

Developments in standardless analysis

Where can FP take us?

Kristiansand

Sept 2010

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?

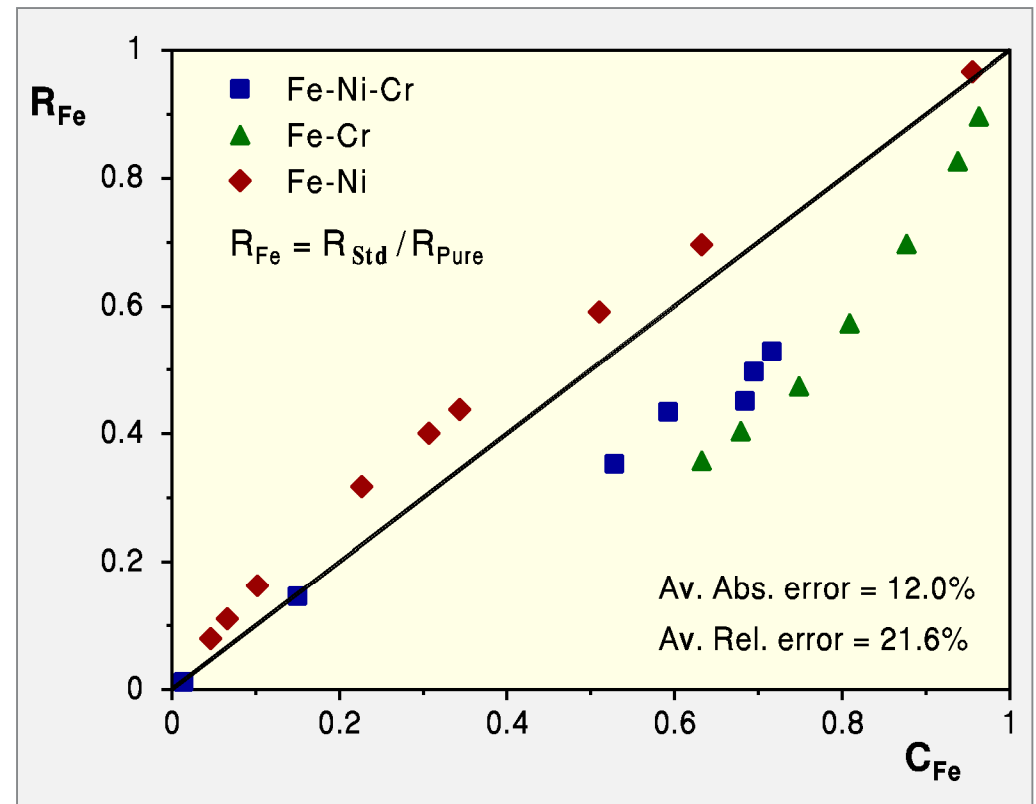
Based on

- **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, CH₂=balance, 35 mm diameter, Mylar 3.6μm foil, Helium atmosphere
- Oxide sample, 10g, 40mm diameter, prepared as fused bead 1g + 10g Li₂B₄O₇
- Steel, 10mm thick, 40mm diameter
- Sewage sludge, 20g, 35mm diameter, CH₂=balance
- Tap water, 20ml, d=1, H₂O=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

$C_{18}H_{36}O$ 99%, P 1%	1 μm
Zn 94 %, Al 1%, Fe 5%	5-10 μm
Substrate = Steel, Fe 99.3 %, Si 0.5%, Mn 0.15% rest <0.05%	1.5 mm

- 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

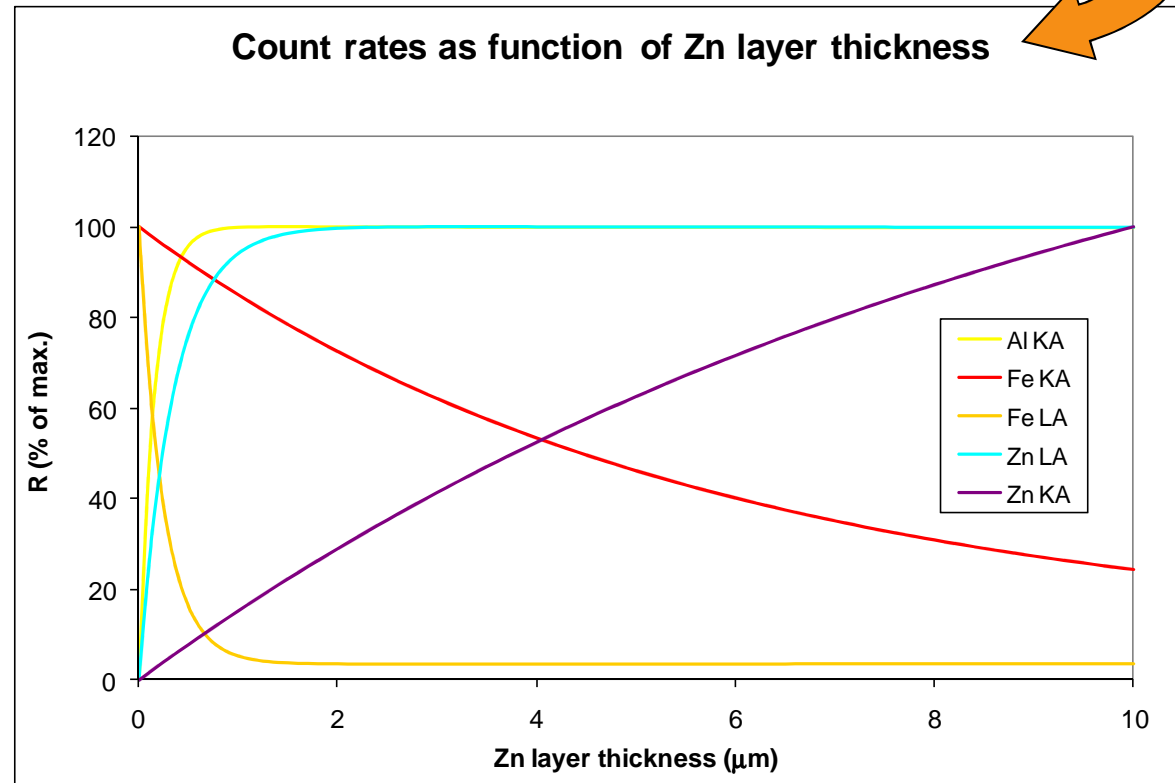
$C_{18}H_{36}O$ 99%, P 1%
Zn 94 %, Al 1%, Fe 5%
Substrate = Steel, Fe 99.3 %, Si 0.5%, Mn 0.15% rest <0.05%

1 μm

5-10 μm

1.5 mm

Varied in thickness



(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 $K\alpha$ (or absorption of Zn/Al)
- Zn Layer:
thickness based on Zn $K\alpha$
 C_{Zn} based on Zn $L\alpha$
 C_{Al} based on Al $K\alpha$
 $C_{Fe} = 100\% - C_{Zn} - C_{Al}$ (or from total Fe $K\alpha$)

Typical results


- Cr on galvanized steel:

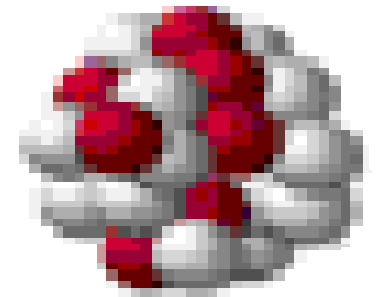
Cr

Zn

Steel

Zn layer: $7.129 \mu\text{m} \pm 0.008 \mu\text{m}$ (8 nm)

