

# ALTERNATIVE APPLICATIONS USING WDXRF

COMPILED BY

XRF SPECIALIST

CARMEN KAISER BRÜGMANN



**Rigaku**

POWERING NEW PERSPECTIVES

# Content

- Introduction
- WDXRF Instrument
- Instrument configuration
- SQX Scatter FP
- Loose powder measured in Vacuum
- Oil solidification Method
- Ultra Carry Micro Carry
- Summary

# Introduction

## A brief overview

- Founded 1951 in Japan
- Biggest analytical & industrial X-ray company globally
  - Today more than 1400 direct employees
  - Hundreds of innovations in:
    - X-ray Crystallography
    - X-ray Diffraction
    - X-ray Fluorescence, first WDX 1962,
      - thousands of installations all over the world



WDX

XRD

Simultix 15



ZSX Primus IV



ZSX Primus IV*i*



ZSX Primus III <sup>NEXT</sup>



Supermini200



Excellent spectral resolution  
(Less line overlaps)  
High precision analysis

## WDX

### ZSX Primus III <sup>NEXT</sup>



Standard system

Normal sample throughput

### ZSX Primus IV



Standard system

High sample throughput

### ZSX Primus IV*i*



Small footprint

If liquids needed

Normal to High sample throughput

### Supermini200



Backup-System

If liquids needed

Best Light element

### Simultix 15



Most powerful system

High sample throughput

Small footprint

## Sequential WDXRF

ZSX Primus IV



Tube Above

ZSX Primus IV*i*



Tube below

ZSX Primus III <sup>NEXT</sup>



Tube Above



## Configuration Summary

- 4 kW Rh-Tube with 30 $\mu$ m Be-Window
- Tube above Geometry
- Dual Detector Configuration with Scintillation Counter (SC) and Proportional Counter (PC)
- 48 Position Sample Changer
- 10 Position Analyzing Crystal Changer
- 5 Diaphragms
- 5 Primary Beam Filters
- 3 Collimation Slits



## Features and benefits

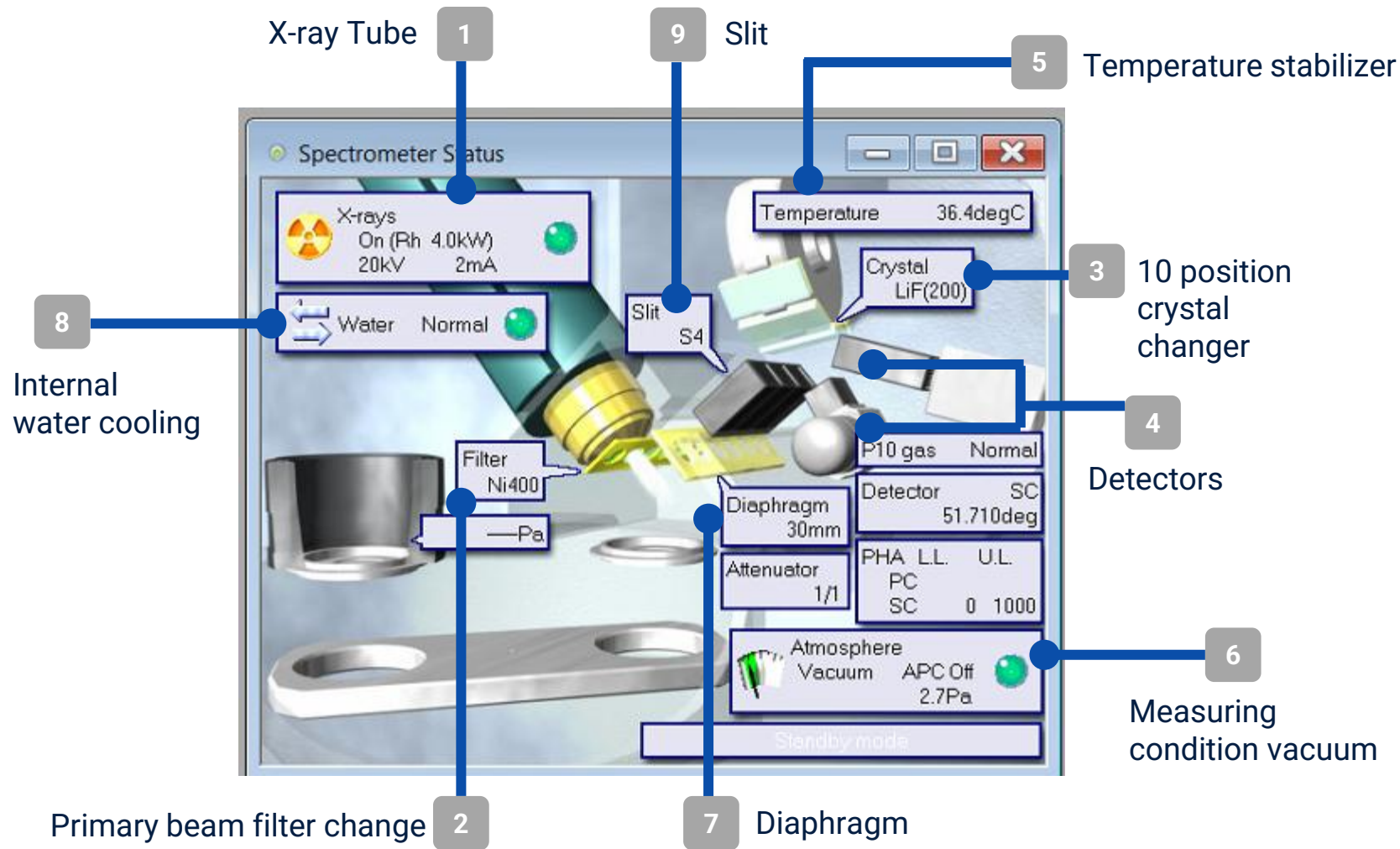
- Thin Be30 $\mu$ m window on the X ray tube results in 40% more intensity especially beneficial for light element detection resulting in lower limit of detection
  - High sensitivity enables high precision or short measurement time, and low detection limit.
- Tube above system ensures the long-term usage of the X-ray Tube, no dust on the thin Be window, loss of intensity is reduced, thus offering enhanced reliability and durability. Accidental contamination of the goniometer or inadvertent damage to the X-ray tube is minimized
- Vacuum partition saves on the consumption of He gas resulting in reduced cost of consumables
- Automatic central wire cleaning mechanism controlled by the user and the software, resulting in reduced service costs, improved resolution on the F-PC detector better light element detection with less variation



## Features and benefits

- Various Algorithm Correction models available, best automatic overlap corrections without the need for additional standards
- Automatic Quantitative method setup with all measuring conditions chosen based on the elements, concentration range and sample type
  - Built-in expertise method development made fast and easy
- Special sample cells and solutions for tiny sample analysis in vacuum mode, resulting in better precision and accuracy
- SQX FP quantification of all RDF waste materials example elephant grass ,nut shells ,sludges ,waste ,plastic etc...

# ZSX Primus IV instrument configuration

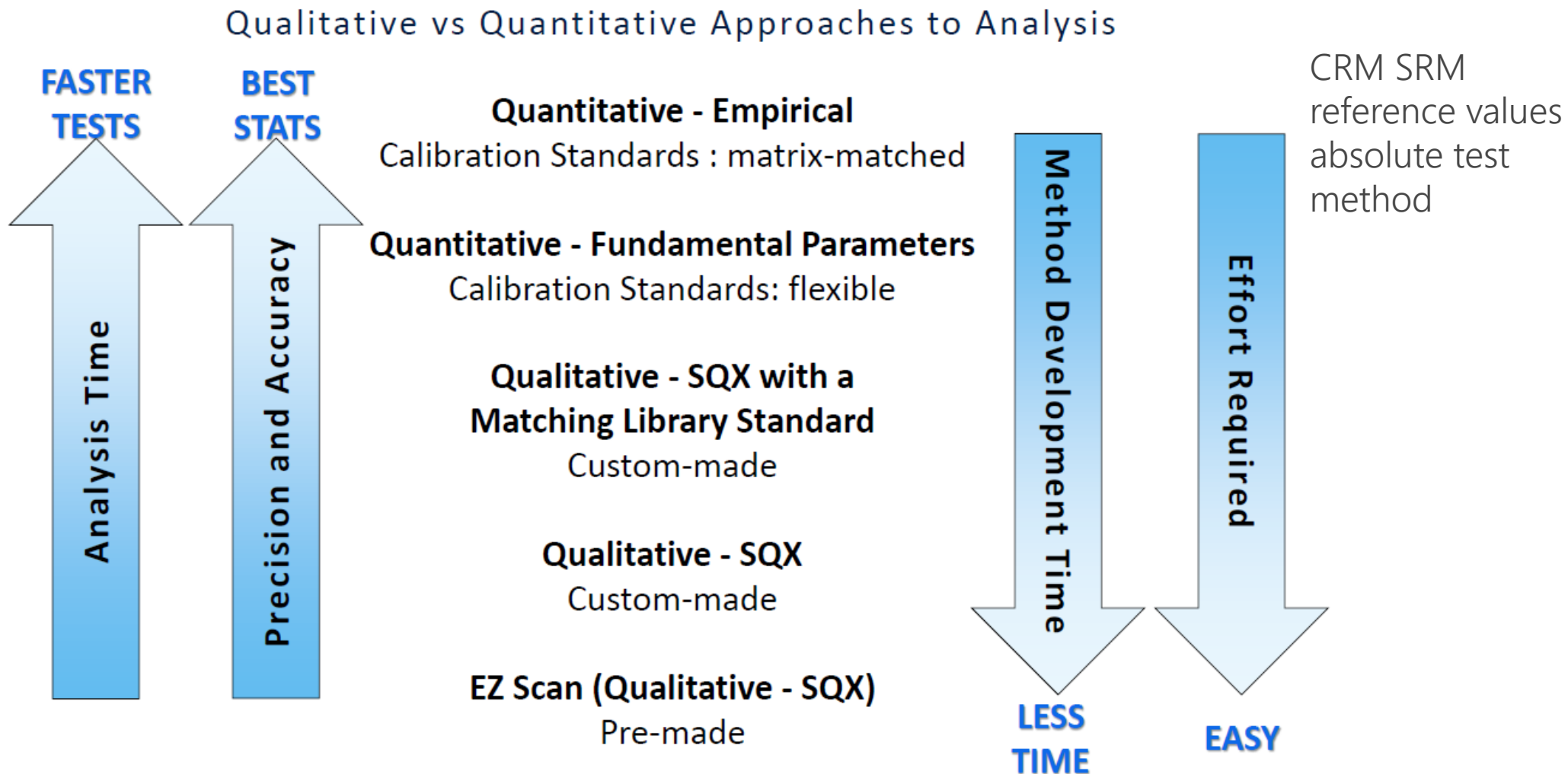


# ZSX Primus IV instrument configuration

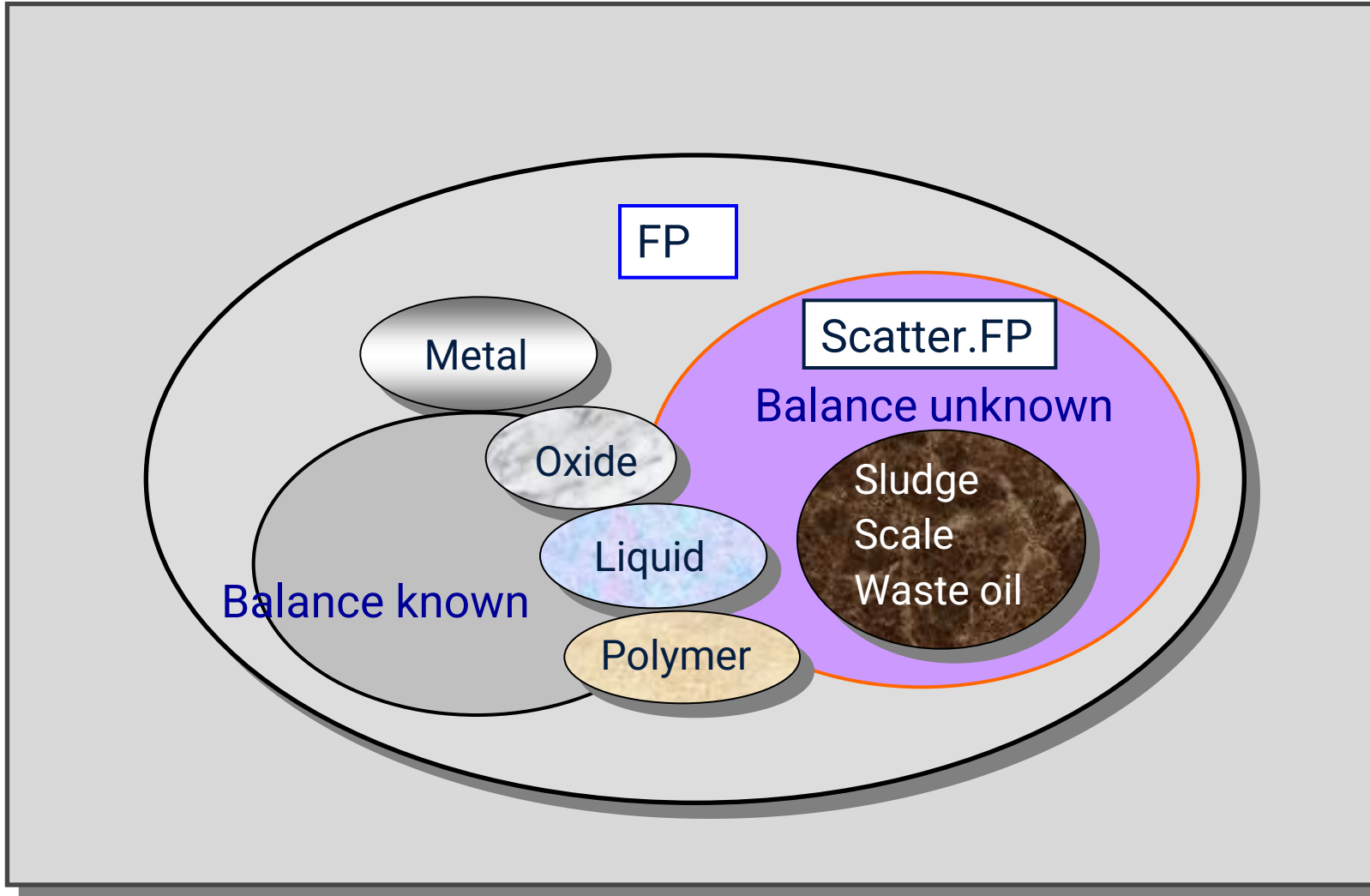
Configuration	
X-ray source	4 kW Rh X-ray tube 60kV 150 mA
Detector	Scintillation counter (SC)
Detector	Proportional counter (PC)
Crystal	LiF200
Crystal	RX25
Crystal	GeH
Crystal	PETH
Crystal	LiF420
Crystal	RX61
Crystal	RX45
Crystal	LiF220
Crystal	RX35
Crystal	RX85

Configuration	
Primary beam filter	Be30
	Ni400
	Ni400
	Al125
	Al25
Diaphragm	30 mm
	20 mm
	10 mm
	1 mm
	0.5 mm
Attenuator	30mm
Collimator	S2
	S4
	S8

# GENERAL TRENDS OF ACCURACY AND TIME



# SQX Scatter FP



## *Function:*

Scatter lines are used in FP calculation of SQX Analysis to estimate the influence of the components that are not measured, typically H, C, N and O.

