Webinar
Investigation of Concrete by Means of micro-XRF

Dr. Andrew H. Menzies and Dr. Max Buegler
Bruker Nano Analytics, Berlin, Germany
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Introduction
Presenters / Moderators

Andrew Menzies, PhD

Sr. Application Scientist Geology and Mining,
Bruker Nano Analytics, Berlin, Germany

Max J.L. Bügler, PhD

Applications Specialist,
Bruker Nano Analytics, Berlin, Germany

Construction Materials - Concrete
Outline

- Brief introduction
  - M4 TORNADO
  - Micro-XRF
- Construction Materials - Concrete
  - Alkali-Silicate- (ASR) and Alkali-Carbonate-Reaction (ACR)
  - AMICS (mineralogy)
  - SEM-EDX
- Mapping of relevant elements
- Analytical approaches
- Comparison of anodes materials
- Practical demonstration
- Summary

M4 TORNADO
Micro-XRF Spectrometer

30 W micro-focus Rh tube with polycapillary lens
for excitation spot sizes < 20 µm (for Mo-Kα)

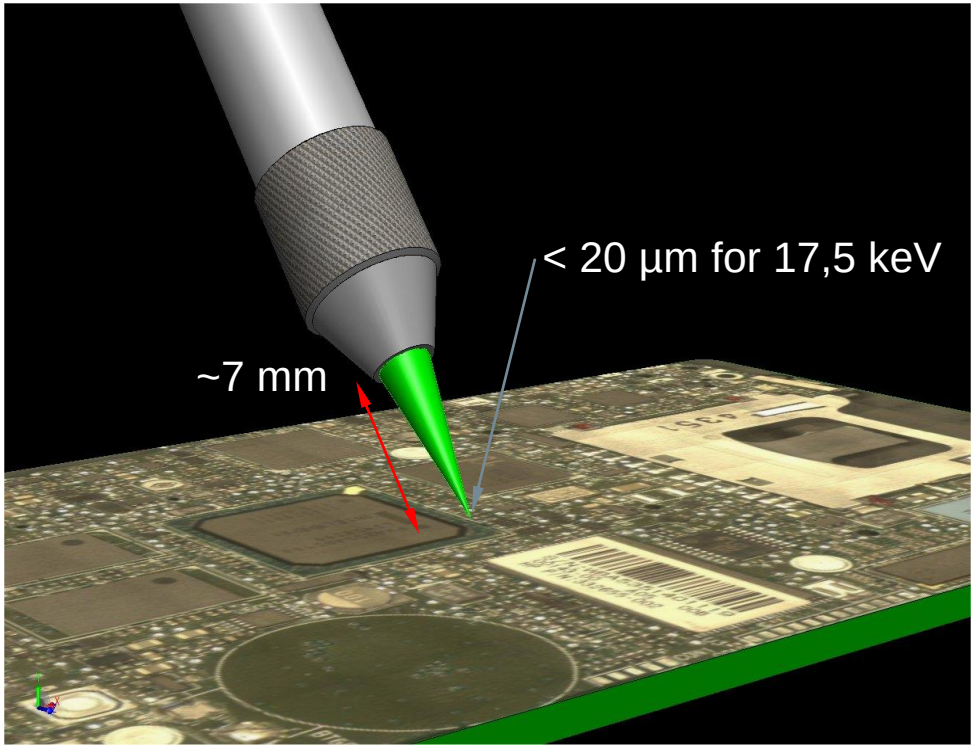
Optional 40 W micro-focus W tube with collimator
for excitation of 'heavy' elements, embedded in lighter matrices

Up to two Silicon drift detectors (SDD)
with 30 or 60 mm² active area each energy resolution < 145 eV
(for Mn-Kα @ 130 kcps throughput)

Sealed sample chamber with adjustable pressure between 1 mbar and atmospheric pressure for detecting elements down to Na

Sample stage with measureable area of 200 mm x 160 mm, maximum sample height 120 mm, maximum sample weight 5 kg, and sample stage speed up to 100 mm/s, minimum step size 4 µm

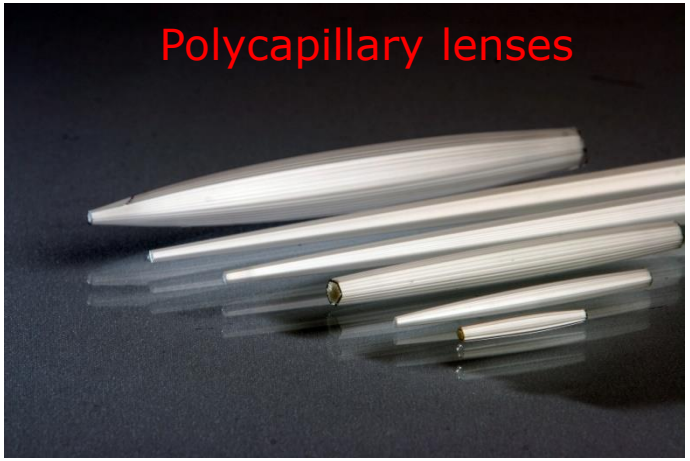
M4 TORNADO Instrument Design
Focusing by Poly-Capillary Lens

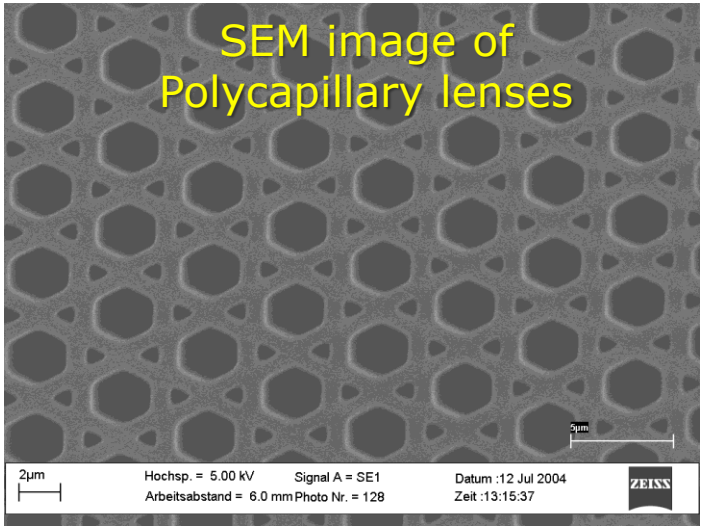


Poly-capillary lens collects
large solid angle of tube radiation

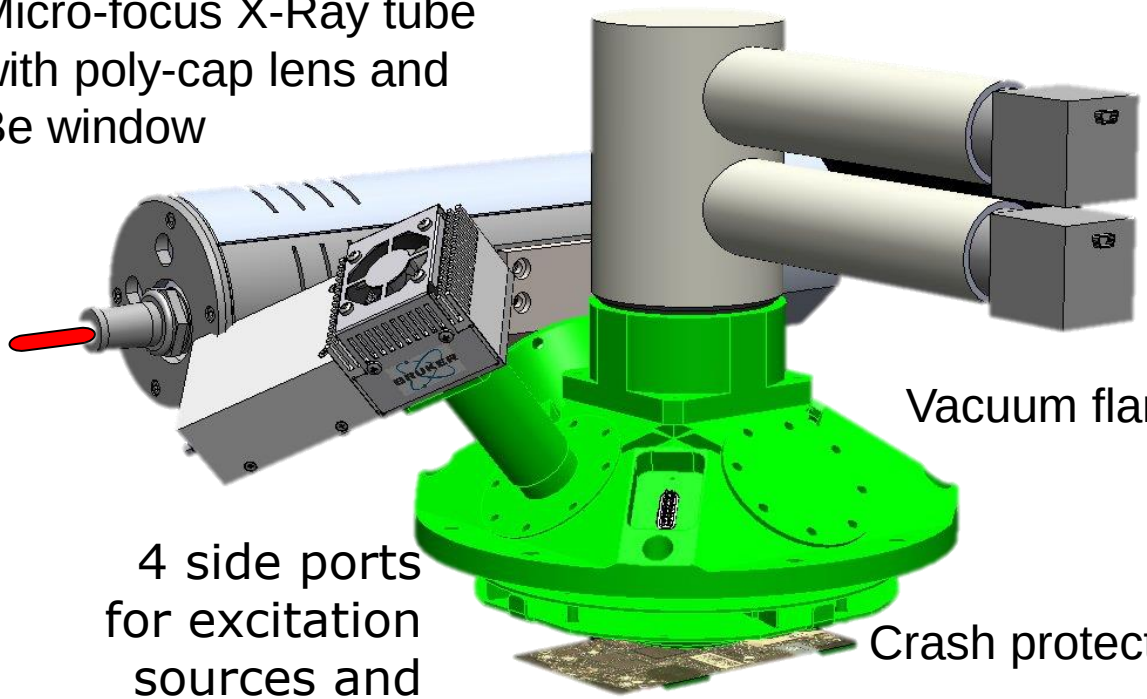
Concentrates beam at sample into small spot

