

Advances in table top ED-XRF

New applications within reach.

By A.Jonkers

Contents

- Some historic data (briefly)

Hardware performance improvements

In resolution

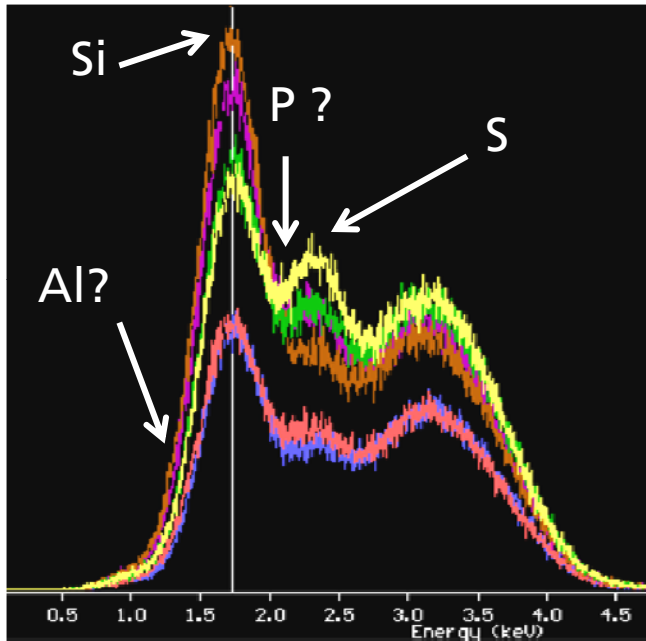
In elemental range

In maximum count rate

- Recent application performance improvements

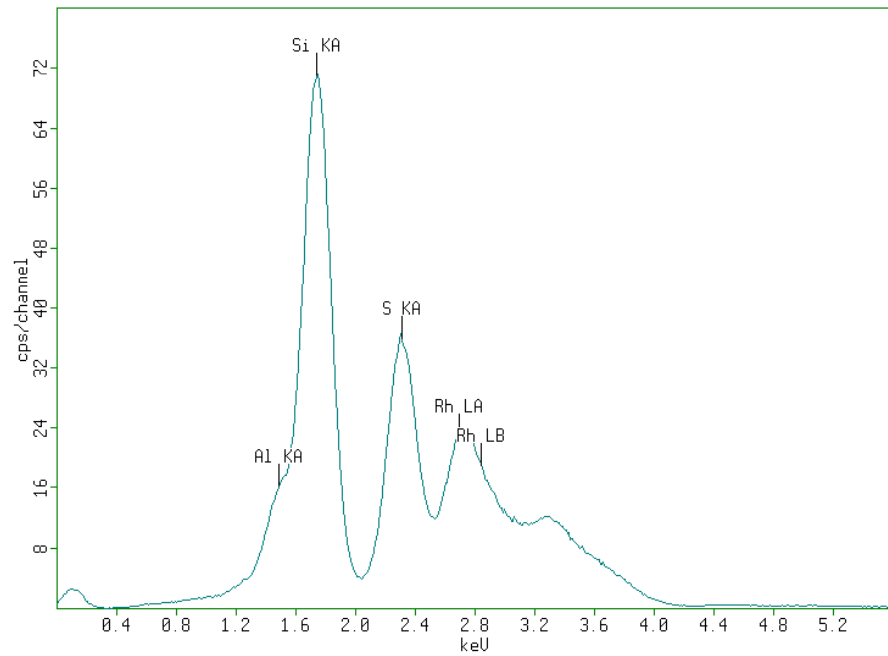
Sealed detector

Si-Pin



Resolution $\approx 800\text{eV}$

≈ 1998

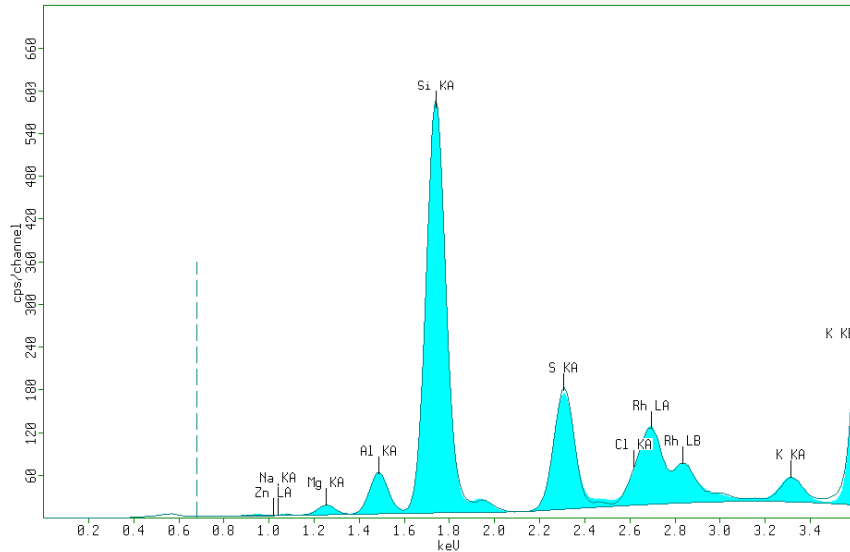


Resolution $\approx 185\text{eV}$

≈ 2002

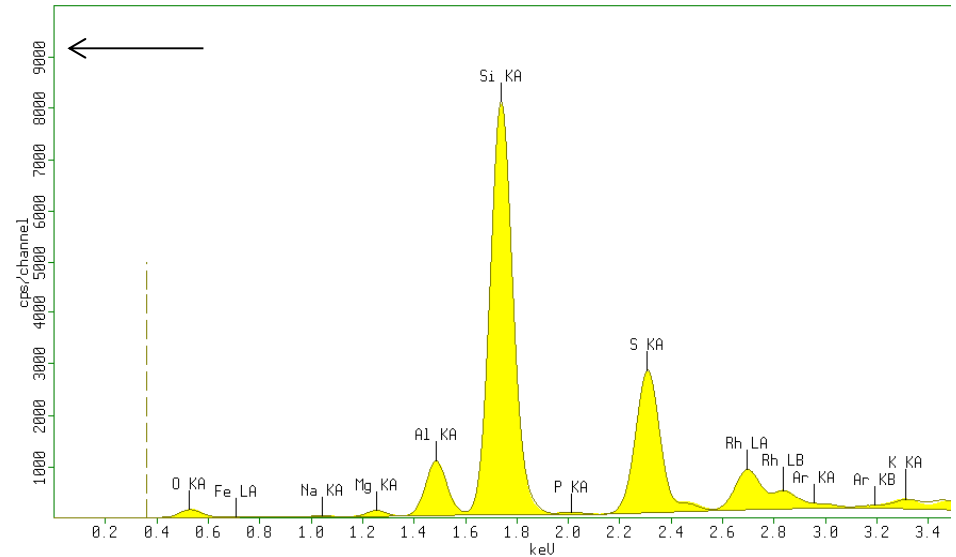
1st gen. SDD vs

2nd gen. high transmission SDD



Resolution <145 eV

2006



Resolution <145 eV

2014

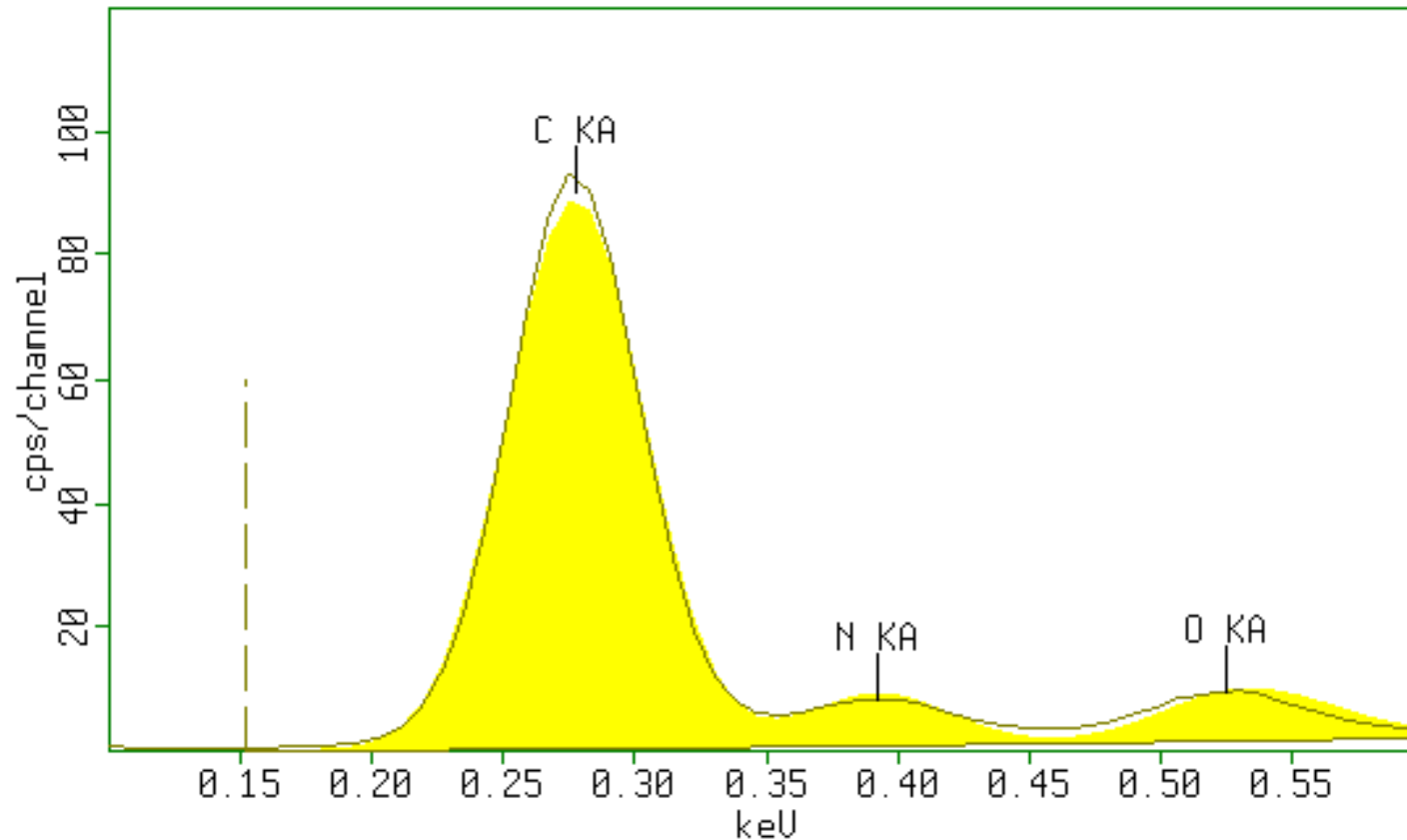
Opening a route to new, improved applications !

Advances in ED-XRF

- In less than 2 decades:
 - Max count rate from 6,000 cps to >> 200,000 cps, depending on application
 - Resolution from 800eV improved to better than 145eV
 - Lowest energy from 1.486 keV (Al) extended to 0.27 keV (C)

