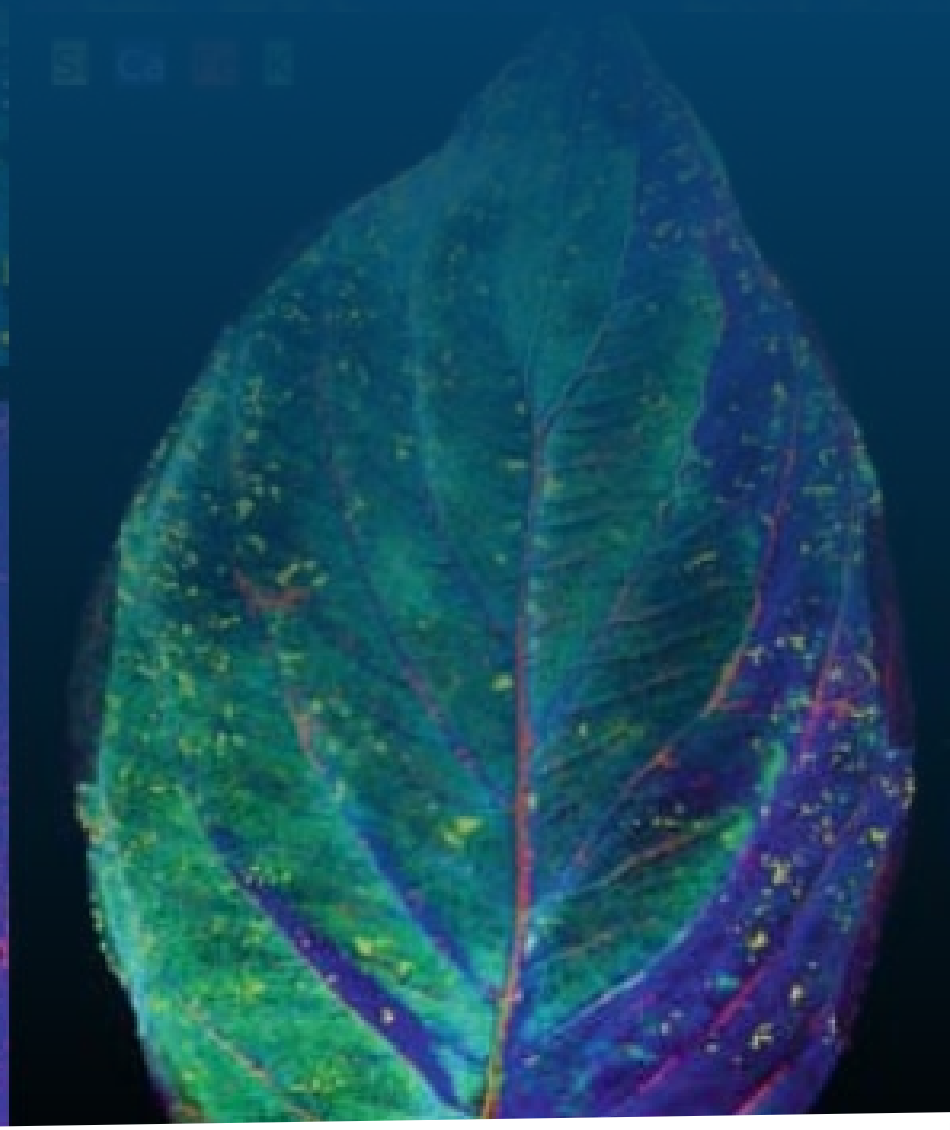
Micro-XRF
Back to the Roots – Part V



The speakers

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Overview

- Part I of this series introduced micro-XRF as a technique and gave an overview of the individual components.
- Part II focused on qualitative micro-XRF analysis, showing how much information can be gained without knowing the composition of a sample.
- Part III discussed quantitative XRF analysis already, focusing on the range of application.
- Part IV introduced micro-XRF on the SEM, showing where this secondary excitation allows to extend the analytical capabilities.

- Part V shall show that today XRF quantification does not have to be based on standards anymore.
  - Which samples can be quantified and what to expect from quantification?
  - What is the difference between standard-based and (standard-supported) FP quantification?

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Setting the scene
What is a homogeneous sample?

- When looking from far away, everything looks homogeneous. Planet earth, for example, looks pale blue. Only when getting closer large-scale inhomogeneities, like water versus land are revealed.
- On the other end, not even the atoms themselves are homogeneous. They have inner structure, created by different sub-atomic particles.
- Ultimately, the sample homogeneity depends on how close a look we take, i.e. what **analytical technique** we use to asses it.

- So what is homogeneity and why do we bother?

Pale Blue Dot – The earth photographed by Voyager 1 at a distance of 6 billion kilometers.

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Setting the scene
Why does homogeneity matter?

- The earth's surface is made from 71 % of water and only 29 % of landmass. ...and luckily we are not inhabitants of a homogenously muddy planet.
- So the heterogeneity may be a sample property that we need to know to truly understand that sample.
- Sometimes, of course, we only need to know a general number, that we can use to compare one sample to the next. (Jupiter weighs 318 times as much as Earth)

- So not only the measurement method, but also our **analytical question** dictates, whether we can assume the sample to be homogeneous or not.

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Setting the scene
Sample and analytical method

- Some samples **are homogeneous**.
- Some samples **appear homogeneous**, because the analytical method cannot resolve the inhomogeneities or averages over all individualities.
- Some samples **can be considered homogeneous**, because the possible level of heterogeneity wouldn't affect the answer to our analytical question.
- ...and there are the other cases:
  - The method cannot resolve inhomogeneities, but the sample is too heterogeneous to give "good results".
  - The analytical question itself is about the (in)homogeneity of the sample.

- Some methods can analyse a wide variety of samples and/or answer very different analytical questions.
- In general, the analytical method should match both, the analytical question and the sample!

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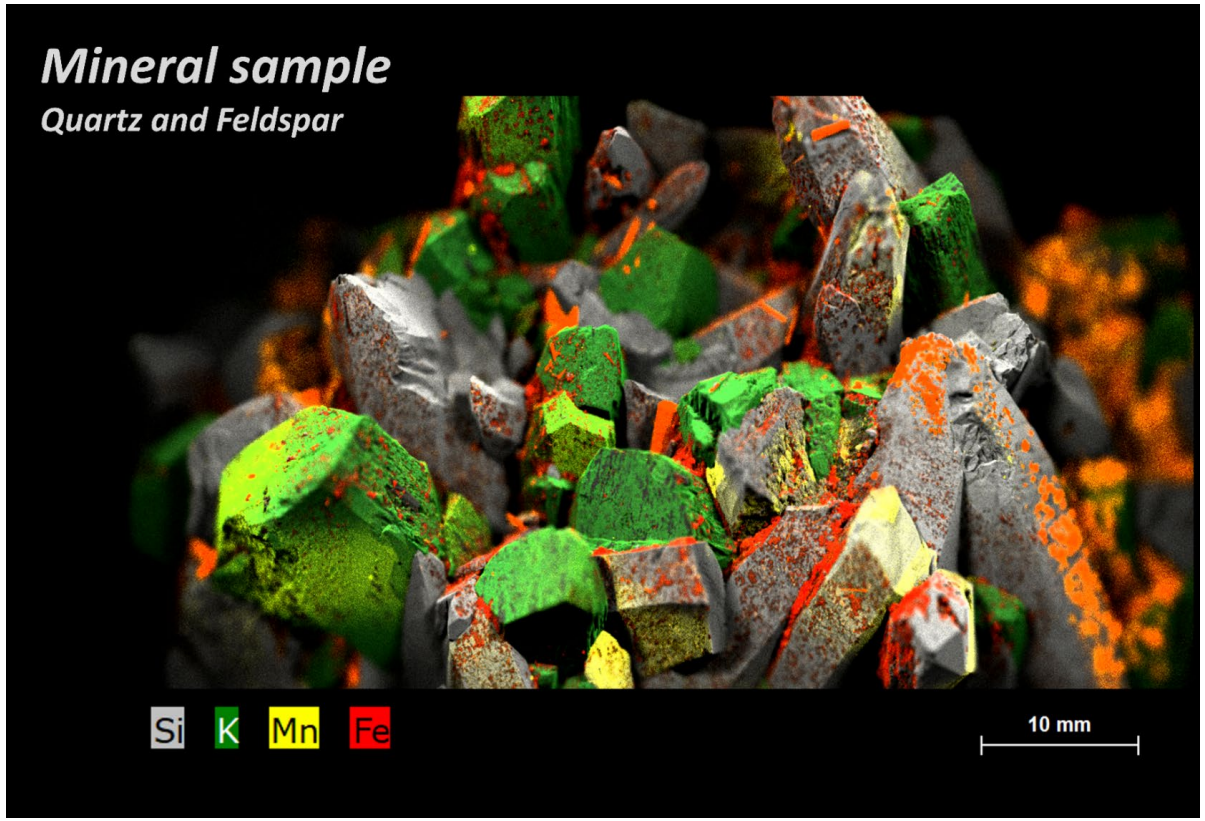
Setting the scene
Homogeneity and Quantification

- When a heterogeneous sample is investigated with a method that can resolve the respective heterogeneities, individual parts of the sample can be analyzed independent of each other.



- With XRF we determine element abundance as the sample property of interest.
- Micro-XRF resolves lateral structures down to 20 µm.
- The X-ray information can be obtained from depths up to some Centimeter!
- Depending on the matrix, the analytical volume is between 20 µm³ and 200 µm³.
- If we want to quantify individual parts of our sample, these parts should be **homogeneous within the analytical volume**!

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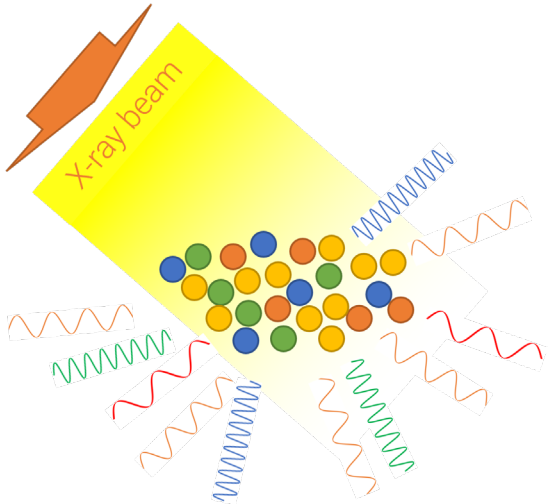
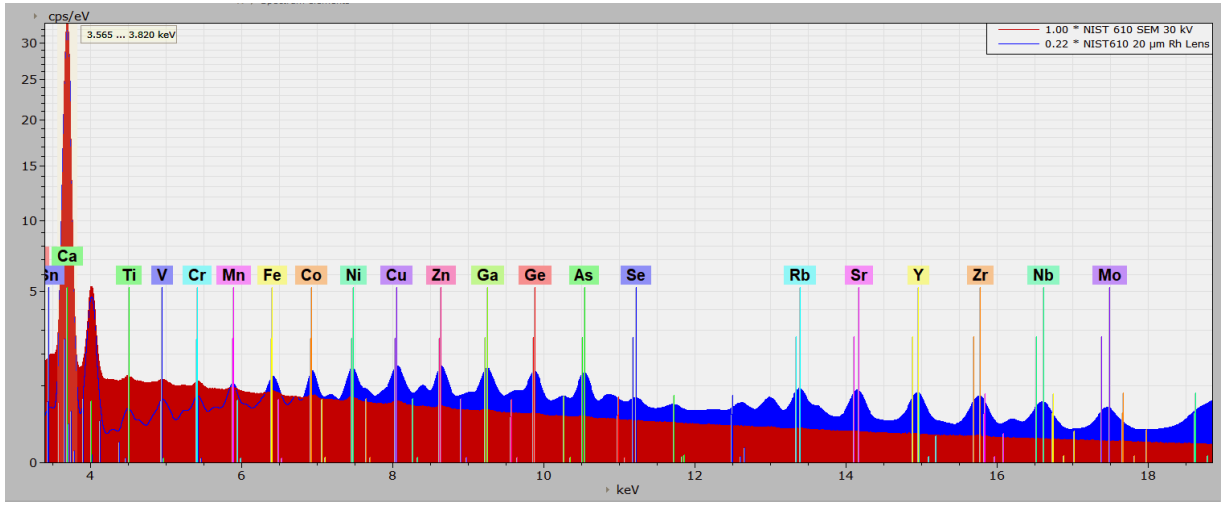
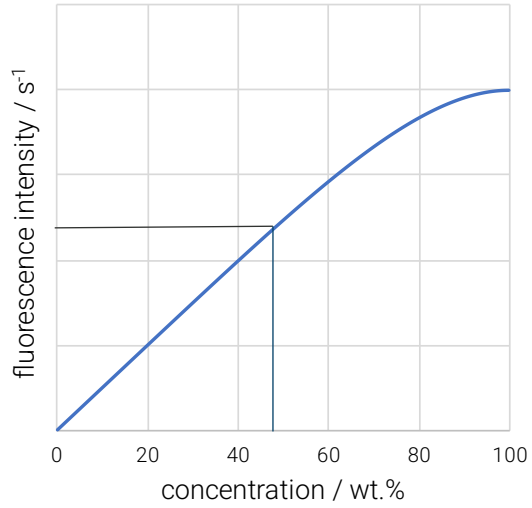
Setting the scene
What is XRF quantification?