Cr layer $8.02 \text{ nm} \pm 0.03 \text{ nm}$ 



- 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
 - SiO₂ on polymer: 2.9 nm ± 0.4 nm
 - Sn & Silicone coating on tin-cans
 - TiO₂ 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

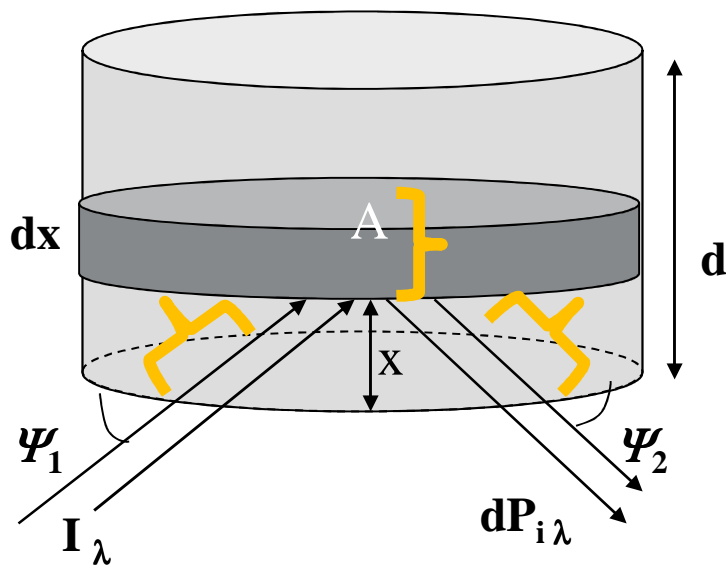
Contribution of slice with thickness dx at depth x to the intensity of element i in a sample

$$dP_{i\lambda}(x) = e^{-\rho x \mu'_{s\lambda}} \underbrace{A \rho \epsilon_{i\lambda} w_i \tau_{i\lambda} I_{\lambda}}_{\text{production of fluorescence in slice}} \frac{dx}{\sin \psi_1} \underbrace{e^{-\rho x \mu''_{s\lambda}}}_{\text{absorption of fluorescent radiation}}$$

absorption of incoming radiation

production of fluorescence in slice

absorption of fluorescent radiation



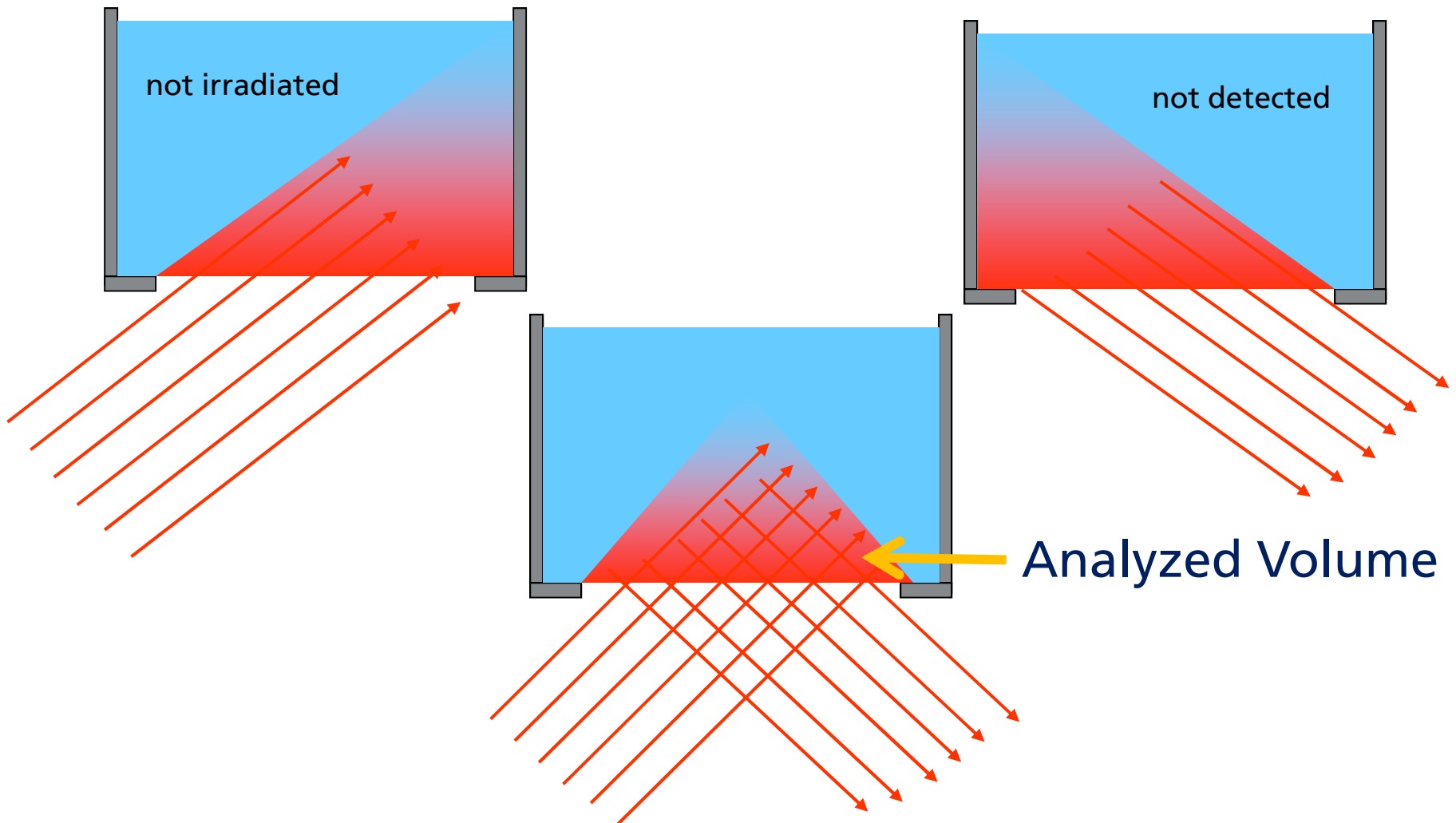
Important:

A = area of slice

x = depth of slice

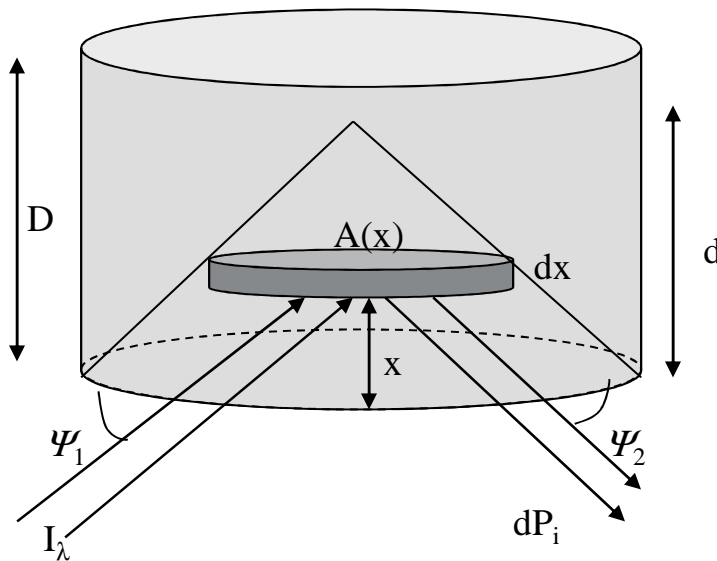
ρ = sample density

Wedge or shadow effect



Extended Sherman Equation

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

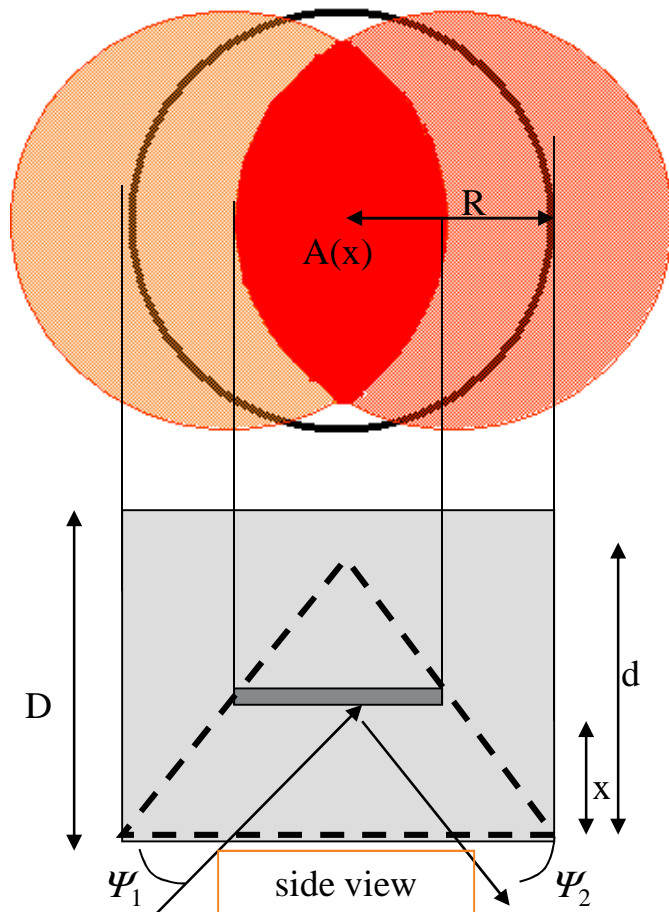


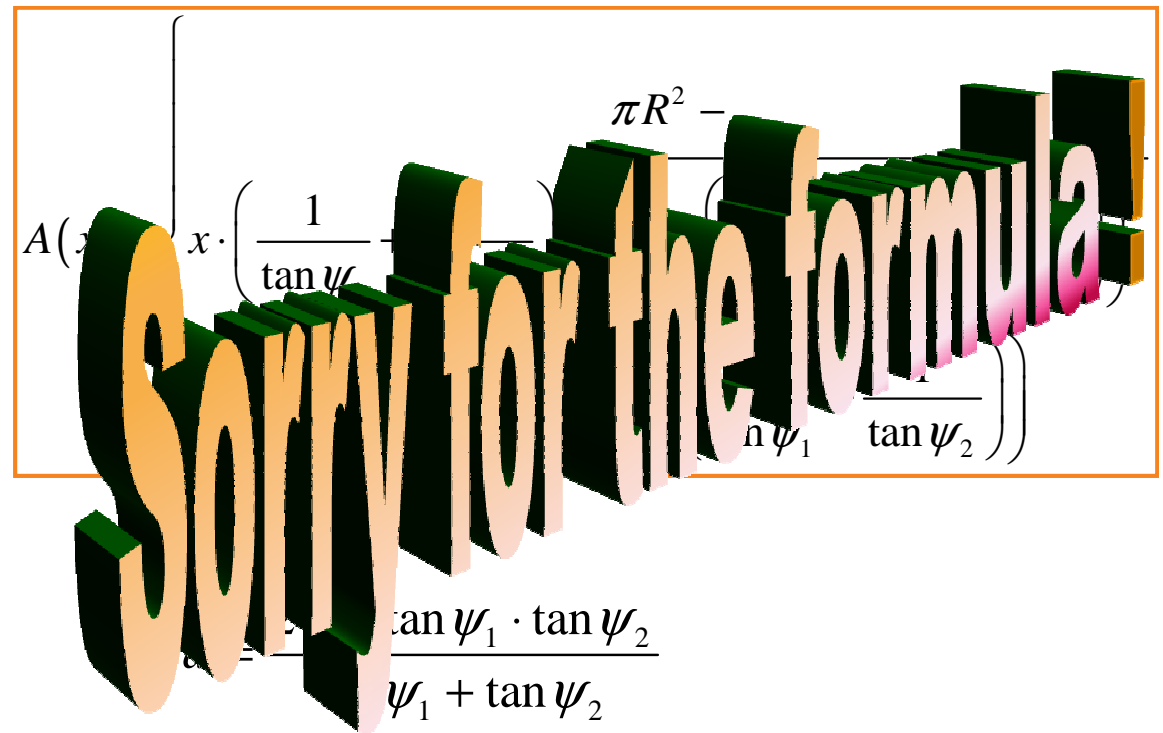
HOWEVER..

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

Area at depth x for circular samples

top view at depth x

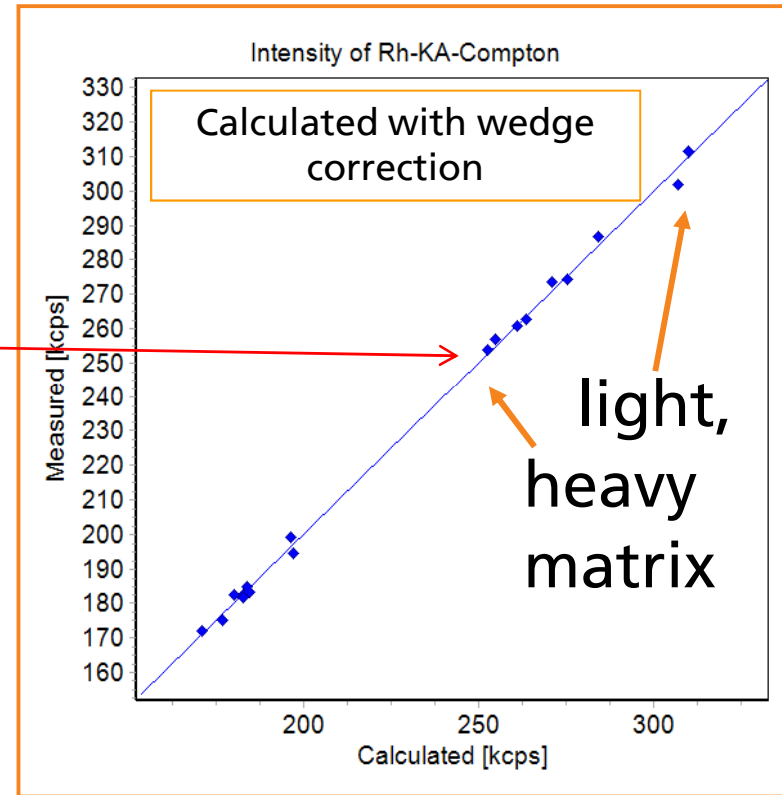
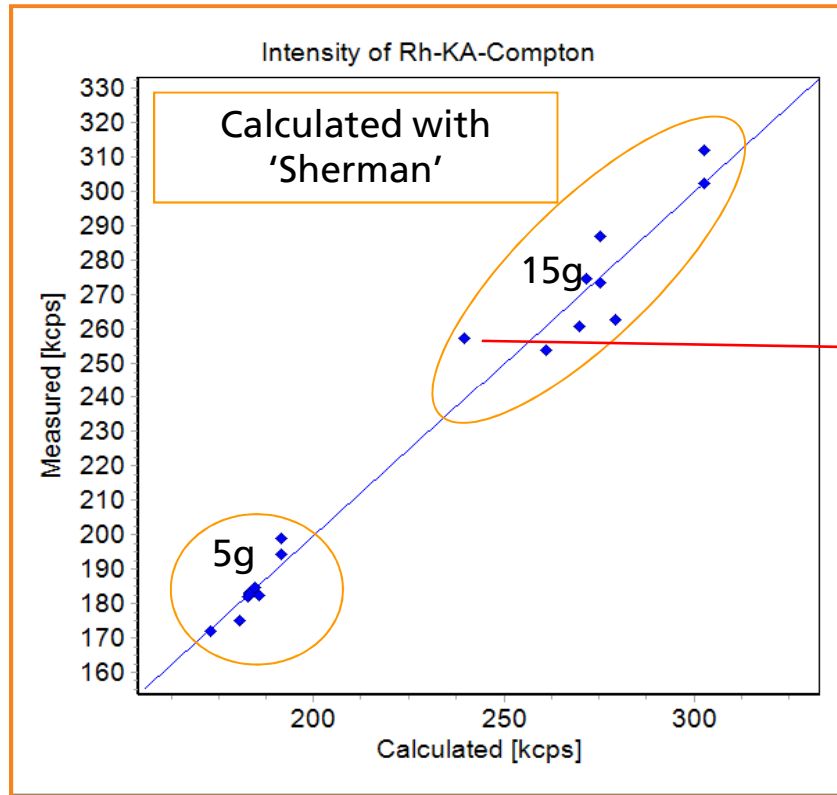