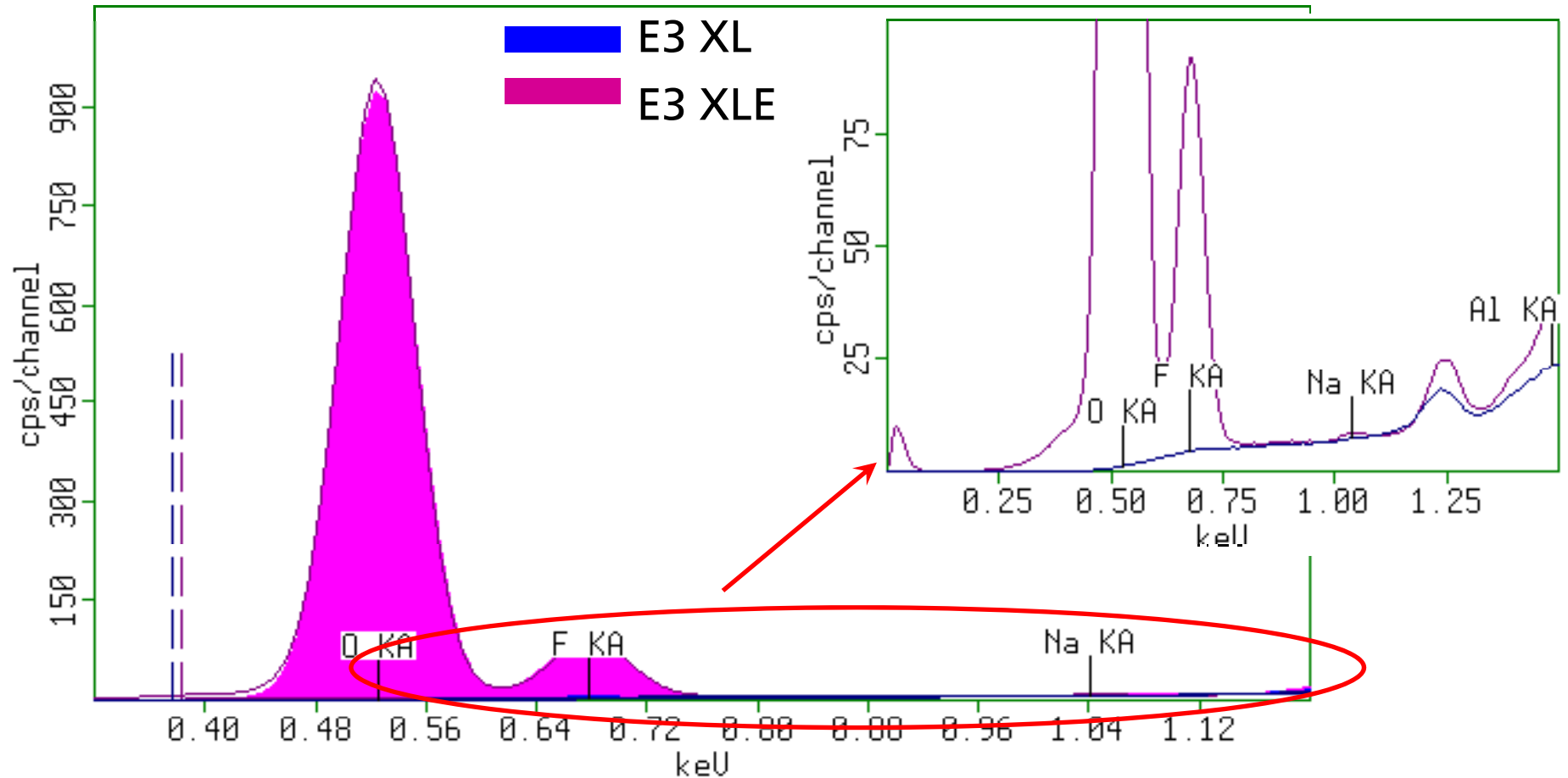
Detection down to C with E3 XLE

- Example: a spectrum obtained of a sample foil



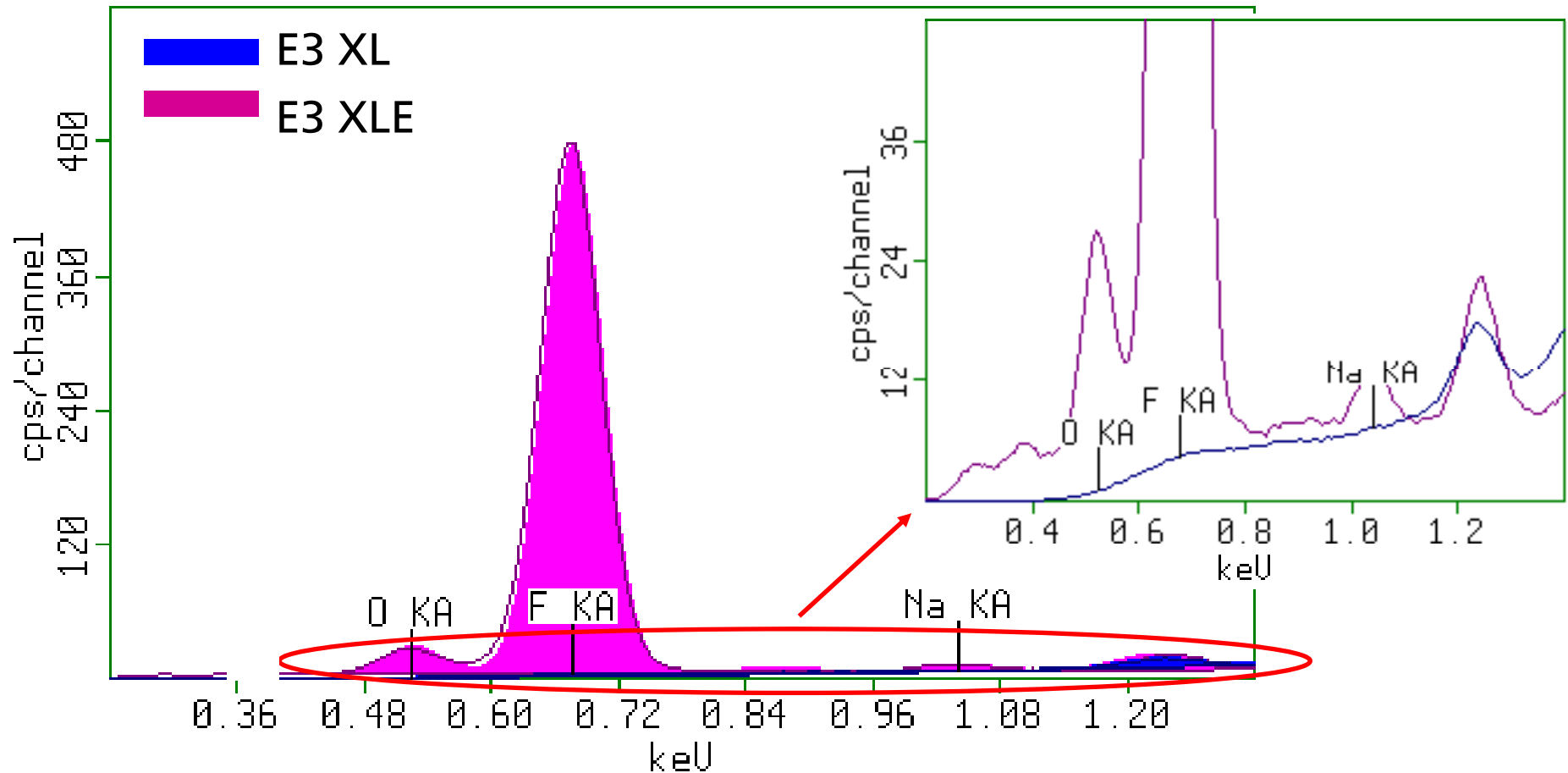
