Considerations for optimizing Agronomic analysis by ICP OES

Dion Tsourides, Director ICP, SPECTRO Analytical Instruments, Mahwah NJ

Agenda

- 1. Hardware : Optical / Plasma Orientation (Plasma Viewing)
- 2. Advances in Plasma Torch Alignment : DSOI
- 3. Experimental, Calibration Strategies/Results (Soils, Plant Tissues, Feeds and Fertilizers –P2O5)
- 4. Accessories/Options

The Sensitivity Dilemma

- Since the beginning of ICP-OES engineers strive to improve its sensitivity
  - *Innovative sampling techniques improving the performance were developed.*

- But: every advantage seems to comes at a price. Apparently, no possibility to improve the sensitivity without creating a disadvantage!

- Axial technique for most industrial applications not an option
  - *Efforts were made to improve light collection and transfer*

- With DIRECT RADIAL VIEW, the radial sensitivity of ICP OES systems can be increased by a factor of two, BUT

There is POTENTIAL for more – because:

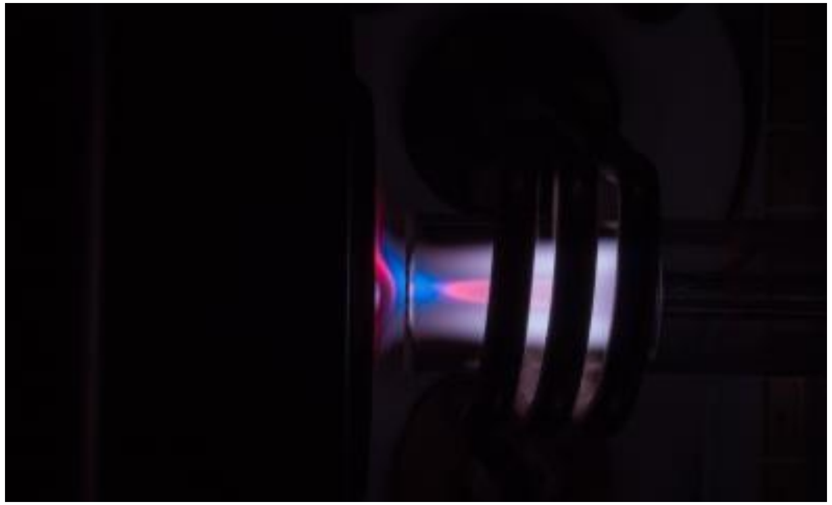
➔ **The more light that is captured, the higher the light transfer, the higher the sensitivity gain.**

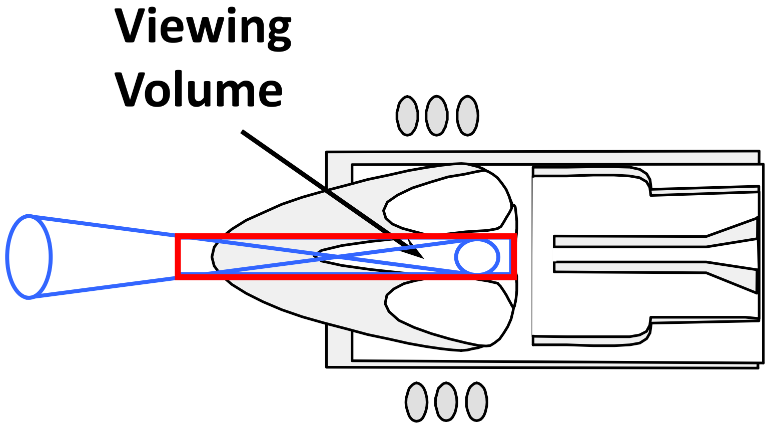
Axial Plasma Observation – Pros and Cons

- Axial plasma observation improves the sensitivity by sampling the emitted light from the entire excitation channel

- However, it also suffers from stronger influences, since all phenomena present in the excitation are viewed

- Pros and Cons:
  - *High sensitivity*
  - *Stronger matrix effects i.e. recombination, EIE*
  - *Less suitable for high TDS and applications with organic solutions*



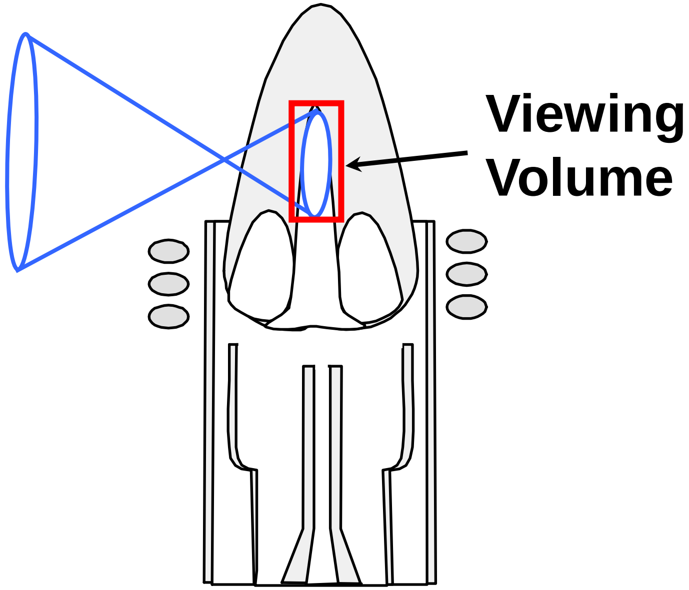


Radial Plasma Observation – The choice for high stability, high TDS and organic solutions

- Radial plasma observation provides lower sensitivity since the central channel is only partially view

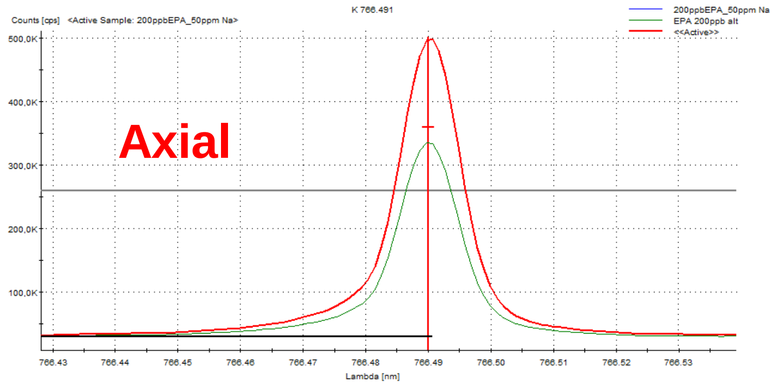
- However, it provides high stability and freedom from matrix effects since the affected zones in the plasma are blanked out

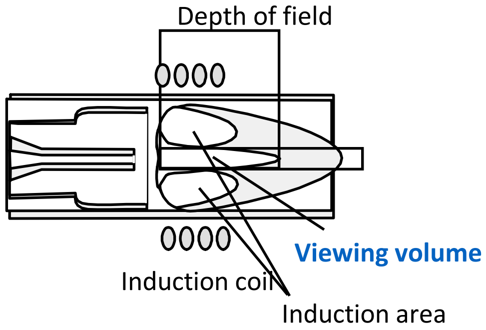
- Pros and Cons:
  - - *High stability*
  - - *High matrix tolerance*
  - - *High linear dynamic range*
  - - *Freedom from matrix effects*
  - - *Lower sensitivity*



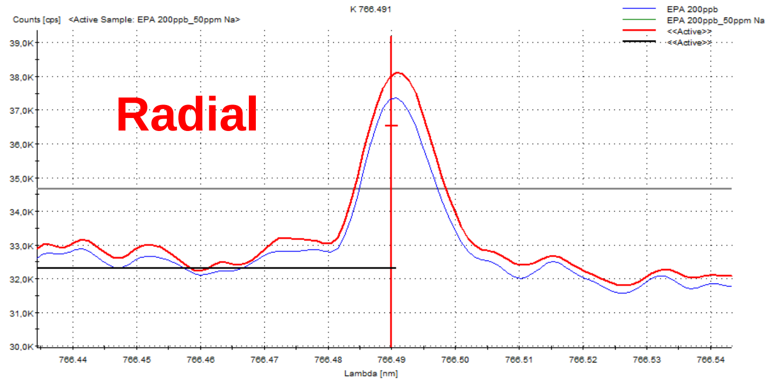
Axial Plasma Observation – Easy ionizable element effect

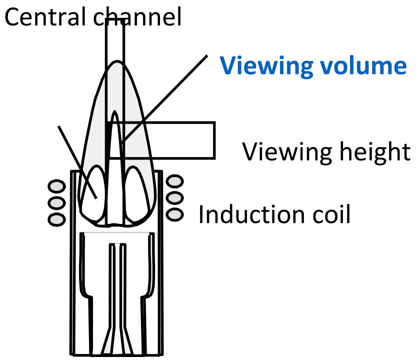
Influence of 50 ppm Sodium on Potassium using axial and radial plasma observation





Axial: Strong Effect

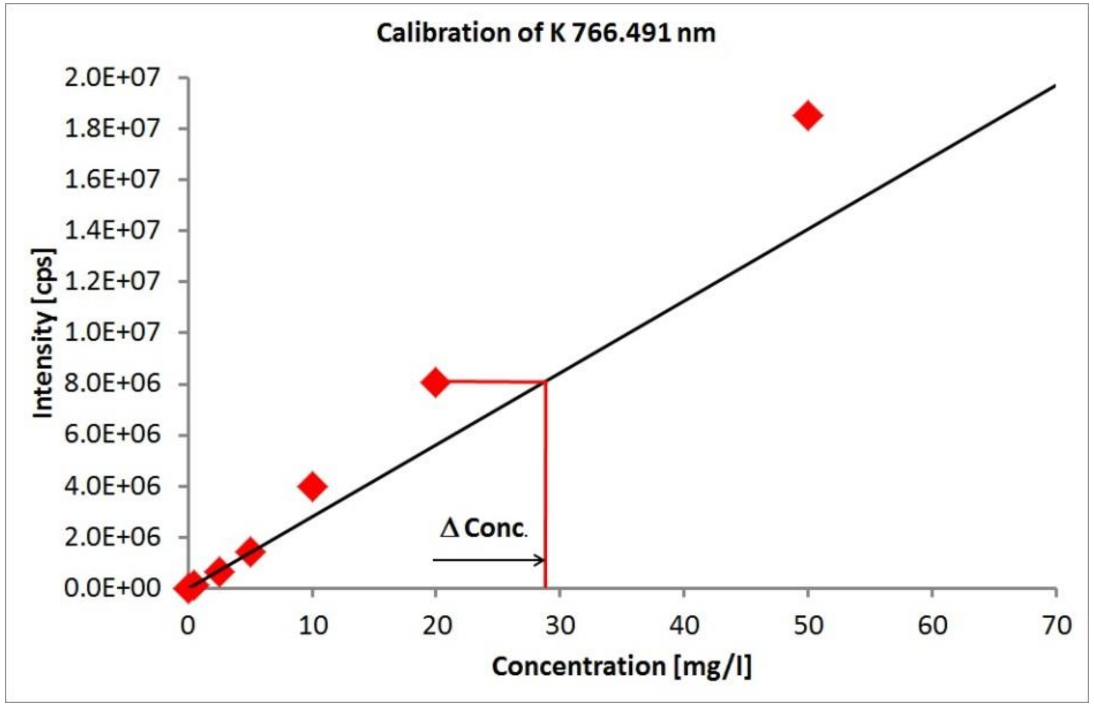




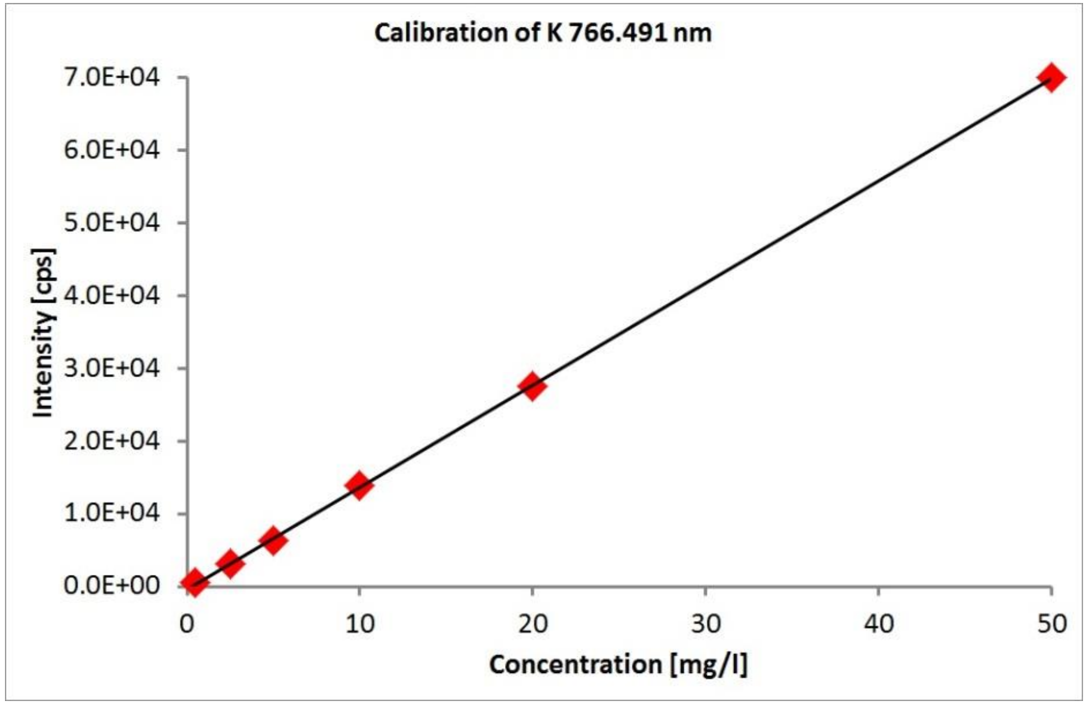
Radial: Effect visible, but greatly reduced

Dual- Axial-Radial Analytical Performance: Linearity, K 766.491 nm

Axial mode



Radial mode



- For alkali elements linearity drastically reduced
- Linearity: R^2=0.99
- Rel. deviation of the standards up to 25%

- Linearity, R^2=0.99998
- Rel. deviation of the standards < 5%

Dual Plasma Observation Axial-Radial

- Used to reduce matrix interferences, i.e. for the accurate determination of alkali elements in the presence of a varying alkali/earth alkali matrix (i.e. mineral waters) with axial ICP-OES
  - ➔ *The EIE (Easy Ionizable Element = EXTREMELY POOR accuracy using AXIAL for Grp I (K, Na, Li)), therefore effect is greatly reduced since the alkali/earth alkali elements are measured in radial mode*
  - ➔ *No need for the use of an ionization buffer (Cs or Li)*
    - ➔ Cost reduction, reduced risk of contamination
  - ➔ *Toxic elements can still be determined with great sensitivity since they are measured in axial mode*
  - ➔ *Dynamic range and linearity can be further expanded*
  - ➔ ***BUT......there are compromises in terms of speed, maintenance, sensitivity and flexibility!***

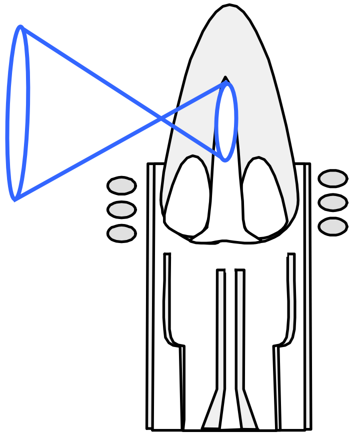
Torch Alignment NOT Plasma Viewing!

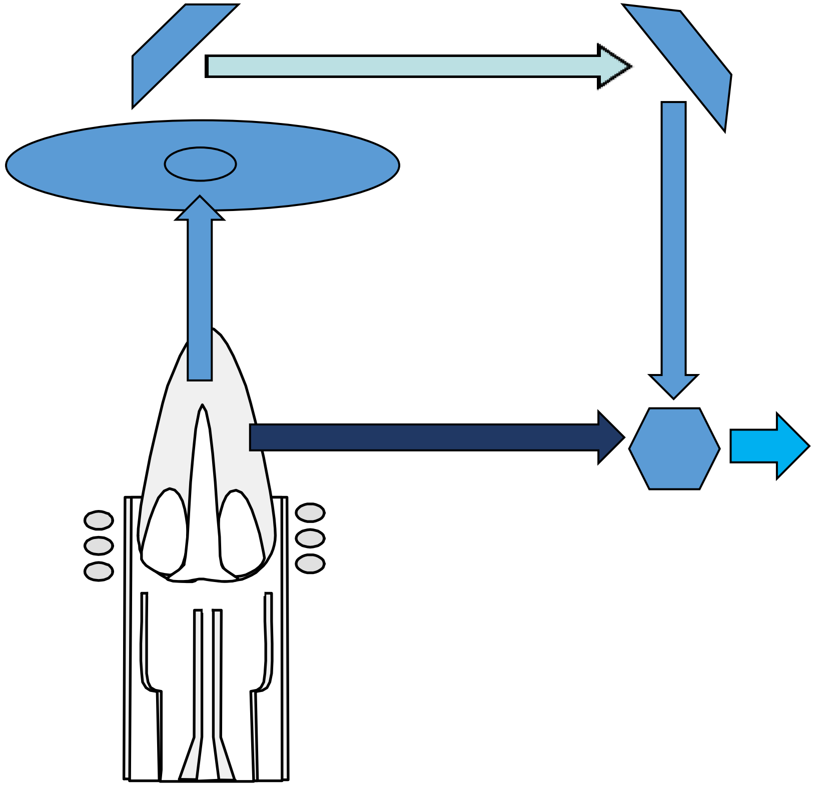
- A radially MOUNTED TORCH is NOT necessarily A RADIAL VIEWED TORCH!
- An Axially MOUNTED TORCH (horizontal) can be radially viewed.
- Vertical and Horizontally mounted torches ARE NOT what defines VIEWING configuration.
- Confused??? You should be...
- How a torch is mounted, is a PHYSICAL trait that MAY or MAY NOT (!) have perceived and practical benefits. (True Radial versus a Radially mounted Axial viewed torch)...
- You must know and UNDERSTAND your hardware to configure it best for your application. Watch the funny man now try and visualize this for you...

