Practical applications of TXRF in fruits, beverages, wines and fining agents

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Welcome

Speakers

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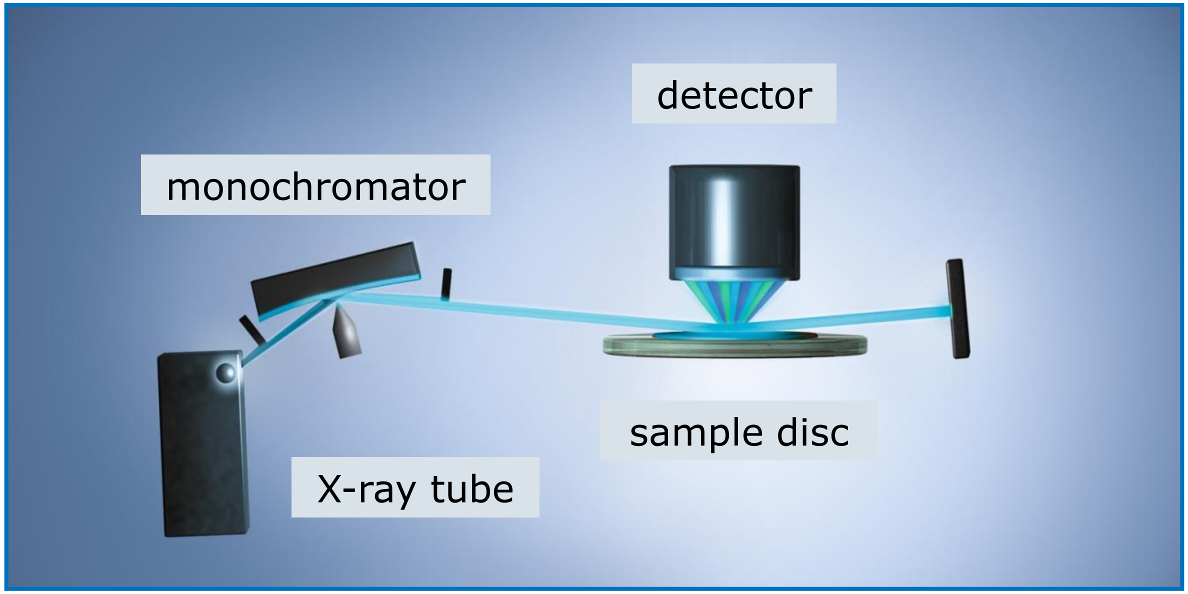
Itinerary

- Principles of TXRF
- Examples for the analysis of wine, fruits and fining agents
- TXRF analysis of beer and wort
- Q & A

Principles of TXRF

Principles of TXRF
Technical background

Total reflection X-ray fluorescence spectroscopy



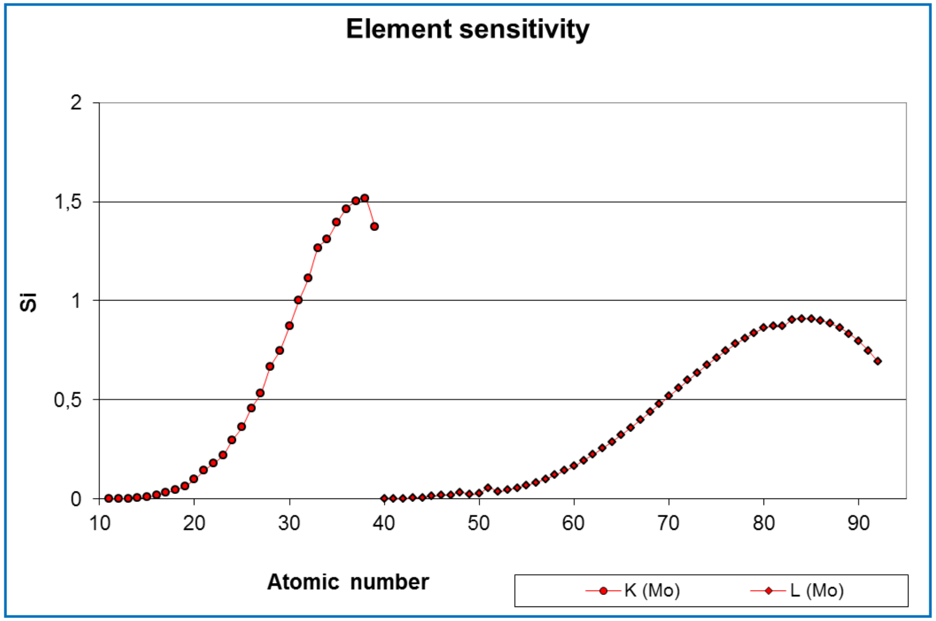
Beam angle: 0˚ / 90˚

- Samples must be prepared on a reflective media
- Polished quartz glass or polyacrylic glass disc
- Dried to a thin layer, or as a thin film or microparticle
- Matrix effects are negligible

Principles of TXRF Quantification

$$C_i = \frac{C_{IS} \cdot N_i \cdot S_{IS}}{N_{IS} \cdot S_i}$$

C_i: Element concentration
C_{IS}: Internal standard concentration
N_i: Element net countrate
N_{IS}: Internal standard net countrate
S_i: Element sensitivity factor
S_{IS}: Internal standard sensitivity factor



Principles of TXRF
Bruker Product Portfolio

BRUKER

S2 PICOFOX

- Most compact design — transportable, for on-site analysis
- Fixed excitation mode — easy to use, most suitable for teaching
- about 300 installations worldwide — well established technology

S4 T-STAR

- Multiple excitation modes — to detect most elements of the PSE
- Large area detectors — improved sensitivity for lowest limits of detection
- Motorized beam path — automatic beam adjustment and QC procedures
- Large sample capacity — up to 90 sample discs, multi-user operation

Examples for the analysis of wine, juices and fining agents

Overview

- How to measure ?
  - Short explanation of sample preparation

- Examples from the beverage industry
  - Hazes, turbidity in beverages
  - Fining agents
  - Wine
  - Fruits

- *Some Pros and Cons*

Total Reflection X-Ray Fluorescence Spectroscopy
S2 PICOFOX (Bruker)

