Different Approaches to Bulk Quantification

Bruker Nano Analytics, Berlin, Germany
Webinar, June 01, 2017

M4 TORNADO Webinar
Outline

- Introduction
  - Presenters
  - The M4 instrument
  - Micro-XRF
- Bulk quantification
  - The basics
- Examples
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  - Lucas-Tooth quantification: Au-alloys
  - Polynomial calibration: S in oil
- Live part
  - Polynomial calibration: oxidic samples
- Summary

M4 TORNADO Webinar
Presenters / Moderators

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M4 Tornado micro-XRF spectrometer
Standard configuration

30 W micro-focus Rh tube with polycapillary lens
for excitation spot sizes < 25 µm (for Mo-Kα)
Option: second X-ray tube for different excitation conditions (collimated)

30 mm² silicon drift detector (SDD)
with energy resolution < 145 eV (for Mn-Kα)
Option: second detector with independent SPU for double pulse throughput
Option: 60 mm² detector(s)

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

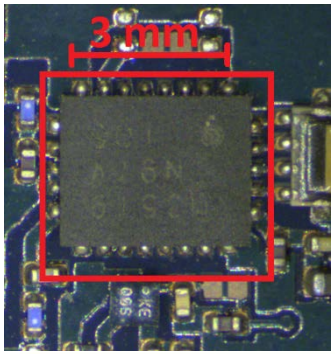
Sample stage with measureable area of 190 mm x 160 mm

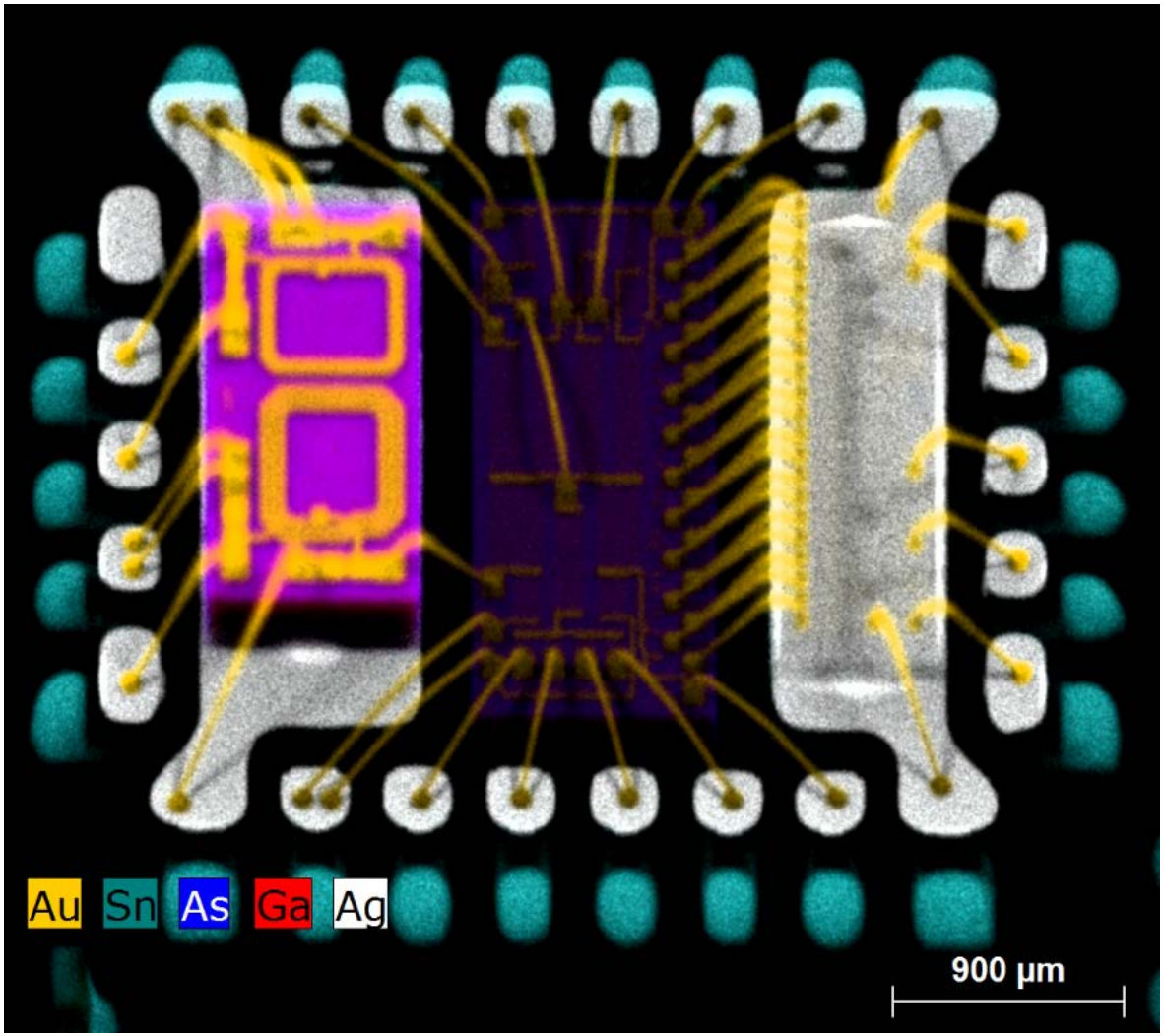
Maximum sample height 120 mm, maximum sample weight 5 kg

Sample stage speed up to 100 mm/s, minimum step size 4 µm

Micro-XRF features and benefits
At a glance

- Little or no sample preparation
- Non-destructive
- Elemental information
- Small spot analysis
- Information from within the sample
- Large-scale
- Quantification

