BAM
Bundesanstalt für Materialforschung und -prüfung

Sicherheit in Technik und Chemie

26.09.2019

BESTIMMUNG VON HALOGEN IN METALLEN MITTELS SPEKTROMETRISCHER VERFAHREN

Silke Richter, Jens Pfeifer, Carlos Abad, Maria Dommaschk, Sebastian Recknagel

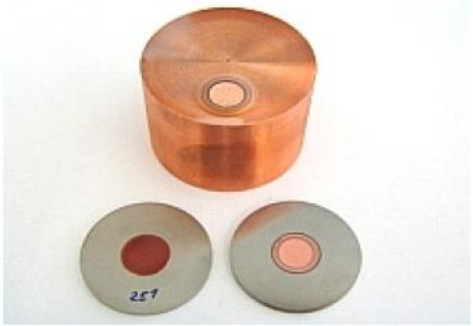
Overview

Why halogenes in pure metals?

Short excursion into Metrology

How
Calibration with liquid doped pressed powder pellets
Calibration with sintered samples

Improvement
Comparison
Summary and Outlook



Metrology

Why?

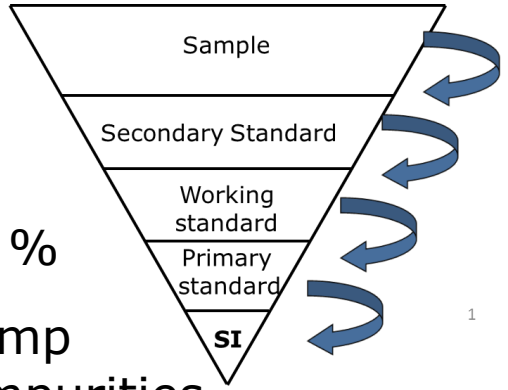
The science of measurement

- **Comparability** of measurement data e.g. results of blood test, data in industrial and research labs
- For **Quality Assurance** (ISO/EN 17025) and **Safety**

How?

High Purity Materials

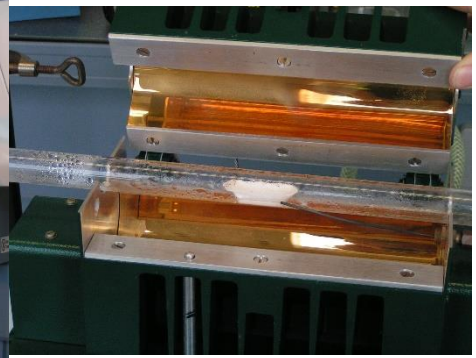
- serve as primary standards for chemical measurements
- used to establish SI traceability

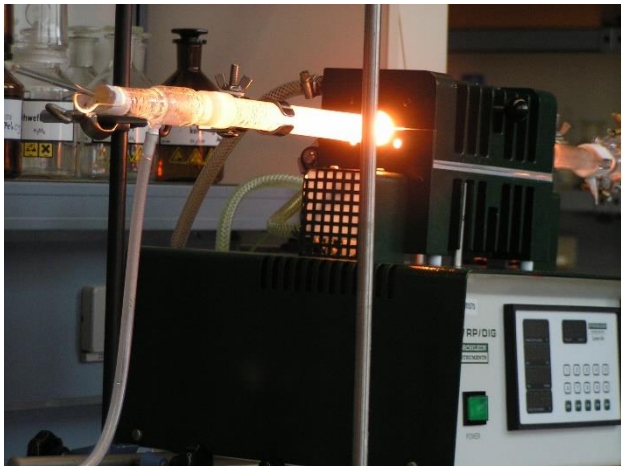


Target: $u(w(E)) \leq 0.01$ %

$\Rightarrow$ approach: 100 % - ΣImp
measurement of **all** impurities
(incl.N, Cl, F ...)

DIN 51723:2002-06 Determination of fluorine content





Reference: Lucelia Hoehne et. al, Feasibility of pyrohydrolysis as a clean method for further fluorine determination by ISE and IC in high purity nuclear grade alumina. Microchemical Journal **2019,** *146*, 645-649.