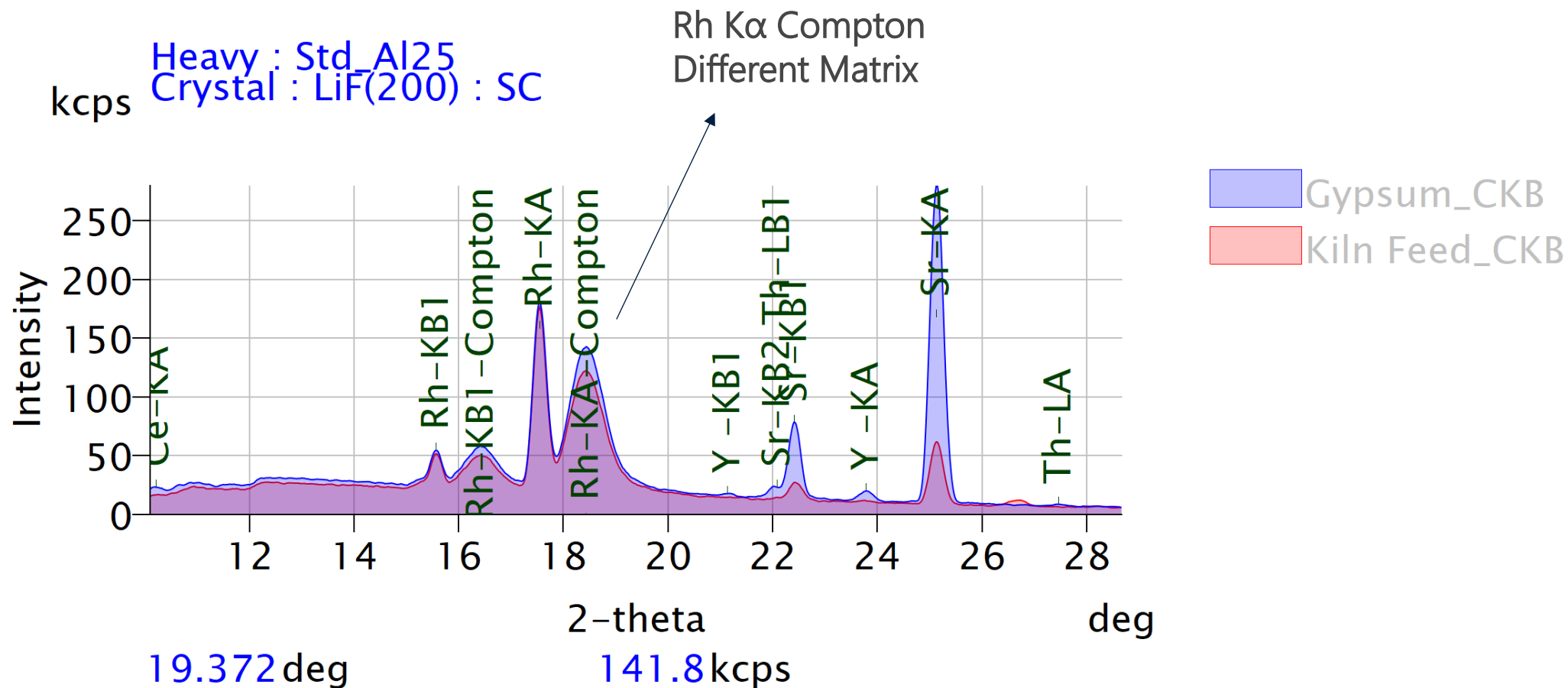
## *Typical samples and applications:*

Samples containing a significant amount of H, B, C, N and O, such as waste materials, organic samples, fly ash, soil, limestone and plastics.

## *Requirement:*

“SQX Analysis” option is required.  
For “Powder” and “Polymer”, a 20mm-opening mask and a backscatter-elimination cup are required.

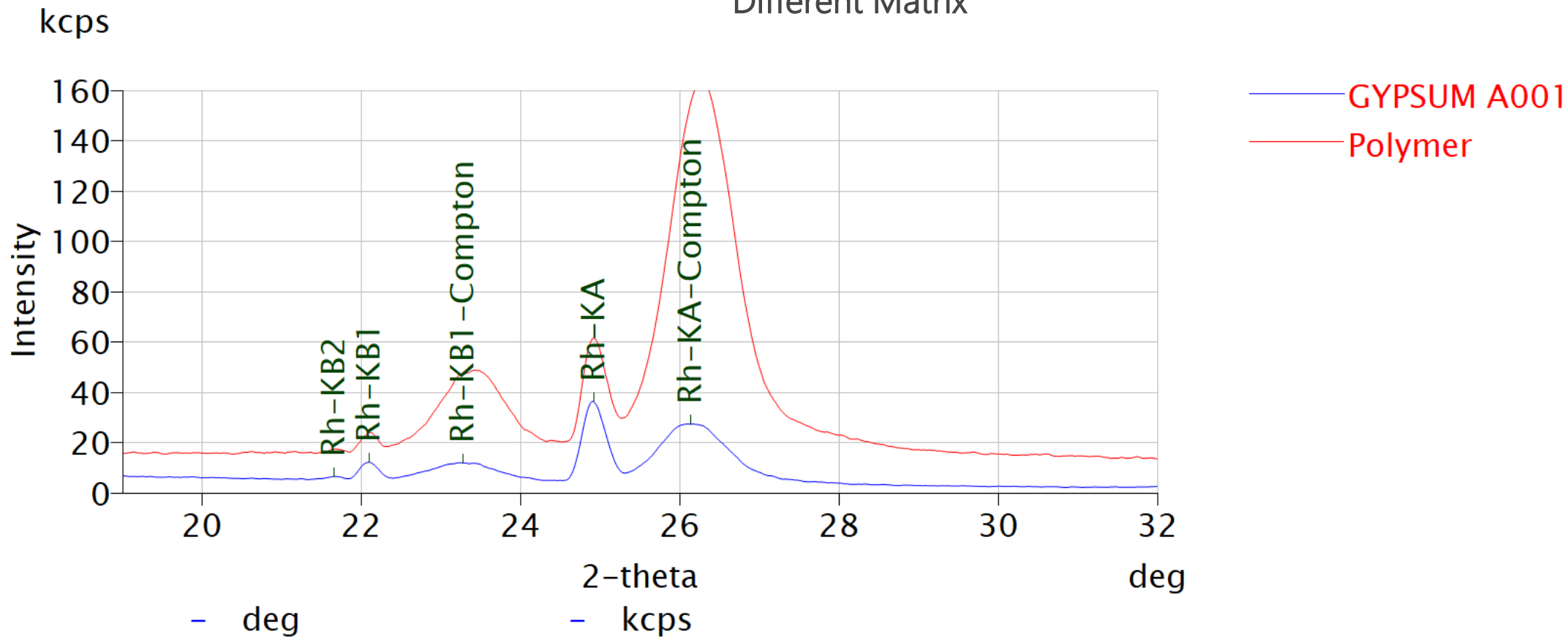
# SQX Scatter FP method



# SQX Scatter FP method

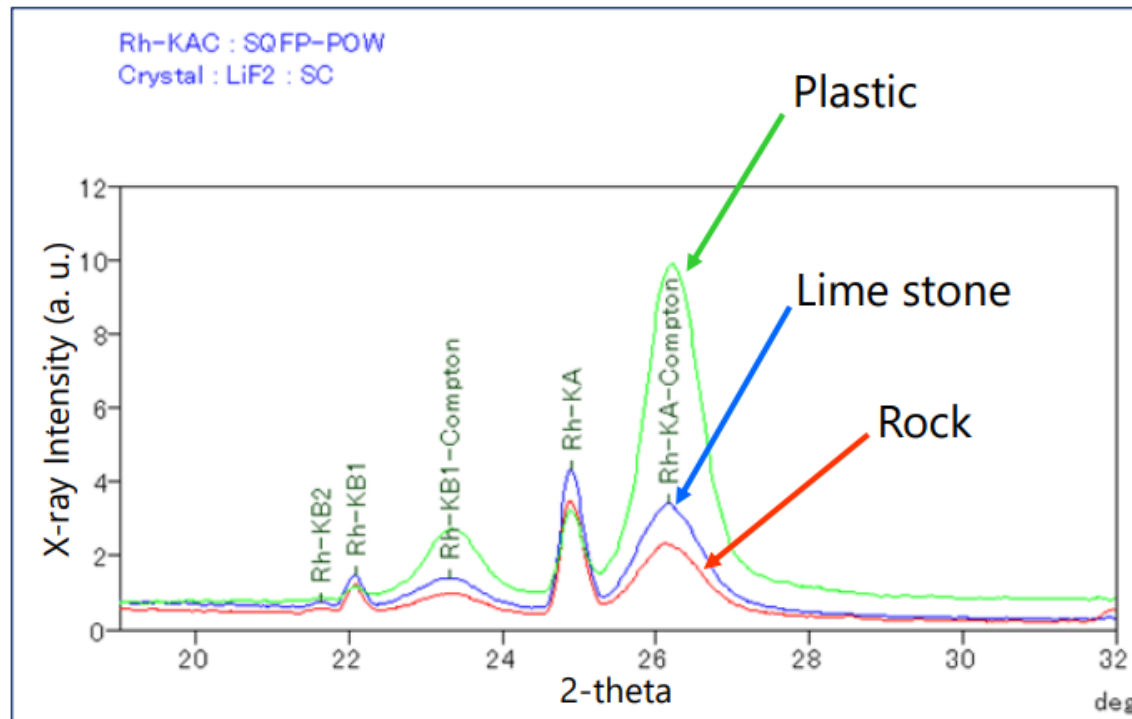
Scatter. : SQFP-POW  
Crystal : LiF(220) : SC

Rh K $\alpha$  Compton  
Different Matrix



# Automatic Estimation of Balance Component —SQX Scattering FP Method—

Optional



Estimate influences of ultra-light elements (H – O)

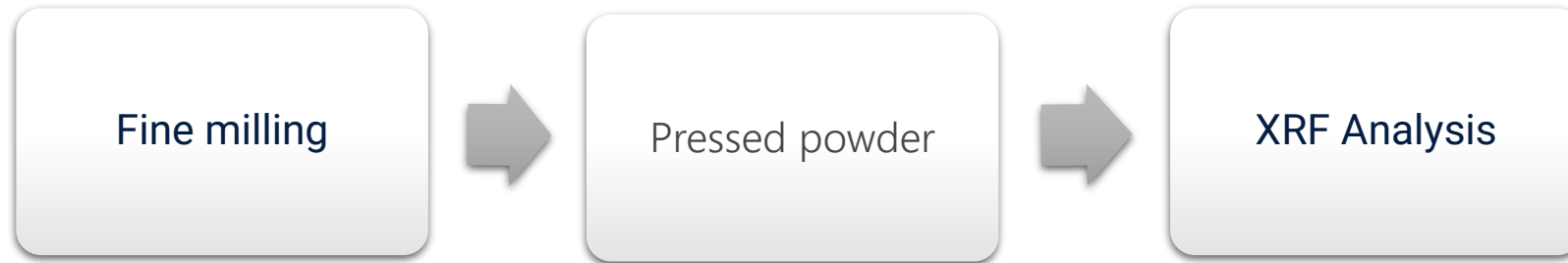
# Alternative Fuels

Sample	Description	Status
1	Alternative fuel 19 12 10 Bulky beige grey material	Ok for testing

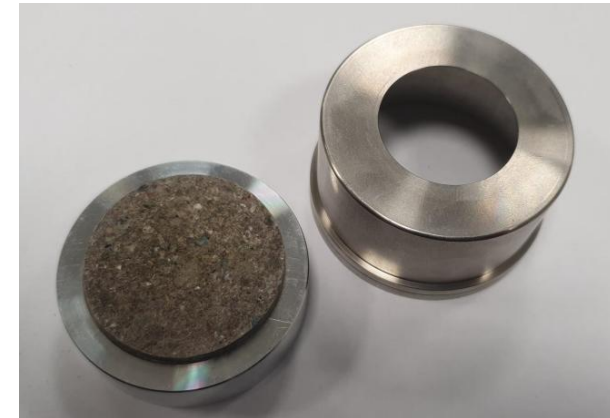
Original sample recieved



# Sample preparation



- ✓ Samples ( $6.00 \pm 0.01$ g) were pressed with wax as the binder (Cereox,  $1,50 \pm 0.01$ g) in ratio of 0.25 which is specified by all results as S-BLEND
- ✓ Pressed powder was prepared using Fluxana press (Veneox 25t manual)



- SQX Scatter FP method was set for the Alternative fuel sample

Qual Flow Bar

RDF Waste

Application File

Select Element Range

Sample Preparation

Parameters

Check Measuring Condition

Output Information

Exit

SQX  
Scatter  
FP



Repeatability  
measurements



Precision at the 95 %  
confidence level

Check Measuring Condition

Spectrum	Library	Target	KV-mA	Filter	Att.	Slit	Crystal	Defec...	PHA
Heavy	Standard	Rh	50-60	OUT	1/1	S2	LiF(200)	SC	100-30
Cd-KA	Std_Ni400	Rh	50-60	Ni400	1/1	S2	LiF(200)	SC	150-25
2 Cd-KA	Std_Ni400	Rh	50-60	Ni40	1/1	S2	LiF(200)	SC	100-27
Br-KA	Std_Ni40	Rh	50-60	Ni40	1/1	S2	LiF(200)	SC	100-27
2 Br-KA	Std_Ni40	Rh	50-60	Ni40	1/1	S2	LiF(200)	SC	100-27
Pb-LB1	Std_Ni40	Rh	50-60	Ni40	1/1	S2	LiF(200)	SC	100-27
2 Pb-LB1	Std_Ni40	Rh	50-60	Ni40	1/1	S2	LiF(200)	SC	100-27
Hg-LA	Std_Ni40	Rh	50-60	Ni40	1/1	S2	LiF(200)	SC	100-27
2 Hg-LA	Std_Ni40	Rh	50-60	Ni40	1/1	S2	LiF(200)	SC	100-27
Cr-KA	Standard	Rh	50-60	OUT	1/1	S2	LiF(200)	SC	100-30
2 Cr-KA	Standard	Rh	50-60	OUT	1/1	S2	LiF(200)	SC	100-30
Ca-KA	Standard	Rh	40-75	OUT	1/1	S4	LiF(200)	PC	100-30
K-KA	Standard	Rh	40-75	OUT	1/1	S4	LiF(200)	PC	100-30
CH-KA	Standard	Rh	30-100	OUT	1/1	S2	GeH	PC	150-30
S-KA	Standard	Rh	30-100	OUT	1/1	S4	GeH	PC	150-30
P-KA	Standard	Rh	30-100	OUT	1/1	S4	GeH	PC	150-30
SH-KA	Standard	Rh	30-100	OUT	1/1	S4	PETH	PC	100-30
AH-KA	Standard	Rh	30-100	OUT	1/1	S4	PETH	PC	100-30
Mg-KA	Standard	Rh	30-100	OUT	1/1	S4	RX26	PC	100-25
Na-KA	Standard	Rh	30-100	OUT	1/1	S4	RX26	PC	100-25
F-KA	Standard	Rh	30-100	OUT	1/1	S4	RX26	PC	100-25

Mass change

Tube wattage

Protection filter

Time

Measuring order

Wavelength

Scanning condition

Peak 15.560 deg

Start 5.000 deg

End 90.000 deg

Step 0.050 deg

Time 0.025 sec

Speed 120 deg/min

Total measuring time 21 min.