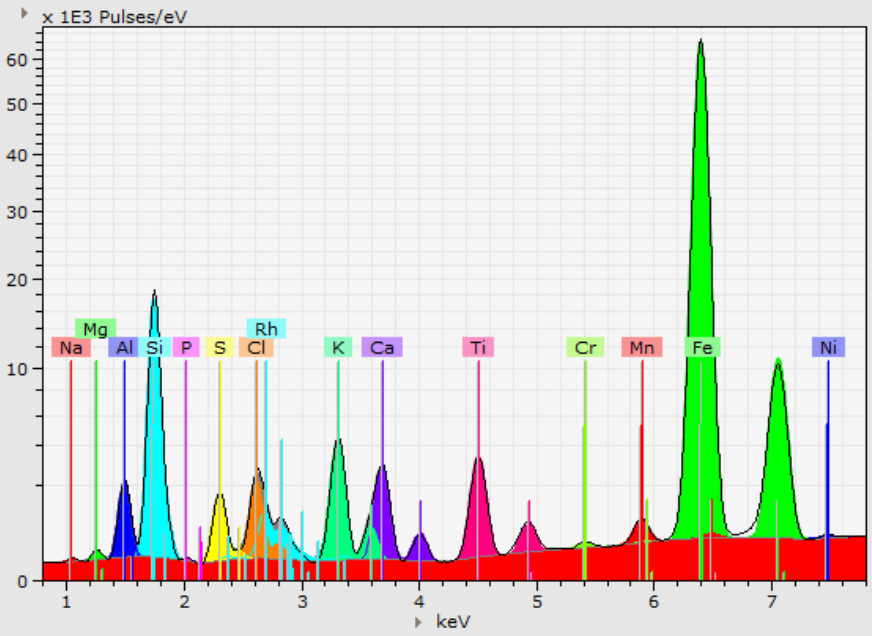




Bulk Quantification
The basics – what means quantification?

The aim is to derive the concentration of an element within a sample from the measured fluorescence signal of the respective element

This prerequisites a correlation between the concentration and the measured fluorescence intensity



Bulk Quantification
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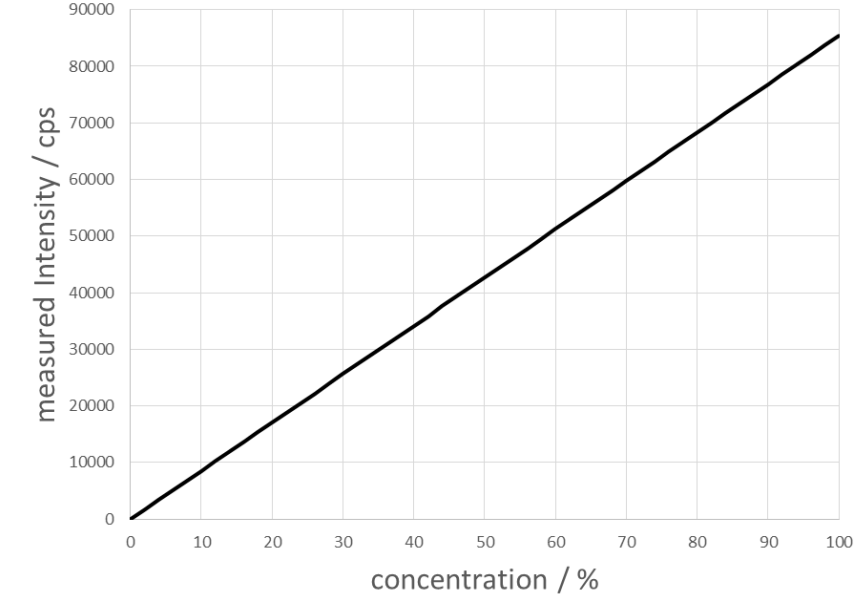
Ideally this correlation is linear



Bulk Quantification
The basics – what means quantification?

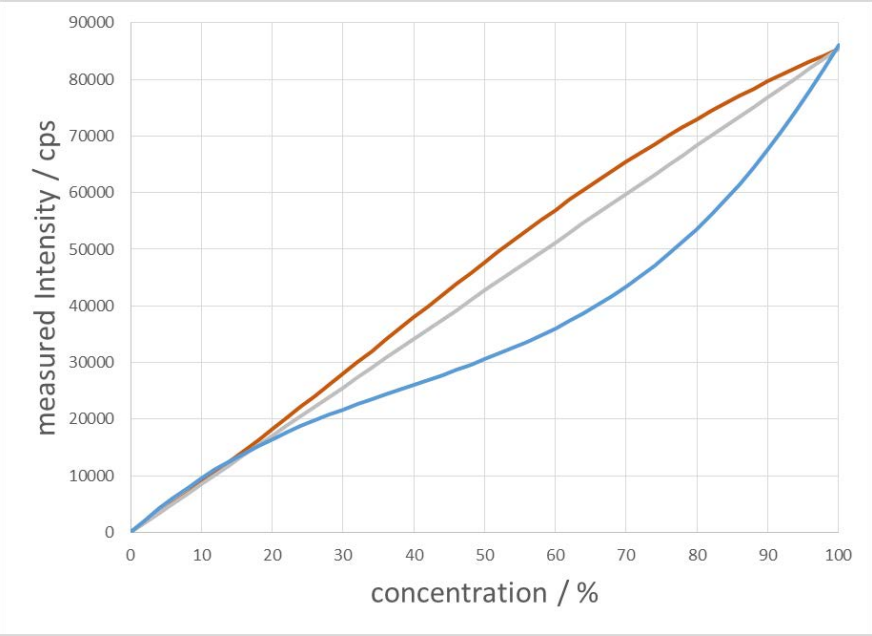
The aim is to derive the concentration of an element within a sample from the measured fluorescence signal of the respective element

This prerequisites a correlation between the concentration and the fluorescence intensity

Ideally this correlation is linear

In reality **inter-element effects** cause deviations from perfect linearity

To correlate measured intensities to elemental concentrations **quantification models** are needed



These models can be of **different complexity** and should reflect the sample systems complexity

Bulk Quantification
The basics – quantification models

There are several ways of quantification. These can be sorted in three groups:

- Physical models (Fundamental parameter methods)
  - Calculating with **known cross sections and probabilities** of “all” physical processes taking place
  - No standards needed
  - Sample must fit the model
- Mathematical models (Empirical methods)
  - Direct correlation between measured intensities and concentrations
  - measured spectra are compared to **sufficiently similar reference spectra**
  - (many) standards needed
- Mixed models
  - Either **standard-supported FP** or FP-supported empirical methods

Bulk Quantification
The basics – quantification models

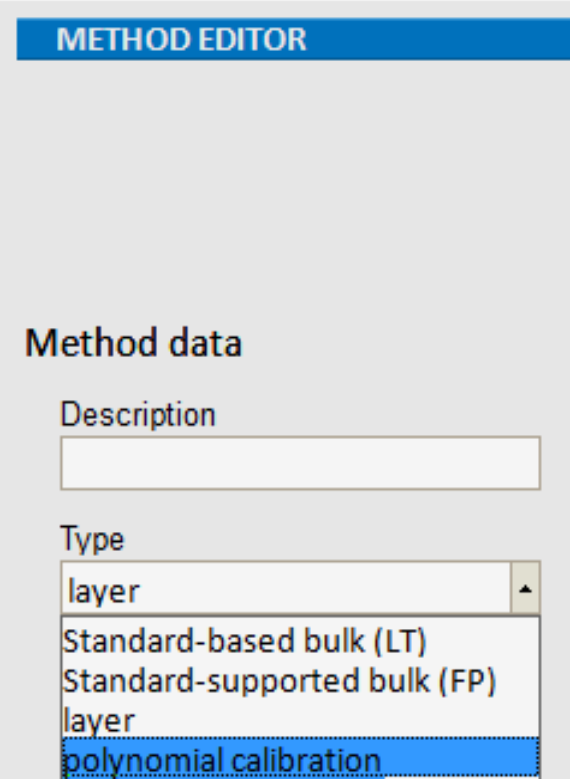
The M4 software already offers the MQuant FP routine which can be adapted to specific sample types (Type calibration)

→ see Webinar and/or Lab Report (XRF 465) on steel quantification

The XMethod software package is a tool to manage standards and additional quantification methods

- layer FP (not discussed here)
- bulk FP with multi-standard calibration (non-linear, offset)
- Lucas-Tooth (simple math, fast for multi-element samples)
- Polynomial calibration

Bulk Quantification
The basics – XMethod

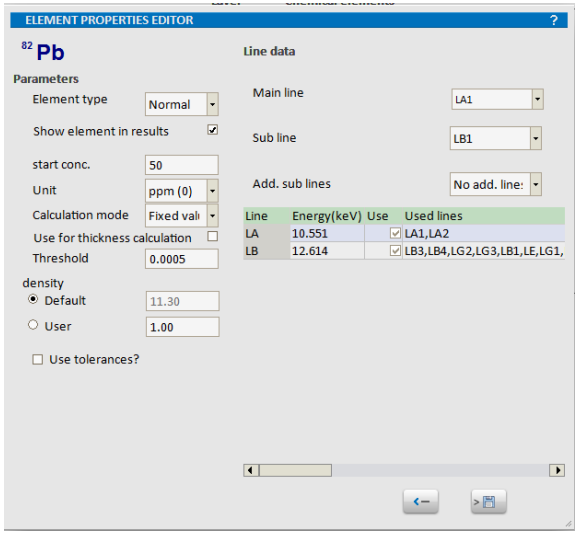


XMethod is an add-on to the M4 software.

It provides a database for standards and method development and offers several quantification and calibration models which can be selected and adapted.

The XMethod software package allows to calibrate the quantification method if standards are available or to create non-calibrated FP methods.

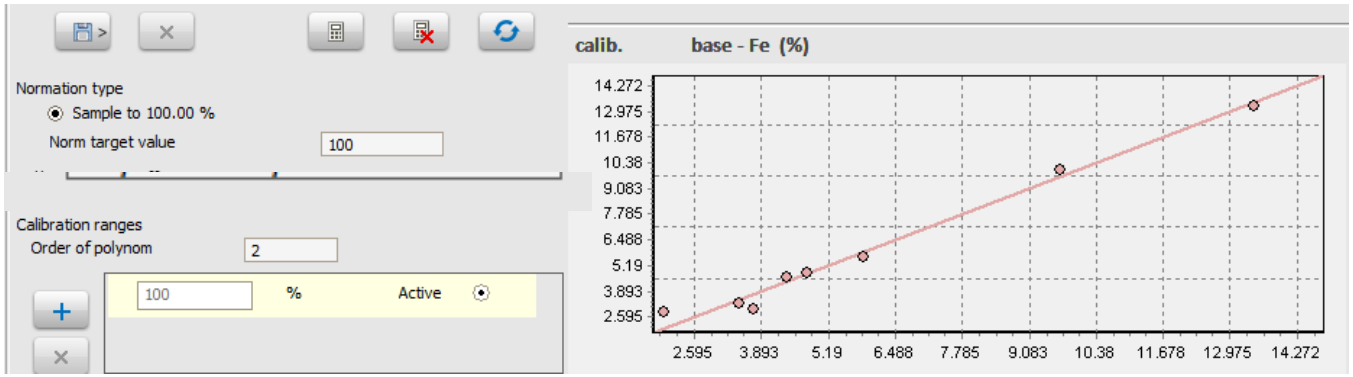
Bulk Quantification
The basics – XMethod



The software provides a variety of options for optimizing methods. These options include different models for deconvolution, selection of used fluorescence (K or L-series, or even change from Lα to Lβ).

Most quantification models allow for different calibration curves for each individual element.

The created methods can be used directly in the M4 Tornado software.



