



Shimadzu Vendor Seminar

In food we trust – the passion of food analysis

Prague, 08.11.2017

Uwe Oppermann
Shimadzu Europa GmbH, Duisburg



Program

In food we trust – the passion of food analysis

Advanced beer aroma analysis:

Erich Leitner, TU Graz, Institute of Analytical Chemistry and Food Chemistry, Graz, Austria

Characterization of the Oxygen Heterocyclic Compounds (Coumarins, Psoralens and Polymethoxylated Flavones) in Food Products

Mariosimone Zoccali, Francesca Rigano, Luigi Mondello, Chromaleont s.r.l., c/o University of Messina, Messina, Italy

Adriana Arigò, Paola Dugo, Luigi Mondello, Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, University of Messina, Italy

Marina Russo, Paola Dugo, Luigi Mondello, University Campus Bio-Medico of Rome, Italy

How Safe is Safe? Analytical Tools for Tracing Contaminants in Beer

Uwe Oppermann, Jan Knoop, Carola Schultz, Anja Grüning, Shimadzu Europa GmbH

HOW SAFE IS SAFE? ANALYTICAL TOOLS FOR TRACING CONTAMINANTS IN BEER

Uwe Oppermann, Jan Knoop, Carola Schultz & Anja Grüning

Shimadzu Europa GmbH, Duisburg

Food Analysis

Is our food safe????

Nobody can answer this question.....

.....but It has never been checked better than today



Dioxin scandal: Germans warned about contaminated eggs

Germans have been urged to keep an eye out for eggs that may have been tainted by contaminated animal feed.

Thousands of chickens have been culled and 1,000 farms ordered to stop selling their products after toxic dioxin was found in poultry and pig feed.

Authorities say more than 100,000 eggs that may have been contaminated have been produced by two farms in the past two weeks.



The dioxin is believed to have come from feed contaminated with industrial fats

EC Approach to Food Safety *

- Every European has the right to know how food is produced, processed, packaged, labelled and sold
- The goal of the EC's Food Safety policy is to ensure a high level of protection of human health regarding the food industry — Europe's largest manufacturing and employment sector
- The EC's guiding principle is to apply an integrated approach from farm to fork (white paper)
- http://ec.europa.eu/food/index_en.htm

Food Quality.....

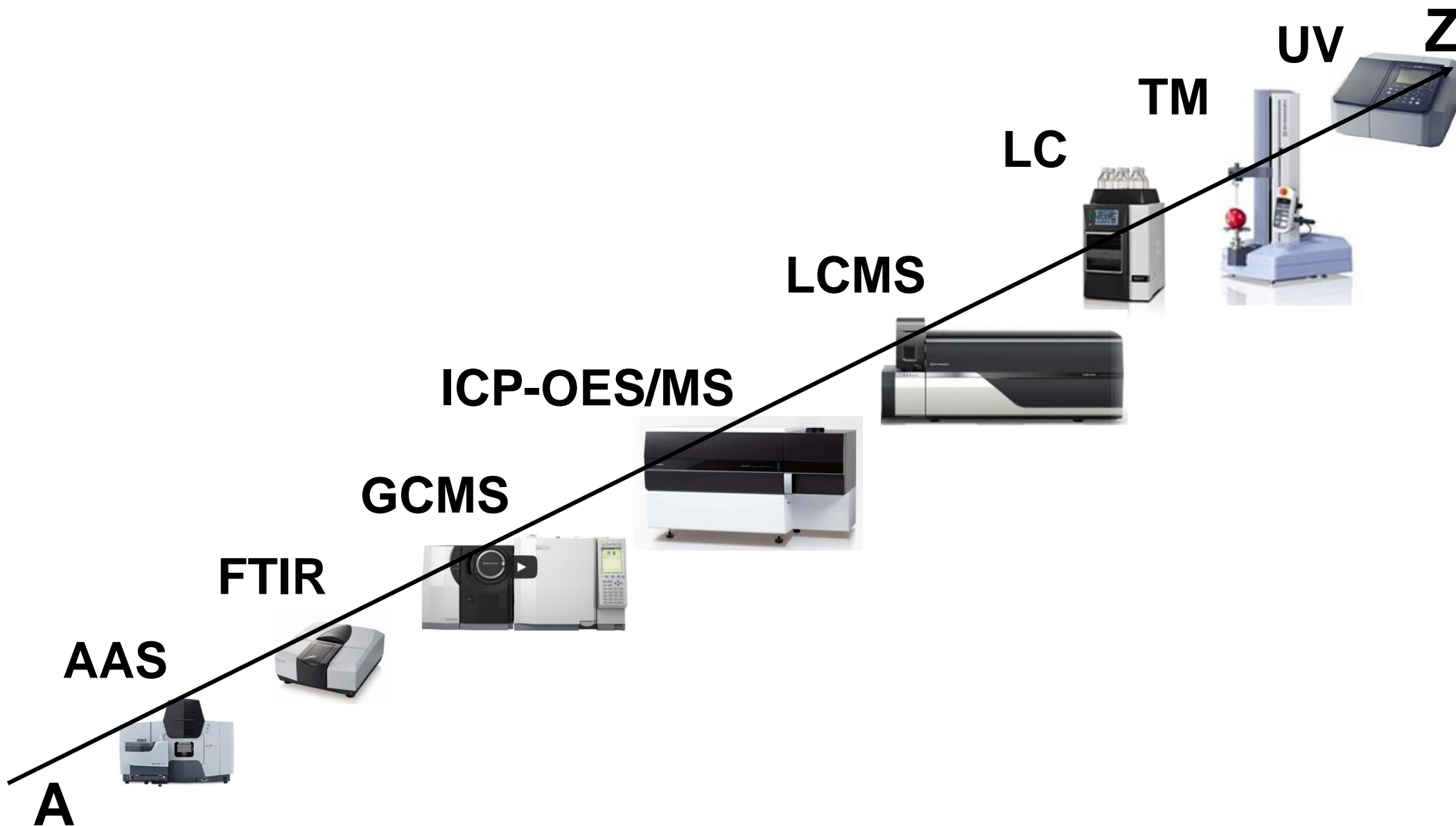
Properties to determine:

- **Composition**
- **Essential Elements**
- **Toxic Elements**
- **Taste, Color.....**
- **Contaminants**

Laws and Regulations:

- **Drinking Water Regulation**
- **Beer Purity Law**
- **Foodstuff and commodity Act**
- **European Food Law**
- **European Food Safety Authority**

One Stop Vendor in Food Analysis



Beer Analysis - Overview

- Introduction
- European Regulations
- Analysis of Beer
- Spectroscopy
- Chromatography
- Mass Spectrometry



Regulations

● 500 Years German Beer Purity Law

- Oldest Food Law in the world since 23 April 1516
- Beer is the most popular alcoholic beverage in Europe. In Germany, beer enjoys a particularly high status due to the German Beer Purity Law of 1516 (the “Reinheitsgebot”).....
- https://www.shimadzu.eu/sites/default/files/beer_catalogue_c10g-e049.pdf



