The Abdus Salam International Centre for Theoretical Physics

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Joint ICTP-IAEA Workshop on Advanced Synchrotron Radiation Based X-ray Spectrometry Techniques

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Chemical characterization of environmental particulate matter

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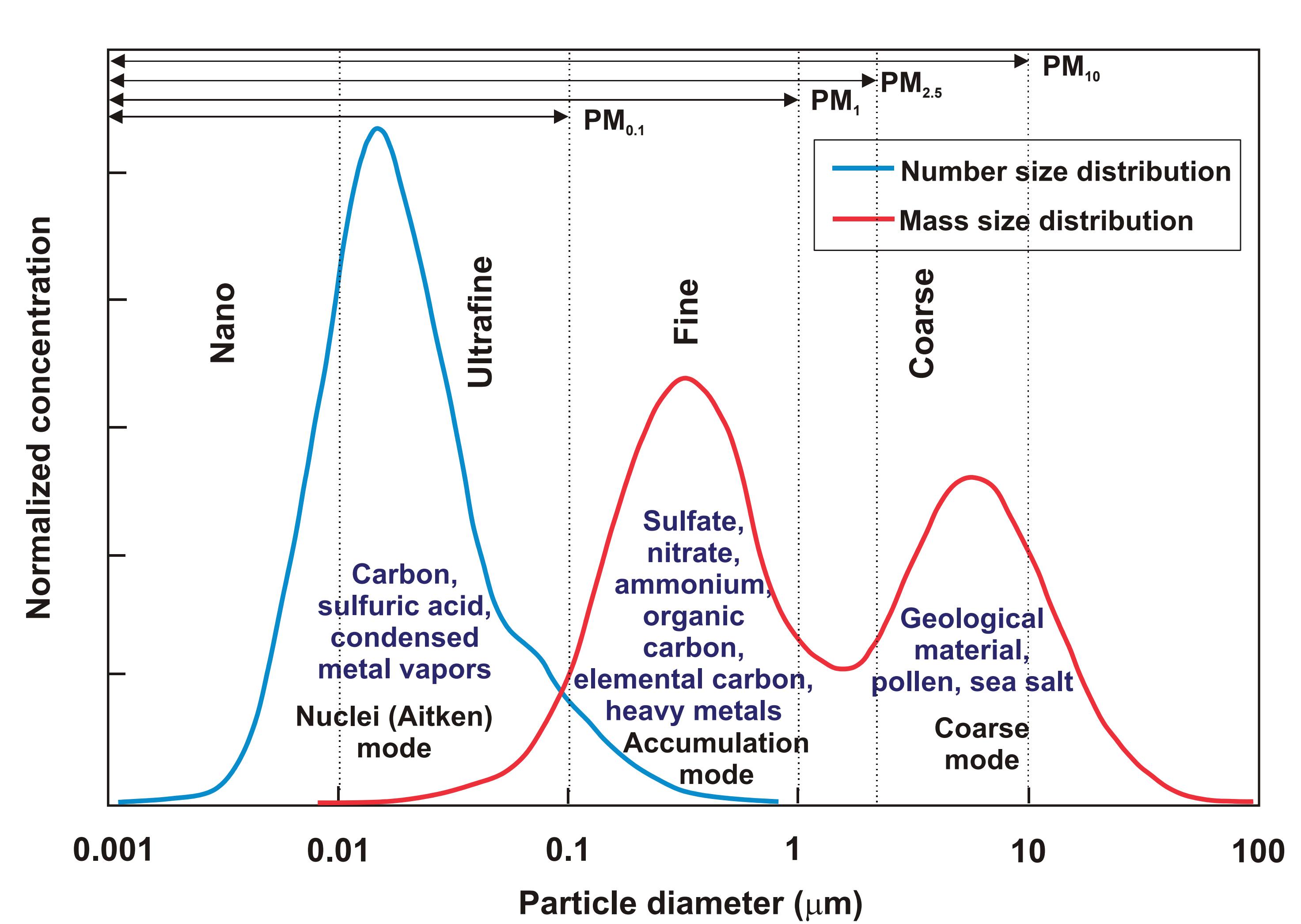
Introduction

- Fine and ultrafine aerosol fraction (d < 2.5 µm)
  - respirable aerosol – important health effects
  - climate effect – optical characteristics, chemical composition, structure
  - time dependence of physical and chemical characteristics
    - meteorological circumstances, mobile sources (traffic)
- Characteristics of sources – „fingerprints”
  - chemical composition
    - air concentration of major and trace components
    - compounds, chemical forms
  - morphological parameters (diameter, shape)
- Sediment and water-suspended particles, tire debris
  - sources and fate

Size distribution of aerosol particles



Health effect: stochastic lung model calculations

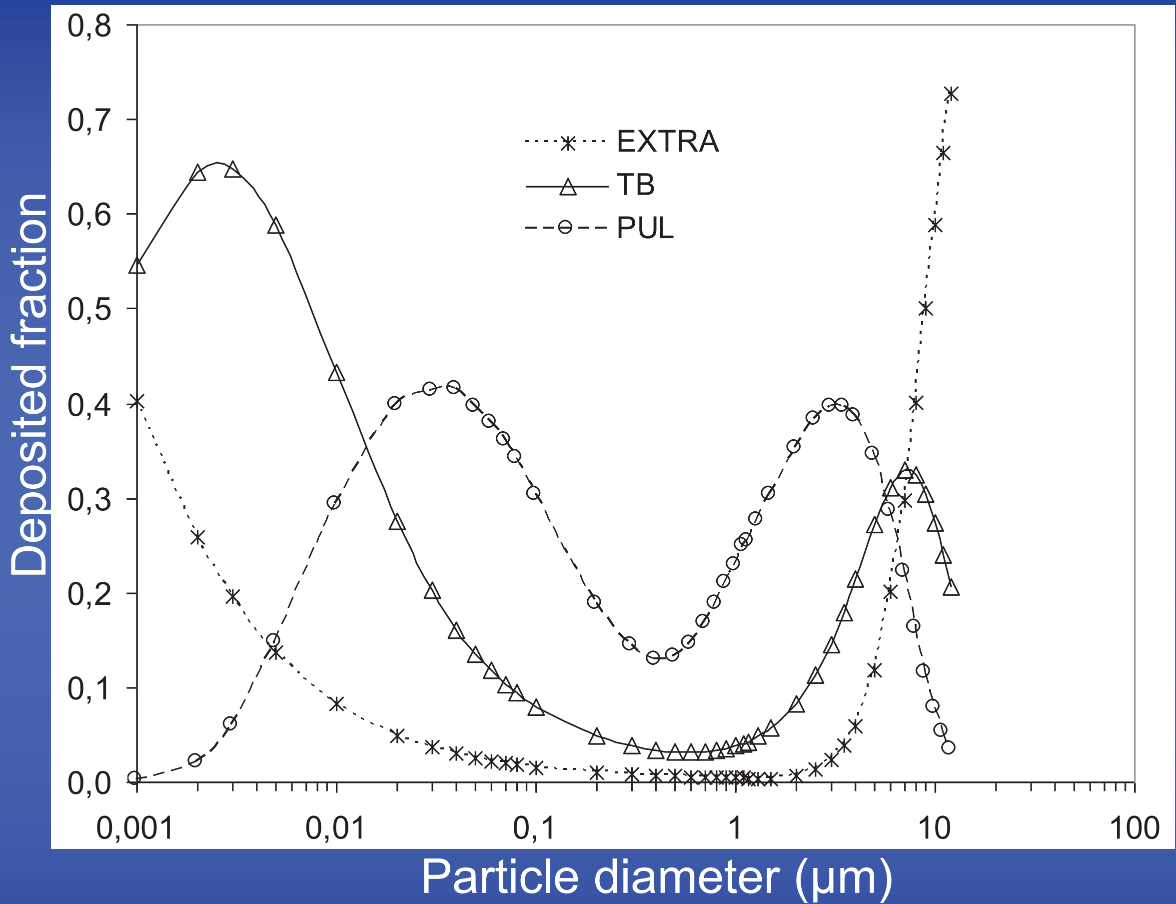
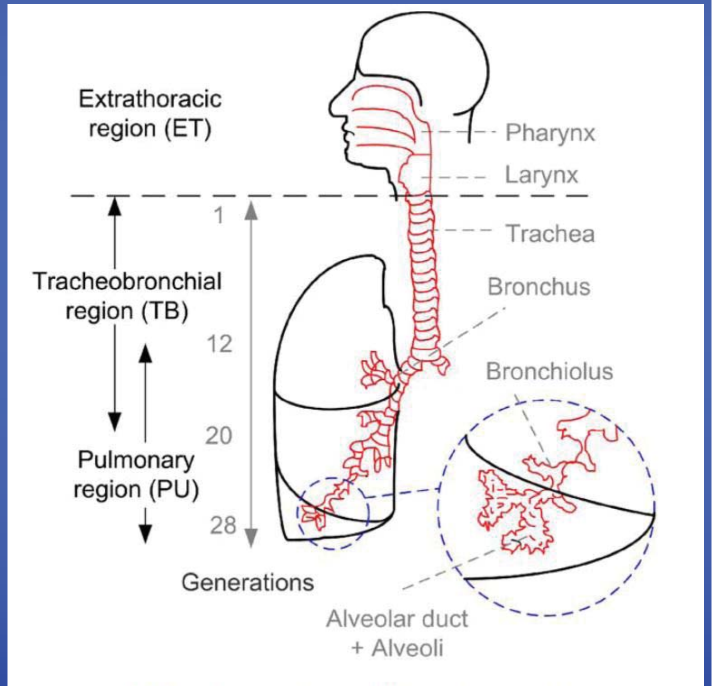


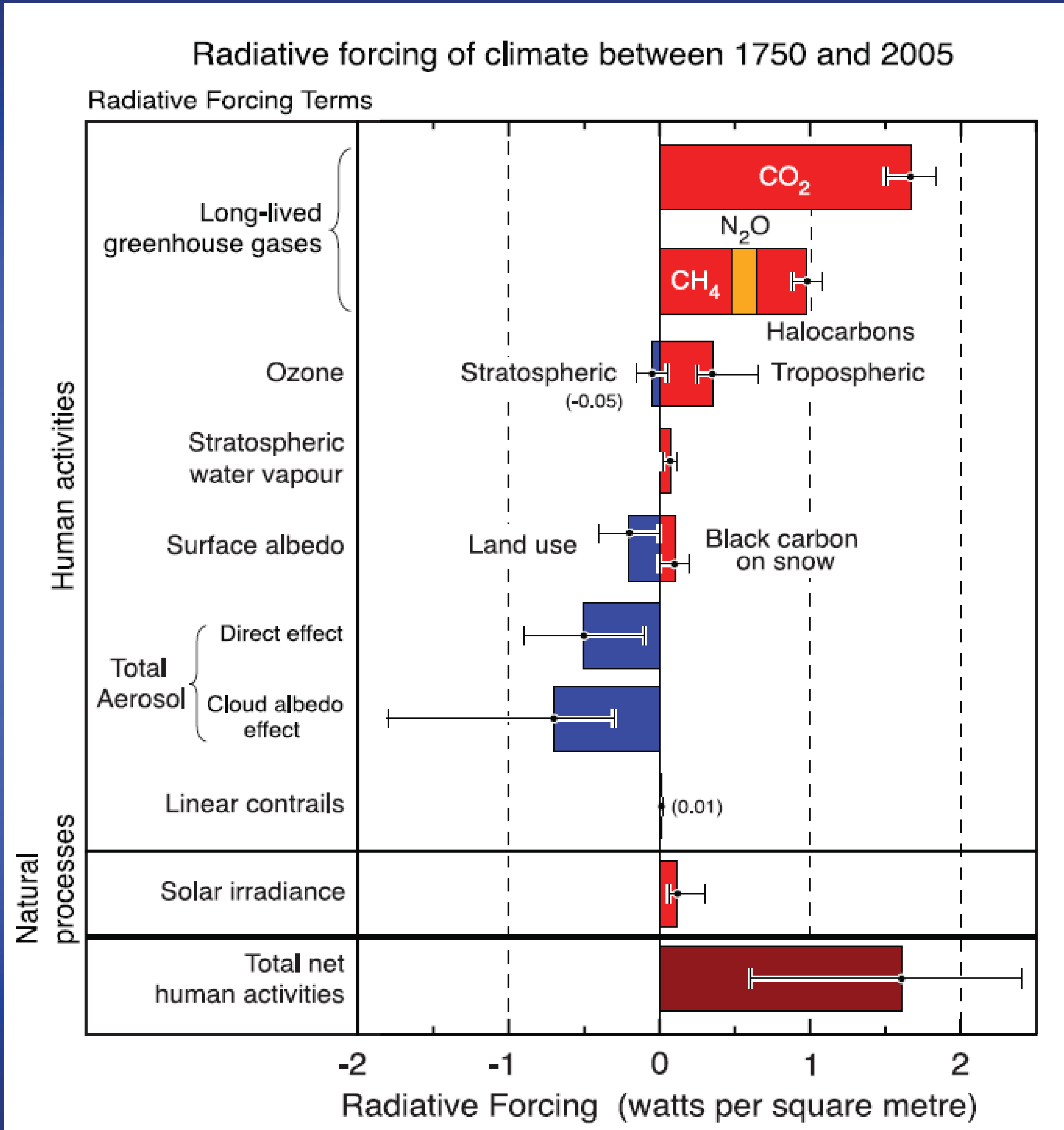
Figure courtesy: Imre Balásházy, MTA EK

medium deep breathing,
HP = 5 s, BH = 0 s, TV = 1.5 l
EXTRA: extrathoracic region,
TB: tracheobronchial region
PUL: pulmonar (acinar) region



A schematic representation of the human respiratory tract.

Health effect of ultrafine particles might not be closely associated with particle mass, but 50 µg/m^3 might be fatal, toxicity increases with decreasing particle size, e.g. inflammatory response depends on surface area



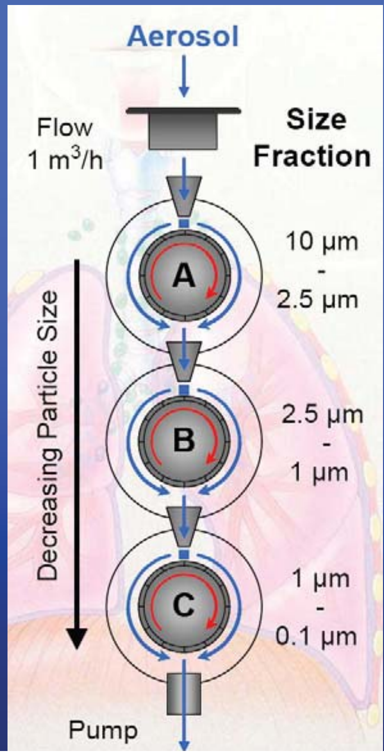
Inaccuracy of indirect aerosol forcing≈ GHG forcing

Application of synchrotron radiation

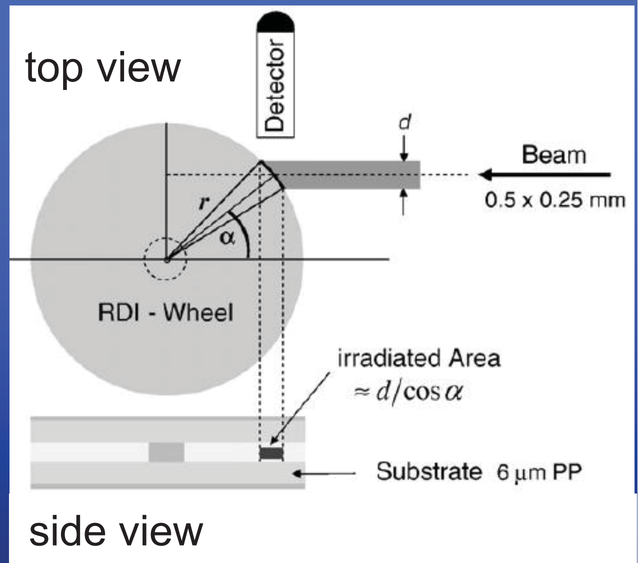
- Size fractionated aerosol
  (sampling using cascade impactor)
  - elemental composition
    - increase of time or size resolution
    - test of new methods for laboratory applications
    (SR-XRF, SR-TXRF)
  - determination of chemical species
    - chemical form of major components (C, N, S), trace elements (XAFS, TXRF-XAFS)
    - organic compounds (ATOFMS)
- Measurement of individual particles
  - chemical forms of light elements (STXM, XAFS)
  - distribution and chemical state of metals (µXRF, XAFS)

Elemental composition – SR-XRF

- Aim:
  - Increase of (atmospheric) size resolution (24 h → 1 h)
- Harmonization of sampling and analysis
  - rotating drum impactor, 3 size fractions
  - design of drums, substrate (6 µm polypropilene foil) optimized to SR-XRF measurements



Measurement setup (HASYLAB *L*, SLS *microXAS*):



N. Bukowiecki et al., Spectrochim Acta Part B 63 (2008) 929-938

Elemental composition – SR-XRF

- Detection limits

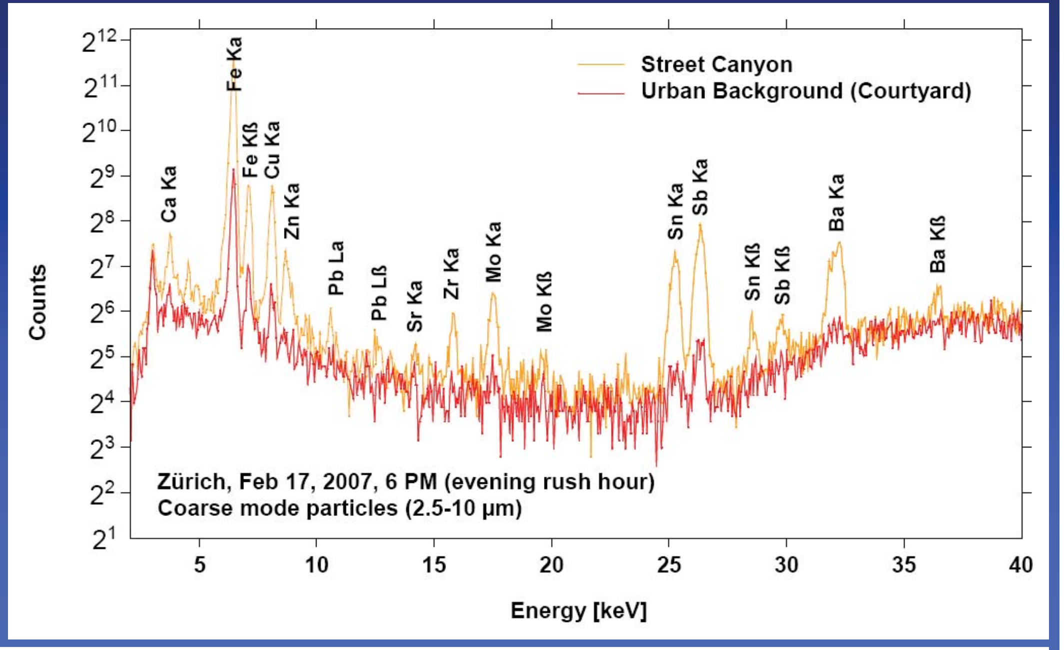
  1–10 µg/g → 10–100 pg/m^3
  (20 s measurement time, monochromatic, white beam)