Sorry for the formula!

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

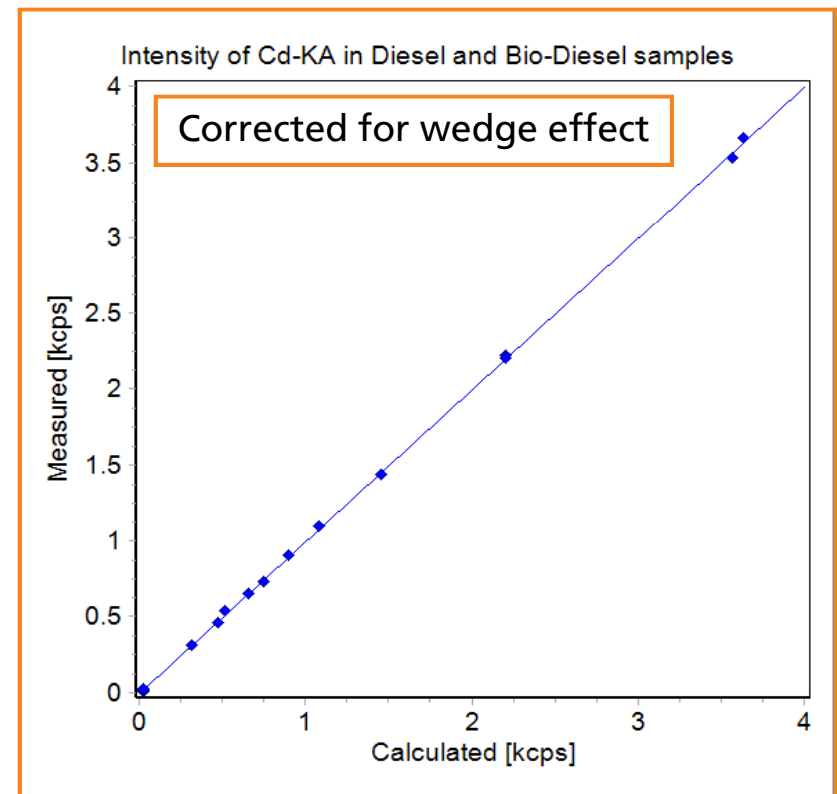
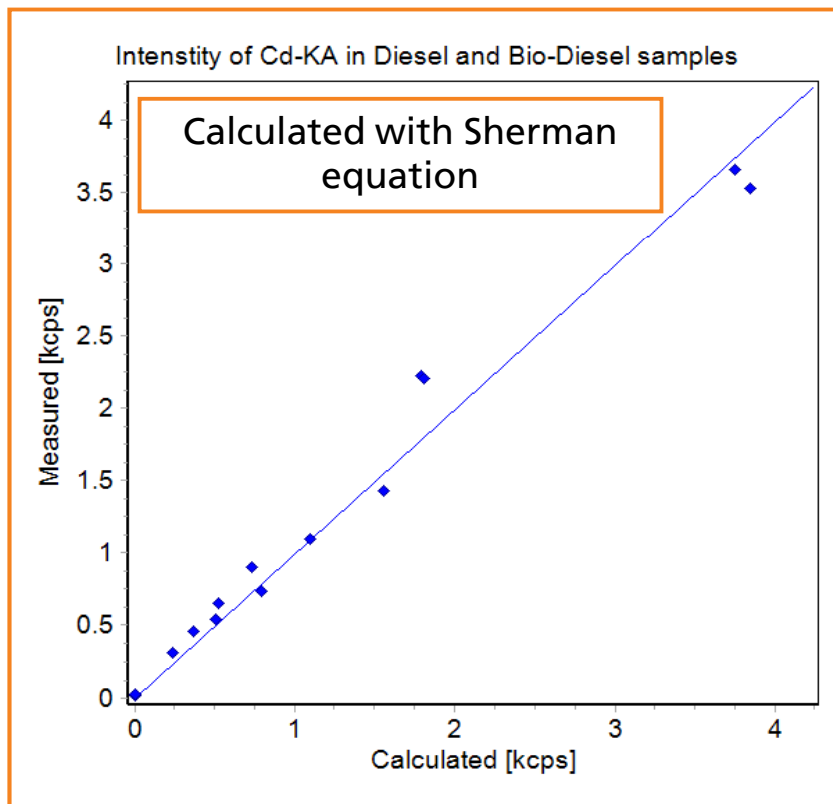
Effect of FVG correction on Rh-K α -Compton



FVG (Fluorescent Volume Geometry) correction

Intensities of Cd-K α in Diesel and Bio-Diesel

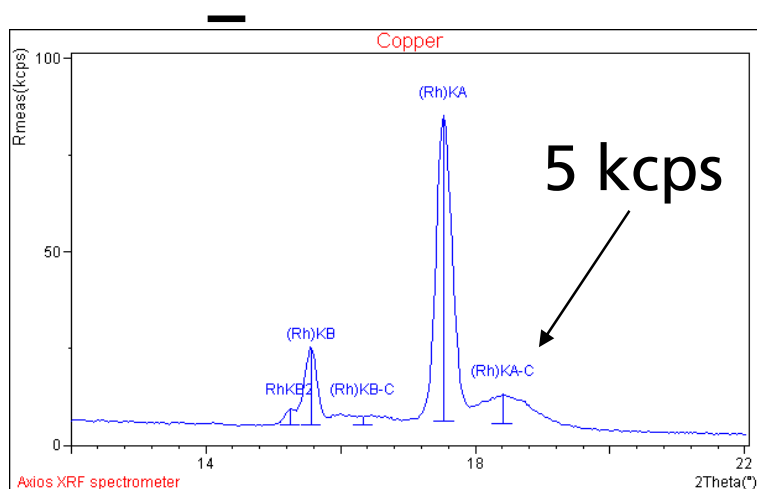
Sample weight between 5g and 15g,
 Bio-Diesel : $\rho = 0.907$, Diesel : $\rho = 0.838$