Small spot size guarantees
high brilliance for data collection

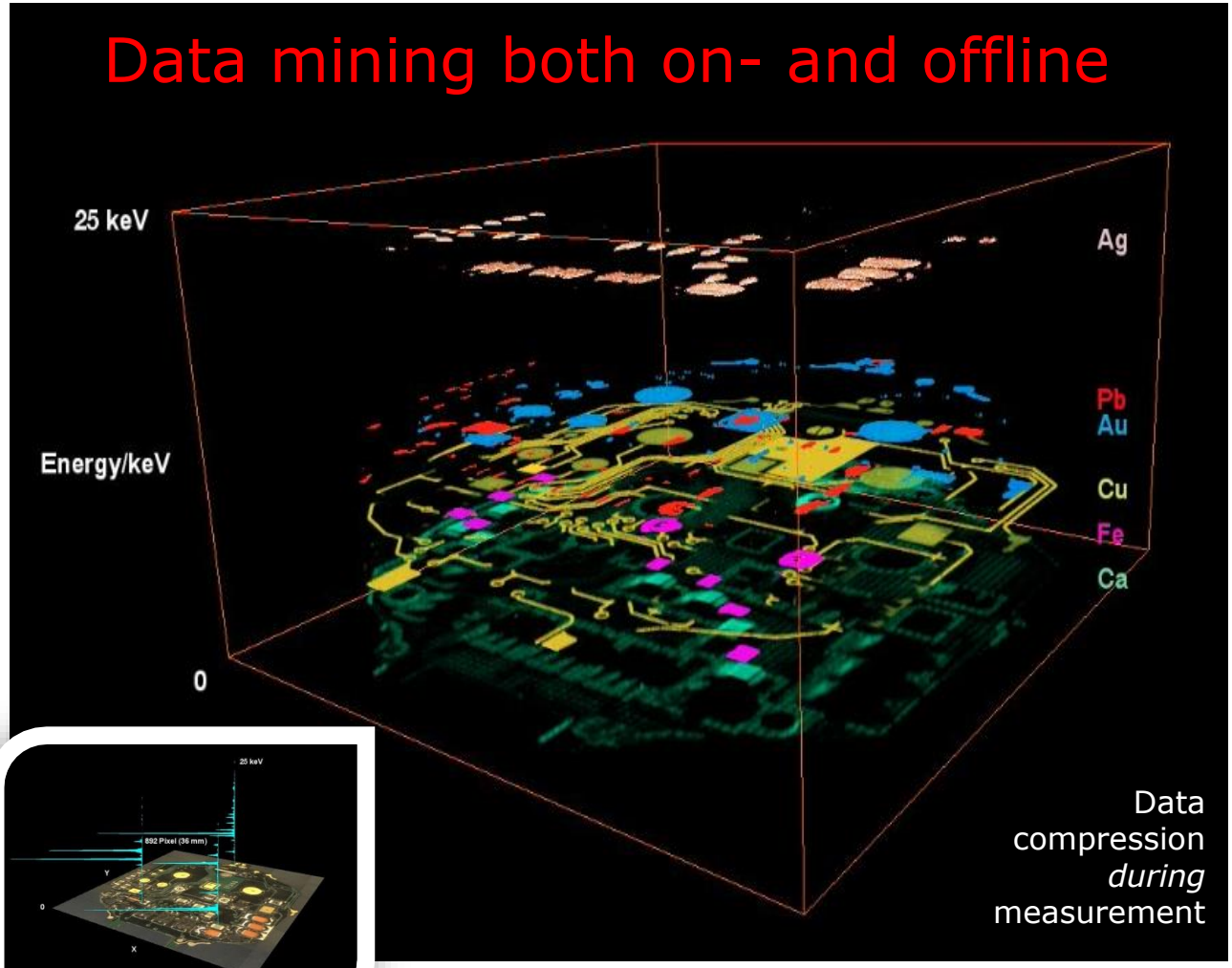




M4 TORNADO Instrument Design
Design and Safety



HyperMap Data Accumulation
Position-Tagged Spectrometry (PTS)



What is a HyperMap?

Complete X-ray spectrum for every measured pixel saved.

Generates 4D data cube

2D – Spatial Distribution

3D – Spectral Distribution (E)

4D – Intensity of every spectral channel

Measurement time/pixel down to 1 ms

Introduction
XRF on Different Scales and Fields

X-TRACE
(on SEM)

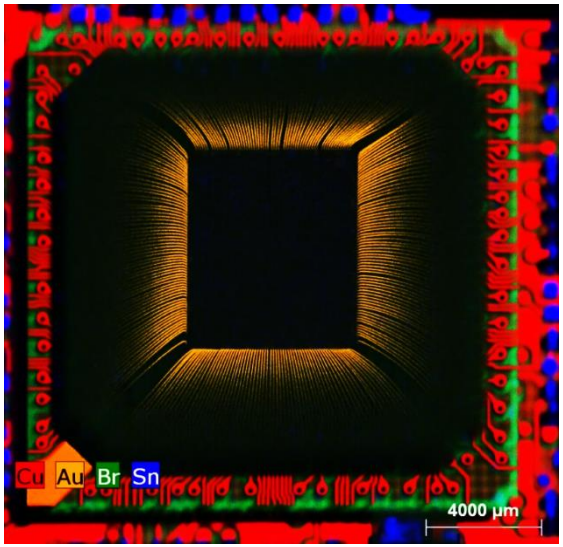
M4 Tornado

M6 Jetstream

Tracer

19 mm

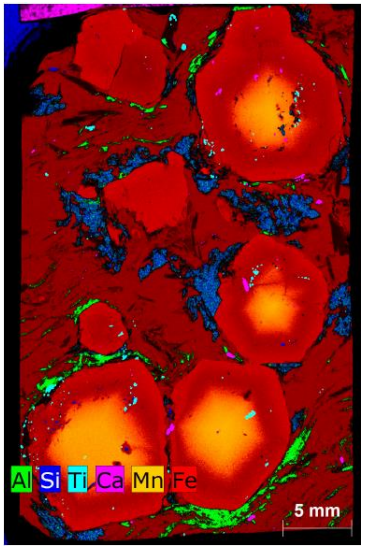
19 mm



Information from different depths of the sample

25 mm

38.7 mm



Trace element sensitive

37.5 cm

46.5 cm

No sample preparation

Concrete
Applications

- Concrete has been used as building material since the Mesopotamian ages and became very popular with Greek and Roman builders
- It withstands immense pressure and has a high durability
- It can be poured into almost any shape
- If reinforced with steel cable or mesh as pre- or post-tensioned it can bridge wide distances

Concrete
Weathering

- Concrete can last thousands of years under the right conditions
- Nowadays we frequently find images of cracked and weathered concrete
- As concrete is a mixture of many complex chemical compounds its durability depends on environmental conditions
- Saltwater for example leads to chemical reactions that change the volume and lead to stress and strain in the structure

Concrete
Alkali–Silica Reaction (ASR)

- Aggregates containing certain forms of silica will react with alkali hydroxide in concrete to form a gel that swells as it adsorbs water from the surrounding cement paste or the environment.
- These gels can induce enough expansive pressure to damage concrete.
- The final reaction can be schematically represented by:

$$Ca(OH)_2 + H_4SiO_4 \rightarrow Ca^{2+} + H_2SiO_4^{2-} + 2H_2O$$

$$Ca^{2+} + H_2SiO_4^{2-} + 2H_2O \rightarrow CaH_2SiO_4 \bullet 2H_2O$$

- Which is a reaction that will terminate during maturation of the concrete as the acidity goes down

Concrete
Alkali–Silica Reaction (ASR)

- In the presence of alkaline hydroxides (NaOH / KOH) the pH level is significantly increased, and the reaction can continue. In the presence of such alkaline hydroxides a sodium silicate can form:

$$\mathbf{2Na(OH) + H_4SiO_4 \rightarrow Na_2H_2SiO_4 \bullet 2H_2O}$$

$$\mathbf{Na_2H_2SiO_4 \bullet 2H_2O + Ca(OH)_2 \rightarrow CaH_2SiO_4 \bullet 2H_2O + 2NaOH}$$

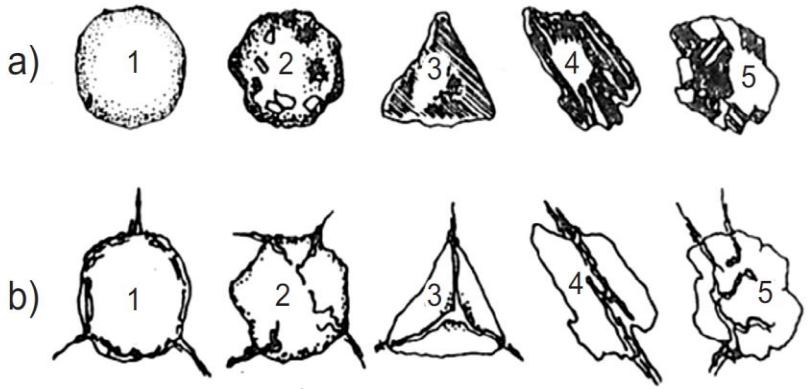
- The hygroscopic sodium silicate will expand as it absorbs water.
- This expansive pressure in the solid matrix may induce spalling of material, formation of macroscopic cracks, and a consequently a loss of structural integrity.
- However, this ASR can be controlled using certain supplementary cementitious materials.

Concrete
Alkali–Silica Reaction (ASR)

In order of decreasing potential to cause alkali-silica reaction.

