THE ANALYSIS OF FERRO-SILICON ALLOYS

Fused beads vs pressed powder
WD-XRF vs ED-XRF

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- Short introduction Eagon 2 Fusion device
- Comparison Fused Beads vs Pressed Powders
- Comparison Axios vs Axios^{mAX}
- Evaluation of Epsilon 3 and Epsilon 3-XL
- Conclusion

Fused beads vs pressed powder

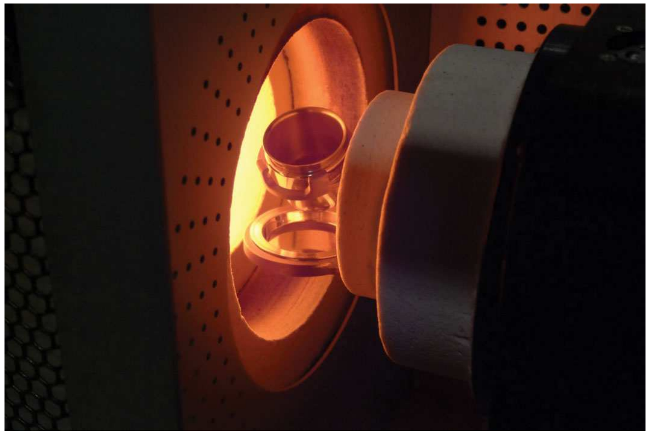
< 40 min

< 5 min

Eagon 2 fusion device

- No gas required (only electrical)
  - Insensitive for gas composition, operator and draft
- Cold to cold operation (safe)
- Can be automated
- Flexible
  - User-defined programs

- 2 beads simultaneously
- Max 1200 °C
- Meets C114 performance



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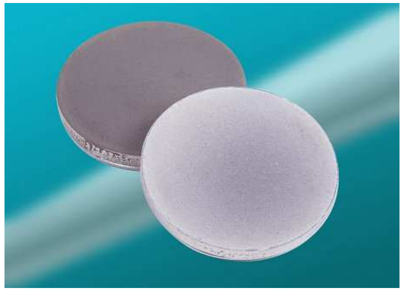
FeSi alloys preparation with the Eagon 2

- One single Fusion program for
  - Fe-Si + Fe-Si-Cr + Fe-Si-Mn (+ Si-Ca ,not discussed here)
- For 32 mm beads: 0.2g sample (<100µm), + 7.5g flux ($5g\ Li_2B_4O_7$, $1.5g\ Li_2CO_3$, $1g\ KIO_4$) $\Rightarrow$ 6.2g flux
- Careful mixing
- 3 Oxidation steps
- Fusion at 1052 °C
- 40 minutes for 2 samples

Pressed tablet

- Ground to < 100 µm
- 10g sample, + 1g wax
- Pressed 30s @ 20ton in a 40mm Al cup



Standards and concentration ranges

- 529-1
- F1/3
- F3/3
- FeSi_St_1-a
- FeSi_St_2-a
- HC 14606
- HC 14607
- HC 19602
- HC 25627
- IPT 143
- IPT70
- NIST 59a
- SARM-33
- SL23-15

Majors

	Min (%)	Max (%)
Fe	6.150	80.200
Si	15.600	91.110
Cr	0.004	34.110
Mn	0.040	31.530

Minors / traces

	Min (%)	Max (%)
C	0.0240	1.0100
O	0.2560	10.0900
Mg	0.0051	0.0400
Al	0.2100	2.4500
P	0.0093	0.0430
S	0.0012	0.0060
Ca	0.0420	2.4700
Ti	0.0180	0.1210
V	0.0024	0.0110
Co	0.0031	0.0047
Ni	0.0028	0.2800
Cu	0.0100	0.2900
As	0.0012	0.0015
Sr	0.0140	0.0140
Zr	0.0820	0.0820
Mo	0.0013	0.0110
Sn	0.0003	0.0004
Ba	0.0043	0.1260

A variety of sources $\Rightarrow$ severe mineralogical effects ?