Regulations

- **MEBAK**

- Mid- European brewing commission



- **EBC**



- European brewery convention

- **Testing chemical/ physical parameters**

- Organic components
- Element concentration
- Density
- Turbidity
- Color



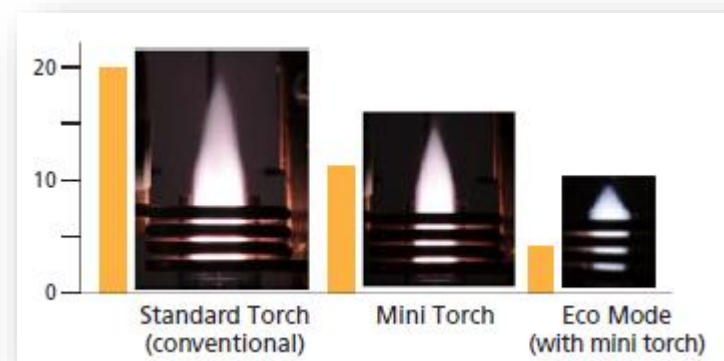
What's inside the Beer ???

Water		95 %
Ethanol		5 %
Aluminium		0,20 mg/L
Arsenic		0,01 mg/L
Lead		0,04 mg/L
Antimony		0,01 mg/L
Cadmium		5,00 µg/L
Copper		0,20 mg/L
Zinc		0,20 mg/L
Tin		0,10 mg/L
Ochratoxin A		5,00 µg/L*
Glyphosate		20,0 mg/L**

* in barley ** in barley

Quantitation of Heavy Metals

....for highly sensitive determination of more than 70 elements using ICPMS-2030



ICP- Spectrometry Coupled to Mass



Mass detector

*Detection, identification
and quantification of
ions*

**Mini Torch
Technology**

● 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																								
*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											

<1ppt
1~10ppt
10~100ppt
autres

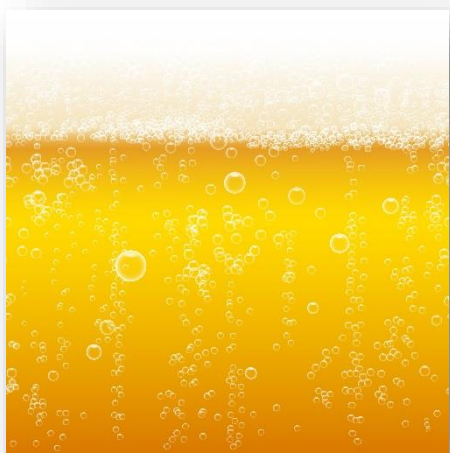
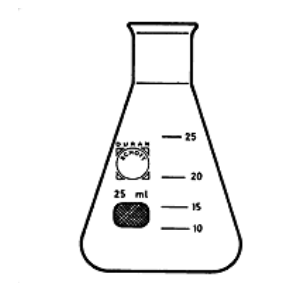
${}^9\text{Be} \leq 0,5 \text{ ppt}$

${}^{115}\text{In} \leq 0,05 \text{ ppt}$

${}^{209}\text{Bi} \leq 0,01 \text{ ppt}$

Sample Preparation

- Direct analysis with internal standard or
- Dilution with H₂O 1:1 or 1:10
- Ultrasonic pretreatment
- Alcohol concentration approx. 2,5 %
- HNO₃ concentration 0.1 %
- Calibration range: 0.002 µg/L to 20 mg/L.



Argon Plasma with Minitorch

System Parameters:

- RF Power 1.2 kW
- PL Gas 10 L/min
- AX Gas 0.6 L/min
- CA Gas 0.7 L/min
- Exposure time 15 sec



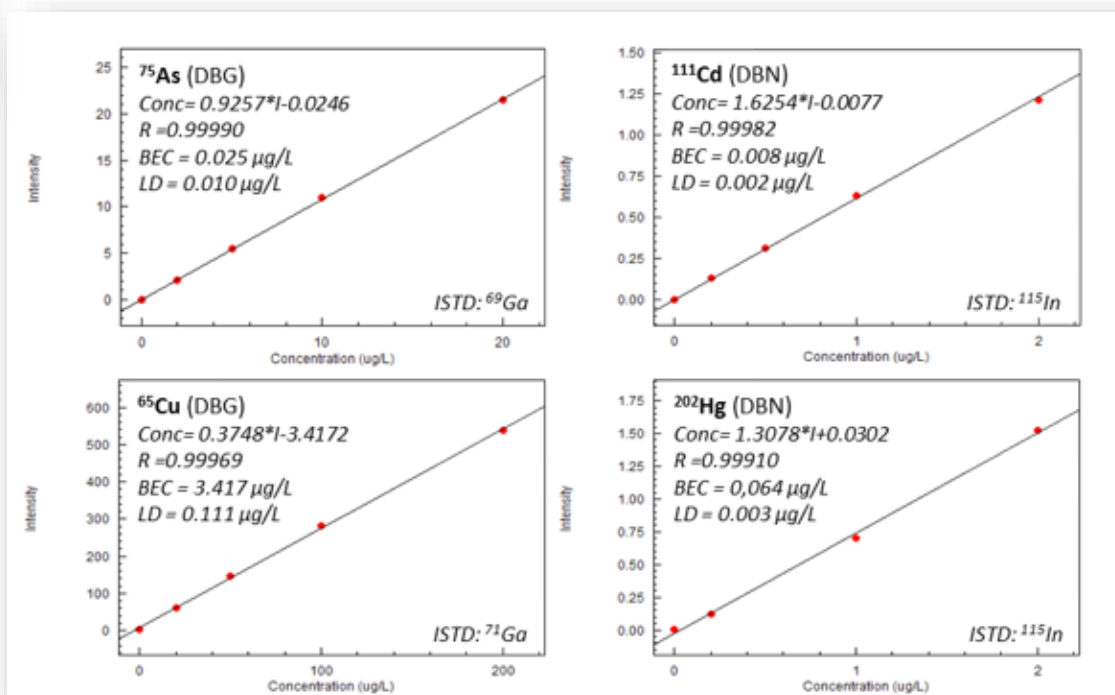
Water Analysis

Element	EPA Max. Limit Value for Drinking Water (µg/L)	Samples: JSAC0301-3		Samples: JSAC0302-3	
		Quantitation Value	Certified Value	Quantitation Value	Certified Value
Unit: µg/L					
Al	200	16	15±1	66.9	66±1
As		0.20	0.20±0.01	5.29	5.2±0.1
B		8.52	8.2±0.3	58.0	59±1
Ba	2000	0.55	0.53±0.01	0.55	0.52±0.01
Cd	5	0.0018	0.0018 (Reference value)	0.991	1.00±0.02
Cr ⁶⁺	100	0.17	0.16±0.01	10.0	10.0±0.2
Cu	1300	0.4	0.37±0.03	10.0	9.9±0.1
Fe	300	6.5	6.4±0.2	58.5	58±1
Mn	50***	0.21	0.2±0.01	5.3	5.1±0.1
Mo		0.30	0.290±0.004	0.30	0.290±0.004
Ni				9.63	9.5±0.3
Pb	15	0.005	0.007 (Reference value)	9.68	9.9±0.2
Se		0.2	0.08 (Reference value)	4.95	5.0±0.2
Zn	5000***	0.17	0.17±0.04	10.5	9.8±0.2
Unit: mg/L					
K		0.48	0.47±0.02	0.48	0.48±0.02
Na		4.53	4.34±0.07	4.47	4.32±0.07
Mg		3.37	3.34±0.07	3.34	3.32±0.06
Ca	250***	13.2	13.0±0.2	13.1	13.0±0.1

