Monitoring the feedstock quality of coal conversion processes by means of ETV-ICP OES
Joint research projects in cooperation with IEC-TUBAF

- KORRISTENT (FKZ: 03ET7066A, BMWi-funded)
- Lausitz Energie Kraftwerke AG (LEAG), RWE Power AG

Goal of the research activities

Development of solution strategies to realize a slagging- or corrosion-free operation of plants → especially for mineral rich energy resources
Estimation of fouling or slagging behaviour of energy resources

For estimation of fouling or slagging behavior of energy resources (coals, sewage sludge, biomass)

→ Early identification of critical impurities for plant operation
→ IAC: Development of an analysis method for monitoring the feedstock quality
Need of an analysis method for monitoring the feedstock quality

**Traditional analytical methods**

- **Determination of element-concentrations**
  - Ultimate analysis (C, H, N, S, O-difference)
  - X-ray fluorescence spectroscopy (RFA) – previous ashing
  - ICP OES or -MS – previous digestion
  - CV-AAS (Hg)
  - TXRF
  - Neutron activation analysis (NAA)

- **Determination of element-species**
  - X-ray diffraction (XRD)
  - Scanning electron microscopy with energy dispersive X-ray spectroscopy (REM-EDX)
  - NAA – previous cold-plasma ashing
  - Infrared spectroscopy (IR)
  - Chemical extraction
  - Light microscopy

**Time-consuming analysis of process-relevant elements**

Sample alteration during ashing or digestion

**Requirement of a sensitive solid sampling analysis technique**
Advantages of ETV for sample introduction

**ETV – electrothermal vaporization**
- Approximately 3 mg of sample weighed in graphite boat
- Resistive heating in graphite tube
- Heating program up to 3000 °C (2400°C); max. heating rate 800 K/s
- Temperature-dependent vaporization of analytes
Coupling ETV-ICP OES

ICP OES – atomic emission spectroscopy with inductive coupled plasma (SPECTRO Analytical Instruments GmbH)

ETV – electrothermal vaporization
ETV 4000c – with autosampler AWD 50 (Spectral Systems)

ICP OES – atomic emission spectroscopy with inductive coupled plasma
- Excitation of electrons to a higher energy level
- Relaxion of electrons to a lower state - Emission of energy difference in form of radiation - Detection of element-specific radiation
Advantages of ETV-ICP OES analysis

ETV-ICP OES: Multi-element method with high dynamic measurement range

- Simultaneous determination of all relevant elements in energy feedstocks
- Traces to main elements in the same measurement run
- Temperature dependent release
### Method development – ETV-ICP OES

#### ETV (solid sampling unit)
- Graphit-tubes
- Graphit-boats
- Gas-flows
- Reaction-gases
- Transportsystem

#### ICP OES (spectrometer)
- Wavelength selection
- Plasma parameters
- Calibration
- Ar-Correction
  - calculation of signals in consideration of Ar-Emission for compensating fluctuations of plasma-temperature
- Wet plasma

#### Validation
- ICP OES / MS with previous digestion
- RFA, TXRF
- Hg-/ O-analyzer
- NAA
- REM EDX
- XRD
- Argonne Premium Coals
Determination of major, minor and trace elements in energy resources

Argonne Premium Coals (APC)

- 8 north american coal reference materials – prepared and stored under controlled conditions
- Used in various studies worldwide – reference values verified with various analytical methods
- Rank from lignite (lig: ND) to semi-anthracite (lvb: POC)
- High variation of ash content (5 - 20 %) and ash composition (B/A and D/A)
Direct determination of major, minor and trace elements of solid fuels by means of ETV-ICP OES

- coals* (rank from lignite to semi-anthracite, high variation of ash content and ash composition)
- coal adjacent sediments
- biomass (sewage sludge, wood, bamboo)
- mercury in coals
- oxygen in coals**

** Anal. Chem (2015) DOI: 10.1021/acs.analchem.5b02530
Transient signal ETV-ICP OES – element speciation

Discrimination of organic and inorganic bound oxygen
(carbonates, sulfates, clay, quartz)


Discrimination of organic and inorganic bound sulfur
(pyrite FeS$_2$, sulfates)

On-site visit of coal-fired boiler (2017)

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Motivation

Basics

Experiments

Results

Summary

Estimation of critical feedstock-quality for prevention slagging or corrosion of plants

- pyrite-content or clay-content \(\Rightarrow\) indicator for process-behaviour of feedstock
- Development of an analysis method for monitoring the feedstock quality
  \(\Rightarrow\) early identification of critical impurities for plant operation
Estimation of critical feedstock-quality for prevention slagging or corrosion of plants

Clay-/quartz content and pyrite content in feedstock of high relevance for estimation the corrosion or slagging potential

Model of formation mechanism
*Guilin Hu et al. in Progress in Energy and Combustion Science 2006
Monitoring the feedstock quality in 42 coal samples (3 times per day)

Discrimination of organic and inorganic bound oxygen

Discrimination of organic and inorganic bound sulfur
O-speciation in coals by means of ETV-ICP OES

Motivation

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Summary
O-speciation in coals by means of ETV-ICP OES

Motivation
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Summary

- Intensity [cps]
- Temperature [°C]
- O
- Si
- Al
- O

mineral-poor coal
mineral-rich coal
clayey coal
sandy coal
silty coal

Intensity [cps]
Temperature [°C]
Summary – ETV-ICP OES

- Fast solid sampling multielement-method with high dynamic range
  - possibility of simultaneous determination of process-relevant elements
  - trace- (Hg-ppb) to major (O-%) elements in fuels in the same measuring run

- Minimal sample preparation
  - homogenization (< 250 µm)
  - weight in (mg) → but problems with inhomogeneous samples

- Direct solid sampling method
  - no digestion (Si-underestimation)
  - no loss of analytes (S-evaporation)

- S- and O-Speciation
  - early identification of critical impurities for plant operation

- Short analyses time → process-accompanying analyses
  - autosampling (50-fold autosampler)
  - analysis time (s)
Acknowledgment

Thank you for your attention.