Project Boron – quantitative analyses for Boron by XRF

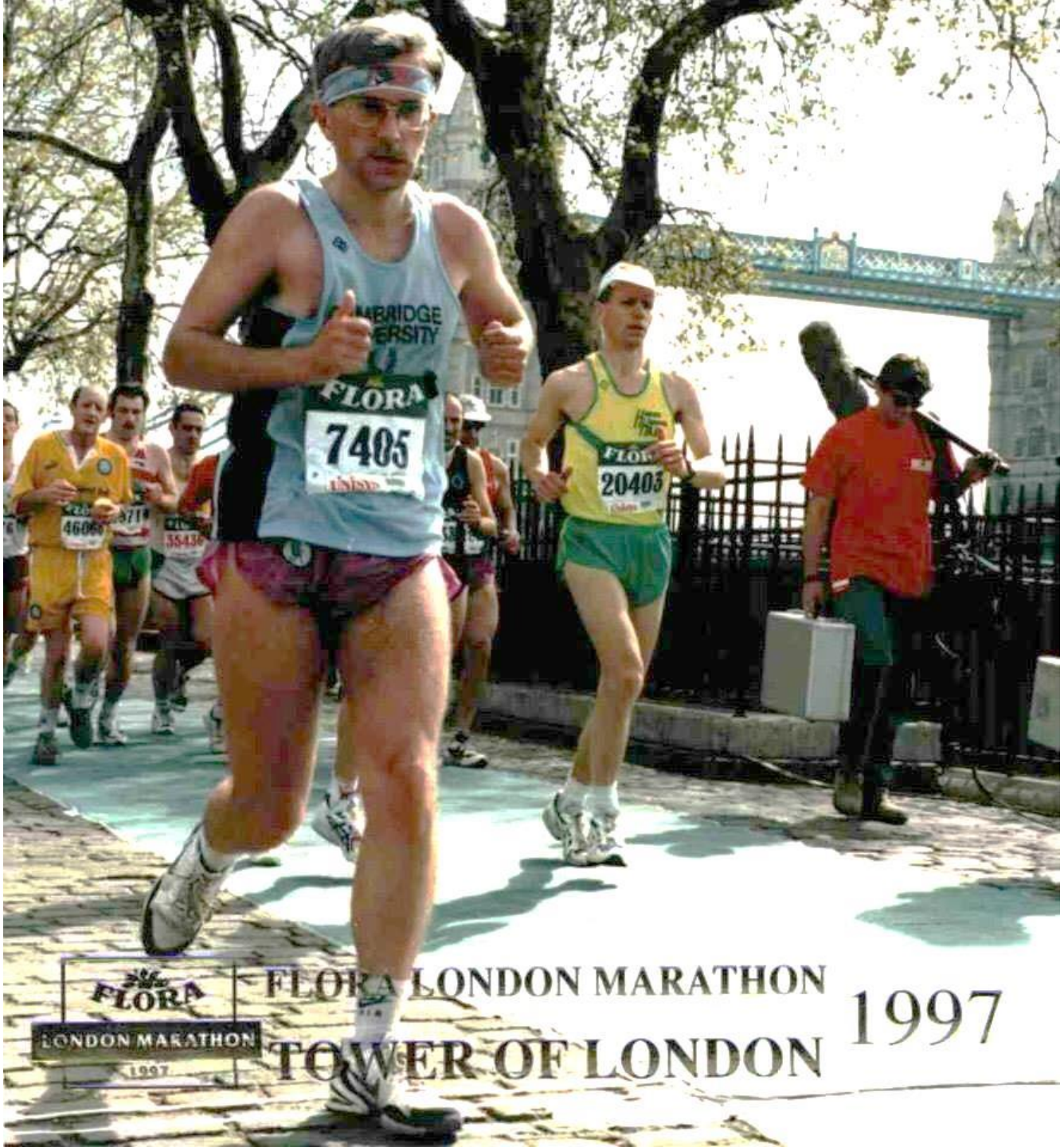
BELL, Anthony <http://orcid.org/0000-0001-5038-5621>

The “OXI” XRF standard analysis method on a new XRF spectrometer.

Dr. Tony Bell

ESG15 – NCM15 Cambridge 2024

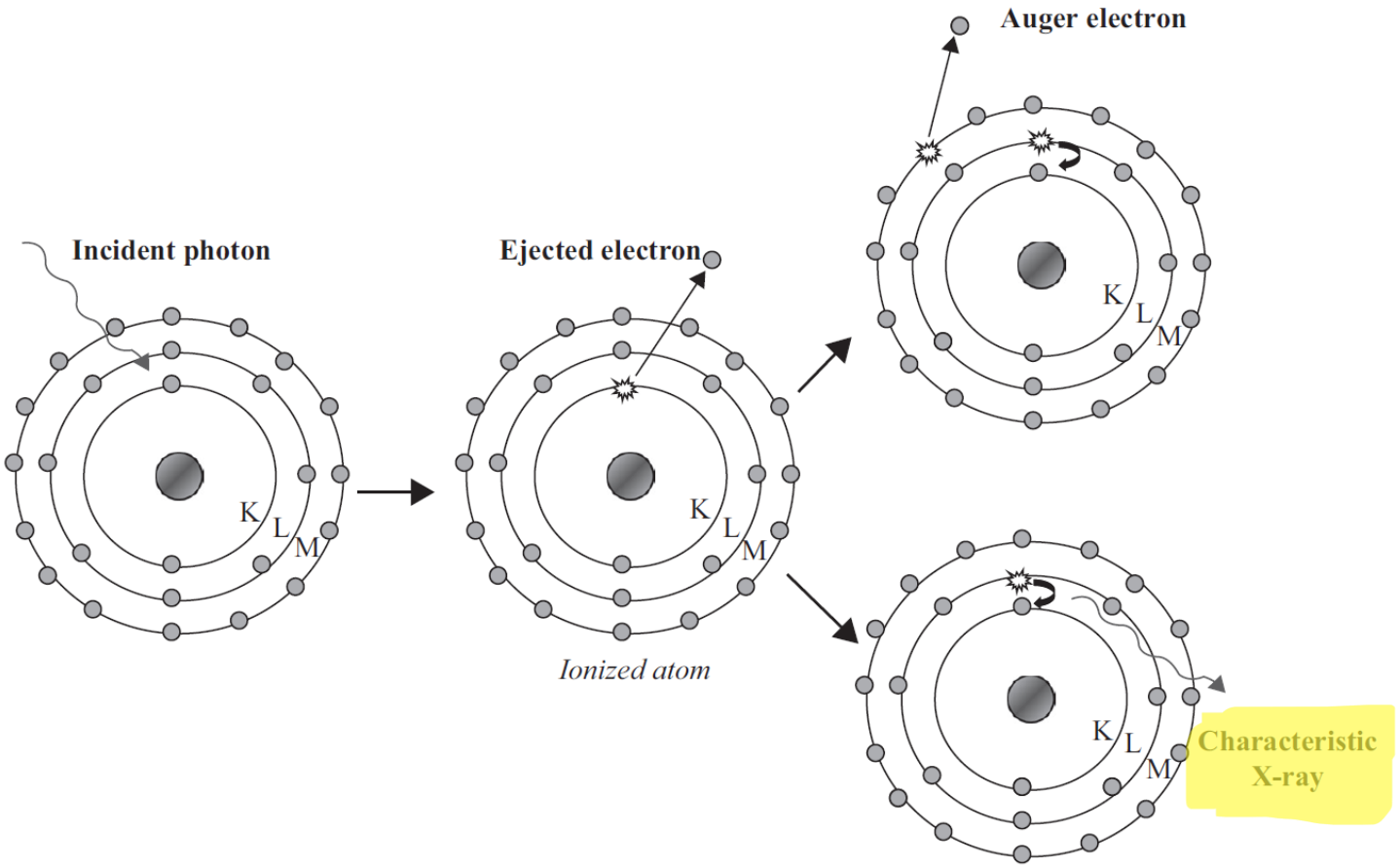
Sheffield Hallam University | Materials and Engineering Research Institute



FLORA LONDON MARATHON

TOWER OF LONDON 1997

X-ray Fluorescence (XRF)



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- XRF is a very useful technique with strengths and limitations.
- XRF is not a magic black box that produces results out of thin air!


PW2540 vrc sample changer
PHILIPS
MagiX PRO
PHILIPS
PHILIPS
MagiX PRO

MagiX PRO XRF spectrometer

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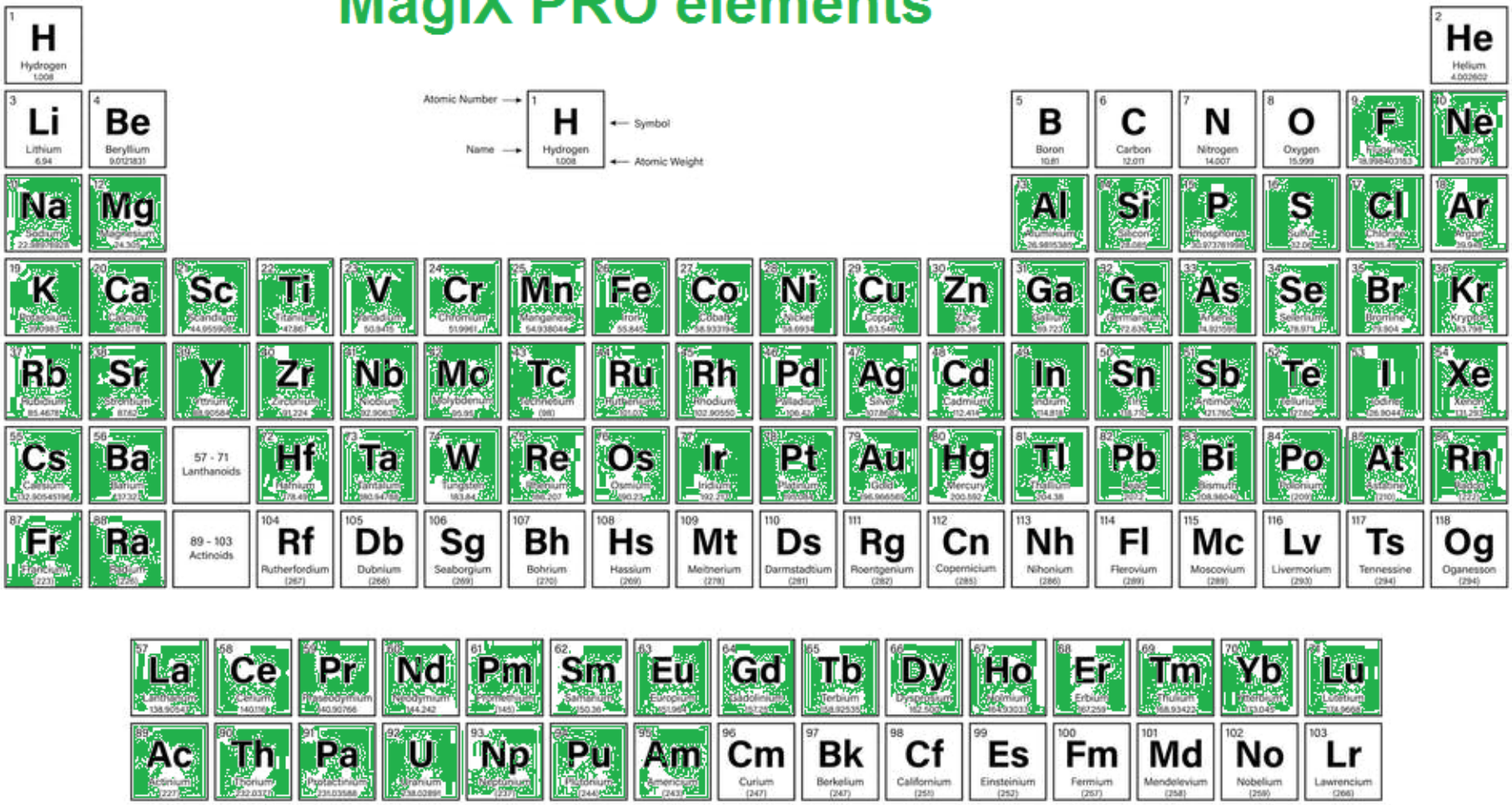
- Glass samples made into **fused beads**.

Periodic Table of the Elements

MagiX PRO elements



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- However, these **IQ+** results were only semi-quantitative.
- More accurate results were needed.

Bring back

OXI

X-RAY SPECTROMETRY, VOL. 24, 205–218 (1995)

Simple Approach to the Analysis of Oxides, Silicates and Carbonates Using X-Ray Fluorescence Spectrometry

H. L. Giles*
Materials Research Institute, Sheffield Hallam University, Pond Street, Sheffield, S1 1WB, UK

P. W. Hurley†
Analytical Consultant, 'Endian', Gore Tree Road, Hemingford Grey, Huntingdon, Cambs., PE18 9BP, UK

H. W. M. Webster
Philips Analytical X-ray, York Street, Cambridge, CB1 2QU, UK

X-ray fluorescence spectrometry has always been considered to be a comparative method of analysis requiring chemically analysed samples or reference materials for calibration. The fusion technique, which is widely used as the method of sample preparation to eliminate particle size and mineralogical effects, allows the use of synthetic 'standards' as the means of calibration, but most laboratories use large numbers to establish the primary calibration line and calculate empirical interelement correction coefficients. In the 1970s, de Jongh proposed the use of theoretically based correction coefficients, and his concept of 'apparent concentration,' which is related linearly to the measured intensity, means that in principle only two samples are necessary to define the primary calibration line. This paper describes the use of this principle to calibrate a spectrometer for the 13 most commonly occurring oxides, plus six others, over wide composition ranges. Each calibration line requires one sample, which is made from a commercially available source of the element, a blank or zero sample, which is used for all calibration lines, and a set of theoretical α coefficients calculated using de Jongh's program. Sample preparation is by fusion in $Li_2B_4O_7$. The calibration was tested using reference materials and was found to be accurate for every element except sulphur.

INTRODUCTION

In x-ray fluorescence spectrometry, concentration is related to intensity by an algorithm of the type

$$C_i = D_i + E_i R_i (1 + \Sigma\alpha_{i,j} \cdot C_j) \quad (1)$$

where i is the analyte element, j is an interfering element (j can be i), C_i is the concentration of the analyte i, E_i and D_i are the slope and intercept, respectively, of the primary calibration line, R_i is the dead-time corrected net intensity for element i, α_{ij} is the interelement correction factor for element j on element i (j can be i) and C_j is the concentration of the intefering element j (j can be i).