***: National Secondary Drinking Water Regulations

Beer Data

Element	Beer 1	Beer 2	Beer 3	Beer 4	Beer 5
⁷⁵ As	2.05	3.49	2.39	1.46	0.39
¹¹¹ Cd	0.07	0.05	0.07	0.08	0.15
⁶⁵ Cu	29.10	28.70	40.50	38.20	22.40
⁶⁶ Zn	5.28	23.90	5.04	2.83	29.20
⁶⁰ Ni	2.25	5.62	1.53	2.58	4.47
²⁰⁸ Pb			< LQ		
¹²¹ Sb	0.39	0.19	2.15	0.45	0.55



Mycotoxin Analysis

Consumers want to trust in safe, non-toxic food

EU: strictest regulations of the world

Aflatoxins: Aflatoxin B1, B2 (AFB1, AFB2), G1, G2 (AFG1, AFG2) **(Grain)**
AFB1: most genotoxic and carcinogenic



Ochratoxin A (OTA), Zearalenone (ZON), Deoxynivalenol (DON), Nivalenol (NIV)
(Grain)



Aflatoxin M1 (AFM1) **(Milk)**



and Patulin (PAT) **(Fruits)**



Features of Mycotoxin System

High sensitivity

- EU directive level (*)
(* not applicable for baby food)
- no derivatization
- combination of PDA detector and RF-20Axs

Fast and easy screening

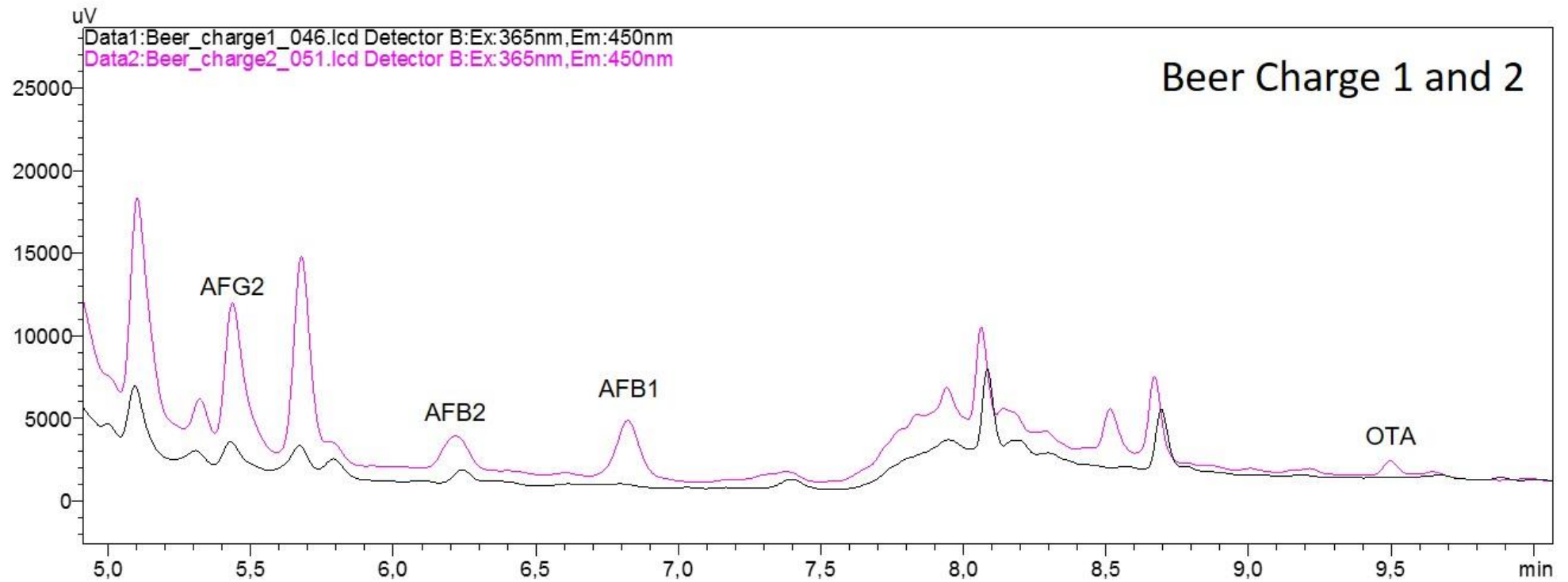
- 10 mycotoxins are monitored in 14-minutes.
- Step-by-step explanation