Important Mineral Phases:

- Amorphous silica: volcanic glass, opal,
- Unstable silica polymorphs (tridymite and cristobalite),
- Chalcedony,
- Other forms of cryptocrystalline silica,
- Deformed quartz
- Strained quartz
- Quartz with crystallization imperfections,
- Quartz in crystalline forms



Grains of aggregate with different mineral composition and morphology:
a) initial condition,
b) with ASR - induced characteristic micro-cracks

DARIA JÓWIAK-NIEDWIEDZKA ,KAROLINA GIBAS MICHAL A. GLINICKI, 2017, PETROGRAPHIC IDENTIFICATION OF REACTIVE MINERALS IN DOMESTIC AGGREGATES AND THEIR CLASSIFICATION ACCORDING TO RILEM AND ASTM RECOMMENDATIONS, DOI: 10.7409/rabdim.017.015

Concrete
Alkali–Carbonate Reaction (ACR)

- Dedolomitization, the breaking down of dolomite, is normally associated with expansion.
- The reaction in this case can be schematically represented by:

$$\mathbf{CaMg(CO_3)_2 + 2NaOH \rightarrow Mg(OH)_2 + CaCO_3 + Na_2CO_3}$$

- In another step the sodium-carbonate in combination with calcium hydroxide (portlandite) can react again into :

$$\mathbf{Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH}$$

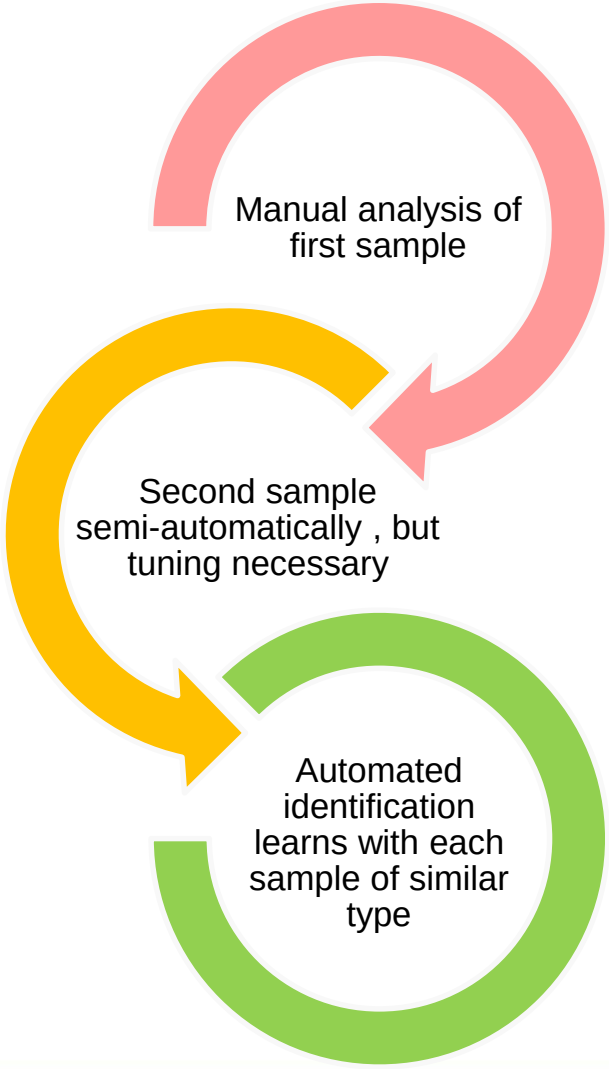
- Under the presence of calcium hydroxide, the dolomite reacts as follows:

$$\mathbf{CaMg(CO_3)_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + 2CaCO_3}$$

- This reaction and subsequent crystallization of brucite ($\mathbf{Mg(OH)_2}$) may cause considerable expansion.

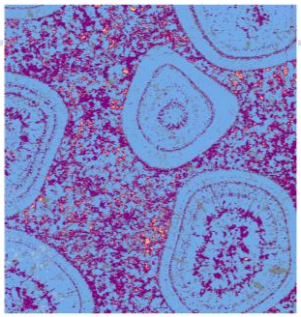
Advanced **M**ineral **I**dentification and **C**haracterization **S**ystem (AMICS)

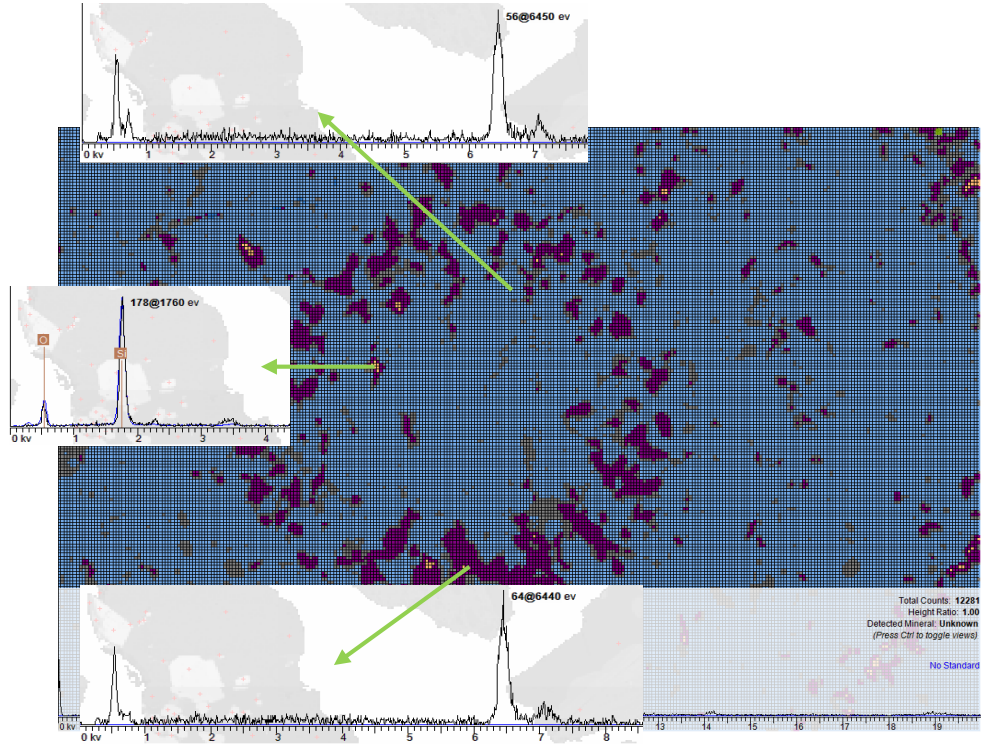
- AMICS software package applies finger printing to spectra for pixels in order to identify the minerals in a mapping
- The system comes with a preloaded comprehensive set of typical spectra for more than 2000 minerals for quick starting a custom database
- For each material system an individual database is developed as samples are characterized
- Based on the sample the database is extended by standard spectra created from the identified regions of a specimen.
- Statistical tools to calculate mass fractions and areal coverage across the specimen

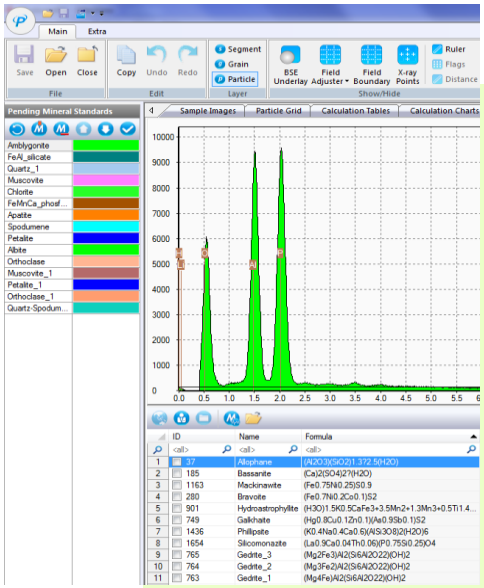


AMICS
How does AMICS work?

Micro-XRF Analysis: Hypermap
Mineralogy Workflow Schematic







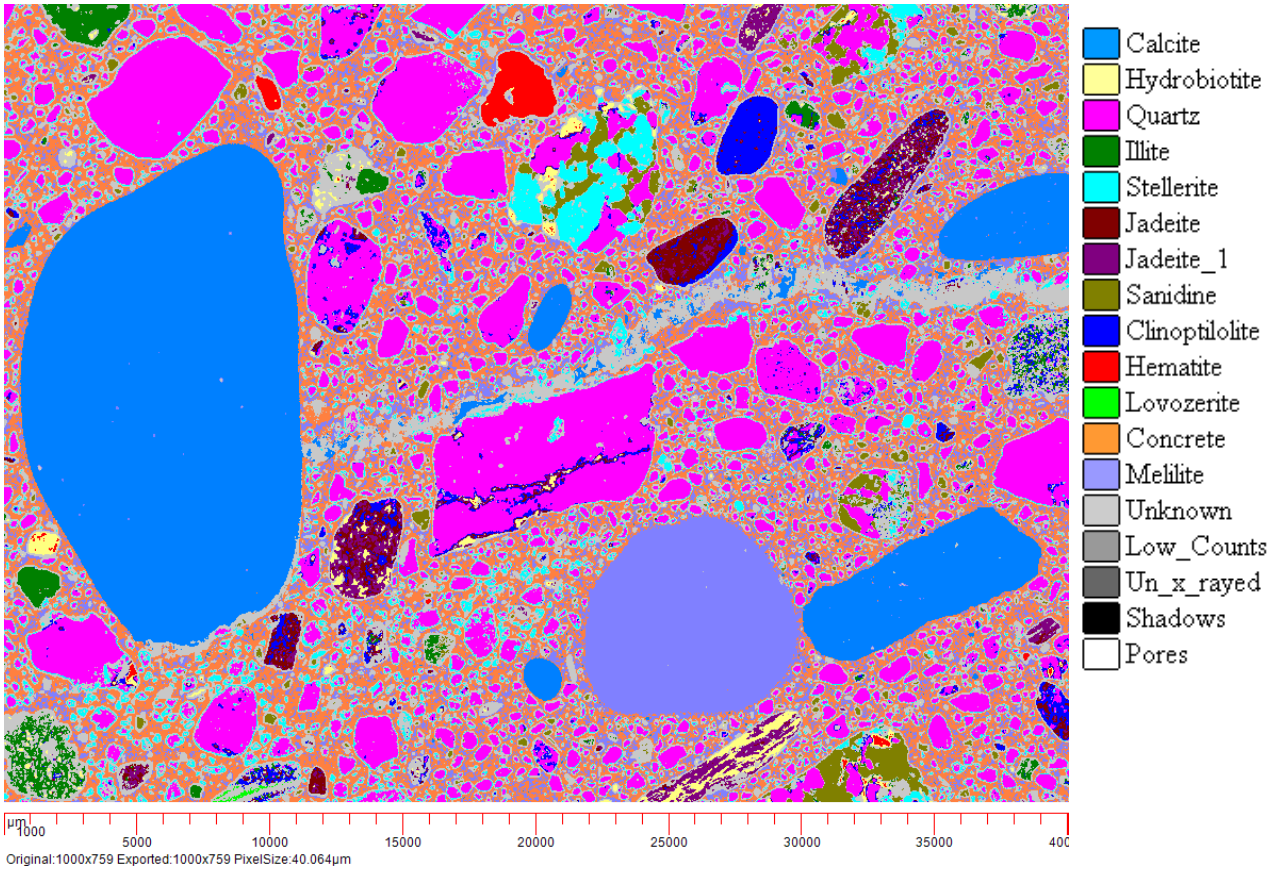
Classification

- Acquires spectrum for each segment
- Identifies minerals based on spectral information

