Residual highly polar pesticides in beer

Jan Stenzler
Application specialist LCMS
Product group LCMS
Shimadzu Deutschland GmbH

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Glyphosate: background

Feb 2016:

- Glyphosate residues found in 14 german beers significant above the maximum residue limit of 0,1 µg/l for german drinking water
- Method: ELISA (LOD in beer 0,075 µg/l)
- ADI: 0,3 mg/kg body weight
- Federal Institute for risk assessment (BfR): no risk < 1000 l/day

Glyphosate: exemplary methods

- Vegetables: EURL-SRM Quick Polar Pesticides Method (QuPPe)
- Mother‘s milk: BfR-method for Glyphosate (J. Agric. Food Chem. 2016, 64, 1414−1421), LOQ 1 ng/ml
- Environment: PROMOTE project (UFZ)

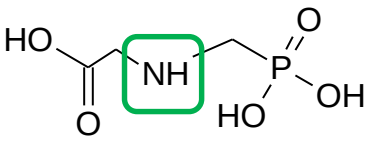
Beer is a difficult matrix due to

- ion suppression for highly polar compounds
- interferences during derivatisation with FMOC

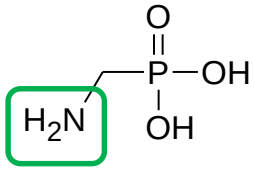
Highly polar compounds such as glyphosate...

- ...have a low mass and less product ions
- ...are amphoter

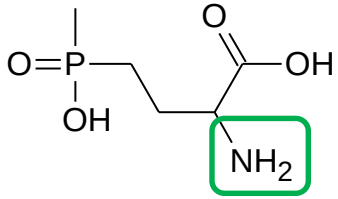
Derivatisation with FMOC



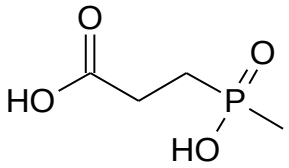
Glyphosate



AMPA



Glufosinate



MPPA

Analyte	With derivatisation	Without derivatisation
Glyphosate	Yes	Yes
AMPA	Yes	Not possible
Glufosinate	Yes	Yes
MPPA	Not possible	Yes

Two workflows

[1] Residual highly polar pesticides in beer: A comparative study about sample pretreatment with and without derivatization, Poster 11th EPRW, Limassol, Cyprus, May 2016
Sigrid Baumgarten[1]; Anja Grüning[1]; Julia Sander[1]; Rebecca Kelting[1]
[1] Shimadzu Europa GmbH, Duisburg, Germany

Two workflows

With derivatisation

500 µl supernatant

+ 25 µl EDTA-borate buffer

+ 75 µl FMOC

60 min incubation at 50 °C

30 µl 0,2 % phosphoric acid

+ 125 µl water

Without derivatisation

1 ml beer + 1 ml methanol, vortex

centrifuge, 15 min, 12000 rpm

500 µl residue

Multiplexing with Nexera MX and LCMS-8060

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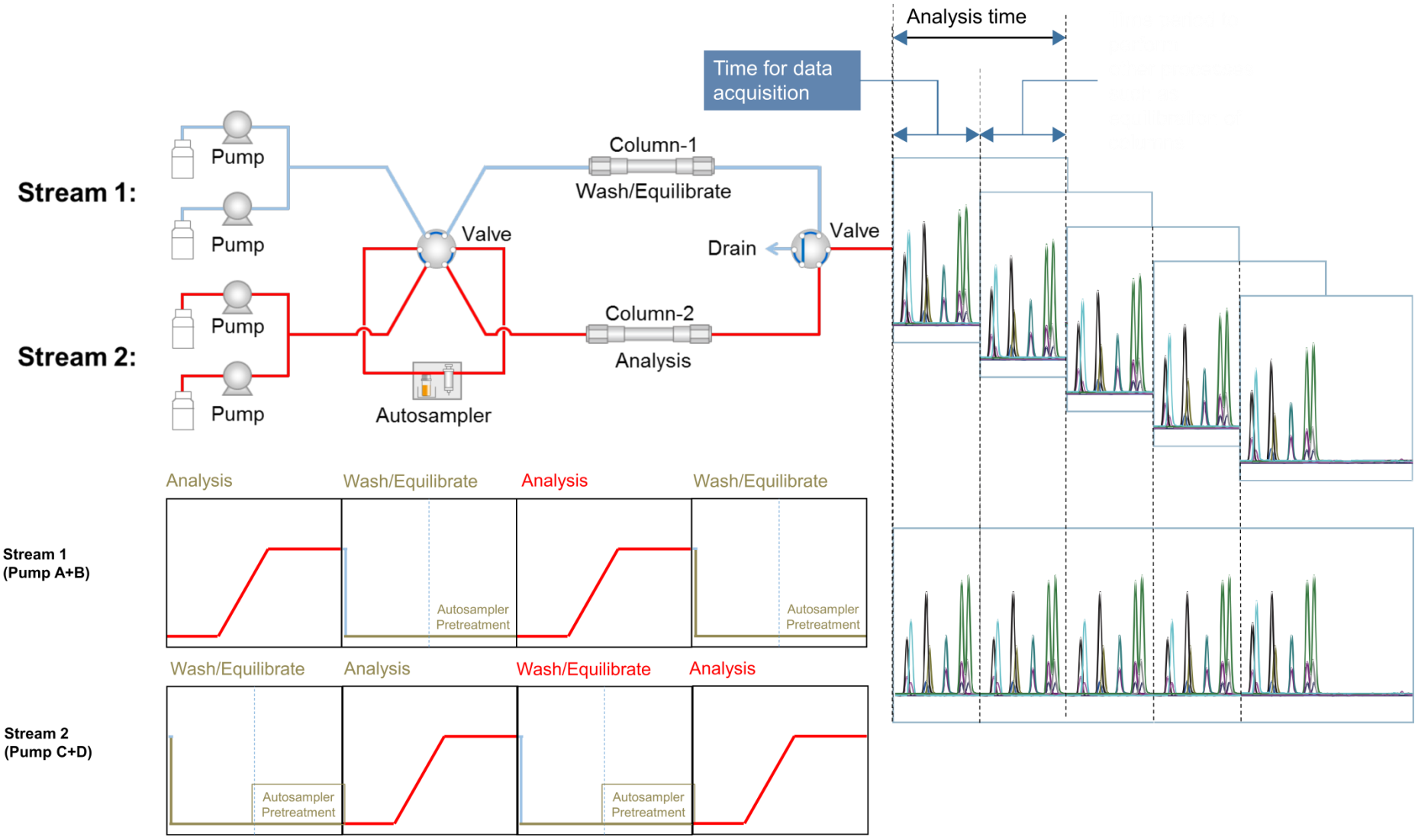
Nexera MX



