Joint EURL-FV & SRM Workshop 2018 - Almería

News on EURL-SRM

European Commission

EURL-SRM

M. Anastassiades

27.09.2018

Highly Polar Pesticides

EURL-SRM EU Reference Laboratories for Residues of Pesticides
Single Residue Methods

Quick Method for the Analysis of numerous Highly Polar Pesticides in Foods of Plant Origin via LC-MS/MS involving Simultaneous Extraction with Methanol (QuPPe-Method)

Version 9.3 (August 2017, Document History, see page 73)

Authors: M. Anastassiades; D. I. Kolberg; A. Benkenstein; E. Eichhorn; S. Zechmann; D. Mack; C. Wildgrube; I. Sigalov; D. Dörk; A. Barth

Note: Changes from V9.2 to V9.3 are highlighted in yellow

Version 10 coming-up soon

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Interlaboratory QuPPe Validation

•Study Round 1: Finished;
Method 4.1 ("Quats & Co Obelisc R")

•Study Round 2: Finished
Method 1.4 (PerChlorPhos)

•Study Round 3: In preparation
Method 1.3 "Glyphosate & Co."

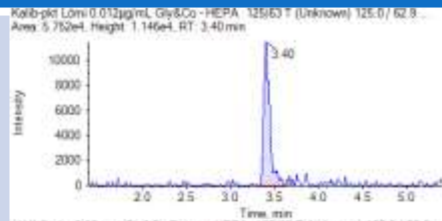
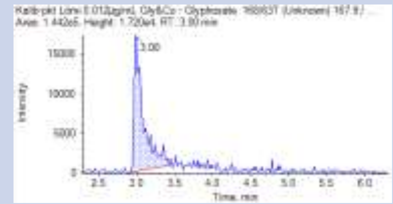
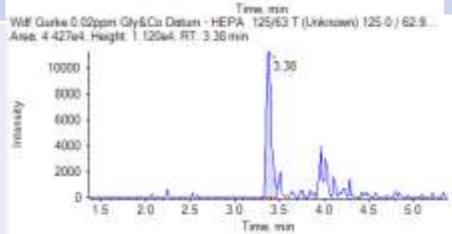
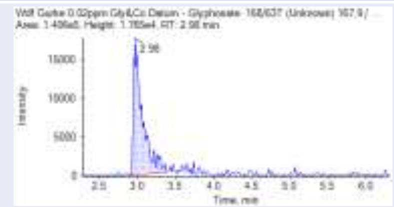
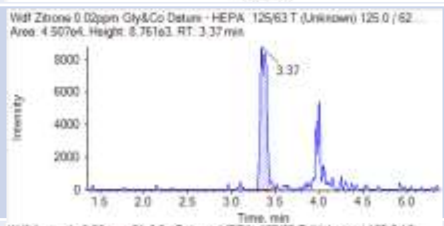
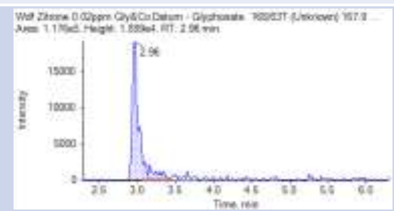
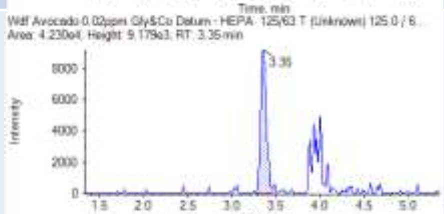
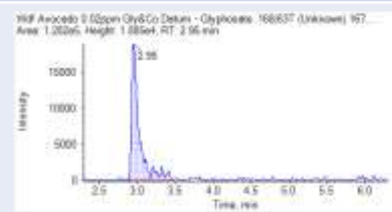
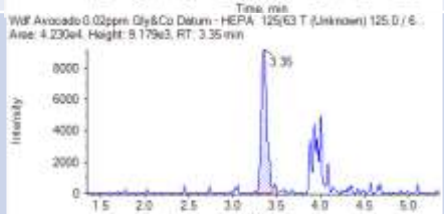
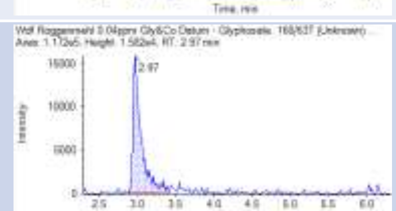
Currently planned …

Carbon-based	HILIC	HILIC
Hypercarb	**Torus DEA**	**Acclaim Trinity Q1**
(Porous Graphitic Carbon)	(Diethylamine)	(Mixed-mode silica based)
by Thermo Scientific	*by Waters*	*by Thermo Scientific*

Torus™DEA – Method

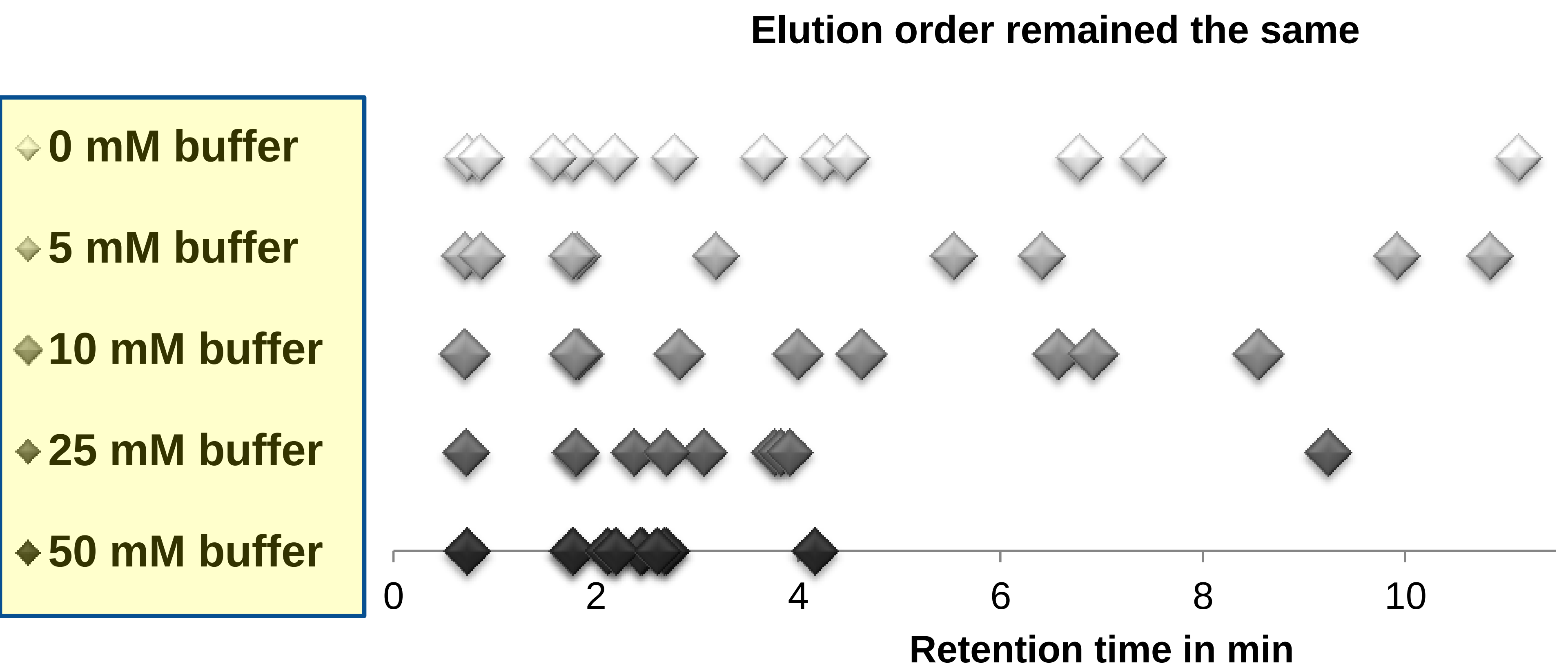
Instrument parameters	Current Conditions	
Column	Torus™DEA 2.1 mm x 100 mm; 1.7 µm (Waters)	
Pre-column	Torus™DEA VanGuard™ 2.1 mm x 5 mm; 1.7 µm (Waters)	
Eluent A	1.2% FA in water	**Current Conditions** (keep acidity low during equilibr. & after sequence)
Eluent B	0.5 % FA in ACN	
Gradient	**Time (min)**	**%A**
	0	10
	1.5	90
	17	90
	22	10
Flow rate	0.5 mL/min	
Column temp.	50 °C	
Inj. volume	10 µL	

Torus DEA (Waters): Exemplary Peak Shapes

	HEPA 125/63 T	Glyphosate 168/63 T
Solvent 0.012 µg/mL		
Cucumber 0.02 ppm		
Lemon 0.02 ppm		
Avocado 0.02 ppm		
Rye flour 0.04 ppm		

First Tests

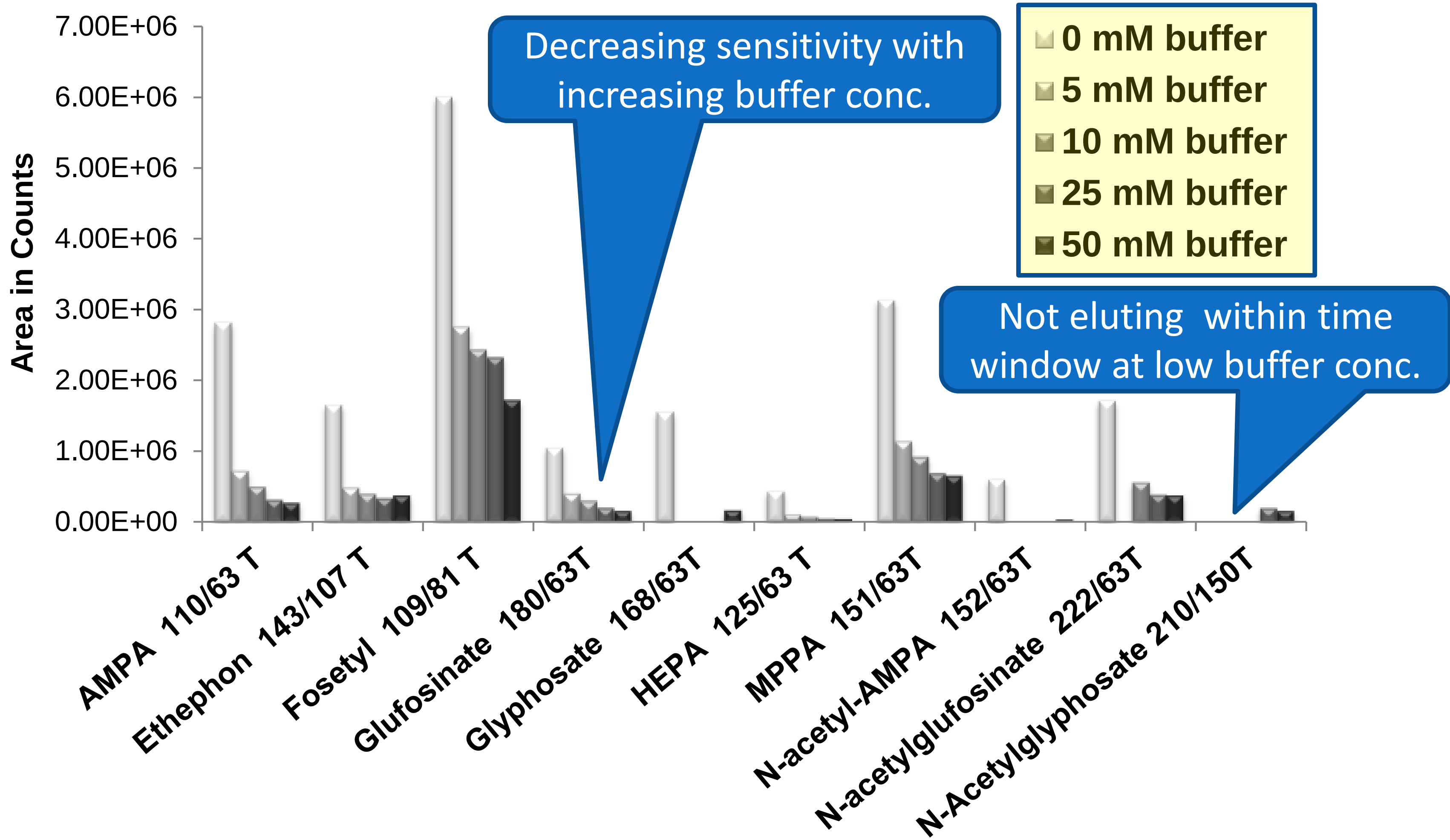
Impact of Buffer Concentration on Retention Times



Eluent A	0.9% formic acid in water **+ Ammonium Formate Buffer X mM**
Eluent B	0.9% formic acid in ACN

First tests …

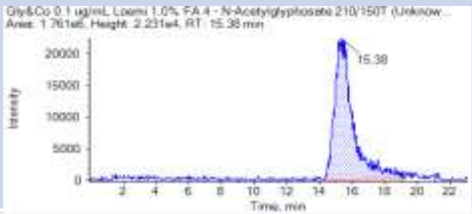
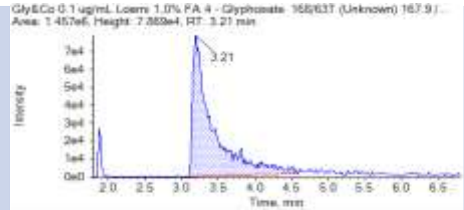
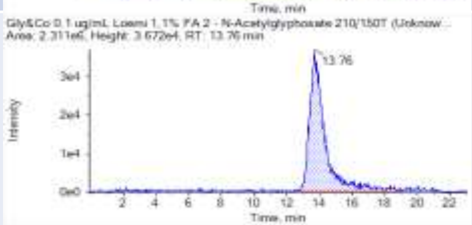
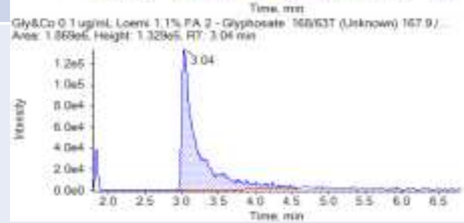
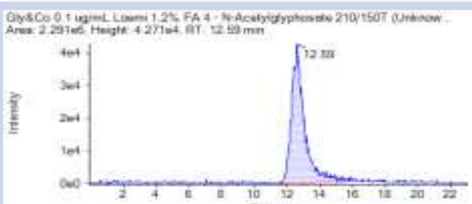
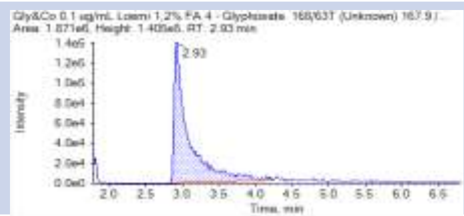
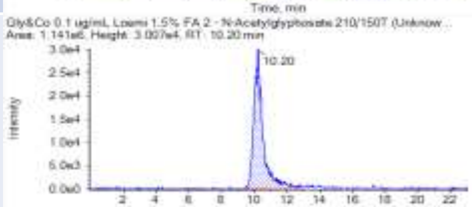
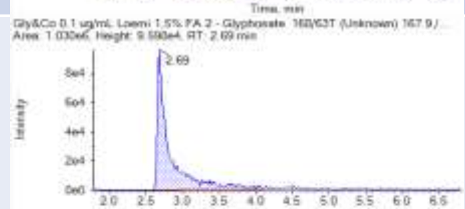
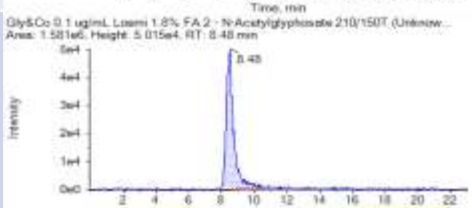
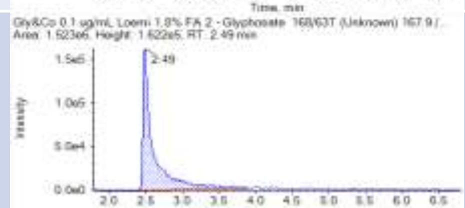
Impact of Buffer Concentration on Peak Intensity



Eluent A	0.9% formic acid in water + **Ammonium Formate Buffer X mM**
Eluent B	0.9% formic acid in ACN

First tests …

Impact of Acid Content on Retention Times & Peak Shapes

<table>
<tr><th></th><th>N-Acetyl-Glyphosat
210/150 T</th><th>Glyphosat
168/63 T</th></tr>
<tr><td>1,0 % FA;
pH 1,96</td><td>
</td><td>
</td></tr>
<tr><td>1,1 % FA;
pH 1,93</td><td>
</td><td>
</td></tr>
<tr><td>1,2 % FA;
pH 1,91</td><td>
</td><td>
</td></tr>
<tr><td>1,5 % FA;
pH 1,86</td><td>
</td><td>
</td></tr>
<tr><td>1,8 % FA;
pH 1,82</td><td>
</td><td>
</td></tr>
</table>

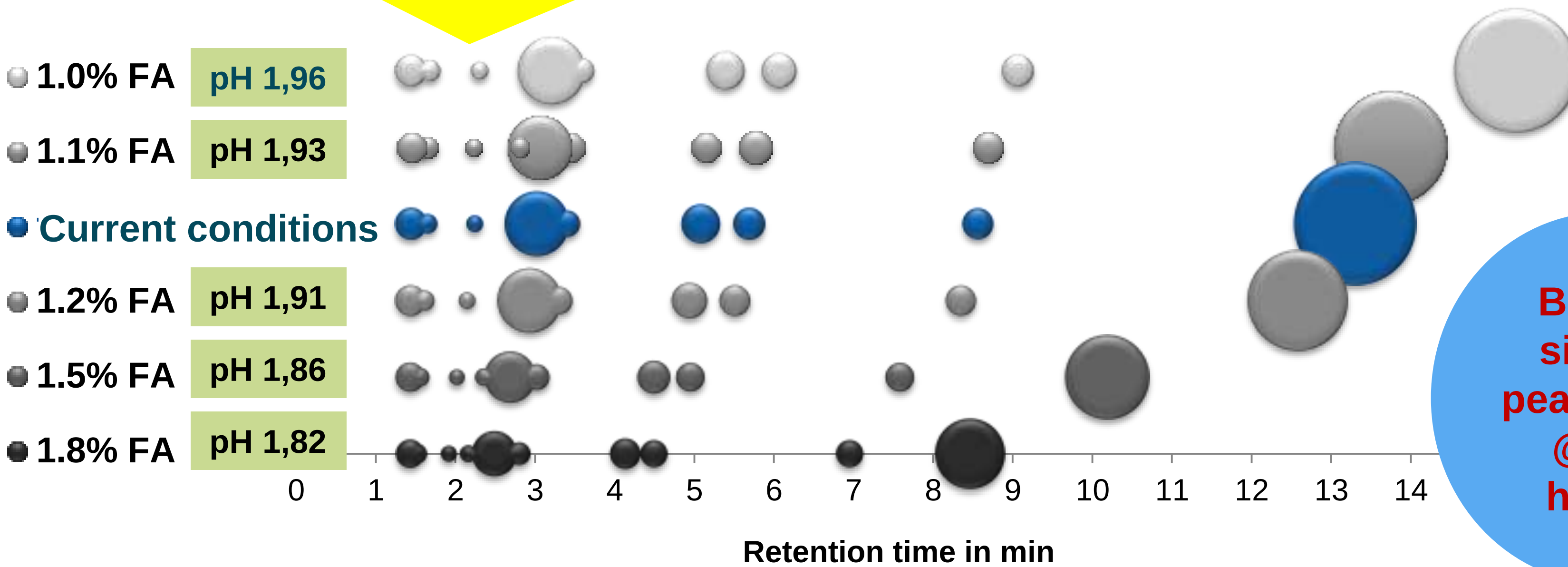
Same Gradient profile but w/o buffer (only with FA)

Manufacturer Recommendation: lowest operating pH of column: 2 !

