

Practical Aspects of the X-ray Characterisation of Silicate and Alumino-silicate Industrial Minerals

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Principal Scientist

Presentation Outline

Brief Introduction to Sibelco

XRF Instruments and Sample Preparation

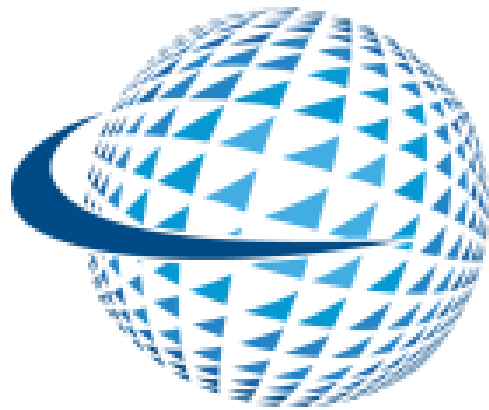
Glass Sands and Clays

Mineralogy – XRF and XRD

Quartz Standards and Crystallinity

Presentation Outline

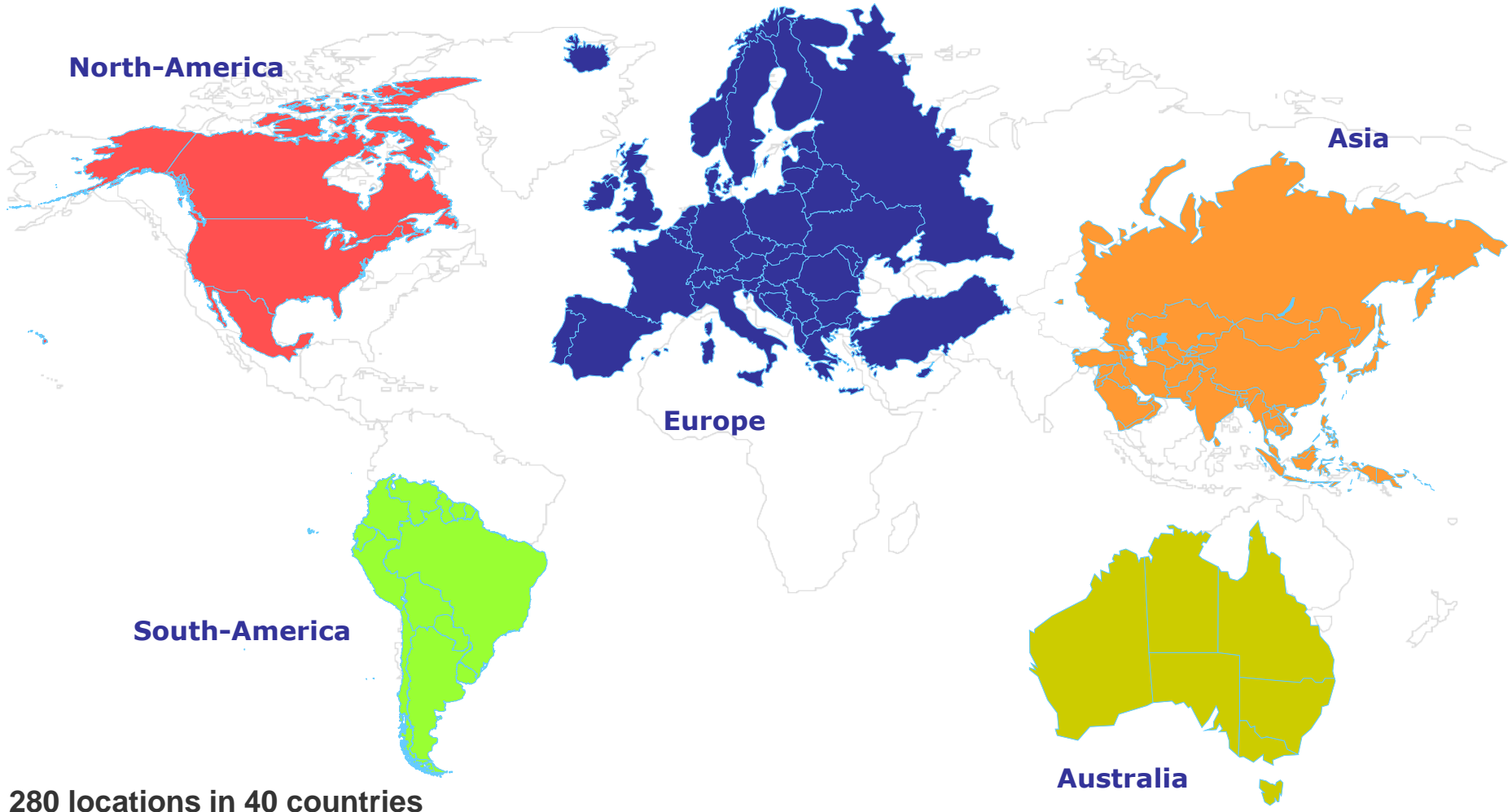
Brief Introduction to Sibelco



SIBELCO®

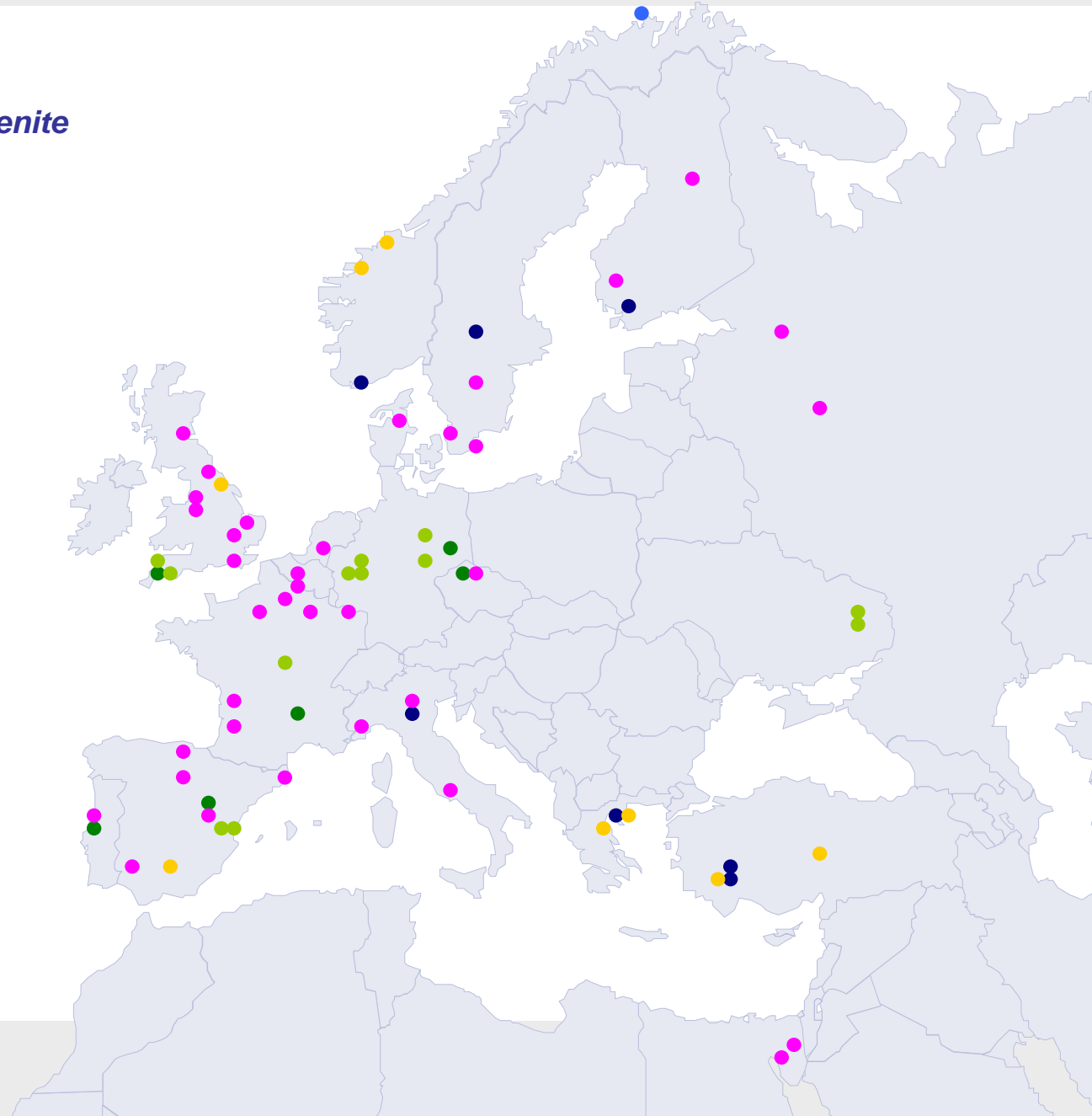
GLOBAL RESOURCES • LOCAL SOLUTIONS

Sibelco



Ceramic Related Technical Centres

- Silica Sand
- Feldspar and Nepheline Syenite
- Plastic Clay and Kaolin
- Other Minerals



Sibelco Group

Sibelco is one of the top five industrial mining groups in the world, holding leading market shares across a number of key mineral groups

Product	Estimated Worldwide Market Position
Silica Sand	1
High Purity Quartz	1
Ball Clay	1
Feldspathic Minerals	1
Olivine	1

Sibelco and XRF

- For QC:
 - Routine for dispatches of Glass Grade Minerals
 - Energy Dispersive – Fe_2O_3 and K_2O
 - Fixed Channel if Al_2O_3 as well
- For QA, exploration and calibration support:
 - High power sequential spectrometers
- Several Thousand XRFs per week
 - ~10 Sequential spectrometers in Europe
 - >50 ED or Fixed Channel Instruments
- XRD less common – support from 'central' laboratories

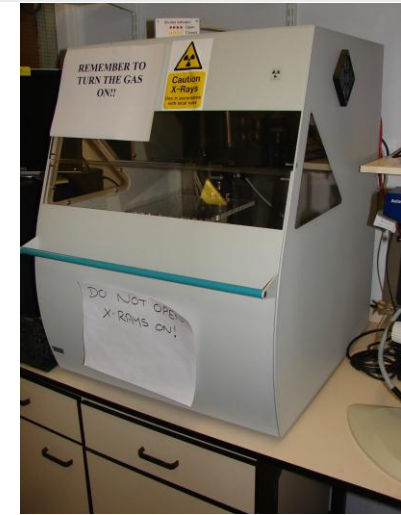
Presentation Outline

XRF Instruments and Sample Preparation

XRF Instruments



Wavelength Dispersive XRF



Energy Dispersive Scanning XRF



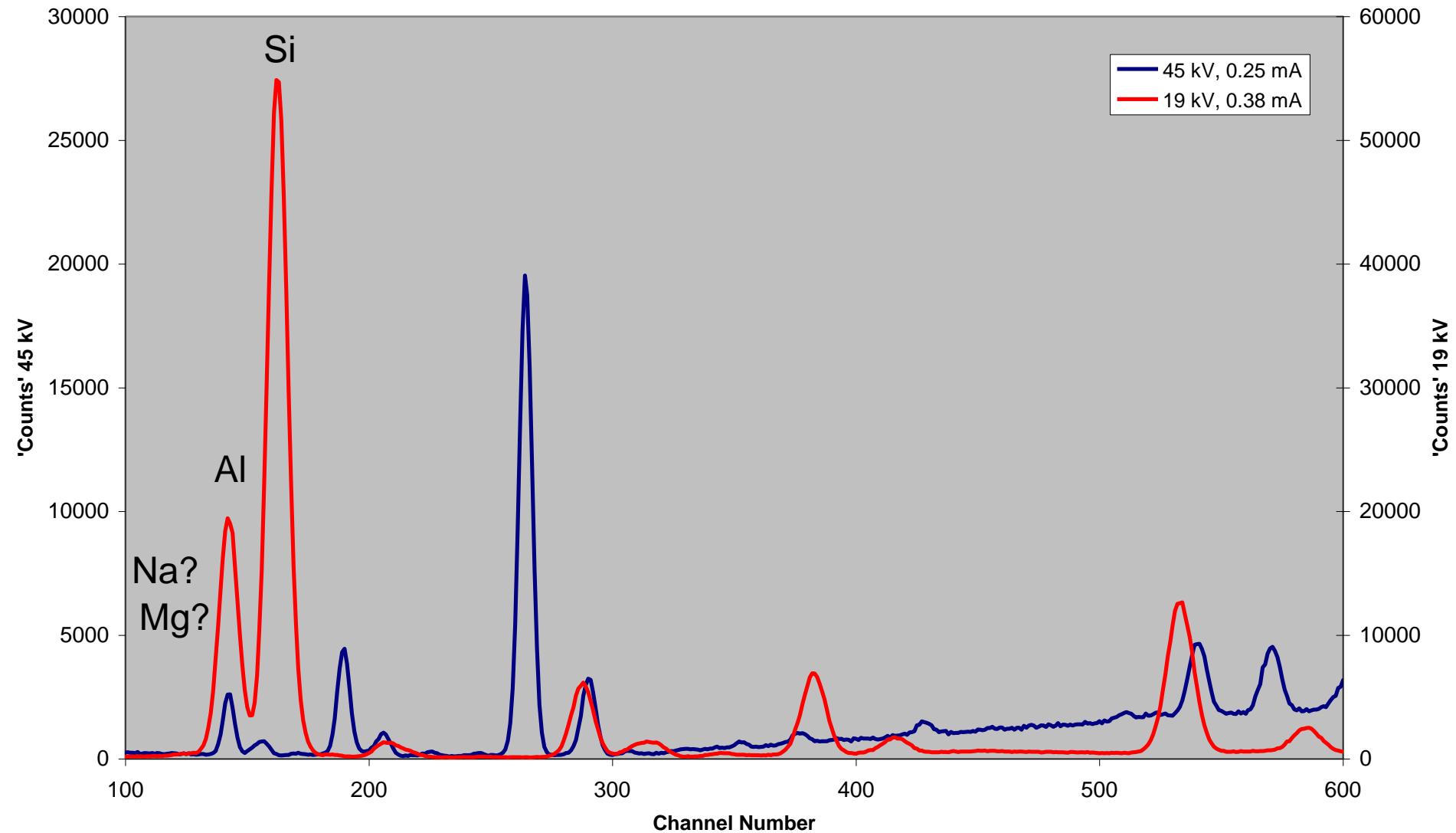
Powder XRD
- Used for routine analyses -