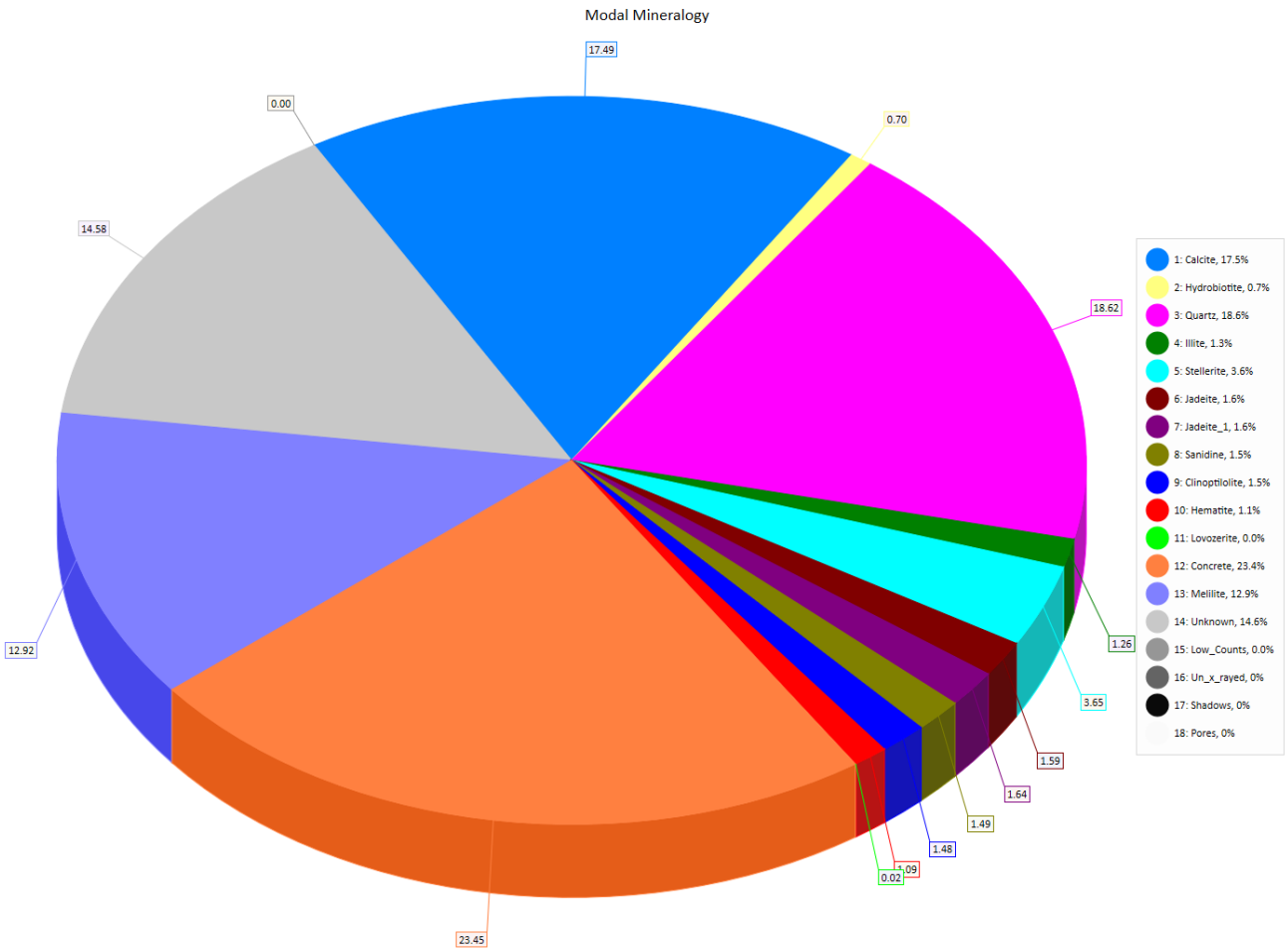
Concrete Hypermap Example
Starting with AMICS

With the preloaded database the concrete sample was analyzed and a according database of minerals with according spectra was defined.

The analysis shows the spatial distribution of each of the identified minerals along the sample surface.



Concrete Sample Mineralogy
Visualizing Results with AMICS



Resulting modal composition of the investigated area.

Relatively large unknown portion due to edge area around grains, that cannot be properly assigned to either one phase.

Higher resolution scan and longer exposure can reduce the amount of unknown material.

AMICS:
Relevant Mineralogical Information

Modal Mineralogy: How much of each mineral is present.

Elemental Assay: How much of each element is present (Whole Rock).

Elemental Distribution: How is the element of interest (EOI) distributed in each mineral? E.g. Cr in Chromite vs Pyrope Garnet.

Particle (Grain) Size Distribution: Classify sizes of particles (grains). Provide P-80, P-50 and P-20 values

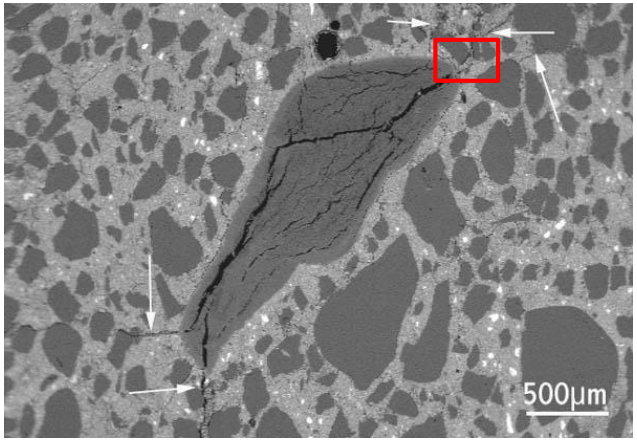
Mineral Association: Identify how the minerals are associated with each-other, e.g. Chromite and Garnet and Clinopyroxene etc.

Grain Shape Factor: The shape of the grain, i.e. euhedral, elongated.

Mineral Density Distribution: Classify densities of minerals. Identify how the minerals are distributed among the densities.

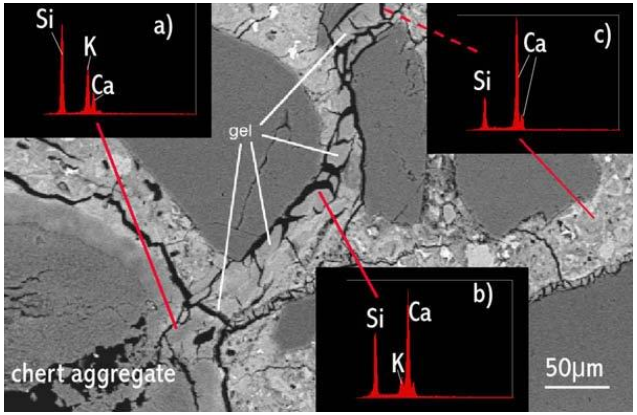
Academic Research
EDX and X-TRACE

As the spot in micro-XRF is in the range of 15 µm for higher energies and about 30 µm for elements such as Si, to resolve the micrometer and sub-micrometer scale an alternative method is required. The common approach is an e-beam excitation of the fluorescence in a SEM.



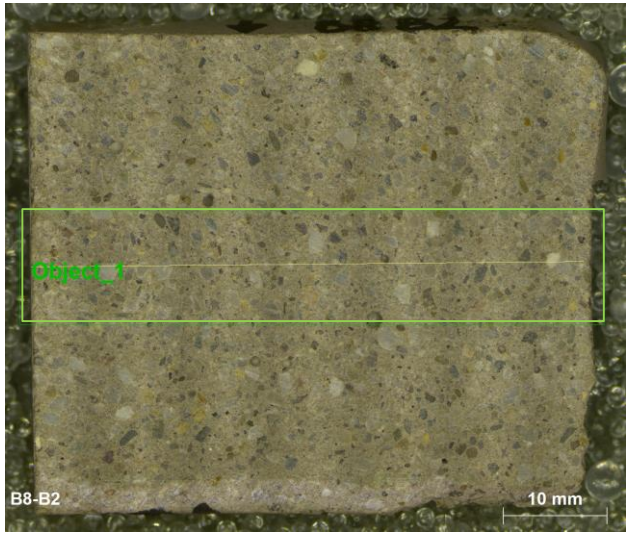
To correlate this information with micro-XRF results, X-TRACE provides an X-ray excitation on SEM. This allows for direct correlation of micro-XRF results with the sub-micrometer features in heterogeneous samples.

This adds complimentary information at a superior resolution,
its high sensitivity for light elements down to boron. Where micro XRF outperforms an EDX for elements with Z > 20 in detection limits, below that threshold the EDX has superior sensitivity and detection limits.