True Direct Viewing vs Periscope Viewing

TRUE RADIAL SYSTEM versus a DUAL VIEW SYSTEM in a VERTICAL CONFIGURATION, is sensitivity effected?

TRUE RADIAL (no mirrors, periscope, no interfaces/cones)





Dual View, Twin Interface, DSDV, etc.

“Dual View” – really the best of both worlds?

- **Dual View serves a purpose!**
  - *Without any doubt DV is well suited for EPA work, where sensitivity and the elimination of matrix interferences need to be combined in one measurement...*

But is it always the best solution?!

- Only one view uses the direct light path, the other is compromised

➔ *Sensitivity loss due to additional optical components*

➔ Further compromised if interference filters are used to combine the views

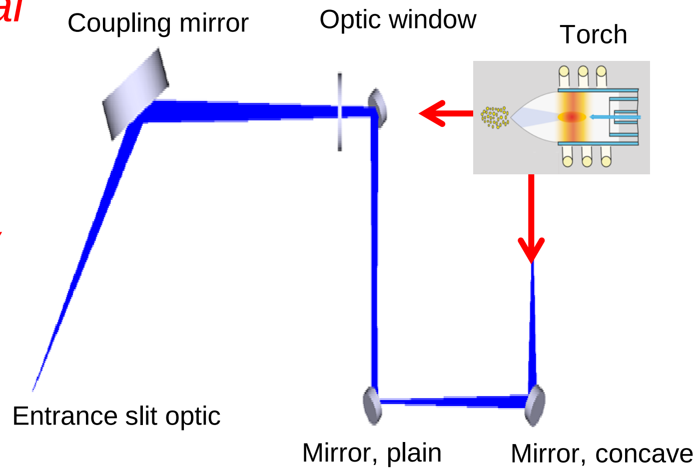
➔ *Sensitivity loss in the UV since the light path cannot be purged effectively*

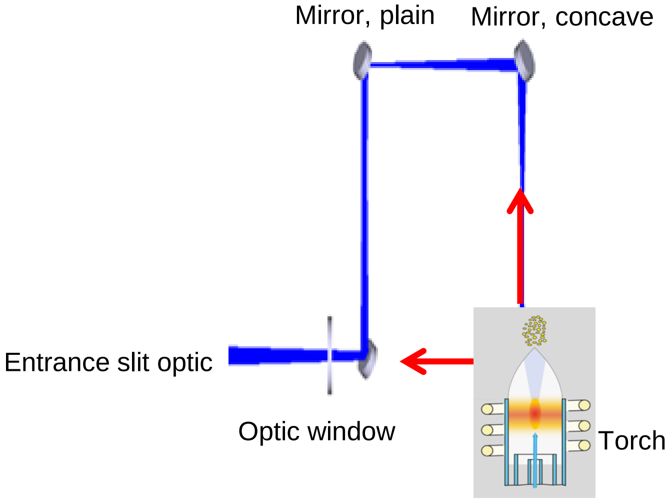
➔ *Requires two measurements (speed loss)*

➔ *Contamination risk if positioned above the plasma*

➔ *High thermal stress if positioned above the plasma*

➔ *Lose the ability to measure VUV (Al 167, Pb 168, P 177/178, S 166/180/182, etc) in some systems!*

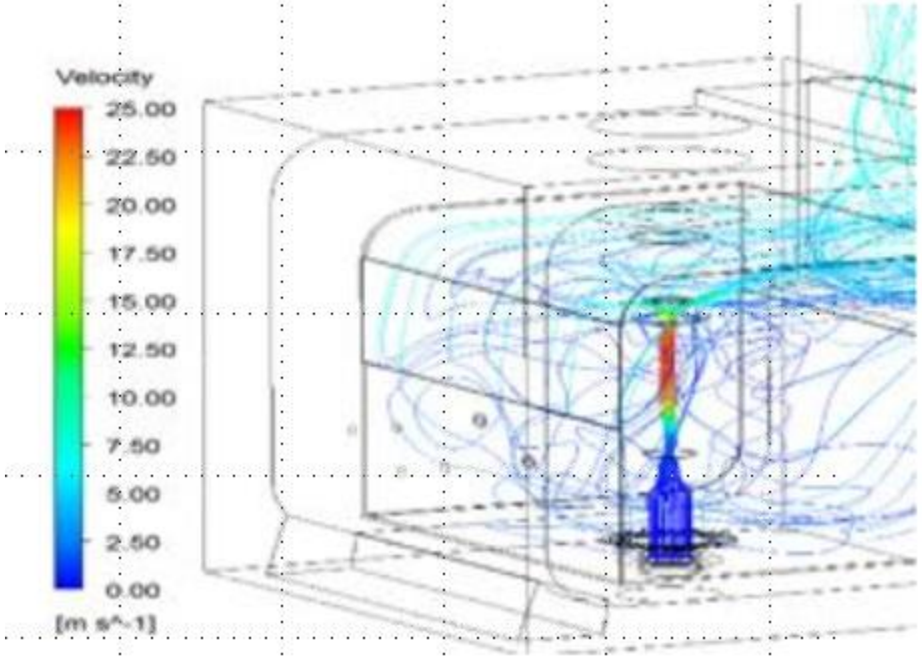




Vertically mounted Axial View ICP-OES Interface – (Echelle)

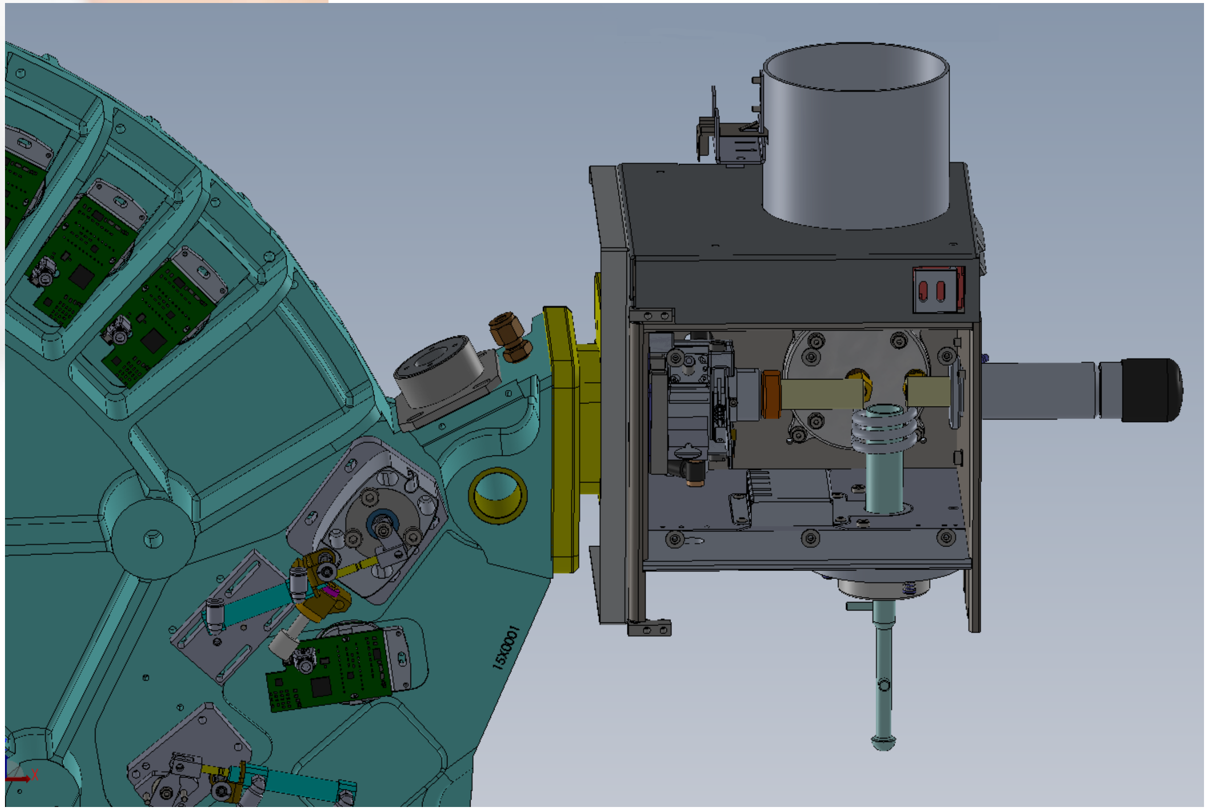
All VMAV systems have the extraction on the right upper side of the torch box

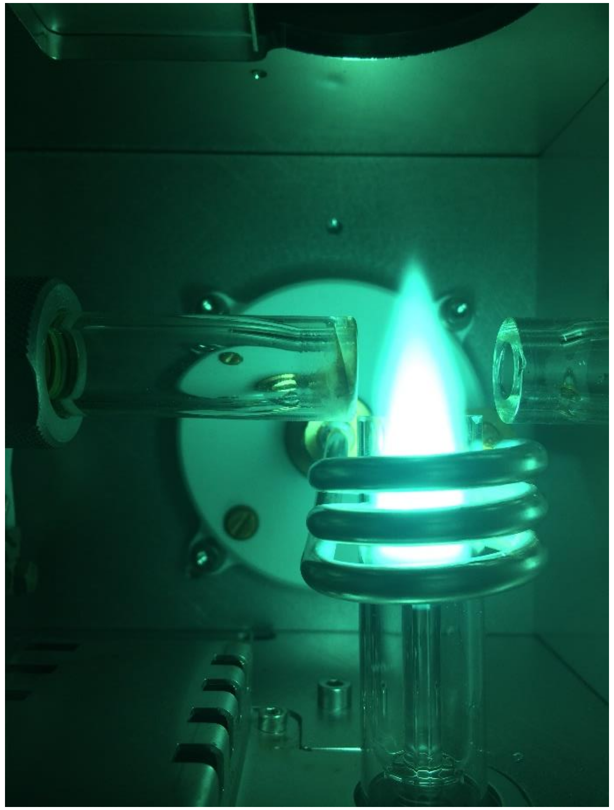
- *It is clear that the axial interface reflects the heat and all sample matter and contaminates the torch box.*
- ***This affects VUV performance (O2 ingress thru turbulence or use of an "air knife")***
- *The axial view is compromised because of the periscope (i.e. S 166/180/182, Halogens, etc.)*



Radial View and Axial/Dual View is there a better option?

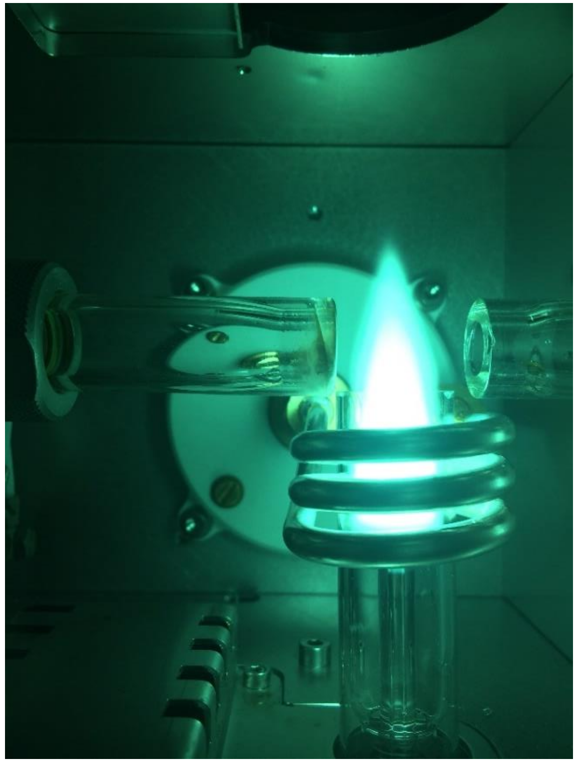
Dual Side-On Interface : A superior option to non-EPA DV analysis

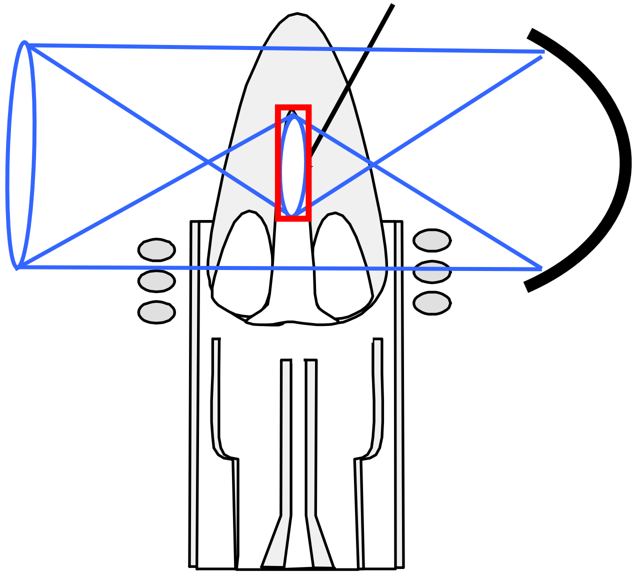




Dual Side-On Plasma Observation – How does it work?

- Since the light emitted into two directions is transferred into the optical system the sensitivity is in average improved by a factor of two
- In addition, the vertical torch provides high stability and freedom from matrix effects since the affected zones in the plasma are blanked out



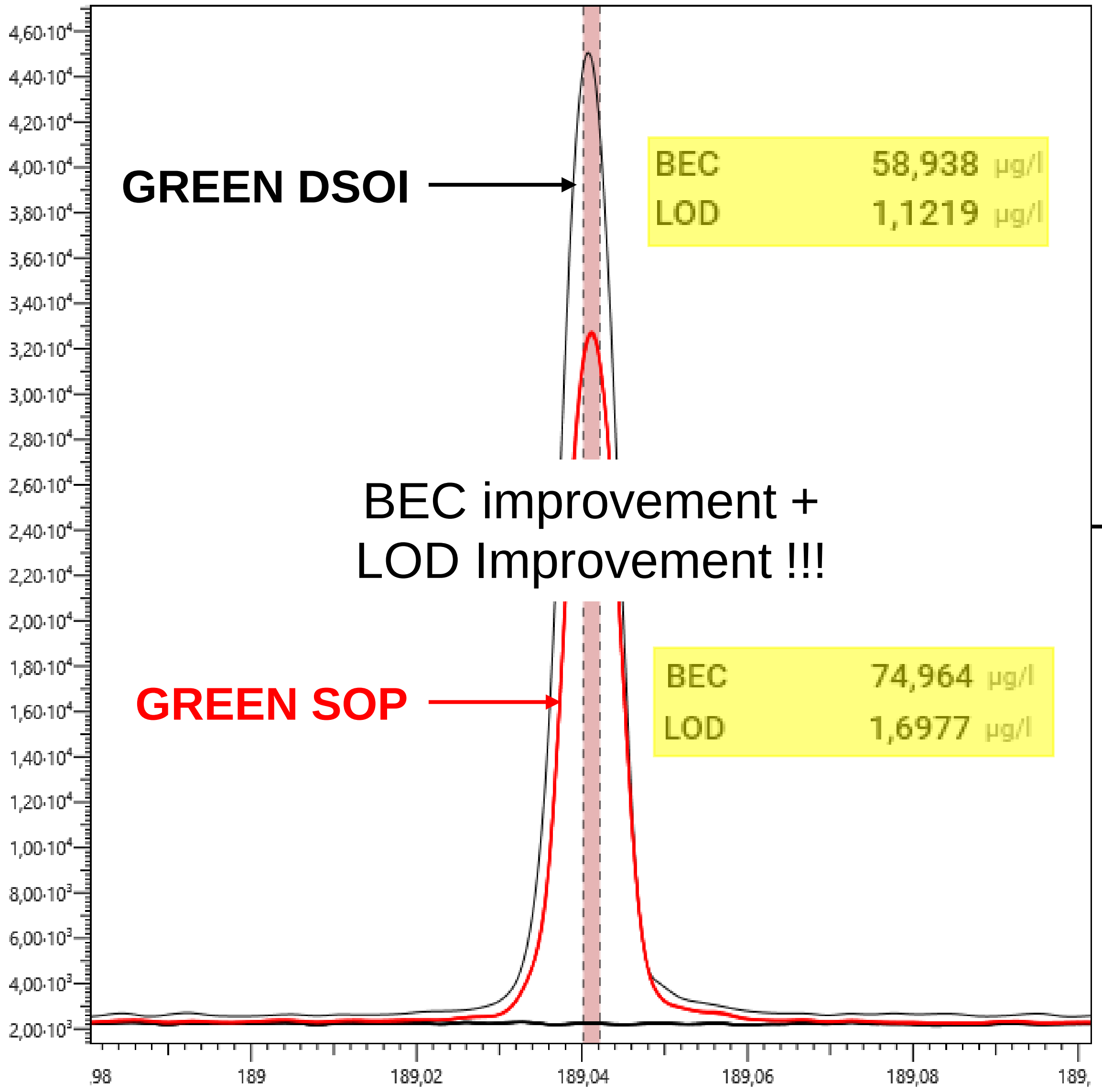


- Pros and Cons:
  - *High stability*
  - *High matrix tolerance*
  - *High linear dynamic range*
  - *Freedom from matrix effects*
  - *All with one measurement*
  - *Only slightly lower sensitivity compared to a direct light path axial view*