Sample preparation solids

- Transfer quantitatively to a tube

- Suspend in 1 to 2 ml detergent solution

- Add standard

- Homogenize carefully

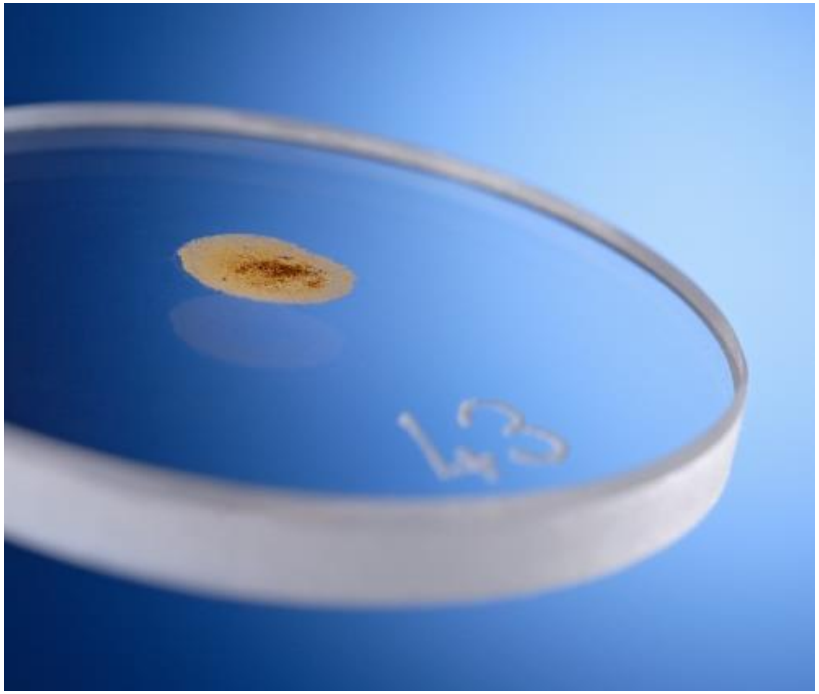
- Pipette 5 to 20 µl on carrier

sample preparation
drying and measuring

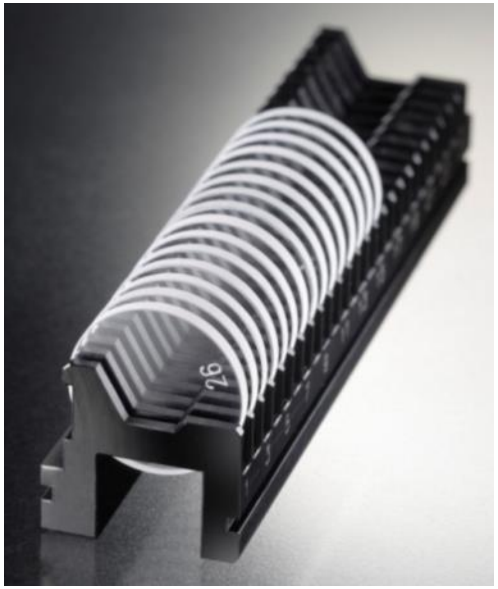
■ Dry through heat or vacuum

■ Load the instrument

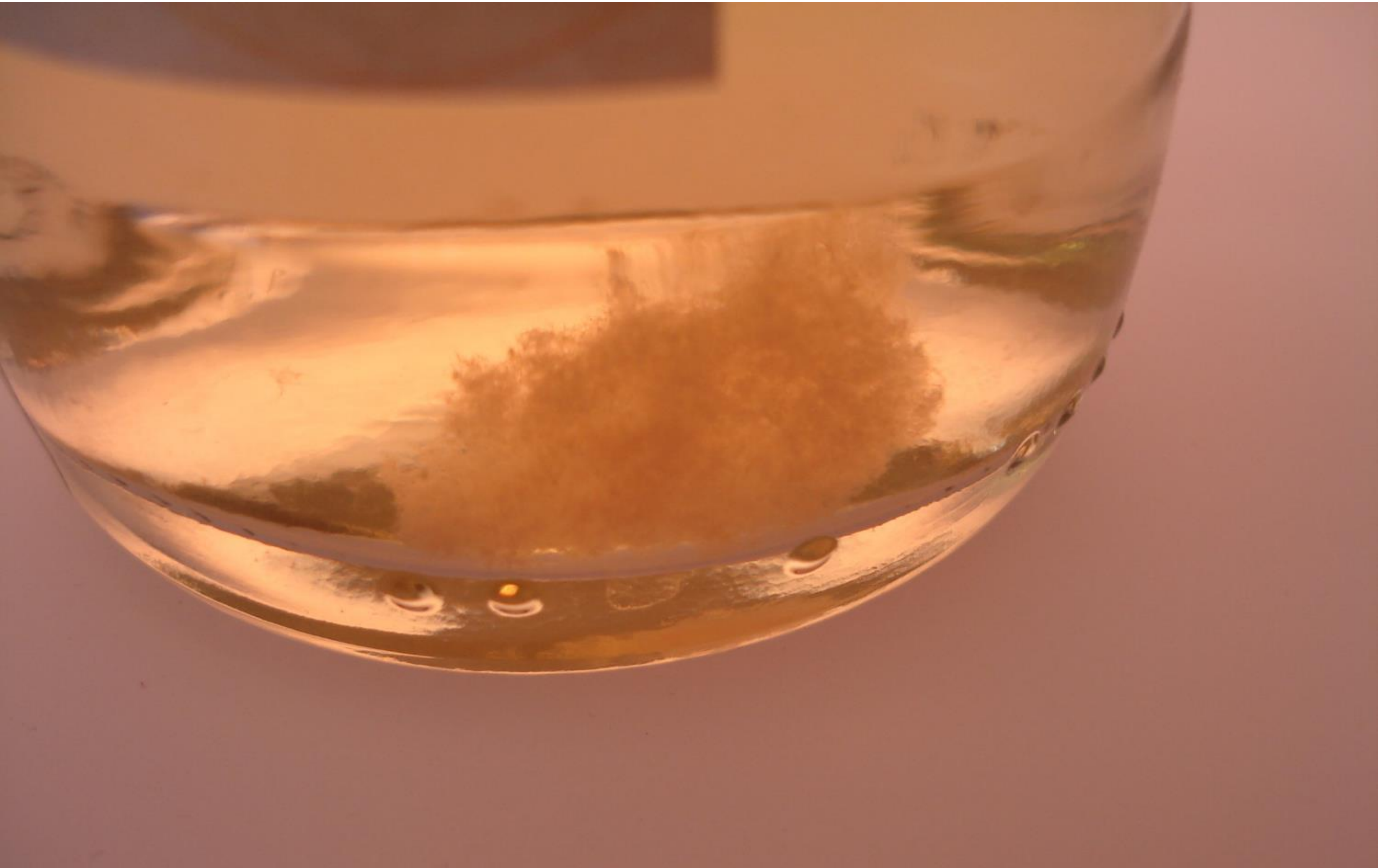
30 mm labelled quartz disc



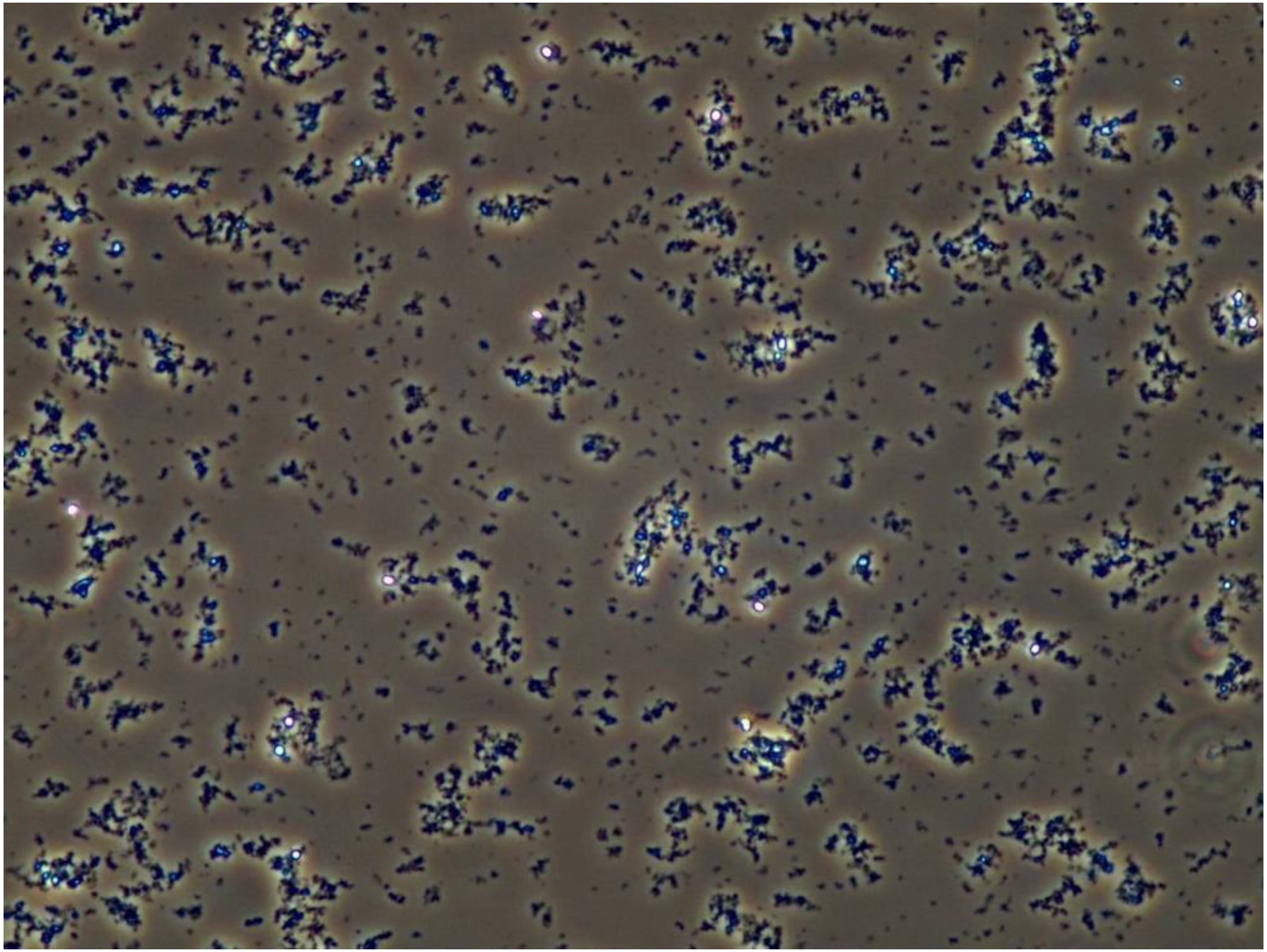
sample casette for 25 samples



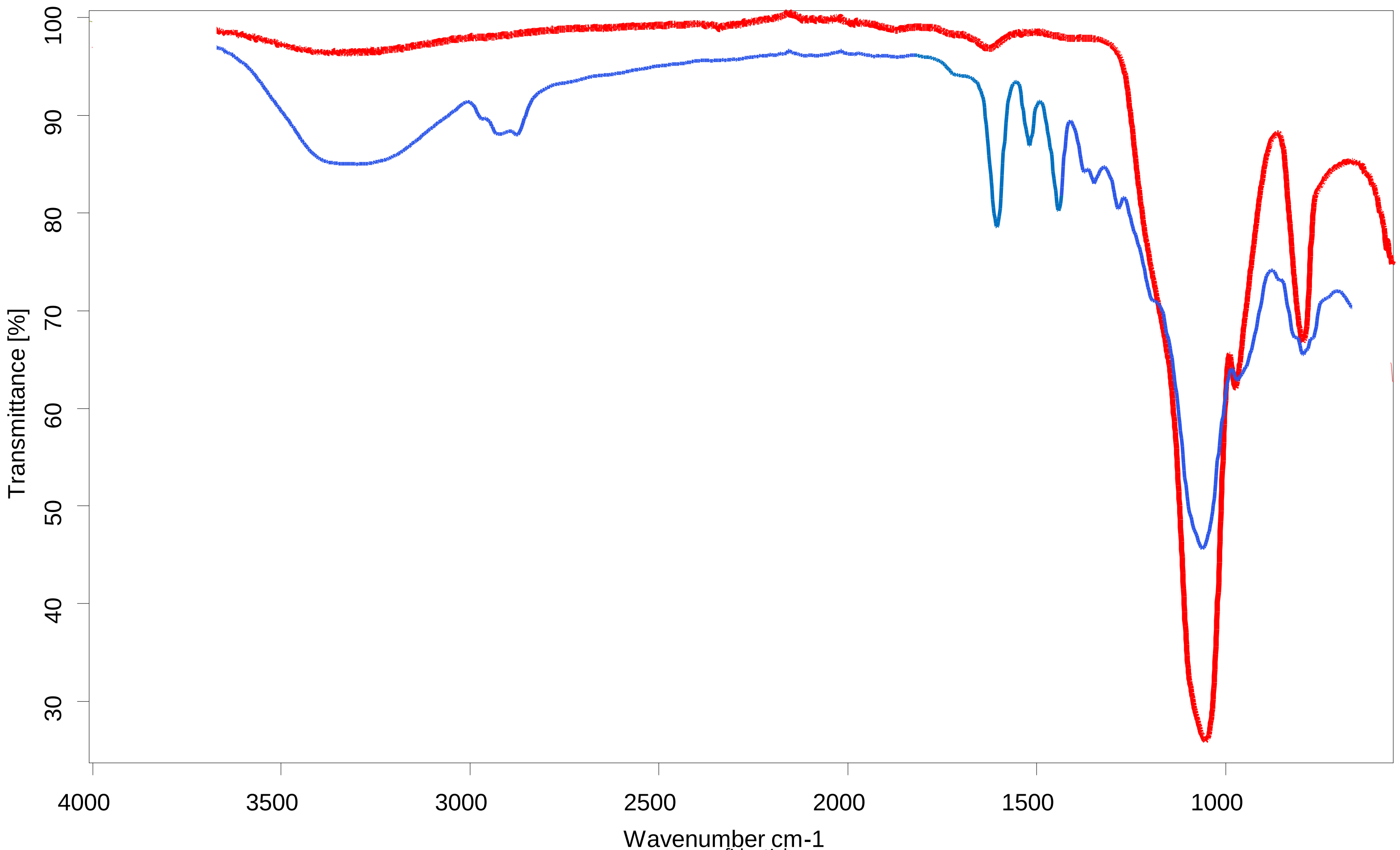
Damages to beverages due to hazes and turbidities



Hazes from roséwine
125x

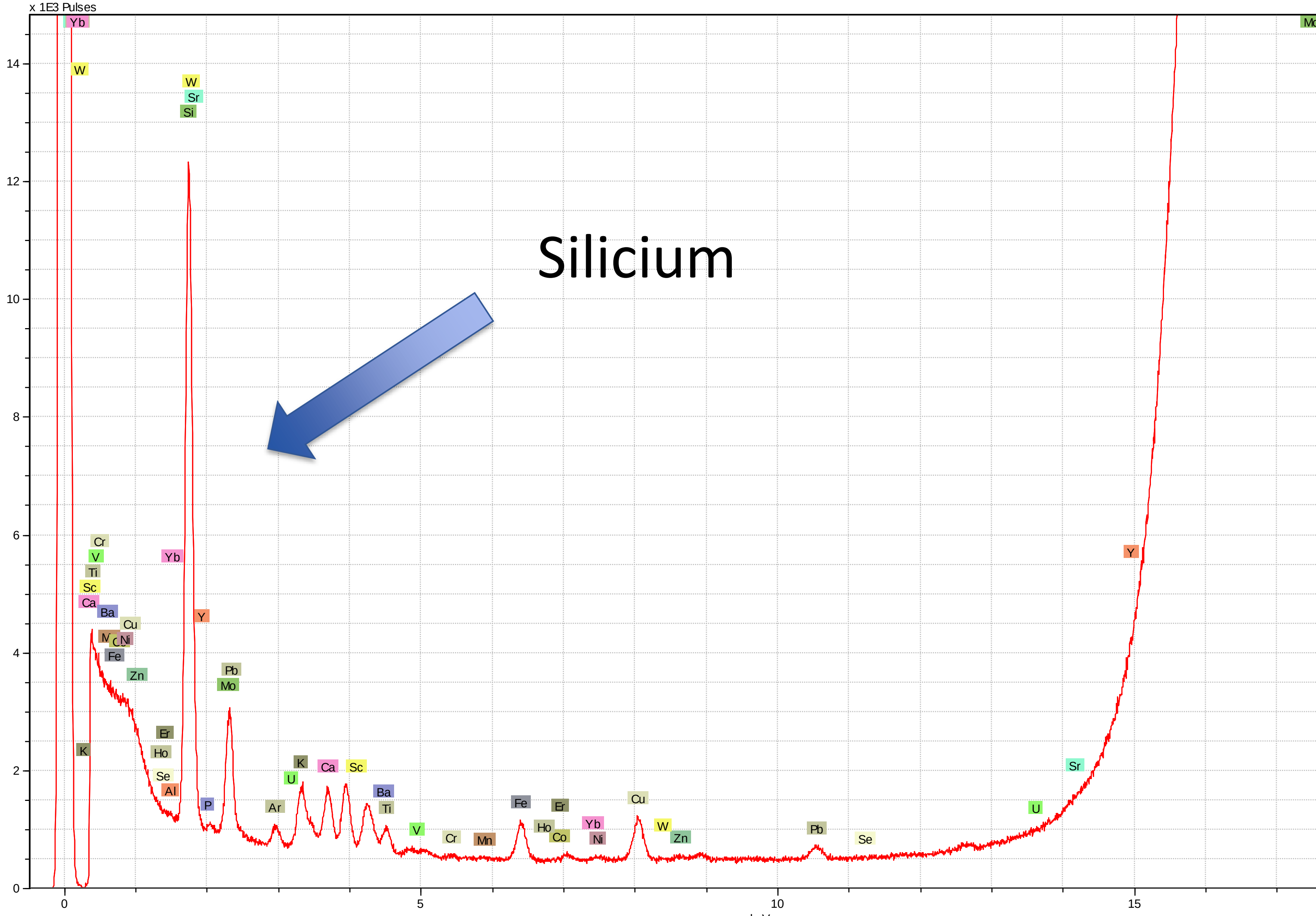


Hazes from roséwine (blue) FTIR comparision with SiO_2 (red)