To solve this equation for C_i in a multi-element situation, the values of E_i, D_i and α_{ij} must be known, and then iteration or matrix inversion can be used to solve the set of equations for C_i using measured values of R_i.

Several approaches can be used to obtain values for the constants D_i, E_i and α_{ij}.

1. The use of a 'close range' calibration, where the interelement correction term $(1 + \Sigma\alpha_{ij})$ is assumed to be constant and is incorporated in D_i and E_i. These latter being determined either graphically or by least squares fit from a small number of standards.
2. The use of many standards including binaries and pseudobinaries with graphical solution.
3. The use of fewer standards than in 2 above, and multilinear regression analysis.
4. The use of theoretically determined values of α_{ij} by, for instance, the method of de Jongh[1] to obtain an apparent concentration, where:

$$C_{\text{apparent}(i)} = \frac{C_{\text{true}(i)}}{1 + \Sigma\alpha_{i,j} \cdot C_j} \quad (2)$$

followed by a simple graphical or algebraic solution for D_i and E_i from Eqn (3), which results from the combination of Eqns (1) and (2).

$$C_{\text{apparent}(i)} = D_i + E_i R_i \quad (3)$$

Provided that the values of $C_{\text{apparent}(i)}$ and R_i are precisely known, Eqn (2) may be solved using only two values of $C_{\text{apparent}(i)}$, e.g. a high concentration plus a zero. In this work, we applied this concept and tested its validity.

In a later paper[2] de Jongh proposed that by using loss/gain on ignition (L.O.I.) as the eliminated component in the theoretical coefficients calculation, then the samples need not be pre-ignited before fusion, and that the loss or gain on ignition is represented by the difference between 100% and the arithmetic sum of the

* Formerly of London & Scandinavian Metallurgical Co. Ltd., Fullerton Road, Rotherham, S. Yorks, S60 1DL, UK

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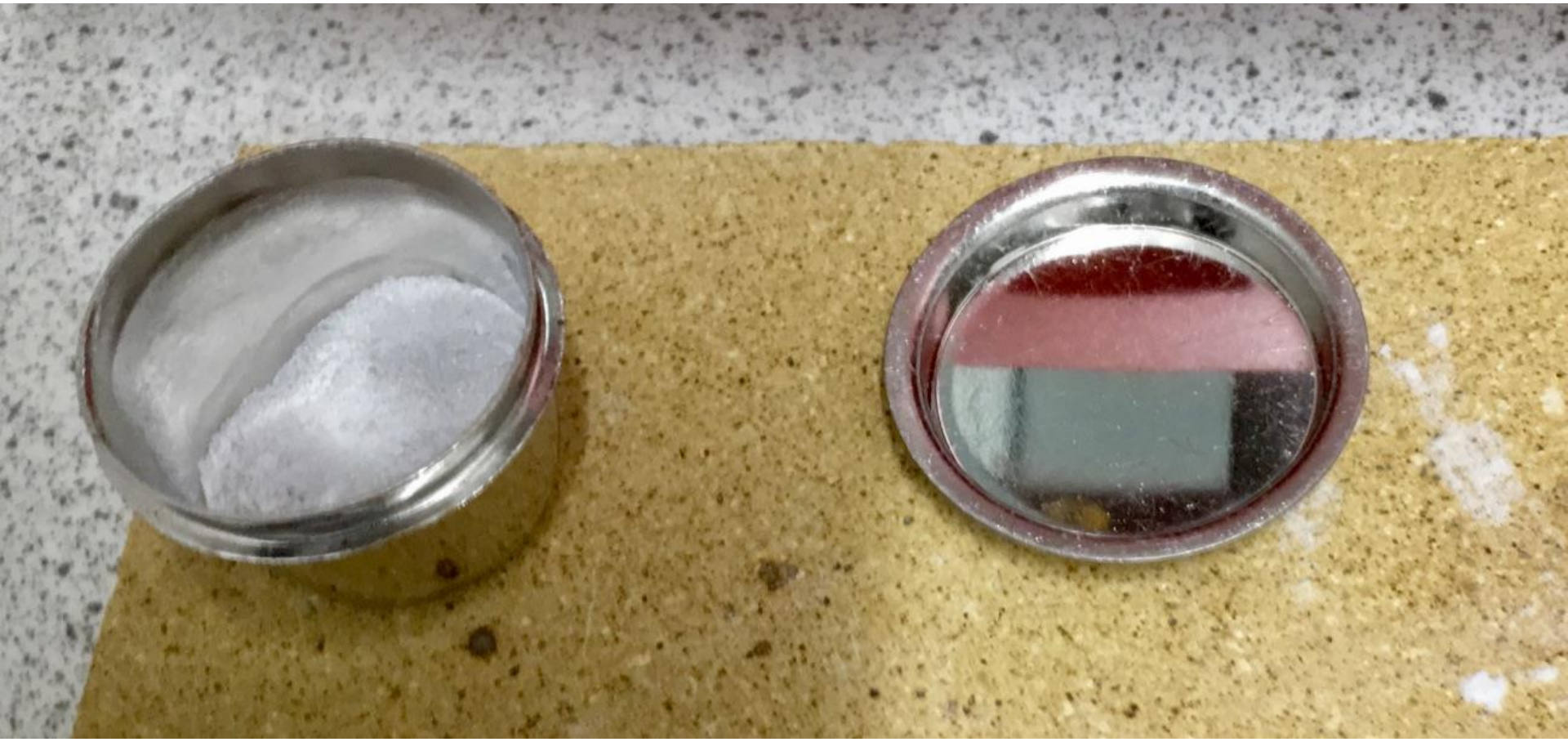
- Standards made by mixing material of interest with 10g of $Li_2B_2O_7$ (doped with 0.5% LiI) flux in a 95%Pt:5%Au crucible.



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CLAISSE
THE FIRST AND FINEST IN FUSION
Home
25°C
EMERGENCY
STOP
LE neo
FLUXER
4 ALFIE

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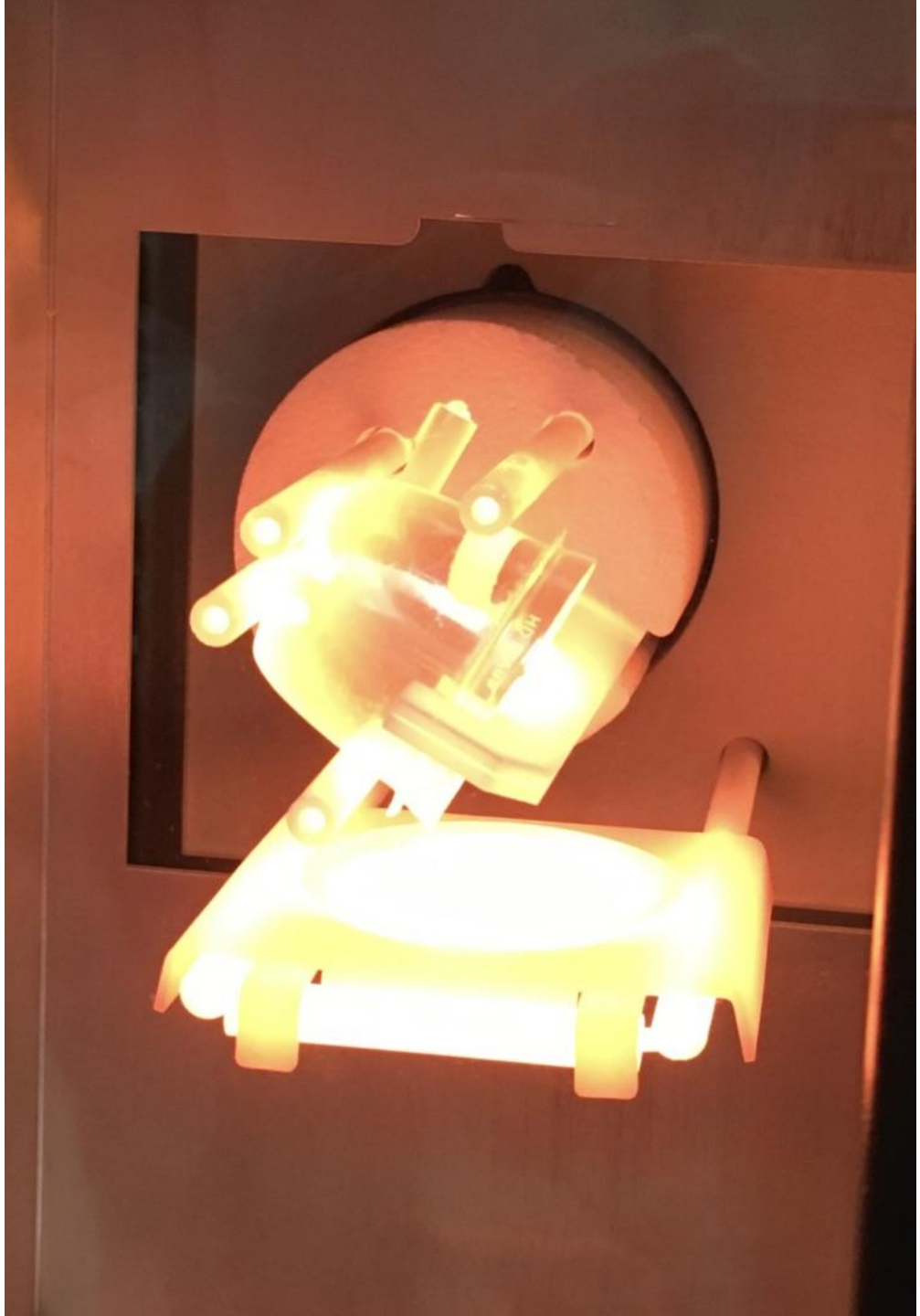
Fusion
1065°C
Disk - High refractory materials
00:21:45
Step number
1/7
Step type
Heating
Step duration
00:06:00
Setpoint
1065°C
Rocking speed
0 RPM
Rocking angle
0°
Select...
Time
Start



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- Cool to form a fused bead.
- All OXI standards consist of an oxide dissolved in a fused bead.

OXI standards

starting material	OXI oxide	starting material	OXI oxide
Na_2CO_3	Na_2O	Cr_2O_3	Cr_2O_3
MgO	MgO	MnO_2	Mn_3O_4
Al_2O_3	Al_2O_3	Fe_2O_3	Fe_2O_3
SiO_2	SiO_2	ZnO	ZnO
$NH_4H_2PO_4$	P_2O_5	$Sr(NO_3)_2$	SrO
Li_2SO_4	SO_3	Y_2O_3	Y_2O_3
K_2CO_3	K_2O	ZrO_2	ZrO_2
$CaCO_3$	CaO	$BaCO_3$	BaO
TiO_2	TiO_2	HfO_2	HfO_2
V_2O_5	V_2O_5		

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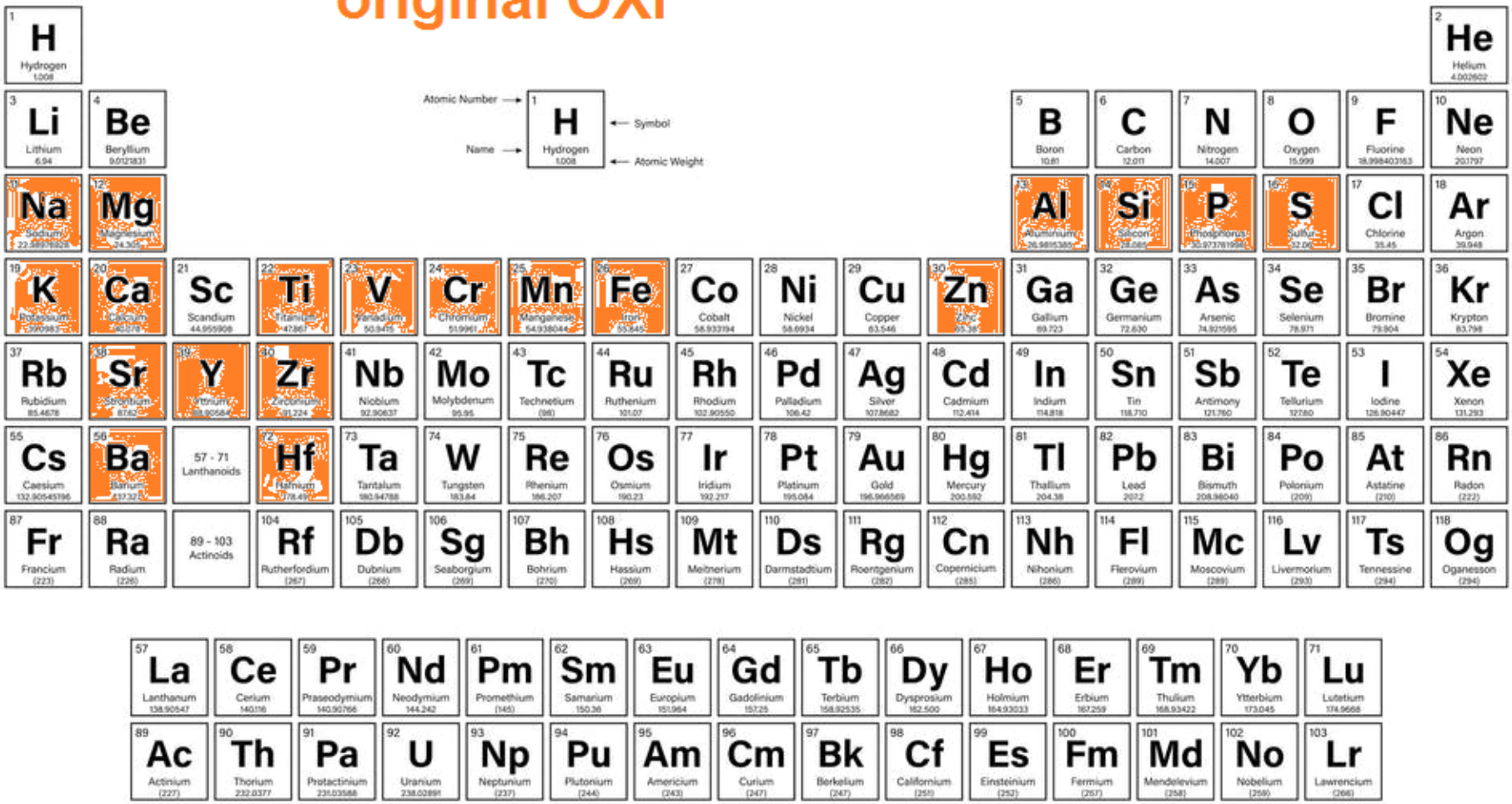
original OXI



new OXI standards

- Clay standard sample
- CRM-309 sillimanite
- CRM-348 ball clay
- CRM-375 soda feldspar
- CRM-376 potash feldspar
- CRM-525 low iron float glass
- CRM-528 standard glass sand
- CRM-531 low iron sand

