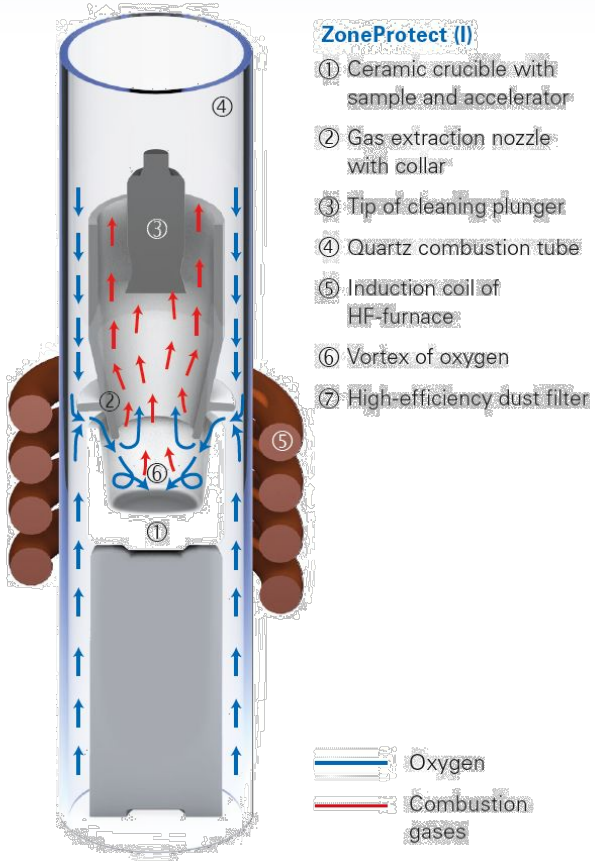
Metals/Minerals + O_2
= particulate oxides = DUST

G4 ICARUS Series 2
Intelligent Design: ZoneProtect™

ZoneProtect™

- More efficient combustion on a wider variety of samples
- Superior gas flow design for better analytical quality

  ⇒ Oxygen supply through annular flow gap & turbulences ensure perfect oxygen supply to the sample
- Reduces splattering, maximizes component lifetime
- Combustion gases, dust & particles transported through the extraction nozzle upward
- Integrated auto cleaner



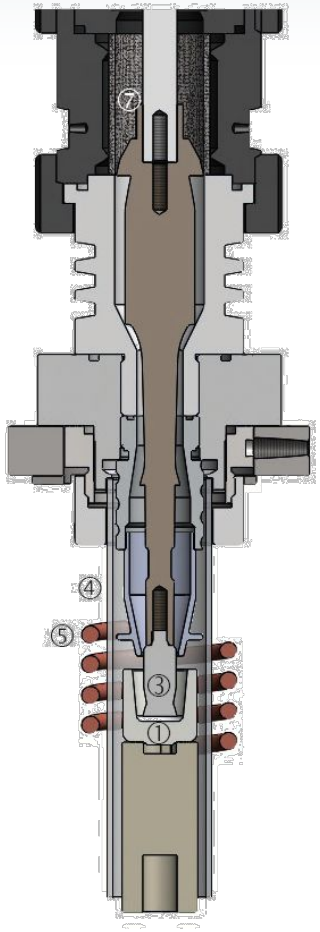
G4 ICARUS Series 2

Easy Maintenance: ZoneProtect™

Integrated dust removal system:

- Vacuum & noise-free cleaning system
- Waste disposal into the crucible
- Brush-free cleaning operated by solid plunger
- High efficiency, integrated dust filter (3µm pore size) for cleaner environment and analytical precision

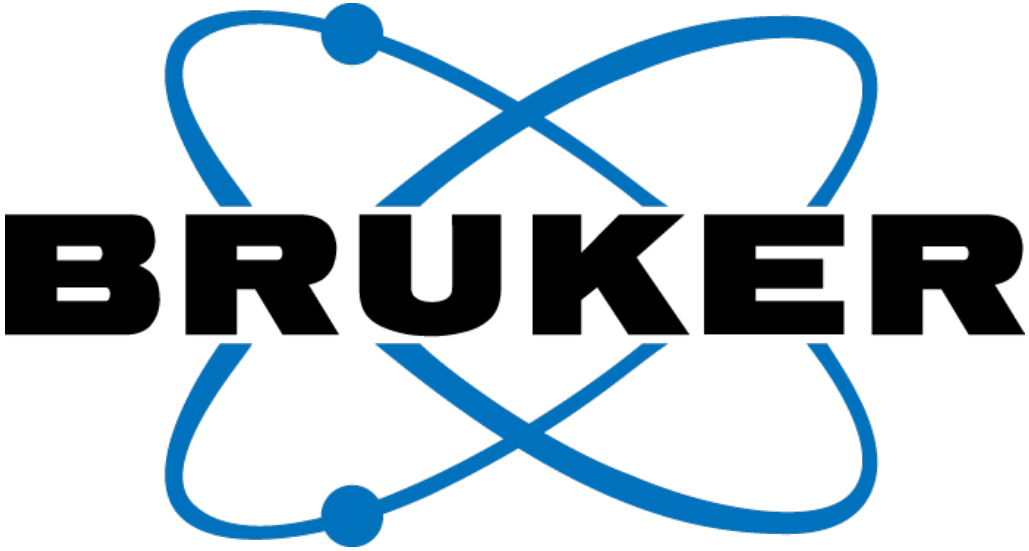
Efficient dust removal into the crucible



G4 ICARUS Series 2 – CS Analyzer
Key points

High precision C and S analysis in inorganic materials by combustion

- Combustion by combination of high frequency induction and pressurized oxygen gas flow in a closed system
- Solid sample is weighed into a ceramic crucible and conductive accelerator material added
- Combustion and liberation of CO_2 and SO_2 from the sample
- Transport of sample gas by oxygen carrier gas towards the detection system
- Detection of CO_2 by NDIR detector and SO_2 by UV-LED detector
- Integration of detector signal, calculation of result
- Automatic cleaning



Innovation with Integrity

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