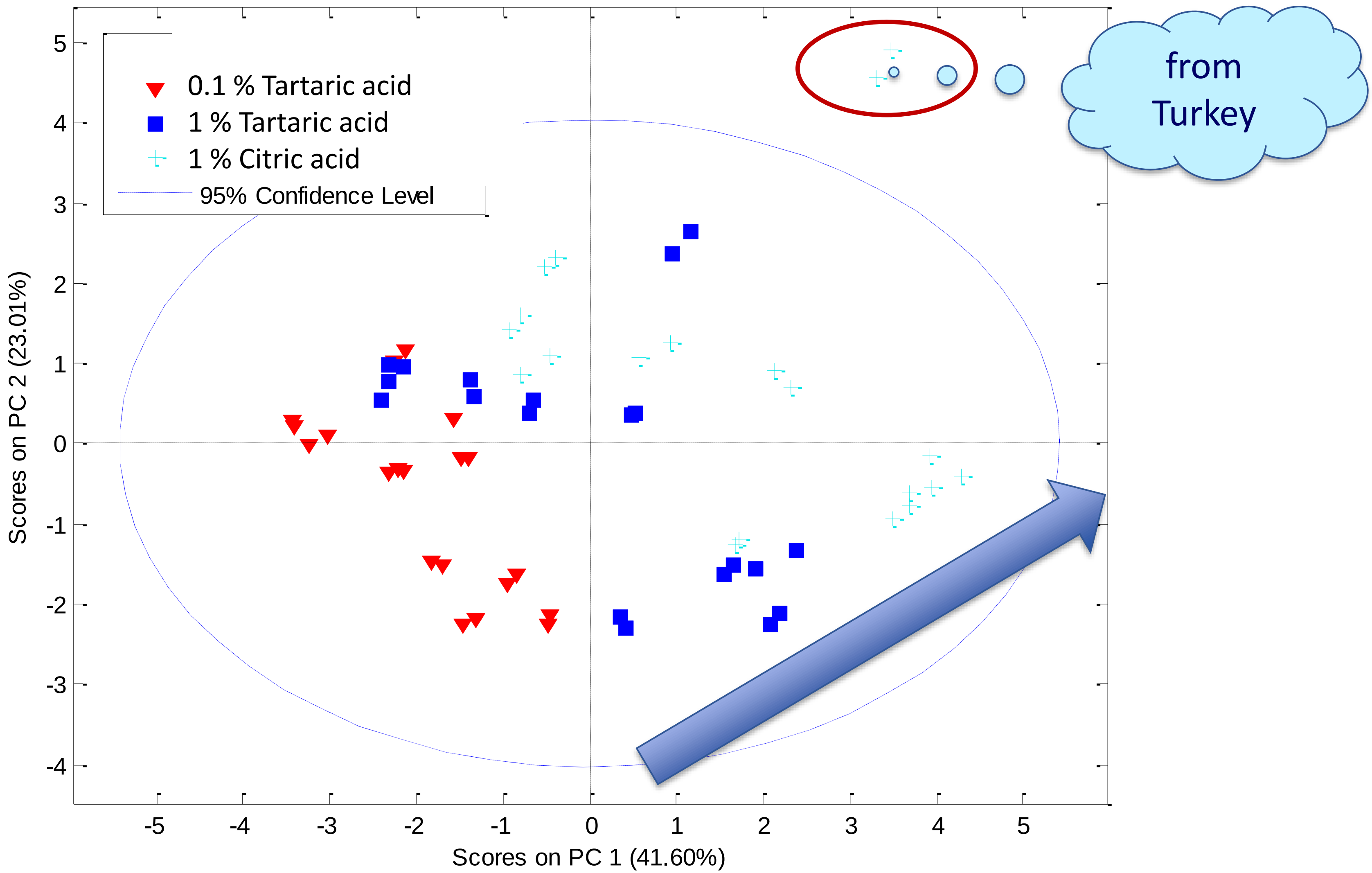
- confidential -

Hazes from roséwine
TXRF on a plastic plate



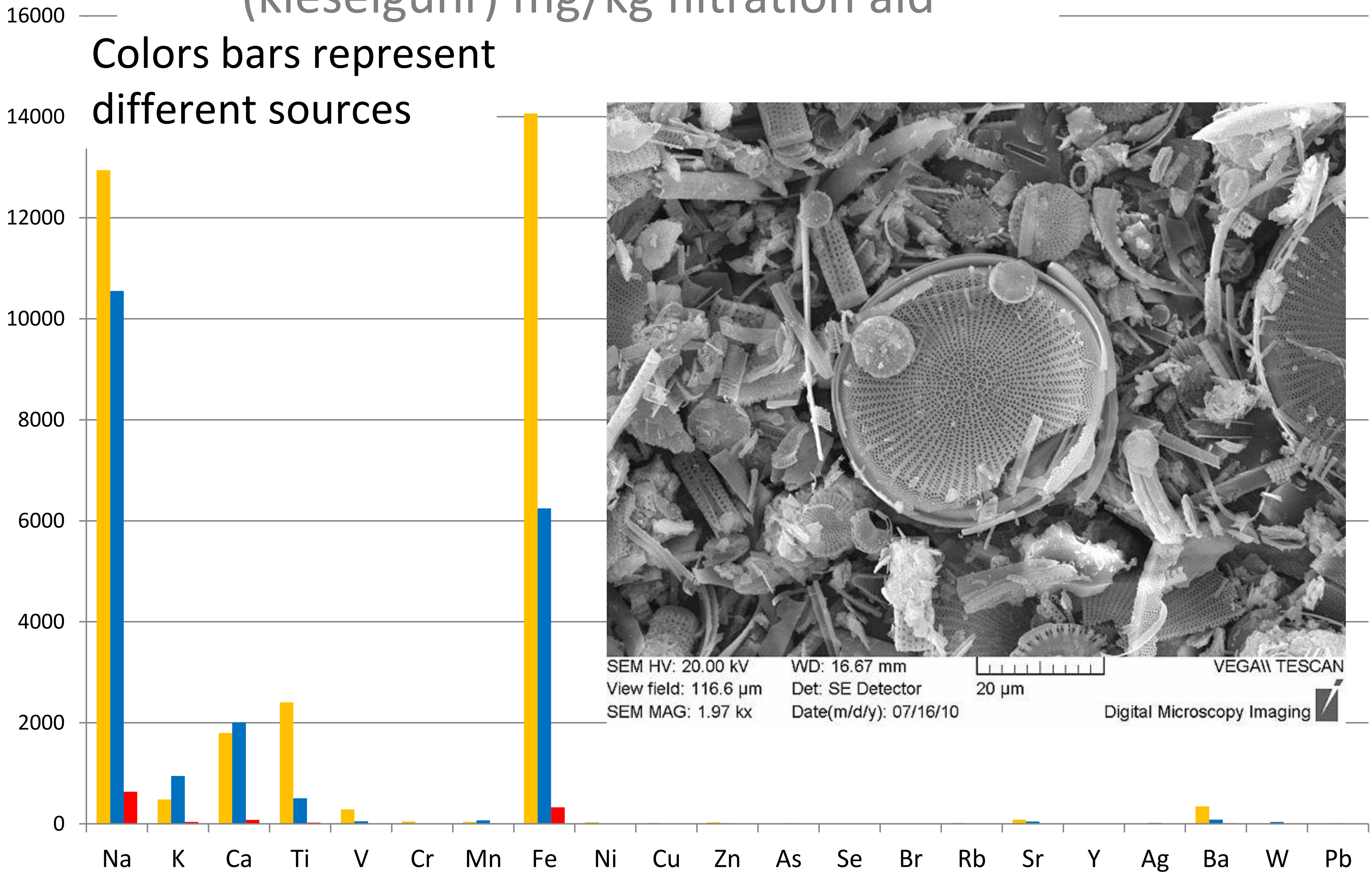
Multielement PCA
Eluted elements from bentonite

(0,5 g bentonite /100 mL 0,1% TA; 1% TA; 1% CA)



Different diatomaceous earth
(kieselguhr) mg/kg filtration aid

Colors bars represent different sources



diatomaceous earth (kieselguhr) mg/kg

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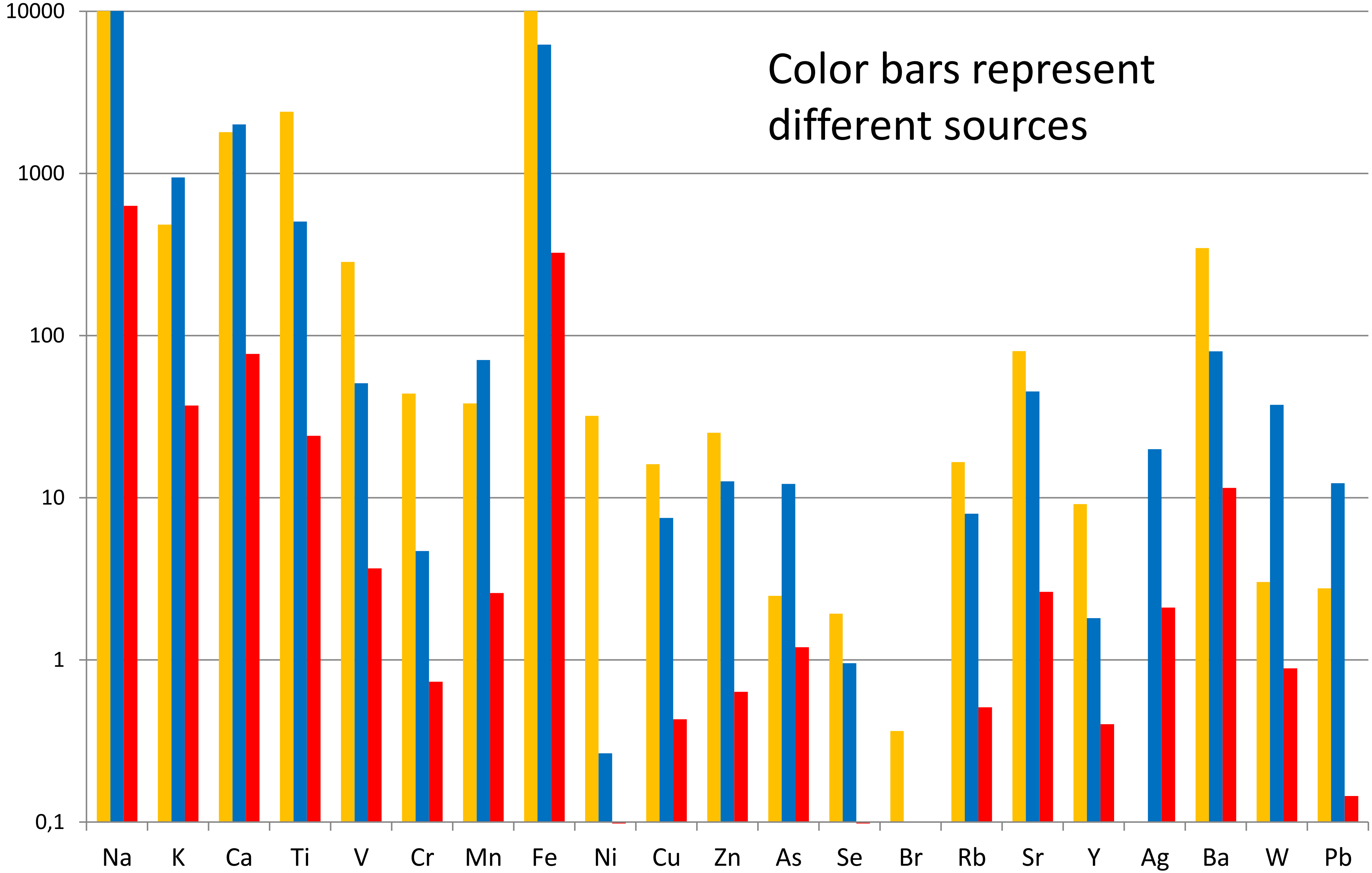
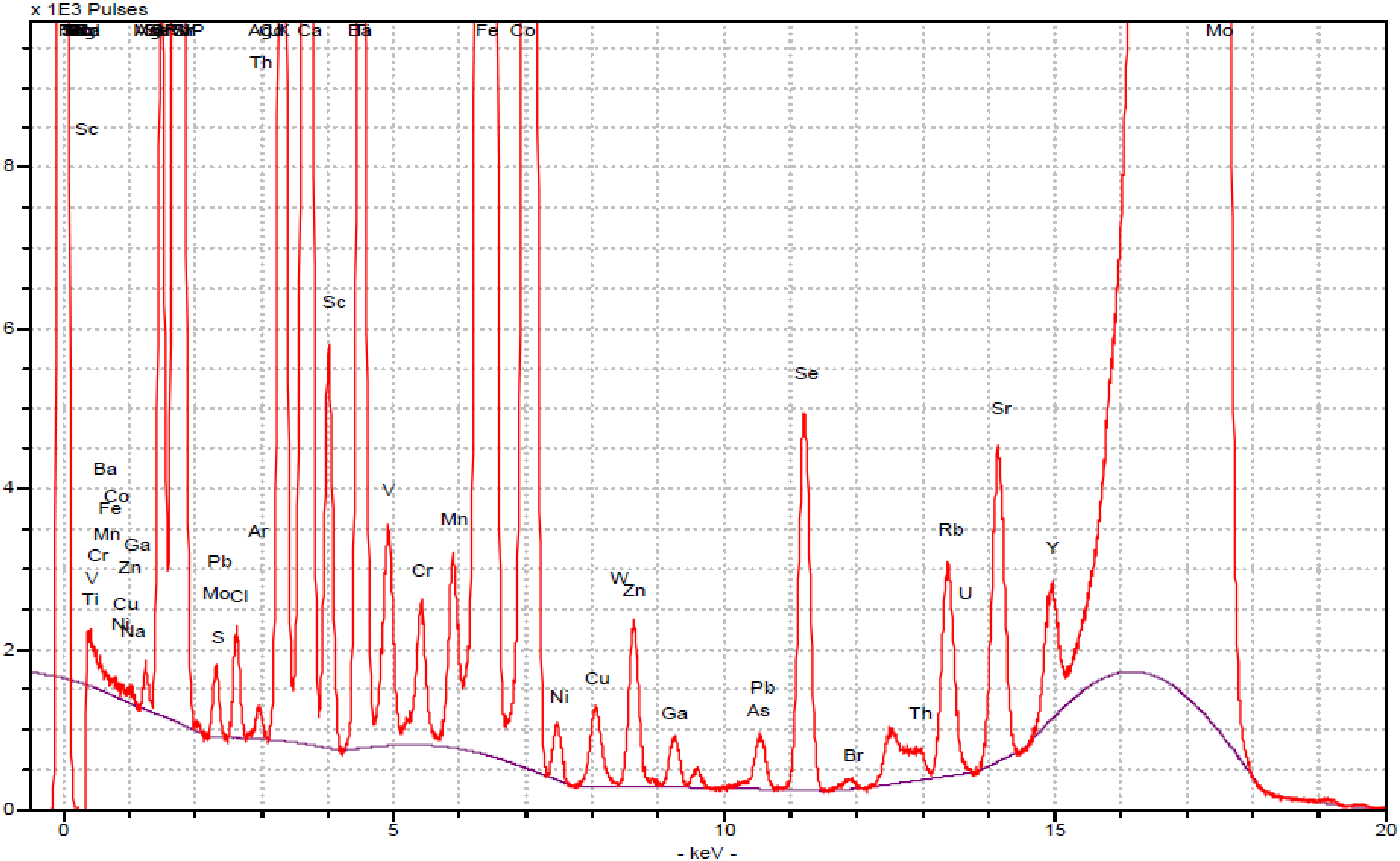