Standard-supported FP
Sherman's equation

One of many ways to write down Sherman's equation:

$$I_{\mathrm{fl},i} = K_i \cdot \int_{E_{\mathrm{abs},i}}^{E_{\max}} \int_{x=0}^{D} I_0(E) \cdot e^{\frac{-\mu_S(E)\cdot\rho_S\cdot x}{\sin(\varphi_{\mathrm{in}})}} \cdot C_i \cdot \tau_{i,E} \cdot Q_i(E, E_{\mathrm{fl}}) \cdot e^{\frac{-\mu_S(E_{\mathrm{fl}})\cdot\rho_S\cdot x}{\sin(\varphi_{\mathrm{out}})}} \cdot \frac{\Omega}{4\pi} \cdot \varepsilon^{\mathrm{D}} \, \mathrm{d}x \, \mathrm{d}E$$

Excitation spectrum (as it reaches the sample)

Attenuation of excitation radiation when penetrating into the sample

Sample composition and interaction probabilities

Attenuation of fluorescence radiation when leaving the sample

Solid angle of detection and detector sensitivity

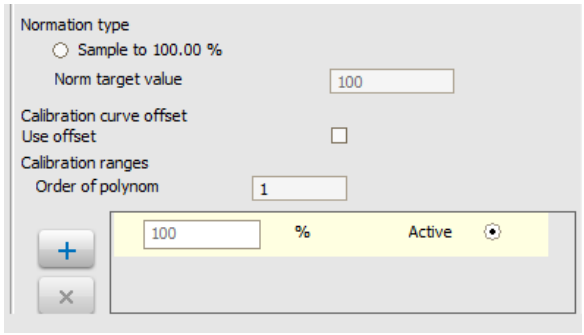
Instrument sensitivity for the respective element

Standard-supported FP
Al in Cu-alloys

- Light element in heavy matrix → vastly different information depths
- Uncertainty of fundamental parameters
- Mobility of Al and Cu atoms?

Calibration samples

	Layer		Cu(%)		Ni(%)		Fe(%)		Mn(%)		Cr(%)		Al(%)		Sn(%)		Pb(%)		Zn(%)	
	Parameter		Std	FP	Std	FP	Std	FP	Std	FP	Std	FP	Std	FP	Std	FP	Std	FP	Std	FP
No.	Sample	W.																		
97	82B CDA 655	1	95.30	97.54	0.01	0.02	0.08	0.18	1.04	0.84	0.00	0.04	0.00	0.68	0.02	0.06	0.01	0.01	0.38	0.63
92	77B CDA 510	1	95.20	95.80	0.00	0.01	0.00	0.08	0.00	0.00	0.00	0.05	0.00	0.42	4.66	3.40	0.02	0.01	0.01	0.24
96	81B CDA 642	1	91.20	93.22	0.00	0.01	0.05	0.13	0.01	0.00	0.00	0.04	6.70	5.94	0.01	0.13	0.01	0.14	0.18	0.39
89	72B CDA 314	1	90.08	89.83	0.00	0.01	0.01	0.10	0.00	0.00	0.00	0.06	0.00	0.56	0.03	0.07	1.99	1.39	7.81	7.99
94	79B CDA 623	1	88.40	89.31	0.08	0.07	2.13	2.05	0.16	0.12	0.00	0.03	9.19	7.74	0.02	0.49	0.00	0.00	0.01	0.20
98	84B CDA 706	1	87.89	87.61	10.03	9.73	1.30	1.19	0.62	0.50	0.00	0.05	0.00	0.60	0.01	0.09	0.01	0.02	0.08	0.20
93	78B CDA 544	1	87.70	89.58	0.08	0.06	0.02	0.11	0.00	0.00	0.00	0.08	0.00	0.59	4.73	3.10	3.87	2.83	3.55	3.65
99	86C CDA 836	1	84.60	86.19	0.27	0.23	0.24	0.31	0.00	0.00	0.00	0.10	0.00	0.59	4.37	3.22	5.03	3.92	5.38	5.44
101	91C CDA 932	1	83.20	85.65	0.46	0.43	0.03	0.11	0.00	0.00	0.00	0.07	0.00	0.40	6.77	5.39	6.80	5.19	2.62	2.76
95	80B CDA 630	1	81.20	82.39	4.69	4.65	3.31	3.13	0.54	0.45	0.00	0.02	10.19	9.03	0.02	0.13	0.01	0.01	0.08	0.19
102	92C CDA 937	1	80.20	84.39	0.35	0.33	0.00	0.16	0.00	0.00	0.00	0.03	0.00	0.44	9.70	7.58	9.23	6.87	0.04	0.21
90	73B CDA 360	1	61.50	61.56	0.06	0.05	0.17	0.30	0.00	0.00	0.00	0.02	0.00	0.55	0.15	0.03	2.71	1.99	35.30	35.51
100	87B CDA 857	1	60.90	60.87	0.00	0.08	0.29	0.31	0.01	0.01	0.00	0.04	0.20	0.89	0.78	0.08	1.58	1.29	36.10	36.42
91	76B CDA 485	1	60.50	60.74	0.02	0.01	0.06	0.13	0.00	0.00	0.00	0.02	0.01	0.59	0.69	0.08	1.94	1.40	36.71	37.02
	Deviation (σ)			1.79		0.10		0.10		0.11				1.10		1.00		0.99		0.21



Calibration options:

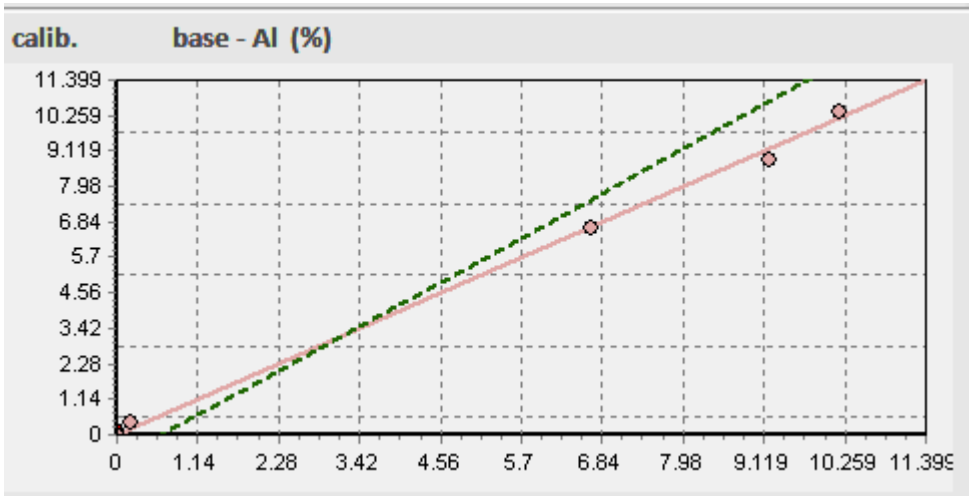
Deselect samples or individual values
Normalization to 100 % y/n
Polynomial degree
Use offset
Calibration ranges