- When a sample is irradiated with X-rays, any irradiated atom in it will begin to fluorece. → X-ray fluorescence
- Each element has its own characteristic fluorescence energy, and when the XRF spectrum is recorded, it is easy to see which elements are in the sample. → Qualitative analysis
- Quantification is the process to derive the concentrations of the elements from the fluorescence intensities.







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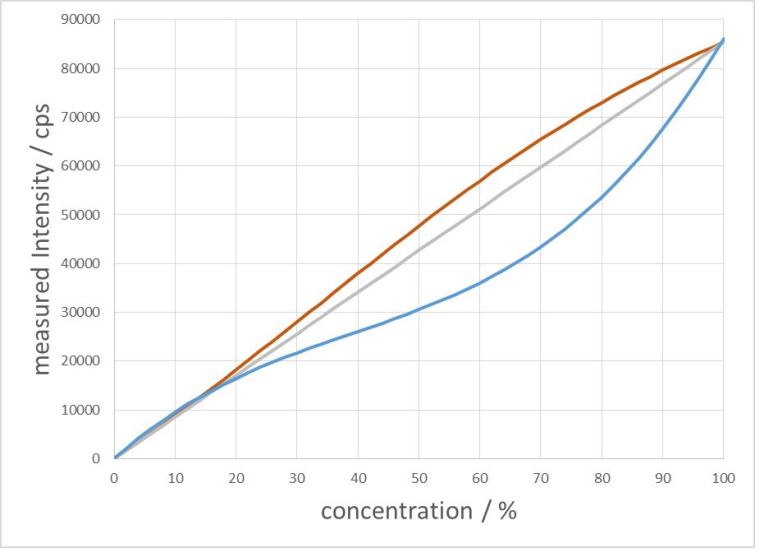
Setting the scene
What is XRF quantification?

- The relation between the concetration and the fluorescence intensity of an element is not always easily described.
- Other elements in the sample can lead to **line overlap** or significantly enhance or attenuate the fluorescence, causing the so-called **inter-element effects.**
- With increasing number of elements the correlations become increasingly complex and non-linear.



- Traditionally large sets of **standards** or **reference materials** are used to compared to and compensate for all this non-linearity in complex samples.
- Since almost 70 years* the theoretical foundations are laid out to quantify samples without the use of standards: this is called **fundamental parameter (FP) quantification**.

* J. Sherman, *The theoretical derivation of fluorescent X-ray intensities from mixtures*, Spectrochimica Acta 7 (1955)

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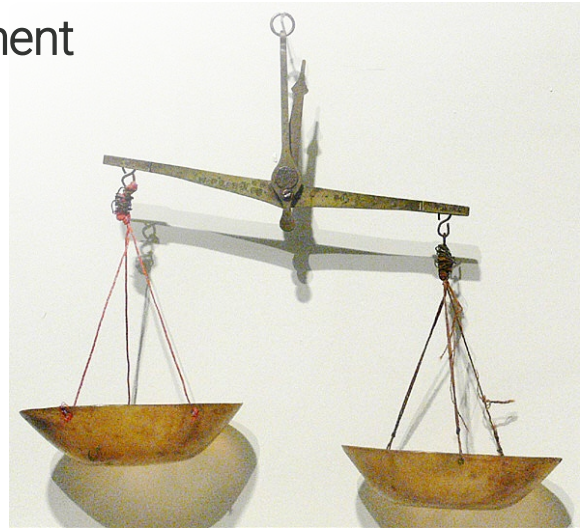
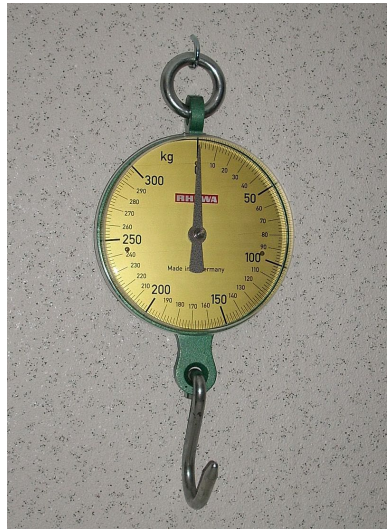
Setting the scene
What are the different ways of quantification?

Standard-based measurement



- Without something of known weight, it's not possible to determine the weight of a sample.

Standard-free measurement



- With known properties of the spring and an understanding of the underlying physics you can directly measure the weight of a sample.
- Still, you would check against something of known weight … just to make sure.

Pictures: https://de.wikipedia.org/wiki/Balkenwaage and /Federwaage

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Setting the scene
Standard-based measurement

- For precise measurements a set of high-quality reference samples is needed.
- Just like in XRF
  - any damage or alteration of or to the sample will directly impact the quality of the measurement results.
  - The comparison against standards does not depend on the environment.
- Unlike in XRF, a set of reference samples can easily be reproduced or extended for a different range or precision.

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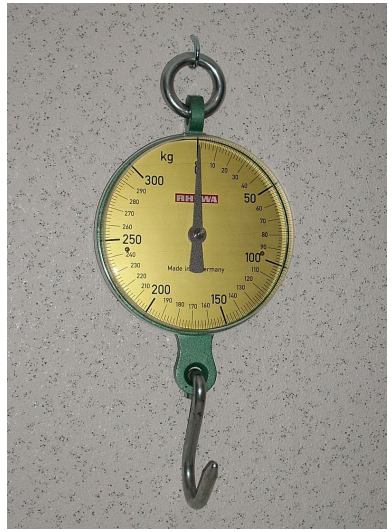
Setting the scene
Measurement based on physics

- Just like in XRF, physical process are fairly well understood.
- First-order processes are easily explained (the gravitational force is elongates a spring until its tension compensates that force).
- The mass *m* then equals the spring constant *k* of the spring divided by the gravitational acceleration *g* times the elongation *x* of the spring.

$$m = \frac{k}{g}x$$



- In order to obtain a higher accuracy, secondary effects need to be taken into account. (local changes of gravity, buoyancy of the object in air, friction, inelastic stress, ...)

- To stay in the picture: the spring constant and the gravitational acceleration at your location would be fundamental parameters, as they are the physical properties that have to be known for the calculation and are tabulated somewhere.

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Setting the scene
Measurement based on physics – FP quantification

- There is an equation that allows the calculation of fluorescence intensities I_{fl} produced by a sample of known composition. (first order effects only!)
- This can be used to calculate spectra from samples with assumed compositions.
- It is an iterative process:

  guess → *spectrum* → *comparison* → *change guess*

  and ultimately a sample composition can be found that produces a spectrum that matches the measurement.
- μ^*, $\tau_{i,E}$, and $Q_i(E, E_{\mathrm{fl}})$ represent the so-called fundamental parameters, which are probabilities for the physical interactions in the fluorescence process.
- They are known (with varying uncertainties, ~ 10 %)

$$I_{\mathrm{fl}} = C_i \cdot K_i \cdot \int_{E_{\mathrm{abs},i}}^{E_{\mathrm{max}}} I_0(E) \cdot \tau_{i,E} \cdot Q_i(E, E_{\mathrm{fl}}) \cdot \frac{1}{\mu^*} \mathrm{d}E$$

μ^*	Attenuation coefficient of the sample
$\tau_{i,E}$	Photoabsorption coefficient
$Q_i(E, E_{\mathrm{fl}})$	Photon production factor
$I_0(E)$	Description of the excitation spectrum
K_i	Instrument parameter
C_i	Concentration(s) of the element(s)

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Setting the scene
Different words for quantification

▪ “Quantification”	What people call a quantification with “acceptable“ error margins.
▪ “Semi-quantitative analysis”	What people call other ways of quantification (error too large).
▪ Standard-based quantification	Use of standards is essential, accuracy and precision can be very high, if the standards are of sufficient quality.
▪ FP quantification	Quantification based on the physics and known instrumentation.
➢ Standard-supported quantification	Results obtained on standard samples were used to adapt “element sensitivities” according to certain sample systems.
➢ Standard-validated quantification	
➢ Standard-less quantification	The quantification works without standards, but the instrument itself has been calibrated (usually with pure elements).
➢ Standard-free quantification	
➢ Reference-free quantification	No standards at all. Knowledge about equipment is as good as it gets today, and the quality of the results is “only” limited by the uncertainties of the fundamental parameters.

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Quantification
Standard-based versus FP quantification

Standard-based

- There have to be some standards (concentration range)
- They have to mirror the sample's structure.
- Origin of reference values?

- If the standards and the samples are equally good, the trueness of the quantification usually is better than FP quantification.

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Quantification
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FP quantification

- Flexibility
- Without basing the quantification on standards it's faster to start measuring
- Traceable uncertainties

- Can be validated
- CAN BE calibrated if trustworthy standards are at hand, but works without…

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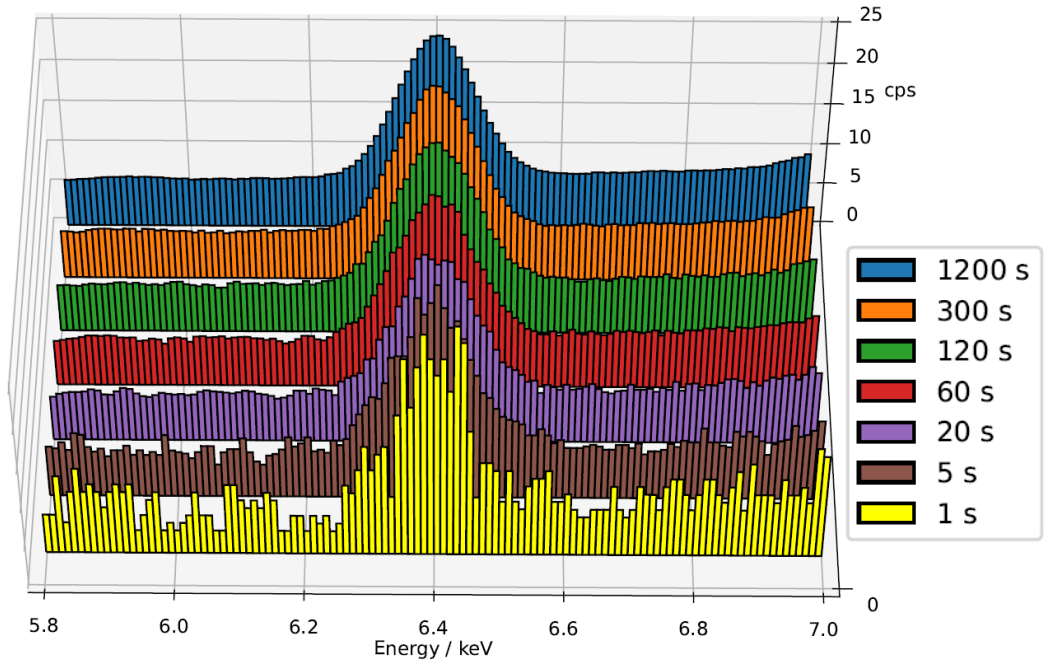
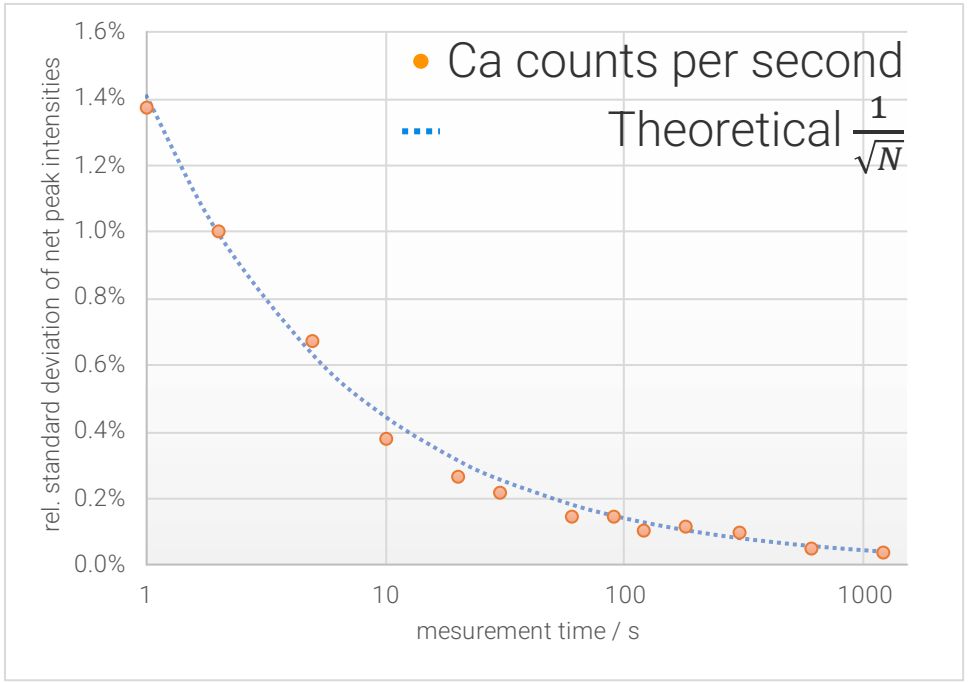
What are prerequisites for quantitative analysis? Uncertainty of the net peak intensity

