High-precision oxygen concentration analysis using a novel high-temperature pyrolysis technique

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PEFTEC 2015

Dr. Marc Ruppenthal

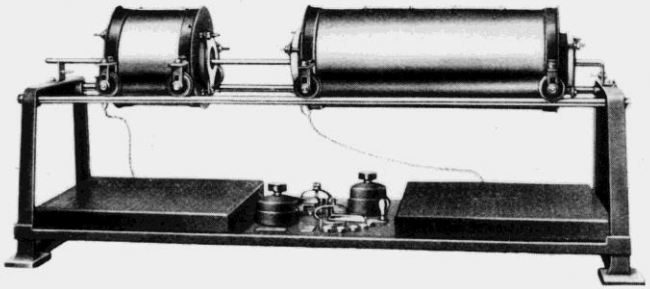
Product Manager Elemental Analysis
and EA-IRMS interfaces

elementargroup.
elementar | isoprime

Content

110 years tradition… Heraeus

Verbrennungsofen



System Heraeus

Zweck des Ofens: Ausführung von Verbrennungen bei der organischen Elementaranalyse.

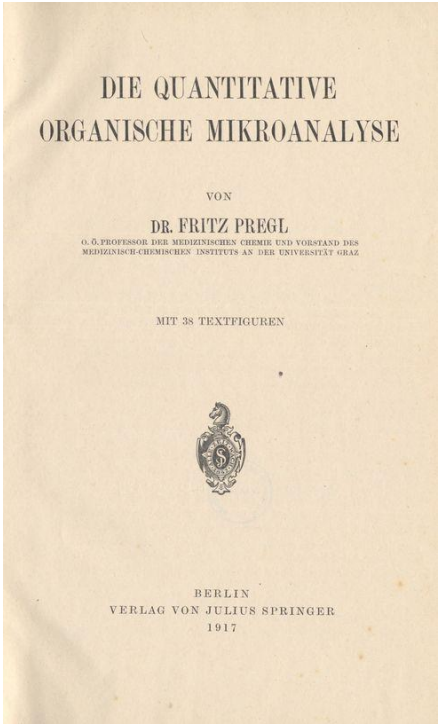
The elementargroup – tradition means trust

- Approx. 1860: W. C. Heraeus utilizes high temperature technologies in order to process platinum
- Approx. 1900: Heraeus produces high purity quartz glass which is soon used in elemental analysis

Wilhelm Carl Heraeus

Pharmacy “White Unicorn”

The elementargroup – tradition means trust


DIE QUANTITATIVE
ORGANISCHE MIKROANALYSE

VON

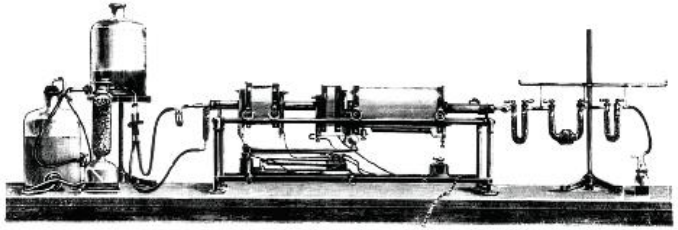
DR. FRITZ PREGL

O. Ö. PROFESSOR DER MEDIZINISCHEN CHEMIE UND VORSTAND DES MEDIZINISCH-CHEMISCHEN INSTITUTS AN DER UNIVERSITÄT GRAZ

MIT 38 TEXTFIGUREN

BERLIN
VERLAG VON JULIUS SPRINGER
1917

- Approx. 1905: First generation of elemental analyzers with electrical furnaces produced by Heraeus

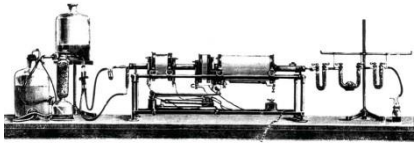


- 1923: Fritz Pregl receives the Nobel Prize in Chemistry for his invention of the *method of micro-analysis of organic substances*, **using dedicated analytical equipment manufactured by Heraeus !**