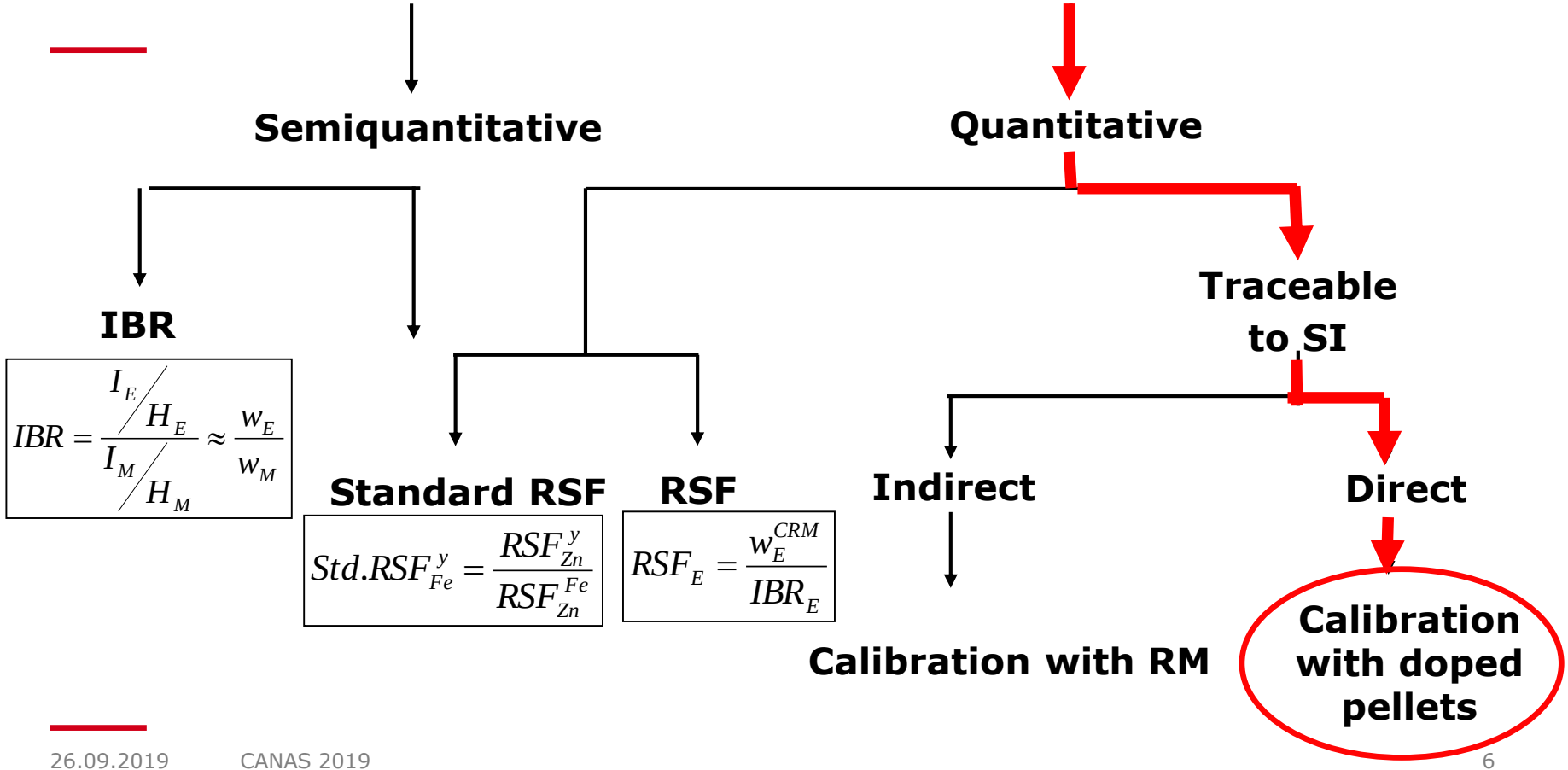
GD-MS has the potential to reduce the effort for purity determination

- Fast sensitive multi-element analysis without extensive sample preparation

- The use of the concept Relative Sensitivity Factors (RSFs) provides good **approximations** specially for high purity materials

- Only works with a wide uncertainty of the results

Quantification with Element GD



Synthetic Standards:

Different Doping Approaches

Pure metal powder

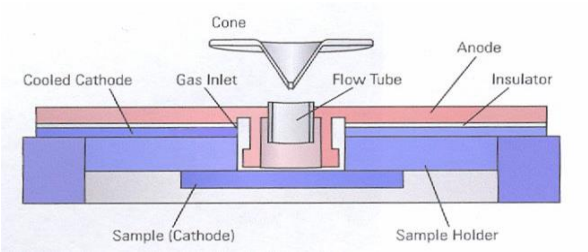
Solid-source doping (oxides, nitrides, etc.)

