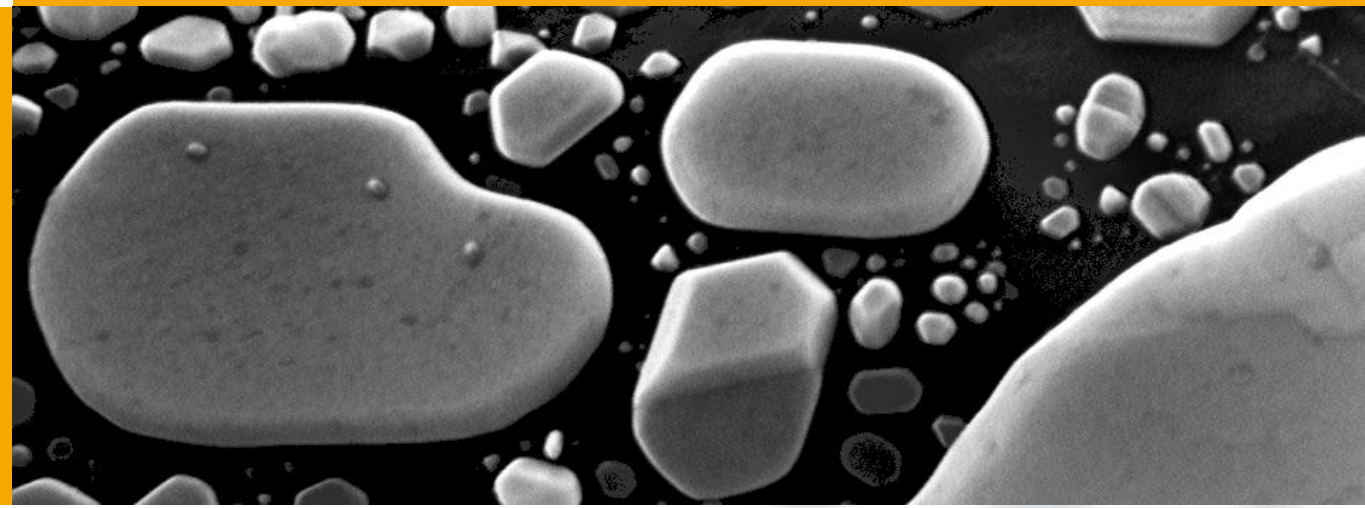
CleanControlling®

Online Basic-Seminar
TECHNICAL CLEANLINESS
VDA 19.1 and VDA 19.2



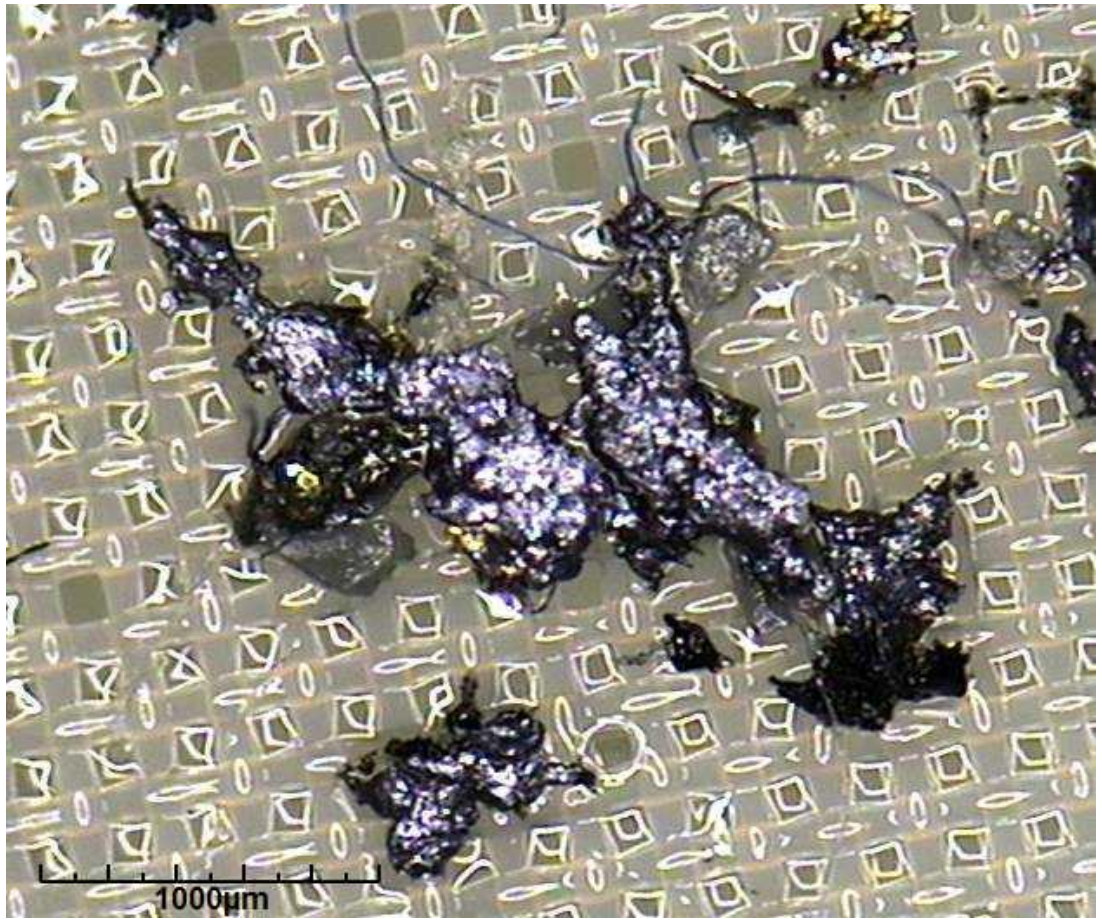
Particle identification using Scanning Electron Microscopy and Infrared Spectroscopy

Simon Schnitzlein, CleanControlling GmbH

EXTENDED ANALYSES

Motivation

Why performing extended analyses?



Extended analyses are performed when additional information is needed:

- Exact measurement of particles < 50 µm
- **Material determination** or derived properties such as hardness or electrical conductivity

EXTENDED ANALYSES

Content

Basics SEM/EDS

Particle identification by means of SEM/EDS

IR-Spectroscopy & particle identification

Analytical methods for testing surface cleanliness

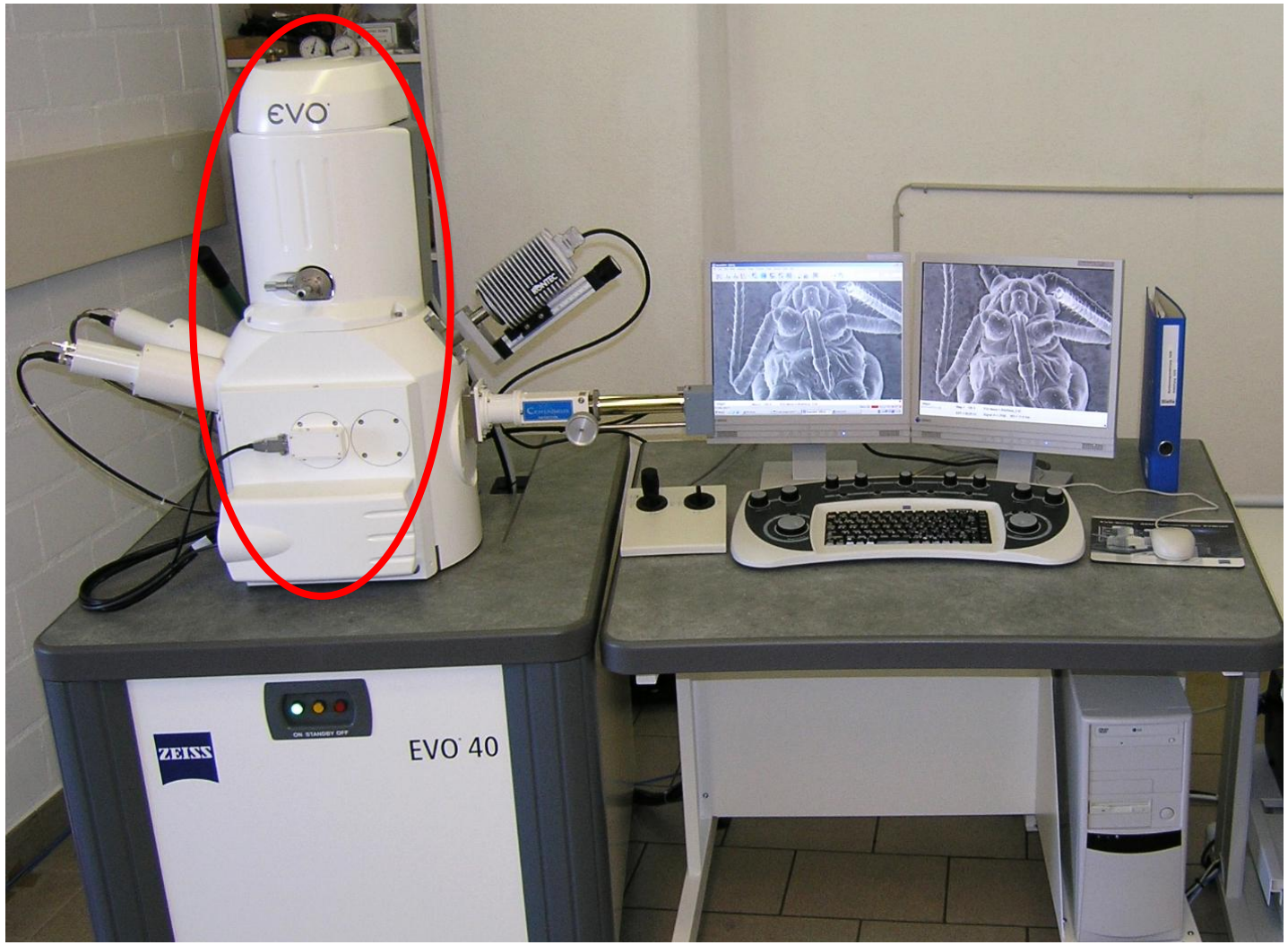
SCANN ELECTRON MICROSCOPE (SEM)

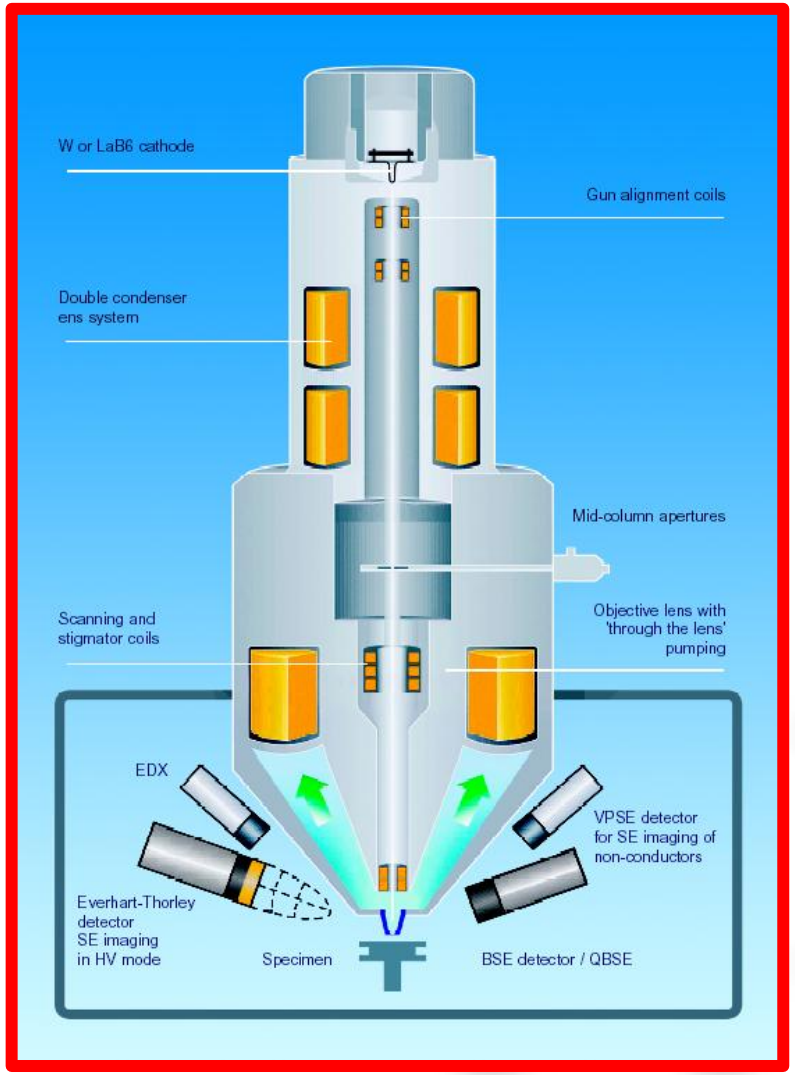
Limits

Instrument	Resolution limit	Magnification	Depth of field
Eye	100 µm	1 : 1	-
Light microscope	0.2 µm	1000 : 1	0.2 µm
Scanning electron microscope (SEM)	0.002 µm	100.000 : 1	0.025 – 2 µm

SCANN ELECTRON MICROSCOPE (SEM)

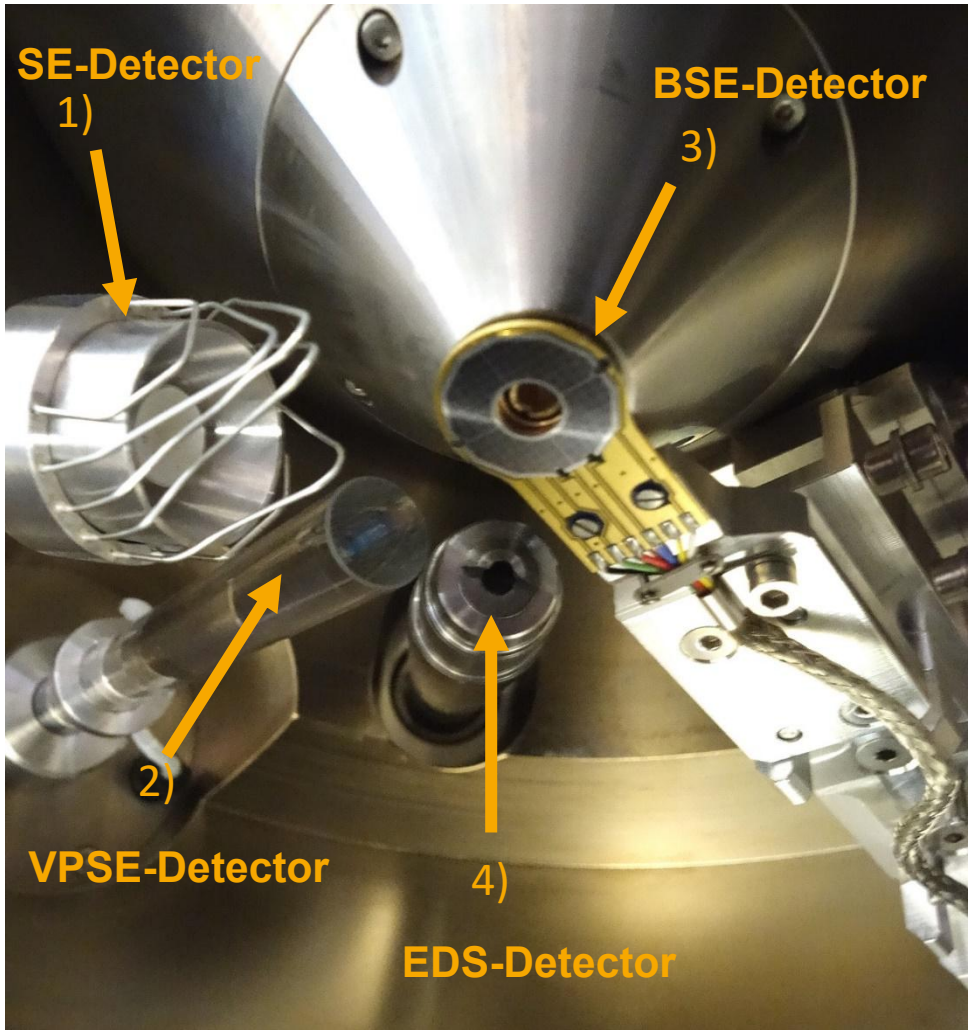
Setup of a scanning electron microscope



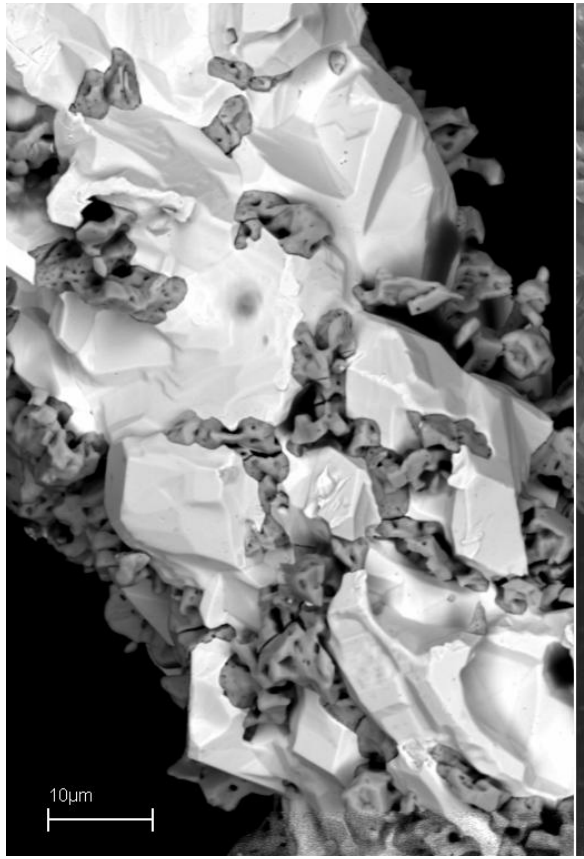


SCANN ELECTRON MICROSCOPE (SEM)