The elementargroup history

1851 Heraeus was founded

1904 Dennstedt patent "über die vereinfachte Elementaranalytik" was the basis for the 1st instrument generation



1932 The first elemental analyzer for simultaneous detection of carbon, hydrogen and nitrogen was invented.

1964 The first Dumas Nitrogen/Protein analyzer was introduced

1973 The High temperature TOC analyzer was introduced

1980 The first fully automatic elemental analyzer with TCD detection was introduced

1995 The EA business of Heraeus was sold in a management buyout and restructured under the brand name Elementar.

The elementargroup history

2006

Introduction of the "cube" platform
vario MICRO cube, vario EL cube,
vario MACRO cube, rapid N cube

2008

Isoprime Ltd was acquired

vario TOC cube

2009

rapid CS cube, vario ISOTOPE cube,
vario PYRO cube

2010

trace SN cube

2012

vario MAX cube, iso TOC cube

2014

rapid N exceed, rapid OXY cube

The elementargroup history

rapid MAX N exceed, rapid MiCRO N cube

2015

Introduction of the inductar series

inductar CS cube, inductar ONH cube,
inductar EL cube

The elementargroup – about us

elementargroup

elementar
EXCELLENCE IN ELEMENTS

isoprime
EXCELLENCE IN ISOTOPES

- The technology leader in
  - Elemental Analysis (EA)
  - Isotope Ratio Mass Spectrometry (IRMS)
- Offers an unmatched combination of
  - innovative technologies,
  - tailor-made solutions and
  - comprehensive support.

The elementargroup – key markets

Chemicals

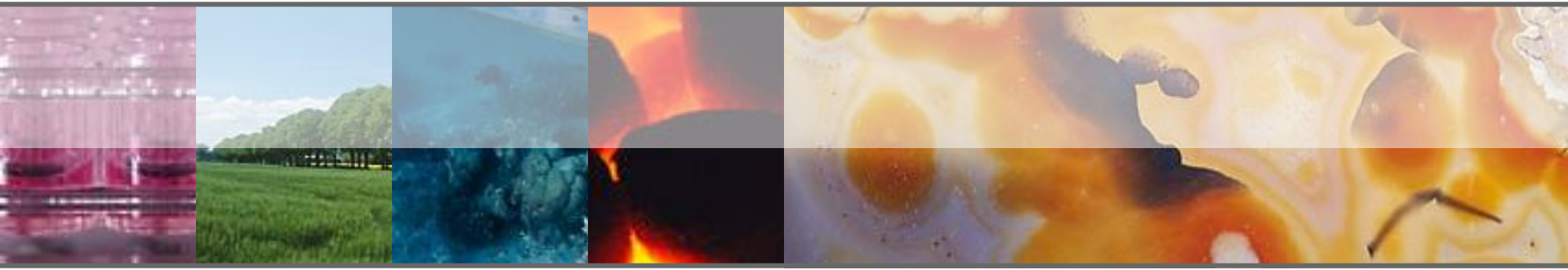
Agriculture

Energy

Forensics

Materials

Environmental



Some of our customers

Content

Why Oxygen Analysis?

- Oxygen is an important parameter to describe:
  - Coke and coal (ASTM D3176)
  - Gasoline and methanol fuels (ASTM D5622)
  - Polymers (fire/decomposition resistance)
  - Fine chemicals (quality control)

- Two approaches:
  - Indirect: 100% - CHNS% - ash% = O%
  - Direct measurement

Indirect Oxygen Analysis

- Indirect approach: 100% - CHN% - S% - ash% = O%
  - Drawbacks:
  - Time and resources consuming
  - Summation of errors
  - Up to three instruments required

"The result so obtained is affected by errors incurred in the other determinations of the ultimate analysis and also by the changes in weight of the ash-forming constituents of ignition." (ASTM D3176)

Direct Oxygen Analysis

- New applications require more precise, direct determination of oxygen

> *"The presence of oxygen-containing compounds in gasoline can promote more complete combustion, which reduces carbon monoxide emissions. The Clean Air Act (1992) requires that gasoline sold within certain, specified geographical areas contain a minimum percent of oxygen by mass (presently 2.7 mass %) during certain portions of the year. The requirement can be met by blending compounds such as methyl tertiary butyl ether, ethyl tertiary butyl ether, and ethanol into the gasoline."* (ASTM D5622-95)