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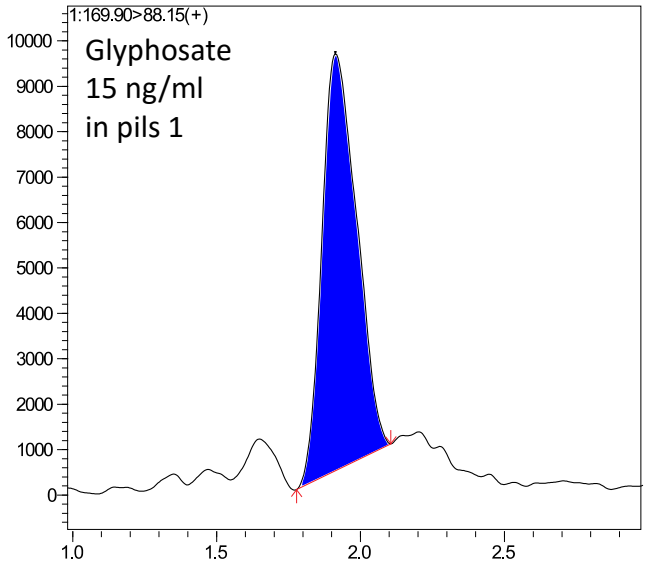
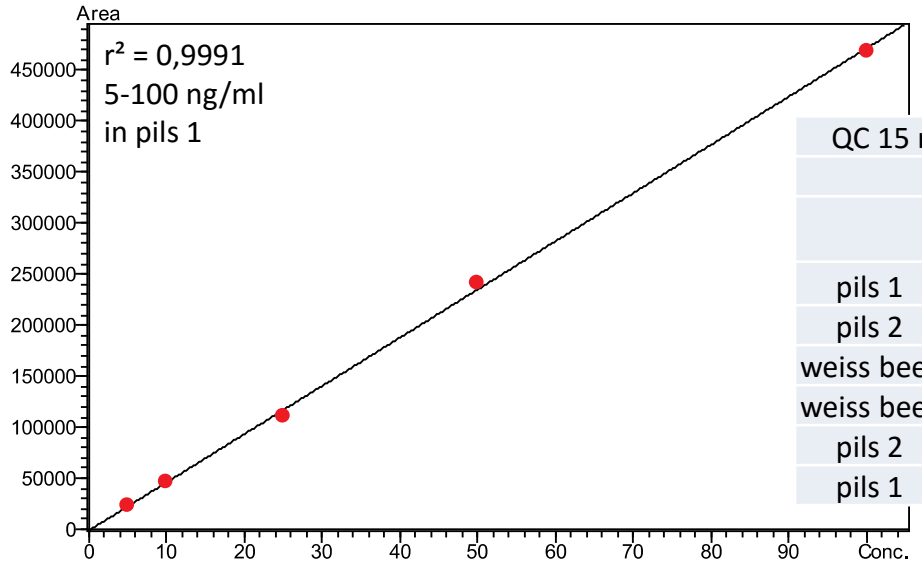
LC-MS/MS parameters

