PANalytical

Developments in standardless analysis

Where can FP take us?

Kristiansand

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Armand Jonkers

Content

- What would be the target?
- What is standardless analysis?
  - Conventional + layers
- How does standardless analysis work?
- What information is hidden in the count rates?
- How was this information used up to now?
- What's next?

What would be the target?

- Full standardless quantitative analysis including
  - Correction for wrong sample identifications
  - Analysis of missing samples
  - Analysis of vacuum

But most of all:

Explanation of unexpected results

What is standardless analysis? – A definition

- Complete composition of unknown materials can be quantified with a single set-up program.
  - Set up with a selected range of spectral interference-free reference materials (dissimilar to unknowns) to determine the instrument response.

How does standardless analysis work?

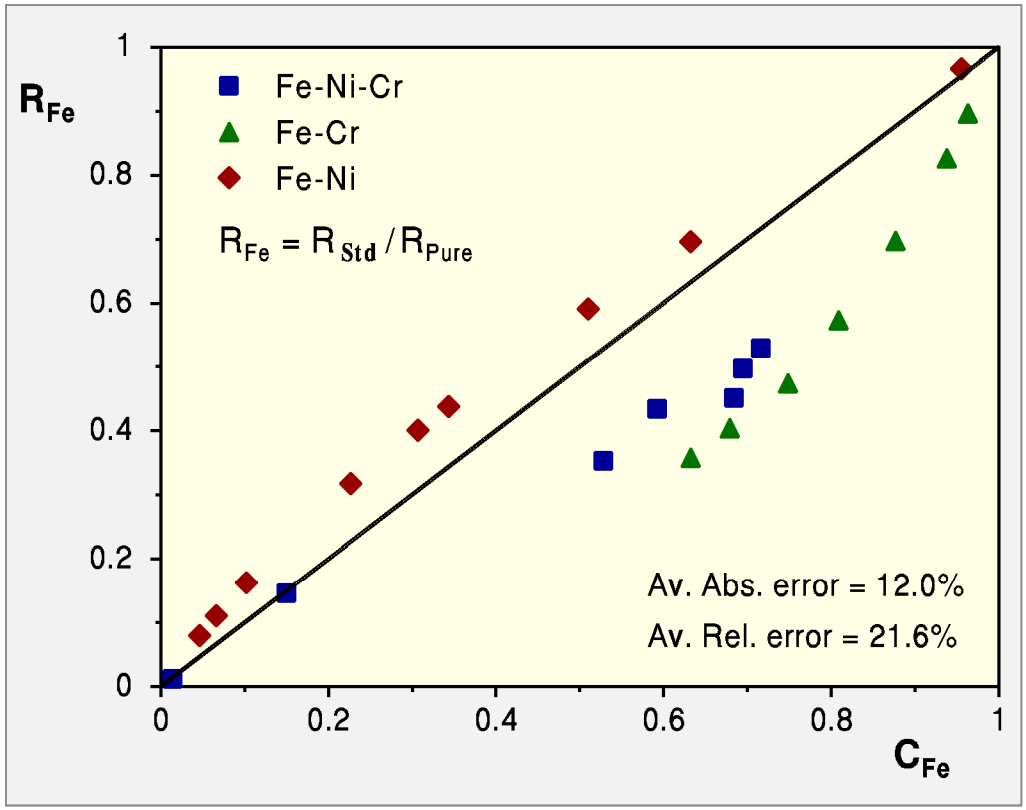
Based on

- Fundamental Parameters
  (Many references in literature)
- A sample model for the sample of concern
  (very specific for each sample analyzed)

FP corrects for matrix effects

Matrix effects:

- Inter-element effects within the sample cause absorption and enhancement.
- In Fe-Ni-Cr steel example:
  - Ni enhances Fe
  - Cr absorbs Fe
- FP corrects for these inter-element effects



How does standardless analysis work?

Required actions

1. Determine elements present
   - Scans and/or channels (Omnian, SuperQ)

   ⇨ Count rates for measured lines
2. Choose/Enter a sample model
   - No of layers, diameter, weight, density, presence of non-measured compounds
3. Calculate concentrations (& thicknesses) by using Fundamental Parameters (FP) in combination with sample model.

Sample models: non-layered

- Oil, 5g in liquid cup, CH_2=balance, 35 mm diameter, Mylar 3.6μm foil, Helium atmosphere
- Oxide sample, 10g, 40mm diameter, prepared as fused bead 1g + 10g $Li_2B_4O_7$
- Steel, 10mm thick, 40mm diameter
- Sewage sludge, 20g, 35mm diameter, CH_2=balance
- Tap water, 20ml, d=1, H_2O=balance, 35 mm diameter, PP 6μm foil, Helium atmosphere

Sample model: layered sample with finite thicknesses

$C_{18}H_{36}O$ 99%, P 1%	1-3 µm
Zn 90-98%, Al 1-2%, Fe 8-10%	5-10 µm
Substrate = Steel, Fe 99.3 %, Si 0.5%, Mn 0.15% rest <0.05%	1 – 1.5 mm

Note: The signal of Zn depends on both layer thickness and on its concentration within the layer.

What information is there in spectra?

- Peak intensities
  - Rayleigh peak of analytes

⇨ Which elements are present?

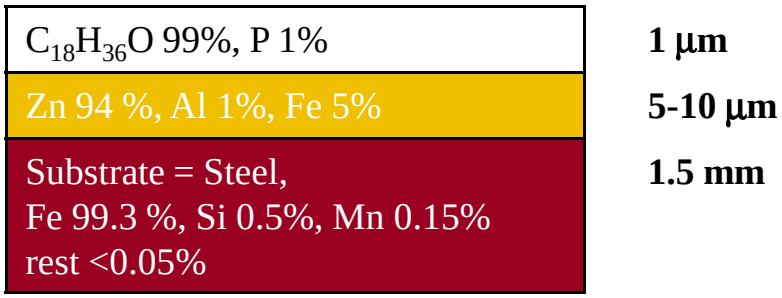
  - Anode element peaks (Rayleigh as well as Compton)

⇨ Total matrix information

  - Ratio between K, L and M lines

⇨ Depth information

Let's have a look at a layered sample



- Let's check whether measurements will be possible
  - Use FP to predict feasibility of measurement
  - Forecast which lines should be measured

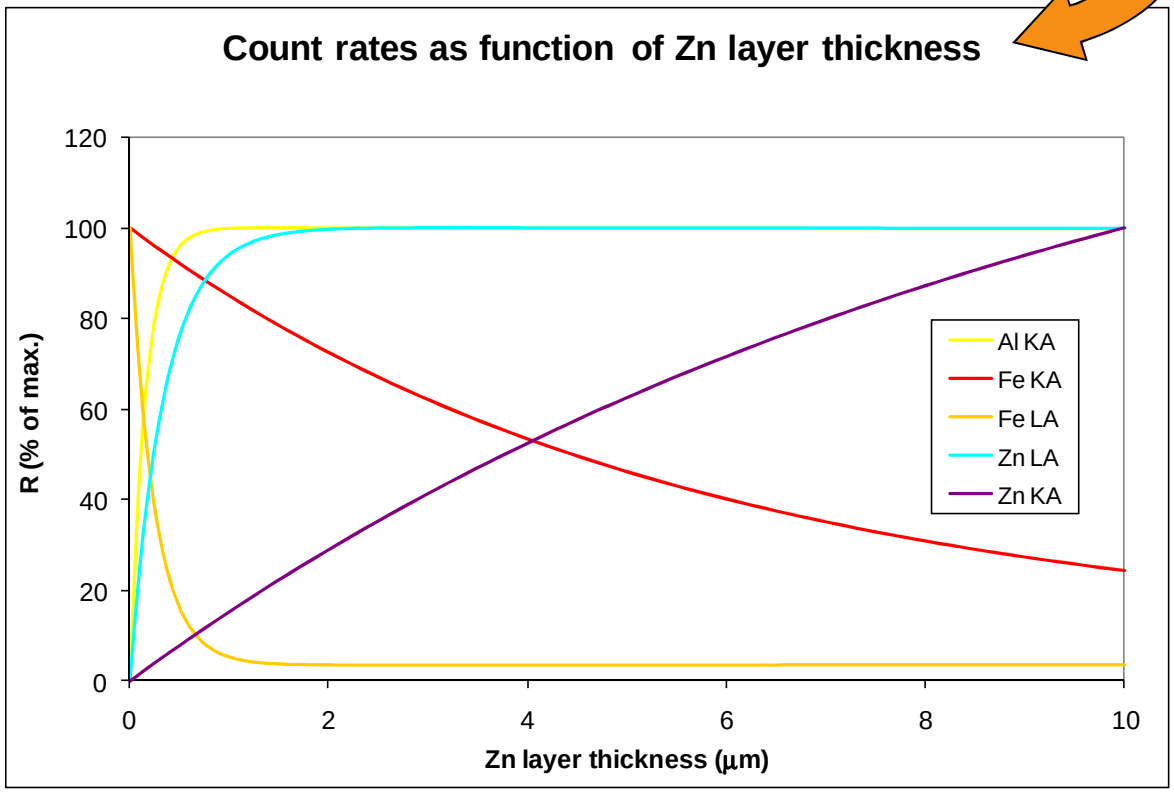
FP calculation of count rates

$C_{18}H_{36}O$ 99%, P 1%
Zn 94 %, Al 1%, Fe 5%
Substrate = Steel, Fe 99.3 %, Si 0.5%, Mn 0.15% rest <0.05%