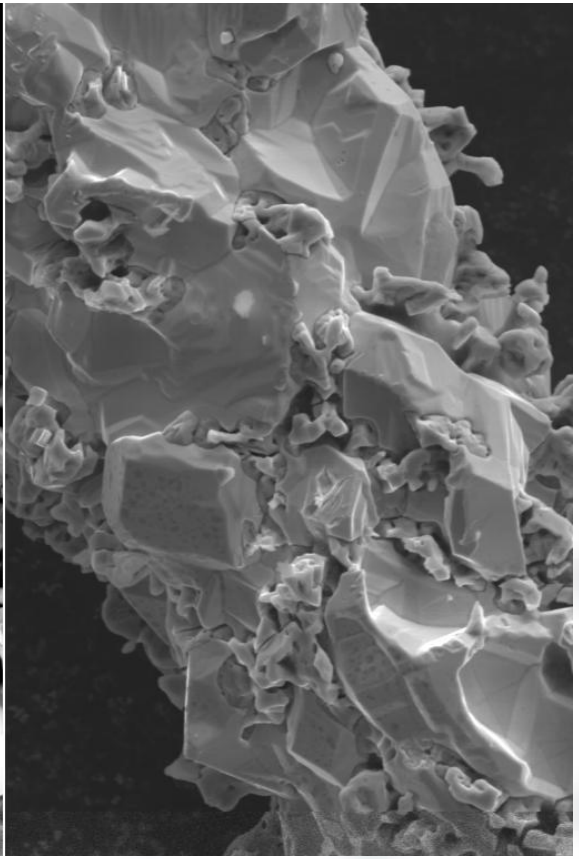
Signals



BSE-Detector



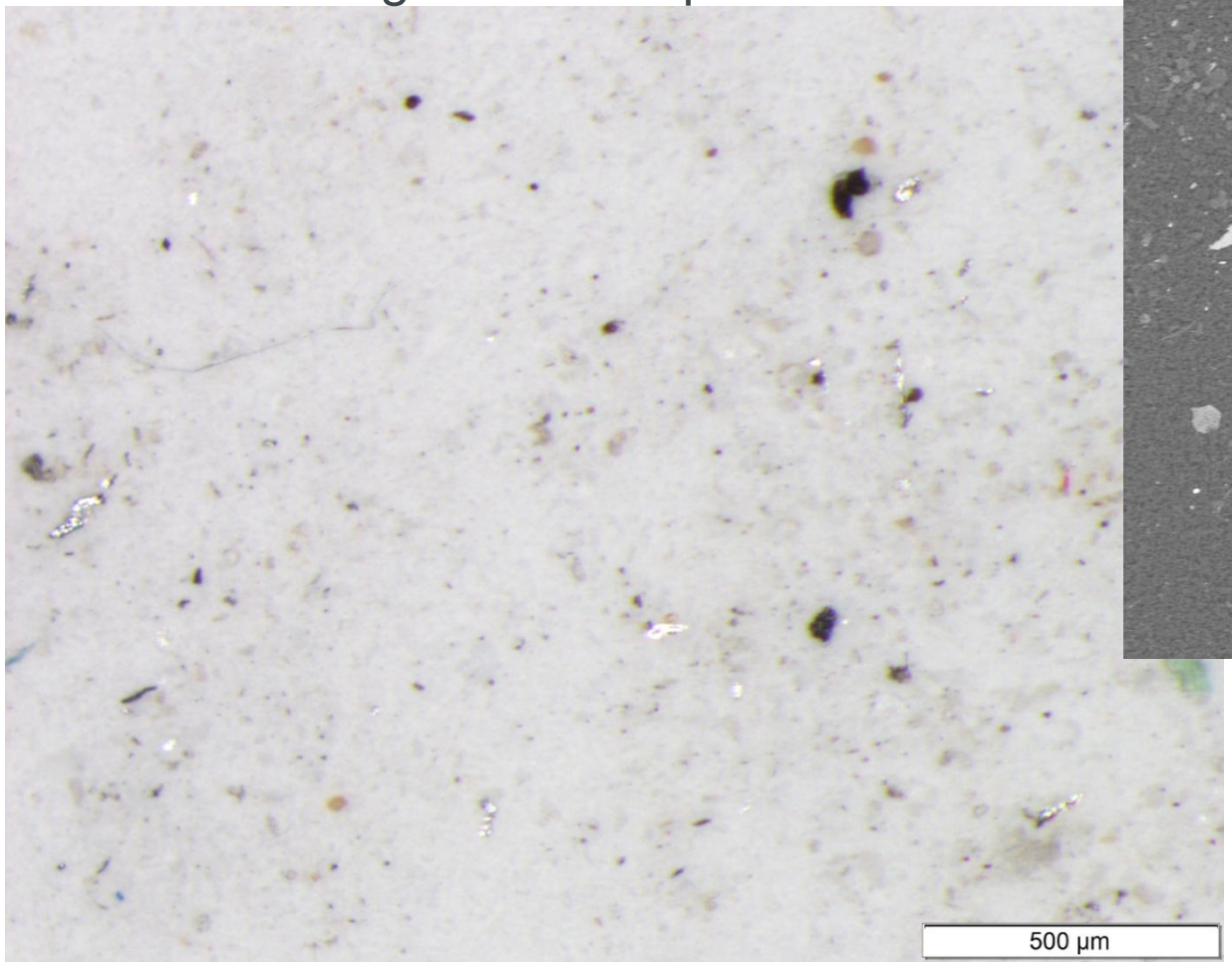
SE-Detector

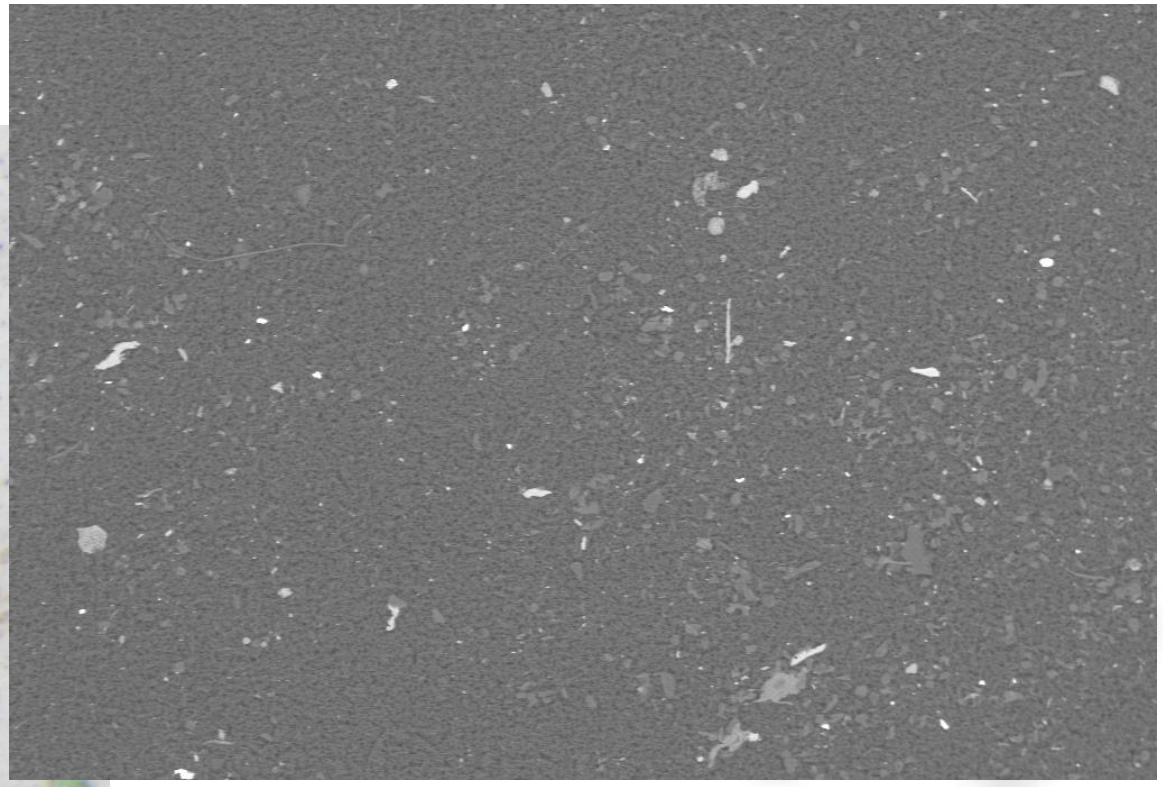


SCANN ELECTRON MICROSCOPE (SEM)

Image comparison

Light microscope



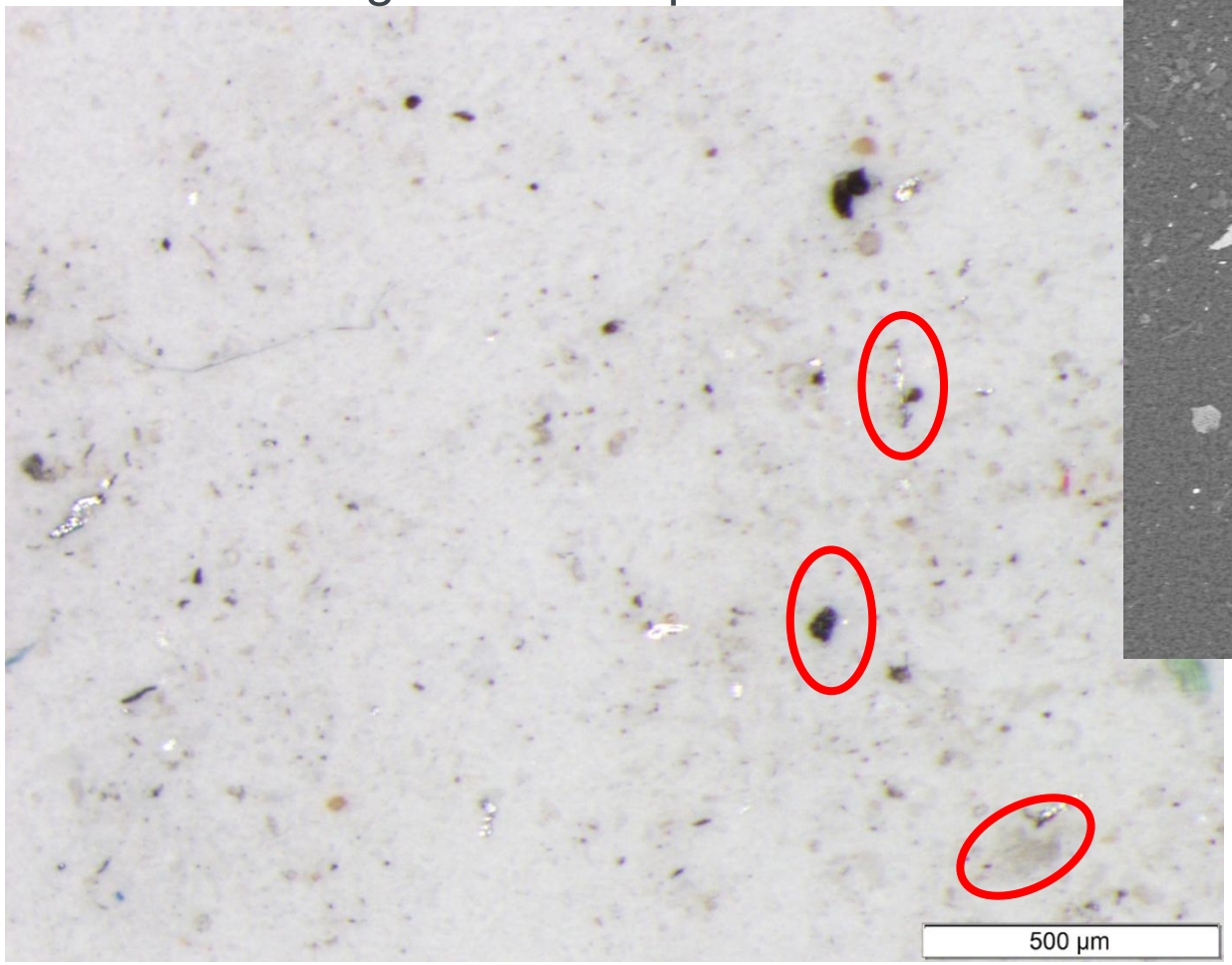


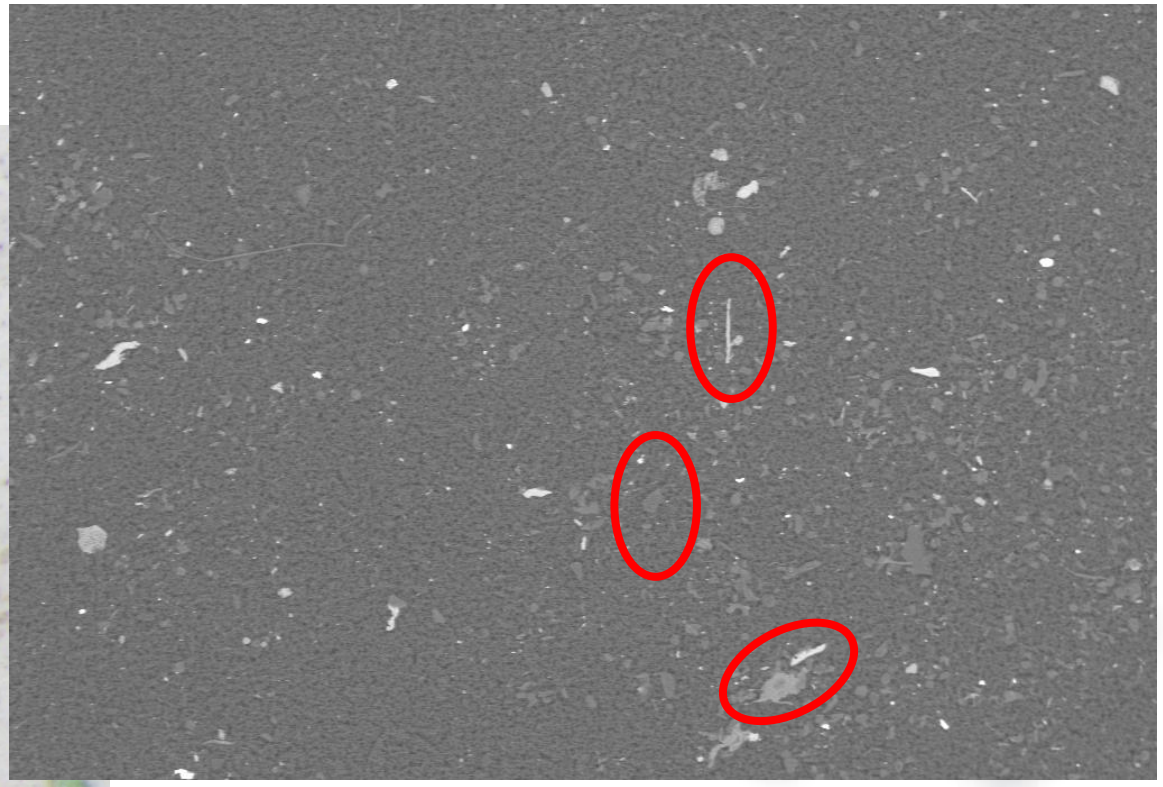
Electron microscope

SCANN ELECTRON MICROSCOPE (SEM)

Image comparison

Light microscope



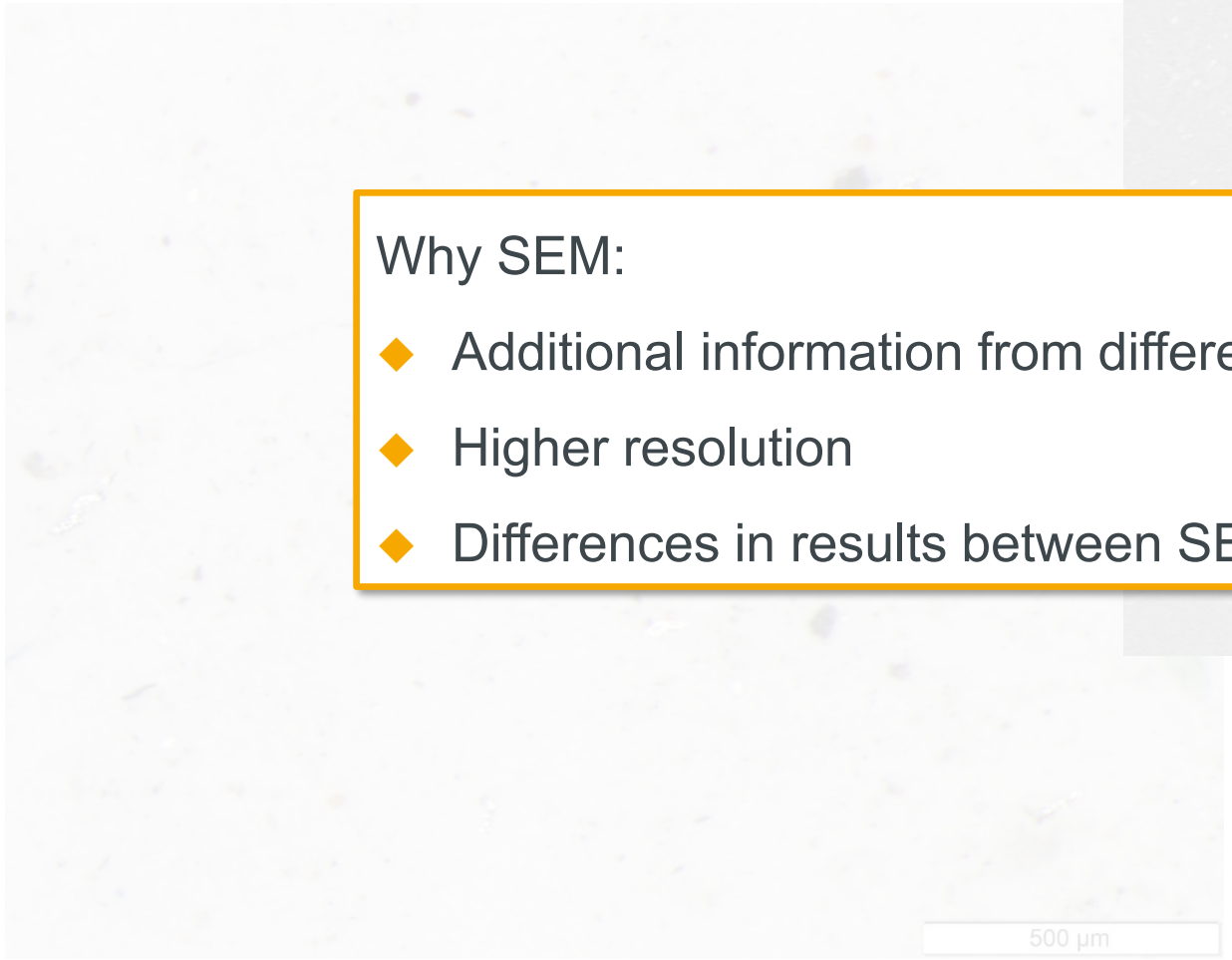


Electron microscope

RASTERELEKTRONENMIKROSKOP (REM)