Powder XRD
- Used for research analyses -

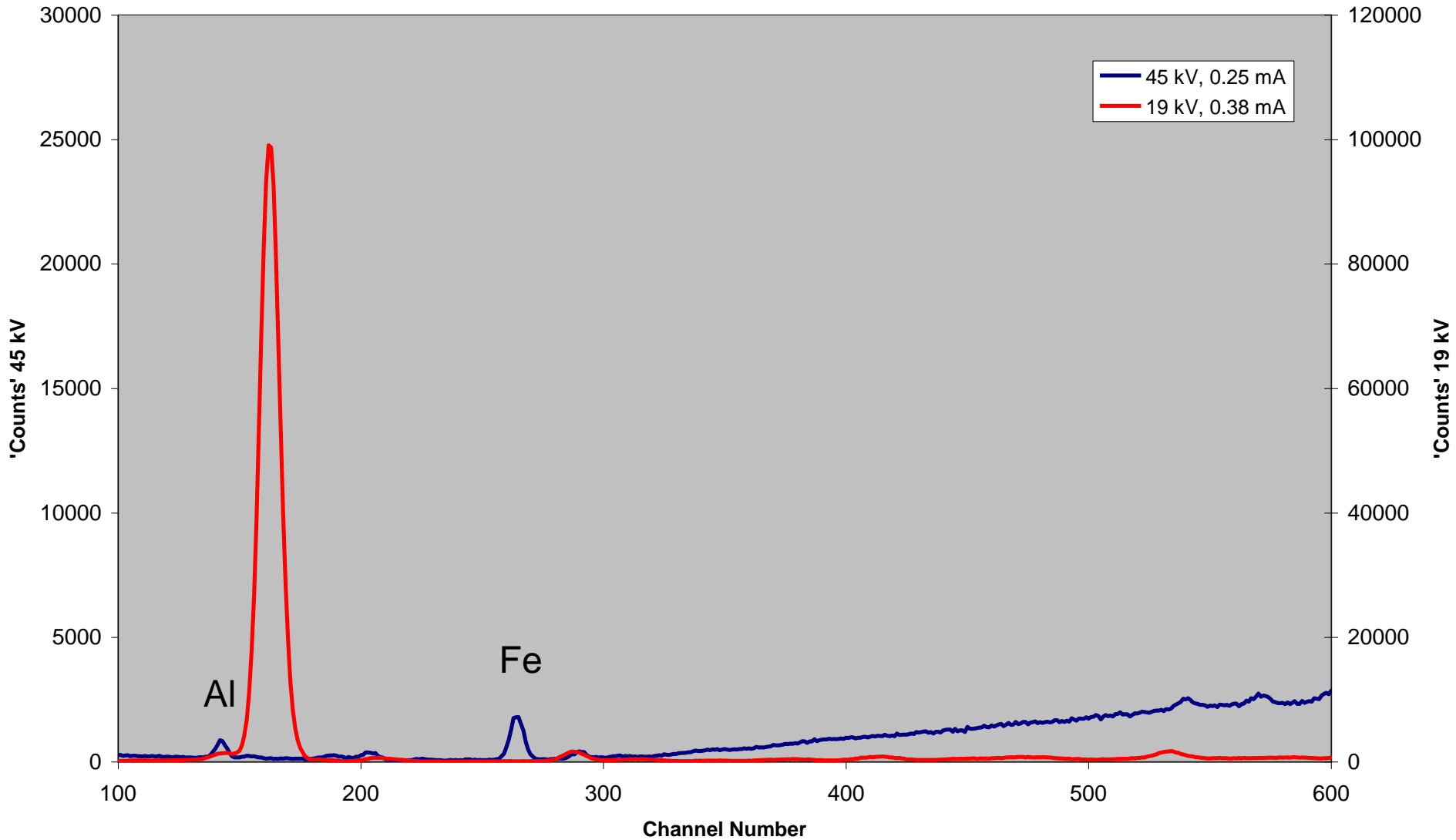
Energy Dispersive XRF

ED-XRF Ball Clay Pressed Pellet



Energy Dispersive XRF

ED-XRF Glass Sand Pressed Pellet



Wavelength Dispersive XRF

3kW Rh Tube

Crystals and Power Settings Optimised for Light Elements

Channel	Type	Line	X-tal	Collimator	Detector	Tube filter	kV	mA
Fe1	Gonio	KA	LiF 200	150 µm	Duplex	None	60	50
Ti1	Gonio	KA	LiF 200	150 µm	Flow	None	40	75
I	Gonio	LA	LiF 200	300 µm	Flow	None	40	75
Ca1	Gonio	KA	LiF 200	300 µm	Flow	None	40	75
K1	Gonio	KA	LiF 200	300 µm	Flow	None	40	75
Si1	Gonio	KA	InSb 111	700 µm	Flow	None	24	125
Al1	Gonio	KA	PE 002	700 µm	Flow	None	24	125
Mg1	Gonio	KA	PX1	700 µm	Flow	None	24	125
Na1	Gonio	KA	PX1	700 µm	Flow	None	24	125

Sample Preparation



Gas Fusion
XRF bead manufacture



Electric Fusion
Produces individual fused glass beads



Pellet Press
Non-glass XRF pellets



Kilns
Loss on Ignition

Pressed Powders or Fused Beads?

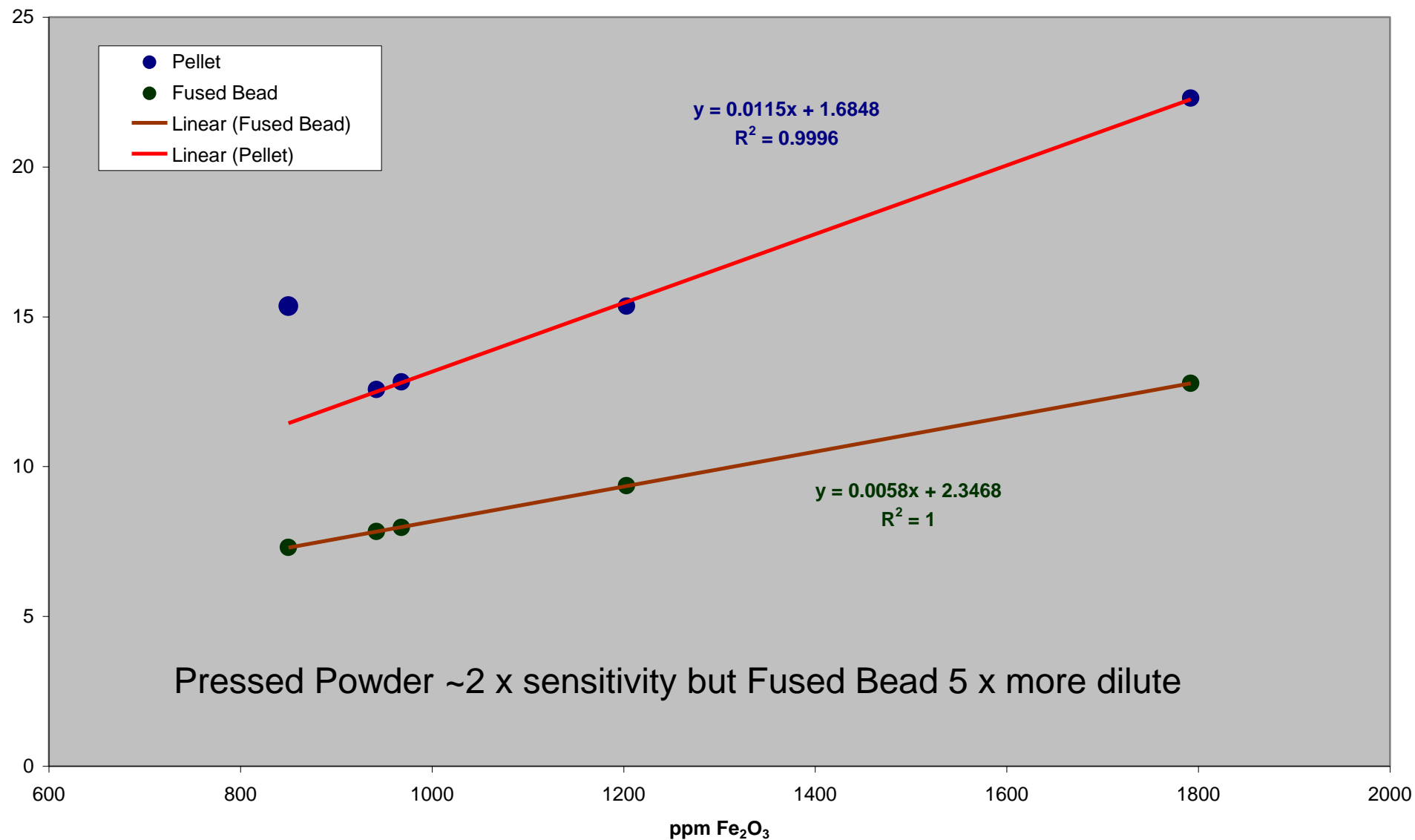
- Pressed Powders

- No Complex Equipment
- Cheap
- High Count Rates?
- Sample Matrix still intact

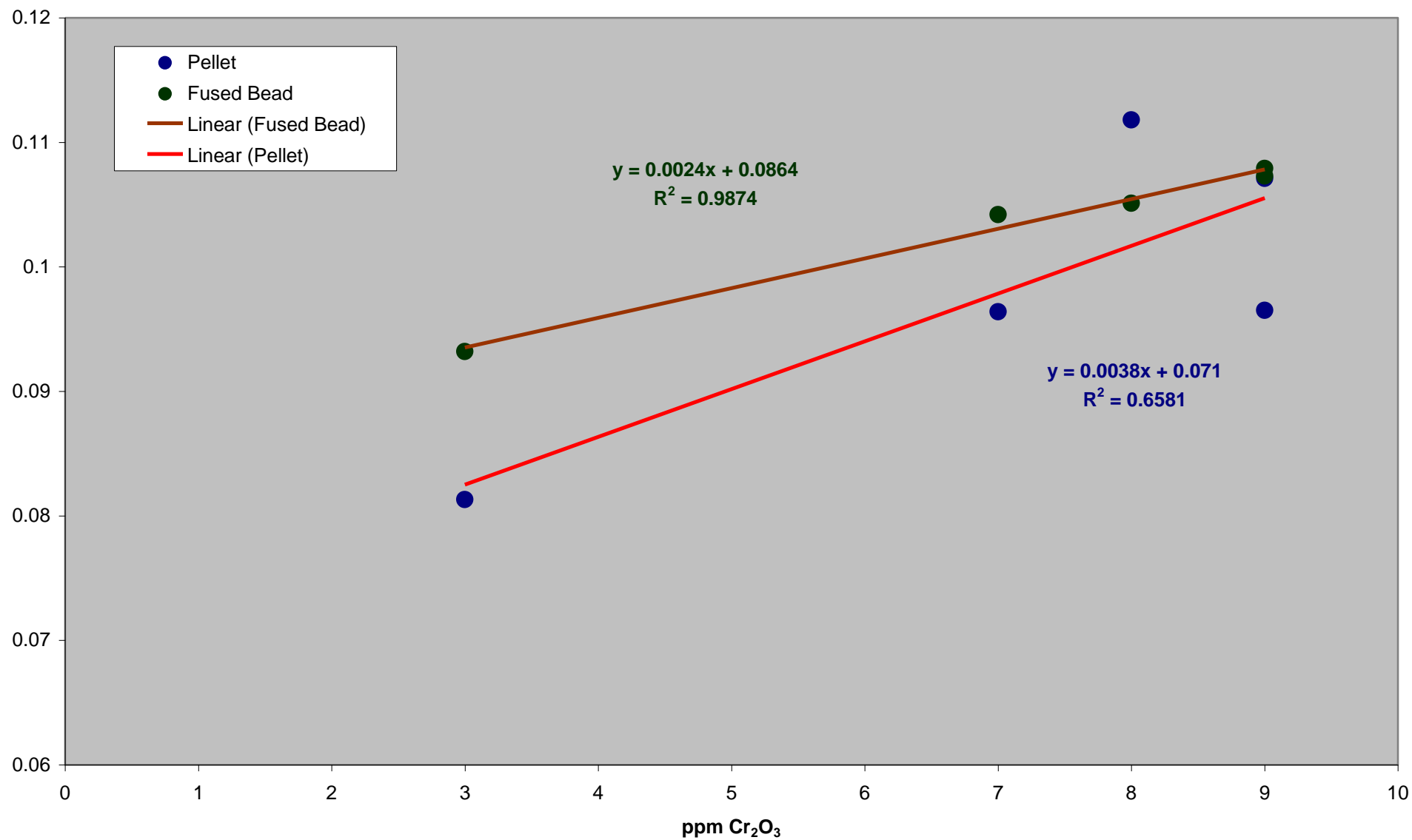
- Fused Beads

- Complicated equipment (gas/electricity supply, etc)
- Equipment and Platinum is expensive
- Complicated to set-up correctly
- Cost of flux is not insignificant
- Glass (sample matrix removed)
- Dilute: inter-element effects reduced