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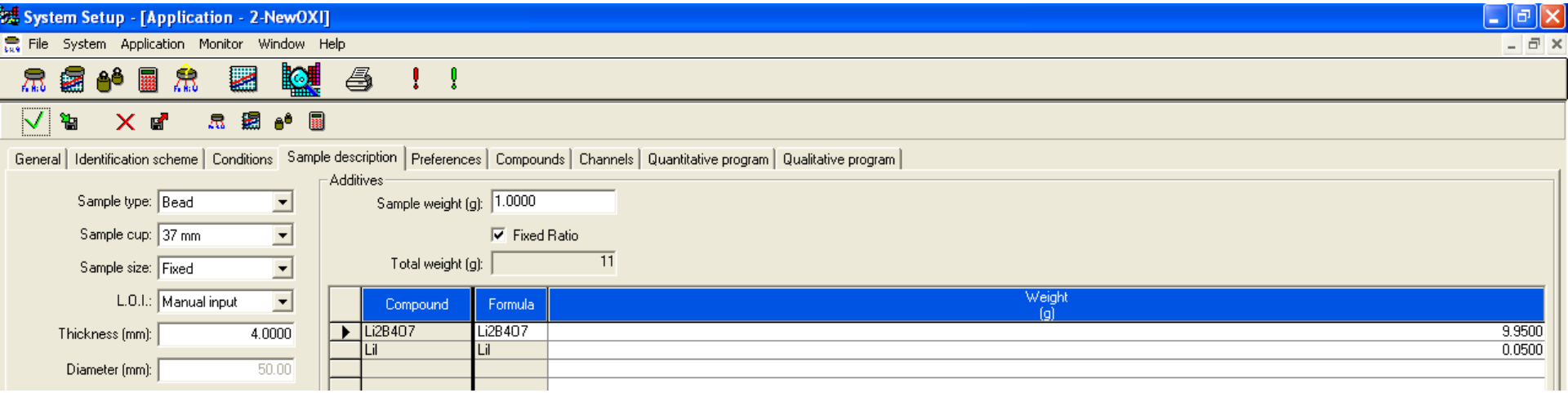

$Li_2B_4O_7$ (with 0.5% LiI anti-cracking agent) flux.

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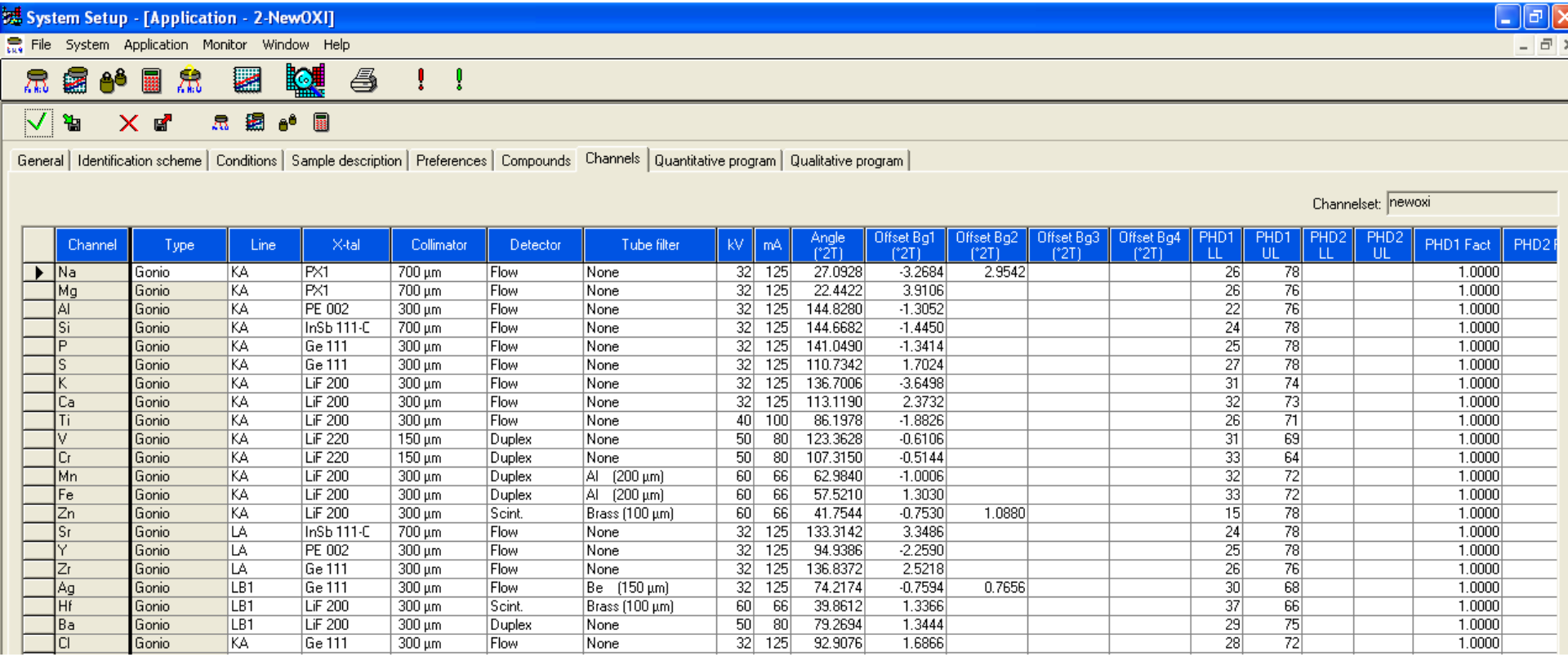

Channel	Type	Line	X-tal	Collimator	Detector	Tube filter	kV	mA	Angle (°2T)	Offset Bg1 (°2T)	Offset Bg2 (°2T)	Offset Bg3 (°2T)	Offset Bg4 (°2T)	PHD1 LL	PHD1 UL	PHD2 LL	PHD2 UL	PHD1 Fact	PHD2 F
Na	Gonio	KA	PX1	700 µm	Flow	None	32	125	27.0928	-3.2684	2.9542			26	78			1.0000	
Mg	Gonio	KA	PX1	700 µm	Flow	None	32	125	22.4422	3.9106				26	76			1.0000	
Al	Gonio	KA	PE 002	300 µm	Flow	None	32	125	144.8280	-1.3052				22	76			1.0000	
Si	Gonio	KA	InSb 111-C	700 µm	Flow	None	32	125	144.6682	-1.4450				24	78			1.0000	
P	Gonio	KA	Ge 111	300 µm	Flow	None	32	125	141.0490	-1.3414				25	78			1.0000	
S	Gonio	KA	Ge 111	300 µm	Flow	None	32	125	110.7342	1.7024				27	78			1.0000	
K	Gonio	KA	LiF 200	300 µm	Flow	None	32	125	136.7006	-3.6498				31	74			1.0000	
Ca	Gonio	KA	LiF 200	300 µm	Flow	None	32	125	113.1190	2.3732				32	73			1.0000	
Ti	Gonio	KA	LiF 200	300 µm	Flow	None	40	100	86.1978	-1.8826				26	71			1.0000	
V	Gonio	KA	LiF 220	150 µm	Duplex	None	50	80	123.3628	-0.6106				31	69			1.0000	
Cr	Gonio	KA	LiF 220	150 µm	Duplex	None	50	80	107.3150	-0.5144				33	64			1.0000	
Mn	Gonio	KA	LiF 200	300 µm	Duplex	Al (200 µm)	60	66	62.9840	-1.0006				32	72			1.0000	
Fe	Gonio	KA	LiF 200	300 µm	Duplex	Al (200 µm)	60	66	57.5210	1.3030				33	72			1.0000	
Zn	Gonio	KA	LiF 200	300 µm	Scint.	Brass (100 µm)	60	66	41.7544	-0.7530	1.0880			15	78			1.0000	
Sr	Gonio	LA	InSb 111-C	700 µm	Flow	None	32	125	133.3142	3.3486				24	78			1.0000	
Y	Gonio	LA	PE 002	300 µm	Flow	None	32	125	94.9386	-2.2590				25	78			1.0000	
Zr	Gonio	LA	Ge 111	300 µm	Flow	None	32	125	136.8372	2.5218				26	76			1.0000	
Ag	Gonio	LB1	Ge 111	300 µm	Flow	Be (150 µm)	32	125	74.2174	-0.7594	0.7656			30	68			1.0000	
Hf	Gonio	LB1	LiF 200	300 µm	Scint.	Brass (100 µm)	60	66	39.8612	1.3366				37	66			1.0000	
Ba	Gonio	LB1	LiF 200	300 µm	Duplex	None	50	80	79.2694	1.3444				29	75			1.0000	
Cl	Gonio	KA	Ge 111	300 µm	Flow	None	32	125	92.9076	1.6866				28	72			1.0000	

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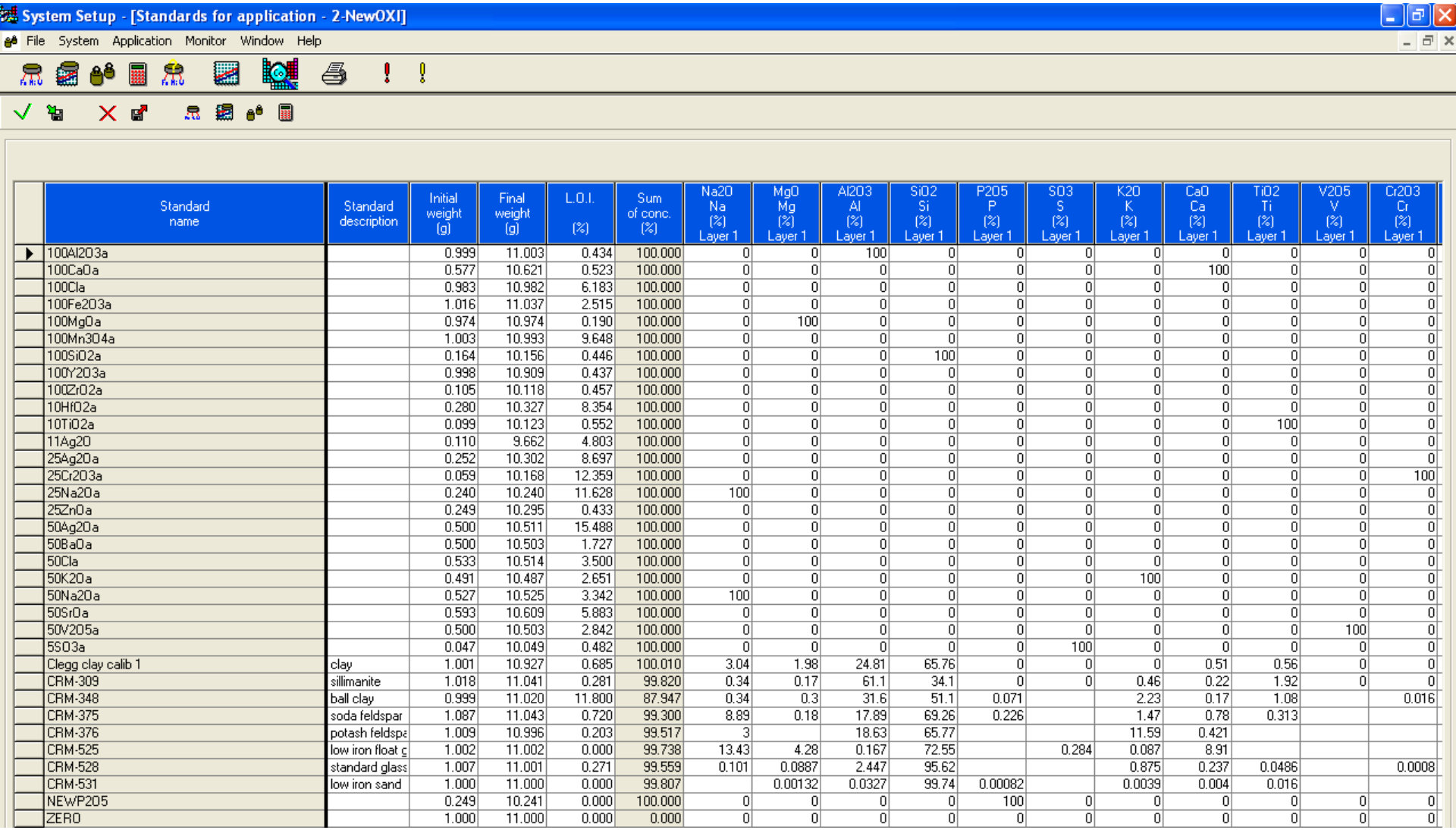
- some standards contain more than one element of interest.