F in fluorite (as bead)

NCS DC 14022, 1 to 10; 46.23%F

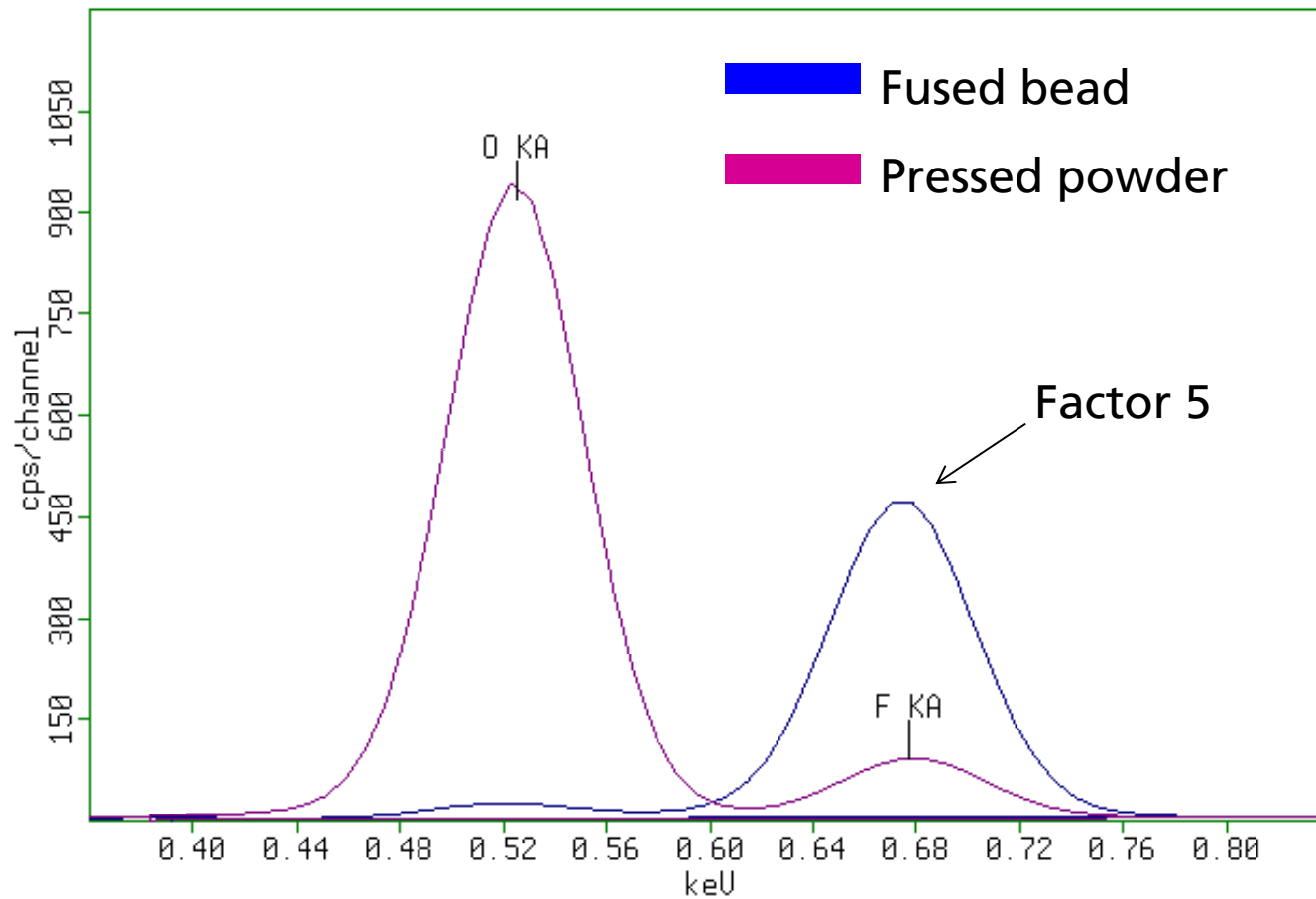


F in fluorite (as pressed powder pellet)