But

➔ ***Offers greater/equivalent sensitivity as Echelle based, vertical torch dual view systems, since there are no additional reflect surfaces in the primary light path***

How is the Sensitivity Gained? - Arsenic



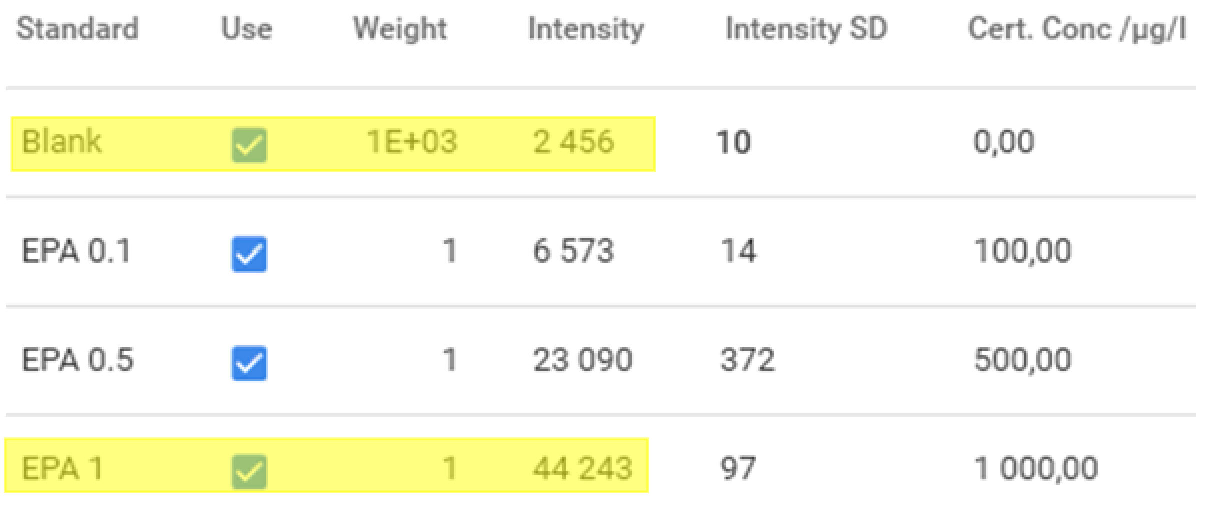
GREEN DSOI

BEC 58,938 µg/l
LOD 1,1219 µg/l

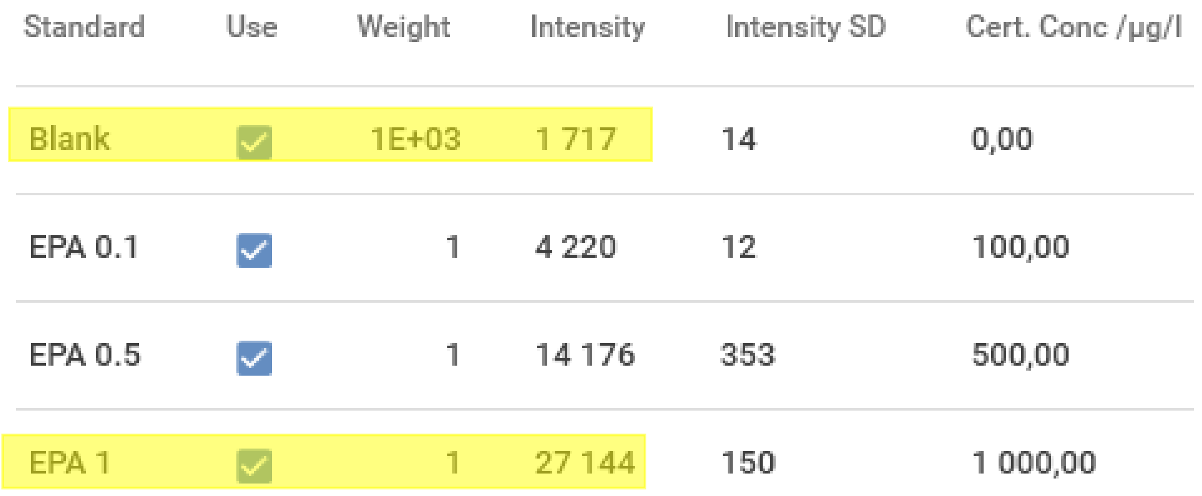
BEC improvement +
LOD Improvement !!!

GREEN SOP

BEC 74,964 µg/l
LOD 1,6977 µg/l

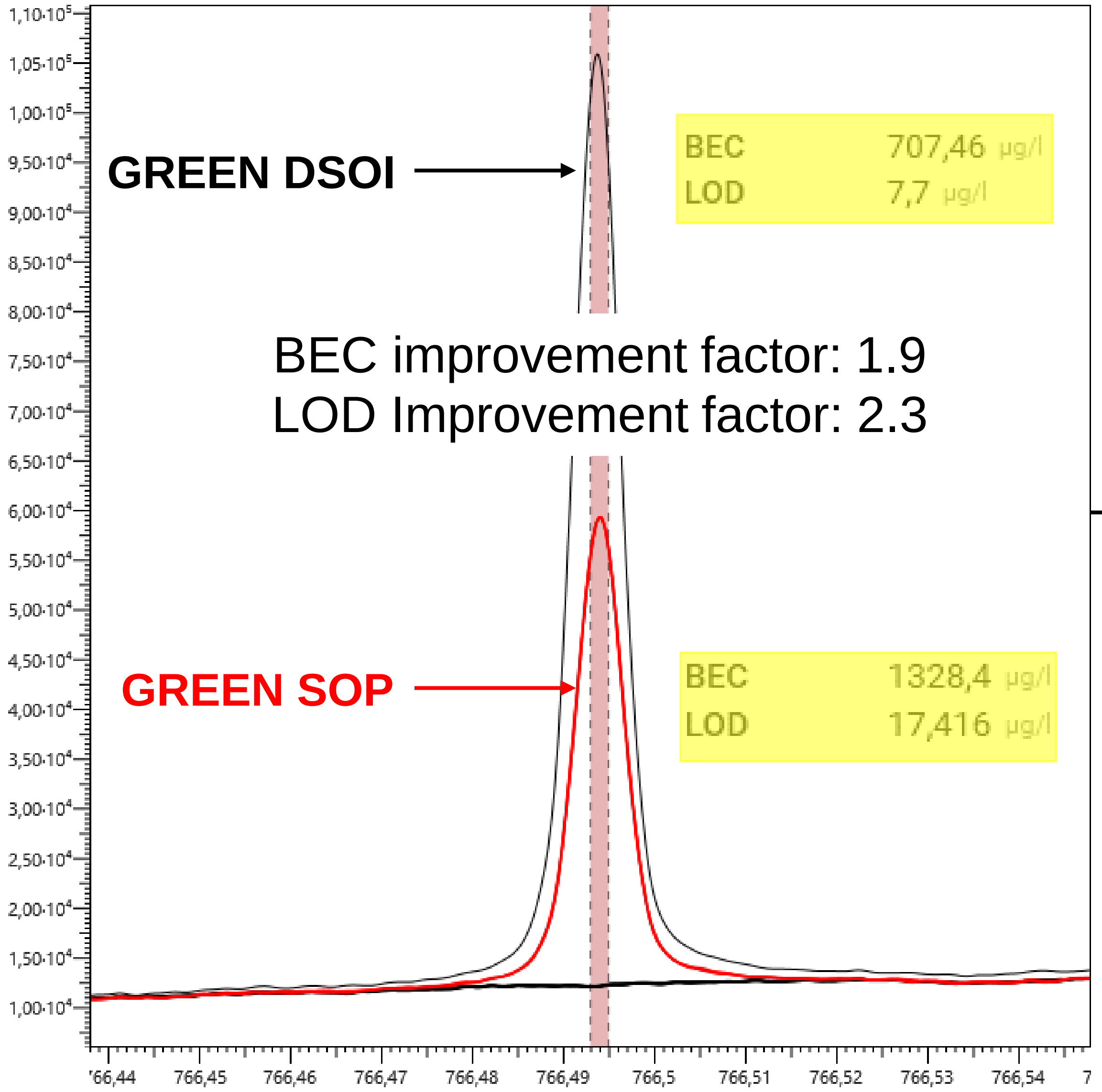


Standard	Use	Weight	Intensity	Intensity SD	Cert. Conc /µg/l
Blank	☑	1E+03	2 456	10	0,00
EPA 0.1	☑	1	6 573	14	100,00
EPA 0.5	☑	1	23 090	372	500,00
EPA 1	☑	1	44 243	97	1 000,00



Standard	Use	Weight	Intensity	Intensity SD	Cert. Conc /µg/l
Blank	☑	1E+03	1 717	14	0,00
EPA 0.1	☑	1	4 220	12	100,00
EPA 0.5	☑	1	14 176	353	500,00
EPA 1	☑	1	27 144	150	1 000,00

How is the Sensitivity Gained? - Potassium



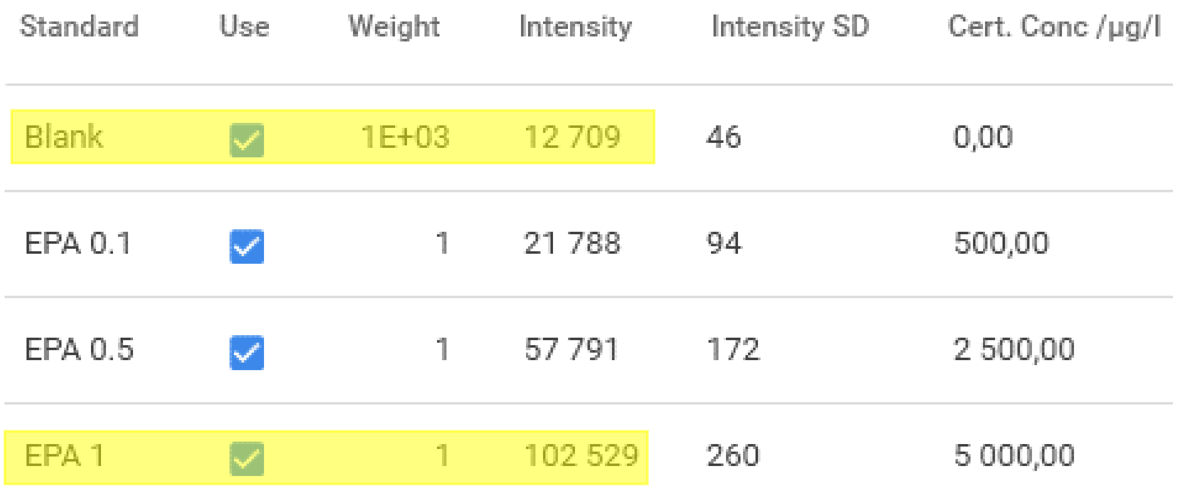
GREEN DSOI →

BEC 707,46 µg/l
LOD 7,7 µg/l

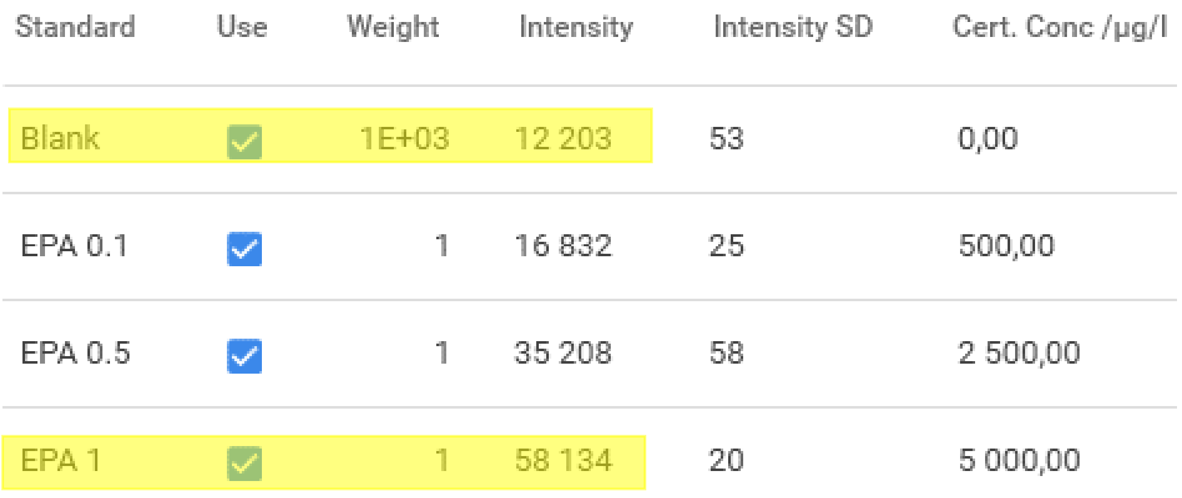
BEC improvement factor: 1.9
LOD Improvement factor: 2.3

GREEN SOP →

BEC 1328,4 µg/l
LOD 17,416 µg/l



Standard	Use	Weight	Intensity	Intensity SD	Cert. Conc /µg/l
Blank	☑	1E+03	12 709	46	0,00
EPA 0.1	☑	1	21 788	94	500,00
EPA 0.5	☑	1	57 791	172	2 500,00
EPA 1	☑	1	102 529	260	5 000,00



Standard	Use	Weight	Intensity	Intensity SD	Cert. Conc /µg/l
Blank	☑	1E+03	12 203	53	0,00
EPA 0.1	☑	1	16 832	25	500,00
EPA 0.5	☑	1	35 208	58	2 500,00
EPA 1	☑	1	58 134	20	5 000,00

Sensitivity Comparison Dual versus Single Side-On

		Single Side-On SOP	Dual Side-On DSOI	SOP/DSOI
	nm	LOD [µg/L]	LOD [µg/L]	Factor
Ag	328.068	1.32	0.39	3.42
Al	167.078	0.14	0.03	4.39
As	189.042	1.65	1.31	1.26
As	193.759	2.67	1.99	1.34
Ba	455.404	0.07	0.03	2.14
Be	313.042	0.04	0.02	2.58
Ca	396.847	0.06	0.02	3.31
Ca	315.887	3.13	1.17	2.68
Cd	214.438	0.10	0.08	1.22
Cd	226.502	0.16	0.11	1.47
Co	228.615	0.32	0.20	1.54
Cr	267.716	0.30	0.27	1.09
Cu	324.754	0.74	0.29	2.60
Fe	259.941	0.18	0.22	0.83
Hg	194.227	1.02	0.56	1.81
K	766.491	50.63	8.45	5.99
Li	670.784	1.07	0.28	3.86
Mg	279.553	0.06	0.02	2.82
Mg	280.270	0.06	0.02	3.26
Mn	257.611	0.05	0.04	1.36
Mo	202.095	0.28	0.24	1.20
Na	589.592	6.01	2.01	2.98
P	177.495	1.55	0.95	1.63
P	178.287	1.99	1.37	1.45
Pb	220.351	1.92	1.60	1.20
Sb	206.833	1.85	1.31	1.41
Se	196.090	2.52	2.15	1.17
Sn	189.991	1.23	0.53	2.29
Sr	407.771	0.04	0.01	3.56
Tl	190.864	5.35	1.23	4.33
V	311.071	1.24	0.35	3.56
Zn	213.856	0.10	0.07	1.39
			Average	2.35

Axial	DSOI	Axial/DSOI
LOD [µg/L]	LOD [µg/L]	Factor
0.51	0.39	1.32
0.05	0.03	1.53
0.81	1.31	0.62
0.95	1.99	0.48
0.05	0.03	1.49
0.03	0.02	1.98
0.02	0.02	1.08
0.79	1.17	0.68
0.04	0.08	0.50
0.06	0.11	0.55
0.12	0.20	0.59
0.15	0.27	0.55
0.31	0.29	1.08
0.08	0.22	0.36
0.42	0.56	0.75
1.7	8.45	0.20
0.04	0.28	0.14
0.005	0.02	0.25
0.03	0.04	0.84
0.15	0.24	0.64
0.4	2.01	0.20
0.59	0.95	0.62
0.79	1.37	0.58
0.68	1.60	0.42
0.87	1.31	0.66
0.98	2.15	0.46
0.28	0.53	0.52
0.01	0.01	0.91
0.59	1.23	0.48
0.46	0.35	1.32
0.05	0.07	0.71
	Average	0.73