Pressed Pellet vs Fused Bead



Pressed Pellet vs Fused Bead



Calibration: CRMs or Primary Standards

- BCS CRM 348 – Ball Clay

ANALYSES

Mean values — mass content in % All results relate to the dried (105°C) sample

Analyst No.	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	Cr ₂ O ₃	LOI	BaO	ZrO ₂	C (Total)	S
1	50.92	31.41	1.066	1.006	0.307	0.320	0.071	11.64
2	51.09	31.69	1.090	1.020	0.170	0.305	0.362	2.255	0.072	0.020	11.64	0.05	0.04	1.63
3	51.39	31.61	1.077	1.042	0.175	0.298	0.334	2.210	0.072	0.014	11.68	0.03	0.03
4	51.03	31.57	1.065	1.038	0.165	0.310	0.358	2.195	0.086	0.015	11.82	0.05	0.03
5	51.34	31.65	1.062	1.041	0.177	0.314	0.312	2.213	0.075	0.018	11.78	0.05	0.02
6	51.00	31.51	1.076	1.042	0.188	0.280	0.340	2.234	0.058	11.82	0.04	1.65	0.1
7	51.14	31.71	1.100	1.068	0.180	0.315	0.353	2.220	0.060	0.015	11.86	0.02
8	51.35	31.37	1.093	1.027	0.172	0.308	2.264	11.95
9	50.92	31.80	1.127	1.082	0.158	0.305	0.370	2.250	11.60
M_M	51.1	31.6	1.08	1.04	0.17	0.30	0.34	2.23	0.071	0.016	11.8
S_M	0.2	0.2	0.02	0.03	0.01	0.01	0.02	0.03	0.009	0.002	0.1

M_M: Mean of the intralaboratory means. S_M: Standard deviation of the intralaboratory means.

Calibration: CRMs or Primary Standards

■ BCS CRM 348 – Ball Clay

SILICA

Analysts Nos. 1, 3, and 4 determined the bulk of the silica gravimetrically after double dehydration, and determined the residual silica photometrically as molybdenum blue. The remaining analysts determined silica by XRF, using a fused bead technique and synthetic calibration with pure materials.

ALUMINA

Analysts Nos. 1, 3, 4 and 9 separated iron and titanium by solvent extraction with cupferron and chloroform. No. 1 determined alumina gravimetrically as the oxinate. Nos. 3, 4 and 9 determined alumina titrimetrically. Nos. 3 and 9 added an excess of EDTA, and back titrated with standard zinc solution. No. 4 used an excess of DCTA. The remaining analysts used XRF.

Analyst No. 9 also determined alumina by XRF and obtained a mean value of 31.92%.

TITANIA

Analysts Nos. 1, 3, 4 and 9 determined titania photometrically, No. 1 with tiron, No. 3 with diantipyrylmethane and Nos. 4 and 9 with hydrogen peroxide. The remaining analysts used XRF.

Analyst No. 9 also determined titania by XRF and obtained a mean value of 1.16%.

FERRIC OXIDE

Analysts Nos. 1 and 3 determined iron photometrically with 1,10-phenanthroline. No. 4 determined iron titrimetrically with titanous chloride solution. The remaining analysts used XRF.

Calibration: CRMs or Primary Standards

- Primary Standards

Element	Report Cpd	Calib Cpd	Drying / C	min Mass / g	Factor
Si	SiO ₂		1200	236.1600	1
Al	Al ₂ O ₃		1200	23.1250	1
Fe	Fe ₂ O ₃		700	1.5075	1
K	K ₂ O	K ₂ CO ₃	220	2.5929	1.4672
Ti	TiO ₂		1000	1.2825	1
Zr	ZrO ₂		1000	1.0800	1
Ba	BaO	BaCO ₃	220	1.3900	1.2870
Ca	CaO	CaCO ₃	220	2.1713	1.7848
Mn	Mn ₃ O ₄	MnO ₂	1000	1.2310	1.1398
Cr	Cr ₂ O ₃		1000	1.0800	1
Na	Na ₂ O	Na ₂ CO ₃	220	2.9844	1.7101
S	S	Li ₂ SO ₄	220	3.7030	3.4287
S		Flux Correction factor			0.2718
Mg	MgO		1200	1.2825	1
W	WO ₃		110	0.9375	1

Calibration: CRMs or Primary Standards

Silica Calibration from Primary Oxides - Jan 2003

Flux 7.5000 g					to 4 Sig. Figs					Dried Sample 1.5000 g																																																	
%	mass / g	No.	mass / g	%	%	mass / g	No.	mass / g	%	%	mass / g	No.	mass / g	%																																													
SiO₂ :					Al₂O₃					SiO₂ :					Na₂O																																												
0	0.0000	1	1.5000	100	99.67	1.4951	49	0.0085	0.33	99.33	1.4900	50	0.0172	0.67	99.00	1.4850	51	0.0257	1.00	96.50	1.4475	52	0.0898	3.50	95.00	1.4250	53	0.1283	5.00	90.00	1.3500	54	0.2565	10.00	85.00	1.2750	55	0.3848	15.00	85.00	1.2750	56	0.3848	15.00															
0	0.0000	2	1.5000	100	SiO₂ :					BaO					SiO₂ :					Fe₂O₃																																							
5	0.0750	3	1.4250	95	99.67	1.4951	57	0.0064	0.33	99.33	1.4900	58	0.0129	0.67	99.00	1.4850	59	0.0193	1.00	99.75	1.4963	62	0.0038	0.25	99.50	1.4925	63	0.0075	0.50	99.25	1.4888	64	0.0113	0.75	99.00	1.4850	65	0.0150	1.00	97.00	1.4550	66	0.0450	3.00	95.00	1.4250	67	0.0750	5.00	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00
10	0.1500	4	1.3500	90	95.00	1.4250	60	0.0965	5.00	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																														
20	0.3000	5	1.2000	80	95.00	1.4250	61	0.0965	5.00	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
30	0.4500	6	1.0500	70	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
40	0.6000	7	0.9000	60	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
50	0.7500	8	0.7500	50	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
50	0.7500	9	0.7500	50	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
60	0.9000	10	0.6000	40	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
70	1.0500	11	0.4500	30	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
80	1.2000	12	0.3000	20	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
90	1.3500	13	0.1500	10	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
92	1.3800	14	0.1200	8	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
94	1.4100	15	0.0900	6	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
96	1.4400	16	0.0600	4	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
98	1.4700	17	0.0300	2	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
100	1.5000	18	0.0000	0	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
100	1.5000	19	0.0000	0	90.00	1.3500	68	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00	90.00	1.3500	69	0.1500	10.00																																			
SiO₂ :					CaO					SiO₂ :					Fe₂O₃																																												
99.67	1.4951	20	0.0088	0.33	99.67	1.4951	20	0.0088	0.33	99.67	1.4951	20	0.0088	0.33	99.67	1.4951	20	0.0088	0.33	99.67	1.4951	20	0.0088	0.33	99.67	1.4951	20	0.0088	0.33	99.67	1.4951	20	0.0088	0.33																									
99.33	1.4900	21	0.0179	0.67	99.33	1.4900	21	0.0179	0.67	99.33	1.4900	21	0.0179	0.67	99.33	1.4900	21	0.0179	0.67	99.33	1.4900	21	0.0179	0.67	99.33	1.4900	21	0.0179	0.67	99.33	1.4900	21	0.0179	0.67																									
99.00	1.4850	22	0.0268	1.00	99.00	1.4850	22	0.0268	1.00	99.00	1.4850	22	0.0268	1.00	99.00	1.4850	22	0.0268	1.00	99.00	1.4850	22	0.0268	1.00	99.00	1.4850	22	0.0268	1.00	99.00	1.4850	22	0.0268	1.00																									

Calibration: CRMs or Primary Standards

96.50	1.4475	23	0.0937	3.50
95.00	1.4250	24	0.1339	5.00
95.00	1.4250	25	0.1339	5.00
SiO ₂		:	TiO ₂	
99.67	1.4951	26	0.0050	0.33
99.33	1.4900	27	0.0101	0.67
99.00	1.4850	28	0.0150	1.00
96.50	1.4475	29	0.0525	3.50
95.00	1.4250	30	0.0750	5.00
95.00	1.4250	31	0.0750	5.00
SiO ₂		:	K ₂ O	
99.67	1.4951	32	0.0073	0.33
99.33	1.4900	33	0.0147	0.67
99.00	1.4850	34	0.0220	1.00
98.50	1.4775	35	0.0330	1.50
97.50	1.4625	36	0.0550	2.50
95.00	1.4250	37	0.1100	5.00
90.00	1.3500	38	0.2201	10.00
85.00	1.2750	39	0.3301	15.00
85.00	1.2750	40	0.3301	15.00
SiO ₂		:	ZrO ₂	
99.67	1.4951	41	0.0050	0.33
99.33	1.4900	42	0.0101	0.67
99.00	1.4850	43	0.0150	1.00
95.00	1.4250	44	0.0750	5.00
95.00	1.4250	45	0.0750	5.00
SiO ₂		:	WO ₃	
99.50	1.4925	46	0.0075	0.50
99.00	1.4850	47	0.0150	1.00
99.00	1.4850	48	0.0150	1.00

SiO ₂		:	MgO	
99.67	1.4951	70	0.0050	0.33
99.33	1.4900	71	0.0101	0.67
99.00	1.4850	72	0.0150	1.00
96.50	1.4475	73	0.0525	3.50
95.00	1.4250	74	0.0750	5.00
95.00	1.4250	75	0.0750	5.00
SiO ₂		:	Cr ₂ O ₃	
99.67	1.4951	76	0.0050	0.33
99.33	1.4900	77	0.0101	0.67
99.00	1.4850	78	0.0150	1.00
95.00	1.4250	79	0.0750	5.00
95.00	1.4250	80	0.0750	5.00
SiO ₂		:	Mn ₃ O ₄	
99.67	1.4951	81	0.0056	0.33
99.33	1.4900	82	0.0115	0.67
99.00	1.4850	83	0.0171	1.00
95.00	1.4250	84	0.0855	5.00
95.00	1.4250	85	0.0855	5.00
SiO ₂		:	S	
99.67	1.4951	86	0.0170	0.33
			7.4954	Flux
99.33	1.4900	87	0.0345	0.67
			7.4906	Flux
99.00	1.4850	88	0.0514	1.00
			7.4860	Flux
95.00	1.4250	89	0.2572	5.00
			7.4301	Flux
95.00	1.4250	90	0.2572	5.00
			7.4301	Flux

Calibration: CRMs or Primary Standards

α – Correction Beads

Alumina Beads

% Oxide 5.00 Mass Bead / g **1.5000** [5 % by Mass of Oxide + 95 % Al₂O₃]