Darstellungsvergleich

Licht-Mikroskop



Elektronenmikroskop

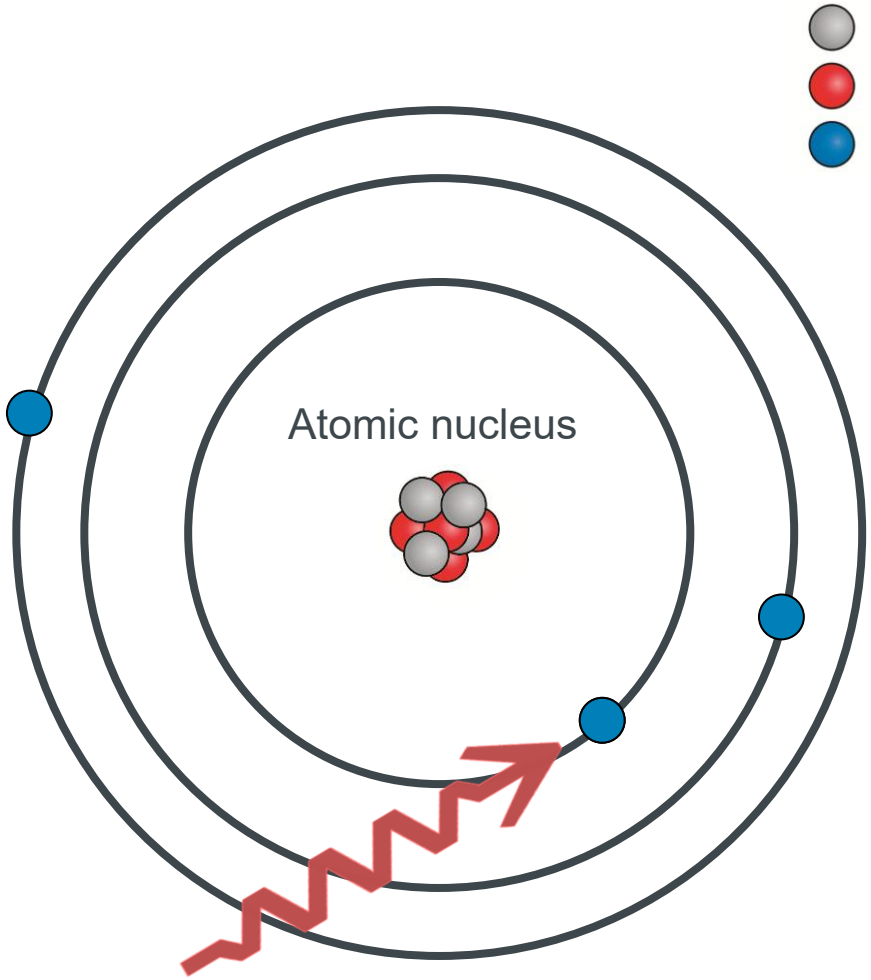


Why SEM:

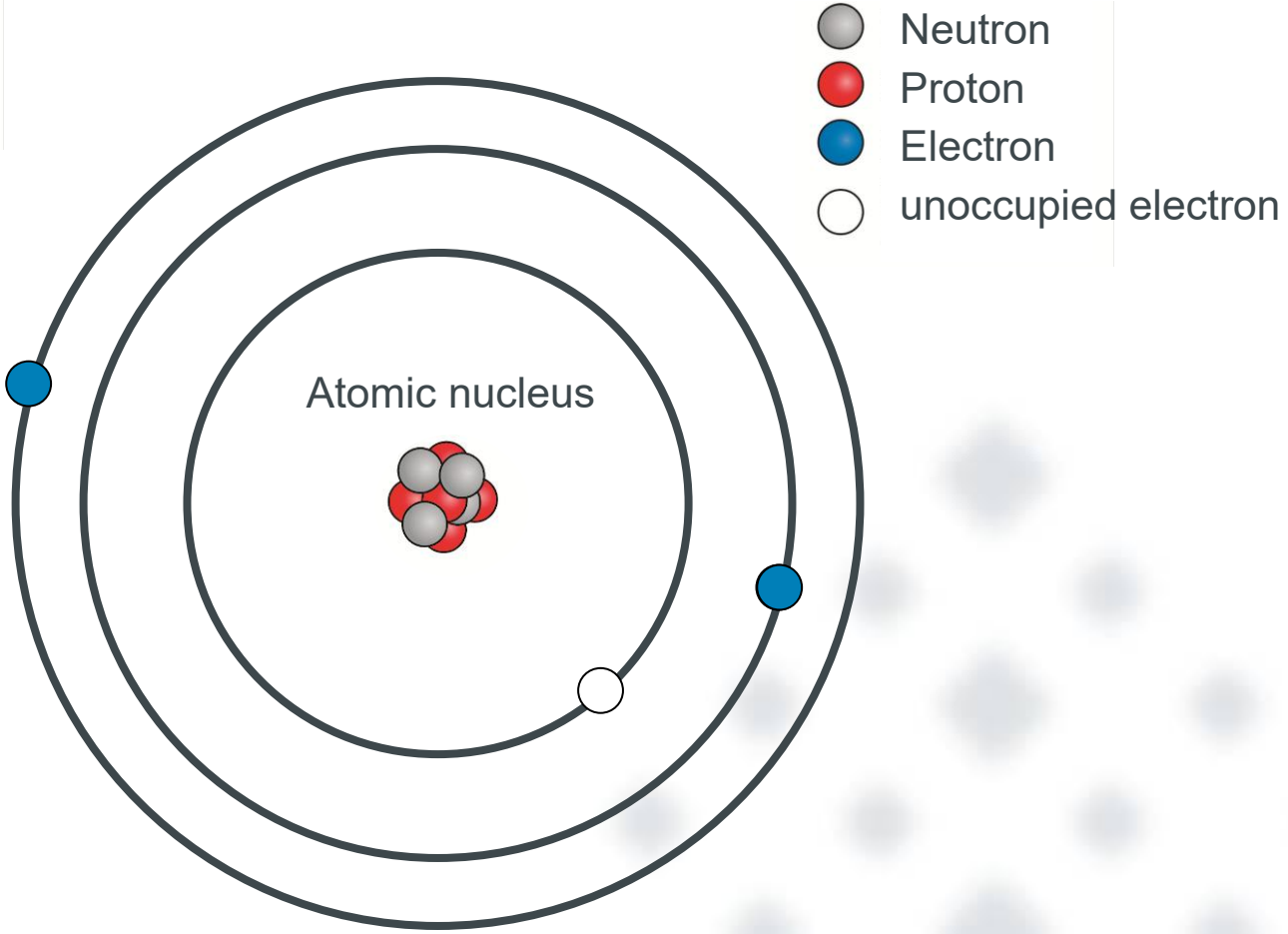
- Additional information from different microscopy technique
- Higher resolution
- Differences in results between SEM and light microscopy

ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS)

Energy-dispersive x-ray spectroscopy (EDS)

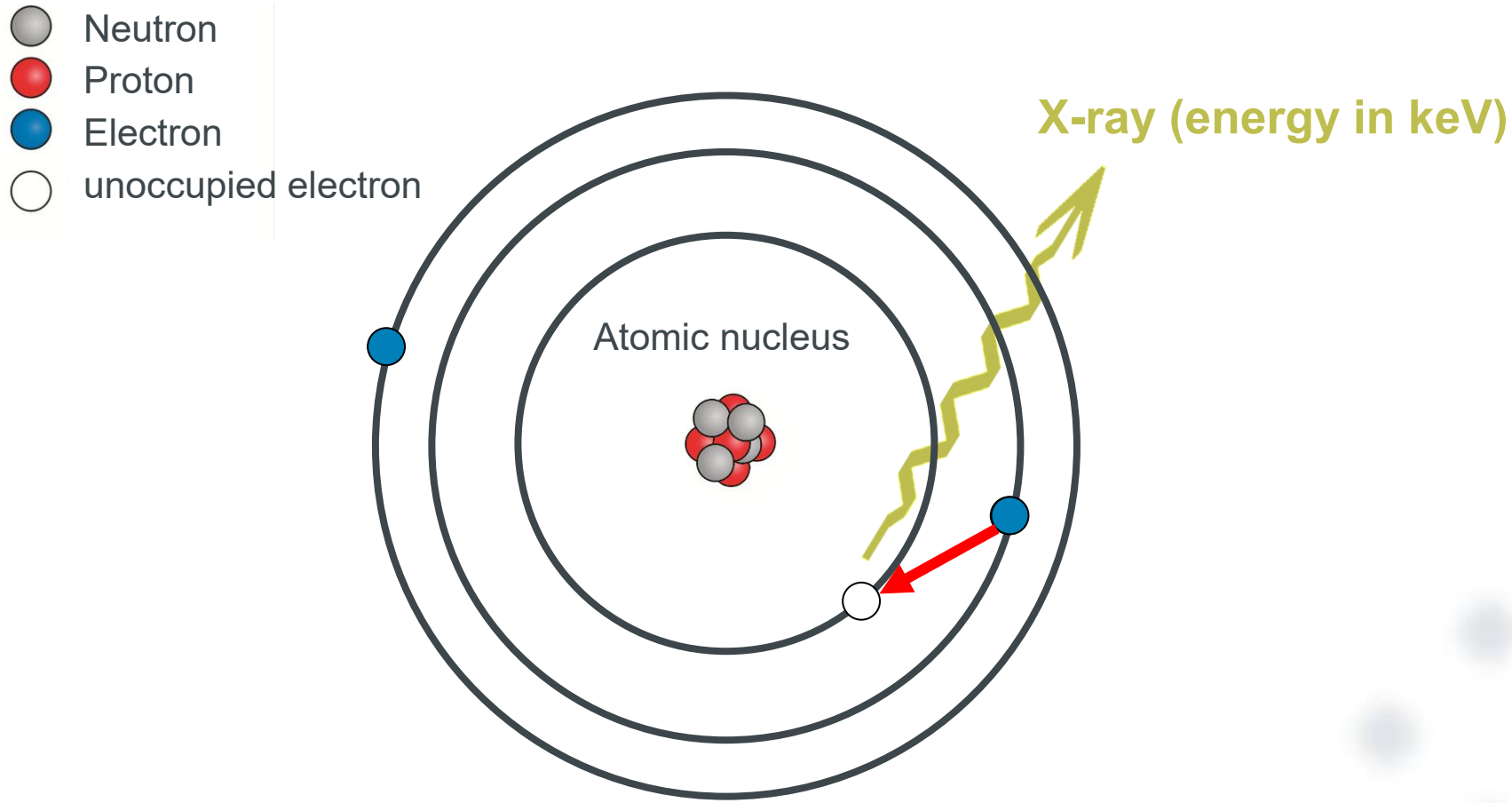


High energy



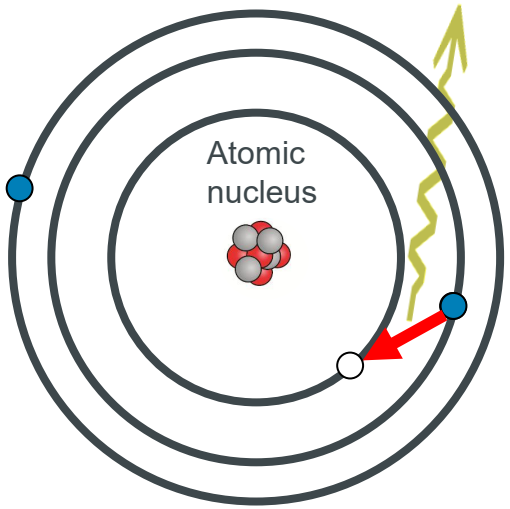
ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS)

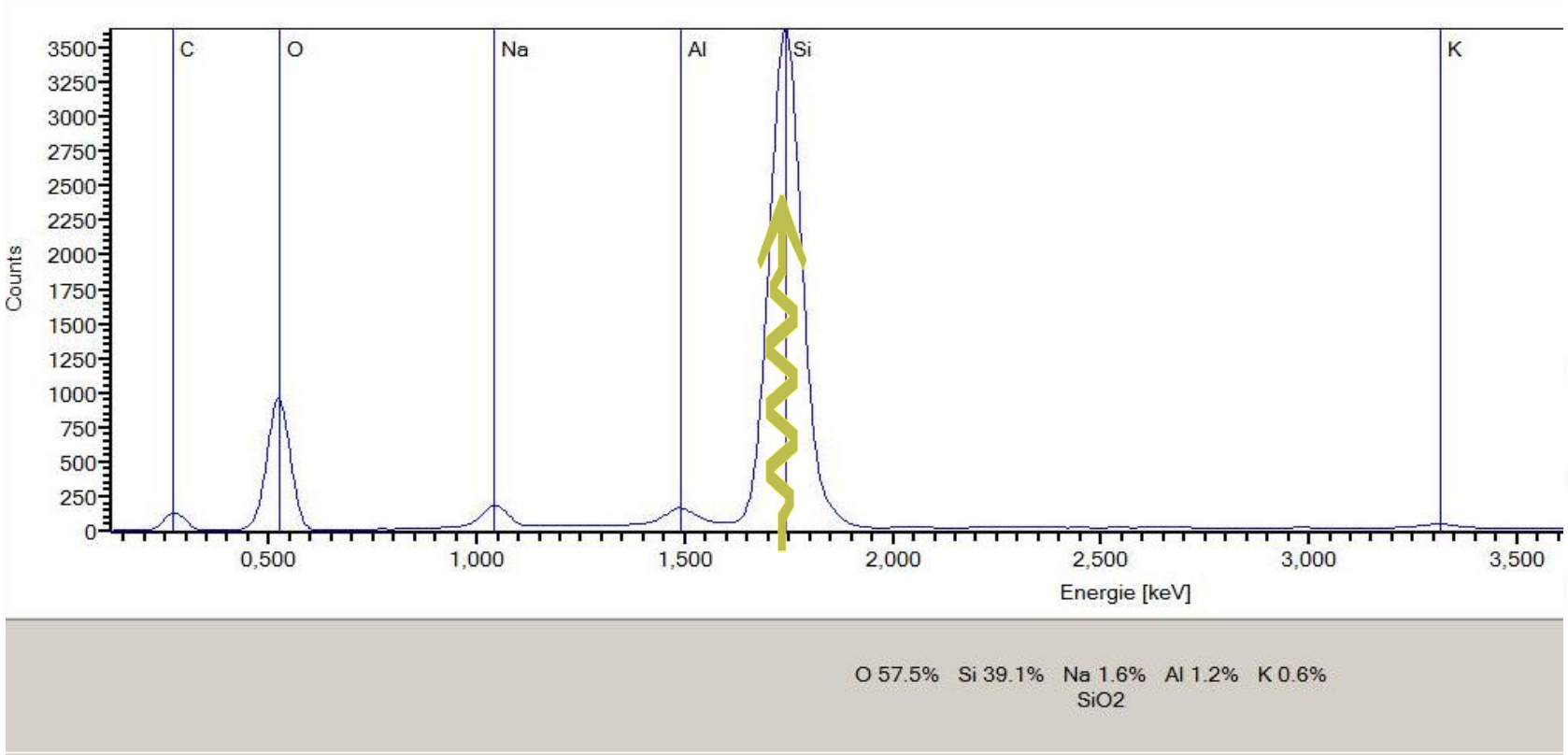
Energy-dispersive x-ray spectroscopy (EDS)



ENERGIEDISPERSIVE RÖNTGENANALYSE (EDX)

Energie-Dispersive Röntgen (X-ray) Spektroskopie (EDX)





Every chemical element has a unique EDS signature!