Measurements

- WD-XRF
  - Axios and Axios^{mAX}

&

- EDXRF
  - Epsilon 3 and Epsilon 3XL

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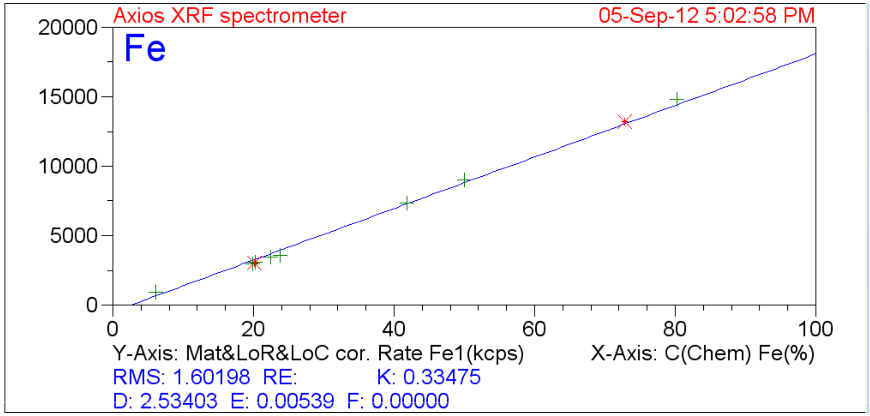
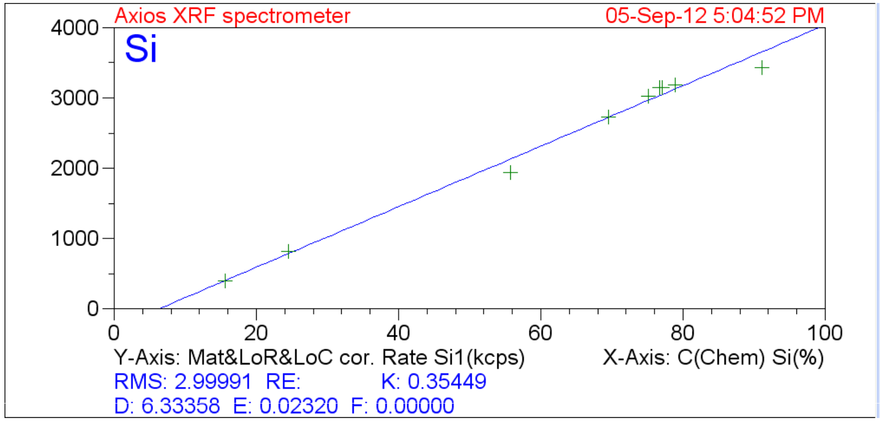
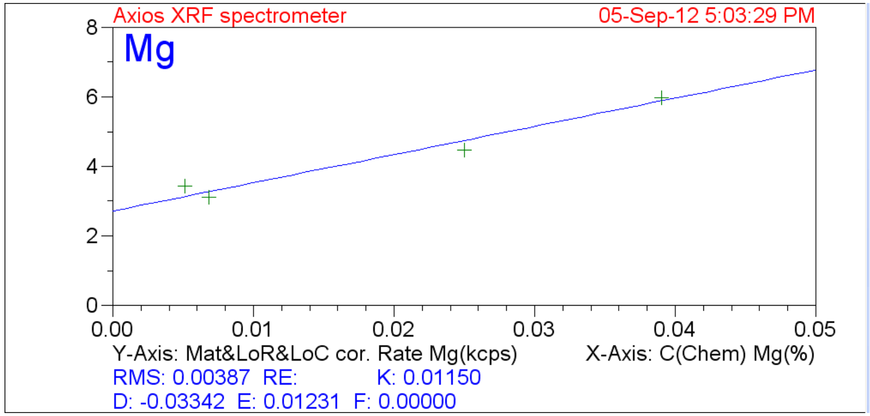
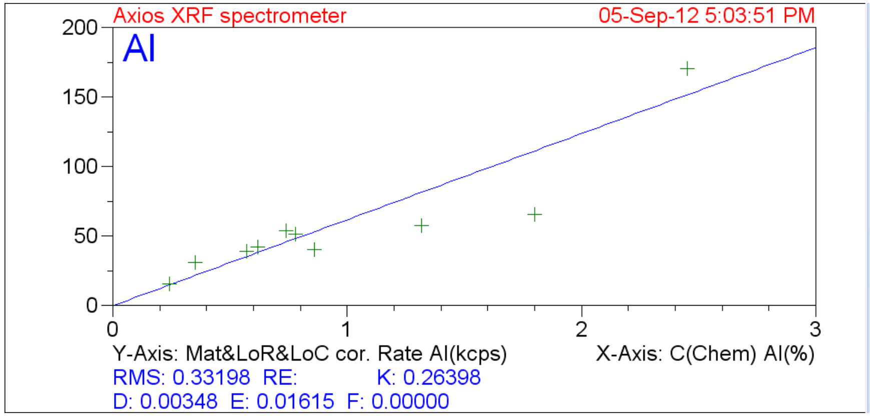
Calibrations on pressed powders (Axios^{mAX} 4kW)