	Compared	Final
Columns, without derivatisation [2]	Obelisc R, SM-C18, SW-C18, ZIC-HILIC, ZIC-cHILIC, Hypercarb and Synergi Fusion C18	Hypercarb (100 mm x 2.1 mm, 5 µm)
Mobile phases, without derivatisation [2]	Different concentrations of ammonium acetate, ammonium formate, ammonium hydroxide, formic acid and acetic acid. Methanol, acetonitrile	1% acetic acid, methanol + 1% acetic acid
Columns, with derivatisation [1]	Raptor Biphenyl, Raptor C18 and other C18-columns	Raptor C18 (100 mm x 2.1 mm, 2.7 µm)
Mobile phases with derivatisation [3]	Shimadzu application note	5 mM ammonium acetate Acetonitrile
Ion Source Parameters, for both [1]	Drying Gas, Nebulising Gas, Heating Gas, ESI-Voltage, Desolvation Line Temperature, Heat Block Temperature, Interface Temperature	DG 3.00 l/min, NG 3.00 l/min, HG 15.0 l/min, ESI + 4 / - 3 kV, DLT 150°C, HBT 400 °C, IFT 325 °C

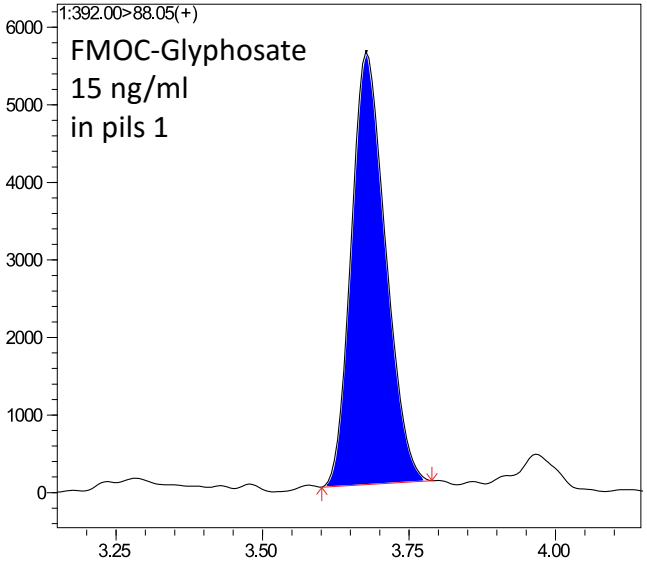
[2] Highly Polar Pesticide Analysis in Food Samples by LC-MS/MS, WP-351, ASMS 2014, Poster WP-351
David R. Baker[1], Mikaël Levi[2], Eric Capodanno[3]
[1]Shimadzu, Manchester, UK [2]Shimadzu, Marne-La-Vallée, France [3]Phytocontrol, Nimes, France
[3] Application News 120, Analysis of Glufosinate, Glyphosate, and AMPA in Drinking Water Using a Triple Quadrupole LC/MS/MS System, Nov. 2015