Chitosan

exoskeleton of crustaceans (such as crabs and shrimp)



Chitosan

from marine organisms

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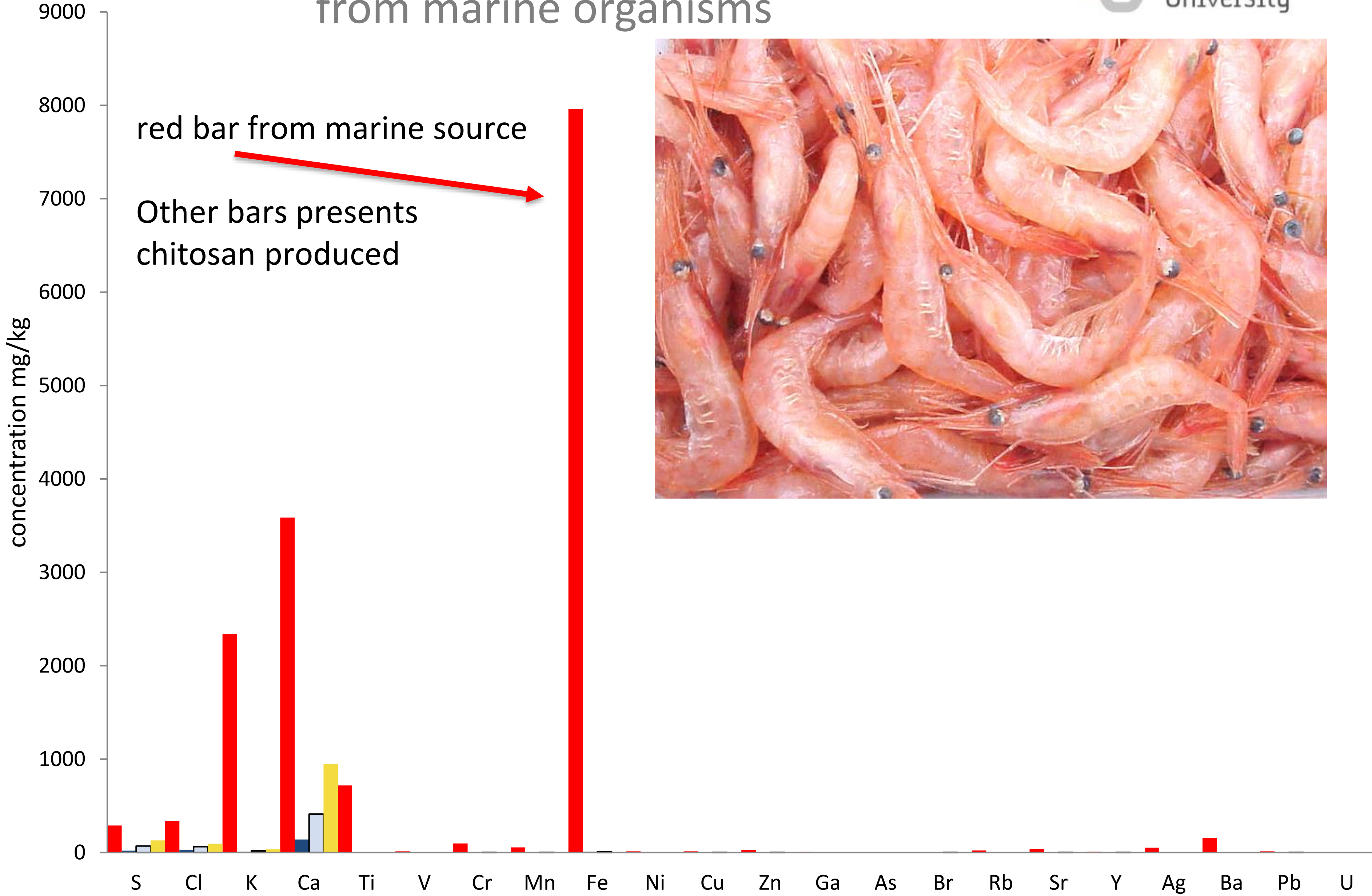
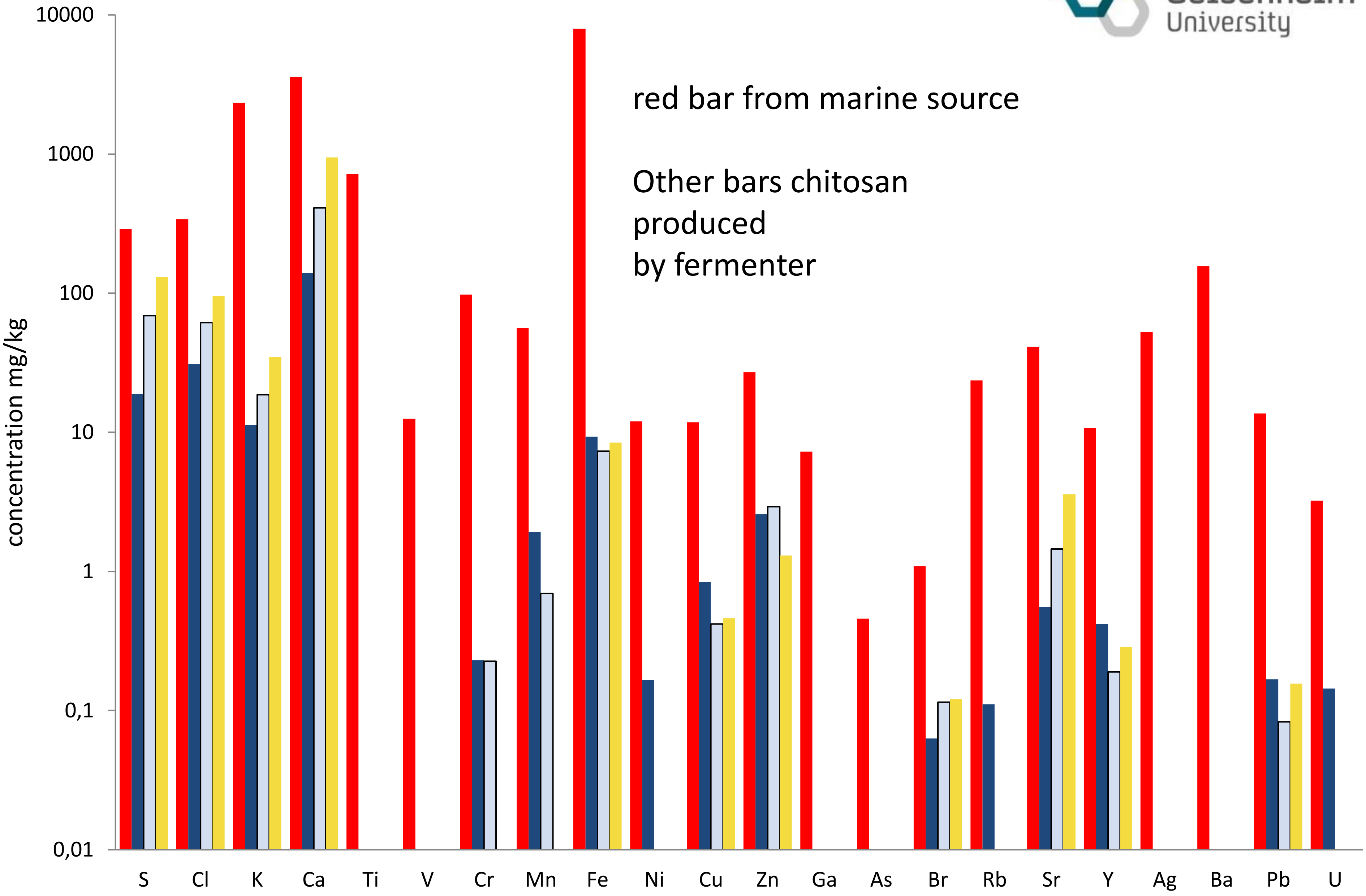


