

QUANTITATIVE ANALYSIS OF ELEMENTS IN WINE USING “STATE OF THE ART” SPECTROSCOPY

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Wine Analysis - Overview

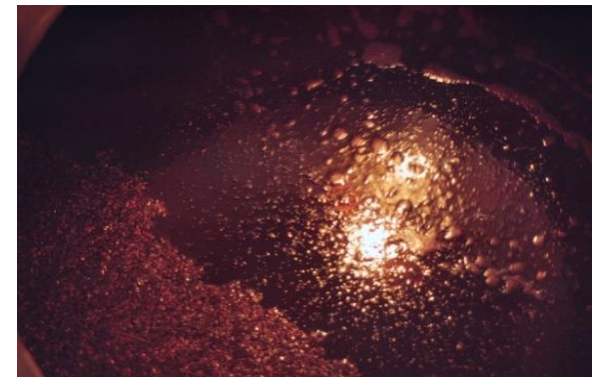
- Introduction
- European Norms EN/DIN
- Analysis of Wine
- AAS: sequential
- ICP-OES: simultaneous
- ICP-MS: ultra trace



Wine Production



1. Vintage
2. Mashing
3. Wine pressing
4. Fermentation
5. Tapping
6. Aging
7. Storage



Regulations



- European Union wine regulation

- Latest update from 9th March 2012

- Testing physical parameters

- Density
- Turbidity
- Color



Control Limits

Aluminium	8.00 mg/l
Arsenic	0.10 mg/l
Lead	0.25 mg/l
Boron	80 mg/l
Cadmium	0.01 mg/l
Copper	2.00 mg/l
Zinc	5.00 mg/l
Tin	1.00 mg/l

Trichloromethane	0.10 mg/l
Trichloroethene	0.10 mg/l
Tetrachloroethene	0.10 mg/l
Trichloromethane, Trichloroethene & Tetrachlorethene (total)	0.20 mg/l

Copper/ Zinc

Concentration

- Metallic bitter taste > 1.0 mg/L
- Generate turbidity > 0.5 mg/L
- Copper oxidation > 0.5 mg/L
- Reducing the flavour >0.5 mg/L
- Influence on fermentation > 20 mg/L

Table 1: Influence of copper concentrations in wine

Boron

- Fertilizer
- 5 – 500 g/ha
- Accumulated in the ground
- B consumption during growth 200 g/ha

Sulfur

- Conservation, to prevent Oxidization
- European Limits:
- Dry Wine: 160 – 260 mg/L
- Medium Wine: 300 – 350 mg/L
- Sweet Wine: 400 mg/L

Antimony?

Wine in PET- Bottles – Prof. Dr. Rainer Jung, University Rhein/Main



Languedoc Producer SKALLI in 2010: 2,5 Mio. PET bottles

<http://blog.campus-geisenheim.de/index.php/2010/12/wein-aus-pet-flaschen-und-bechern-prof-dr-rainer-jung-im-interview-mit-dem-wiesbadener-kurier/>

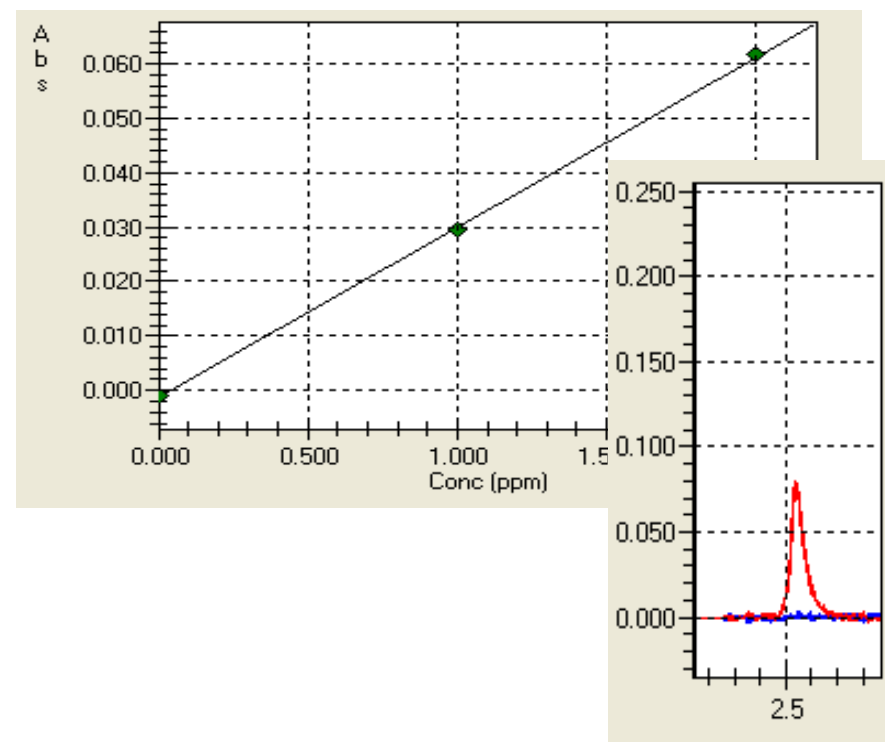
Quantitative Analysis (1)

Sequential.....

...in Flame and furnace atomization using AA-7000

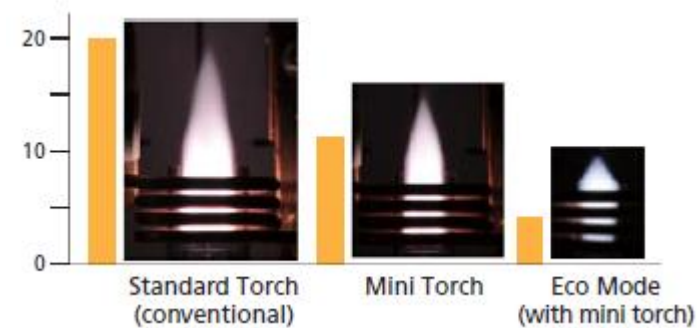
Determination of Cu, Zn, Al, Cd, Pb, und P