Determination of non-metallic impurities (Si, O, N, S, P)

Liquid doping with standard solutions

Determination of metallic impurities

Calibration using pellets of pure metal powders



Preparation of synthetic pellets

Pure metal matrix powder (5N) weigh and dope with standard solutions of analytes

Pipette

Standard solution

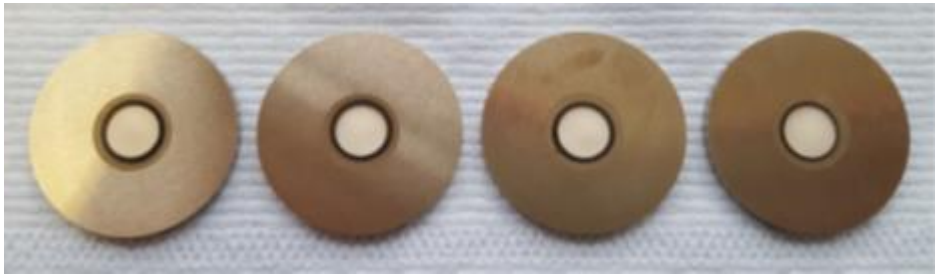
Doped powder

Pure metal powder

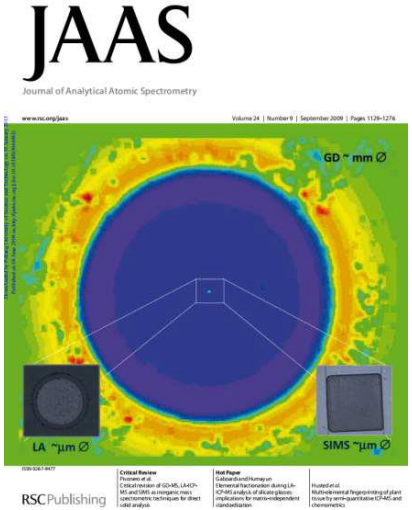
Vessel

adopted from T. Gusarova

Pressed powder pellets for GDMS

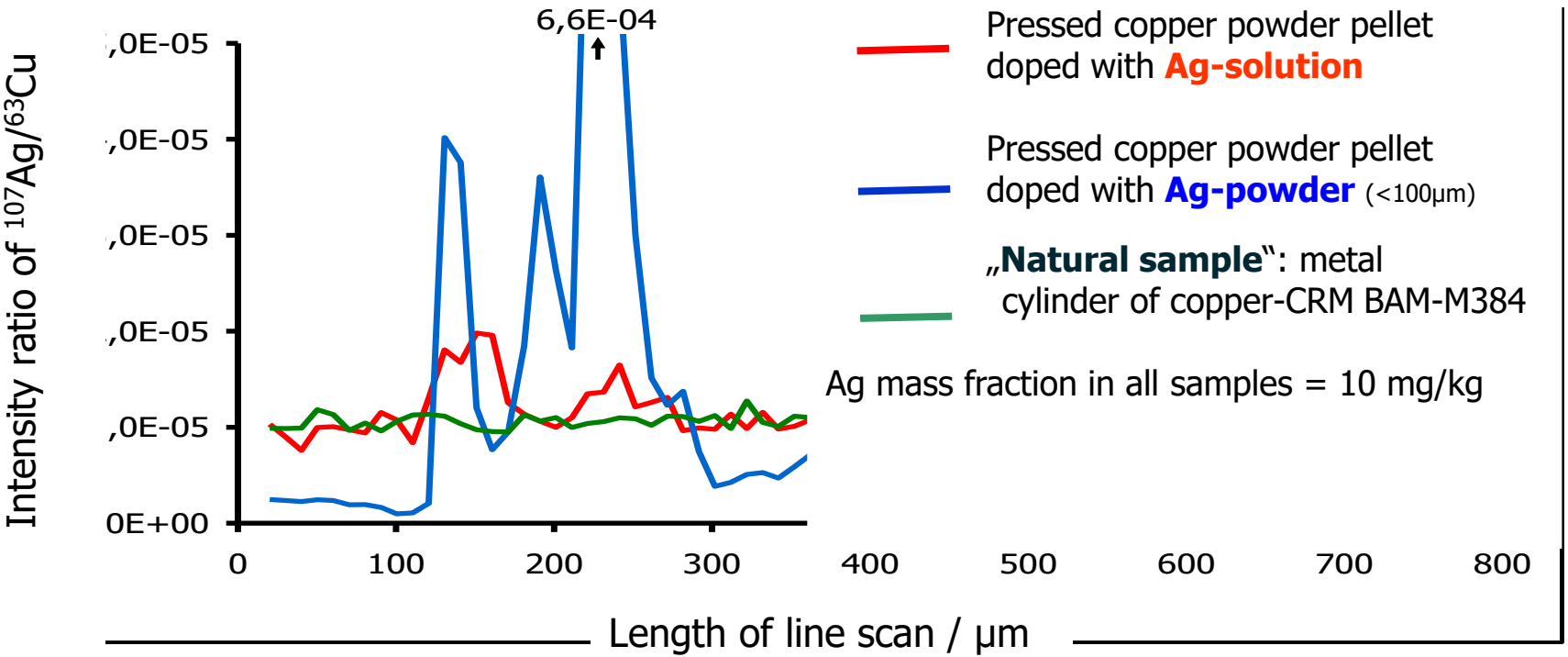


Cu+ KF KCl KJ KBr



Appearance of copper and nickel samples

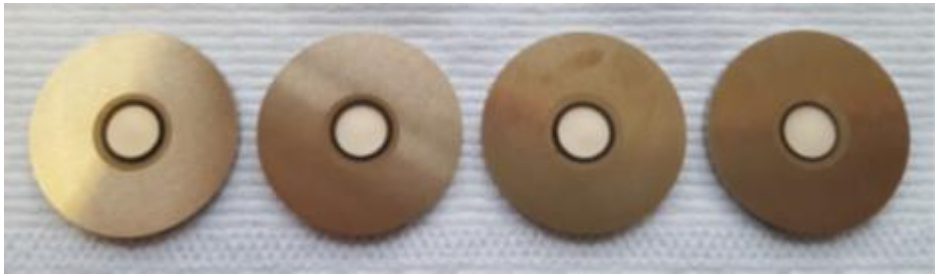
Checking `micro´-homogeneity of doped pellets