First tests …

Impact of Acid Content on Retention Times & Peak Width

Early eluters less impacted
⇨ Reduce acid in B and start with low FA and increase during run



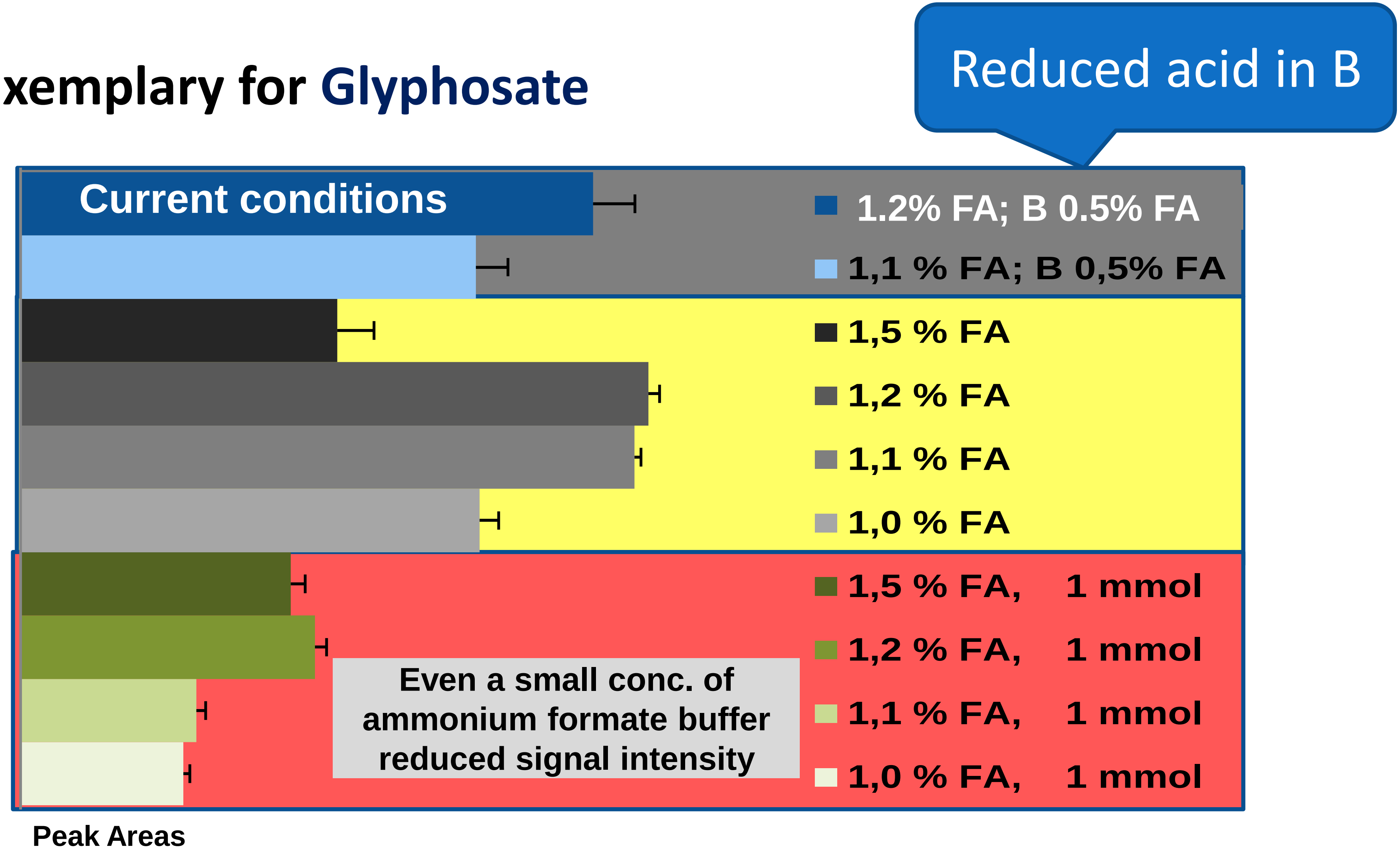
Bubble sizes = peak width @ 5% height

Same Gradient profile but w/o buffer (only with FA)

Manufacturer Recommendation: lowest operating pH of column: 2 !

Impact of Buffer on Peak Intensity

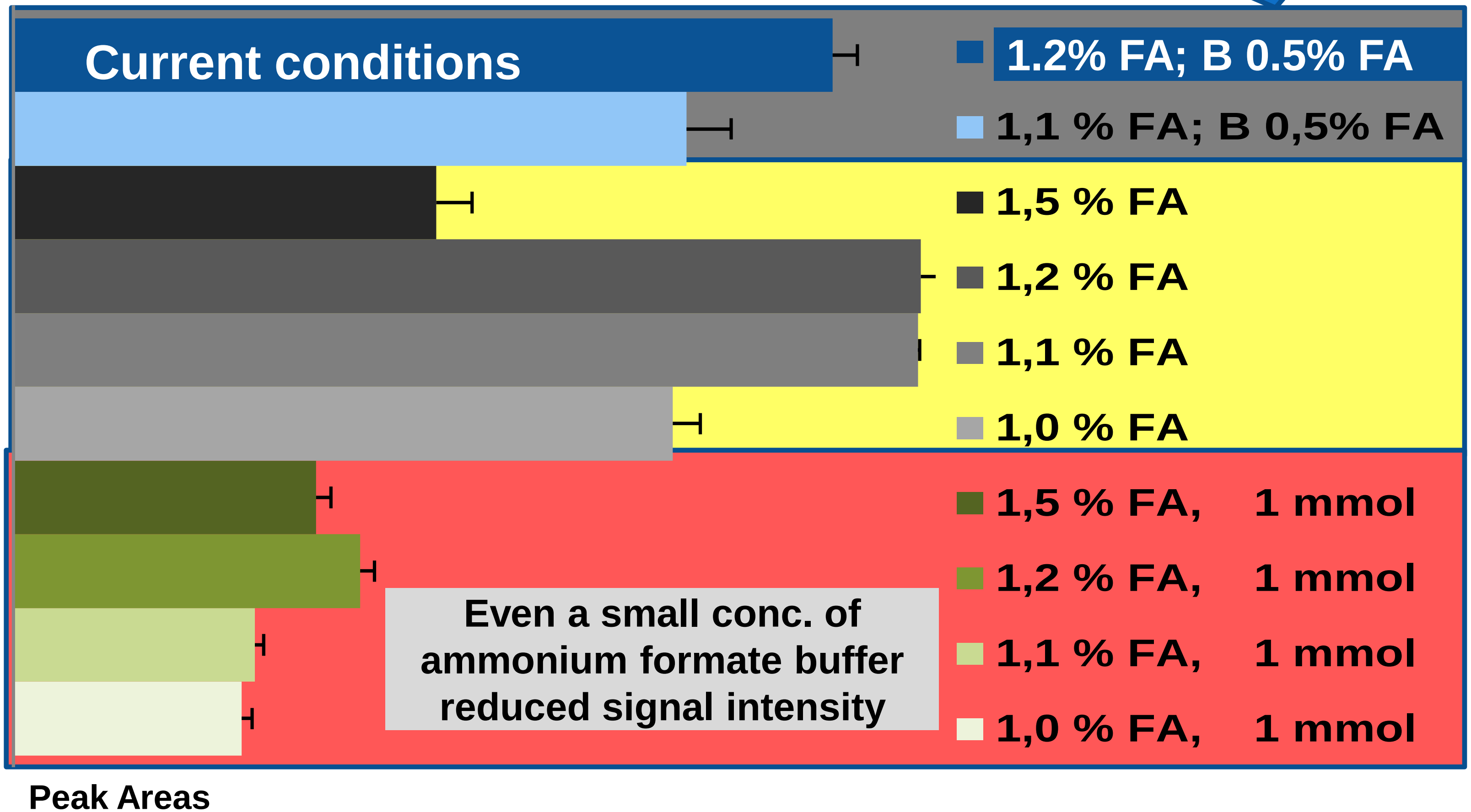
Exemplary for Glyphosate



Impact of Buffer on Peak Intensity

Exemplary for N-Acetyl-Glyphosate

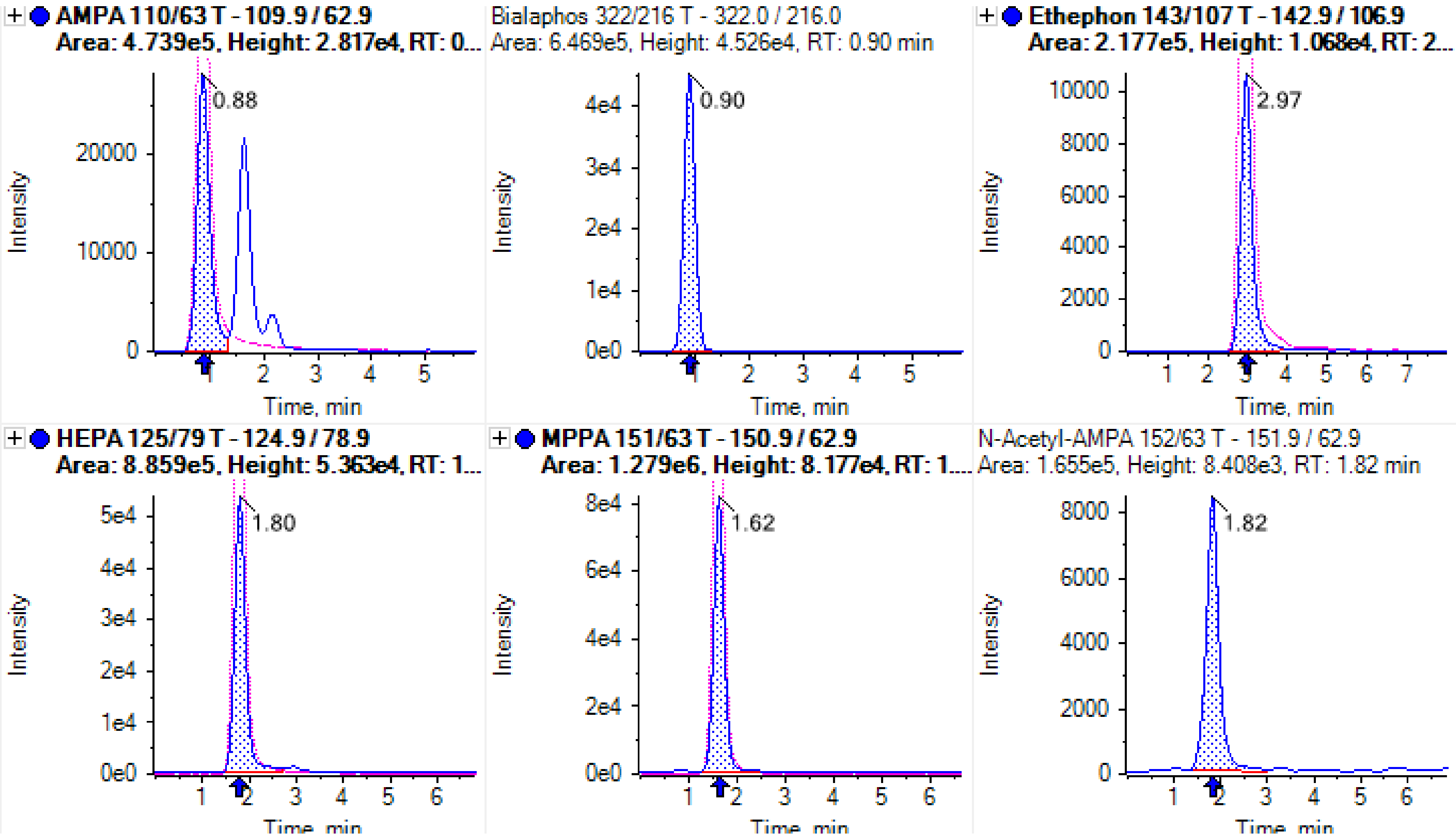
Reduced acid in B



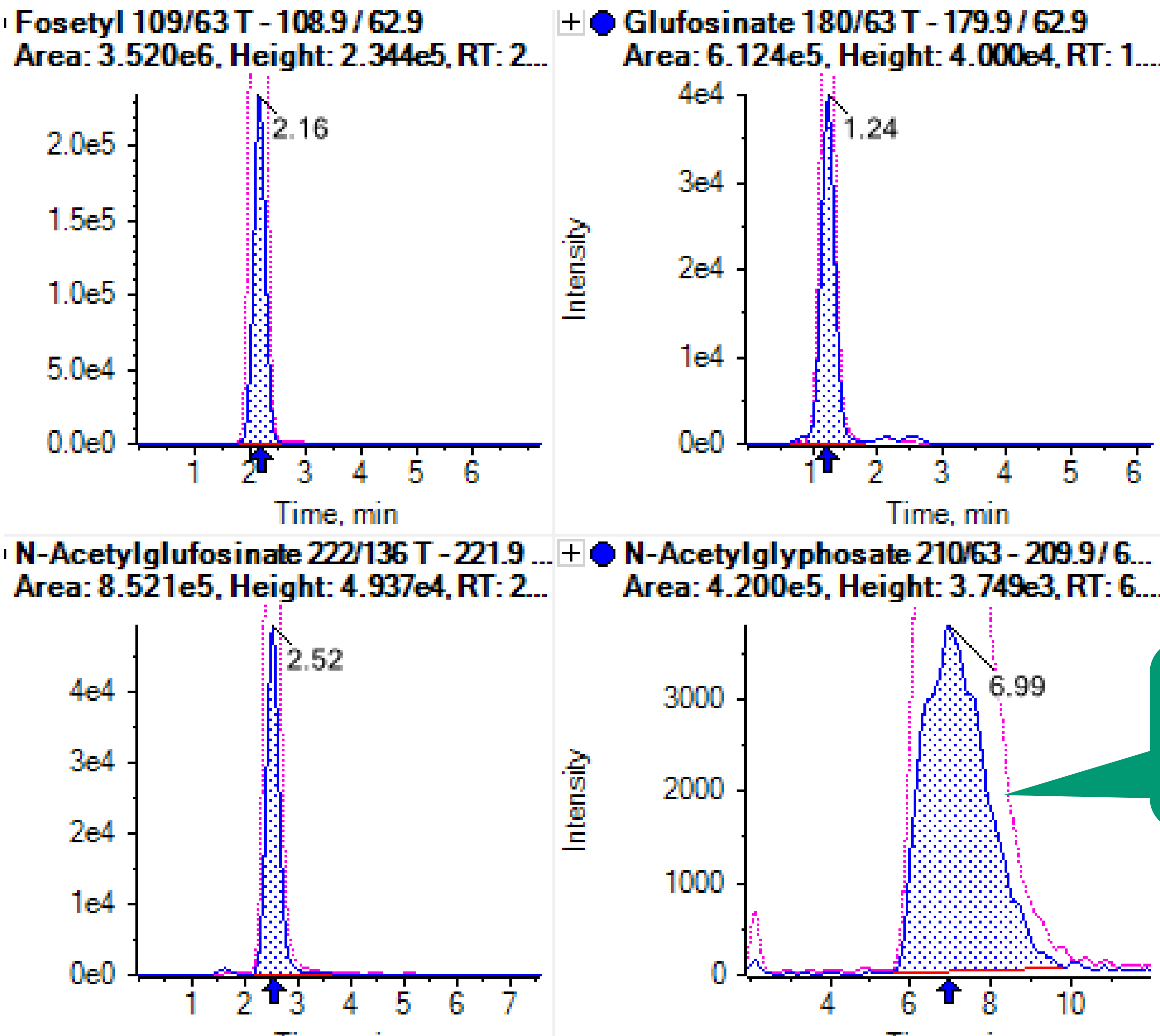
Trinity Q1 – Method

Instrument parameters	Conditions	
Column	Acclaim Trinity Q1 2.1 mm x 100 mm, 3 um (ThermoFisher Scientific)	
Pre-column	Acclaim Trinity Q1 Guard Cartridge 2.1 mm x 10 mm, 5 um	
Eluent A	50 mmol/L NH4-formiate (pH 2.9) in water+acetonitrile 6+4	
Eluent B	Acetonitrile	
Gradient	**Time (min)**	**% A**
	0	100
	10	100
	10.1	18.2 (≙ 90 % ACN)
	13	18.2 (≙ 90 % ACN)
	13.1	100
	18	100
Flow rate	0.5 mL/min	
Column Temp.	30 °C	
Injection Vol.	10 µL	