- The relative error of counting statstics is $\frac{1}{\sqrt{N}}$
- The more counts, the smaller the relative uncertainty of the measurement → it needs time!





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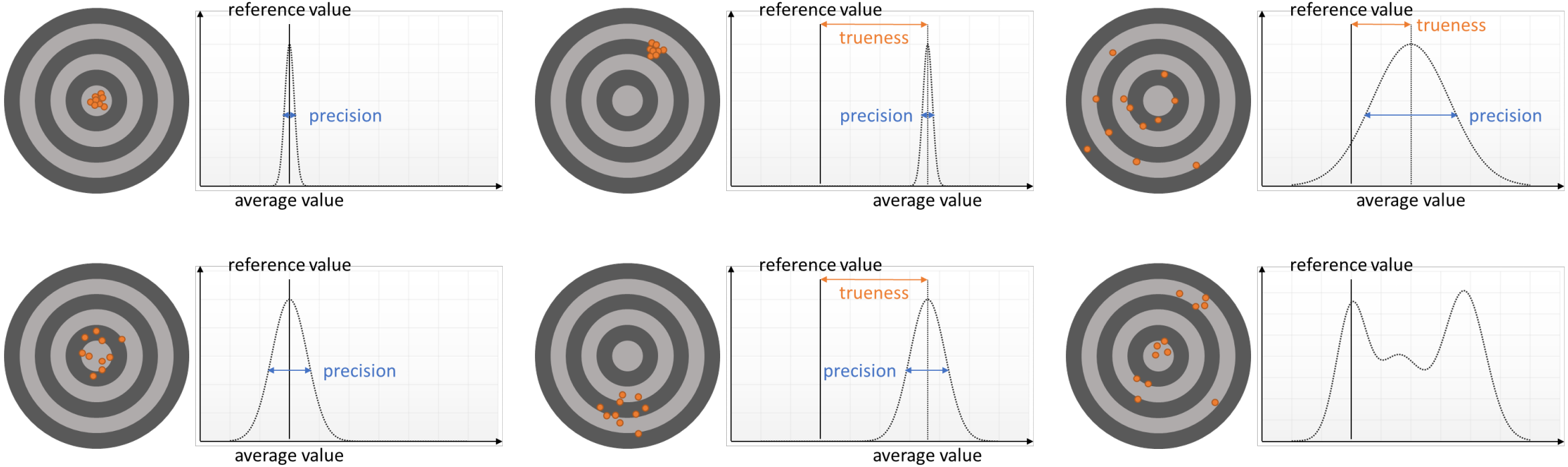
Quantification
What quality to expect?

- Since 1994 ISO 5725-1 defines accuracy as a convolution of trueness and precision.



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What's the composition of a sample?

- Does a rock have "a composition"?
- Powders can be considered homogeneous for bulk-XRF, but what part of the hand specimen was crushed and milled?
- Is that part representative?
- Does the initial hand specimen actually describe the site it's been taken from?
- Is it a true sample?
- (Is "the composition" of a rock really a meaningful analytical question?)

Gypsum sample – hand specimen and powder.

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What's a known sample?

- As can be seen with almost any reference material the spread of published values is ... significant
- Often there is a mismatch between the carefully selected "preferred values" and the certified compositions.

GSR-2 (andesite powder) [National Research Centre of Geoanalysis, , *26 Baiwanzhuang Dajie, Beijing 100037, China*] Info

☐ Select for single values or click chemical item for individual element data

H2O+	**1.5 %m/m - 1.54 %m/m**	2 values compiled
CO2	**3.46 - 3.47 %m/m**	2 values compiled
Na2O	**3.28 - 3.91 %m/m**	23 values (compiled: **3.86 %m/m**)
MgO	**1.38 - 1.88 %m/m**	23 values (compiled: **1.72 %m/m**)
Al2O3	**14.41 - 16.45 %m/m**	23 values (compiled: **16.17 %m/m**)
SiO2	**56.6 - 61.6 %m/m**	23 values (compiled: **60.62 %m/m**)
P2O5	**0.2 - 0.27 %m/m**	22 values (compiled: **0.24 %m/m**)
K2O	**1.68 - 1.9 %m/m**	24 values (compiled: **1.89 %m/m**)
CaO	**4.63 - 5.35 %m/m**	23 values (compiled: **5.2 %m/m**)
TiO2	**0.309 - 0.54 %m/m**	22 values (compiled: **0.52 %m/m**)
MnO	**0.07 - 0.08 %m/m**	22 values (compiled: **0.08 %m/m**)
Fe2O3	**4.38 - 5.03 %m/m**	6 values

GeoReM: A New Geochemical Database for Reference Materials and Isotopic Standards Geostandards and Geoanalytical Research 29 (3) [2005] 333-338

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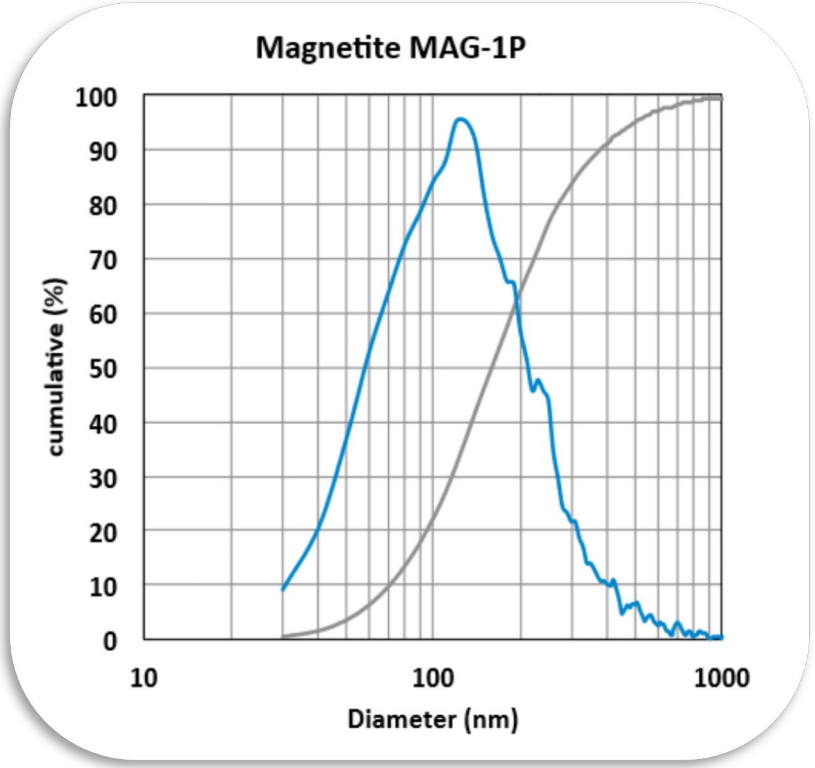
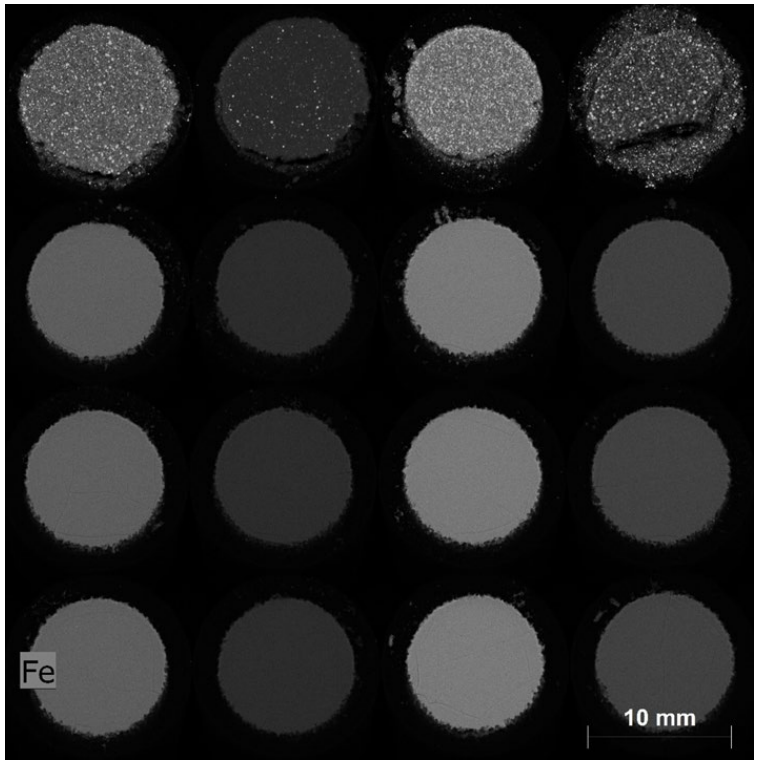
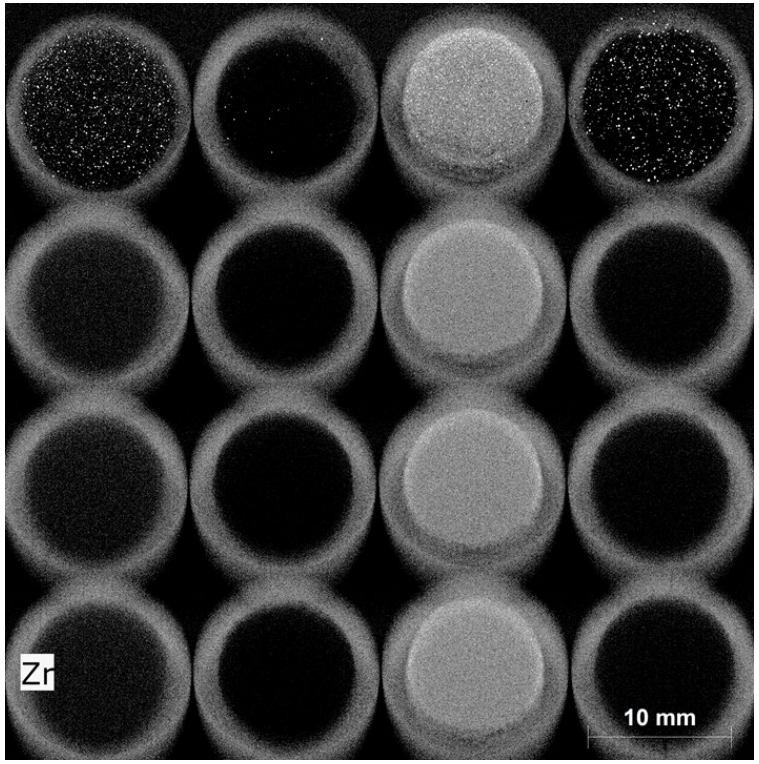
Is there a perfect standard?