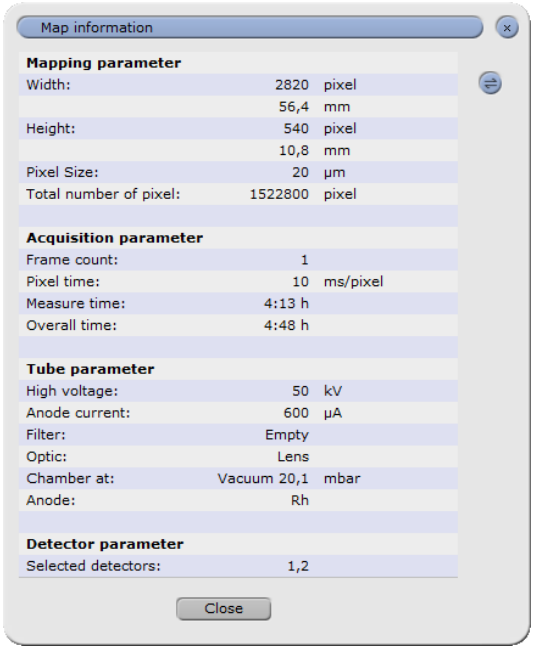


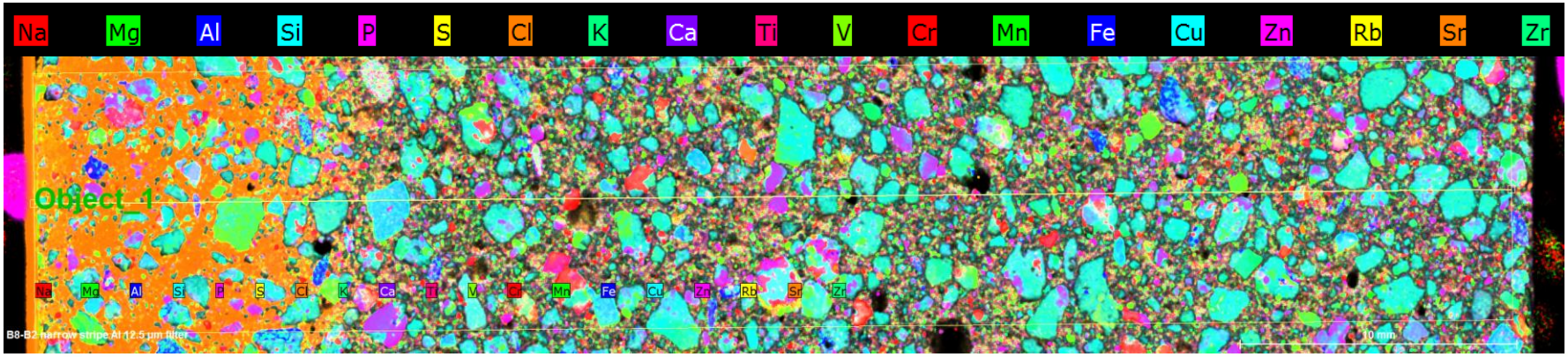
https://www.understanding-cement.com/alkali-silica.html

Analyzing Concrete
Measurement Conditions

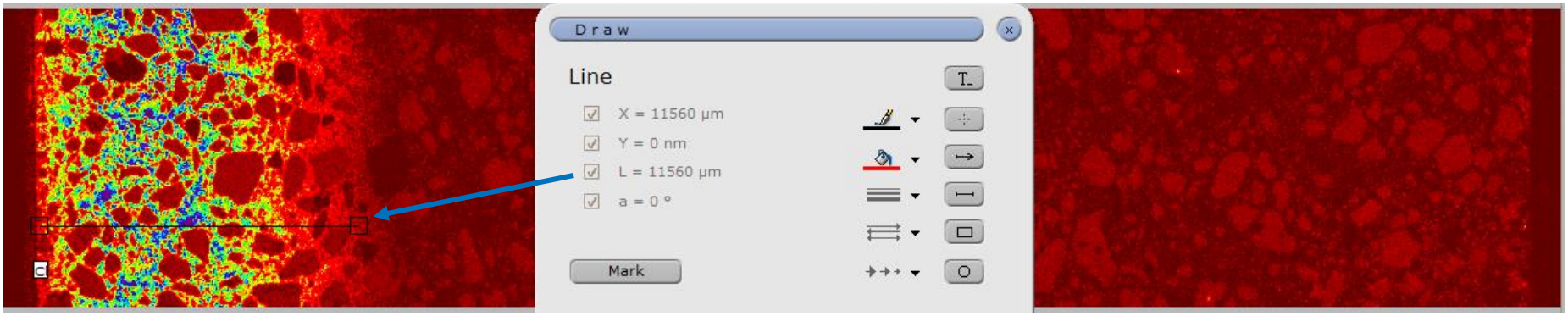


- Map of of 56.4 mm by 10.8 mm with 20 µm pixel size and 10 ms pixel time was measured on a standard M4 TORNADO utilizing 2x30 mm² detectors and a Rhodium anode
- 4 h scan on a region from left to right (thin green frame)
- Gradient in Cl distribution (orange) clearly visible



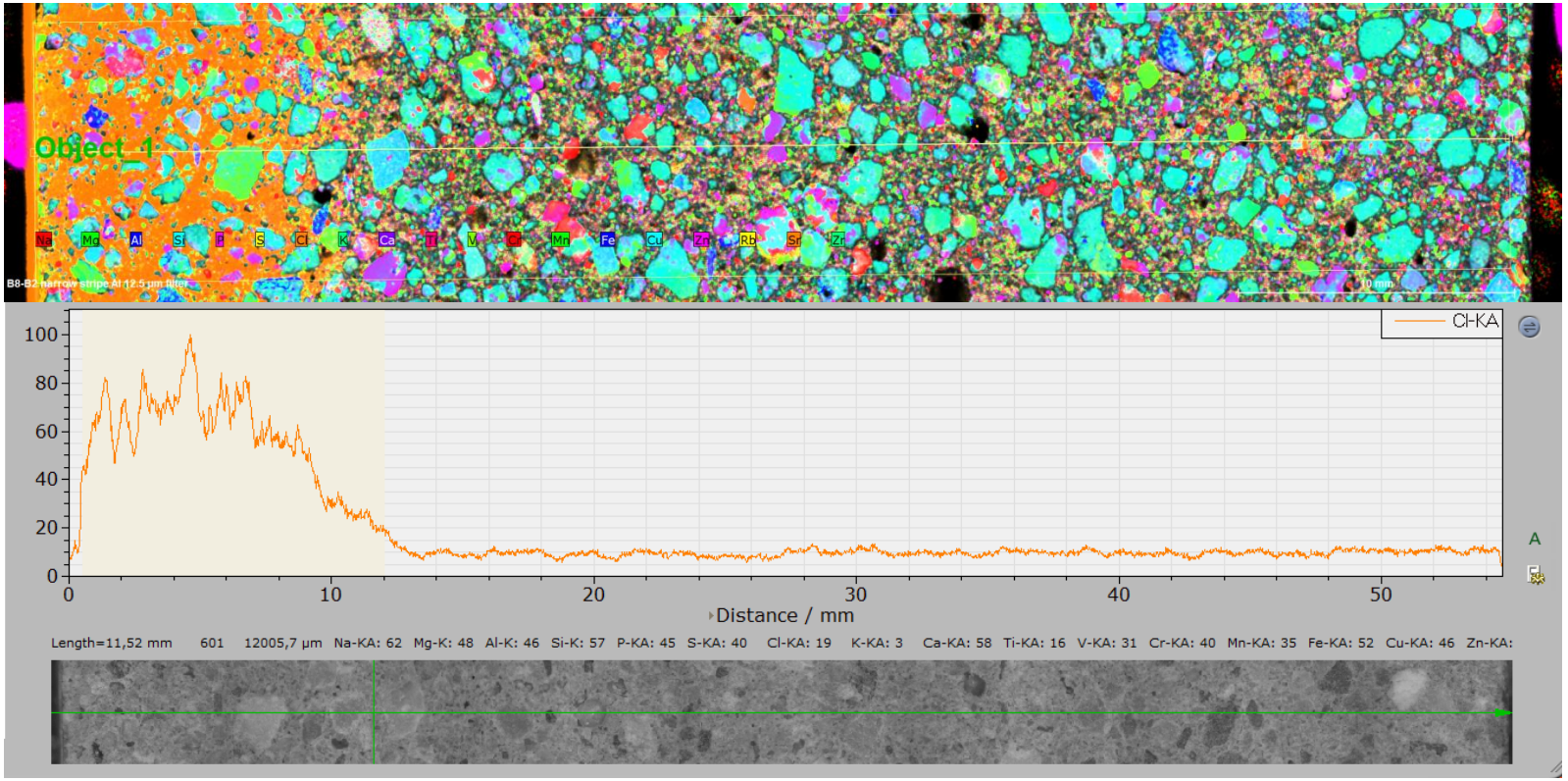


Analyzing Concrete
Enhanced Visualization and Dimensions



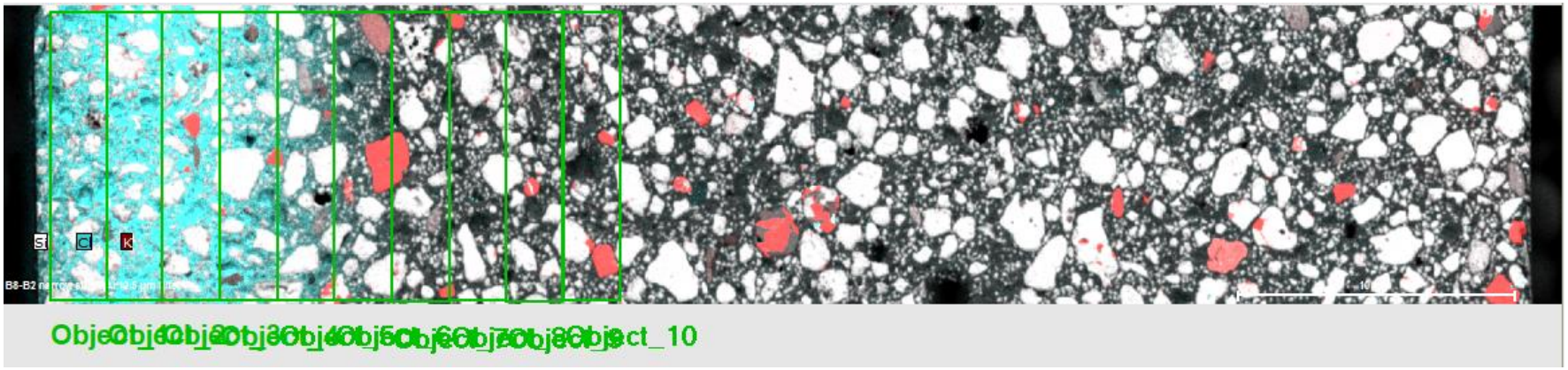
- False color representation of the chlorine concentration to enhance dynamic to the human eye for small changes
- The chemical gradient of Cl is clearly visible by the color changing accordingly to the element's fluorescence intensity
- With the *drawing tool* based on the visualization, a line has been drawn (shown above) and is 11.5 mm long, which gives an indication of the depth of Cl diffusion into the concrete