"Glyphosate&Co. Trinity Q1" 0.1 µg/mL



“Glyphosate&Co. Trinity Q1” 0.1 µg/mL



N Acetyl-Glyphosate broader peak

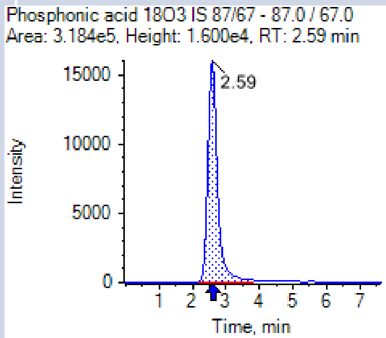
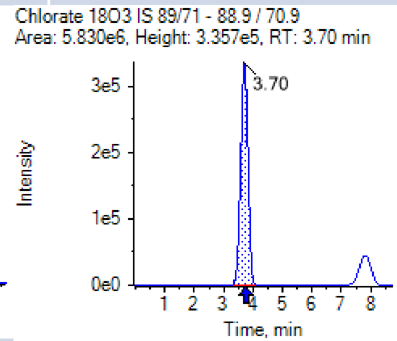
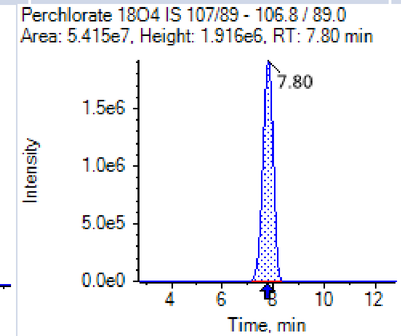
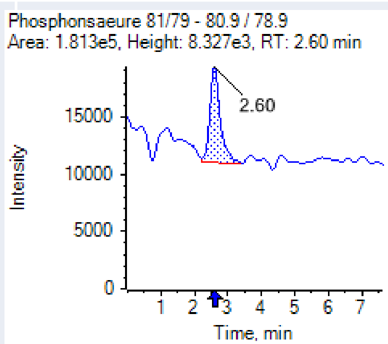
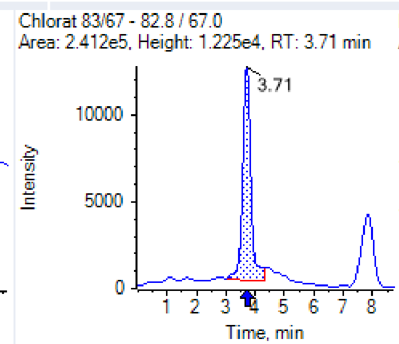
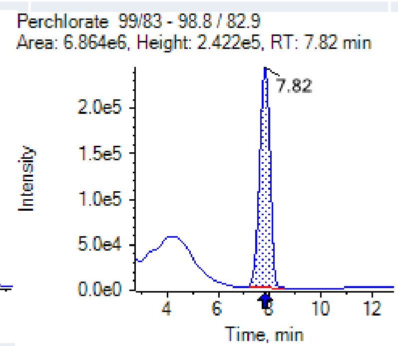
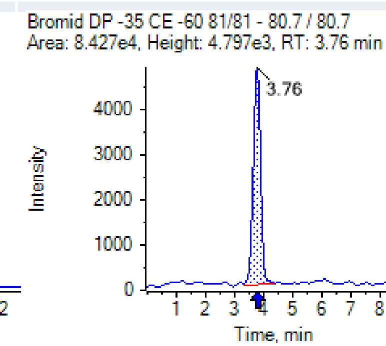
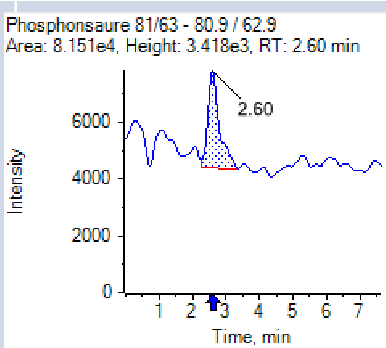
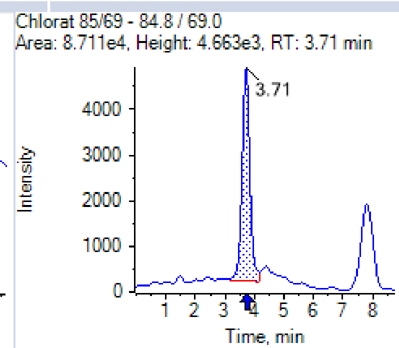
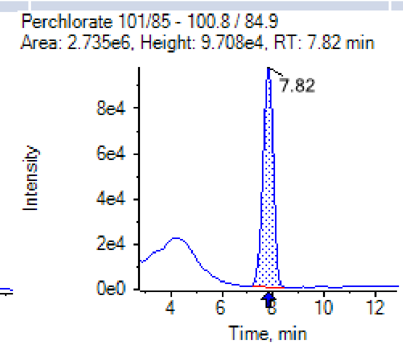
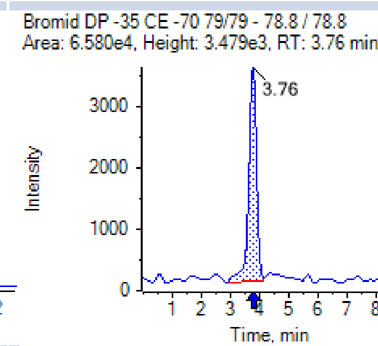
"Glyphosate&Co. Trinity Q1"

Remarks:

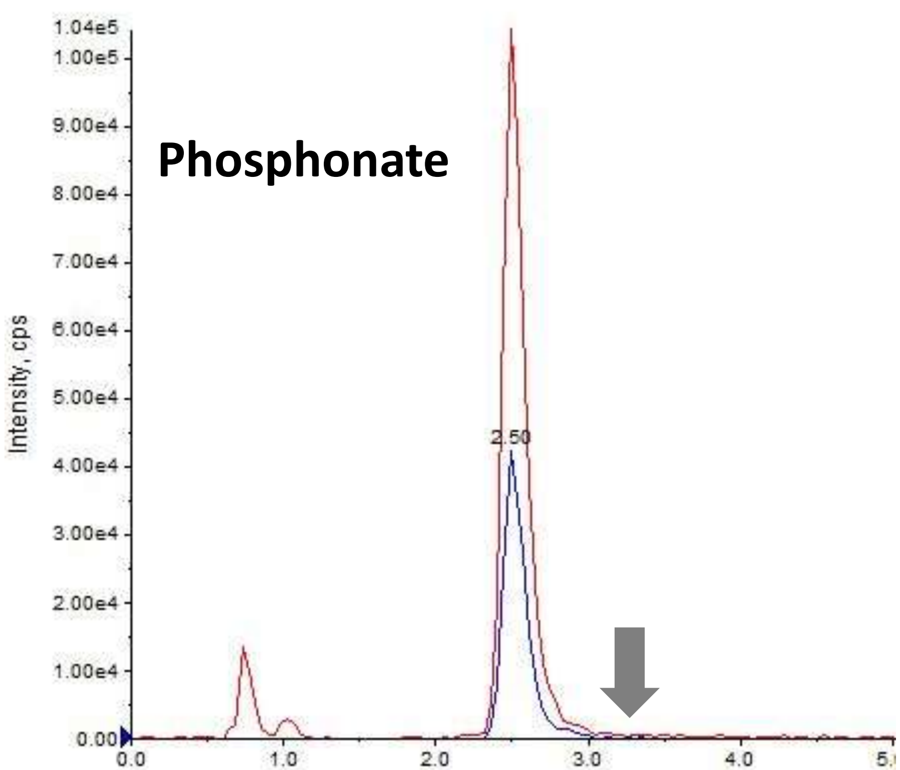
- Overall good peak shapes
- More stable RTs than Hypercarb approach
- Less pampering needed compared to Hypercarb
- A bit less sensitive detection than by Hypercarb approach
- Some initial problems with badge-to-badge differences (hopefully now solved)
- Also covers very well "PerChloPhos" analytes

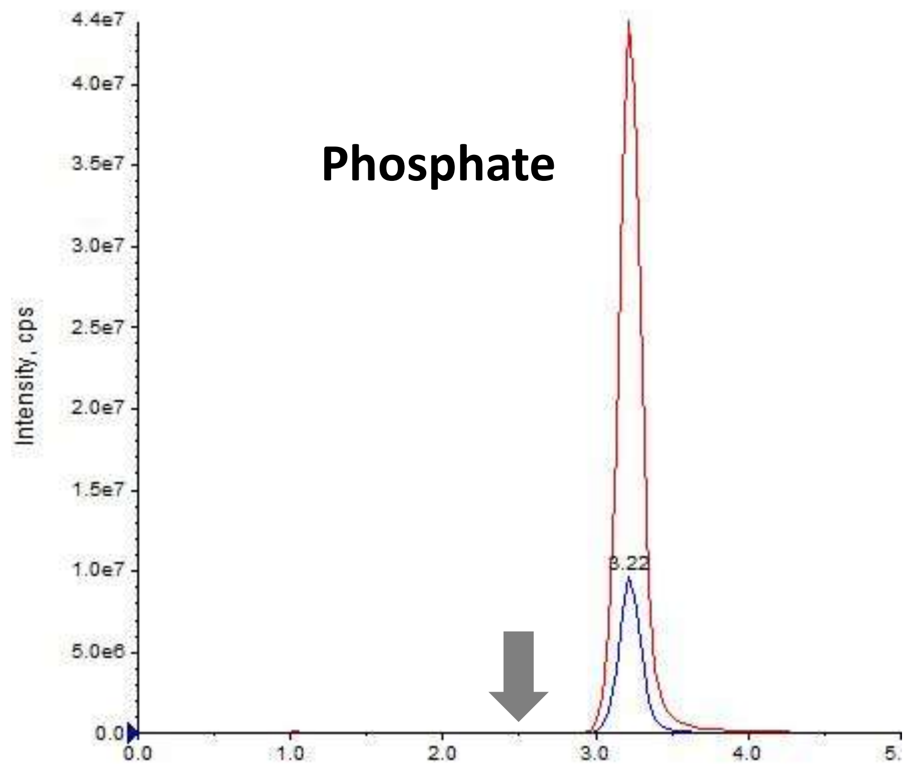
EURL-SRM

„PerChloPhos“ compounds

	Phosphonic acid 0.025 µg/mL	Chlorate 0.0025 µg/mL	Perchlorate 0.0025 µg/mL	Bromide 0.01 µg/mL
ILIS				**No ILIS for bromide**
Native comp. Quant. MRM				
Native comp. Qual. MRM				

Better separation between Phosphate and Phosphonate



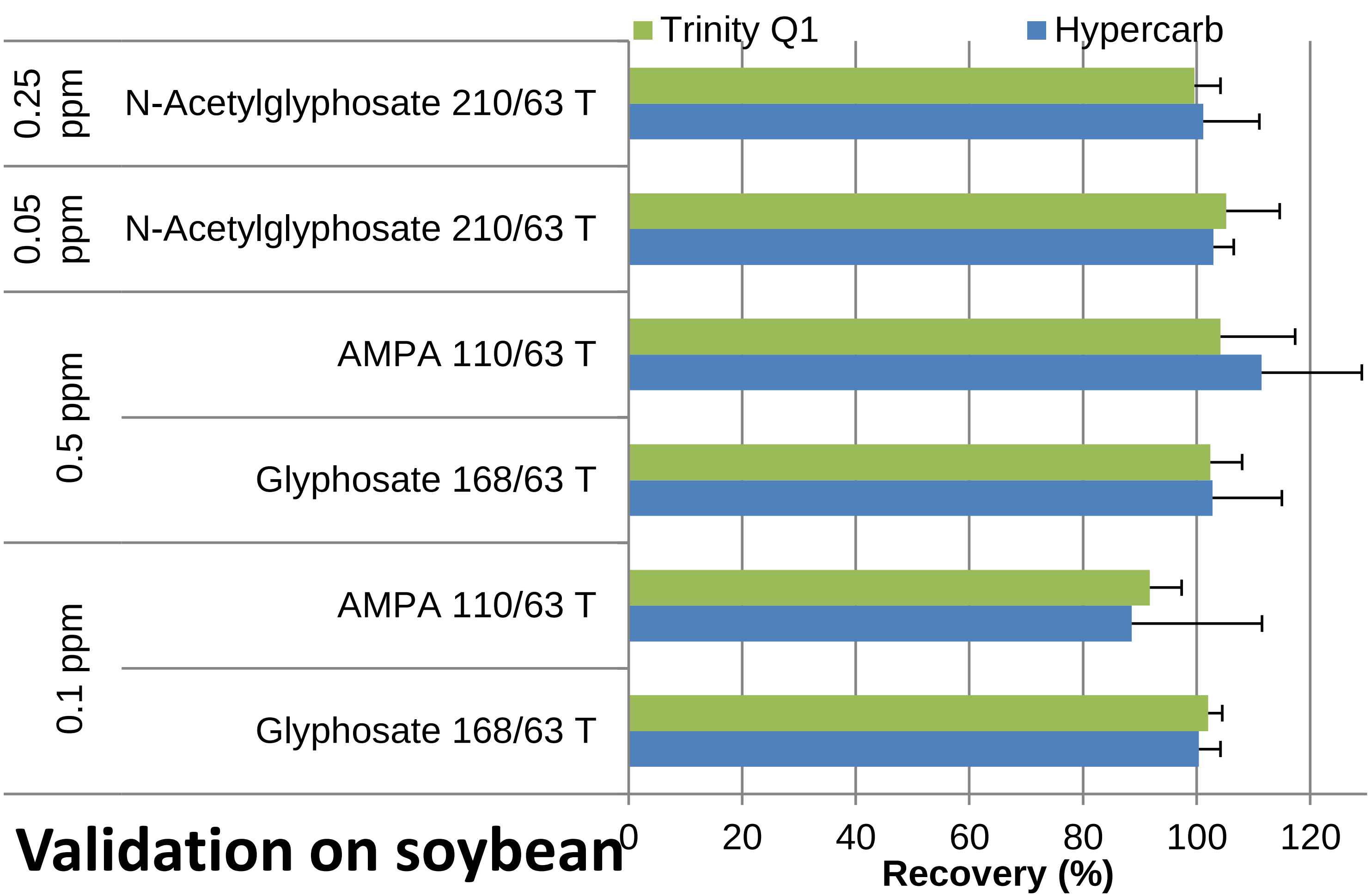


Situation with Hypercarb

Phosphate elutes just prior to phosphonate and has a strong tailing

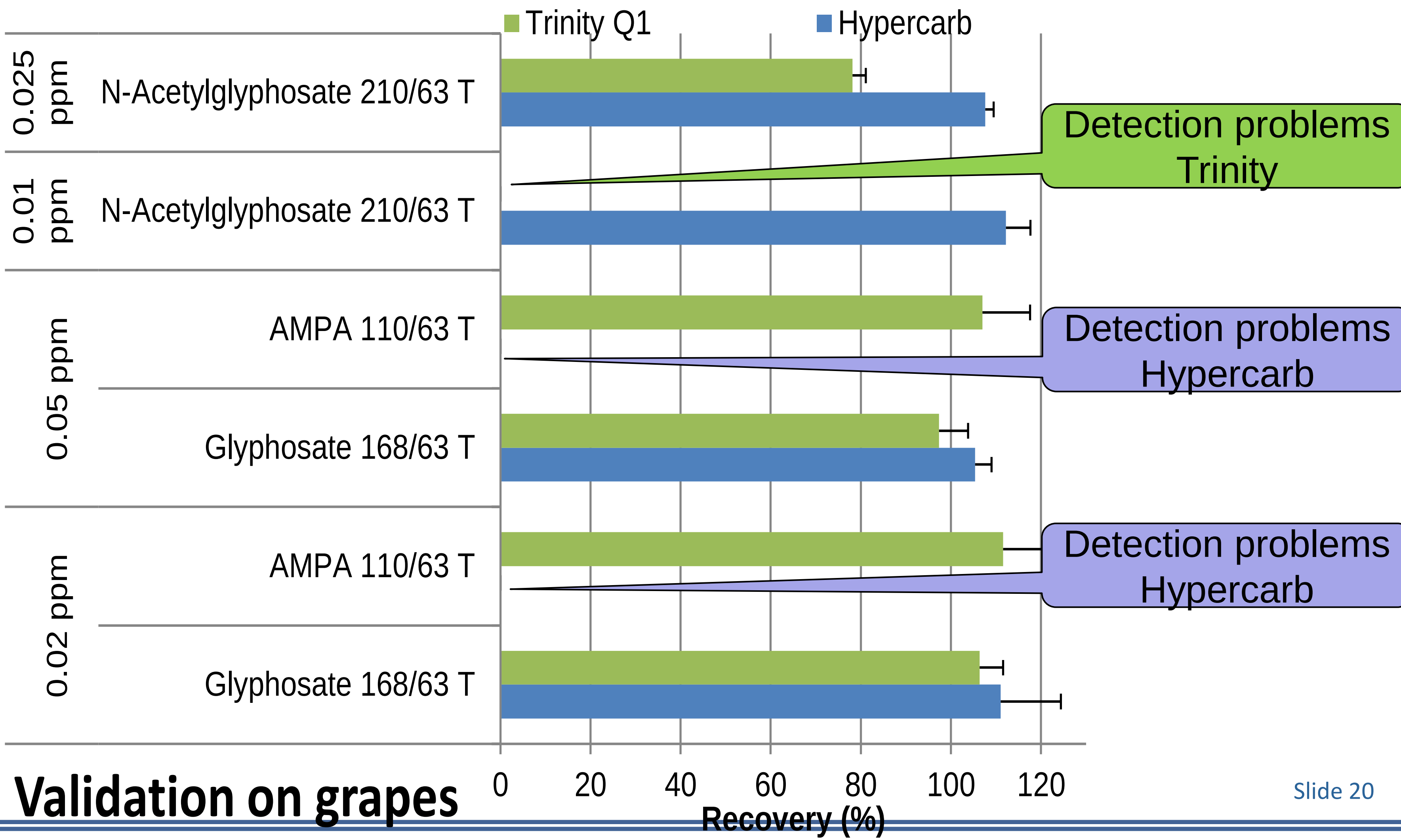
Separation between phosphate and phosphonate sometimes compromized.