Important: BGC SR/D₂

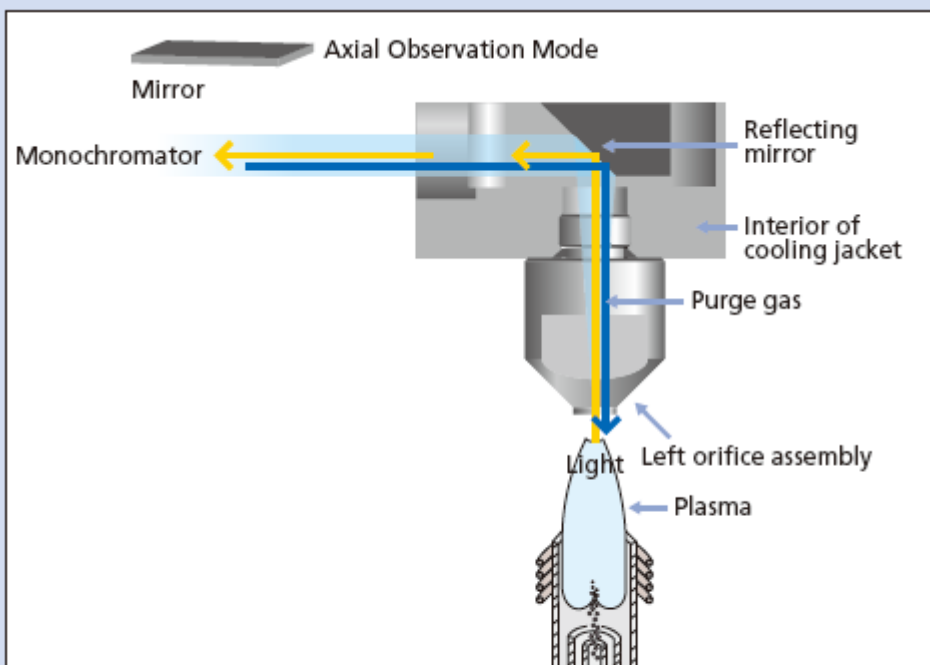


Quantitation of Heavy Metals(2)

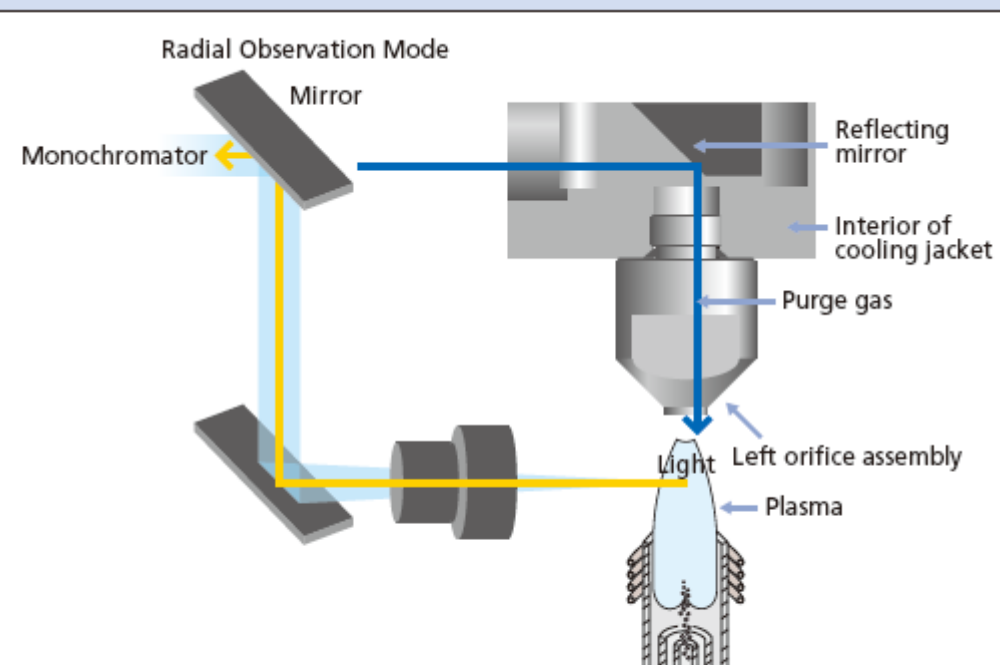
...using simultaneous ICP-OES: ICPE-9820