Al ₂ O ₃	1.4250	91	0.0750	Fe ₂ O ₃	
Al ₂ O ₃	1.4250	92	0.0750	Fe ₂ O ₃	
Al ₂ O ₃	1.4250	93	0.1100	K ₂ O	
Al ₂ O ₃	1.4250	94	0.1100	K ₂ O	
Al ₂ O ₃	1.4250	95	0.0750	TiO ₂	
Al ₂ O ₃	1.4250	96	0.0750	TiO ₂	
Al ₂ O ₃	1.4250	97	0.0750	MgO	
Al ₂ O ₃	1.4250	98	0.0750	MgO	
Al ₂ O ₃	1.3500	99	0.2565	Na ₂ O	10 % Na ₂ O, therefore 90 % alumina
Al ₂ O ₃	1.3500	100	0.2565	Na ₂ O	10 % Na ₂ O, therefore 90 % alumina
Al ₂ O ₃	1.4250	101	0.1339	CaO	
Al ₂ O ₃	1.4250	102	0.1339	CaO	

Silica Beads

% Oxide 5.00 Mass Silica / g **1.3500** [5 % by Mass of each Oxide + 90 % SiO₂]

Fe ₂ O ₃	0.0750	103	0.1100	K ₂ O	
Fe ₂ O ₃	0.0750	104	0.1100	K ₂ O	
Fe ₂ O ₃	0.0750	105	0.0750	TiO ₂	
Fe ₂ O ₃	0.0750	106	0.0750	TiO ₂	
Fe ₂ O ₃	0.0750	107	0.0750	MgO	
Fe ₂ O ₃	0.0750	108	0.0750	MgO	
Fe ₂ O ₃	0.0750	109	0.2565	Na ₂ O	Silica 1.275 g 10 % Na ₂ O, therefore 85 % silica
Fe ₂ O ₃	0.0750	110	0.2565	Na ₂ O	Silica 1.275 g 10 % Na ₂ O, therefore 85 % silica
Fe ₂ O ₃	0.0750	111	0.1339	CaO	
Fe ₂ O ₃	0.0750	112	0.1339	CaO	

Calibration: CRMs or Primary Standards

- CRMS
 - Limited range of elements covered
 - Vital Calibration Check Materials
- Primary Oxides
 - ~ 200 Combinations for Main Calibrations:
 - Quartz Glass Sands
 - Quartz Sand Exploration and Mineral Processing
 - Clays – Kaolins and Ball Clays
 - Feldspars – Alkali and plagioclase
- Beads at least in duplicate!!!
- Used to Analyse Appropriate Local Minerals
 - In-house Secondary Standards

Glass Sands and Clays

Challenges – Glass Sands

Browse SAMPLEPARAM rows related to sample(s)

File Table

SAMPLE_ID	ME_NAME	DOC PA	PA_NAME	SRESULT	ORESULT	TRESULT	STATUS	PARAM_UI	LIMIT1LO	LIMIT1HI	LDL	UDL	TA
100002725	LOI MDC		Wgt Boat	28.6034	28.6034		ev	g					
100002725	LOI MDC		Wgt Sample	3.9070	3.9070		ev	g					
100002725	LOI MDC		Wgt Boat & Sample	32.5104	32.510400		ev	g					
100002725	LOI MDC		Wgt After Ignition	32.5022	32.5022		mv	g					
100002725	LOI MDC		LOI	0.21	.209880		mv	%					
100002725	XRF SILICA MDC		Fe2O3	0.032	0.0316		tv	%			0.002		
100002725	XRF SILICA MDC		Al2O3	0.73	0.731		tv	%			0.01		
100002725	XRF SILICA MDC		Cr2O3	0.0007	0.0007		tv	%			0.0002		
100002725	XRF SILICA MDC		CaO	0.01	0.010		tv	%			0.01		
100002725	XRF SILICA MDC		TiO2	0.083	0.083		tv	%			0.002		
100002725	XRF SILICA MDC		K2O	0.35	0.345		tv	%			0.01		
100002725	XRF SILICA MDC		S=	0.009	0.009		tv	%			0.002		
100002725	XRF SILICA MDC		SiO2	98.28	98.281		tv	%			0.01		
100002725	XRF SILICA MDC		Na2O	<0.05	0.022		tv	%			0.05		
100002725	XRF SILICA MDC		MgO	<0.03	0.012		tv	%			0.03		
100002725	XRF SILICA MDC		Mn3O4	<0.0002	-0.0005		tv	%			0.0002		
100002725	XRF SILICA MDC		BaO	0.01	0.012		tv	%			0.01		
100002725	XRF SILICA MDC		ZrO2	0.01	0.011		tv	%			0.01		
100002725	XRF SILICA MDC		WO3	0.001	0.001		tv	%			0.001		
100002725	XRF SILICA MDC		TRUE SUM	99.55	99.548		tv	%					
100002725	XRF SILICA MDC		Sum of XRF & LOI	99.76	99.757880		tv	%			99.5	100.5	
100002725	XRF SILICA MDC		I	0.83	0.83		tv	kps				1	
100002725	SiO2 BY DIFFERENCE		SiO2 by Difference	98.52	98.521000		tv	%					

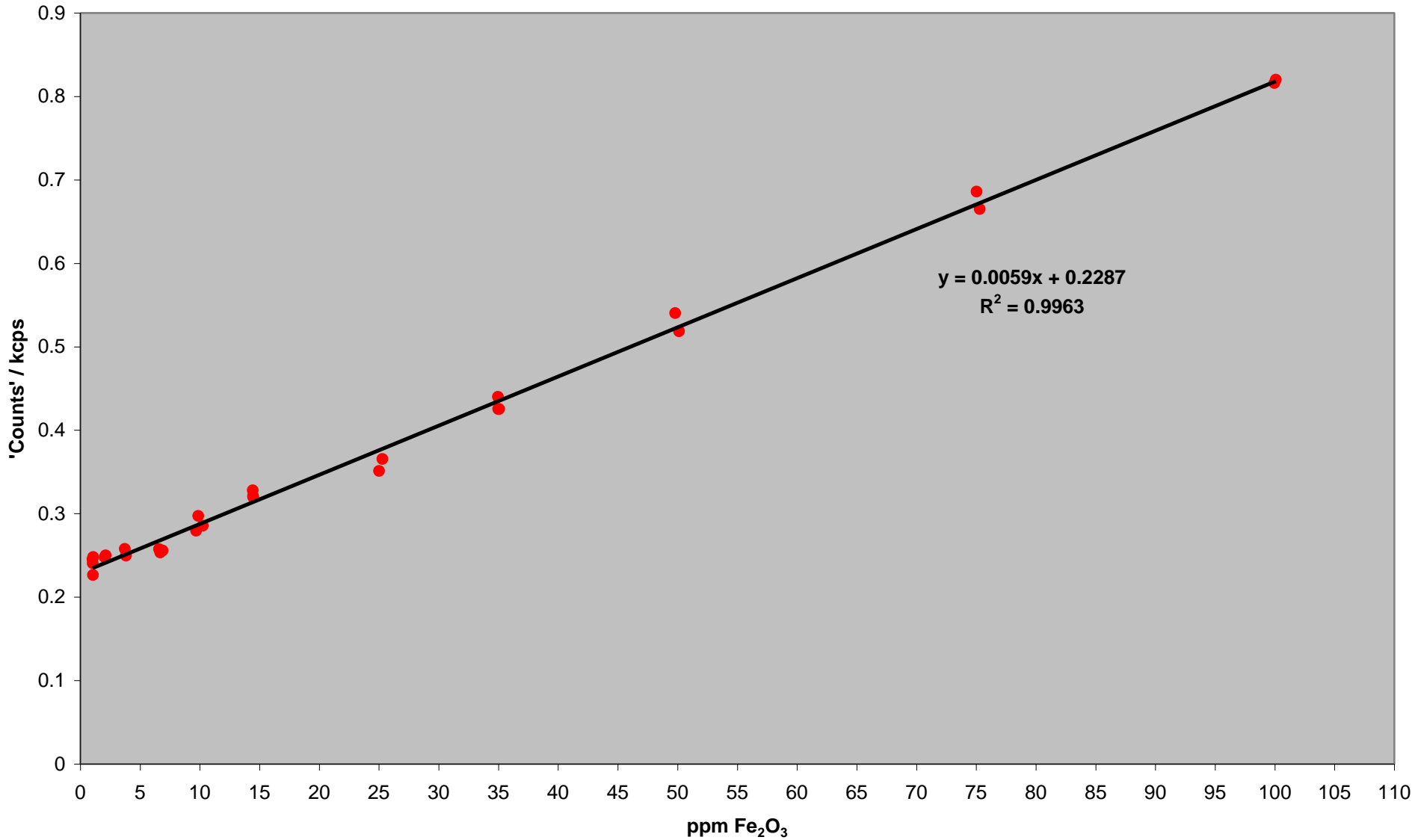
NUM

Glass Sands

- Require very low levels of:
 - Refractory Oxides – Cr_2O_3
 - Usually ICP as ~ 5 ppm
 - Colouring oxides – Fe_2O_3
 - 50 – 350 ppm
- Becoming more challenging:
- Solar Glass
- Coated Glass

- No alpha corrections required for dilute beads


Glass Sand – Low Fe₂O₃ Calibration



Challenges – Clays and Feldspars

Browse SAMPLEPARAM rows related to sample(s)

File Table



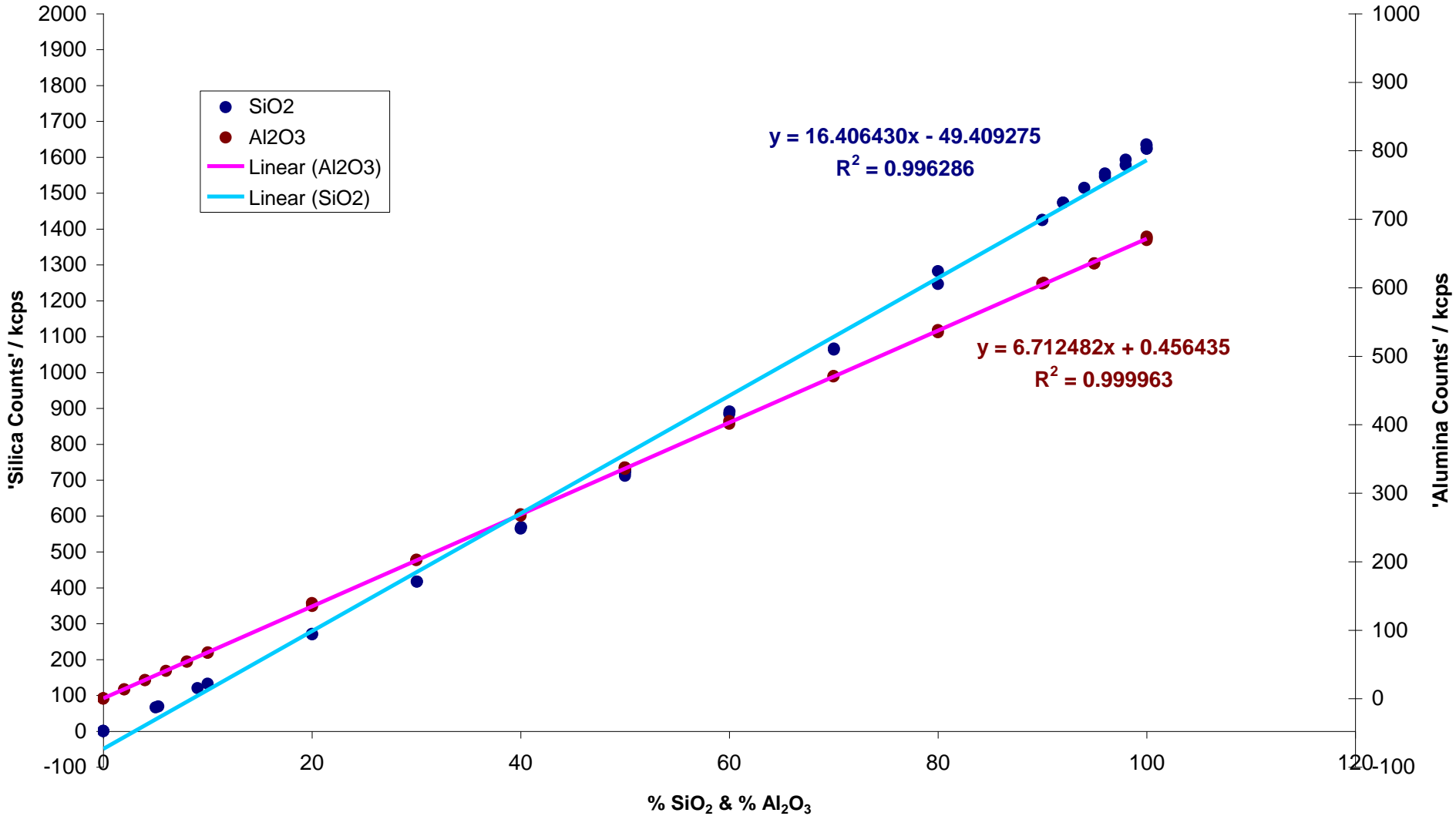
SAMPLE_ID	ME_NAME	DOC PA	PA_NAME	SRESULT	ORESULT	TRESULT	STATUS	PARAM_U	LIMIT1LO	LIMIT1HI	LDL	UDL
100003277	CL PREP RAW MATERIA		Raw Material Prep Complet	Yes	Yes		ev					
100003277	CL WET SIEVE +125um		Initial Dry Wgt	1000.00	1000		ev	g				
100003277	CL WET SIEVE +125um		Residue Wgt 125um	0.31	.31		ev	g				
100003277	CL WET SIEVE +125um		Res >125um	0.03	.031000		ev	%				
100003277	CL WET SIEVE +125um		Res <125um	99.97	99.969000		ev					
100003277	LOI MDC		Wgt Boat	28.6185	28.6185		ev	g				
100003277	LOI MDC		Wgt Sample	7.5243	7.5243		ev	g				
100003277	LOI MDC		Wgt Boat & Sample	36.1428	36.142800		ev	g				
100003277	LOI MDC		Wgt After Ignition	35.3728	35.3728		ev	g				
100003277	LOI MDC		LOI	10.23	10.233510		ev	%				
100003277	XRF CLAY		XRF Fe2O3	1.1618	1.161823948		tv					
100003277	XRF CLAY		XRF Al2O3	29.6286	29.62860194		tv					
100003277	XRF CLAY		XRF CaO	0.1622	0.162200376		tv					
100003277	XRF CLAY		XRF TiO2	1.5333	1.533252607		tv					
100003277	XRF CLAY		XRF K2O	2.1810	2.181033981		tv					
100003277	XRF CLAY		XRF SiO2	64.6108	64.61083641		tv					
100003277	XRF CLAY		XRF Na2O	0.3285	0.328481264		tv					
100003277	XRF CLAY		XRF MgO	0.3938	0.393769465		tv					
100003277	XRF CLAY		XRF I	0.5000	0.5		tv					1
100003277	XRF CLAY		TRUE SUM	100.00	100		tv				98	100.5
100003277	XRF CLAY		SiO2	58.0	57.996880		tv	%			0.01	
100003277	XRF CLAY		Al2O3	26.6	26.596556		tv	%			0.01	
100003277	XRF CLAY		Fe2O3	1.04	1.042929		tv	%			0.002	
100003277	XRF CLAY		TiO2	1.38	1.376347		tv	%			0.002	
100003277	XRF CLAY		CaO	0.15	.145602		tv	%			0.01	
100003277	XRF CLAY		K2O	1.96	1.957638		tv	%			0.01	
100003277	XRF CLAY		Na2O	0.29	.294866		tv	%			0.01	
100003277	XRF CLAY		MgO	0.35	.353473		tv	%			0.01	
100003277	LECO CARBON SULPHU		Carbon	1.735	1.735		ev	%				