Exemplary validation data using Trinity Q1 column



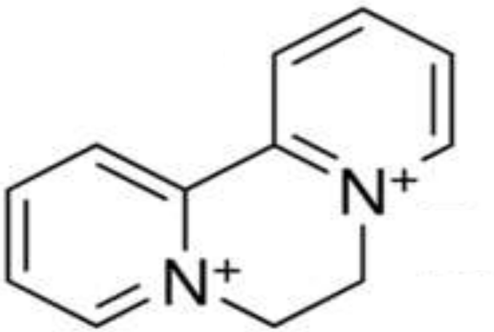
Validation on soybean

Exemplary validation data using Trinity Q1 column



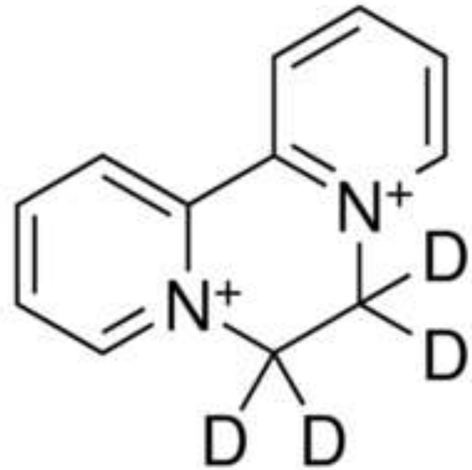
Validation on grapes

Diquat Analysis



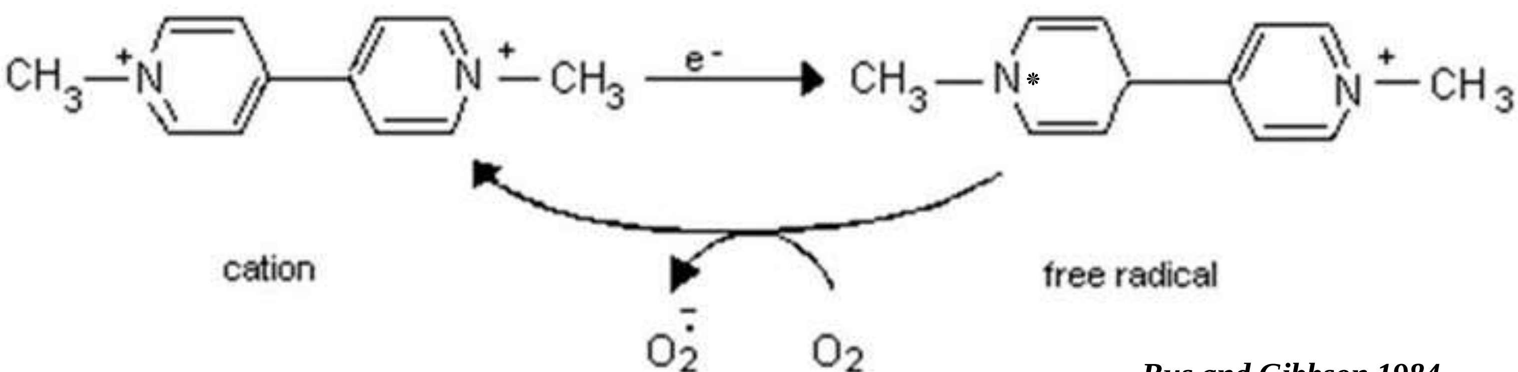
Diquat

Commercially
available



Diquat D4

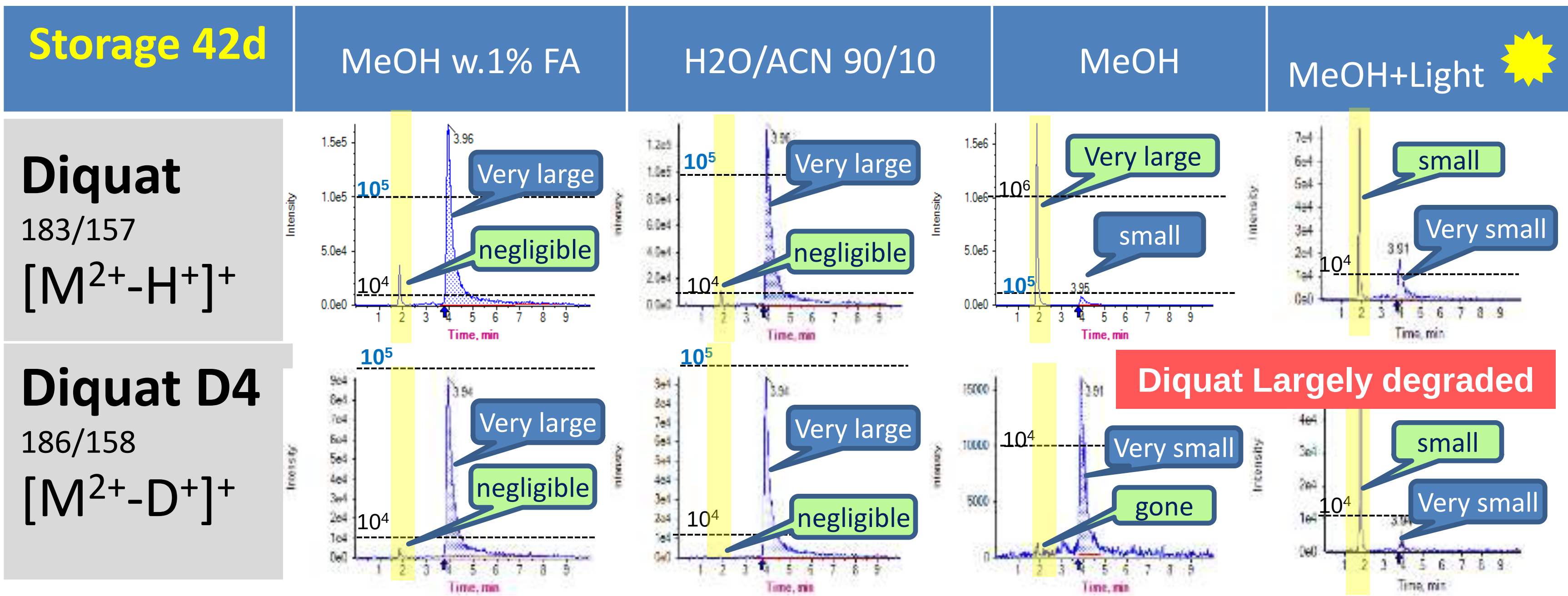
Redox reactions involving radical formation



Bus and Gibbson 1984

Observations when analyzing Diquat

- Diquat /Diquat D4 **unstable when exposed to light**
- **Diquat D4 less stable** than native Diquat solutions
- Calculating **via Diquat D4 recovery rates often more biased** than w/o ILIS
- When storing diquat (or diquat D4) **2nd peak appears** (solvent dependent)
- **Formation of native diquat** in diquat D4 solutions



2^{nd} Peak possibly deprotonated diquat in solution ($[M^{2+}-H^{+}]^{+}$)

Observations when analyzing Diquat

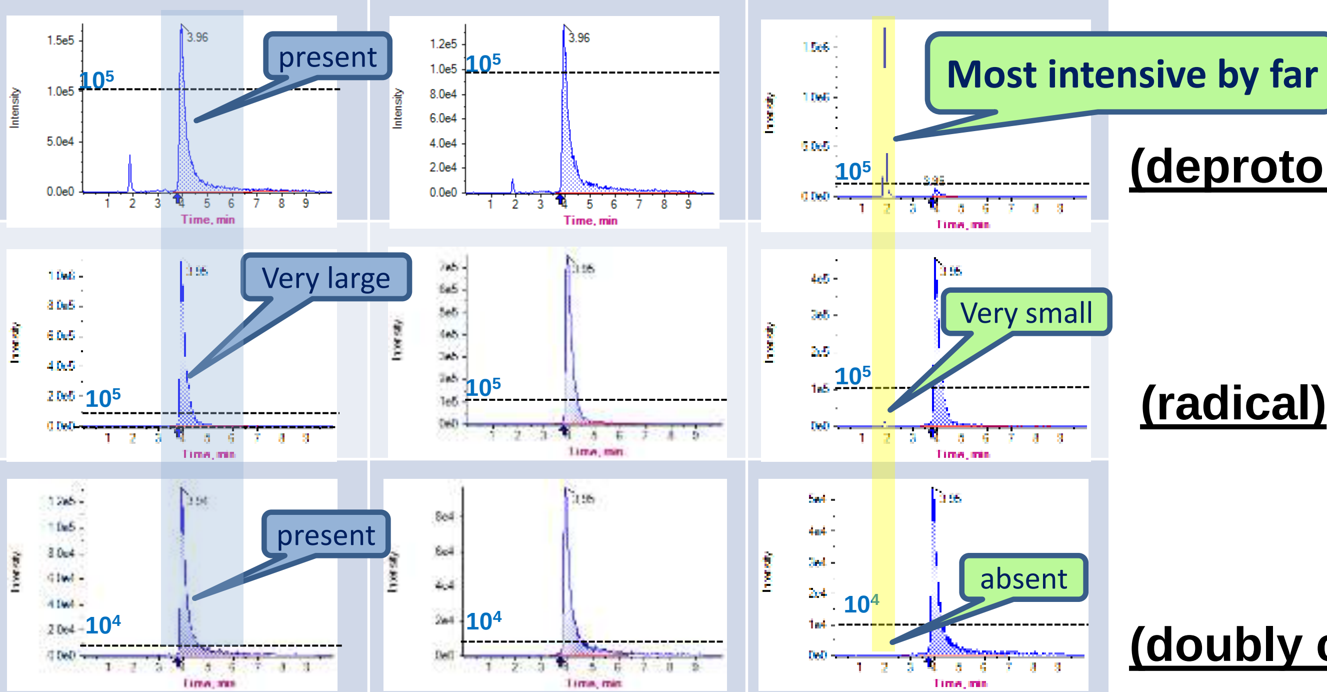
2nd Peak possibly deprotonated diquat in solution ($[M^{2+}-H^+]^+$)

Indications supporting ($[M^{2+}-H^+]^+$) theory:

(1) ESI-Pos ion profile:

Measured on ObeliscR

Native Diquat Stored 42d	MeOH w. 1% FA	H2O/ACN 90/10	MeOH
183/157 $[M^{2+}-H^+]^+$ (deprotonated)			
184/169 $[M]^{+\bullet}$ (radical)			
92/84 $[M]^{2+}$ (doubly charged)			



(1)

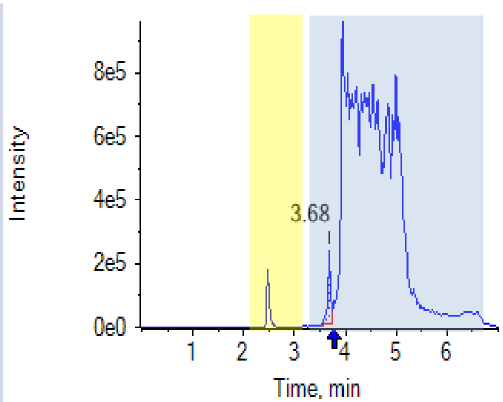
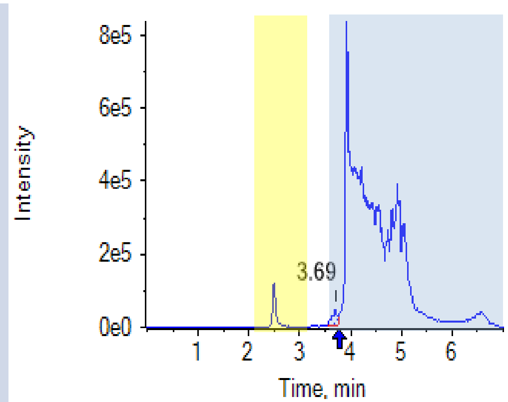
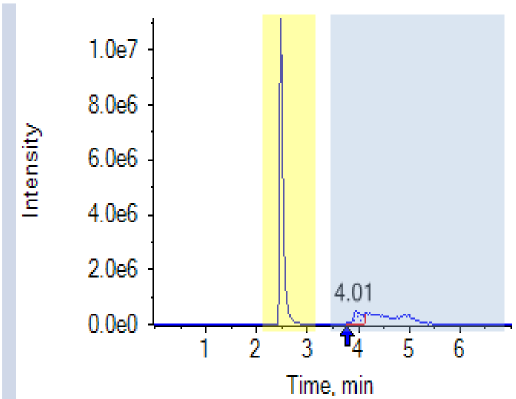
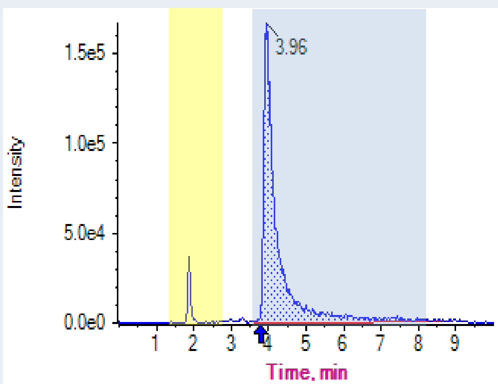
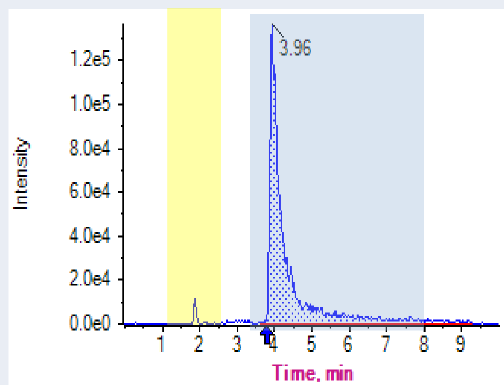
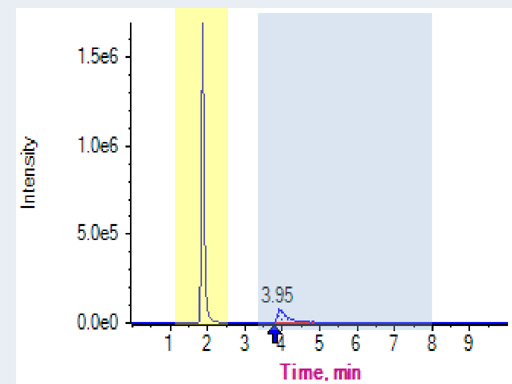
(2) Reversibility: adding acid 2nd peak shrinks ↓; actual later eluting peak increases ↑

(3) Sharper Peak form: Indication of reduced chelating ability,

Observations when analyzing Diquat

Diquat 183/157

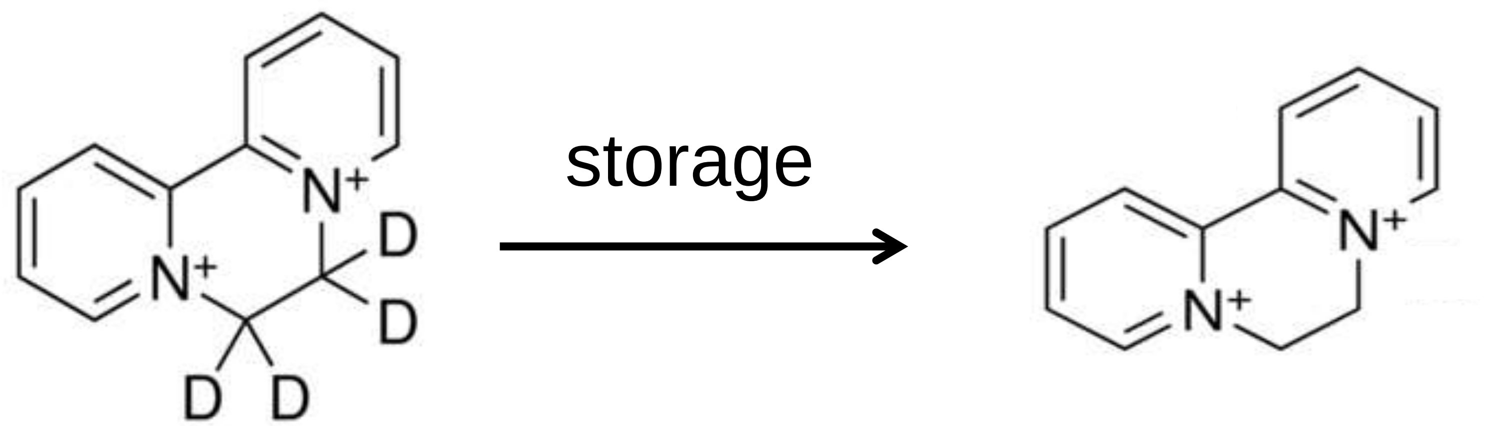
$[M^{2+}-H^{+}]^{+}$

	MeOH w.1% FA	H2O/ACN 90/10	MeOH
BEH Amide			
Obelisc R			

Avoid quantifying via 2nd peak, even use for screening critical

Observations when analyzing Diquat

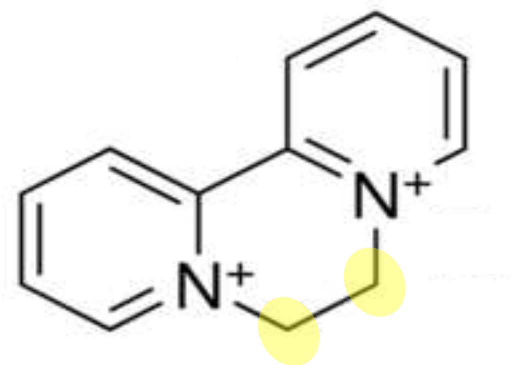
D/H Exchange and Formation of native Diquat from Diquat D4



Diquat D4 Diquat

Storage 42d	MeOH w.1% FA	H2O/ACN 90/10	MeOH	MeOH+light
Stored Sln	**<u>Native Diquat</u> formation** during **storage of 42 days**			
Diquat D4 (0.1 µg/mL)	0	0	**0.059 µg/mL!**	0.0080

Synthesis of Diquat $^{13}C_2$



Diquat $^{13}C_2$

No formation of native Diquat during storage ☺

	MeOH w.1% FA	H2O/ACN 90/10	MeOH	MeOH+light
Stored Sln	**Native Diquat formation** during **storage of 42 days**			
Diquat D4 (0.1 µg/mL)	0	0	**0.059 µg/mL!**	0.0080
Diquat $^{13}C_2$ (0.1 µg/mL)	0	0	0	0

Still care needed …

- Diquat $^{13}C_2$ degrades in MeOH w. sunlight exposure (radical quenchers to be tested)
- Some MRMs of $^{13}C_2$ Diquat are interferred by native Diquat ⇨ use specific MRMs