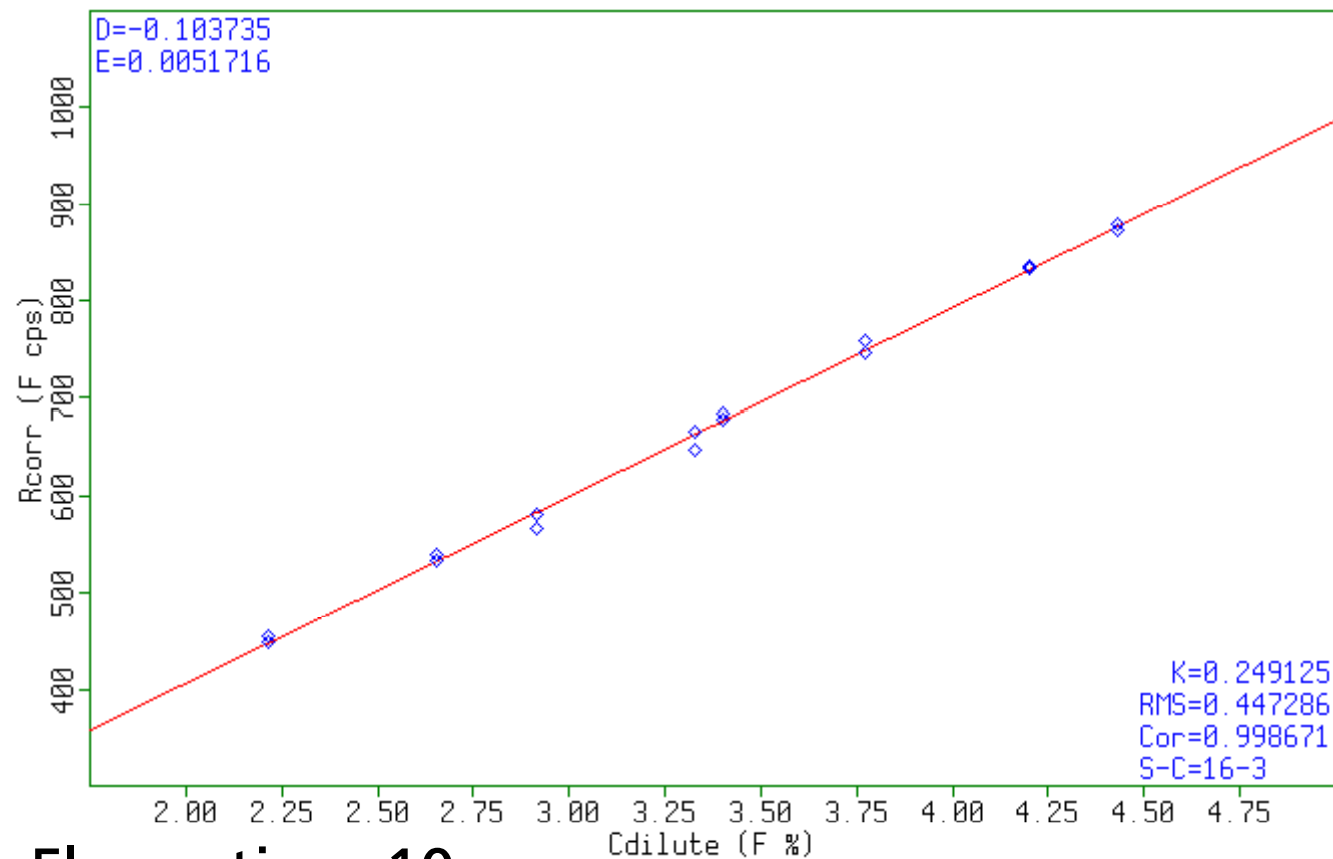
NCS DC 14022 : 46.23%F



F in fluorite, NCS DC 14022



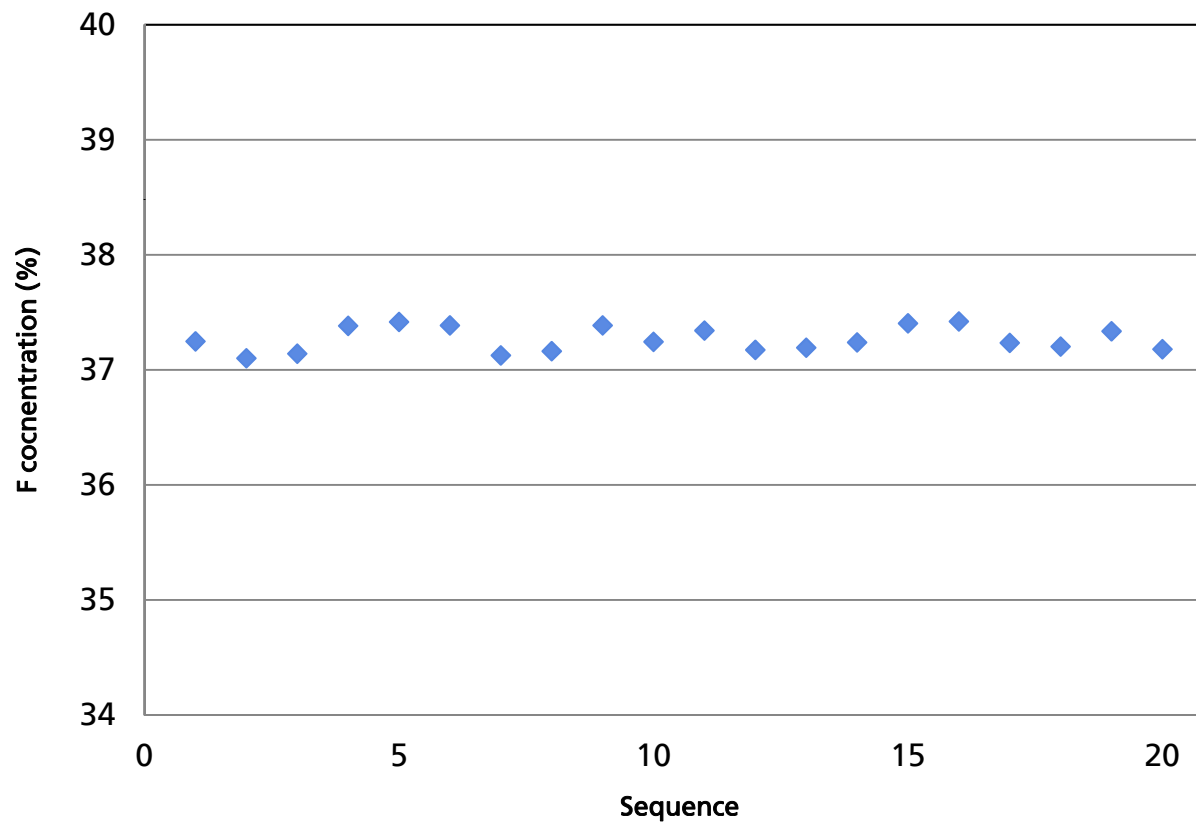
E3 XLE for F in Fluorite fused bead : accuracy



Sample:Flux ratio = 10

E3 XLE for F in Fluorite fused bead : precision

Sample DC 14048



Average = 37.266

RMS = 0.108%

Certified = 37.404

Cement

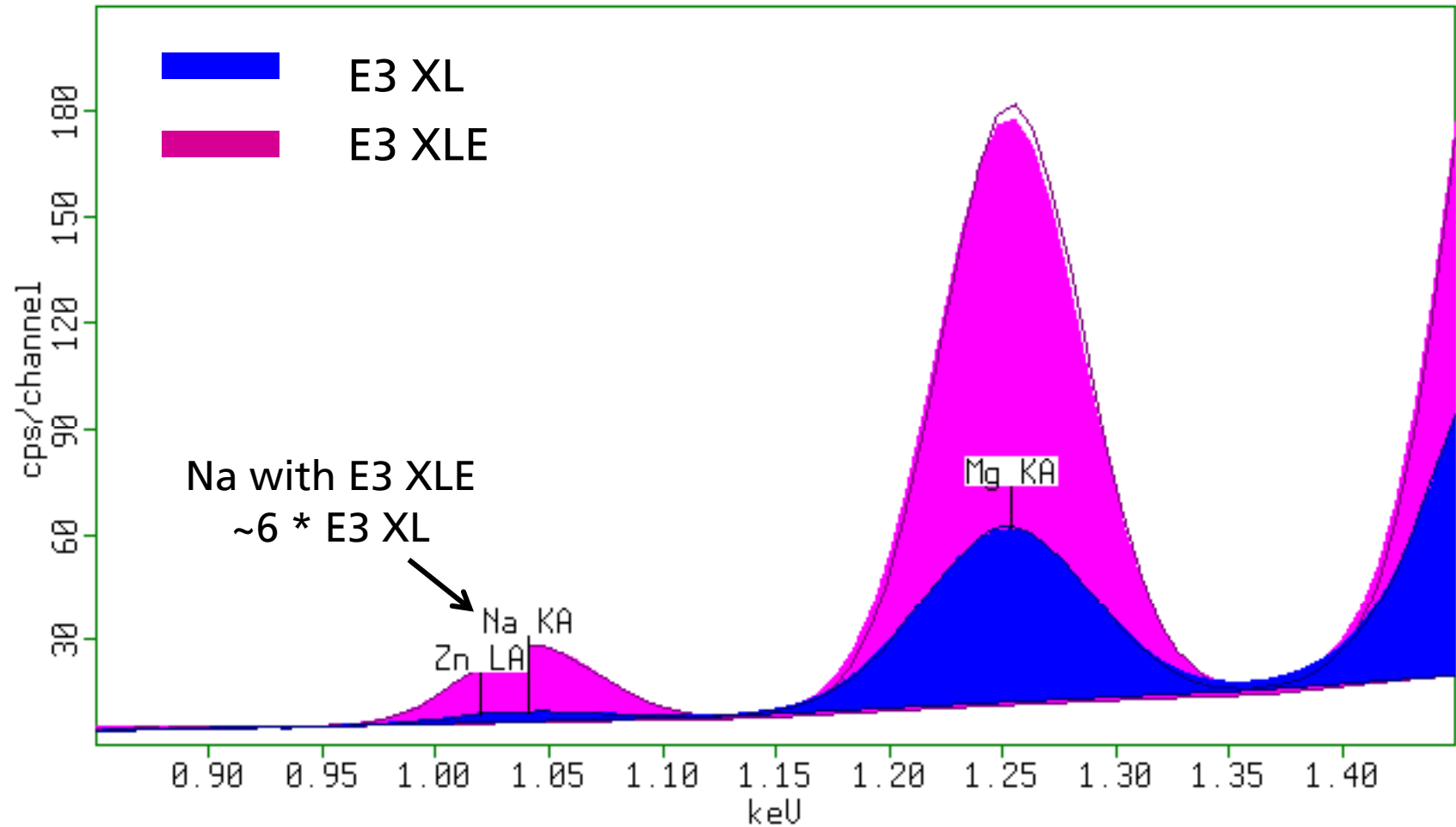
- Sample preparation:
 - Fused bead made with Eagon2
 - 1g sample + 5 g flux
 - Diameter: 32 mm
- Measurement conditions



