Analytical Techniques for Grade and Quality Control in Coal Mining

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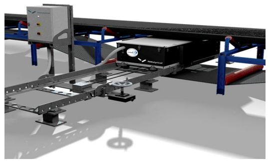
Dr Paul O’Meara

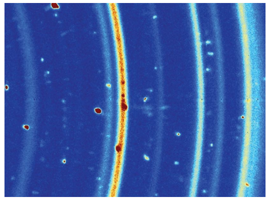
XRD Application Specialist

Topics



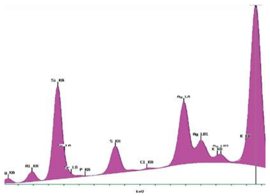
Pulsed Fast & Thermal Neutron Activation (PFTNA)

Cross-belt Elemental Analysis of Coal



X-Ray Diffraction (XRD) & Computed Tomography (CT)

Phase and Structural Analysis of Coal



X-ray Fluorescence (XRF)

Elemental Analysis of Unashed Coal

Cross-belt Elemental Analysis of Coal

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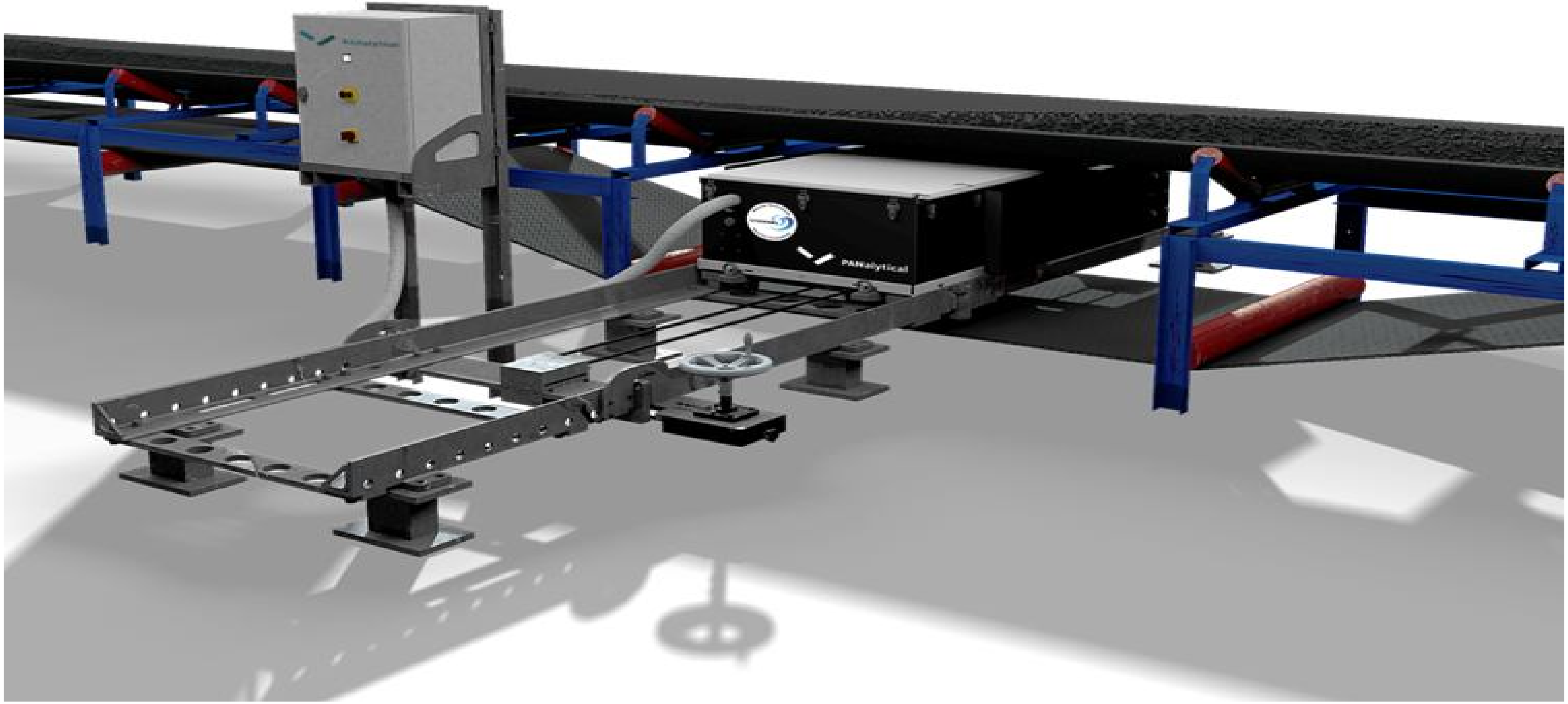

Introduction

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- Coal is a high-volume commodity
- Continuous grading necessary to determine appropriate pricing and use
  - total moisture
  - inherent moisture
  - volatile matter
  - fixed carbon
  - ash content
  - total sulfur
  - calorific value
  - HGI
  - grain size
- Representative sampling is complicated and unreliable
- Cross-belt analyzers eliminate sampling difficulties by measuring the material on moving conveyor belts
- Cross-belt analyzers deliver “real-time” results, which can be used for process optimization

Introduction

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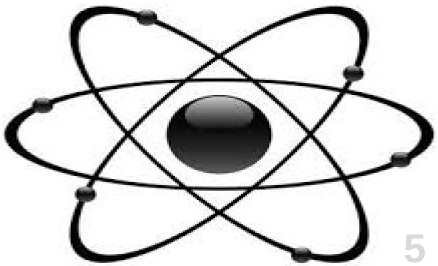
- The majority of cross-belt analyzers are, in fact, neutron activation analyzers (NAA)
- Neutrons are used because:
  1. they are highly-penetrating particles, which means they can access large volumes of material (often through reinforced conveyor belts)
  2. they interact with atomic nuclei and induce characteristic gamma (γ) photon emissions, which are also highly penetrating and can, therefore, escape the sample and enter the detector



The principle

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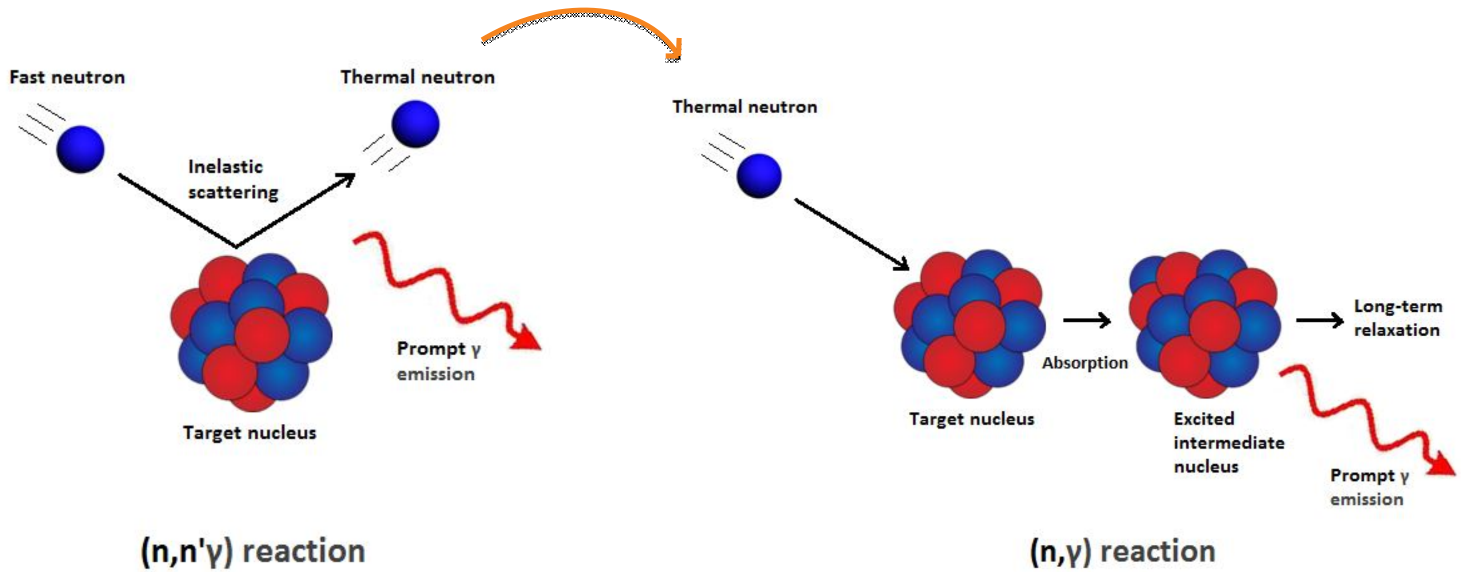

Cross-section

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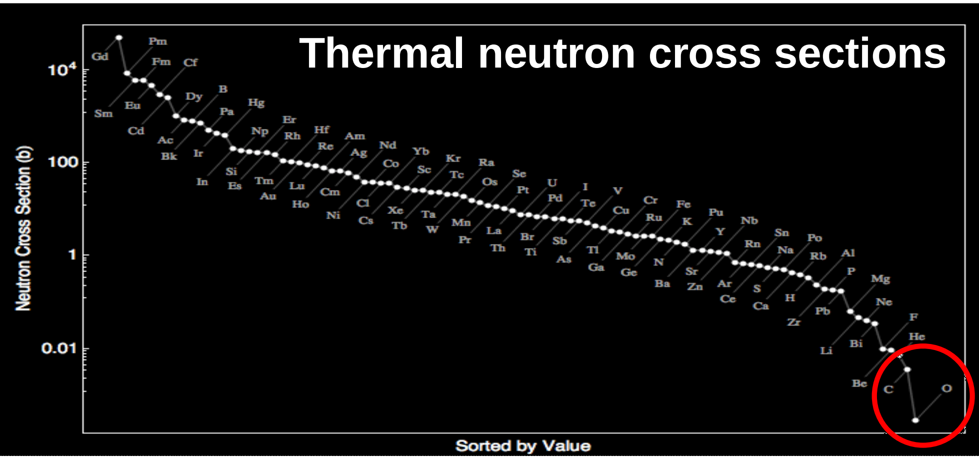
- The probability of interaction between neutrons and atomic nuclei is dependant on the so-called “neutron cross section”
  1. the target element
  2. the type of reaction (absorption, scattering, etc.)
  3. the incident particle energy