Quick result

- Results and reports are produced automatically after analysis



Comparison of Beer Charges



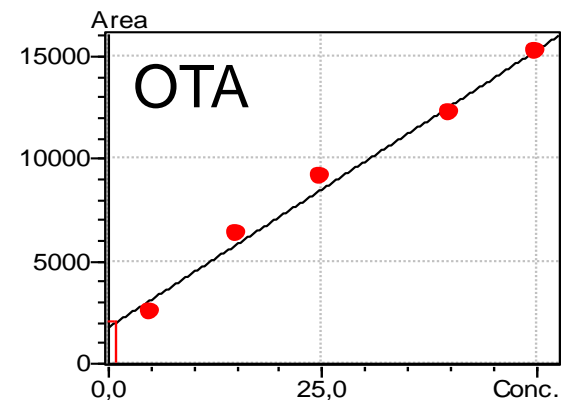
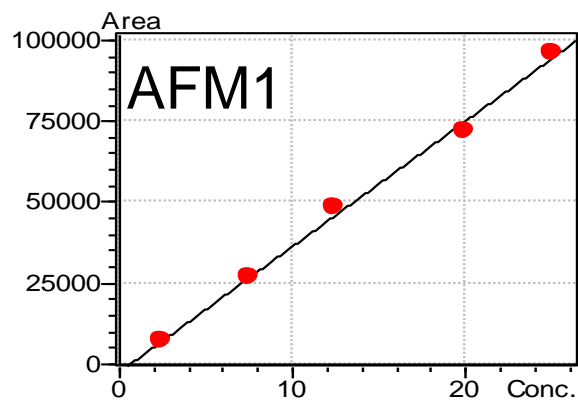
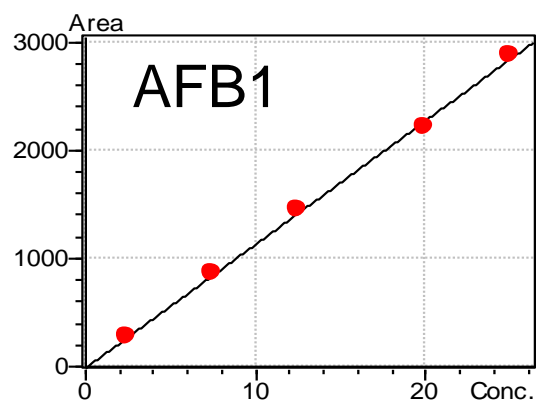
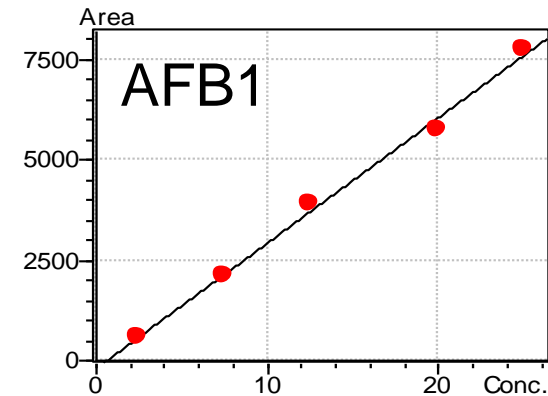
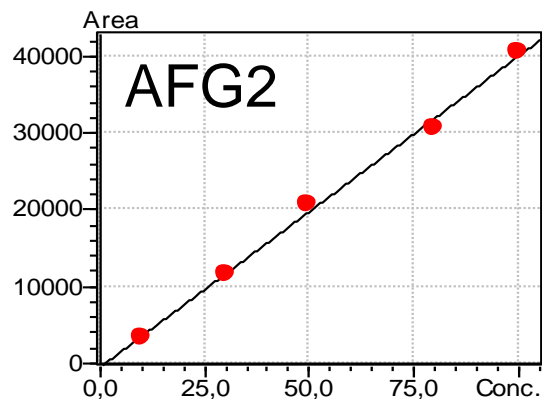
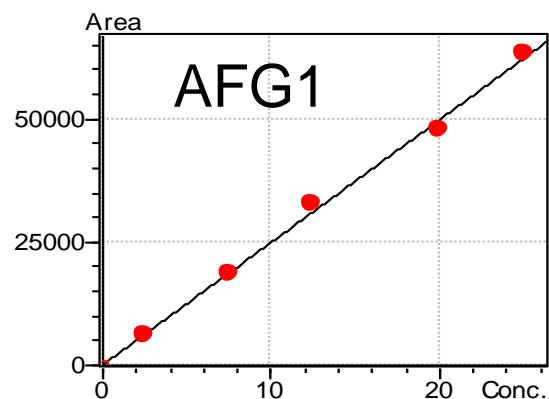
Clear differences concerning the mycotoxin content in different charges of the same beer

Determination at EU Regulations

Target compound	Examples of targeted product	EU	US (Codex)	Japan
Aflatoxin B1,B2,G1,G2 (AFB1,B2,G1,G2)	Grain, Grain product (Flour etc.)	Total 4~15 µg/kg AFB1 2~12 µg/kg	Total 10~15 µg/kg	Total 10 µg/kg
Aflatoxin M1 (AFM1)	Milk	0.05 µg/kg	0.5 µg/kg	0.5 µg/kg
Ochratoxin A (OTA)	Wheat, Wheat flour	2~10 µg/kg	5 µg/kg	Not regulated
Patulin (PAT)	Apple	25~50 µg/kg	50 µg/kg	50 µg/kg
Deoxynivalenol (DON)	Wheat, Wheat flour	500~1750 µg/kg	1000 µg/kg	1100 µg/kg (provisional standard value)
Nivalenol (NIV)	Wheat, Wheat flour	Not regulated		
Zearalenone (ZON)	Grain, Grain product (Flour etc.)	20~400 µg/kg (feed : 2~3 mg/kg)	Not regulated	Not regulated (feed : 1 mg/kg)