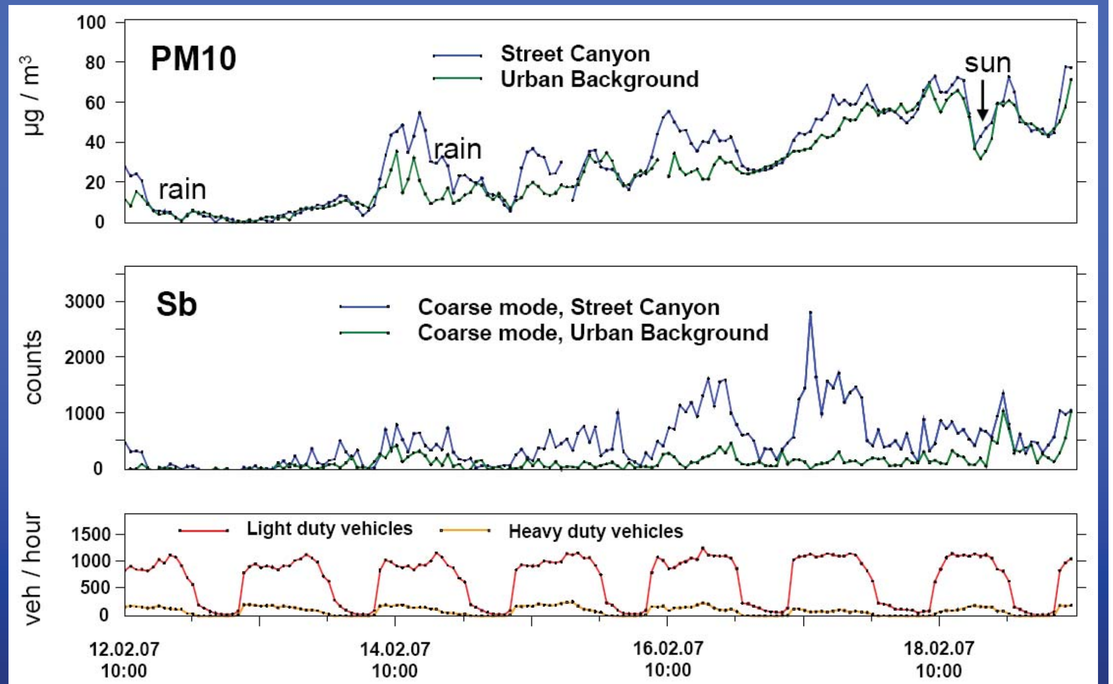
- Application example

  elements characteristic for brake wear (Mo, Sn, Sb, Ba) in coarse fraction of urban aerosol

  correlation: traffic density, PM_{10} near road

  (high number of hourly measurements are necessary for source profiling)





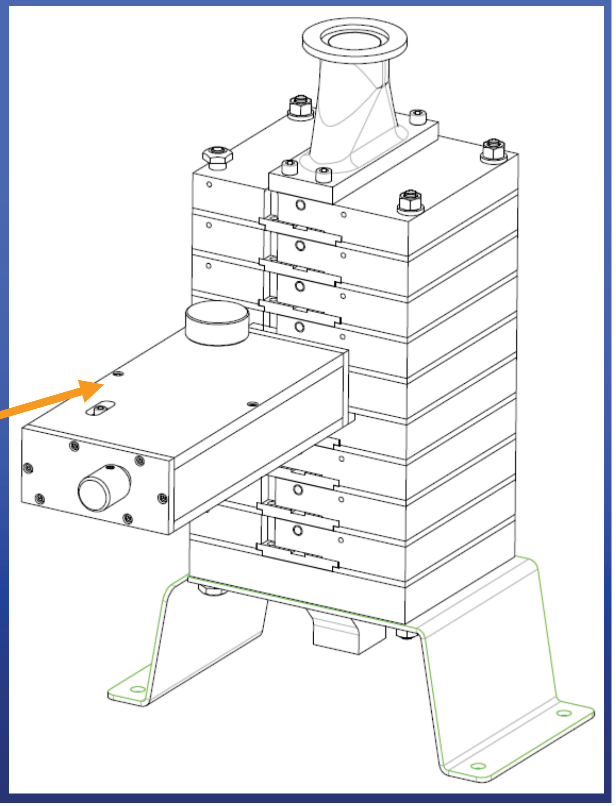
N. Bukowiecki et al., Spectrochim Acta Part B 63 (2008) 929-938
N. Bukowiecki et al., HASYLAB Annual Report 2007, pp. 1287-1288

Elemental composition – SR-TXRF

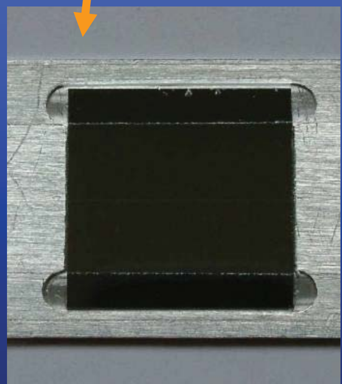
- Aim:
  - development of analytical procedure based on cascade impactor sampling and laboratory or portable total-reflection X-ray fluorescence measurements
  - size fractionation and non-destructive determination of elemental composition of aerosols collected from small air masses
  - Standardization for routine measurements
- Application of synchrotron radiation
  - versatility of measurement setup → test of samples and standards
  - better size and time resolution

Sampling of size fractionated aerosol

- Seven-stage May-type cascade impactor
- d_{50} (20 l/min) 16; 8; 4; 2; 1; 0,5; 0,25 µm
- Different sampling times possible on different stages
- sampling: directly to reflector (Si wafer)
- 20-3200 l air depending on aerosol concentration and size fraction
- **Further development:**
- 9 stages (extension to 0.07-0.25 µm fractions)

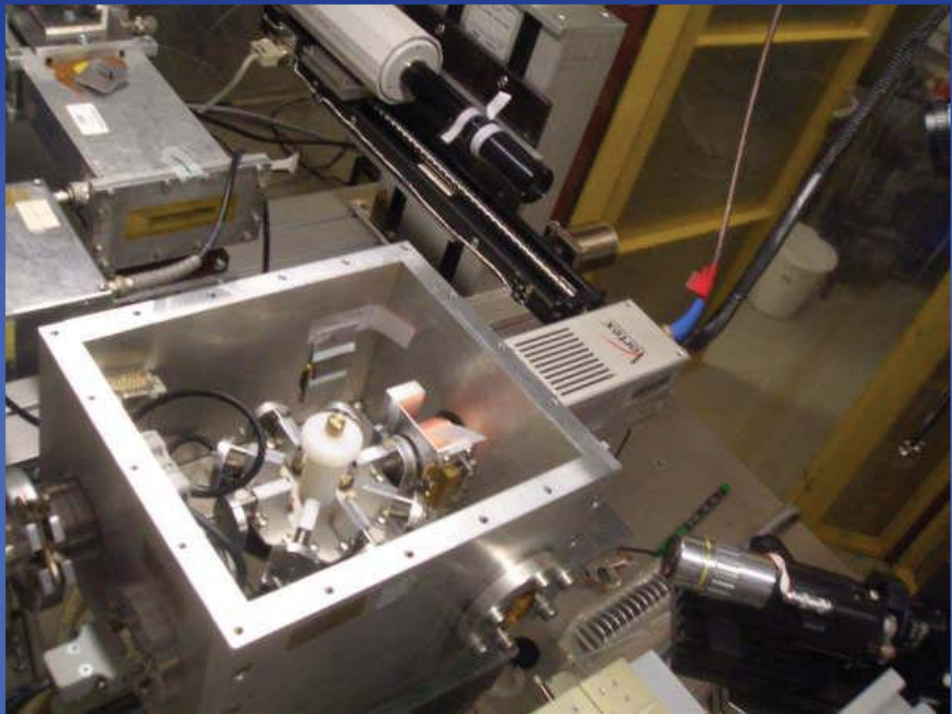


Deposited particles form a stripe of 200-500 µm width on the 20x20 mm^2 Si plate



- Docking to avoid contamination and ease of sample change

SR-TXRF measurements



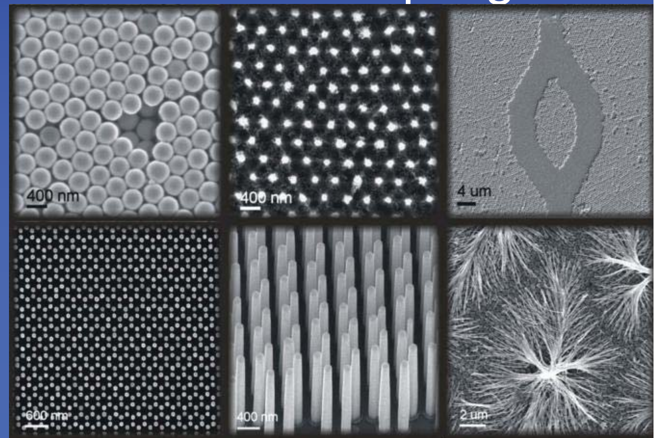
- vacuum chamber [1] at HASYLAB beamline L
- automatic sample loader, easy sample change
- various sizes and shapes of samples can be measured

[1] *Streli C., Pepponi G., Wobrauschek P., Jokubonis C., Falkenberg G., Zaray G., 2005:. A new SR-TXRF vacuum chamber for ultra-trace analysis at HASYLAB, Beamline L. X-Ray Spectrom., 34, 451–455*

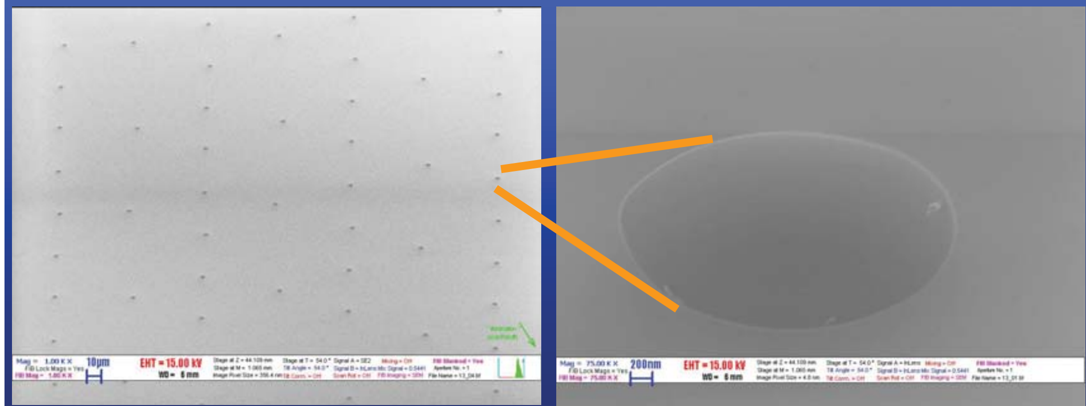
- SR beam dimensions 1.4 mm (vertical) x 0.2 mm (horizontal)
- SDD with 1.4 mm wide Mo slit collimator (sample geometry)
- **TXRF:** E_0=18.4 keV, ΔE/E=0.02 (multilayer monochromator)
  beam perpendicular to the strip: scan in order to test homogeneity of the deposited aerosol particles
- beam parallel to the strip: measurement of the whole sample

Standard development

- Objective: put “aerosol like objects” with know composition mass and shape on Si plates mimicry a May-impactor stage after aerosol sampling



- Institute for Materials Science experience in growing micro and nano structures on Si surface
- Reference chip for TXRF measurements: 20x20 mm^2 Si-plate on median 7 rows of 2250 objects with 2,7 µm diameter 10–100 nm height Cr or „permalloy” (FeNi) with „lift-off” technique
- Rectangular shape of Si is cost efficient

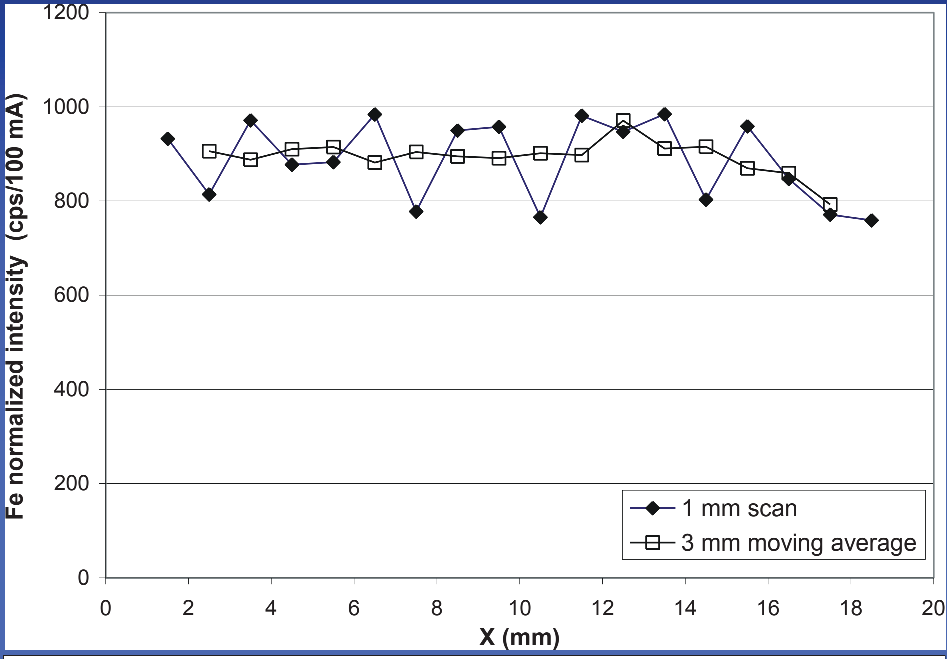


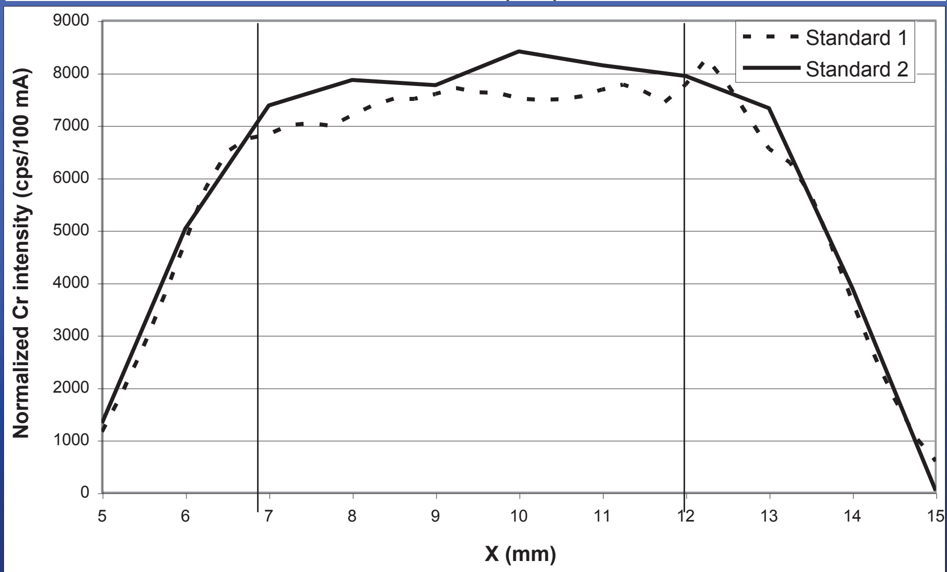
Wätjen U, Bársony I, Dücső C. Microchim Acta 2000, 132, 521–525

Osán J, Reinhardt F, Beckhoff B, Pap AE, Török S. ECS Trans 2009, 25, 441–451

Reinhardt F, Osán J, Török S, Pap AE, Kolbe M, Beckhoff B. J Anal At Spectrom 2012, 27, 248–255

Homogeneity test of sample and standard



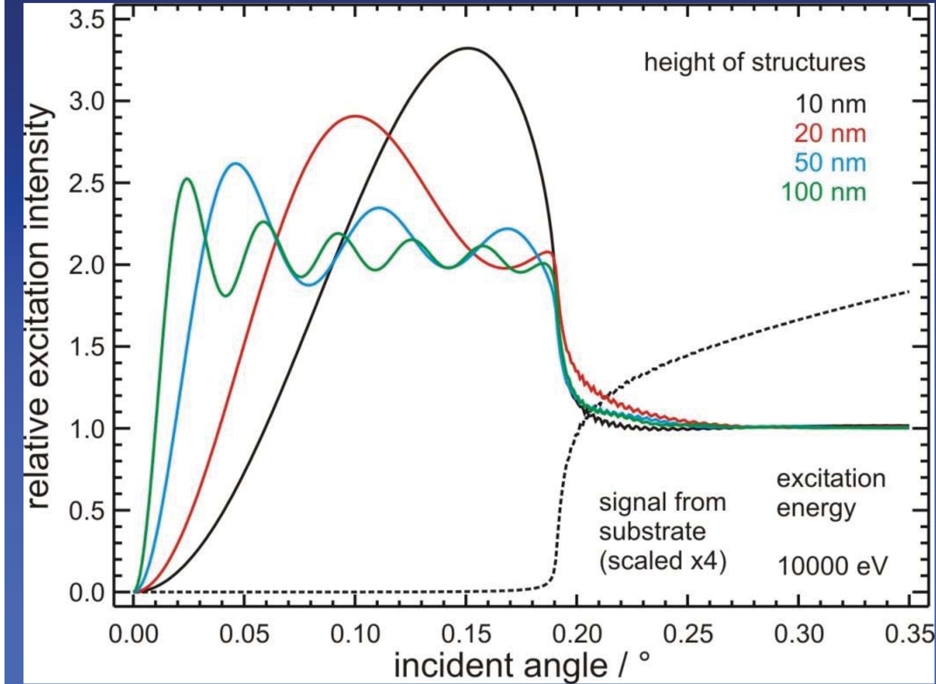


Successive height scans of a stage 6 sample (0,5-1 μm) collected at Mátra

Fe intensities normalized to ring current vary within 10% relative standard deviation during the three scans

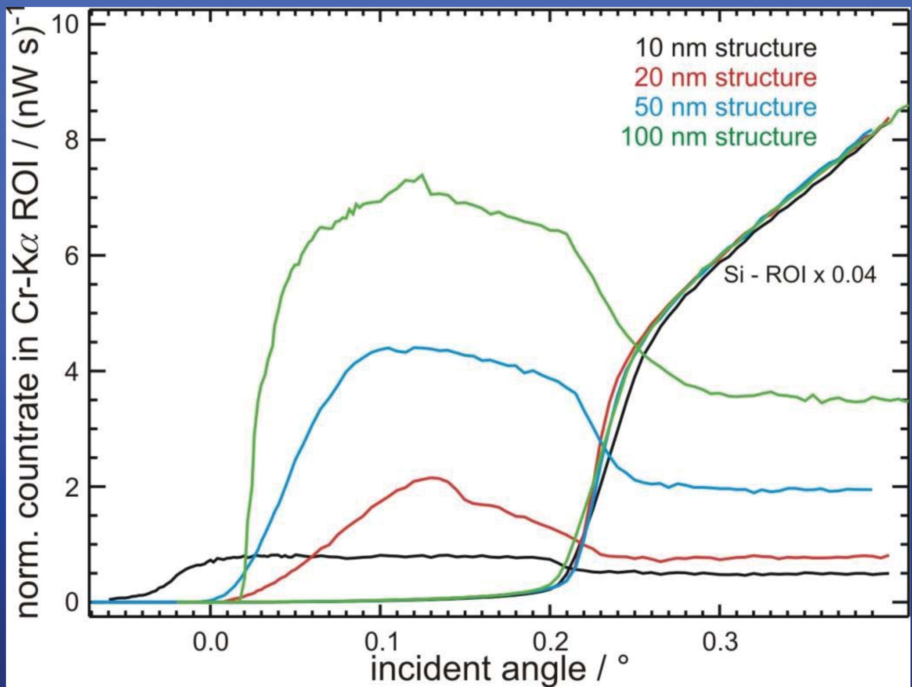
Height scan of two independent standard Si wafers containing 7 ng Cr in a homogenous strip

homogeneity and reproducibility supports suitability as internal standard



Theoretical GIXRF angular scans at 10 keV calculated for structures of different heights – IMD[a] simulations of the X-ray standing wave field