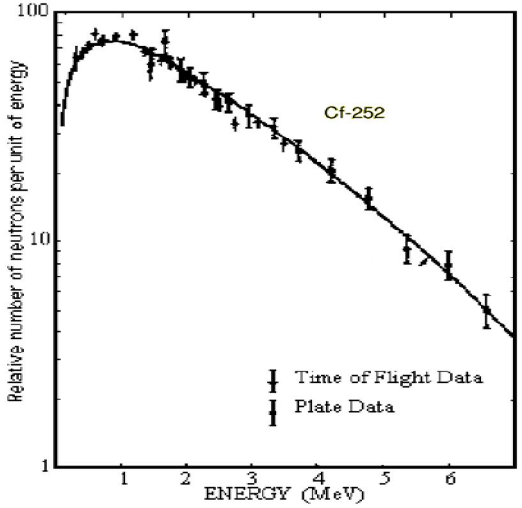
Sources

- The most common source of neutrons in cross-belt analyzers is the spontaneous fission of californium-252 by α-decay

$$^{252}_{98}\mathrm{Cf} \rightarrow {}^{248}_{96}\mathrm{Cm} + \alpha \text{ (where } \alpha = 2\mathrm{p} + 2\mathrm{n})$$

- 70 % of neutrons produced by this process have energies between 0.3 and 1.8 MeV and a maximum energy of approximately 6.5 MeV (low but detectable flux)

NO C AND O ANALYSIS!!!



Sources

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- Neutron generators, like those used in our CNA[3] Coal, offer significant advantages over isotope-based sources:
  1. pulsed 14 MeV neutrons via the fusion of deuterium and tritium

     $${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow \mathrm{n} + {}^{4}_{2}\mathrm{He}$$

  2. programmable flux eliminates interruptive drift corrections and recalibrations and maintains precision
  3. the source can be switched off
  4. reduced import and export limitations and safety requirements

Electric Neutron Generator

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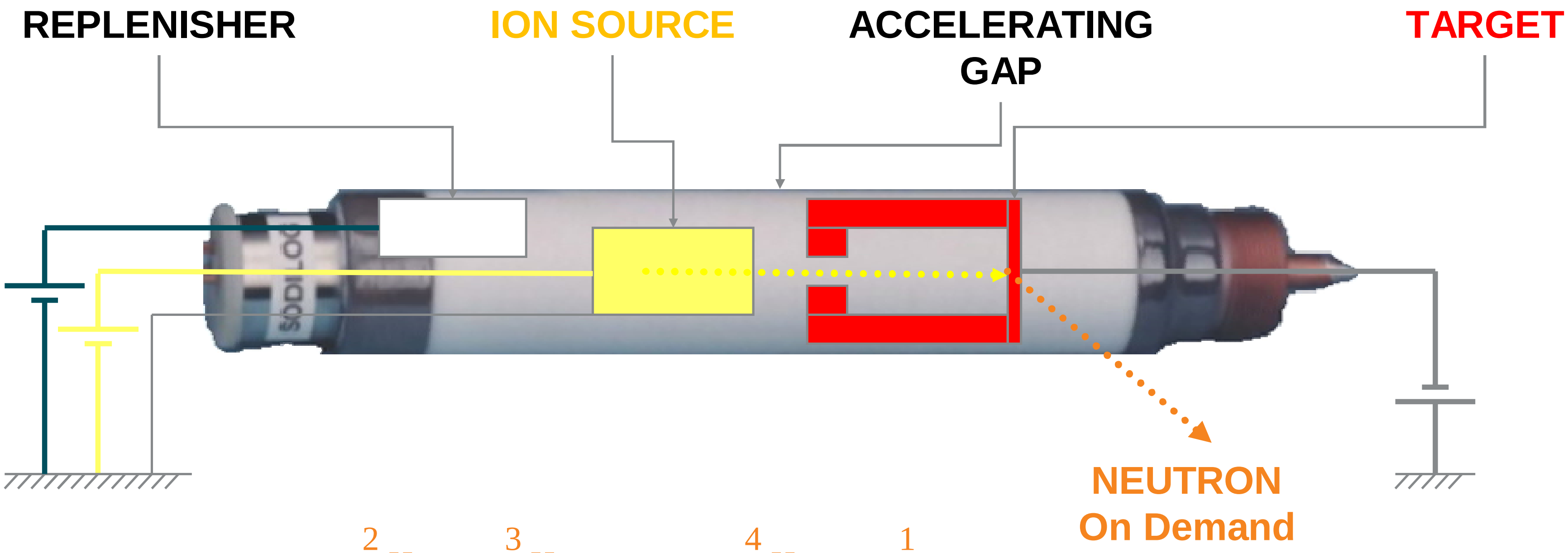
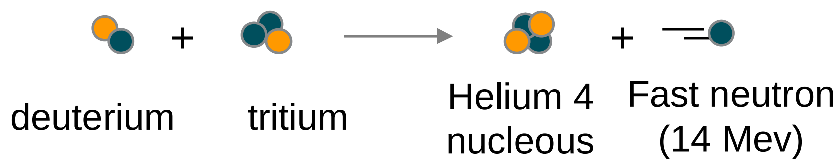


$$ {}^{2}_{1}H + {}^{3}_{1}H \cdots\cdots\rightarrow {}^{4}_{2}He + {}^{1}_{0}n $$



Safety

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- Californium-252

1.2 mSv/h

- Sodern Neutron Generator

natural background radiation

Neutron Activation Analysis

Coal analysis

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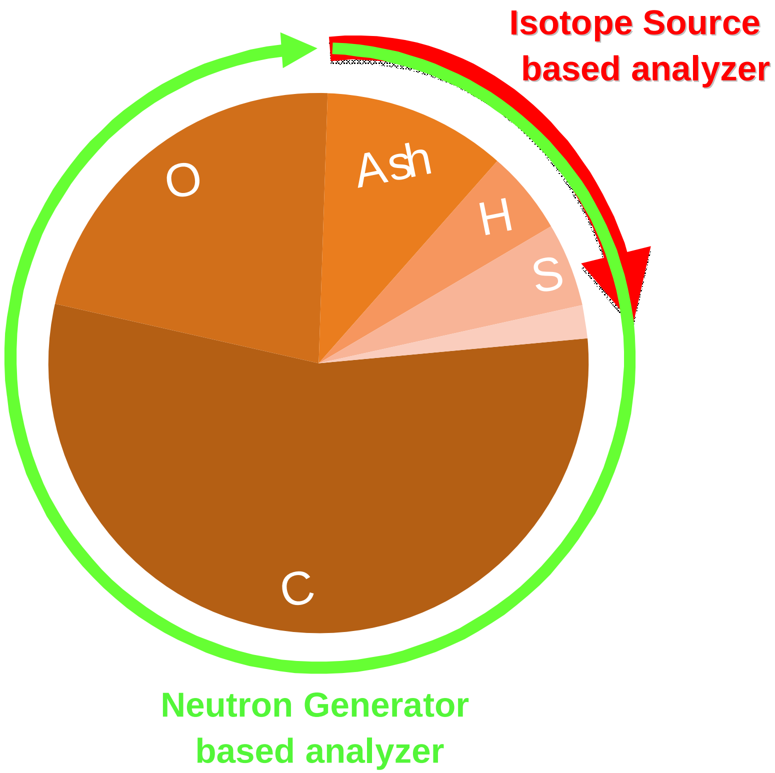

- Real-time elemental analysis (H, C, N, O, Na, Al, Si, S, Fe, K, Ca, Ti & Mn – as received basis)
- Accurate calculation of:
  1. ash content
  2. moisture content
  3. calorific value

Example data

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$$Q = [145.44[C] + 620.28[H] + 40.5[S] - 77.54[O]]$$

Straight PRB al Example

CNA3 Coal Real-time Data

Element	Concentration (%)
C	51
O	37
H	6.67
S	0.23
N	0.68
Cl	0
Si	1.00
Al	0.50
Ti	0.05
Fe	0.20
Ca	0.75
Mg	0.15
K	0.05
Na	0.10

ASTM Stve Parameters

Moisture H	28.89%
Moisture O	32.40%
Average	30.65%
Ash	5.62%
Volatile	31.19%
Fixed Carbon	30.79%
Calorific Value	8.426Btu/lb