Use of Compton count rates, additional scan required

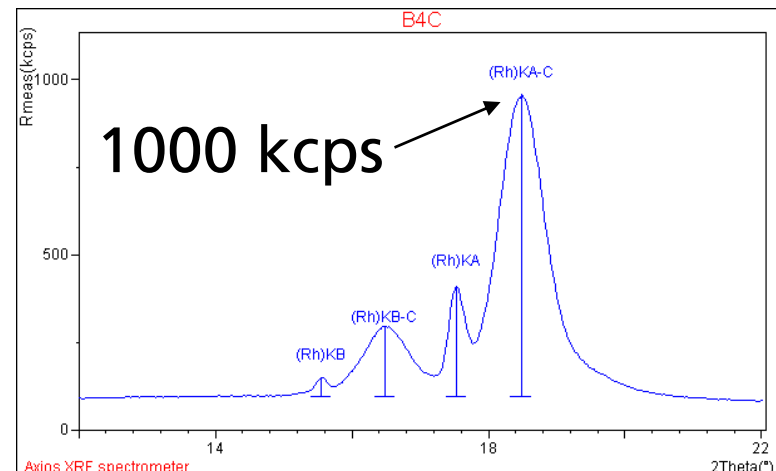
Heavy matrix

⇒ low Compton count rate



Light matrix

⇒ high Compton count rate

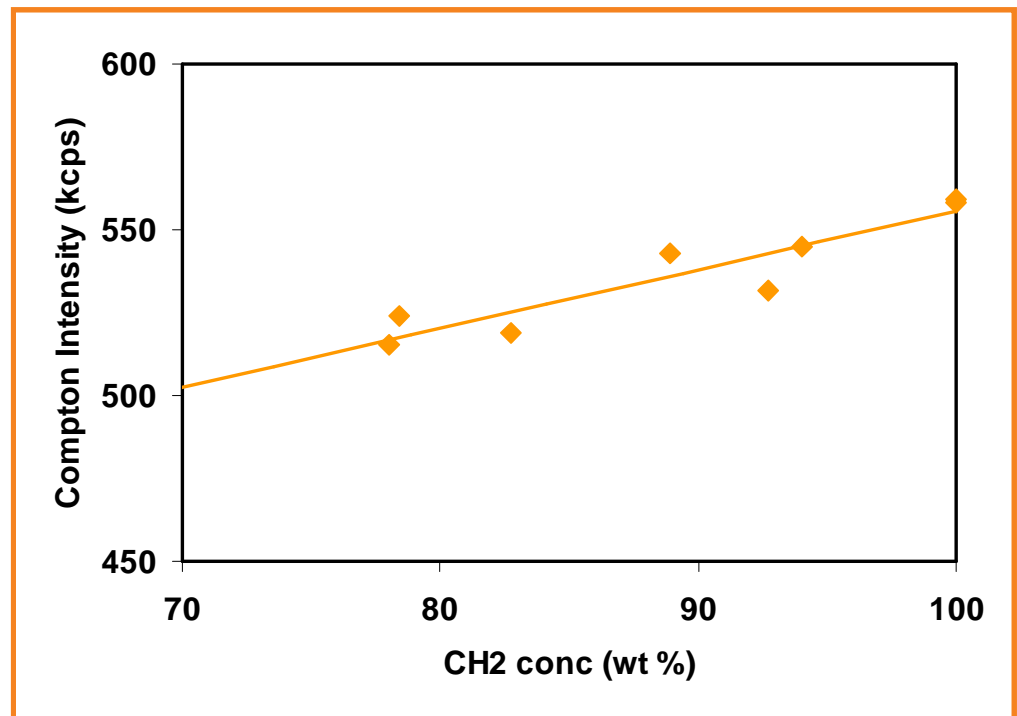


- Works well for light matrices
 - Improves quantitative calibrations
 - Can be used to derive 'extra' information like e.g. non-measured compounds, or validation of standardless results.

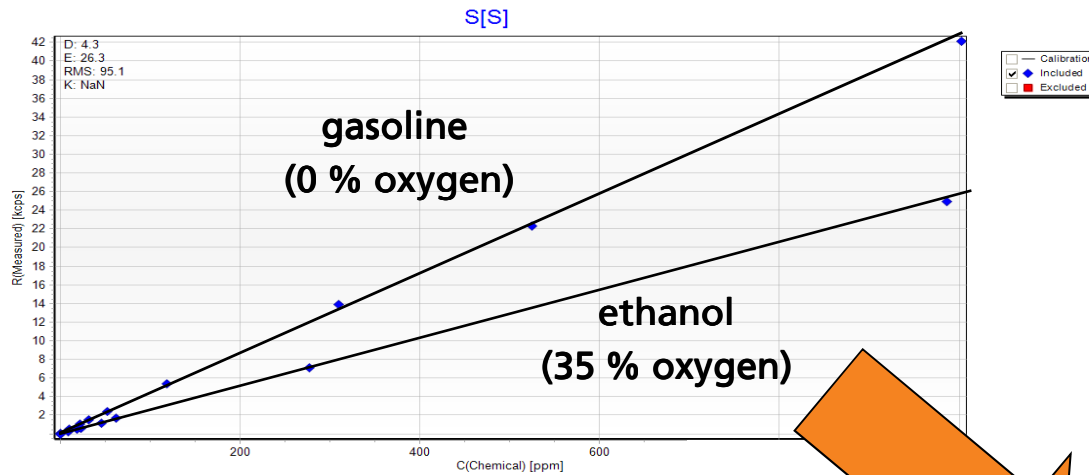
The use of $R_{\text{Rh Compton}}$ in oil analysis (oil-trace)