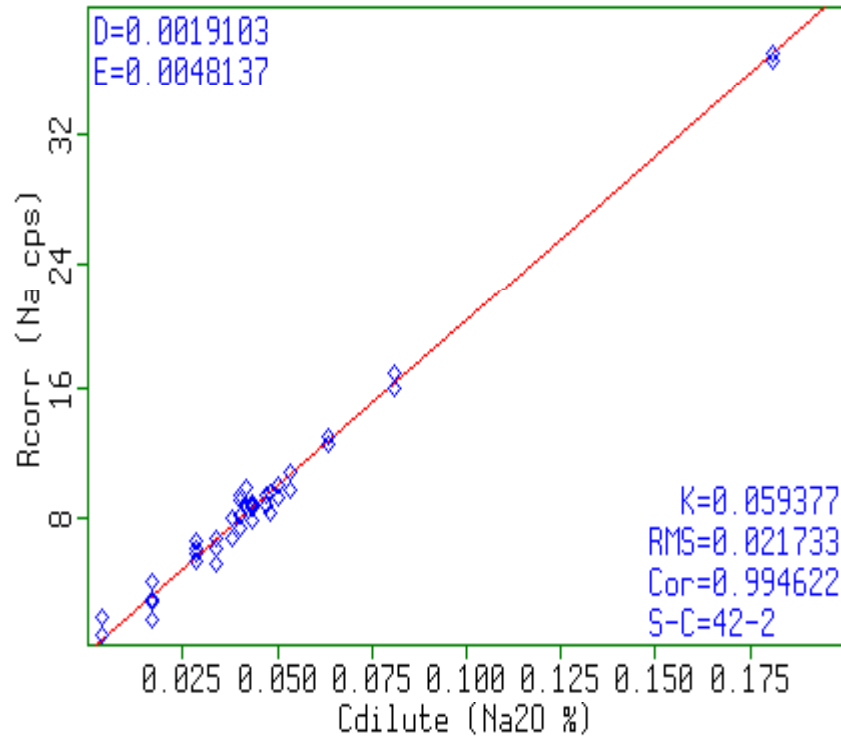
Condition	kV	Filter	Medium	Time (s)	Elements
1	50	Ag	Air	60	Zn, Sr
2	14	Al-50	Helium	120	K, Ca, Ti, Mn, Fe
3	4.5	<none>	Helium	420	Na, Mg, Al, Si, P, S

- Tube anode: Ag

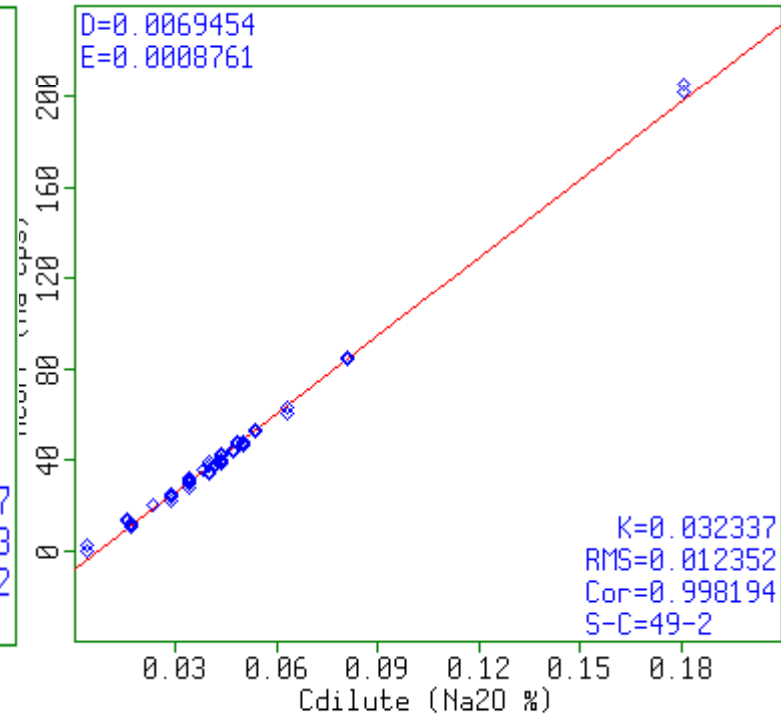
Na in Cement fused bead: spectra (NIST 1885a)



Na in Cement fused bead: accuracy



E3 XL



E3 XLE

C114: Cement fused bead

	Maximum difference between duplicates		
	Measured		Allowed
	E3 XL	E3 XLE	
	%	%	%
SiO ₂	0.05	0.1	0.16
Al ₂ O ₃	0.03	0.04	0.2
Fe ₂ O ₃	0.03	0.09	0.1
CaO	0.16	0.14	0.2
MgO	0.04	0.03	0.16
SO ₃	0.01	0.02	0.1
Na ₂ O	0.06	0.02	0.03
K ₂ O	0.02	0.01	0.03
TiO ₂	0.01	0.01	0.02
P ₂ O ₅	0.01	0.01	0.03
ZnO	0.002	0.002	0.03
Mn ₂ O ₃	0.003	0.004	0.03

	Max. diff. of the average of duplicates from certified conc.		
	Measured		Allowed
	E3 XL	E3 XLE	
	%	%	%
	0.18	0.12	0.2
	0.1	0.08	0.2
	0.02	0.04	0.1
	0.2	0.21	0.3
	0.04	0.08	0.2
	0.06	0.06	0.1
	0.08	0.02	0.05
	0.03	0.04	0.05
	0.01	0.02	0.03
	0.01	0.01	0.03
	0.003	0.002	0.03
	0.004	0.01	0.03

ISO 29581: accuracy, NIST 1888b fused bead

Validation with CRM

Compound	Certified	Difference		Accuracy limit	
		E3XL	E3XLE	Normal	Expert
	(%)	(%)	(%)	(%)	(%)
SiO ₂	20.77	0.07	-0.02	0.38	0.15
Al ₂ O ₃	4.35	0.03	-0.04	0.2	0.08
Fe ₂ O ₃	3.114	0.006	0.003	0.2	0.08
CaO	64.2	0.07	0.07	0.63	0.25
MgO	3.622	0.009	-0.067	0.2	0.08
SO ₃	2.679	0.018	0.000	0.2	0.08
P ₂ O ₅	0.074	0.005	0.002	0.05	0.02
K ₂ O	0.669	0.013	-0.031	0.08	0.03
Na ₂ O	0.139	0.038	0.001	0.05	0.02
TiO ₂	0.232	0.000	-0.002	0.05	0.02
Mn ₂ O ₃	0.065	0.003	0.004	0.05	0.02
ZnO	0.013	0.001	-0.001	0.05	0.02
SrO	0.101	0.002	-0.001	0.05	0.02