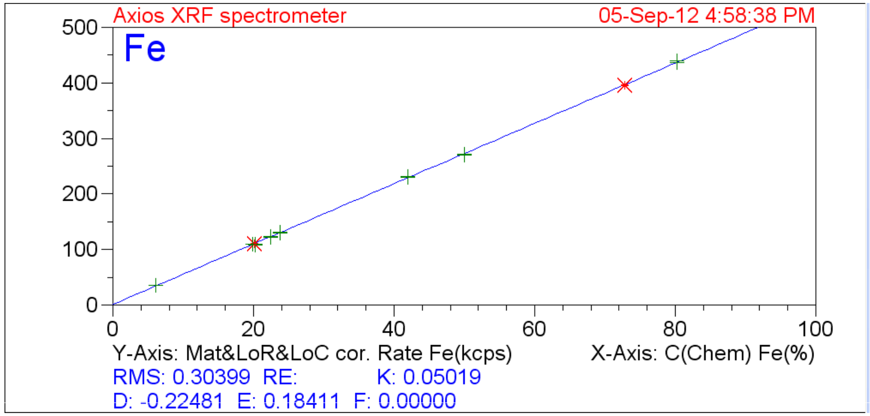


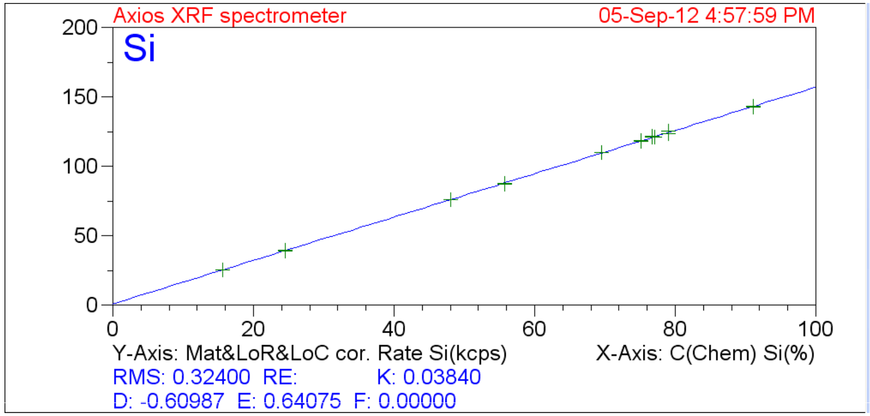


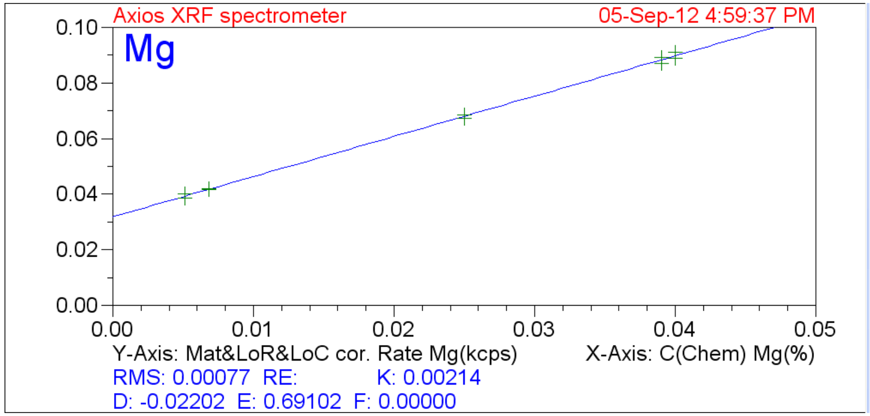


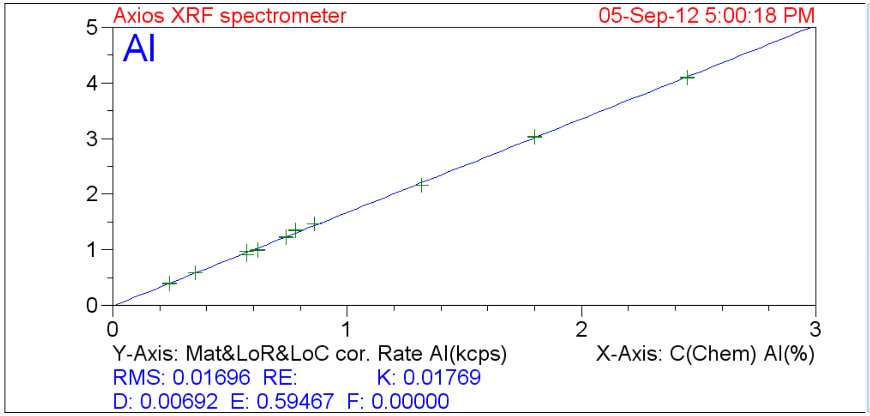


Calibrations on Fused beads: (Axios^{mAX} 4kW)









Calibration: Fused beads vs pressed powder (Axios 4kW)

	Min (%)	Max (%)	RMS beads (%)	RMS Pressed powder (%)
Al	0.21	2.45	0.0170	0.3320
As	0.0012	0.0015		
Ba*	0.0043	0.126	0.0049	0.0008
Ca	0.042	2.47	0.0151	0.0575
Co	0.0031	0.0047		
Cr	0.0044	34.11	0.0038	0.0330
Cu	0.01	0.29	0.0101	0.0044
Fe	6.15	80.2	0.3040	1.6020
Mg	0.0051	0.04	0.0008	0.0039
Mn	0.04	31.53	0.0044	0.0278

	Min (%)	Max (%)	RMS beads (%)	RMS Pressed powder (%)
Mo	0.0013	0.011		
Ni	0.0028	0.28	0.0032	0.0024
P	0.0093	0.043	0.0013	0.0019
S	0.0012	0.006		
Si	15.6	91.11	0.3240	2.9999
Sn	0.0003	0.0004		
Sr	0.014	0.014		
Ti	0.018	0.121	0.0031	0.0086
V	0.0024	0.011		
Zr	0.082	0.082		