Dual View: Axial & Radial

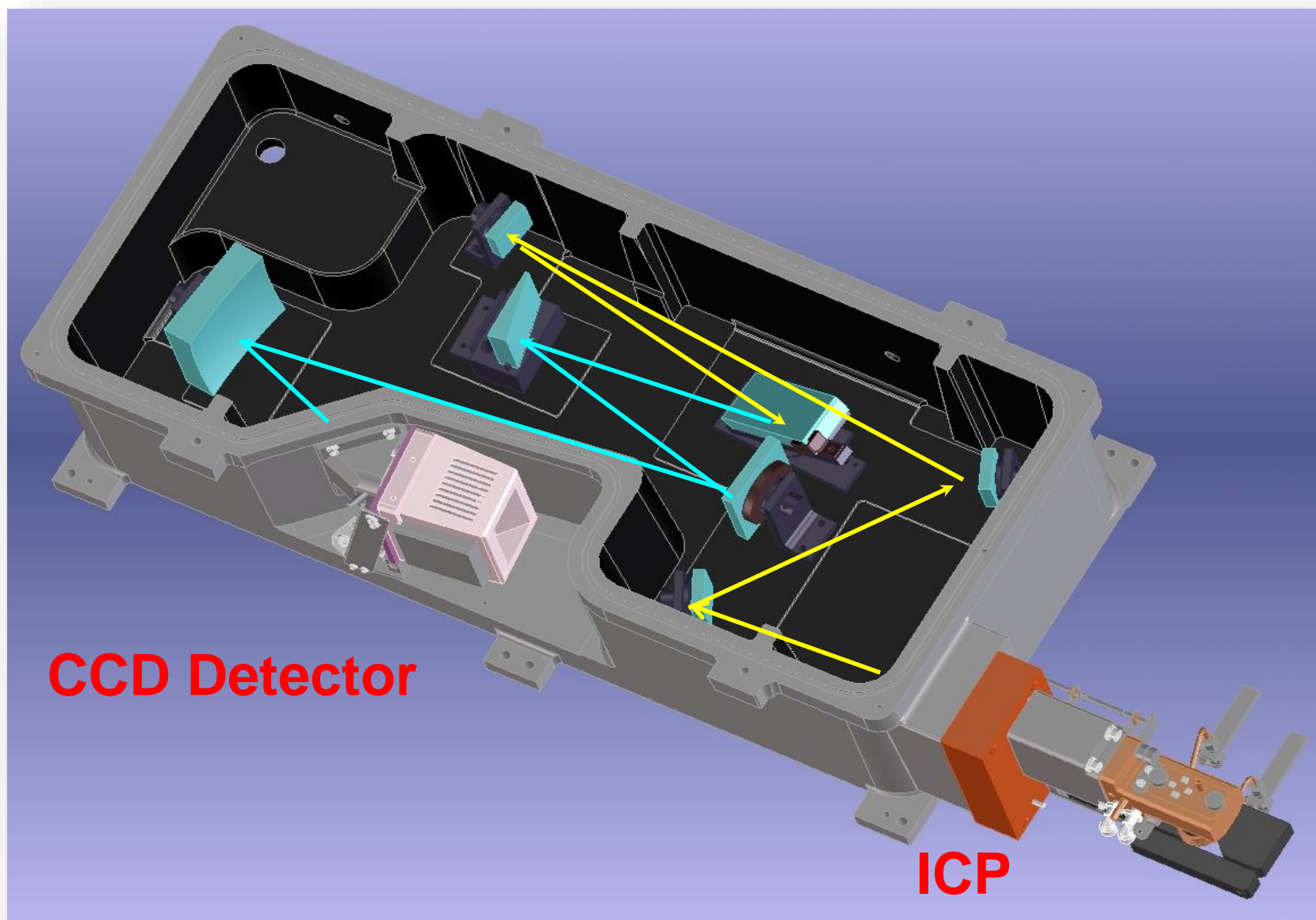


Axial Observation

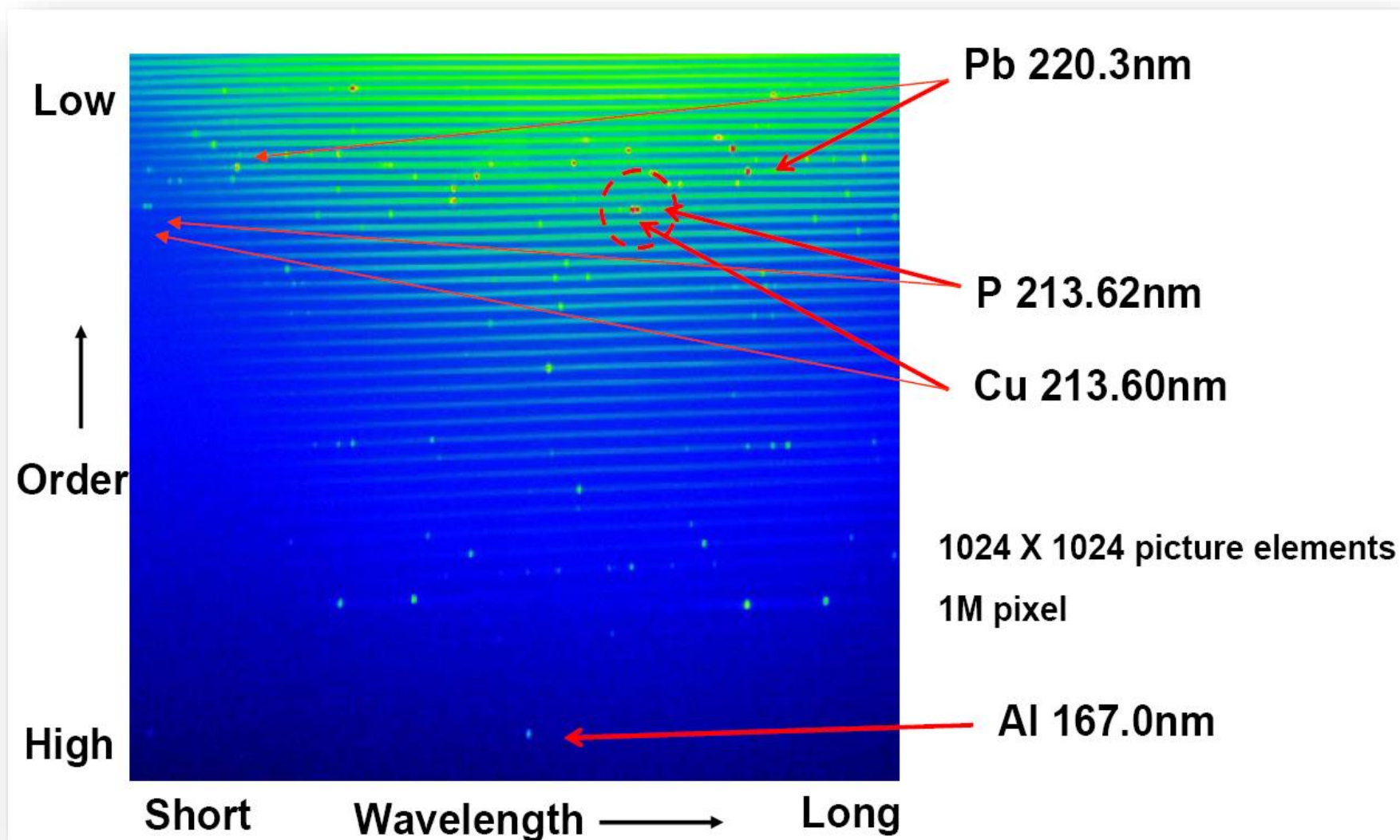


Radial Observation

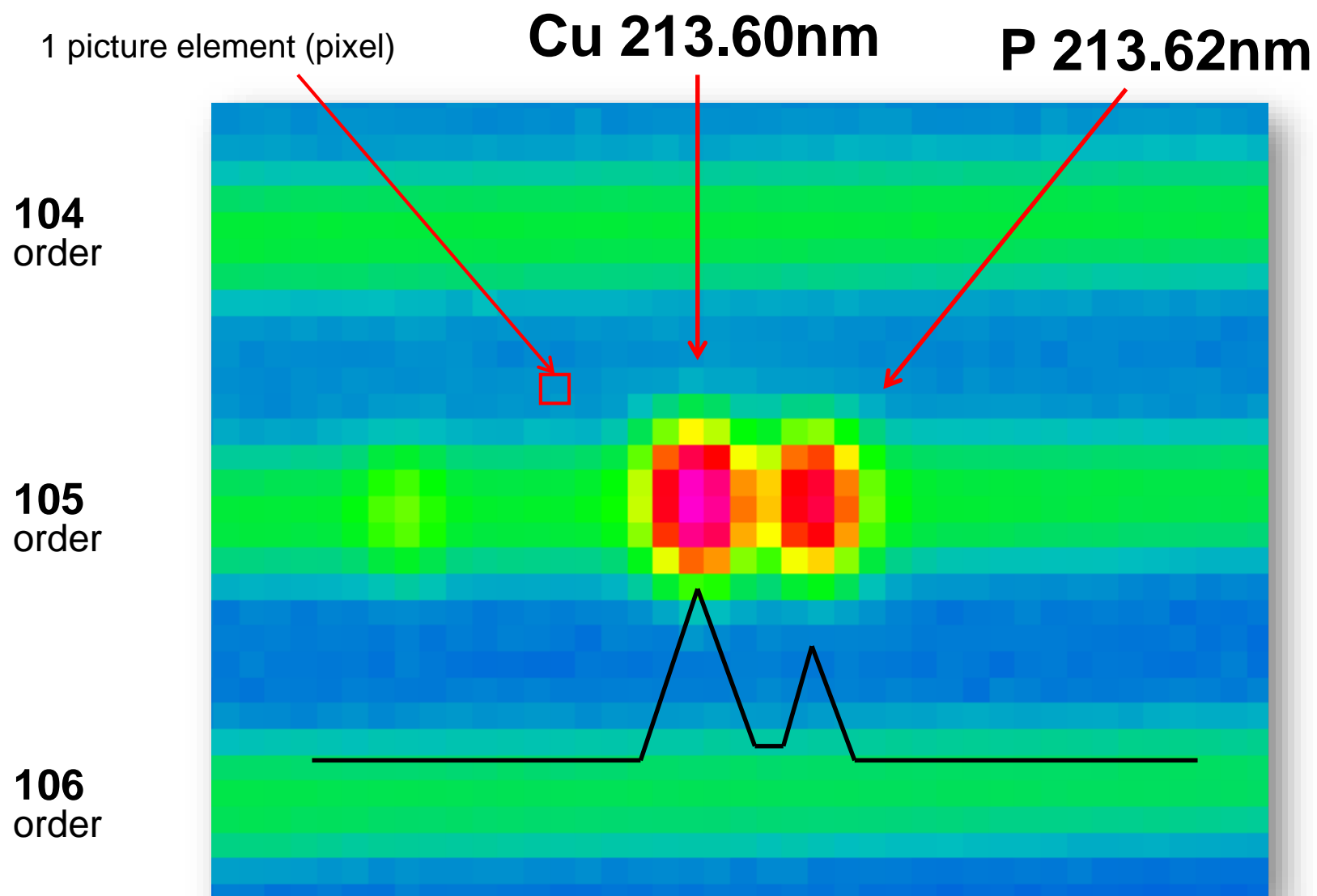
Vacuum Spectrometer



Echelle Spectrum

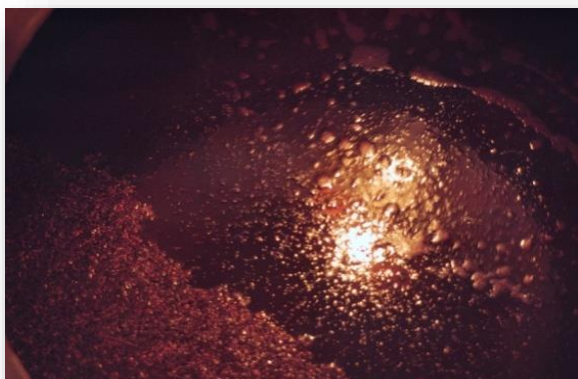
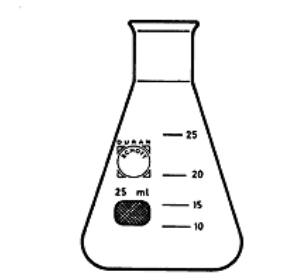


Echelle Spectrum



Sample Preparation

- Dilution with H₂O 1:1
- Alcohol concentration approx. 5 %
- HNO₃ concentration 0.1 %
- Calibration range: 0.005 to 50 mg/L.