Standard-supported FP
Al in Cu-alloys

- Low Al concentration expose a trend to overestimated Al values
  - Possibly surface contaminations, overestimated sensitivity?
- Higher Al concentrations are generally underestimated
  - FP values?

Calibration samples

	Layer		FP		Calib.	
	Parameter		Al(%)		Al(%)	
No.	Sample		Std	FP	Std	calib.
97	82B CDA 655		0.00	0.68	0.00	0.11
92	77B CDA 510		0.00	0.42	0.00	0.00
96	81B CDA 642		6.70	5.94	6.70	6.66
89	72B CDA 314		0.00	0.56	0.00	0.00
94	79B CDA 623		9.19	7.74	9.19	8.84
98	84B CDA 706		0.00	0.60	0.00	0.02
93	78B CDA 544		0.00	0.59	0.00	0.01
99	86C CDA 836		0.00	0.59	0.00	0.00
101	91C CDA 932		0.00	0.40	0.00	0.00
95	80B CDA 630		10.19	9.03	10.19	10.36
102	92C CDA 937		0.00	0.44	0.00	0.00
90	73B CDA 360		0.00	0.55	0.00	0.00
100	87B CDA 857		0.20	0.89	0.20	0.37
91	76B CDA 485		0.01	0.59	0.01	0.00
	Deviation (σ)			1.10		0.21



Linear calibration with offset yields good results

Standard-supported FP
Al in Cu-alloys

Usually a calibration curve of 1st or 2nd order is sufficient for a wide calibration range of all selected elements

In special cases (detection limits for traces, systematic effects like described here) offset should be considered

Calibration samples

	Layer																		
	Parameter		Cu(%)		Ni(%)		Fe(%)		Mn(%)		Cr(%)		Al(%)		Sn(%)		Pb(%)		Zn(%)	
No.	Sample	W.	Std	calib.	Std	calib.	Std	calib.	Std	calib.	Std	calib.	Std	calib.	Std	calib.	Std	calib.	Std	calib.
97	82B CDA 655	1	**95.30**	98.08	**0.01**	0.02	**0.08**	0.14	**1.04**	0.95	~~0.00~~	0.04	~~0.00~~	0.11	**0.02**	0.17	**0.01**	0.00	**0.38**	0.48
92	77B CDA 510	1	**95.20**	95.25	~~0.00~~	0.01	~~0.00~~	0.03	~~0.00~~	0.00	~~0.00~~	0.05	~~0.00~~	0.00	**4.66**	4.57	**0.02**	0.00	**0.01**	0.08
96	81B CDA 642	1	**91.20**	92.54	~~0.00~~	0.01	**0.05**	0.08	**0.01**	0.01	~~0.00~~	0.04	**6.70**	6.66	**0.01**	0.26	**0.01**	0.17	**0.18**	0.23
89	72B CDA 314	1	**90.08**	89.90	~~0.00~~	0.01	**0.01**	0.06	~~0.00~~	0.00	~~0.00~~	0.06	~~0.00~~	0.00	**0.03**	0.17	**1.99**	1.87	**7.81**	7.92
94	79B CDA 623	1	**88.40**	87.99	**0.08**	0.07	**2.13**	2.17	**0.16**	0.14	~~0.00~~	0.03	**9.19**	8.84	**0.02**	0.72	~~0.00~~	0.00	**0.01**	0.04
98	84B CDA 706	1	**87.89**	87.72	**10.03**	10.17	**1.30**	1.20	**0.62**	0.57	~~0.00~~	0.05	~~0.00~~	0.02	**0.01**	0.21	**0.01**	0.01	**0.08**	0.05
93	78B CDA 544	1	**87.70**	88.36	**0.08**	0.07	**0.02**	0.07	~~0.00~~	0.00	~~0.00~~	0.09	~~0.00~~	0.01	**4.73**	4.19	**3.87**	3.77	**3.55**	3.45
99	86C CDA 836	1	**84.60**	84.63	**0.27**	0.25	**0.24**	0.29	~~0.00~~	0.00	~~0.00~~	0.10	~~0.00~~	0.00	**4.37**	4.35	**5.03**	5.19	**5.38**	5.17
101	91C CDA 932	1	**83.20**	82.92	**0.46**	0.46	**0.03**	0.07	~~0.00~~	0.00	~~0.00~~	0.07	~~0.00~~	0.00	**6.77**	7.18	**6.80**	6.79	**2.62**	2.50
95	80B CDA 630	1	**81.20**	80.67	**4.69**	4.81	**3.31**	3.33	**0.54**	0.53	~~0.00~~	0.02	**10.19**	10.36	**0.02**	0.25	**0.01**	0.00	**0.08**	0.03
102	92C CDA 937	1	**80.20**	80.54	**0.35**	0.35	~~0.00~~	0.12	~~0.00~~	0.00	~~0.00~~	0.04	~~0.00~~	0.00	**9.70**	10.01	**9.23**	8.88	**0.04**	0.05
90	73B CDA 360	1	**61.50**	61.63	**0.06**	0.06	**0.17**	0.27	~~0.00~~	0.00	~~0.00~~	0.02	~~0.00~~	0.00	**0.15**	0.12	**2.71**	2.65	**35.30**	35.25
100	87B CDA 857	1	**60.90**	61.02	~~0.00~~	0.09	**0.29**	0.28	**0.01**	0.01	~~0.00~~	0.04	**0.20**	0.37	**0.78**	0.19	**1.58**	1.72	**36.10**	36.28
91	76B CDA 485	1	**60.50**	60.92	**0.02**	0.02	**0.06**	0.09	~~0.00~~	0.01	~~0.00~~	0.02	**0.01**	0.00	**0.69**	0.19	**1.94**	1.87	**36.71**	36.89
	Deviation (σ)			0.91		0.06		0.06		0.04				0.21		0.38		0.14		0.11