1 µm

5-10 µm → Varied in thickness

1.5 mm



(Calculated by FP-Multi in simulation mode)

Solution to layered sample: FP-Multi

$C_{18}H_{36}O$ 99%, P 1%	**1 μm**
Zn 90-98%, Al 1-2%, Fe 2-7%	**5-10 μm**
Substrate = Steel, Fe 99.3 %, Si 0.5%, Mn 0.15% rest <0.05%	**1.5 mm**

- Organic top layer:

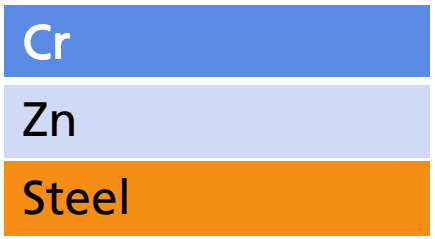
  thickness based on P Kα (or absorption of Zn/Al)

- Zn Layer:

  thickness based on Zn Kα
  C_{Zn} based on Zn Lα
  C_{Al} based on Al Kα
  C_{Fe} = 100% - C_{Zn} – C_{Al} (or from total Fe Kα)

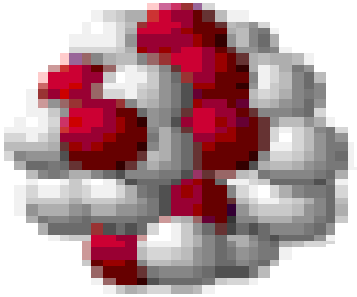
Typical results

- Cr on galvanized steel:



Zn layer: 7.129 µm ± 0.008 µm (8 nm)

Cr layer 8.02 nm ± 0.03 nm



- 0.03 nm, that's about 0.2 atoms thick!

Non-destructive, typical measurement time: 2 minutes

Some more layer applications

- Ag and Halides on photographic film
- SiO_2 on polymer: 2.9 nm ± 0.4 nm
- Sn & Silicone coating on tin-cans
- TiO_2 coatings on tiles
- Glue on stickers
- Ni, Cu and Zn coatings on coins
- Al/Si on Al metal
- Semi-conductor industry
- Glass coatings (e.g. sun protection for offices)

} e.g. 8 layers !

And many more !

What about sample thickness?

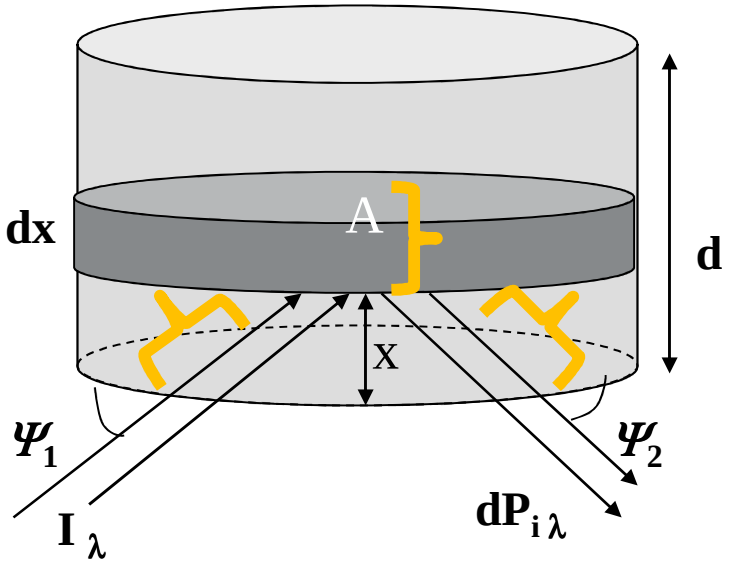
- The layer analysis is possible since these layers are very thin.
  - There are no geometrical problems
  - The signals are not completely absorbed
- What if samples get thicker?

The Sherman Equation: R from a thin layer

Contribution of slice with thickness *dx* at depth *x* to the intensity of element *i* in a sample

$$dP_{i\lambda}(x) = e^{-\rho x \mu'_{s\lambda}} A\rho\varepsilon_{i\lambda} w_i \tau_{i\lambda} I_\lambda \frac{dx}{\sin\psi_1} e^{-\rho x \mu''_{s\lambda_i}}$$

absorption of incoming radiation	production of fluorescence in slice	absorption of fluorescent radiation



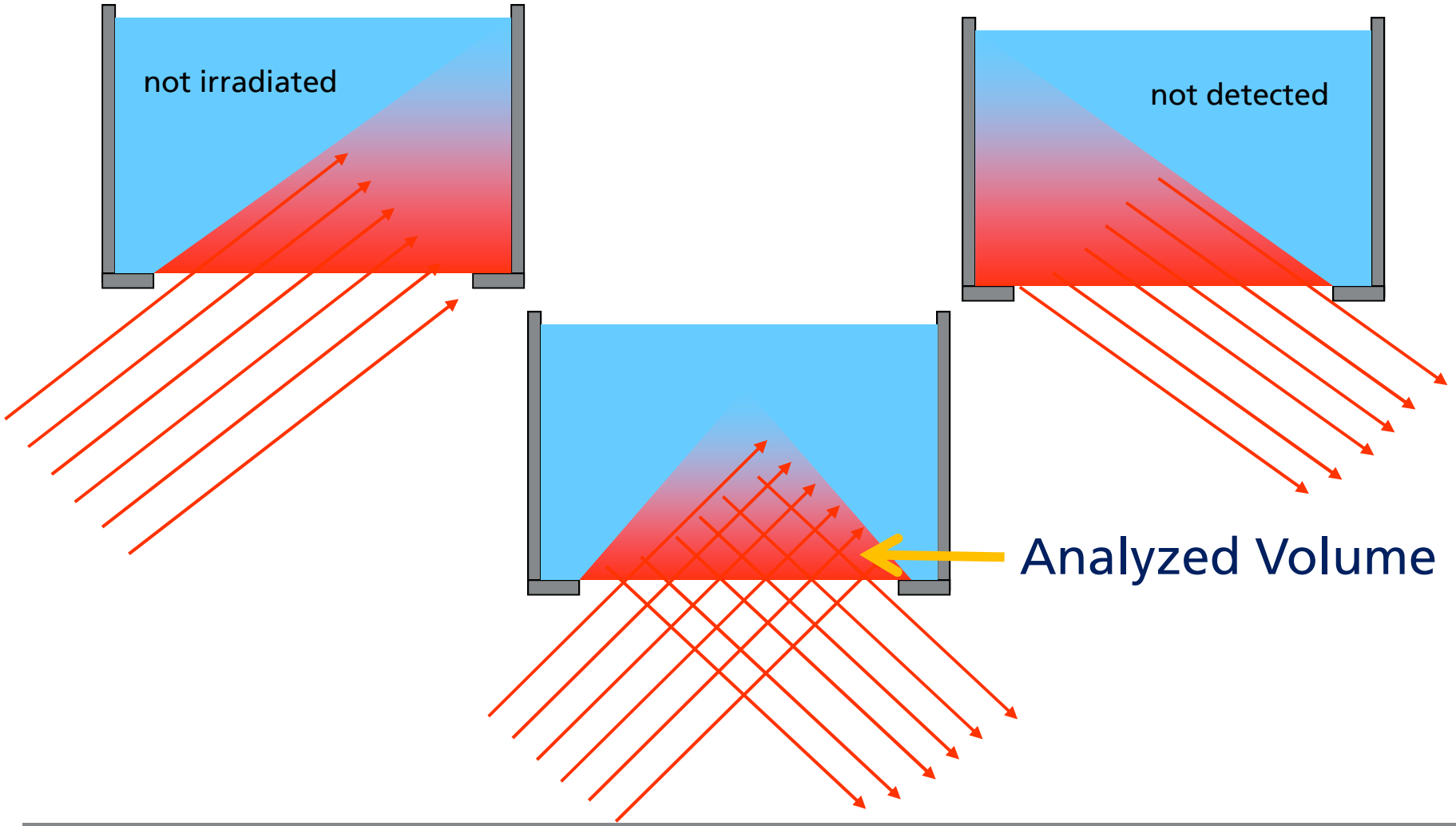
Important:

A = area of slice

x = depth of slice

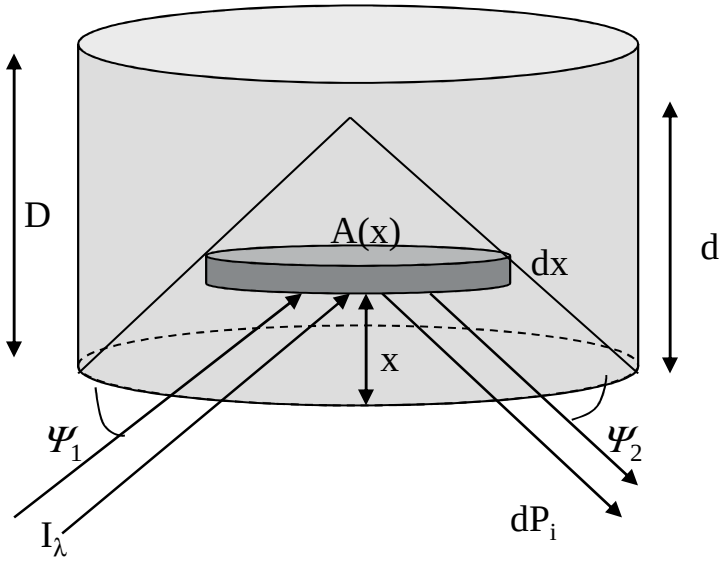
ρ = sample density

Wedge or shadow effect



Extended Sherman Equation

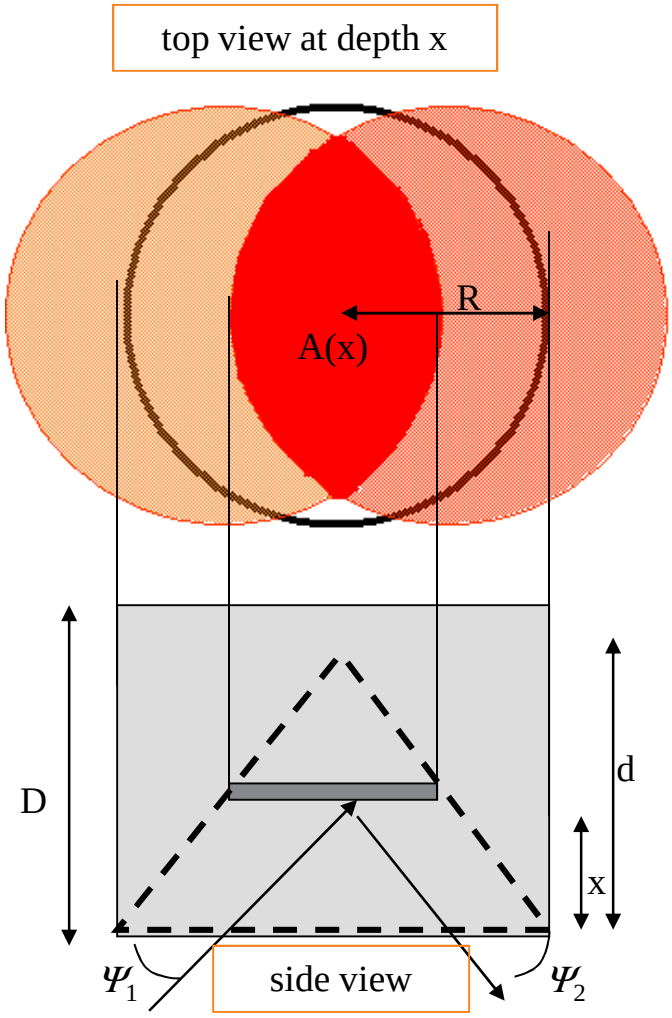
$$dP_{i\lambda}(x) = e^{-\rho x \mu'_{s\lambda}} \mathbf{A(x)} \rho \varepsilon_{i\lambda} w_i \tau_{i\lambda} I_\lambda \frac{dx}{\sin \psi_i} e^{-\rho x \mu''_{s\lambda_i}}$$



HOWEVER..

For a parallel beam the slice is not circular……..

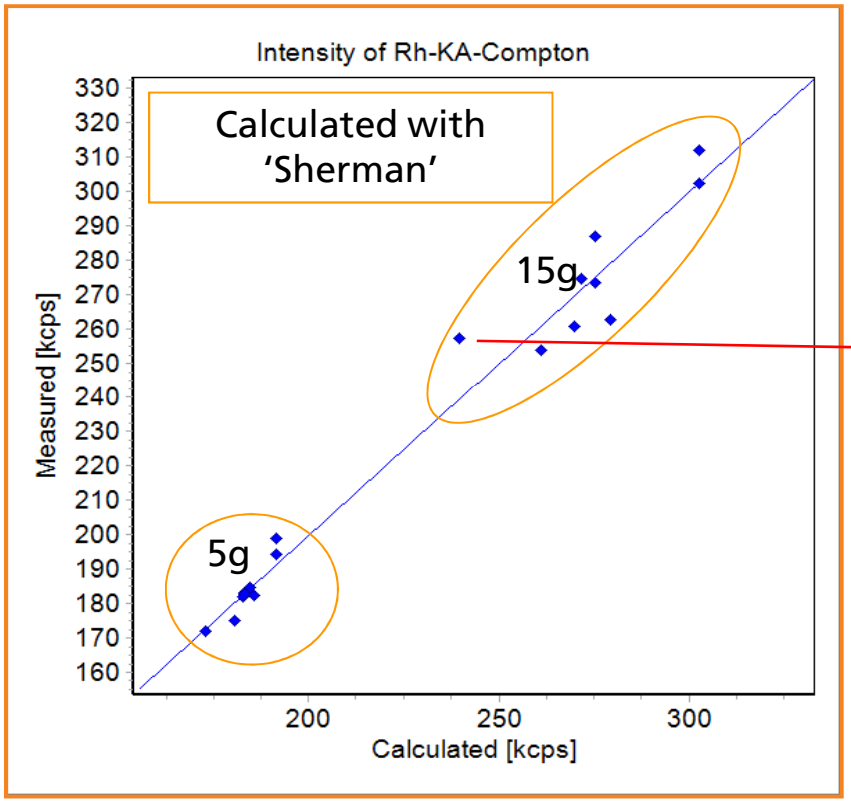
Area at depth x for circular samples

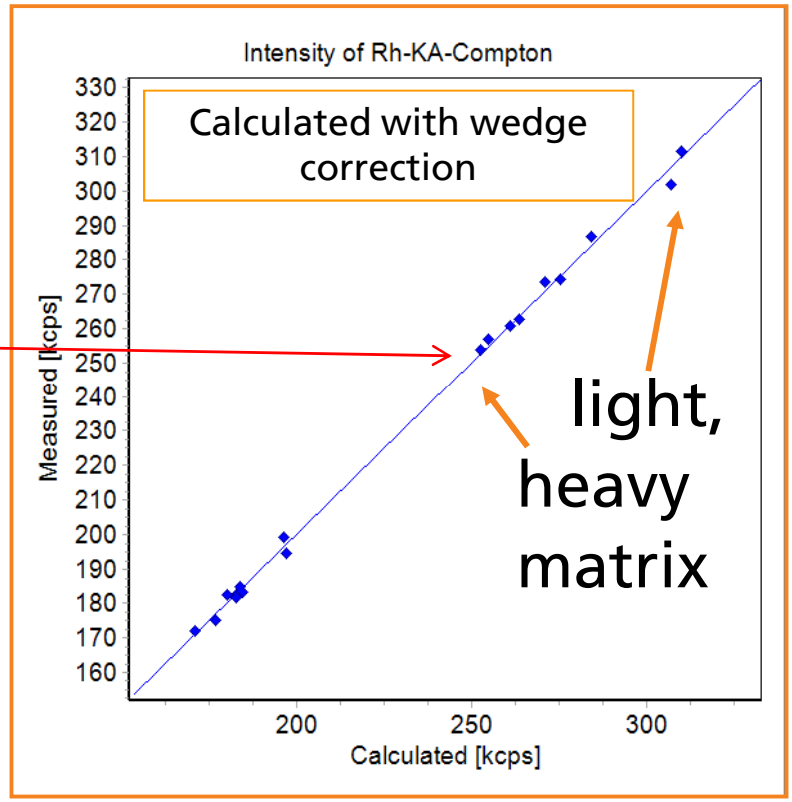


$$A(x) = \pi R^2 - x \cdot \left(\frac{1}{\tan\psi_1} + \frac{1}{\tan\psi_2} \right)$$