ISO 29581: precision cement fused bead

10 measurements within 1 week

E3XL	Average	Stdev	Repeatability limit	
			normal	expert
Comp.	(%)	(%)	(%)	(%)
Na ₂ O	0.063	0.026	0.019	0.008
MgO	2.014	0.014	0.045	0.018
Al ₂ O ₃	4.68	0.013	0.052	0.021
SiO ₂	20.83	0.030	0.112	0.045
P ₂ O ₅	0.265	0.004	0.019	0.008
SO ₃	3.006	0.008	0.045	0.018
K ₂ O	1.056	0.006	0.037	0.015
CaO	64.53	0.030	0.188	0.075
TiO ₂	0.245	0.002	0.019	0.008
Mn ₂ O ₃	0.051	0.001	0.019	0.008
Fe ₂ O ₃	3.174	0.003	0.045	0.018
ZnO	0.034	0.001	0.019	0.008
SrO	0.13	0.001	0.019	0.008

E3XLE	Average	Stdev	Repeatability limit	
			Normal	Expert
Comp.	(%)	(%)	(%)	(%)
Na ₂ O	0.202	0.005	0.057	0.023
MgO	2.983	0.006	0.135	0.054
Al ₂ O ₃	7.1	0.011	0.202	0.081
SiO ₂	22.56	0.029	0.335	0.134
P ₂ O ₅	0.142	0.003	0.057	0.023
SO ₃	3.419	0.006	0.135	0.054
K ₂ O	1.261	0.003	0.2	0.08
CaO	58.47	0.012	0.542	0.217
TiO ₂	0.369	0.002	0.057	0.023
Mn ₂ O ₃	0.106	0.002	0.057	0.023
Fe ₂ O ₃	3.137	0.005	0.135	0.054
ZnO	0.048	0.001	0.057	0.023
SrO	0.037	0.000	0.057	0.023

Fused Bead Calibration

The Residual Standard Deviation (RMS) obtained on the calibration curves

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	P ₂ O ₅	SO ₃	K ₂ O	Na ₂ O
Calibration RMS E3 XL	0.09	0.05	0.02	0.14	0.03	0.01	0.03	0.02	0.16
Calibration RMS E3 XLE	0.06	0.04	0.02	0.13	0.03	0.01	0.03	0.01	0.013

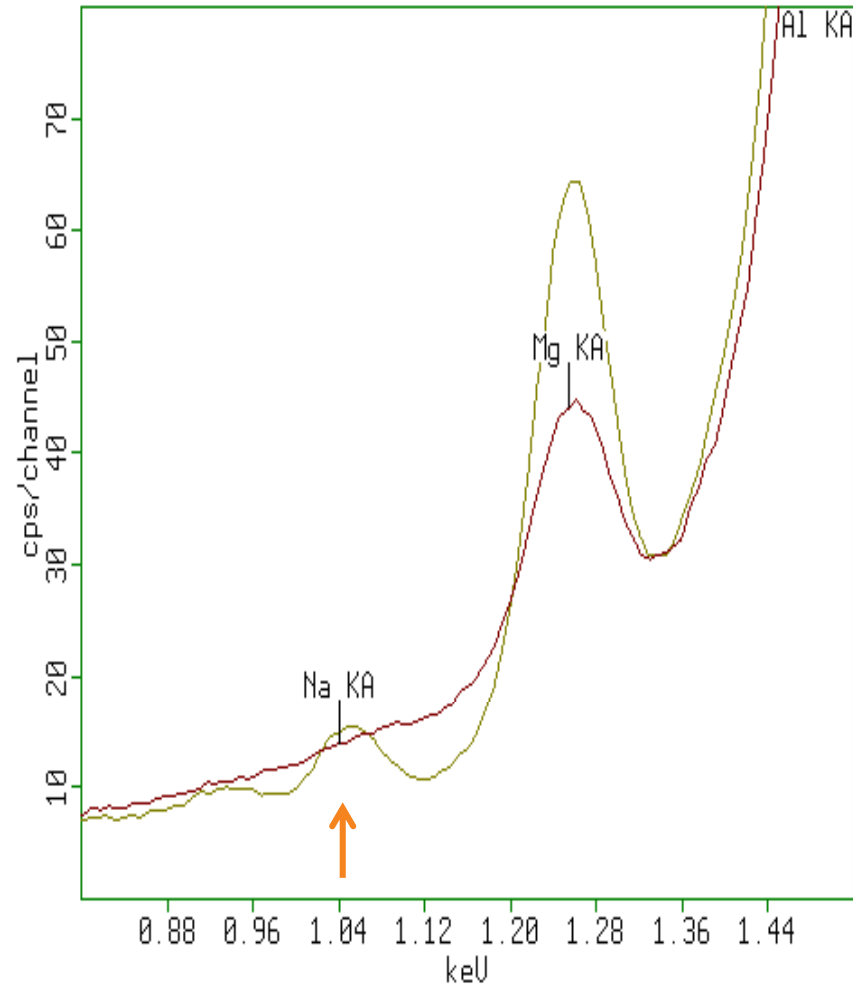
Fused Bead Validation

Difference between certified and measured conc. (%)

Identification	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	P ₂ O ₅	SO ₃	K ₂ O	Na ₂ O
	%	%	%	%	%	%	%	%	%
E3 XL									
NIST 1888b-1	0.06	0.04	0.01	0.05	0.01	0	0.02	0.02	0.03
NIST 1888b-2	0.02	0.04	0.01	0.03	0.01	0.01	0.01	0.01	0.01
XRF13-1	0.08	0	0	0.07	0.02	0	0.02	0.03	0.09
XRF13-2	0.11	0	0.01	0.1	0.02	0	0.01	0.03	0.07
E3 XLE									
NIST 1888b-1	0.07	0.04	0.00	0.12	0.08	0.01	0.01	0.03	0.02
NIST 1888b-2	0.05	0.05	0.00	0.11	0.07	0.00	0.00	0.03	0.01
XRF13-1	0.00	0.01	0.00	0.08	0.03	0.01	0.02	0.00	0.01
XRF13-2	0.00	0.01	0.00	0.10	0.02	0.01	0.01	0.00	0.01