Lucas-Tooth
fast Au quantification

Lucas-Tooth model: $c_i = o_i + s_i I_i + \sum_{n \neq i} (e_{ni} I_n)$

o_i: offset for Element *i*

s_i: “sensitivity” for element *i*

I_i: measured intensity for element *i*

\+ inter-element effects

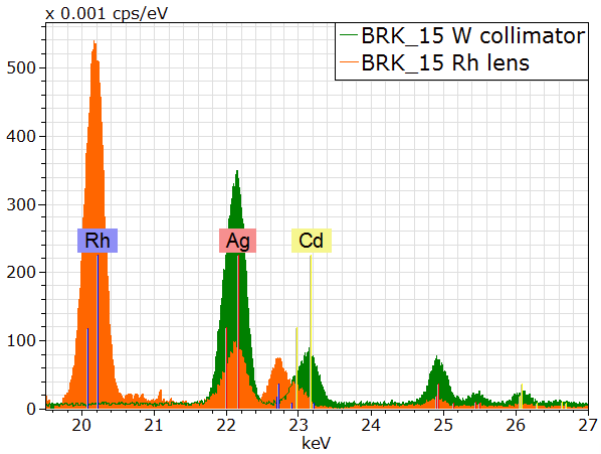
(corrections based on intensities of other elements)

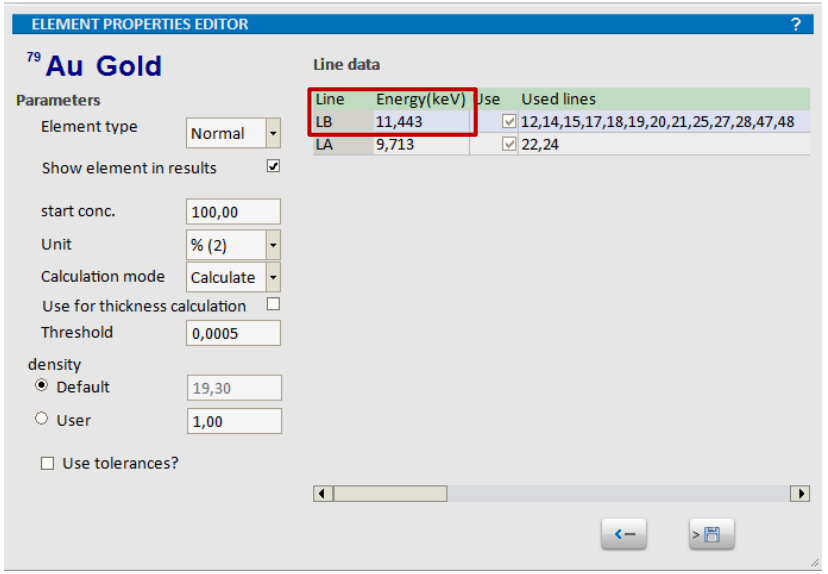
Much simpler math than FP → faster calculations

Lucas-Tooth
fast Au quantification

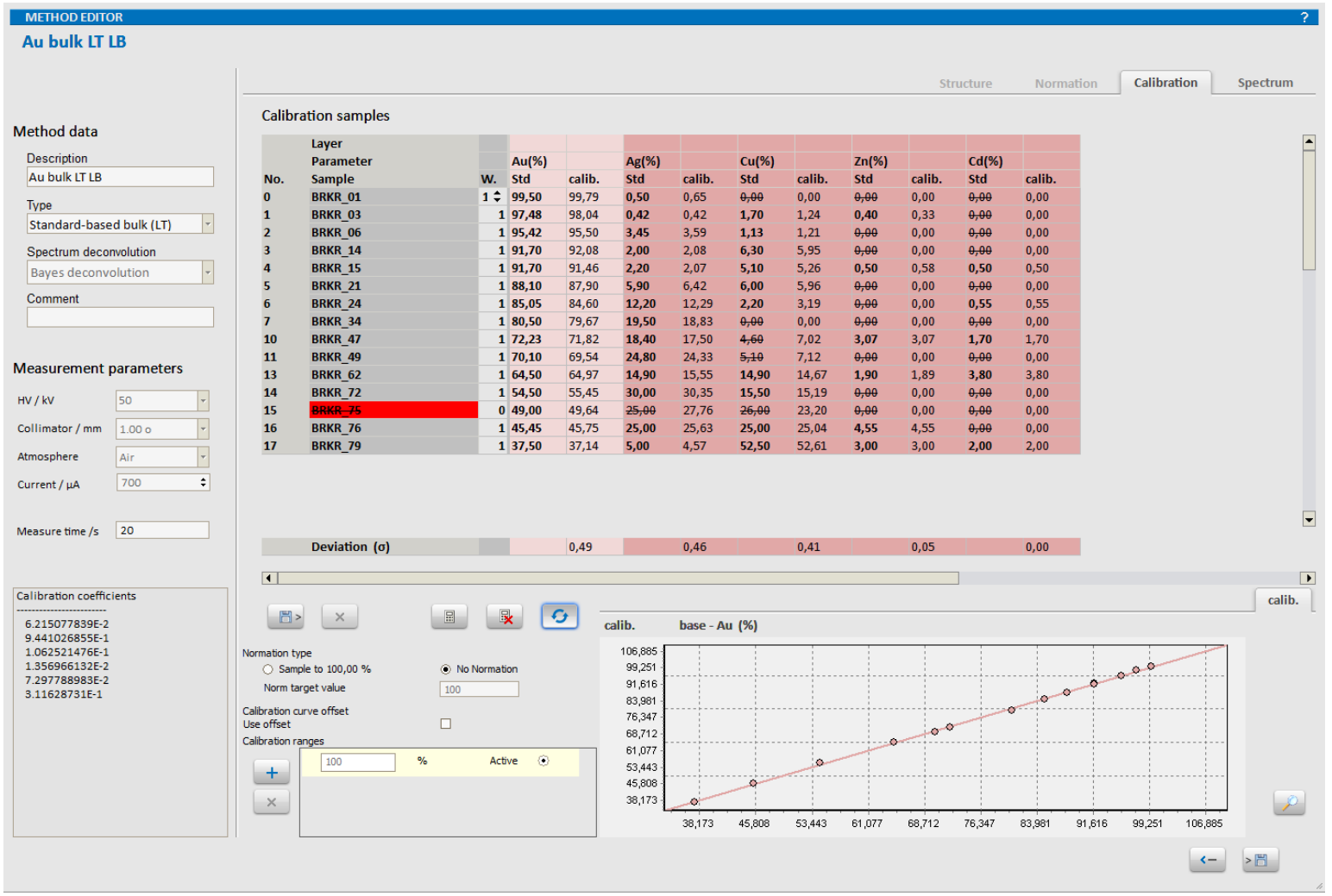
Measurement conditions:

- W tube (no crosstalk for Ag/Cd with Rh lines)
- ø 1 mm collimator (to average over inhomogeneities, high-Z efficiency)
- 50 kV / 700 µA
- Strong 200 µm Al + 200 µm Ti filter (to block characteristic W lines from spectrum)
- Ambient pressure (heavy elements suffer only little from air absorption)
- 1x 30 mm² SDD
- 60 s live time



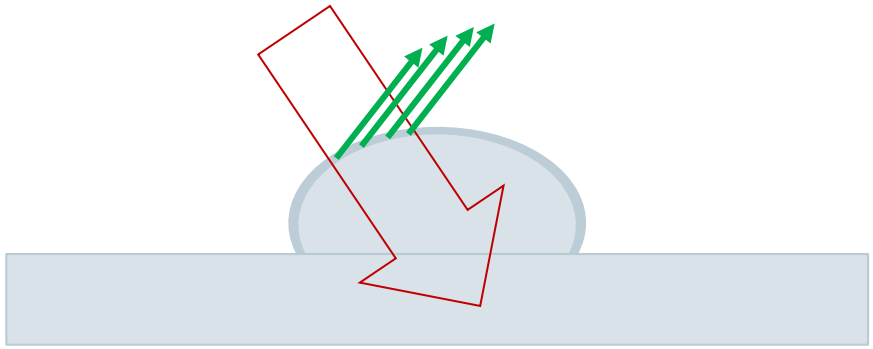


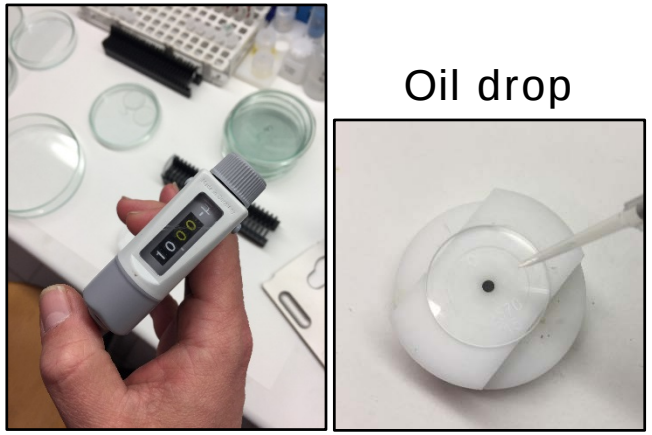
Lucas-Tooth
fast Au quantification



Polynomial Calibration
S in oil

- Sample can hardly be described by a model (shape, density, …)
- Very limited information depth for Sulfur
- Negligible self-absorption





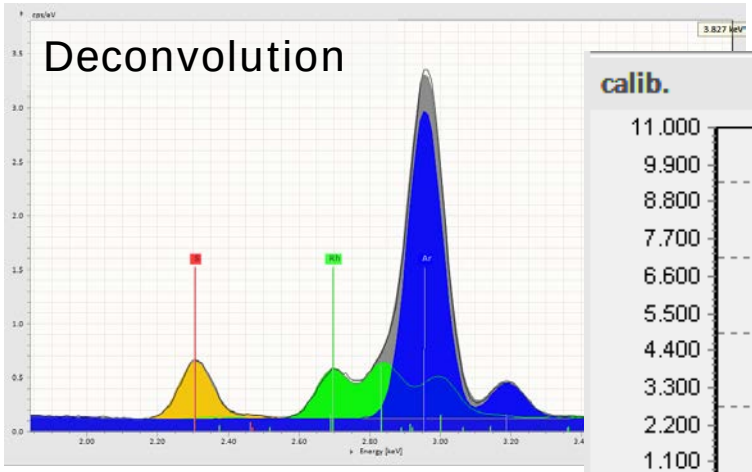
- Simple model: concentration of S oil is linear with intensity