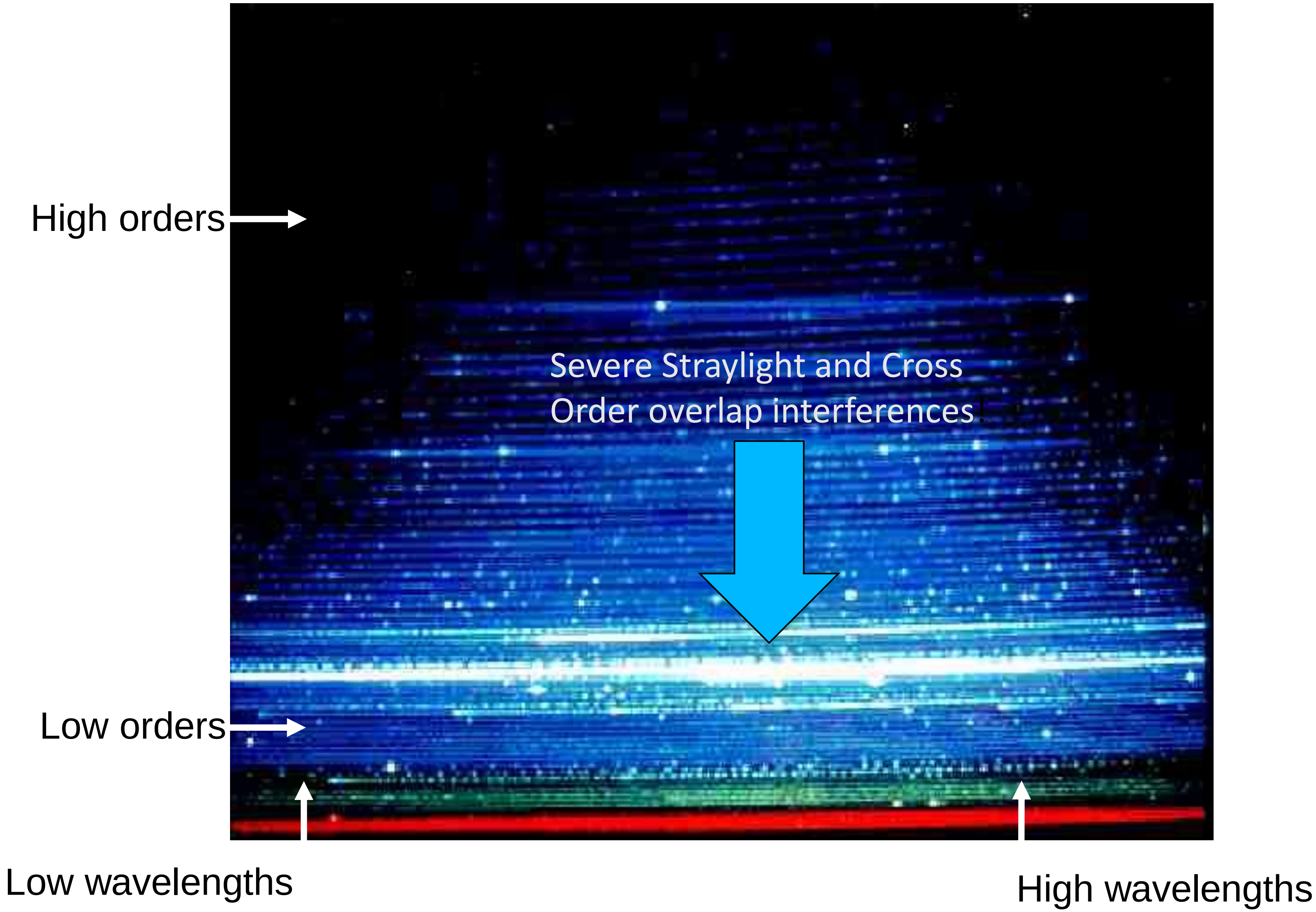
- Clearly improved sensitivity compared to the single side on (∅ factor 2.35)
  - *Biggest effect for alkali/earth for alkali elements*

- Even when compared to the direct path axial observation there is not a big difference (∅ factor 0.73)
  - *Again the alkali/earth for alkali elements show the highest improvement using the axial view*

  - *For Routine work the remaining factor is marginal*
  - *The huge advantages of the vertical torch, radial interface of the DSOI likely outweigh the sensitivity differences for many applications*

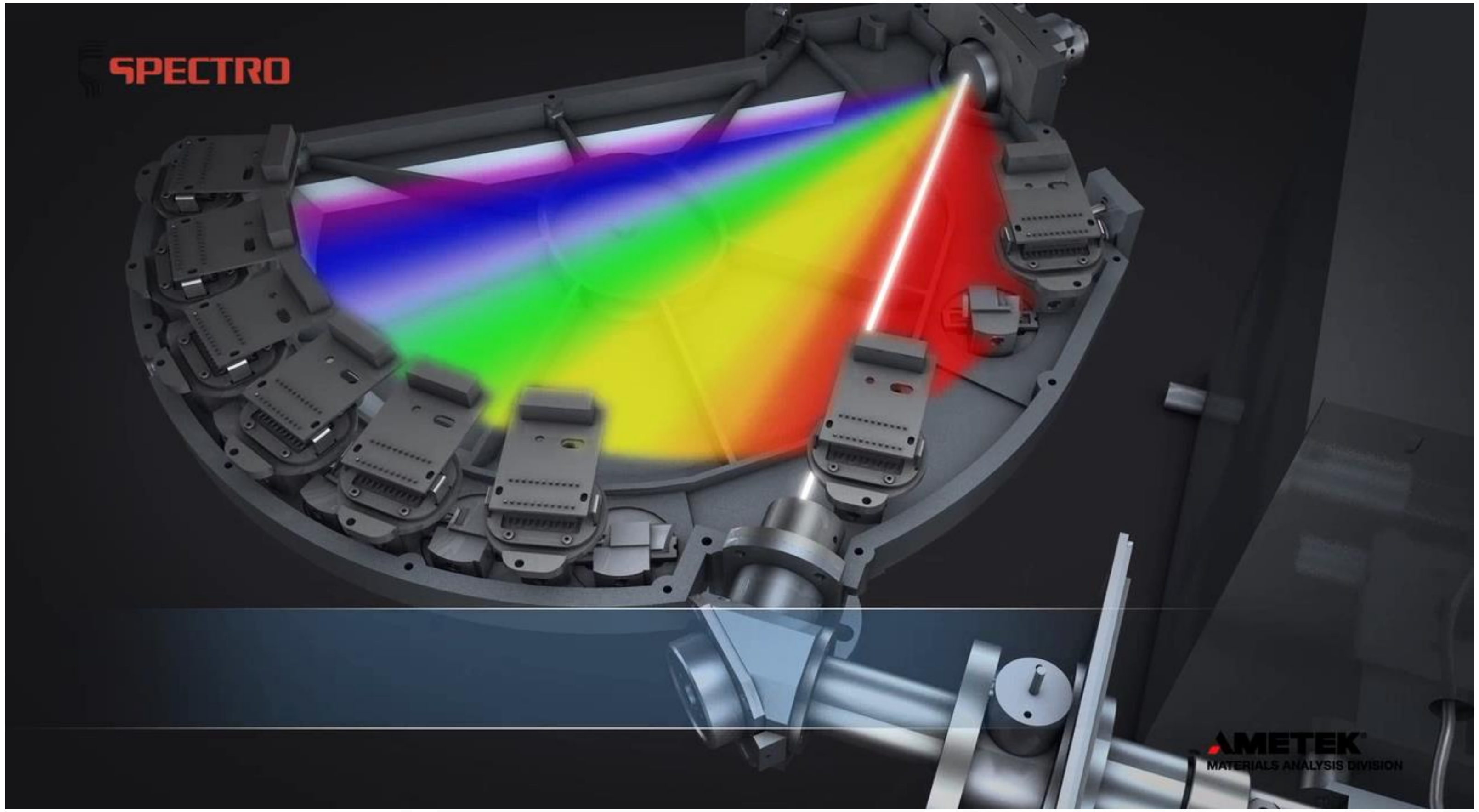
- However, the 27% difference between DSOI and True Axial View is COMPLETELY MITIGATED when using a Periscope! That means DSOI Radial is “equal to or better” than Axial systems using a periscope on critical elements (Mo, As, Pb, S, P, etc)!

Echellogram Based ICP



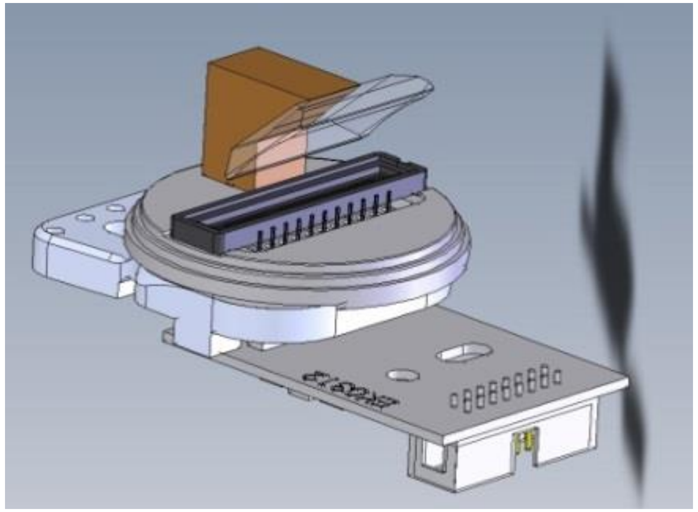
Severe Straylight and Cross Order overlap interferences

SPECTRO ORCA Polychromator



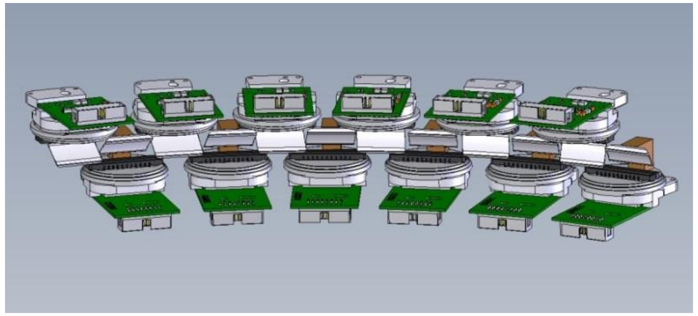
ORCA polychromator with fully simultaneous detection of the spectrum

SPECTRO CMOS Technology



- Novel CMOS line array technology
  - *Outstanding behavior at extreme light intensities*

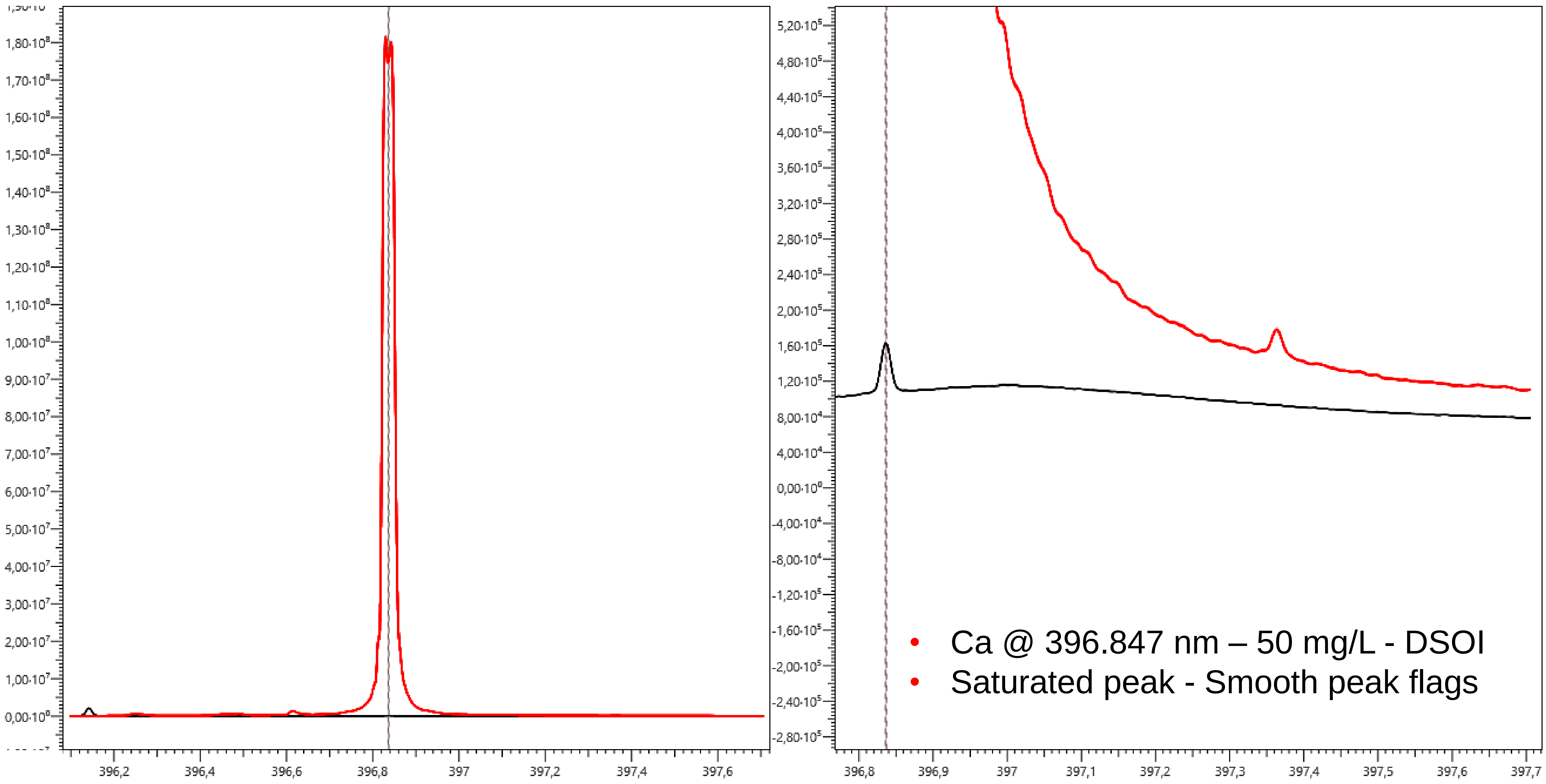
  ➔ *Does not bloom at all (not even with the light of a laser pointer)*
  ➔ *Determination of low signals in the presence of intense matrix peaks*
  ➔ *Single unit costs are drastically lower compared to 2D detectors*
  ➔ *High availability*
  ➔ *In case one detector fails the others remain operational*



- Requires no On-Chip cooling
  - *Thermally stabilized (through optical system) at 32° C*

  ➔ *No problems with condensing or freezing humidity*

SPECTRO CMOS Technology – High Intensity Behavior



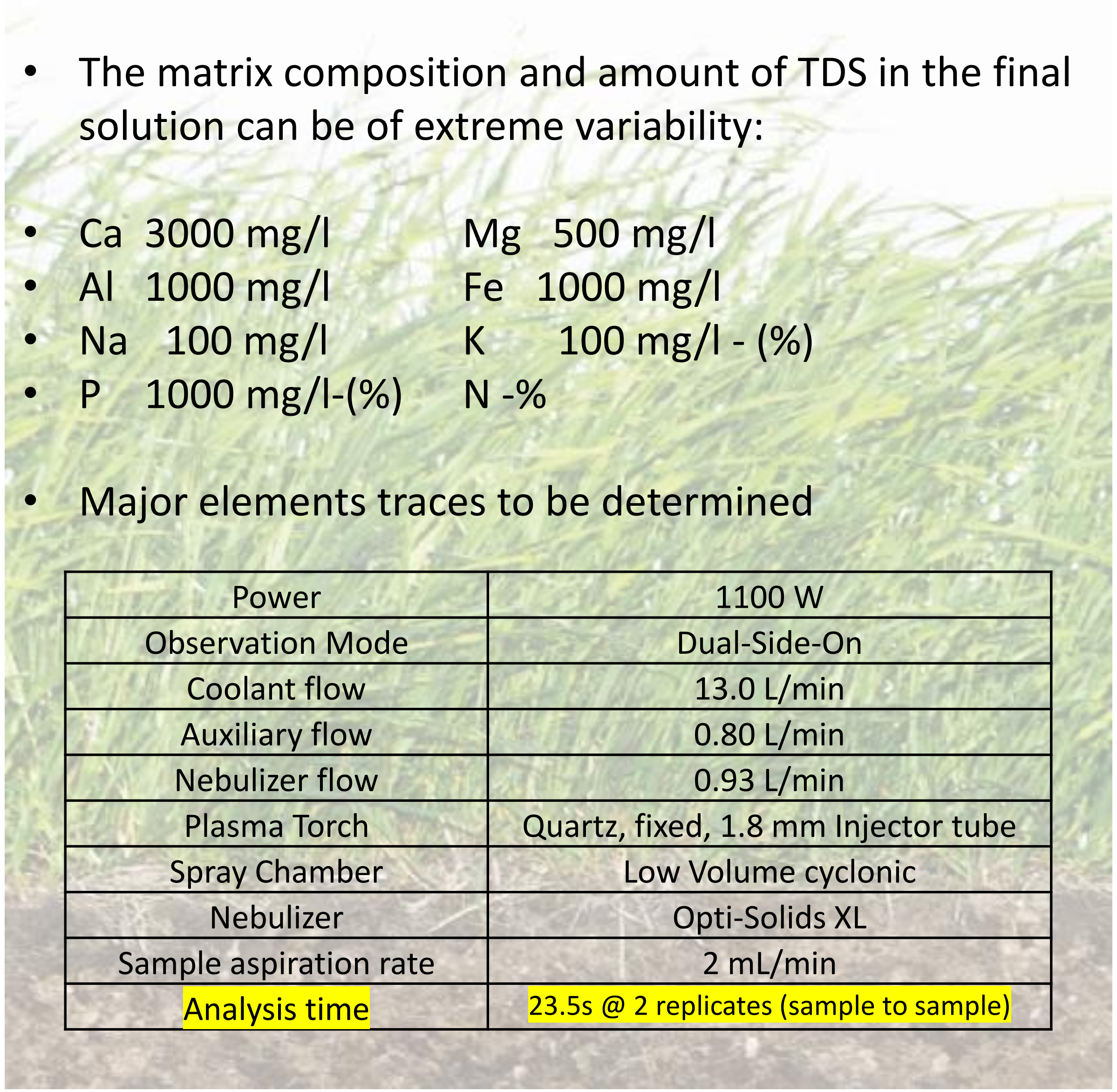
- Ca @ 396.847 nm – 50 mg/L - DSOI
- Saturated peak - Smooth peak flags

Added design benefits ORCA

1. Eliminated the water chiller
2. Linear SSD have a lower heat load and noise level than 2D detectors = No detector icing and lower noise levels at room temperature than a 2D detector at -40C. Much shorter down time after a power outage!
3. Linear CMOS detector replacement (for the life of the system) is about $900 versus $12k-$22k for a 2D camera replacement
4. No purge gases, no air compressors! The **optical system is sealed** and recirculated and requires service once every 24 months. The cost savings is typically $3000-$5000 per year based on sample load making it the LOWEST (not "Lower") cost of operational ownership. No Plasma = No Argon usage...ever!
5. Extended capabilities VUV (Cl, Br, I, Ga, S, etc.) down to 130nm. The ORCA Optical layout is 10-1000x more sensitivity in the VUV region than an Echelle based system (this is simply the physics of using multiple optical surfaces which lead to light loss and aberrations in an Echelle).