Combustion Calculations

Fuel Ratio	0.99
SO2/Mbtu	0.52

B&W T-250	2284
W&F T-250	1934
N&R T-250	2229

ASTM Ash Chemistry

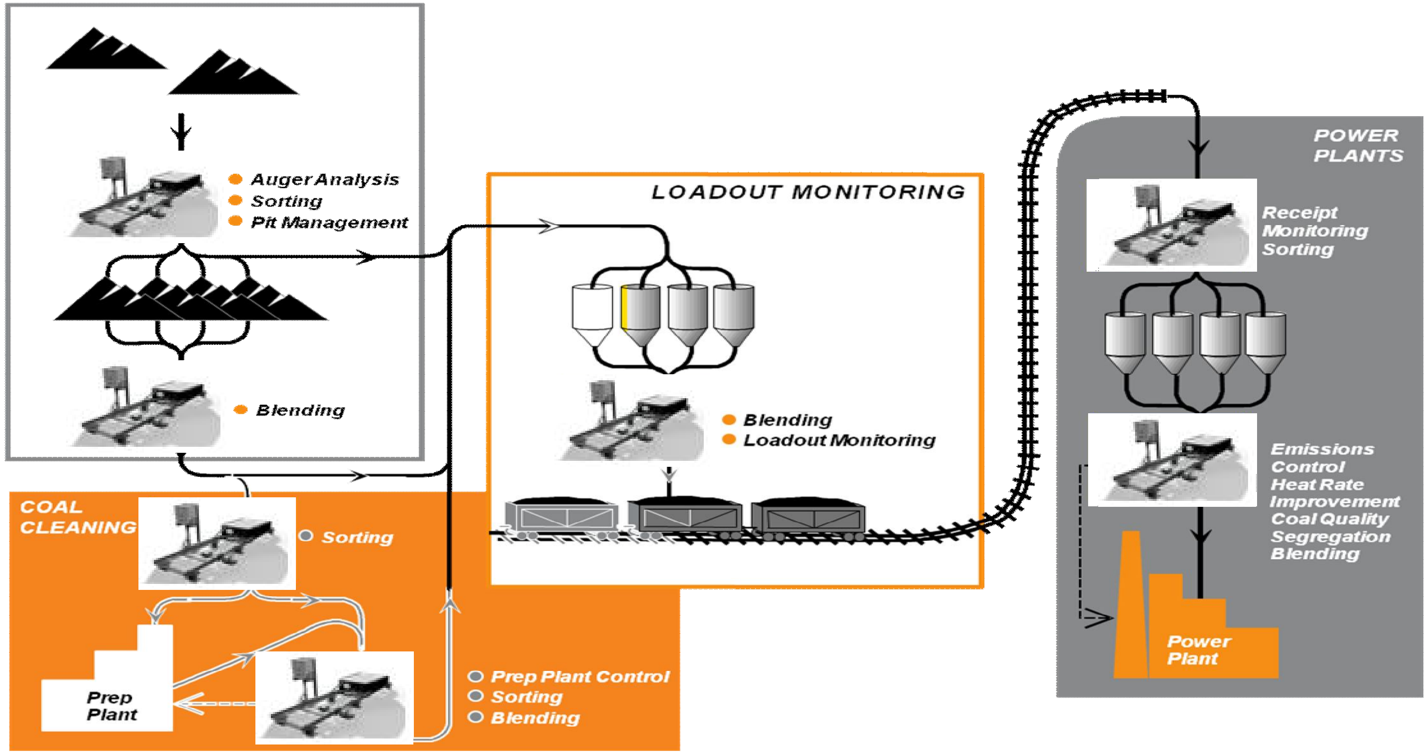
SiO2	39,85%
Al2O3	17,60%
TiO2	1,55%
Fe2O3	5,33%
CaO	19,55%
MgO	4,66%
K2O	1,13%
Na2O	2,51%
SO3	7,82%

Ash Properties

Lbs Ash/Mbtu	6.67
B/A Ratio	0.56
Slag Index	0.12
Foul Index	1.41
Silica%	57.4
SiO2/Al2O3	2.26

Input values from CNA3 Coal
Calculated values from CCI software

CNA³ Coal positions



Benefits for power plants

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- Improved combustion efficiency by approximately 0.4%
- Reduced boiler downtime and, therefore, production
  - ✓ reduced costs associated with oil restarts
  - ✓ reduced fines for non-production
- Reduced coal costs through accurate blending
- Reduced maintenance costs
  - ✓ elimination of sampling system
  - ✓ reduced corrosion and cokefaction in pipes
  - ✓ reduced downtime to remove slags

Payback estimated at 1.5 to 2 years

Phase and Structural Analysis of Coal

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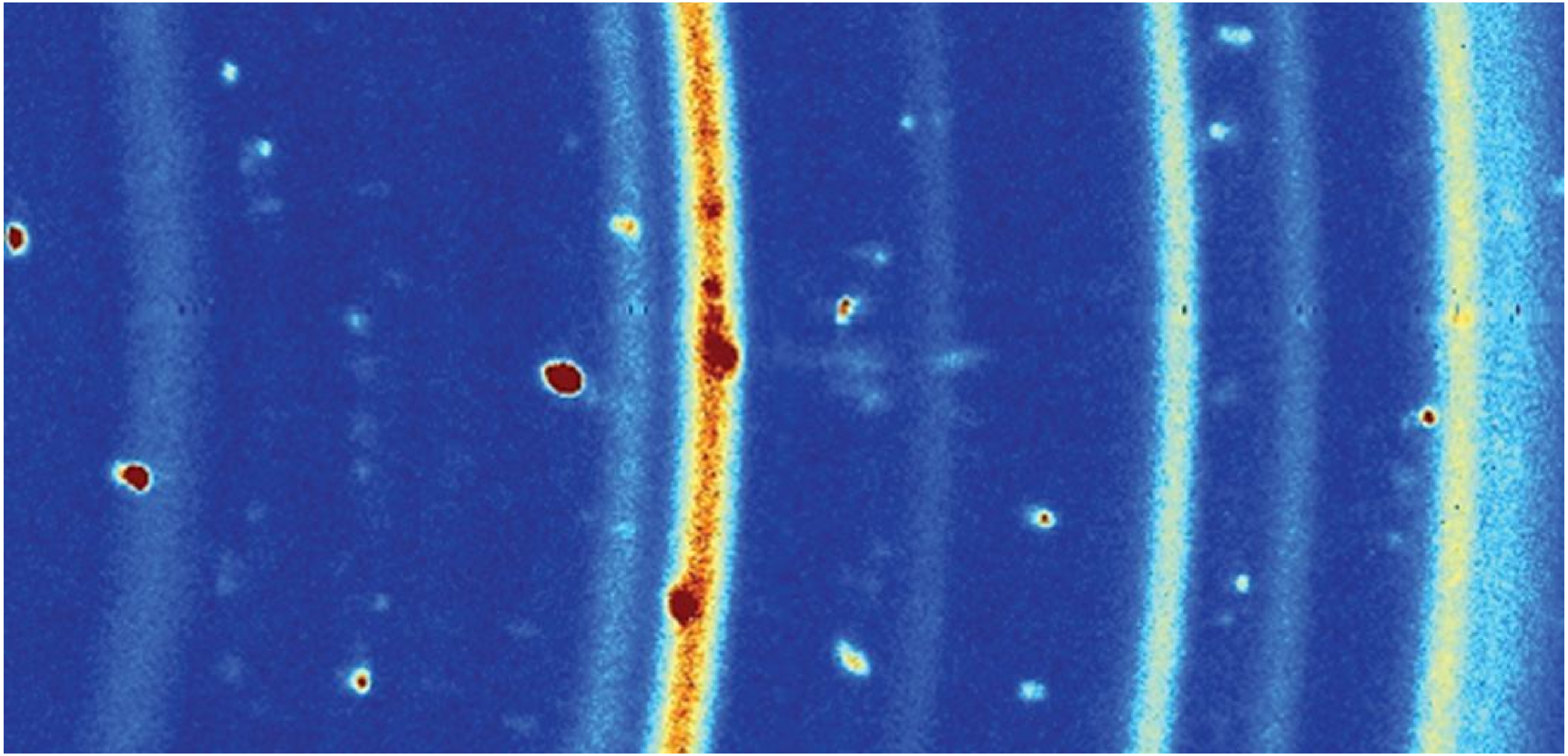
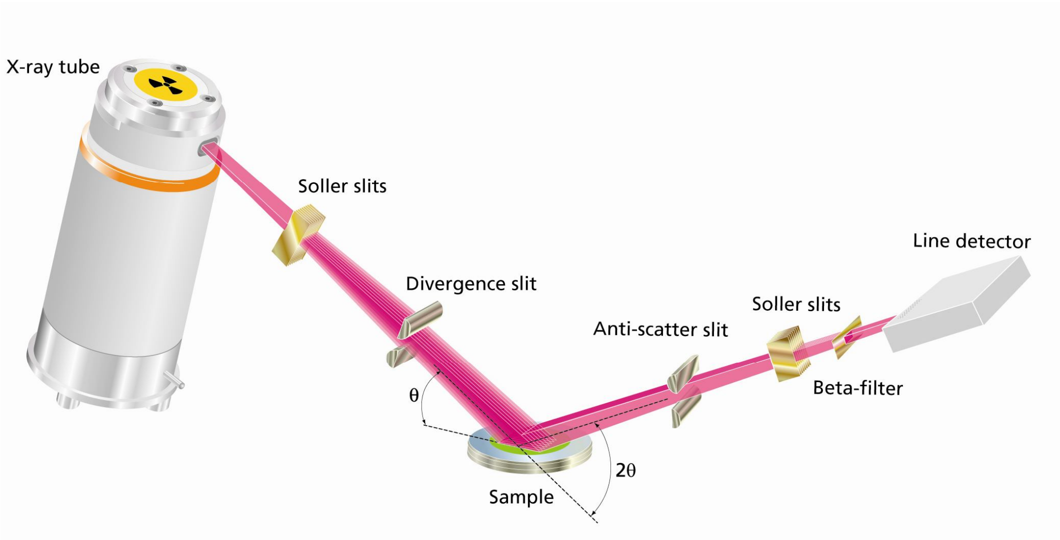
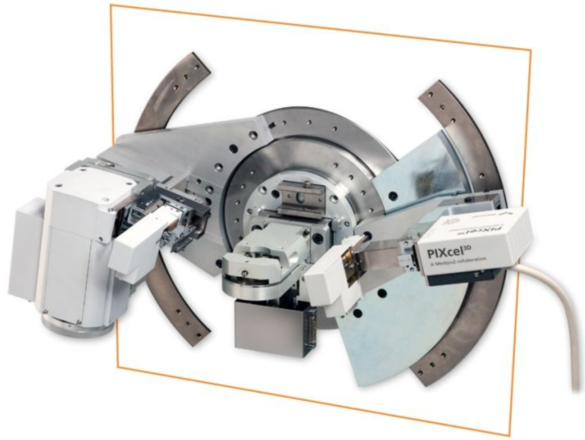


What is X-ray diffraction (XRD) ?