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

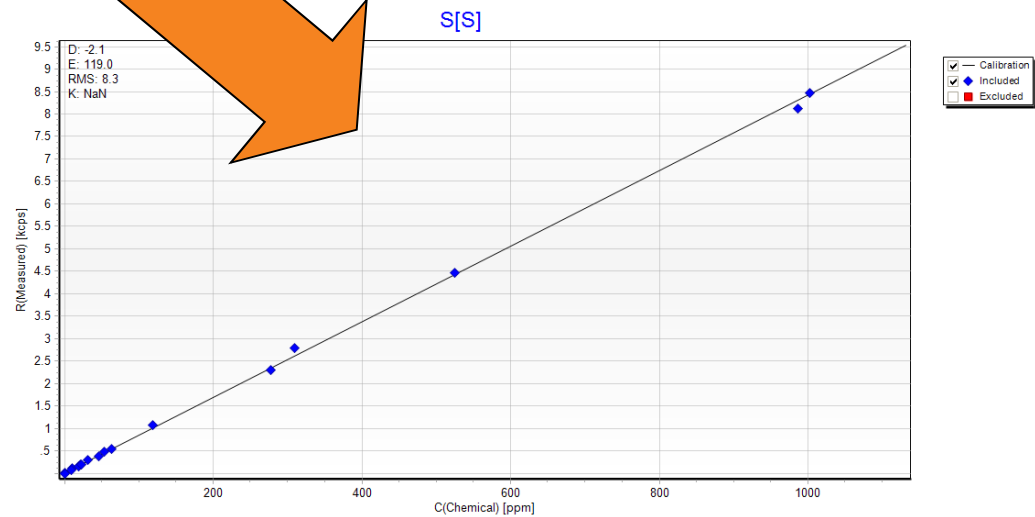
CH_2 from regression,
Oxygen = balance



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

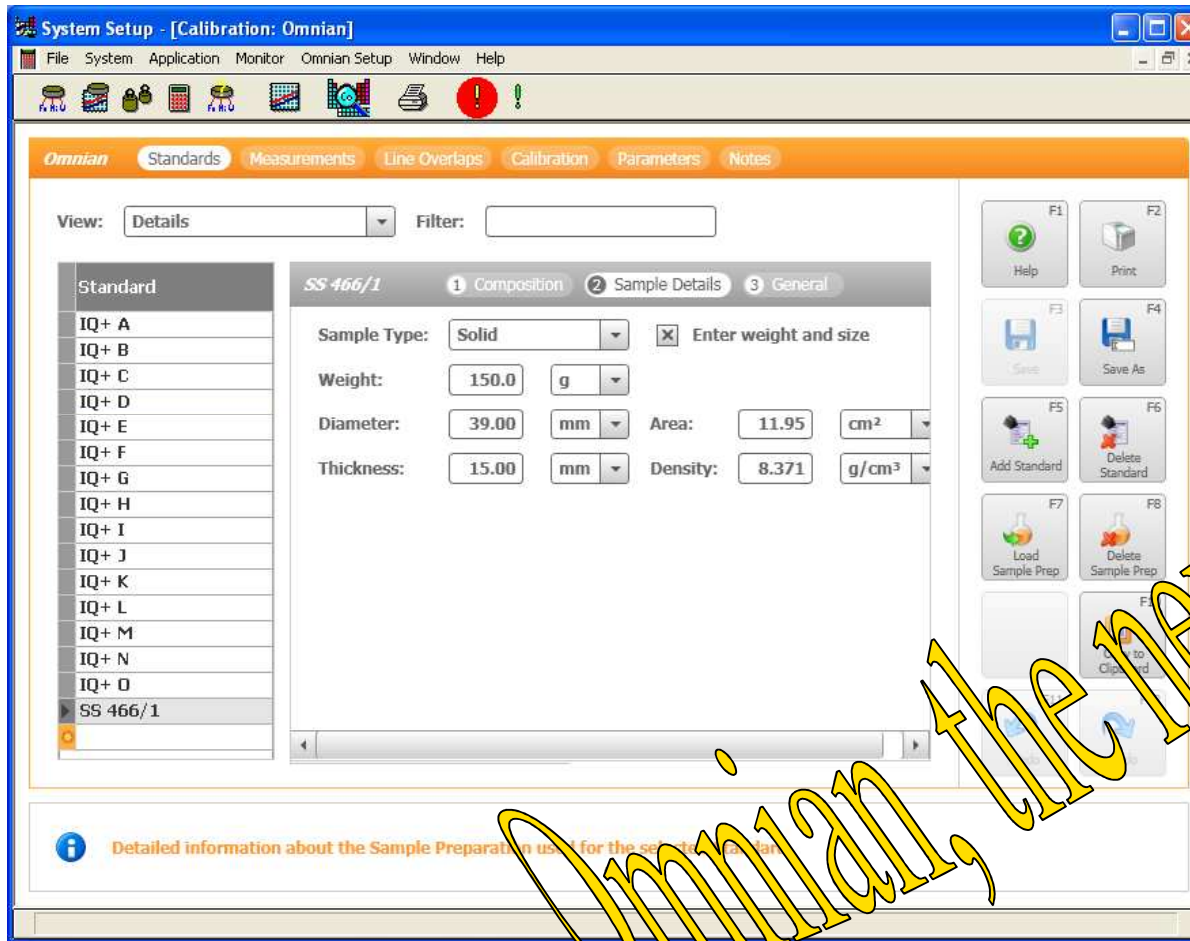


Without oxygen correction



With oxygen correction (from Rh Compton)

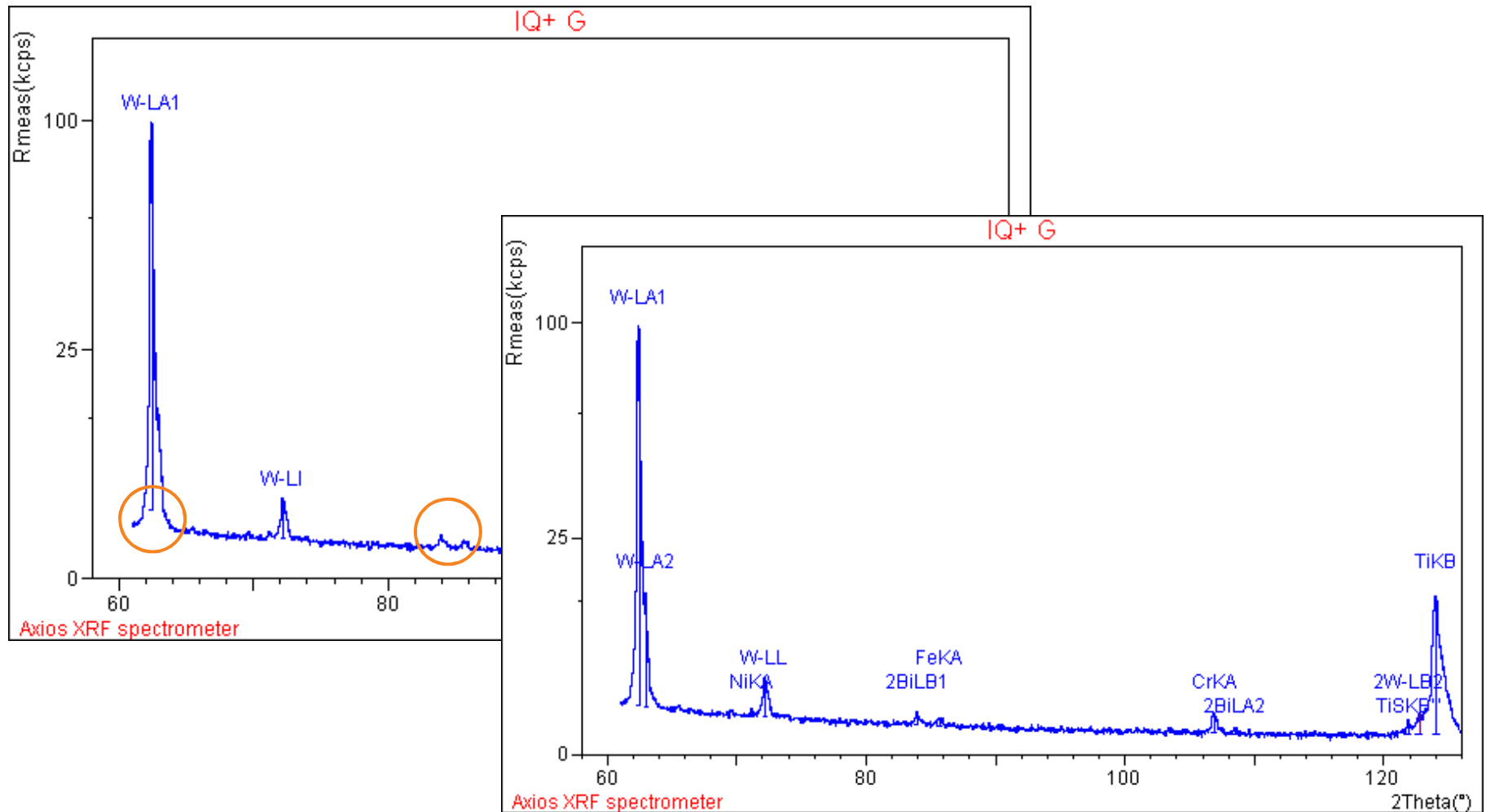
So what are we talking about?