[a] D.L. Windt, IMD—Software for modeling the optical properties of multilayer films, Comp. Phys. 1998, 12, 360-370



Measured GIXRF angular scans at 8.04 keV for Cr pads

No pronounced oscillations observed in measured GIXRF angular scans of Cr structures – suitability for internal standard

Measurements: PTB@BESSYII, FCM beamline

J. Osán, F. Reinhardt, B. Beckhoff, A.E. Pap, S. Török, Probing patterned wafer structures by means of grazing incidence X-ray fluorescence analysis, ECS Transactions 2009, 25, 441–451

SR-TXRF detection limit

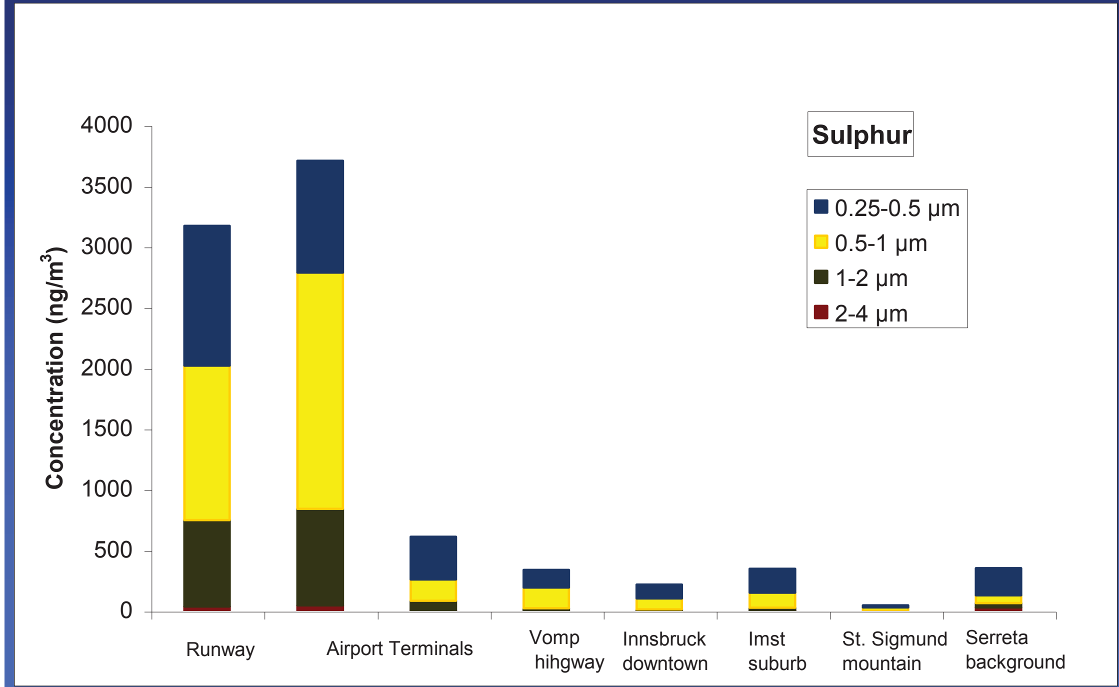
	Detection limit (pg/m3)	
Element	A	B
S	451.3	164.0
Cl	282.8	102.7
Ca	70.2	25.5
Ti	48.7	17.7
Cr	23.4	8.5
Fe	12.4	4.5
Cu	4.5	1.6
Zn	3.5	1.3
Se	2.6	0.9
Br	2.4	0.9
Sr	3.4	1.2
Pb	5.3	1.9

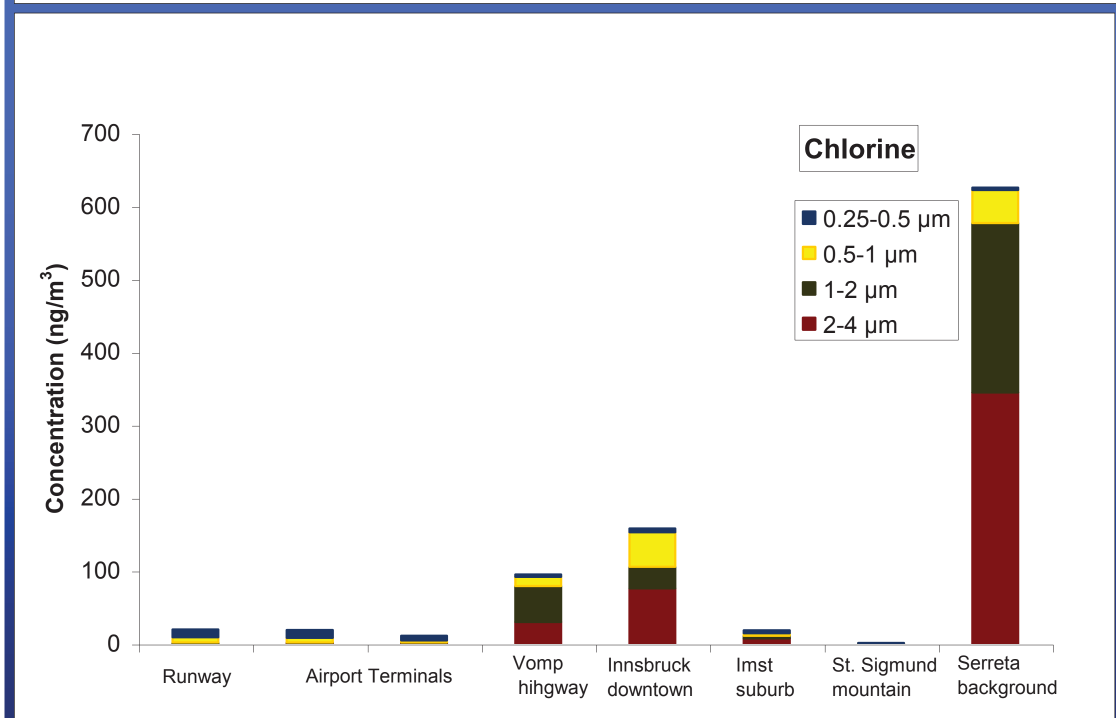
Sample volume: 1000 l
Measurement time: 100 s
Ring current: 100 mA

A:
sample strip perpendicular to beam
B:
sample strip parallel to beam

V. Groma, J. Osán, S. Török, F. Meirer, C. Streli, P. Wobrauschek, G. Falkenberg
Trace element analysis of airport related aerosols using SR-TXRF
Időjárás 112 (2008) 83-97

TXRF results





Size distribution of sulphur concentrations:
in accordance with data obtained from high volume samples

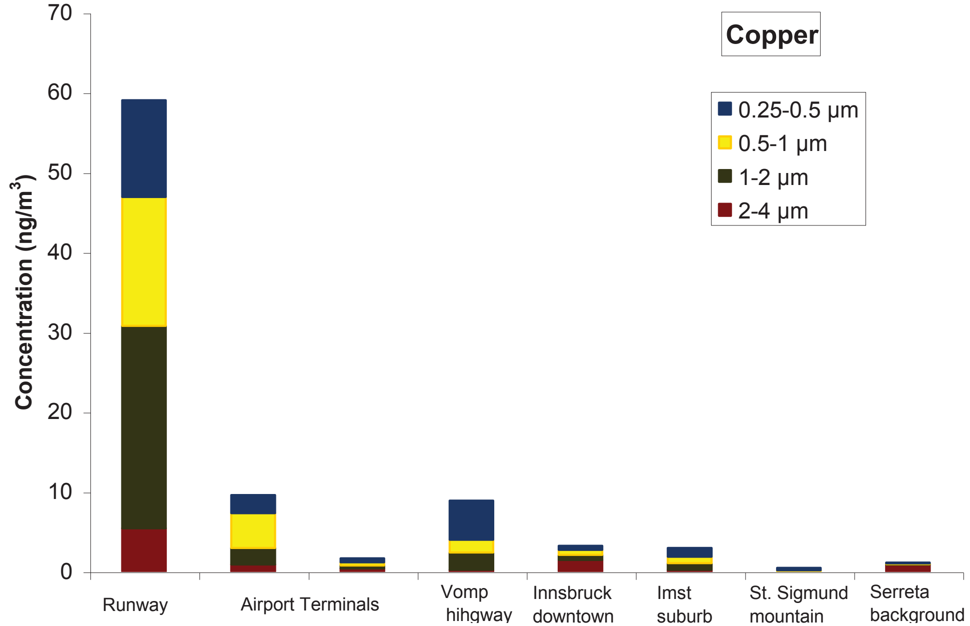
sulfate shows a maximum at
~ 0.3 µm for rural and
~ 0.7 µm for urban aerosols

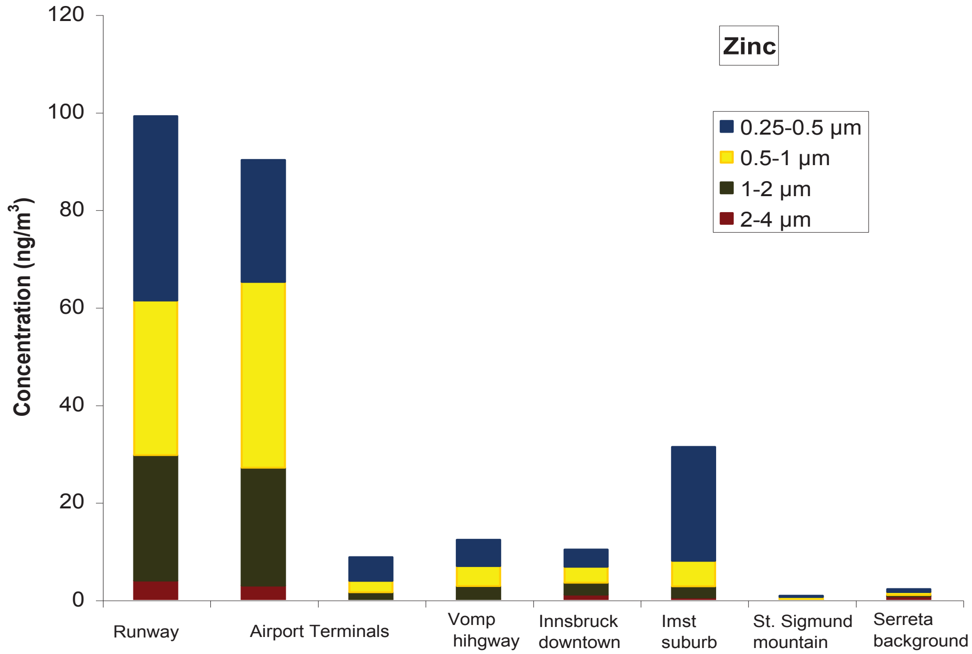
Chlorine dominant in aerosols of marine origin

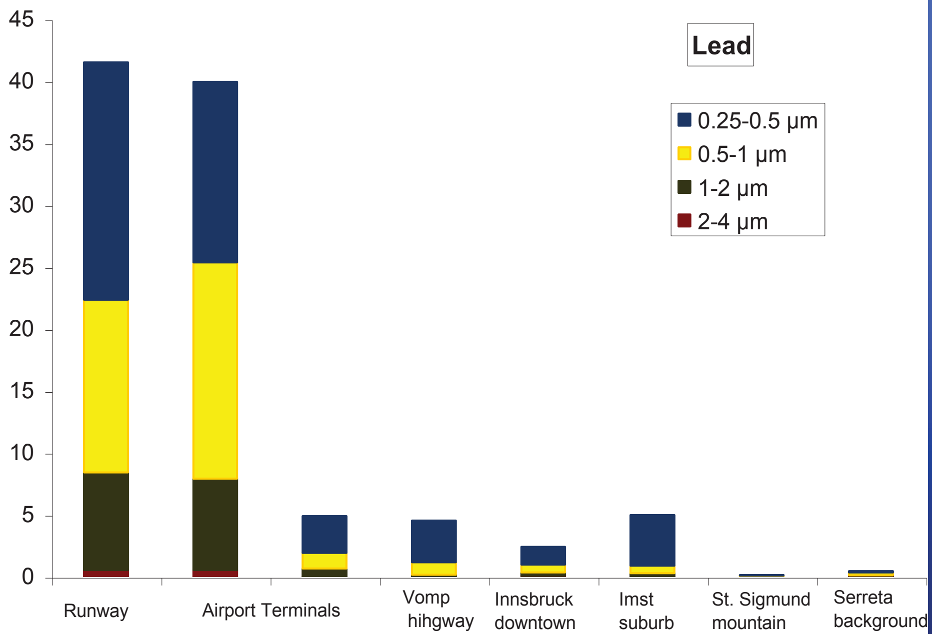
TXRF results

Heavy metals dominant in the submicrometer fractions → indicator of anthropogenic origin

Zn and Pb are related to areas where traffic sources dominate



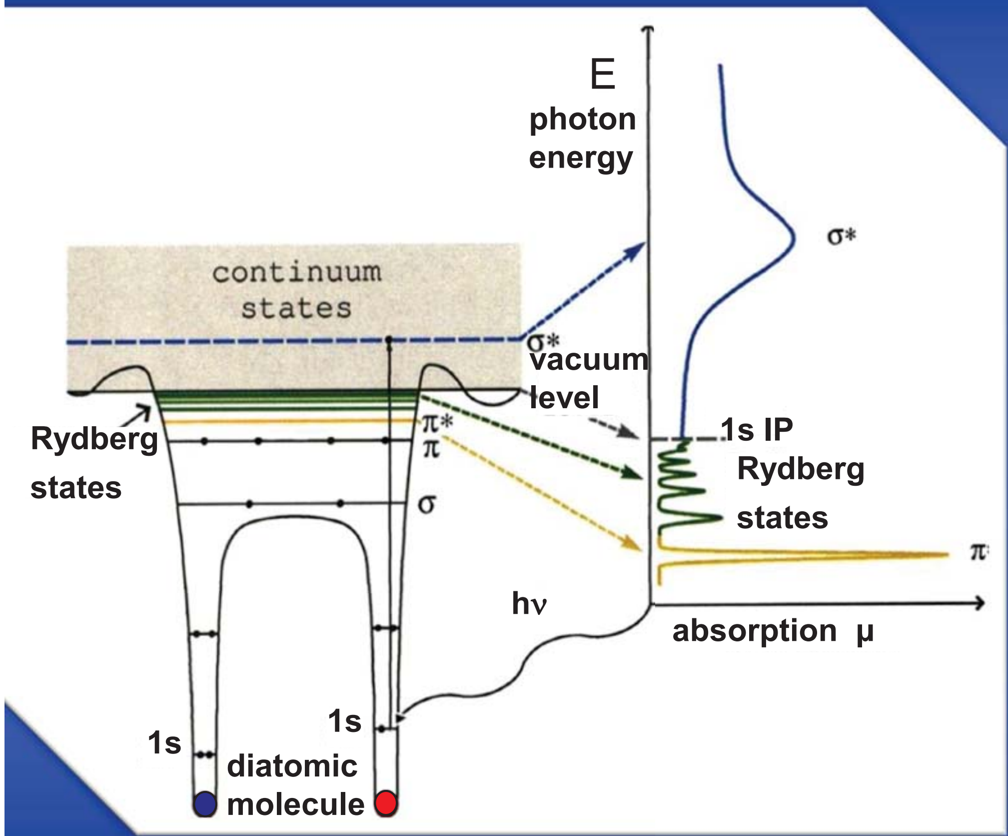




Near-Edge X-ray Absorption Fine Structure (NEXAFS)

recorded in a TXRF mode employing soft x-rays

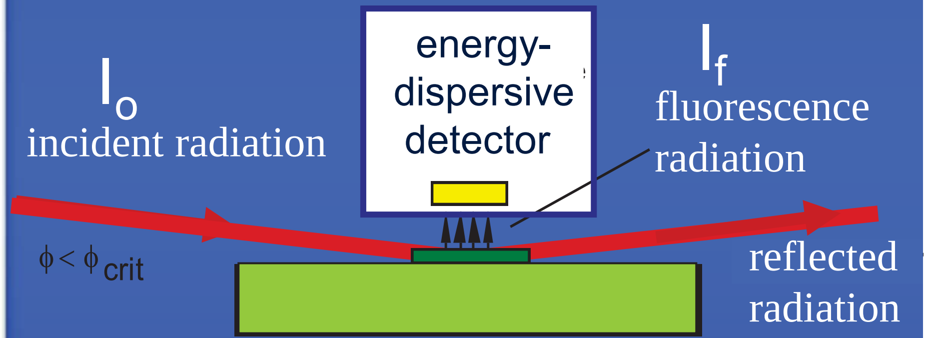
X-ray spectrometry



NEXAFS arises from electronic transitions of an inner shell electron to energy levels (orbitals in molecules) which are normally unoccupied

fluorescence detection

$$I_f \sim \mu \ \text{ as } \ \mu \approx \tau \ \text{ for soft x-rays}$$



<u>advantages of the TXRF mode:</u>

- low scattering background due to small penetration depth
- large solid angle of detection
- absolute detection limits in the fg range

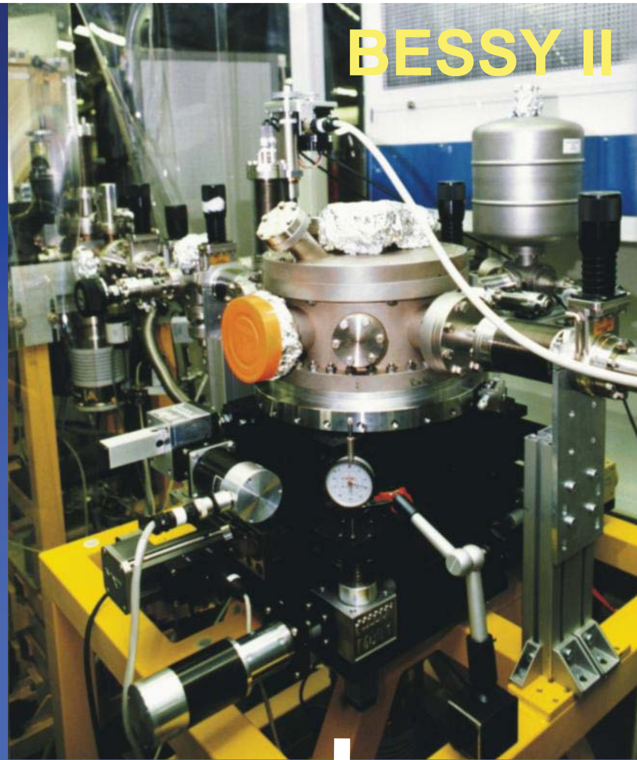
B. Beckhoff

TXRF-NEXAFS measurements

BESSY II (Berlin), PGM (PTB)
plane grating monocromator beamline

TXRF-NEXAFS:
2.5°, 274–330 eV, 396–425 eV,
0.1–0.5 eV steps, 10–30 s/point
(information about C and N chemical forms)

TXRF:
1222 eV, 1.2°, 300 s spectra
(information on light elements, reference free analysis)