Clays and Feldspars

- For dilute beads and primary oxides:
 - Linear calibration lines
 - Simple calculation of alpha corrections
- Lachance-Trail:
 - $C=c + m*I*(1+\sum\alpha_i C_i)$
- Primary Oxides therefore reduces to single term
- clay and feldspar.xls – Now as Slides

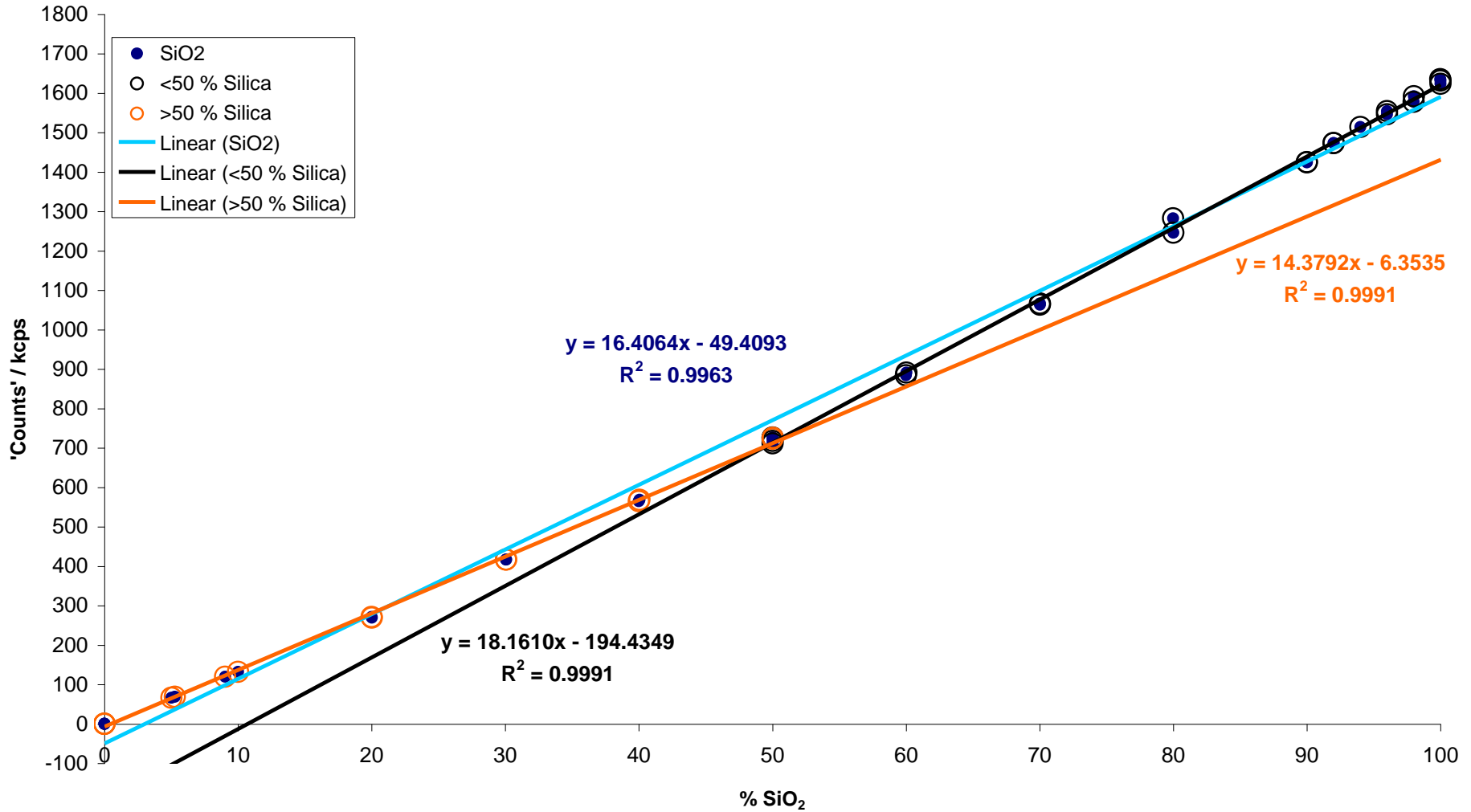
α -Correction

Silica Alumina Calibration



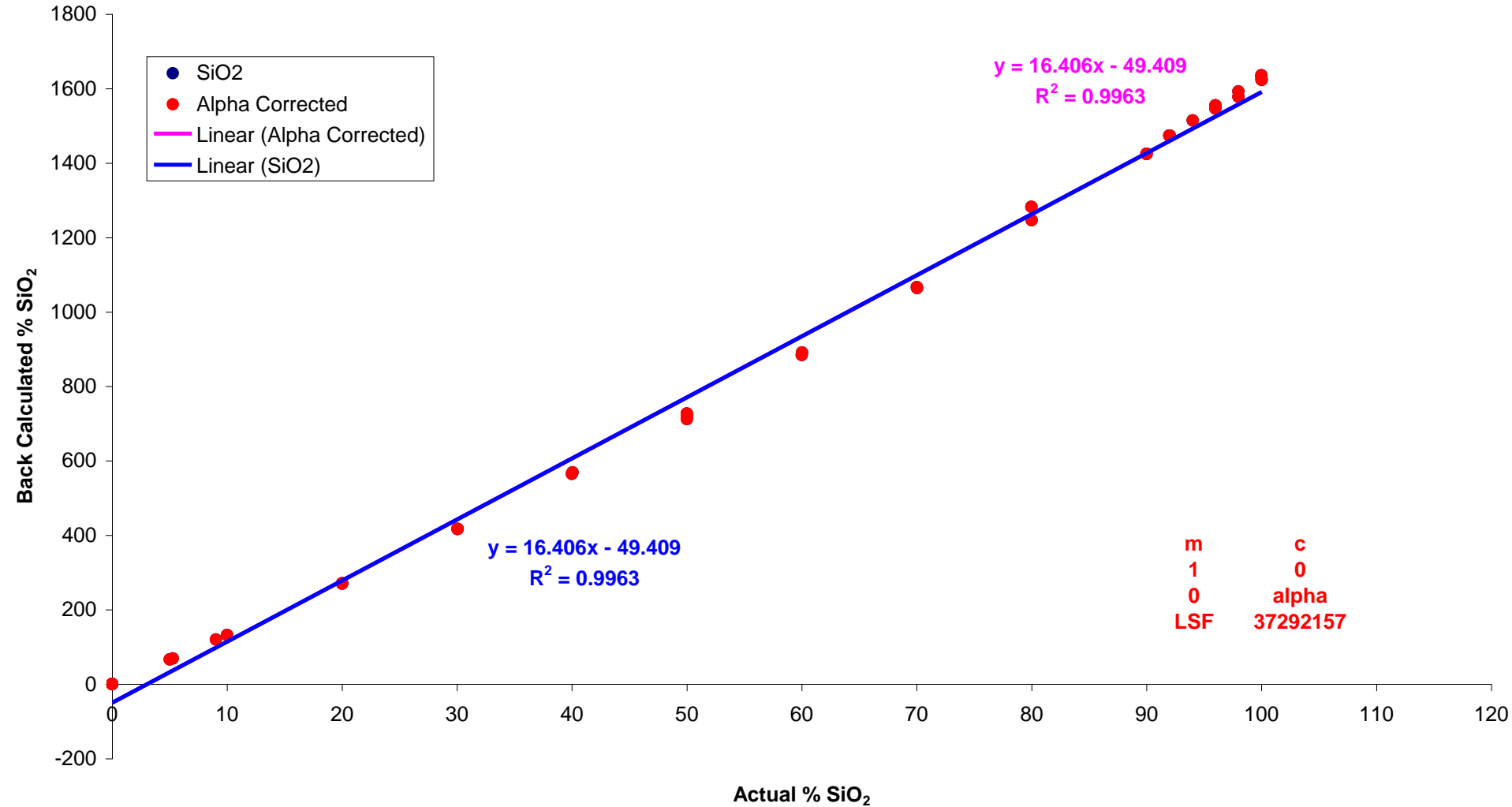
α -Correction

Silica Calibration - no α



α -Correction

Calculated vs Actual % SiO₂ - pre-calculation



α -Correction

m	c
1	0
0	alpha
LSF	37292157



			m	c	1.24696		
			0.06126	0.077116	1.024744		
			0.00247	alpha			
			LSF	9.803414		Al2O3	

Solver Parameters [X]

Set Target Cell: [icon]

Equal To: Max Min Value of:

By Changing Cells: [icon]