* Ba measured on L-line (FB) resp. K-line (PP)

Fused beads vs. pressed powder

- Average sensitivity (kcps/%) pressed powder = 30 * fused beads.
  - Measurement time Axios 1kW = 14 minutes on fused beads still acceptable
  - Much longer sample preparation time for beads and
  - Higher (investment and running) costs for bead sample preparation

BUT

- Accuracy up to 20! times better in fused beads due to absence of severe metallurgical effects.
  - Pressed powder analysis only for fixed metallurgy and trace element analysis, production control rather than incoming goods.
  - Higher costs are easily paid back by the higher accuracy that is obtained.

Ferro-alloy producer: 40 tons weight lost between incoming and outgoing material analysis in 1 year time,

A loss of 1 M€ !!

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How reproducible is the analysis?

- Bead preparation error versus measurement error
  - Prepare 1 bead 10 times and measure each bead once
  - Take one bead and measure it 10 times
  - Compare the RMS values

Fused bead reproducibility (Axios 1kW)

		Fe	Si	Mg	Al	Ca
		(%)	(%)	(%)	(%)	(%)
Same bead 10*	Average	19.046	76.996	0.049	1.728	0.461
Same bead 10*	Stdev	0.038	0.039	0.003	0.011	0.009
10 beads 1*	Average	19.147	76.883	0.048	1.730	0.461
10 beads 1*	Stdev	0.114	0.110	0.003	0.017	0.009

- Outstanding sample preparation reproducibility!
- 1kW Axios suffices for major elements, but at low concentration the measurement error is dominant.

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Comparison Axios^{mAX} 4kW and Axios 1kW

		Axios^{mAX} 4 kW	Axios 1 kW
	Average	Stdev	Stdev
Mg (%)	0.053	0.001	0.003
Al (%)	1.723	0.007	0.017
Si (%)	76.999	0.083	0.110
P (%)	0.041	0.001	0.002
S (%)	0.003	0.000	0.000
Ca (%)	0.458	0.006	0.009
Ti (%)	0.166	0.003	0.007
V (%)	0.010	0.001	0.008
Cr (%)	0.094	0.002	0.004
Mn (%)	1.130	0.004	0.008
Fe (%)	19.197	0.077	0.114
Co (%)	0.004	0.000	0.000
Ni (%)	0.020	0.001	0.001
Cu (%)	0.040	0.002	0.003
As (%)	0.001	0.000	0.000
Sr (%)	0.007	0.000	0.001
Zr (%)	0.025	0.001	0.001
Mo (%)	0.009	0.002	0.006
Sn (%)	0.000	0.000	
Ba (%)	0.021	0.007	0.011

Comparison made on 10 different beads: sample preparation error and measurement error are reflected at the same time.

(Total error)

Comparison Axios^{mAX} 4kW and Axios 1kW: LLD

	1 kW	4 kW
Mg	55.3	27.3
Al	22.4	8.8
Si	96.1	59.8
P	8.6	4.1
S		
Ca	33.8	17.6
Ti	45.4	21.1
V		
Cr	31.7	16.8
Mn	34.7	16.4
Fe	47.3	26.9
Co		
Ni	12.2	6.4
Cu	13.0	6.8
As		0.5
Sr	4.7	2.3
Zr	5.6	2.5
Mo		
Ba	83.6	47.4

Fused beads, measured with collimator mask = 27mm, LLD 100s (ppm)

Comparison Axios^{mAX} 4kW and Axios 1kW

- Axios 1kW can do same as Axios^{mAX} 4kW
  - But the measurement time of Axios^{mAX} is 4* shorter
- Axios 4kW can partly compensate for loss in sensitivity (measurement time) by switching from pressed powder to fused bead.
- Very acceptable measurement times (14 minutes vs 3½ minutes).

Comparison FB and PP : LLD (Axios^{mAX} 4kW)

Fused beads, versus pressed powders, both measured at 27mm

	Bead	Powder
Mg	27.3	1.5
Al	8.8	1.2
Si	59.8	
P	4.1	
S		
Ca	17.6	0.6
Ti	21.1	1.4
V		
Cr	16.8	3.1
Mn	16.4	3.1
Fe	26.9	
Co		
Ni	6.4	1.5
Cu	6.8	1.3
As		
Sr	2.3	0.3
Zr	2.5	0.3
Mo		1.4
Ba	47.4	3.1

LLD (ppm), 100s

Accuracy: Some standards measured (Axios 1kW)

		Certified	Bead 1	Bead 2
Mg	(%)		0.017	0.018
Al	(%)	1.96	1.88	1.89
Si	(%)	77.7	78.24	78.24
P	(%)	0.025	0.028	0.027
S	(%)	0.0023	0.000	0.004
Ca	(%)	0.4	0.388	0.384
Ti	(%)	0.121	0.142	0.143
V	(%)		0.003	0.009
Cr	(%)	0.095	0.094	0.094
Mn	(%)	0.122	0.122	0.119
Fe	(%)	**18.926**	18.94	18.92