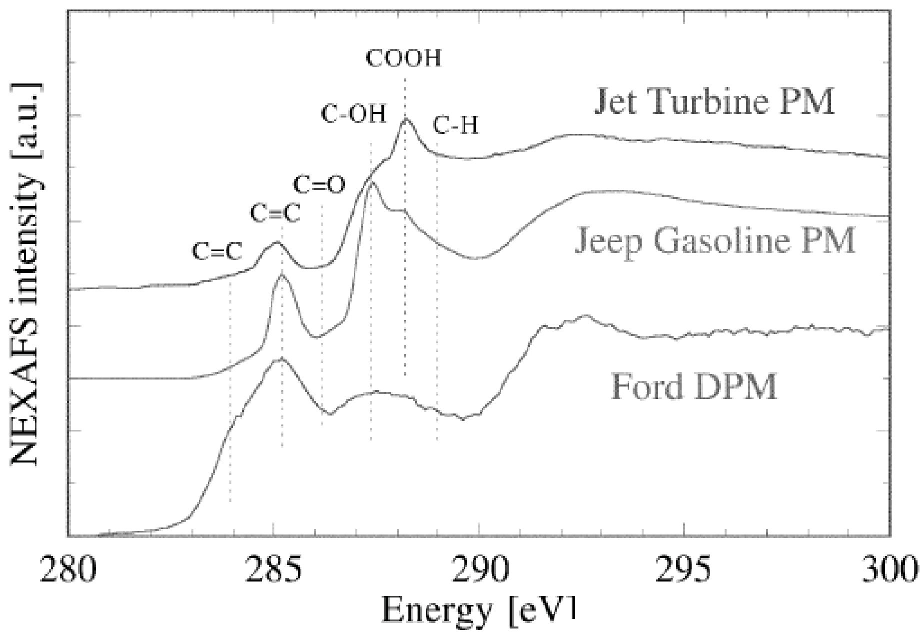


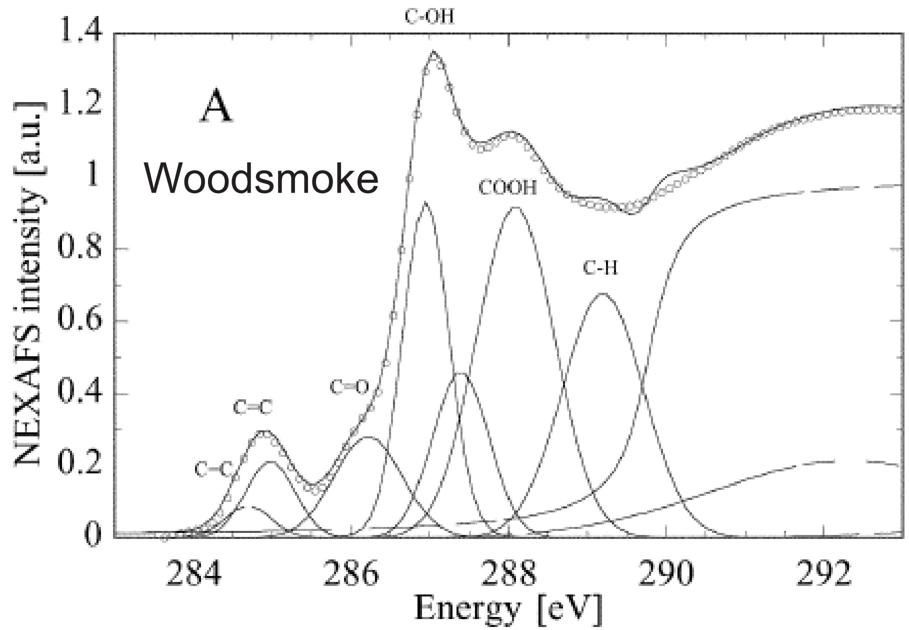
C species in aerosols – NEXAFS

eV	Transition	Functionality
283.7	1s-π*	Quinone
	1s-π*	Protonated/alkylated
284.9–285.5		Aromatic and PNA
	1s-π*	Carbonyl substituted
285.8–286.4		Aromatic, phenolic
	1s-π*	Aromatic C–OH
		Ketone-C=O
287.1–287.4		Aliphatic
	1s-π*	Aromatic carbonyl
287.7–288.3		C=O
287.6–288.2	1s-3p/σ*	CH_3, CH_2, CH
288.2–288.6	1s-π*	COOH
289.3–289.5	1s-3p/σ*	C–OH, alcohol

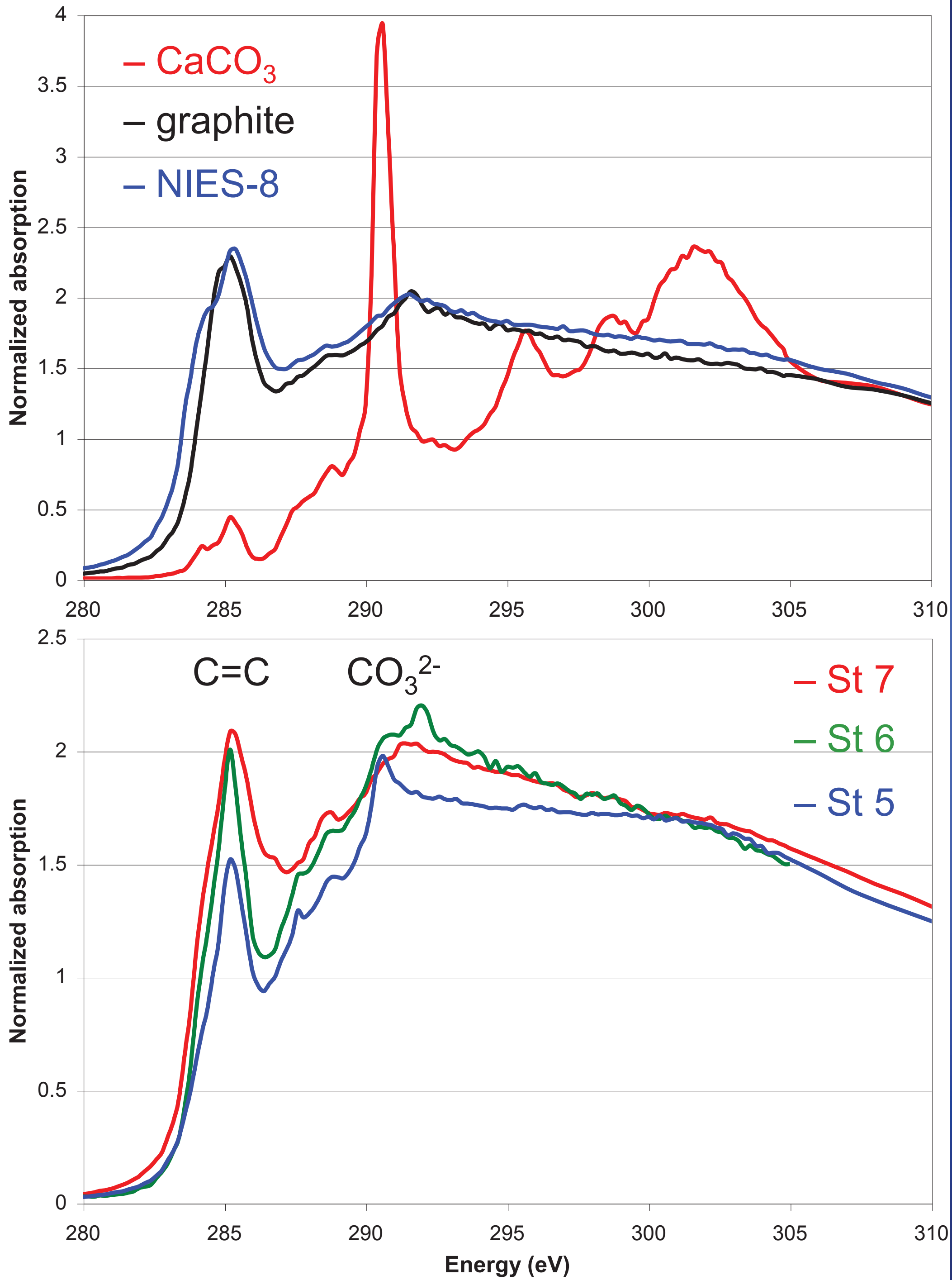
Analysis of carbonaceous particles
Typical emissions from traffic and energy generation
detection: electron yield normal geometry

Cody GD, et al. Org Geochem 1998; 28(7–8):441–55.





Braun A. J. Environ. Monit., 2005, 7, 1059–1065



TXRF-NEXAFS spectra at C-K absorption edge

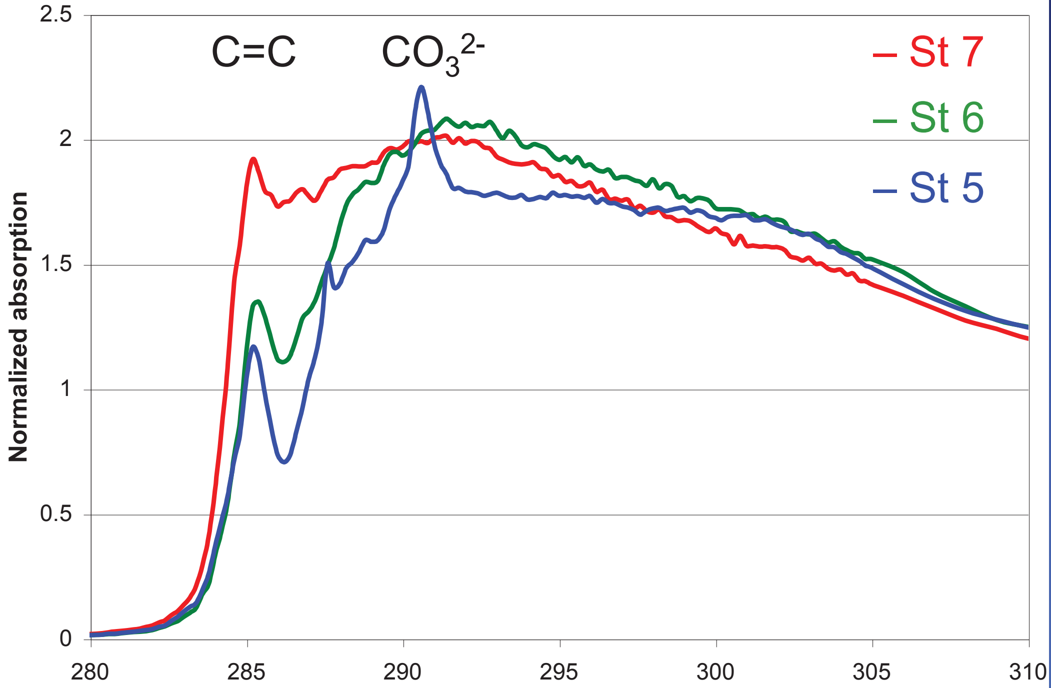
Carbonate, graphite and NIES-8 (urban aerosol) standards

Measurement:
PTB@BESSY II (Berlin),
PGM beamline
2.5°, 274–330 eV,
0.1–0.5 eV steps,
10–30 s/point

Budapest airport terminal

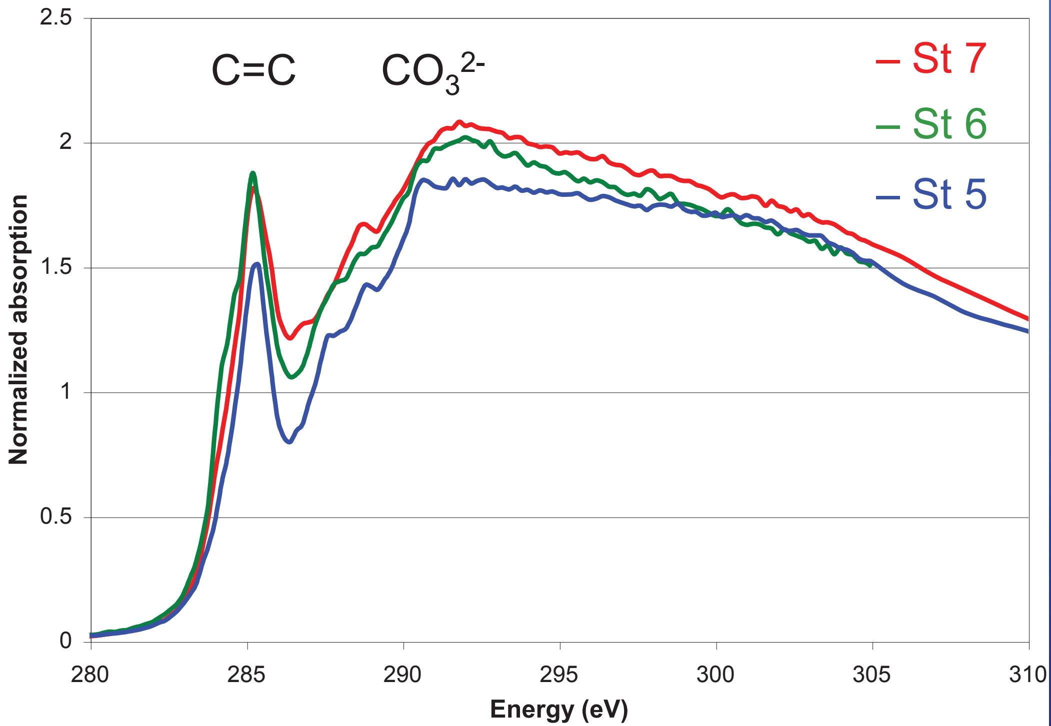
impactor stage 7,6,5
(0.25-0.5, 0.5-1, 1-2 µm)

TXRF-NEXAFS spectra



Budapest airport,
runway **peak hour**

impactor stages 7,6,5
(0.25-0.5, 0.5-1, 1-2 µm)

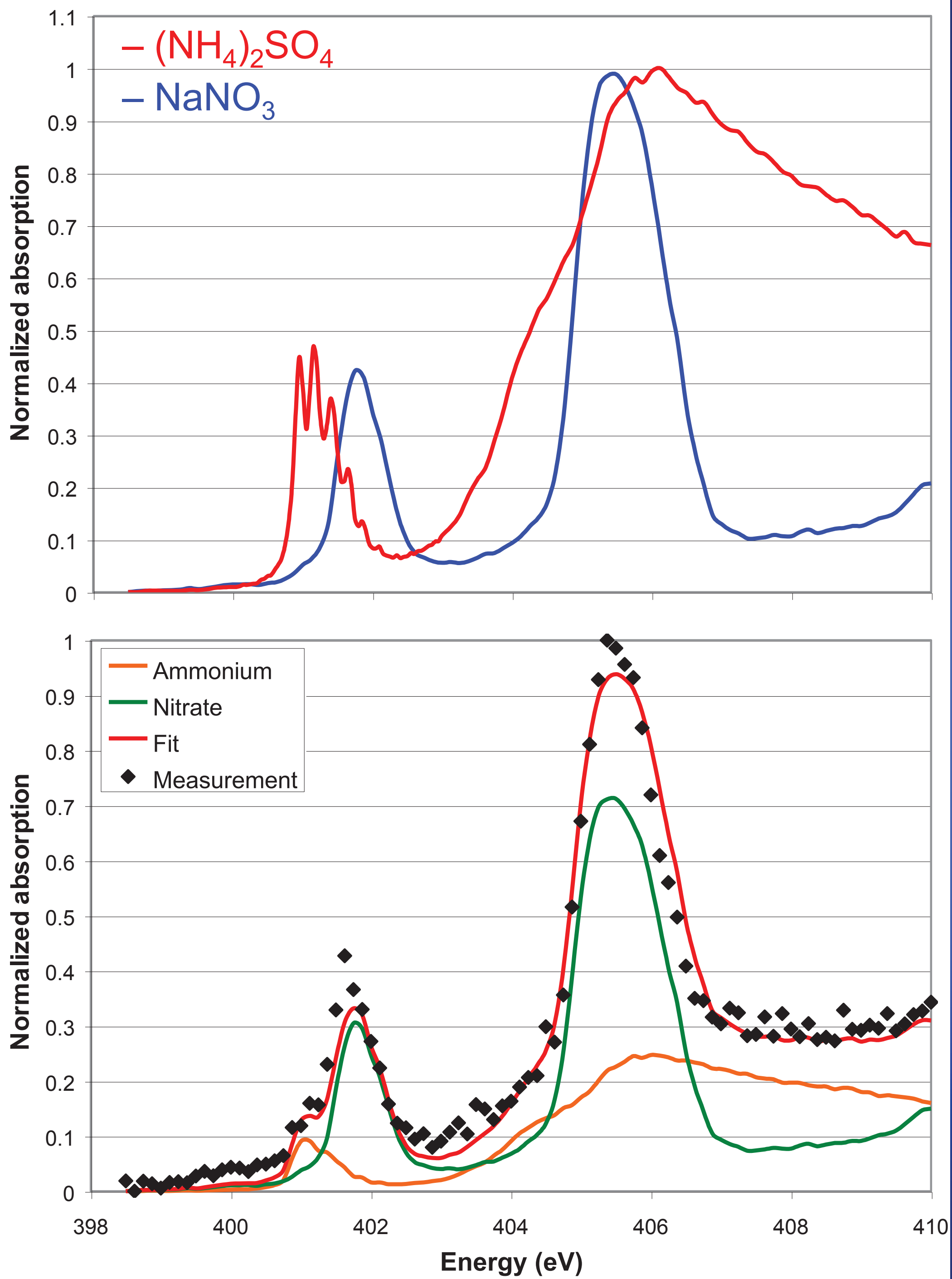


Budapest airport
close to runway
low traffic

Measurement:
PTB@BESSY II (Berlin)