Experimental and Results
(Soils, Plant Tissues, Feeds and Fertilizers)

Soil - Plasma and Measurement Parameters



- The matrix composition and amount of TDS in the final solution can be of extreme variability:

- Ca 3000 mg/l Mg 500 mg/l
- Al 1000 mg/l Fe 1000 mg/l
- Na 100 mg/l K 100 mg/l - (%)
- P 1000 mg/l-(%) N -%

- Major elements traces to be determined

Power	1100 W
Observation Mode	Dual-Side-On
Coolant flow	13.0 L/min
Auxiliary flow	0.80 L/min
Nebulizer flow	0.93 L/min
Plasma Torch	Quartz, fixed, 1.8 mm Injector tube
Spray Chamber	Low Volume cyclonic
Nebulizer	Opti-Solids XL
Sample aspiration rate	2 mL/min
Analysis time	23.5s @ 2 replicates (sample to sample)

Element	Std.1 [mg/L]	Std.2 [mg/L]	Std.3 [mg/L]	Std.4 [mg/L]	Std.5 [mg/L]	Std.6 [mg/L]
Ag	0	0.1	0.25	0.5		
Al	700	600.4	501	402	300	200
As	0	0.4	1	2	20	30
B	0	0.4	1	2		
Ba	0	0.4	1	2		
Be	0	0.4	1	2		
Ca	**1000**	**1100.4**	**1301**	**1502**	**1800**	**1400**
Cd	0	0.4	1	2	0.5	0.1
Co	0	0.4	1	2		
Cr	0	0.4	1	2	5	
Cu	0	0.4	1	2	10	20
Fe	400	500.4	601	702	450	550
Hg	0	0.4	1	2		
K	**0**	**2**	**5**	**10**	**20**	**50**
Li	0	0.4	1	2	10	
Mg	200	100.4	51	2	10	
Mn	0	0.4	1	2		
Mo	0	0.4	1	2		
Na	50	10.4	1	2		
Ni	0	0.4	1	2		
P	**800**	**602**	**205**	**410**	**100**	**50**
Pb	0	0.4	1	2	10	
Sb	0	0.4	1	2		
Se	0	0.4	1	2		
Si	0	0.4	1	2		
Sn	0	0.4	1	2		
Sr	0	0.4	1	2		
Tl	0	0.4	1	2		
V	0	0.4	1	2		
Zn	0	0.4	1	2	10	

Soil - LODs and Recoveries (BCR-320R)

	λ [nm]	DSOI LOD (3σ) [mg/kg]	Axial LOD (3σ) [mg/kg]		λ [nm]	DSOI LOD (3σ) [mg/kg]	Axial LOD (3σ) [mg/kg]
Ag	328.068	0.06	0.035	Mn	257.611	0.01	0.01
As	189.042	0.23	0.21	Mo	202.095	0.08	0.06
B	249.677	0.05	0.1	Ni	221.648	0.05	0.03
Ba	455.404	0.01	0.006	Pb	220.353	0.4	0.2
Be	313.042	0.002	0.002	Sb	206.833	0.5	0.4
Cd	228.802	0.02	0.01	Se	196.090	0.5	0.4
Co	228.616	0.04	0.02	Sn	189.991	0.14	0.1
Cr	267.716	0.04	0.03	Sr	407.771	0.007	
Cu	324.754	0.06	0.03	Tl	190.864	0.4	0.2
Hg	184.950	0.08	0.07	V	311.071	0.05	0.05
Li	670.780	0.04	0.003	Zn	213.856	0.03	0.03

Sample dilution: 1:33 (0.75g/25ml)

Element	Certified Concentrations [mg/kg]	Measured Concentrations [mg/kg]			Recovery [%]		
		Analysis No. 1	Analysis No. 2	Analysis No. 3	Analysis No. 1	Analysis No. 2	Analysis No. 3
As	21.7 ± 2.0	23.0	22.7	22.8	106.0	104.6	105.1
Cd	2.64 ± 0.18	2.63	2.61	2.59	99.6	98.9	98.1
Co	9.7 ± 0.6	9.45	9.37	9.29	97.4	96.6	95.8
Cu	46.3 ± 2.9	45.4	44.7	44.1	98.1	96.5	95.2
Fe	25700 ± 1300	2.45E+04	2.46E+04	2.45E+04	95.5	95.8	95.2
Hg	0.85 ± 0.09	0.855	0.876	0.875	100.6	103.1	102.9
Mn	910. ±50	881	877	871	96.8	96.4	95.7
Ni	27.1 ±2.2	25.2	26.0	25.1	93.0	95.9	92.6
Pb	85 ± 5	86.7	87.0	85.8	102.0	102.4	100.9
Se*	0.96 ± 0.18	0.834	0.857	0.875	86.9	89.3	91.1
Sn*	9.4 ± 1.7	8.50	8.33	8.31	90.4	88.6	88.4
V	46.5 ± 2.8	44.4	44.6	43.9	95.5	95.9	94.4
Zn	319 ± 20	311	312	308	97.5	97.8	96.6

** non-certified concentration, indicative value only*

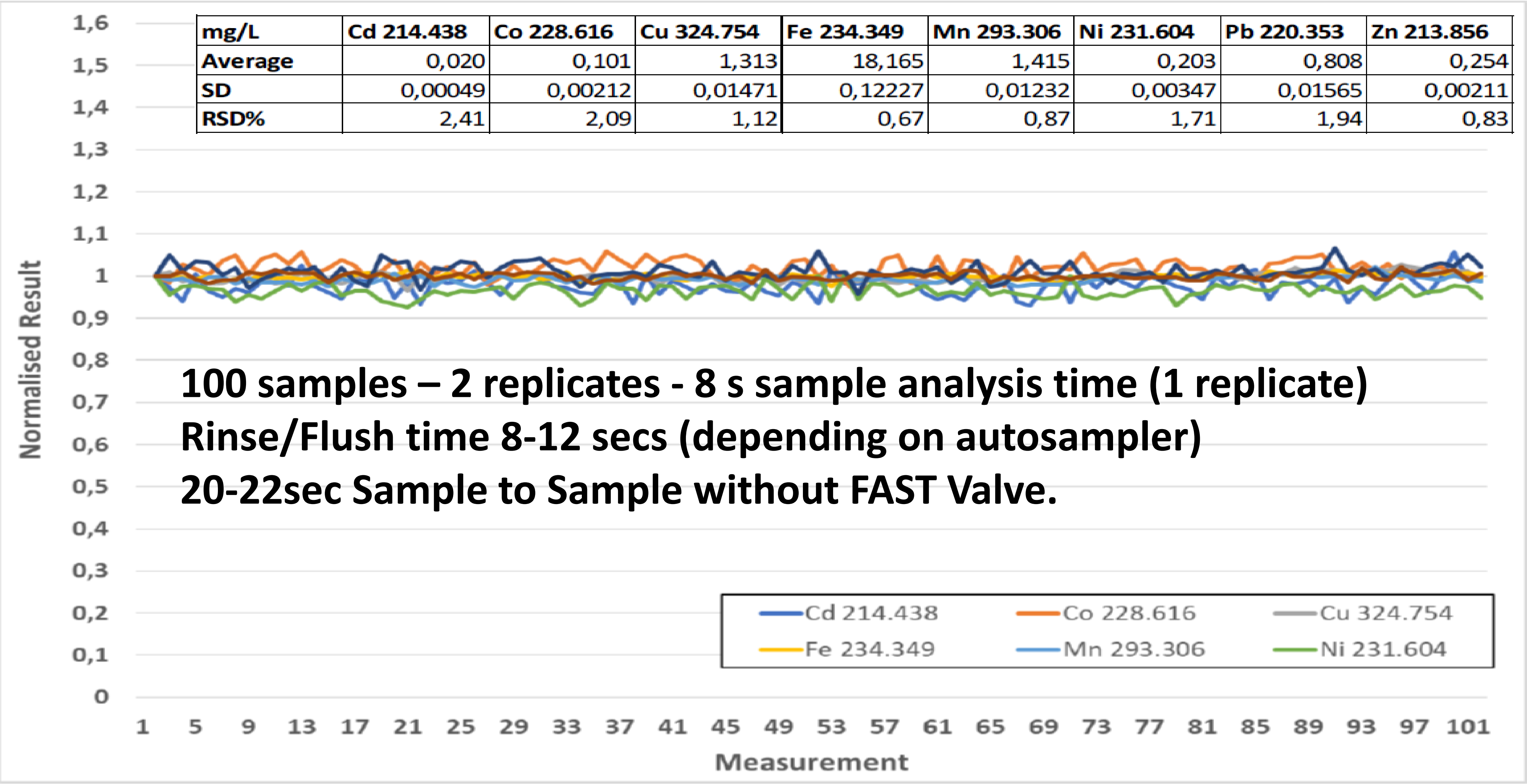
LOD in the SOLID SOIL sample

Table 3: Typical Limits of Detection (LOD) in solid soil samples

Element	λ [nm]	LOD (3σ) [mg/kg] Dual-Side-On
Ag	328.068	0.06
As	189.042	0.23
B	249.677	0.05
Ba	455.404	0.01
Be	313.042	0.002
Cd	228.802	0.02
Co	228.616	0.04
Cr	267.716	0.04
Cu	324.754	0.06
Hg	184.950	0.08
K	766.491	1.2
Li	670.780	0.04

Element	λ [nm]	LOD (3σ) [mg/kg] Dual-Side-On
Mn	257.611	0.01
Mo	202.095	0.08
Ni	221.648	0.05
Pb	220.353	0.4
Sb	206.833	0.5
Se	196.090	0.5
Sn	189.991	0.14
Sr	407.771	0.007
Tl	190.864	0.4
V	311.071	0.05
Zn	213.856	0.03

Soil - Speed



mg/L	Cd 214.438	Co 228.616	Cu 324.754	Fe 234.349	Mn 293.306	Ni 231.604	Pb 220.353	Zn 213.856
Average	0,020	0,101	1,313	18,165	1,415	0,203	0,808	0,254
SD	0,00049	0,00212	0,01471	0,12227	0,01232	0,00347	0,01565	0,00211
RSD%	2,41	2,09	1,12	0,67	0,87	1,71	1,94	0,83

100 samples – 2 replicates - 8 s sample analysis time (1 replicate)
Rinse/Flush time 8-12 secs (depending on autosampler)
20-22sec Sample to Sample without FAST Valve.

Application – S in Fertilizers

DSOI VIEWED ICP for SULFUR

Strengths

- Excellent sensitivity, particularly for non-metals (P and S) and refractory elements
- Freedom from axial interferences
- Better linearity
- Better accuracy
- Lower “S-species” influences
- Simultaneous element detection
- Higher analysis speed
- Fully unattended automatic operation
- Ease of use

Application – Sulfur in Agrochemical

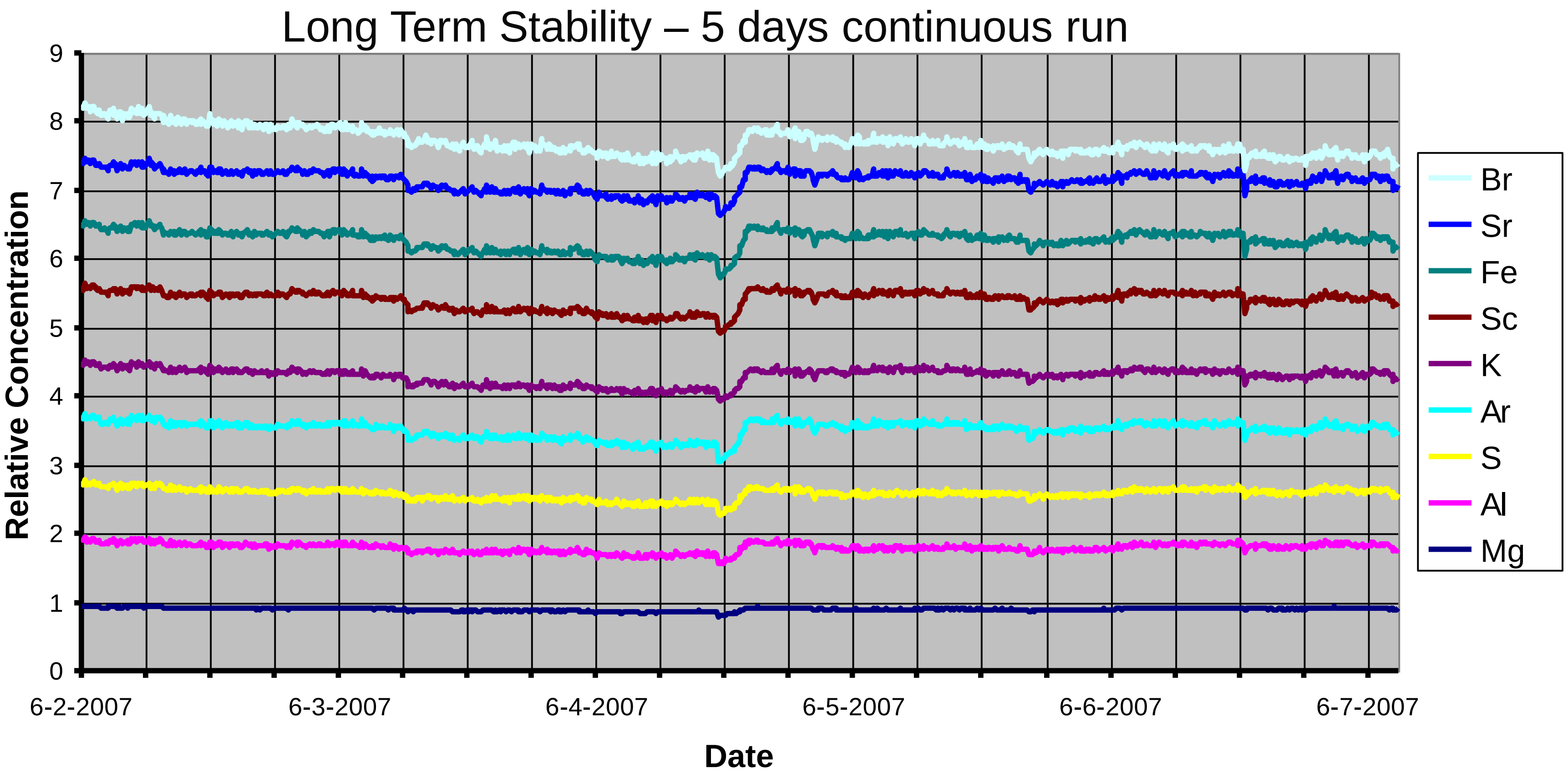
Obstacles

- Calibration (Sulfur is affected by the varying matrix calibration stds)
- Sulfur transport efficiency varies
- UV performance of hardware (optics and O2 ingress)
- IEC’s (Calcium on S 180nm, Phosphorus & Carbon)

Solutions

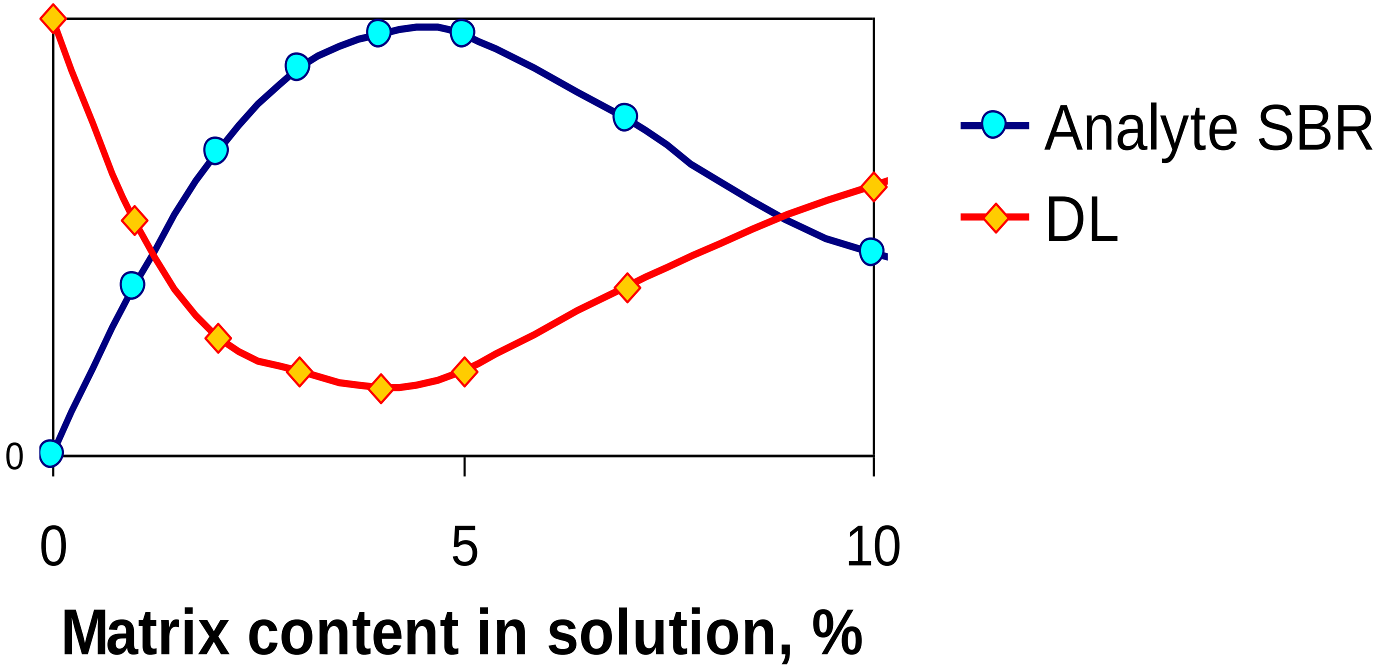
- Matrix match the Sulfur “form” in the calibration to the samples
- Identical sample prep (if possible)
- Use a CRM on the curve prepped the same way as the samples (empirical calibration)
- Stabilize the Sulfur transport efficiency (ISOMIST)
- Access additional Sulfur wavelengths (140nm 142nm, 166nm etc.)