- Milling geo SRMs to < 200 nm gives the resulting powder a glass-like quality.
- There is no measurable inhomogeneity anymore. When pressed, they stick without binder. The grains are smaller than the information depth of the elements! → sounds perfect

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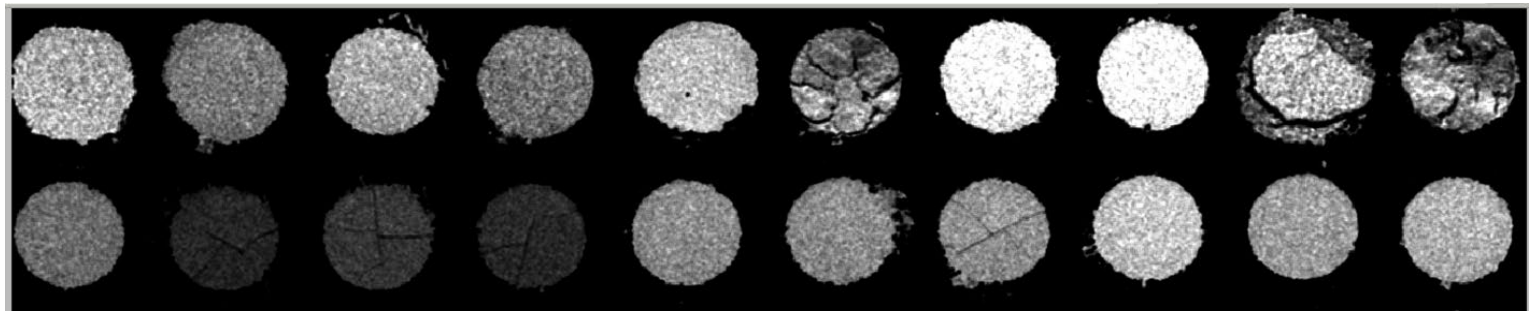
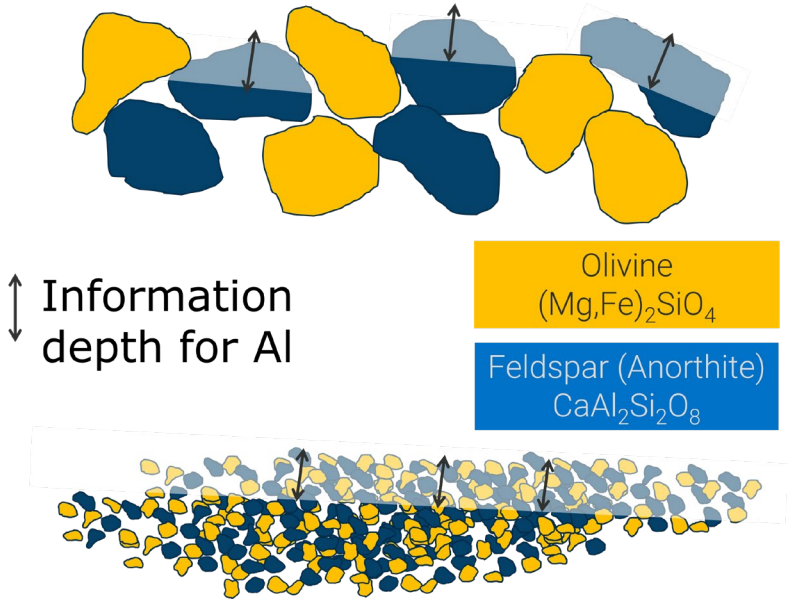
Is there a perfect standard?



Conventionally milled powder (top row) of basaltic samples exhibits much higher Al intensity than the nano-milled samples (bottom row).



For large particles, effectively none of the detected Al fluorescence has interacted with Fe-rich olivine particles.

→ Only if mineral grains are smaller than the information depths, the inter-element effects are according to the sample's composition.

The nano-milled standards can be considered to be ideal for this analytical method ...
But do they reflect the reality (i.e. conventionally milled samples)?

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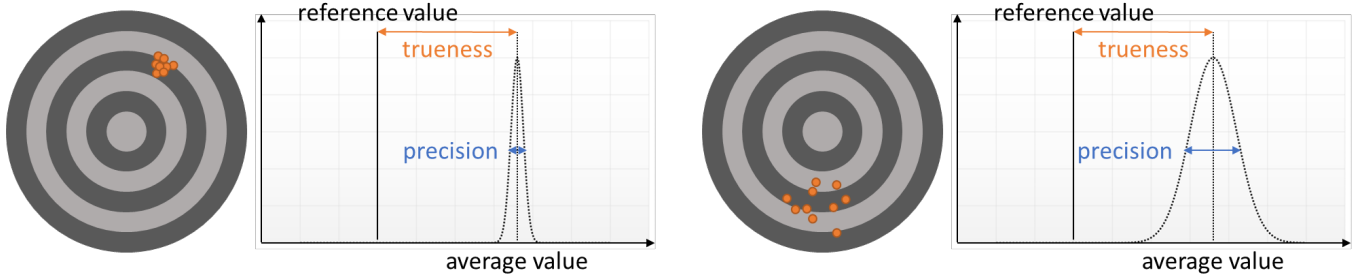
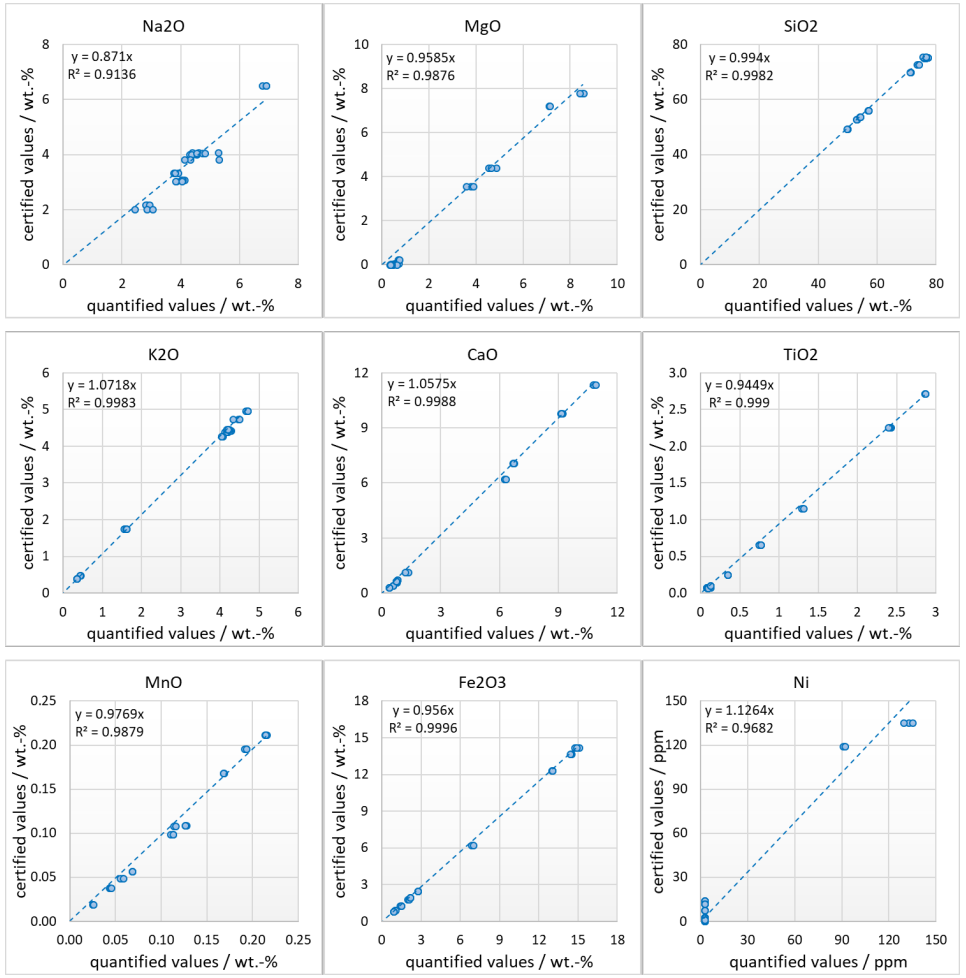
Examples
Major and minor elements in nano-milled geo SRMs

- The recovery rate is very good over a wide concentration range. (especially when considering ~ 50 % “dark matrix”)
- Remember, the quantification assumes a sample composition, based on the selected elements and iteratively calculates all physical effects, like absorption and secondary excitation, and adapts the concentrations until the theoretical spectrum matches the measured one.





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Examples
Major and minor elements in Smithsonian Mineral Standards

Pos	Mineral	Pos	Mineral
1	Anorthite	31	Magnetite
2	Anorthoclase	32	Microcline
3	Apatite (Fluroapatite)	33	Olivine
4	Augite	34	Olivine
5	Chromium Augite	35	Omphacite
6	Benitoite	36	Osumilite
7	Calcite	37	Plagioclase (Labradorite)
8	Chromite	38	Pyrope
9	Corundum	39	Quartz
10	Diopside	40	Scapolite (Meionite)
11	Dolomite	41	Siderite
12	Fayalite	42	Strontianite
13	Gahnite	43	Zircon
14	Garnet	44	$CePO_4$
15	Garnet	45	$DyPO_4$
16	Glass	46	$ErPO_4$
17	YPO_4	47	$EuPO_4$
18	Glass	48	$GaPO_4$
19	Glass	49	$HoPO_4$
20	Glass	50	$LaPO_4$
21	Glass	51	$LuPO_4$
22	Glass	52	$NdPO_4$
23	Glass	53	$PrPO_4$
24	Glass	54	$SmPO_4$
25	Glass	55	$ScPO_4$
26	Glass	56	$TbPO_4$
27	Hornblende	57	$TmPO_4$
28	Hornblende	58	$YbPO_4$
29	Hypersthene	59	Faraday Cup
30	Ilmenite		

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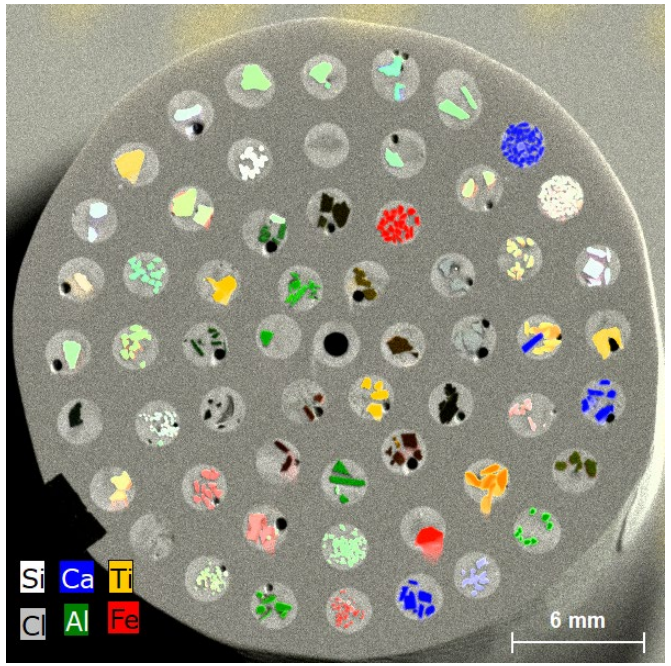
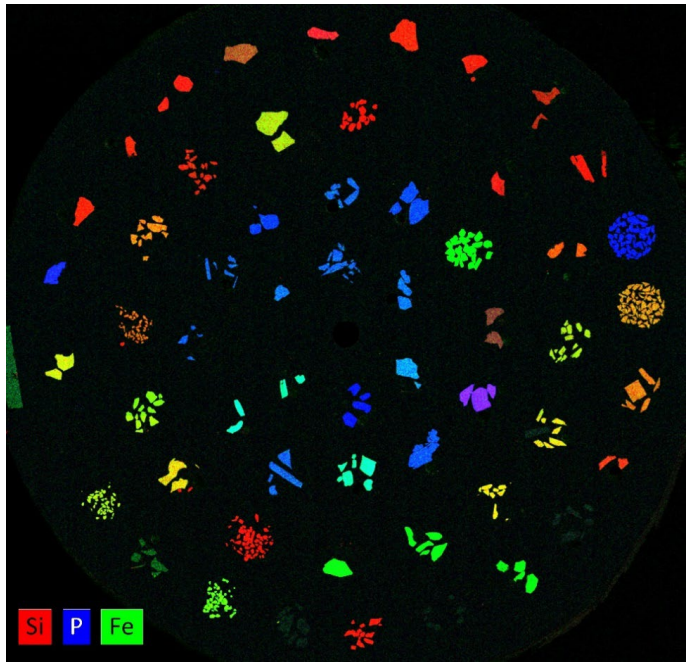
[J. Res. Natl. Inst. Stand. Technol. 107, 681–685 (2002)]