- Versatile, nondestructive analytical technique
- Identification and quantitative determination of the various crystalline phases of compounds present in powdered and solid samples
- Quantification of the amorphous content

Mineral identification in coal

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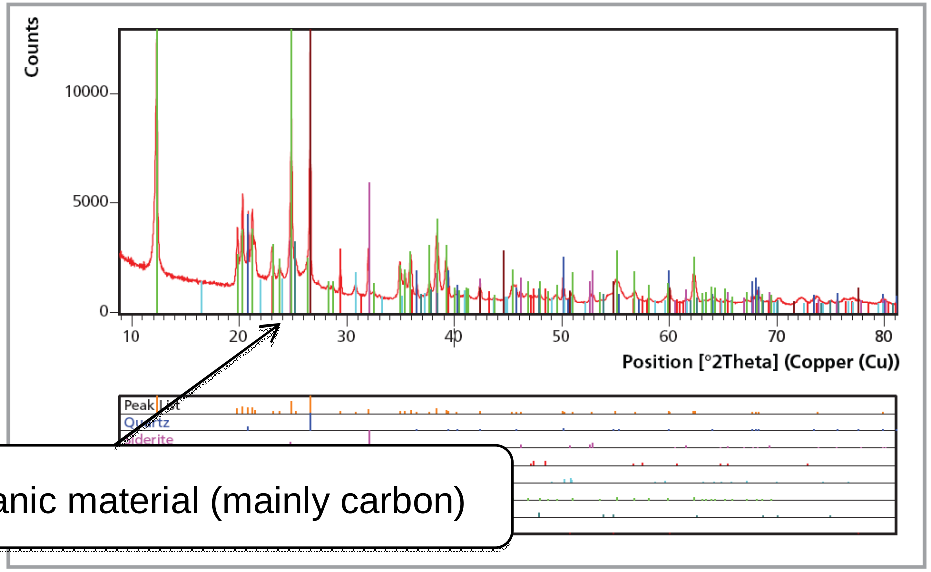
Fast phase ID of minerals in coal and coal related materials compared to microscopy

- Raw coal sample with high mineral content
  - Graphitic carbon (C)
  - Quartz (SiO_2)
  - Kaolinite ($Al_2Si_2O_5(OH)_4$)
  - Calcite ($CaCO_3$)
  - Dolomite ($CaMg(CO_3)_2$)
  - Siderite ($FeCO_3$)
  - Anatase (TiO_2)

Ash



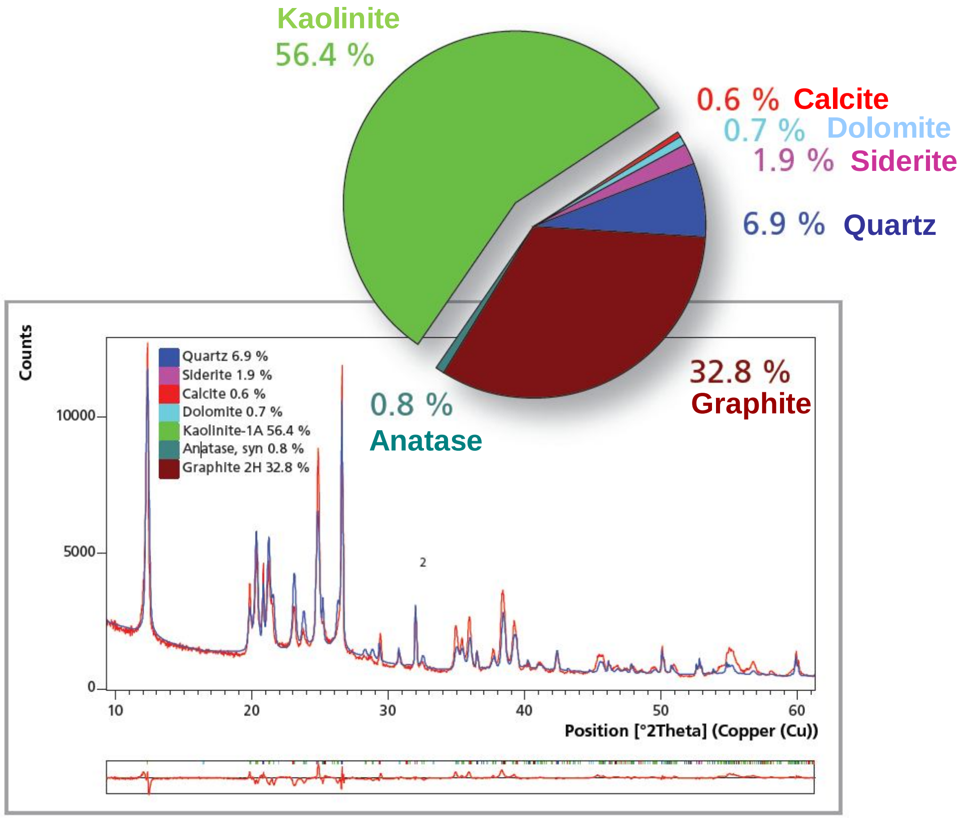
Organic material (mainly carbon)

Mineralogical quantification of coal

None destructive analysis of the coal/ash ratio

Control erosion and abrasion of the mills by monitoring mineral content

- automatable
- operator independent
- non-destructive
- no chemicals required
- easy sample preparation



Characterization of graphitic carbon

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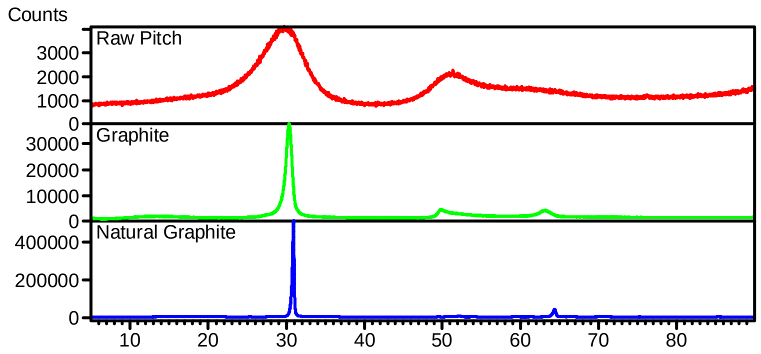
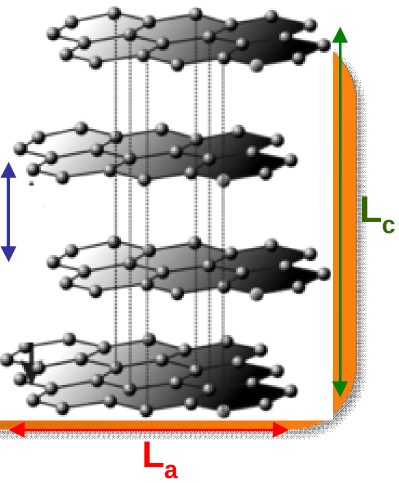
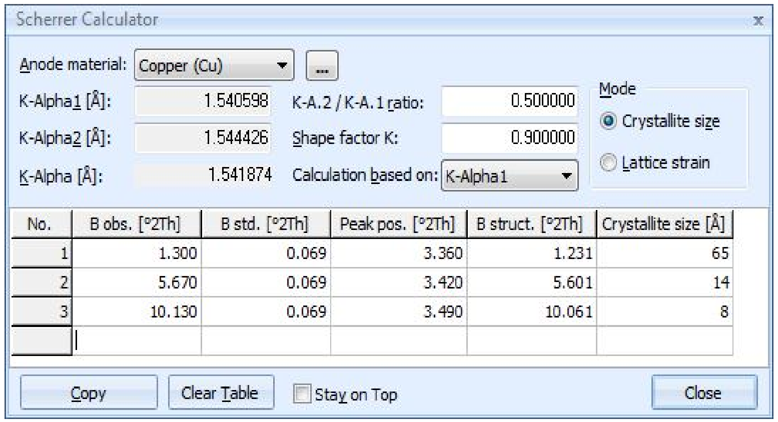
- Process of graphitization *g* (heat treatment) courses an increase in the degree of ordering within crystal structure of graphitic carbon
- Changes within lattice parameters d_{002} and crystallite size L_c
- d_{002} can be used as indicator for the graphitization g



Easy determination of
size (L_c) and graphitiz
- Better performance
materials (resistivity,
thermal expansion, ef
anodes for aluminium





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CubiX^3 Minerals

- Industrial diffractometer
- Fulfills modern international safety standards
- Dust protection for rough environments
- Analysis time of less then 5 minutes
- Handling of all common sample holder rings
- Ready for automation