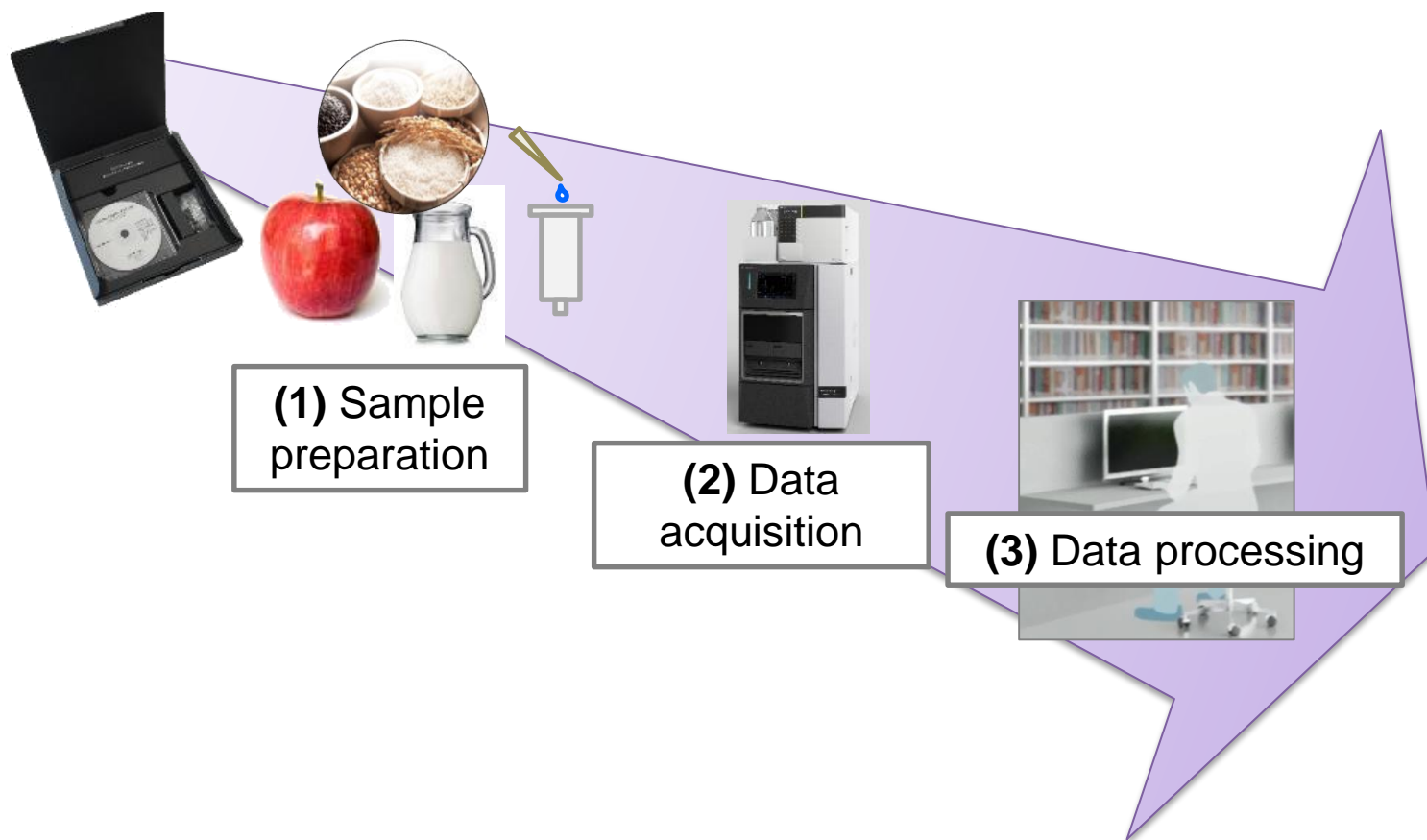
Quantification

Quantification was conducted in the range of EU regulations until 10 x EU regulations



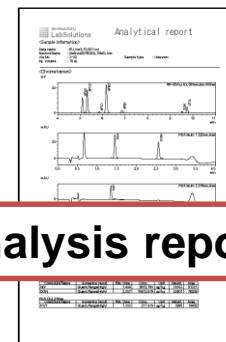
Features

Quick feedback: Reports are immediately available



Data browser

14	Bier frisch ohne MT_046.lcd	
15	Bier frisch ohne MT_047.lcd	
16	Bier frisch mit MT_048.lcd	Quant. Range(High)
17	Bier frisch mit MT_049.lcd	Quant. Range(High)
18	Bier alt ohne MT_050.lcd	
19	Bier alt ohne MT_051.lcd	
20	Bier alt mit MT_052.lcd	Quant. Range(High)
21	Bier alt mit MT_053.lcd	Quant. Range(High)



Analysis report

SHIMADZU

Sample	Peak	Area	Height	Retention	Label
1	1	12345	1000	1.234	Peak 1
1	2	67890	5000	2.345	Peak 2
1	3	11111	100	3.456	Peak 3
1	4	22222	200	4.567	Peak 4
1	5	33333	300	5.678	Peak 5
1	6	44444	400	6.789	Peak 6
1	7	55555	500	7.890	Peak 7
1	8	66666	600	8.901	Peak 8
1	9	77777	700	9.012	Peak 9
1	10	88888	800	10.123	Peak 10
1	11	99999	900	11.234	Peak 11
1	12	101010	1000	12.345	Peak 12
1	13	112112	1100	13.456	Peak 13
1	14	123213	1200	14.567	Peak 14
1	15	134314	1300	15.678	Peak 15
1	16	145415	1400	16.789	Peak 16
1	17	156516	1500	17.890	Peak 17
1	18	167617	1600	18.901	Peak 18
1	19	178718	1700	19.012	Peak 19
1	20	189819	1800	20.123	Peak 20
1	21	190920	1900	21.234	Peak 21
1	22	201021	2000	22.345	Peak 22
1	23	212122	2100	23.456	Peak 23
1	24	223223	2200	24.567	Peak 24
1	25	234324	2300	25.678	Peak 25
1	26	245425	2400	26.789	Peak 26
1	27	256526	2500	27.890	Peak 27
1	28	267627	2600	28.901	Peak 28
1	29	278728	2700	29.012	Peak 29
1	30	289829	2800	30.123	Peak 30
1	31	290930	2900	31.234	Peak 31
1	32	301031	3000	32.345	Peak 32
1	33	312132	3100	33.456	Peak 33
1	34	323233	3200	34.567	Peak 34
1	35	334334	3300	35.678	Peak 35
1	36	345435	3400	36.789	Peak 36
1	37	356536	3500	37.890	Peak 37
1	38	367637	3600	38.901	Peak 38
1	39	378738	3700	39.012	Peak 39
1	40	389839	3800	40.123	Peak 40
1	41	390940	3900	41.234	Peak 41
1	42	401041	4000	42.345	Peak 42
1	43	412142	4100	43.456	Peak 43
1	44	423243	4200	44.567	Peak 44
1	45	434344	4300	45.678	Peak 45
1	46	445445	4400	46.789	Peak 46
1	47	456546	4500	47.890	Peak 47
1	48	467647	4600	48.901	Peak 48
1	49	478748	4700	49.012	Peak 49
1	50	489849	4800	50.123	Peak 50
1	51	490950	4900	51.234	Peak 51
1	52	501051	5000	52.345	Peak 52
1	53	512152	5100	53.456	Peak 53
1	54	523253	5200	54.567	Peak 54
1	55	534354	5300	55.678	Peak 55
1	56	545455	5400	56.789	Peak 56
1	57	556556	5500	57.890	Peak 57
1	58	567657	5600	58.901	Peak 58
1	59	578758	5700	59.012	Peak 59
1	60	589859	5800	60.123	Peak 60
1	61	590960	5900	61.234	Peak 61
1	62	601061	6000	62.345	Peak 62
1	63	612162	6100	63.456	Peak 63
1	64	623263	6200	64.567	Peak 64
1	65	634364	6300	65.678	Peak 65
1	66	645465	6400	66.789	Peak 66
1	67	656566	6500	67.890	Peak 67
1	68	667667	6600	68.901	Peak 68
1	69	678768	6700	69.012	Peak 69
1	70	689869	6800	70.123	Peak 70
1	71	690970	6900	71.234	Peak 71
1	72	701071	7000	72.345	Peak 72
1	73	712172	7100	73.456	Peak 73
1	74	723273	7200	74.567	Peak 74
1	75	734374	7300	75.678	Peak 75
1	76	745475	7400	76.789	Peak 76
1	77	756576	7500	77.890	Peak 77
1	78	767677	7600	78.901	Peak 78
1	79	778778	7700	79.012	Peak 79
1	80	789879	7800	80.123	Peak 80
1	81	790980	7900	81.234	Peak 81
1	82	801081	8000	82.345	Peak 82
1	83	812182	8100	83.456	Peak 83
1	84	823283	8200	84.567	Peak 84
1	85	834384	8300	85.678	Peak 85
1	86	845485	8400	86.789	Peak 86
1	87	856586	8500	87.890	Peak 87
1	88	867687	8600	88.901	Peak 88
1	89	878788	8700	89.012	Peak 89
1	90	889889	8800	90.123	Peak 90
1	91	890990	8900	91.234	Peak 91
1	92	901091	9000	92.345	Peak 92
1	93	912192	9100	93.456	Peak 93
1	94	923293	9200	94.567	Peak 94
1	95	934394	9300	95.678	Peak 95
1	96	945495	9400	96.789	Peak 96
1	97	956596	9500	97.890	Peak 97
1	98	967697	9600	98.901	Peak 98
1	99	978798	9700	99.012	Peak 99
1	100	989899	9800	100.123	Peak 100