Smithsonian Microbeam Standards



Micro-XRF map



SEM-EDX map

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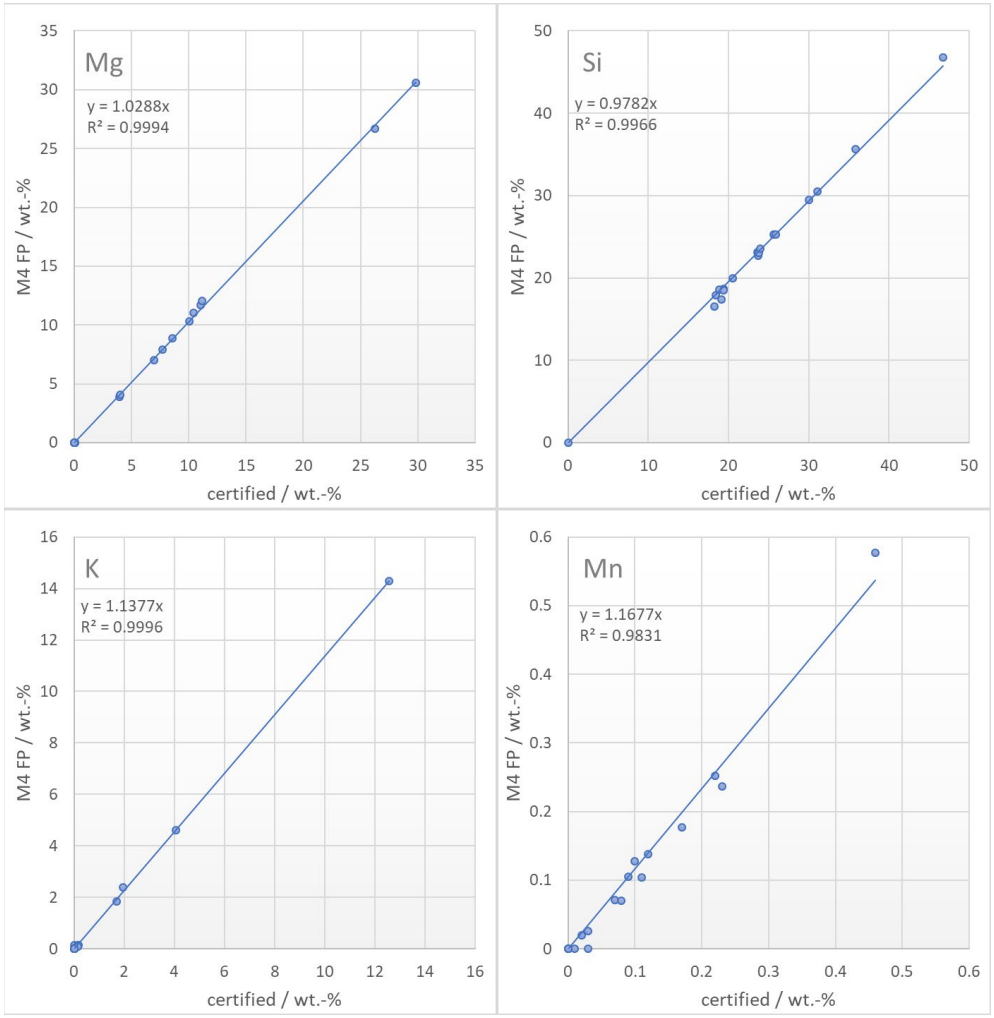
7	Calcite	37	Plagioclase (Labradorite)
8	Chromite	38	Pyrope
9	Corundum	39	Quartz
10	Diopside	40	Scapolite (Meionite)
11	Dolomite	41	Siderite
12	Fayalite	42	Strontianite
13	Gahnite	43	Zircon
14	Garnet	44	$CePO_4$
15	Garnet	45	$DyPO_4$
16	Glass	46	$ErPO_4$
17	YPO_4	47	$EuPO_4$
18	Glass	48	$GaPO_4$
19	Glass	49	$HoPO_4$
20	Glass	50	$LaPO_4$
21	Glass	51	$LuPO_4$
22	Glass	52	$NdPO_4$
23	Glass	53	$PrPO_4$
24	Glass	54	$SmPO_4$
25	Glass	55	$ScPO_4$
26	Glass	56	$TbPO_4$
27	Hornblende	57	$TmPO_4$
28	Hornblende	58	$YbPO_4$
29	Hypersthene	59	Faraday Cup
30	Ilmenite		



- Again, over a wide concentration range there is good linearity between certified values and FP quantification.
- Inter-element effects are “taken care of” by the quantification, making this relation very linear and easy to calibrate.

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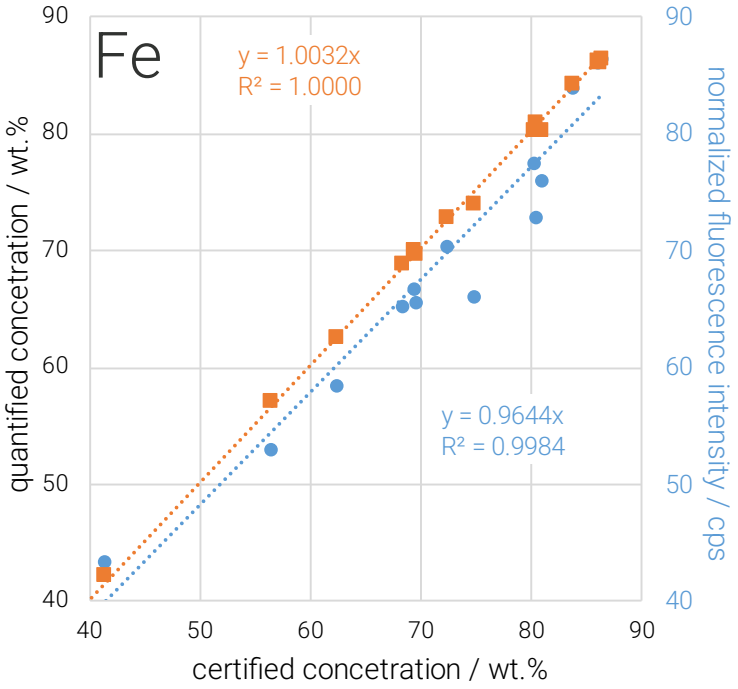
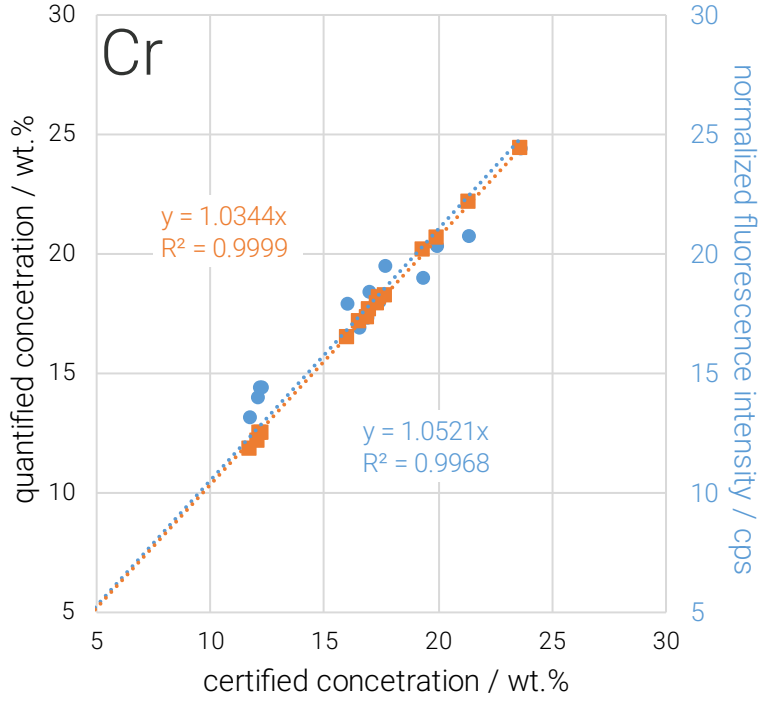
Examples
Mn, Cr, Fe, Ni in stainless steels

- In a stainless steels, there are 3 elements in high concentrations that influence each other significantly: Cr, Fe, and Ni do absorb and enhanve each others fluorescence lines.
- Even though the measured intensities scatter quite a bit, the concentrations have a $R^2 = 1$





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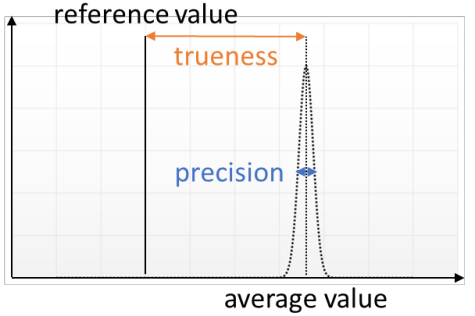
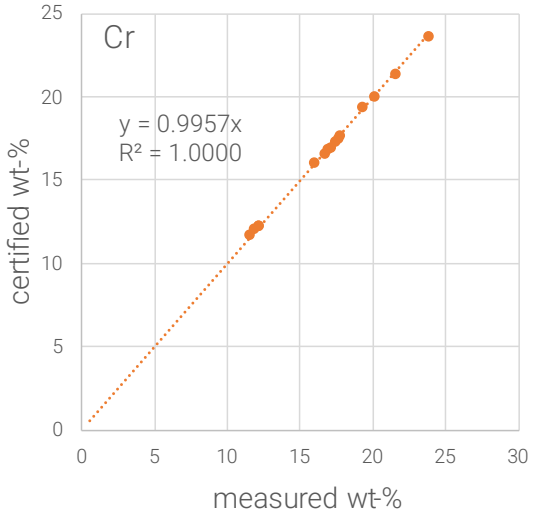
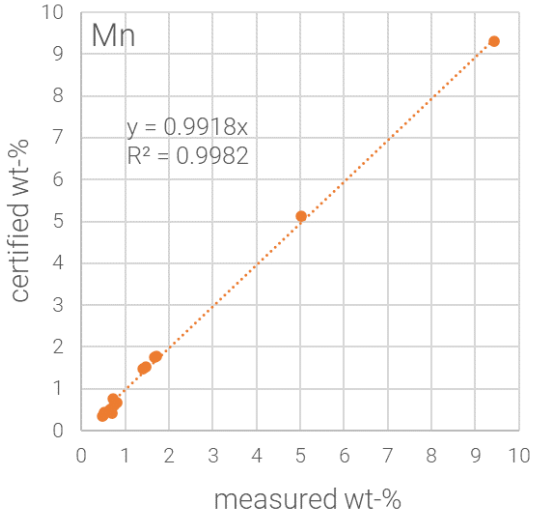
Examples
Mn, Cr, Fe, Ni in stainless steels

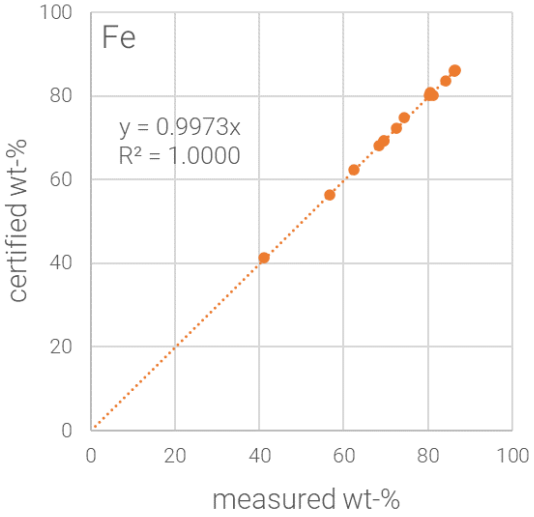
- In stainless steels the precision of FP quantification is very high.
- In metals diffraction peaks can cause wrong values for minor elements.