Analyzing Concrete
Cl Penetration Depth from Line Profile

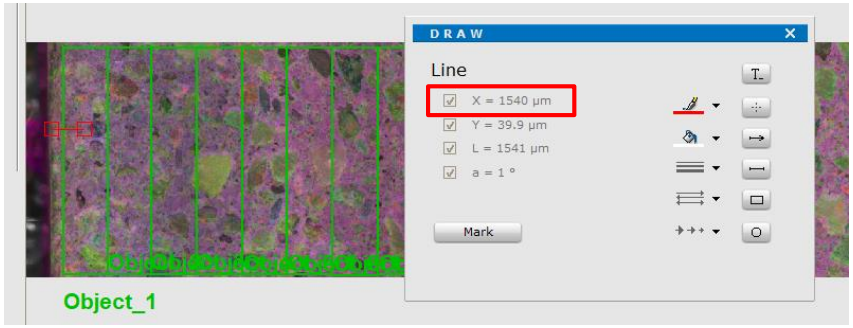


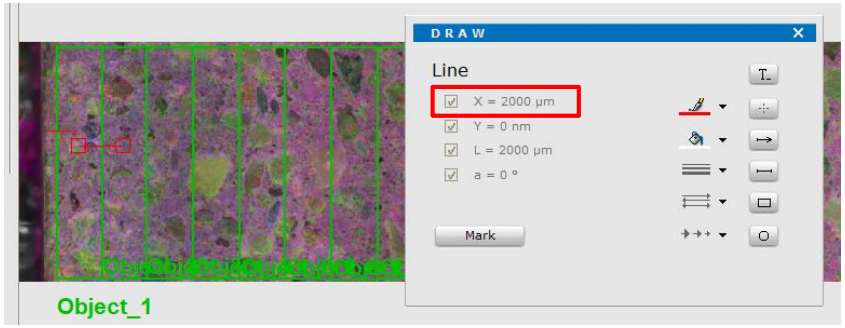
- A line object can be drawn into the Hypermap, creating a line profile along the sample.
- Additionally, the line was widened to average points perpendicular to the line. The Cl signal is higher in the first ~ 11.5 mm (from the left).
- The strong modulation is a result of the large agglomerates in the matrix.

Analyzing Concrete
… a more Quantitative Approach: Objects



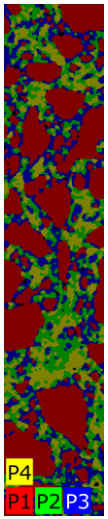
Objects with a width of 2 mm and almost the full height are created next to each other. Their center position with respect to the sample surface are determined with the help of the “draw tools”. The individual objects are saved as new individual maps, using the “save all objects” function.

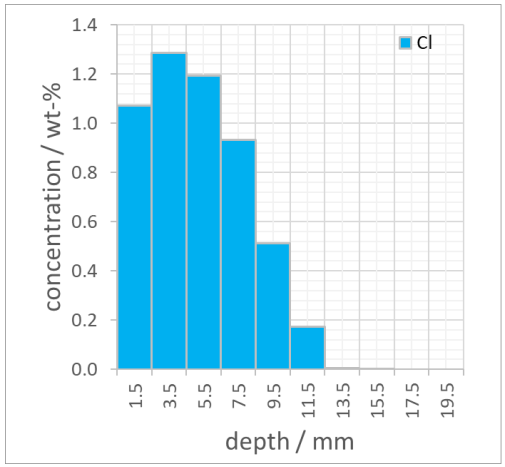


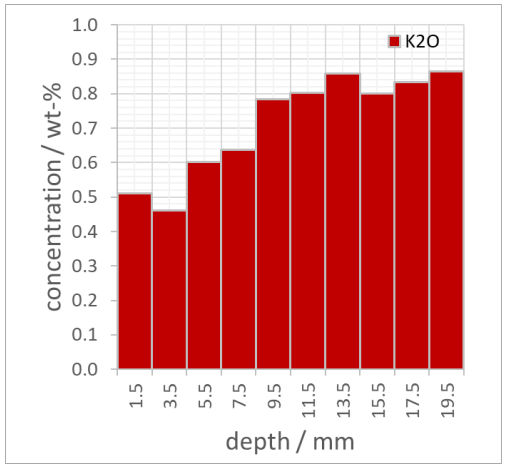


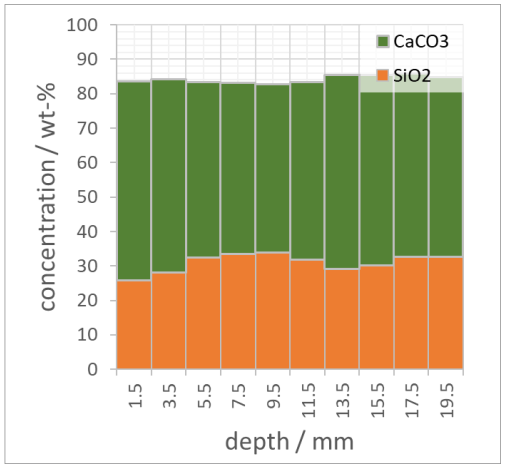
Analyzing Concrete
Phase Analysis and Concentrations

- Load each object
- Select only a signature element of the cement (here P)
- Press auto phase
- Select the cement phase (phases and sum them up if necessary)
- Create sum spectrum of the according (sum-)phase
- Quantify the according spectrum with appropriate method
- Move the spectrum to the project (or save to disk)
- Import (drag and drop) all sum spectra into point mode
- Export results table to Excel → plot