Sorry for the formula

Effect of FVG correction on Rh-Kα-Compton



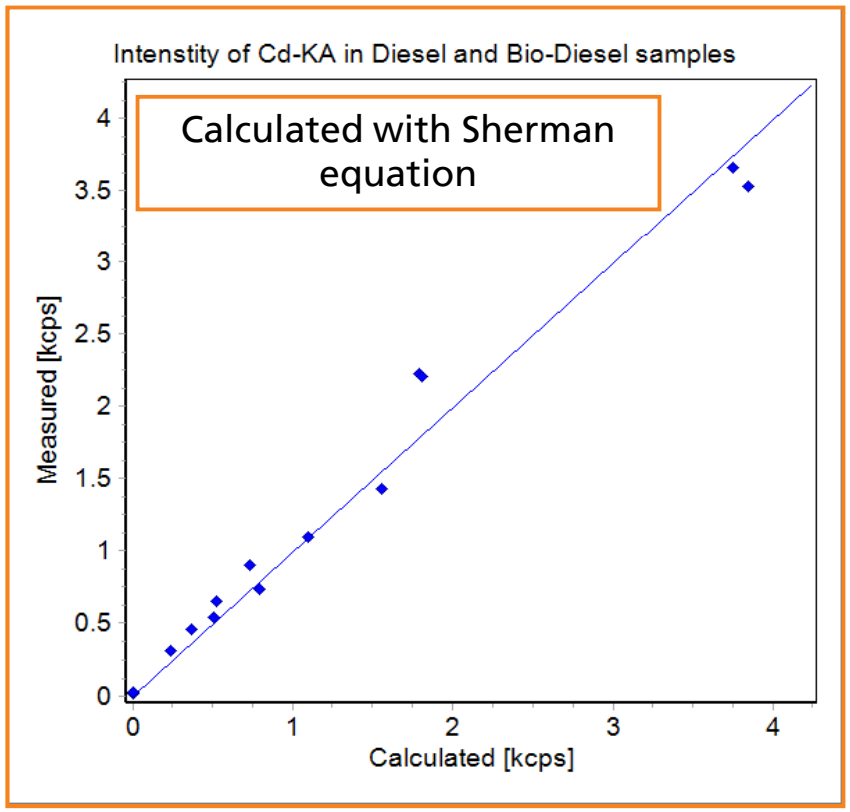


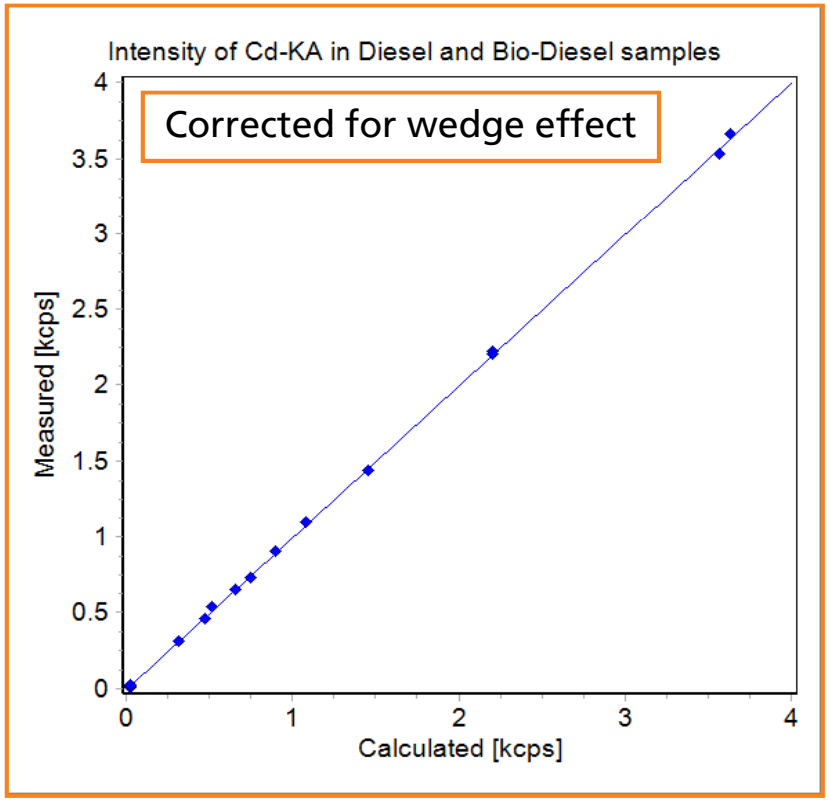
FVG (Fluorescent Volume Geometry) correction

Intensities of Cd-Kα in Diesel and Bio-Diesel

Sample weight between 5g and 15g,

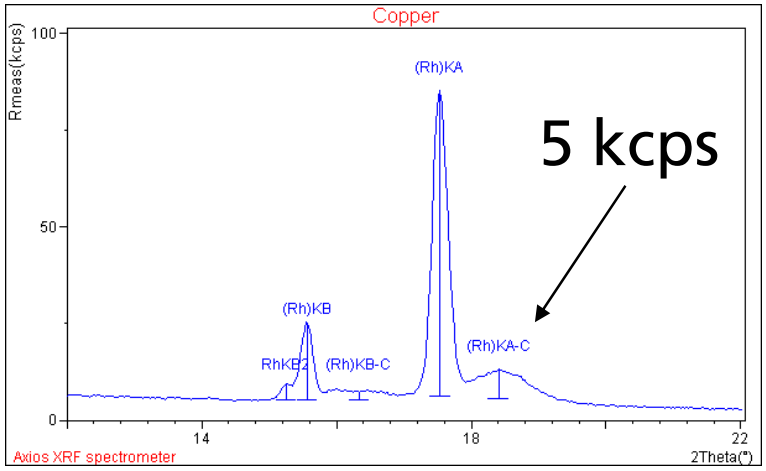
Bio-Diesel : ρ = 0.907, Diesel : ρ = 0.838