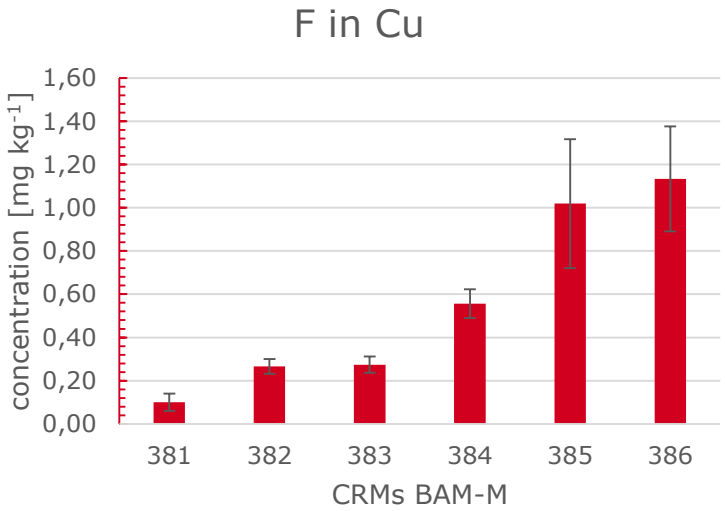
by H. Traub

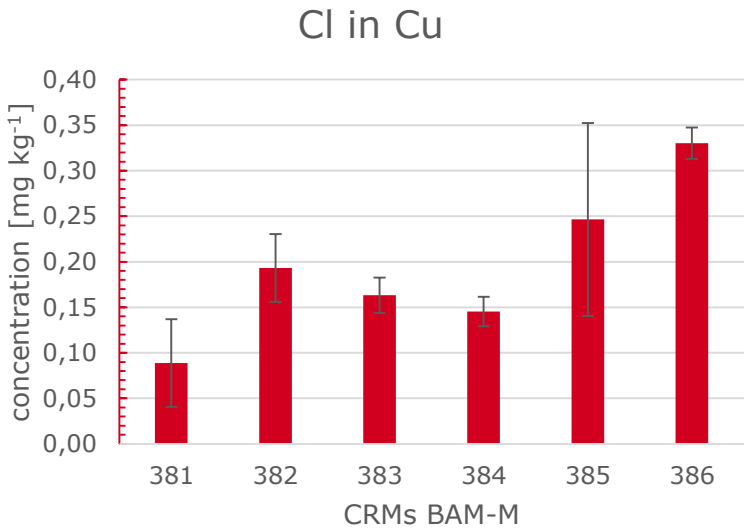
Advantages of calibration with pressed powder pellets

- Available for any material what can be pressed into pellets
- Wide variety of analyte (trace) elements and their concentration range
- more accurate results and more direct traceability to SI
- smaller uncertainties
- down to ppb



Content of F and Cl in Cu- CRMs





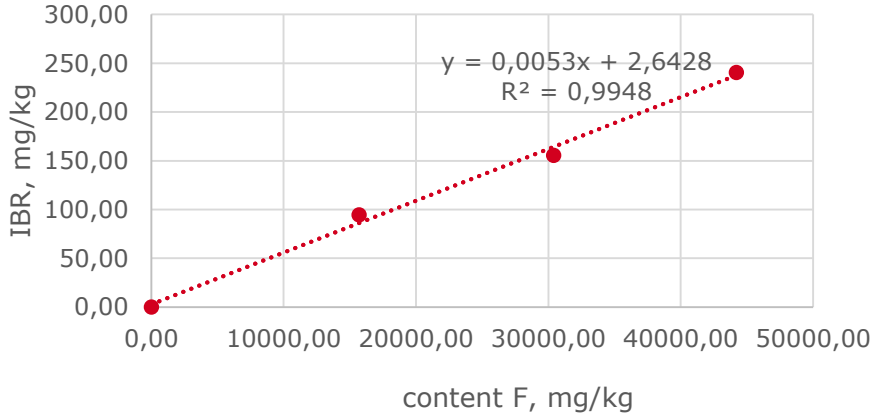
	F [mg/kg]	**Cl [mg/kg]**
LOQ	0.17±0.06	0.08±0.03

Preparation of Sintered Powder Mixtures

Powder is mixed (5 min)
Sintering Process (30 min)

Cu matrix  Cu CaF2

Sintering conditions
Temperature: 600 °C
Pressure: 150 kN
Inert gas: Ar



Properties: ∅ = 20 mm, h ≈ 20 mm, grindable
density > 95% - vacuum tight
homogeneous in mm range