Next Cancel

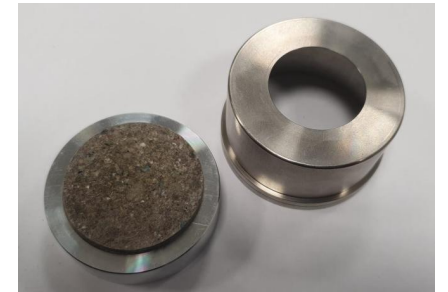
Twenty measurements

# Alternative fuel results expressed as oxides

Pressed powder

Alternative Fuel	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	K <sub>2</sub> O	CaO	TiO <sub>2</sub>
	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
Average	0.608	0.334	2.37	3.82	0.347	1.01	1.10	0.627	5.68	0.667
Std dev.	0.0158	0.0077	0.0191	0.0245	0.0052	0.0093	0.0129	0.0033	0.0357	0.0072
2σ	0.0316	0.0154	0.0382	0.049	0.0104	0.0186	0.0258	0.0066	0.0714	0.0144
Precision	0.608 ± 0.03	0.334 ± 0.02	2.37 ± 0.04	3.82 ± 0.05	0.347 ± 0.01	1.01 ± 0.02	1.10 ± 0.03	0.627 ± 0.007	5.68 ± 0.07	0.667 ± 0.01
95 % Confidence level										

Alternative Fuel	Cr <sub>2</sub> O <sub>3</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	NiO	CuO	ZnO	SrO	ZrO <sub>2</sub>	Scatter FP estimate
	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
Average	0.033	0.032	0.853	0.009	0.024	0.072	0.004	0.012	82.41
Std dev.	0.001	0.0009	0.0063	0.0004	0.0004	0.0005	0.0001	0.0002	
2σ	0.002	0.0018	0.0126	0.0008	0.0008	0.001	0.0002	0.0004	
Precision	0.033 ± 0.002	0.032 ± 0.002	0.853 ± 0.01	0.009 ± 0.0008	0.024 ± 0.0008	0.072 ± 0.001	0.004 ± 0.0002	0.012 ± 0.0004	
95 % Confidence level									

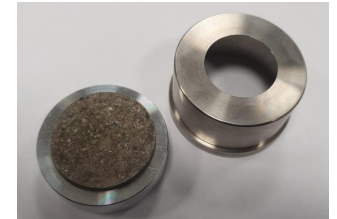


The variation in the results is shown with the small standard deviation of repeatability

# Alternative fuel results expressed as elements

Alternative Fuel	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti
	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
Average	0.3814	0.1716	1.0886	1.5403	0.1309	0.3503	0.9834	0.4569	3.5561	0.3497
Std dev.	0.0158	0.0077	0.0191	0.0245	0.0052	0.0093	0.0129	0.0033	0.0357	0.0072
2σ	0.0316	0.0154	0.0382	0.049	0.0104	0.0186	0.0258	0.0066	0.0714	0.0144
Precision	0.38 ± 0.03	0.172 ± 0.02	1.09 ± 0.04	1.54 ± 0.05	0.131 ± 0.01	0.350 ± 0.02	0.983 ± 0.03	0.456 ± 0.007	3.556 ± 0.07	0.350 ± 0.01
95 % Confidence level										

Pressed powder



Alternative Fuel	Cr	Mn	Fe	Ni	Cu	Zn	Br	Sr	Zr	Scatter FP estimate
	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
Average	0.0189	0.0233	0.5229	0.0062	0.0166	0.0504	0.0039	0.0087	0.0078	90.33
Std dev.	0.001	0.0009	0.0063	0.0004	0.0004	0.0005	0.0001	0.0002	0.0002	
2σ	0.002	0.0018	0.0126	0.0008	0.0008	0.001	0.0002	0.0004	0.0004	
Precision	0.019 ± 0.002	0.023 ± 0.002	0.523 ± 0.01	0.0062 ± 0.0008	0.017 ± 0.0008	0.050 ± 0.001	0.004 ± 0.0002	0.0087 ± 0.0004	0.0078 ± 0.0004	
95 % Confidence level										

The variation in the results is shown with the small standard deviation of repeatability



# FURTHER XRF APPLICATIONS IN CEMENT INDUSTRY

## Liquid

- Waste oil
- Solvents
- Animal fat
- Sewage sludge

## Solid

- Petcoke
- Tyres chipped or complete
- Animal meal + Bone meal
- Dried Sewage sludge
- RDF – refuse derived fuel from:
  - Pulp, paper and cardboard;
  - plastics; Packaging;
  - Textile industry;
  - Scrap wood



## Scattering FP method

Tyres	Mass %	Mass %
	Sample A	Sample B
Na	0.08	0.19
Mg	0.05	
Al	0.13	0.09
Si	0.21	0.21
P	0.03	
Si	0.84	0.89
Cl	0.24	0.18
K	0.09	
Ca	0.22	0.14
Cr	0.09	0.08
Fe	0.17	0.06
Cu	0.08	
Zn	3.56	2.85
FP Balance C	94.21	95.31
Total	100	100



Benefit quantification with low measurement of uncertainty

## RDF Quality testing



## Scattering FP method

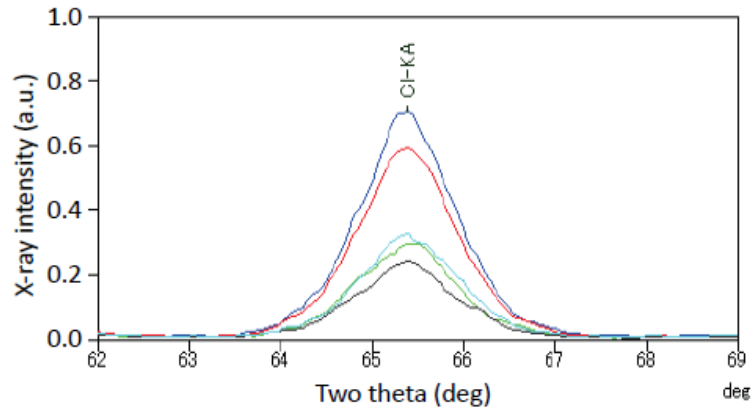


Figure 1 Cl-K $\alpha$  chart on Supermini200 with a Pd

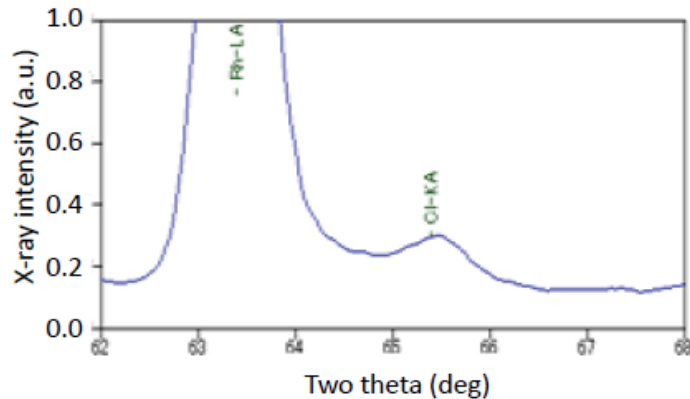


Figure 2 Cl-K $\alpha$  chart with a Rh target X-ray tube.

Element	Sample number				
	1	2	3	4	5
Al	0.08	0.11	0.30	0.17	0.19
Si	0.19	0.31	0.10	0.33	0.26
P	0.005	< LOD	< LOD	< LOD	< LOD
Si	0.009	0.018	0.011	0.021	0.03
Cl	0.14	0.30	0.24	0.16	0.12
FP Balance					
C	99.6	99.3	99.4	99.8	99.9

Benefit quantification with low measurement of uncertainty

# Application 1: Rock

- Sample: Dolomitic Limestone
- Support film (Mylar) was used.  
(C and O can not be analyzed.)

Analyte	Std. value	SQX Scatter FP	FP (O balance)
Ca	21.4	21.2	24.0
Mg	12.7	11.4	12.7
Al	0.18	0.28	0.31
Si	0.52	0.70	0.79
K	0.09	0.10	0.12
Mn	0.012	0.013	0.015
Fe	0.19	0.21	0.24
Sr	0.006	0.006	0.007

Unit: mass%

# Application 2: Ash

- Sample: Incineration ash of municipal waste
- Support film (Mylar) was used.

Unit: mass%

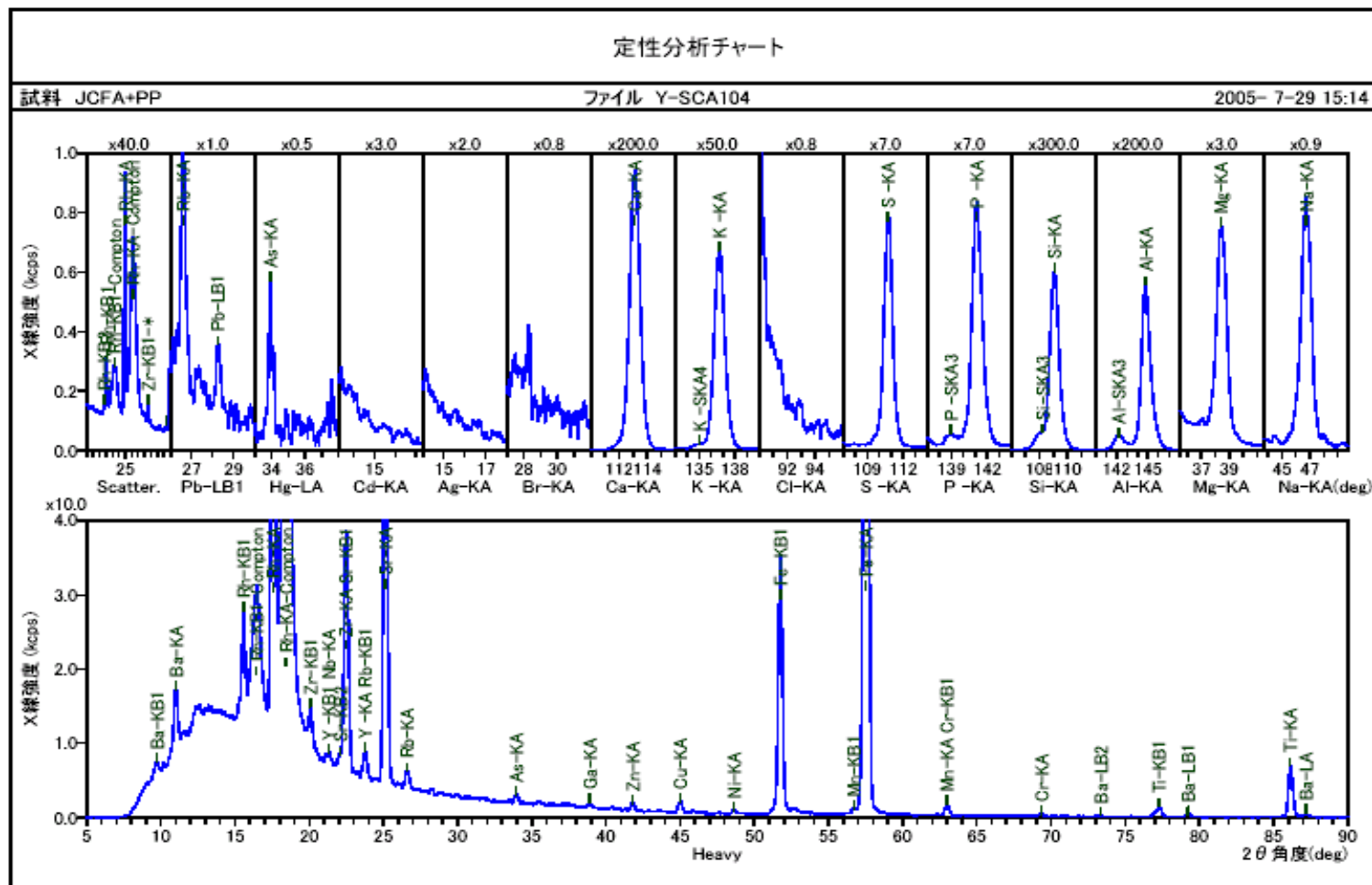
Analyte	Std. value	SQX Scatter FP	FP (O balance)
Ti	<b>0.851</b>	<b>0.883</b>	0.807
Cr	<b>0.086</b>	<b>0.089</b>	0.082
Mn	<b>0.14</b>	<b>0.13</b>	0.12
Fe	<b>2.13</b>	<b>1.96</b>	1.79
Ni	<b>0.012</b>	<b>0.013</b>	0.012
Cu	<b>0.13</b>	<b>0.13</b>	0.12
Zn	<b>2.6</b>	<b>2.5</b>	2.3
Se	<b>0.0041</b>	<b>0.0041</b>	0.0038
Cd	<b>0.047</b>	<b>0.044</b>	0.042
Sb	<b>0.04</b>	<b>0.05</b>	0.05
Pb	<b>1.09</b>	<b>1.02</b>	0.94

# Application 3: Dust

- Sample: Particulate material in automobile exhaust gas
- Support film (Mylar) was used.

Unit: mass%

Element	Mg	Al	Si	P	S	Cl	K	Ca	Ti
<b>Std. value</b>	<b>0.10</b>	<b>0.33</b>	<b>-</b>	<b>0.051</b>	<b>-</b>	<b>0.085</b>	<b>0.115</b>	<b>0.53</b>	<b>0.027</b>
<b>SQX Scatter FP</b>	<b>0.07</b>	<b>0.26</b>	<b>0.82</b>	<b>0.049</b>	<b>2.35</b>	<b>0.067</b>	<b>0.11</b>	<b>0.54</b>	<b>0.031</b>
FP (O balance)	0.12	0.50	1.58	0.09	4.39	0.13	0.20	0.99	0.054
Element	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As
<b>Std. value</b>	<b>0.0017</b>	<b>0.0025</b>	<b>0.0075</b>	<b>0.49</b>	<b>0.0003</b>	<b>0.0019</b>	<b>0.0067</b>	<b>0.104</b>	<b>0.0003</b>
<b>SQX Scatter FP</b>	<b>0.0017</b>	<b>0.0029</b>	<b>0.007</b>	<b>0.47</b>	<b>0.0005</b>	<b>0.0022</b>	<b>0.0075</b>	<b>0.108</b>	<b>0.0001</b>
FP (O balance)	0.0029	0.0051	0.012	0.82	0.0010	0.0039	0.013	0.19	0.0017
Element	Br	Sr	Zr	Sn	Pb				
<b>Std. value</b>	<b>0.0056</b>	<b>0.0089</b>	<b>-</b>	<b>-</b>	<b>0.0219</b>				
<b>SQX Scatter FP</b>	<b>0.0068</b>	<b>0.0091</b>	<b>0.0006</b>	<b>0.0018</b>	<b>0.0237</b>				
FP (O balance)	0.012	0.014	0.0006	0.0021	0.0382				



# Application 4: Fly ash

- Sample: JCFA Coal Fly Ash
- Support film (polypropylene) was used.
- Loose powder method

Unit: mass%

Element	Na	Mg	Al	Si	P	S	K	Ca	Ti
<b>Std. value</b>	<b>1.69</b>	<b>1.27</b>	<b>12.8</b>	<b>23.6</b>	<b>0.26</b>	<b>0.196</b>	<b>1.05</b>	<b>6.36</b>	<b>0.79</b>
<b>SQX Scatter FP</b>	<b>2.14</b>	<b>1.08</b>	<b>12.6</b>	<b>20.3</b>	<b>0.25</b>	<b>0.28</b>	<b>1.04</b>	<b>6.23</b>	<b>0.79</b>
FP (C balance)	1.20	0.59	6.74	10.7	0.13	0.14	0.534	3.19	0.40
Element	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
<b>Std. value</b>	<b>0.0243</b>	<b>0.0075</b>	<b>0.05</b>	<b>3.64</b>	<b>0.0037</b>	<b>0.0032</b>	<b>0.0122</b>	<b>0.0063</b>	<b>(0.0045)</b>
<b>SQX Scatter FP</b>	<b>0.025</b>	<b>0.0112</b>	<b>0.0515</b>	<b>3.42</b>	<b>0.0049</b>	<b>0.0055</b>	<b>0.013</b>	<b>0.0064</b>	<b>0.0044</b>
FP (C balance)	0.013	0.0057	0.0258	1.72	0.0025	0.0028	0.0066	0.0033	0.0022
Element	As	Rb	Sr	Y	Zr	Nb	Ba	Pb	
<b>Std. value</b>	<b>0.0029</b>	<b>0.0054</b>	<b>0.11</b>	<b>(0.0054)</b>	<b>(0.0460)</b>	<b>(0.0025)</b>	<b>(0.1740)</b>	<b>0.0047</b>	
<b>SQX Scatter FP</b>	<b>0.0035</b>	<b>0.0052</b>	<b>0.113</b>	<b>0.0046</b>	<b>0.031</b>	<b>0.0015</b>	<b>0.014</b>	<b>0.0038</b>	
FP (C balance)	0.0017	0.0027	0.0586	0.0024	0.017	0.0008	0.0687	0.0019	

# Application 5: Tissue

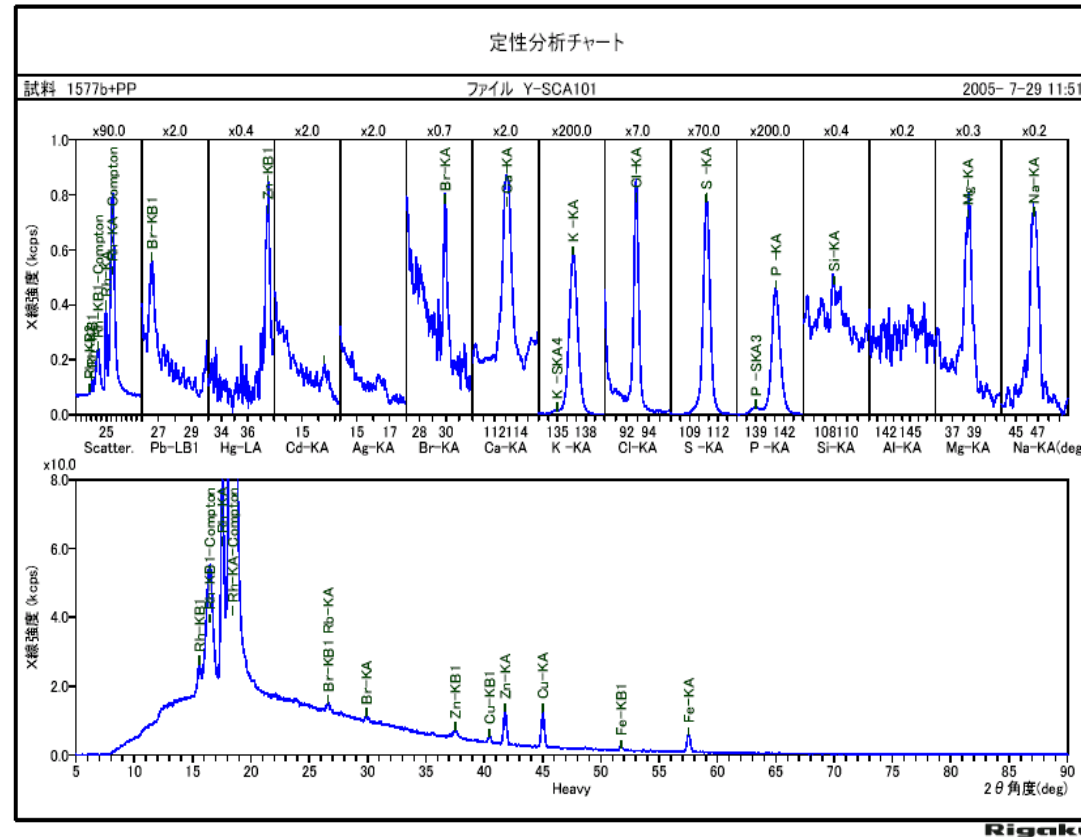
- Sample: Mid-gut (digestive) gland
- Support film (Mylar) was used.