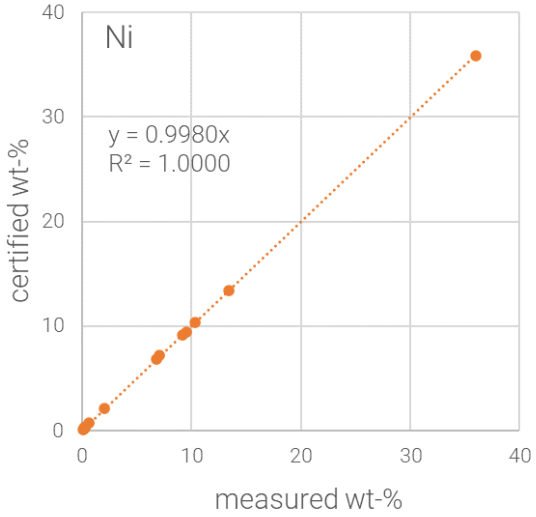


- The trueness can be improved using one sample of known composition.









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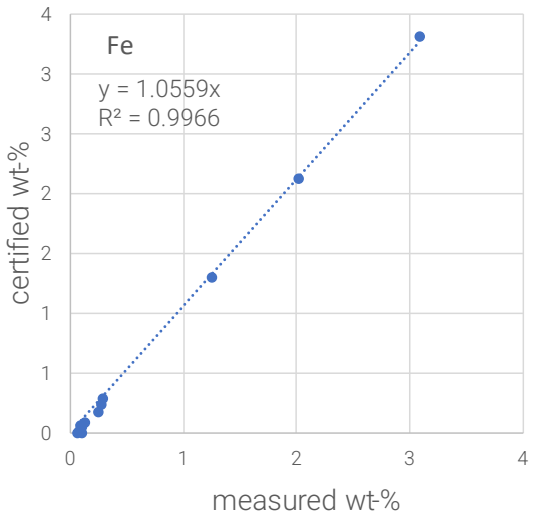
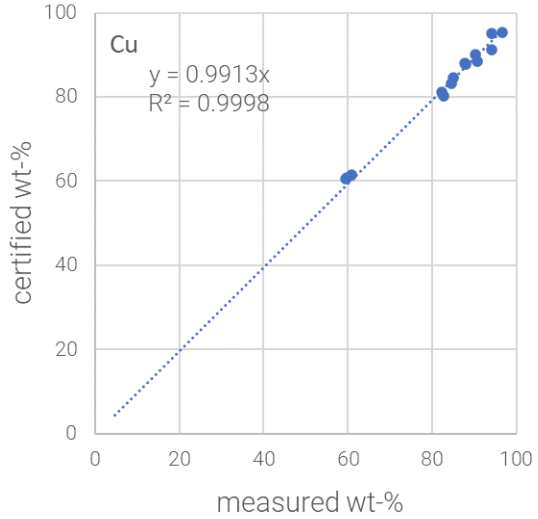
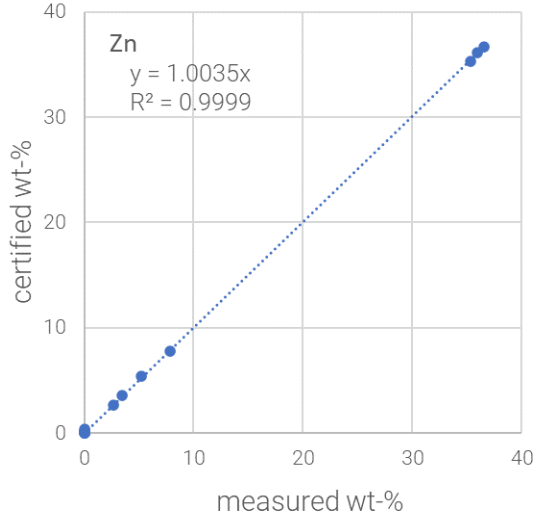
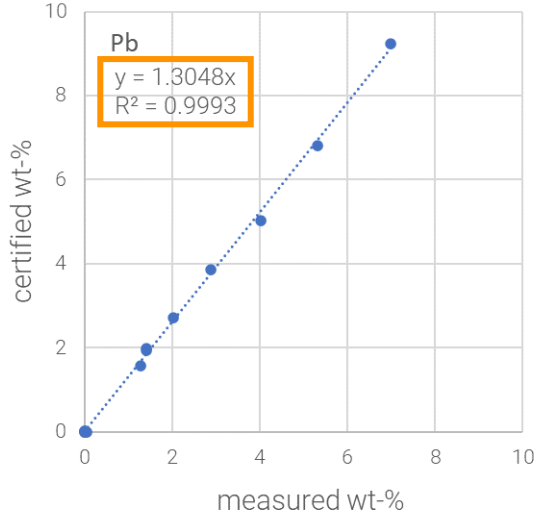
Examples
Cu, Zn, Sn, and Pb in copper-alloys

- In Cu alloys the quantification, again, takes care of the complex inter-element effects.
- Over the whole concetration range, there is very nice correlation.
  ...for most elements
- Note that Lead has a $R^2 = 1$ but is consictently off by 30 %









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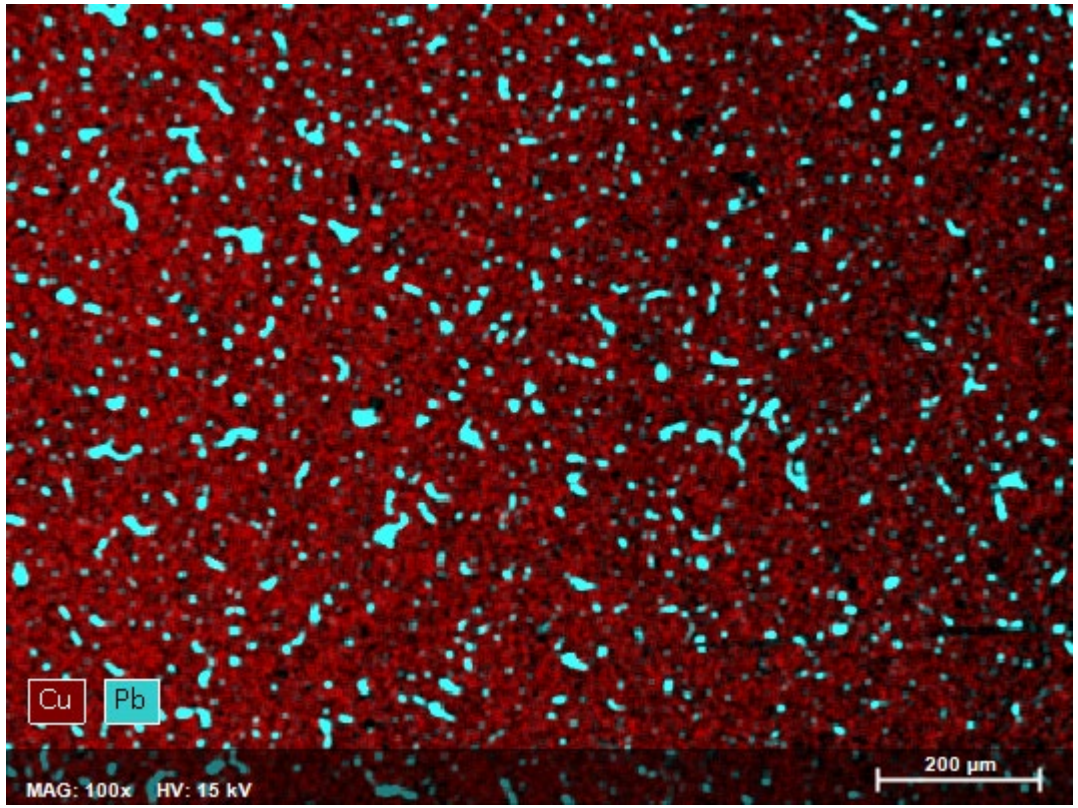
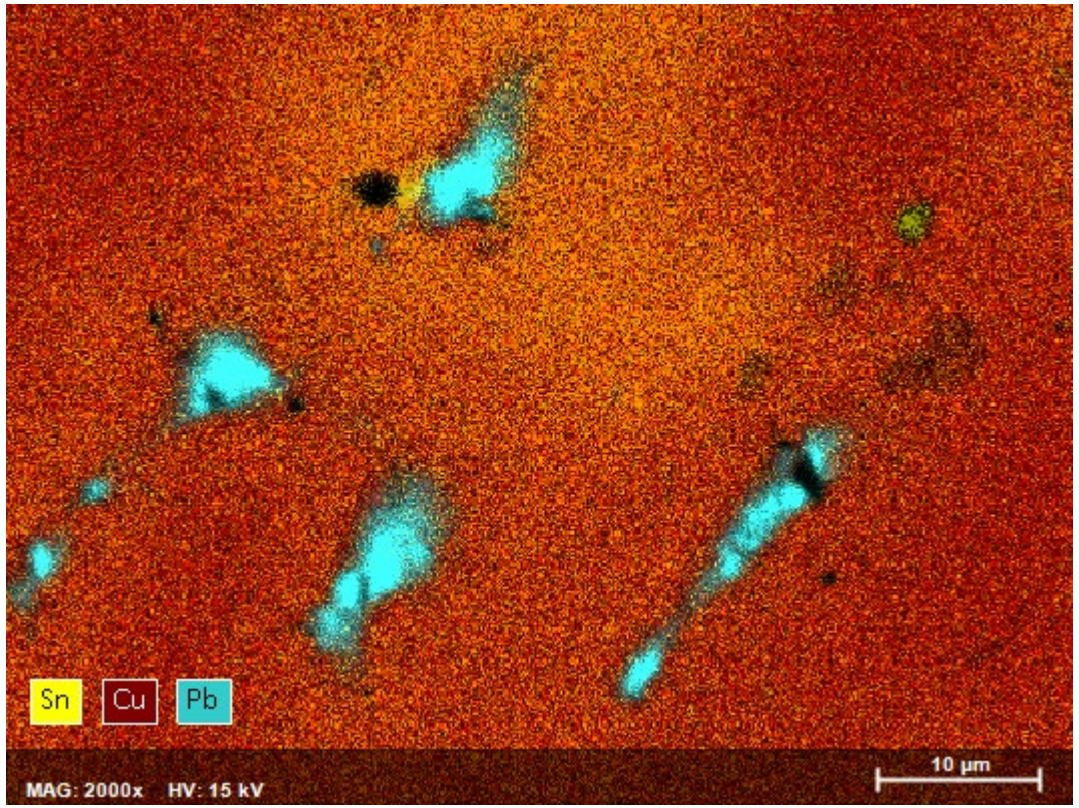
Examples
Exsolutions in copper-alloys

- Cu alloys are heterogeneous on a scale that micro-XRF notices!
- Lead forms small “islands” → most Pb radiation comes from a Pb-rich part of the sample.





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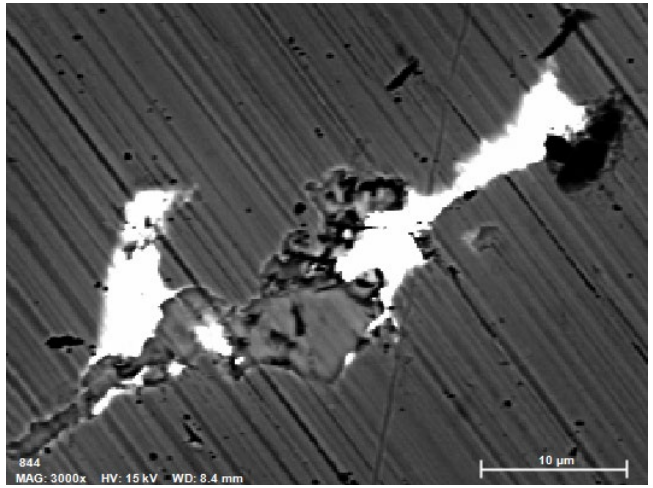
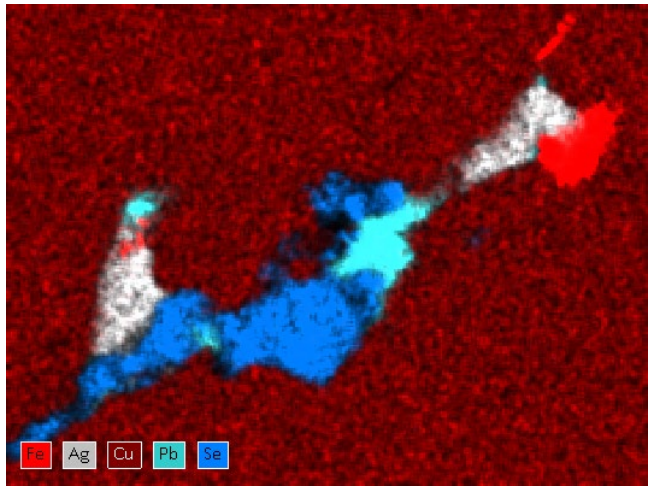
Examples
Exsolutions in copper-alloys





- All elements in the alloy form exsolutions, but to different extent.
- Larger scale measurements will not notice the heterogeneities (see scale).
- Luckily it's the same for standards
  - The effect is automatically corrected for by standard-based quantification!