→ Material identification is possible

EXTENDED ANALYSES

Content

Basics SEM/EDS

Particle identification by means of SEM/EDS

IR-Spectroscopy & particle identification

Analytical methods for testing surface cleanliness

PARTICLE IDENTIFICATION (SEM/EDS)

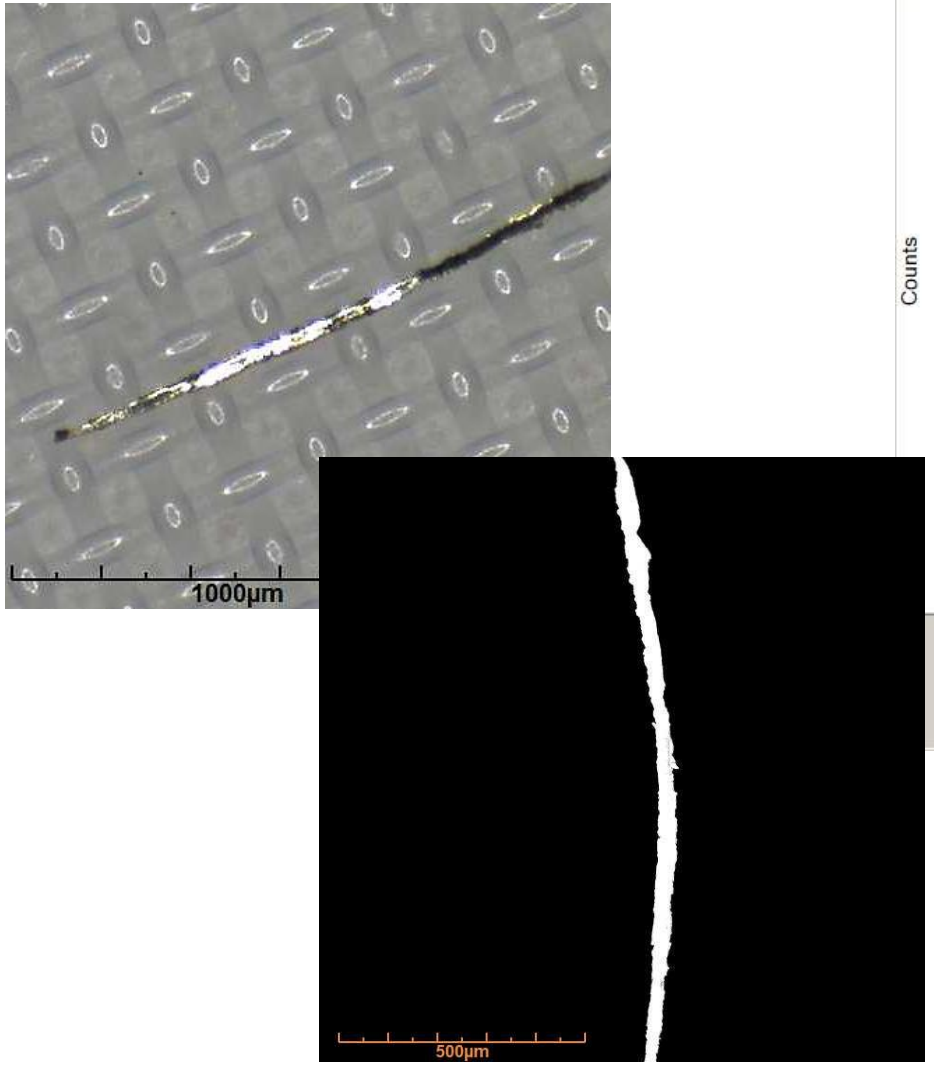
Particle analysis options

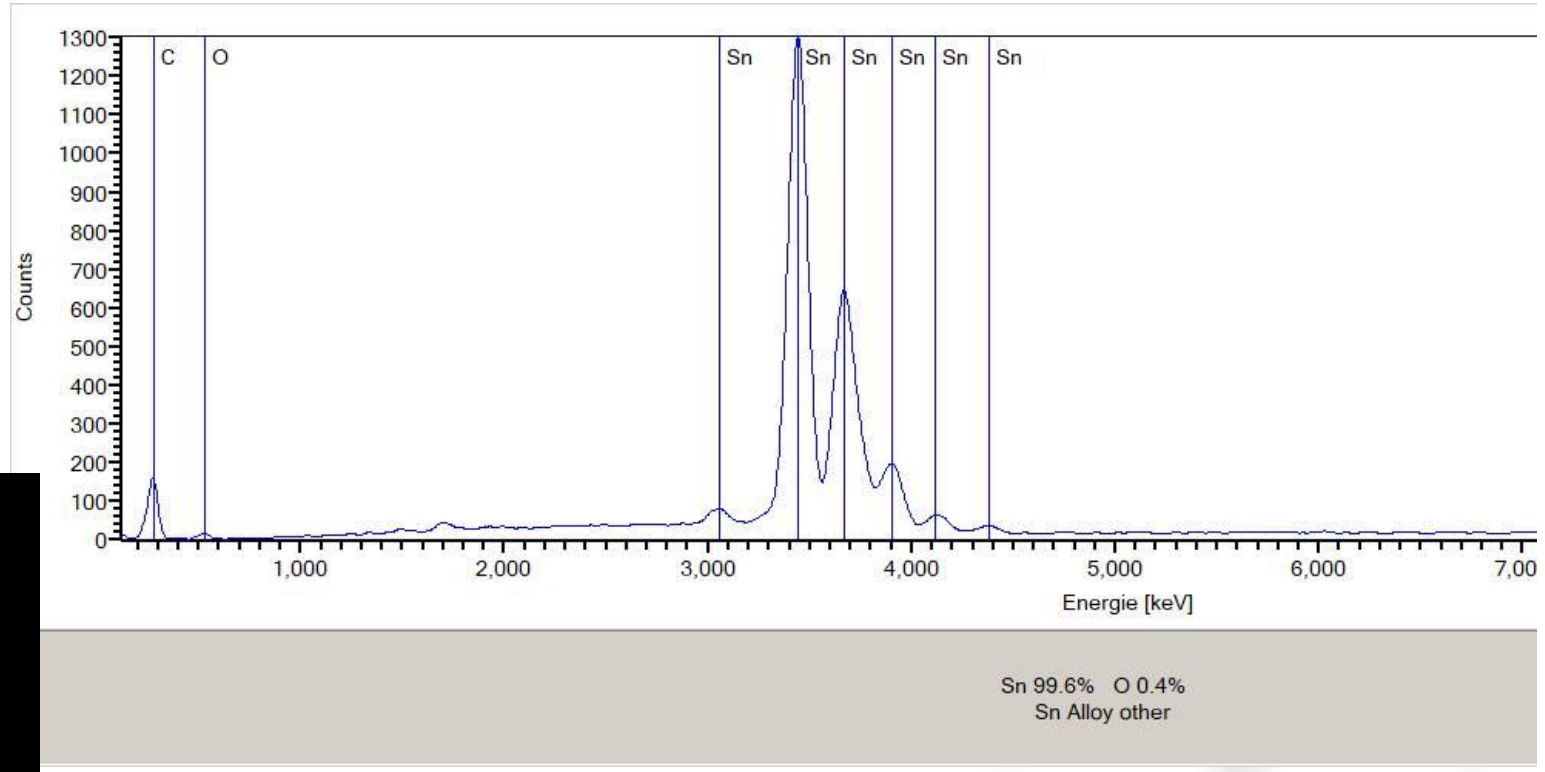
- Single particle analysis
  - \+ Fast and cost-effective identification of materials of individual (critical) particles
  - \- Re-Identification of the desired particles (particles are either directly addressed on the filter membrane or manually transferred)



PARTICLE IDENTIFICATION (SEM/EDS)

Single particle analysis

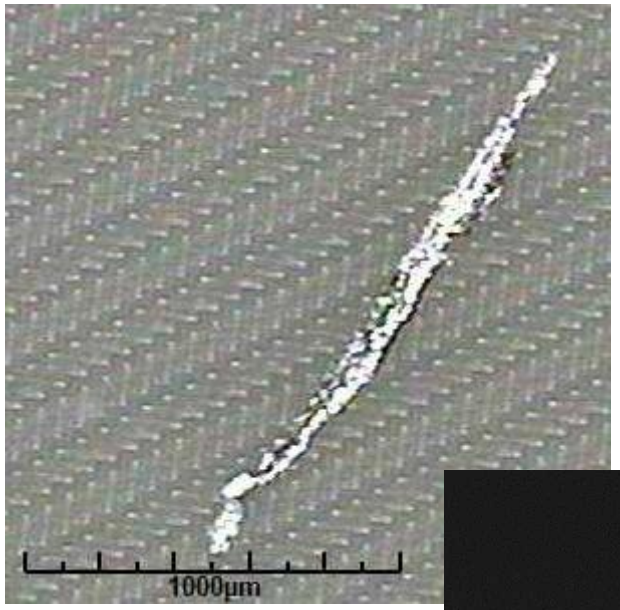


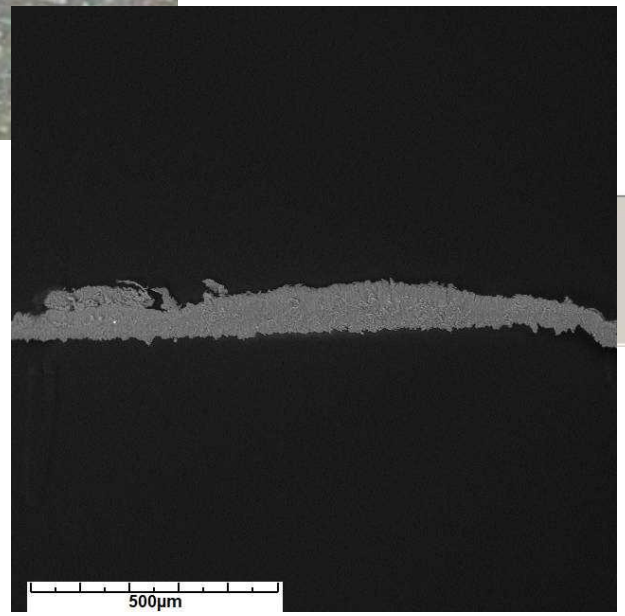


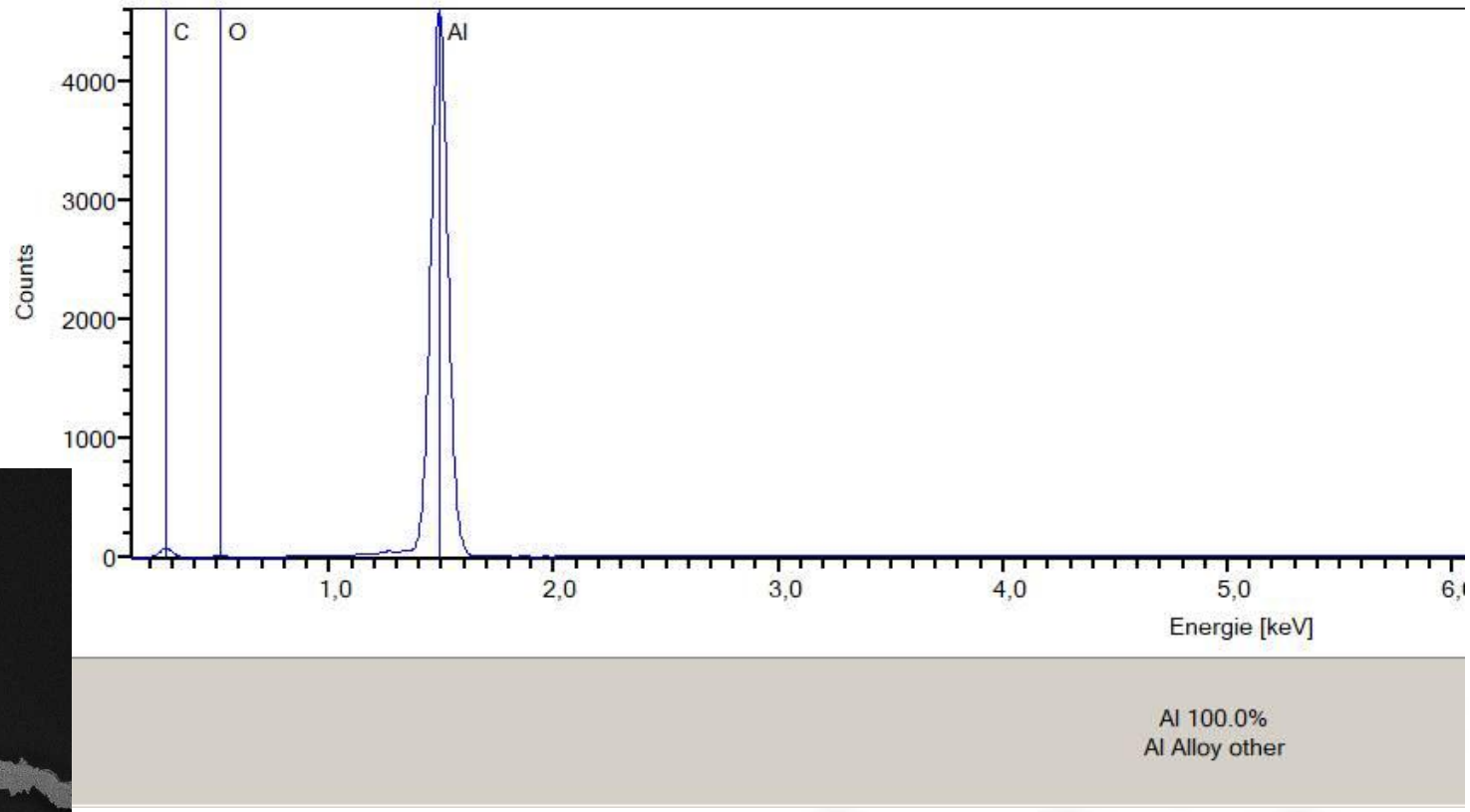
- Definitely tin particle!

PARTICLE IDENTIFICATION (SEM/EDS)

Single particle analysis



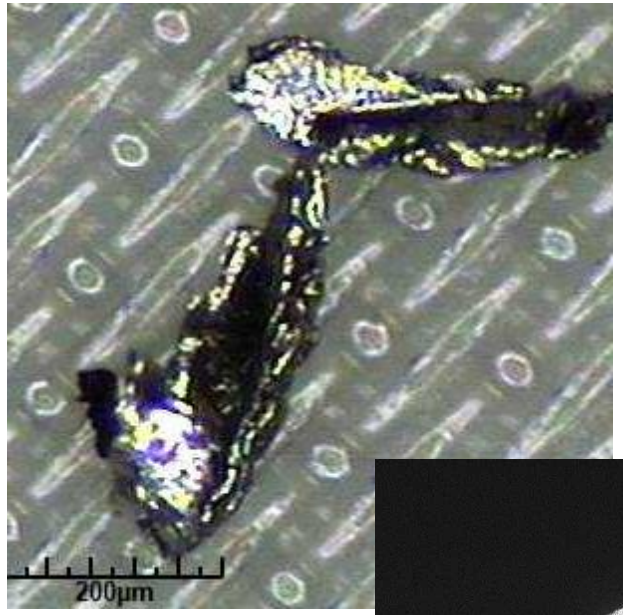




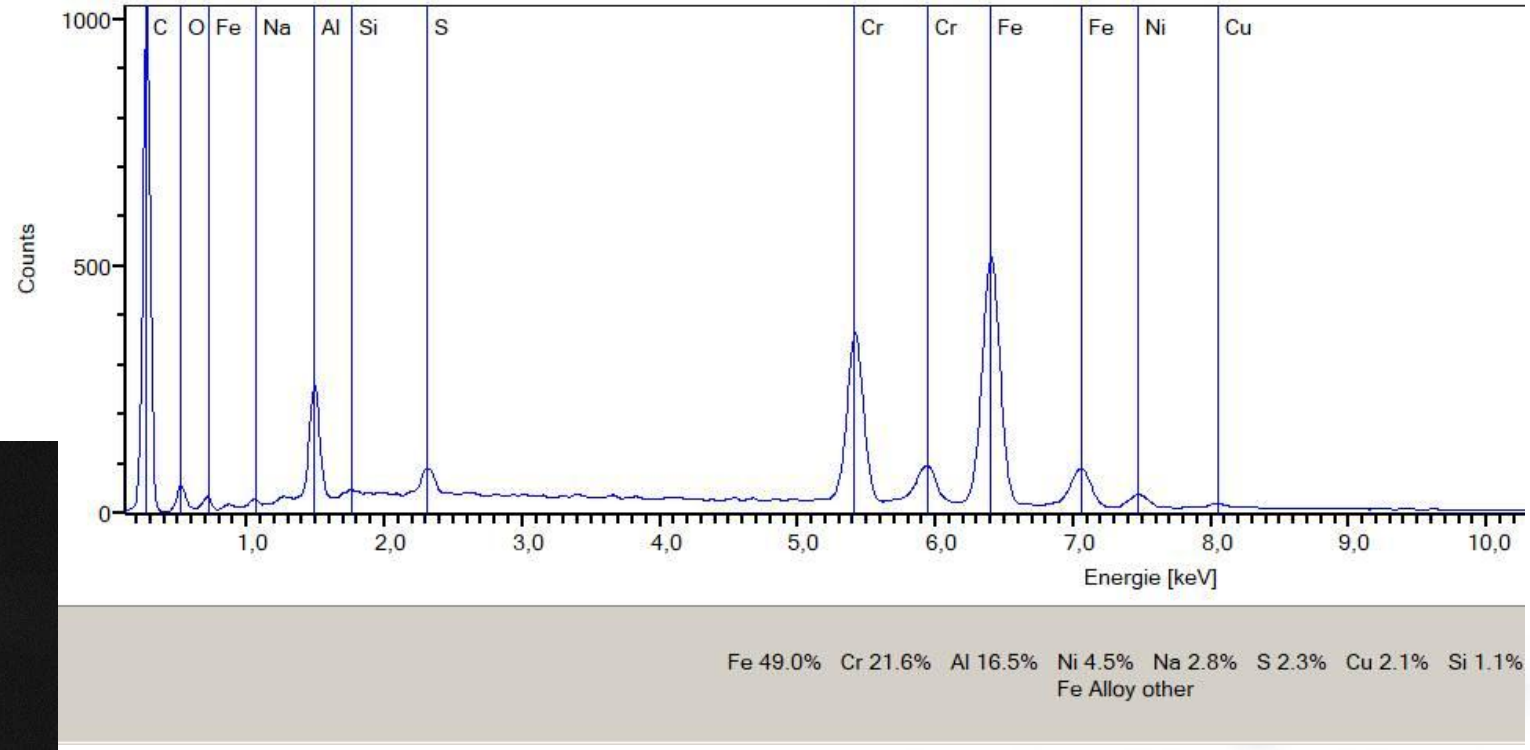
- Definitely an aluminium particle!