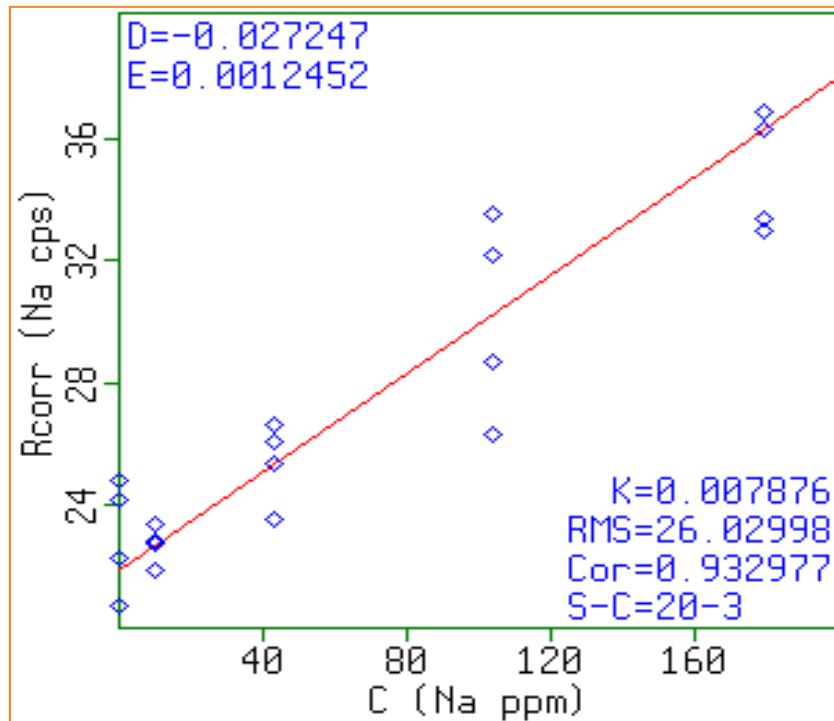
Adpol: sensitivity for Na, 189 ppm Na

█ E3 XL
█ E3 XLE

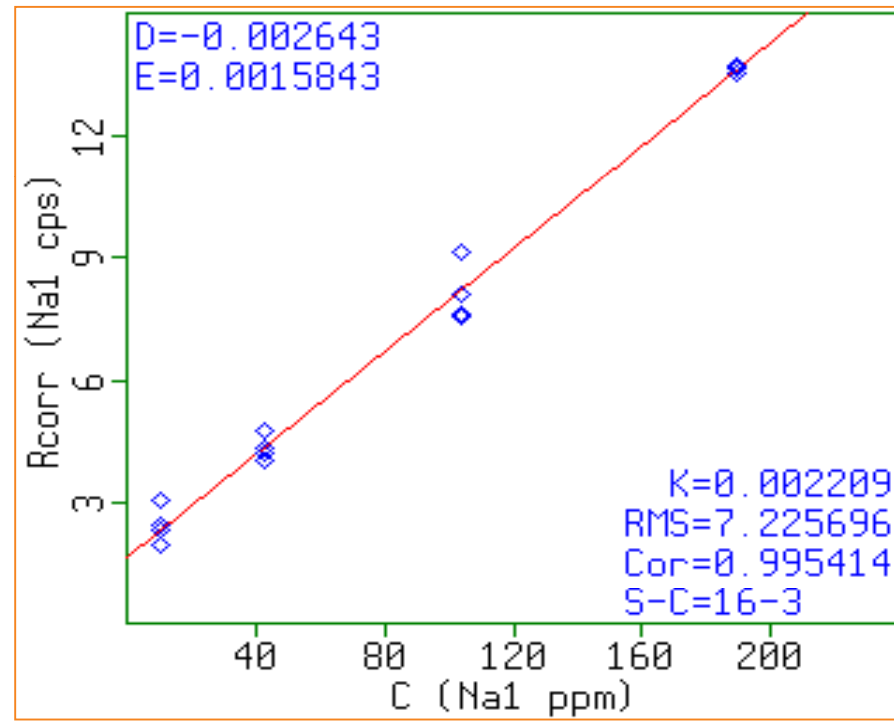


ADPOL: accuracy for Na

E3 XL



E3 XLE

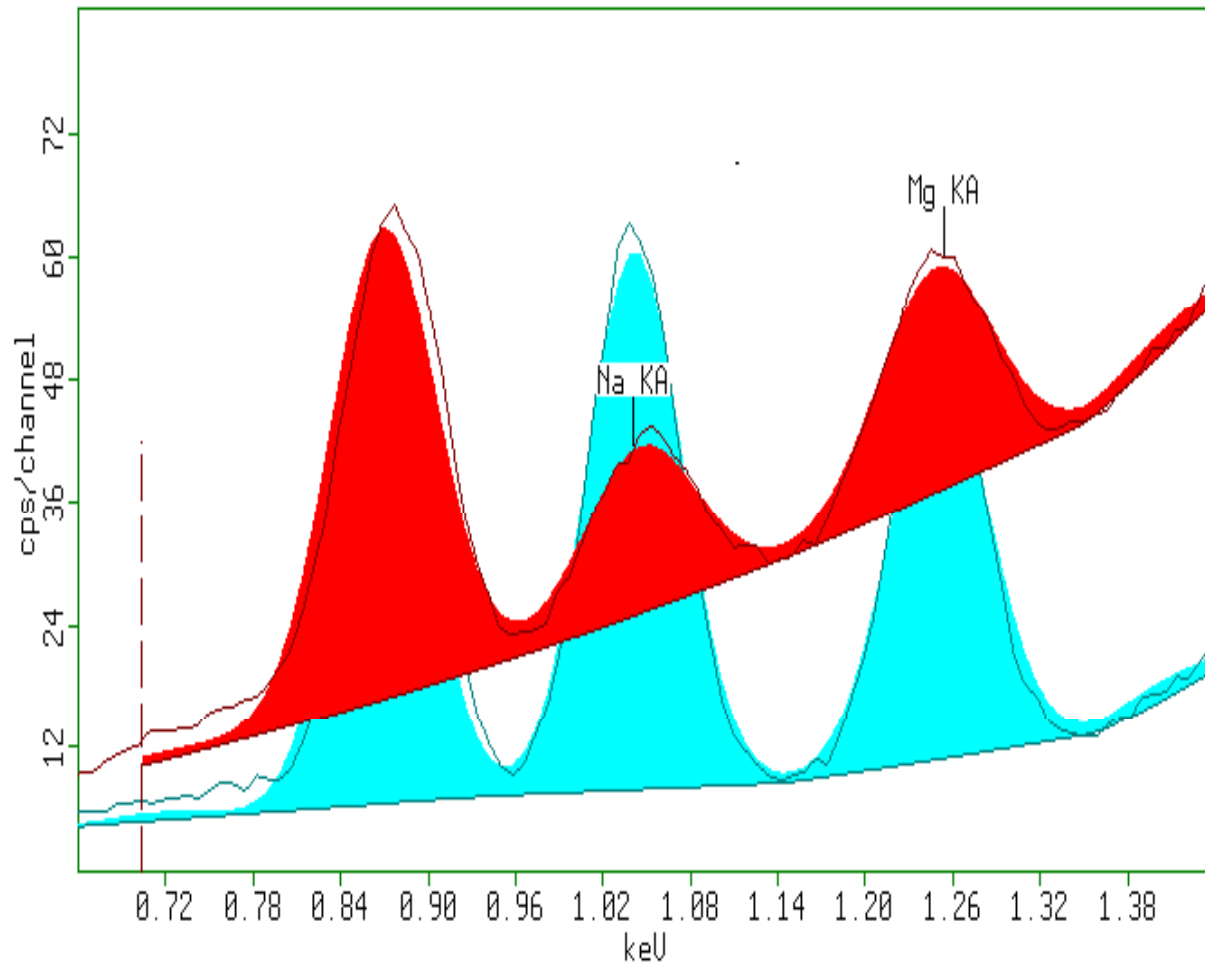


ADPOL: precision

20 measurements for Adpol RM4

Element	Certified Conc. (ppm)	E3 XL		E3 XLE	
		Average (ppm)	RMS (ppm)	Average (ppm)	RMS (ppm)
Na	104	71.0	11.9	99.0	6.9
Mg	102	94.0	6.1	91.9	3.0
Al	209	214.6	5.0	210.7	1.3
Si	125	127.6	2.5	134.3	0.8
P	29	28.4	1.0	29.3	0.4
S	30	29.3	0.6	29.6	0.3
Ca	66	63.1	0.7	64.7	0.5
Ti	19	18.3	0.4	18.5	0.2
Zn	59	57.8	0.4	58.0	0.4