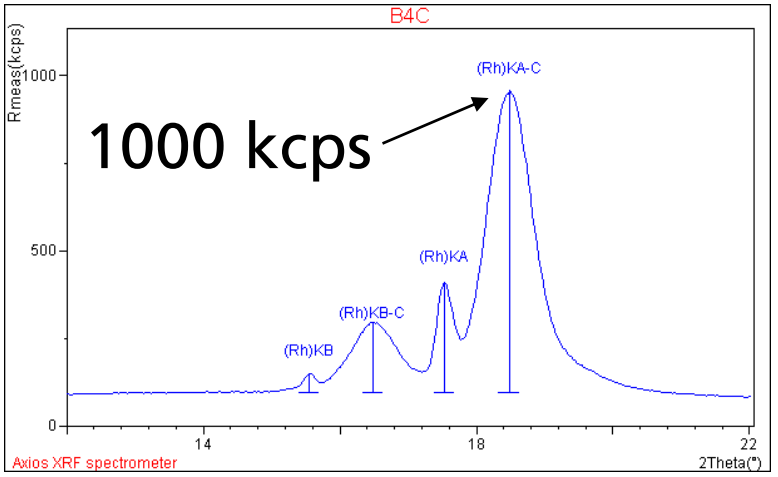


Use of Compton count rates, additional scan required

Heavy matrix
⇒ low Compton count rate



Light matrix
⇒ high Compton count rate



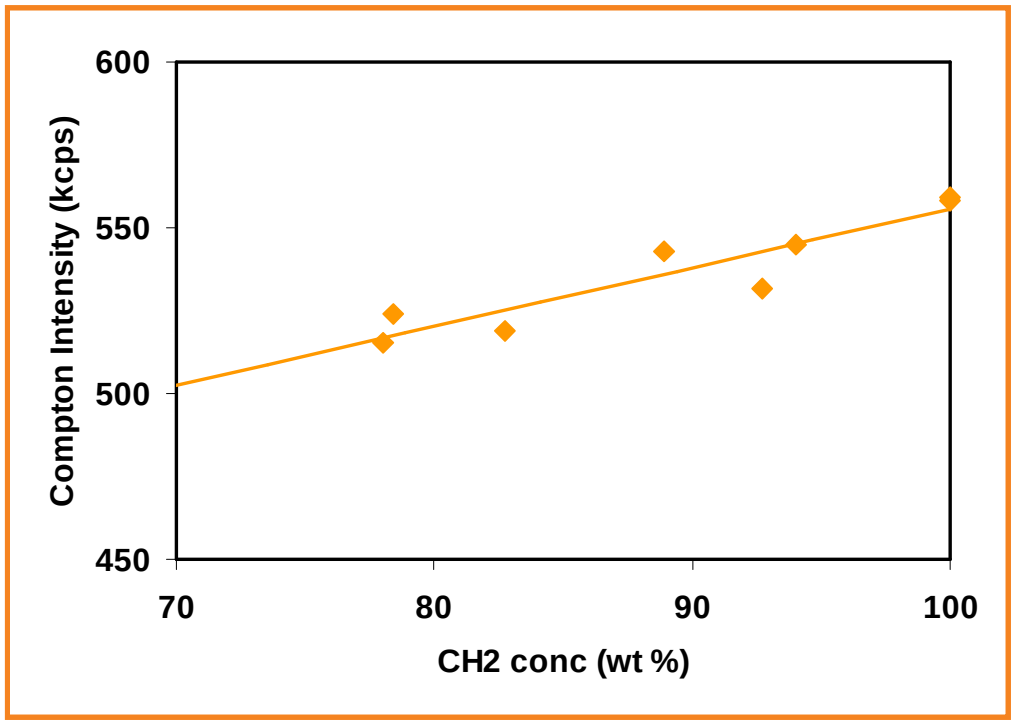
- Works well for light matrices
  - Improves quantitative calibrations
  - Can be used to derive 'extra' information like e.g. non-measured compounds, or validation of standardless results.

The use of $R_{\text{Rh Compton}}$ in oil analysis (oil-trace)

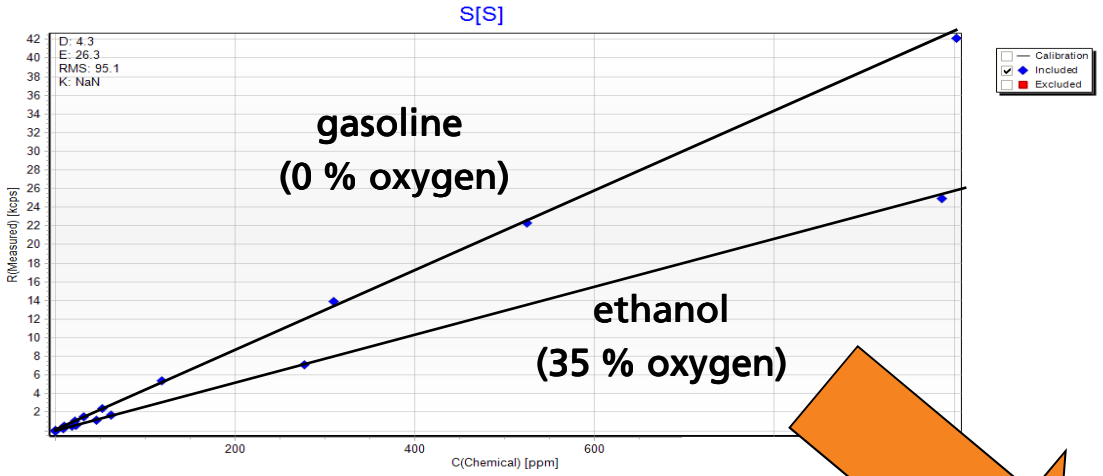
All major and minor elements are analyzed: the matrix is known except for: CH_2 / Oxygen ratio

CH_2 from regression,

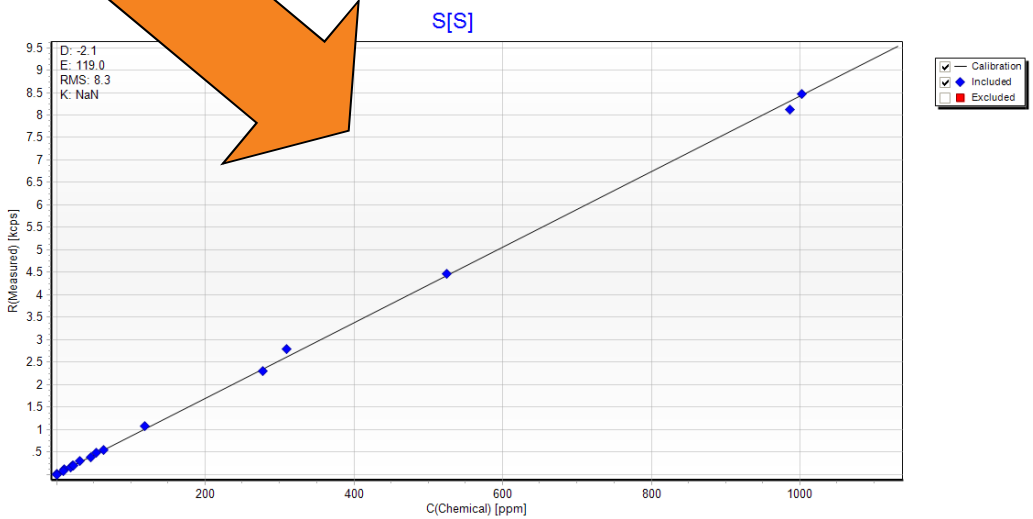
Oxygen = balance



S in oil: Correction for oxygen content (Oil-trace)