TXRF-NEXAFS spectra

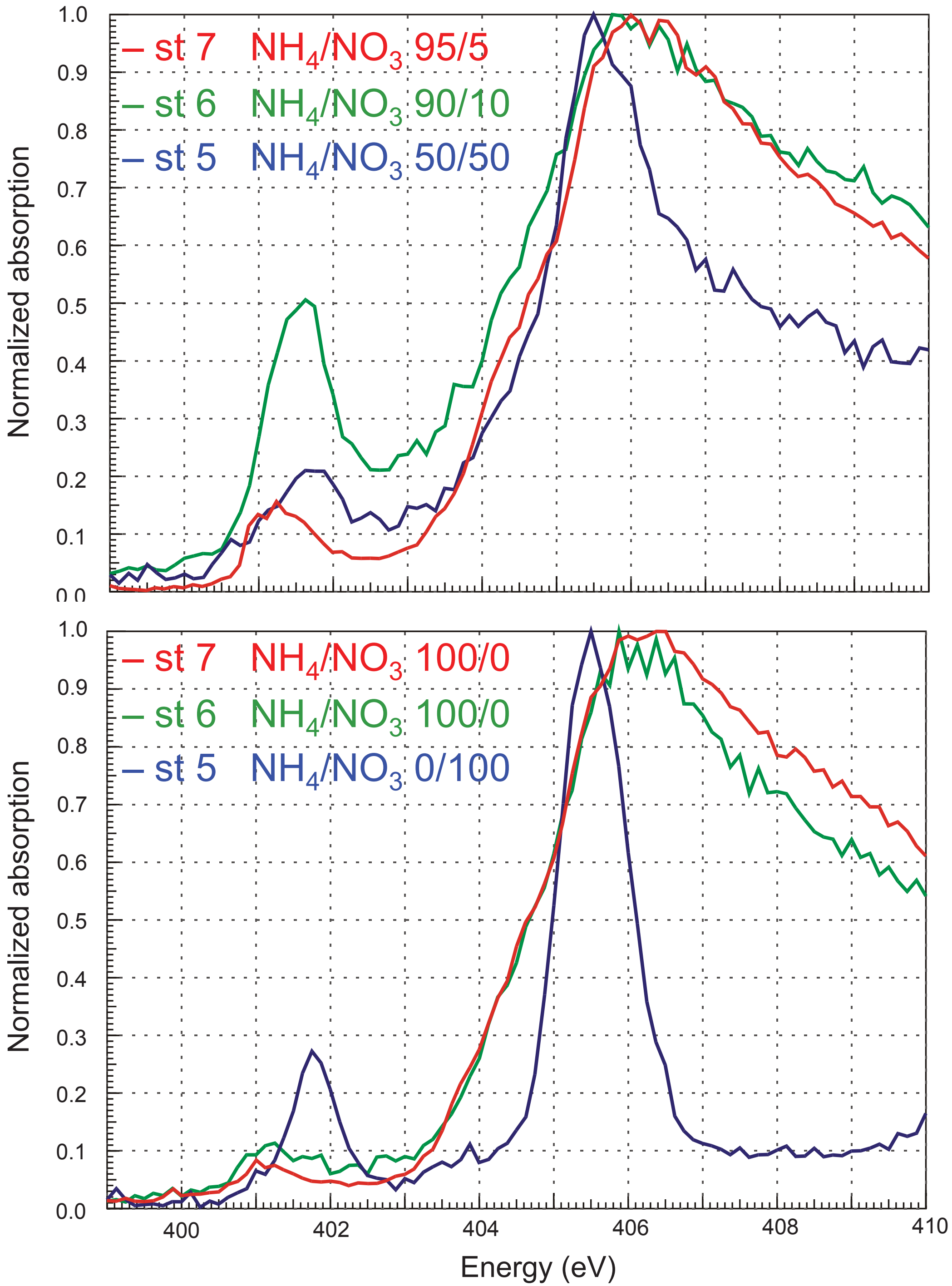
N-K absorption edge



NEXAFS spectra of ammonium and nitrate containing particles as standards

Mátra, stage 5(1-2 μm)

Fit using linear combination of standard spectra → ammonium/nitrate molar ratio can be determined (25%/75% present case)



TXRF-NEXAFS spectra

N-K absorption edge

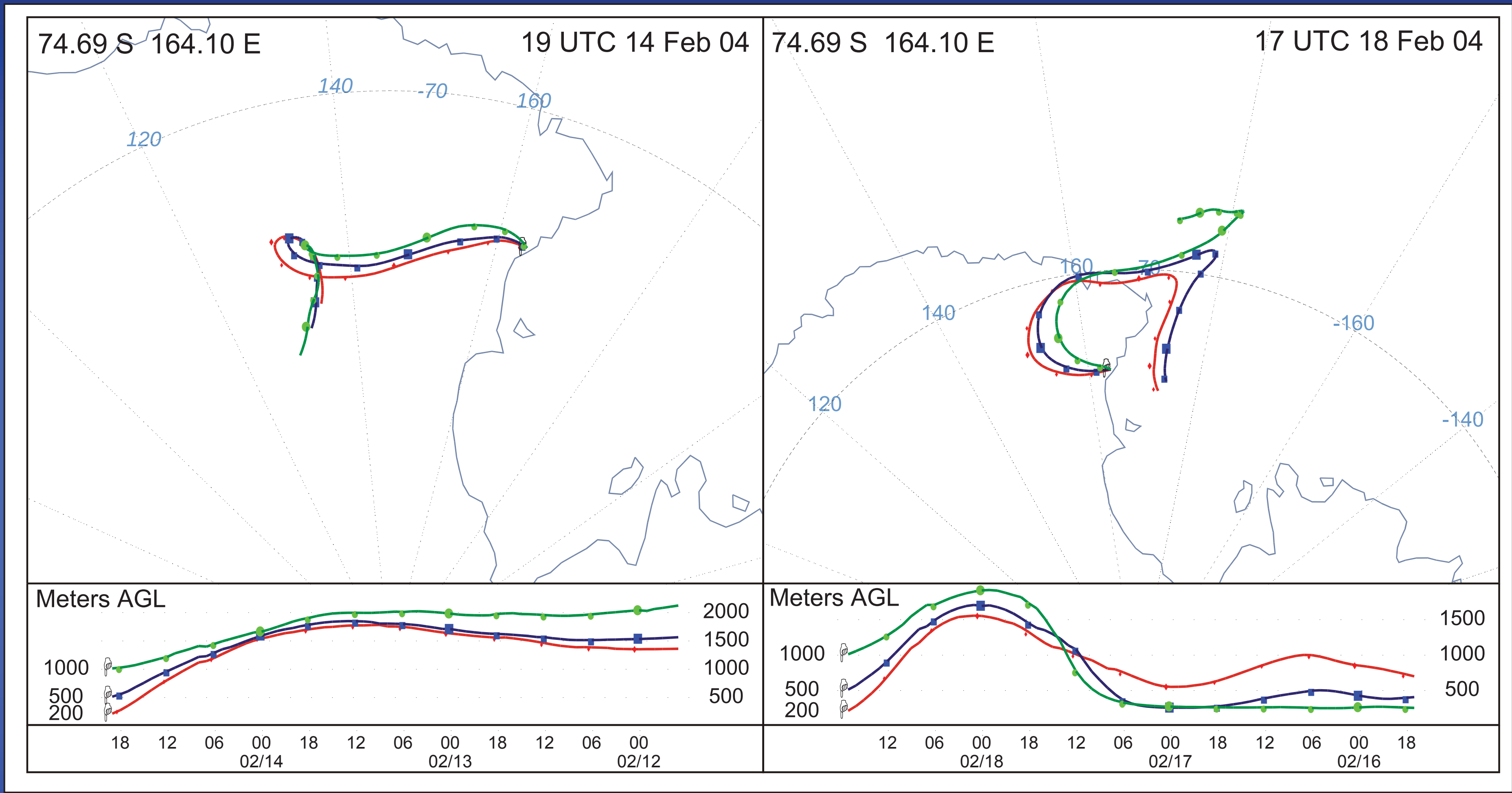
Terra Nova Bay (Antarctica)

Impactor stage 7,6,5
(0.25-0.5, 0.5-1, 1-2 µm)

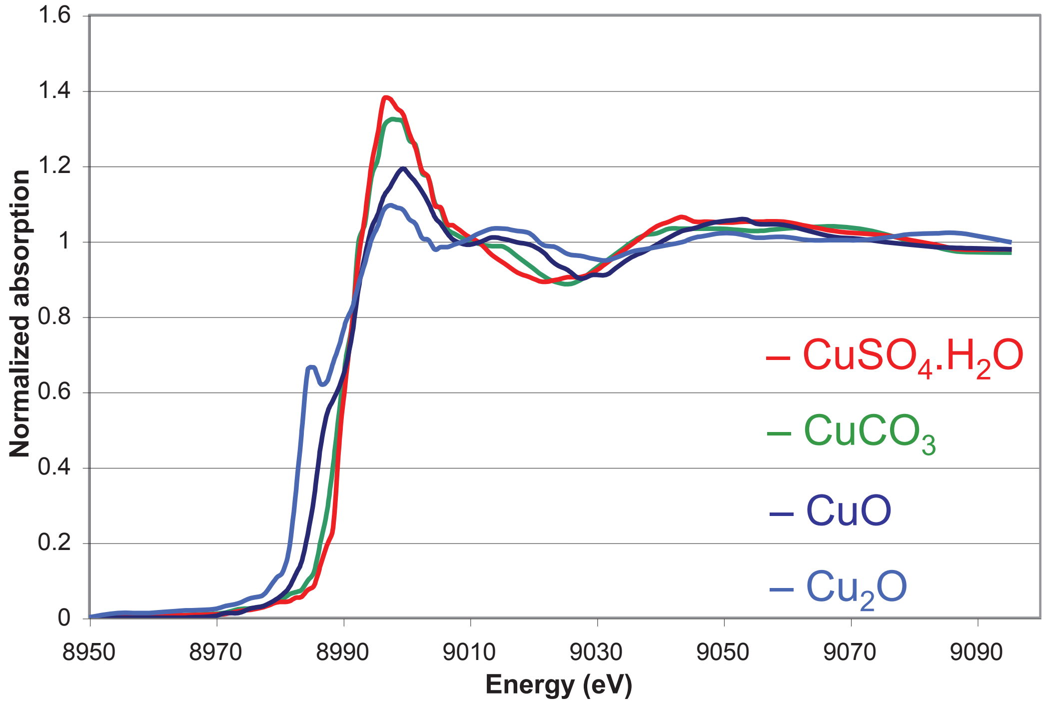
Alghero (Sardinia, Italy)

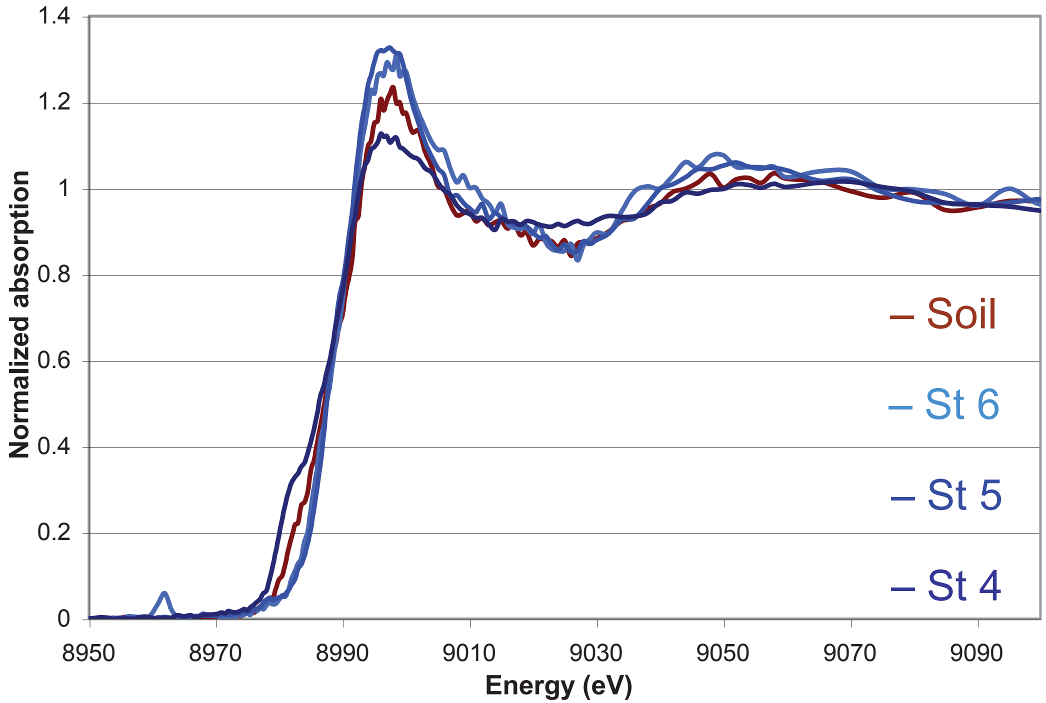
J. Osán, S. Török, B. Beckhoff, G. Ulm, H. Hwang, C.-U. Ro, C. Abete, R. Fuoco Nitrogen and sulfur compounds in coastal Antarctic fine aerosol particles - an insight using non-destructive X-ray microanalytical methods, Atmos. Environ. 40 (2006) 4691-4702

Air mass trajectories: Antarctica



Impactor stage	TXRF (O=1000) C	N	Na	NEXAFS NH_4^+ (%)	NO_3^- (%)	Impactor stage	TXRF (O=1000) C	N	Na	NEXAFS NH_4^+ (%)	NO_3^- (%)
7	9.4	63.8	310	95	5	7	14.6	32.5	120	92	8
6	2.0	19.5	1060	90	10	6	3.7	11.7	750	90	10
5	1.4	2.1	2050	50	50	5	0.0	2.3	3740	40	60





TXRF-XANES spectra Cu-K absorption edge

XAFS spectra of Cu standards

TXRF-XANES
Budapest airport, near runway

St 6,5: Cu connected mostly to sulfates
Soil: CuO and $CuCO_3$

St 4: mostly Cu(I) and Cu(II) oxides, speciation different from Cu in soil
→
source brake pad wear rather than soil resuspension

Osán J, Meirer F, Groma V, Török S, Ingerle D, Streli C, Pepponi G. Speciation of copper and zinc in size-fractionated atmospheric particulate matter using TXRF-XANES. Spectrochim Acta B 65 (2010) 1008–1013

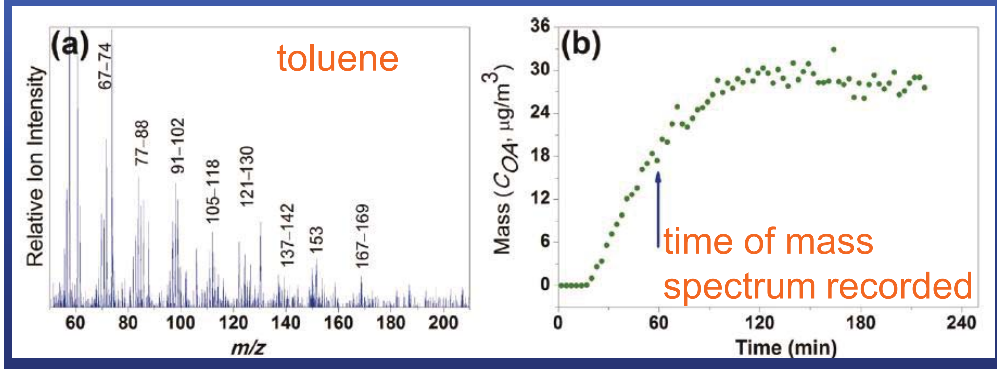
Single particle analysis

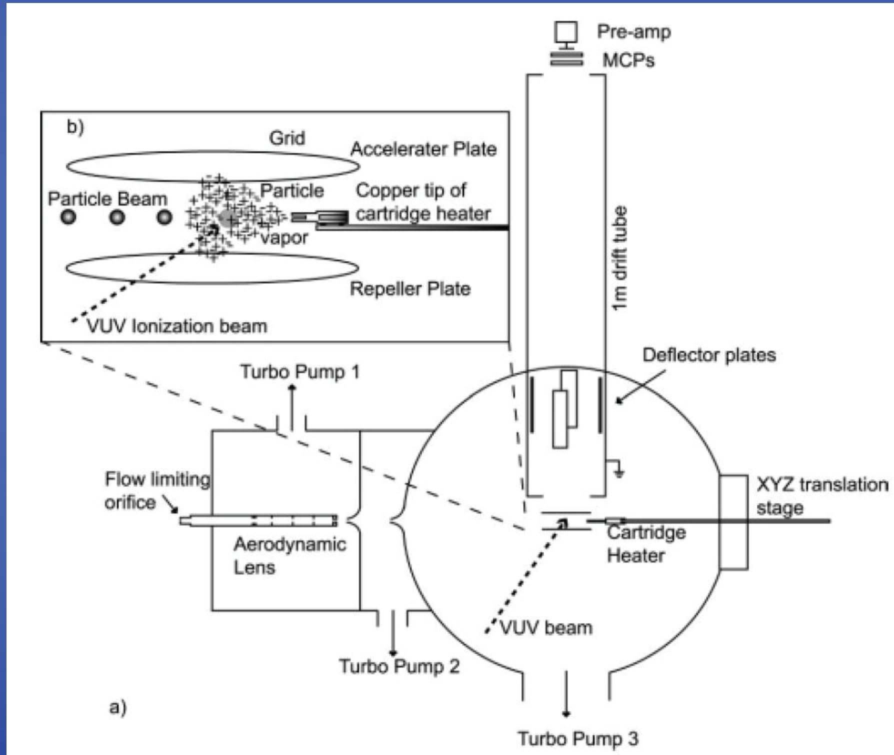
- **Statistical characterization of particulate matter for monitoring:**
  - measurement of large numbers of particles
  - limited quantification
- **Specific environmental analysis:**
  - Measurement of carefully selected particles
  - Usually complementary
  - Quantitative (trace) elemental analysis (EPMA, micro-XRF)
  - Chemical state of selected elements (micro-XANES)
  - Identification of crystalline phases (micro-XRD)

Analysis of individual aerosol particles

- Aerosol TOFMS for analysis of organic compounds in ultrafine particles
- tunable VUV photoionization – synchrotron radiation

- study of photoionization efficiency of different organic compounds – decrease of fragmentation (e.g. oleic acid, cholesterol)
- monitoring the formation of secondary organic aerosol during photo-oxidation (e.g. toluene, isoprene) in smog chamber



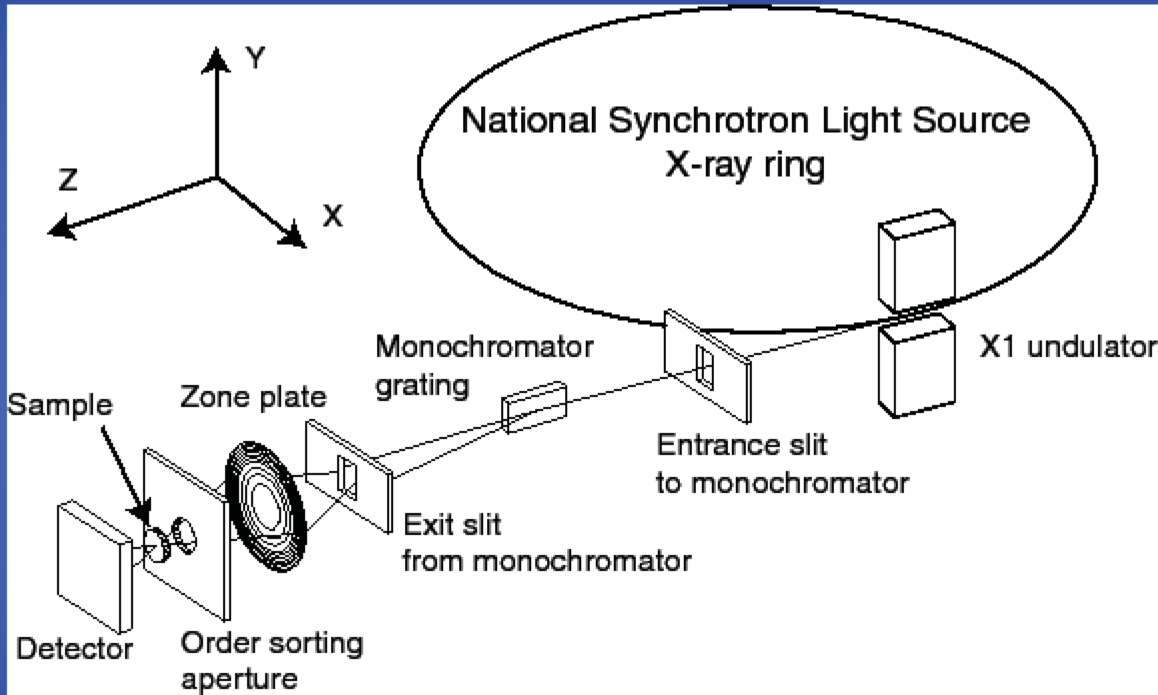


Mysak ER, Wilson KR, Jimenez-Cruz M, Ahmed M, Baer T. Anal Chem 2005, 77, 5953-5960

Fang WZ, Gong L, Shan XB, Liu FY, Wang ZY, Sheng LS. Anal Chem 2011, 83, 9024–9032