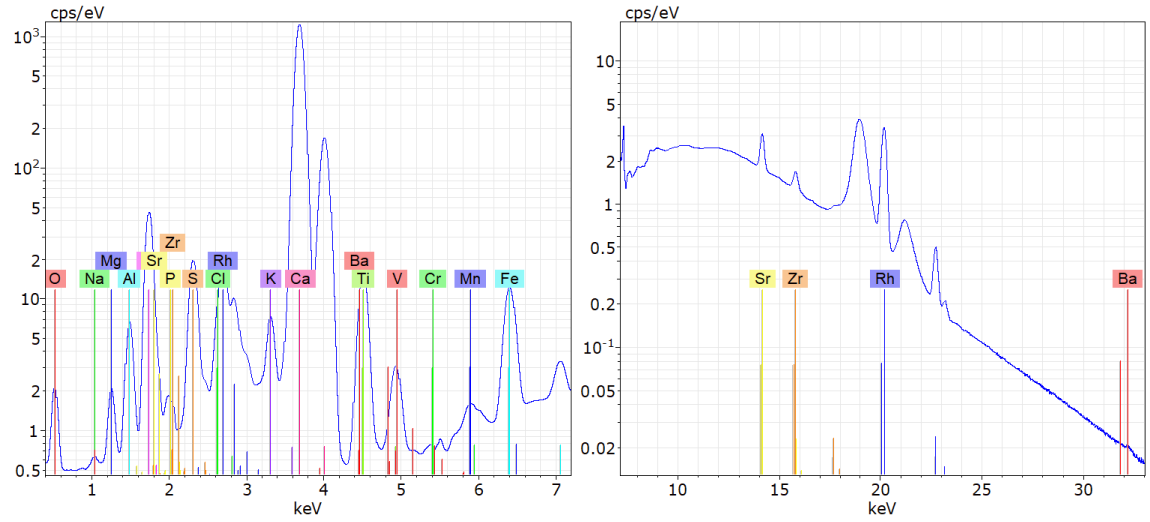


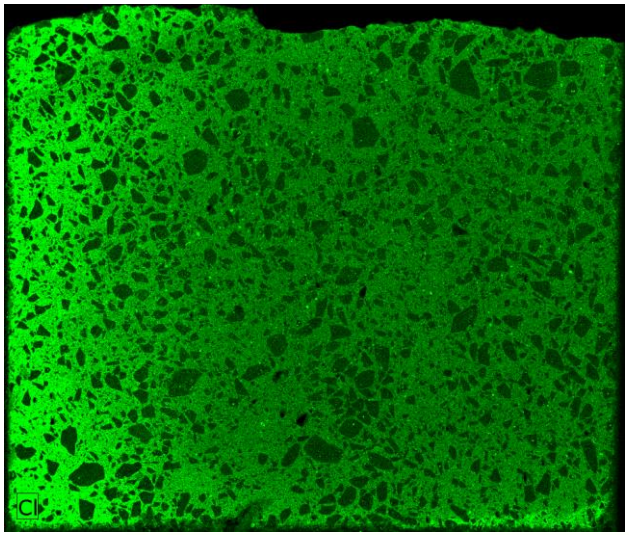






Measuring Concrete
Taking a Map and Visualizing Intensity





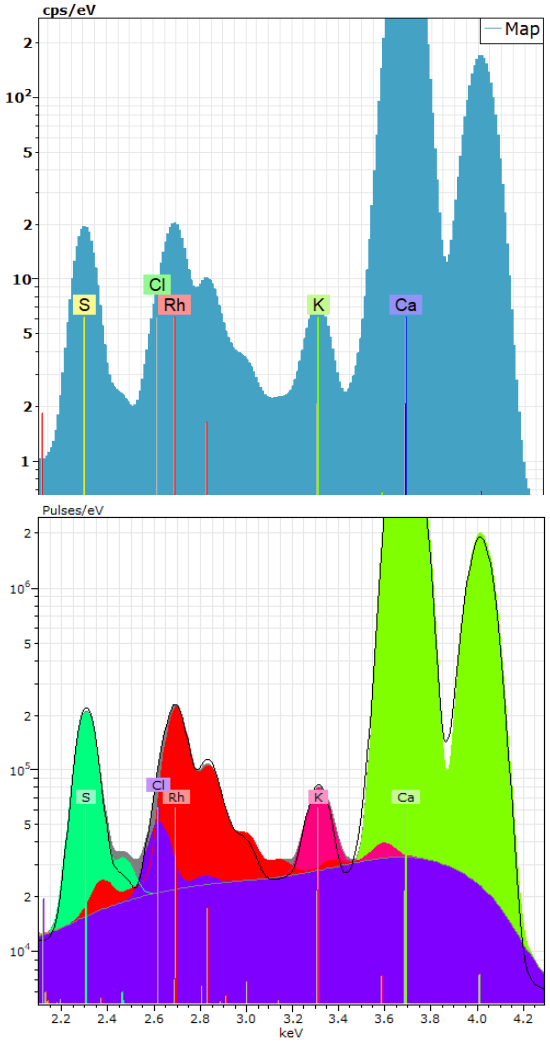
- Drill core of concrete exposed to NaCl was mapped
- The intensity in a Region-Of-Interest (ROI) for Cl-K-line (as proxy for Na) is displayed
- Intensity is found virtually everywhere

MAP INFORMATION

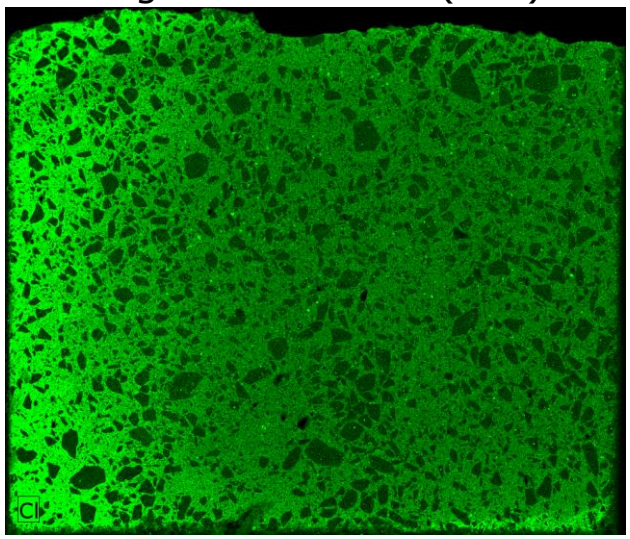
Mapping parameters		
Width:	940	pixel
	70,5	mm
Height:	799	pixel
	59,893	mm
Pixel Size:	75	µm
Total number of pixel:	751060	pixel
Acquisition parameters		
Frame count:	1	
Pixel time:	15	ms/pixel
Measure time:	2:35 h	
Overall time:	3:51 h	
Stage speed:	5,0	mm/s
Stage position (X,Y,Z):	96.968;89.294;78.717	mm
Tube parameter		
High voltage:	50	kV
Anode current:	600	µA
Filter:	Empty	
Optic:	Lens	
Collimator diameter:	0	
SpotSize:	20	
Chamber at:	Air 2	mbar
Flow rate:	---	l/min
Anode:	Rh	
Detector parameters		
Selected detectors:	1,2	
Max. pulse throughput:	275000	cps

Measuring Concrete
Signal-to-Noise-Ratio (SNR)

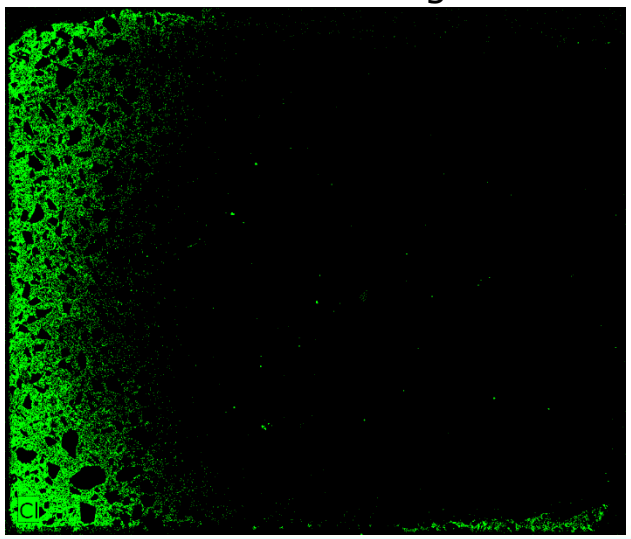
- A look at the spectrum shows a strong overlap of the Cl lines with backscattered Rh-L-line intensity
- Fast algorithm can perform deconvolution of 18 elements in 350 000 spectra in 50 sec, in order to separate Cl from Rh intensity
- Rh-anode yields poor SNR due to overlap, suppressing the Rh-L-line by a filter removes the need for deconvolution at the cost of overall signal and particularly for the light elements



Region of Interest (ROI)

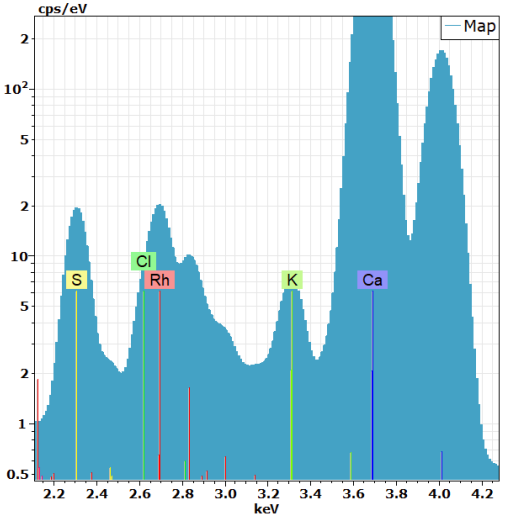


Deconvoluted signal

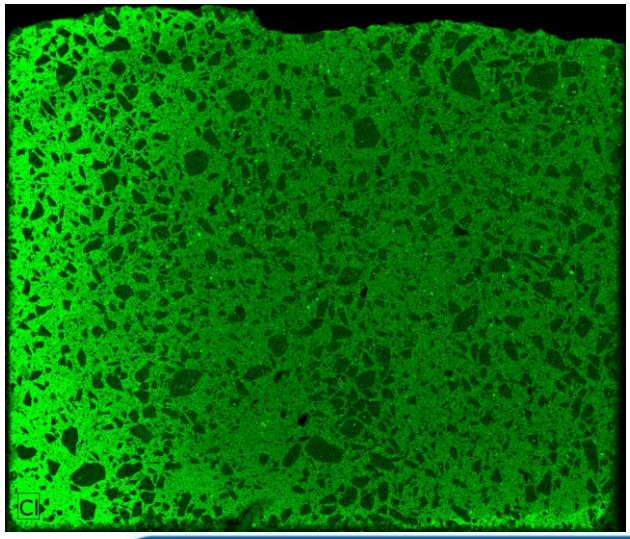


Measuring Concrete
Alternative use of Ag-Anode

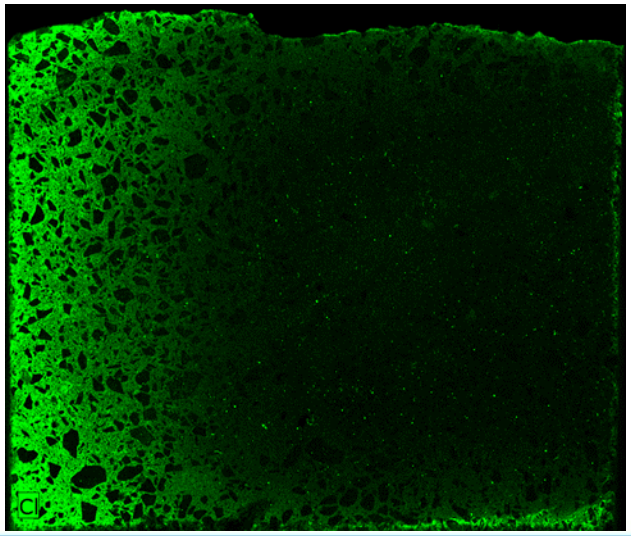
- To avoid the need for deconvolution, or requirement for a filter, alternative anode material should be considered
- For the given analytical question silver offers a much more efficient and potent excitation
- The backscattered Ag-L-line intensity no only does not overlap with the Cl, but it provides a much more efficient excitation of Cl by the 2.82 keV absorption edge
- No filter or deconvolution required