Application – Analytical Performance: Sulfur Stability



Application – Optimizing Sulfur versus the Intro System

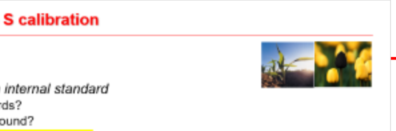
- Optimizing dilution factor around Sulfur



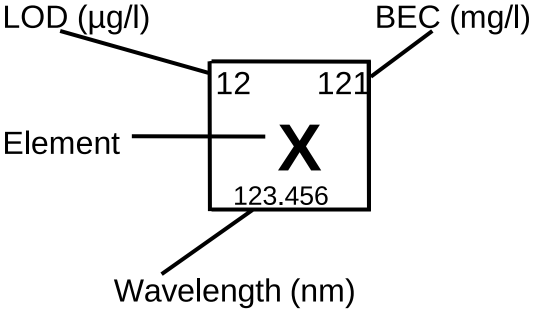
Application – 3 approaches to S calibration

Calibration options

- *Aqueous standard solutions with internal standard*
  - Sample viscosity close to standards?
  - Relatively simple spectral background?
  - Sulfur Std form? Sulfate? Sulfide? IT MATTERS!!!
  - ISOMIST = temperature control of the Sulfur transport
- *Matrix matched calibration*
  - Empirical/CRM used in curve
  - Complex spectral background addressed
- *Method of standard addition*
  - Samples with unknown variable matrix


S calibration
internal standard
rds?
ound?

Application - Intense spectral lines in the VUV (BECs and LODs in Water)

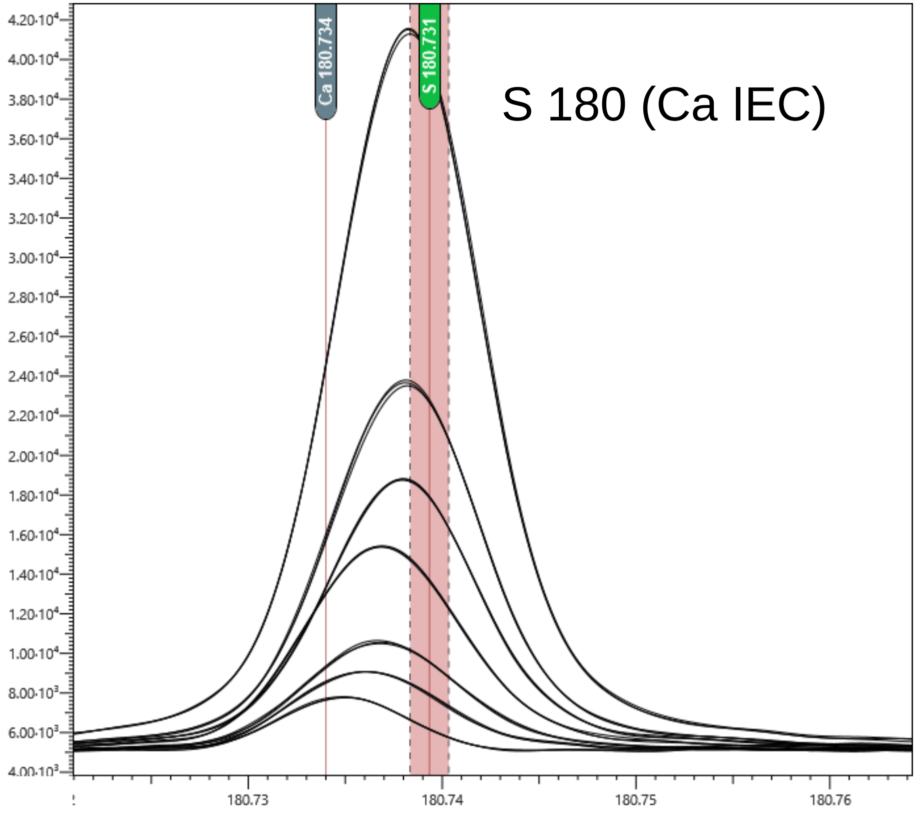


Red: Best SBR for lines <180nm
Blue: Best SBR for lines from 180 - 200 nm
Black: Best SBR for lines > 200 nm

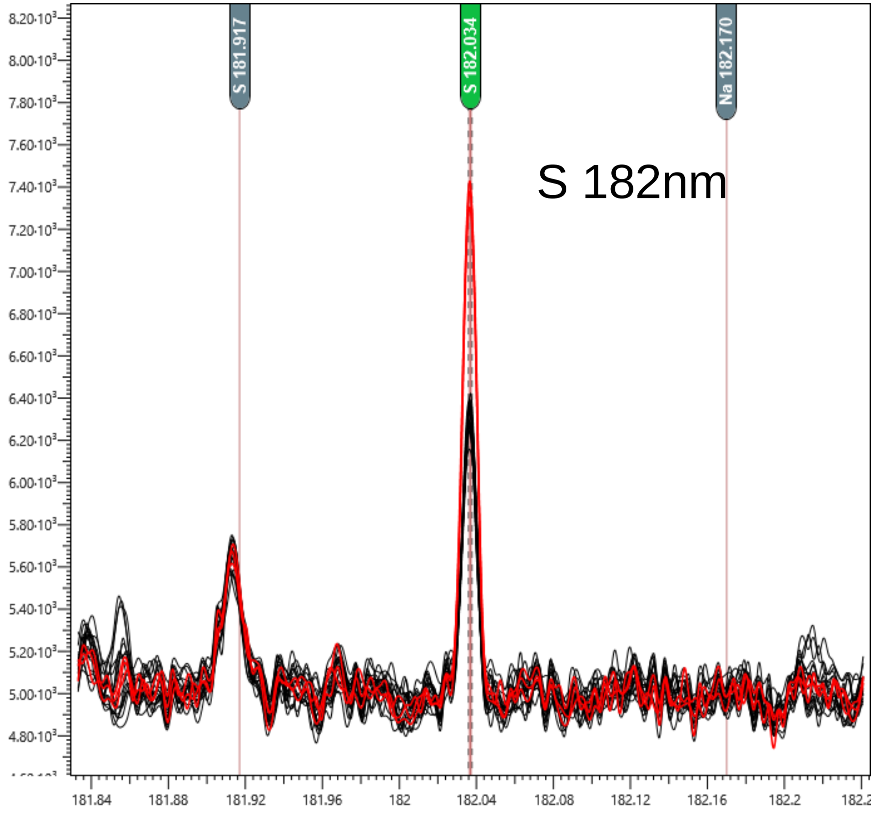
Green: Non ICP elements

								He
			1.2 0.11 B 136.246	500 26 C 193.091	21800 2200 N 149.262	O 130.485	F	Ne
			0.04 0.003 Al 167.078	3.4 0.24 Si 152.672	1 0.12 P 177.495	1.9 0.22 S 180.731	19 2.1 Cl 134.724	Ar
			0.8 0.05 Ga 141.444	1.3 0.11 Ge 164.917	2 0.18 As 189.042	2.7 0.21 Se 196.069	9 1.1 Br 154.065	Kr
			0.09 0.02 In 158.583	1.3 0.25 Sn 147.415	13 0.7 Sb 156.548	3.9 0.38 Te 170.000	13 1.7 I 142.549	Xe
2.3 0.15 Pt 177.709	3.1 0.35 Au 174.047	0.5 0.07 Hg 184.95	1.4 0.1 Tl 190.864	1.8 0.12 Pb 168.215	4.4 0.7 Bi 153.317			

Application – Primary S-Lines in the VUV

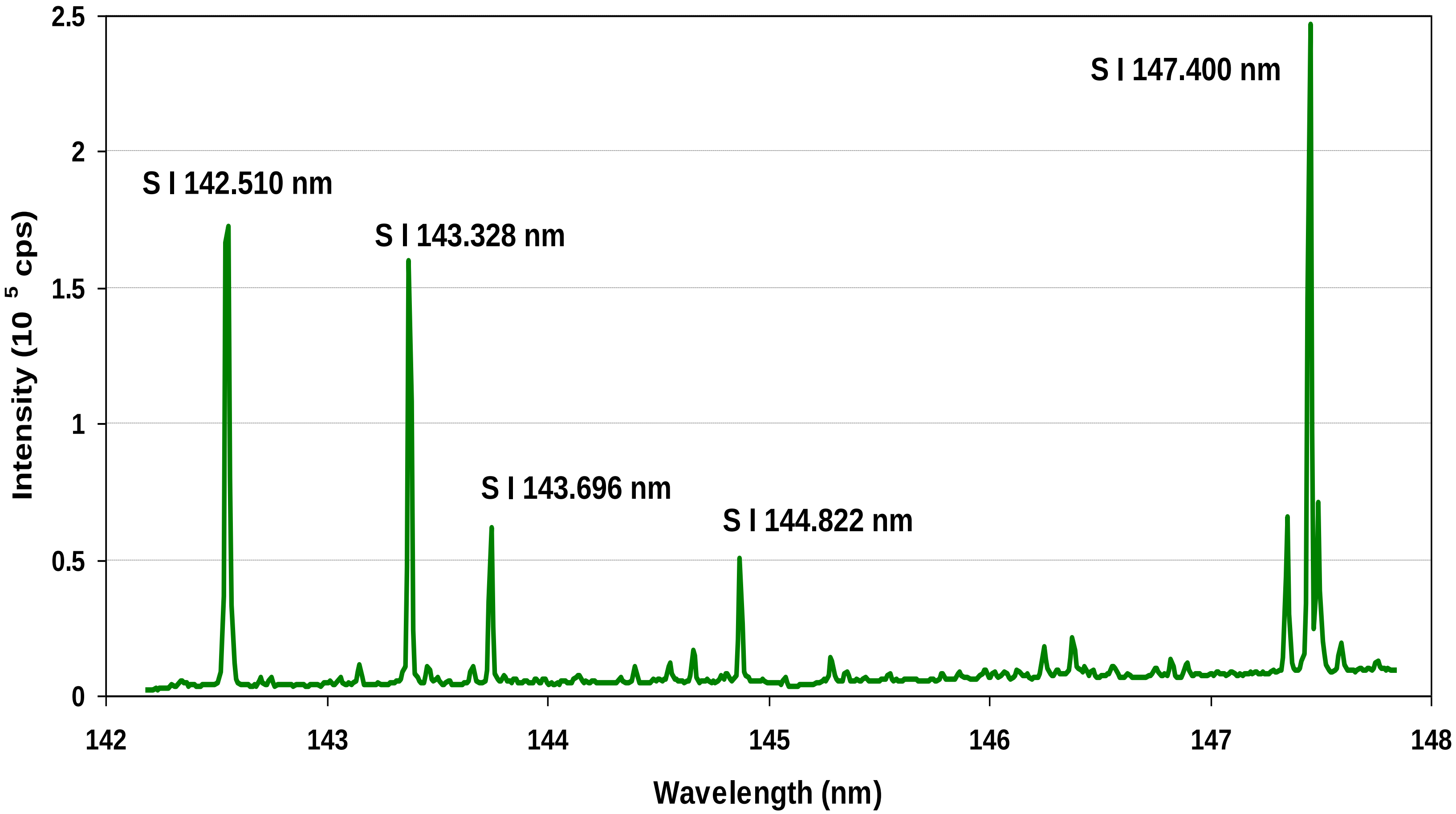


S 180 (Ca IEC)