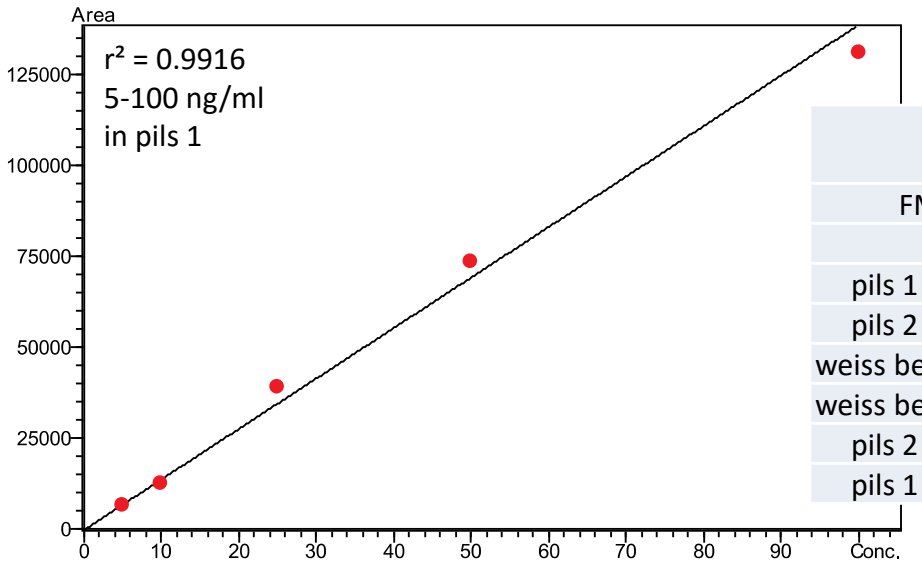
Results: calibration and QC samples





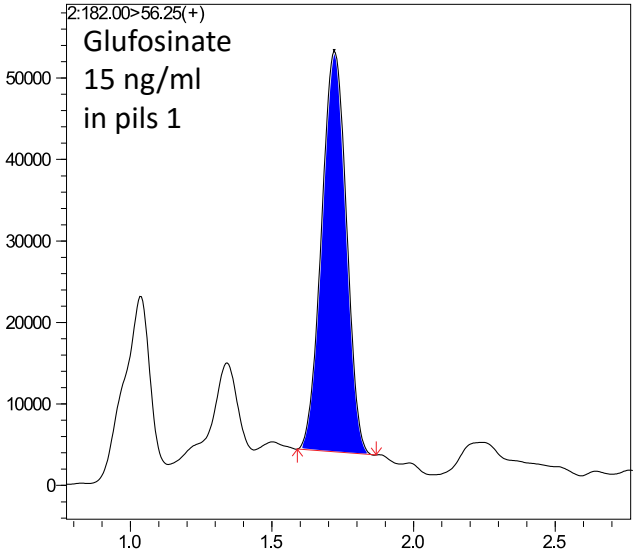
QC 15 ng/mL, spiked in beer Glyphosate		
	Conc.	Accuracy [%]
pils 1	15.81	105.4
pils 2	17.67	117.8
weiss beer	17.3	115.4
weiss beer	17.48	116.6
pils 2	15.62	104.1
pils 1	16.57	110.5

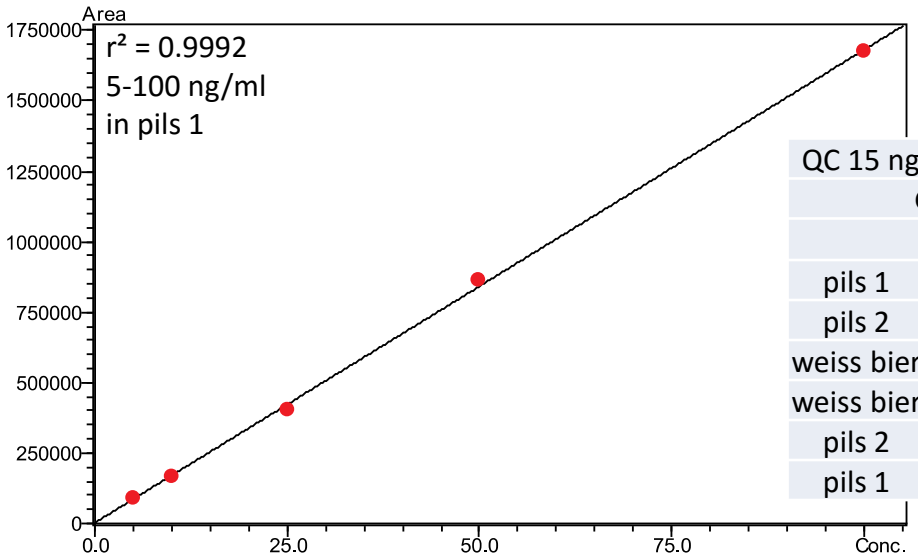




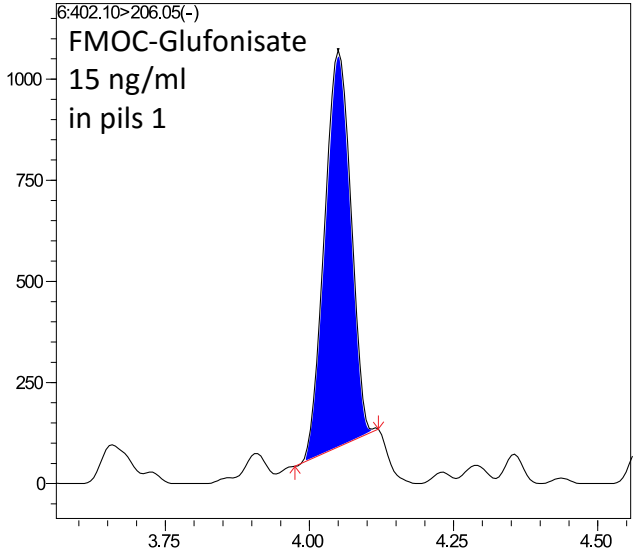
QC 15 ng/mL, spiked in beer FMOC-Glyphosate		
	Conc.	Accuracy [%]
pils 1	18.28	121.8
pils 2	13.04	86.9
weiss beer	16.68	111.2
weiss beer	13.32	88.8
pils 2	17.1	114
pils 1	14.42	96.1