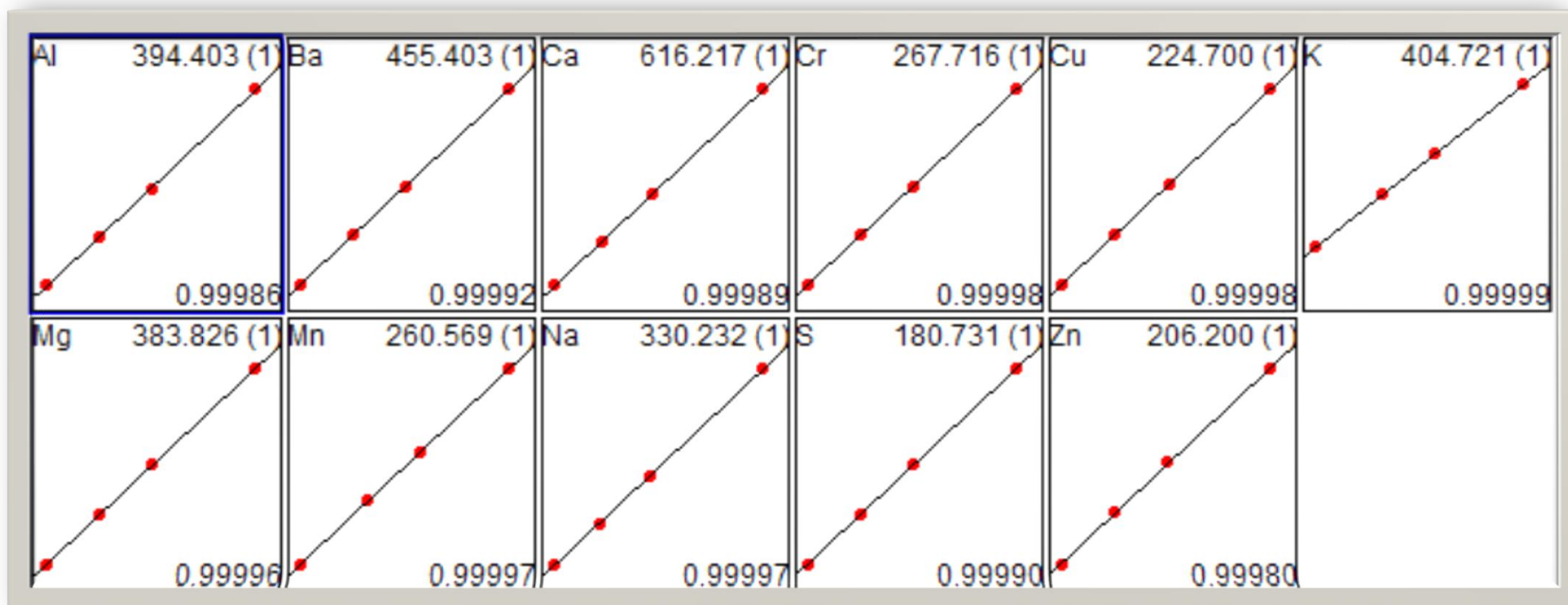
Argon Plasma with Minitorch

Parameters for element concentrations acc. to European wine directive:

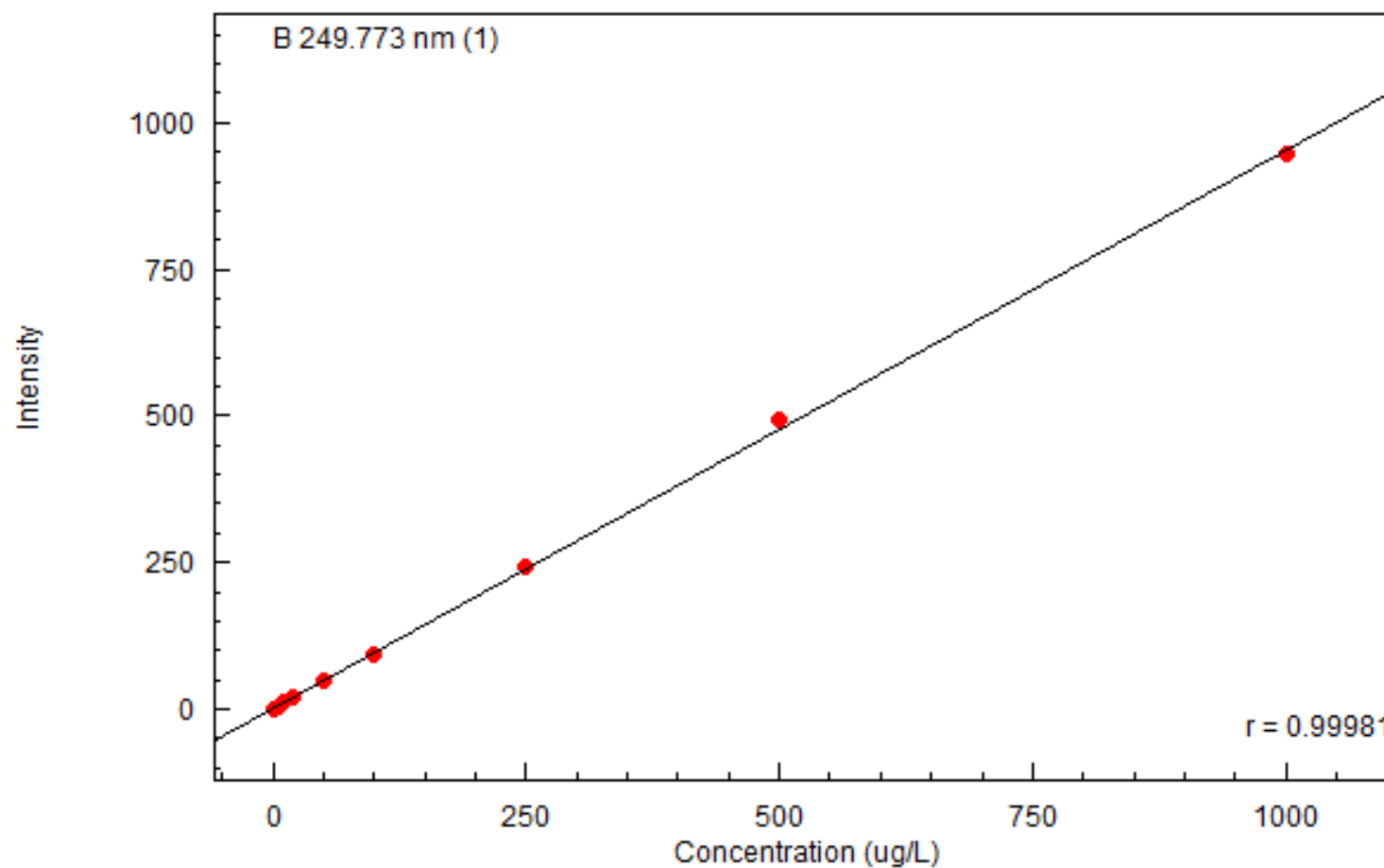
- RF Power 1.2 kW
- PL Gas 10 L/min
- AX Gas 0.6 L/min
- CA Gas 0.7 L/min