Standard name	Standard description	Initial weight (g)	Final weight (g)	L.O.I. (%)	Sum of conc. (%)	Na2O Na (%) Layer 1	MgO Mg (%) Layer 1	Al2O3 Al (%) Layer 1	SiO2 Si (%) Layer 1	P2O5 P (%) Layer 1	SO3 S (%) Layer 1	K2O K (%) Layer 1	CaO Ca (%) Layer 1	TiO2 Ti (%) Layer 1	V2O5 V (%) Layer 1	Cr2O3 Cr (%) Layer 1
100Al2O3a		0.999	11.003	0.434	100.000	0	0	100	0	0	0	0	0	0	0	0
100CaOa		0.577	10.621	0.523	100.000	0	0	0	0	0	0	0	100	0	0	0
100Cla		0.983	10.982	6.183	100.000	0	0	0	0	0	0	0	0	0	0	0
100Fe2O3a		1.016	11.037	2.515	100.000	0	0	0	0	0	0	0	0	0	0	0
100MgOa		0.974	10.974	0.190	100.000	0	100	0	0	0	0	0	0	0	0	0
100Mn3O4a		1.003	10.993	9.648	100.000	0	0	0	0	0	0	0	0	0	0	0
100SiO2a		0.164	10.156	0.446	100.000	0	0	0	100	0	0	0	0	0	0	0
100Y2O3a		0.998	10.909	0.437	100.000	0	0	0	0	0	0	0	0	0	0	0
100ZrO2a		0.105	10.118	0.457	100.000	0	0	0	0	0	0	0	0	0	0	0
10HfO2a		0.280	10.327	8.354	100.000	0	0	0	0	0	0	0	0	0	0	0
10TiO2a		0.099	10.123	0.552	100.000	0	0	0	0	0	0	0	0	100	0	0
11Ag2O		0.110	9.662	4.803	100.000	0	0	0	0	0	0	0	0	0	0	0
25Ag2Oa		0.252	10.302	8.697	100.000	0	0	0	0	0	0	0	0	0	0	0
25Cr2O3a		0.059	10.168	12.359	100.000	0	0	0	0	0	0	0	0	0	0	100
25Na2Oa		0.240	10.240	11.628	100.000	100	0	0	0	0	0	0	0	0	0	0
25ZnOa		0.249	10.295	0.433	100.000	0	0	0	0	0	0	0	0	0	0	0
50Ag2Oa		0.500	10.511	15.488	100.000	0	0	0	0	0	0	0	0	0	0	0
50BaOa		0.500	10.503	1.727	100.000	0	0	0	0	0	0	0	0	0	0	0
50Cla		0.533	10.514	3.500	100.000	0	0	0	0	0	0	0	0	0	0	0
50K2Oa		0.491	10.487	2.651	100.000	0	0	0	0	0	0	100	0	0	0	0
50Na2Oa		0.527	10.525	3.342	100.000	100	0	0	0	0	0	0	0	0	0	0
50SrOa		0.593	10.609	5.883	100.000	0	0	0	0	0	0	0	0	0	0	0
50V2O5a		0.500	10.503	2.842	100.000	0	0	0	0	0	0	0	0	0	100	0
5SO3a		0.047	10.049	0.482	100.000	0	0	0	0	0	100	0	0	0	0	0
Clegg clay calib 1	clay	1.001	10.927	0.685	100.010	3.04	1.98	24.81	65.76	0	0	0	0.51	0.56	0	0
CRM-309	sillimanite	1.018	11.041	0.281	99.820	0.34	0.17	61.1	34.1	0	0	0.46	0.22	1.92	0	0
CRM-348	ball clay	0.999	11.020	11.800	87.947	0.34	0.3	31.6	51.1	0.071		2.23	0.17	1.08		0.016
CRM-375	soda feldspar	1.087	11.043	0.720	99.300	8.89	0.18	17.89	69.26	0.226		1.47	0.78	0.313		
CRM-376	potash feldspa	1.009	10.996	0.203	99.517	3		18.63	65.77			11.59	0.421			
CRM-525	low iron float g	1.002	11.002	0.000	99.738	13.43	4.28	0.167	72.55		0.284	0.087	8.91			
CRM-528	standard glass	1.007	11.001	0.271	99.559	0.101	0.0887	2.447	95.62			0.875	0.237	0.0486		0.0008
CRM-531	low iron sand	1.000	11.000	0.000	99.807		0.00132	0.0327	99.74	0.00082		0.0039	0.004	0.016		
NEWP2O5		0.249	10.241	0.000	100.000	0	0	0	0	100	0	0	0	0	0	0
ZERO		1.000	11.000	0.000	0.000	0	0	0	0	0	0	0	0	0	0	0

Creating a new OXI program

- Run each standard sample, measure intensities for each element of interest and background points.

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- some points can be deleted to improve fit.

INTRODUCTION

In x-ray fluorescence spectrometry, concentration is related to intensity by an algorithm of the type

$$C_i = D_i + E_i R_i (1 + \Sigma\alpha_{i,j} \cdot C_j) \quad (1)$$

where i is the analyte element, j is an interfering element (j can be i), C_i is the concentration of the analyte i, E_i and D_i are the slope and intercept, respectively, of the primary calibration line, R_i is the dead-time corrected net intensity for element i, α_{ij} is the interelement correction factor for element j on element i (j can be i) and C_j is the concentration of the intefering element j (j can be i).

To solve this equation for C_i in a multi-element situation, the values of E_i, D_i and α_{ij} must be known, and then iteration or matrix inversion can be used to solve the set of equations for C_i using measured values of R_i.

Several approaches can be used to obtain values for the constants D_i, E_i and α_{ij}.

1. The use of a 'close range' calibration, where the interelement correction term $(1 + \Sigma\alpha_{ij})$ is assumed to be constant and is incorporated in D_i and E_i. These latter being determined either graphically or by least squares fit from a small number of standards.
2. The use of many standards including binaries and pseudobinaries with graphical solution.
3. The use of fewer standards than in 2 above, and multilinear regression analysis.
4. The use of theoretically determined values of α_{ij} by, for instance, the method of de Jongh[1] to obtain an apparent concentration, where:

$$C_{\text{apparent}(i)} = \frac{C_{\text{true}(i)}}{1 + \Sigma\alpha_{i,j} \cdot C_j} \quad (2)$$

followed by a simple graphical or algebraic solution for D_i and E_i from Eqn (3), which results from the combination of Eqns (1) and (2).

$$C_{\text{apparent}(i)} = D_i + E_i R_i \quad (3)$$

Provided that the values of $C_{\text{apparent}(i)}$ and R_i are precisely known, Eqn (2) may be solved using only two values of $C_{\text{apparent}(i)}$, e.g. a high concentration plus a zero. In this work, we applied this concept and tested its validity.

In a later paper[2] de Jongh proposed that by using loss/gain on ignition (L.O.I.) as the eliminated component in the theoretical coefficients calculation, then the samples need not be pre-ignited before fusion, and that the loss or gain on ignition is represented by the difference between 100% and the arithmetic sum of the

* Formerly of London & Scandinavian Metallurgical Co. Ltd., Fullerton Road, Rotherham, S. Yorks, S60 1DL, UK

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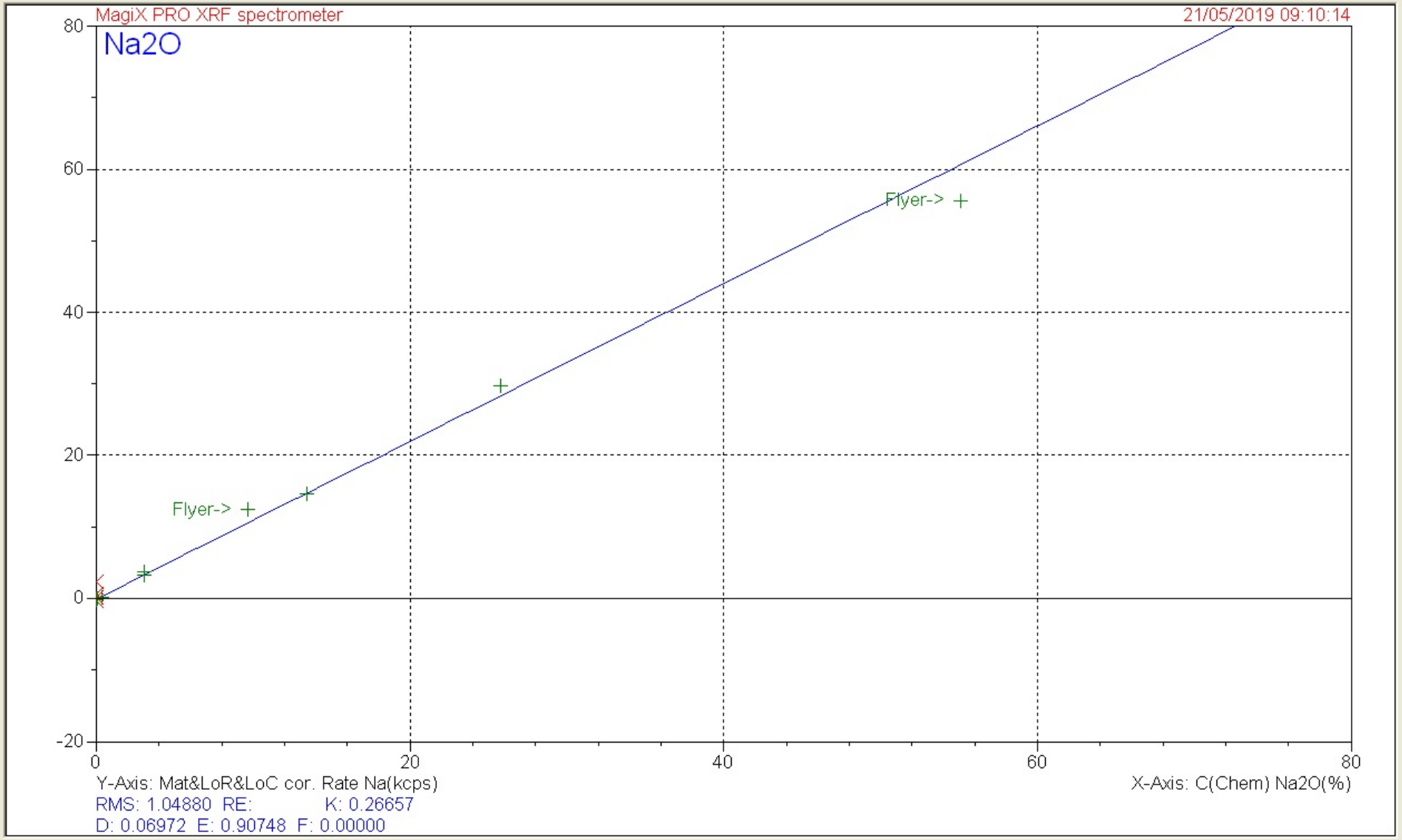
Received 11 October 1994
Accepted 10 February 1995

Calibration results

☑ Show RMS, RE, K ☐ Show Exponent, Exp. const. ☐ Hide excl. standards

☑ Show D, E, F ☑ Show (0,0) lines



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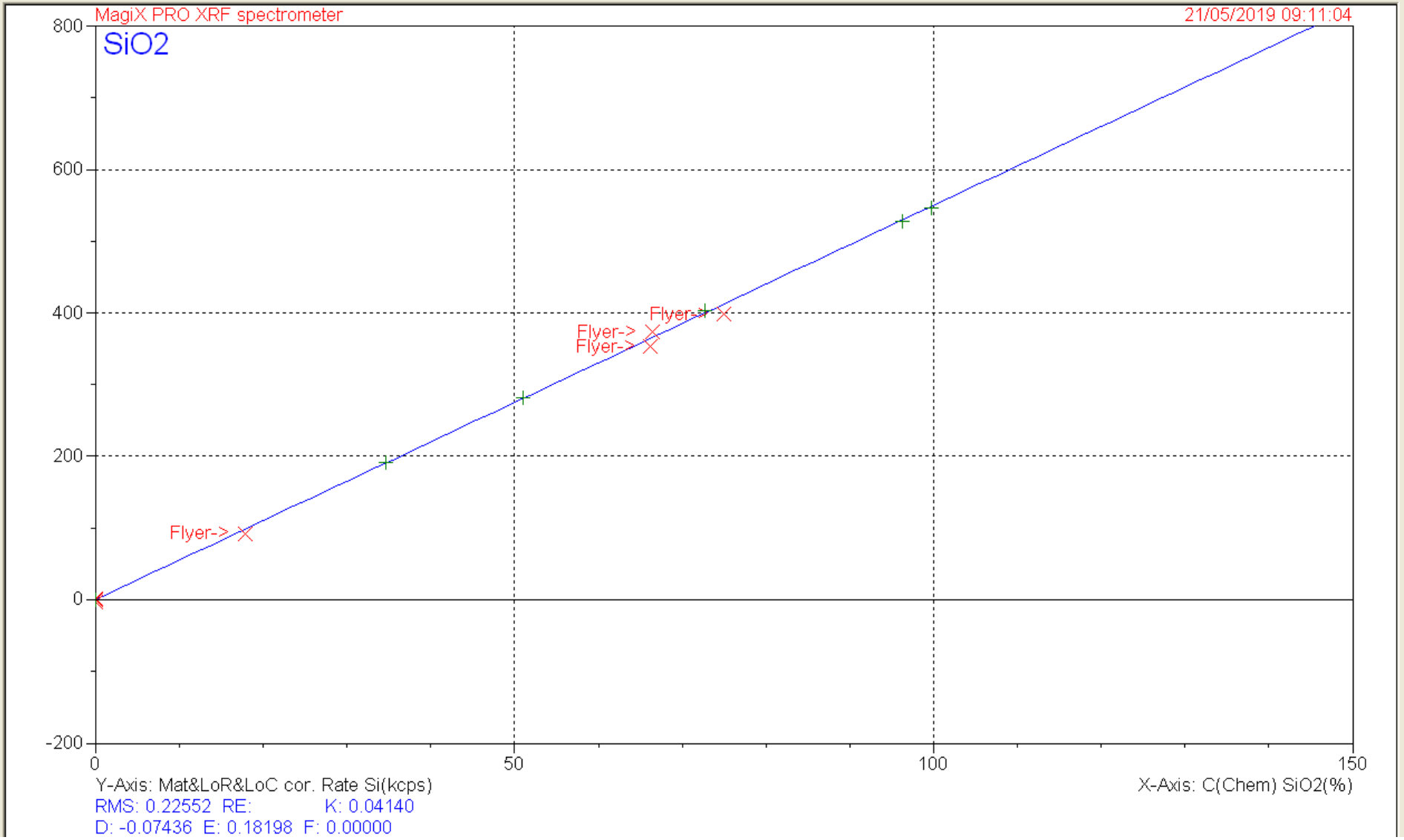