Chitosan



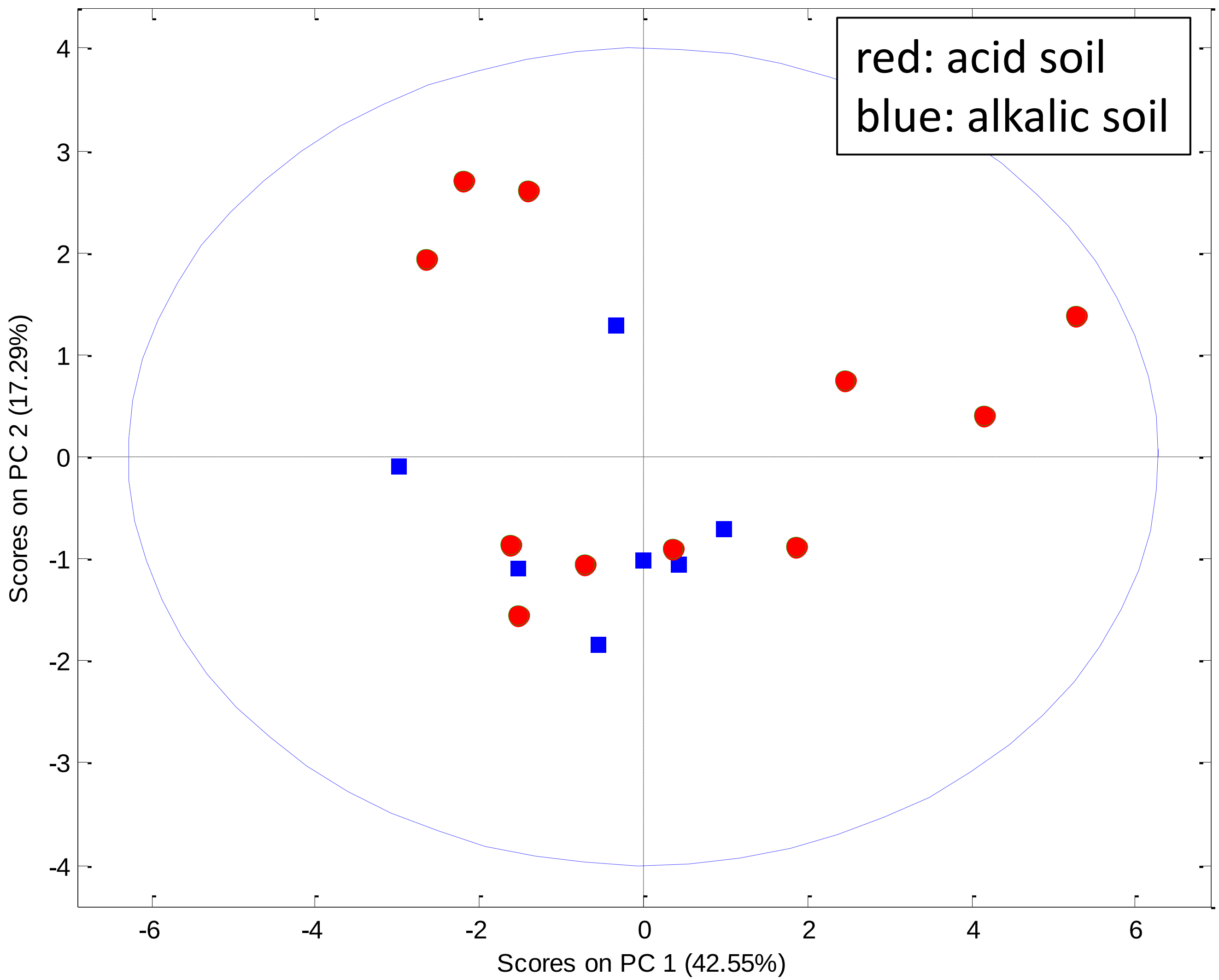
red bar from marine source

Other bars chitosan produced by fermenter

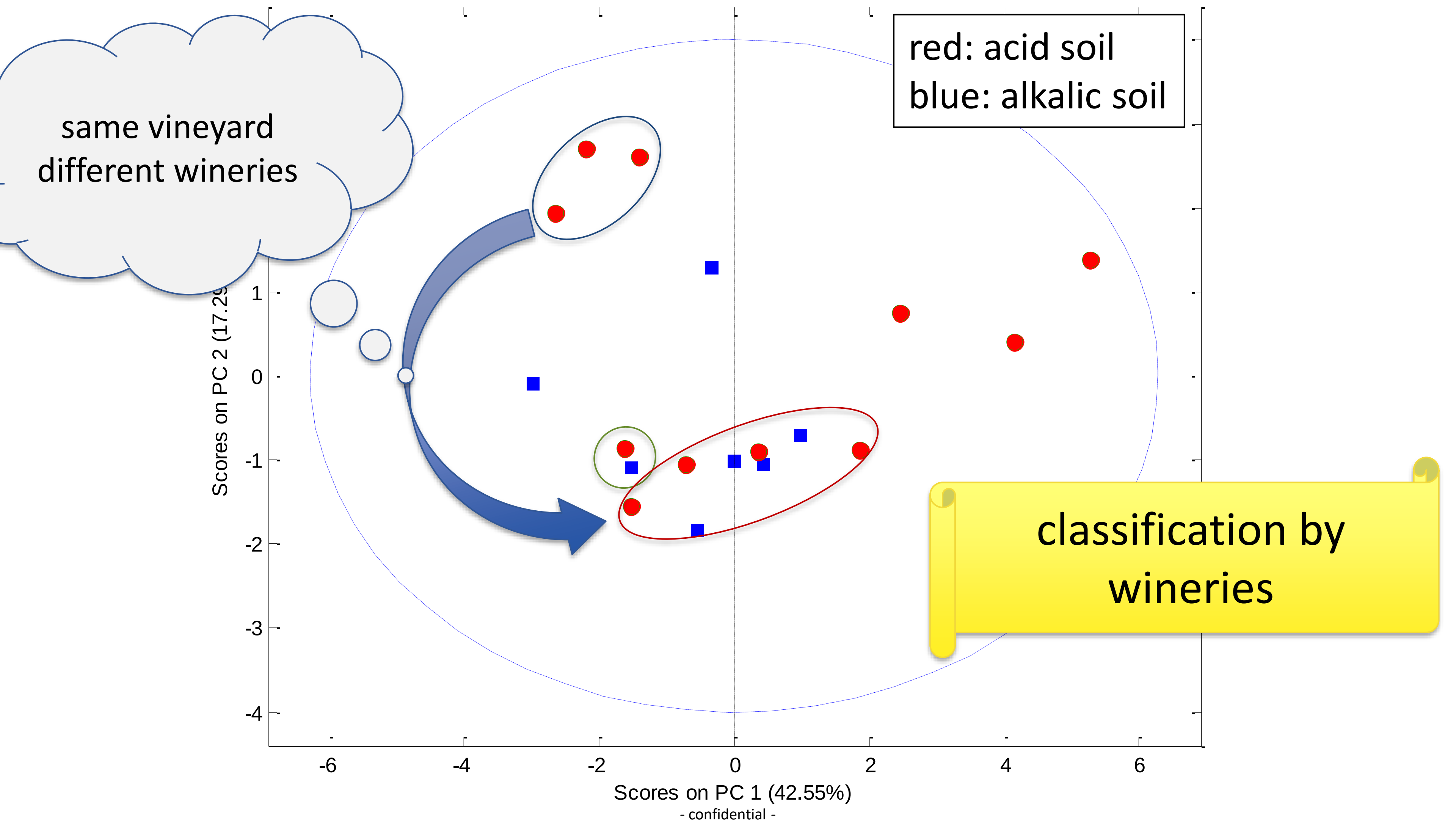
Terroir ?

From French: *soil, earth, origin, provenance, site, vineyard*

Terroir ?
PCA of the multielement spectra



Terroir ?
Element composition is mainly influenced by the winery and not by the soil



Amphora wine

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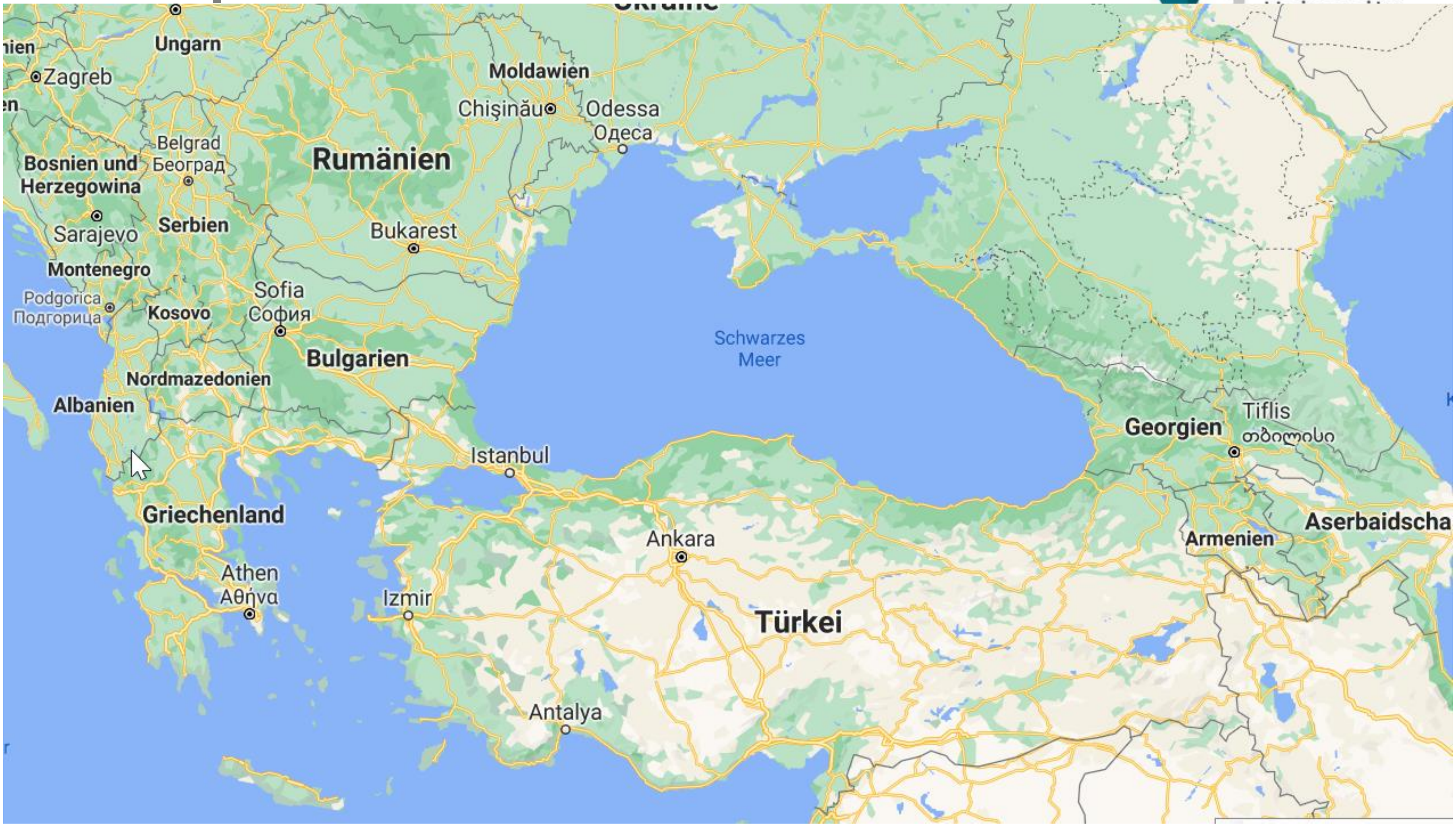
Kvevri from
Western Georgia

Amphora wine



Kvevri from

Western Georgia

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Kvevri from
Western Georgia

	clay chard		withewine	redwine
	mg/kg		mg/L	mg/L
Al	41740		2,9	15,3
P	158,1		124,3	154,2
S			66,6	63,8
Cl	26,5		15,4	10,6
K	9461		1235	1362
Ca	4341		65	65
Ti	1948			
V	54,6		0,06	0,04
Cr	90,9			
Mn	151		0,44	0,37
Fe	27170		0,47	0,69
Ni	37,7		0,01	0,01
Cu	24,8		0,42	0,51
Zn	38,2		0,96	0,86
Ga	10,3			
As	12,2			
Se	261	IST	1,00	1,00
Br	33,9		0,04	0,05
Rb	61,8		0,53	0,45
Sr	66,2		1,47	0,67
Y	9,5		0,02	
Ag	27			
Ba	583		0,08	
W	1,6			
Pb	21,5		0,04	0,04
U	1,81		0,05	0,02

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Amphora wine

Wine prepared in concrete barrel

	concrete barrel mg/l	Control stainless steel barrel mg/l
P	92	93
S	59	52
Cl	0,7	2,8
K	875	814
Ca	96	125
Sc	100 IST	100 IST
Cr	0,027	
Mn	1,2	0,9
Fe	11,2	2,3
Co		0,027
Ni	0,021	0,008
Cu	0,025	0,016
Zn	0,64	0,72
As		
Br	0,087	0,08
Rb	0,52	0,52
Sr	1,08	0,56
Ba	0,213	
Ce		
Pb	0,060	0,053

Legal limits for wine

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	Treshold value*	AAS	ICP-OES	TXRF
Al	8 mg/l	☺	☺	😐
As	0,10 mg/l	☺	☺	☺
Pb	0,25 mg/l	☺	☺	☺
H_3BO_3	80 mg/l	☺	☺	☹
Br	1 mg/l	☹	☹	☺
F	1 mg/l	☹	☹	☹
Cd	0,01 mg/l	☺	☺	☹
Cu	2 mg/l	☺	☺	☺
Zn	5 mg/l	☺	☺	☺
Sn	1 mg/l	☺	☺	☺

*: Wine regulation (new version from May, 14th 2002 [BGBI. IS. 1583])