- Increasing need for a direct and precise determination of oxygen concentrations, especially in the solid and liquid fuel industry

Direct Oxygen Analysis: Reductive Pyrolysis

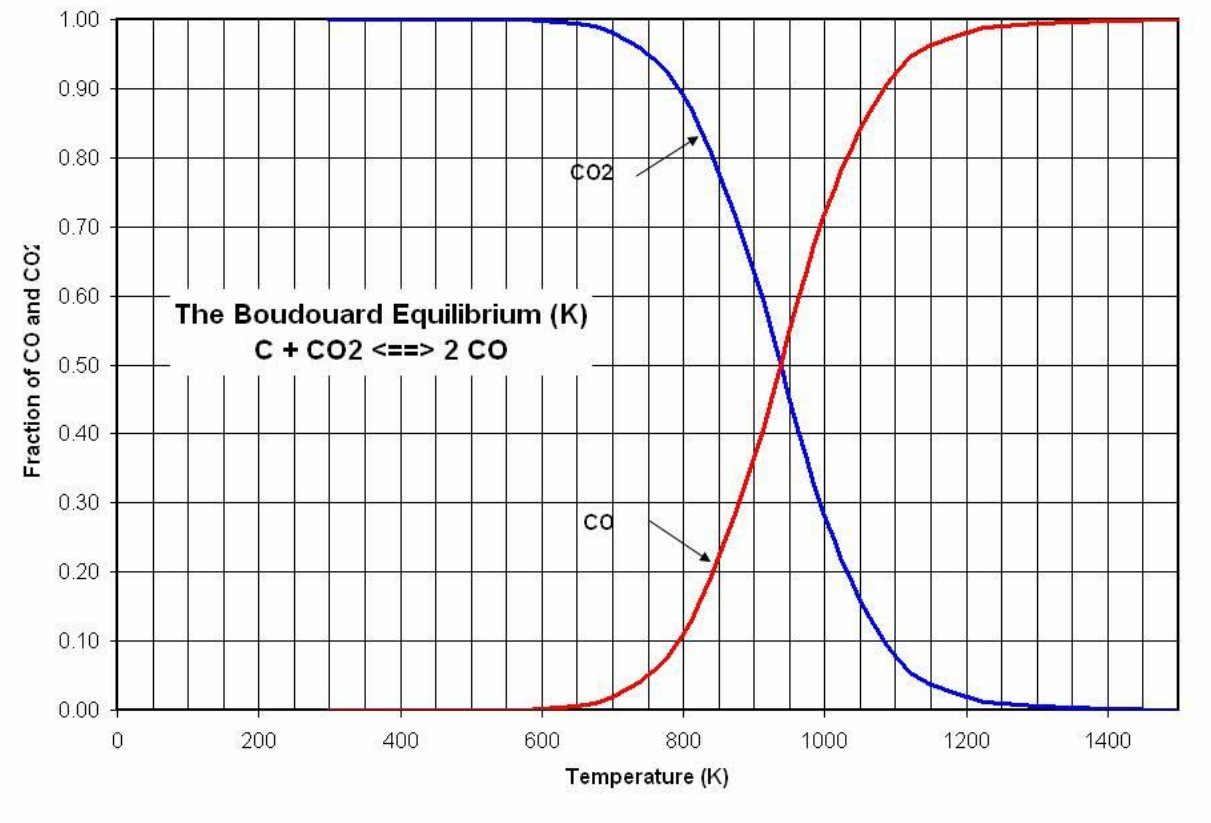
- Sample is pyrolyzed in helium atmosphere in presence of carbon black
  - Sample oxygen (O) is converted to carbon monoxide (CO)
  - CO is detected
  - Boudouard equilibrium:

$$CO_2 + C \rightarrow 2\ CO$$

$$2\ CO \rightarrow CO_2 + C$$

- Only quantitative conversion to CO results in matrix-independence

Boudouard euqilibrium



We want CO! Simplified Pyrolysis Chemistry

- The higher the temperature, the more CO!
- Temperatures around 1200° C for sub-percent CO_2 formation
- But: Temperatures > 1200° C require unique technical solutions!