		Certified	Bead 1	Bead 2
Co	(%)		0.004	0.004
Ni	(%)		0.052	0.048
Cu	(%)		0.055	0.049
As	(%)		0.001	0.002
Sr	(%)		0.008	0.008
Zr	(%)		0.010	0.009
Mo	(%)		0.006	0.002
Ba	(%)		0.015	0.027
Mn	(%)	0.122	0.122	0.119
Cr	(%)	0.095	0.094	0.094

Standard F3/3 (not included in calibration), NF 1.003

Accuracy: Some standards measured (Axios 1kW)

		Certified	Bead 1	Bead 2
Mg	(%)	0.016	0.012	0.014
Al	(%)	0.21	0.206	0.203
Si	(%)	44.7	44.97	44.84
P	(%)	0.018	0.024	0.020
S	(%)	0.006	0.000	0.000
Ca	(%)	0.16	0.135	0.138
Ti	(%)	0.018	0.049	0.048
V	(%)		0.000	0.000
Cr	(%)	0.046	0.045	0.044
Mn	(%)	0.283	0.285	0.288
Fe	(%)	54.1	54.16	54.30

		Certified	Bead 1	Bead 2
Co	(%)		0.004	0.004
Ni	(%)	0.022	0.024	0.021
Cu	(%)	0.066	0.064	0.067
As	(%)		0.002	0.001
Sr	(%)		0.001	0.001
Zr	(%)		0.006	0.003
Mo	(%)		0.000	0.000
Ba	(%)		0.016	0.021
Mn	(%)	0.283	0.285	0.288
Cr	(%)	0.046	0.045	0.044

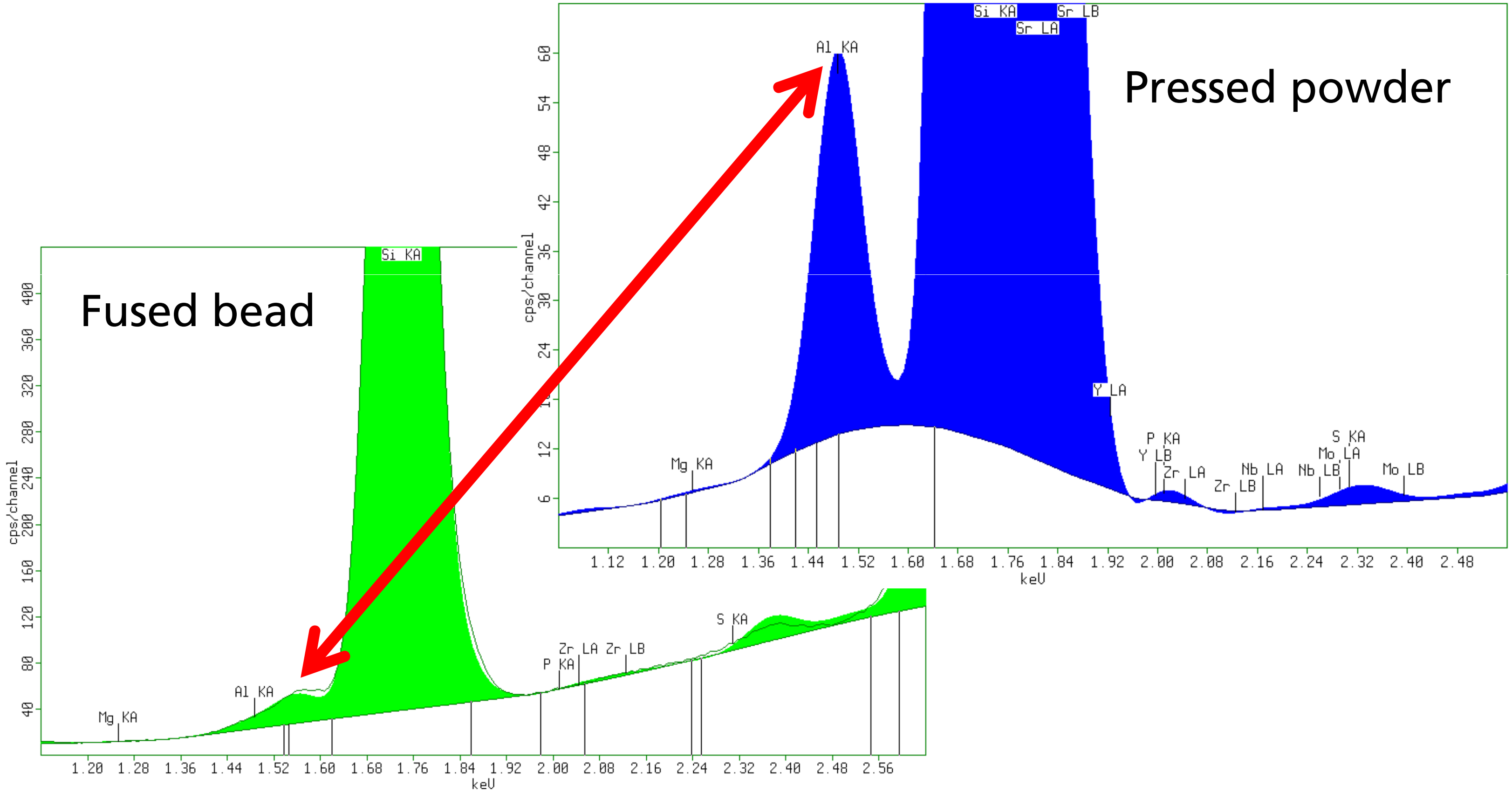
Standard IPT70 (not included in calibration): NF 0.997

