

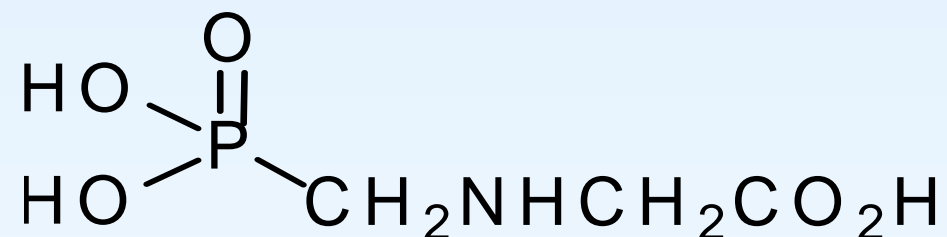


Analysis of Glyphosate in cereals

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Glyphosate



- Zwitterion structure
- Many different analytical methods (with/without derivatisation) , among others
 - GC-MS
 - HPLC fluorescence
 - LC-MS/MS

Usage

Glyphosate (N-phosphonomethyl glycine) (Round up) is used world wide as a herbicide e.g. towards weeds, couch grass and for withering of commodities before harvest.

It is a systemic pesticide that, when translocated throughout the plant inhibits the production of some aromatic amino acids essential for plant growth. The pre-harvest interval is 10 days.

Usage in Denmark:	2003	2004	2005
	1033 t	1073 t	963 t

~ ca 20% of the total Danish pesticide usage (a.i.)

MRL, health aspects

- FAO/WHO has established an ADI at 0.3 mg/kg bw/day
- The exposure of glyphosate through the intake of an average diet with cereals is estimated to negligible in relation to ADI
- The MRL (in cereals):
 - Wheat, rye, triticale 10 mg/kg p,
 - barley, oats, sorghum 20 mg/kg p,
 - maize 1 mg/kg p,
 - other cereals 0,1p*.

Analytical method

Glyphosate

- Extraction with water
- HPLC, anion exchange column
- On-line ion suppression to remove Na⁺
- Quantification by MS/MS (ESI-)
- ISTD: ¹³C¹⁵N-glyphosat

MRM transitions:

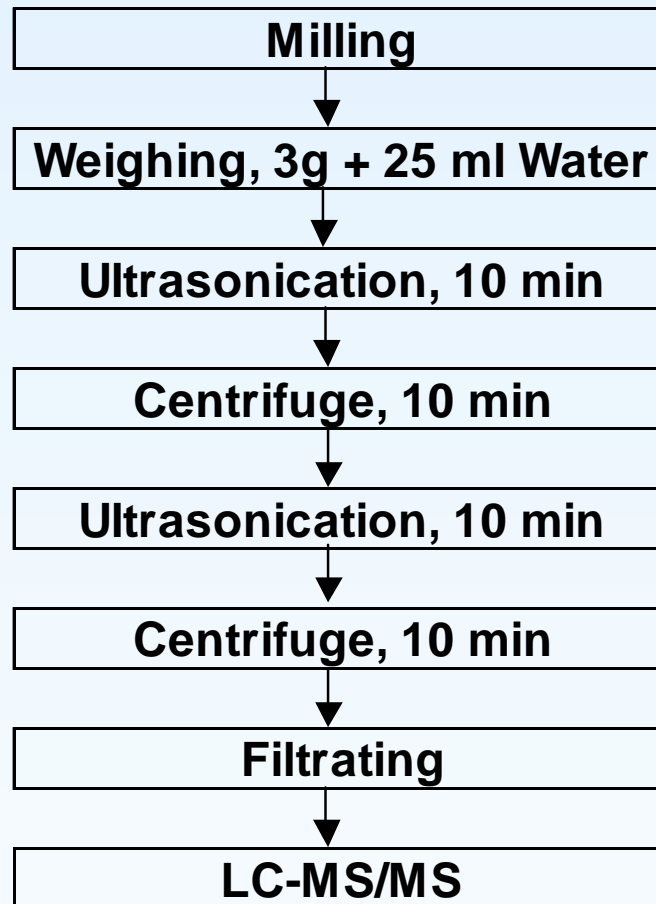
- 168 → 150 (quantification)
- 168 → 124 (qualification/verification)
- 170 → 152 (2-¹³C-N-glyphosate (i.s.))