Depending on temperature, a mixture of CO and CO_2 is produced

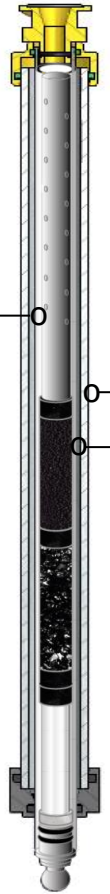
→ biased oxygen measurement (matrix effects!)

Get OXYted about oxygen analysis - rapid OXY cube -

- Temperature 1450° C
- **Matrix independent**, no CO_2 formation
- No matrix standards needed
- Excellent, highly accurate results
- Ready to go, stand-alone analyzer

Content

Get OXYted! - Blank free pyrolysis reactor -



Blank free, long-life glassy carbon tube

Outer protective ceramic tube

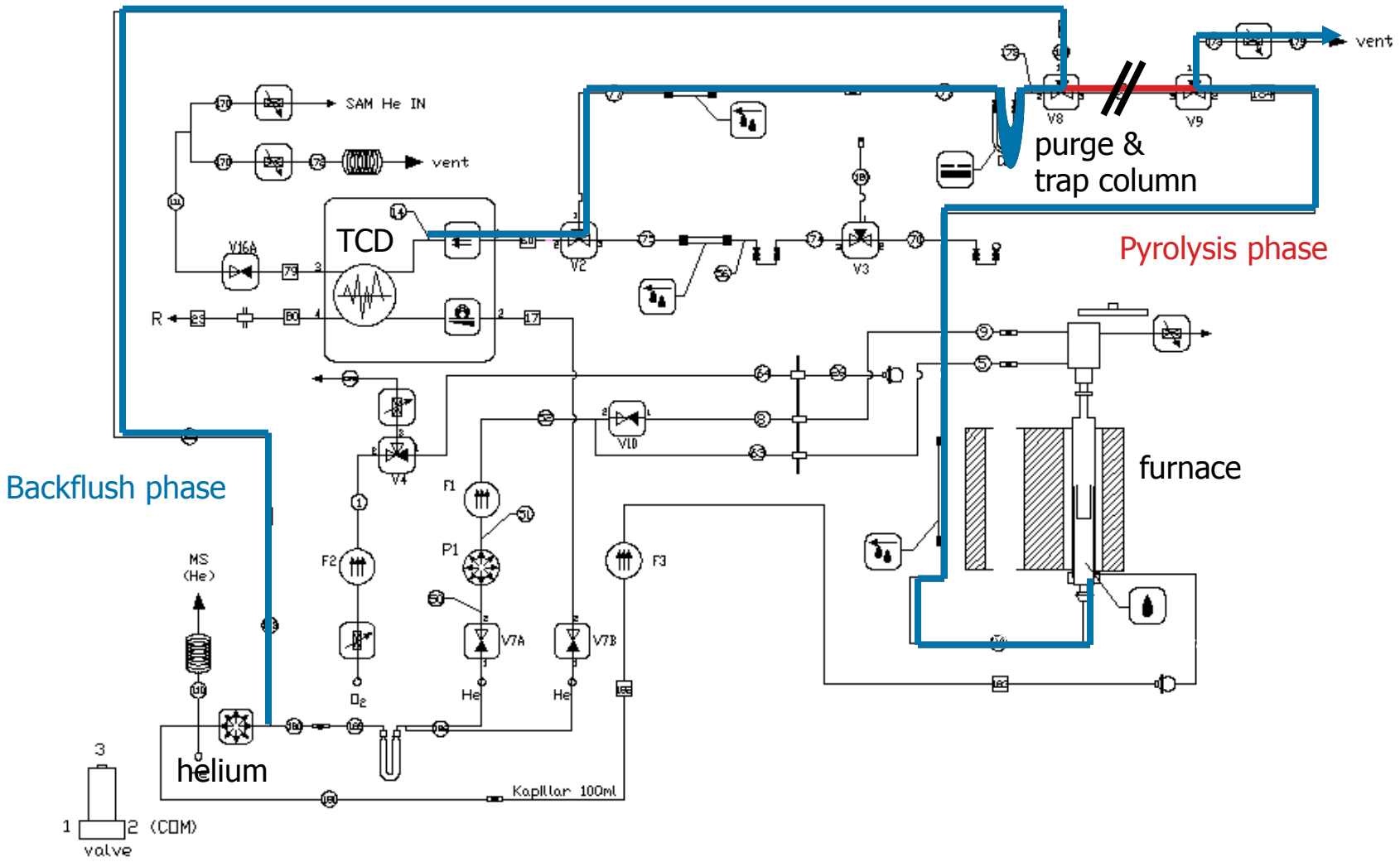
Helium (or argon) purged cavity between outer and inner tube, complete separation of carrier gas from protective gas