Unit: mass%

Element	Na	Mg	Si	P	S	Cl	K	Ca
Std. value	-	-	-	-	-	-	-	-
<b>SQX Scatter FP</b>	<b>1.51</b>	<b>0.11</b>	<b>0.02</b>	<b>0.84</b>	<b>0.90</b>	<b>1.7</b>	<b>0.78</b>	<b>0.27</b>
FP (CH <sub>2</sub> balance)	1.31	0.094	0.02	0.082	0.868	1.7	0.73	0.25
Element	Cr	Mn	Fe	Ni	Cu	Zn	As	Se
<b>Std. value</b>	<b>0.0001</b>	<b>0.0013</b>	<b>0.0105</b>	<b>0.0003</b>	<b>0.0106</b>	<b>0.0180</b>	<b>0.0022</b>	<b>0.0006</b>
<b>SQX Scatter FP</b>	<b>0.0004</b>	<b>0.0008</b>	<b>0.0099</b>	<b>0.0005</b>	<b>0.0087</b>	<b>0.0152</b>	<b>0.0019</b>	<b>0.0006</b>
FP (CH <sub>2</sub> balance)	0.0003	0.0007	0.009	0.0005	0.0081	0.0142	0.0018	0.0006
Element	Br	Sr	Cd					
<b>Std. value</b>	<b>-</b>	<b>0.0045</b>	<b>0.0027</b>					
<b>SQX Scatter FP</b>	<b>0.0141</b>	<b>0.0040</b>	<b>0.0020</b>					
FP (CH <sub>2</sub> balance)	0.0138	0.0039	0.0008					

# Application 6: Tissue

- Sample: NIST1577b Bovin liver
- Support film (polypropylene) was used.



# Application 6: Tissue

- Sample: NIST1577b Bovin liver
- Support film (polypropylene) was used.

Unit: mass%

Element	Na	Mg	P	S	Cl	K	Ca
<b>Std. value</b>	<b>0.242</b>	<b>0.0601</b>	<b>1.1</b>	<b>0.785</b>	<b>0.278</b>	<b>0.994</b>	<b>0.0116</b>
<b>SQX Scatter FP</b>	<b>0.297</b>	<b>0.066</b>	<b>1.3</b>	<b>0.91</b>	<b>0.32</b>	<b>1.2</b>	<b>0.0145</b>
FP (CH <sub>2</sub> balance)	0.179	0.0393	0.768	0.528	0.188	0.693	0.0083
Element	Mn	Fe	Cu	Zn	Br	Rb	
<b>Std. value</b>	<b>0.0011</b>	<b>0.0184</b>	<b>0.016</b>	<b>0.0127</b>	<b>0.0010</b>	<b>0.0014</b>	
<b>SQX Scatter FP</b>	<b>0.0014</b>	<b>0.022</b>	<b>0.019</b>	<b>0.0136</b>	<b>0.0009</b>	<b>0.0015</b>	
FP (CH <sub>2</sub> balance)	0.0008	0.0124	0.0133	0.0086	0.0007	0.0013	

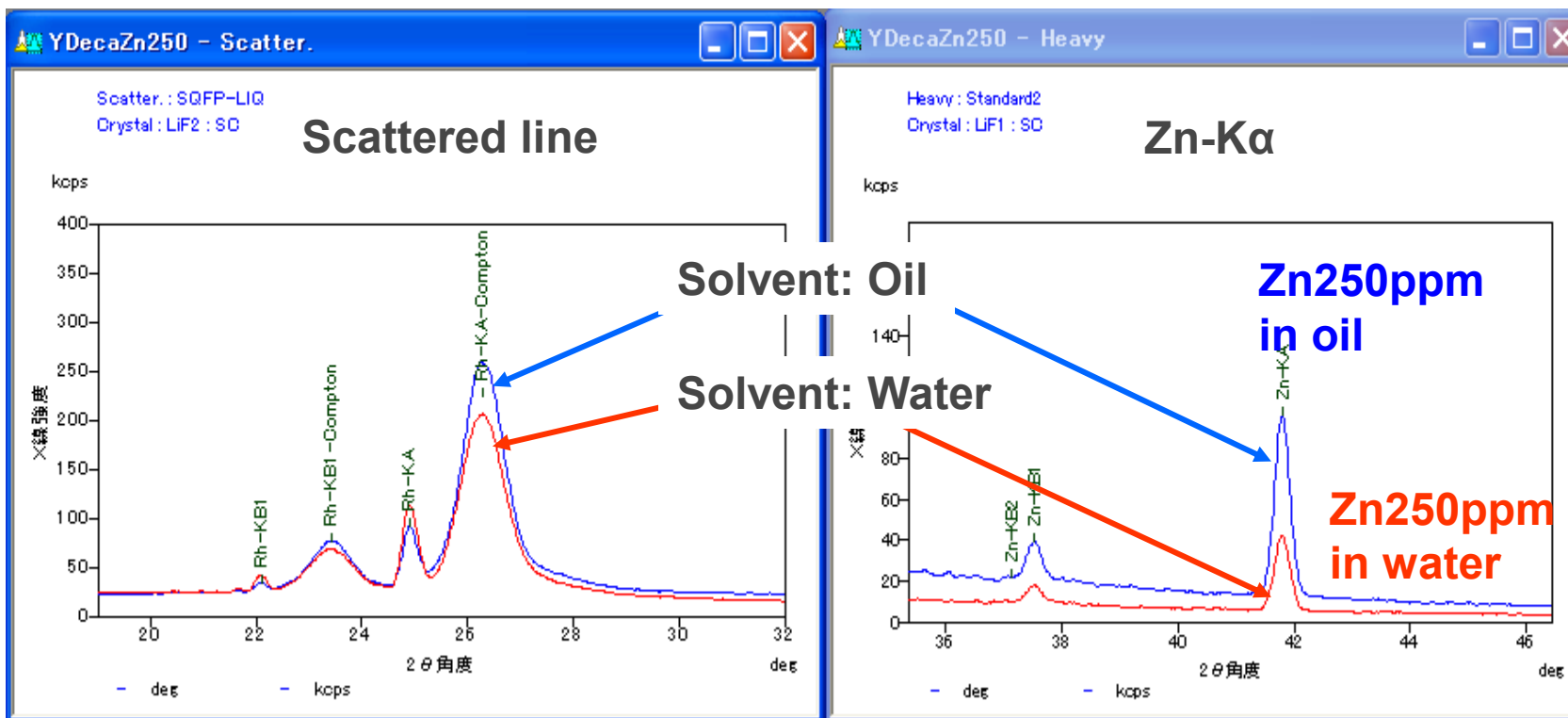


# Application 7: Tissue

- Sample: Human Hair
- Support film (polypropylene) was used.

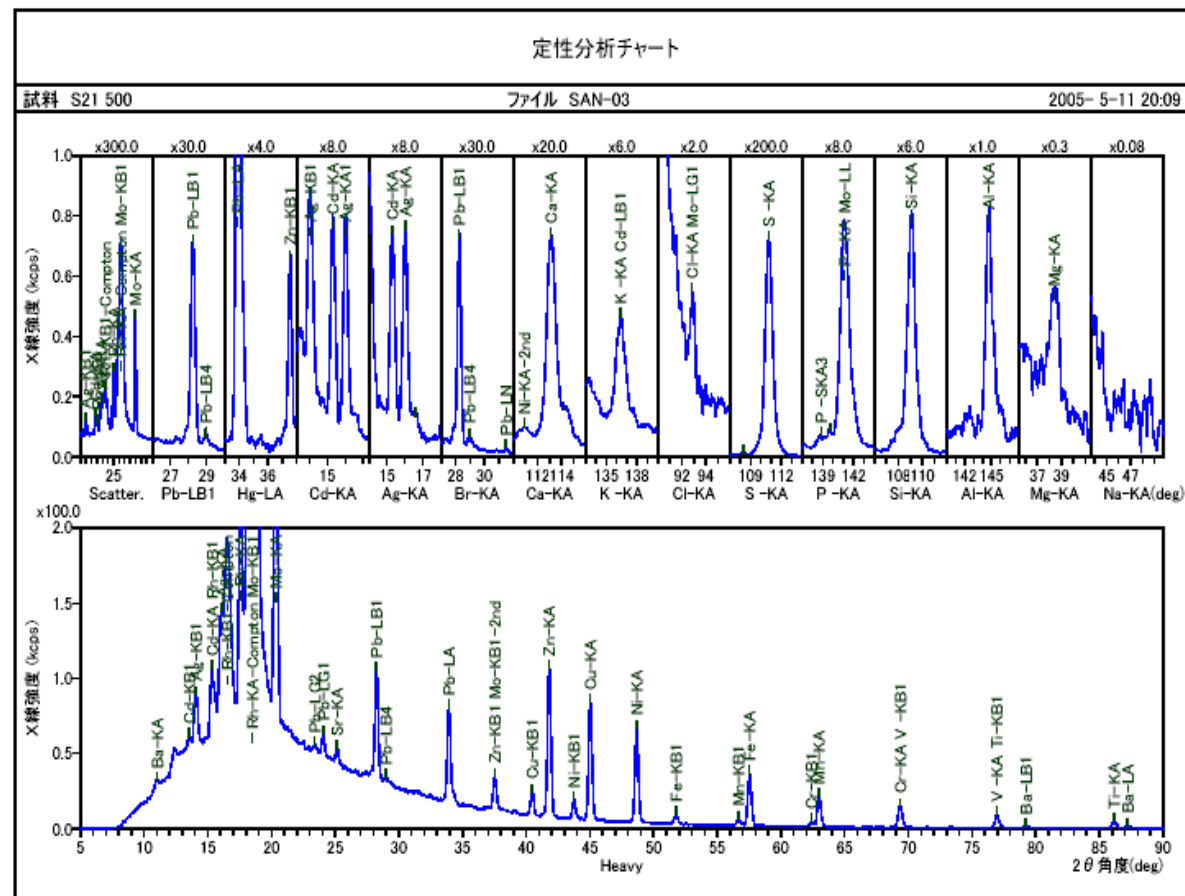
Unit: mass%

Element	Mg	Si	P	S	Cl	K	Ca
<b>Std. value</b>	<b>0.0208</b>	<b>-</b>	<b>(0.0165)</b>	<b>-</b>	<b>(0.0250)</b>	<b>0.0034</b>	<b>0.0728</b>
<b>SQX Scatter FP</b>	<b>0.032</b>	<b>1.00</b>	<b>0.0183</b>	<b>5.08</b>	<b>0.0304</b>	<b>0.0045</b>	<b>0.0815</b>
FP (CH <sub>2</sub> balance)	0.0199	0.615	0.0112	3.09	0.0185	0.0027	0.0492
Element	Ti	Fe	Cu	Zn	Br	Pb	Hg
<b>Std. value</b>	<b>(0.0022)</b>	<b>0.0225</b>	<b>0.0016</b>	<b>0.0169</b>	<b>(0.0090)</b>	<b>(0.0006)</b>	<b>0.0004</b>
<b>SQX Scatter FP</b>	<b>0.0021</b>	<b>0.0245</b>	<b>0.0018</b>	<b>0.0169</b>	<b>0.0103</b>	<b>0.0002</b>	<b>0.0004</b>
FP (CH <sub>2</sub> balance)	0.0013	0.0146	0.0011	0.0113	0.0085	0.0009	0.0003



# Application 8: Liquid (Oil)

- Sample: Oil standard solution
- Path atmosphere: He
- Support film (Mylar) was used.



# Application 8: Liquid (Oil)

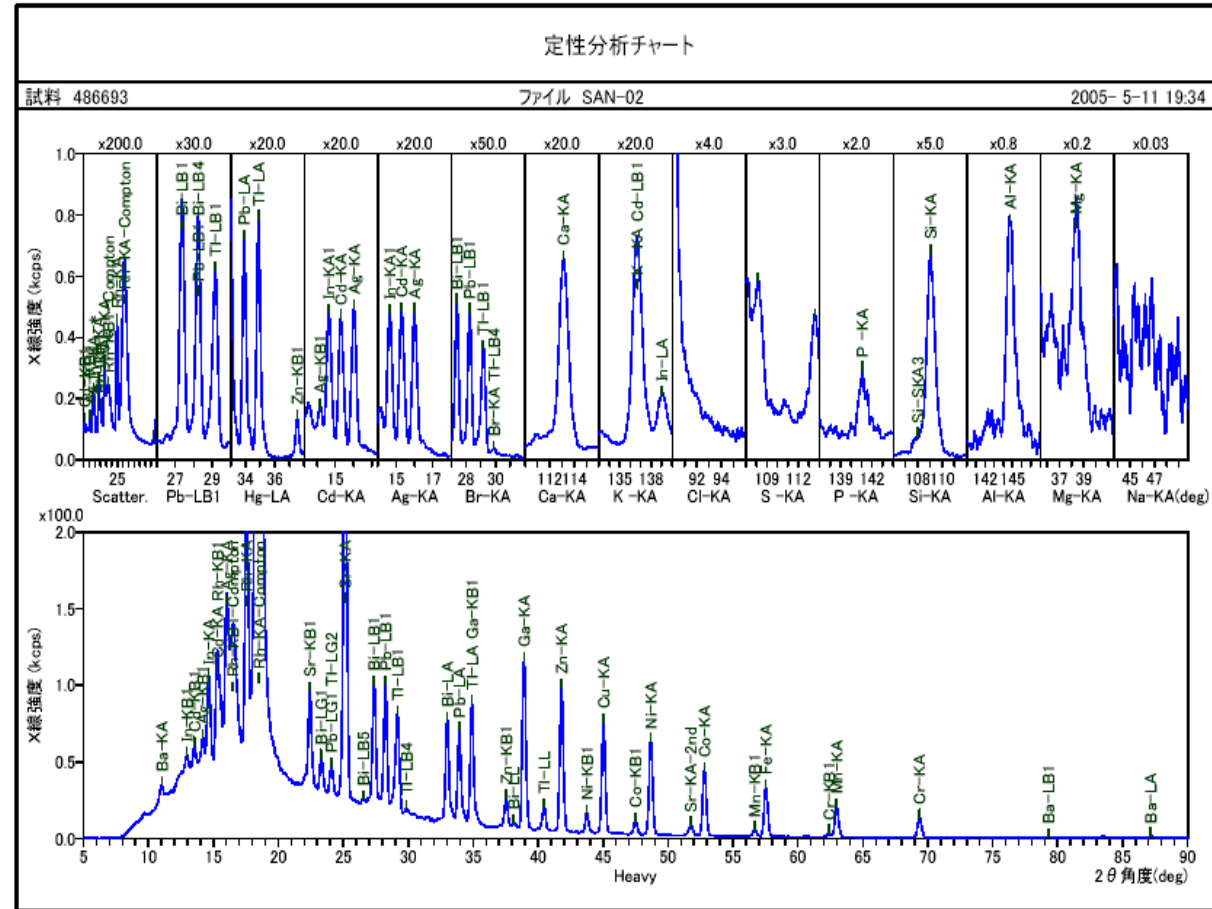
- Sample: Oil standard solution
- Path atmosphere: He
- Support film (Mylar) was used.