PARTICLE IDENTIFICATION (SEM/EDS)

Single particle analysis







- Difficult to classify:
- A combination of an aluminium and a steel component

PARTICLE IDENTIFICATION (SEM/EDS)

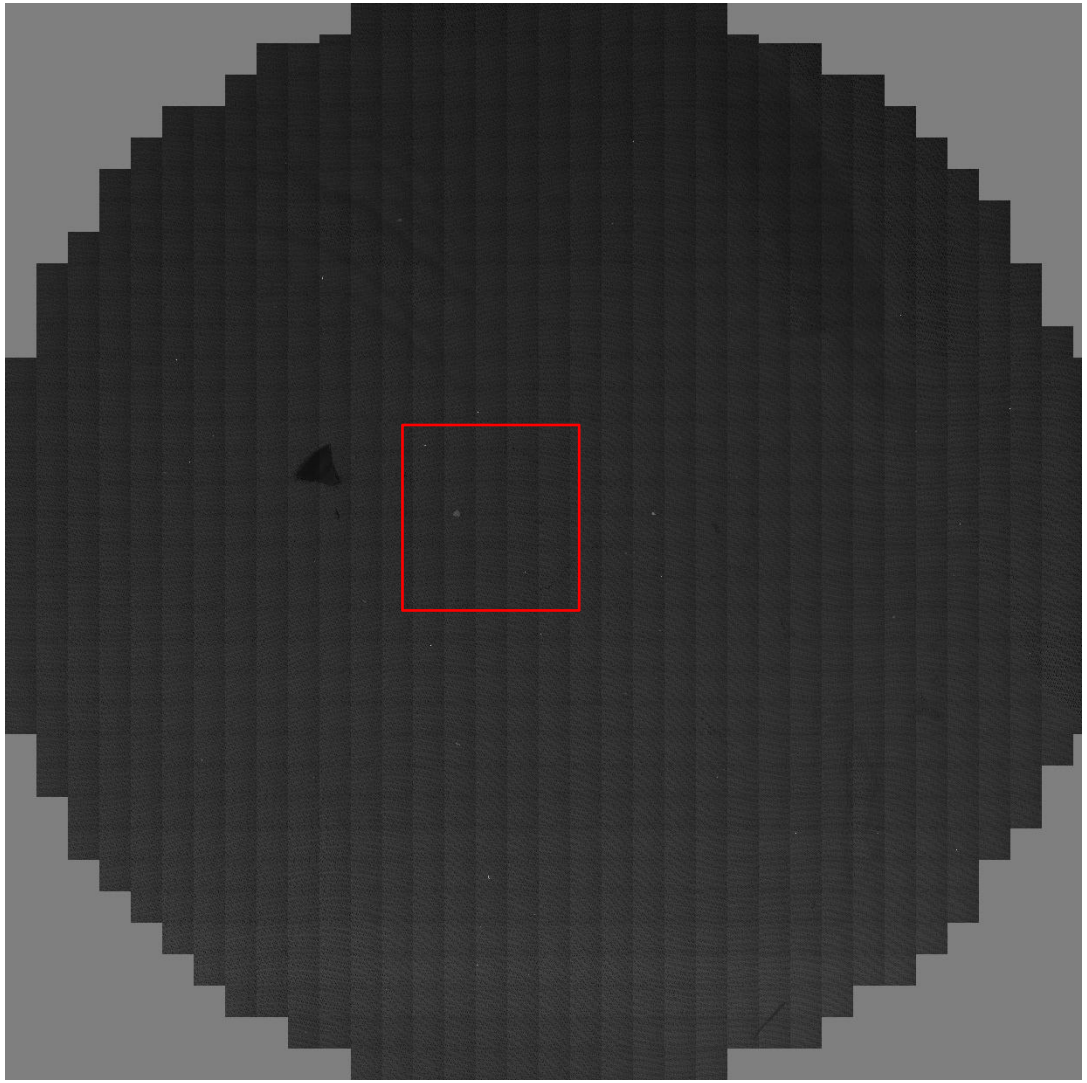
Filter scan

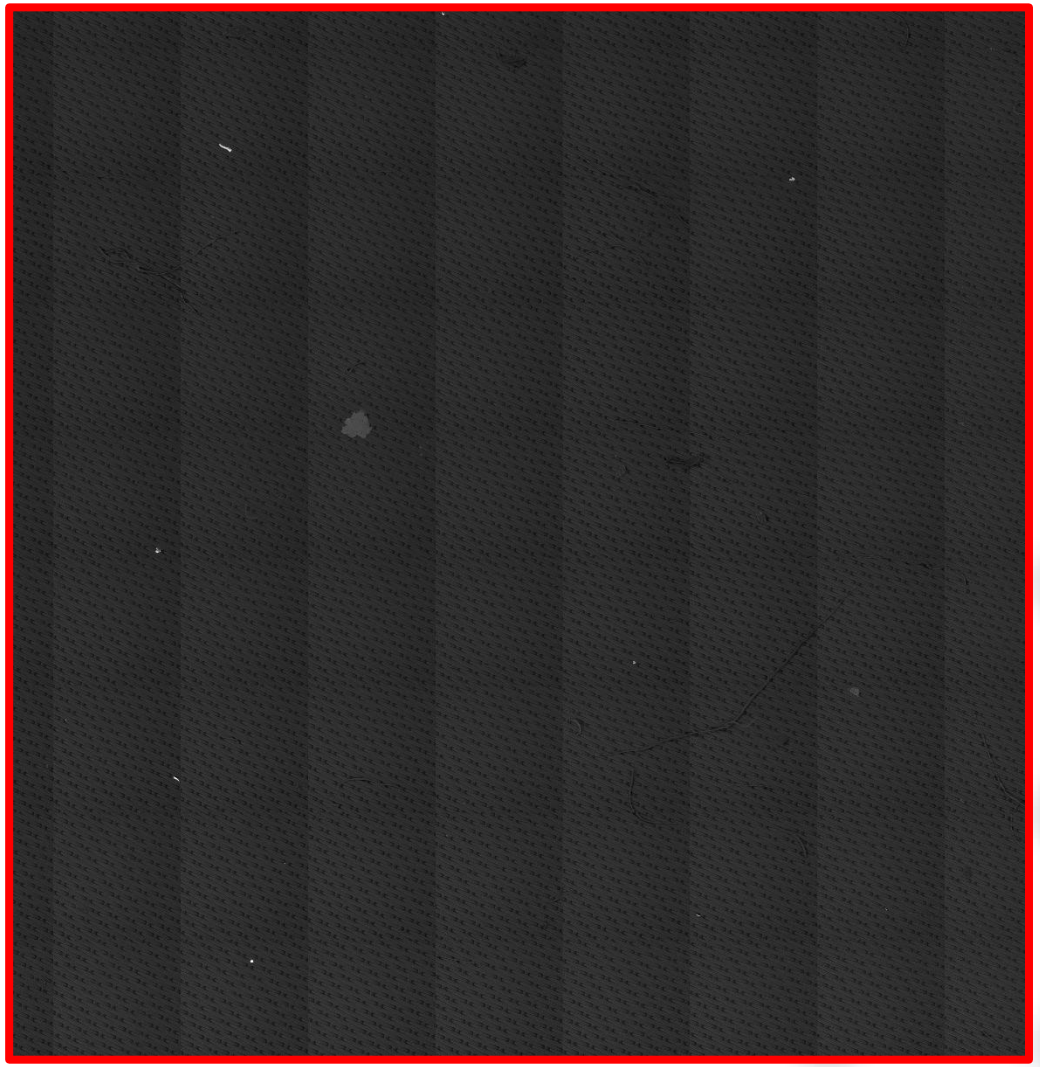
- Filter scan
  - \+ Scan of the entire filter membrane
  - \+ Overview of all inorganic particles on the filter
  - \+ Detection of abrasive particles
  - \- Higher costs
  - \- Longer measurement time



PARTICLE IDENTIFICATION (SEM/EDS)

Filter scan



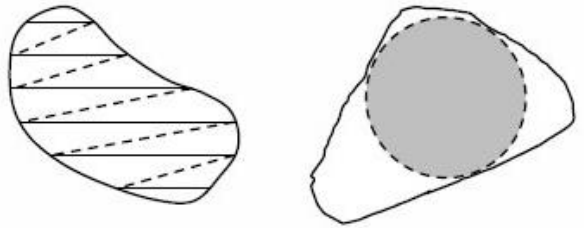


PARTICLE IDENTIFICATION (SEM/EDS)

SEM/EDS Standard Analysis

- Particle size of 50µm or larger
- Low vacuum to prevent charging effects (particle adhesions is generally possible)
- Recommended voltage of 20kV
- Image detection using a BSE detector

	Partikel ≥ 50 µm (REM/EDX-Standardanalyse)
zu verwendender Filter	5 µm PET- bzw. PA-Siebgewebe
zu verwendende Auflösung (siehe Tabelle 8-4)	≤ 5 µm/pxl
ausgewertete Fläche des Filters	vollflächig (100 %)
EDX-Analyse (siehe Abbildung 8-36)	flächige EDX-Analyse

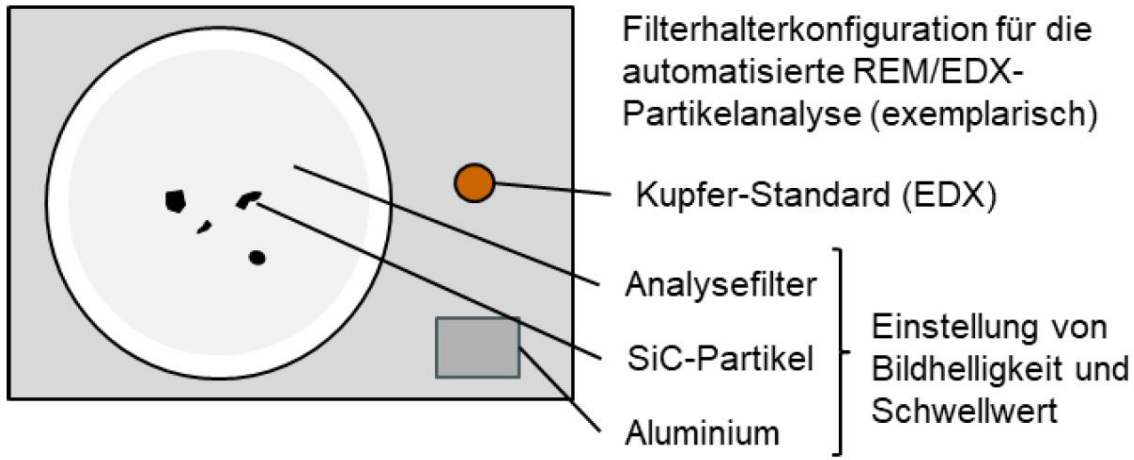


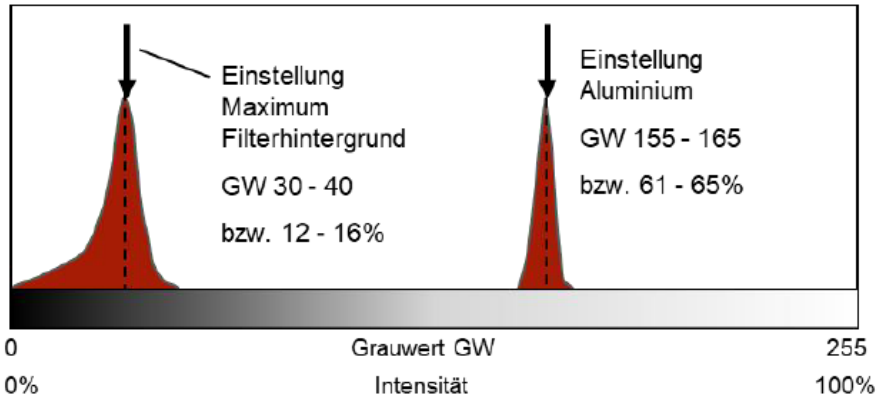
flächige EDX-Analyse (z. B. Inkreis) geeignet bei größeren Partikeln

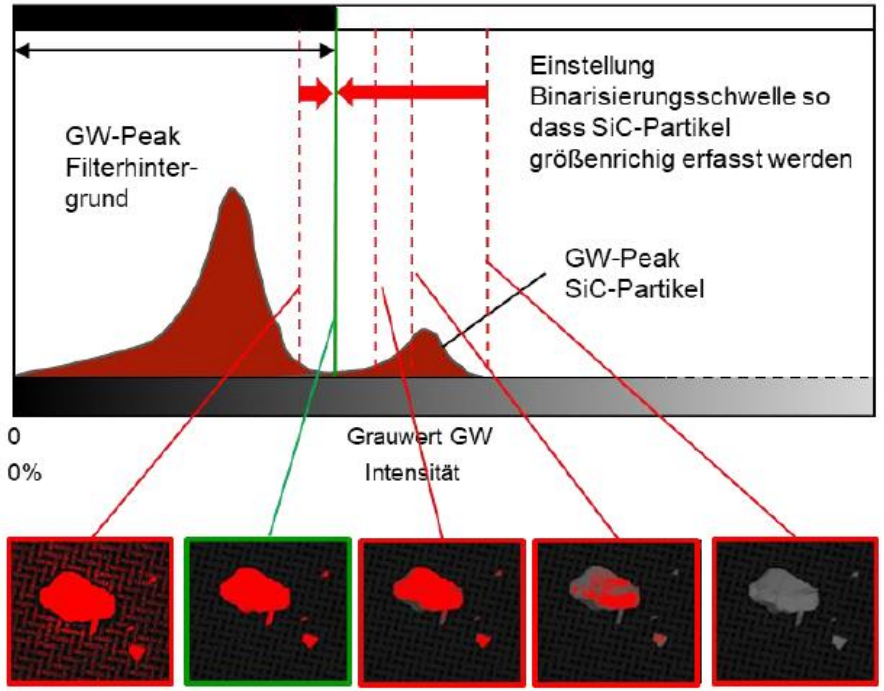
PARTICLE IDENTIFICATION (SEM/EDS)

SEM/EDS Standard Analysis

- Setting the threshold value using a reference filter with aluminium and SiC
- Gray value setting: Aluminium 160 / Background 35
- Setting the threshold value using SiC reference particles



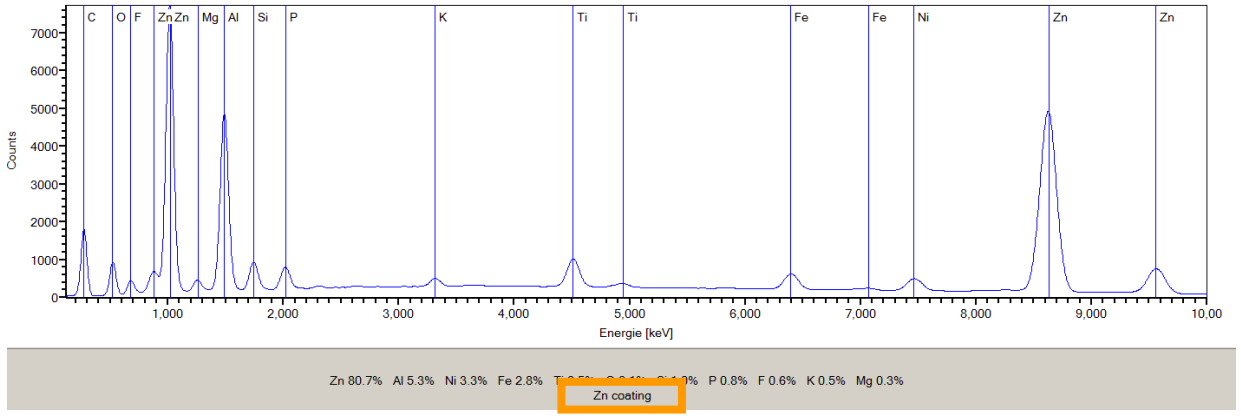




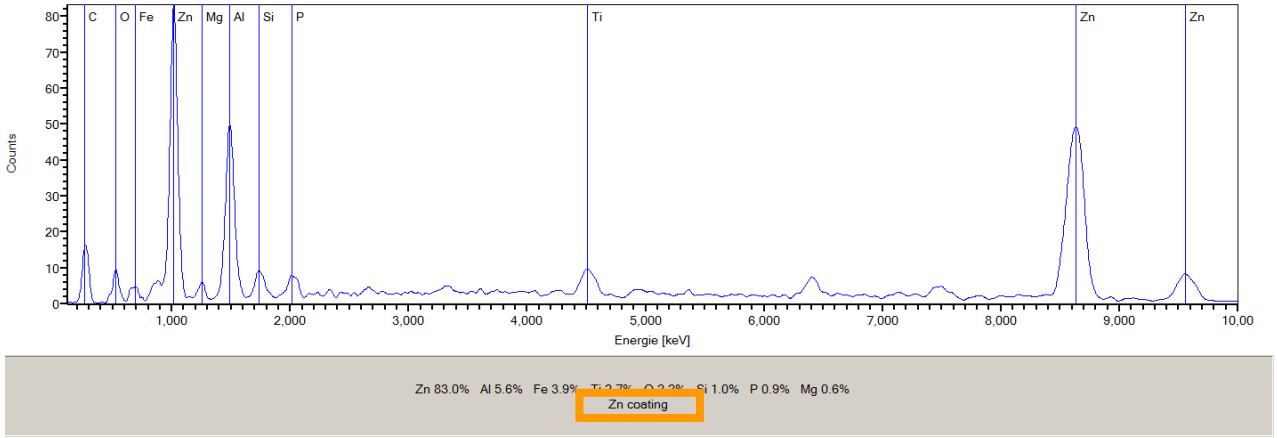
PARTICLE IDENTIFICATION (SEM/EDS)