Automation

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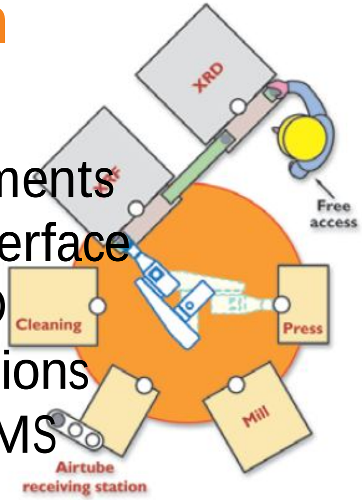
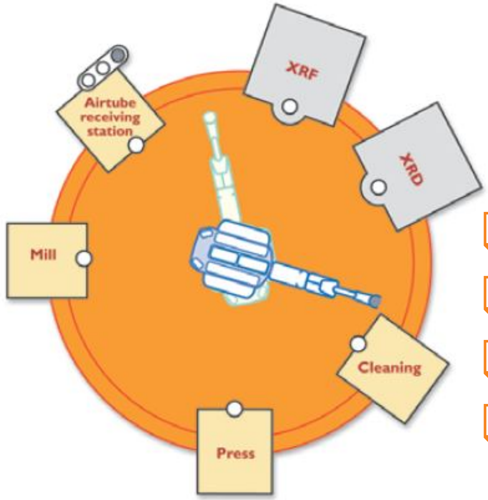
- TWo INstruments
- One user interface
- XRF and XRD
- Belt connections
- Result via LIMS

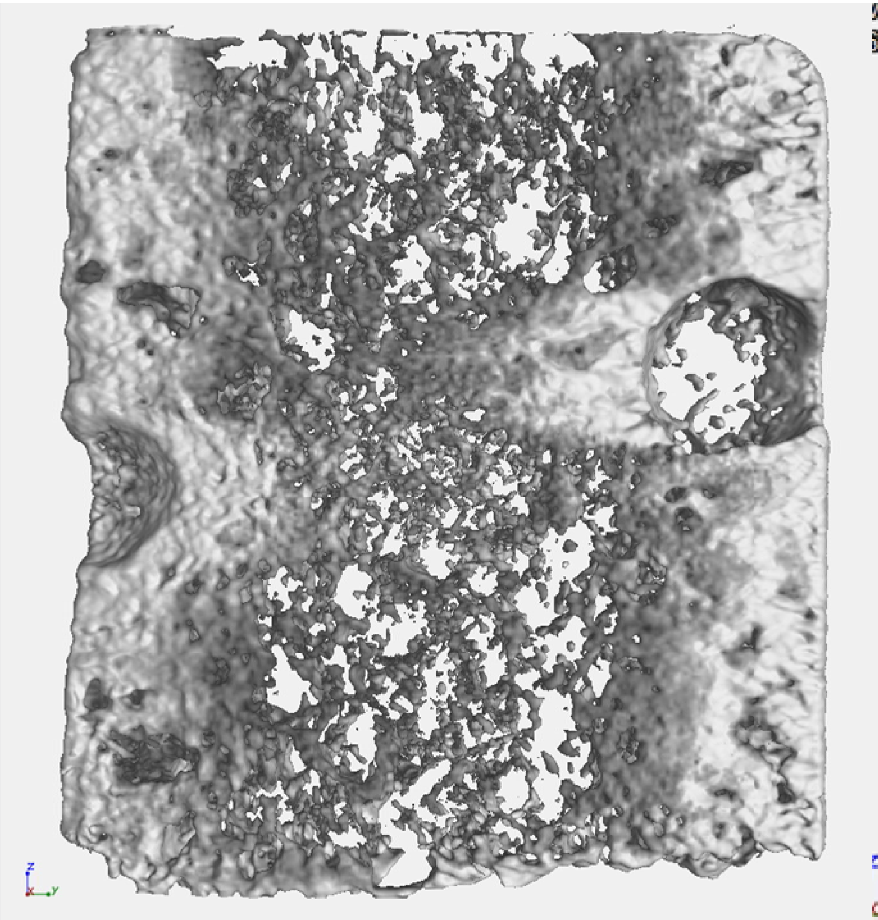


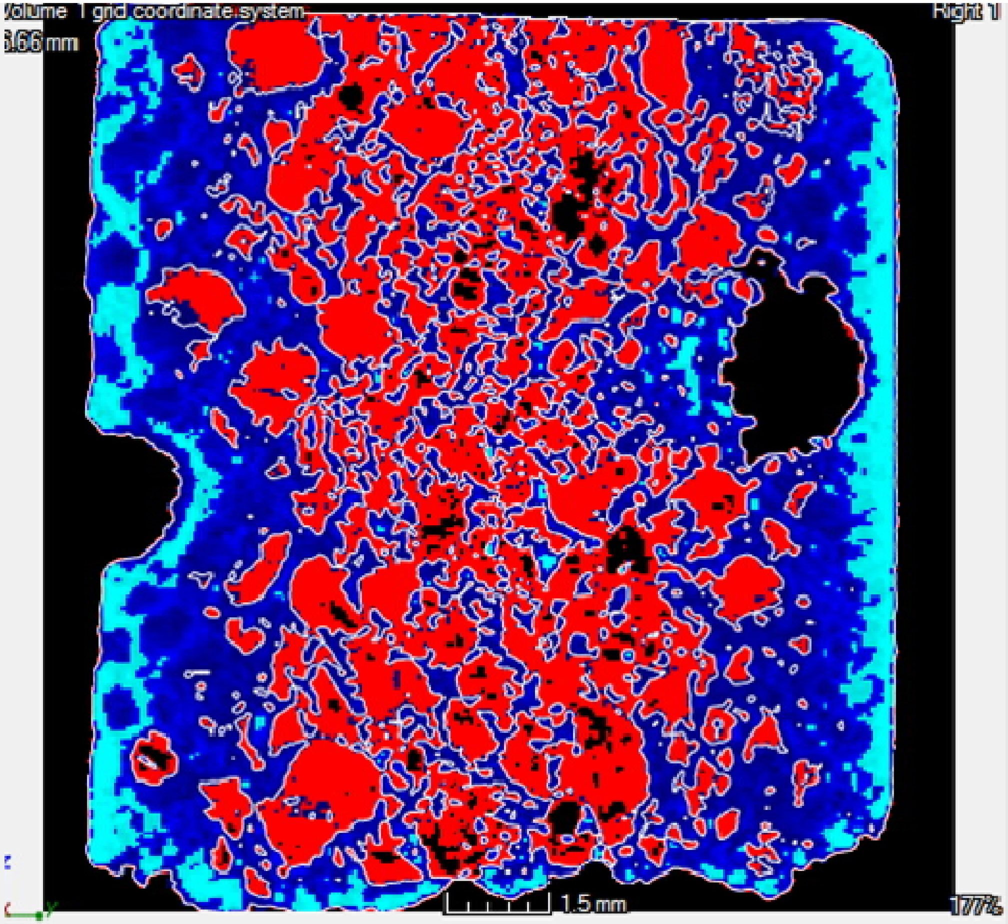


- Container laboratory
- Sample preparation
- Analytics
- Result via LIMS

- Robot automation
- Sample via airtube
- Automatic sample preparation
- Analytics
- Result via LIMS

3D imaging - Computed tomography (CT)





Combined CT - XRD

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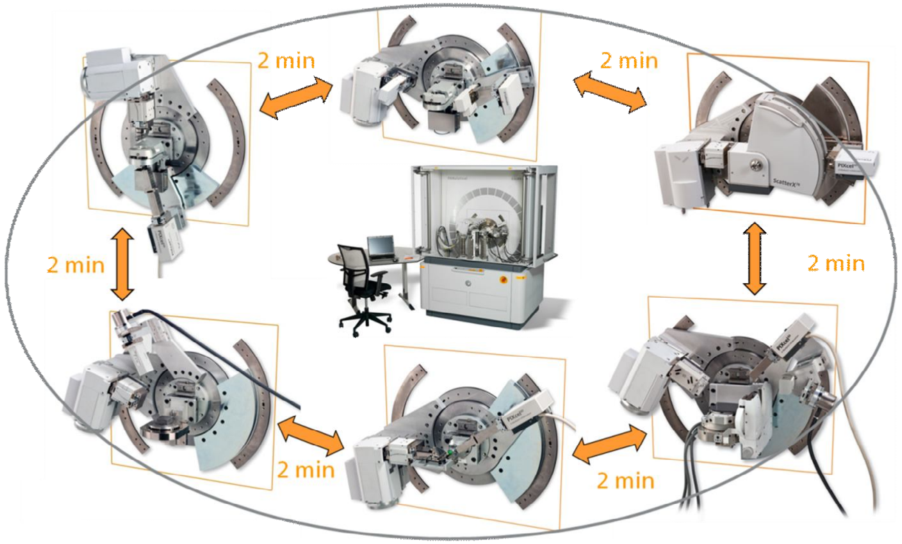
- Computed Tomography (CT) as an analytical tool for material science has been mostly restricted to dedicated CT-instruments or large scale facilities
- We will demonstrate CT measurements on coal samples performed on an Empyrean multipurpose diffraction platform