Unit: mass%

Element	Al	Si	P	S	Ca	Ti	V
<b>Std. value</b>	<b>0.050</b>	<b>0.050</b>	<b>0.050</b>		<b>0.050</b>	<b>0.050</b>	<b>0.050</b>
SQX Scatter FP	0.0632	0.0457	0.0488	1.25	0.0535	0.0535	0.0524
FP (H <sub>2</sub> O balance)	0.132	0.0976	0.107	2.75	0.0317	0.119	0.120
Element	Cr	Mn	Fe	Ni	Cu	Zn	Sr
<b>Std. value</b>	<b>0.050</b>	<b>0.050</b>	<b>0.050</b>	<b>0.050</b>	<b>0.050</b>	<b>0.050</b>	—
SQX Scatter FP	0.0501	0.0531	0.0537	0.0532	0.0507	0.0485	0.0017
FP (H <sub>2</sub> O balance)	0.132	0.123	0.124	0.123	0.117	0.112	0.0034
Element	Mo	Cd	Sn	Ba	Pb		
<b>Std. value</b>	<b>0.050</b>	<b>0.050</b>	<b>0.050</b>	<b>0.050</b>	<b>0.050</b>		
SQX Scatter FP	0.0418	0.0444	0.0443	0.0474	0.0463		
FP (H <sub>2</sub> O balance)	0.0721	0.0593	0.0567	0.108	0.0971		

# Application 9: Liquid (Water)

- Sample: Water standard solution
- Path atmosphere: He
- Support film (Mylar) was used.



# Application 9: Liquid (Water)

- Sample: Water standard solution
- Support film (Mylar) was used.
- Path atmosphere: He
- On ZSXPrimus

Unit: mass%

Element	Al	K	Ca	Cr	Mn	Fe	Co
<b>Std. value</b>	<b>0.0993</b>	<b>0.1080</b>	<b>0.1040</b>	<b>0.1080</b>	<b>0.1060</b>	<b>0.1050</b>	<b>0.1040</b>
SQX Scatter FP	0.1006	0.1010	0.0994	0.1005	0.1005	0.1003	0.1013
FP (CH <sub>2</sub> balance)	0.0396	0.0359	0.0390	0.0402	0.0397	0.0392	0.0390
Element	Ni	Cu	Zn	Ga	Sr	Ag	Cd
<b>Std. value</b>	<b>0.1006</b>	<b>0.1006</b>	<b>0.1008</b>	<b>0.1001</b>	<b>0.1015</b>	<b>0.1006</b>	<b>0.1007</b>
SQX Scatter FP	0.1070	0.1000	0.0985	0.1030	0.1020	0.0897	0.0948
FP (CH <sub>2</sub> balance)	0.0402	0.0379	0.0376	0.0396	0.0480	0.0644	0.0703
Element	In	Ba	Tl	Pb	Bi		
<b>Std. value</b>	<b>0.0989</b>	<b>0.1003</b>	<b>0.1005</b>	<b>0.1009</b>	<b>0.1001</b>		
SQX Scatter FP	0.0887	0.1100	0.1080	0.1010	0.1110		
FP (CH <sub>2</sub> balance)	0.0667	0.0413	0.0467	0.0454	0.0452		

- **It seems simple and easy method, but it is not.**
- **Still sample preparation is important. In the FP calculation, it is assumed that the sample is homogeneous.**
- **Matching Library could improve accuracy.**
- **It is necessary to input all information about specimens, such as binder, flux, balance component, etc.**

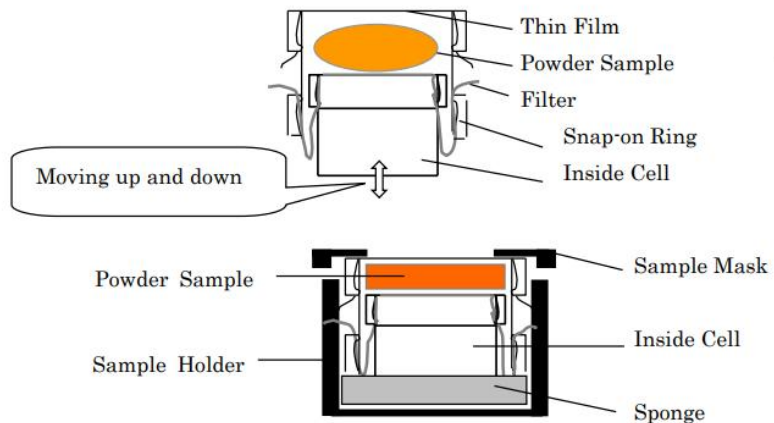
# Loose powder

Loose Powder cell RS640 and the 6 $\mu$ m polypropylene film

Maximum cell diameter  
Internal 35 mm  
External 40 mm

## 2-6-1 POWDER SAMPLE CELL FOR VACUUM (FOR TUBE ABOVE or BELOW OPTICS)

The powder sample cell for a vacuum has been so designed that it can be put in the sample holder of your X-ray fluorescence spectrometer. The cell can be used for any analyzer as long as its holder can house the cell. In case of tube below optics set thin film side to downward.



## XRF consumable RS640

Powder Sample Cell for Vacuum (For tube above or below optics)

Cat. No.	Name	Specification (Material and Shape)	Unit
<b>RS640</b>	Vacuum Powder Sample Cell	Cell: Polyethylene 40mm (OD) × 31mm (ID) × 23mm (H) Thin film: 6μm polypropylene Filter: Nylon 95mm × 95mm Sponge: Polyurethane	6 pcs./set

Note: Thin Film: 85mm × 85mm × 6μm 6 sheets for setting and 6 spare sheets, 12 sheets in total  
Filter: 6 sheets fixed to cells and 6 spare sheets, 12 sheets in total

Select the consumables from Consumables for Powder Sample Cells for Vacuum list.

Standards mass %

STD No	Cl	S	Cu	Mo	Ni	P	Si	Pt	K
CIS 1	0	0.0015							
CIS 2	0.2417	0.0006						0.31	2.3
CIS 3	2.1013	0.0005						0.28	1.04
CIS 4	1.5168	0.0005				0.3			
CIS 5	1.0507	0.0765							
CIS 6	0.9907	0.1417							
CIS 7	3.4426	0.0169							
CIS 8	0.0105	1.7025							
CIS 9	0	0.3816			15				
CIS 10	0	0.7369	5.69				0.0113		
CIS 11	0.2476	1.0528							
CIS 17	0.085	0.9205		8.82	2.56		0.0269		

# Measuring conditions

**Quant Flow Bar**

C/S Catalyst

Application File

Component Selection

Sample Preparation

Standard Samples

Composition Information

**Parameters**

Optimize MC's

Run Standards

Drift Correction Samples

Run Drift Corr. Samples

Calibration

Limit Ranges

Check Samples

Comment >>

**Parameters**

Analysis Information Measuring Condition

Diameter 30mm Atmosphere Helium/Vacuum Sealing IN

El.line	Type	Target	KV-mA	Filter	Att.	Slit	Crystal	Detector	PHA
CH-KA	Private	Rh	40-70	OUT	1/1	S2	GeH	PC	135-275
S-KA	Private	Rh	40-70	OUT	1/1	S4	GeH	PC	120-295
Cu-KA	Private	Rh	40-70	OUT	1/1	S2	LiF(200)	SC	95-510
Mo-LA	Private	Rh	50-60	OUT	1/1	S4	GeH	PC	150-300
Ni-KA	Private	Rh	40-70	OUT	1/1	S2	LiF(200)	SC	75-500
P-KA	Private	Rh	40-70	OUT	1/1	S4	GeH	PC	125-295
Si-KA	Private	Rh	40-70	OUT	1/1	S4	PETH	PC	100-300
Pt-LA	Private	Rh	40-70	OUT	1/1	S2	LiF(200)	SC	100-300
K-KA	Private	Rh	40-70	OUT	1/1	S4	LiF(200)	PC	110-295

Mass change

Tube wattage

Protection filter

Time + -

Advanced

Angle & Time

Peak 92.806 deg  
12 sec

Background  
4 points

BG1 93.700 deg  
6 sec

BG2 93.650 deg  
6 sec

Total time 4 min.

Property

Next Cancel

**Measuring Condition**

Element line CH-KA Type Private

Excitation Target Rh Tube voltage 40 Tube current 70 Filter OUT

Optics Attenuator 1/1 Slit S2 Crystal GeH Detector PC

PHA Lower level 135 Upper level 275

Peak & Background

Peak	2-theta(deg)	Time(sec)
Peak	92.806	12
BG1	93.700	6
BG2	93.650	6
BG3	91.600	6
BG4	91.500	6
BG5		

Background method Cubic

Intensity control No

Advanced

OK Cancel

**Measuring Condition**

Element line S-KA Type Private

Excitation Target Rh Tube voltage 40 Tube current 70 Filter OUT

Optics Attenuator 1/1 Slit S4 Crystal GeH Detector PC

PHA Lower level 120 Upper level 295

Peak & Background

Peak	2-theta(deg)	Time(sec)
Peak	110.704	12
BG1	108.700	6
BG2	112.100	6
BG3		
BG4		
BG5		

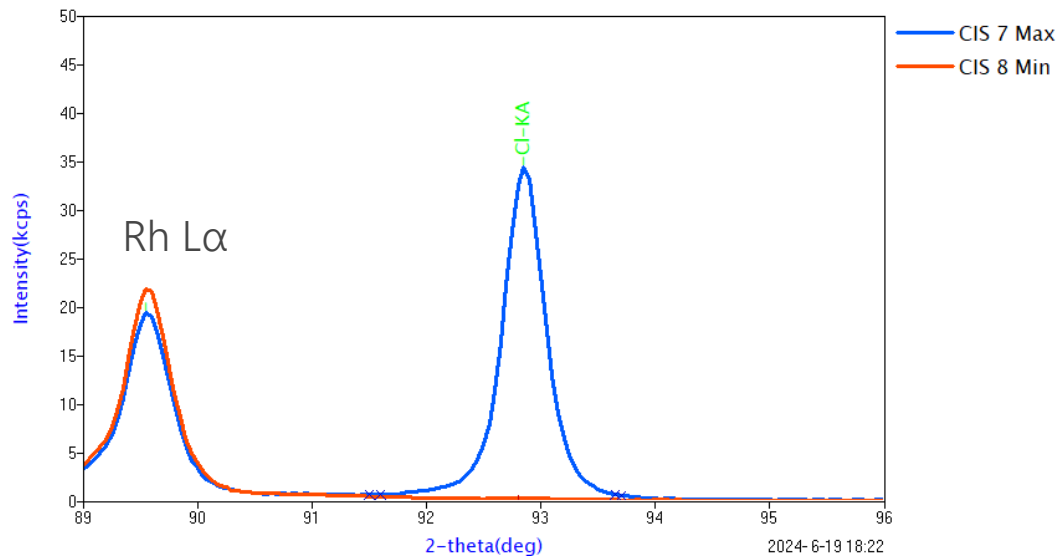
Background method Linear

Intensity control No

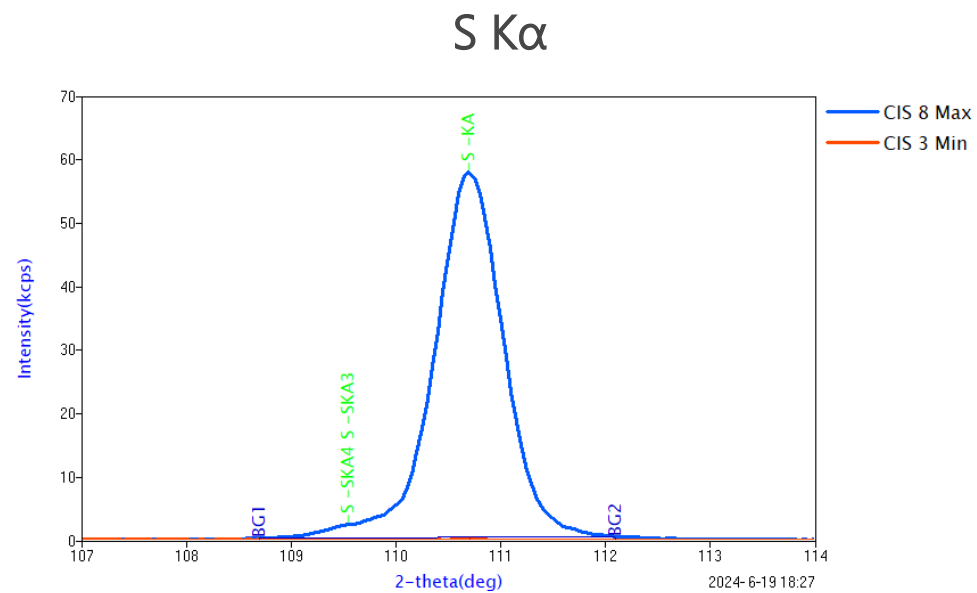
Advanced

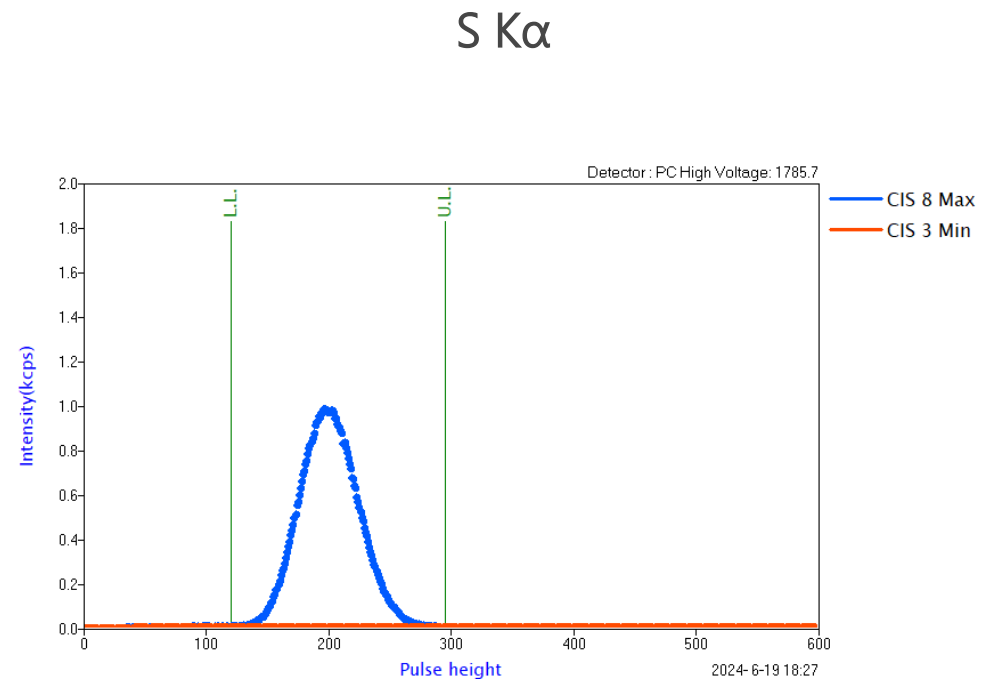
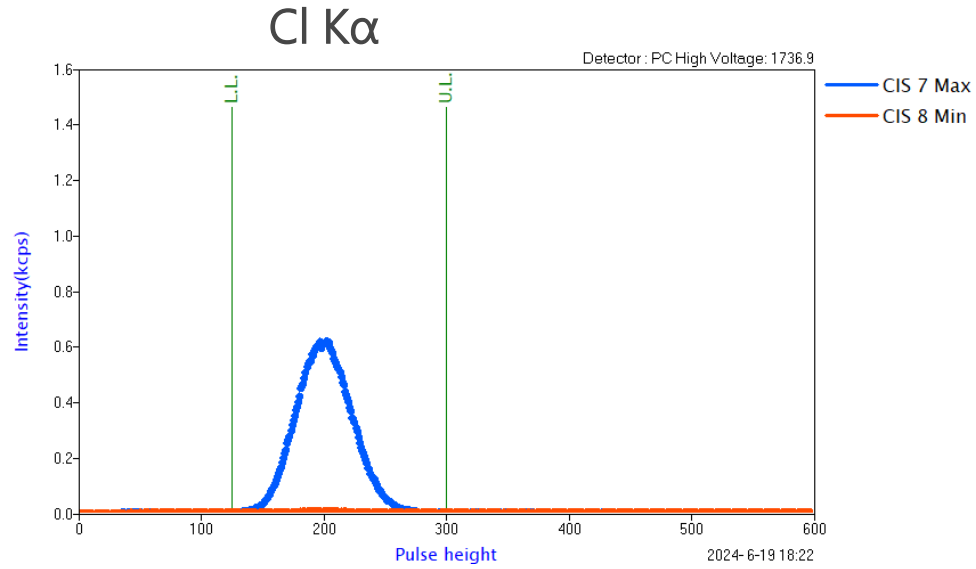
OK Cancel