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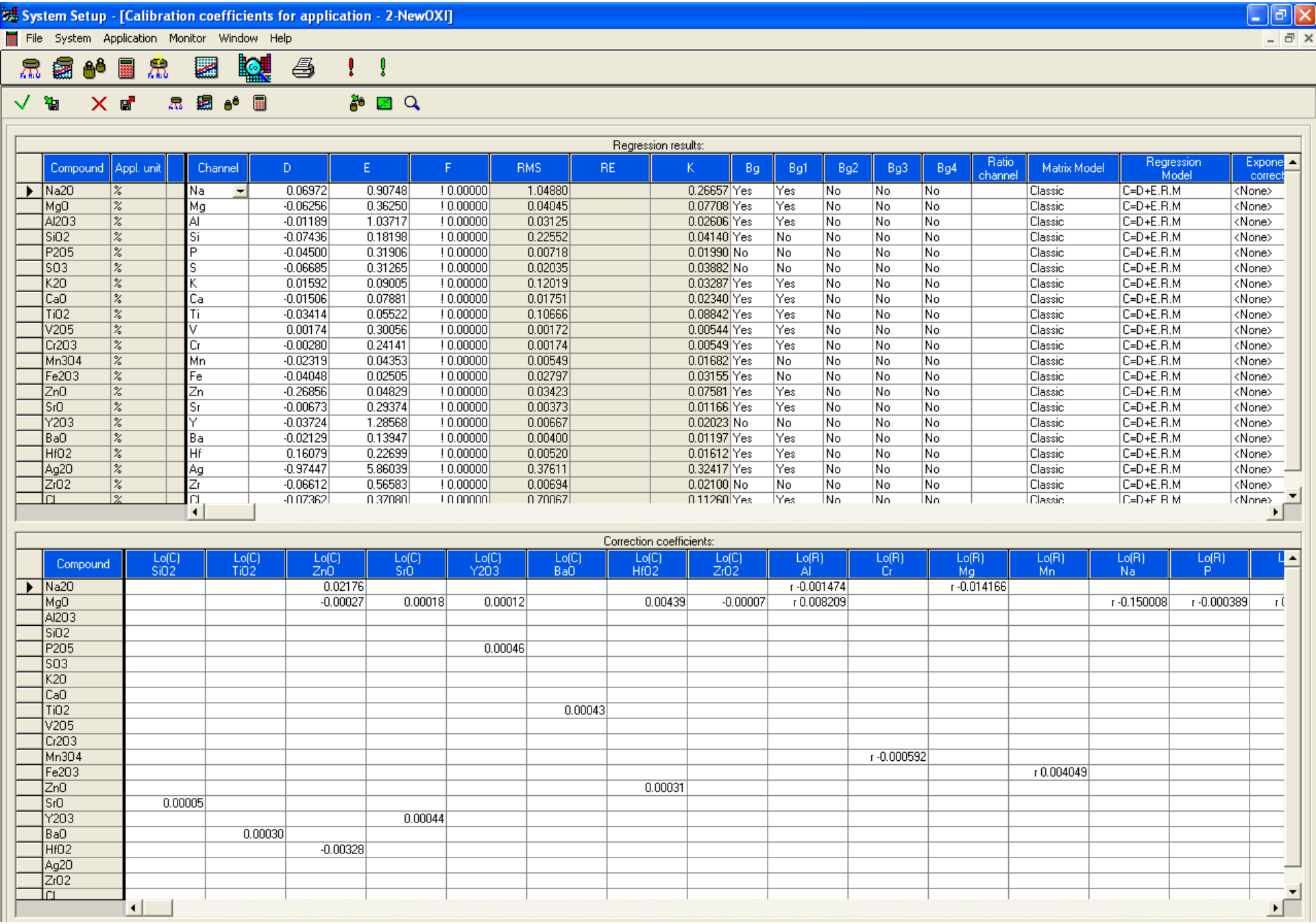

System Setup - [Calibration coefficients for application - 2-NewOXI]
File System Application Monitor Window Help
Regression results:
Compound | Appl. unit | Channel | D | E | F | RMS | RE | K | Bg | Bg1 | Bg2 | Bg3 | Bg4 | Ratio channel | Matrix Model | Regression Model | Expone correct
Na2O % Na 0.06972 0.90748 ! 0.00000 1.04880 0.26657 Yes Yes No No No Classic C=D+E.R.M <None>
MgO % Mg -0.06256 0.36250 ! 0.00000 0.04045 0.07708 Yes Yes No No No Classic C=D+E.R.M <None>
Al2O3 % Al -0.01189 1.03717 ! 0.00000 0.03125 0.02606 Yes Yes No No No Classic C=D+E.R.M <None>
SiO2 % Si -0.07436 0.18198 ! 0.00000 0.22552 0.04140 Yes No No No No Classic C=D+E.R.M <None>
P2O5 % P -0.04500 0.31906 ! 0.00000 0.00718 0.01990 No No No No No Classic C=D+E.R.M <None>
SO3 % S -0.06685 0.31265 ! 0.00000 0.02035 0.03882 No No No No No Classic C=D+E.R.M <None>
K2O % K 0.01592 0.09005 ! 0.00000 0.12019 0.03287 Yes Yes No No No Classic C=D+E.R.M <None>
CaO % Ca -0.01506 0.07881 ! 0.00000 0.01751 0.02340 Yes Yes No No No Classic C=D+E.R.M <None>
TiO2 % Ti -0.03414 0.05522 ! 0.00000 0.10666 0.08842 Yes Yes No No No Classic C=D+E.R.M <None>
V2O5 % V 0.00174 0.30056 ! 0.00000 0.00172 0.00544 Yes Yes No No No Classic C=D+E.R.M <None>
Cr2O3 % Cr -0.00280 0.24141 ! 0.00000 0.00174 0.00549 Yes Yes No No No Classic C=D+E.R.M <None>
Mn3O4 % Mn -0.02319 0.04353 ! 0.00000 0.00549 0.01682 Yes No No No No Classic C=D+E.R.M <None>
Fe2O3 % Fe -0.04048 0.02505 ! 0.00000 0.02797 0.03155 Yes No No No No Classic C=D+E.R.M <None>
ZnO % Zn -0.26856 0.04829 ! 0.00000 0.03423 0.07581 Yes Yes No No No Classic C=D+E.R.M <None>
SrO % Sr -0.00673 0.29374 ! 0.00000 0.00373 0.01166 Yes Yes No No No Classic C=D+E.R.M <None>
Y2O3 % Y -0.03724 1.28568 ! 0.00000 0.00667 0.02023 No No No No No Classic C=D+E.R.M <None>
BaO % Ba -0.02129 0.13947 ! 0.00000 0.00400 0.01197 Yes Yes No No No Classic C=D+E.R.M <None>
HfO2 % Hf 0.16079 0.22699 ! 0.00000 0.00520 0.01612 Yes Yes No No No Classic C=D+E.R.M <None>
Ag2O % Ag -0.97447 5.86039 ! 0.00000 0.37611 0.32417 Yes Yes No No No Classic C=D+E.R.M <None>
ZrO2 % Zr -0.06612 0.56583 ! 0.00000 0.00694 0.02100 No No No No No Classic C=D+E.R.M <None>
Cl % Cl -0.07362 0.37080 ! 0.00000 0.70067 0.11260 Yes Yes No No No Classic C=D+E.R.M <None>
Correction coefficients:
Compound | Lo(C) SiO2 | Lo(C) TiO2 | Lo(C) ZnO | Lo(C) SrO | Lo(C) Y2O3 | Lo(C) BaO | Lo(C) HfO2 | Lo(C) ZrO2 | Lo(R) Al | Lo(R) Cr | Lo(R) Mg | Lo(R) Mn | Lo(R) Na | Lo(R) P
Na2O 0.02176 r -0.001474 r -0.014166
MgO -0.00027 0.00018 0.00012 0.00439 -0.00007 r 0.008209 r -0.150008 r -0.000389
P2O5 0.00046
TiO2 0.00043
Mn3O4 r -0.000592
Fe2O3 r 0.004049
ZnO 0.00031
SrO 0.00005
Y2O3 0.00044
BaO 0.00030
HfO2 -0.00328

System Setup - [Application - 2-NewOXI]

File System Application Monitor Window Help

General | Identification scheme | Conditions | Sample description | Preferences | Compounds | Channels | Quantitative program | Qualitative program

☑ Normalise Normalise to (%): 100.00 ☑ Lock normalise

Compound	Formula	El.	Layer	Source	Unit	Dec.	Minimum	Maximum	Report
Na2O	Na2O	Na	1	XRF	%	3			Yes
MgO	MgO	Mg	1	XRF	%	3			Yes
Al2O3	Al2O3	Al	1	XRF	%	3			Yes
SiO2	SiO2	Si	1	XRF	%	3			Yes
P2O5	P2O5	P	1	XRF	%	3			Yes
SO3	SO3	S	1	XRF	%	3			Yes
K2O	K2O	K	1	XRF	%	3			Yes
CaO	CaO	Ca	1	XRF	%	3			Yes
TiO2	TiO2	Ti	1	XRF	%	3			Yes
V2O5	V2O5	V	1	XRF	%	3			Yes
Cr2O3	Cr2O3	Cr	1	XRF	%	3			Yes
Mn3O4	Mn3O4	Mn	1	XRF	%	3			Yes
Fe2O3	Fe2O3	Fe	1	XRF	%	3			Yes
ZnO	ZnO	Zn	1	XRF	%	3			Yes
SrO	SrO	Sr	1	XRF	%	3			Yes
Y2O3	Y2O3	Y	1	XRF	%	3			Yes
BaO	BaO	Ba	1	XRF	%	3			Yes
HfO2	HfO2	Hf	1	XRF	%	3			Yes
Ag2O	Ag2O	Ag	1	XRF	%	3			Yes
ZrO2	ZrO2	Zr	1	XRF	%	3			Yes
Cl	Cl	Cl	1	XRF	%	3			Yes

Add Compound... | Add Compound from Periodic... | Remove Compound | Edit Compound...

System Setup - [Application - 2-NewOXI]

File System Application Monitor Window Help

Open instrument monitor

General | Identification scheme | Conditions | Sample description | Preferences | Compounds | Channels | Quantitative program | Qualitative program

Minimum time (s): 464

Maximum time (s): 464

Channel	Time (s)	CSE (%)	No. Bg's	Drift corr.	Bg const (kcps)	Bg of channel
Na	60		1	Yes		
Mg	10		1	Yes		Na
Al	20		1	Yes		
Si	20		0	Yes		Al
P	16		1	Yes		
S	10		1	Yes		
K	10		1	Yes		
Ca	10		1	Yes		
Ti	6		1	Yes		
V	10		1	Yes		
Cr	10		1	Yes		
Mn	6		0	Yes		Cr
Fe	6		0	Yes		Cr
Zn	2		1	Yes		
Sr	6		1	Yes		
Y	30		1	Yes		
Zr	26		1	Yes		
Ag	10		2	Yes		
Hf	10		1	Yes		Zn
Ba	10		1	Yes		
Cl	10		1	Yes		