Multielement Calibration

Selected Calibration range from: 0 - 1000 $\mu\text{g/L}$



Boron Calibration 5 to 1000 µg/L



Equation: $\text{Conc} = a * I^3 + b * I^2 + c * I + d$

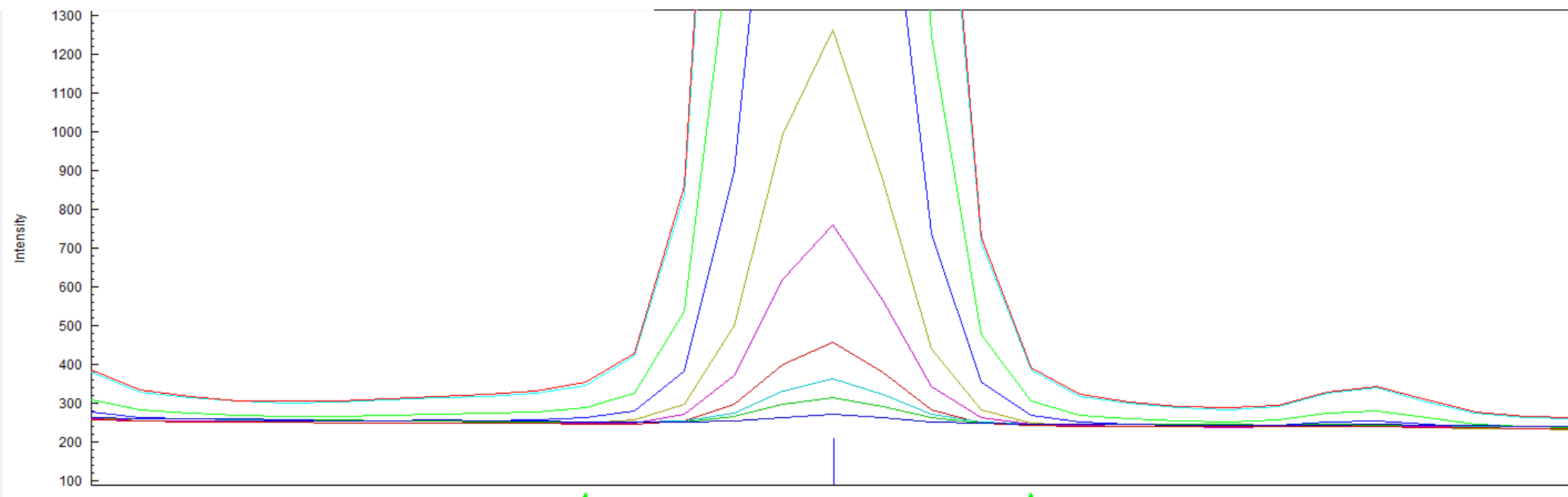
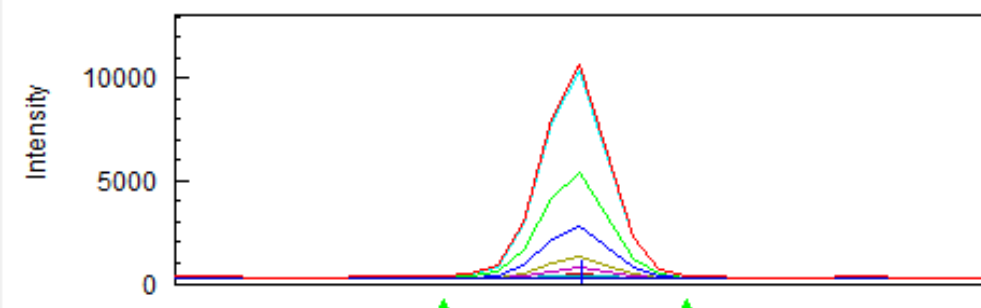
Factor: $a = 0.0000000$ $c = 1.050763$
 $b = 0.0000000$ $d = -2.384529$
Detection Limit (3s) = 0.7177392