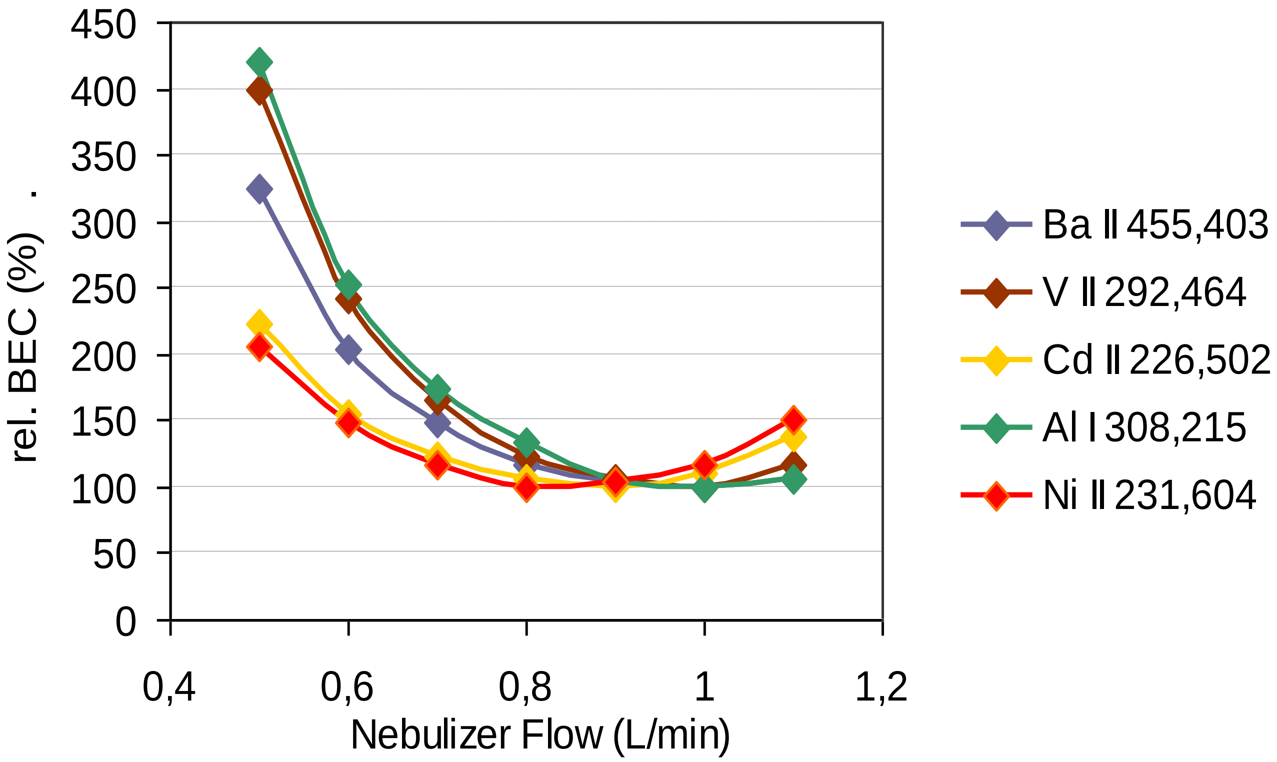
S 182nm

Application - Less intense S-Lines in the VUV



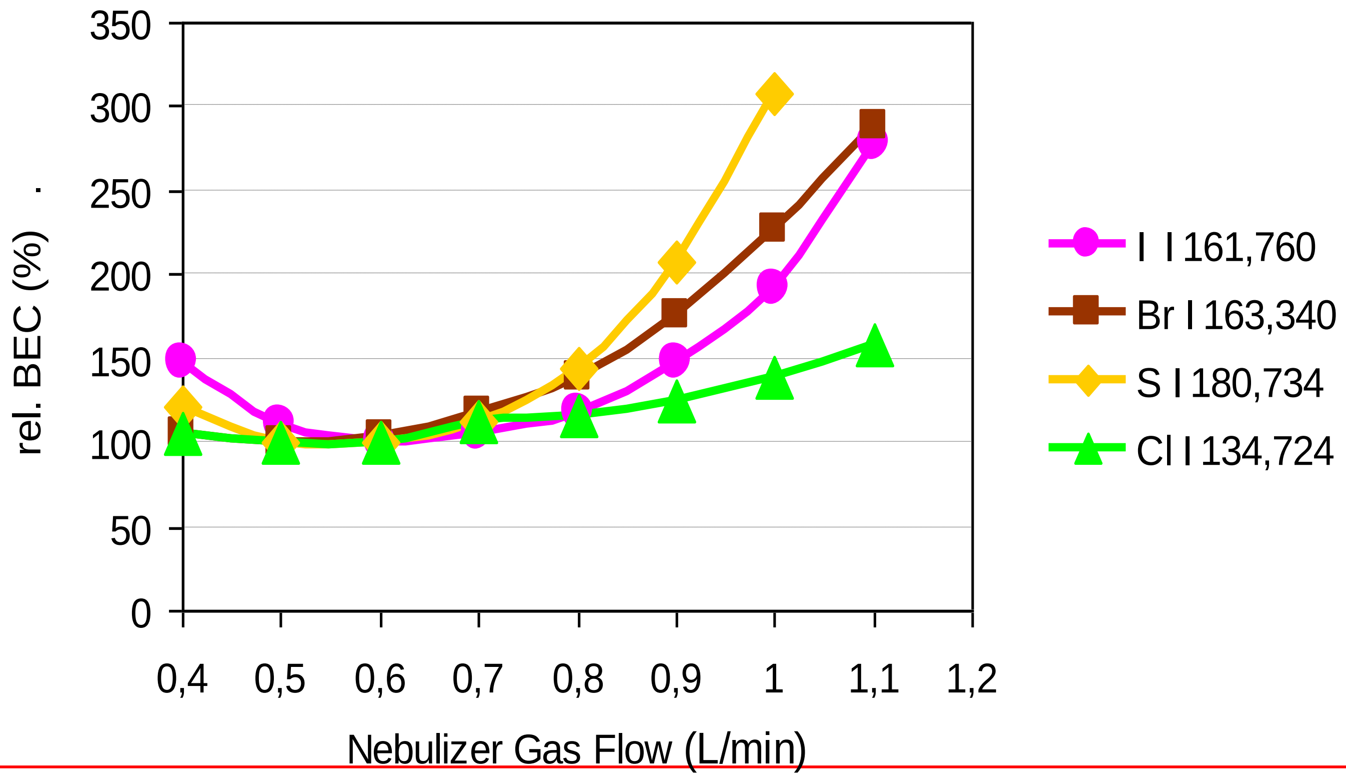
Application

- Nebulizer gas flow influence (Metals)



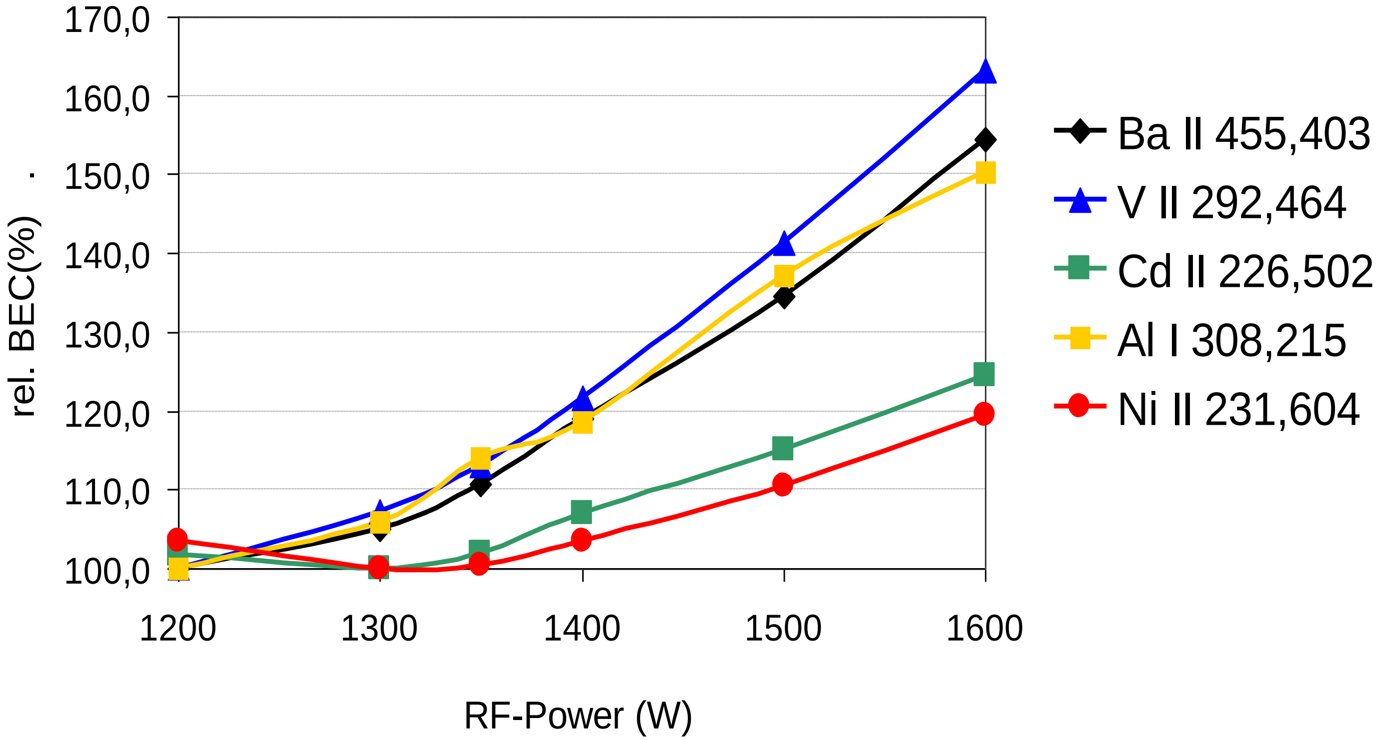
Application

- Nebulizer gas flow influence (Non-Metals)!!!



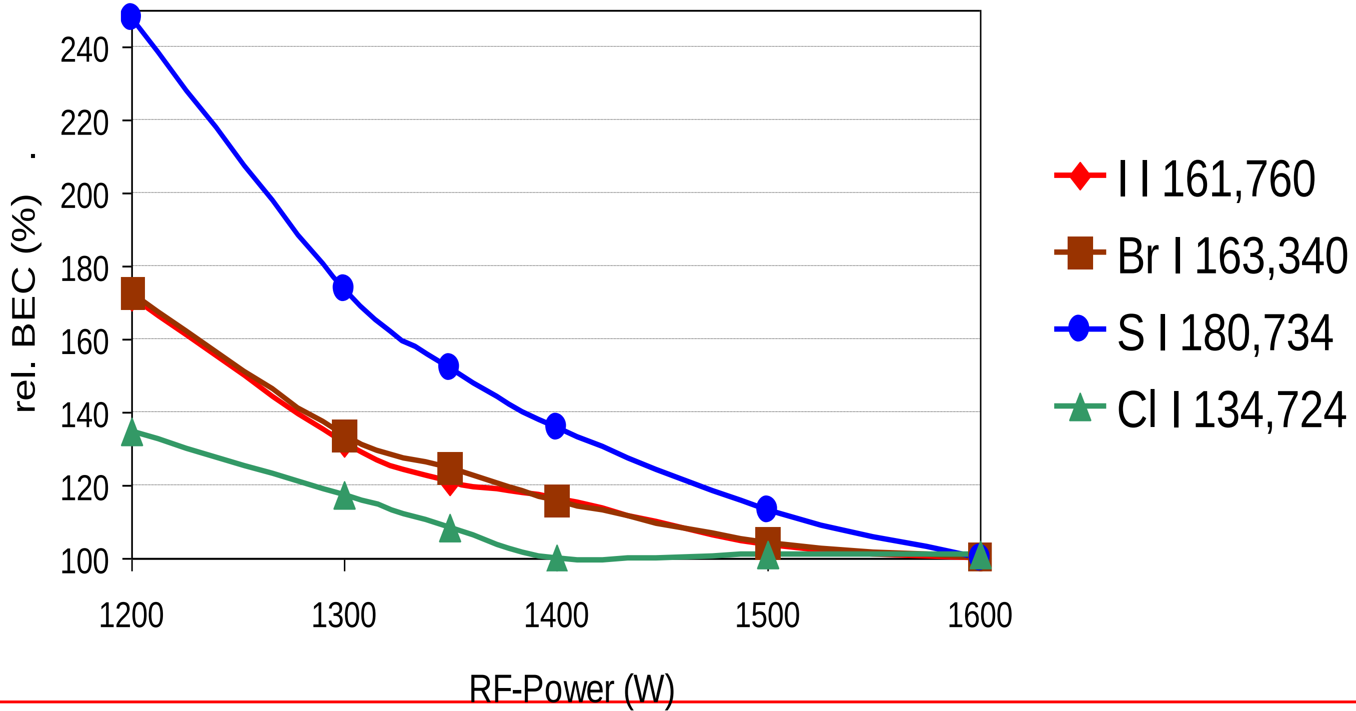
Application – RF Power

- RF-Power Influence (Metals)



Application – RF Power Non-Metals!

- RF-Power Influence (Non-Metals)

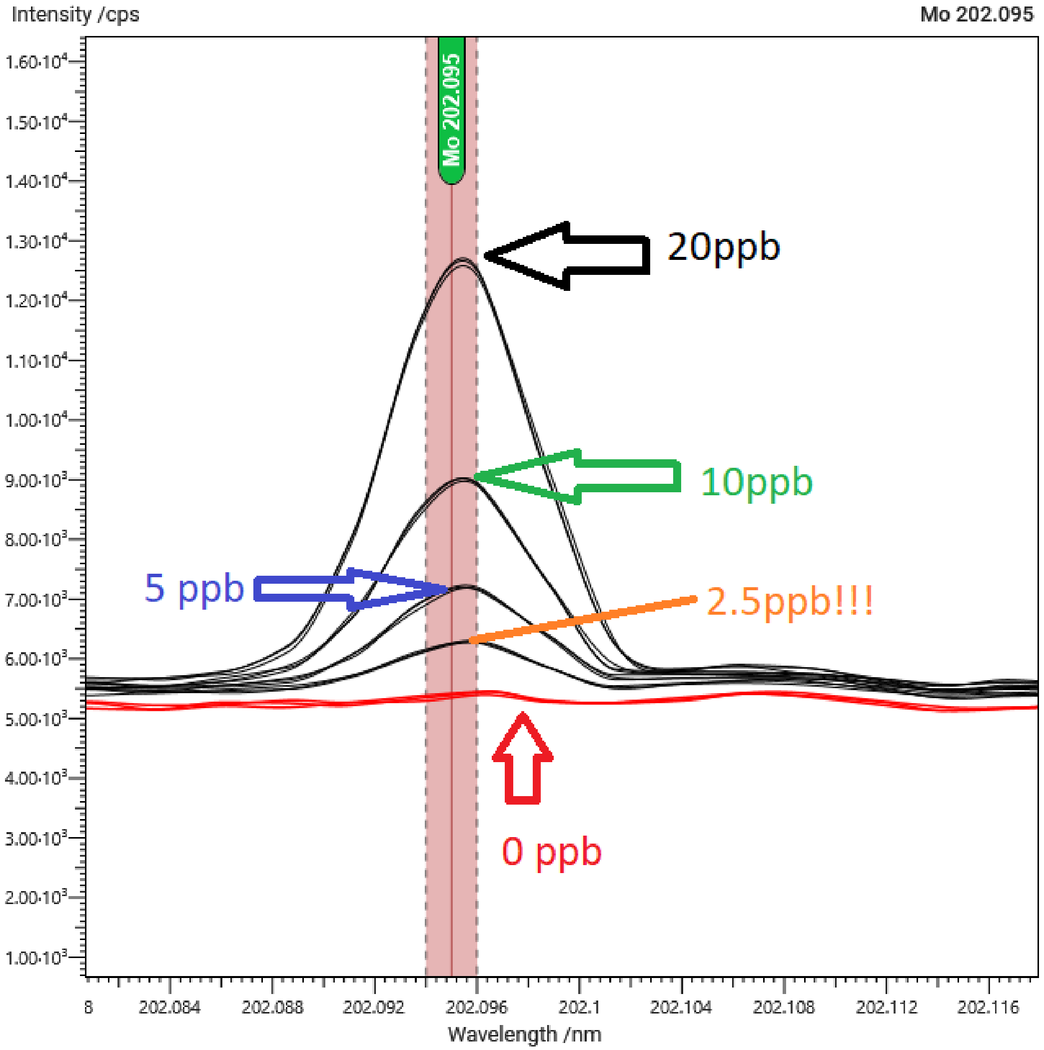


Overview

- Non Metals like Sulfur require a different approach:
  - *Know your hardware and its limitations/capabilities*
  - *Focus on the analyte*
  - *Heated spray chamber / sample introduction system*
- Calibration:
  - *3 options, pick what is best for your needs and STICK TO IT!*
  - *Pick the right Internal Std*
  - *Chilled spray chamber*
- Optimization “Plasma Loading” / Signal Depression
  - *Robust Plasma*
  - *Intro optimization (different for non-metals)*

Plant Tissue (Mo = 0.68 ppb DL) using an 18 sec integration strategy

Mo in plant tissue. Target LOQ = 0.2ppm in the plant tissue or 0.002ppm (2 ppb) in solution!



Application - Internal Standardization

Why is Internal Standardization needed?

(I) Compensation of non-spectral interferences

- Sample introduction system, differences in
  - Viscosity / Transport efficiency
  - Salt content
  - Surface tension
  - Vapor pressure
- Plasma
  - Temperature changes by matrix elements
  - Effect of easy ionizable elements

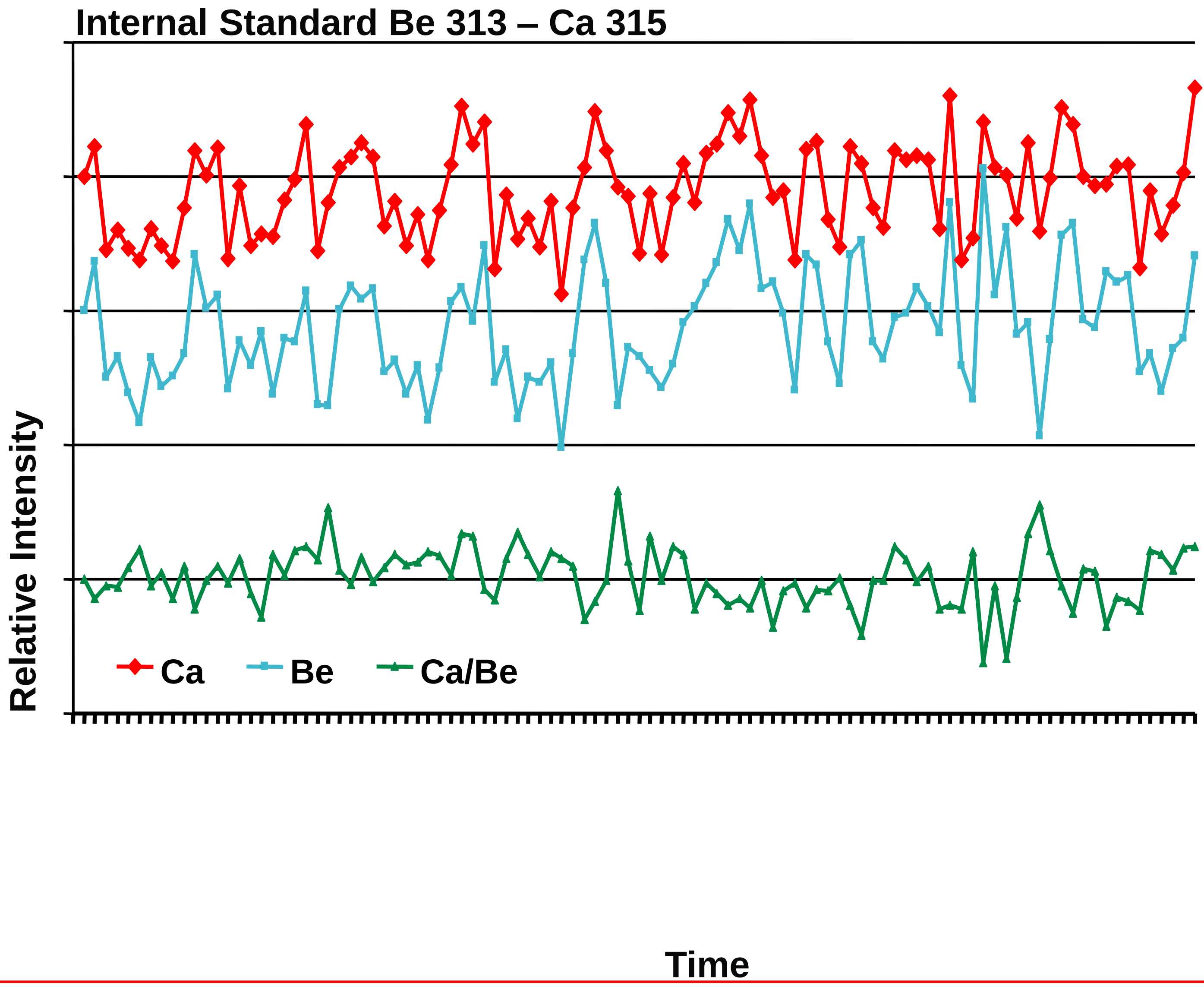
(II) Improvement of the precision

Application - Internal Standardization

- **The internal standard is added to all samples and calibration samples in the same concentration and with high accuracy**

- The internal standard should be “matched” to Sulfur! (Te vs Y)
- Is not in the sample before prior to its addition
- Has a high purity
- Does not produce spectral interferences
- Is in the samples soluble and stable
- Intensity = Intensity of analytes
- Is detected simultaneously with the analytes

Application - Internal Standardization



Experimental (Magruder Fertilizers)

- Radial ICP OES (DSOI)
- Cyclonic Chamber with Seapray nebulizer, 1.8mm injector
- 1350 W, 14 L/min Coolant, 1.4 L/min Aux, 0.8 L/min Nebulizer, (+ 0.2 L/min Aux)
- Standard Calibration
- Empirical Calibration
- Varying Internal Standards
- Various Calibration standards (P, **PO4**, PPO4)
- Digestion concerns (P volatility)
- The same techniques discussed will apply to optimizing the K results!