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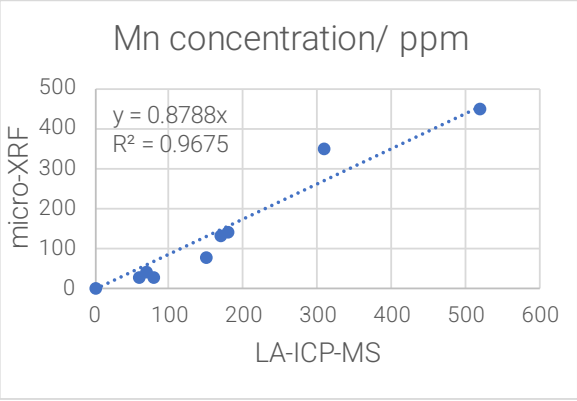
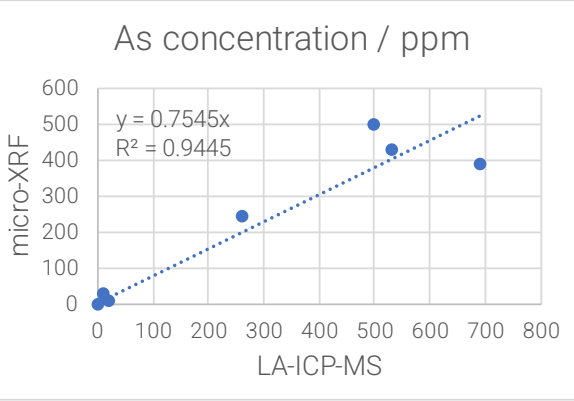
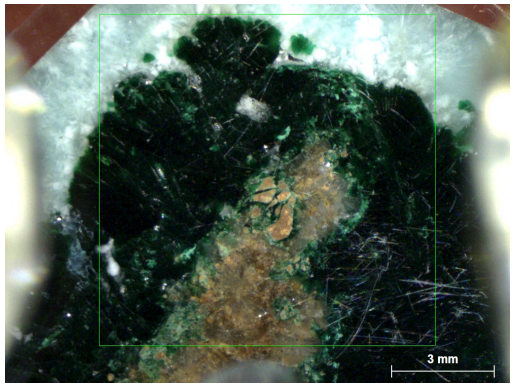
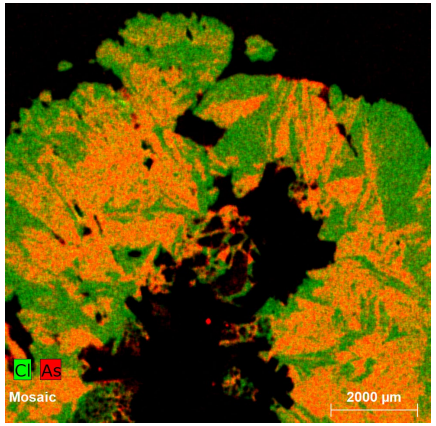
Examples
Trace elements and crystal zonation

Atacamite: Individual Crystal Trace Element Zonation
Key element concentrations correspond to LA-ICP-MS Results

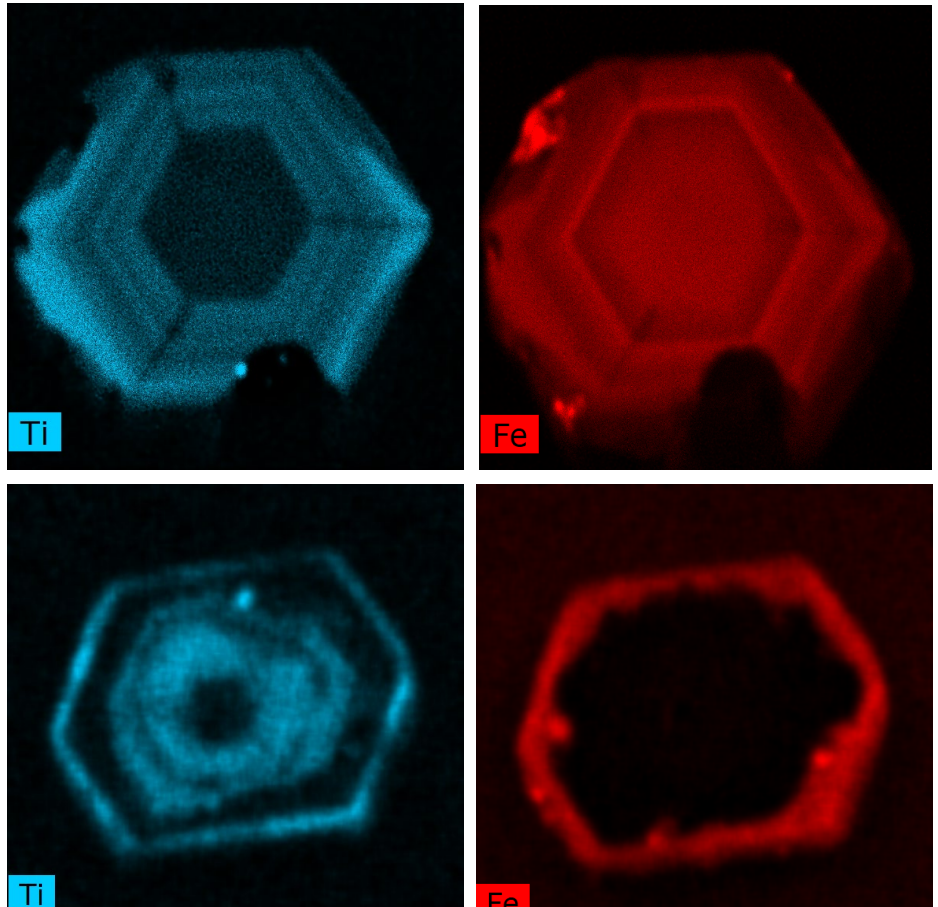








Sapphires:
Individual Crystal Trace Element Zonation



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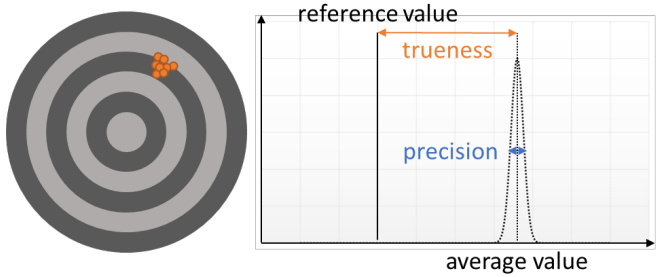
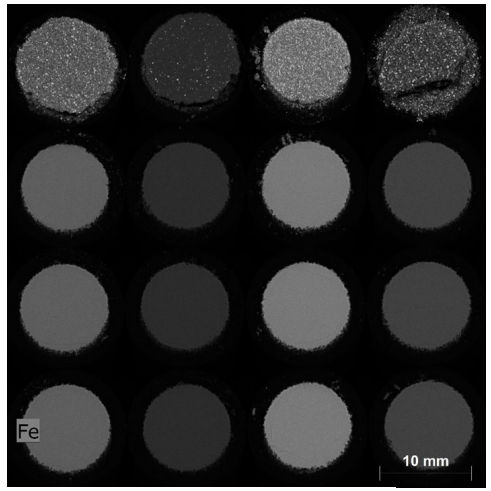
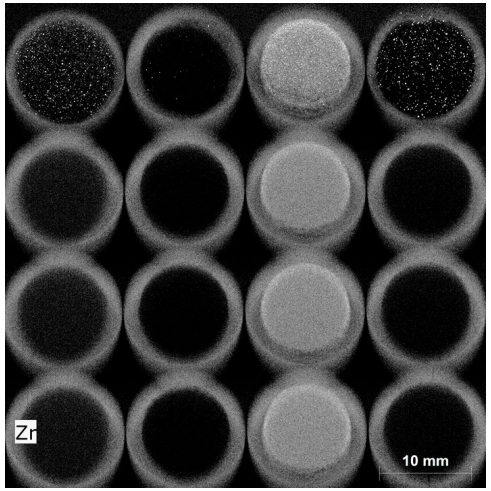
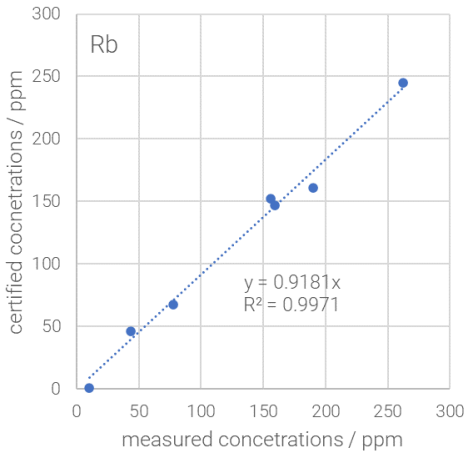
Today's quality of FP quantification ... when applied to ideal samples

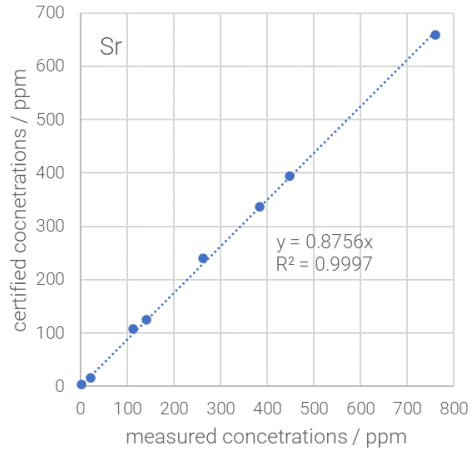
- In ideal samples, trace element quantification is even more stable:

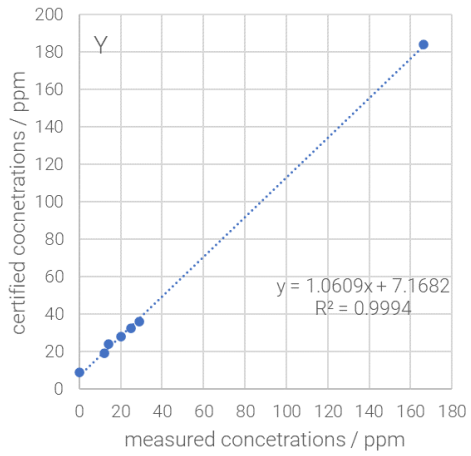


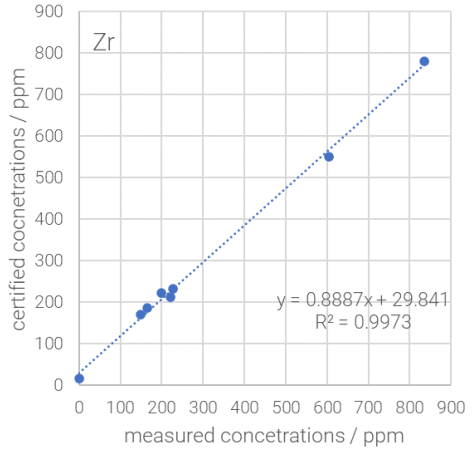












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Today's quality of FP quantification
Where is the limit for result quality?

- The same quantification algorithm can be applied to copper alloys, stainless steels, mineral samples, either carbonates, sulfates or oxides, ores, layered samples, glasses, ceramics.
- The recovery rate may not be 1 but the correlation is linear, thus the methods an easily be type-calibrated.
- One trustworthy standard can be enough, since all the results fall on one line.

- Usually the quality of the results is limited by the sample itself much more than by the FP algorithm
  - nano-milled powders and glasses are ideal samples and give "perfect" correlations.

- So ... How much help can standards be to improve the quality of this approach?