Additional gases

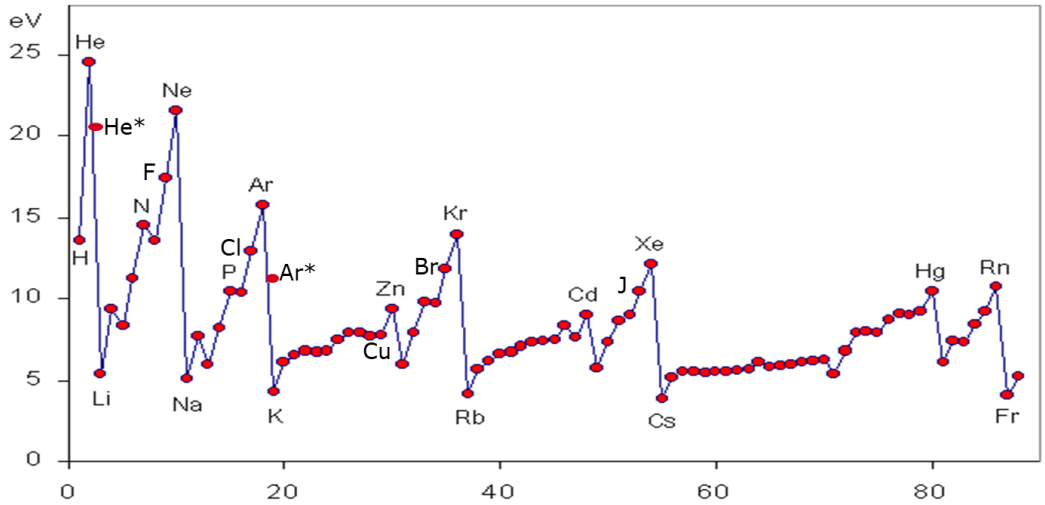
Helium additional to Argon
(Ar needed for sputtering)

Intensity increased for:

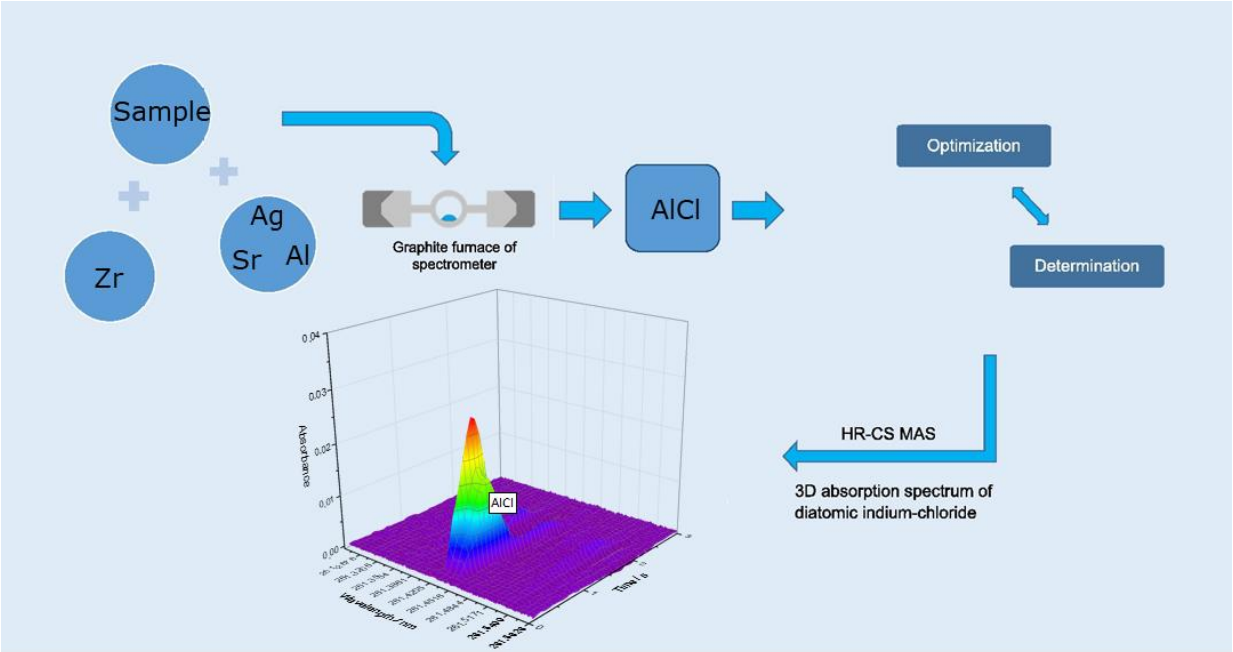
F (f ~10)
Cl (f ~ 5)