SEM/EDS Standard Analysis

- Challenge: Measuring an entire filter membrane (often >1000 particles)
- Automatic analysis required (=assigning the spectrum to a material class)
- Only a short measurement time is possible (1-3 s/particles)



1 000 000 counts (~100 sec)



10 000 counts (1 sec)

PARTICLE IDENTIFICATION (SEM/EDS)

SEM/EDS Standard Analysis

- Restricting all elements of the periodic table to a specific selection: overlapping lines as a potential problem

Tabelle 8-1: für die Standardanalyse nach VDA 19.1 auszugebende Elemente

zu berücksichtigende Elemente
O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Zr, Mo, Ag, Sn, Ba, Au, Pb

- Implementation of „Zero Rules“ for improved material calssification

Zero-Element Rule (Element “x” wird auf “0” gesetzt, wenn...)	
O	(Al+Si)<15
O	O<15
O	Fe≥30

- Short measurement time per measurement point: 3000 – 5000 counts; up to 1 second

PARTICLE IDENTIFICATION (SEM/EDS)

Material Classes

- Introduction of a total of 30 material classes
- Material classes can be added and modified at the customer's request
  - Introducing a new material class, check where they are to be inserted
  - Check whether zero rules have an impact on the material class

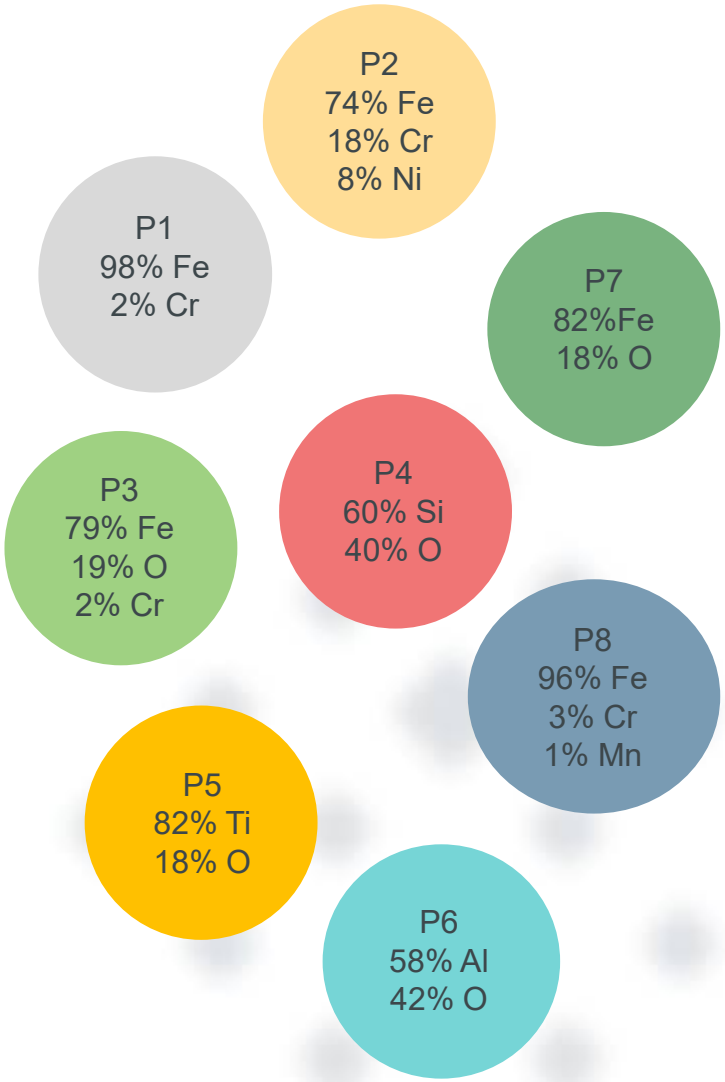
#	Name	Regel
1	Cr- Schicht	P<5 AND Fe≥10 AND E1=Cr AND (Fe+Cr)≥35 AND Zn<20 AND Cu<5 AND Mn<5 AND Ti<5
2	Zn- Schicht	P<5 AND Fe≥10 AND E1=Zn AND (Fe+Zn)≥35 AND Cr<20 AND Cu<5 AND Mn<5 AND Ti<5
3	Mn-Phosphate	P≥5 AND Mn≥10 AND Fe≥5 AND (P+Fe+Mn) ≥50 AND Cl<5 AND K<5 AND Zn<5 AND Cu<5 AND Ti<5 AND Cr<5
4	Zn-Phosphate	P≥5 AND Zn≥10 AND Fe≥5 AND Cr<2 AND (Fe+Zn+P)≥40 AND Cu<5 AND Mn<5 AND Ti<5
5	unlegierter Stahl	Fe≥75 AND Cr<1 AND Mn<1 AND Ni<0.5 AND Zn<5 AND Cu<5 AND Ti<3
6	niedrigleg. Stahl	Fe≥65 AND (Mn>0 OR Cr>0 OR Ni>0) AND (Cr+Mn+Ni)<5 AND Zn<5
7	hochleg. Stahl	Fe≥50 AND (Cr≥5 OR Mn≥5 OR Ni≥5)
8	mittelleg. Stahl	Fe≥65 AND (Mn<5 AND Cr<5 AND Ni<5) AND (Cr+Mn+Ni) ≥5 AND Zn<5
9	Eisen reich	E1=Fe AND Fe≥30
10	Si-O	((E1=Si AND E2=O) OR (E1=O AND E2=Si)) AND O≥20 AND Ca<3 AND Mg<3 AND Al<3 AND K<3 AND Na<3
11	Si - (SiC - SiN)	E1=Si AND Al<3 AND Mg<3 AND Ca<3 AND O<20 AND K<3 AND Na<3
12	Silikate (Si-XX-O)	(Si+Al+Ca+K+Na+Fe+O)≥60 AND Si≥10 AND K<50 AND Ca<50 AND Mg<5 AND Al<50 AND Na<50 AND O≥15
13	Si-Mg-O	(Si+Mg+O)≥60 AND Si≥10 AND Mg≥5 AND Mg<50 AND Ca<3 AND K<3 AND Al<3
14	Al-O	((E1=Al AND E2=O) OR (E1=O AND E2=Al)) AND Al<65 AND O≥25 AND Si<8 AND Ca<3 AND Mg<3 AND K<3 AND Cu<1 AND F<3
15	Aluminiumlegie-rung	E1=Al AND Al≥30 AND O<30 AND Si<22 AND Cu<12 AND Mg<8 AND Na<3 AND (K+Ca)<5
16	Zirkon reich	E1=Zr AND Zr≥30
17	Silizium reich	Si≥25 AND Al<60
18	Aluminium reich	E1=Al AND Al≥30
19	Messing	((E1=Cu AND E2=Zn) OR (E1=Zn AND E2=Cu)) AND Cu≥15 AND Zn≥15
20	Kupfer reich	E1=Cu AND Cu≥30
21	Zink reich	E1=Zn AND Zn≥30
22	Zinn reich	E1=Sn AND Sn≥30
23	Titan reich	E1=Ti AND Ti≥30
24	Nickel reich	E1=Ni AND Ni≥30
25	Silber reich	E1=Ag AND Ag≥30
26	Gold reich	E1=Au AND Au≥30
27	Fluor reich	E1=F AND F≥30
28	Festschmier-stoffe	(Mo+S+Pb+Ba)≥50
29	Chlor reich	E1=Cl OR E2=Cl
30	P/S/Na/Mg/K/Ca	E1=P OR E2=P OR E1=S OR E2=S OR E1=Na OR E2=Na OR E1=Mg OR E2=Mg OR E1=K OR E2=K OR E1=Ca OR E2=Ca

PARTICLE IDENTIFICATION (SEM/EDS)

Material Classes

Class order are mixed up!

Klasse	Definition	Partikel im Siebturm
Eisenreich	Fe ≥ 30	
Niedriglegierter Stahl	Fe ≥ 65% und Cr+Mn+Ni < 5 und Zn < 5 und Mn/Cr/Ni > 0	
Hochlegierter Stahl	Fe ≥ 50 und Mn/Cr/Ni ≥ 5	
Silizium reich	Si ≥ 25 und Al < 60	
Titan reich	Ti ≥ 30	
Aluminium reich	Al ≥ 30	

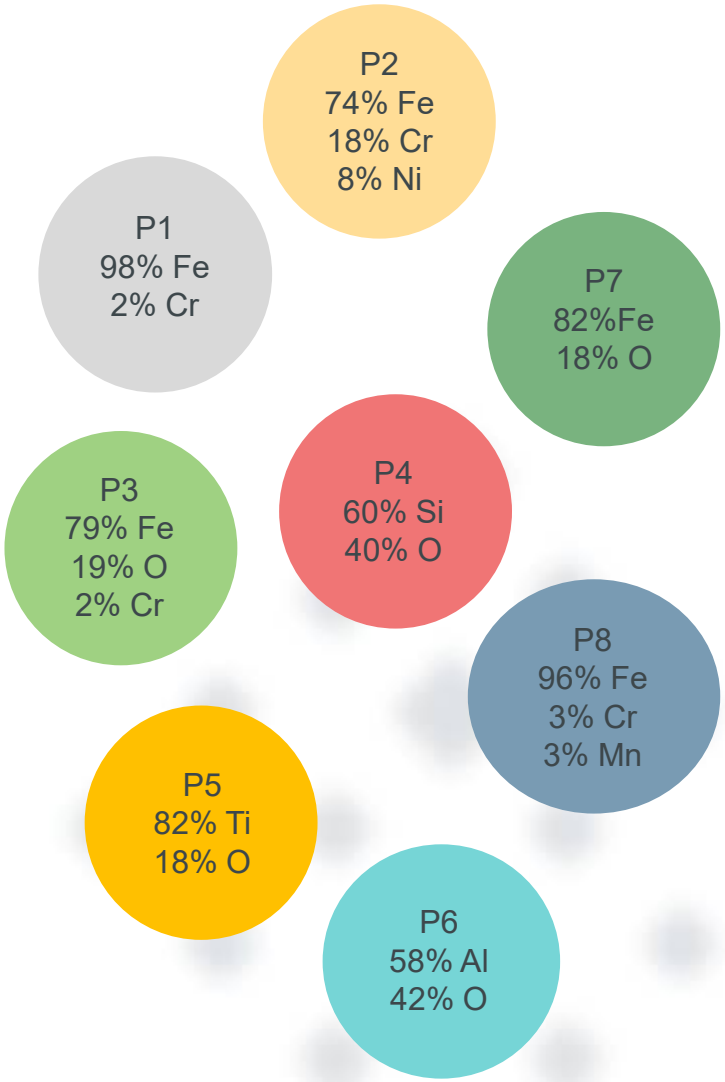


PARTICLE IDENTIFICATION (SEM/EDS)

Material Classes

Class orderd as in VDA 19.1

Klasse	Definition	Partikel im Siebturm
Niedriglegierter Stahl	Fe ≥ 65% und Cr+Mn+Ni < 5 und Zn < 5 und Mn/Cr/Ni > 0	
Hochlegierter Stahl	Fe ≥ 50 und Mn/Cr/Ni ≥ 5	
Eisenreich	Fe ≥ 30	
Silizium reich	Si ≥ 25 und Al < 60	
Titan reich	Ti ≥ 30	
Aluminium reich	Al ≥ 30	



PARTICLE IDENTIFICATION (SEM/EDS)

Material properties

- Correlation between materials and physical properties: Vickers hardness and electrical conductivity
- Potential damage, such as hardness or conductivity, cannot be directly detected using EDX.
  - However, it can be deducted from the combination of elements
- Categorization of material classes based on the pure substance and the ‘worst-case’ scenario

Name	Potentially hard	Potentially conductive
Unalloyed Steel	V2	+
Salt	V1	-
Titan/Titan dioxide	V2	+
SiC	V3	-

V1: < 400 HV

V2: 400-1000 HV

V3: > 1000 HV

+: potentialy conductive

-: nonconductive

PARTICLE IDENTIFICATION (SEM/EDS)

Limitations of EDS-Analysis

- Classification based purely on chemical composition using EDS
  - Incorrect automatic classification possible
  - Overlapping particles
  - Short EDS measurement time

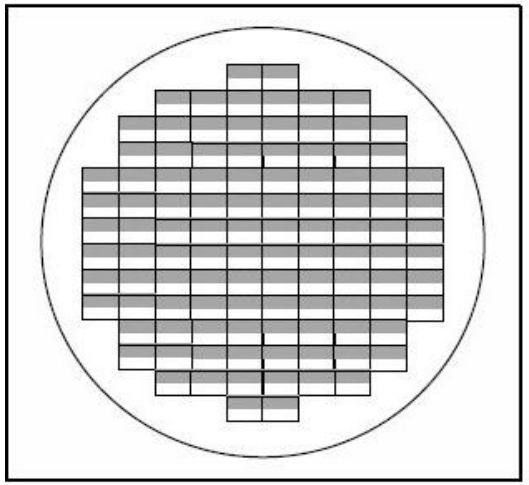
- Example 1: A silicone particle is classified into a mineral class on the basis of its elemental composition and is therefore classified as ‘potentially hard’
- Example 2: A large particle with small particles attached to it may, under certain circumstances, be classified according to the material class of the attached particles

- **Manual check is very important!**

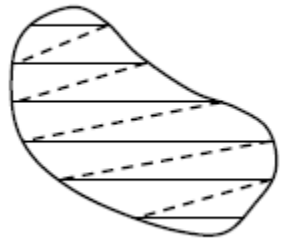
PARTICLE IDENTIFICATION (SEM/EDS)

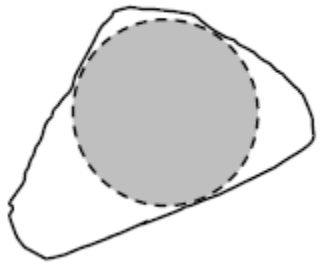
Deviation from the standard analysis

- Particle measurement < 50 µm – no full scan requiered
  - Partial scan followed by extrapolation is possible
    - Use of a foamed polyamid filter
    - EDS analysis may be point-based for small particles
    - Adjustment of pixel criterion possibly needed
- Use of metal-coated filter possible





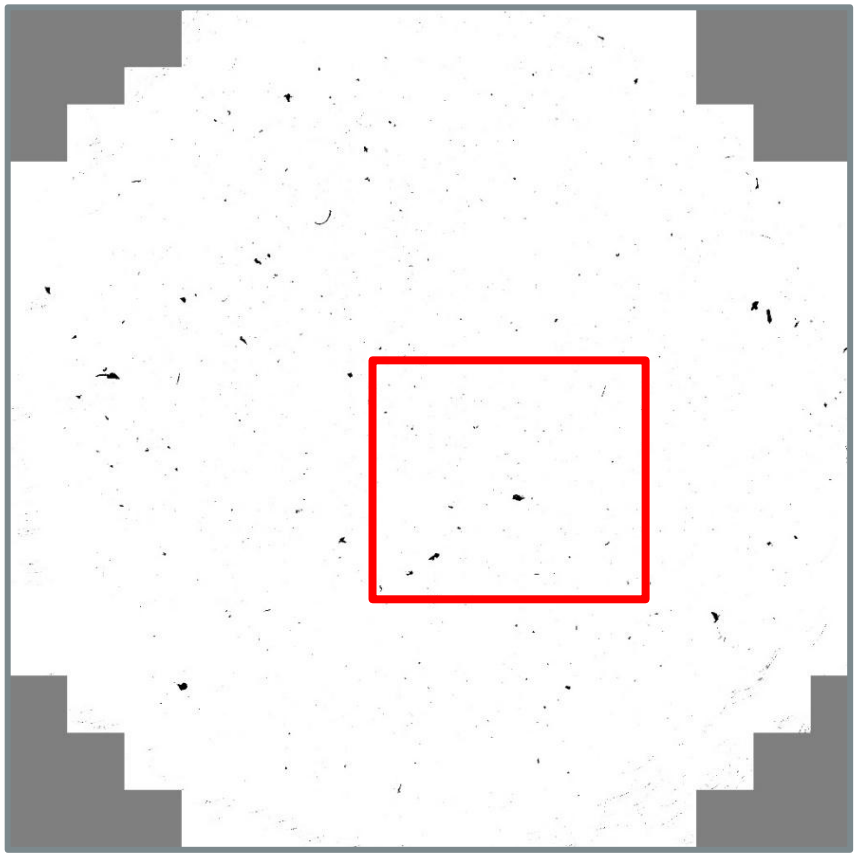


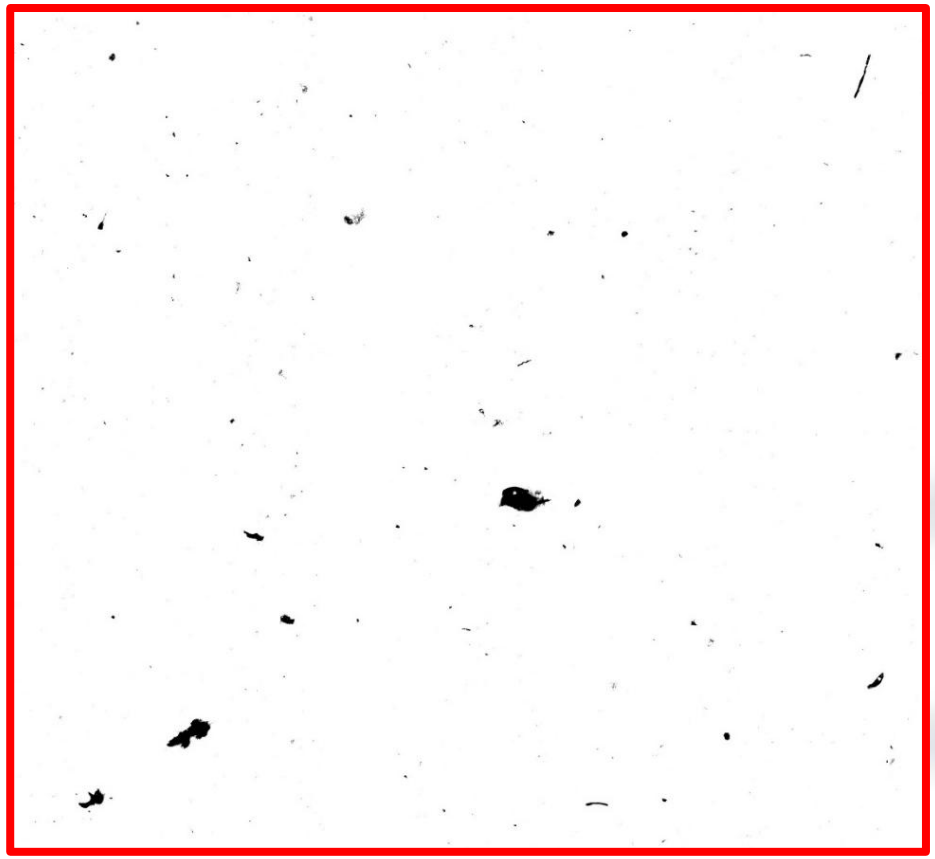


PARTICLE IDENTIFICATION (SEM/EDS)