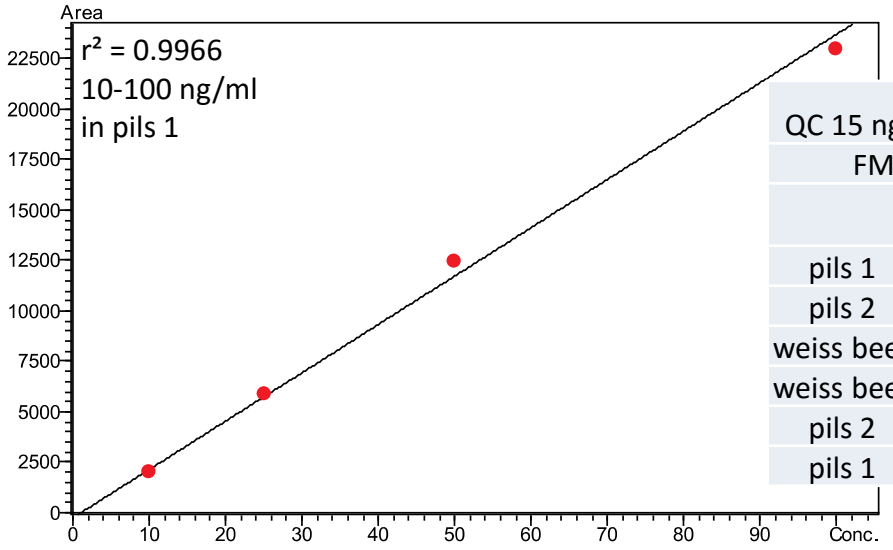
Results: calibration and QC samples





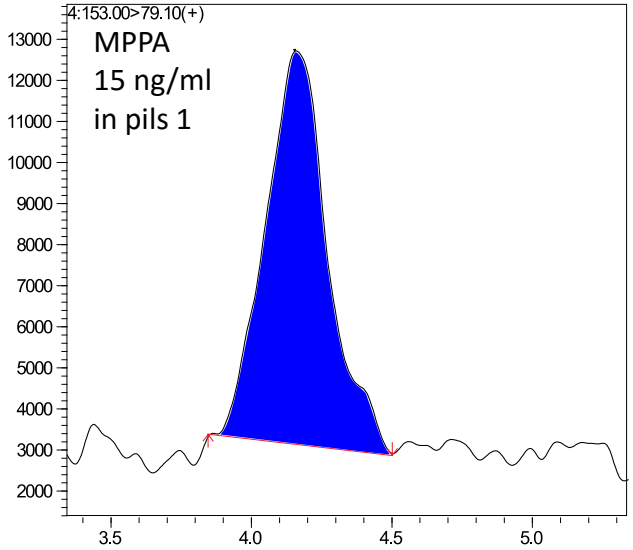
QC 15 ng/mL, spiked in beer Glufosinate		
	Conc.	Accuracy [%]
pils 1	17.12	114.1
pils 2	17.07	113.8
weiss bier	17.85	119
weiss bier	17.63	117.6
pils 2	15.35	102.3
pils 1	14.81	98.7