Background of channel: Na

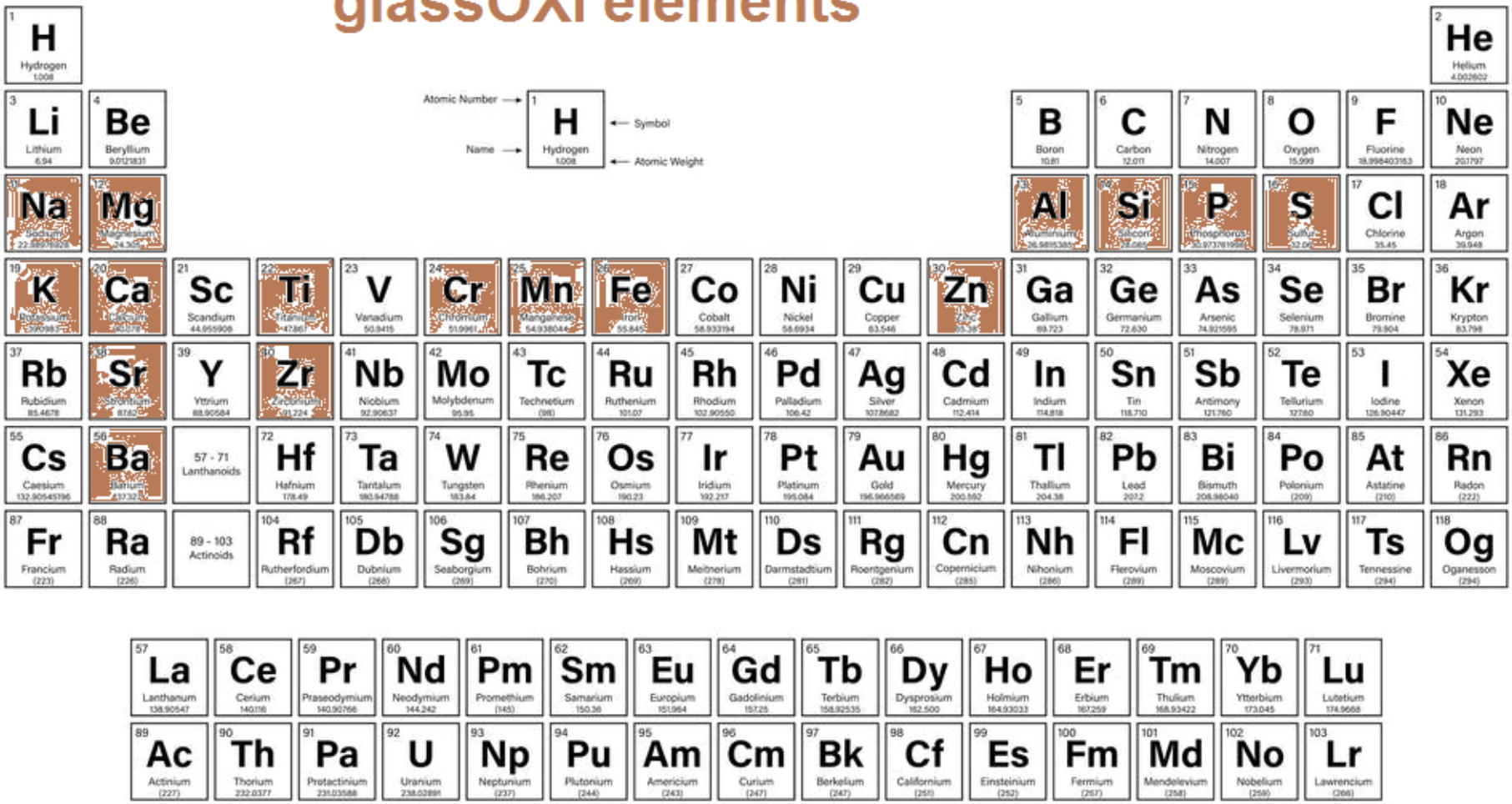
Background method: Calc. factors

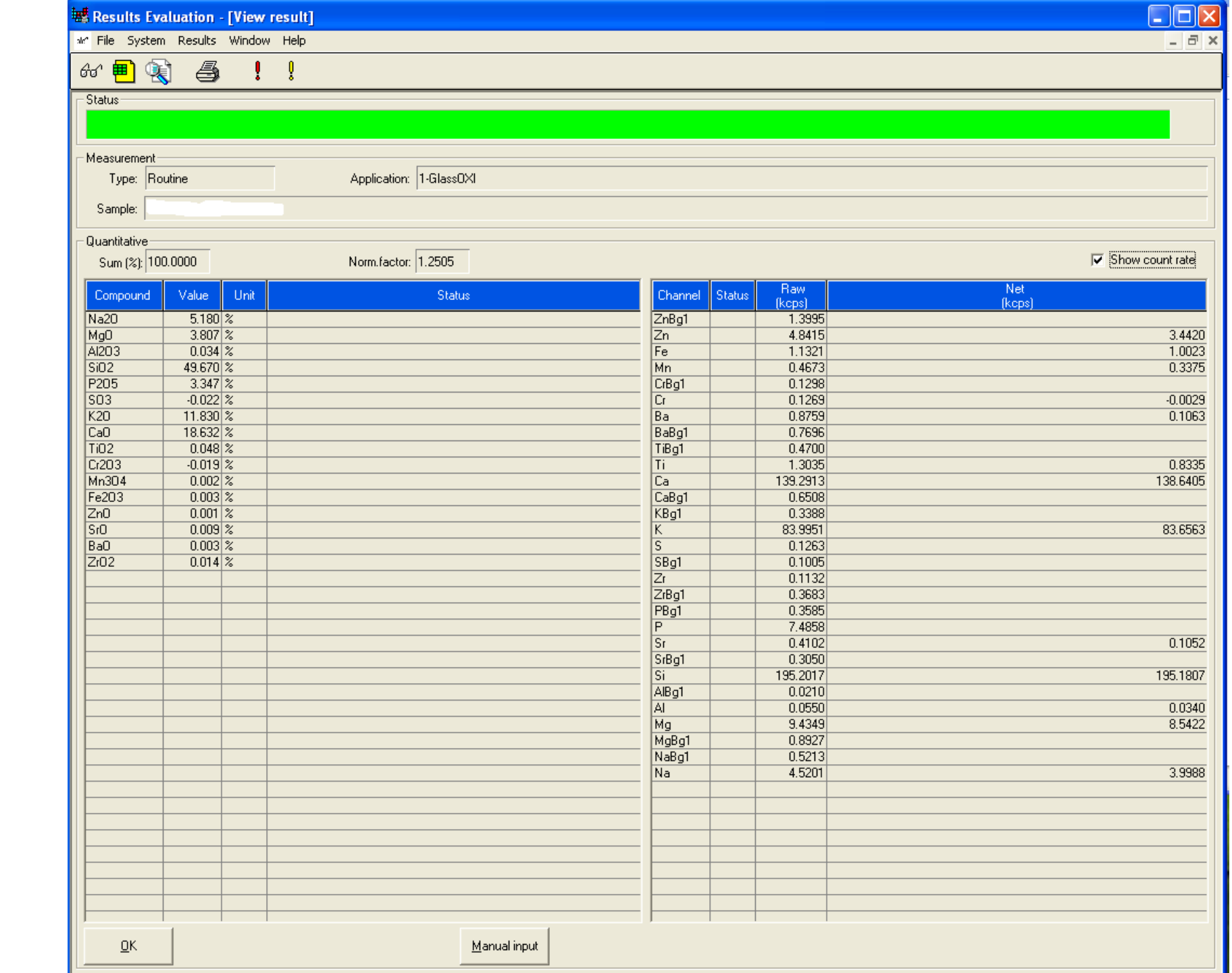
No.	Channel	Time (s)	CSE (%)	Factor
1	NaBg1	20		1.0000
2				
3				
4				

Add Channel... | New Channel... | Remove Channel | Sort High->Low | Set default Background

Periodic Table of the Elements

glassOXI elements




Results Evaluation - [View result]
File System Results Window Help
Status
Measurement
Type: Routine
Application: 1-GlassOXI
Sample:
Quantitative
Sum (%): 100.0000
Norm.factor: 1.2505
Show count rate
Compound Value Unit Status
Na2O 5.180 %
MgO 3.807 %
Al2O3 0.034 %
SiO2 49.670 %
P2O5 3.347 %
SO3 -0.022 %
K2O 11.830 %
CaO 18.632 %
TiO2 0.048 %
Cr2O3 -0.019 %
Mn3O4 0.002 %
Fe2O3 0.003 %
ZnO 0.001 %
SrO 0.009 %
BaO 0.003 %
ZrO2 0.014 %
Channel Status Raw (kcps) Net (kcps)
ZnBg1 1.3995
Zn 4.8415 3.4420
Fe 1.1321 1.0023
Mn 0.4673 0.3375
CrBg1 0.1298
Cr 0.1269 -0.0029
Ba 0.8759 0.1063
BaBg1 0.7696
TiBg1 0.4700
Ti 1.3035 0.8335
Ca 139.2913 138.6405
CaBg1 0.6508
KBg1 0.3388
K 83.9951 83.6563
S 0.1263
SBg1 0.1005
Zr 0.1132
ZrBg1 0.3683
PBg1 0.3585
P 7.4858
Sr 0.4102 0.1052
SrBg1 0.3050
Si 195.2017 195.1807
AlBg1 0.0210
Al 0.0550 0.0340
Mg 9.4349 8.5422
MgBg1 0.8927
NaBg1 0.5213
Na 4.5201 3.9988
OK
Manual input

CRM-529 anorthic feldspar

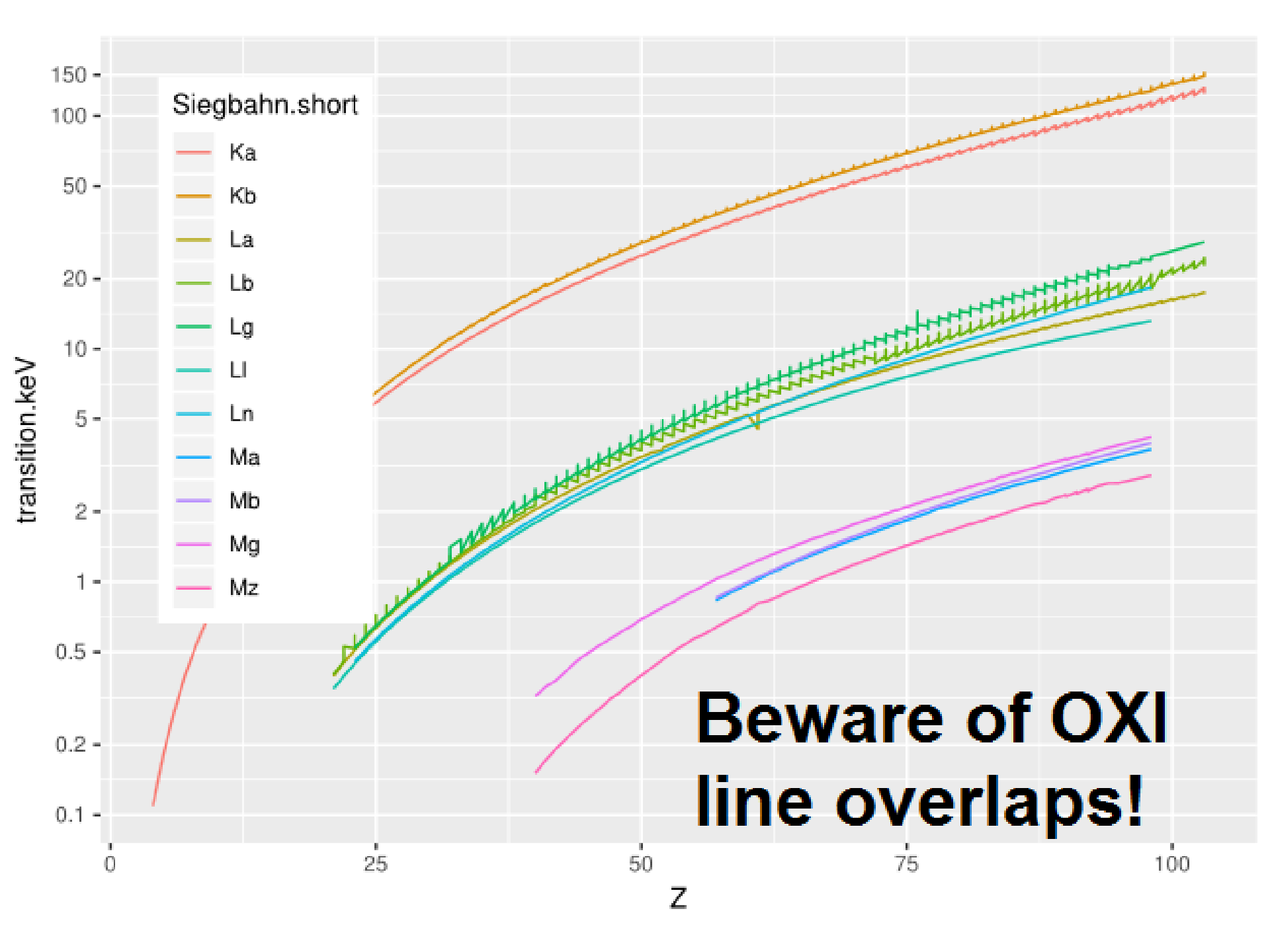
Oxide	Value (%)	BASRID (%)	diff
Na_2O	5.564	5.251	0.313
MgO	0.007	0.041	-0.034
Al_2O_3	27.111	26.977	0.134
SiO_2	56.543	57.661	-1.118
K_2O	0.459	0.371	0.088
CaO	10.000	9.370	0.630
Fe_2O_3	0.316	0.329	-0.014

CRM-532 Swedish feldspar

Oxide	Value (%)	BASRID (%)	diff
Na_2O	4.283	4.244	0.039
MgO	0.153	0.172	-0.018
Al_2O_3	13.453	13.944	-0.491
SiO_2	77.722	77.700	0.021
K_2O	3.981	3.536	0.445
CaO	0.206	0.253	-0.046
Fe_2O_3	0.201	0.152	0.050

Creating a new OXI program

- measure intensities for a particular XRF line for each element, use standard samples.
- make sure it doesn't overlap another XRF line for an element of interest.


Siegbahn.short
Ka
Kb
La
Lb
Lg
Ll
Ln
Ma
Mb
Mg
Mz
transition.keV
150
100
50
20
10
5
2
1
0.5
0.2
0.1
0
25
50
75
100
Z
Beware of OXI line overlaps!


PW2540 vrc sample changer
PHILIPS
MagiX PRO
PHILIPS
PHILIPS
MagiX PRO
died in 2021


Rigaku
ZSX PrimusIV
Primus IV
arrived 2022

Primus IV XRF spectrometer

- Wavelength dispersive spectrometer.

Primus IV XRF spectrometer

- Wavelength dispersive spectrometer.
- Primus IV **B-Cm** scans over 16 different energy ranges.

Primus IV XRF spectrometer

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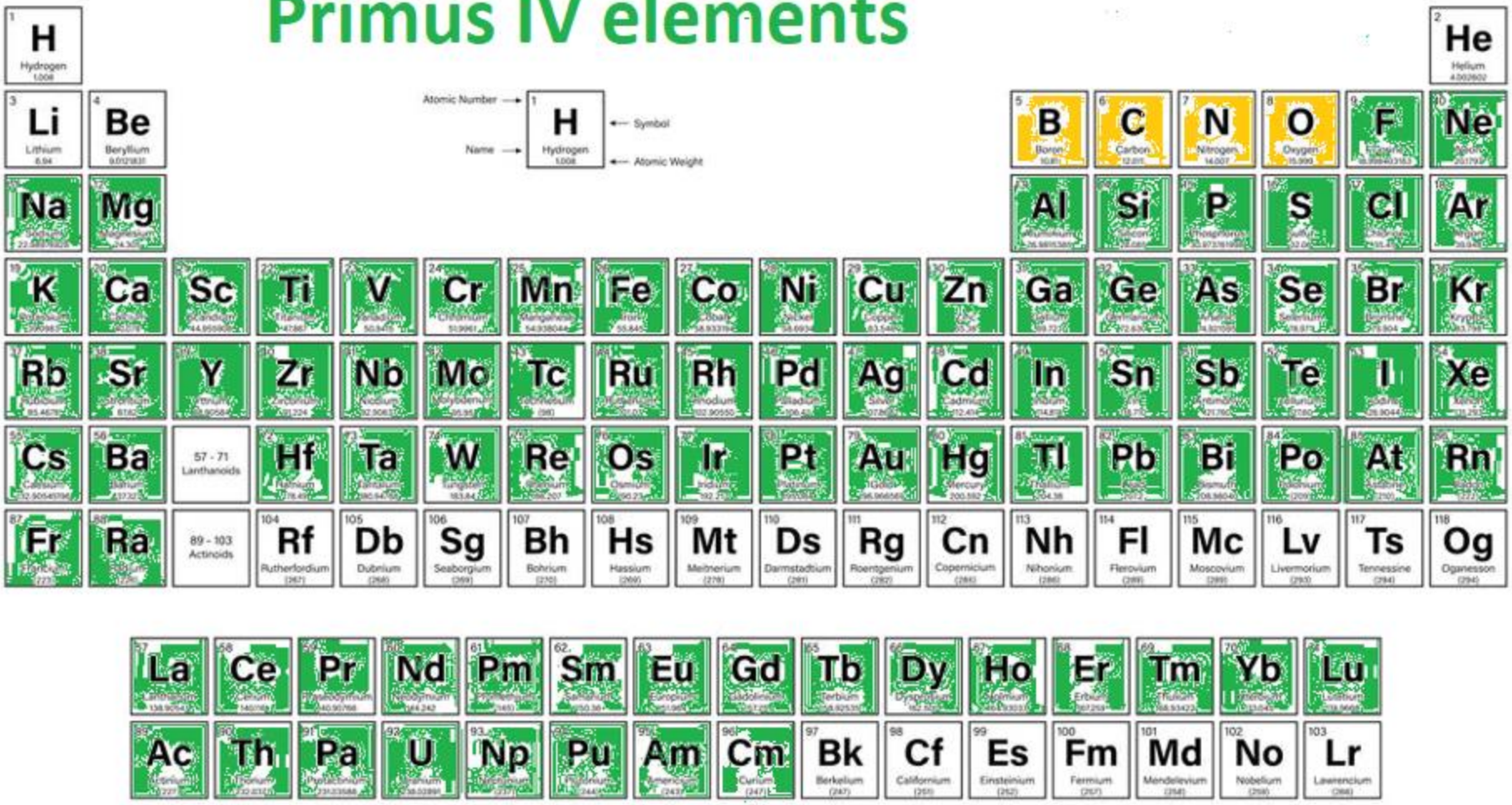
- Primus IV **F-Cm** scans over 12 different energy ranges.