Metal-coated filter

- Detection of all particles with an atomic number lower than that of gold
- Detection and identification of inorganic and organic materials





PARTICLE IDENTIFICATION (SEM/EDS)

Automated particle analysis using SEM/EDS – Advantages and Disadvantages

Advantages

- Reliable distinction between inorganic and organic particles (rather than shiny/non-shiny)
- (Better) identification of white, transparent and abrasive particles
- Elemental composition of the particles
- Allows certain material properties to be assigned (hardness / electrical conductivity)

Disadvantages

- Long measurement times
- The influence of the environment (substrate, beam scattering) and particle quality (inhomogeneity, possible contamination with deposits) can have a massive impact on the result of the EDX measurement
- Manual follow-up checks are necessary

EXTENDED ANALYSES

Content

Basics SEM/EDX

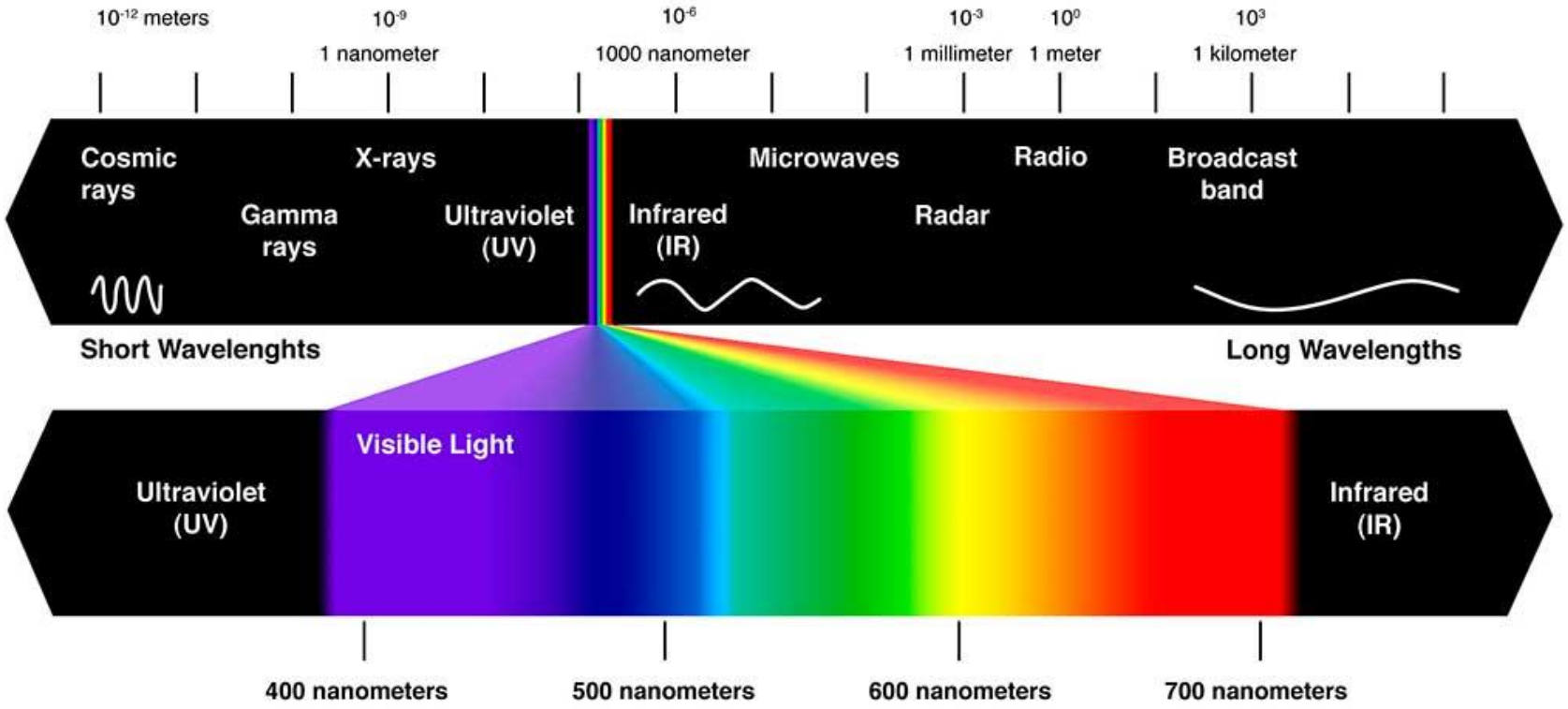
Particle identification by means of SEM/EDS

IR-Spectroscopy & particle identification

Analytical methods for testing surface cleanliness

IR-SPEKTROSKOPY

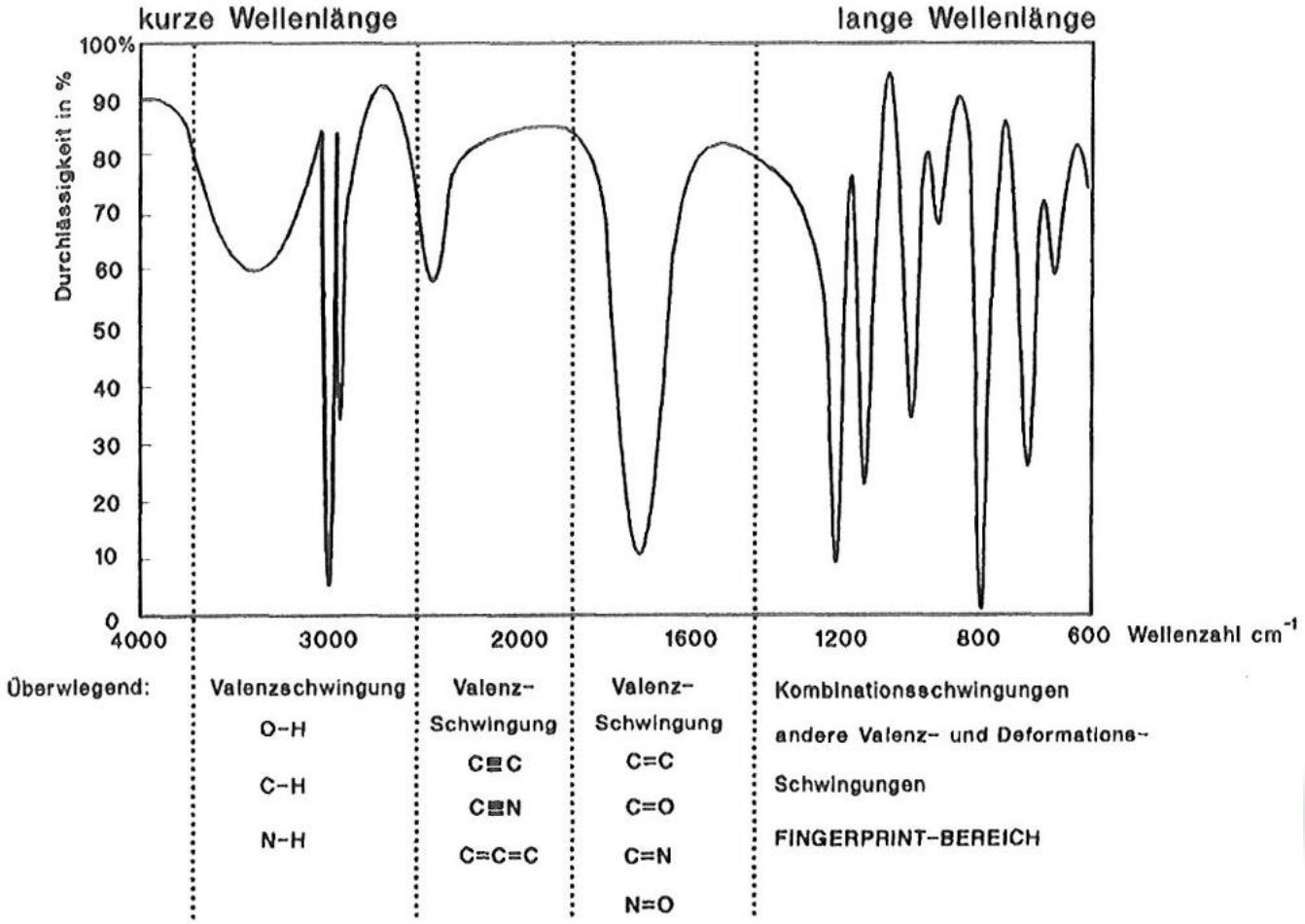
Basics



- Wavelength range used: 2.5 – 50 µm
- Organic molecules absord specific wavelength of IR radiation

IR-SPEKTROSKOPY

Basics



Einteilung nach Schwingungsform

IR-SPEKTROSKOPY

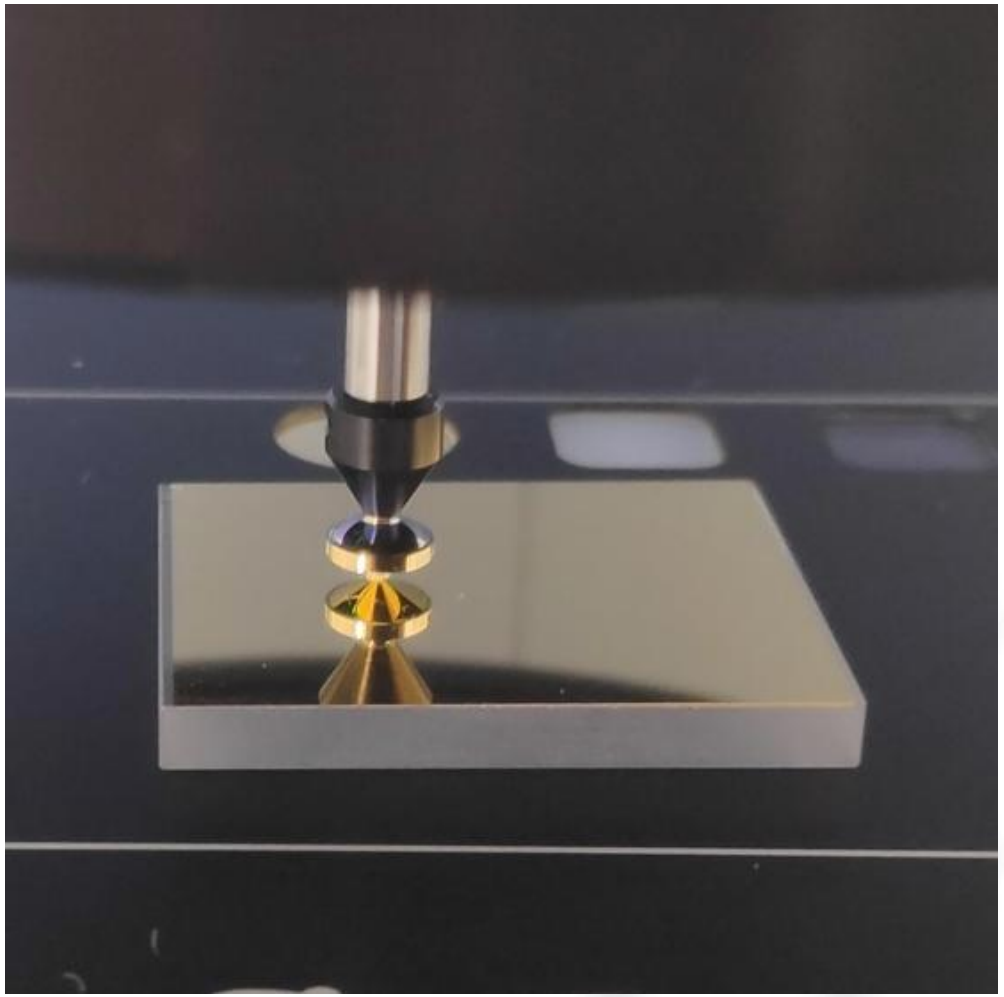
Basics

Measurement IR spectroscopy using IR microscope:

Challenges:

- Filter material also consists of organic polymer
  - Particle must be prepared on metallic support manually
  - Particle must be large enough

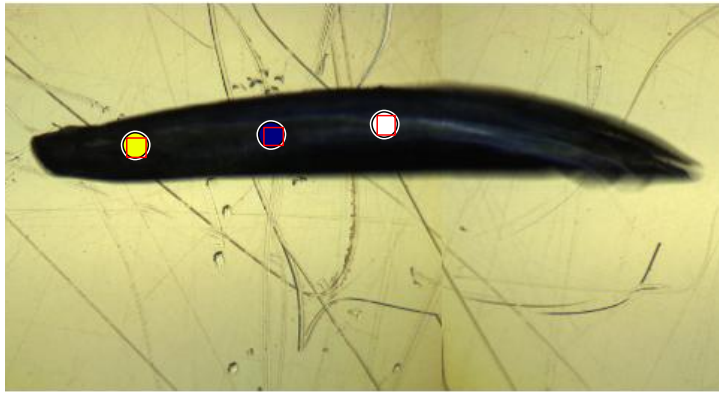
The smaller the particle, the more difficult!