Technical details

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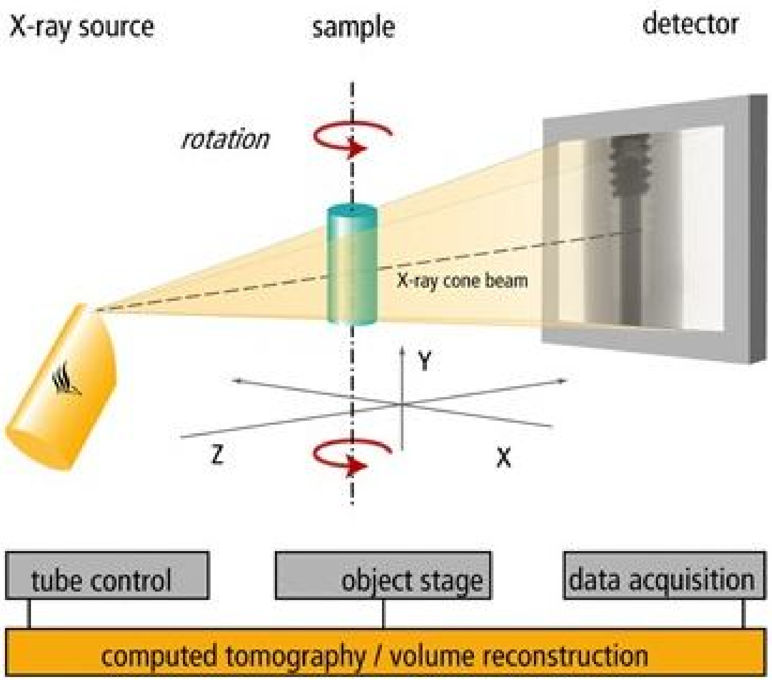
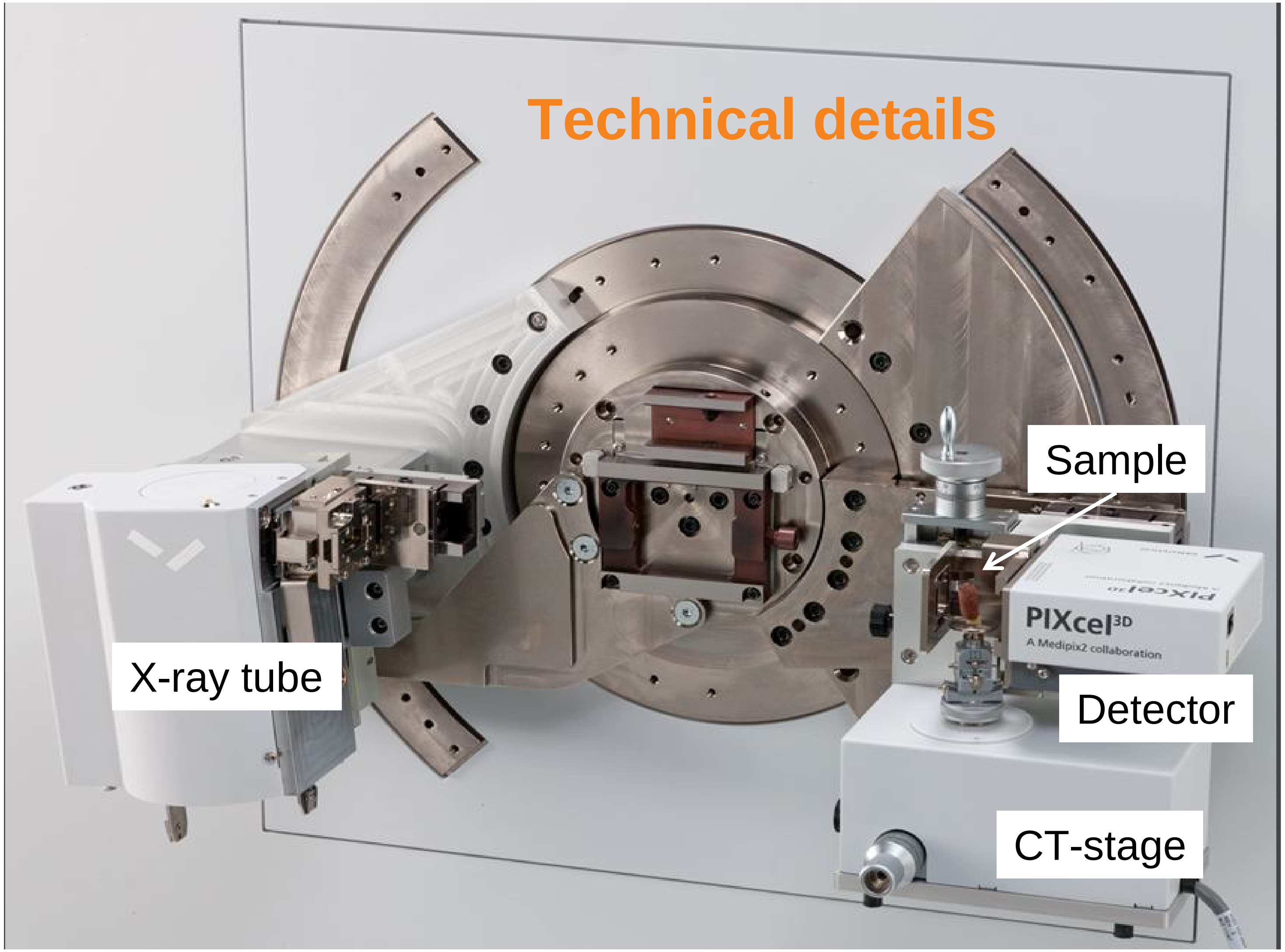


Technical details



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Technical details

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Computed tomography (CT) on coal

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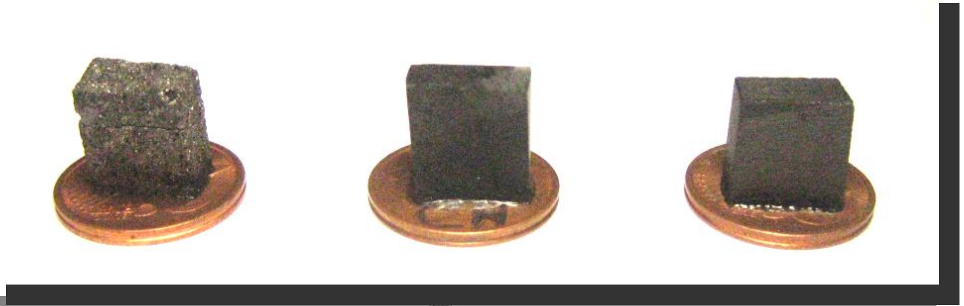
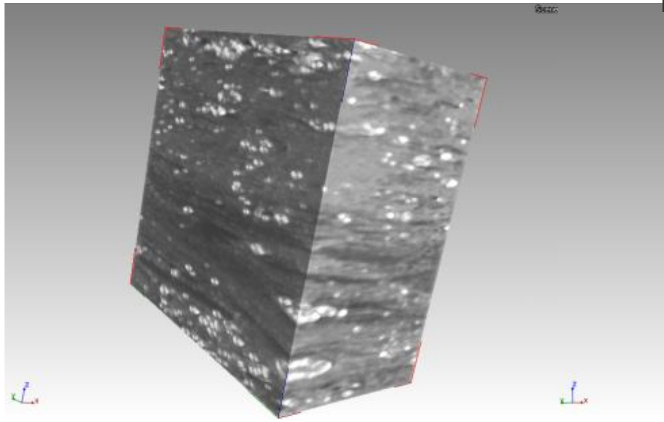
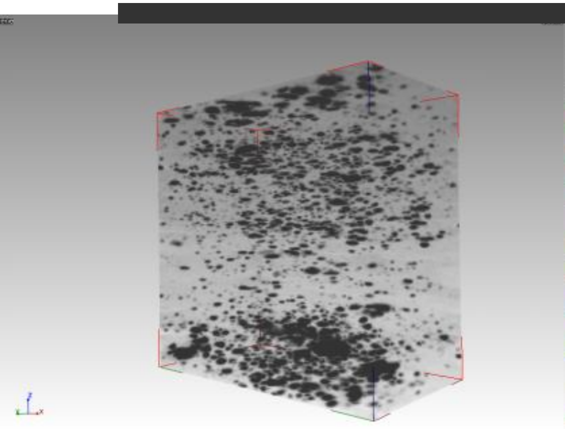


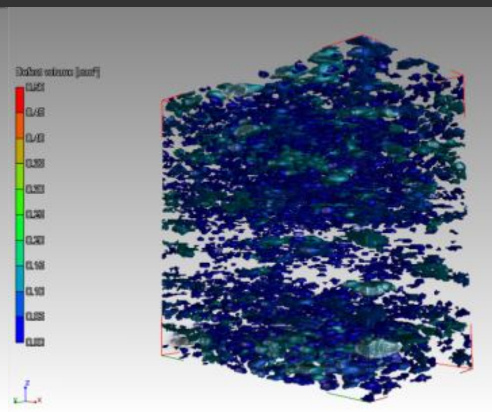
Sample size: 12 x 12 x 8 mm



Mineral distribution



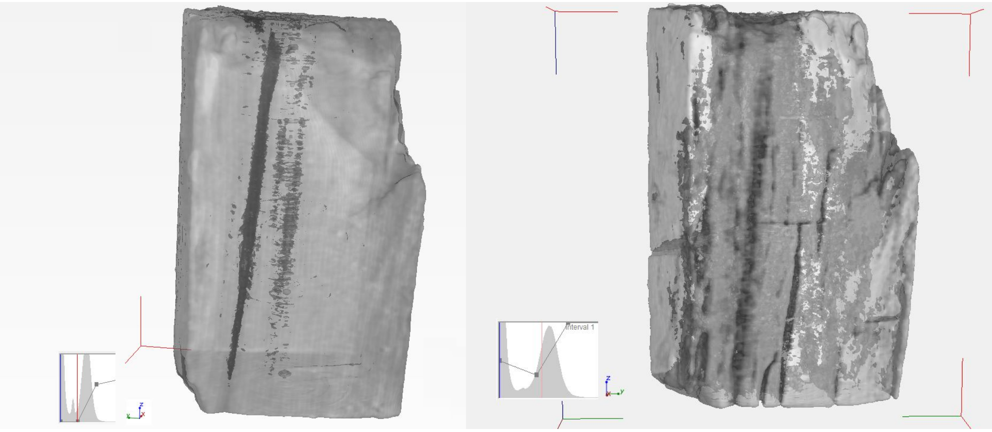
Pore size distribution



Mineral size distribution

Heat treatment of coal samples

- Samples were heat treated to simulate the char process
- Comparison of volume, void, composition changes