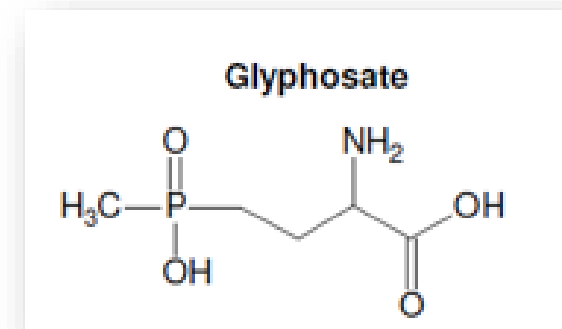
Flagged screening report*

* Multi data report (LabSolutions DB/CS)

Analysis of Pesticides

....for highly sensitive determination of Glyphosate in Beer using LCMS-8060

Glyphosate Herbicide Found In 14 Popular Beer Brands From Germany
Germany's farm federation denies responsibility 



Glyphosate: Background

February 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 test
- Acceptable Daily Intake: 0,3 mg/kg body weight
- Federal Institute for risk assessment (BfR):
no risk < 1000 L/day



Glyphosate: Existing 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:

■ interferences during derivatisation with FMOC

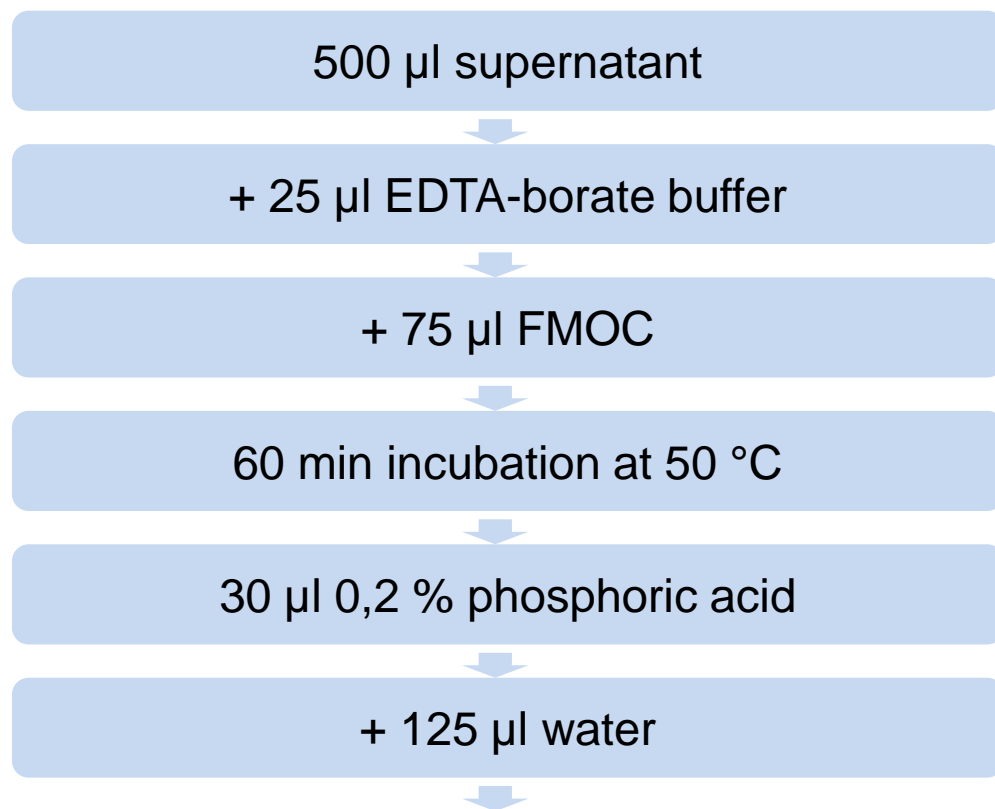
Highly polar compounds such as glyphosate...