Analysis of individual aerosol particles

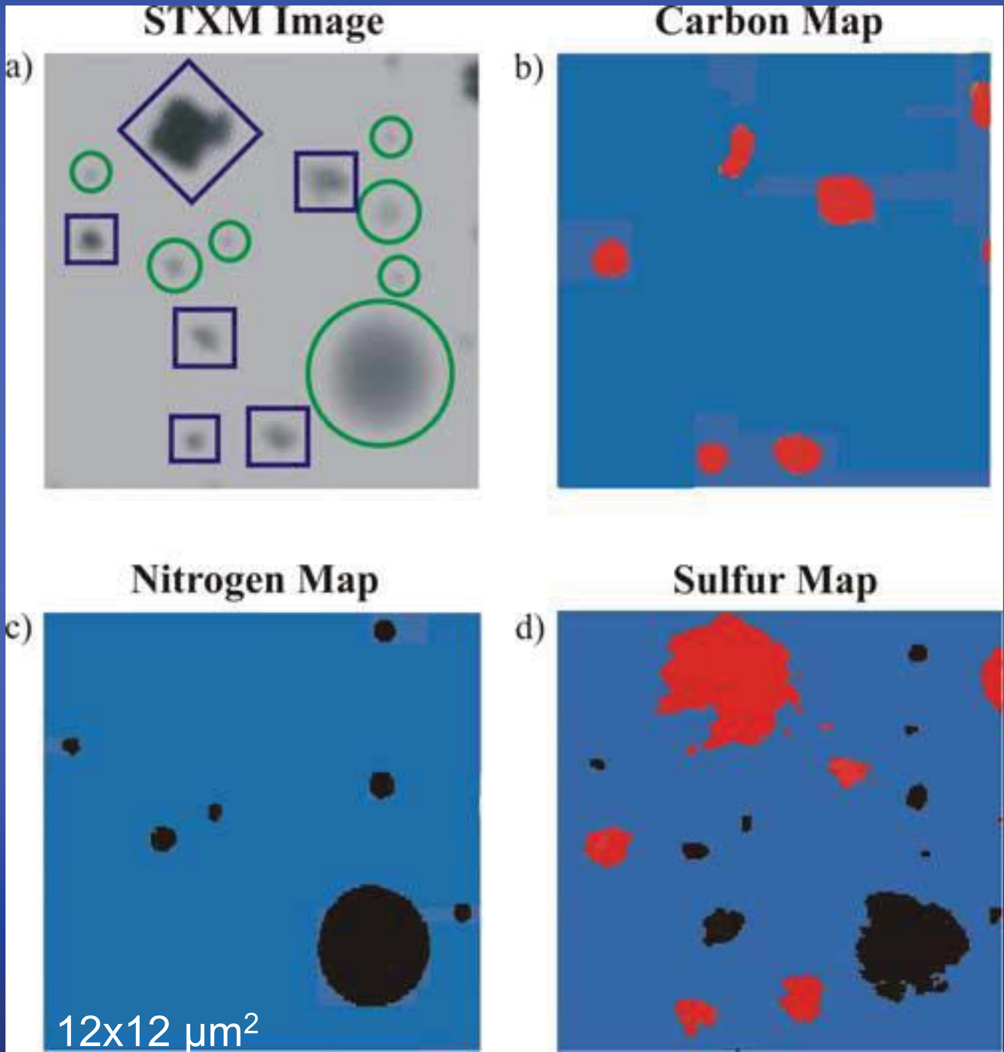
- Scanning transmission X-ray microscope (NSLS, ALS)
  soft X-ray range



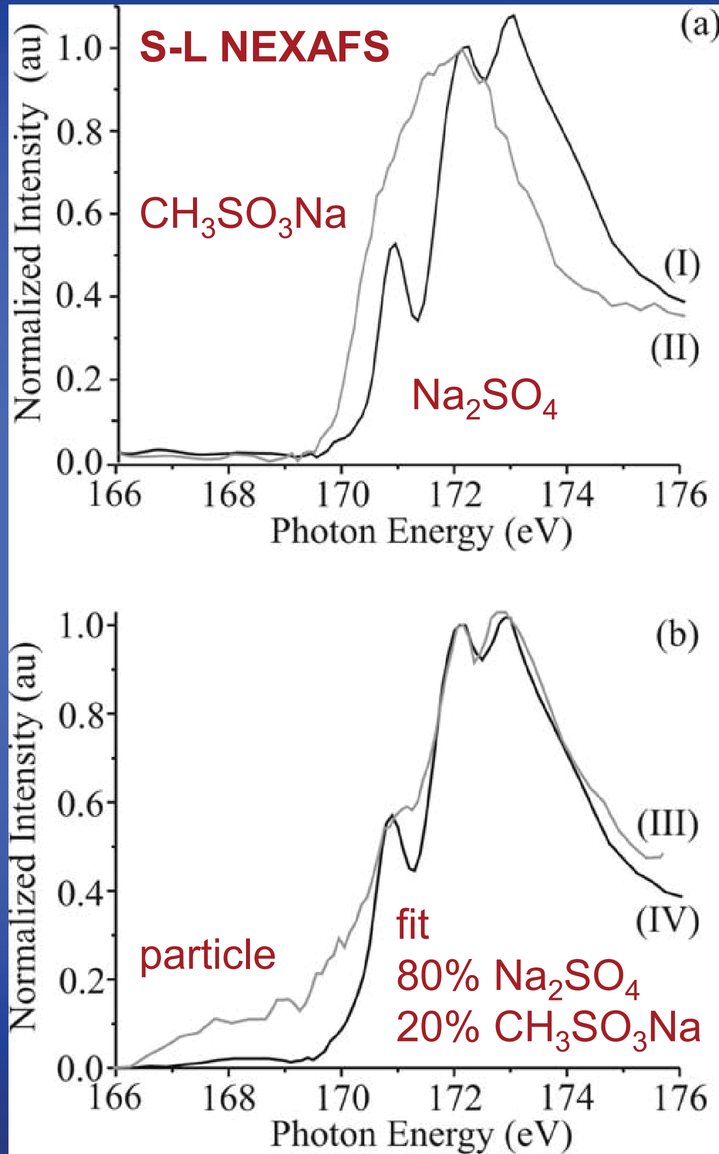
- lateral resolution 30-50 nm (particle diameter above 100 nm)
- substrate 30 nm thick Si_3N_4 → impactor sampling
- measurements in He atmosphere
- NEXAFS in transmission mode (C-K, N-K, O-K, S-L)
  0,1 eV steps, 120 ms / point

Analysis of individual aerosol particles

- Chemical forms of sulfur in marine aerosol



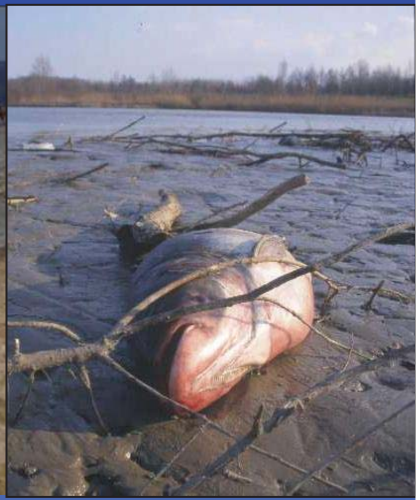
□ sea salt + S ○ $(NH_4)_2SO_4$ + H_2SO_4



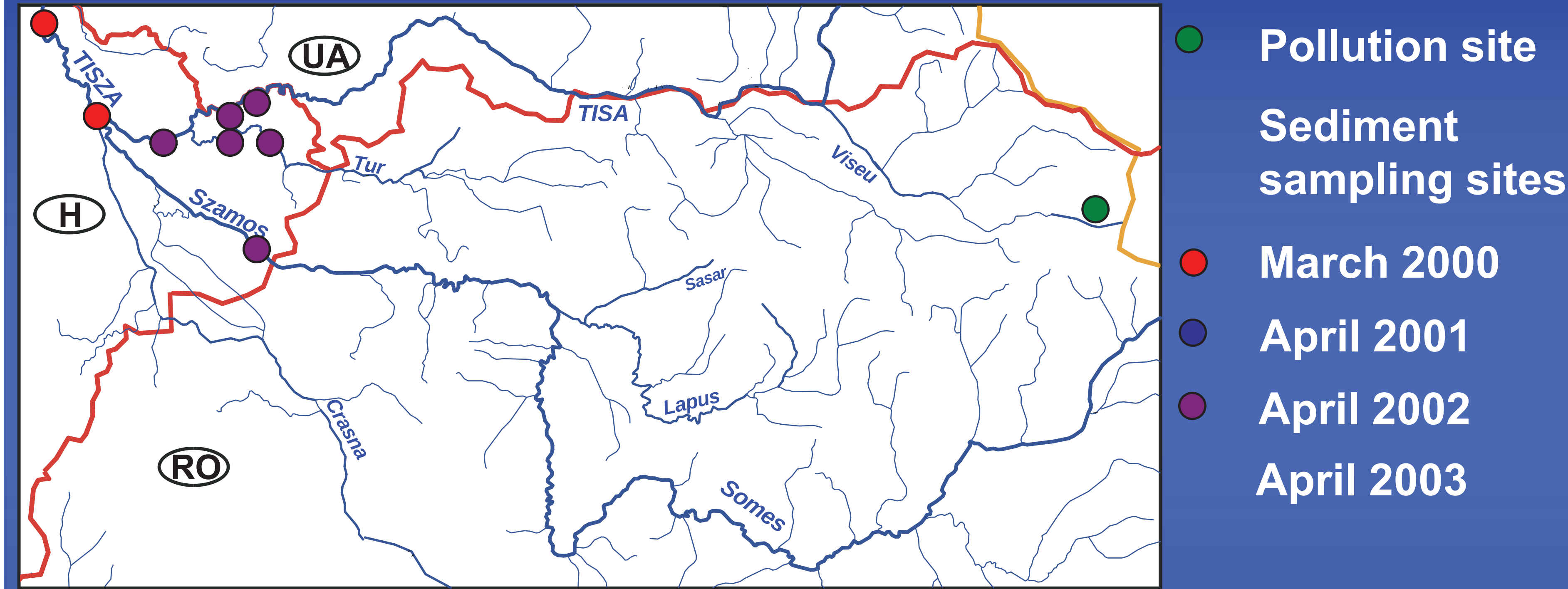
R.J. Hopkins et al., *J Geophys Res – Atmos* 113, D04209, 2008

Water pollution accidents

- 20 Aug. 1995: Omai gold mine in Guyana → cyanide and heavy metal pollution of rivers Omai and Essequibo
- 25 Apr. 1998: Alnazcollar mine in Spain → heavy metal pollution of river Guadiamar affected the Donana National Park
- 30 Jan. 2000: gold extraction facility at Baia Mare, Romania → 100 thousand m^3 waste water with high concentrations of cyanide was spilled into the tributary of river Szamos
- 11 March 2000: mine tailing failure at Baia Borşa, Romania → heavy metal pollution of river Tisza, the leached zinc content of the river grow to 230 µg/l and the lead was 130 µg/l



Upper Tisza Region (Hungary)



- Mine tailings failure at Baia Borşa 11 March 2000
- Surface sediment and water sampling from the main riverbed of Tisza, Szamos and Túr
- Sample preparation: Nuclepore, Si, Ag substrates

XRF and EPMA results

XRF

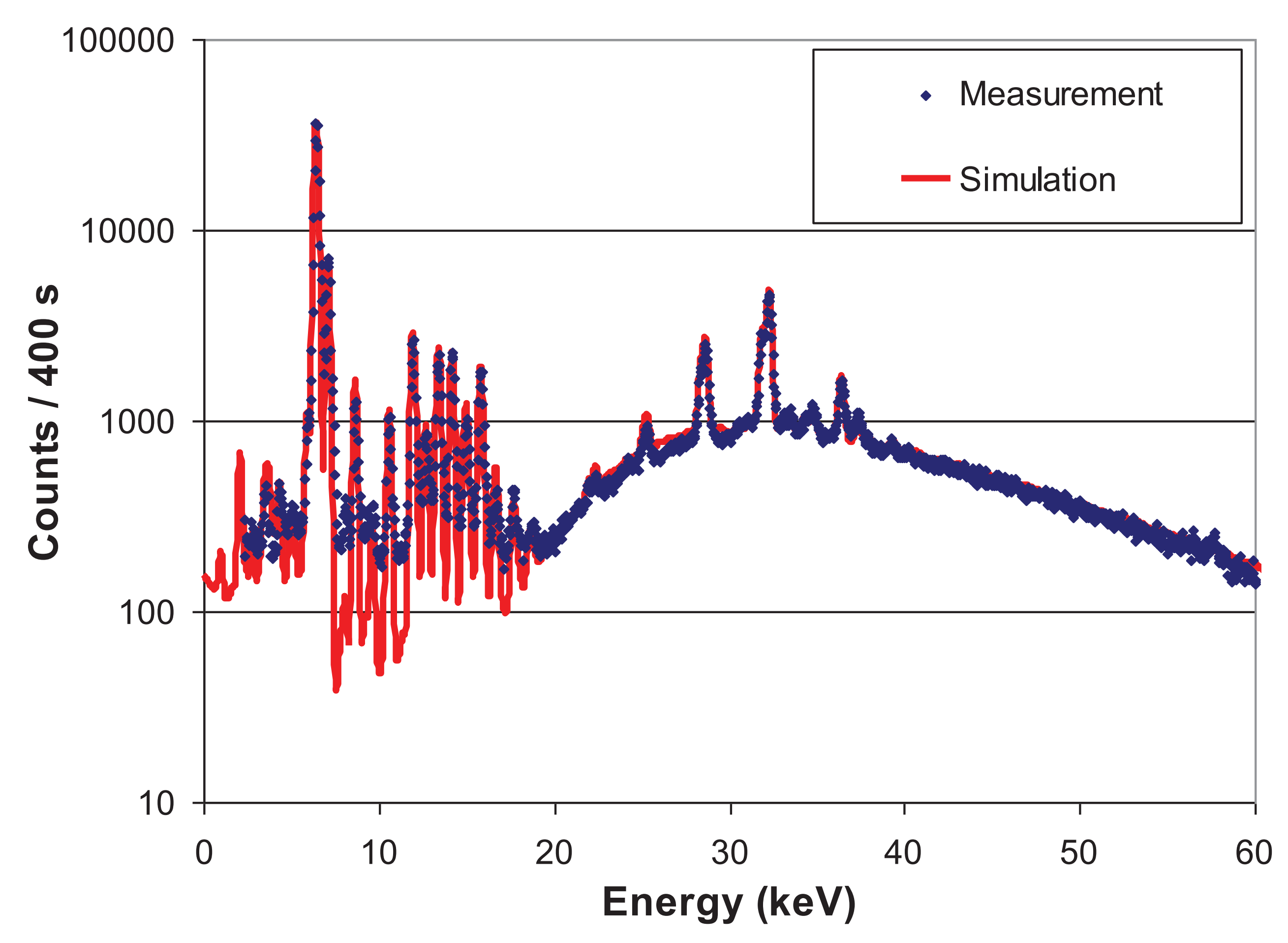
River	Year	Concentration (μg/g)						
		Mn	Ni	Cu	Zn	As	Br	Pb
Tisza	2000	1050	<48.1	1250.0	3200	148.0	6.89	2100.0
Tisza	2001	641	<25.2	42.1	126	<19.6	2.54	<41.0
Tisza	2002	391	<20.2	40.8	84	<6.8	<2.8	20.9
Szamos	2001	1527	38.3	167.5	1259	52.5	4.87	79.9
Szamos	2002	1374	<41.5	182.9	885	16.7	<5.0	189.6
Túr	2001	2384	<23.8	51.3	2074	<26.2	5.39	<52.8
Túr	2002	2071	<27.2	73.6	1637	<7.9	5.25	33.0
Öreg-Túr	2002	2467	<24.1	32.2	1025	<13.7	4.59	23.5

No significant decrease of heavy metal concentrations was observed in the Szamos and Túr surface sediment

EPMA

- Pollution-related particle groups: pyrite, Mn and Zn-rich aluminosilicates, Zn-rich particles, observed also in the water samples
- Average diameter and major elemental composition of particles could be determined

White-beam micro-XRF

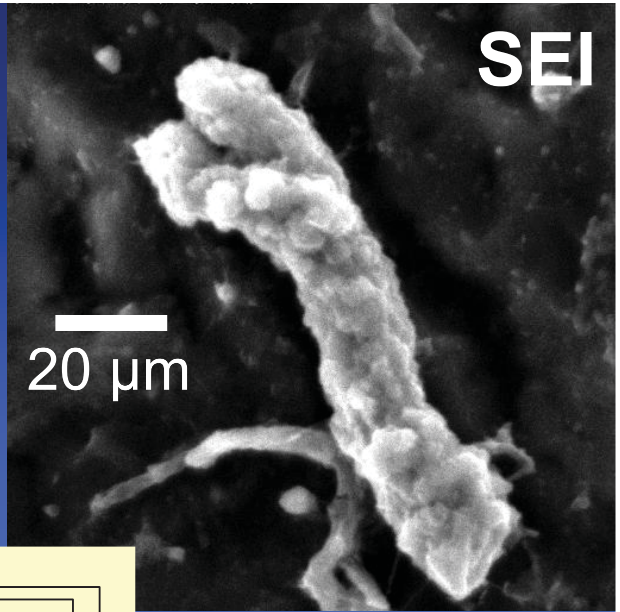


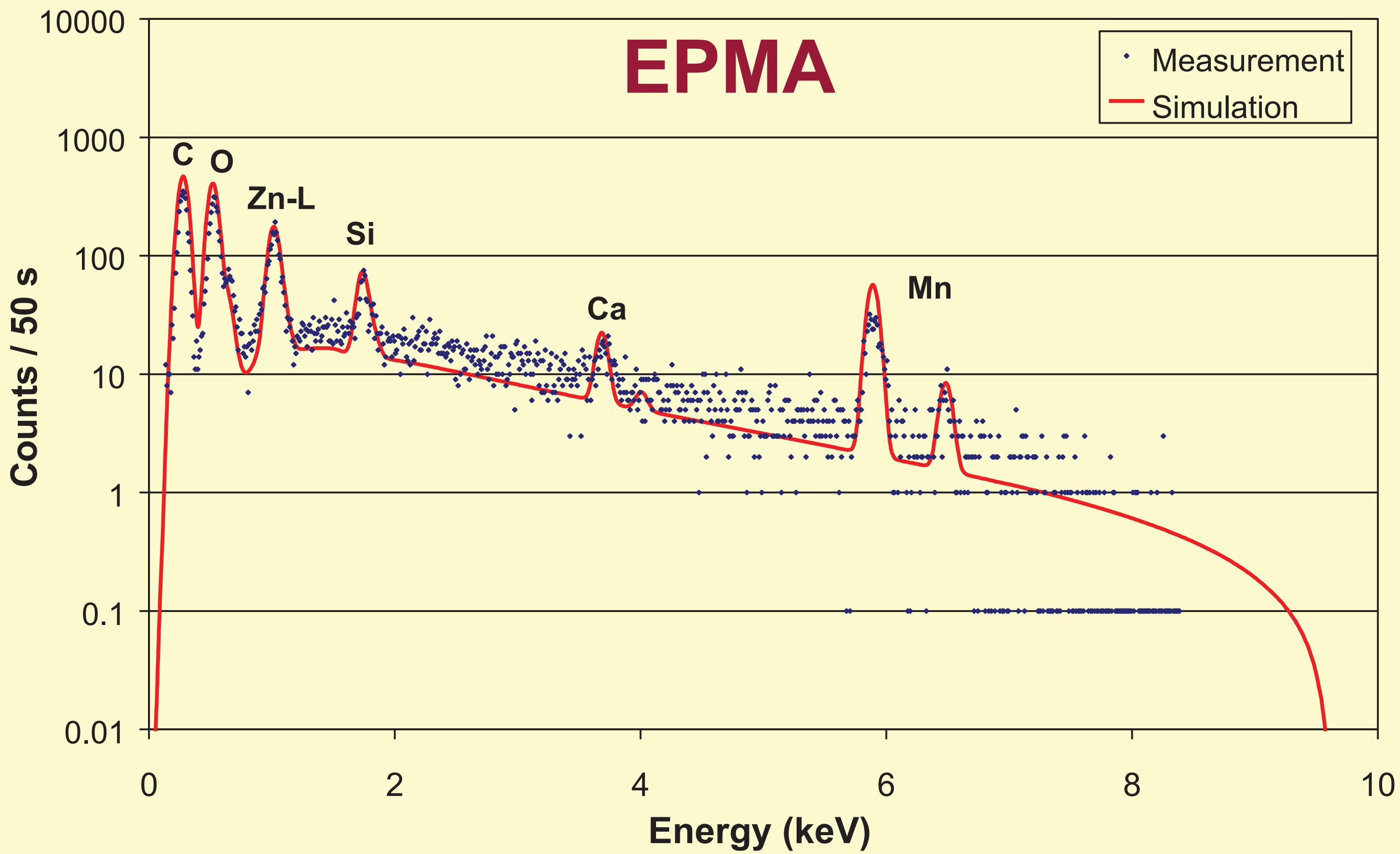
Elemental composition	
O	49.30 wt%
Mg	3.50 wt%
Al	12.00 wt%
Si	27.40 wt%
S	0.52 wt%
Cl	1.69 wt%
K	1.48 wt%
Ca	2.65 wt%
Mn	500 ppm
Fe	1.44 wt%
Cu	10 ppm
Zn	150 ppm
Br	130 ppm
Rb	70 ppm
Sr	70 ppm
Y	20 ppm
Zr	40 ppm
Nb	10 ppm
Sn	10 ppm
I	70 ppm
Ba	200 ppm
La	10 ppm
Ce	20 ppm
Pb	100 ppm