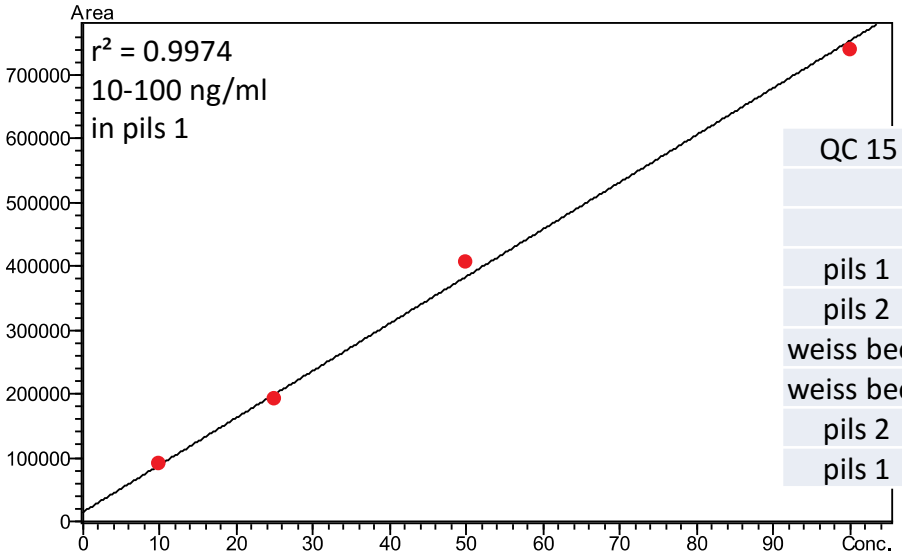




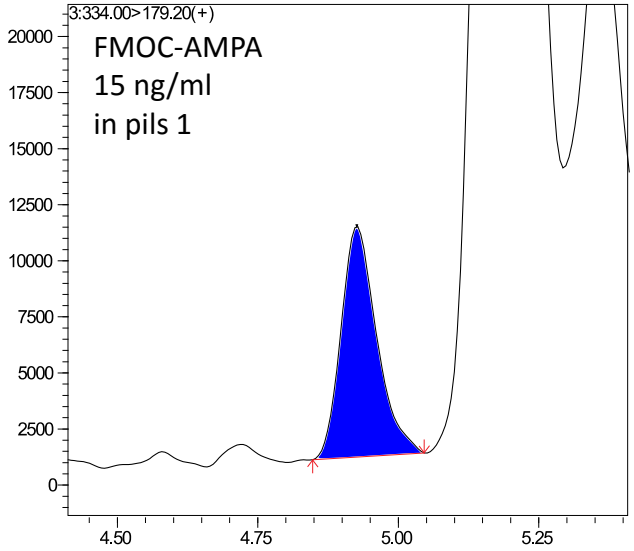
QC 15 ng/mL, spiked in beer FMOC-Glufosinate		
	Conc.	Accuracy [%]
pils 1	18.97	126.4
pils 2	15.58	103.9
weiss beer	19.77	131.8
weiss beer	16.27	108.5
pils 2	14.14	94.3
pils 1	19.81	132.1

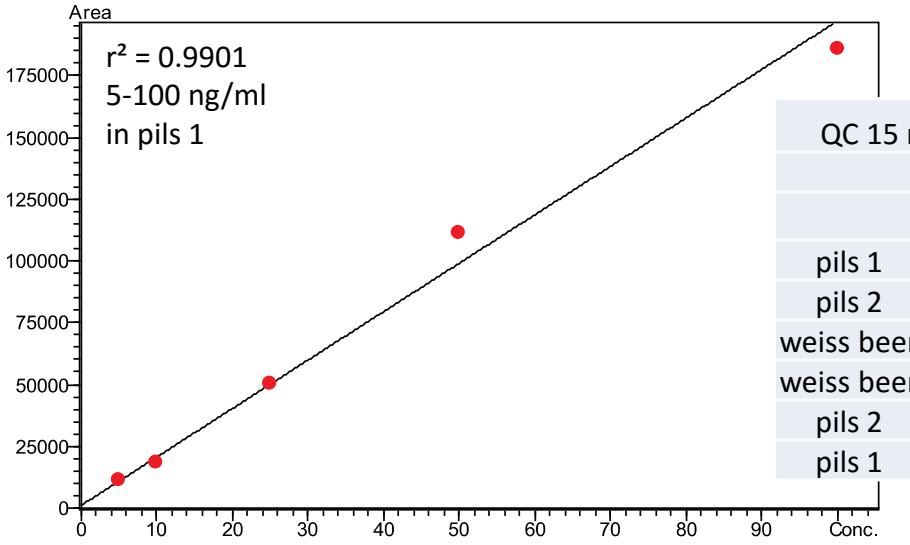
Results: calibration and QC samples





QC 15 ng/mL, spiked in beer		
MPPA		
	Conc.	Accuracy [%]
pils 1	18.71	124.7
pils 2	15.23	101.5
weiss beer	17.91	119.4
weiss beer	17.09	113.9
pils 2	14.08	93.9
pils 1	18.12	120.8





QC 15 ng/mL, spiked in beer		
FMOC-AMPA		
	Conc.	Accuracy [%]
pils 1	22.7	151.4
pils 2	13.31	88.7
weiss beer	15.9	106
weiss beer	17.53	116.9
pils 2	12.85	85.6
pils 1	16.98	113.2