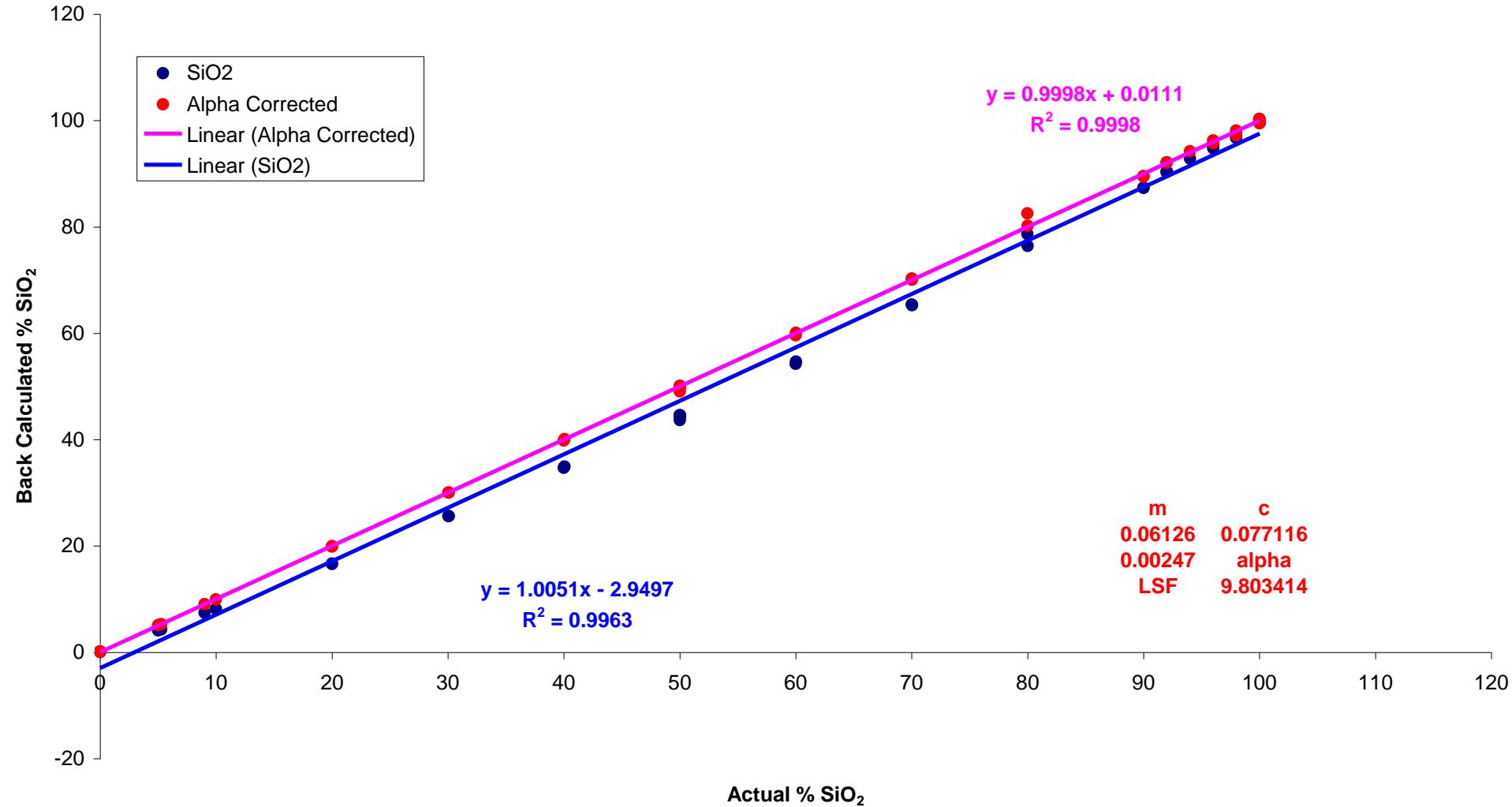
Subject to the Constraints:

[List Box]

1044 | 44.42705 | 31.21044 | 49.90200 | 0.01202 | 013.330 | 49.90701 | 330.13

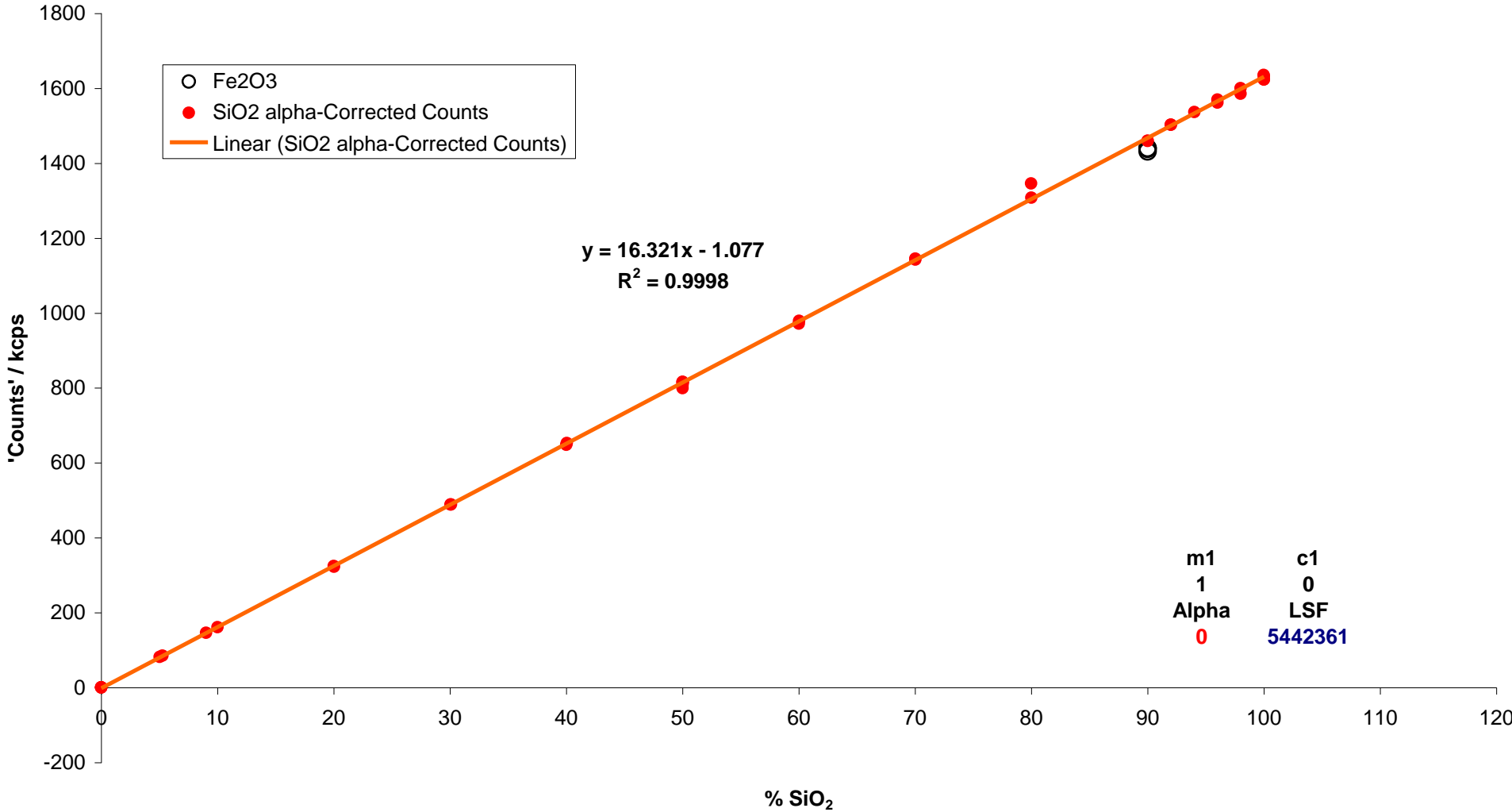
α -Correction

Calculated vs Actual % SiO₂ - post-calculation



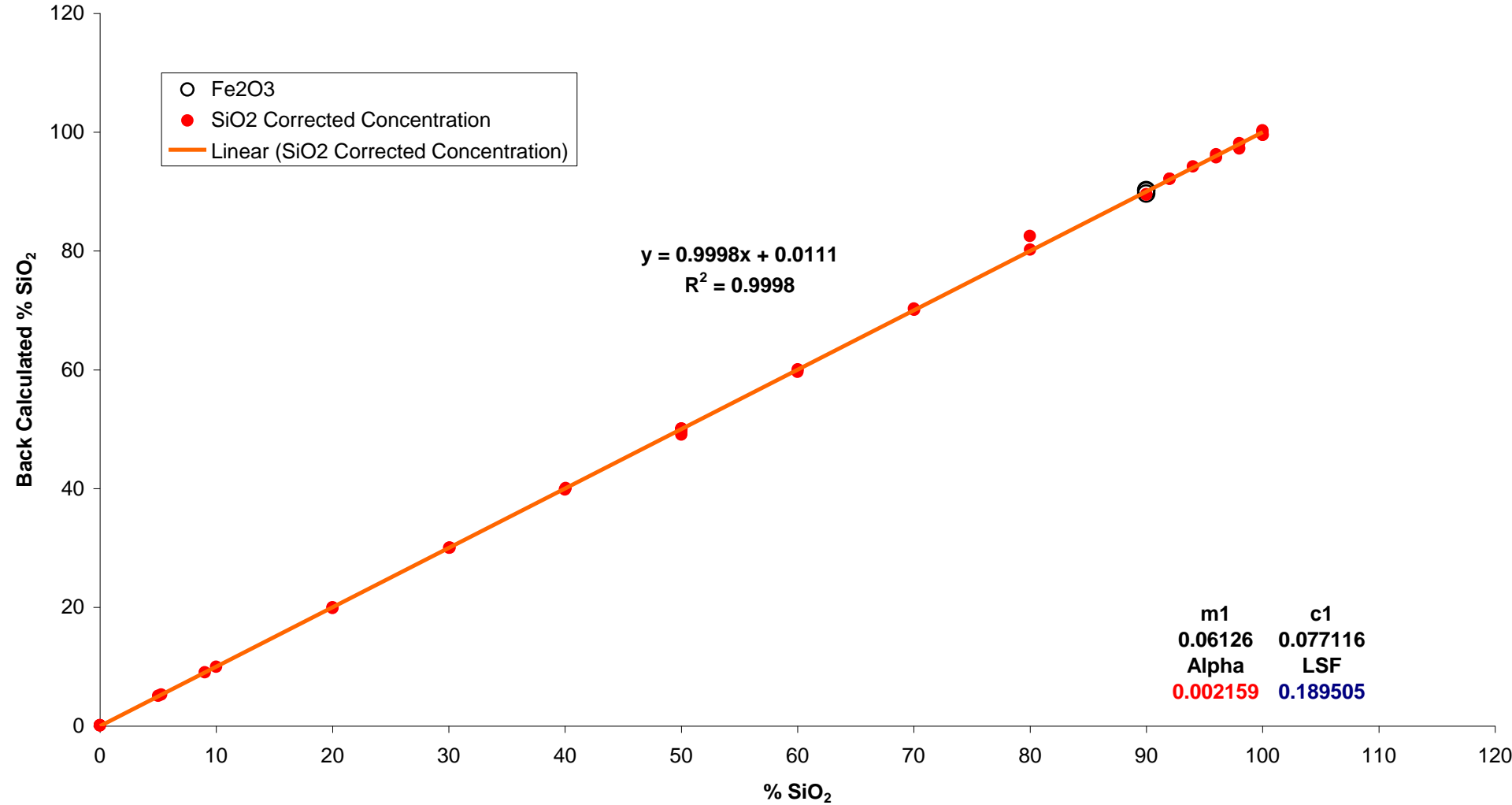
Fe₂O₃ α-Correction

Additional Alphas



Fe₂O₃ α-Correction

Silica Slope and Intercept from previous fit



Alpha Corrections Alumino Silicates

Compound	Calibrated	Channel	D	E	F	RMS	RE
SiO2	Yes	Si1	-0.04301	!0.06129	!0.00000	0.46253	
Al2O3	Yes	Al1	-0.00875	!0.14878	!0.00000	0.22432	
Fe2O3	Yes	Fe1	-0.00406	!0.01858	!0.00000	0.03644	
TiO2	Yes	Ti1	!0.00095	!0.11808	!0.00000	0.01502	
CaO	Yes	Ca1	!0.00020	!0.05757	!0.00000	0.01256	
K2O	Yes	K1	!0.00072	!0.06249	!0.00000	0.03646	
Na2O	Yes	Na1	-0.05418	!0.34628	!0.00000	0.02676	
MgO	Yes	Mg1	-0.07444	!0.14409	!0.00000	0.01794	
I	Yes	I	!0.00000	!1.00000	!0.00000	1.96346	
Correction coefficients:							
Compound	Alpha	Alpha	Alpha	Alpha	Alpha	Alpha	Alpha
	Al2O3	Fe2O3	TiO2	CaO	K2O	Na2O	MgO
SiO2	!0.2555	!0.1812	!0.0084	!0.0004	-0.0855	!0.1377	!0.2283
Al2O3		!0.1691	!0.1674	!0.1067	!0.0497	!0.2281	!0.3615
Fe2O3	-0.0687		!0.8289	!0.8150	!0.6999	-0.2795	-0.3570
TiO2	-0.0484	-0.3257		!1.0152	!0.8114	-0.2159	-0.2378
CaO	-0.0586	-0.2728	-0.4232		!0.7852	-0.1340	-0.1472
K2O	-0.0446	-0.1648	-0.1856	!0.4367		!0.6431	!0.0199
Na2O	-0.0202	!0.3091	!0.2423	!0.2059	!0.2370		!0.0487
MgO	-0.0616	!0.0585	!0.0440	!0.6165	!0.0425	!0.3219	
I							