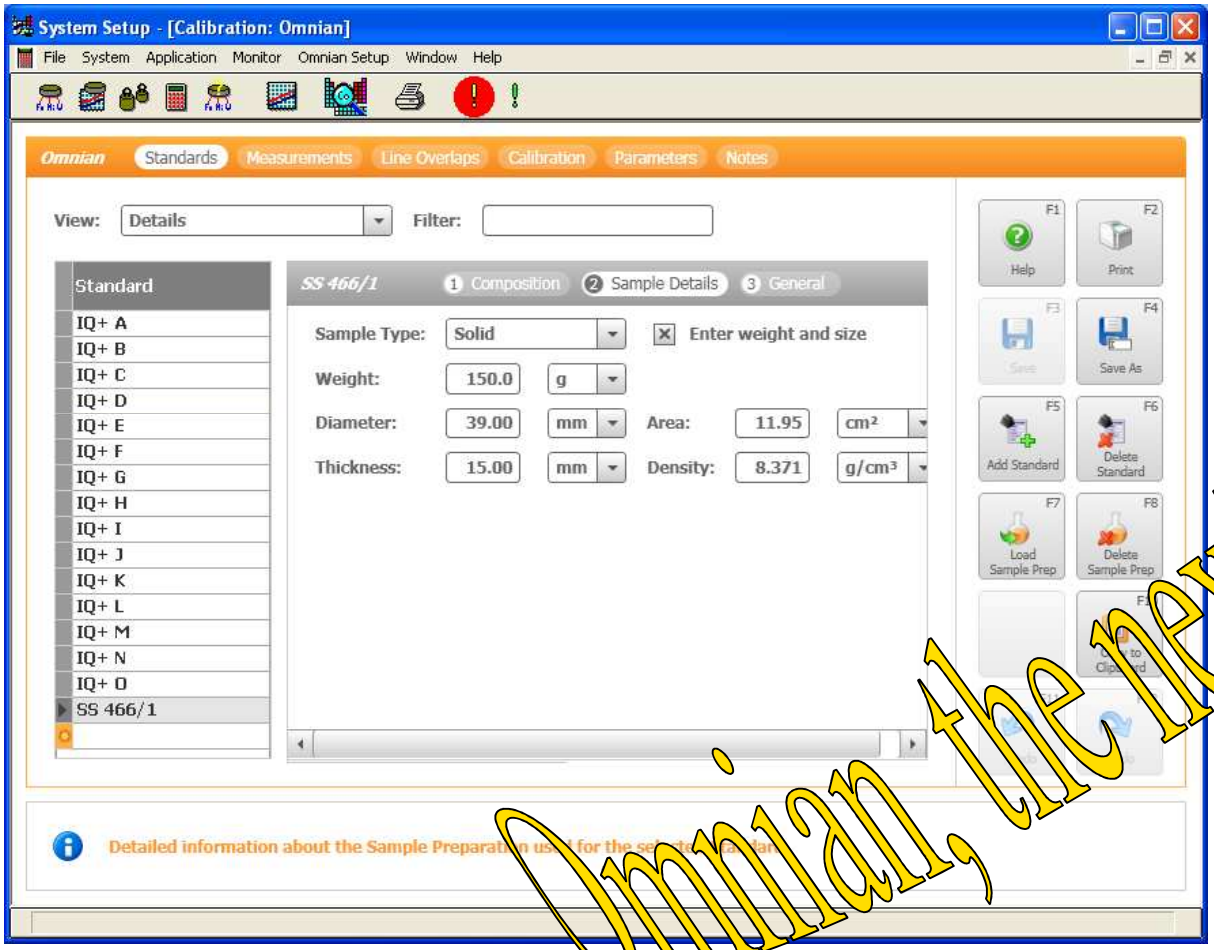


Without oxygen correction



With oxygen correction (from Rh Compton)

So what are we talking about?

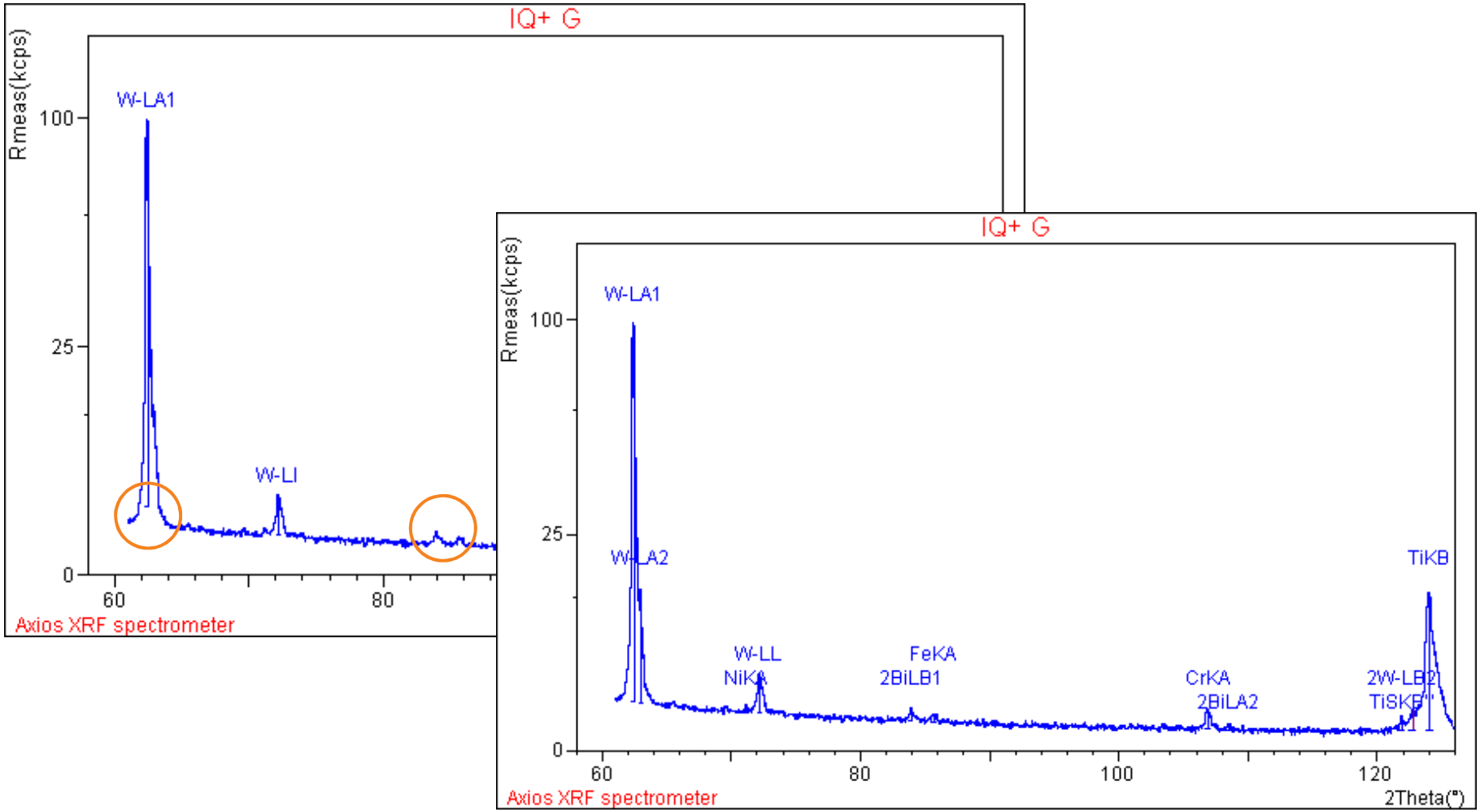


Omnian, the next generation

Various new functions

- Integration in SuperQ
- New program, new user interface
- View, edit and recalculation in results evaluation, of multiple samples at the same time.
- Improved search and match as well as background fit
- Automatic monitor correction
- Theoretical monitor correction

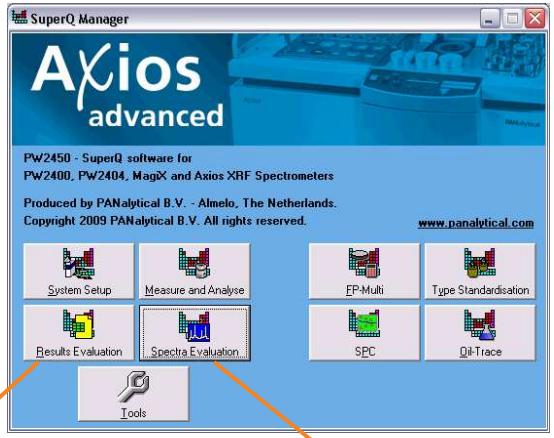
Omnian : improved search, match & Background



Results can be viewed in Results Quantitative

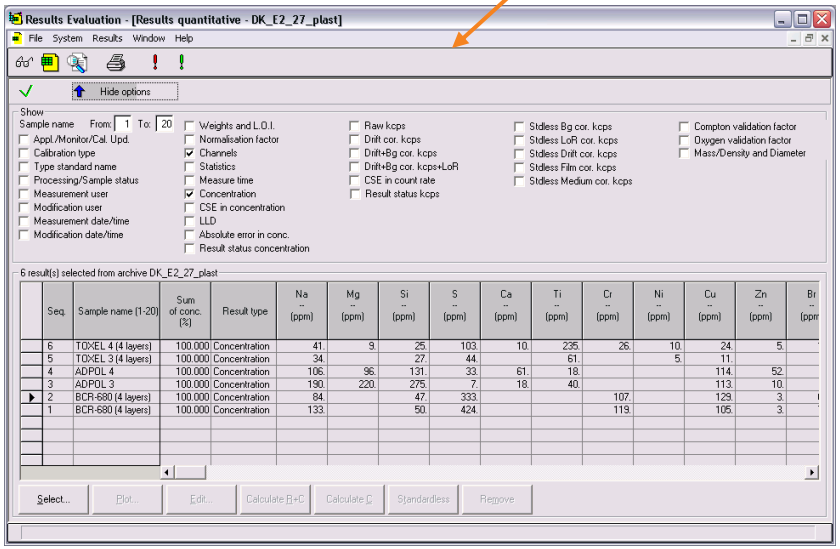
Results Evaluation

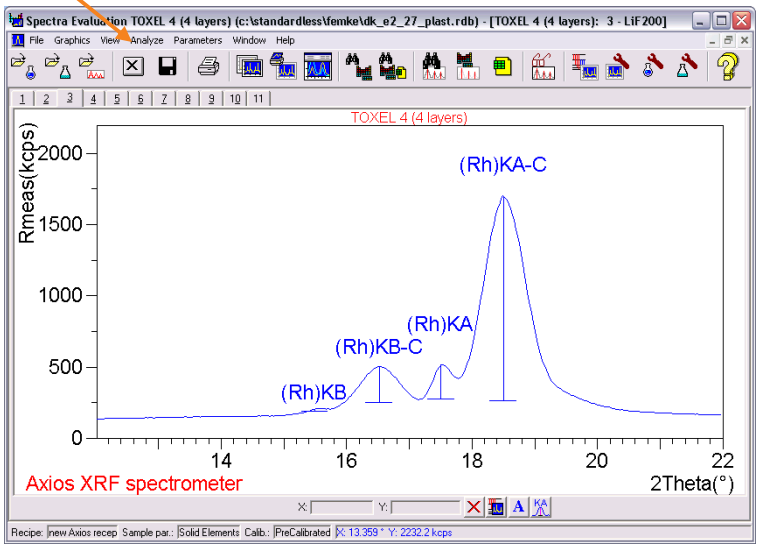
- For general purpose results viewing and recalculating
- Possibility to compare results