Get OXYted! - Patented backflush -

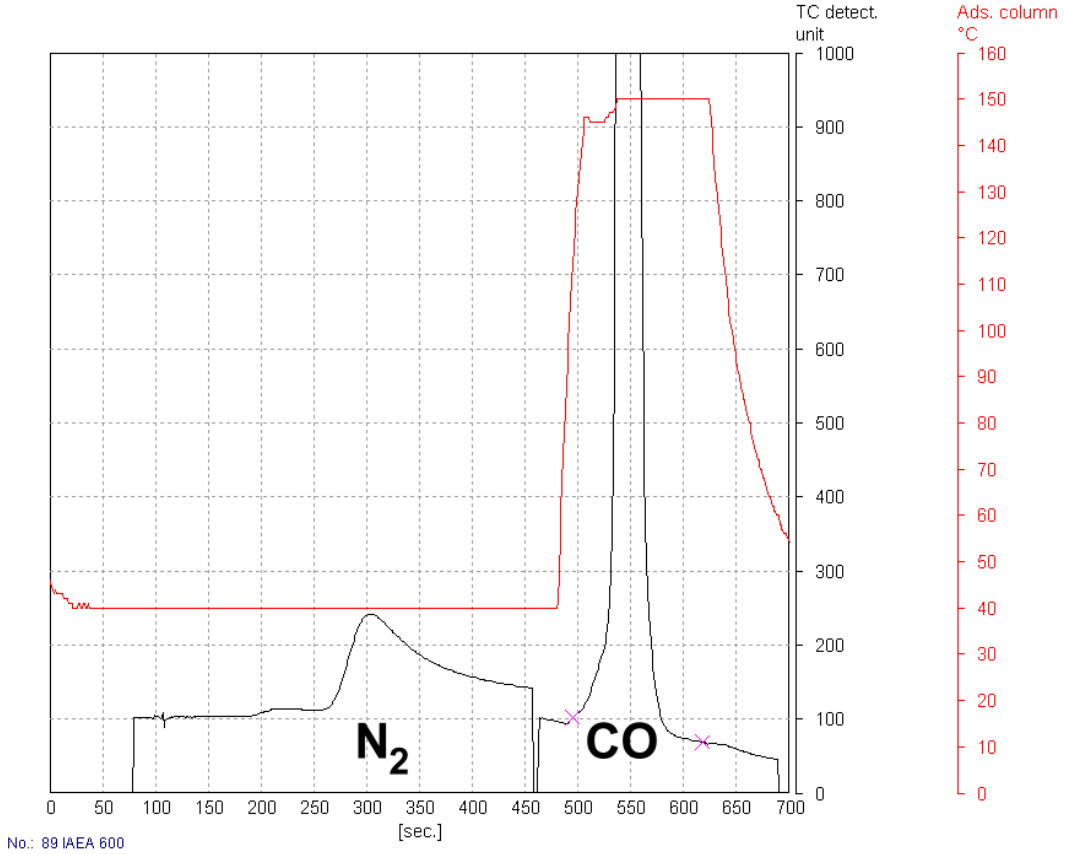
- **Problem:** Pyrolysis is not as well defined as combustion. Interferences can lead to wrong results.
- Function of backflush system:
  - Adsorption of CO during pyrolysis phase
  - Desorption with clean helium and temperature ramp
  - Tailing from pyrolysis byproducts does not enter the TCD but goes to vent
  - Focused peak due to temperature ramp