Accuracy controls

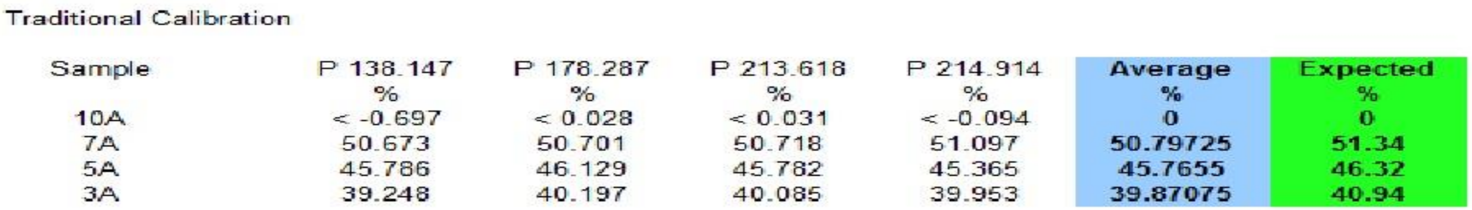
1. Linearity : An ICP (all ICP's) typically have +/- 2% error in the calibration curve. What does that mean? Using the exact same conditions, intro system and solutions...each time you calibrate, the accuracy of the curve can vary up to 2%. So, on a 50% check solution a range of 49-51% is expected.
2. Adding empirical calibration controls can reduce this to 0.5% or less.
3. Additional gas flow (intro system) can produce a more consistent sample delivery with less plasma effects (efficiency/cooling/EIE).
4. Internal Standard selection and error from using a Blank.
5. Wavelength averaging.

Anatomy of an active plasma stream

- High Na matrix to show the plasma has a “skin depth effect” which causes much of the sample to pass around the plasma and not complete through the plasma.
- Additional gas option forces the sample stream through the plasma.

Optional Gas adapter (laminar flow to force sample into plasma and avoid external cooling of plasma).

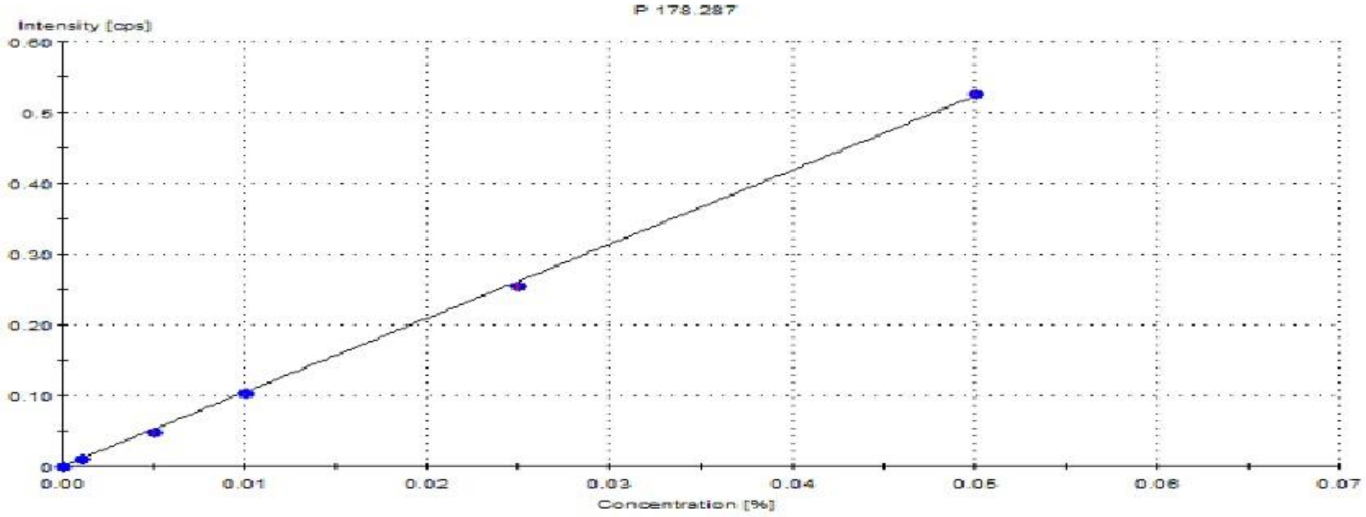
Traditional without Additional Gas (lower trend)



Traditional Calibration

Sample	P 138.147 %	P 178.287 %	P 213.618 %	P 214.914 %	**Average %**	Expected %
10A	< -0.697	< 0.028	< 0.031	< -0.094	**0**	**0**
7A	50.673	50.701	50.718	51.097	**50.79725**	**51.34**
5A	45.786	46.129	45.782	45.365	**45.7655**	**46.32**
3A	39.248	40.197	40.085	39.953	**39.87075**	**40.94**

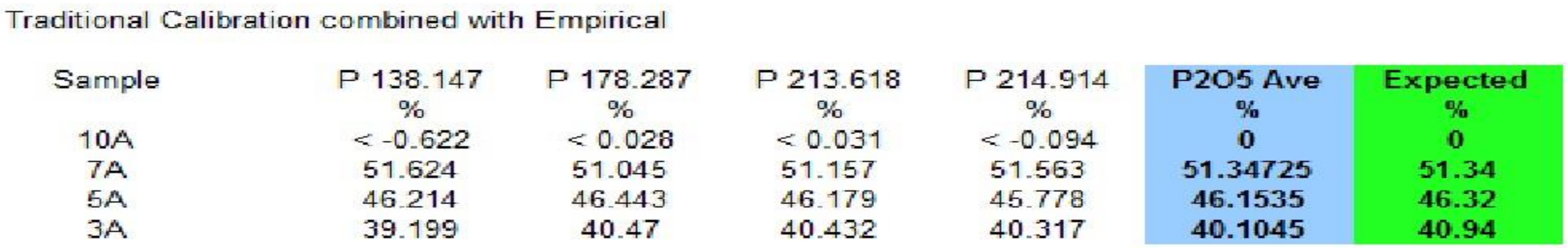
Calibration = 0, 10, 50, 100, 250, 500ppm Phos



Method defined calibration with Additional Gas

Sample		**P2O5**	**Expected**
		%	**%**
10B		**! 0.012**	**0**
7B		**51.62**	**51.34**
5B		**46.029**	**46.32**
3B		**40.54**	**40.94**

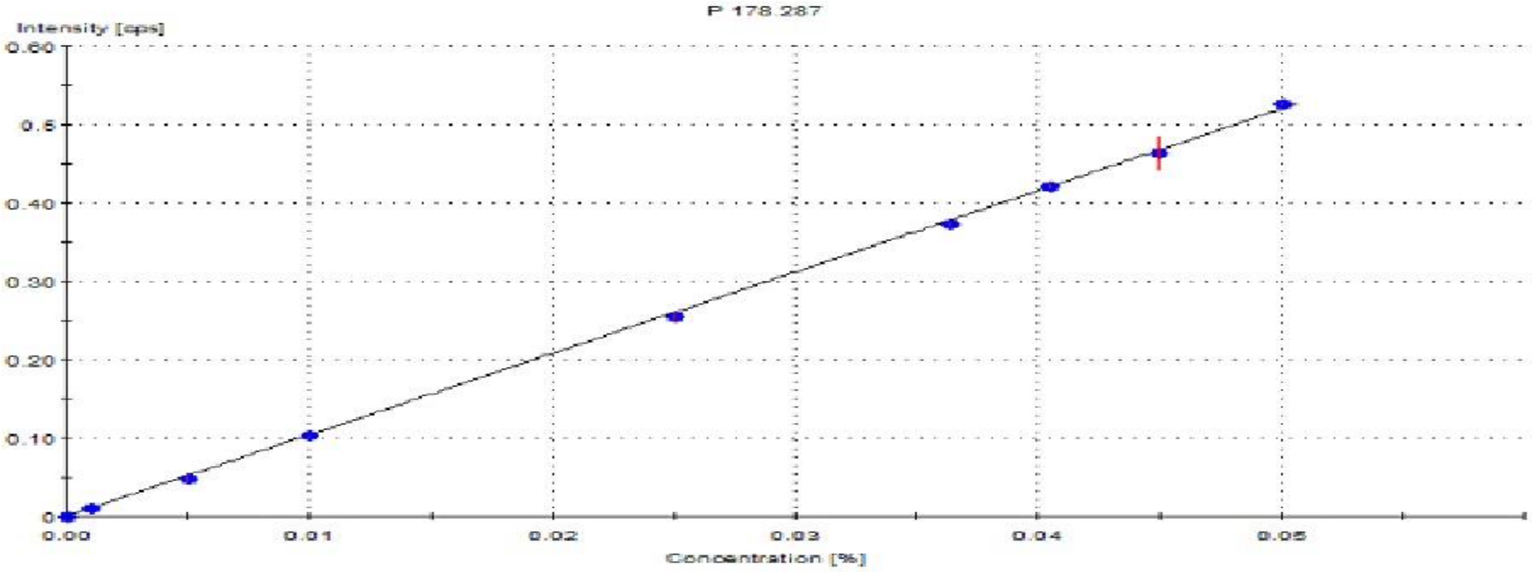
Traditional with partial Empirical (closer to expected)



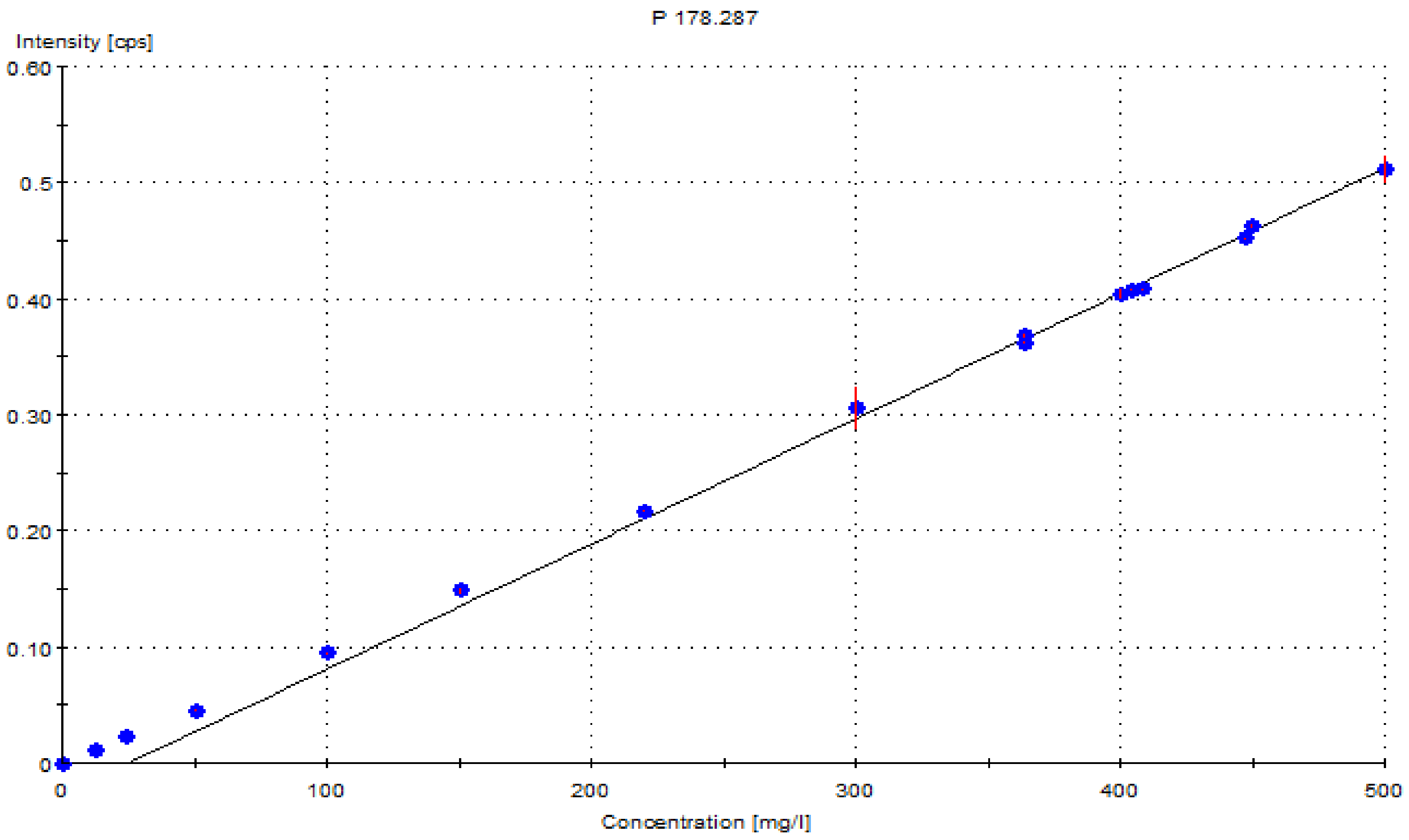
Traditional Calibration combined with Empirical

Sample	P 138.147 %	P 178.287 %	P 213.618 %	P 214.914 %	P2O5 Ave %	Expected %
10A	< -0.622	< 0.028	< 0.031	< -0.094	**0**	**0**
7A	51.624	51.045	51.157	51.563	**51.34725**	**51.34**
5A	46.214	46.443	46.179	45.778	**46.1535**	**46.32**
3A	39.199	40.47	40.432	40.317	**40.1045**	**40.94**

Calibration = 0, 10, 50, 100, 250, 500ppm Phos + 4 Empirical Stds



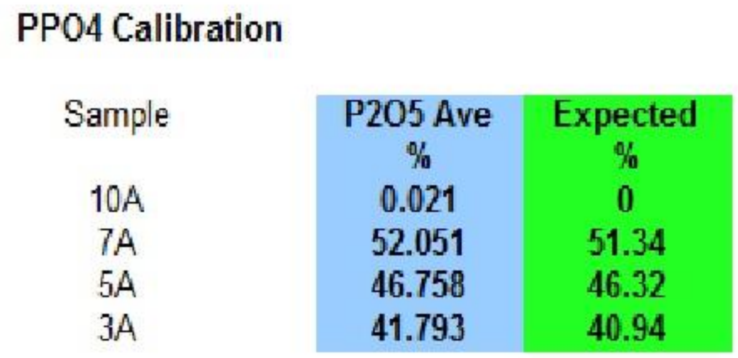
Curve biased based on Empirical Weighting (Magruder)



Other Phosphorus based calibrations

PPO4 calibration gave a biased higher than expected results.

Needs to be re-worked and confirmed.



PPO4 Calibration

Sample	P2O5 Ave %	Expected %
10A	0.021	0
7A	52.051	51.34
5A	46.758	46.32
3A	41.793	40.94

PO4 – precipitates in the presents of high salt matrices, not suitable for this application.

Comments and recommendations

1. Additional carrier gas seems to help accuracy.
2. In a traditional calibration the biggest limiting factor is the ICP's linear error (2%).
3. Empirical calibrations help accuracy and long term precision....! Wt./Wt. Dilution 0.5012g/0.5g
4. Calibration standards (species) affect accuracy as does digestion!
5. Internal standard, wavelength selection, and averaging also help accuracy.
6. Varying tubing sizes and dilution rate helps based on specific instrumentation more than on the methodology.

Accessories and Improvements that are available

- Detectors/Optics change and improve, know what you are using.

- Intro systems are constantly being updated, check precision, stability and sensitivity with your systems compatibility!

- Try hybrid systems (HydraMIST or Isomist)!

- Solid Sampling (ETV)

- Anything else?

- The DSOI Technology was specifically developed for Agronomic samples allowing one system to measure soils, fertilizers and plant tissues without the high maintenance requirements of Axial/Dual View or compromising sensitivity and speed!

Thank You for Your Attention!

Dion.Tsourides@ametek.com