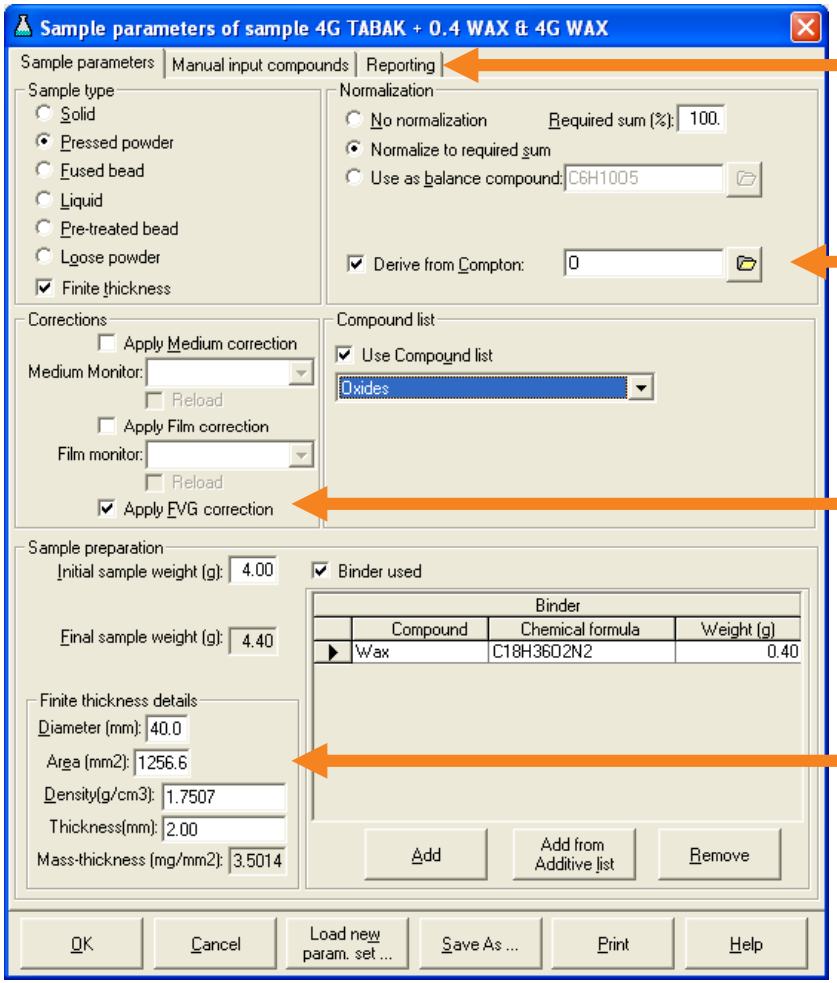
Spectra Evaluation

- For more advanced results viewing and reprocessing
- Possibility to view scans



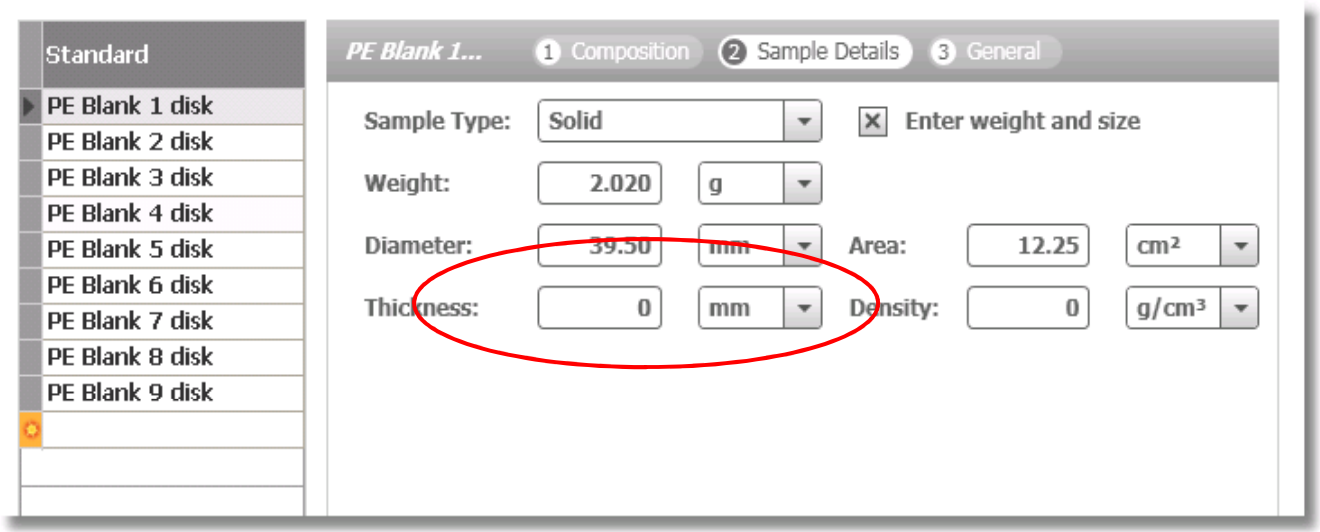


Various new functions

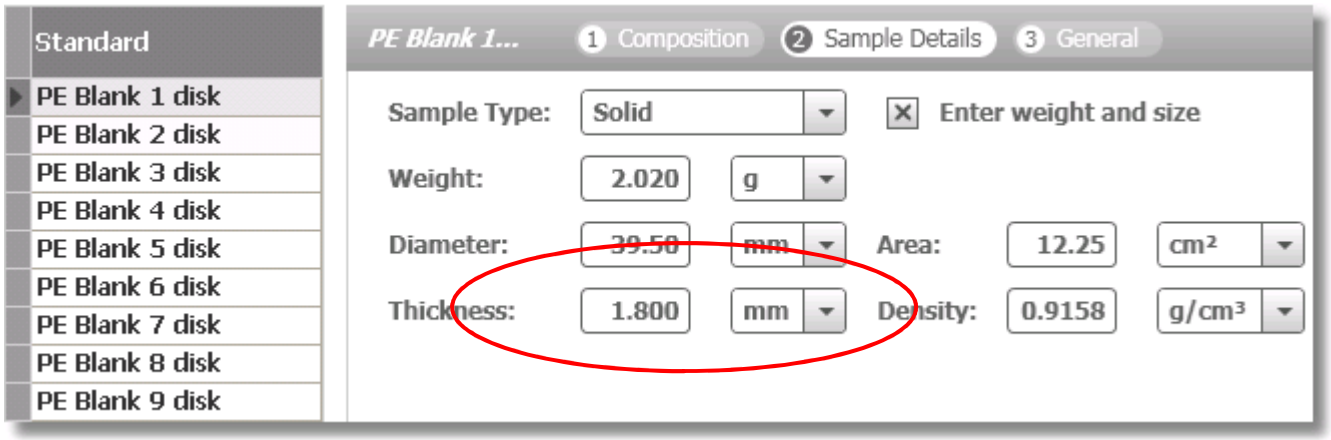


- New reporting in ppm and %
- Compton correction
- FVG correction
- Finite thickness correction

FVG correction: in calibration



No FVG



With FVG

Next step to take

Now we:

- Know the analyte peak intensities,
- Corrected for wedge effect,
- Know the black matrix,
- Know the sample model,

Is this enough for full quantitative analysis?

Destination full quantitative analysis reached?

- No: the sample model is often not complete due to:
  - Incomplete FP data (CH_2 or CH_2O or $C_{18}H_{36}ON$?)
  - Not-modeled physical effects (e.g. sample prep.)
  - Mineralogical effects (powders)
  - Metallurgical effects
    - Corrected for by type standardization in quantitative analysis.
- In quantitative analysis these effects are accounted for by using in-type standards.