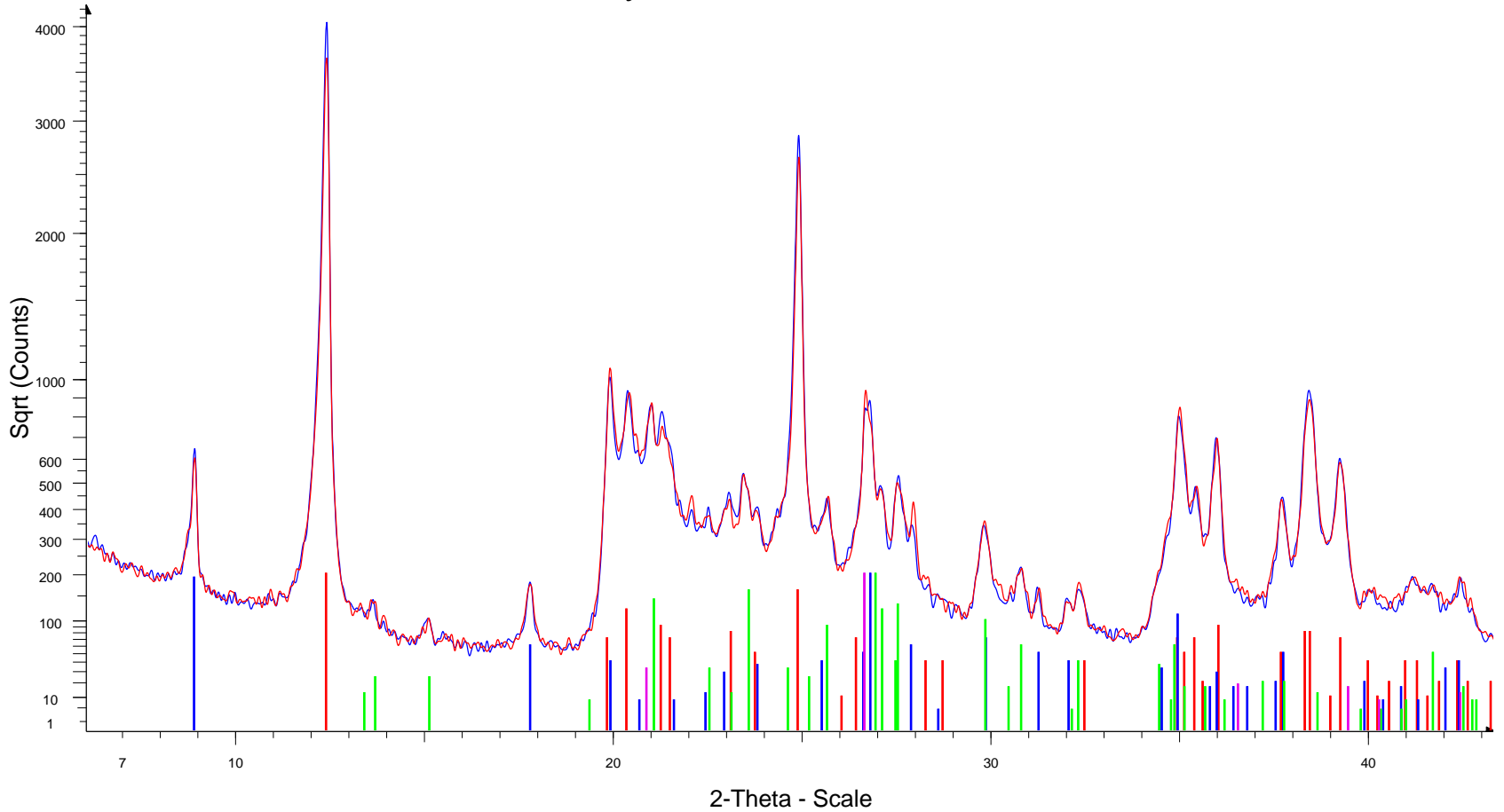
Should be <1 for dilute beads

Presentation Outline

Mineralogy – XRF and XRD

Mineralogy Refined Kaolin

Powder X-ray Diffraction Refined Kaolin



9/5/03 Old(New) K67(73) M16(10) F11(15) - File: 230011122.raw - Type: 2Th/Th locked - Start: 2.000 ° - End: 70.019 ° - Step: 0.006 ° - Step time: 1. s - Temp.: 25 °C (Room) - Time Started: 0 s - 2-Theta: 2.000 ° - The
2/6/03 Old(New) K72(70) M04(11) F18(17) - File: 230013338.raw - Type: 2Th/Th locked - Start: 2.000 ° - End: 70.019 ° - Step: 0.006 ° - Step time: 1. s - Temp.: 25 °C (Room) - Time Started: 0 s - 2-Theta: 2.000 ° - The
00-014-0164 (I) - Kaolinite-1A - Al₂Si₂O₅(OH)₄ - Y: 5.00 % - d x by: 1. - WL: 1.54056 - Triclinic - a 5.155 - b 8.959 - c 7.407 - alpha 91.68 - beta 104.9 - gamma 89.94 - Base-centered - C1 (0) - 2 - 330.431 - F30= 35(0
00-006-0263 (I) - Muscovite-2M1 - KAl₂(Si₃Al)O₁₀(OH,F)₂ - Y: 5.00 % - d x by: 1. - WL: 1.54056 - Monoclinic - a 5.19 - b 9.03 - c 20.05 - alpha 90.000 - beta 95.77 - gamma 90.000 - Base-centered - C2/c (15) - 4 - 93
00-031-0966 (*) - Orthoclase - KAlSi₃O₈ - Y: 5.00 % - d x by: 1. - WL: 1.54056 - Monoclinic - a 8.556 - b 12.98 - c 7.205 - alpha 90.000 - beta 116.01 - gamma 90.000 - Base-centered - C2/m (12) - 4 - 719.122 - F30=
00-046-1045 (*) - Quartz, syn - SiO₂ - Y: 5.00 % - d x by: 1. - WL: 1.54056 - Hexagonal - a 4.91344 - b 4.91344 - c 5.40524 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P3221 (154) - 3 - 113.010 - I/c P

Presentation Outline

Quartz Standards and Crystallinity

Quartz Standards and Crystallinity

- Issue is Amorphous Content –
 - Is it really there?
- Important for:
 - Respirable Silica Analysis
 - New STOT Labelling Regulations

Quartz Standards and Crystallinity

Edit Crystal

Spacegroup:

Lattice Parameters:

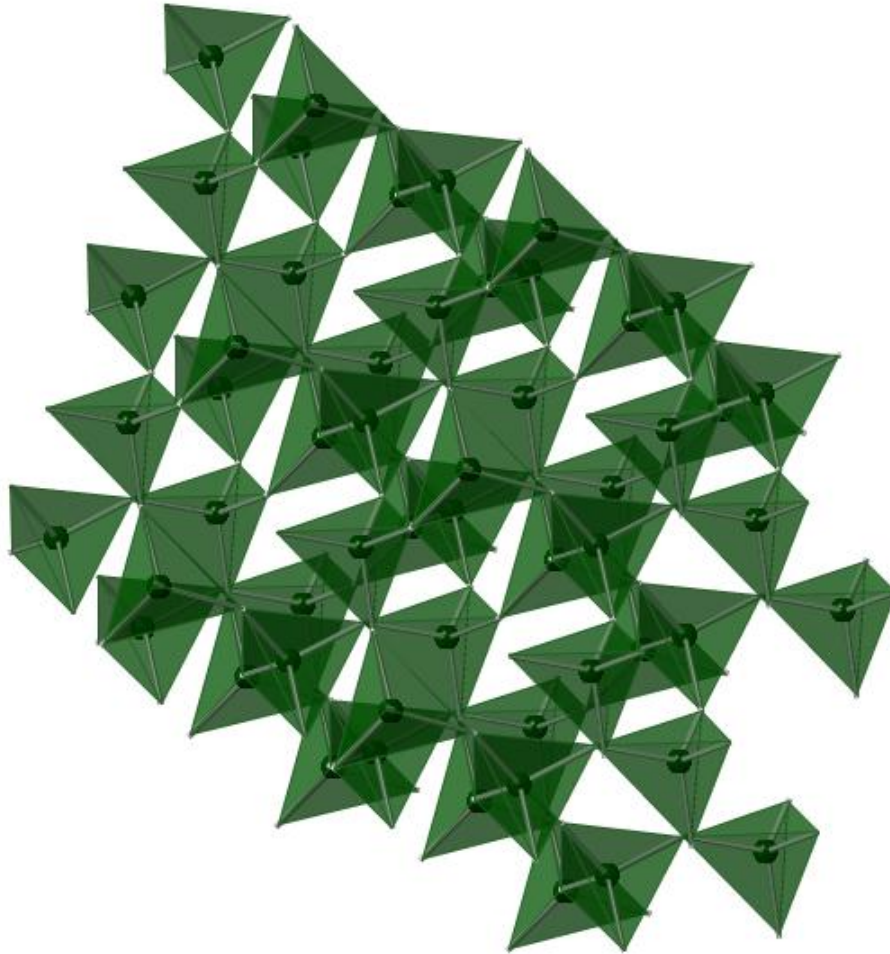
a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]
<input type="text" value="4.91344"/>	<input type="text" value="4.91344"/>	<input type="text" value="5.40512"/>	<input type="text" value="90.0"/>	<input type="text" value="90.0"/>	<input type="text" value="120.0"/>

Asymmetric Unit: Use Displacement Parameters Selection Type:

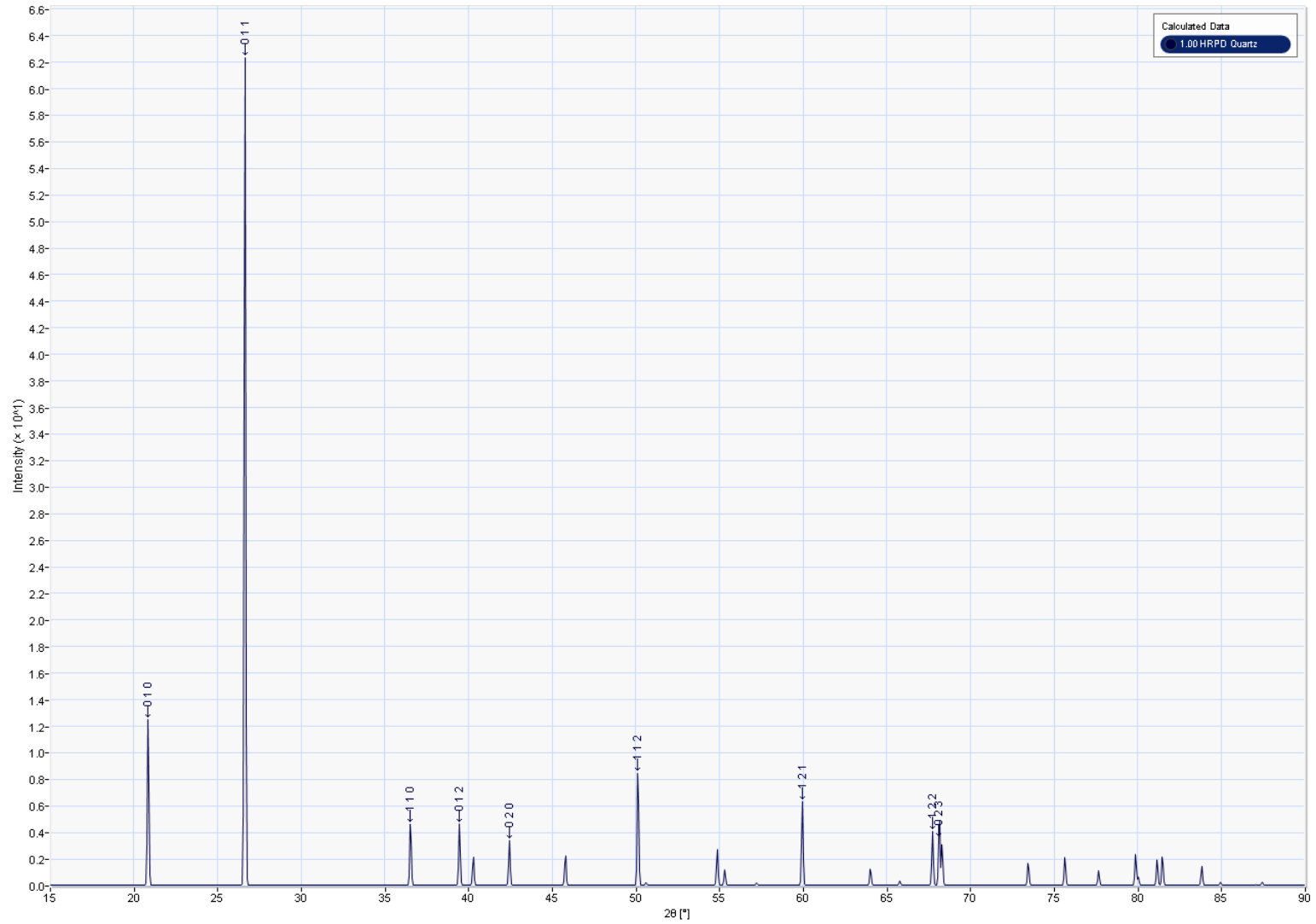
Show:

#	Label	Site Occupancy	x	y	z
1	O	O 1.00	0.4146	0.2678	0.7854
2	Si	Si 1.00	0.4700	0.0000	0.6667

Quartz Standards and Crystallinity



Quartz Standards and Crystallinity



Quartz Standards and Crystallinity

Parameters F2

All range dependent | Rwps | Path | Display | Rpt/Text

	Use	Value	Code	Error	Min	Max
Background						
Chebychev	<input checked="" type="checkbox"/>		@			
Order	<input checked="" type="checkbox"/>	5				
1/X Bkg	<input type="checkbox"/>	1000	Refine	0		
Goniometer radii						
Primary radius (mm)	<input type="checkbox"/>	173				
Secondary radius (mm)	<input type="checkbox"/>	173				
Equatorial Convolutions						
Point detector	<input checked="" type="checkbox"/>					
Receiving Slit Width (mm)	<input checked="" type="checkbox"/>	1e-005	R5W	0		
FDS Shape, angle(°)	<input checked="" type="checkbox"/>	0.3229493	FDS	0		
Beam spill, sample length	<input checked="" type="checkbox"/>	5.169418	B5	0		
Correct Intensity	<input checked="" type="checkbox"/>					
VDS irradiated length (mm)	<input type="checkbox"/>	12	Fix	0		
VDS Scale Intensity	<input type="checkbox"/>					
Capillary	<input type="checkbox"/>					
Linear PSD	<input type="checkbox"/>					
Tube Tails	<input checked="" type="checkbox"/>					
Source Width (mm)	<input type="checkbox"/>	1e-005	TSW	0		
Z1 (mm)	<input type="checkbox"/>	-1.000079e-	TZ1	0		
Z2 (mm)	<input type="checkbox"/>	1e-005	TZ2	0		
Fraction	<input type="checkbox"/>	0.00025413	Fra	0		
Axial Convolutions						
Full Axial Model	<input checked="" type="checkbox"/>					
Source length (mm)	<input type="checkbox"/>	7.788147	SL	0		
Sample length (mm)	<input type="checkbox"/>	4.288364	SmL	0		
RS length (mm)	<input type="checkbox"/>	7.965917	RSL	0		
Prim. Soller (°)	<input type="checkbox"/>	2.3	Fix	0		
Sec. Soller (°)	<input type="checkbox"/>	2.3	Fix	0		
N Beta	<input type="checkbox"/>	30				
Finger_et_al	<input type="checkbox"/>					
Simple Axial Model (mm)	<input type="checkbox"/>	12	Fix	0		
Peak shift						
Zero error	<input type="checkbox"/>	0.04840861	@	0		
Sample displacement (mm)	<input checked="" type="checkbox"/>	-0.0605372	@	0		
Intensity Corrections						
LP Factor	<input checked="" type="checkbox"/>	29.49359	LP	0		
Surface Rghnss Pitschke et .	<input type="checkbox"/>					
Surface Rghnss Suortti	<input type="checkbox"/>					
Sample Convolutions						
Absorption (1/cm)	<input checked="" type="checkbox"/>	550	@	0	0.9*SmA	1.1*SmA
Sample Thickness (mm)	<input checked="" type="checkbox"/>	5.932153	@	0	0.9*SmT	1.1*SmT
Scale Intensity	<input checked="" type="checkbox"/>					
Sample Tilt (mm)	<input checked="" type="checkbox"/>	0.0001	=(Tilt)	0		
Miscellaneous						
Conv. Steps	<input type="checkbox"/>	1				
Start X	<input checked="" type="checkbox"/>	15				

Add Structure
 Add Peaks Phase
 Add hkl Phase
 Load STR(s)
 Load CIF(s)

Quartz Standards and Crystallinity

Parameters F2

Structure Peak Type hkl's Additional Convolutions Rpt/Text

	Use	Value	Code	Error	Min	Max
Use Phase	<input checked="" type="checkbox"/>					
Spacegroup		P3221				
a (Å)		4.9134572 @		0.0000000		
c (Å)		5.4046778 @		0.0000000		
Scale	<input checked="" type="checkbox"/>	0.01111714 @		0		
Cry Size						
Cry size L (nm)	<input checked="" type="checkbox"/>	589.7 @		0.0		
Cry size G (nm)	<input checked="" type="checkbox"/>	198.2 @		0.0		
LVol-IB (nm)	<input type="checkbox"/>	0.000		0.000	k:	1
LVol-FWHM (nm)	<input type="checkbox"/>	0.000		0.000	k:	0.89
Strain						
Strain L	<input checked="" type="checkbox"/>	0.0001 @		0		
Strain G	<input checked="" type="checkbox"/>	0.05504779 @		0		
e0	<input type="checkbox"/>	0.00000		0.00000		
Wt% Rietveld		100.000		0.000		
Wt% of Spiked	<input type="checkbox"/>	0.000				
Cell Mass		180.252		0.000		
Cell Volume (Å ³)		112.99905		0.00000		
Cry LAC (1/cm)		95.387		0.000		
Cry Density (g/cm ³)		2.649		0.000		
R Bragg		2.211				

Save Structure in STR format
View/Hide Structure
Create hkl's phase
Delete Structure
Paste INP to Node/Selections

Parameters F2

Structure Peak Type hkl's Additional Convolutions Rpt/Text

	Use	Value	Code	Error	Min	Max
Use Phase	<input checked="" type="checkbox"/>					
Spacegroup		P3221				
a (Å)		4.9138216 @		0.0000000		
c (Å)		5.4053297 @		0.0000000		
Scale	<input checked="" type="checkbox"/>	0.01233748 @		0		
Cry Size						
Cry size L (nm)	<input checked="" type="checkbox"/>	416.6 @		0.0		
Cry size G (nm)	<input checked="" type="checkbox"/>	234.0 @		0.0		
LVol-IB (nm)	<input type="checkbox"/>	0.000		0.000	k:	1
LVol-FWHM (nm)	<input type="checkbox"/>	0.000		0.000	k:	0.89
Strain						
Strain L	<input checked="" type="checkbox"/>	0.02556693 @		0		
Strain G	<input checked="" type="checkbox"/>	0.00010000 @		0		
e0	<input type="checkbox"/>	0.00000		0.00000		
Wt% Rietveld		100.000		0.000		
Wt% of Spiked	<input type="checkbox"/>	0.000				
Cell Mass		180.252		0.000		
Cell Volume (Å ³)		113.02944		0.00000		
Cry LAC (1/cm)		95.362		0.000		
Cry Density (g/cm ³)		2.648		0.000		
R Bragg		2.065				

Save Structure in STR format
View/Hide Structure
Create hkl's phase
Delete Structure
Paste INP to Node/Selections

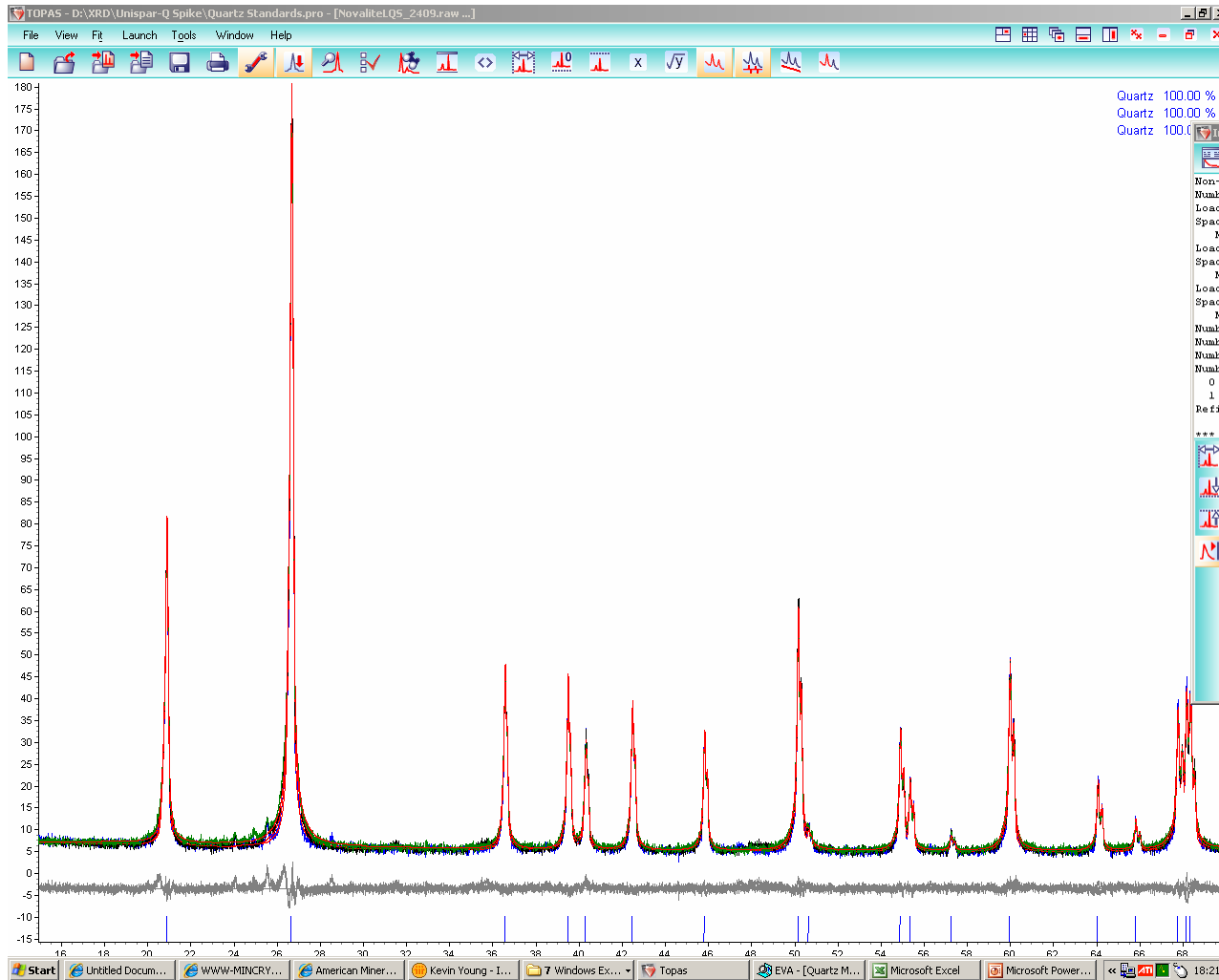
Parameters F2

Structure Peak Type hkl's Additional Convolutions Rpt/Text

	Use	Value	Code	Error	Min	Max
Use Phase	<input checked="" type="checkbox"/>					
Spacegroup		P3221				
a (Å)		4.9138732 @		0.0000000		
c (Å)		5.4055581 @		0.0000000		
Scale	<input checked="" type="checkbox"/>	0.01207324 @		0		
Cry Size						
Cry size L (nm)	<input checked="" type="checkbox"/>	293.4 @		0.0		
Cry size G (nm)	<input checked="" type="checkbox"/>	267.0 @		0.0		
LVol-IB (nm)	<input type="checkbox"/>	0.000		0.000	k:	1
LVol-FWHM (nm)	<input type="checkbox"/>	0.000		0.000	k:	0.89
Strain						
Strain L	<input checked="" type="checkbox"/>	0.05841871 @		0		
Strain G	<input checked="" type="checkbox"/>	0.0001 @		0		
e0	<input type="checkbox"/>	0.00000		0.00000		
Wt% Rietveld		100.000		0.000		
Wt% of Spiked	<input type="checkbox"/>	0.000				
Cell Mass		180.252		0.000		
Cell Volume (Å ³)		113.03659		0.00000		
Cry LAC (1/cm)		95.356		0.000		
Cry Density (g/cm ³)		2.648		0.000		
R Bragg		1.575				

Save Structure in STR format
View/Hide Structure
Create hkl's phase
Delete Structure
Paste INP to Node/Selections

Quartz Standards and Crystallinity



Interface Mode

Non-linear least squares (c) 1992-2007 Alan A. Coelho
Number of independent parameters : 90
Loading xyz's for P3221 from file C:\Topas4-2\sg\p3221.sg
Space group P3221 is not centrosymmetric
Number of equivalent positions 6
Loading xyz's for P3221 from file C:\Topas4-2\sg\p3221.sg
Space group P3221 is not centrosymmetric
Number of equivalent positions 6
Loading xyz's for P3221 from file C:\Topas4-2\sg\p3221.sg
Space group P3221 is not centrosymmetric
Number of equivalent positions 6
Number of independent parameters : 90
Number of hkls generated for C:\Topas4-2\sg\p3221.sg 27
Number of hkls generated for C:\Topas4-2\sg\p3221.sg 27
Number of hkls generated for C:\Topas4-2\sg\p3221.sg 27
0 Time 1.91 Rwp 10.084 0.000 MC 0.00 0
1 Time 2.95 Rwp 10.085 0.000 MC 100.00 0
Refinement converged

*** Parameter(s) close to limit(s)

Interface Mode

- **Sorry for being late**

- **Thank You for Listening**