■ ...have a low mass and less product ions

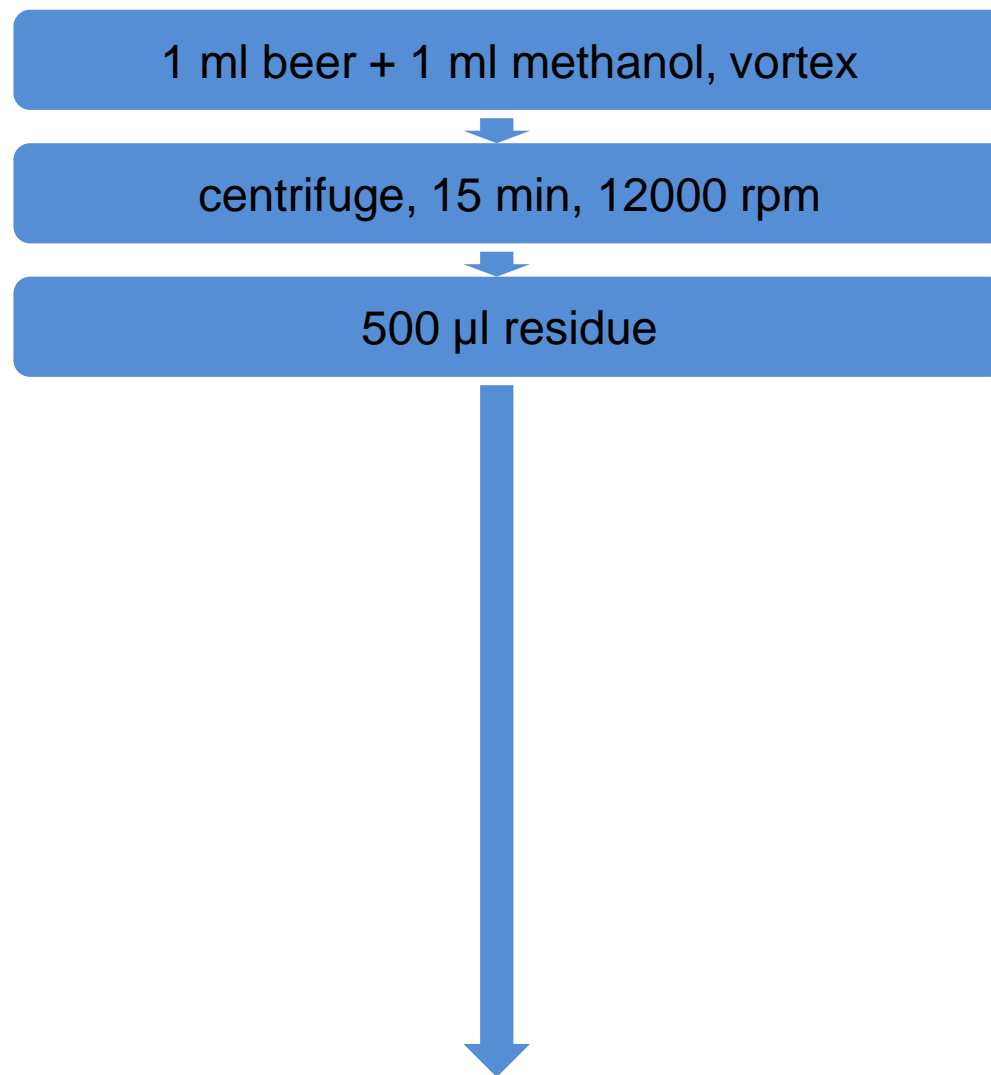


Two Workflows

With derivatisation



Without derivatisation



Analysis with Nexera MX and LCMS-8060

Nexera MX with LCMS-8060

UPLC
ULTRA FAST MASS SPECTROMETRY



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

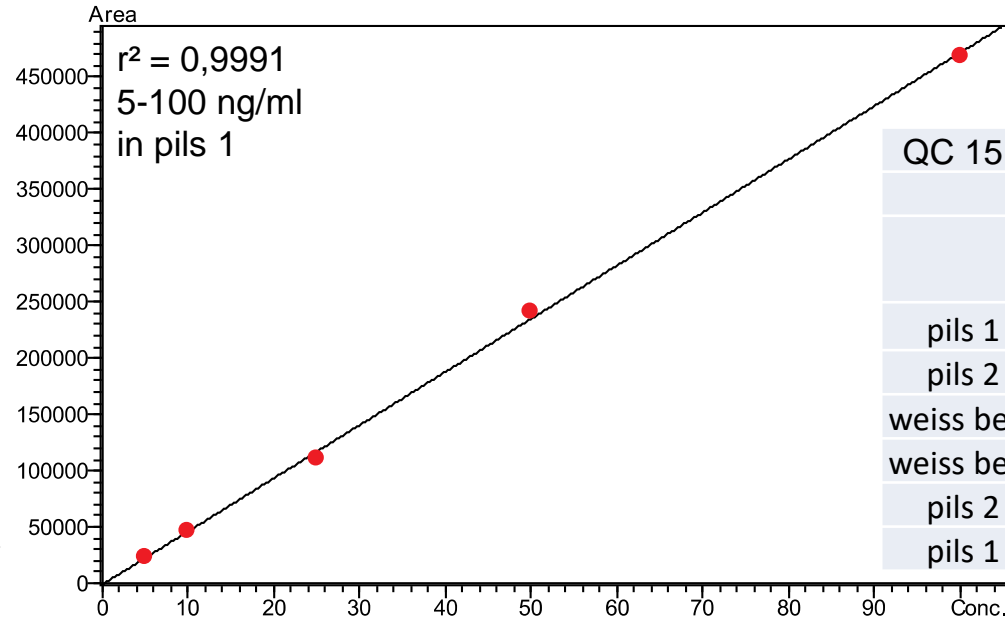
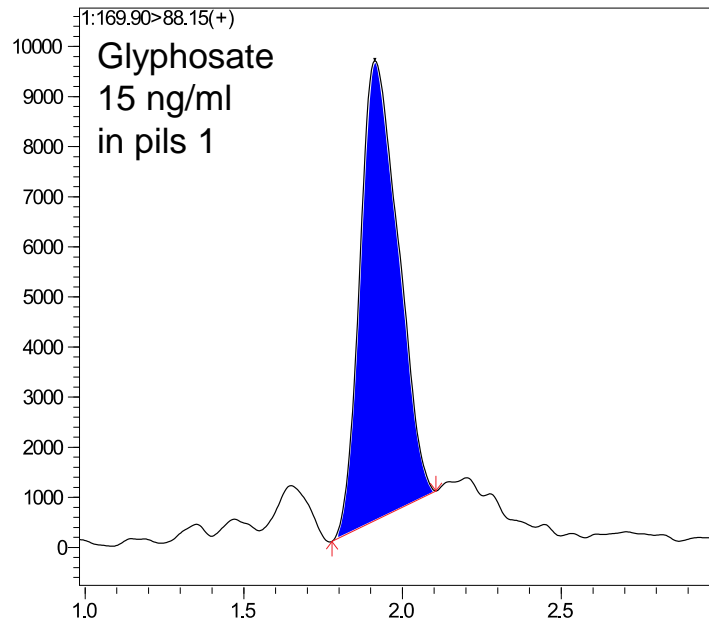
[2] Highly Polar Pesticide Analysis in Food Samples by LC-MS/MS, WP-351, ASMS 2014, Poster WP-351

David R. Baker¹, Mikaël Levi², Eric Capodanno³

¹Shimadzu, Manchester, UK ²Shimadzu, Marne-La-Vallée, France ³Phytocontrol, Nimes, France

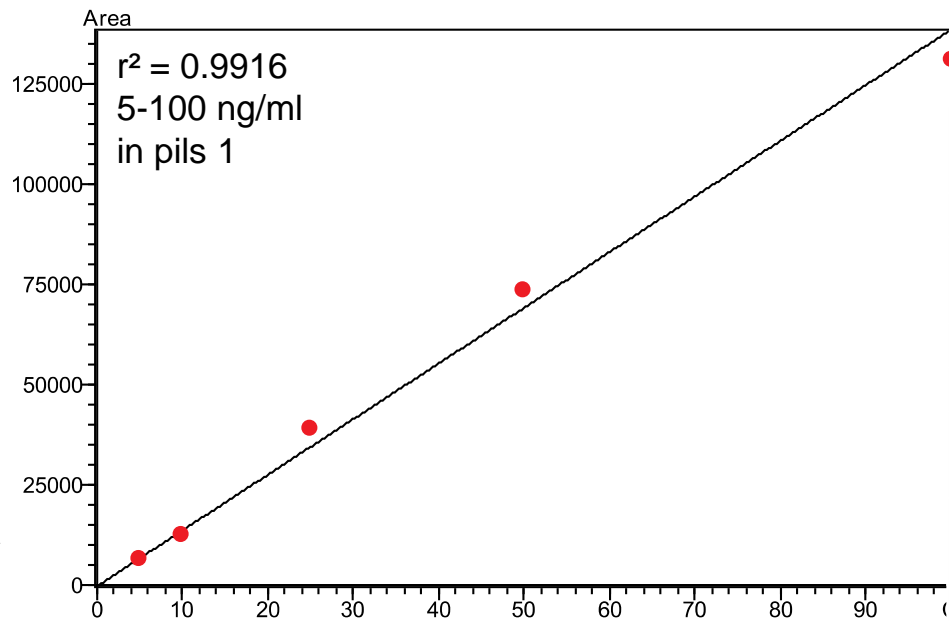
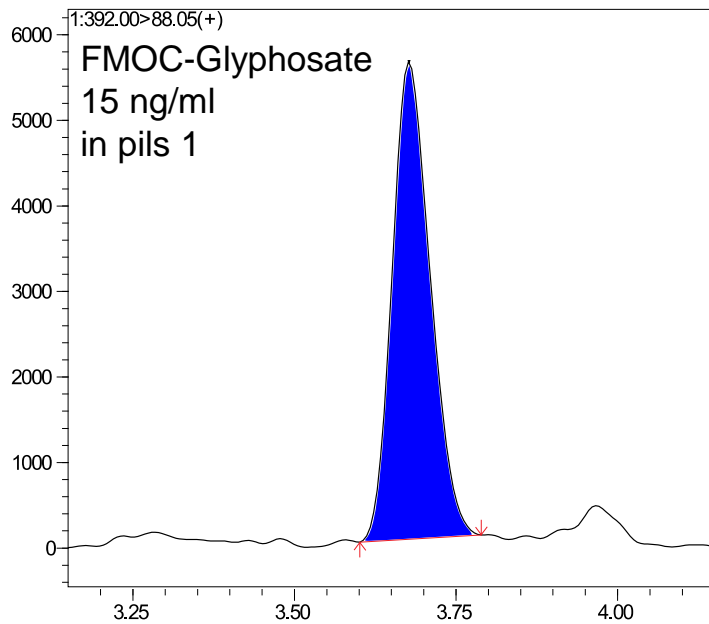
[3] Application News 120, Analysis of Glufosinate, Glyphosate, and AMPA in Drinking Water Using a Triple Quadrupole LC/MS/MS System, Nov. 2015