Xylem juice from vine plants

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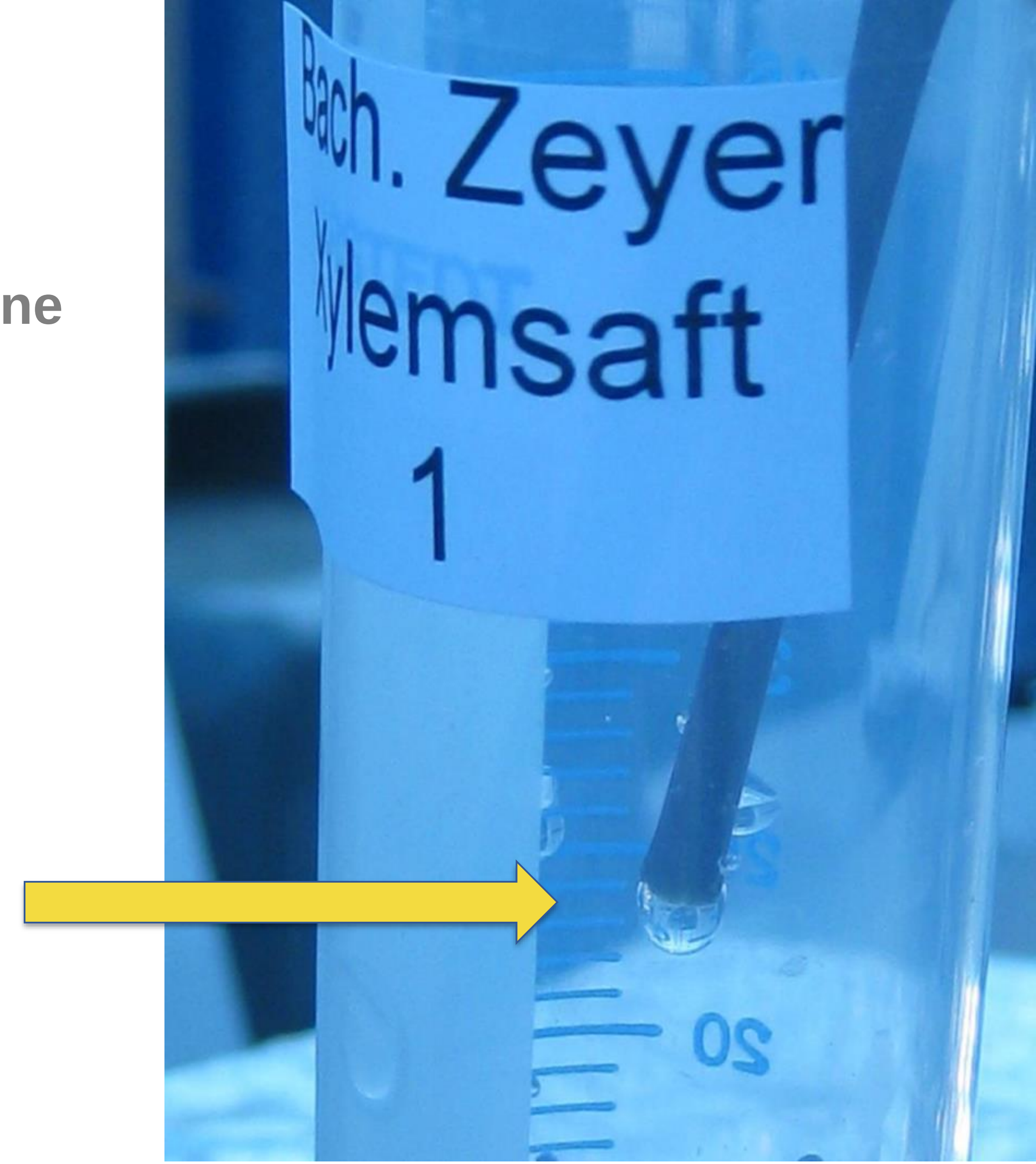
Xyleme juice from vine



Element	Line	Conc./ mg/l	RSD/ %	LLD/ mg/l	Net area
Na	K12	53	21,6	24	759
Mg	K12	67,7	6,4	8,6	2619
Al	K12	5,10	12,5	1,31	1284
P	K12	40,75	0,7	0,32	44641
S	K12	26,72	0,6	0,17	57373
Cl	K12	0,407	12,6	0,106	1377
K	K12	75,49	0,2	0,05	608920
Ca	K12	205,26	0,2	0,02	2306118
Sc	K12	Not det.		0,01	1
Ti	K12	Not det.		0,01	1
V	K12	Not det.		0,01	1
Cr	K12	Not det.		0,01	95
Mn	K12	1,024	0,6	0,005	41143
Fe	K12	0,247	1,2	0,004	12589
Co	K12	Not det.		0,003	1
Ni	K12	Not det.		0,002	1
Cu	K12	0,012	8,9	0,002	1030
Zn	K12	0,355	0,7	0,002	34341
Ga	K12	Not det.		0,002	1
As	K12	Not det.		0,001	1
Se (IS)	K12	1,000	0,4	0,001	145777
Br	K12	0,008	8,0	0,001	1257
Rb	K12	0,015	4,8	0,001	2489
Sr	K12	0,029	3,2	0,002	4939
Y	K12	Not det.		0,002	4
Ag	L1	Not det.		0,171	351

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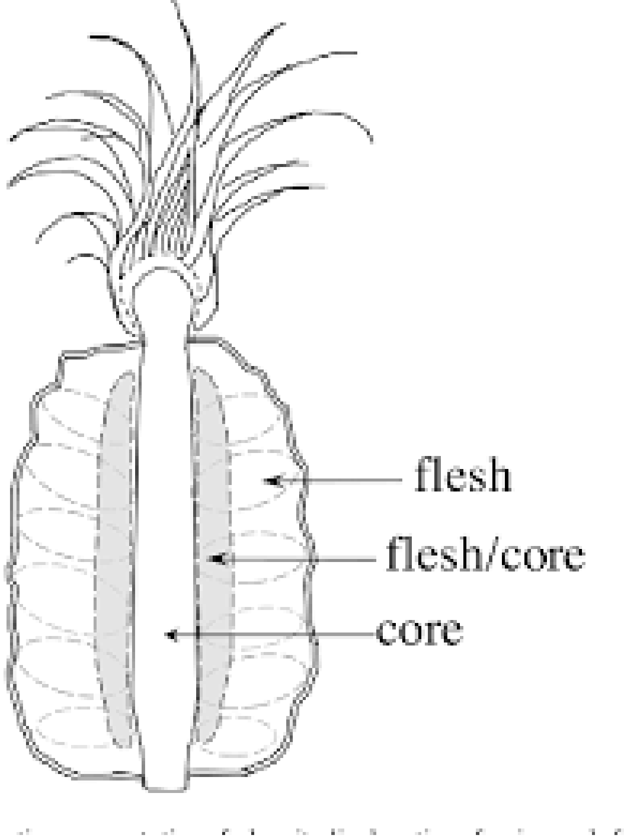
Xylem „juice“

TXRF

generated report

Element	Line	Conc./ mg/l	RSD/ %	LLD/ mg/l	Net area
W	L1	Not det.		0,002	1
Pb	L1	Not det.		0,002	107
U	L1	Not det.		0,003	144