Some more notes

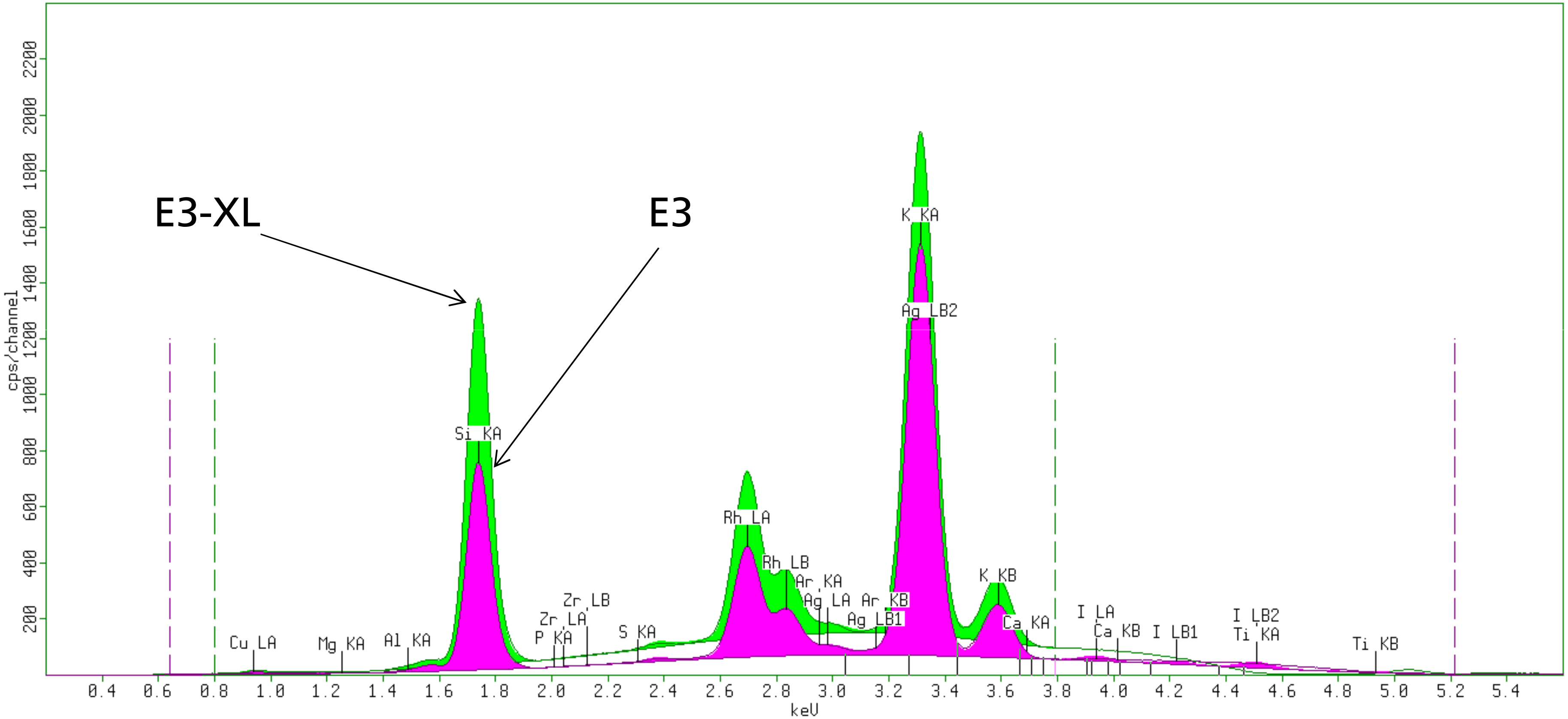
- Measurement times/element were not optimized yet.
- Measurement times at 37mm (instead of 27mm)
  - 9 minutes on Axios 1kW
  - 2½ minutes on Axios^{mAX} 4kW
- Combined analysis fused bead/pressed powder possible, in order to reduce total measurement time and optimize majors as well as traces.
- Increased accuracy with CNO analyzer results can be included in calculations. (C not homogeneous)

But what about ED-XRF?