# Spectra 2 theta peak angle



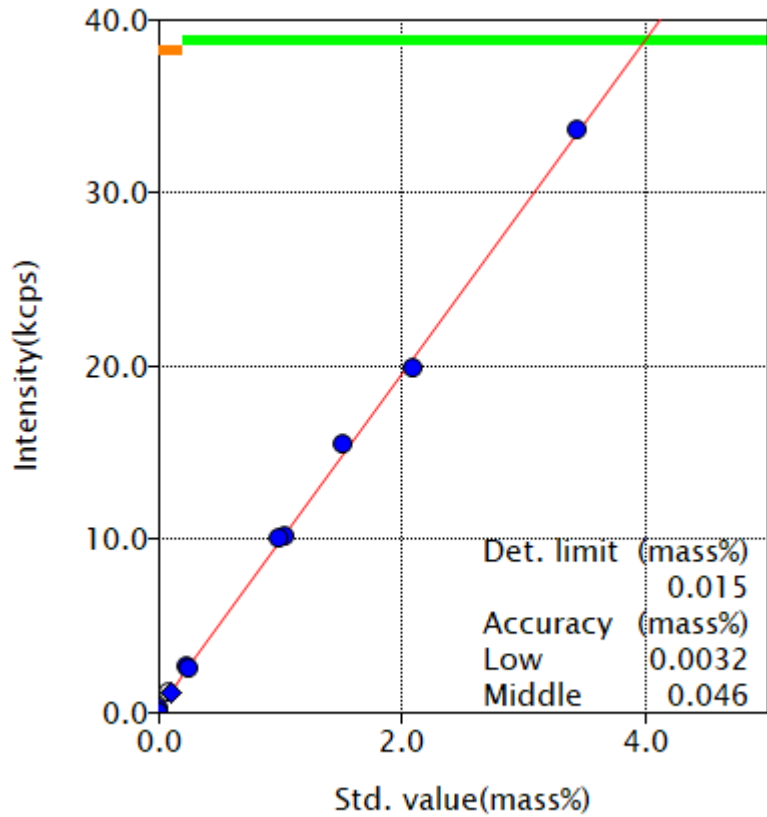
Cl K $\alpha$





# Calibrations

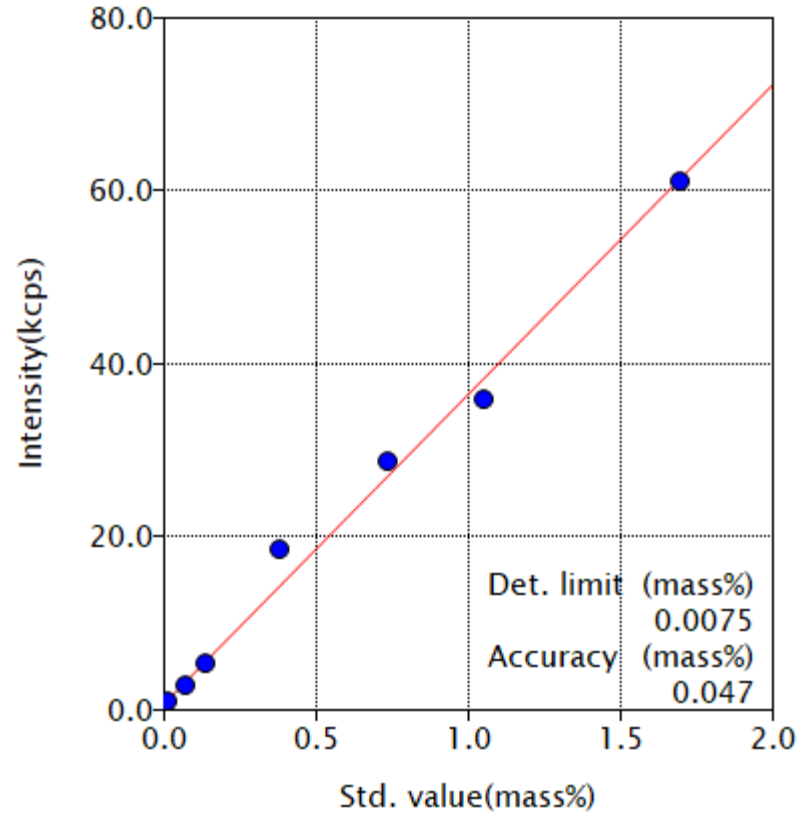
Comp. Cl El. line Cl-KA PHA 135 - 275



● Certified ● Uncertified ● Deselected ◇ Corrected

Mo overlap correction

Comp. S El. line S -KA PHA 120 - 295



● Certified ● Uncertified ● Deselected ◇ Corrected

Mo overlap correction  
Pt overlap correction

# Definition of Sensitivity

The sensitivity  $S_i$  of the spectrometer for an element  $i$ ,

It is the number of detected X-ray photons  $N$  ("counts"), divided by the measurement time  $t$ , divided by the concentration  $W_i$  of the element  $i$

$$S_i = \frac{N}{t \cdot W_i}$$

( kcps / % or kcps / ppm )

Element	Sensitivity kcps/%	counts	counting time Peak and BKG	Conc
		kcps	Seconds	%
Cl	0.2732	7.9380	36	0.8072
S	1.2129	12.2074	24	0.4194

# Repeatability

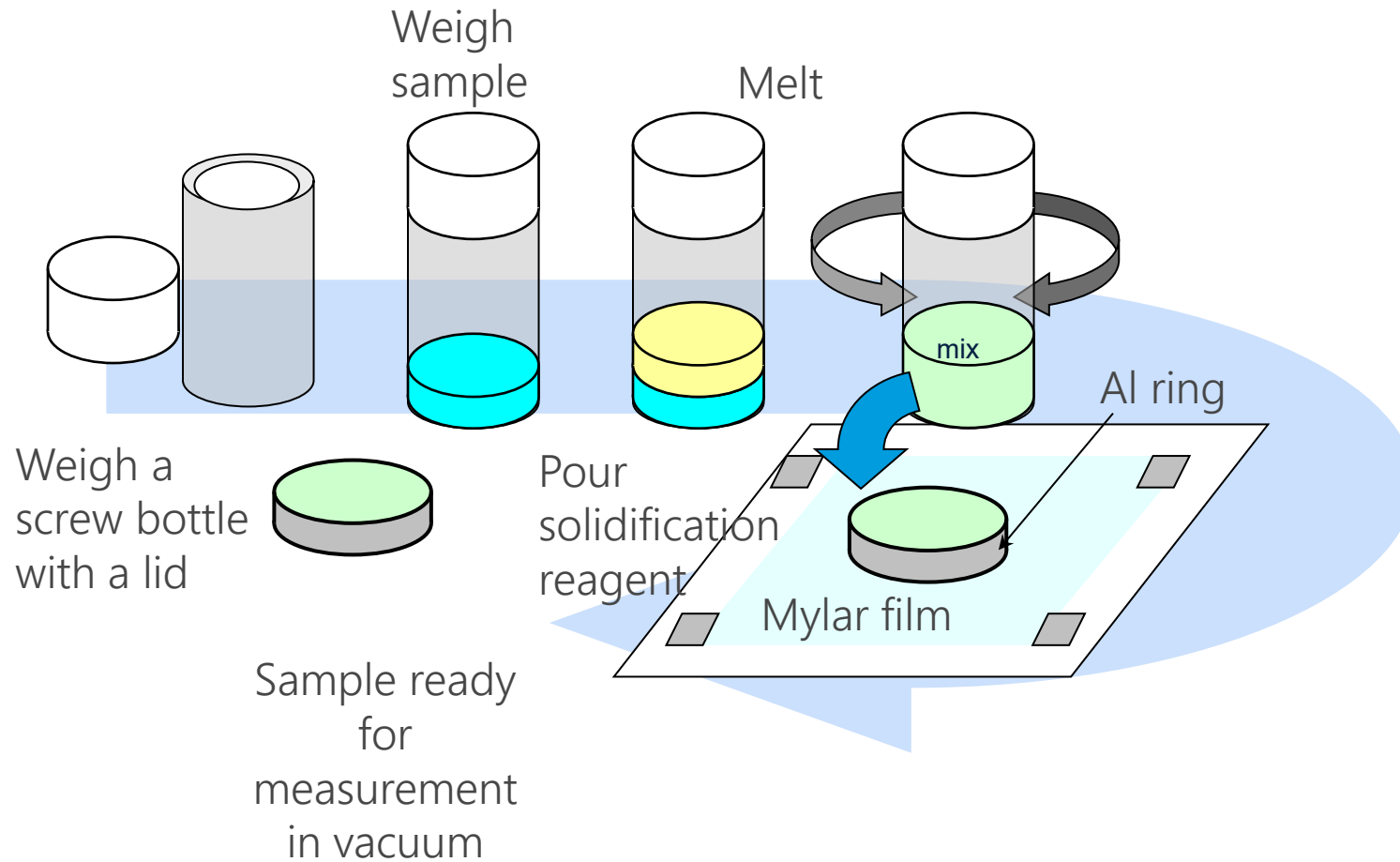
Sample name	CI	S
	mass%	mass%
CI S 12-1	1.038	0.050
CI S 12-2	0.958	0.051
CI S 12-3	0.950	0.052
CI S 12-4	1.079	0.054
CI S 12-5	1.000	0.054
CI S 12-6	0.975	0.055
CI S 12-7	1.114	0.056
CI S 12-8	1.028	0.057
CI S 12-9	0.990	0.057
CI S 12-10	1.102	0.059
Number	10	10
Average	1.023	0.055
Maximum	1.114	0.059
Minimum	0.950	0.050
Range	0.165	0.009
Std dev.	0.059	0.003

Static repeatability  
New cell for each measurement

Std Dev for repeatability shows small variation in results

# *Oil Solidification*

# Oil solidification method



## DRAWBACKS OF TRADITIONAL OIL/FUEL ANALYSES

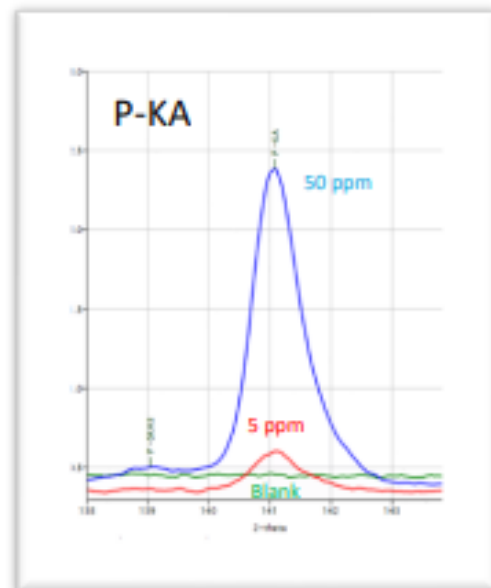
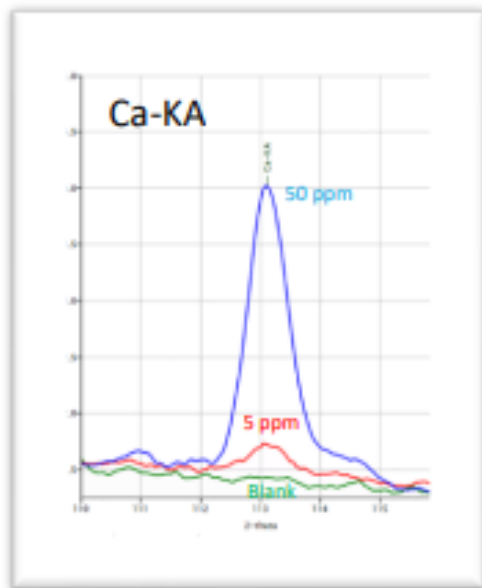
- Leakage can occur during analysis or in batch
- 2) Settling can give rise to higher or lower than nominal values
- 3) Helium consumption/sourcing – logistics and cost issues
- 4) Reduced sensitivity to light element analytes



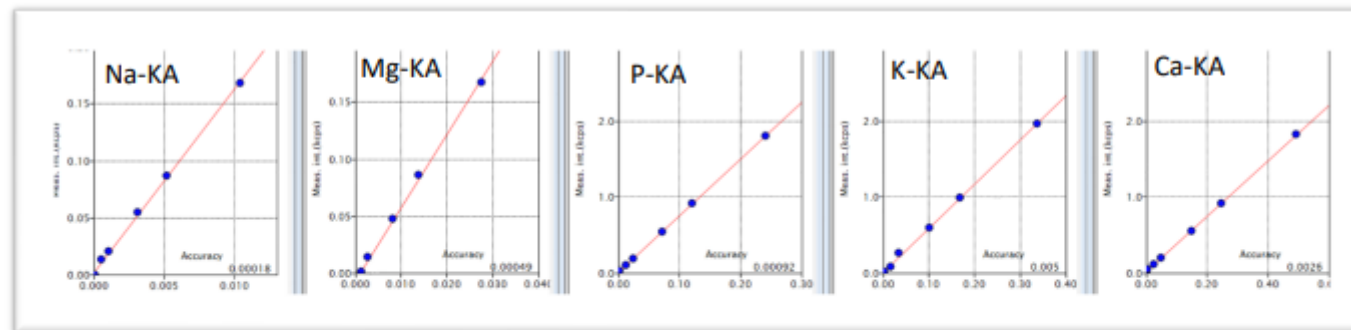
## THE SOLUTION: OIL SOLIDIFICATION

Oil solidification sample prep techniques provide a potential solution to all these challenges, as well as providing additional benefits. Pre-mixed wax blends are simply melted, combined with oil samples and quickly cooled in a mold. The resulting solidified puck can then be conveniently analyzed in a vacuum atmosphere, without the need for films, and providing the best sensitivity for light elements like Na and Mg. This also provides an added benefit that samples can simply be left on the sample changer in queue without the worry of settling or leaking





**REPRESENTATIVE SCANS:** Light elements (such as Na, Mg, P, etc.) can easily be detected in a wax pellet over traditional liquid oil samples in a cup. Samples can be analyzed repeatedly without the worry of spillage or film breakage.



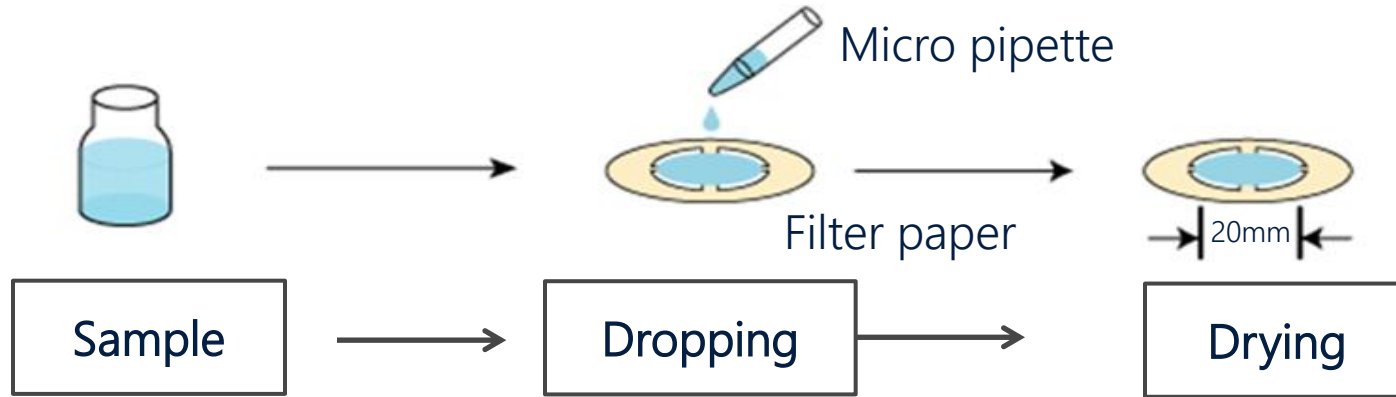
**CALIBRATION CURVES:** Linear range of wax pellets were prepared at 1-50 ppm. Correlation factors were better than 0.999 for all elements.

Measurement No.	Na (ppm)	Mg (ppm)	P (ppm)	K (ppm)	Ca (ppm)
1	5.3	5.9	4.8	4.9	4.1
2	5.1	4.6	4.9	4.8	4.5
3	6.0	5.4	5.0	5.1	5.2
Mean	5.5	5.3	4.9	4.9	4.6
Nominal	5.0	5.0	5.0	5.0	5.0
Std Dev	0.49	0.64	0.09	0.18	0.54
%RSD	8.97	12.11	1.81	3.6	11.73

**REPEATABILITY:** A wax pellet prepared at a nominal concentration at 5 ppm demonstrated good repeatability with %RSD < 15% for all elements.

# Ultra Carry Micro Carry

# Liquid analysis by droplet (filter paper) method



There are cases that adding fixed amount of internal standard element reduce errors caused by variations of diffusion and amount of liquid.