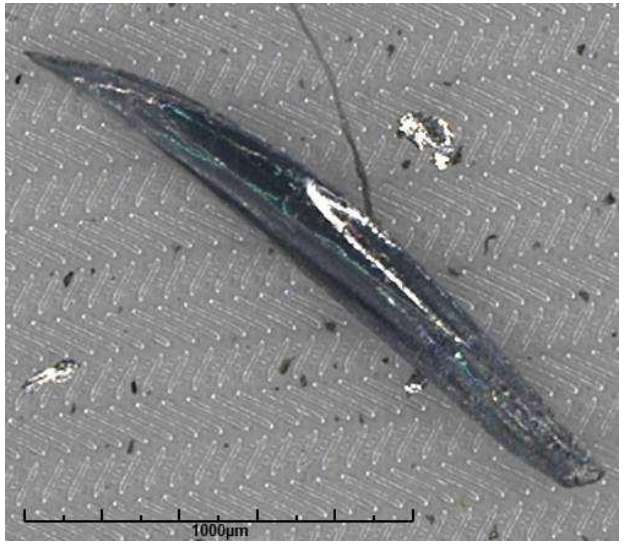


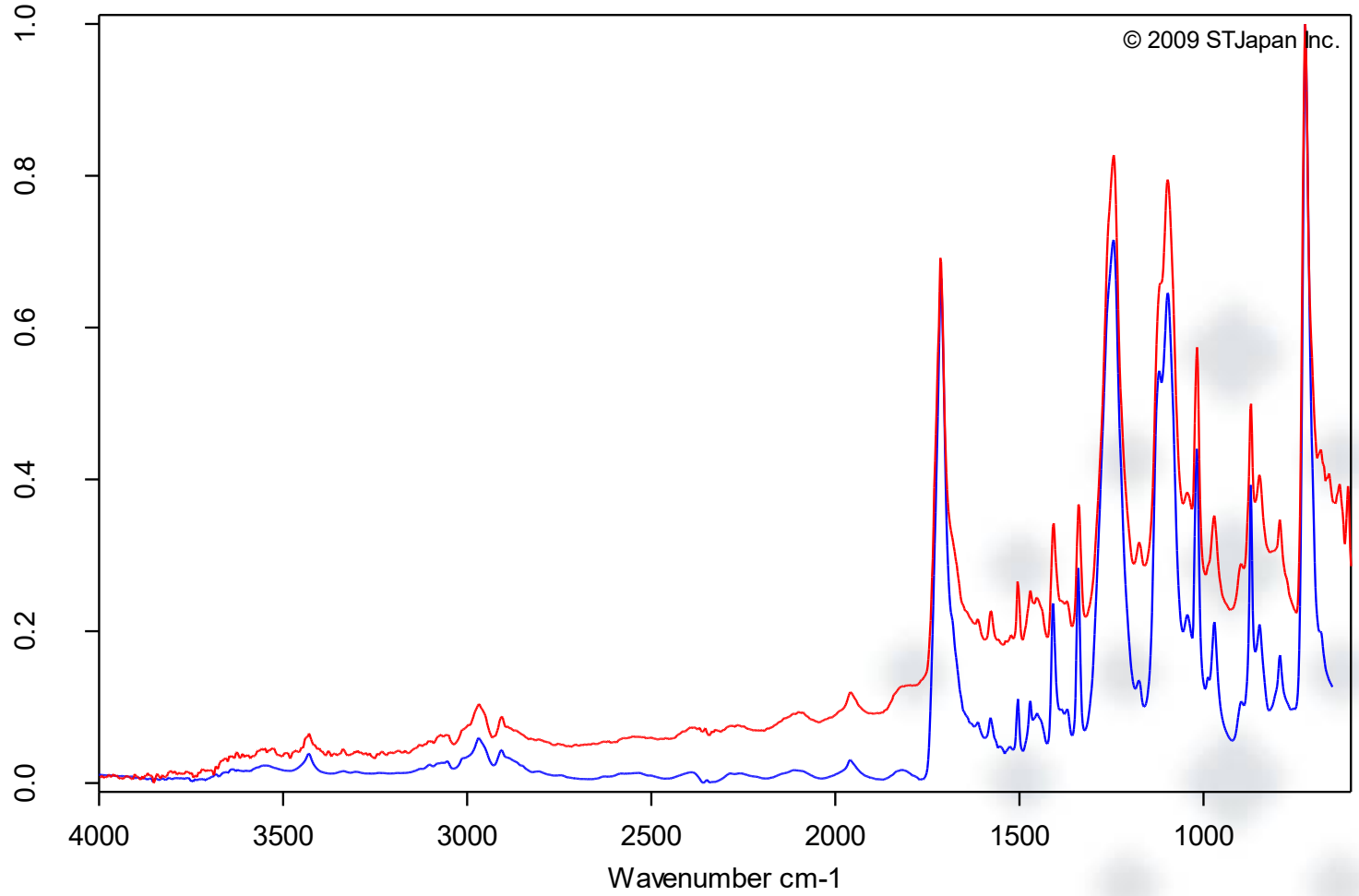
IR-SPEKTROSKOPY

Single particle analysis

Polyester



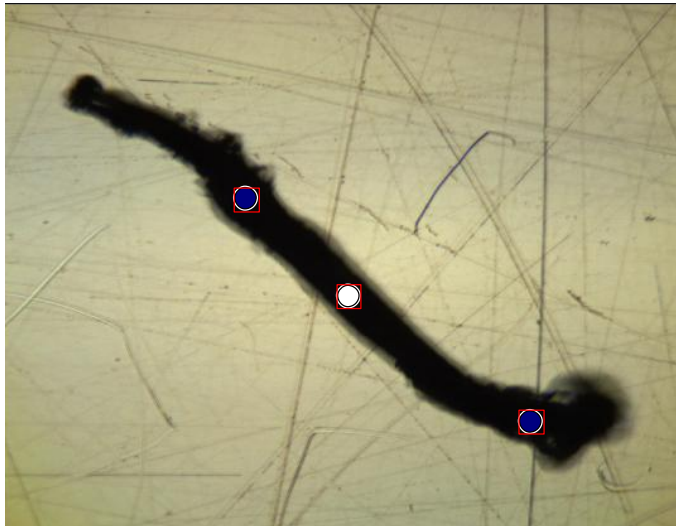


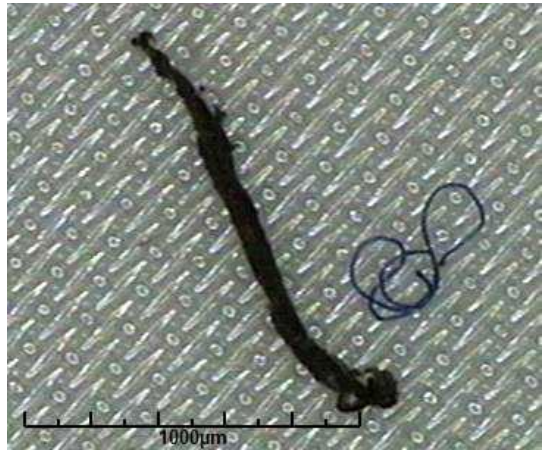


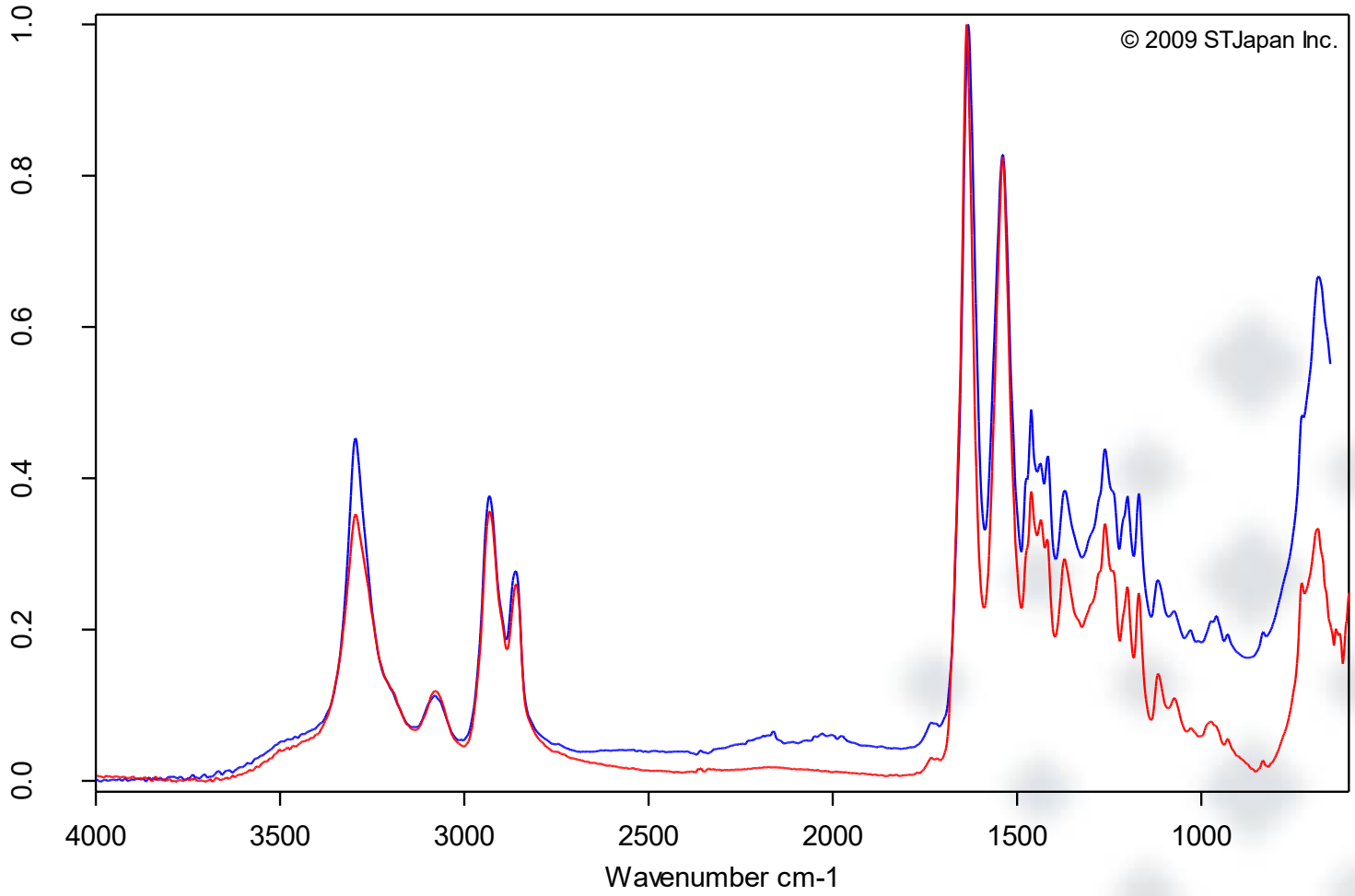
IR-SPEKTROSKOPY

Single particle analysis

Polyamid



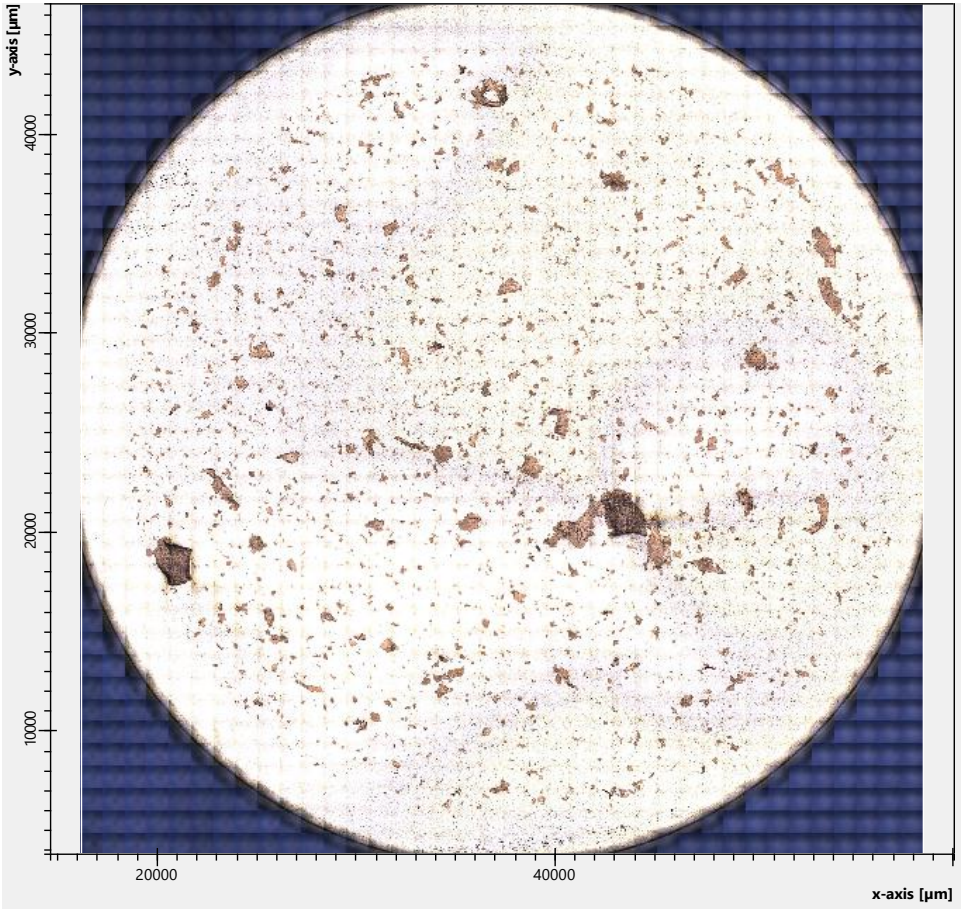


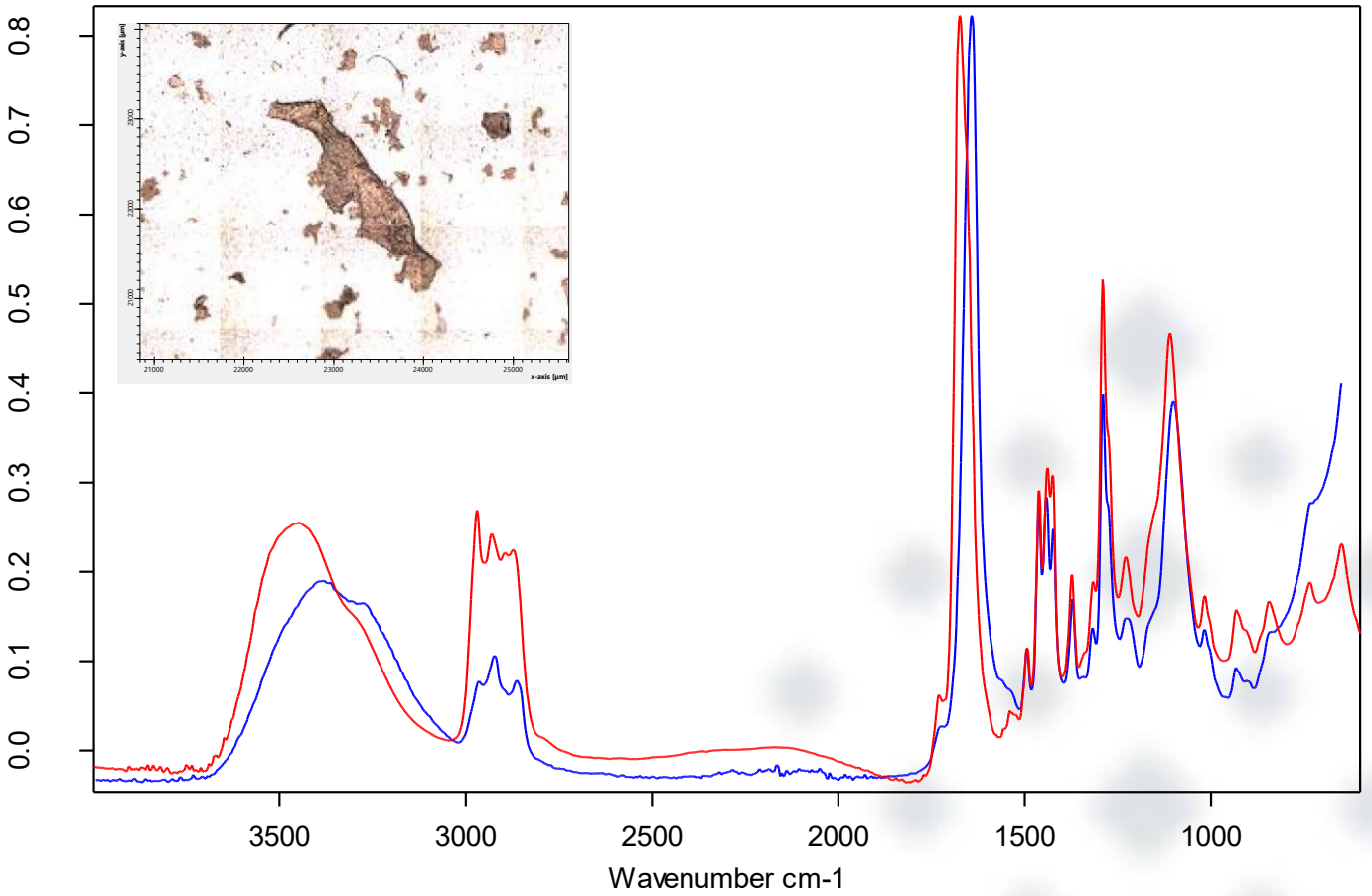


IR-SPEKTROSKOPY

Filter scan

- Detection of organic particles and fibres





PVP (Polyvinylpyrrolidon)

IR-SPEKTROSKOPY

Summary

Advantages

- Material often can be determined very accurately due to characteristic absorption and comparison with extensive database
- Single particle and filter scan analyses possible

Disadvantages

- Particles have to be prepared one by one
- Detection of sizes starting around 100 µm
- Interpretation of the obtained spectra required experience/chemical knowledge

FURTHER ANALYSIS & SURFACE CLEANLINESS

Content

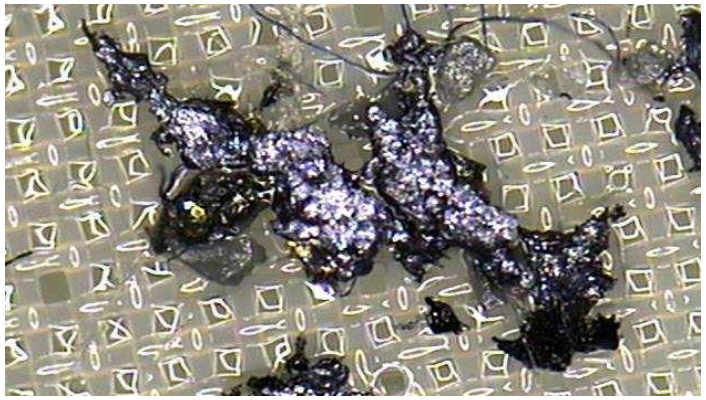
- Basics SEM/EDX
- Particle identification by means of SEM/EDS
- IR-Spectroscopy & particle identification
- Analytical methods for testing surface cleanliness

ANALYTICS FOR TESTING SURFACE CLEANLINESS

Basics

Types of surface contamination

Particles



Organic contaminants



Inorganic contaminants



ANALYTICS FOR TESTING SURFACE CLEANLINESS

Basics

Types of surface contamination

Particles

Organic contaminants

- Corrosion protection
- Machine oil
- Cleaning residues

Inorganic contaminants

- Cleaning residues
- Production residues (e.g. solder)





ANALYTICS FOR TESTING SURFACE CLEANLINESS

Basics

Types of surface contamination

Organic contaminants



Analytical methods:

Sum-parameter:

- TOC (**T**otal **O**rganic **C**arbon)
  - water-soluble organic compounds (e.g. surfactants)
- AGREE (**A**nalysis of **G**ravimetrically detectable **R**esidues by **E**fficient **E**xtraction)
  - "Gravimetric" determination of non-evaporable residues

Single-parameter:

- GC-MS (**G**as **C**hromatography with **M**ass **S**pectrometer
  - Separation and characterization of an extract of the test component

ANALYTICS FOR TESTING SURFACE CLEANLINESS

Basics

Types of surface contamination

Inorganic contaminants



Analytical methods:

Sum-parameter:

- ROSE (**R**esistivity **O**f **S**olvent **E**xtract)
  - Extraction of the test part, measurement of the increase in conductivity of the extract

Single-parameter:

- IC (**I**on **c**hromatography)
  - Separation and characterization of an extract of the test component

QUESTIONS



Do you have any questions?

Chat



E-Mail

seminar@cleancontrolling.de

Thank you for your attention