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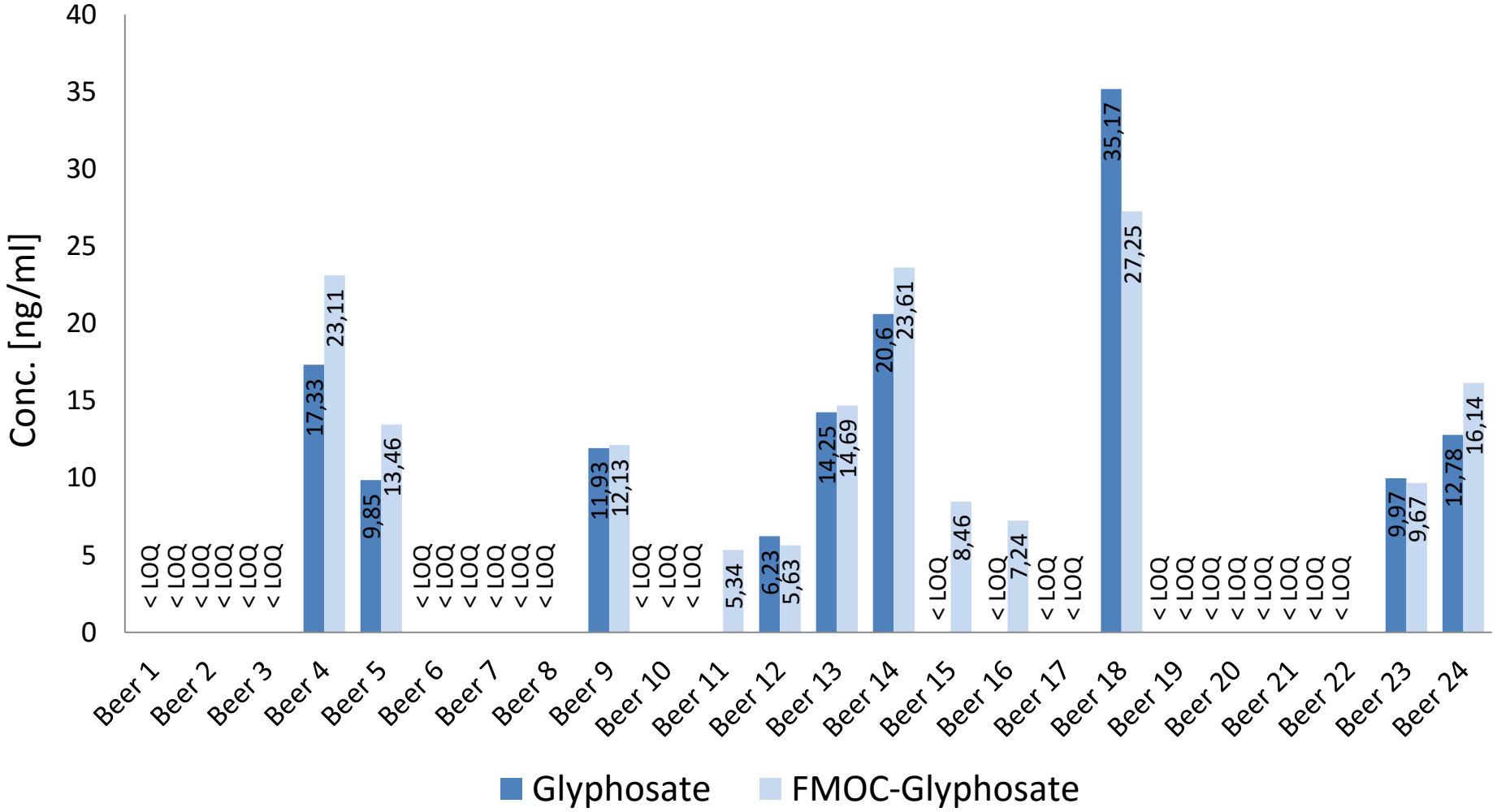
Results: beer samples



Glyphosate and AMPA in food

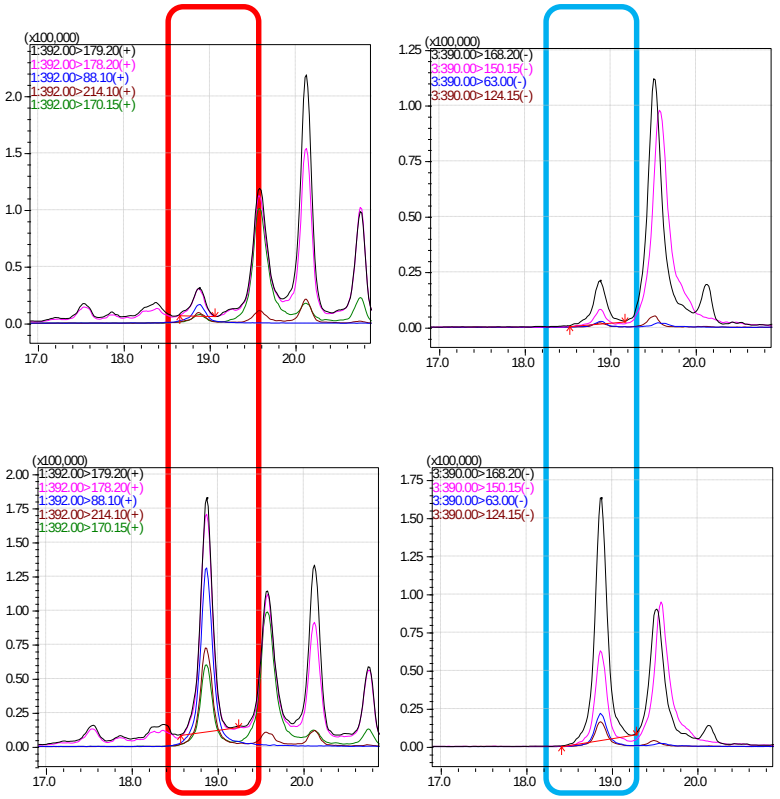
LCMS-8050: confirm results at low levels with fast polarity switching (5 msec)

organic grain sample

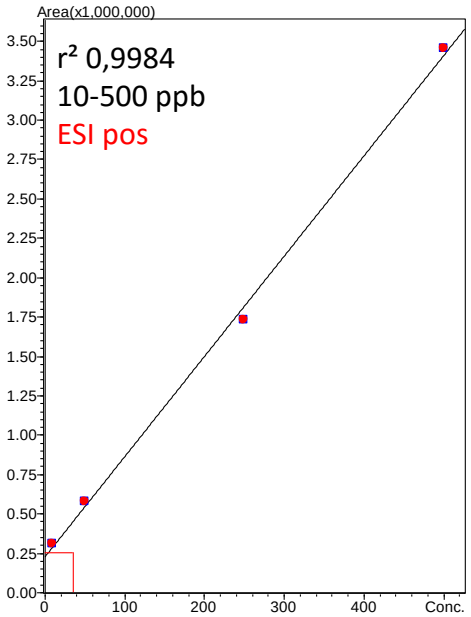
organic grain sample
+ 250 ppb

FMOC-Glyphosate
(ESI positive)