Primus IV XRF spectrometer

- Wavelength dispersive spectrometer.
- Primus IV **B-Cm** scans over 16 different energy ranges.
- Primus IV **F-Cm** scans over 12 different energy ranges.
- Rh anode for X-ray tube, see Rh fluorescence lines from the tube.

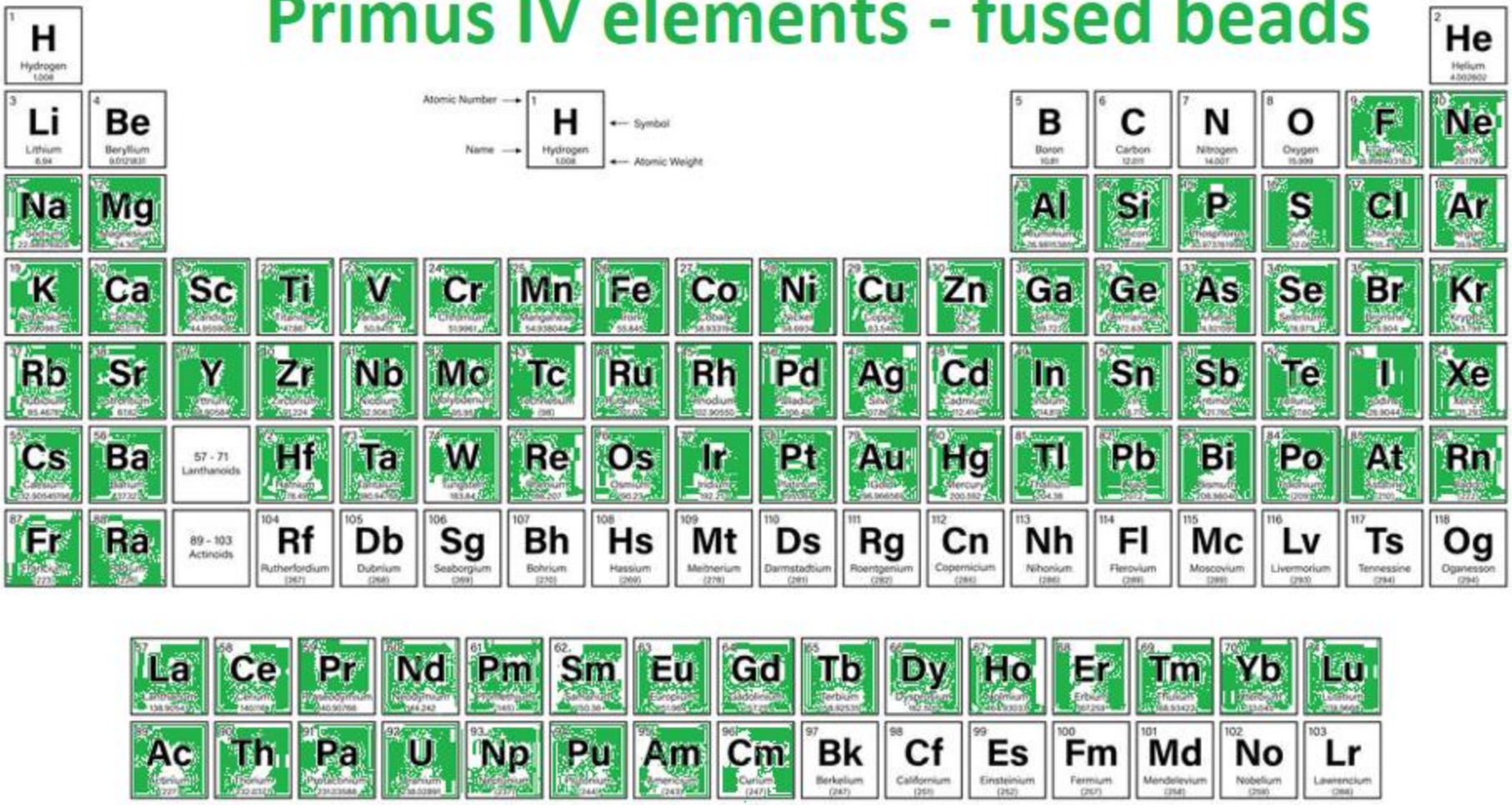
Periodic Table of the Elements

Primus IV elements



Periodic Table of the Elements

Primus IV elements - fused beads



NewOXI program for Primus IV

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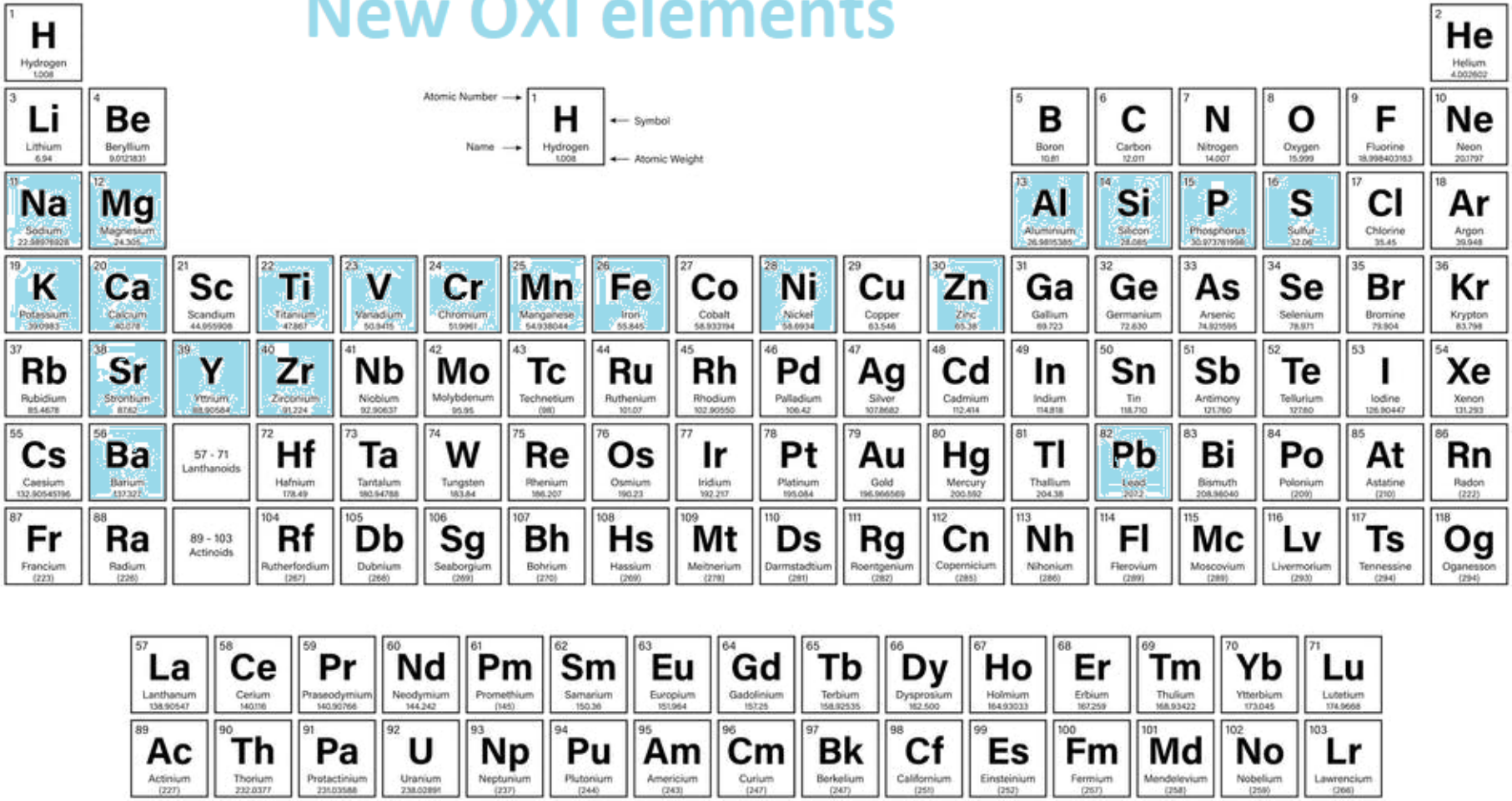
- Then as before, measure intensities for a particular XRF line for each element, use standard samples.
- **NewOXI** standard calibration program.

NewOXI standards

starting material	OXI oxide	starting material	OXI oxide
Na_2CO_3	Na_2O	Cr_2O_3	Cr_2O_3
MgO	MgO	MnO_2	Mn_3O_4
Al_2O_3	Al_2O_3	Fe_2O_3	Fe_2O_3
SiO_2	SiO_2	NiO	NiO
$NH_4H_2PO_4$	P_2O_5	ZnO	ZnO
Li_2SO_4	SO_3	Y_2O_3	Y_2O_3
K_2CO_3	K_2O	ZrO_2	ZrO_2
$CaCO_3$	CaO	$SrCO_3$	SrO
TiO_2	TiO_2	$BaCO_3$	BaO
V_2O_5	V_2O_5	PbO	PbO

Periodic Table of the Elements

New OXI elements



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- This did not always give accurate results, especially for samples containing light elements.
- The problem was particularly bad for Na_2O and MgO.

X-RAY SPECTROMETRY, VOL. 26, 97–104 (1997)

Assessment of the Accuracy of the Determination of Low Levels of Sodium in Fused Beads†

H. L. Giles[1] and P. W. Hurley[2]*
[1] Materials Research Institute, Sheffield Hallam University, Pond Street, Sheffield S1 1WB, UK
[2] Philips Analytical X-Ray, 7602 EA Almelo, The Netherlands

In an earlier study, the accuracy of the determination of Na_2O below about 0.5% (m/m) in samples prepared as fused beads was found to be poor with an RMS of 0.14 and a k factor of 0.11. Three possible sources of this inaccuracy were studied, and an improvement to an RMS of about 0.025 and a k factor of 0.025 was achieved by a combination of more careful determination of spectral overlap correction coefficients, allowance for crystal fluorescence in the setting of the pulse height selector and, most important, the preparation of new 'clean' beads. A comparison of the performance of a W–Si synthetic multilayer (PX1) and TlAP for the determination of Na_2O in fused beads has emerged from this study. © **1997 by John Wiley & Sons Ltd.**

X-Ray Spectrom. **26**, 97–104 (1997) No. of Figures: 7 No. of Tables: 3 No. of References: 5

INTRODUCTION

The assessment of test methods was proposed originally by Johnson[1] using the k factor method, and more recently by Hughes and Hurley,[2] and is substantiated in ISO 5725.[3] It has been shown that the standard deviation of a population of analytical results is related to the square root of the concentration by the following expression:

$$s = k(C + c)^{0.5}$$

where: s is the standard deviation, k is a constant, C is the concentration and c is a weighting factor, often given a value of 0.1.[1,2]

The constant k can be considered as a quality factor, which has been found to have values between 0.01 and 0.10 for round-robin studies in the steel industry using International (ISO) or British (BS) Standard methods of analysis.[2] For oxide analysis the values of k are generally between 0.02 and 0.07.[2]

In an earlier study,[4] the accuracy of the proposed method for the analysis of oxides, silicates and carbon-

(3) contaminated beads (fingerprints 'bloom' on the surface).

In order to simplify this study, a sub-set of 15 of the original 43 RMs was made (Table 1). The points marked with squares in Fig. 1 were chosen for this study. As can be seen, two groups of samples were chosen: one group around 0.15% Na_2O and the other around 0.35% Na_2O. Two feldspars, BCS 376 (2.83% Na_2O) and BCS 375 (10.40% Na_2O) and BCS 393 at 0% were also included to help to fix the least-squares fit line.

EXPERIMENTAL AND RESULTS

The original 43 RMs had been in use for 2 years or more and, although they had been stored in sealed polythene bags, many of them had become 'bloomed' on the surface. It has recently been reported[5] that this bloom consists of NaCl, kerotin and phospholipids

Table 1. Reference materials used

X-RAY SPECTROMETRY, VOL. 26, 97–104 (1997)

Assessment of the Accuracy of the Determination of Low Levels of Sodium in Fused Beads†

H. L. Giles[1] and P. W. Hurley[2]*
[1] Materials Research Institute, Sheffield Hallam University, Pond Street, Sheffield S1 1WB, UK
[2] Philips Analytical X-Ray, 7602 EA Almelo, The Netherlands

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NewOXI solution

- As the old Na_2O and MgO standards gave problems then make new standards.