Results: Calibration and QC Samples



QC 15 ng/mL, spiked in beer
Glyphosate

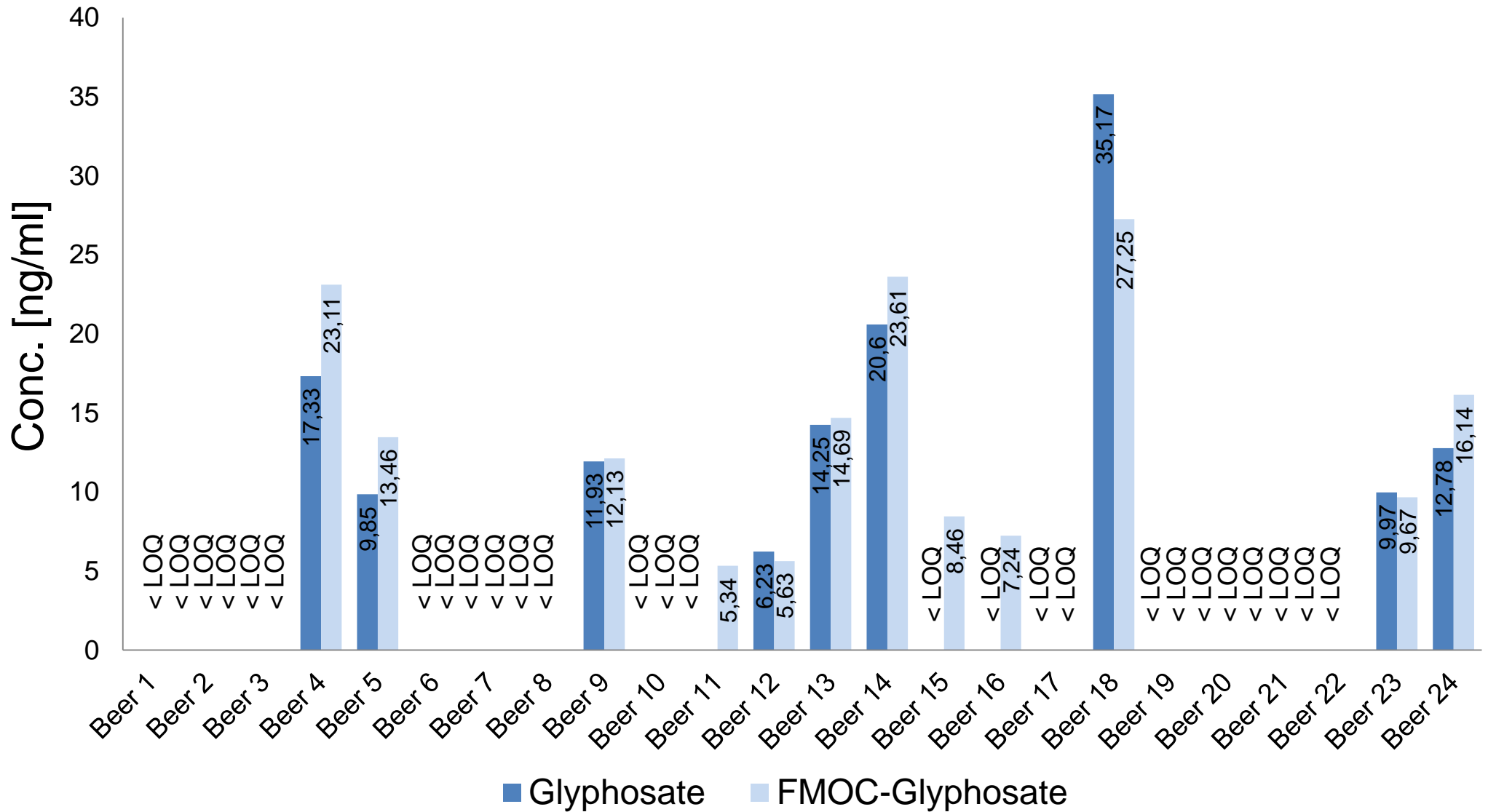
	Conc	Accuracy [%]
pils 1	15.81	105.4
pils 2	17.67	117.8
weiss beer	17.3	115.4
weiss beer	17.48	116.6
pils 2	15.62	104.1
pils 1	16.57	110.5



QC 15 ng/mL, spiked in beer
FMOG-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

Results: Beer Samples



Summary

- A routine method for the determination of Glyphosate was developed
- 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

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

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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

Conclusion

Shimadzu is offering the full range of instruments for „state of the art“ solutions in beer analysis in order to maintain the highest level of food quality and food safety.



Thank You!

....and please enjoy your beer !



Brand Statement "Excellence in Science"

We in the Shimadzu Group have delivered products and services to enable our customers around the world to develop a diverse range of new products, to protect and improve the environment, and to improve the health and lives of mankind. This brand statement represents our sense of pride in this endeavor. It is our commitment to society and ourselves that Shimadzu remains dedicated in our pursuit of technology and accumulation of knowledge, so that we can offer even more outstanding technologies, products, and services, so as to be recognized for excellence in the field of science.