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

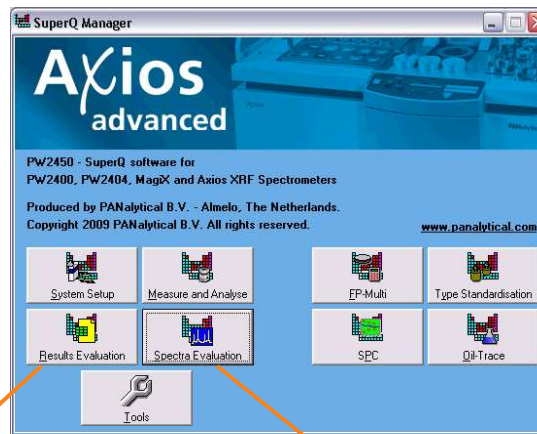
Omnian : improved search, match & Background



Results can be viewed in Results Quantitative

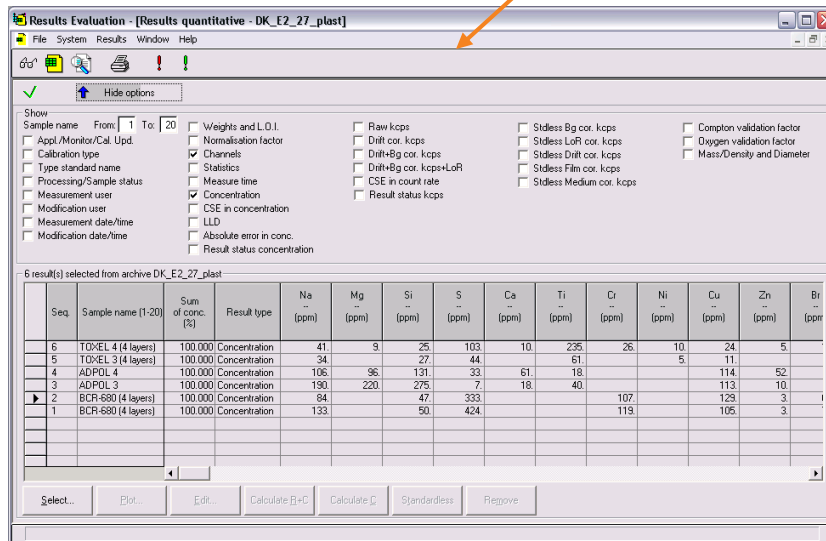
Results Evaluation

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



Spectra Evaluation

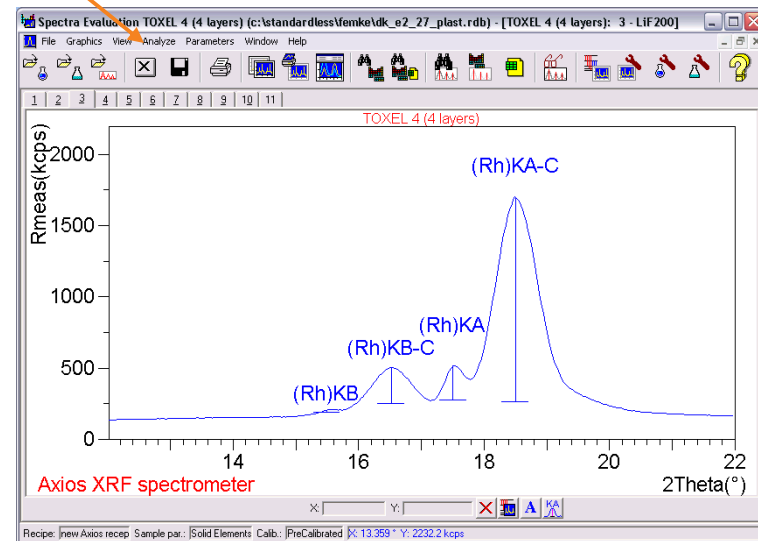
- For more advanced results viewing and reprocessing
- Possibility to view scans



Results Evaluation - [Results quantitative - DK_E2_27_plast]

6 result(s) selected from archive DK_E2_27_plast

Seq	Sample name (1-20)	Sum of conc. (%)	Result type	Na (ppm)	Mg (ppm)	Si (ppm)	S (ppm)	Ca (ppm)	Ti (ppm)	Cr (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Br (ppm)
6	TOXEL 4 (4 layers)	100.000	Concentration	41	9	25	103	10	235	26	10	24	5	
5	TOXEL 3 (4 layers)	100.000	Concentration	34		27	44		61			5	11	62
4	ADPOL 4	100.000	Concentration	106	96	131	33	61	18				114	10
3	ADPOL 3	100.000	Concentration	190	220	275	7	18	40				113	10
2	BCR-680 (4 layers)	100.000	Concentration	84		47	333			107			129	3
1	BCR-680 (4 layers)	100.000	Concentration	133		50	424			113			105	3



Various new functions

Sample parameters of sample 4G TABAK + 0.4 WAX & 4G WAX

Sample parameters | Manual input compounds | Reporting

Sample type

- Solid
- Pressed powder
- Fused bead
- Liquid
- Pre-treated bead
- Loose powder
- Finite thickness

Normalization

- No normalization Required sum (%): 100.
- Normalize to required sum
- Use as balance compound: C6H10O5

Derive from Compton: 0

Corrections

- Apply Medium correction
- Medium Monitor:
- Reload
- Apply Film correction
- Film monitor:
- Reload
- Apply FVG correction

Compound list

- Use Compound list
- Oxides

Sample preparation

Initial sample weight (g): 4.00

Final sample weight (g): 4.40

Finite thickness details

Diameter (mm): 40.0

Area (mm²): 1256.6

Density(g/cm³): 1.7507

Thickness(mm): 2.00

Mass-thickness (mg/mm²): 3.5014

Binder used

Binder		
Compound	Chemical formula	Weight (g)
Wax	C18H36O2N2	0.40

Add Add from Additive list Remove

OK Cancel Load new param. set ... Save As ... Print Help

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

FVG correction: in calibration

Standard	PE Blank 1...	1 Composition	2 Sample Details	3 General
PE Blank 1 disk	Sample Type:	Solid	<input checked="" type="checkbox"/> Enter weight and size	
PE Blank 2 disk	Weight:	2.020	g	
PE Blank 3 disk	Diameter:	39.50	mm	Area: 12.25 cm ²
PE Blank 4 disk	Thickness:	0	mm	Density: 0 g/cm ³
PE Blank 5 disk				
PE Blank 6 disk				
PE Blank 7 disk				
PE Blank 8 disk				
PE Blank 9 disk				

No FVG

Standard	PE Blank 1...	1 Composition	2 Sample Details	3 General
PE Blank 1 disk	Sample Type:	Solid	<input checked="" type="checkbox"/> Enter weight and size	
PE Blank 2 disk	Weight:	2.020	g	
PE Blank 3 disk	Diameter:	39.50	mm	Area: 12.25 cm ²
PE Blank 4 disk	Thickness:	1.800	mm	Density: 0.9158 g/cm ³
PE Blank 5 disk				
PE Blank 6 disk				
PE Blank 7 disk				
PE Blank 8 disk				
PE Blank 9 disk				

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 $\text{C}_{18}\text{H}_{36}\text{ON}$?)
 - 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'