➢ **Result:** Full baseline separation of CO from interfering gases and full recovery

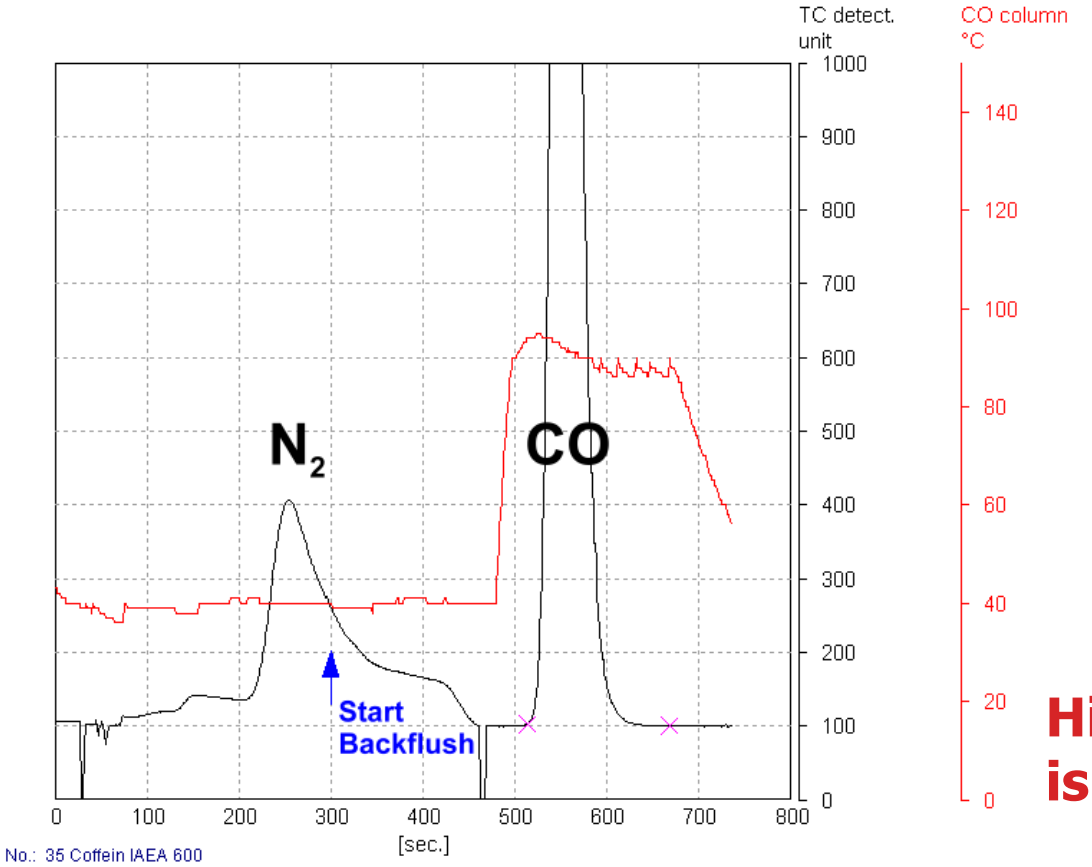
patented backflush



Analysis of caffeine without backflush



Analysis of caffeine with backflush



Highest accuracy is guaranteed!