Parameter	Room temperature	950°C
Size (mm)	5.4 x 6.6 x 11.2	4.8 x 5.9 x 10.1
Volume (mm^3)	399.168	286.032
Shrink factor volume (%)	100.0	-28.336
Size (mm) [CT]	7.18 x 7.94 x 11.91	6.61 x 7.25 x 10.8
Volume (mm^3) [CT]	353.1	287.51
Shrink factor (%) [CT]	100.0	-18.575

Density distribution

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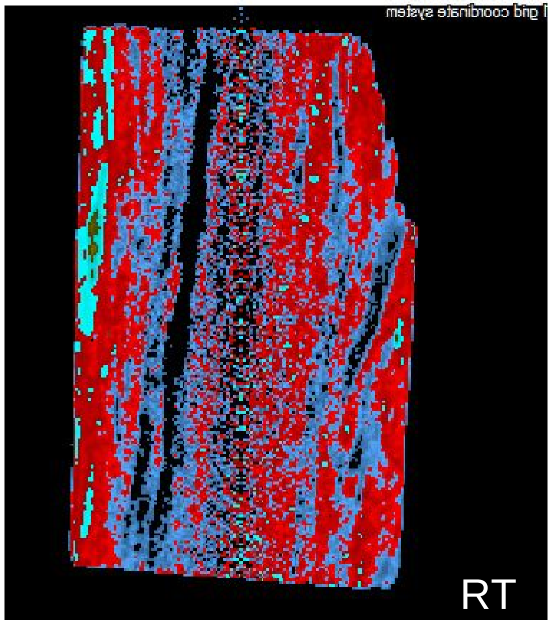
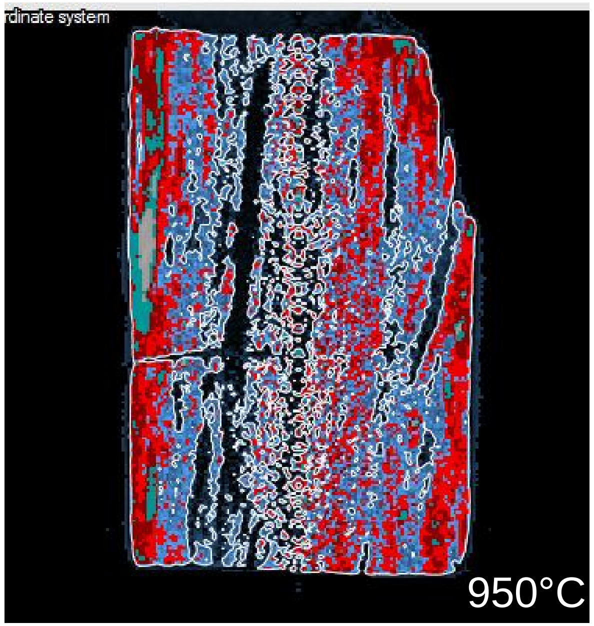
Coal with different densities = Colored

Inclusions/cracks = Black





Elemental Analysis of Unashed Coal

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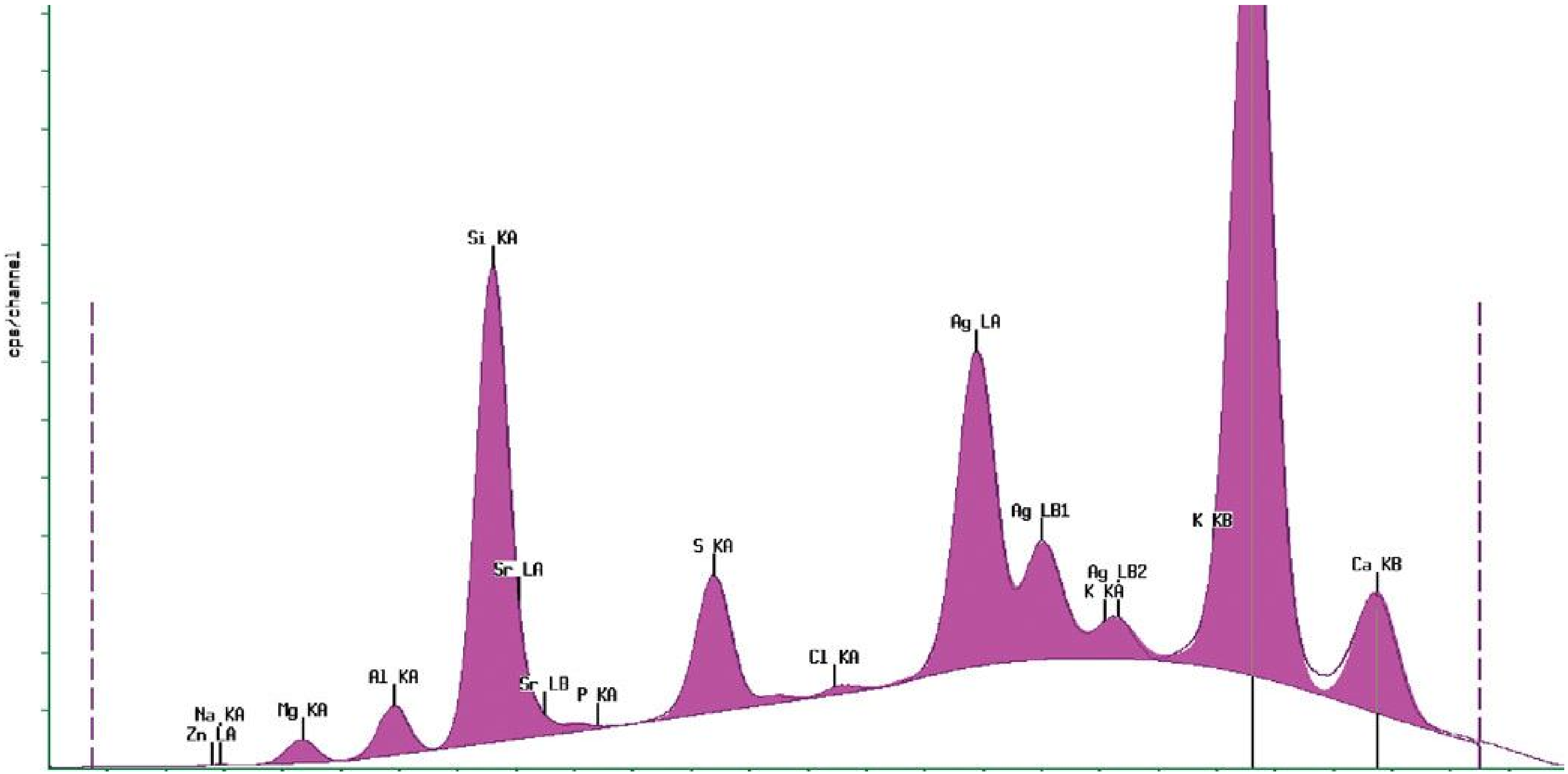

Introduction

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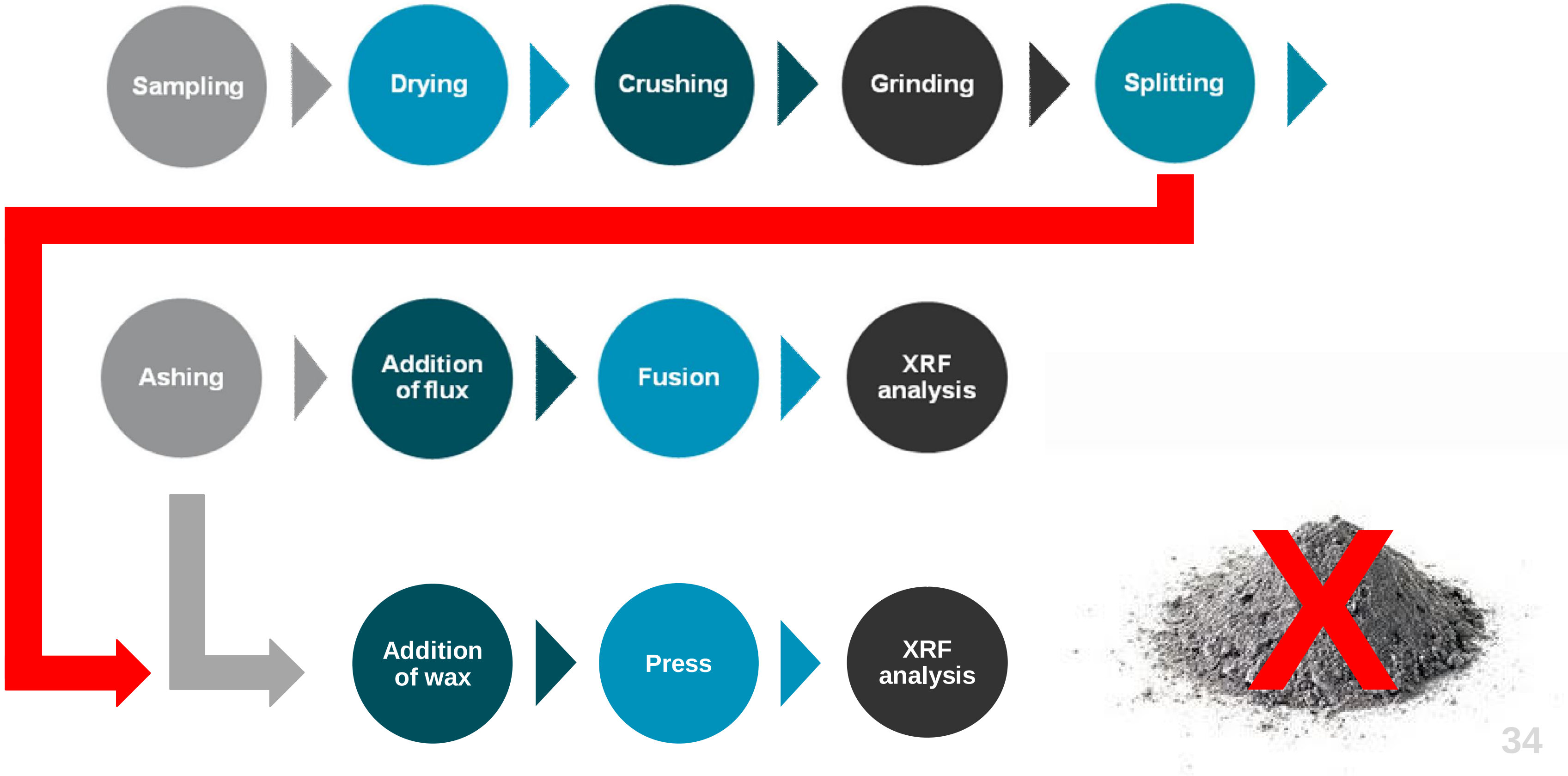
- Coal is often graded and priced according to the concentration of sulfur, phosphorus, volatile materials and ash content