- Pressed powder versus Fused bead

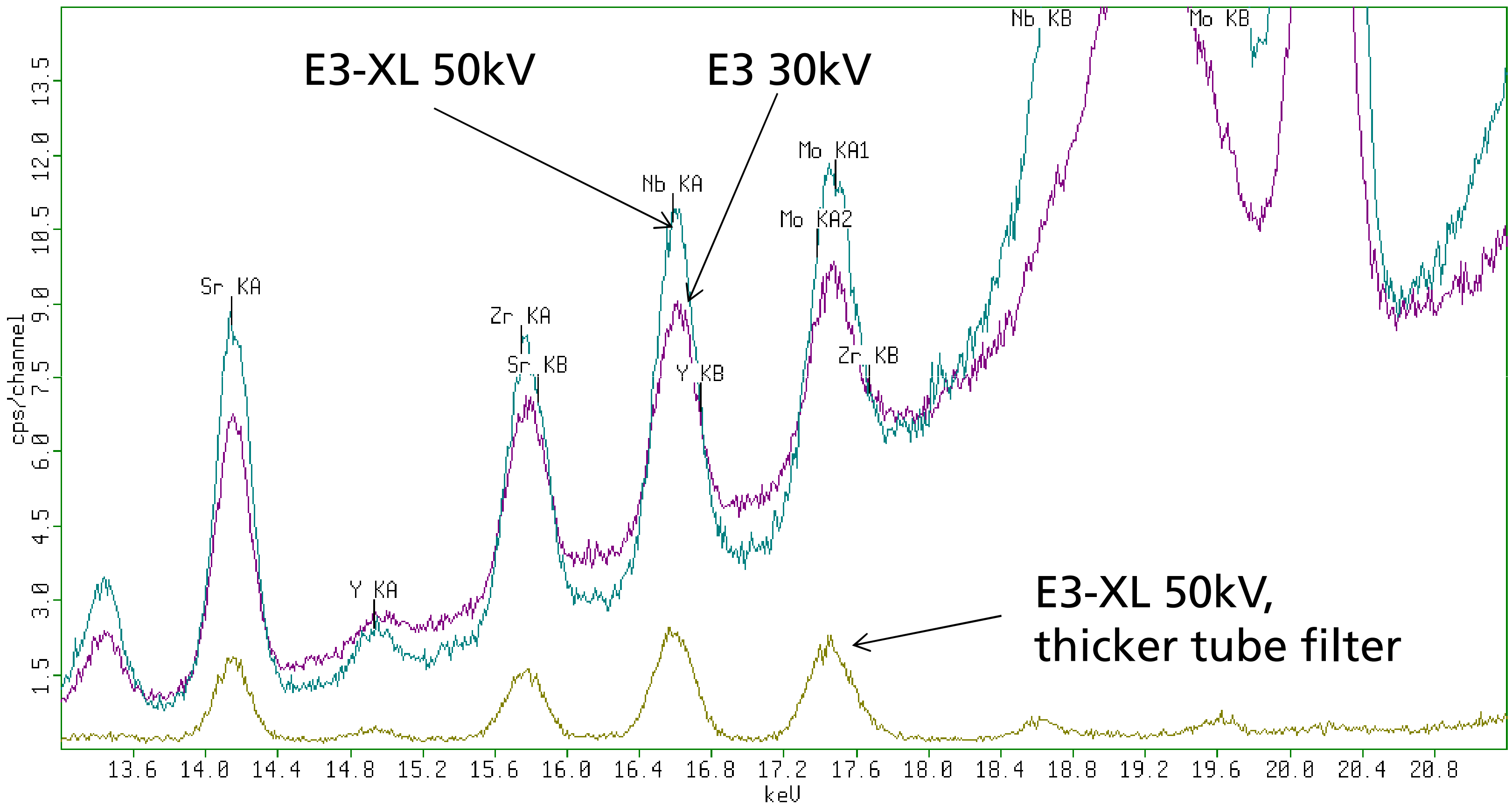


Epsilon 3 (9W) versus Epsilon 3XL (15W)