Content

Oxygen analysis has never been more reliable

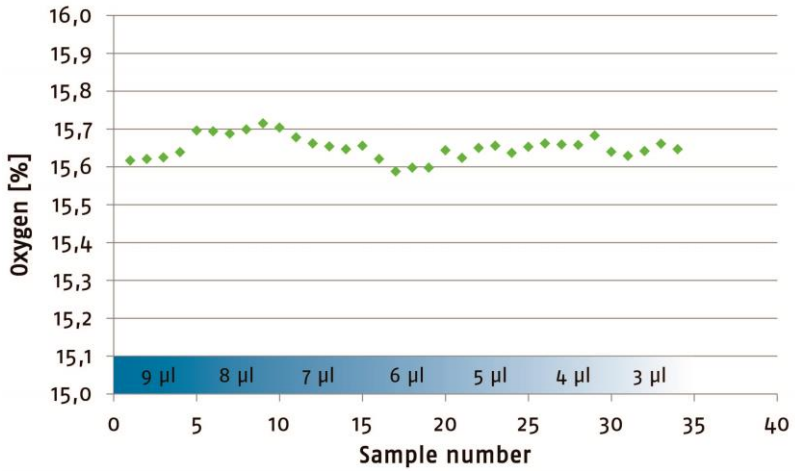
elementar
EXCELLENCE IN ELEMENTS

SAMPLE	O [%]	ABS. SD [%]
OIL 1	0,34	0,03
OIL 2	0,66	0,04
COKE 1	3,93	0,05
COKE 2	1,88	0,10
COAL	6,32	0,08
CAFFEINE	16,94	0,07
ACETANILIDE	11,97	0,05
SULFANILIC ACID	27,77	0,07
SIVER PHOSPHATE	15,35	0,15
BARIUM SULFATE	27,72	0,44
FLUOROBENZOIC ACID	23,50	0,12

rapid OXY cube liquid injection

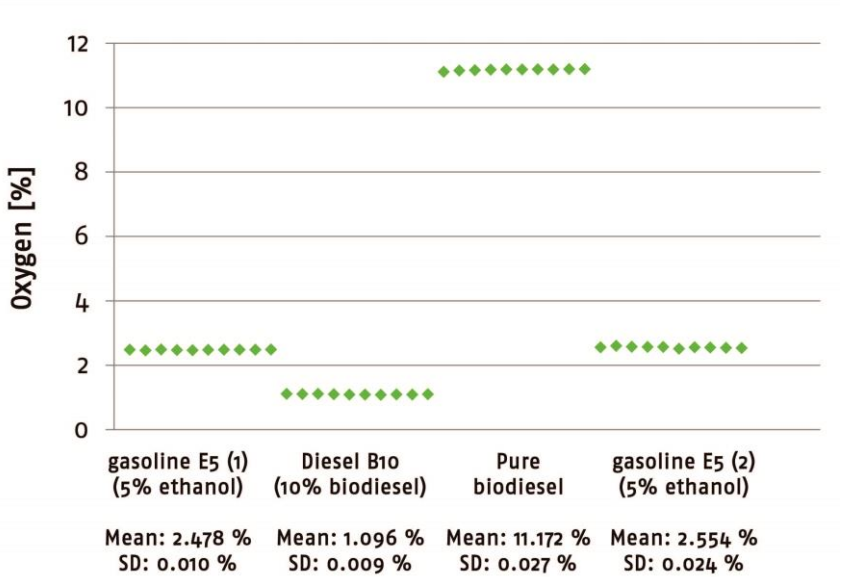
- rapid OXY cube + VLS

Liquid samples: Proof of principle



- 34 consecutive hexanol injections over wide range of injection volumes (3-9 µl)
- Theoretical value: 15.66%
- Mean: 15.65%
- Abs. SD: 0.03%
- Excellent results
- Excellent repeatability
- Excellent accuracy

Oxygen Content in Gasoline Blending



- Oxygen content corresponds to unwanted CO emission in engines
- Minimum oxygen content is legal requirement (e.g. Clean Air Act)
- Pure fossil gasoline with low oxygen content is blended with high oxygen content biofuels
- Excellent repeatability
- No memory effects

Content

Highlights

elementar
EXCELLENCE IN ELEMENTS

- Highest accuracy and data reliability
- Patented backflush for blank-free oxygen analyses
- Designed for unattended 24/7 operation
- Unmatched operating comfort through sophisticated self-diagnosis
- High robustness – low maintenance

Elementar thanks for your attention !