- Trace composition refined using Monte Carlo simulations
- Matrix composition estimated from the single-particle EPMA results

Pollution particles in river Túr

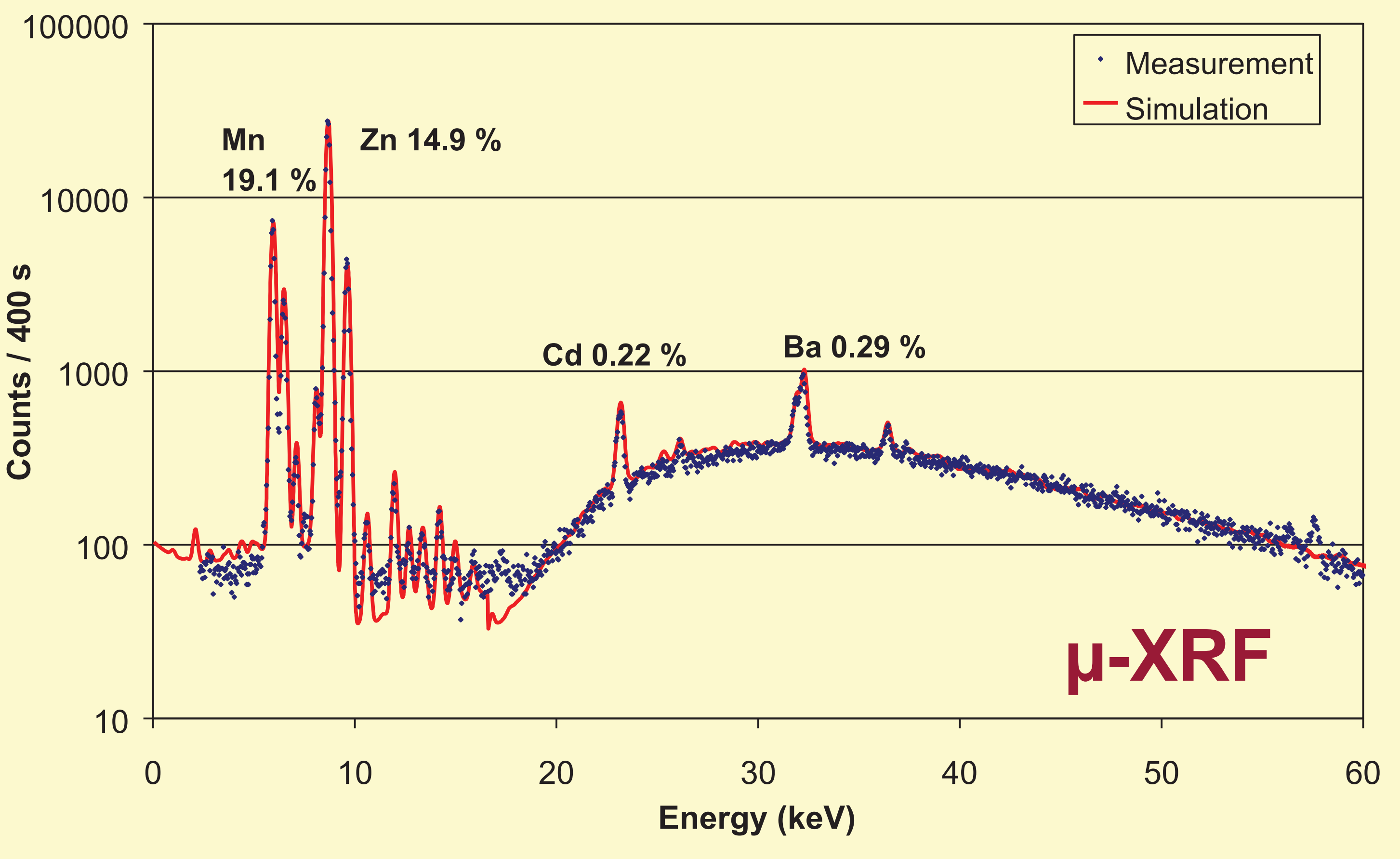
Measurement: JEOL 733 electron microprobe
OXFORD Pentafet Si(Li) detector
MOXTEK AP1.4 thin window, E_0 = 10 keV





Element	C (wt.%)
C	39.7
O	23.2
Si	2.0
Ca	1.1
Mn	19.1
Zn	14.9

Pollution particles in river Túr



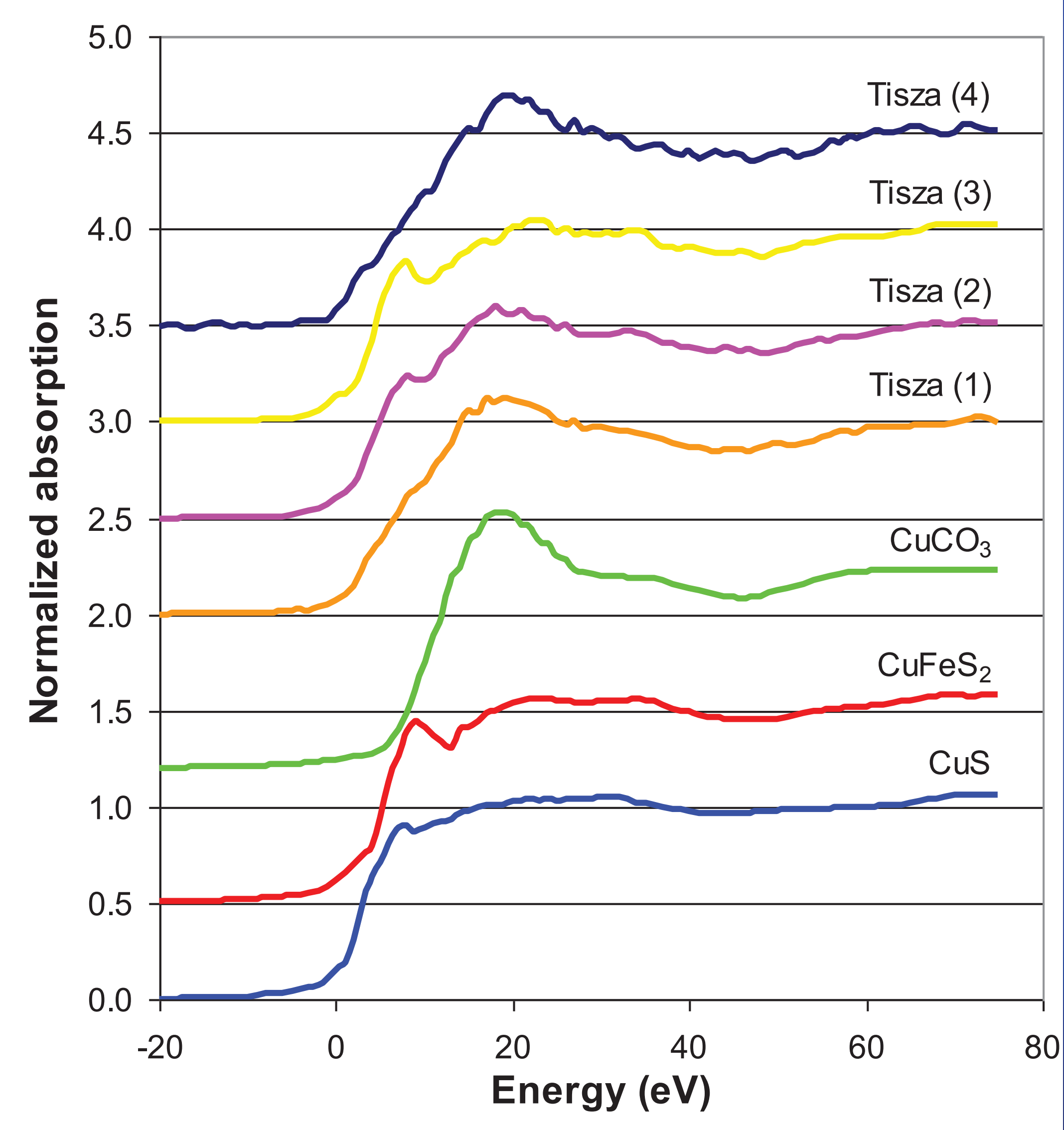
Measurement:
HASYLAB Beamline L
white excitation,
70 µm
4 mm Al absorber

- High amount of cadmium was present in the pollution particles in river Túr, in correlation with zinc concentration

Osán J, Török S, Alföldy B, Alsecz A, Falkenberg G, Baik SY, Van Grieken R. Spectrochim. Acta Part B 62 (2007) 123-136

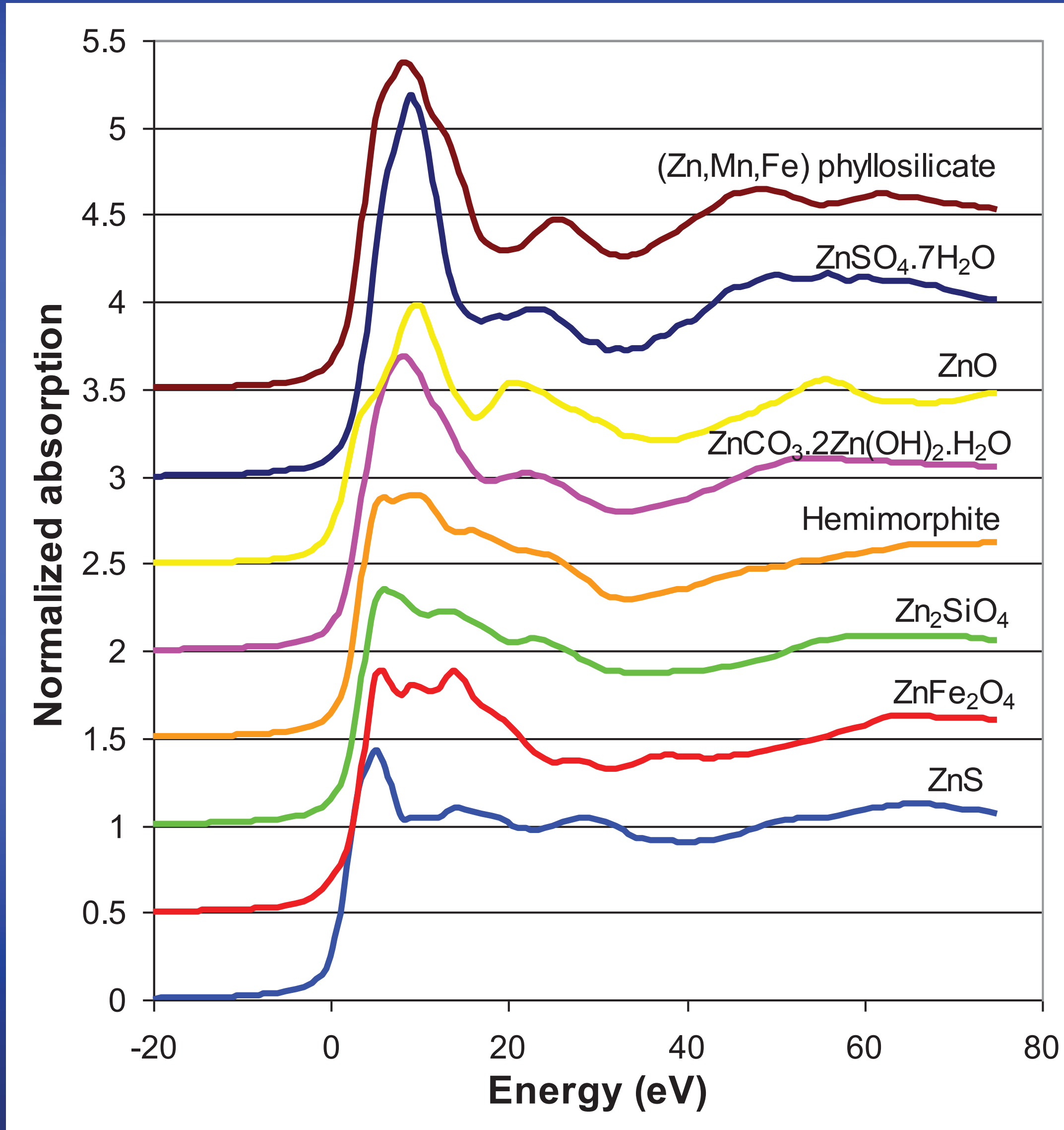
Micro-XANES, Cu K-edge

- Particles from the Tisza (2000) sediment sample
- Particulate and diluted bulk standards
- The co-existence of CuS and $CuFeS_2$ is possible in particles 2 and 3
- 40 and 60 % of Cu was present as CuS in these particles

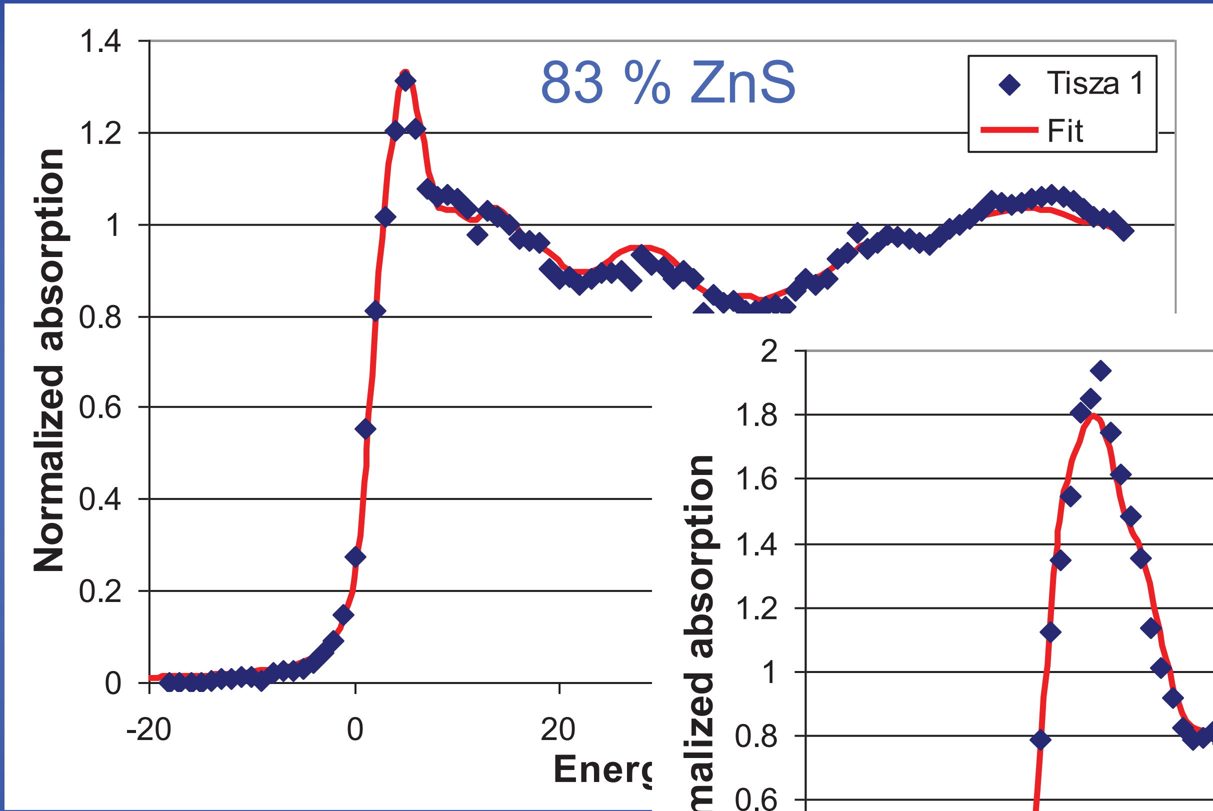


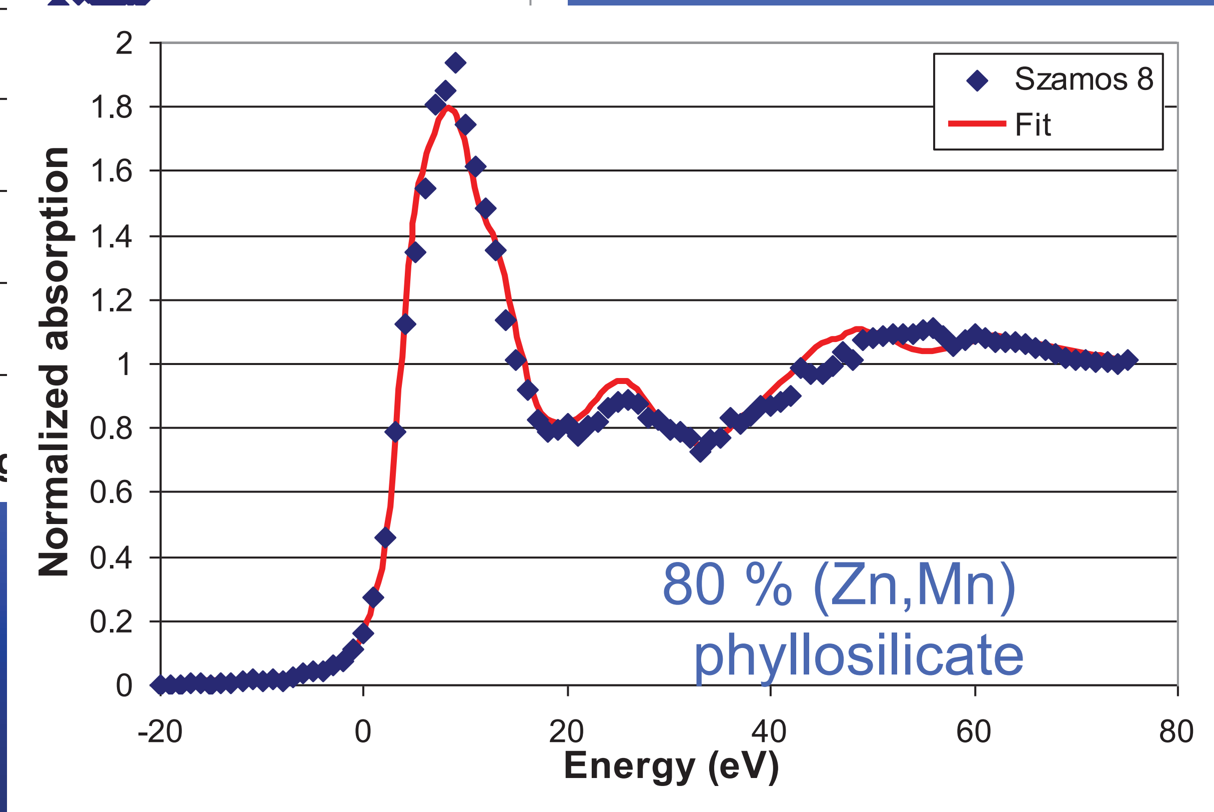
Micro-XANES, Zn K-edge

- Eight standard compounds possibly present in environmental microparticles were selected
- Particles and diluted bulk samples were measured
- Linear combination: five compounds were found to be present in the particles
- Sphalerite (ZnS), Willemite (Zn_2SiO_4), Hemimorphite, $ZnCO_3.2Zn(OH)_2.H_2O$ and (Zn,Mn,Fe) phyllosilicate