Drop with fixed amount of droplet in the center of filter.  
 Typical amount:  
 MicroCarry : 50 - 100  $\mu\text{L}$   
 UltraCarry : 50 - 500  $\mu\text{L}$

After dried, the filters are measured under vacuum atmosphere.

MicroCarry



UltraCarry



Measurable elements  
 ${}^5\text{B}, {}^9\text{F} \sim {}^{92}\text{U}$

# Micro Carry and Ultra Carry

- **Task:**
  - there is the need to analyse aqueous liquids. The situation may be that heavy metals are present in very low (sub-ppm) concentrations, generally non-measurable by XRF
- **Objective:**
  - analyse accurately, precisely and fast sub-ppm levels of light- and heavy elements with WD-XRF using (very) small amounts of sample
- **Key-words:**
  - lower limits of detection (LLD)
  - Small sample quantities

# MicroCarry and UltraCarry

## MicroCarry

- “Conventional” filter paper with low level of impurities
- Ideally for very small sample quantities (10 to 200 $\mu$ l)
- Especially for light elements like F, Na and Mg

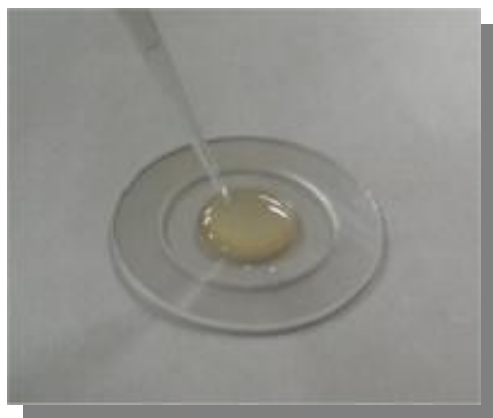
## UltraCarry



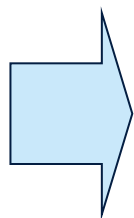
Ultra Carry

- Special paper carrier for trace amounts of heavy elements in solutions
- Low amounts of light elements using UltraCarry Light
- Larger amount can be deposited (500 $\mu$ l)
- Few tens of ppb
- B to U

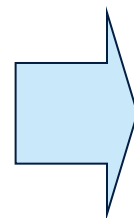
# Micro Carry and Ultra Carry



Place a piece of UltraCarry on a clean surface. Deposit 500 $\mu$ l liquid in the center.

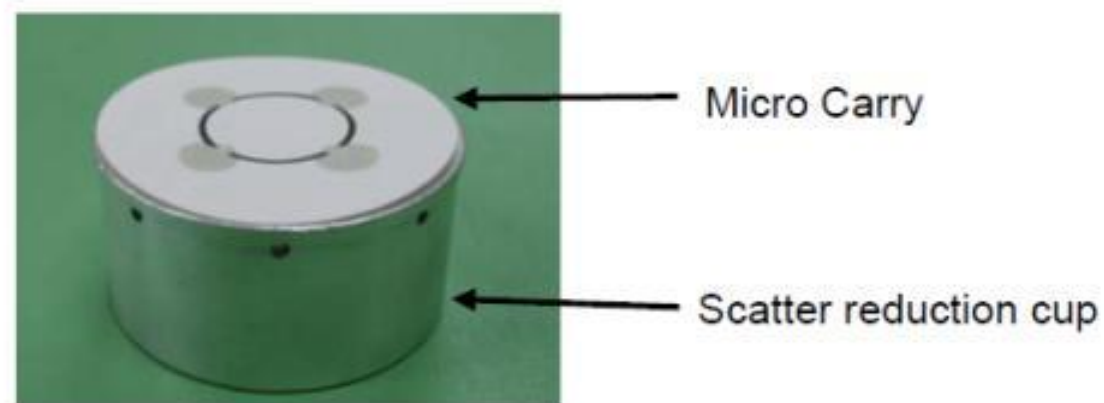


Dry at about 55° C using a drying chamber (vacuum dryer).



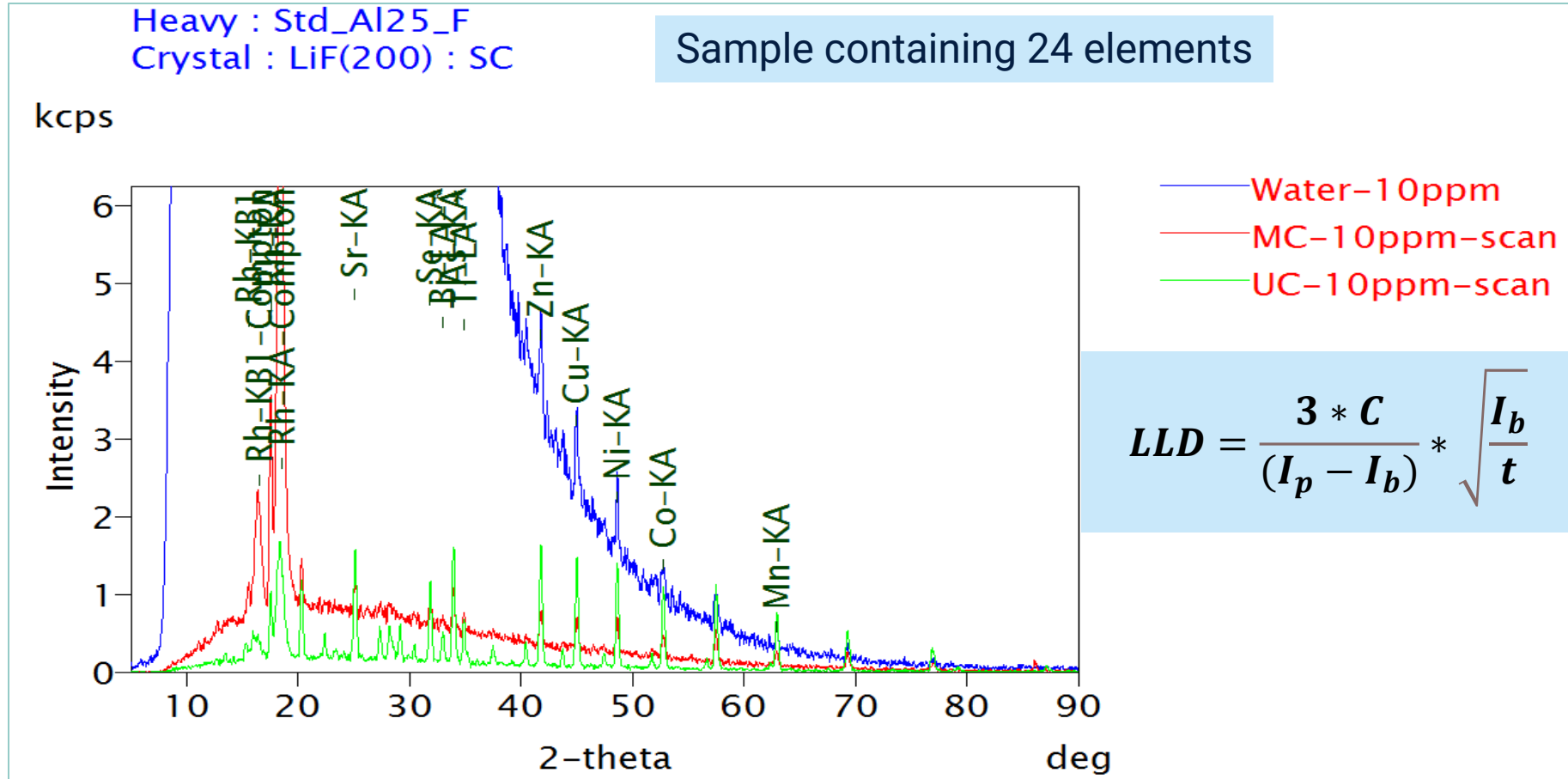
Analyze

# MicroCarry and UltraCarry

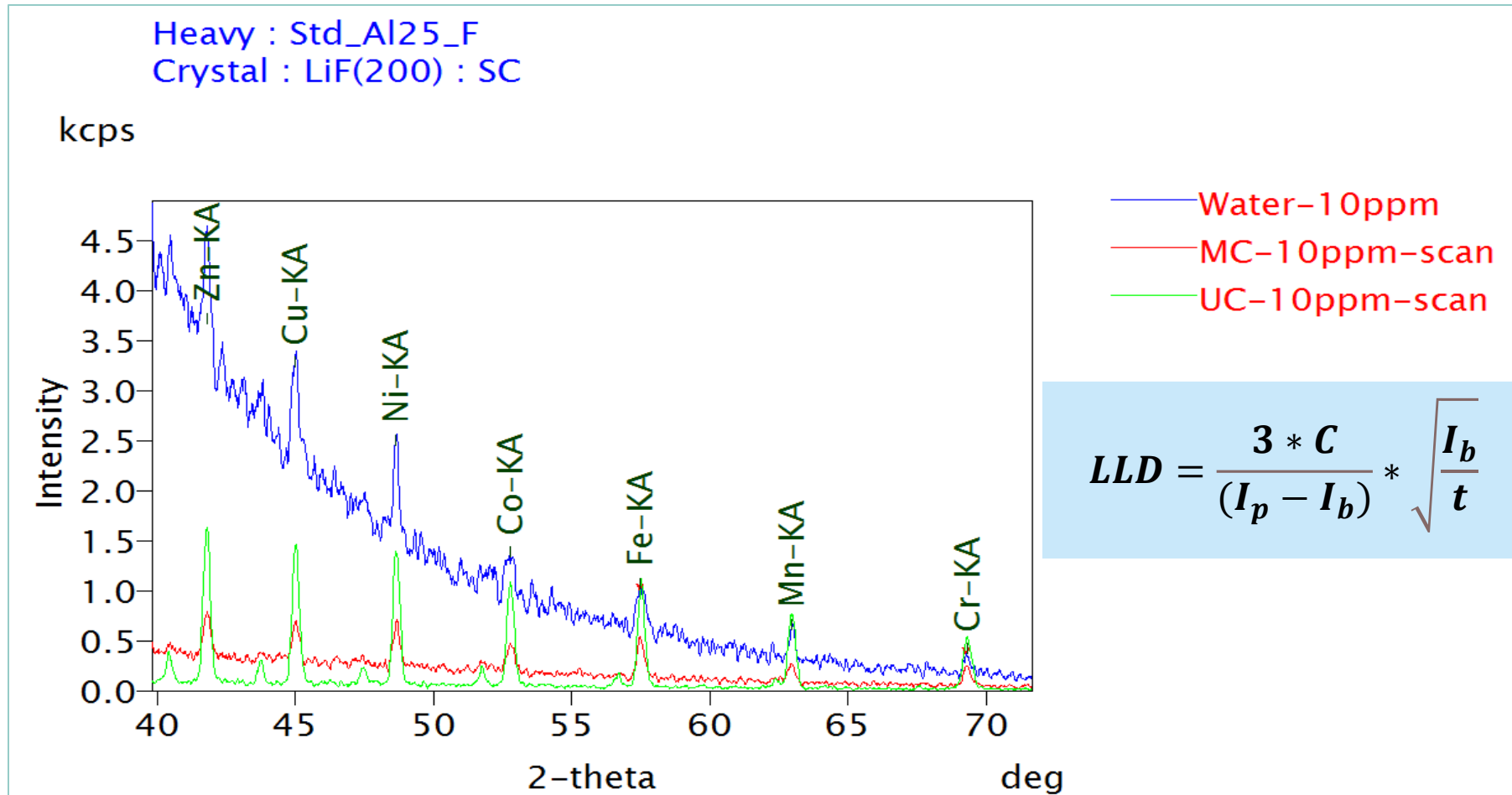


- Use of a Ti, Al or acrylic resin scatter reduction cup
- Up to 30 minutes measurement time for UltraCarry, MicroCarry „much“ longer (hours) @ full power!
- Drying temperature: 40 – 60°C in a dust free environment → vacuum dryer