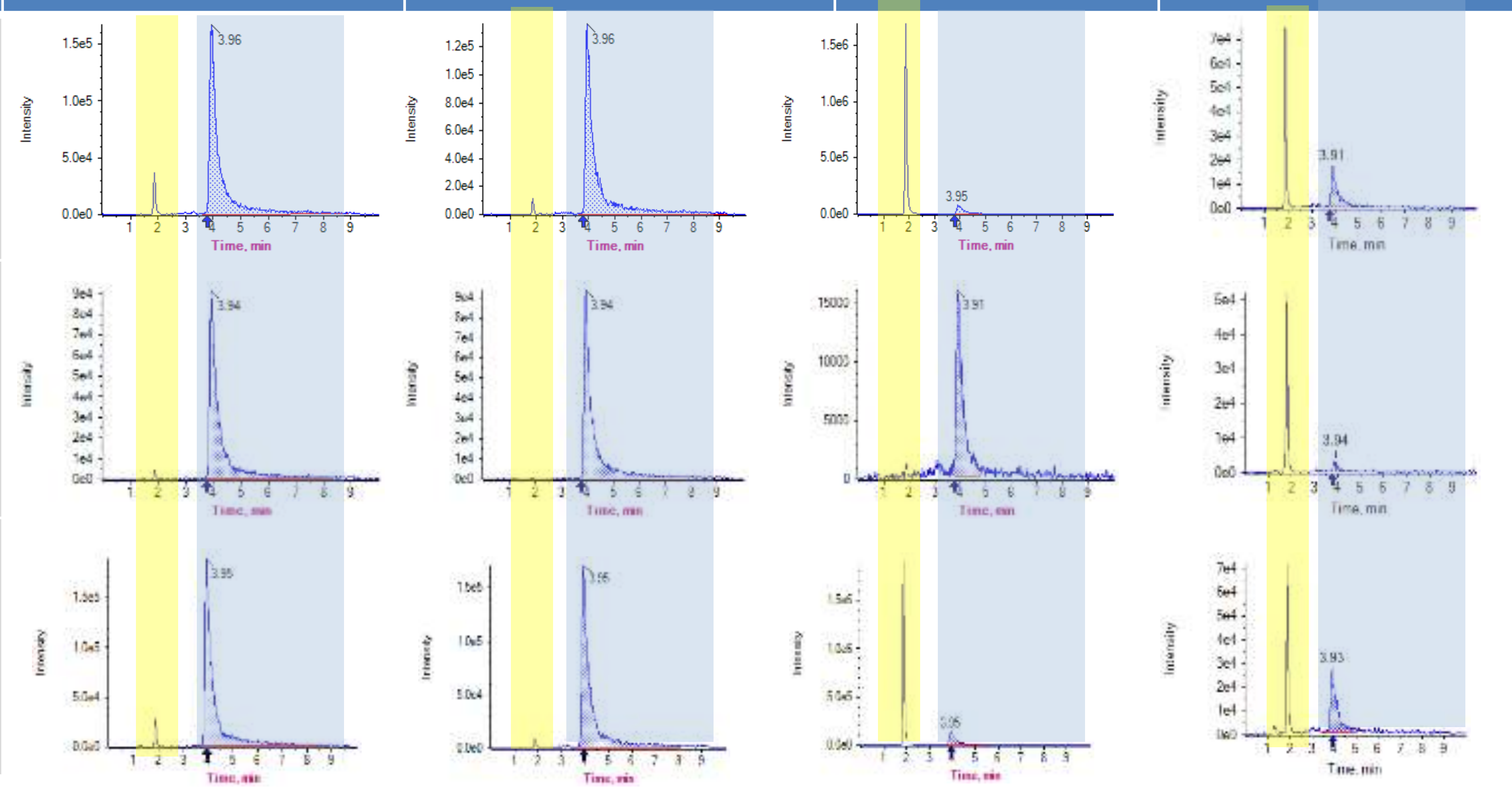
Behaviour of Diquat and its ILISs in different solvents

Storage 42d	MeOH w.1% FA	H2O/ACN 90/10	MeOH	MeOH+Light

Diquat
183/157
$[M^{2+}-H^{+}]^{+}$

Diquat D4
186/158
$[M^{2+}-D^{+}]^{+}$

Diquat $^{13}C_2$
186/158
$[M^{2+}-H^{+}]^{+}$



Diquat and **Diquat $^{13}C_2$** behave simmilarly
Diquat D4 deviates in its behaviour

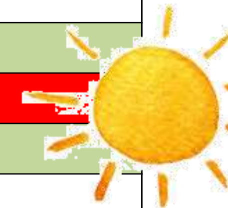
➔ Diquat $^{13}C_2$ better suitable as ILIS

Stability of Diquat and its ILISs in different solvents

Solutions (1 µg/ml) in various solvents stored for 42 days
(measured via later eluting peak)

New ISTD

Storage 42d	**Diquat** original stock sln in H2O	**Diquat D4** original stock sln in D2O	**Diquat ^{13}C2** original stock sln in H2O
MeOH w. 1% FA (**fresh**)	**100**	**100**	**100**
Storage in Fridge			
MeOH w. 1% FA	105	114	114
Methanol	73	7	77
H2O/ACN 90/10	78	86	96
H2O	84	86	80
Storage on Bench			
MeOH w. 1% FA	46	16	83
Methanol	13	0	15
H2O/ACN 90/10	84	83	104
H2O	77	93	94



⇨ H2O/ACN 9:1 is a good solvent for working standards

Highly Volatile Pesticides

Phosphine

Cost-effective + rapidly acting **fumigant**
→ protect food stock **(e.g. cereals, spices) from insects + rodents**

Use increased following phasing-out of MeBr (Montreal Protocol)

APPLICATION FORMS:

- **PH_3 gas** (from gas cylinders or generated from phosphide plates)

Applied in silos against Insects and Rodents

- **Phosphides in Pellet/Tablet Form** (e.g. Al, Mg, Zn phosphides)

a) In **silos/containers**;
b) In **field** (against Rodents)

Phosphides **react with …**

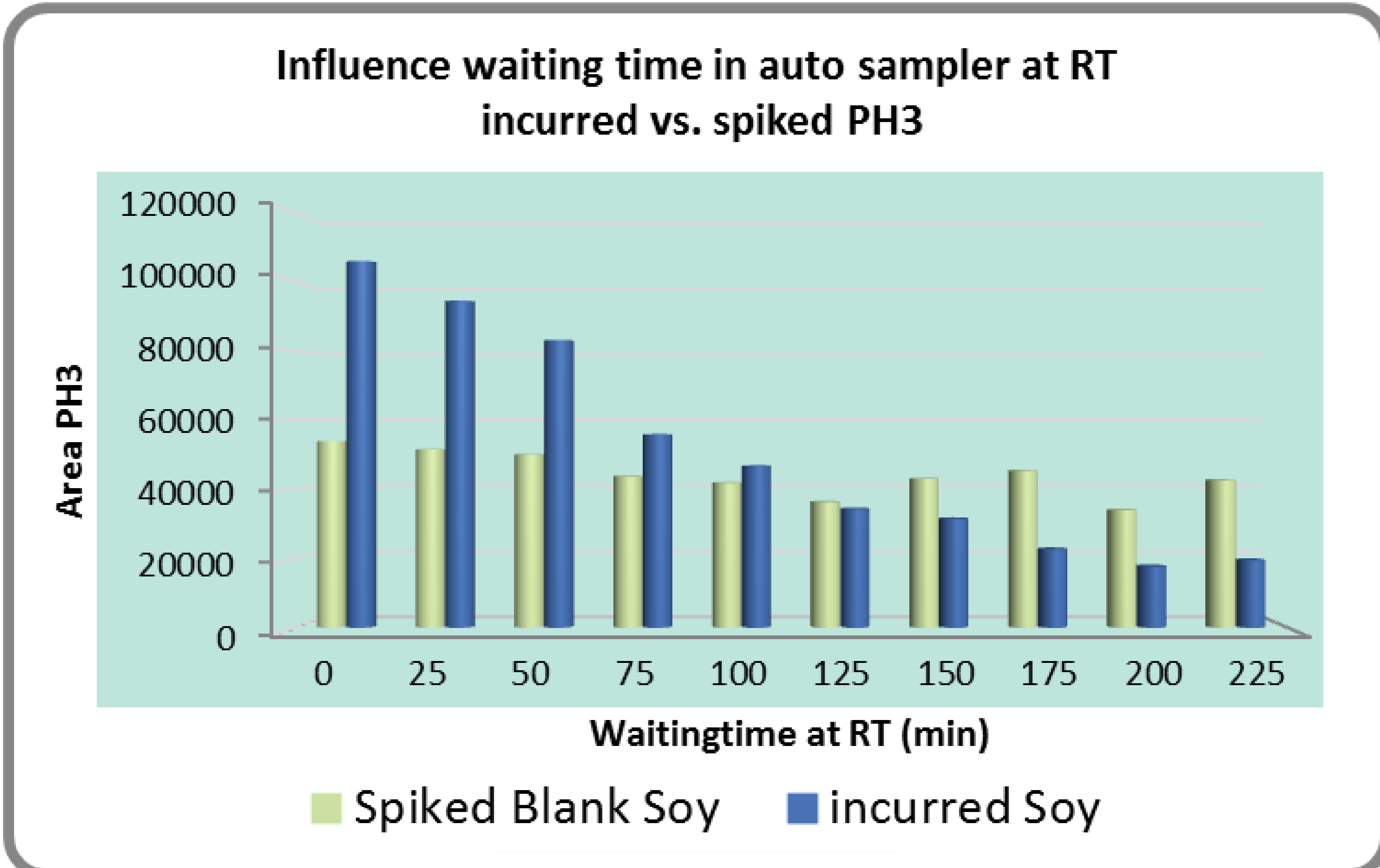
- **Water** (incl. atmospheric **vapor**

$$AlP + 3H_2O \longrightarrow Al(OH)_3 + PH_3$$

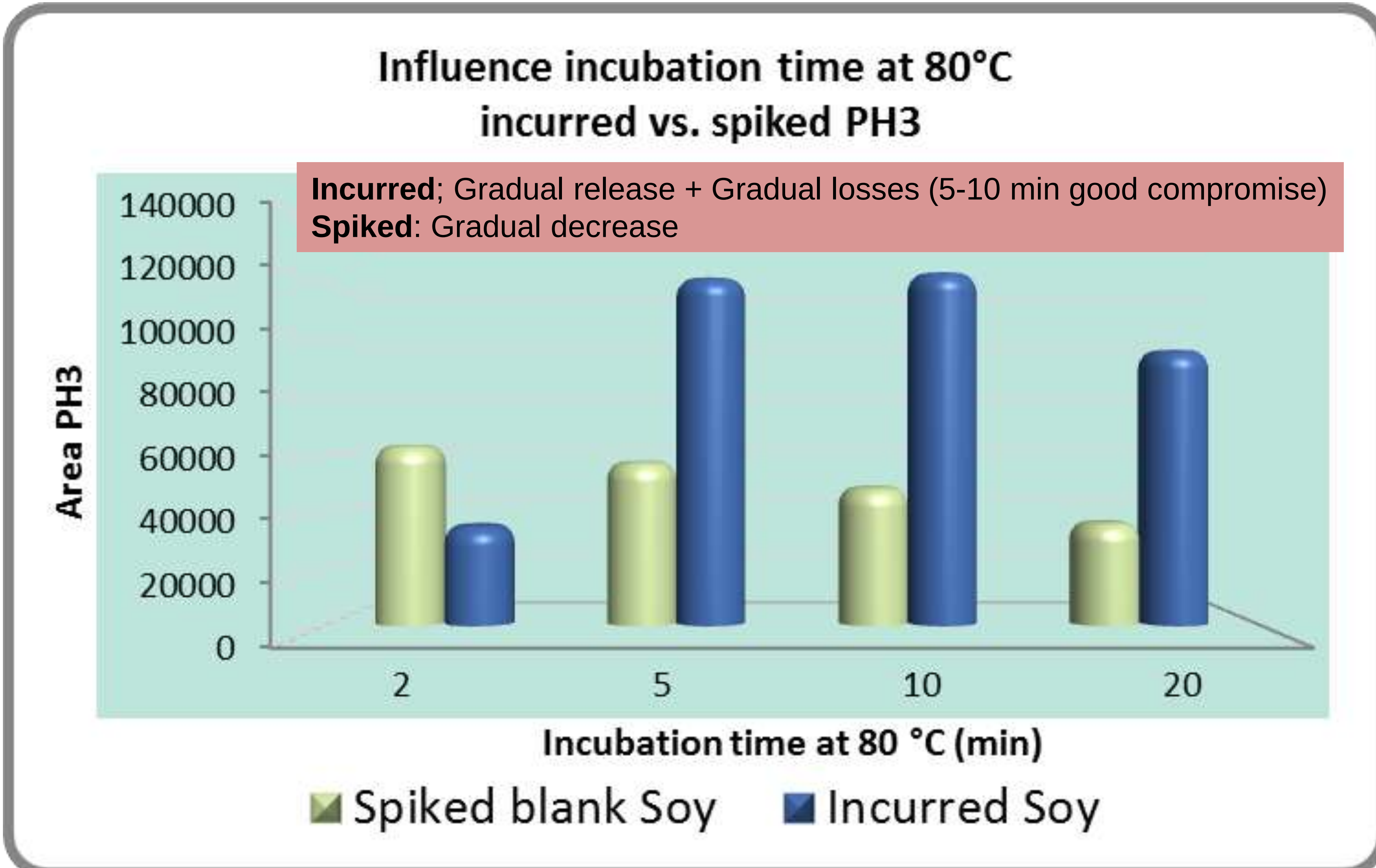
- **Acids** (e.g. in rodents' stomach) accelerate PH_3 formation

$$AlP + 3H^+ \longrightarrow Al^{3+} + PH_3$$

Phosphine = Phosphane (IUPAC) PH_3



Phosphine = Phosphane (IUPAC) PH_3



Sulfurylfluorid SO_2F_2

Fumigant insecticide

Replacement for methyl bromide

Odorless and neurotoxic

Usage (not necessarily in EU)

1. dried fruit,
2. nuts, oily seeds
3. cereals,
4. dried eggs, meat

Also used in buildings (e.g. against termites)

MRLs

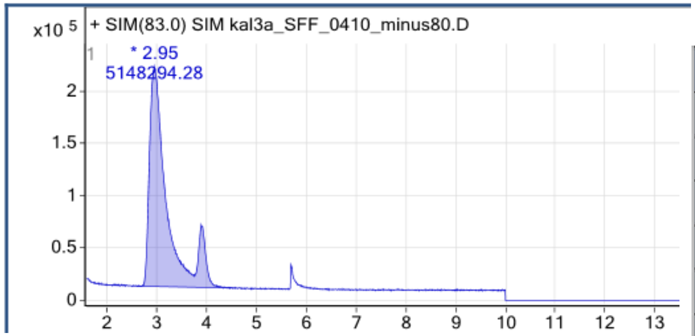
SO_2F_2: e.g. Tree nuts: 10 mg/kg, Herbal infusions; 0.05 mg/kg,
MRL*s = 0.01* mg/kg for most commodities and 0.02* for teas, coffee etc.

Fluoride ion: e.g. Teas: 350 mg/kg, Tree nuts 25 mg/kg, Herbal infusions and Hops 10 mg/kg;
Coffee beans and spices: 5 mg/kg.
MRL* = 2 mg/kg for all commodities of plant origin

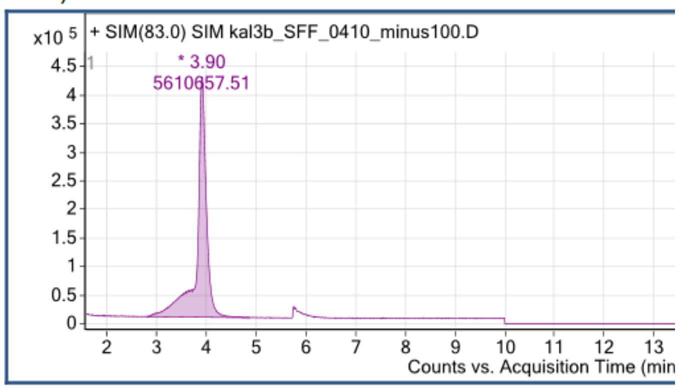
Sulfuryl Fluorid SO_2F_2

Method Optimization

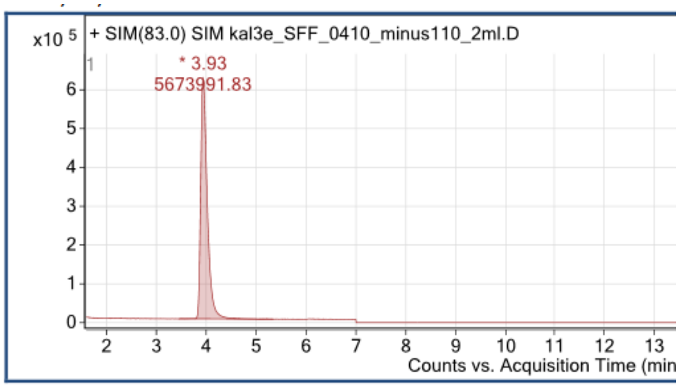
a) -80°C



b) -100°C



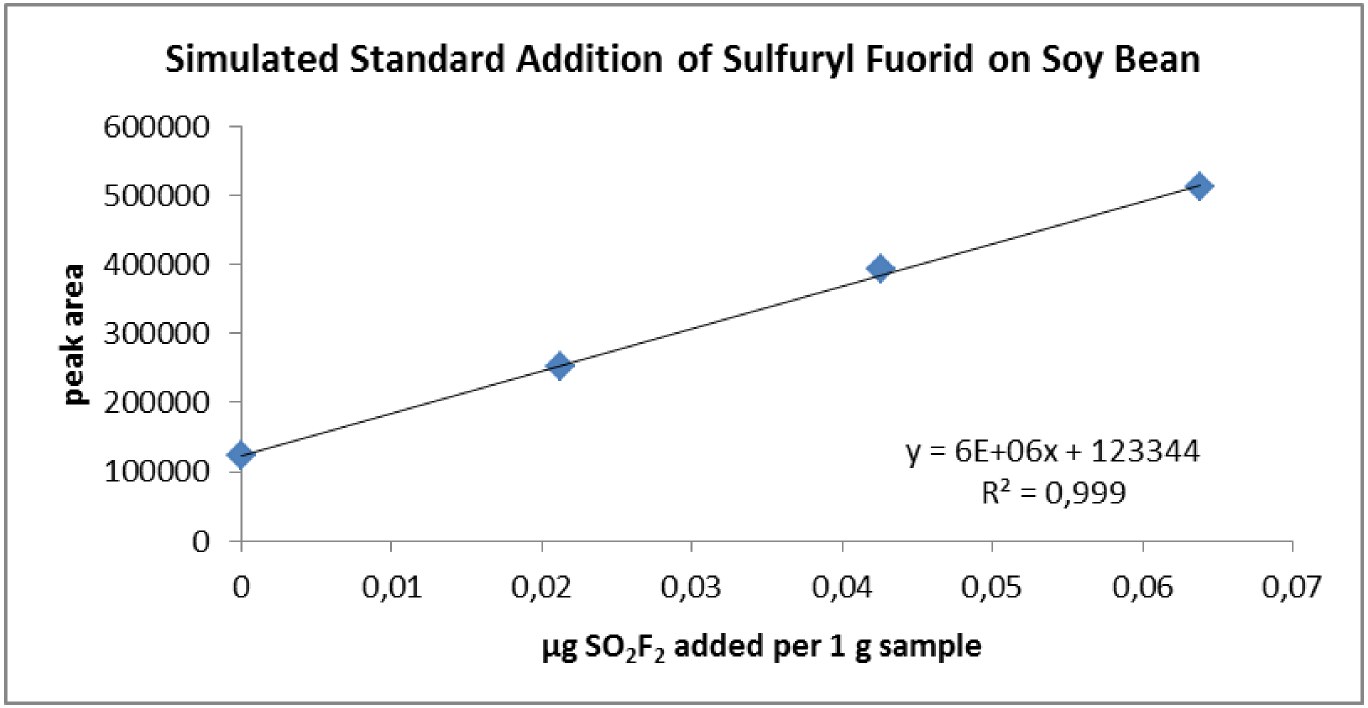
c) -110 °C

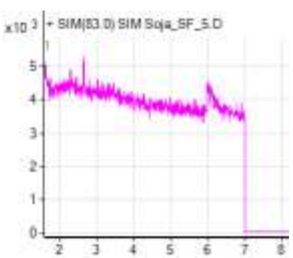


Headspace GC-MS analysis:

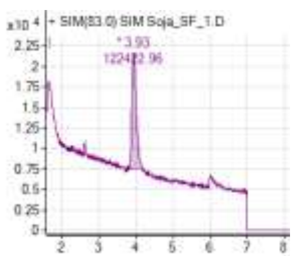
Headspace conditions	
Agitator temperature	80°C
Incubation time	10 min
Shaking speed	500 rotations per min
Shaking interval	5 s followed by a 2 s break
Syringe temperature	85°C
Injection volume	2000 µL
Draw speed	200 µL/s
Injection speed	500 µL/s
PTV conditions	
Initial temperature	-110°C with 0.1. min initial time
Heating ramp	150°C with a rate of 12°C/min
Hold time	2 min
Oven	
Carrier gas flow (Hydrogen)	2.2 mL/min (constant flow mode)
Split ratio	5:1
Oven temperature	35°C for 3 min
Heating ramps	10°C/min to 100°C, then 35°C/min to 200°C
Final time	4 min
Total run time	16.4 min
MSD	
Transfer line temperature	240°C
Solvent delay	4 min
SIM mode recording	m/z 83
Dwell time	100 ms for each ion
Tune mode	Manual tune for very low masses

Method verification through simulated standard addition

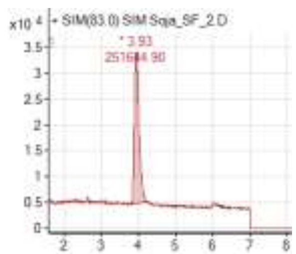




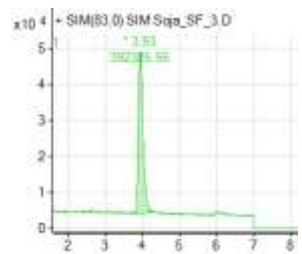
Blank Soy Bean



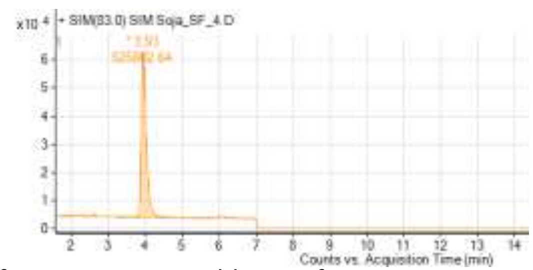
Soy Bean with xy ppm Sulfuryl Fluorid



Soy Bean + Addition of 0,021 µg Sulfuryl Fluorid



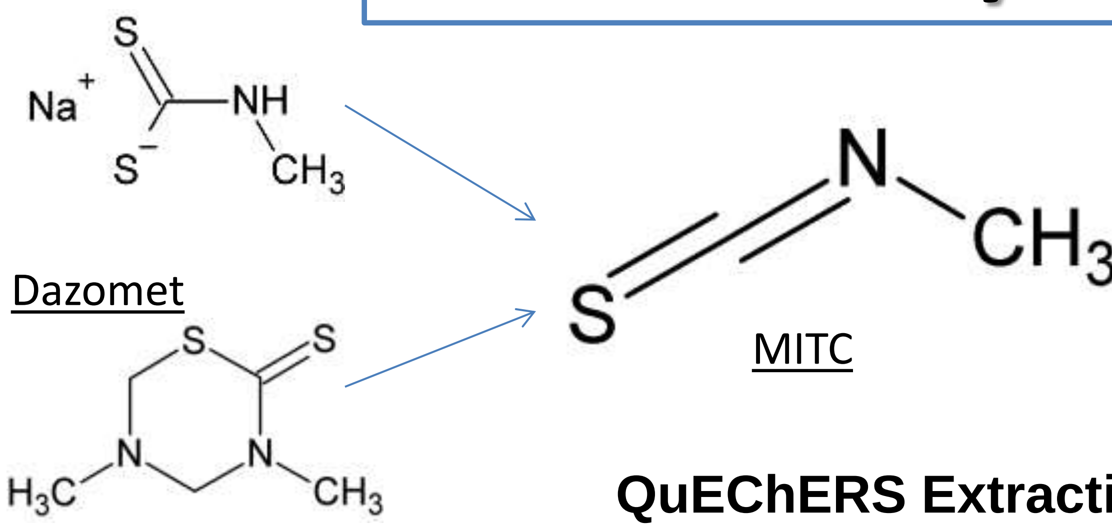
Soy Bean + Addition of 0,042 µg Sulfuryl Fluorid



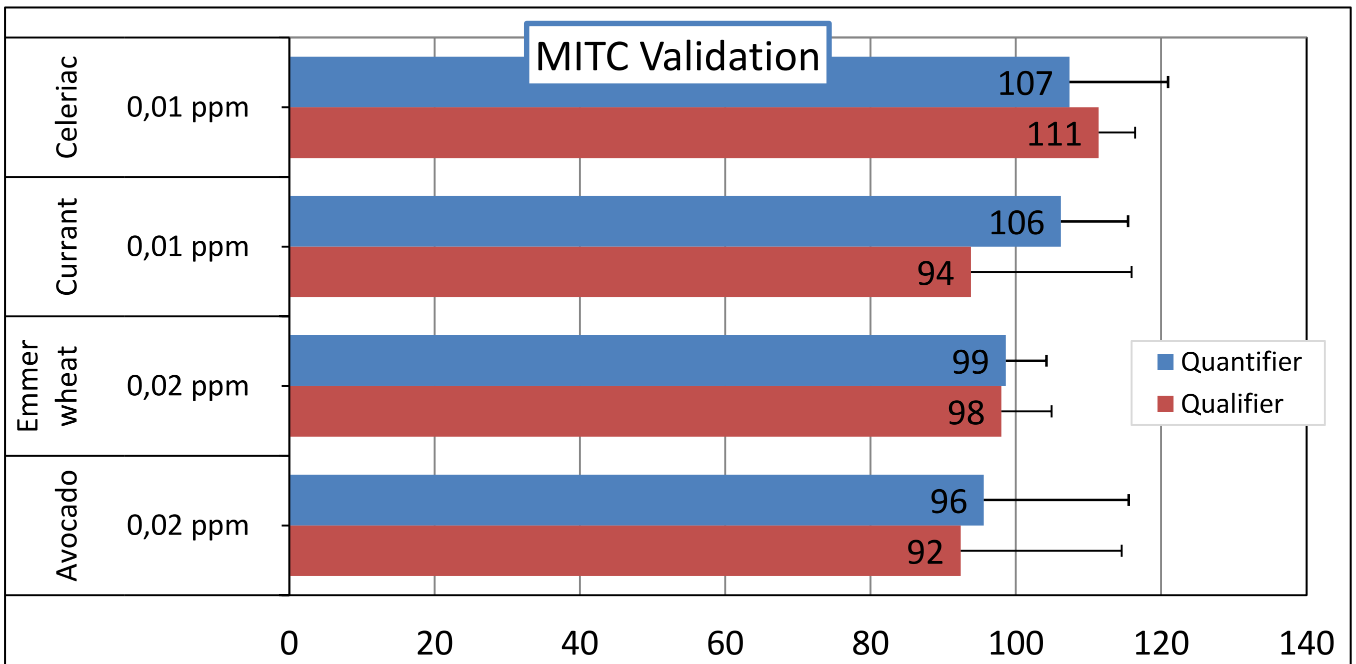
Soy Bean + Addition of 0,063 µg Sulfuryl Fluorid

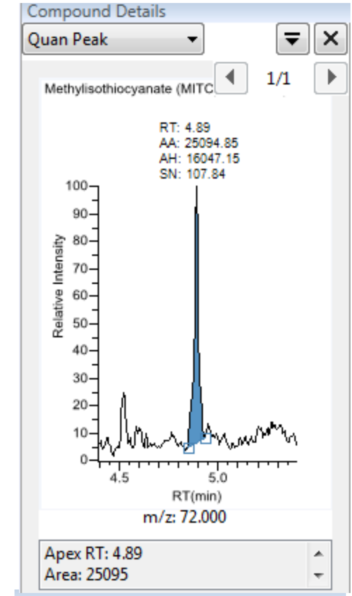
Simulated Standard Addition: Soy Bean spiked with 0,020 ppm
Calculated result via extrapolation 0.0188 (≡ 94 %)

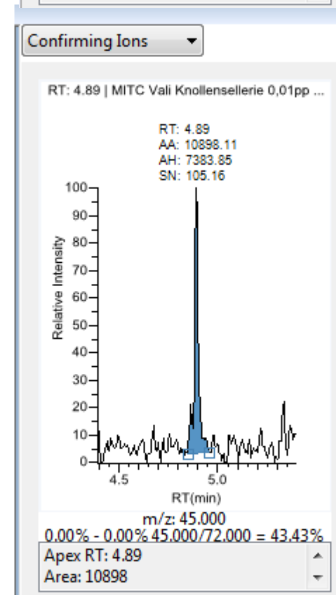
MITC - Methylisothiocyanate



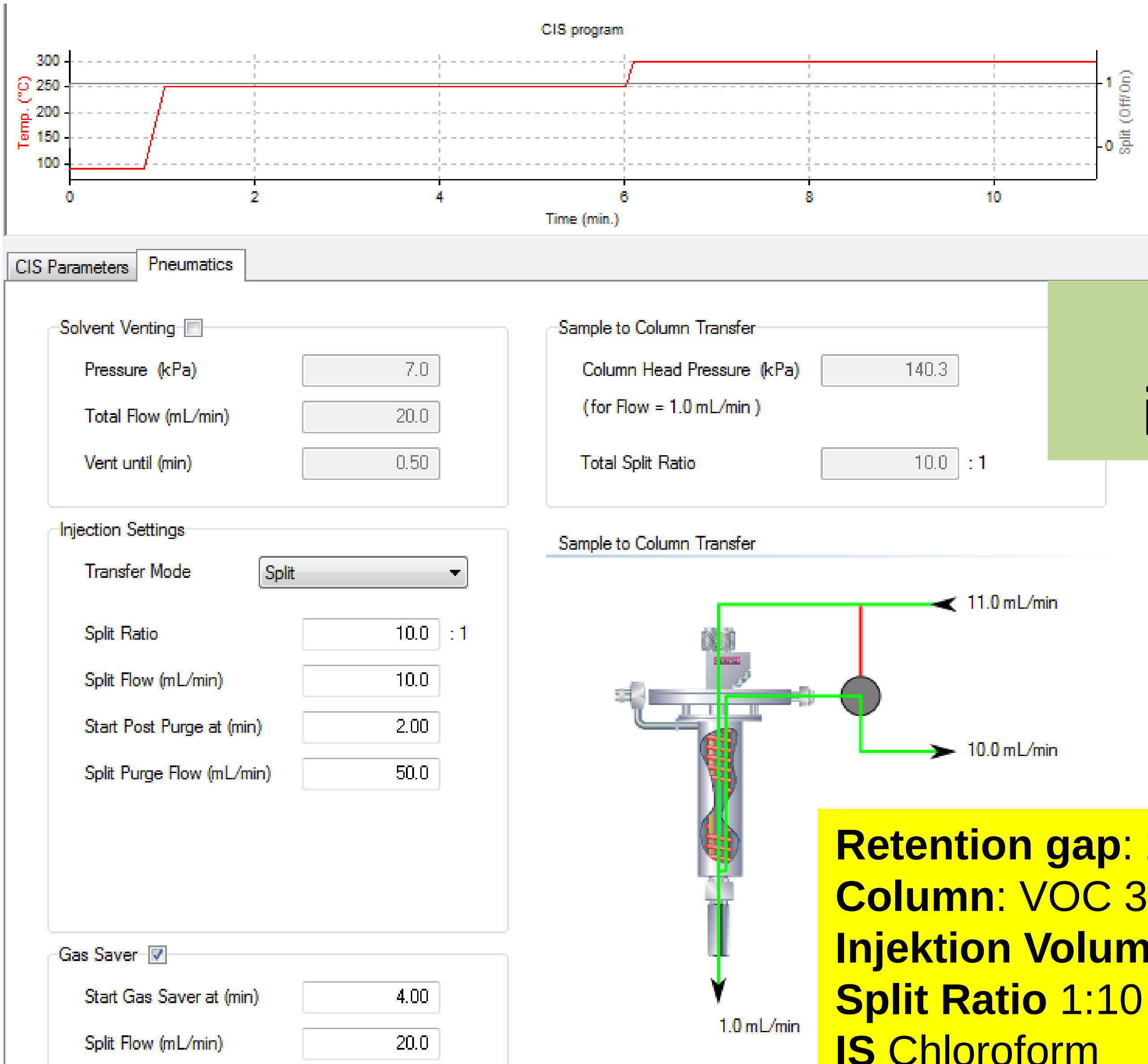
QuEChERS Extraction







MICP - GC-Conditions



Split Inj.
instead of PTV

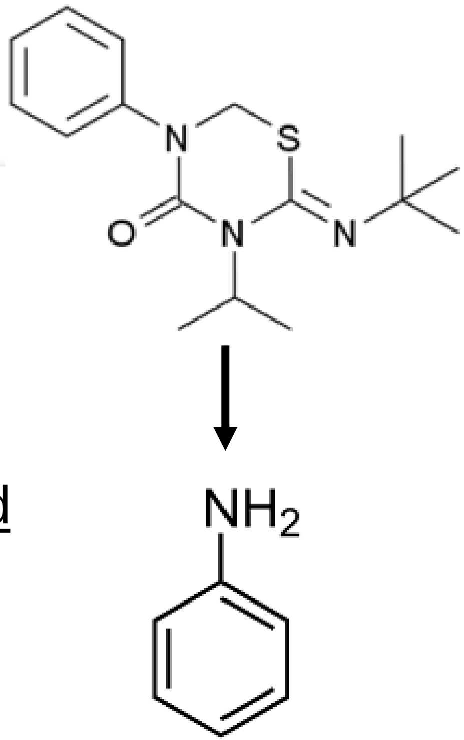
Retention gap: 2 m x 0.25 mm
Column: VOC 30 m x 0.2 mm (1.12 µm film)
Injektion Volume: 2 µl,
Split Ratio 1:10
IS Chloroform

Some other Compounds of Interest and actuality

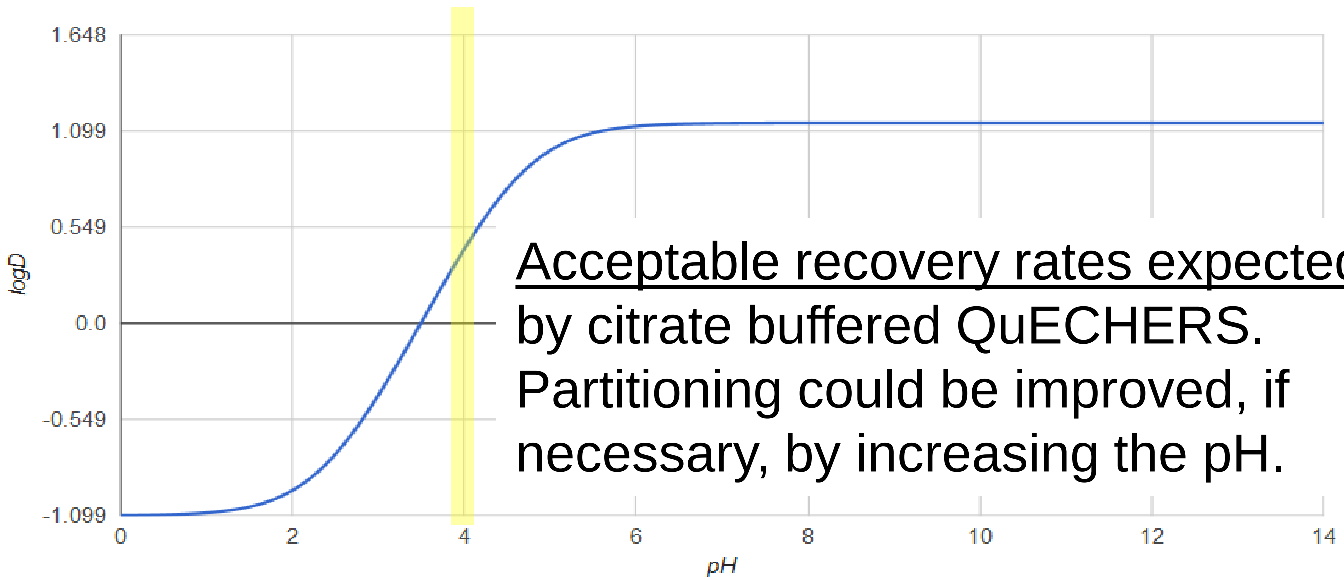
ANILINE

Aniline-forming pesticides and other compounds are in discussion
Anilines suspected to be cancerogenic + genotoxic.
Aniline is formed during **thermal processing of <u>Buprofezine</u>**