Pineapple



Manganese in pineapple fruits*

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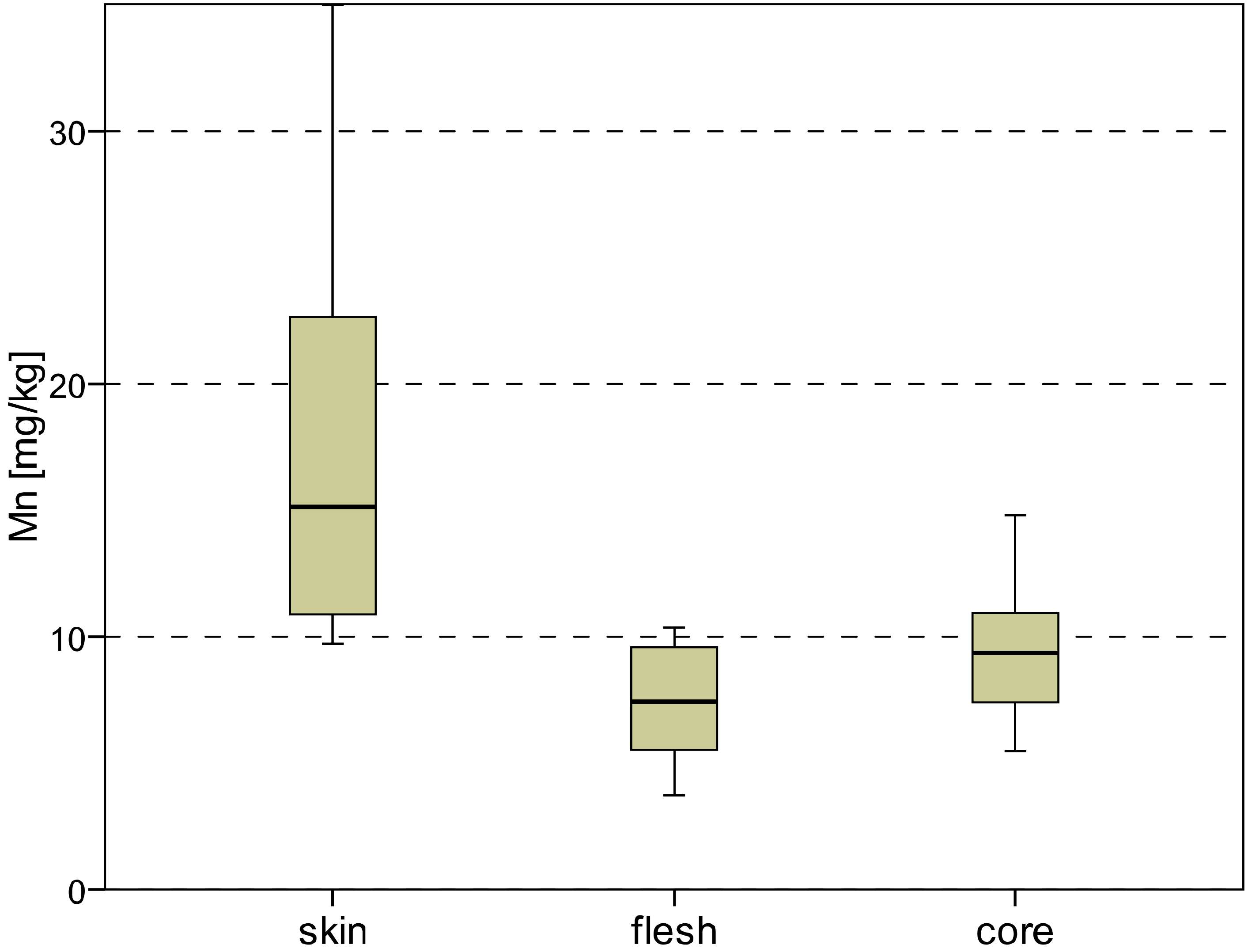
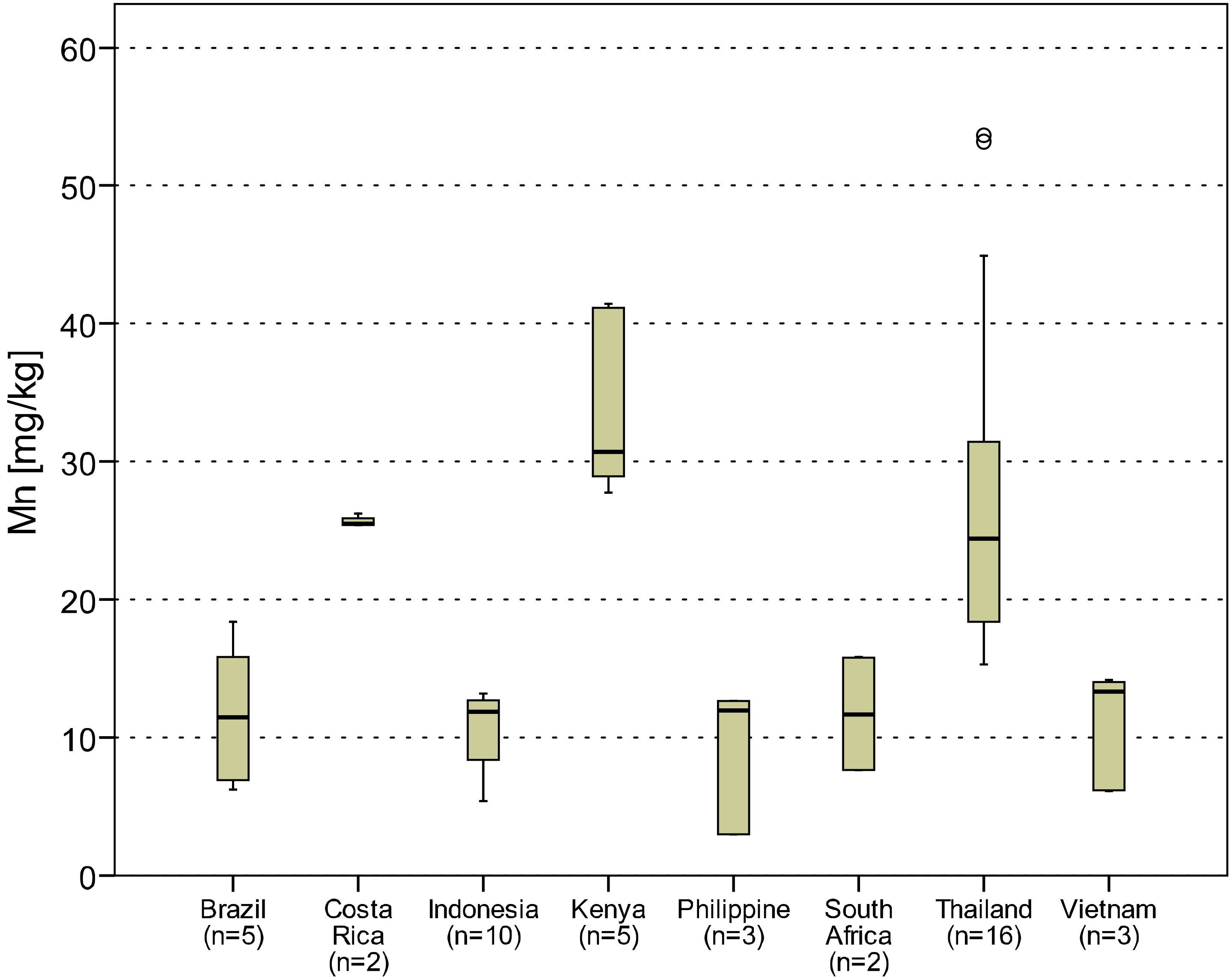
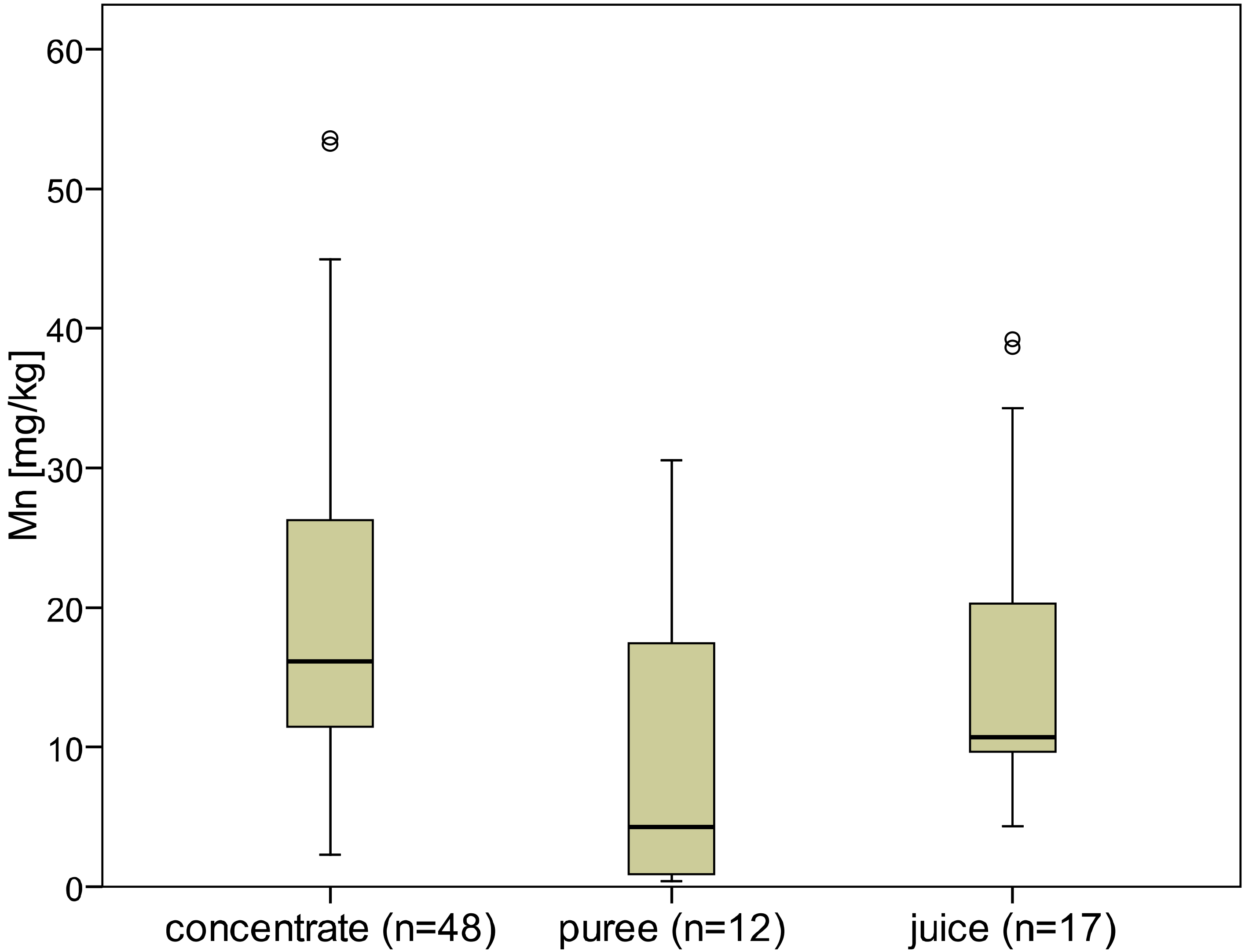


Patz C.-D., Cescutti C., Dietrich H., Andlauer W. Manganese screening of pineapple by total-reflection X-ray fluorescence (TXRF) spectroscopy. Deutsche Lebensmittel-Rundschau. 2013; *109:* 315–319.

Manganese of pineapple products from different countries



Manganese in pineapple products



Pros & Cons

Cons

- Lower intensity for
  Ag, Cd, Sb (only L line)
  dependent from X-Ray (Mo) source
- Low weight elements are less sensitive
- Concentration effects -> „Pile Up Peaks“

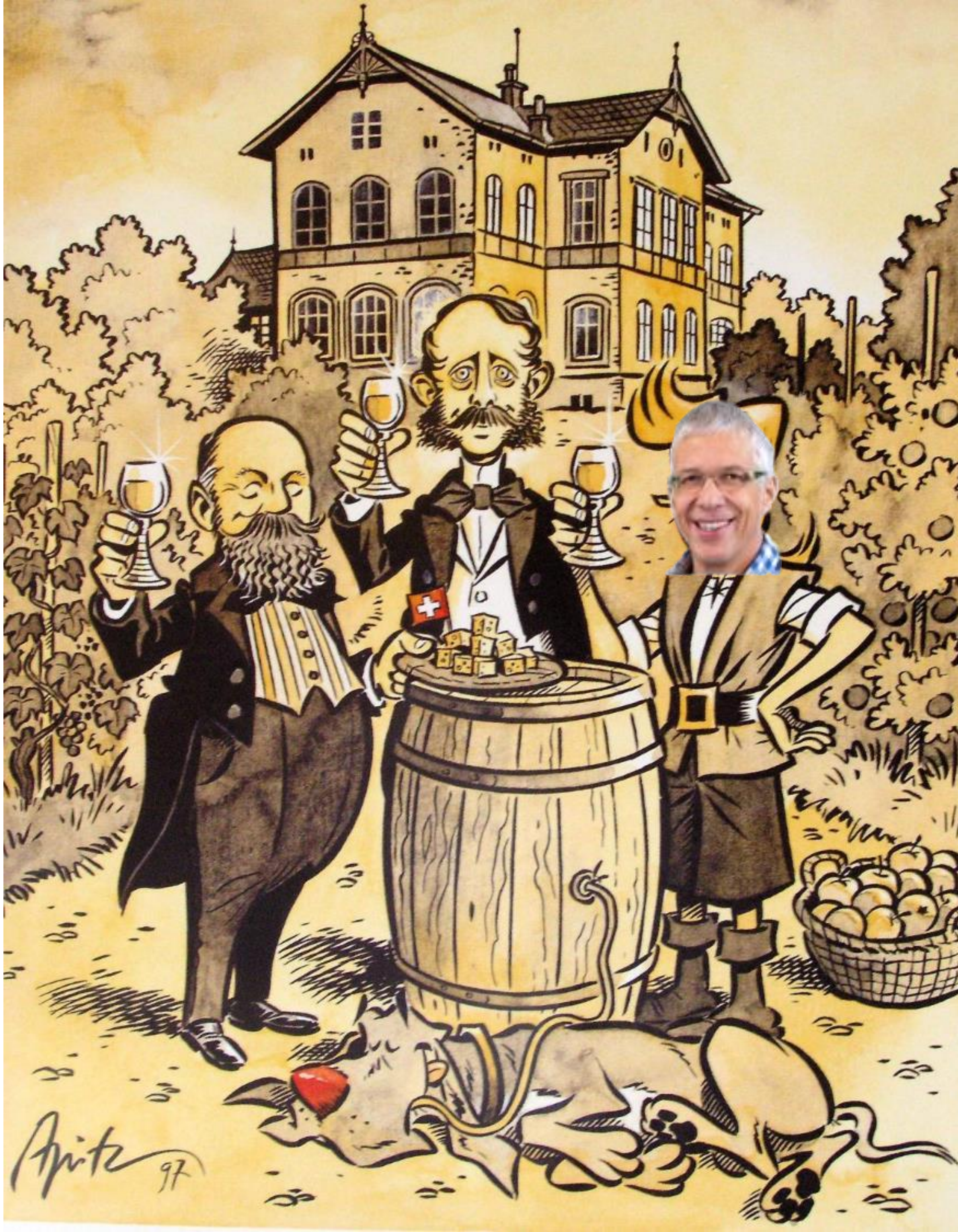
Pros

- Less sample amount (5µg)
- Easy sample preparation
- Fast multielement spectra
- High dynamic range (10^7)
- Solid and insoluble material are measurable
  (e.g. bentonite, kieselguhr, fining agents)

Thanks to

Vicky Bäumer

Carine Cescutti



TXRF analysis of beer and wort

TXRF analysis of beer and wort
Motivation

Motivation for metal analysis during the beer brewing process

- Certain metals, especially Fe and Cu can affect the taste of the final beer products by forming reactive oxygen species
- Metals in form of salts ($CaSO_4$, $MgSO_4$, $ZnSO_4$, $CaCl_2$) are introduced to control pH, adjust taste, improve efficiency and enhance fermentation processes
- Elements in the brewing water can introduce unwanted metals into the brewing process
- Typical analytical task:

Lp.	Sample	Type	Ca mg/l	Zn mg/l	Fe µg/l	Cu µg/l	Mg mg/l	Na mg/l	Mn mg/l
1	Wort not filltered	a.)							
2		b.)							
3		c.)							
4	Wort filltrated	a.)							
5		b.)							
6		c.)							
7	beer	a.)							
8		b.)							
9		c.)							
10	water	A1							

TXRF analysis of beer and wort Samples

Analyzed samples

- 4 beer samples (3 bottles, 1 can)
- 3 filtered wort samples
- 2 unfiltered wort samples
- 1 brewing water sample
- 1 water CRM

TXRF analysis of beer and wort
Sample preparation beer and wort TXRF

Sample preparation beer & wort

- Degassing in ultrasonic bath for 10 min
- Aliquotation of 10 ml sample into centrifugation tubes
- Addition of 50 µl Ga-solution (100 mg/l) for internal standardization
- Addition of 1 ml aqueous polyvinyl alcohol solution (0,3 g/l)
- Homogenization
- Transfer of 10 µl sample to siliconized quartz glass carriers
- Drying on hot plate at 40° C
- All samples were prepared threefold