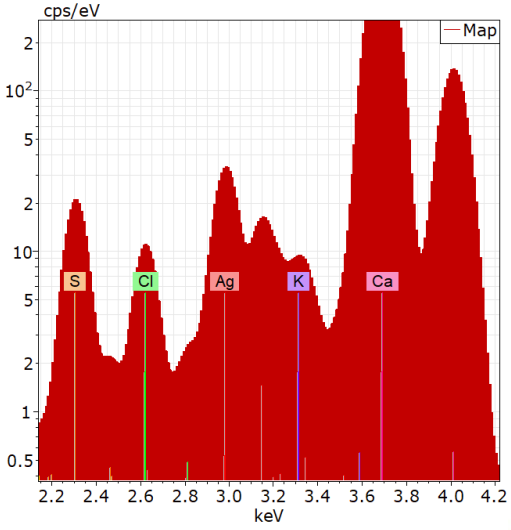


ROI of Cl with Rh-anode

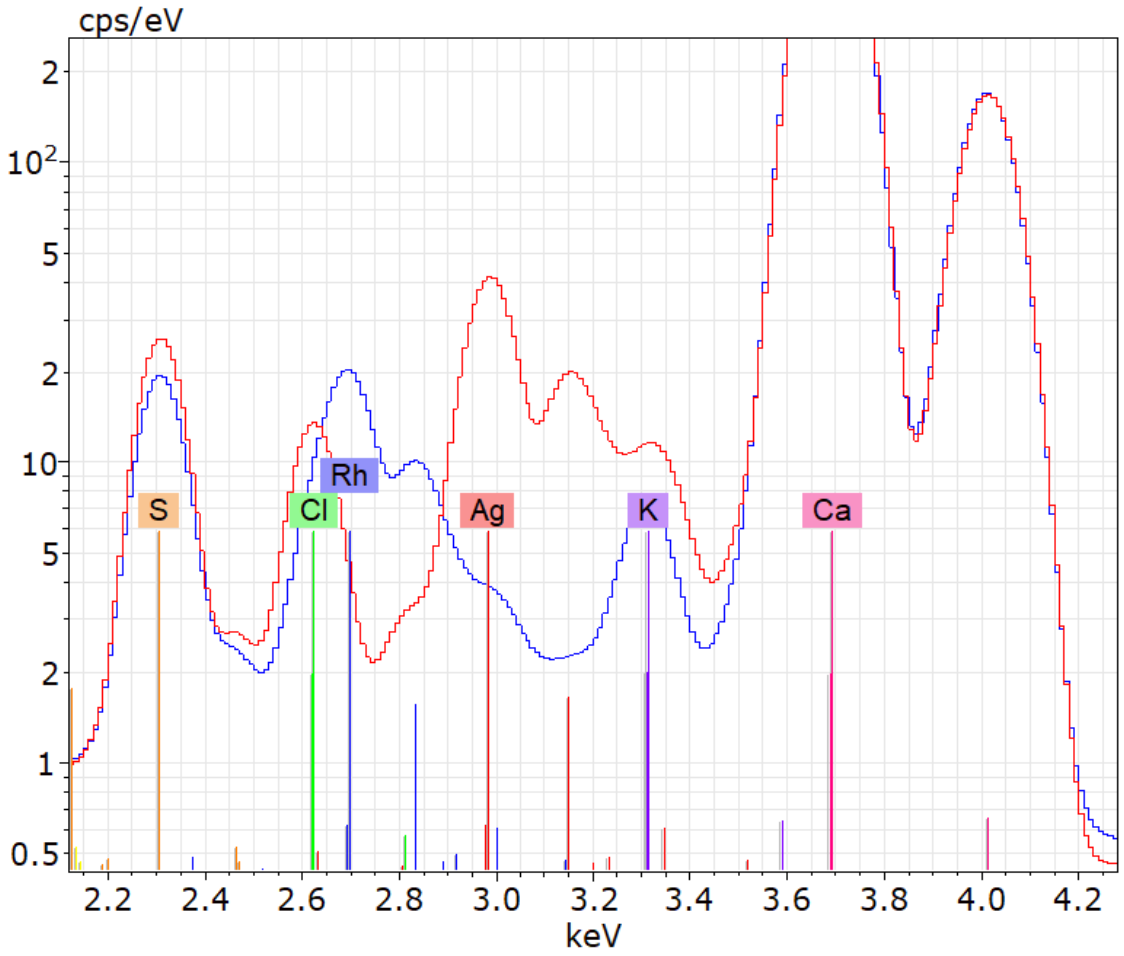


ROI of Cl with Ag-anode





Measuring Concrete
Is there an Ideal Source?



- A direct comparison shows that the Ag excitation comes at a cost as well, it overlaps strongly with K
- As the Ag-L-lines are transmitted more efficiently, it provides better signal for elements with 6 < Z < 18, such as Cl, S, P, etc.
- It is possible to equip the M4 TORNADO with two sources, but only one can be equipped with a poly-capillary lens

From the above, it becomes clear, there is no ideal anode for all questions! In the decision for an excitation source the priority in terms of elements must be considered!

Concrete
Why XRF? From Construction Site to Lab

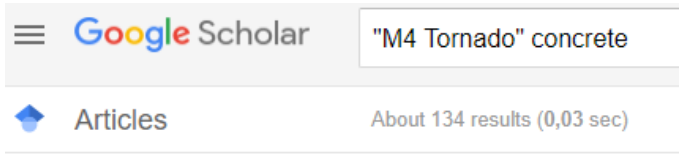
- XRF allows for fast measurement of a surface on site using a handheld XRF, such as the tracer
- On indication of contaminants a drill core can be taken for more in-depth analysis
- An area of up to 19 cm x 16 cm can be mapped with an M4 TORNADO, or an area of up to 80 cm x 60 cm utilizing an M6 JETSTREAM
- The penetration of catalysts, such as NaCl, into the concrete can be visualized and semi-quantitatively analyzed
- For research purposes it can be analyzed even further utilizing EDX in conjunction with X-TRACE, allowing to correlate micrometer and sub-µm-scale element distributions

Live Demonstration
Phase Analysis and Concentrations

Concrete
Summary

- Micro-XRF can provide compositional and mineralogical information across a range of scales
- Fundamental parameter (FP) based quantification allows for quick assessment of composition in points
- Mapping of mineralogy using AMICS yields information about possible ASR and ACR reactions as well as matrix and aggregate compositions
- Mapping of element intensities on a drill core sample can provide visualization of alkaline hydroxide penetration into the volume
- Smart analysis of mapping allows for semi-quantitative analysis of Cl and K concentration in the matrix
- Phase analysis allows for quick estimation of cement to aggregate ratio as well as for semi-quantitative analysis

Literature
M4 TORNADO in Concrete Research



Since in 2015 the first M4 was purchased for the purpose of research in concrete more than 130 publications can be found, and multiple Masters and PhD thesis utilizing the M4 in the field were published. Some example from various groups:

G. Bonifazi et al., "*Hyperspectral imaging applied to the identification and classification of asbestos fibers*," 2015 IEEE SENSORS, Busan, 2015, pp. 1-4, doi: 10.1109/ICSENS.2015.7370458.

K. De Weerdt et al., "*Comparing chloride ingress from seawater and NaCl solution in Portland cement mortar*," Cement and Concrete Research, Volume 115, 2019, pp. 80-89, doi: 10.1016/j.cemconres.2018.09.014.

H. Morillas et al., "*Multianalytical approach to evaluate deterioration products on cement used as consolidant on lithic material: The case of Tello Obelisk, Lima (Peru)*," Microchemical Journal, Volume 139, 2018, pp. 42-49, doi: 10.1016/j.microc.2018.02.017.

G. Plusquellec et al., "*Determining the free alkali metal content in concrete – Case study of an ASR-affected dam*," Cement and Concrete Research, Volume 105, 2018, Pages 111-125, doi: 10.1016/j.cemconres.2018.01.003.

A. Dehghan et al., "*Application of X-ray microfluorescence for the determination of chloride diffusion coefficients in concrete chloride penetration experiments*," Construction and Building Materials, Volume 148, 2017, pp. 85-95, doi: 10.1016/j.conbuildmat.2017.05.072.

T. Danner et al., "*Long-term Influence of Concrete Surface and Crack Orientation on Self-healing and Ingress in Cracks – Field Observations*," Nordic Concrete Research, 58(1), 1-16. doi: https://doi.org/10.2478/ncr-2018-0001

Questions, Thoughts or Comments?

If you have questions or want to contact us during the Webinar, please **type your questions**, thoughts, or comments in the **Q&A box** and **press Submit**.

We ask for your understanding if we do not have time to discuss all comments and questions within the session.

Any unanswered questions or comments will be answered and discussed by e-mail or in another Webex session.

More Information

For more information, please contact us:

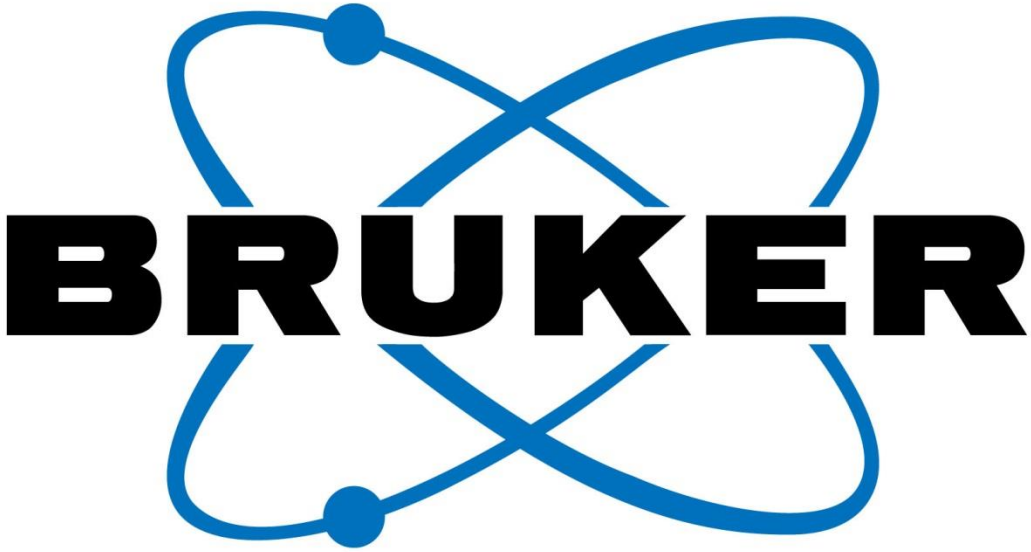
Bruker Nano GmbH

info.bna@bruker.com

Or

Max.Buegler@bruker.com

Andrew.Menzies@bruker.com



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