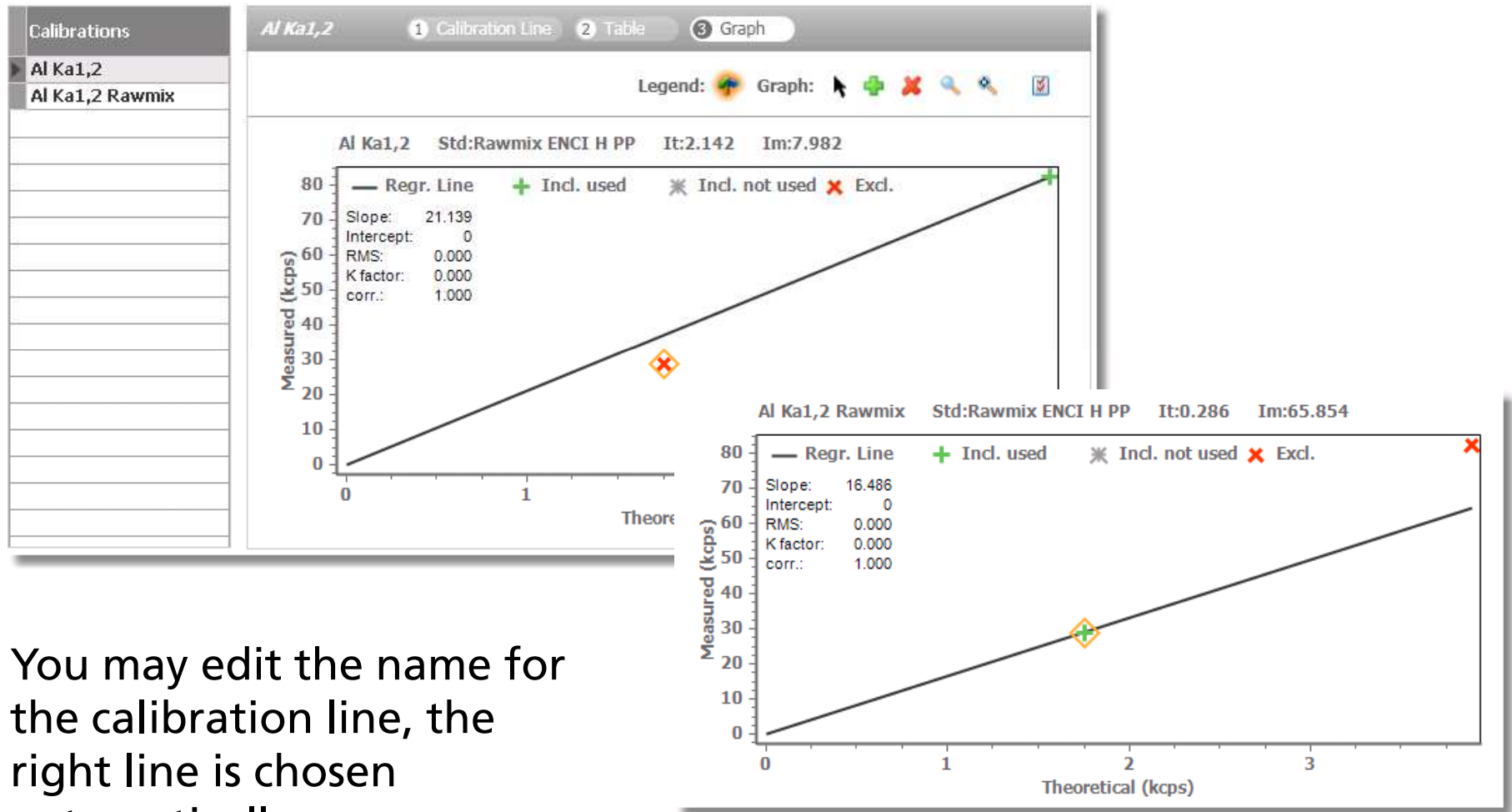
Use FP + in-type standards, (like in quantitative analysis) to get the best of both worlds. Choose tag = 'Cement' during measurement.

Large advantage:

One standard is sufficient

	Certified wt%	Conventional standardless analysis wt%	Standardless Including type standard selection 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

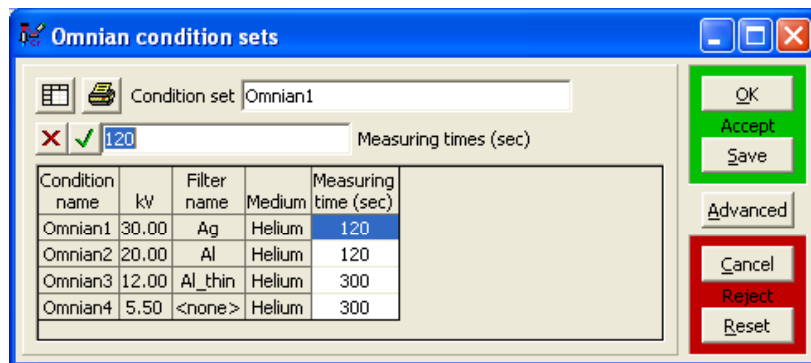
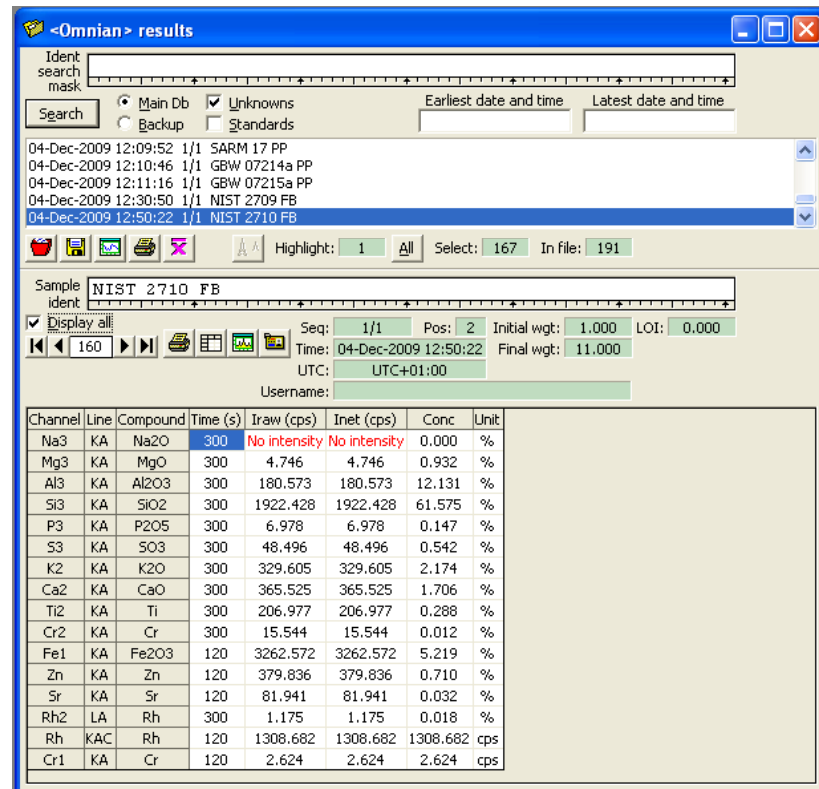
- Using a next generation FP, one can:
 - Correct for widely varying matrix effects,
 - Check for consistency of results,
 - Apply geometry corrections,
 - Apply sample specific corrections (e.g. mineralogy),
 - Determine non-measured compounds,
 - Reduce required no. of standards.

The solution

Omnian

Another solution

- Omnian now also available for MiniPal-4

Sample ident: NIST 2710 FB

Seq: 1/1 Pos: 2 Initial wgt: 1.000 LOI: 0.000
 Time: 04-Dec-2009 12:50:22 Final wgt: 11.000
 UTC: UTC+01:00
 Username:

Channel	Line	Compound	Time (s)	Iraw (cps)	Inet (cps)	Conc	Unit
Na3	KA	Na2O	300	No intensity	No intensity	0.000	%
Mg3	KA	MgO	300	4.746	4.746	0.932	%
Al3	KA	Al2O3	300	180.573	180.573	12.131	%
Si3	KA	SiO2	300	1922.428	1922.428	61.575	%
P3	KA	P2O5	300	6.978	6.978	0.147	%
S3	KA	SO3	300	48.496	48.496	0.542	%
K2	KA	K2O	300	329.605	329.605	2.174	%
Ca2	KA	CaO	300	365.525	365.525	1.706	%
Ti2	KA	Ti	300	206.977	206.977	0.288	%
Cr2	KA	Cr	300	15.544	15.544	0.012	%
Fe1	KA	Fe2O3	120	3262.572	3262.572	5.219	%
Zn	KA	Zn	120	379.836	379.836	0.710	%
Sr	KA	Sr	120	81.941	81.941	0.032	%
Rh2	LA	Rh	300	1.175	1.175	0.018	%
Rh	KAC	Rh	120	1308.682	1308.682	1308.682	cps
Cr1	KA	Cr	120	2.624	2.624	2.624	cps

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