FMOC-Glyphosate
(ESI negative)



Quantification and identification by standard addition



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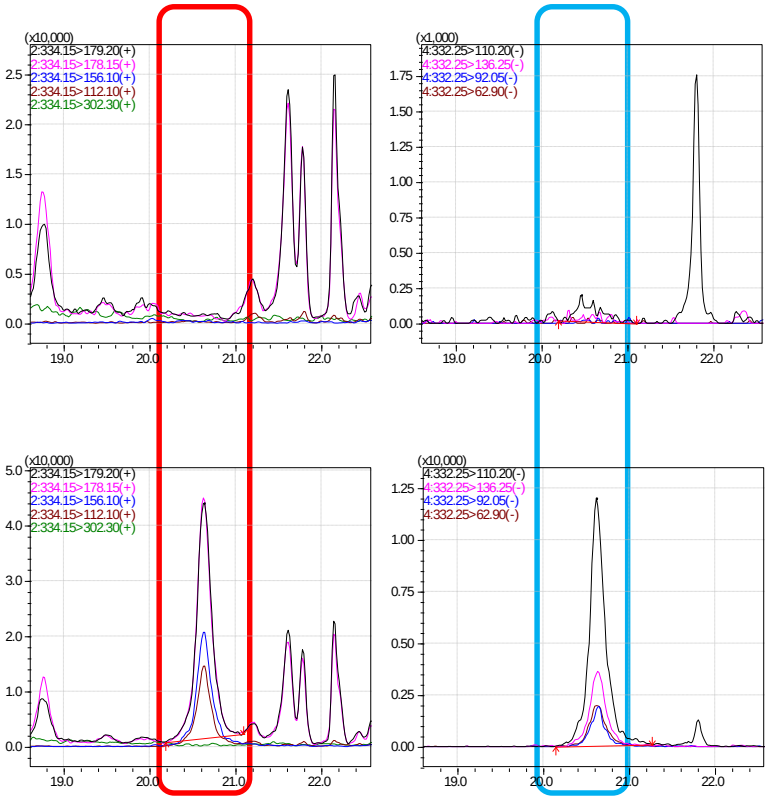

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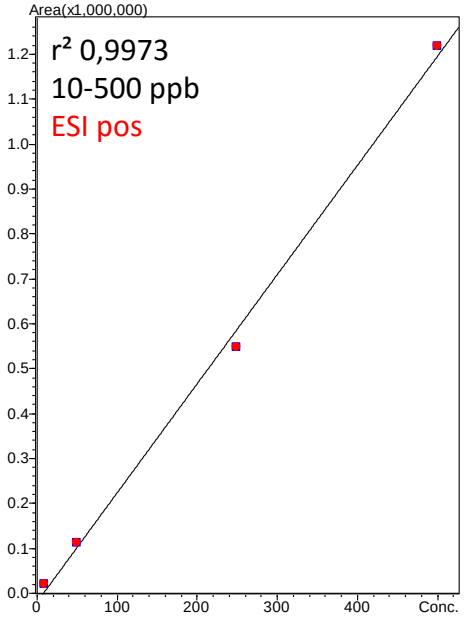

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Summary

- A routine method for the determination of Glyphosate, AMPA, Glufosinolate and MPPA was developped
- LOQ: 10 ng/ml in beer
- Accurate and sensitive quantification without derivatisation
- Nexera MX allows higher sample throughput
- Application Notes available (request: info@shimadzu.eu)

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Residual highly polar pesticides in beer: A comparative study about sample pretreatment with and without derivatization

Sigrid Baumgarten[1]; Anja Grüning[1]; Julia Sander[1]; Rebecca Kelting[1]
[1]Shimadzu Europa GmbH, Duisburg, Germany

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Highly Polar Pesticide Analysis in Food Samples by LC-MS/MS

David R. Baker[1], Mikaël Levi[2], Eric Capodanno[3]
[1]Shimadzu, Manchester, UK [2]Shimadzu, Marne-La-Vallée, France [3]Phytocontrol, Nimes, France

Application News

No.C120

Liquid Chromatography Mass Spectrometry

Analysis of Glufosinate, Glyphosate, and AMPA in Drinking Water Using a Triple Quadrupole LC/MS/MS System

Thank you

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Excellence in Science

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