TXRF analysis of beer and wort
Sample preparation brewing water TXRF

Sample preparation water

- Aliquotation of 1 ml sample into centrifugation tubes
- Addition of 10 µl Ga-solution (100 mg/l) for internal standardization
- Homogenization
- Transfer of 10 µl sample to siliconized quartz glass carriers
- Drying on hot plate at 40 ° C
- All samples were prepared threefold

TXRF analysis of beer and wort
Sample preparation ICP-OES

Measurements at external service lab with ICP-OES

Samples

- Beer
- Filtered wort
- Water

Sample preparation and measurements

- Microwave digestion with HNO_3
- Measurements according to DIN EN ISO 11885:2009-09 (Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES))

TXRF analysis of beer and wort
Measurements

S2 PICOFOX

- Mo tube, 50 kV/1000 µA
- 60 mm^2 XFlash SDD
- 25 position sample changer

S4 TSTAR

- Mo tube, 50 kV/1000 µA
- W-tube, 50 kV/1000 µA
- Monochromator system for Mo-K, W-L and W-Brems monochromatization
- 60 mm^2 XFlash SDD
- 90 position sample changer

Measurements

- Mo-K excitation, 1000 s

TXRF analysis of beer and wort
Results

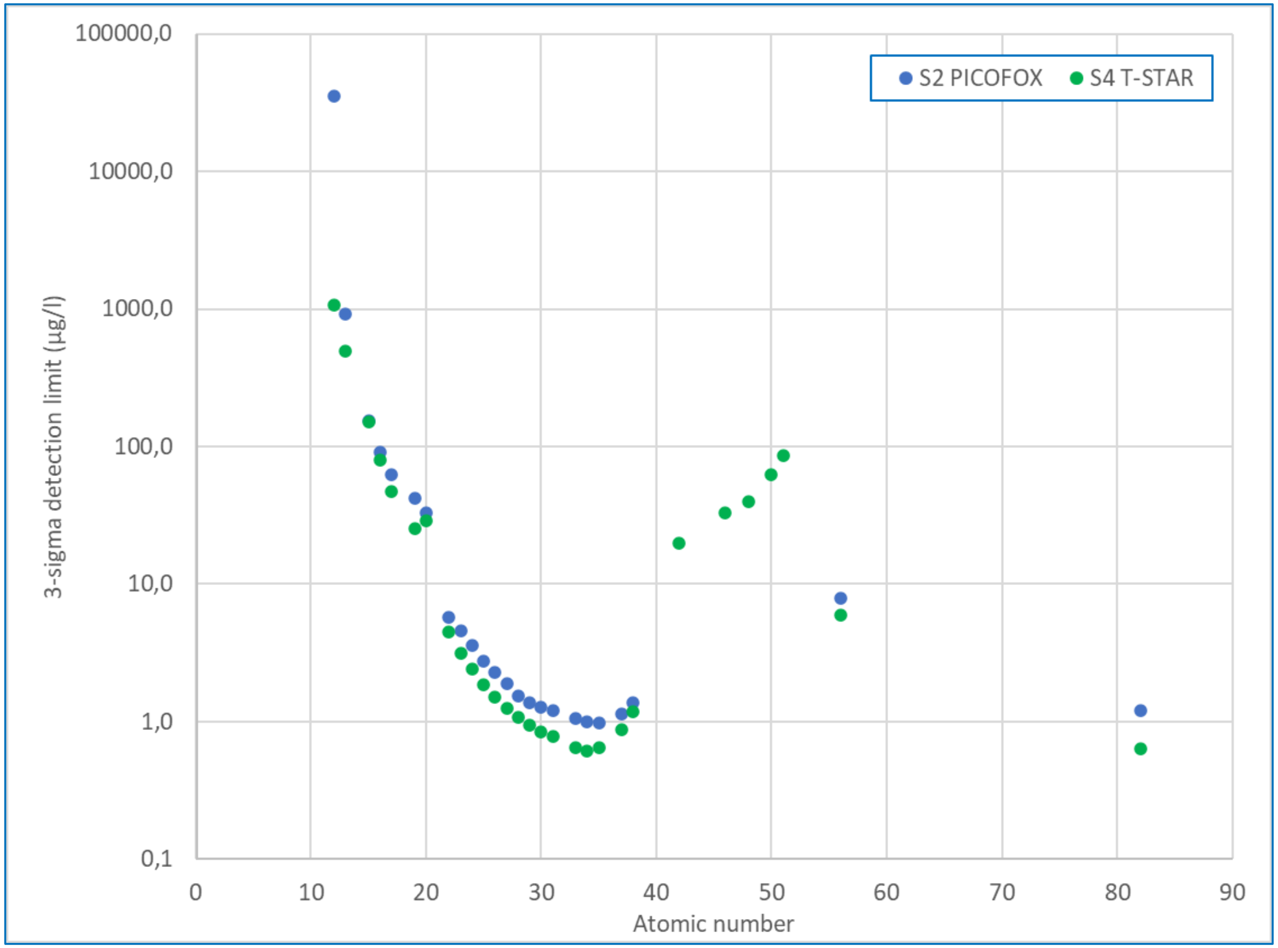
Beer – Reproducibility

	Reproducibility (%)		
Element	S2 PICOFOX	S4 T-STAR	ICP-OES*
Potassium	1,2 - 3,9	2,0 - 3,5	12,7 - 13,4
Calcium	1,3 - 2,2	0,3 - 1,3	11,8 - 12,7
Chromium	2,5 - 11,7	7,9 - 17,5	no data
Manganese	1,6 - 3,3	0,3 - 5,8	no data
Iron	1,4 - 4,1	0,9 - 4,7	no data
Nickel	5,5 - 8,9	9,0 - 12,1	no data
Copper	2,3 - 10,6	0,7 - 7,7	14,2 - 28,6
Zinc	4,6 - 31,1	4,4 - 16,2	17,6 - 23,1

*: Sedin, D. et al. (2006): “Elemental Analysis of Beer and Wort by Inductively Coupled Plasma–Atomic Emission Spectroscopy”, Journal of the American Society of Brewing Chemists, 64:4, 233-237

TXRF analysis of beer and wort
Results

Beer – Detection limits



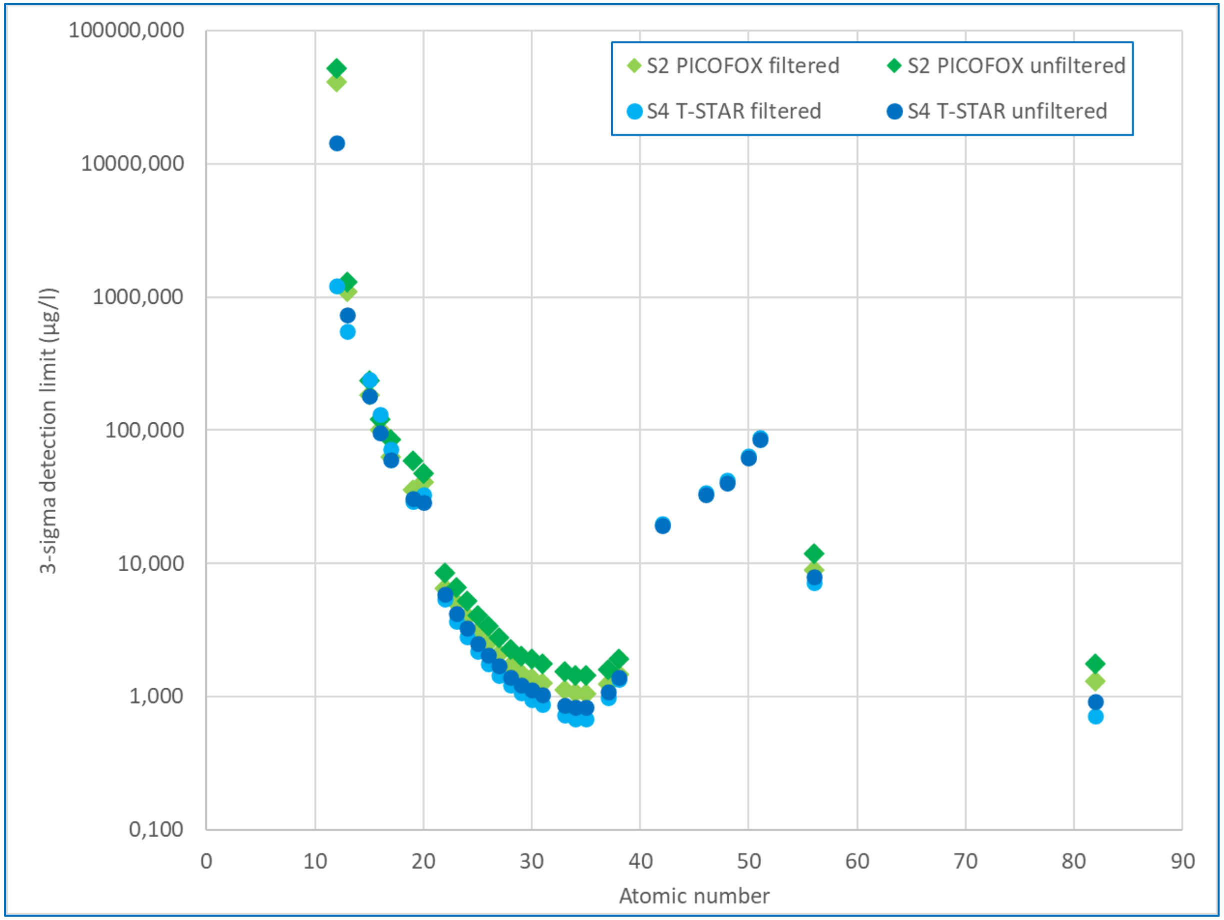
TXRF analysis of beer and wort
Results

Wort - Reproducibility

Element	Reproducibility (%)			
	S2 PICOFOX		S4 T-STAR	
	filtered	unfiltered	filtered	unfiltered
Phosphorus	1,9 - 4,5	0,6 - 10	0,4 - 0,9	0,4 - 3,5
Sulfur	1,0 - 3,6	0,7 - 2,6	0,8 - 1,2	1,2 - 1,5
Chlorine	0,2 - 1,4	3,3 - 6,8	0,8 - 0,9	0,7 - 0,8
Potassium	0,7 - 1,4	0,6 - 5,8	0,4 - 0,5	0,3 - 0,4
Calcium	0,5 - 1,5	1,4 - 8,1	0,6 – 1,3	0,6 - 2,2
Manganese	1,4 - 5,6	2,0 – 11	0,6 - 2,0	0,6 - 5,8
Iron	1,6 - 8,9	10 – 19	4,8 - 7,7	1,8 - 9,5
Nickel	17 – 18	7,3 – 18	9,0 – 10	5,1 - 8,0
Copper	2,4 - 4,9	4,7 - 5,5	4,4 - 8,6	9,3 – 10
Zinc	1,9 - 9,2	1,6 - 9,2	1,7 - 9,2	5,2 - 8,0
Bromine	0,8 - 1,1	0,9 - 1,4	0,6 - 1,4	0,3 - 0,6

TXRF analysis of beer and wort
Results

Wort – Detection limits



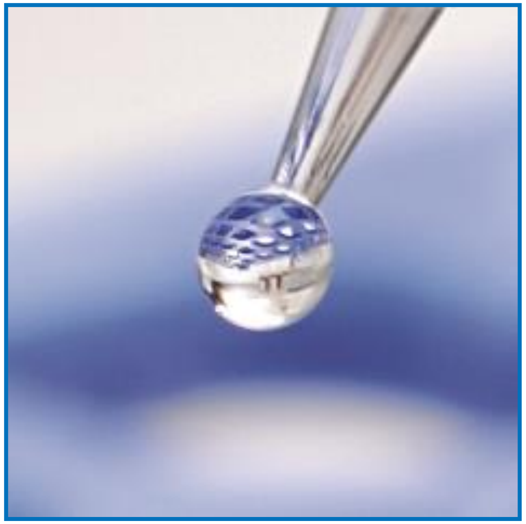
TXRF analysis of beer and wort
Summary

- All macro- and trace elements of interest can easily be analyzed in beer, wort and brewing water samples without the need for digestion procedures
- Other elements of potential interest (S, Cl, Br, Cr, As, Pb etc.) are analyzed simultaneously
- Wort samples can be analyzed filtered and unfiltered (partly distinct differences of the element concentrations were observed)
- Low-concentrated brewing water samples can also be analyzed in one go for trace metal contents (no memory effects)

Q & A

Any Questions?

Please **type in** the questions you may have for our speakers in the **Questions Box** and click **Submit**



Thank you for your attention!

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