- Traditionally, the inorganic content has been quantified (often with XRF) by analyzing coal ash
  - sample preparation is extremely time consuming
  - multiple sample preparation steps introduce errors & contaminants

Analysis process

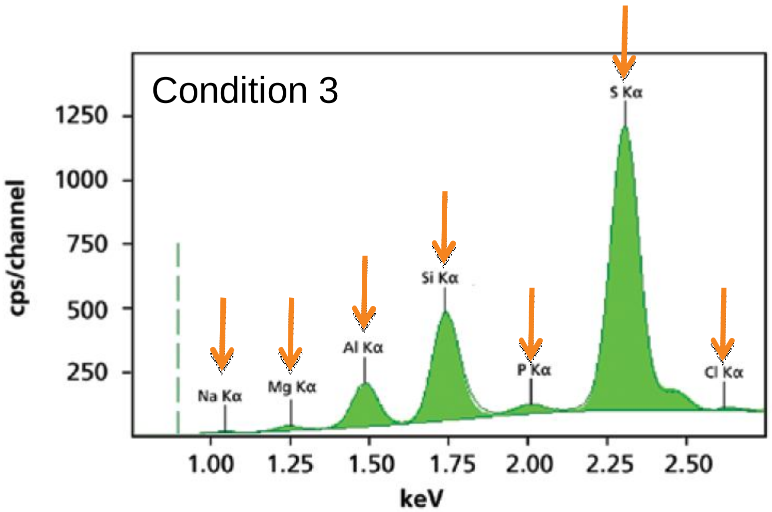


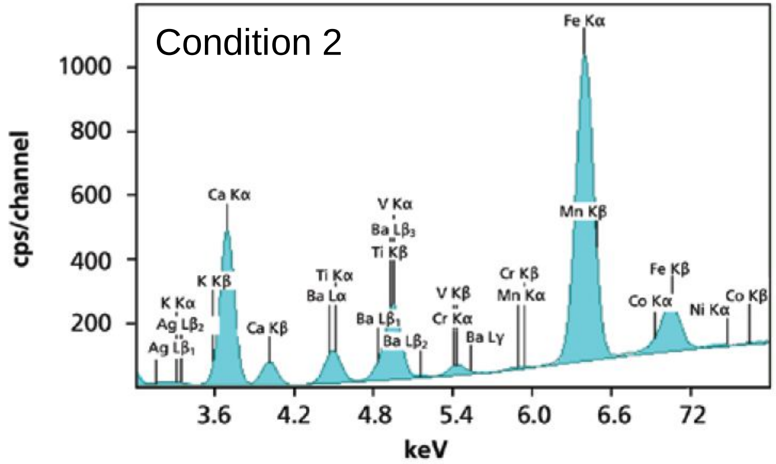
Application example

- Procedure
  1. coal standards acquired (Alpha & SABS)
  2. the standards were dried
  3. the standards were milled
  4. the standards mixed with wax
  5. the mixtures were pressed into pellets
  6. the standards were measured on an Epsilon 3^X

Condition	Elements	kV	µA	Measurement Time (s)	Medium	Filter
1	Sr	30	300	60	Air	Ag
2	K, Ca, Ti, Fe & Ba	12	600	60	Air	Al (thin)
3	Na, Mg, Al, Si, P & S	6	1000	120	Helium	none

Spectrum examples





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Calibration examples

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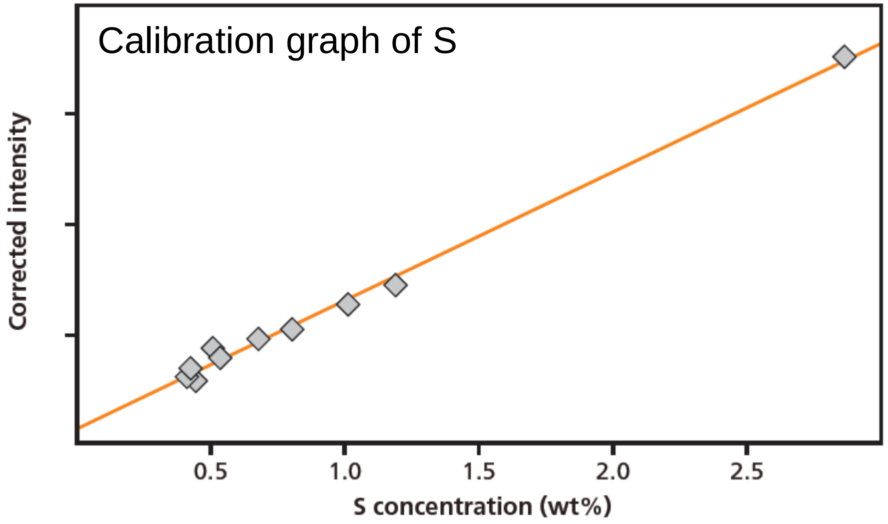

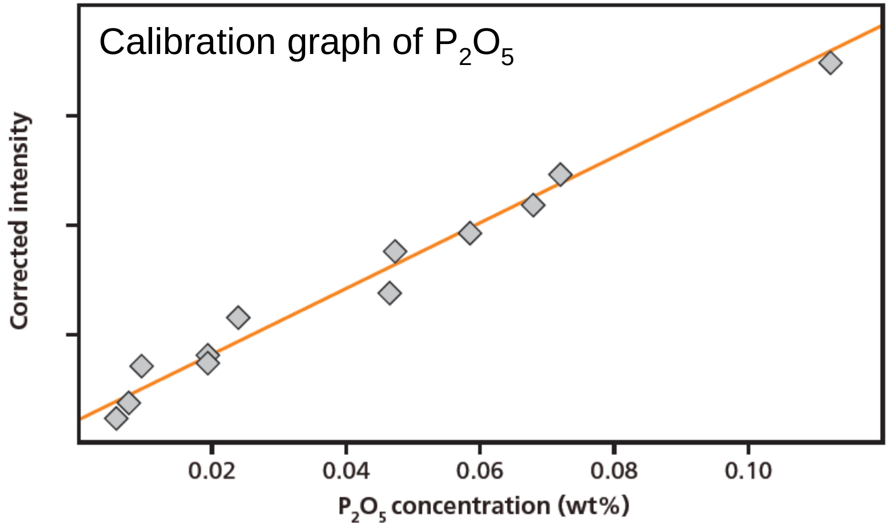

Calibration results

Compound	Concentration Range (wt%)	RMS (wt%)	LLD (ppm)
Na_2O	0.014 – 0.29	0.0131	150
MgO	0.025 – 0.43	0.0111	100
Al_2O_3	0.86 – 11.27	0.1480	55
SiO_2	1.6 – 17.66	0.2810	45
P_2O_5	0.007 – 0.14	0.0067	40
S	0.51 – 3.58	0.0764	10
K_2O	0.029 – 0.215	0.0060	12
CaO	0.044 – 1.87	0.0232	8
TiO_2	0.06 – 0.63	0.0055	7
MnO	0 – 0.02	0.0006	7
Fe_2O_3	0.147 – 3.815	0.0395	6
SrO	0.001 – 0.033	0.0010	2
BaO	0.004 – 0.042	0.0017	20

Precision results

Compound	Average Concentration (wt%)	1σ Standard Deviation (wt%)
Na_2O	0.26	0.009
MgO	0.23	0.007
Al_2O_3	8.05	0.014
SiO_2	15.12	0.044
P_2O_5	0.042	0.004
S	1.40	0.003
K_2O	0.24	0.002
CaO	1.43	0.012
TiO_2	0.35	0.001
MnO	0.021	0.0003
Fe_2O_3	1.75	0.004
SrO	0.014	0.0002
BaO	0.036	0.001

Summary

- Accurate determination of ash, phosphorus and sulfur content is possible without time-consuming ashing procedures

- Inexpensive solution for:
  1. mine/pit management
  2. stockpile sorting
  3. load-in control (specification checking)
  4. coal yard management
  5. blending

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