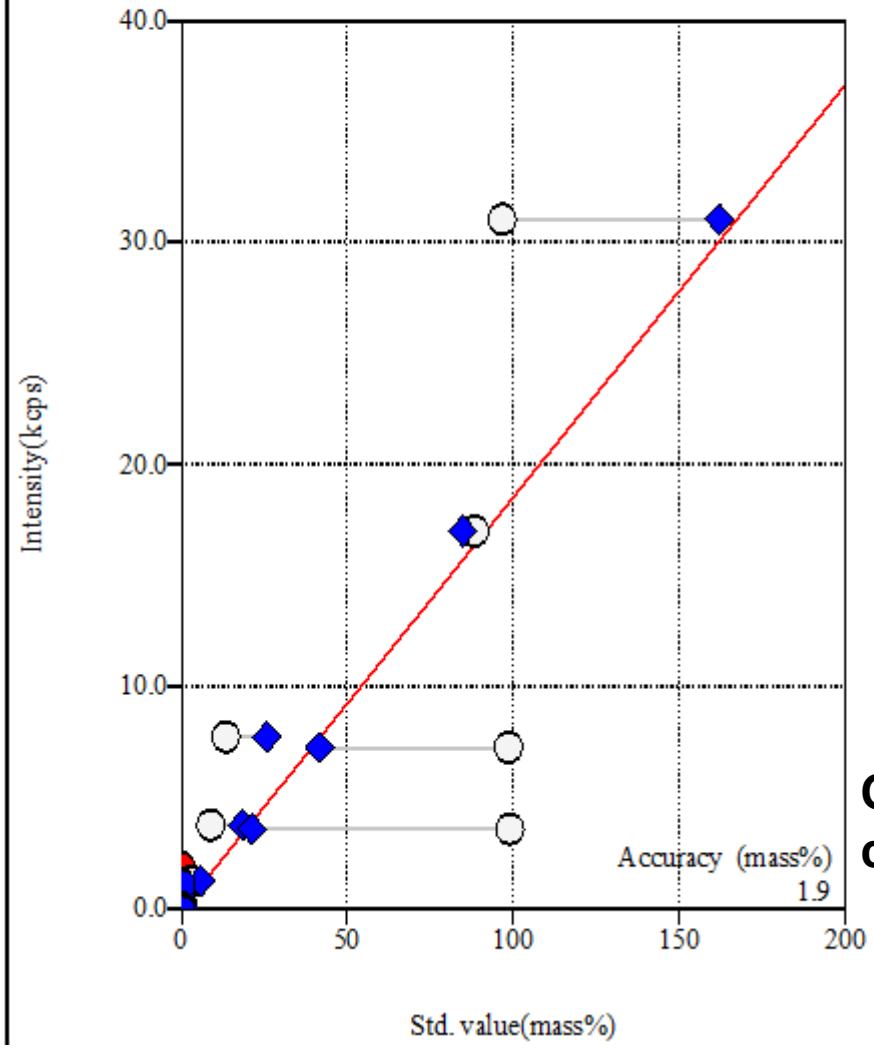
NewOXI solution

- As the old Na_2O and MgO standards gave problems then make new standards.
- Comparison of calibration curves with and without new standards shows the problems.

2024-6-13 08:13

Empirical Calibration

Application NEW OXI



Component	Na2O
Element line	Na-KA
PHA range	110 - 300

$X = AI^3 + BI^2 + CI + D$

Linear(straight)

A=	
B=	
C=	5.38448e+000
D=	1.63525e-001
Accuracy	1.90264e+000
Corr. factor	9.96528e-001
Inter. std	No
Fixed point	No
Weighting	Normal

Old Na_2O standards calibration.

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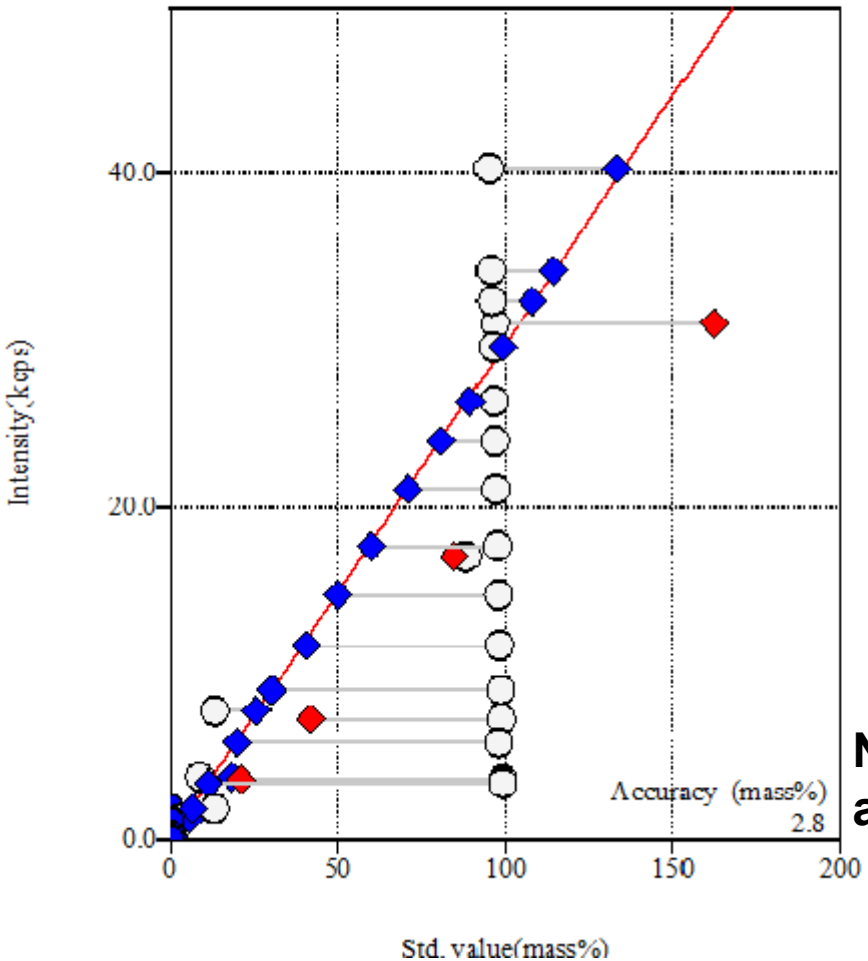
Empirical Calibration

Application NEW OXI APR 2024



Component	Na2O
Element line	Na-KA
PHA range	110 - 300

$X = AI^3 + BI^2 + CI + D$

Ratio(one point)

A=	
B=	
C=	3.35255e+000
D=	
Accuracy	2.75884e+000
Corr. factor	9.96400e-001
Inter. std	No
Fixed point	No
Weighting	Normal

New Na_2O standards added to calibration.

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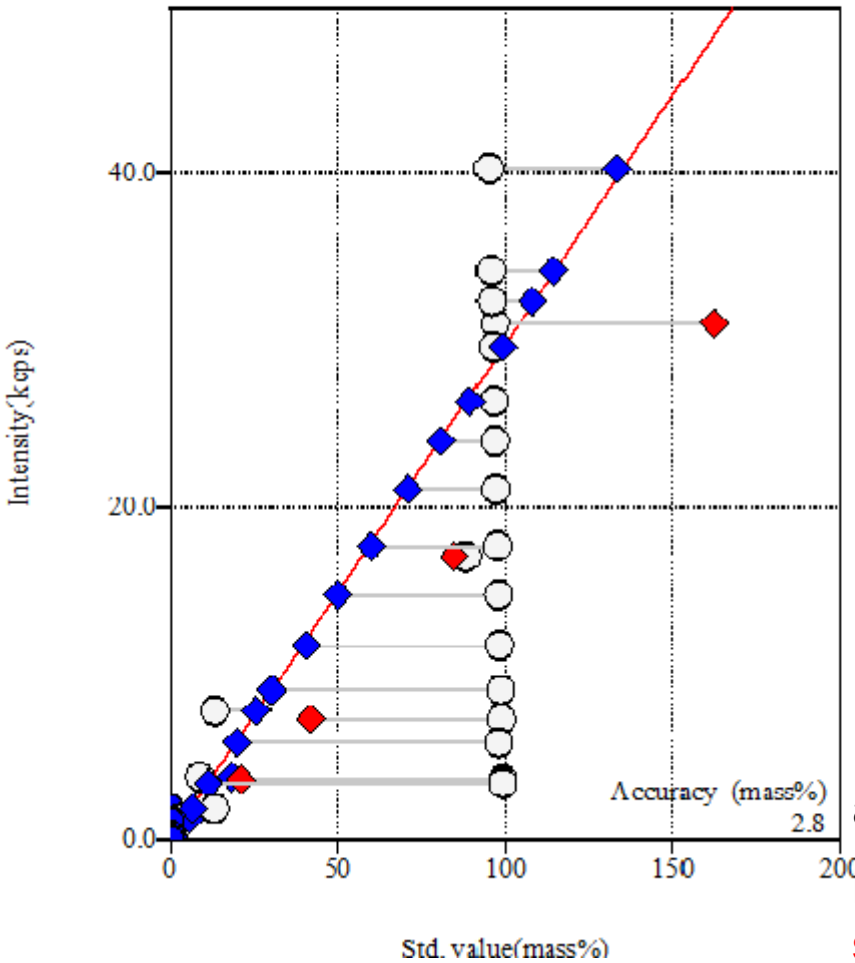
Empirical Calibration

Application NEW OXI APR 2024



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New Na_2O standards added to calibration.

Exclude old Na_2O standards.

	Sample 1		Sample 2	
	New OXI 2023	New OXI 2024	New OXI 2023	New OXI 2024
Na_2O	12.093	11.98(3)	12.220	11.814(8)
MgO	1.491	1.661(3)	1.496	1.67(1)
Al_2O_3	1.695	1.609(1)	1.661	1.596(3)
SiO_2	71.497	71.74(3)	71.530	72.14(1)
K_2O	0.651	0.964(3)	0.702	0.967(3)
CaO	10.904	11.022(8)	11.480	10.828(9)
Fe_2O_3	0.571	0.608(2)	0.558	0.560(1)

	Sample 3		Sample 4	
	New OXI 2023	New OXI 2024	New OXI 2023	New OXI 2024
Na_2O	11.995	11.84(2)	12.177	11.82(2)
MgO	1.473	1.65(2)	1.499	1.67(1)
Al_2O_3	2.221	2.076(7)	1.663	1.600(4)
SiO_2	71.183	71.53(2)	71.581	72.13(1)
K_2O	0.691	0.959(2)	0.705	0.969(3)
CaO	11.343	10.754(9)	11.453	10.816(5)
Fe_2O_3	0.651	0.648(2)	0.571	0.573(2)

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Analyzed Result (Single)

Analysis type : Quant analysis
Sample name : CRM-529
Analysis code : NEW OXI APR 2024
Meas. position : Center
Analysis date : 2024- 6-18 11:30

No.		Result	Unit	Judge
1	Na2O	4.728	mass%	
2	MgO	0.034	mass%	
3	Al2O3	23.262	mass%	
4	SiO2	49.015	mass%	
5	P2O5	0.041	mass%	
6	SO3	0.118	mass%	
7	K2O	0.507	mass%	
8	CaO	8.067	mass%	
9	TiO2	0.123	mass%	
10	V2O5	-0.006	mass%	
11	Cr2O3	0.000	mass%	
12	MnO	0.003	mass%	
13	Fe2O3	0.243	mass%	
14	NiO	0.000	mass%	
15	ZnO	-0.001	mass%	
16	Y2O3	-0.000	mass%	
17	ZrO2	-0.082	mass%	
18	SrO	0.258	mass%	
19	BaO	0.098	mass%	
20	PbO	0.006	mass%	
21	Ig	13.495	mass%	
22	Li2B4O7	9.022		
23	Sample	1.000	g	
24	Bead	10.024	g	

CRM-529 anorthic feldspar

Oxide	Value (%)	BASRID (%)	diff
Na_2O	5.471	5.251	0.220
MgO	0.039	0.041	-0.002
Al_2O_3	26.919	26.977	-0.058
SiO_2	56.721	57.661	-0.940
K_2O	0.591	0.371	0.220
CaO	9.317	9.370	-0.053
Fe_2O_3	0.282	0.329	-0.047

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Analyzed Result (Single)

Analysis type : Quant analysis
Sample name : CRM-532
Analysis code : NEW OXI APR 2024
Meas. position : Center
Analysis date : 2024- 6-18 11:43

No.		Result	Unit	Judge
1	Na2O	3.879	mass%	
2	MgO	0.169	mass%	
3	Al2O3	12.240	mass%	
4	SiO2	70.423	mass%	
5	P2O5	0.013	mass%	
6	SO3	-0.002	mass%	
7	K2O	4.899	mass%	
8	CaO	0.187	mass%	
9	TiO2	0.069	mass%	
10	V2O5	-0.008	mass%	
11	Cr2O3	0.005	mass%	
12	MnO	-0.002	mass%	
13	Fe2O3	0.174	mass%	
14	NiO	-0.000	mass%	
15	ZnO	-0.003	mass%	
16	Y2O3	0.014	mass%	
17	ZrO2	-0.001	mass%	
18	SrO	0.016	mass%	
19	BaO	0.004	mass%	
20	PbO	0.012	mass%	
21	Ig	7.897	mass%	
22	Li2B4O7	18.823		
23	Sample	0.505	g	
24	Bead	10.014	g	

CRM-532 Swedish feldspar

Oxide	Value (%)	BASRID (%)	diff
Na_2O	4.212	4.244	-0.032
MgO	0.184	0.172	0.012
Al_2O_3	13.292	13.944	-0.652
SiO_2	76.474	77.700	-1.226
K_2O	5.320	3.536	1.784
CaO	0.203	0.253	-0.050
Fe_2O_3	0.189	0.152	0.037

Conclusions

- NewOXI has been successfully transferred from the old MagiX PRO to the new Primus IV XRF spectrometer. Some of the original MagiX PRO standards were used to set up this program.

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- However, there was a problem with measurements for light elements, particularly Na_2O and MgO.
- This problem was solved by making fresh Na_2O and MgO standards. Standard samples do not last for ever!

Future work

- This program can be extended by making standards for new elements of interest, provided that a suitable XRF transition can be found that doesn’t overlap with any transitions for existing elements of interest.

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- OXI is currently set up for fused bead samples containing lithium borate glass.
- However, the Primus IV can detect boron. It could be possible to have a BoronOXI program if suitable standards could be made for borate glasses (NOT FUSED BEADS).

Thanks to.....

- **Paul Bingham – SHU**

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- Paul Bingham – SHU
- Ebele Ahizi – SHU
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- Jack Cornwall – SHU
- Casey Walsh – SHU
- Amy Young – SHU
- Erhan Kilinc – SHU
- James Eales – SHU
- Hannah Blystra – SHU
- Elliott Wakelin – SHU

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- **Steve Davies - PANalytical**
- **Andrew Scothern – PANalytical**

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- **John Austin – SciMed**


thank you for listening
Anthony.Bell@shu.ac.uk