Milk powder: NIST 1549, Na=0.497%

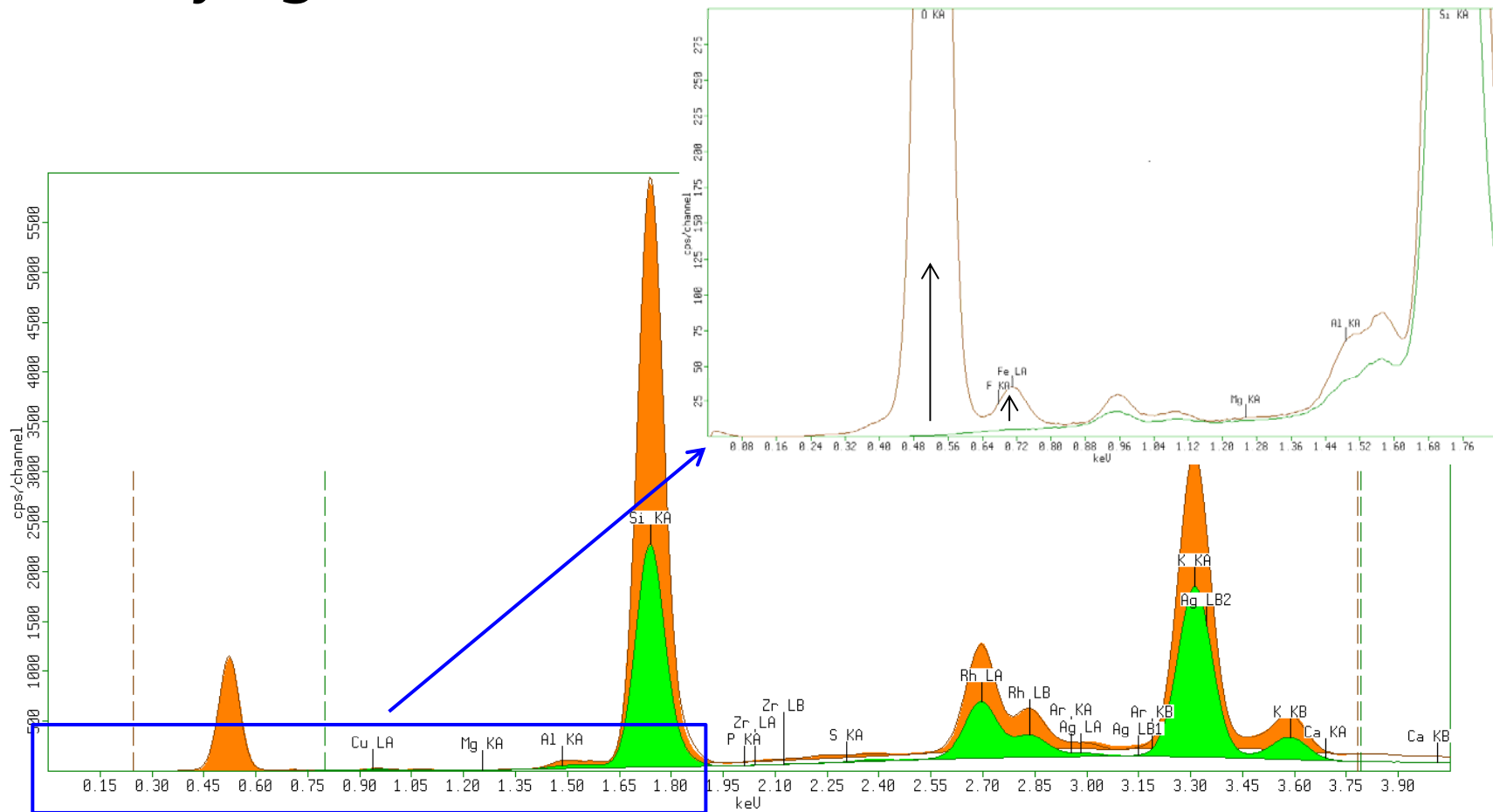


 E3
 E3XLE

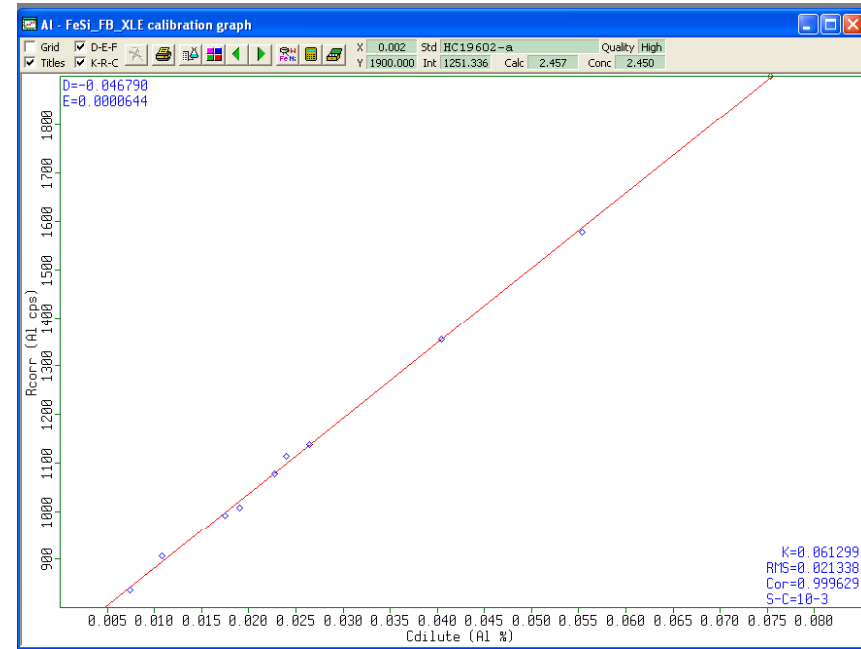
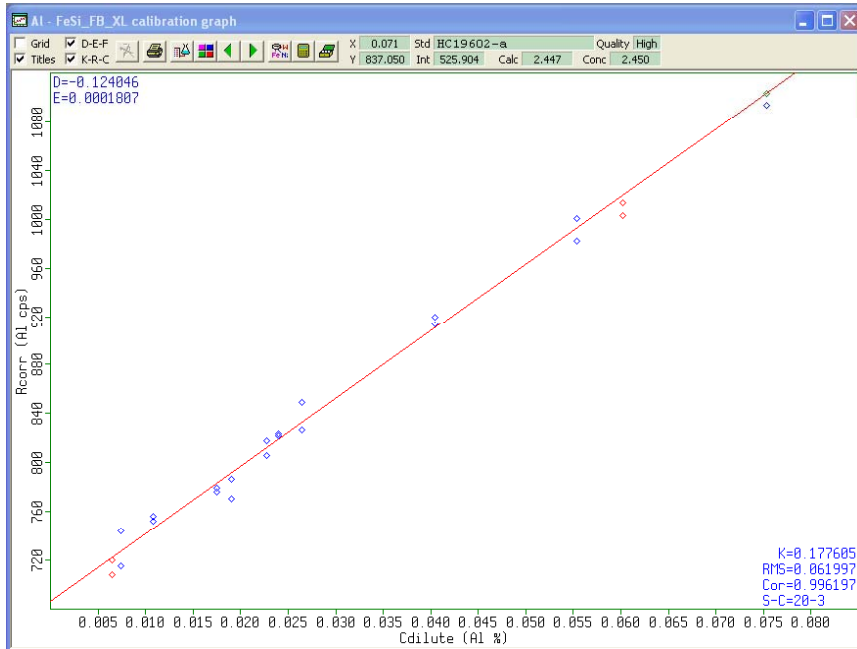
Have a look at the poster for more details.

Ferro-Silicon

- Very light elements now also visible



Calibration of Al in FeSi



FeSi : Fused bead repeatability

El.	Unit	E3 XL	E3 XLE
Mg	%	0.020 +/- 0.014	0.005 +/- 0.004
Al	%	0.480 +/- 0.021	0.472 +/- 0.012
Si	%	77.53 +/- 0.024	76.59 +/- 0.0199
P	%	0.028 +/- 0.008	0.030 +/- 0.004
S	%	0.003 +/- 0.00009	0.003 +/- 0.00007
Ca	%	0.370 +/- 0.011	0.386 +/- 0.0098
Ti	%	0.040 +/- 0.004	0.043 +/- 0.003
Cr	%	0.000 +/- 0.0022	0.0004 +/- 0.0015
Mn	%	0.073 +/- 0.002	0.074 +/- 0.001
Fe	%	21.45 +/- 0.0103	21.20 +/- 0.012
Ni	%	0.004 +/- 0.001	0.003 +/- 0.0009

FeSi : Pressed powder : repeatability

El.	Unit	E3 XL	E3 XLE
Mg	%	0.020 +/- 0.006	0.025 +/- 0.001
Al	%	0.507 +/- 0.004	0.386 +/- 0.002
Si	%	76.558 +/- 0.103	78.671 +/- 0.012
P	%	0.021 +/- 0.001	0.019 +/- 0.002
S	%	0.004 +/- 0.0004	0.004 +/- 0.00003
Ca	%	0.280 +/- 0.002	0.295 +/- 0.002
Ti	%	0.131 +/- 0.0008	0.139 +/- 0.001
Cr	%	0.0722 +/- 0.0026	0.1183 +/- 0.0028
Mn	%	0.156 +/- 0.002	0.154 +/- 0.002
Fe	%	19.031 +/- 0.034	20.117 +/- 0.011
Ni	%	0.025 +/- 0.0008	0.025 +/- 0.0003

Recent changes: E3 XL vs E3 XLE

- **Detector window: Ultra transmission**
 - Sensitivity for light elements is improved very significantly
 - Possible to detect very light elements C, N, O and F
- **Increased detector area**
 - Improved sensitivity for all elements
- **Large software advances**

But more has become available in ED-XRF

- Software:
 - Oil trace, Omnian, fingerprinting, Thin & multi-layer analysis, Virtual analyst
- Epsilon-1 :
 - Additionally pre-calibrations for Lube oils, milk powder, Catalysts



Perhaps more about this next time.