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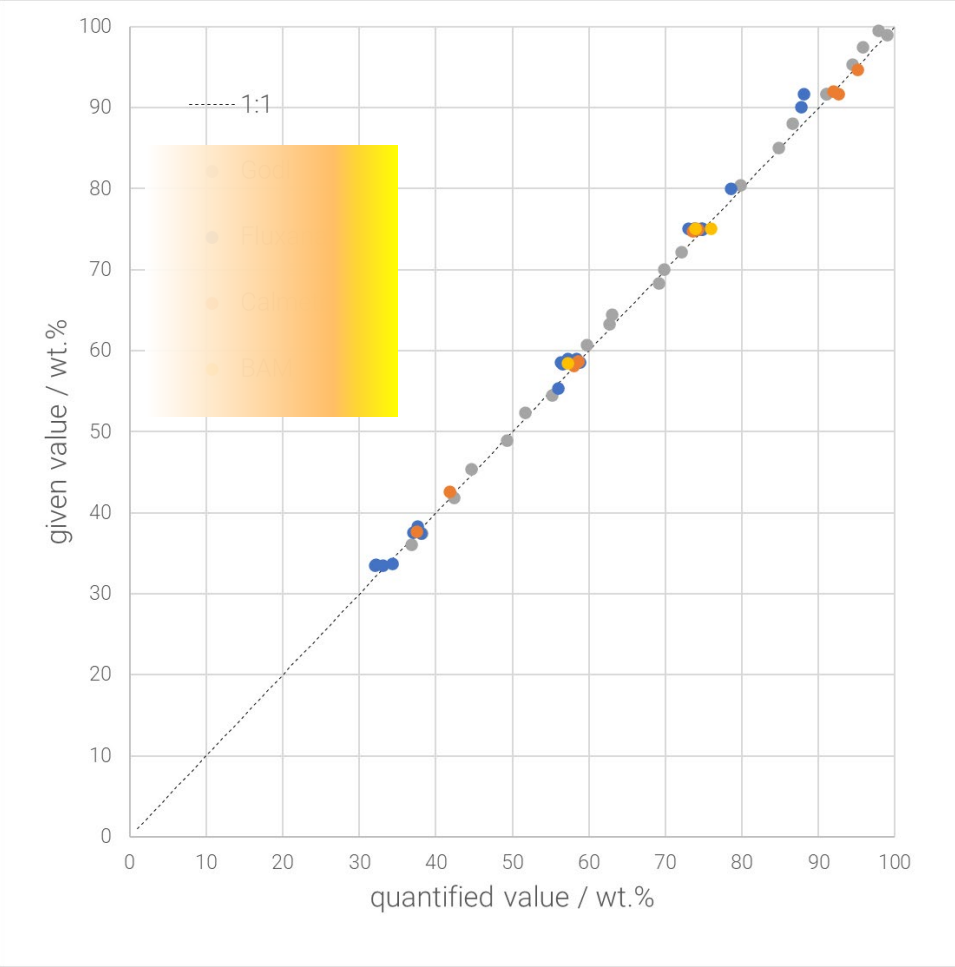
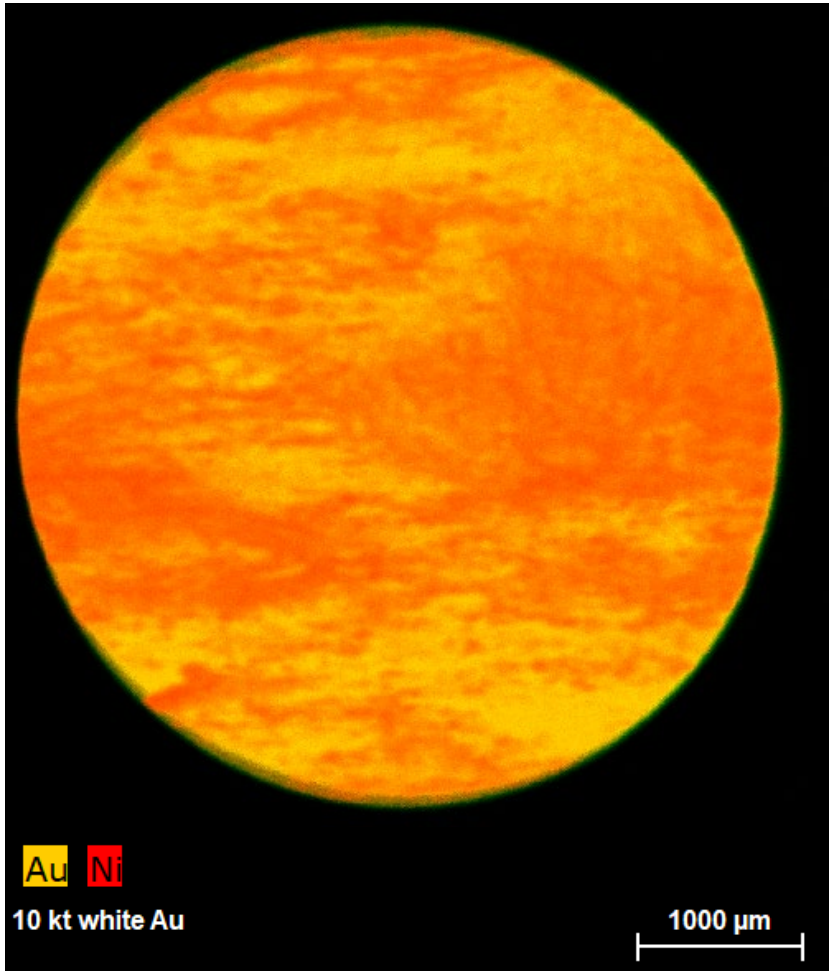
Using reference samples
Gold References from different manufacturers



- Overall, the correlation looks good over the whole concetration range and for different sources for the reference materials.
- But: the quality of some of these standards (or their certified values) is not sufficient to calibrate FP quantification.
- Some examples:



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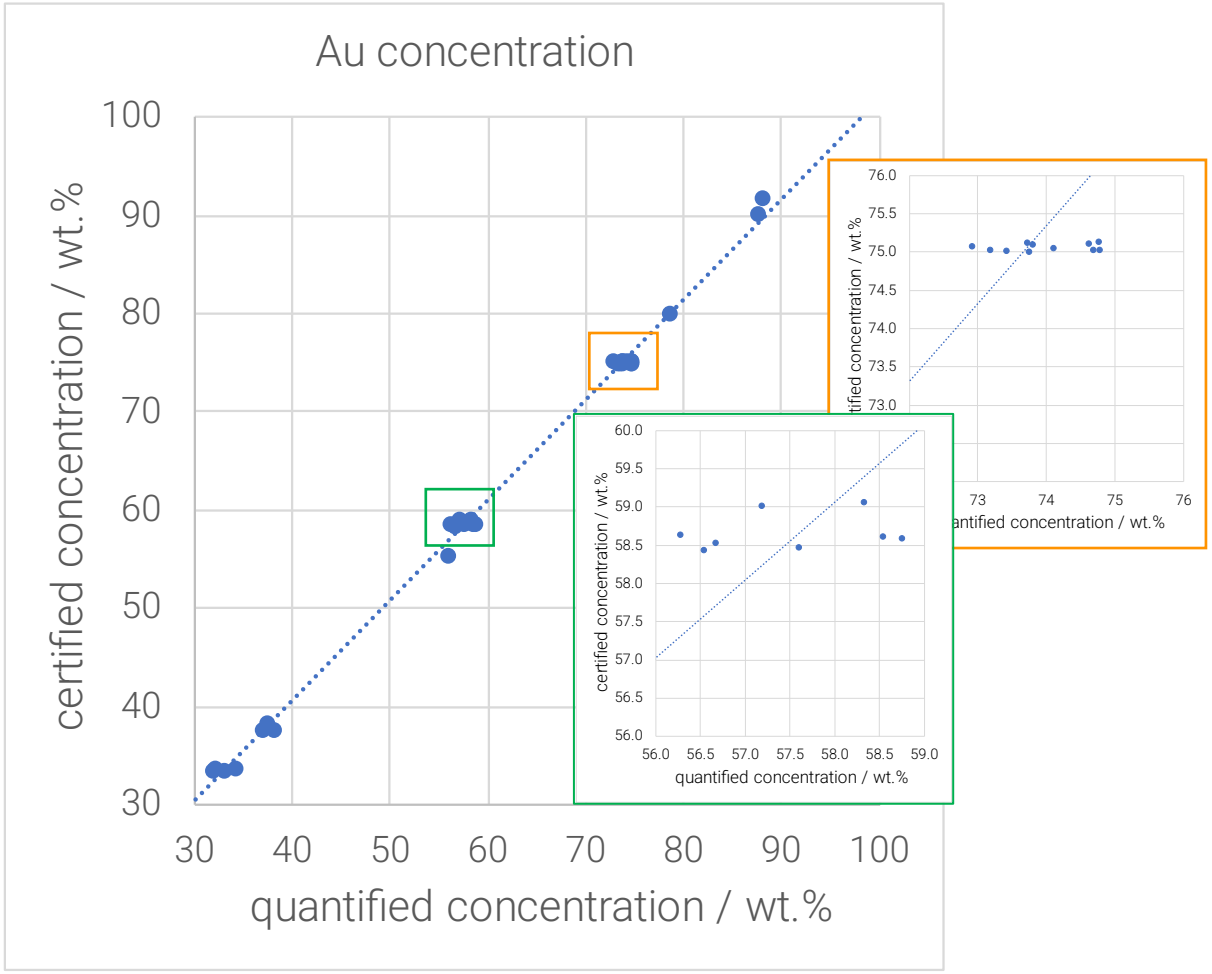
Using reference samples
Reference values based on other XRF



- Given the overall performance of FP quantification, it is save to assume that there is something wrong with these certified values.
- According to the supplier, the reference values were themselves obtained by XRF measurements.
- The reference values are stated with a precision of 2 post-comma-digits ...

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FP Quantification
Today's limits of the algorithm

- The uncertainties of the fundamental parameters:
  - depending on the element an the spectral range they can as high as 40 % (for very light elements), but usually are well below 5 %.

- The instrument parameter is of great importance:
  - Each individual component in the beam path contributes to the overall uncertainties.
  - The uncertainty introduced by the geometry is significant.

$$I_{\mathrm{fl}} = C_i \cdot K_i \cdot \int_{E_{\mathrm{abs},i}}^{E_{\max}} I_0(E) \cdot \tau_{i,E} \cdot Q_i(E, E_{\mathrm{fl}}) \cdot \frac{1}{\mu^*} \,\mathrm{d}E$$

μ^*	Attenuation coefficient of the sample
$\tau_{i,E}$	Photoabsorption coefficient
$Q_i(E, E_{\mathrm{fl}})$	Photon production factor
$I_0(E)$	Description of the excitation spectrum
K_i	Instrument parameter
C_i	Concentration(s) of the element(s)

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Summary

- Micro-XRF is a method designed to analyse and understand samples which are heterogeneous (> 50 µm).
- The accuracy of FP quantification is often higher than the element variations in heterongeneous samples.
- Quantifying each individual (homogeneous) part of the sample based on standards, is a huge effort.
  - It takes time to select the individual quantification methods.
  - It takes huge amounts of time to monitor the validity of all the different calibrations.

  (What is the analytical benefit of a high precision quantification of tiny areas in a heterogeneous sample?)
- FP quantification puts the quantified values on a straight correlation line. → relative changes easily assessible
- FP quantification is accurate enough to validate the quality of standards used for calibration.
- Trustworthy standards CAN be used to calibrate the quantification and increase the accuracy.
- Using small sets of standards to type-calibrate is much more time- and cost-efficient than properly calibrating the instrument geometry and its individual components (windows, detector, lens, a.s.o.).

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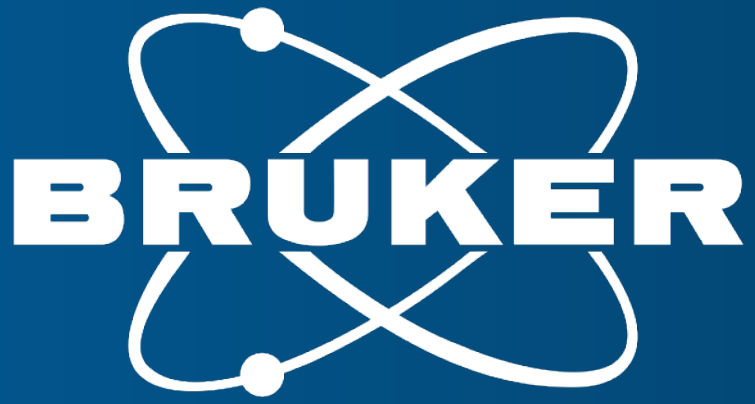

Innovation with Integrity

Thank you!

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