Micro-XANES, Zn K-edge



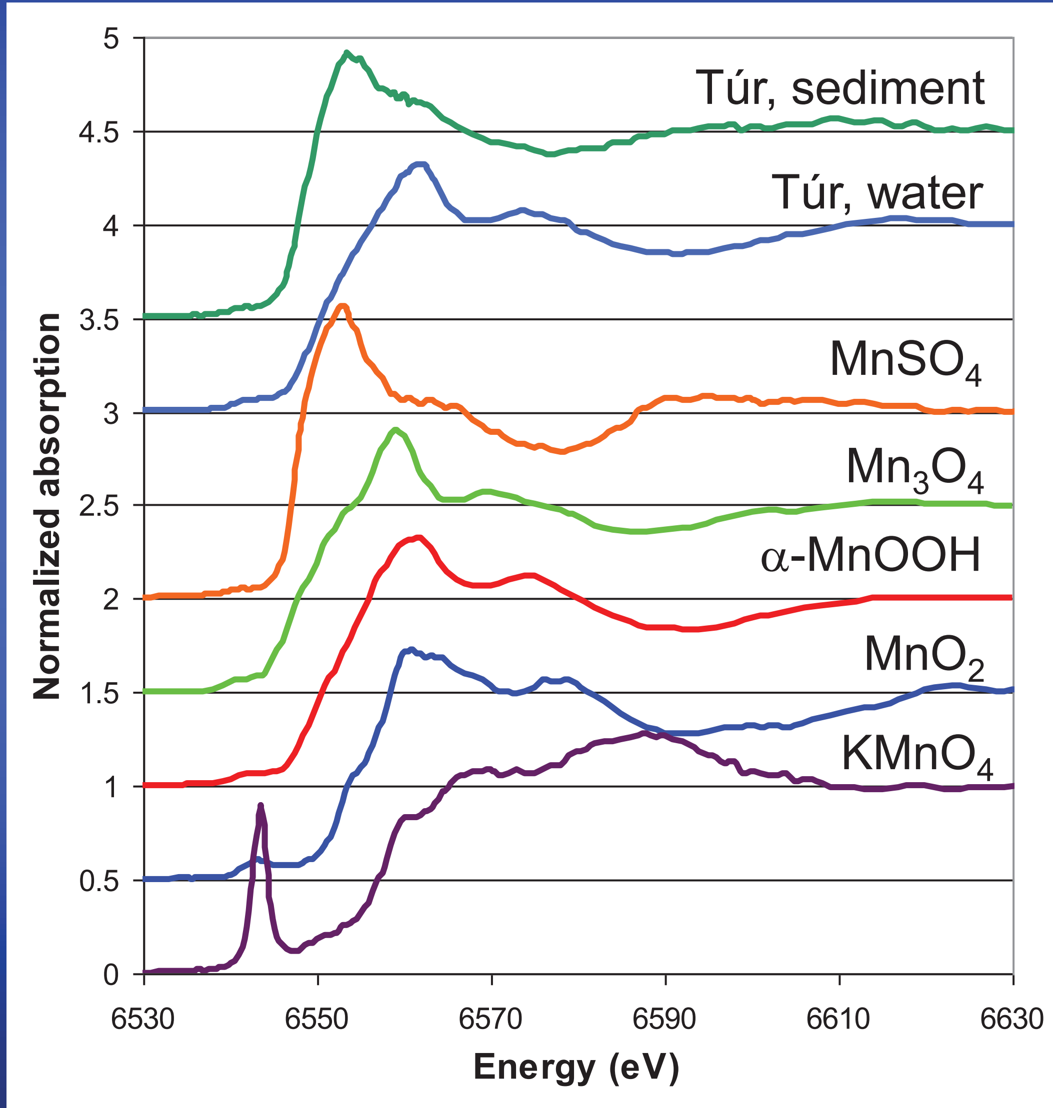


Linear combination of standard spectra yields reasonable fit

(Micro-)XANES, Mn K-edge

- Standard compounds with different Mn oxidation state were selected
- Water suspended particles in River Túr: similar to MnOOH

  (verified using micro-XRD)
- Bulk sediment sample from the same location: mostly Mn(II) compounds



Osán J, Török S, Alföldy B, Alsecz A, Falkenberg G, Baik SY, Van Grieken R. Spectrochim. Acta Part B 62 (2007) 123-136

Tire particles from wear

- **Emitted in various sizes ranging up to >100 µm. aerodynamic diameter,**
- **Have a bimodal size distribution, with about 5% by mass of an aerodynamic diameter <1 µm**
- **make up approx. 5-6% of all respirable (PM10) in the urban atmosphere**
- **Debris loss of ground vehicle tire $5x10^6$ in GB and $40x10^6$ in Italy**
- **Of toxicity Zn and PAH**

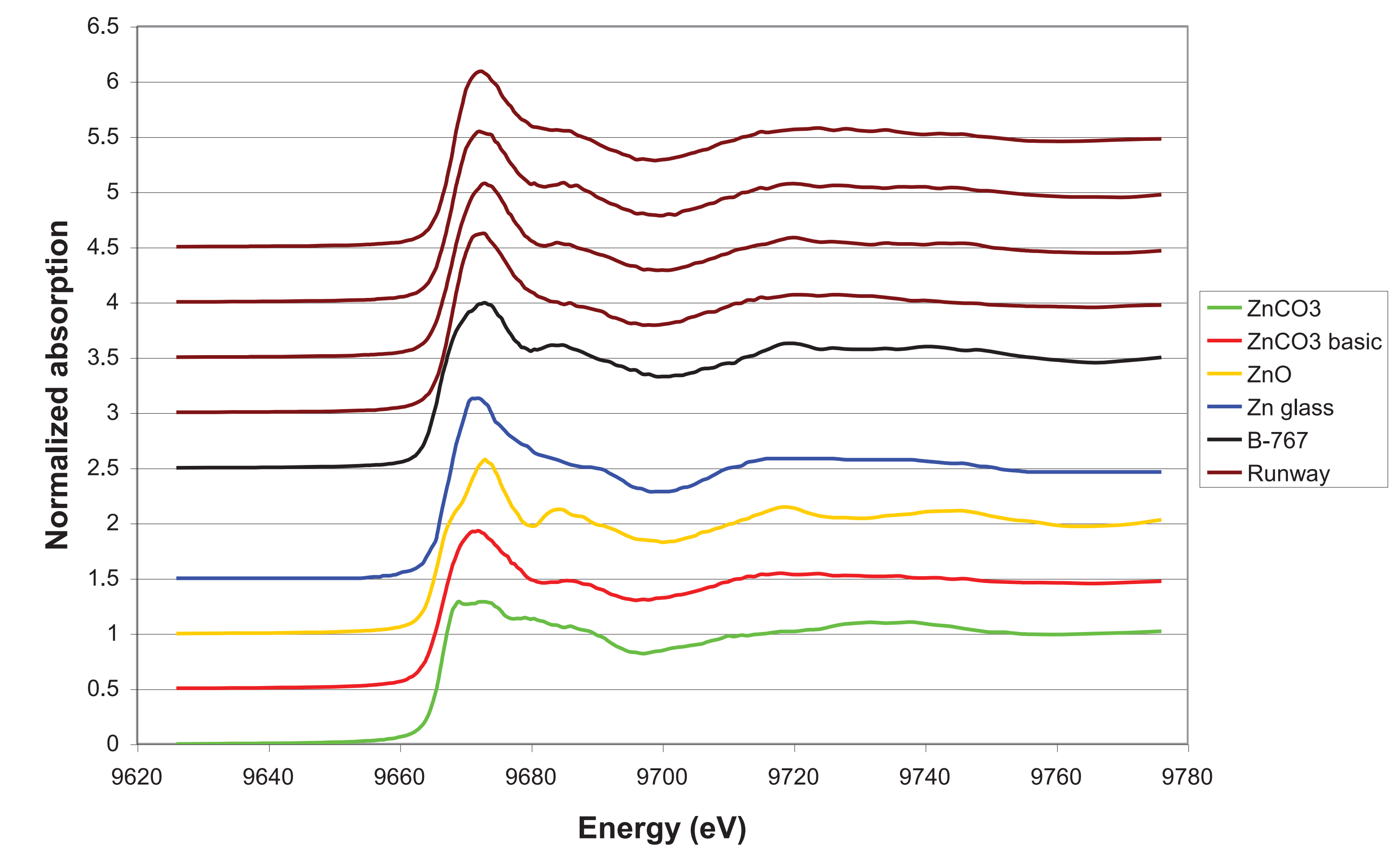
Composition of tire tread

EC adopted in 2004 amending Council Directive 76/769/EEC, proposing restrictions on polycyclic aromatic hydrocarbons in extender oils and tires

- Synthetic rubber (polybutadiene, styrene butadiene rubber) major component
- Natural rubber various %
- Zn is added to tiretread rubber mostly as zinc oxide (ZnO) to facilitate vulcanization of the rubber Zn content of rubber tires reported in the literature range from 0.04 to 1.55 % Zn literature suggests that tire-tread formulations have historically included about 2.5% Zn
- Reinforcing filler carbon black and SiO_2
- From the softening high viscosity aromatic oil 6-8 % in tire mass and 11-16 in tread

Tire debris sampling from runway

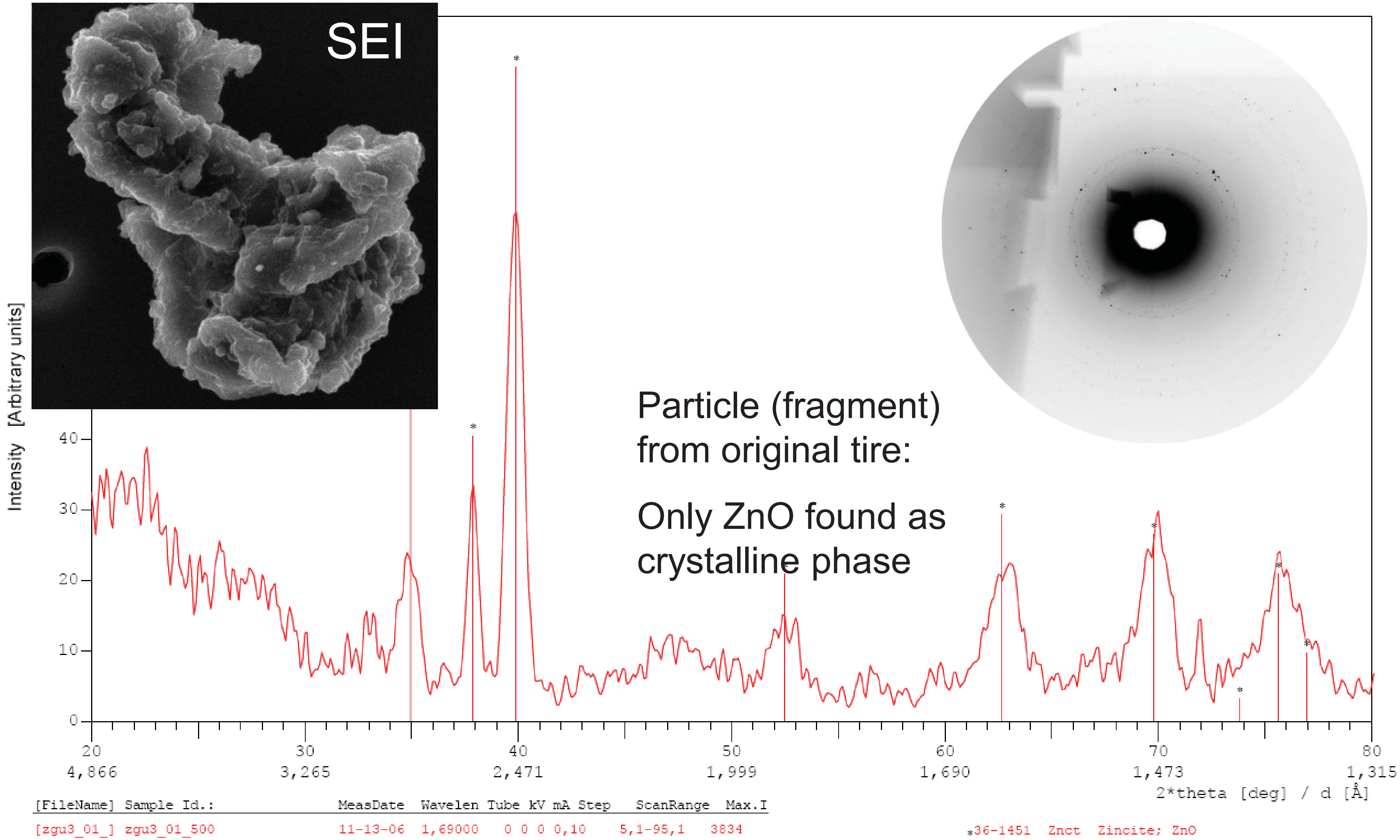
Micro-XANES at Zn K edge



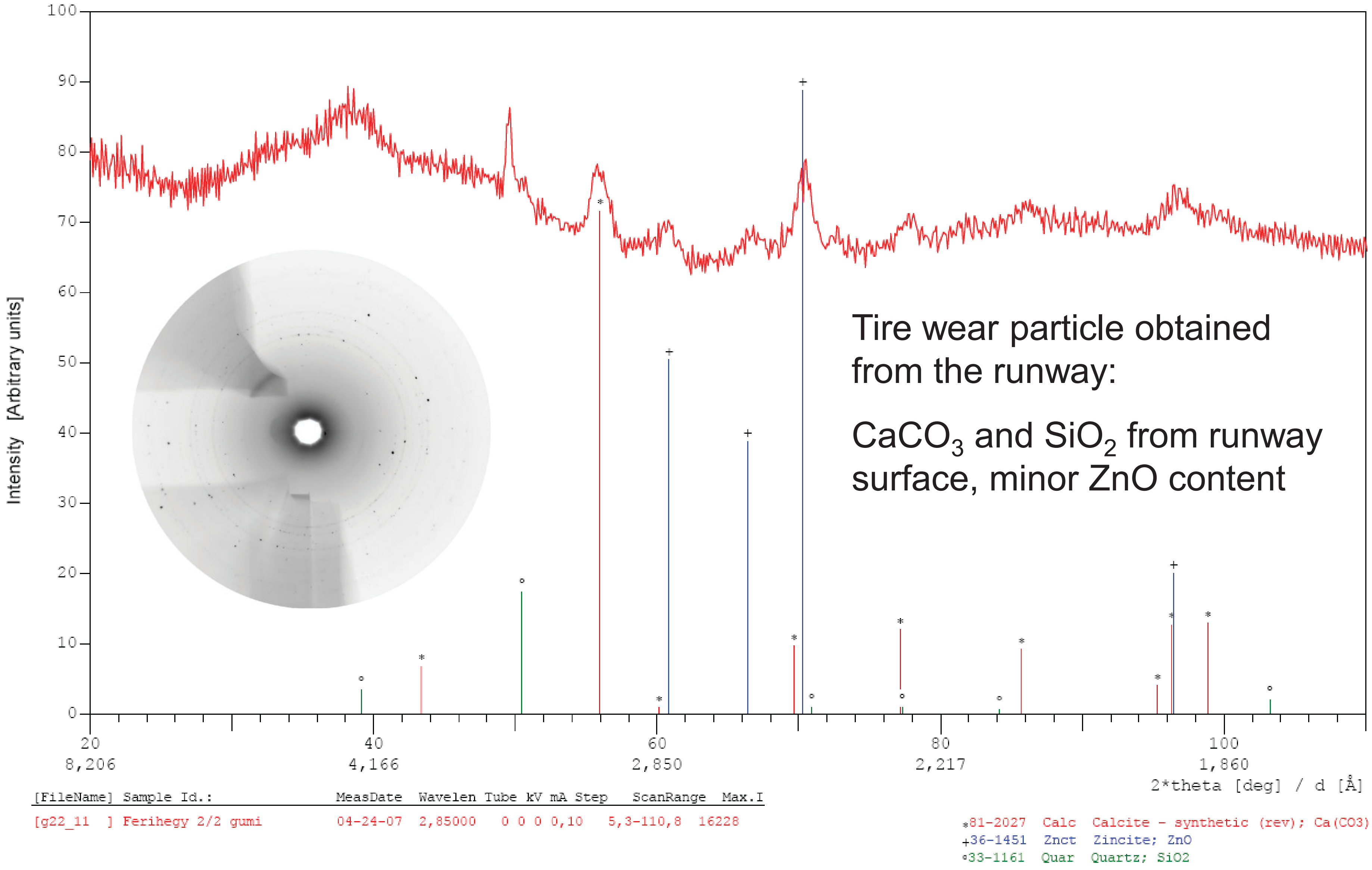
measurement at HASYLAB DORIS Beamline L

B-767 tire tread: 45 % ZnO, 55 % $ZnCO_3$ (of total Zn)
Runway swipe: mostly Zn in glass, max. 15 % ZnO

Micro-XRD at HASYLAB



Micro-XRD at HASYLAB



Tire wear particle obtained from the runway:

$CaCO_3$ and SiO_2 from runway surface, minor ZnO content

Summary

- **Application of synchrotron radiation in analysis of environmental particulate matter**
- composition and chemical form can be determined from minute amount of particulate samples, even from single particles
  (absolute detection limit ~pg for light elements, ~fg for transition metals)
- basically not intended for routine measurements
  careful selection and laboratory pre-characterization of samples to be measured (particles, particle types) is important before synchrotron radiation measurements
- very useful in development of monitoring and laboratory X-ray analytical techniques for measurement of aerosol particles

Acknowledgements

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