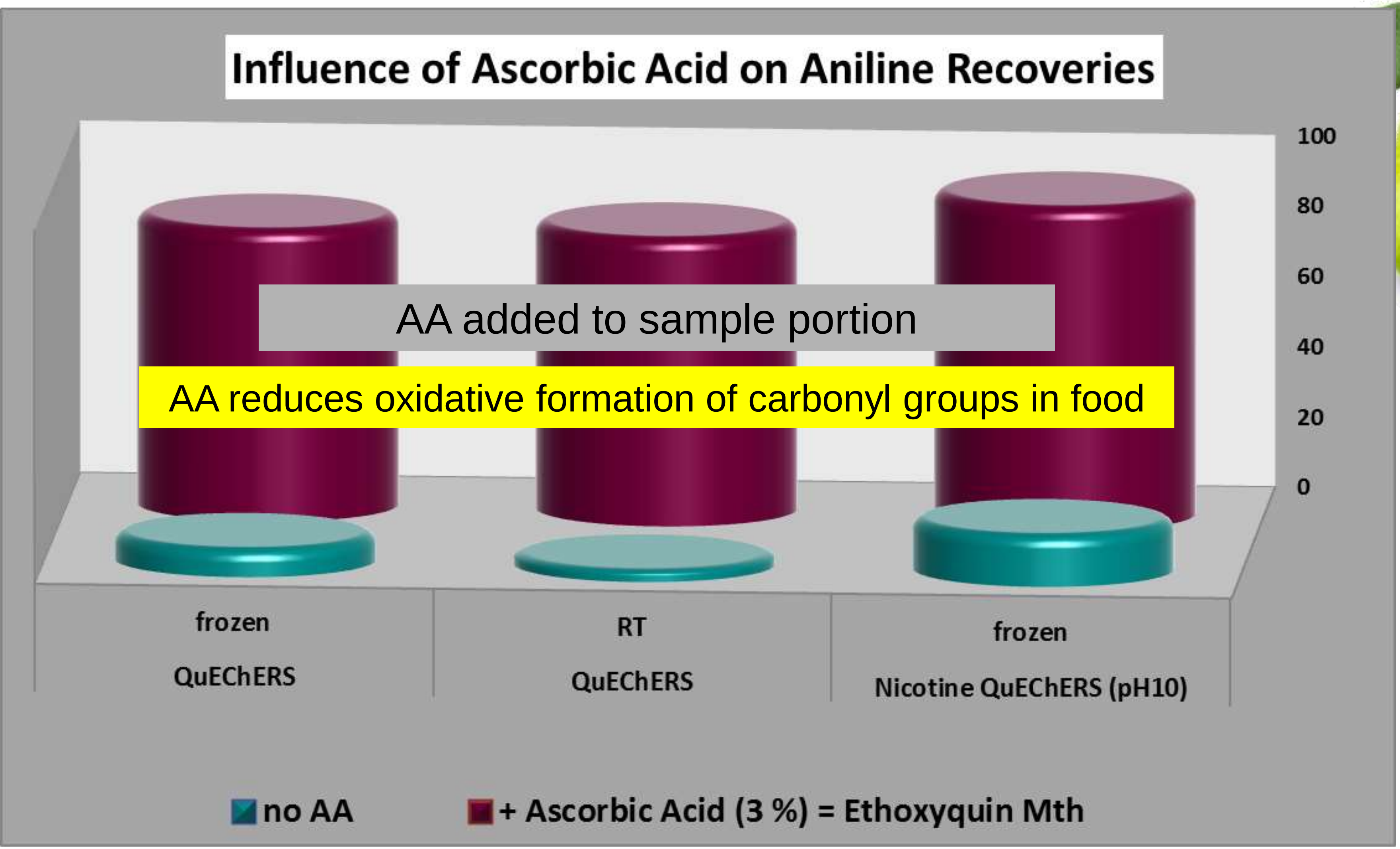
Aniline known to form **conjugates (especially with compounds entailing carbonyl groups)**



LogD-profile of Aniline

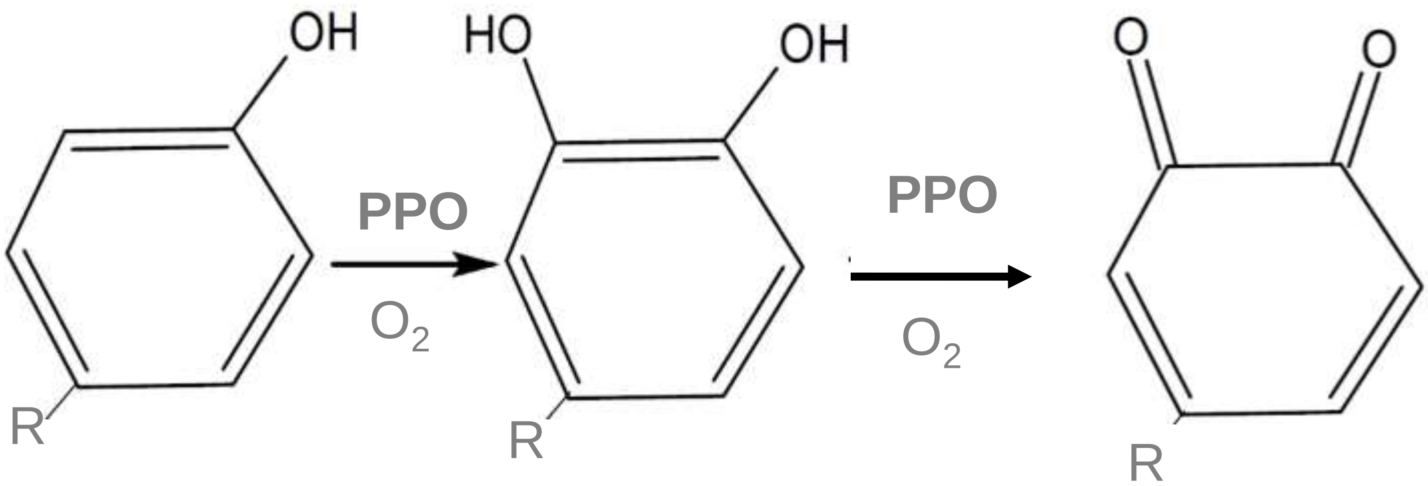


<u>Acceptable recovery rates expected</u> by citrate buffered QuECHERS. Partitioning could be improved, if necessary, by increasing the pH.



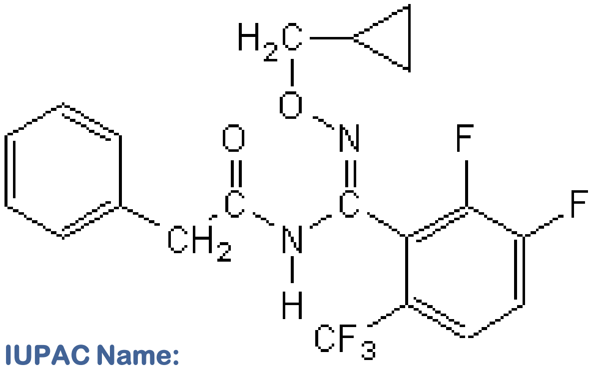
See also work by EURL-FV ⇨ here combination of citric and ascorbic acid

Formation of carbonyl groups through enzymatic browning



PPO = Polyphenoloxidase enzymes

Cyflufenamid



Cyflufenamid = z-isomer (by definition):
Technical material contains low conc. of E-isomer
(no FAO specification on isomeric ratio)

IUPAC Name:
(Z)-N-[α-(cyclopropylmethoxyimino)-2,3-difluoro-6-(trifluoromethyl)benzyl]-2-phenylacetamide

Current Residue definition:

„Cyflufenamid: sum of Cyflufenamid (Z-isomer) and its E-isomer"

Peer Review:
E-isomer was included in RD based on assumption that analytical methods used cannot separate the two isomers
E-isomer up to 4% of TRR (up to 10% of the level of the z-isomer) suggesting some shift of isomer ratio

Availability of analytical Standards:

- **Cyflufenamid** (z-isomer) = **available**
- **E-isomer** of cyflufenamid: **NOT available** (provided to EURL-SRM by applicant)

Q: Is the available standard (z-isomer) suitable for quantitative analysis of sum?

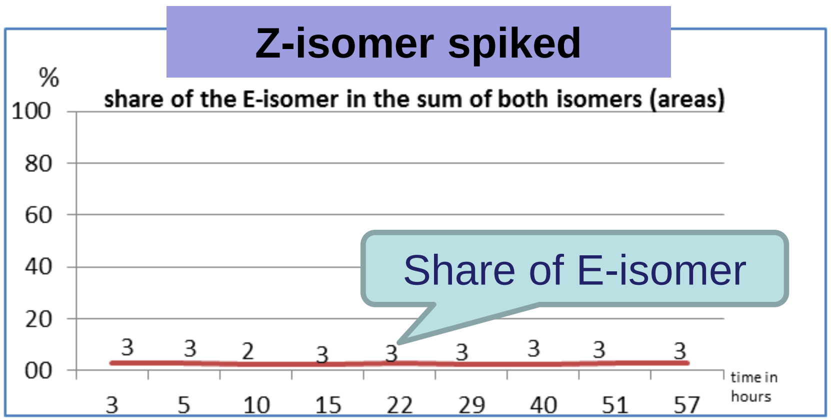
Observations analyzing Cyflufanamid by LC-MS:

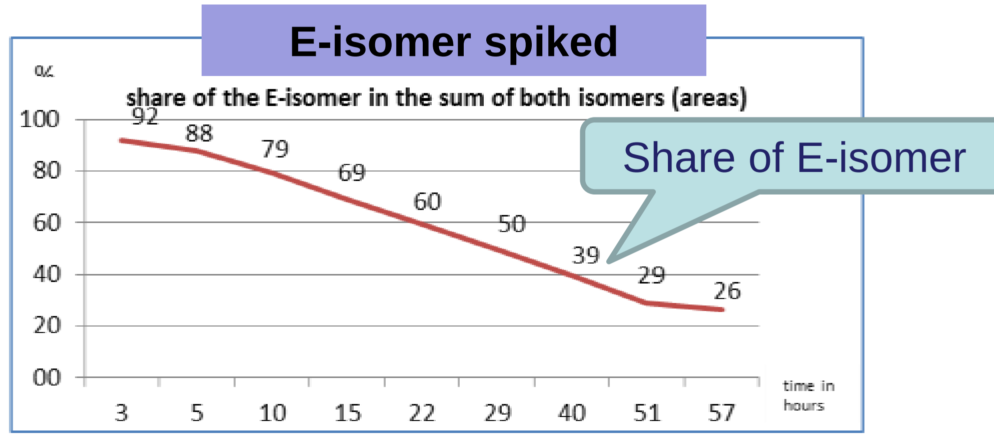
1) **Differing ESI-Ionization/fragmentation profiles of E- and Z-isomers**
2) **Isomerization from E to Z and vice-versa in solutions**

- Irrespective of the initial E/Z-composition isomerization leads to the **establishment of an E/Z equilibrium (**in QuEChERS extracts ~96:4 ratio) (Z-form obviously thermodynamically favored)
- **E➔Z isomerization during QuEChERS** (using frozen samples) is limited when measuring immediately *(E/Z still 95:5 tested with currant, cucumber)*
- **E➔Z isomerization in auto-sampler** in QuEChERS extract + in matrix-based cal. solutions *(E/Z ca 50:50 after 48h, same in currant = cucumber)*
- **E➔Z isomerization in stock and working solutions** (ACN/fridge). In diluted working solutions faster than in stock solutions,
- **Isomerization accelerates at higher temperatures** (activation energy). Heating for 2h@60°C was enough to shift E/Z from 97:3 to 4:96 (equilibrium)

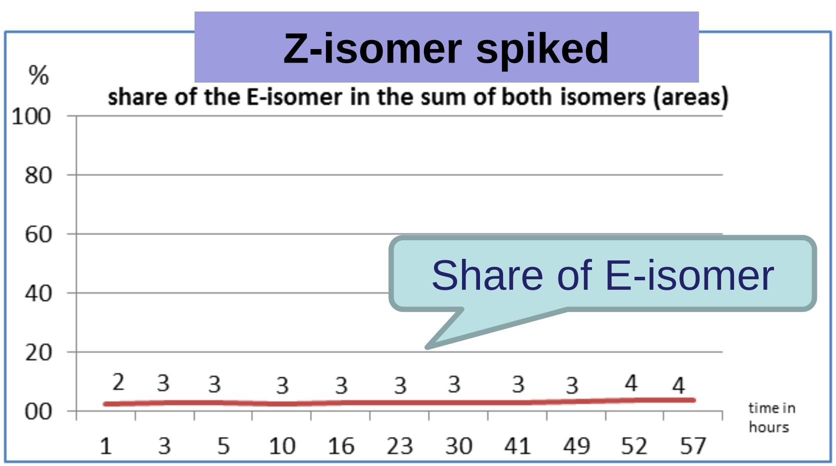
Cyflufenamid Isomerization

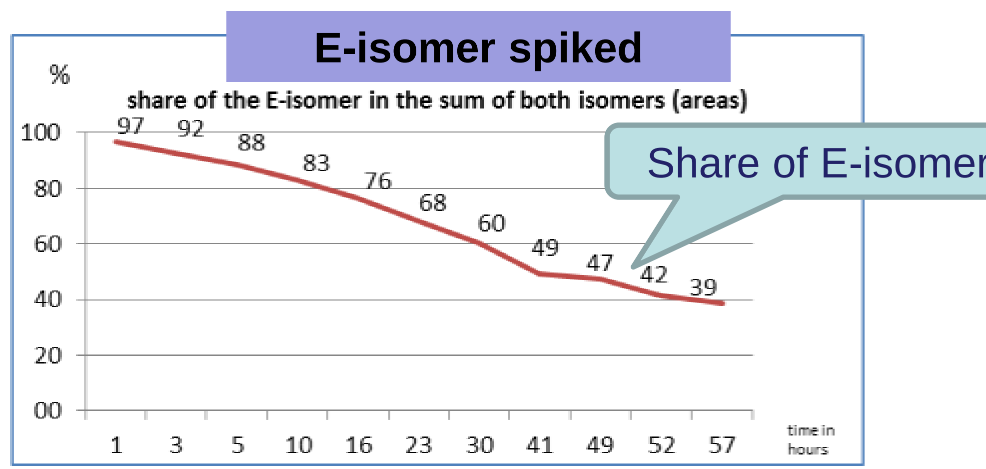
In Solvent



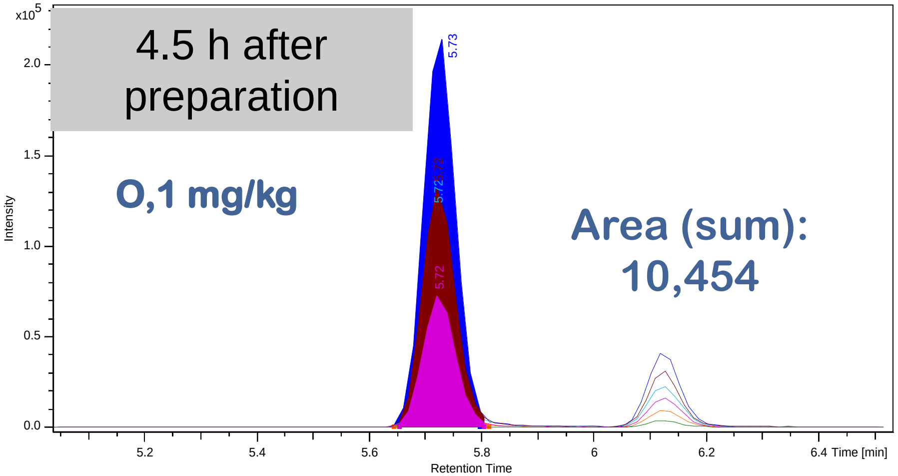


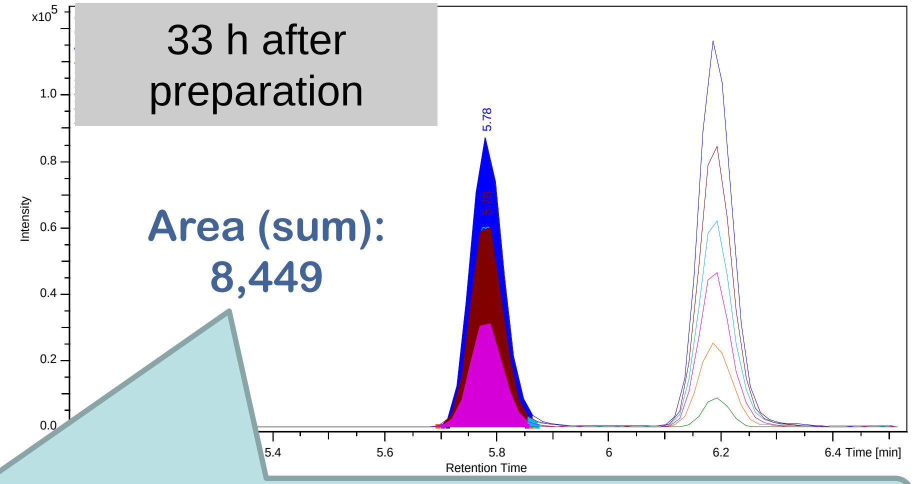
In Cucumber Extract (currant almost identical)





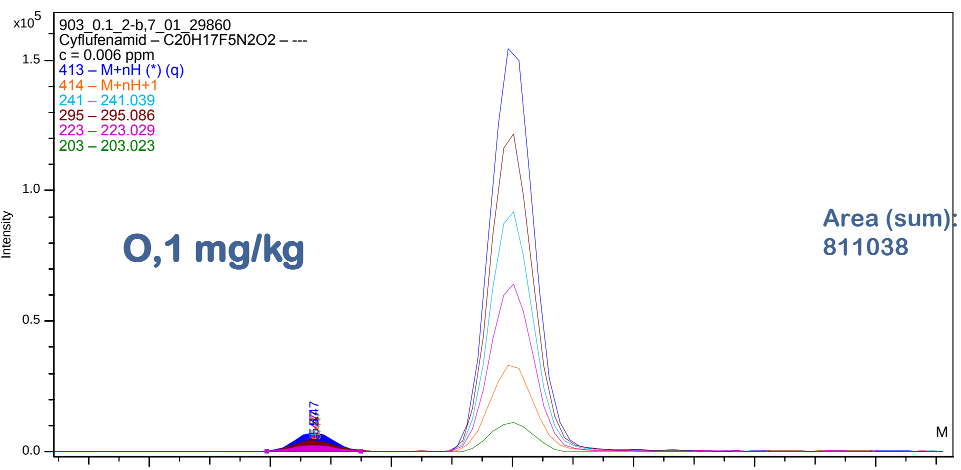
E-Isomer





Summed area decreased because
Z-isomer showed weaker response on used mass trace

E-Isomer



Reflections on Quantification and utility of standards

Q1: How is quantification of cyflufenamid (sum) influenced by differences in signal response and share of E and Z-isomers?

Scenario (realistic):
- Z/E ratio in calibration standard solution: 96:4
- Z/E detection response ratio : 1:1.25 (depends on masses chosen)

Z/E RATIO in sample extract	THEORETICAL BIAS of ‚Cyflufenamid (sum)'
Quantification via Z-ISOMER AREA (disregarding E-isomer)	
90:10	-6.3%
95:5	-1%
Quantification via SUMMED AREA (disregarding different response of E and Z)	
90:10	+1.5% } **preferred**
95:5	+0.25% } **preferred**

Q2: Would an E-isomer calibration standard be usefull or superfluous?

Due to rapid E➔Z conversion in cal. stds
- ➢ Risk of overestimating E-isomer results
- ➢ Risk of underestimating Z-isomer results if E and Z-isomers are within same cal. std mix

CONCLUSIONS:

- **E-isomer std has limited use for routine analysis of cyflufenamid (sum).**
- **Cyflufenamid (sum) can be quantified w. sufficient accuracy using available Z-standard.**

Pesticide Related Compounds from sources other than direct pesticide use

Nicotine Background Levels:

Plants naturally containing Nicotine

- **Pepper, Aubergines, Tomatoes** (ppb levels according to lit.)
- **Goji-Berries** (Under suspicion but contam. During picking likely) …

} ***Solanaceae***

- **Mushrooms,**
- **Tea,**
- **Moringa**.