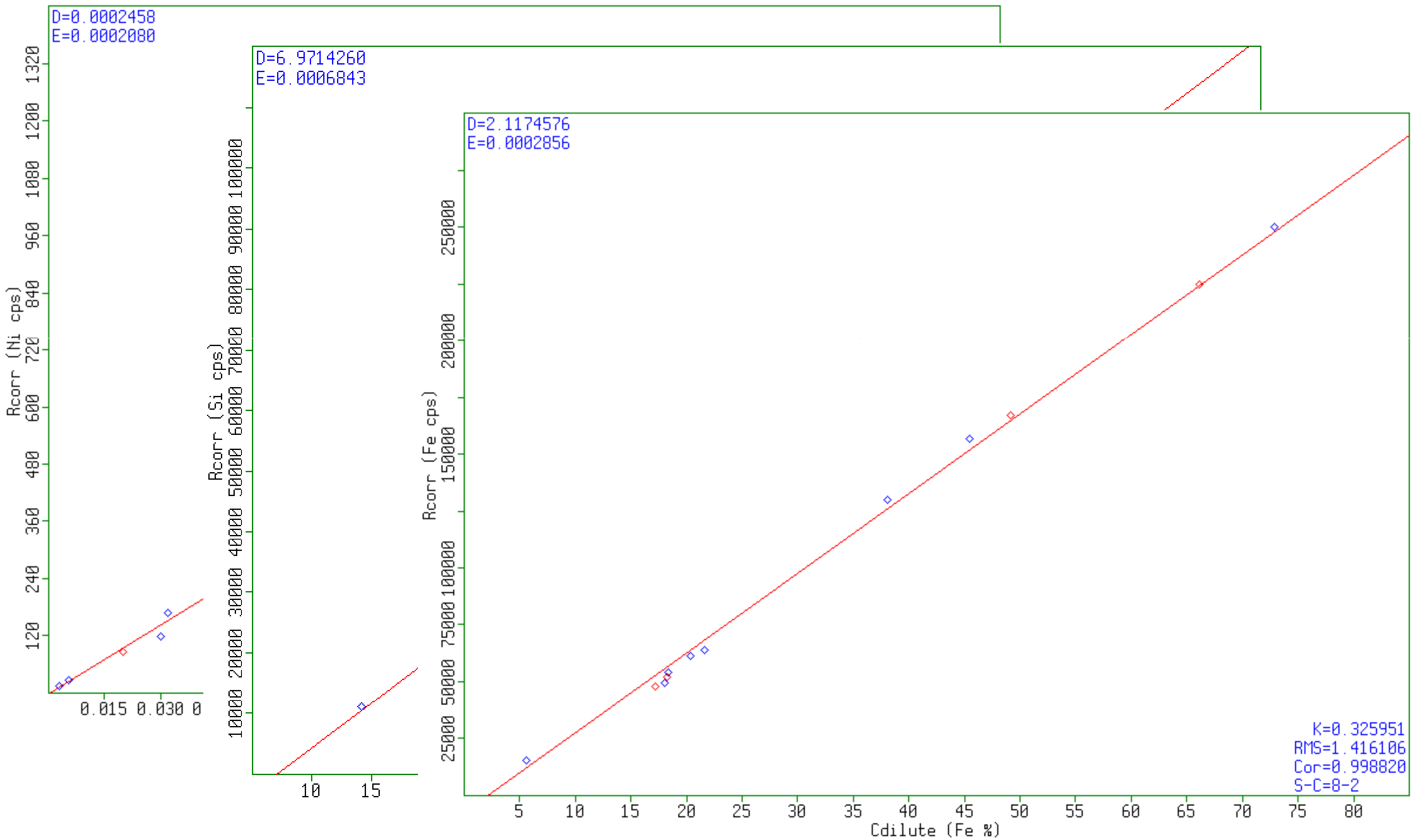
- Clear difference in measurement time

Epsilon 3 (30kV, 9W) versus Epsilon 3XL (50kW, 15W)



- Lower Bg and higher sensitivity E3-XL

Calibration E3-PP



Some data

- Epsilon 3: 480s measurement time
  - Elements covered : Al Ca Cr Cu Fe Mg Mn Ni P S Si Ti
  - Helium required for light elements
  - Suitable for fast production control

    with regular check (using fused beads) on correctness of calibration for the samples analyzed.

Reproducibility E3-XL (PP)

	Conc	Unit
Mg	0.021 +/- 0.006	%
Al	0.523 +/- 0.004	%
Si	79.070 +/- 0.016	%
P	0.022 +/- 0.001	%
S	0.004 +/- 0.0004	%
Ca	0.289 +/- 0.002	%
Ti	0.135 +/- 0.0008	%
Cr	0.0744 +/- 0.0027	%
Mn	0.161 +/- 0.002	%
Fe	19.637 +/- 0.012	%
Ni	0.024 +/- 0.0005	%
Cu	0.022 +/- 0.0006	%
Zr	0.018 +/- 0.000096	%

Normalized results

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Fusion summary

- Only a few recipes to cover:
  - FeSi, FeSiCr, FeSiMn, SiCa
  - Low carbon FeCr, FeMn, high carbon FeCr, FeTi, FeNb, SiMn, FeNb, FeMo …….
  - Geological materials
  - Cement, Lime stone, Sand, Clay, …
  - Many others
- Cookbook delivered with Eagon 2

Before the conclusion(s)

- Special thanks to Alexander Komelkov for the vast amount of work he invested.

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Conclusion

- Fused beads are the way to go for end control
  - Higher costs easily paid back by increased accuracy.
  - Measurement times are not the bottle neck anymore.
  - High sensitivity of a WD-XRF required to cover all elements.
- Pressed powders only work for own production control due to metallurgical effects
  - But is a fast and cheap method that can also be carried out on a cost-effective Epsilon 3

End conclusion

Replace confusion with fusion

By replacing Pressed Powder with fusion

as cheap, fast and accurate is just an illusion