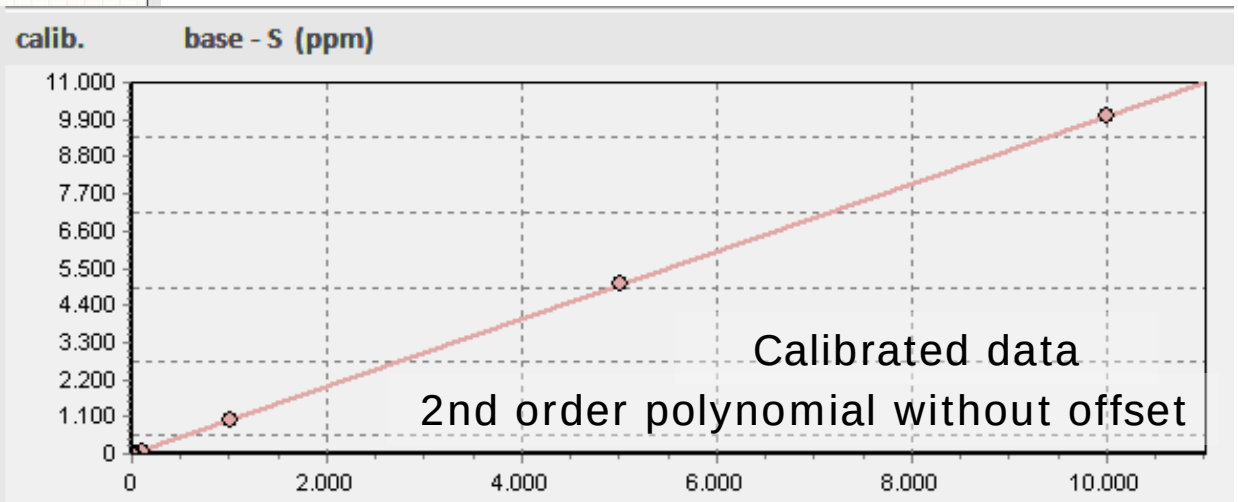
Polynomial Calibration
S in oil

- 10 µl of each reference sample (CONOSTAN) were deposited on a clean SiO_2 disc
- Concentration of S from 0 to 10000 ppm (1 %)

- Measurement conditions:
  - Rh tube with polycapillary lens
  - 50 kV/ 600 µA
  - No filter (Rh-L used to efficiently excite Sulfur)
  - Ambient pressure (to avoid evaporation)
  - 2x 30 mm^2 SDDs
  - 600 s real time (statistic needed especially for low concentrations)

Polynomial Calibration
S in oil





base	S	Rh	Ar

Most simple
sample description

Calibration samples

	Layer							
	Parameter		S(ppm)		Rh(%)		Ar(%)	
No.	Sample	W.	Std	calib.	Std	calib.	Std	calib.
124	S_OIL_ 10000 ppm	1	10000	9993	~~0.00~~	0.00	~~0.00~~	0.00
123	S_OIL_ 5000 ppm	1	5000	5014	~~0.00~~	0.00	~~0.00~~	0.00
122	S_OIL_ 1000 ppm	1	1000	995	~~0.00~~	0.00	~~0.00~~	0.00
120	~~S_OIL_ 500 ppm~~	0	500	458	~~0.00~~	0.00	~~0.00~~	0.00
119	S_OIL_ 100 ppm	1	100	93	~~0.00~~	0.00	~~0.00~~	0.00
118	S_OIL_ 25 ppm	1	25	23	~~0.00~~	0.00	~~0.00~~	0.00
116	S_OIL_0 ppm	1	0	6	~~0.00~~	0.00	~~0.00~~	0.00

Polynomial Calibration
Geological samples - Live

In a sample which is mostly composed of light elements (mainly Oxygen), inter-element effects, such as secondary excitation or self-absorption are no longer dominant effects.

For almost all elements with concentration < 10 % the measured intensity is linear with the element's concentration.

→ Even though most geological samples can be rather complex (> 30 elements), the quantification of most elements can be performed using a simple quantification model.

Summary

- The M4 with XMethod offers 4 different approaches to bulk quantification
- FP methods are most flexible

  Calibration is an option to improve the obtained results and the standards may deviate more from the actual samples than for other approaches.
- LT method is very fast

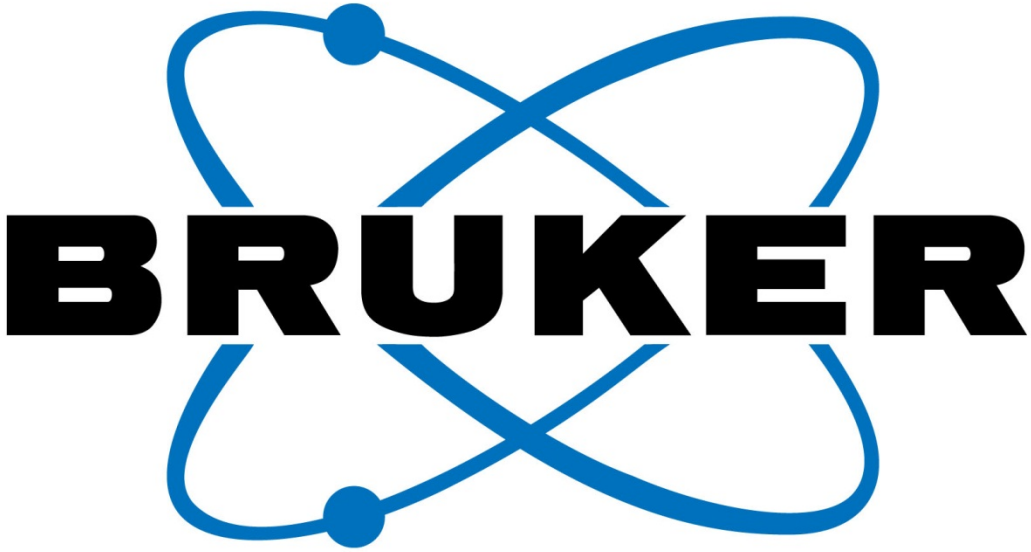
  … as it is based on simple math. A large set of very similar standards is required.
- Polynomial calibration is the most basic approach.

  It is suitable when either most of the sample is not of interest (or “invisible”) and when inter-element effects can be neglected. One standard per element is sufficient but a larger number improves the calibration.

Q&A

Are There Any Questions?

Please type in the questions you might have in the Q&A box and press *Send*.



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