The use of ‘in-type’ standards: ‘Tags’

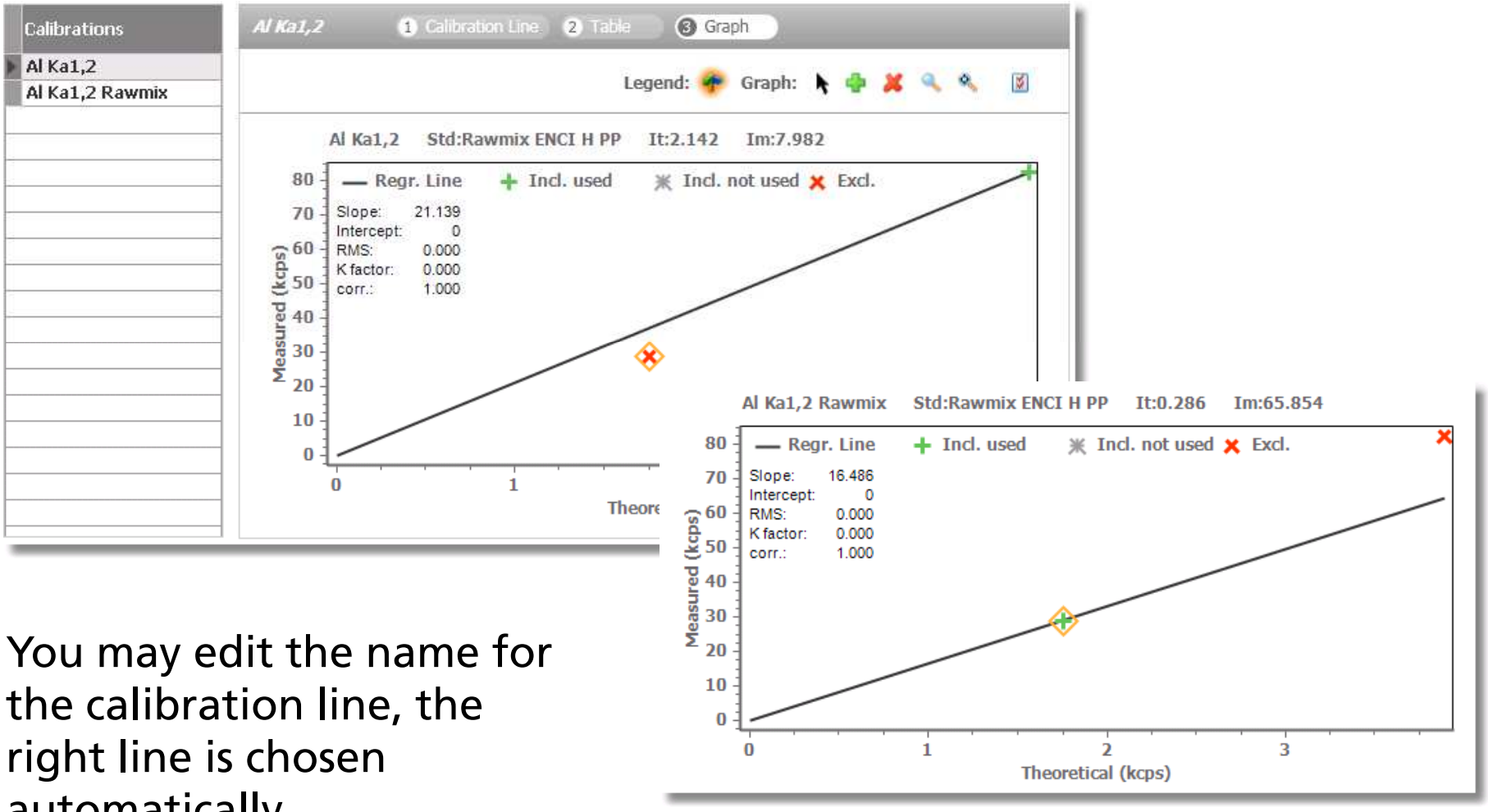
Use FP + in-type standards, (like in quantitative analysis) to get the best of both worlds. Choose tag = ‘Cement’ during measurement.

Large advantage:

One standard is sufficient

	Certified	Conventional standardless analysis	Standardless Including type standard selection
	wt%	wt%	wt%
CO2	42.57	38.397	42.203
MgO	2.29	2.514	2.374
Al2O3	0.77	0.838	0.83
SiO2	1.8	2.032	1.842
SO3	0.755	0.717	0.71
K2O	0.168	0.159	0.158
CaO	51.2	54.7	51.3
Fe2O3	0.446	0.53	0.513

Extra calibration lines are added



You may edit the name for the calibration line, the right line is chosen automatically

Summary

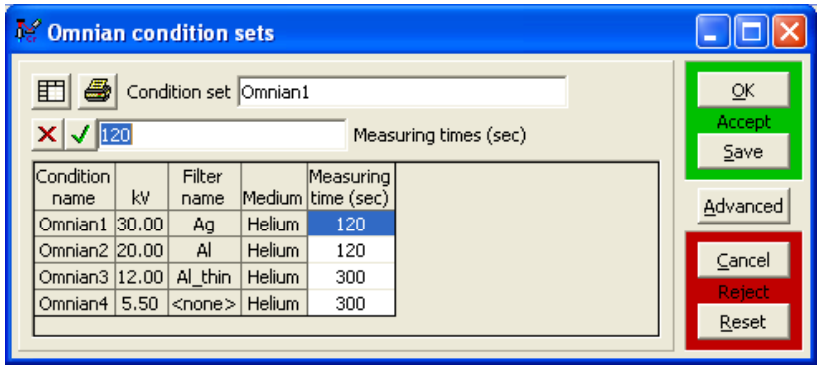
- Using a next generation FP, one can:
  - Correct for widely varying matrix effects,
  - Check for consistency of results,
  - Apply geometry corrections,
  - Apply sample specific corrections (e.g. mineralogy),
  - Determine non-measured compounds,
  - Reduce required no. of standards.

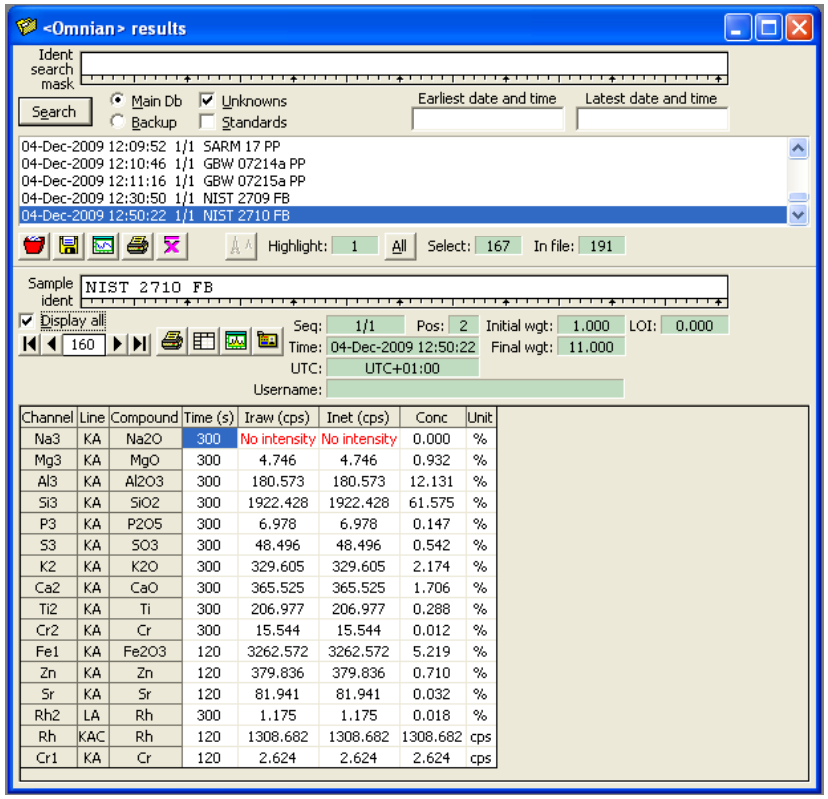
The solution

Omnian

Another solution

- Omnian now also available for MiniPal-4





How far did we get?

Explanation of unexpected results

- Unexpected elements may be found
- Rh and O validation factors help !

The other questions still remain open …..

Thanks for your attention