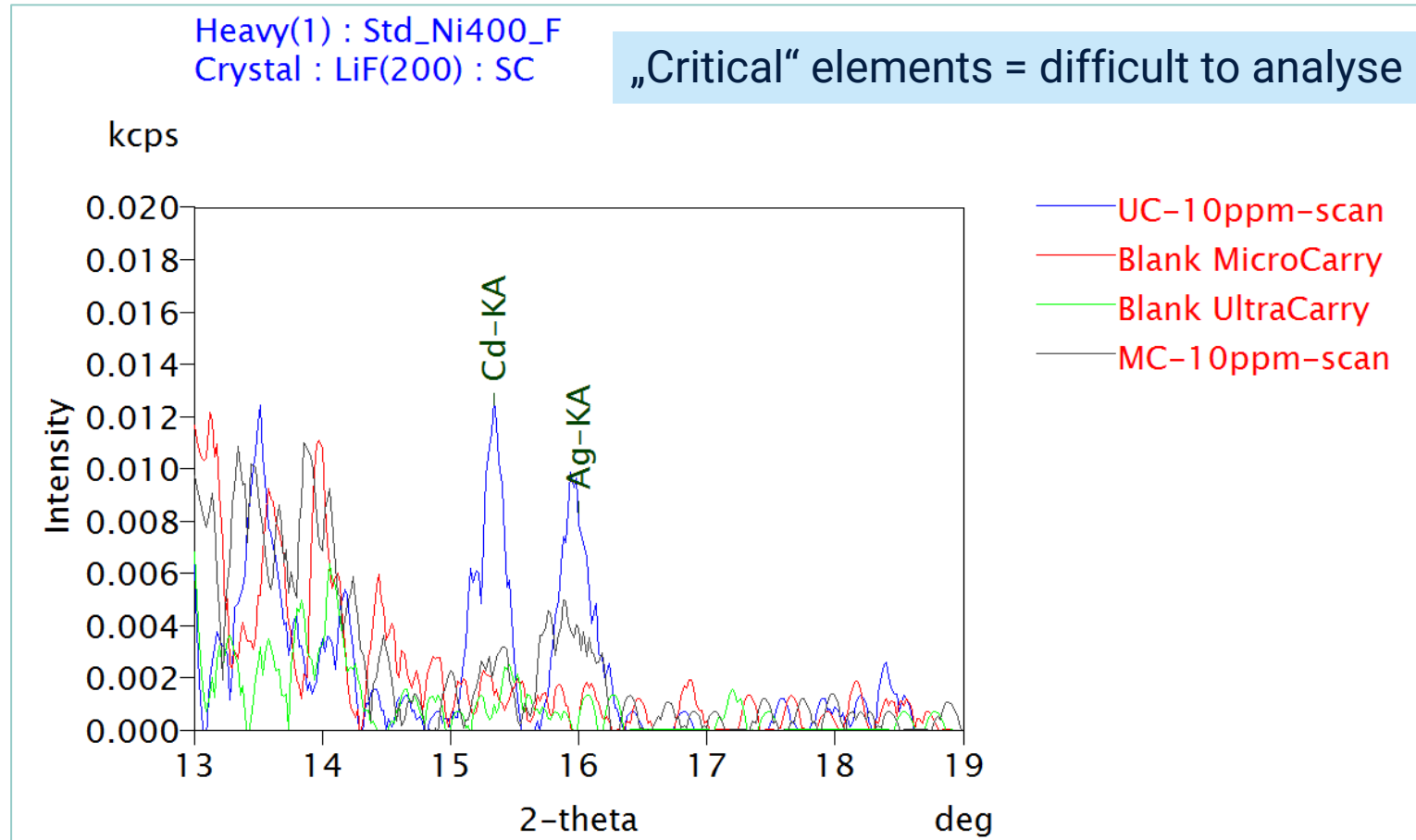
# MICROCARRY AND ULTRACARRY



# MICROCARRY AND ULTRACARRY

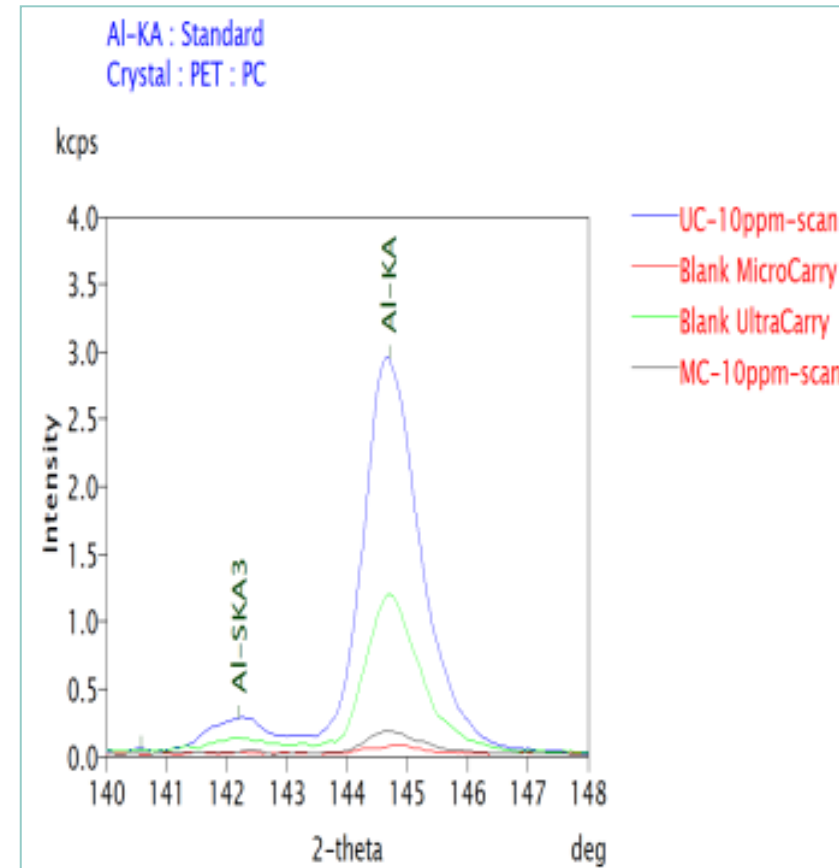
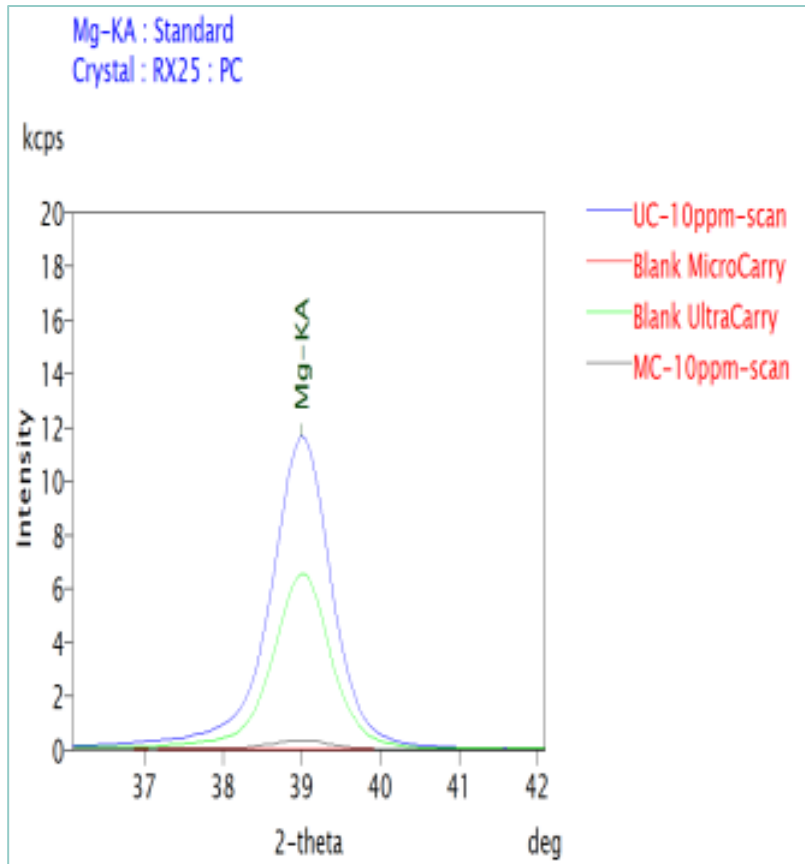


# MICROCARRY AND ULTRACARRY



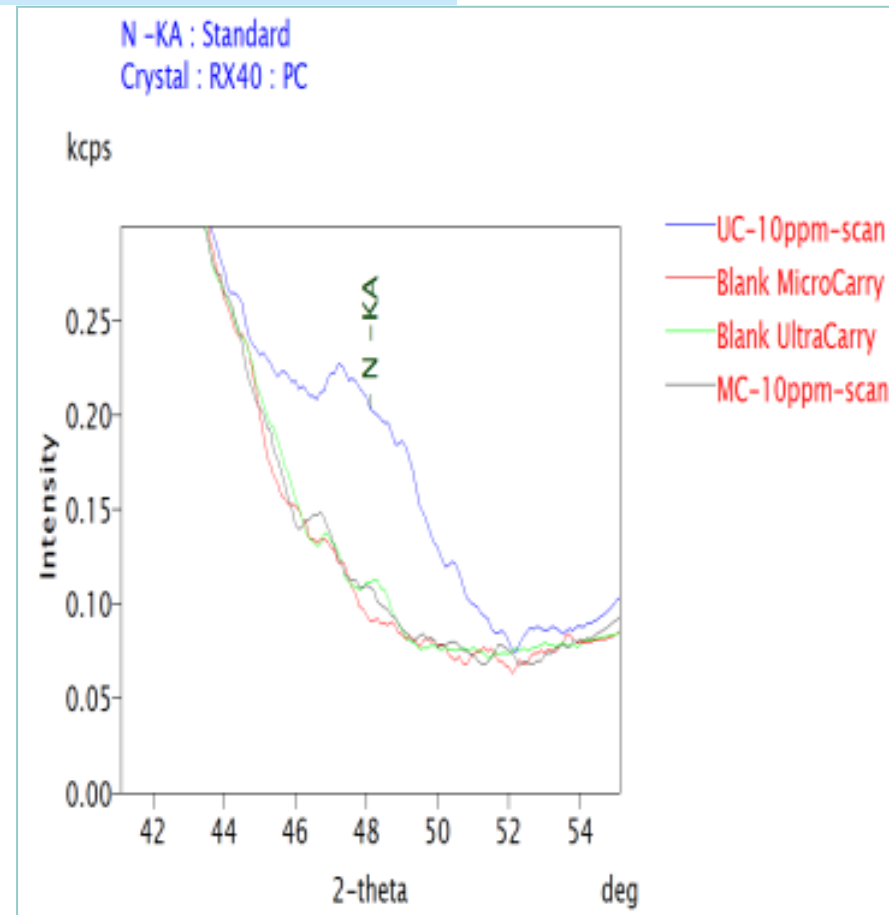
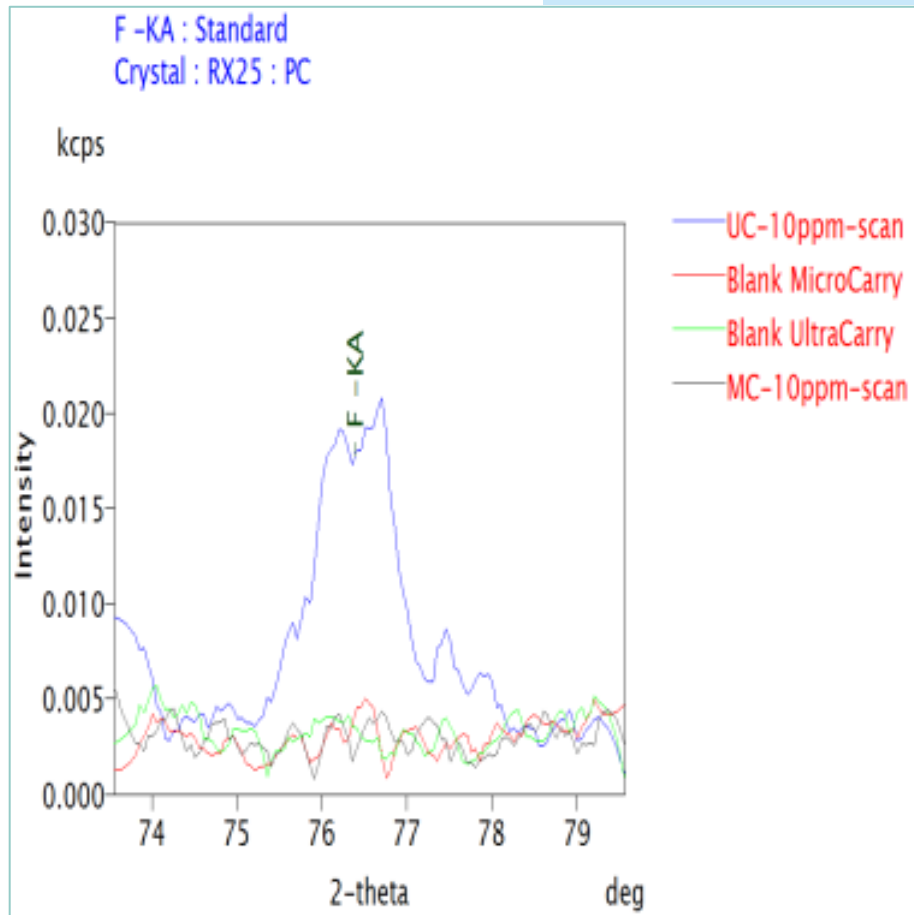
# MICROCARRY AND ULTRACARRY

Is everything perfect? No!



# MICROCARRY AND ULTRACARRY

What about a signal for light elements?



# MICROCARRY AND ULTRACARRY

## Calibration - Details

Element	Ultra Carry						Micro Carry				Sensitivity factor UC/MC	LLD factor MC/UC
	Concentration range (ppm)	Measurement Time (seconds)	Accuracy (ppm)	Sensitivity (cps/ppm)	Background (cps)	LLD (ppm)	Accuracy (ppm)	Sensitivity (cps/ppm)	Background d (cps)	LLD (ppm)		
Al	0 - 10	40	0.73	281	1932	0.074	0.25	61	98	0.077	4.61	0.96
Sb	0 - 10	100	0.13	3.46	12	0.300	0.52	1.5	31	1.114	2.31	3.71
As	0 - 10	60	0.21	38	201	0.144	1.29	18	1200	0.745	2.11	5.16
Ba	0 - 10	100	0.23	54	30	0.030	0.82	4.8	104	0.637	11.25	20.95
Bi	0 - 10	20	0.26	69	192	0.135	0.90	34	1092	0.652	2.03	4.84
Cd	0 - 10	20	0.47	4.1	8.4	0.474	1.10	1.3	14	1.931	3.15	4.07
Cr	0 - 10	10	0.36	115	73	0.070	0.23	36	294	0.452	3.19	6.41
Co	0 - 10	20	0.24	219	105	0.031	0.47	60	543	0.261	3.65	8.30
Cu	0 - 10	10	0.24	254	175	0.049	0.41	72	709	0.351	3.53	7.10
Fe	0 - 10	10	0.32	123	809	0.219	0.20	58	750	0.448	2.12	2.04
Pb	0 - 10	30	0.21	85	209	0.093	0.72	31	1281	0.632	2.74	6.79
Mn	0 - 10	10	0.26	160	93	0.057	0.40	41	328	0.419	3.90	7.33
Mo	0 - 10	10	0.23	164	268	0.095	0.26	94	1568	0.400	1.74	4.22
Ni	0 - 10	10	0.24	254	147	0.045	0.17	72	791	0.371	3.53	8.18
Se	0 - 10	10	0.26	168	186	0.077	0.34	70	1151	0.460	2.40	5.97
Ag	0 - 10	100	0.27	3.8	6.5	0.201	0.50	1.9	14	0.591	2.00	2.94
Sr	0 - 10	10	0.23	246	231	0.059	0.42	75	1365	0.467	3.28	7.97
Tl	0 - 10	20	0.19	97	171	0.090	0.81	31	1025	0.693	3.13	7.66
V	0 - 10	20	0.39	75	45	0.060	0.32	23	171	0.381	3.26	6.36
Zn	0 - 10	10	0.27	268	156	0.044	0.39	77	782	0.345	3.48	7.79
Ca	0 - 100	30	2.00	386	4520	0.095	1.10	140	809	0.111	2.76	1.17
Mg	0 - 100	50	8.50	82	11449	0.554	0.83	12.4	77	0.300	6.61	0.54
K	0 - 100	20	2.90	545	521	0.028	1.80	180	561	0.088	3.03	3.14
Na	0 - 100	20	5.80	33.1	84	0.186	1.40	8.8	28	0.403	3.76	2.17

# MicroCarry and UltraCarry (11)

ULTRA CARRY: 500ML 1PPM  
SOLUTION  
LLD'S (3 SIGMA, 100S)

**WE ARE LOOKING AT SUB-PPM  
LEVELS!**

**LLD = JUST A FEW ppb**



Component	Unit	Result	LLD (ppm)
Al	ppm	1.0	0.300
Sb	ppm	1.0	0.202
As	ppm	1.7	0.080
Ba	ppm	1.1	0.080
Bi	ppm	1.2	0.046
Cd	ppm	0.6	0.100
Cr	ppm	1.1	0.015
Co	ppm	1.0	0.021
Cu	ppm	1.1	0.019
Fe	ppm	1.5	0.013
Pb	ppm	1.3	0.047
Mn	ppm	1.1	0.022
Mo	ppm	0.9	0.027
Ni	ppm	1.1	0.017
Se	ppm	1.0	0.020
Ag	ppm	0.4	0.120
Sr	ppm	1.1	0.022
Tl	ppm	1.2	0.047
V	ppm	1.0	0.022
Zn	ppm	1.0	0.015

# MICROCARRY AND ULTRACARRY

Micro Carry: *Sample Preparation Repeatability, 500µl 3ppm solution*

Component	Unit	Prep. 1	Prep. 2	Prep. 3	Number	Average	Maximum	Minimum	Range	Std dev.	RSD(%)
Al	ppm	2.3	2.6	2.7	3	2.5	2.7	2.3	0.4	0.19	7.63
Sb	ppm	3.5	2.9	2.9	3	3.1	3.5	2.9	0.6	0.33	10.54
As	ppm	3.5	4.5	4.2	3	4.1	4.5	3.5	0.9	0.48	11.77
Ba	ppm	2.4	3.0	2.6	3	2.7	3.0	2.4	0.7	0.34	12.58
Bi	ppm	3.0	3.5	3.4	3	3.3	3.5	3.0	0.5	0.25	7.56
Cd	ppm	2.5	3.5	3.0	3	3.0	3.5	2.5	1.0	0.48	16.11
Cr	ppm	3.1	3.2	3.0	3	3.1	3.2	3.0	0.2	0.11	3.63
Co	ppm	2.6	2.8	2.8	3	2.7	2.8	2.6	0.3	0.15	5.34
Cu	ppm	2.8	2.8	3.1	3	2.9	3.1	2.8	0.4	0.20	6.95
Fe	ppm	2.8	3.0	2.8	3	2.9	3.0	2.8	0.2	0.13	4.46
Pb	ppm	3.3	3.7	3.7	3	3.6	3.7	3.3	0.4	0.23	6.46
Mn	ppm	2.8	2.9	2.8	3	2.8	2.9	2.8	0.1	0.06	1.96
Mo	ppm	2.9	2.9	3.2	3	3.0	3.2	2.9	0.3	0.17	5.56
Ni	ppm	2.9	3.2	3.2	3	3.1	3.2	2.9	0.3	0.16	5.08
Se	ppm	2.9	3.0	3.1	3	3.0	3.1	2.9	0.2	0.09	3.09
Ag	ppm	3.8	3.3	2.6	3	3.2	3.8	2.6	1.2	0.59	18.32
Sr	ppm	2.9	3.1	2.9	3	3.0	3.1	2.9	0.2	0.09	2.93
Tl	ppm	2.8	3.0	3.1	3	3.0	3.1	2.8	0.3	0.16	5.33
V	ppm	2.6	2.9	2.6	3	2.7	2.9	2.6	0.3	0.17	6.37
Zn	ppm	2.9	3.2	2.8	3	3.0	3.2	2.8	0.5	0.25	8.54
Ca	ppm	19.9	21.1	20.8	3	20.6	21.1	19.9	1.1	0.60	2.90
Mg	ppm	20.2	22.6	22.0	3	21.6	22.6	20.2	2.4	1.23	5.70
K	ppm	17.2	17.3	18.7	3	17.8	18.7	17.2	1.5	0.85	4.80
Na	ppm	16.1	17.5	17.8	3	17.1	17.8	16.1	1.7	0.90	5.28

# Sample Preparation - Conclusions

- Sampling and sample preparation depend on many parameters
- Important physical effects have to be taken into account for the specimen preparation
- Powder and liquid samples can be prepared in a relatively simple way
- Many different preparation techniques exist to prepare specimens
- The sample preparation is a crucial event in the chemical analysis

# Sample Preparation

## The one commandment

Whatever sample preparation method you choose, verify its reproducibility before you start preparing the calibration standards



**Prepared by  
XRF Application Scientist  
Carmen Kasier Brugmann**

**Contact us  
[www.Rigaku.com](http://www.Rigaku.com)**