Careful: purity of the gases!
Quenching effect of N and O

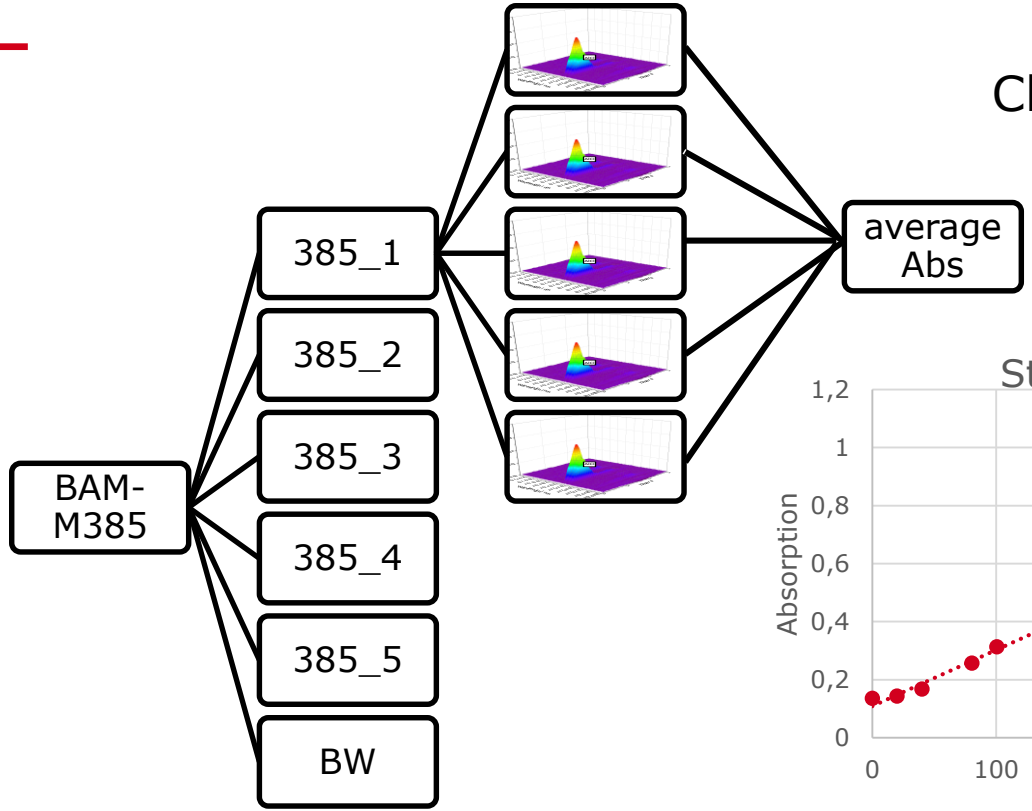
First measurements with Neon



Comparison with other procedures

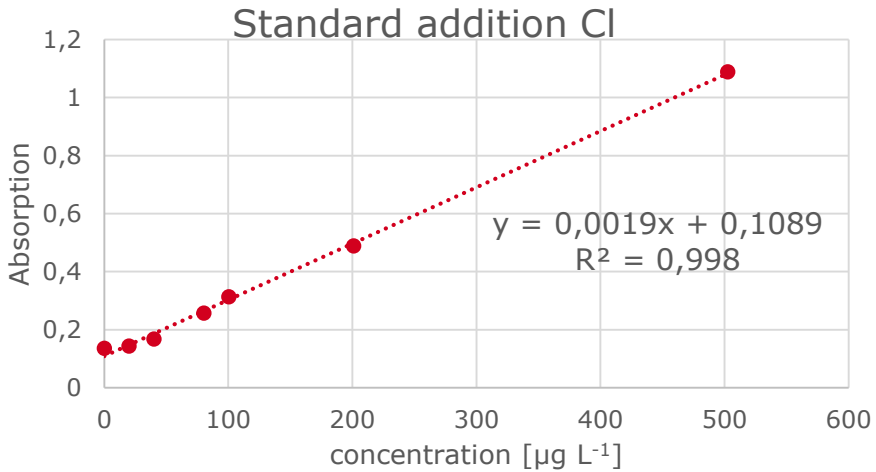


Measurement graphit furnace HR-CD-MAS



Cl+Al(NO3)3 → AlCl

LOD= 15 mg/kg



Conclusion and Outlook

GDMS an alternative to classical F-determination

Quantification strategies with pressed powder pellets/sintered samples

Improvement/Optimization of GD using additional discharge gases

Comparison using other techniques

Further investigations necessary to validate the findings