Weight: None
Origin: None
Limit of Quantity (10s) = 2.392464

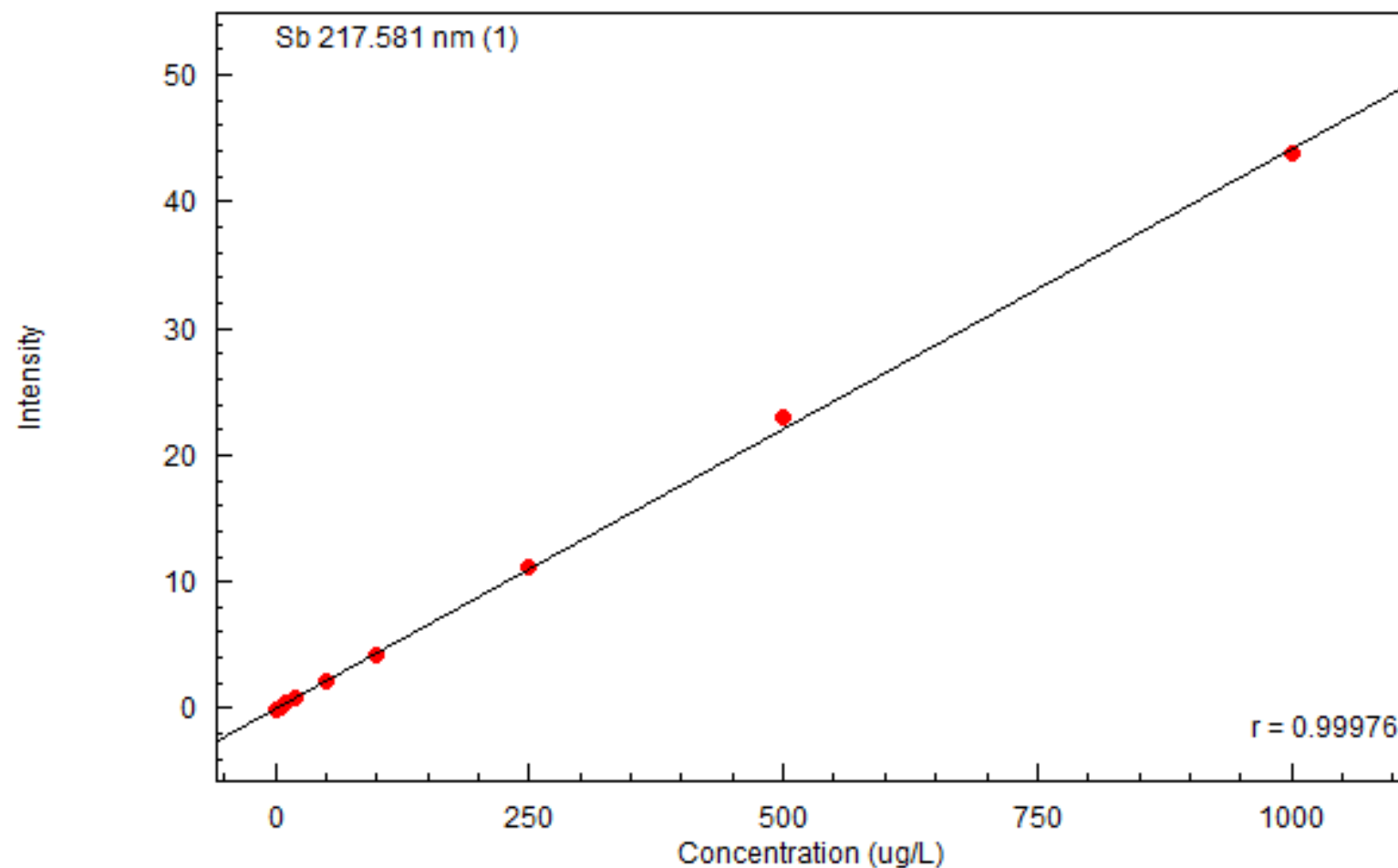
Boron Peak Profile

B 249.773 Best

Cond 1



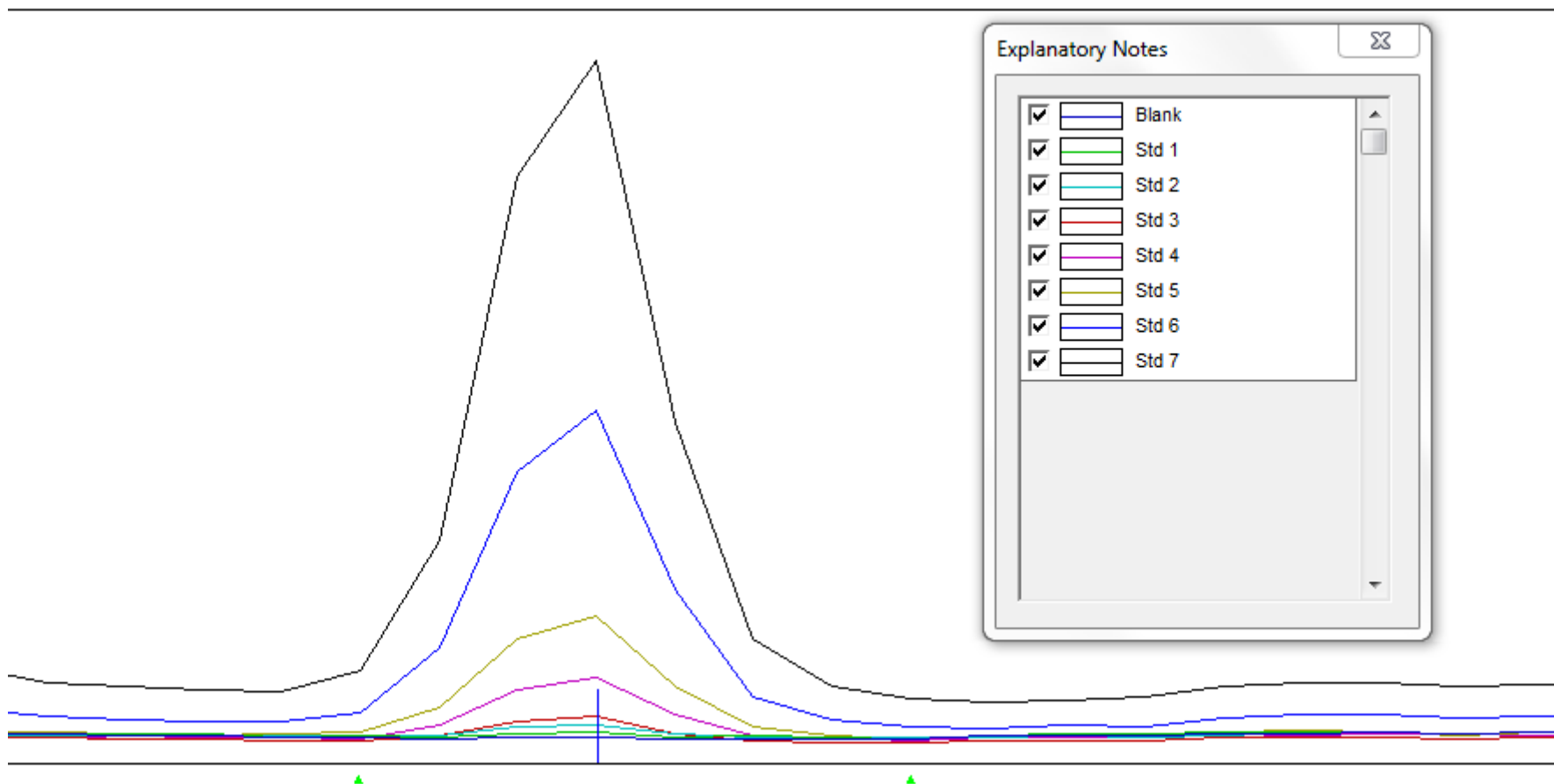
Antimony Calibration 5 to 1000 µg/L



Equation: $\text{Conc} = a * I^3 + b * I^2 + c * I + d$

Factor:	$a = 0.0000000$	$c = 22.63174$	Weight: None
	$b = 0.0000000$	$d = -0.3619756$	Origin: None
	Detection Limit (3s) = 0.9387628		Limit of Quantity (10s) = 3.129209

Antimony Peak Profile



Quantitation of Heavy Metals(3)

....using high sensitivity ICPMS-2030



Parameter	Setting
RF generator power	1.2 kW
Plasma gas	8 l/min
Auxiliary gas	1,1 l/min
Carrier gas	0.7 l/min
Nebulizer type	MicroMist
Sampling depth	6 mm
Spray Chamber temperature	5°C
Coll. Cell gas flow (He)	4 ml/min (std) 8 ml/min for As ⁷⁵ and Se ⁷⁸
Quantified Isotopes	V ⁵¹ , Cr ⁵² , Mn ⁵⁵ , Fe ⁵⁶ , Ni ⁶⁰ , Cu ⁶³ , Zn ⁶⁶ , As ⁷⁵ , Se ⁷⁸ , Cd ¹¹¹ , Sn ¹¹⁸ , Cs ¹³³ , Tl ²⁰⁵ , Pb ²⁰⁸
Internal Standards (ISTD)	Sc ⁴⁵ , Ge ⁷² , Y ⁸⁹ , In ¹¹⁵ , Tb ¹⁵⁹ , Ho ¹⁶⁵ , Lu ¹⁷⁵ , Bi ²⁰⁹



ICP- Spectrometry coupled to Mass



● Analysis Technique:

- **Multi-element analysis** : simultaneous as in ICP-OES
- Extremely sensitive => analysis of ultra-traces (< ppb => ppt).