} ***Suspected***

Study on Moringa:

- Moringa Plants grown in Egypt,
- Sent to our lab by grower immediately after harvest
- Grower claimed no contamination w. nicotine during growing or harvest!
- Grower refered to Univ. Prof. statement that nicotine is formed from nicotinic acid during processing

RESULTS

1) Fresh homogenate : **0.0160 mg/kg**

2) ➔ 8 h @ RT +16h in fridge**: 0.0164 mg/kg**

3) + 200 mg/kg Nicotinic acid ➔ 8 h @ RT +16h in fridge : **0.0164 mg/kg**

4) + 200 mg/kg Nicotinic acid ➔ 8 h @ RT +16h in fridge ➔ dried @ 35°C : **0.0169 mg/kg** (back-calculated to fresh product, F=4.75)

5) ➔ dried @ 35°C : **0.0175 mg/kg** (back-calculated to fresh product)

Assuming no contamination prior to analysis Moringa seems to contain significant natural levels of nicotine. Formation during drying, if at all, very limited

Nicotine Residues - Overview

Product Group	No. Samples	No. Positive	Percentage	Mean mg/kg	Max mg/kg	Min mg/kg
Cereals and cereal products	24	1	4	0,030	0,030	0,03
Fruit	125	16	13	0,011	0,044	0,005
Fruit products	22	3	14	0,277	0,440	0,12
Dry fruits and seeds	39	2	5	0,031	0,033	0,028
Vegetables	184	46	25	0,028	0,610	0,005
Vegetable products	27	16	59	0,157	0,710	0,009
Potatoes and starchy vegetables	10	2	20	0,013	0,013	0,013
Mushrooms	36	9	25	0,021	0,057	0,005
Mushroom products	61	40	66	0,862	3,400	0,012
Tea	28	20	71	0,077	0,230	0,015
Medical tea	12	7	58	0,081	0,190	0,021
Spices, seasonings	23	14	61	0,043	0,088	0,015
Food contact material	8	6	75	0,573	1,300	0,076
Food supplement	3	3	100	5,472	16,000	0,085
Other	10		0			
Total	**612**	**185**	**30**	**0,336**	**16,000**	**0,005**

Source: CVUA Stuttgart

Nicotine Residues - Highest Levels Found

Wild mushroom, dried	Nicotin mg/kg	Country of Origin
	3,4	unknown
	3	unknown
	2,8	unknown
	2,7	unknown
	2,6	unknown
	2,4	unknown
	2,2	Serbia
	1,8	Pakistan
	1,7	unknown
	1,7	India
	1,2	unknown
	1,2	Serbia
	1,1	unknown
	1,1	Serbia
	0,86	Turkey
	0,63	Serbia

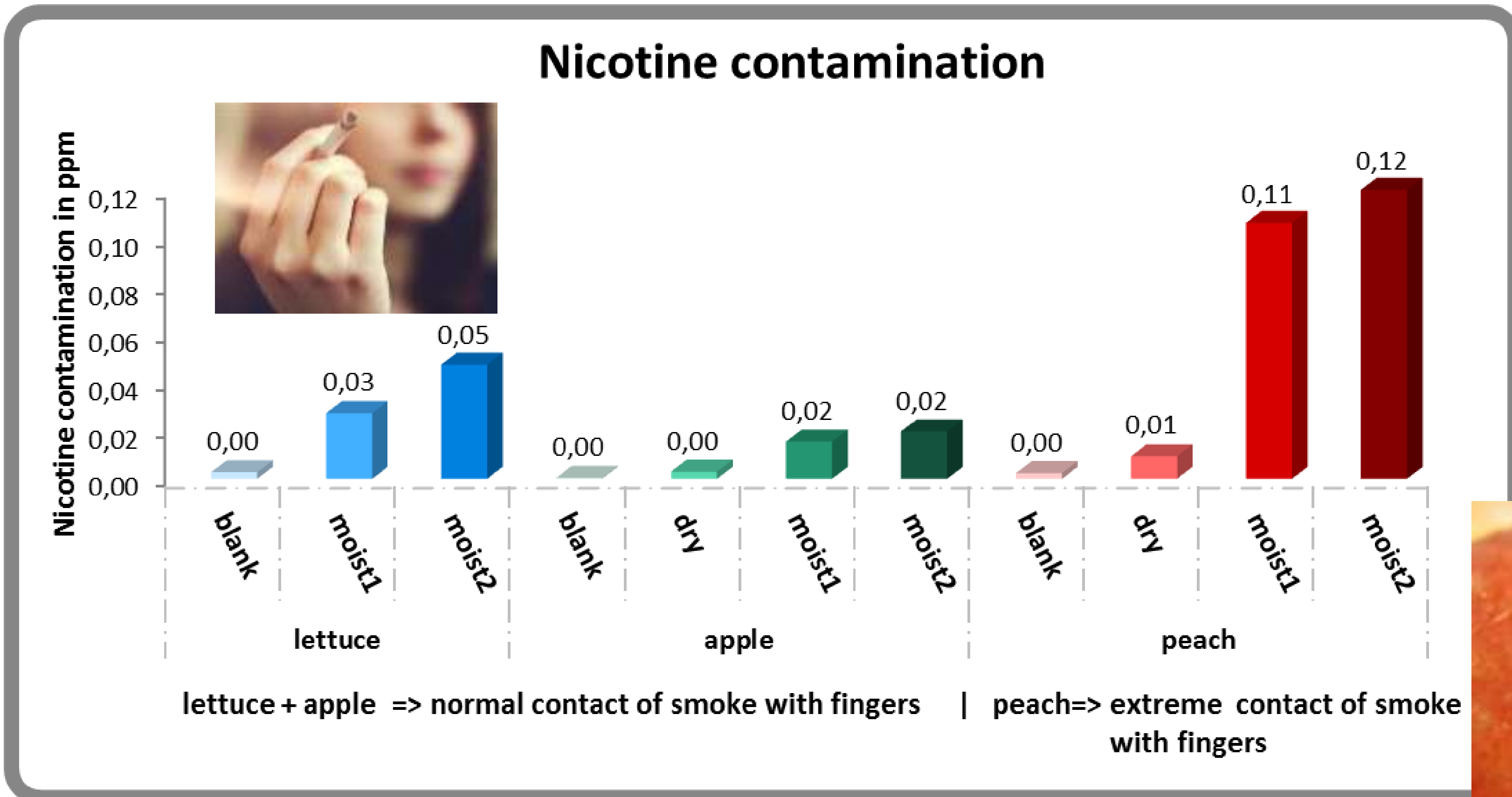
Product	Nicotin mg/kg	Country of Origin
Chives	0,61	Kenia
Food contact material	0,39	unknown
	0,46	unknown
	1,1	unknown
	1,3	unknown
Goji berry, dried	0,44	China

Moringa	Nicotin mg/kg	Country of Origin
	0,33	unknown
	0,38	unknown
	0,71	Philippines
	16	Dom. Republic

Still suitable as a food???

Source: CVUA Stuttgart

Contamination of samples with Nicotine



4 units touched in each case ➔ homogenized and analyzed

dry => product with **dry skin** was **touched** after smoking a cigarette

moist1 => product with **moist skin** was **touched** after smoking a cigarette (e.g. at the weekly market)

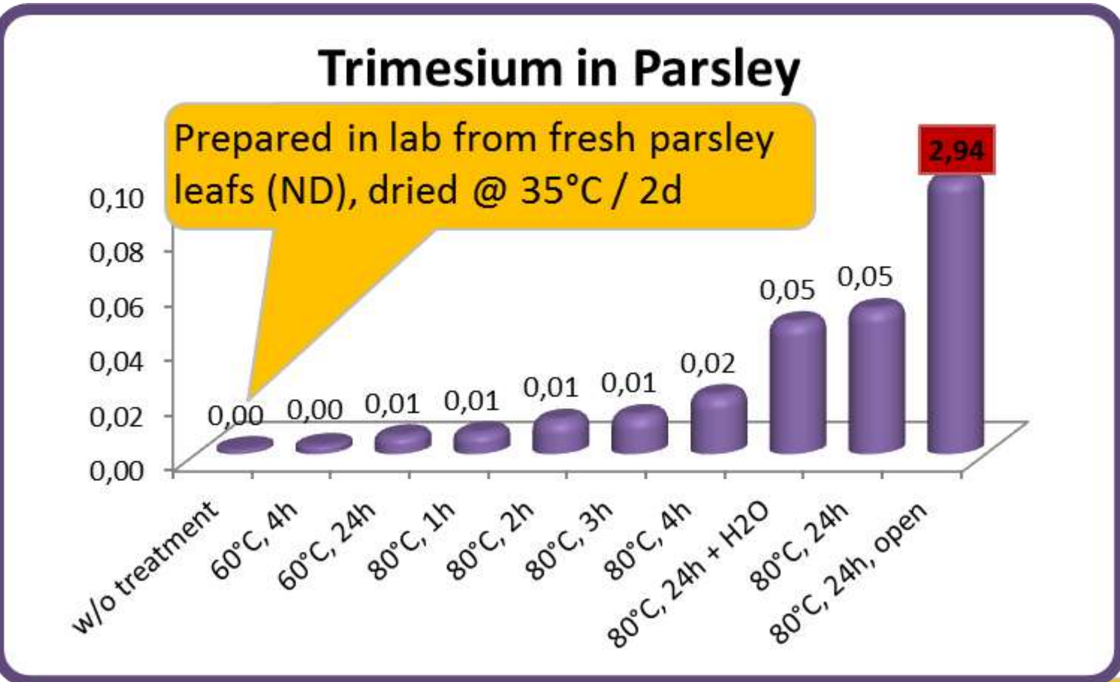
moist2 => product with **moist skin** was **touched and sectioned** after smoking a cigarette (e.g. in the lab)

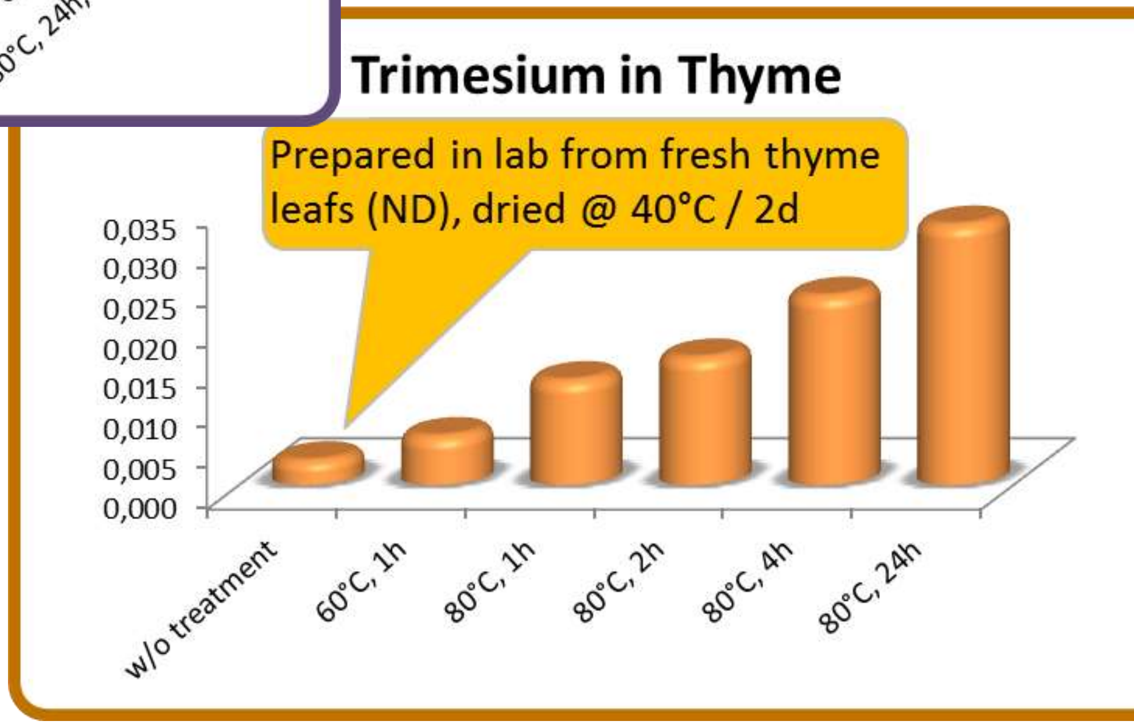


NO!


DON'T TOUCH.

Trimesium formation during processing





Trimesium Levels

Product Group	No. Samples	No. Positive	Percentage	Mean mg/kg	Max mg/kg	Min mg/kg
Samples analyzed since 2010	11414	319	2,8	0,044	0,650	0,001
		thereof with findings				
Baby and infant foods	94	1	1,1	0,016	0,016	0,016
Beer and ingredients	6	2	33,3	0,031	0,047	0,014
Beverages	2	1	50,0	0,044	0,044	0,044
Beverages alcoholfree	126	12	9,5	0,019	0,160	0,005
Cereals and cereal products	257	2	0,8	0,005	0,006	0,003
Dry fruits and seeds	270	12	4,4	0,041	0,340	0,004
Food supplement	16	12	75,0	0,085	0,300	0,002
Fruit	4199	67	1,6	0,016	0,210	0,001
Fruit products	302	10	3,3	0,044	0,170	0,002
Mushroom products	79	20	25,3	0,018	0,077	0,002
Mushrooms	284	60	21,1	0,021	0,120	0,001
Potatoes	253	1	0,4	0,001	0,001	0,001
Spices, seasonings	41	8	19,5	0,052	0,190	0,005
Spread	11	2	18,2	0,015	0,019	0,010
Tea	53	36	67,9	0,132	0,650	0,007
Vegetable products	351	35	10,0	0,079	0,470	0,004
Vegetables	4870	33	0,7	0,031	0,220	0,005
Medical Tea	16	5	31,3	0,044	0,089	0,008

Source:
CVUA Stuttgart

Trimesium levels in Tea

Product	Country of Origin	No of samples	Min (mg/kg)	Max (mg/kg)
Green tea	China	4	0,009	0,2
	Japan	1	0,047	
	Nepal	1	0,34	
	unknown	4	0,042	0,24
Black tea	India	1	0,11	
Peppermint tea	unknown	3	0,027	0,077
Melissa tea	unknown	1	0,036	
Herbal tea	Turkey	1	0,035	
other infusions	unknown	2	0,007	
	India	1	0,28	
Fennel tea	unknown	5		
Mate tea	unknown	1		
Rooibos tea	South Africa	1		
Total		26	0,007	0,34

Source:
CVUA Stuttgart

Fosetyl formation in Wine

	Conc. mg/kg (Mean n=2)	
Datum	Fosetyl	Phosphonate
12.05.16 prior to addition of yeast	-	**13.1** (13,2+12,9)
18.05.2016	**0.0015** (0,0014+0,0015)	**12.4** (12,3+12,4)
26.06.2016	**0.0027** (0,0028+0,0026)	**12.3** (11,97+12,7)
24.01.2017	**0,0087** (0,0088+0,0086)	**13,7** (13,6+13,8)
02.05.2018	**0,0185** (0,0184+0,0186)	**13,2** (13,2+13,2)

Overview of Residue Levels of SRM-Compounds

Dry Products	Freq. >0.01 mg/kg (%)	>MRL (%)	≥5 cases >MRL
Triazole-alanine *(Not Regul. Metab.)*	80,6		
Triazole-acetic acid *(Not Regul. Metab.)*	65,7		
Cyanuric acid *(Not Regul. Metab.)*	48,2		
Trifluoroacetic acid *(Not Regul. Metab.)*	32,5	-	
Phosphonic acid	25,1	1,76	>=5 cases
Diethanolamine	22,0		
Triazole-lactic acid *(Not Regul. Metab.)*	16,0		
Chlormequat	11,1	-	
Triethanolamine	9,0	-	
Chlorate	8,3	1,95	>=5 cases
Bromide	9,7	-	
Glyphosate	6,5	3,27	>=5 cases
Morpholine	4,1	-	
Perchlorate	2,8	-	
HEPA *(Not Regul. Metab.)*	2,6	-	
Mepiquat	1,9	-	
Diquat	1,6	0,41	
Trimethylsulfonium cation	1,1	0,22	
Melamine *(Not Regul. Metab.)*	1,3	-	

Other: Ethephon (0.1%), MPPA (0.2%), Maleic hydrazide (0.2%), Mepiquat- 4-hydroxy, N-Acetyl-AMPA (0.2%), 1,2,4-Triazole (0.7%)

Fruits + Vegetables	Freq. >0.01 mg/kg (%)	>MRL (%)	≥5 cases >MRL
Triazole alanine *(Not Regul. Metab.)*	44.1		
Phosphonic acid	36,7	0,77	>=5 cases
Triazole lactic acid *(Not Regul. Metab.)*	22.3		
Trifluoroacetic acid *(Not Regul. Metab.)*	19,1	-	
Perchlorate *(contaminant)*	15,4	0,05	
Cyanuric acid *(Not Regul. Metab.)*	12,9		
Melamine *(Not Regul. Metab.)*	12,1	-	
Chlorate	10,5	7,52	>=5 cases
Bromide	11,1	0,02	
Triethanolamine	8,7	-	
Triazole acetic acid *(Not Regul. Metab.)*	7,6		
Diethanolamine	5,1	-	
Propamocarb	4,2	0,06	
Propamocarb-N-oxide *(Not Regul. Metab.)*	2,7	-	
Ethephon	2,9	0,45	>=5 cases
Propamocarb-N-desmethyl *(Not Regul. Metab.)*	1,2	-	
HEPA *(Not Regul. Metab.)*	1,7	-	
Cyromazine	0,8	0,01	
Chlormequat	0,5	0,08	>=5 cases
Glyphosate	0,1	0,03	

Other: Bromate (0.4%), Chloridazon-desphenyl (0.5%), Daminozide (0.04%), ETU (0.4%), Fosetyl (0.7%), MPPA (0.5%), Maleic hydrazide (0.6%), Morpholine (0.6%), Nereistoxin (0.1%), PTU (0.1%), Streptomycin (0.9% all < 0.01 mg/kg), 1,2,4-Triazole (0.4%), Trimethylsulfonium cation (0.4%)

Examples of commodities with high detection frequency

Dry Products (Top Commodities with residues)	Matrix	Frequency (%)	>MRL (%)
Phosphonic acid	Rice	46,2	8,11
Glyphosate	Buckwheat	19,3	16,7
Glyphosate	Lentil	22,1	15,6

**(of commodity analyzed)

Fruits + Vegetables (Top Commodities with Residues	Matrix	Frequency (%)	>MRL (%)
Phosponic acid	Pomegranate	51,0	7,7
Phosponic acid	Asparagus	31,0	3,5
Chlorate	Coriander	72,2	61,1
Chlorate	Dill leaves	40,0	37,5
Chlorate	Celery	36,4	36,4
Chlorate	Rucola	37,1	32,9
Chlorate	Basil	40,0	29,3
Chlorate	Aubergine	28,2	25,9
Ethephon	Kumquat	20,0	16,0
Ethephon	Figs	18,0	12,7

**(of commodity analyzed)

Thank you
for your Attendance

European Commission

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