Welcome in the World of Traces

1a	2a	3b	4b	5b	6b	7b	8				1b	2b	3a	4a	5a	6a	7a	0			
H																		He			
Li	Be															B	C	N	O	F	Ne
Na	Mg															Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	*L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	**A																			

<1ppt

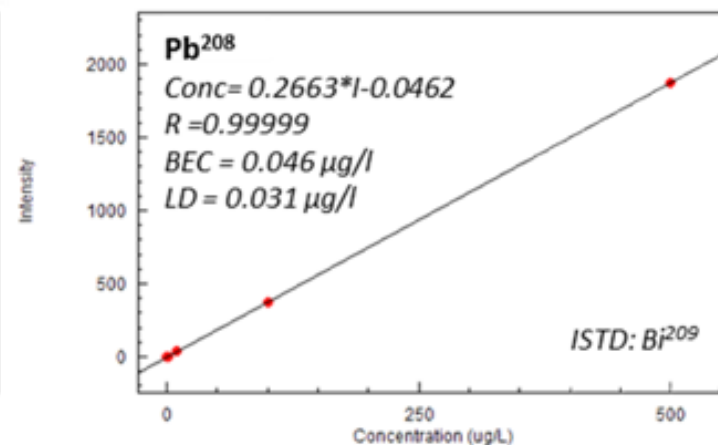
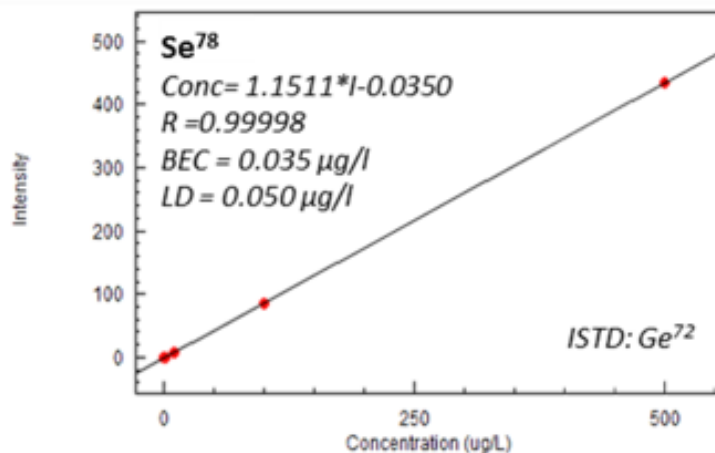
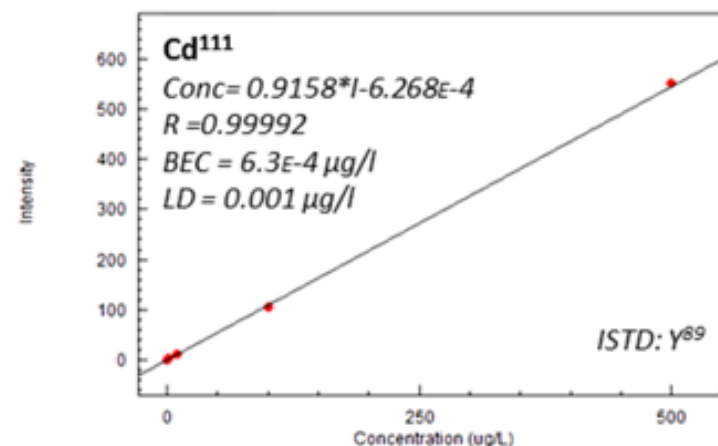
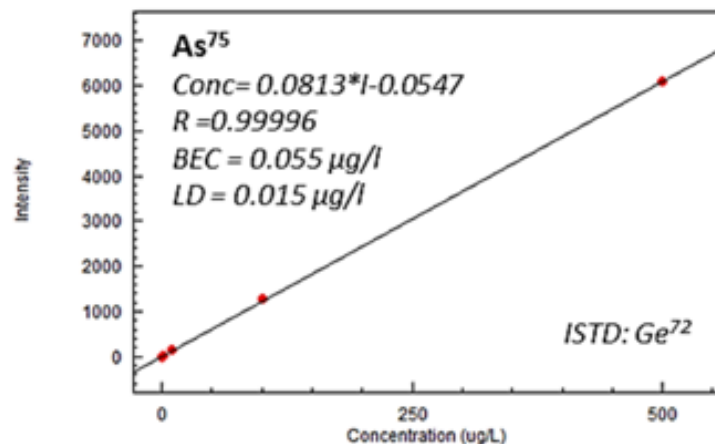
1~10ppt

10~100ppt

Other

*L	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Multielement Analysis



Analytical Results

Sample Name	Date/Time	As 75 (DBG) ug/L	Cd 111 (DBG) ug/L	Cr 52 (DBG) ug/L	Cs 133 (DBG) ug/L	Cu 63 (DBG) ug/L	Fe 56 (DBG) ug/L	Mn 55 (DBG) ug/L	Ni 60 (DBG) ug/L	Pb 208 (DBG) ug/L	Se 78 (DBG) ug/L	Tl 205 (DBG) ug/L	V 51 (DBG) ug/L	Zn 66 (DBG) ug/L
1. [REDACTED]	02.05.2017 13:19	5,39	1,26	18,6	3,11	73,2	793	833	20,6	10,9	2,71	1,26	44,1	1310
2. [REDACTED]	02.05.2017 13:20	5,16	0,246	8,01	10,1	11,4	601	932	22,1	9,9	2,09	0,393	2,46	803
3. [REDACTED]	02.05.2017 13:21	9,08	0,184	7,3	3,41	44,9	784	1510	15,4	21	1,64	0,175	7,31	918
4. [REDACTED]	02.05.2017 13:23	4,13	0,094	16,6	5,24	92,4	802	941	13	2,68	1,56	0,226	55,7	296
5. [REDACTED]	02.05.2017 13:24	2,58	0,106	4,59	0,921	3,2	433	832	7,07	14,8	1,15	0,15	2,43	628

Element concentrations are below MAC 's

Outlook

- Bordeauxmixture: $\text{CaCO}_3 + \text{CuSO}_4$
- Fungicide
- Accumulation in soil
- Ban from 2016?
- Until 2018 tolerated in EU



Conclusion

AAS, ICP-OES and ICP- MS are ideal tools for quantification of wine.

The systems are able to accept a wide variety of samples and offering the flexibility for a perfect match allowing easy operation and high sample throughput.

Thank You....

...and please enjoy your wine!



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