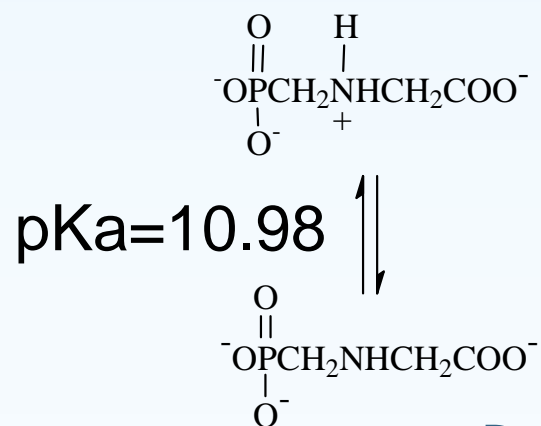
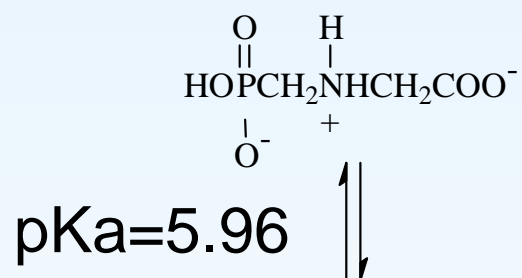
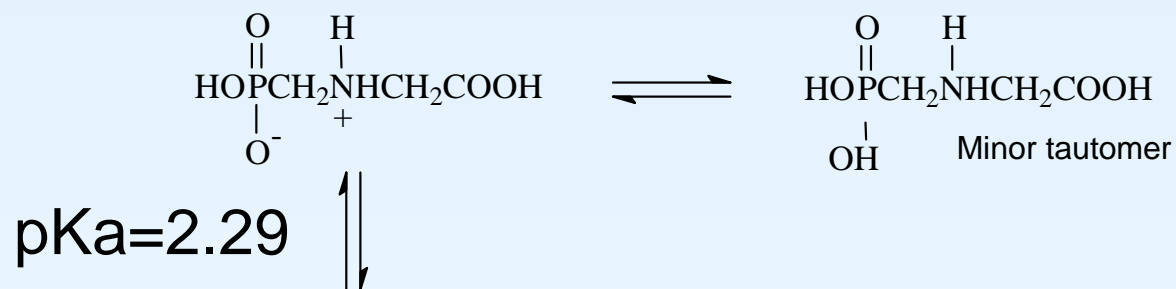
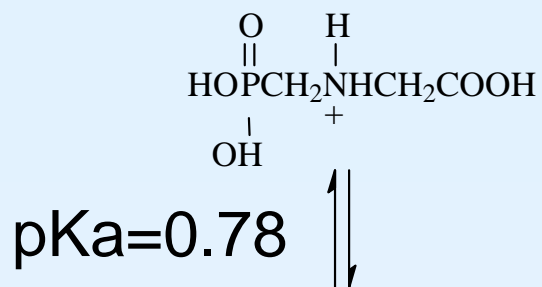
AMPA:

Showed broad peak (2 min), due to retention on the ion suppressor

- Used in the Danish monitoring programme since 2000.

Flowchart of the method

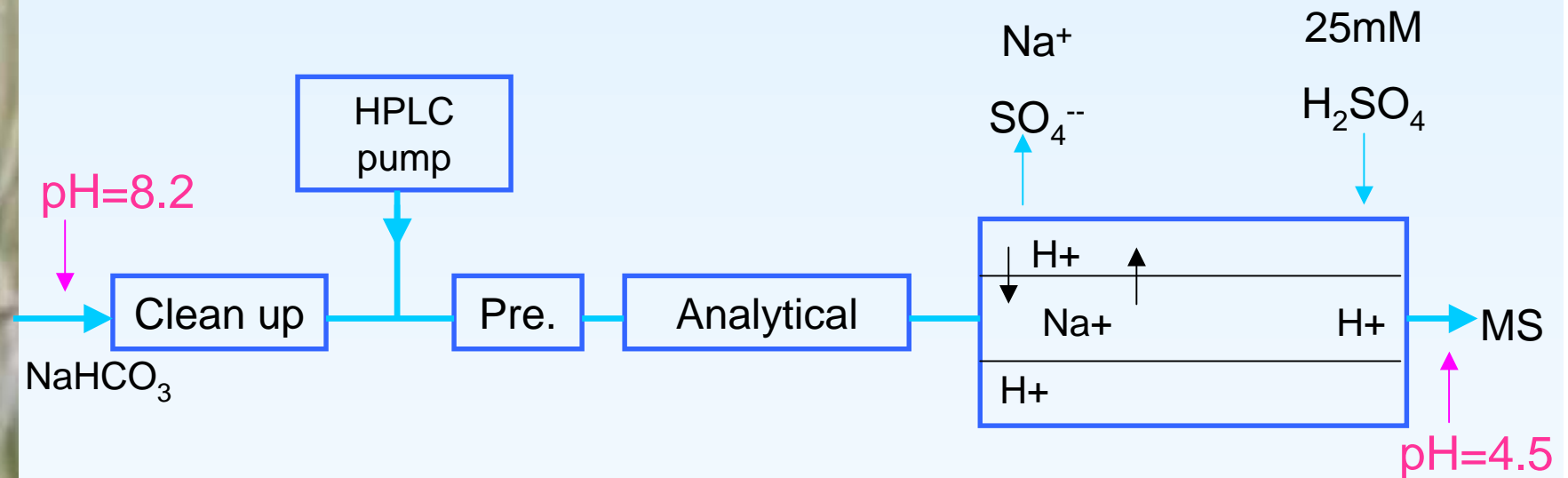




Glyphosate, pH dependency

Ref: Chamberlain et al. (1996). Pestic. Sci., 47.

Schematic set up of columns



Columns

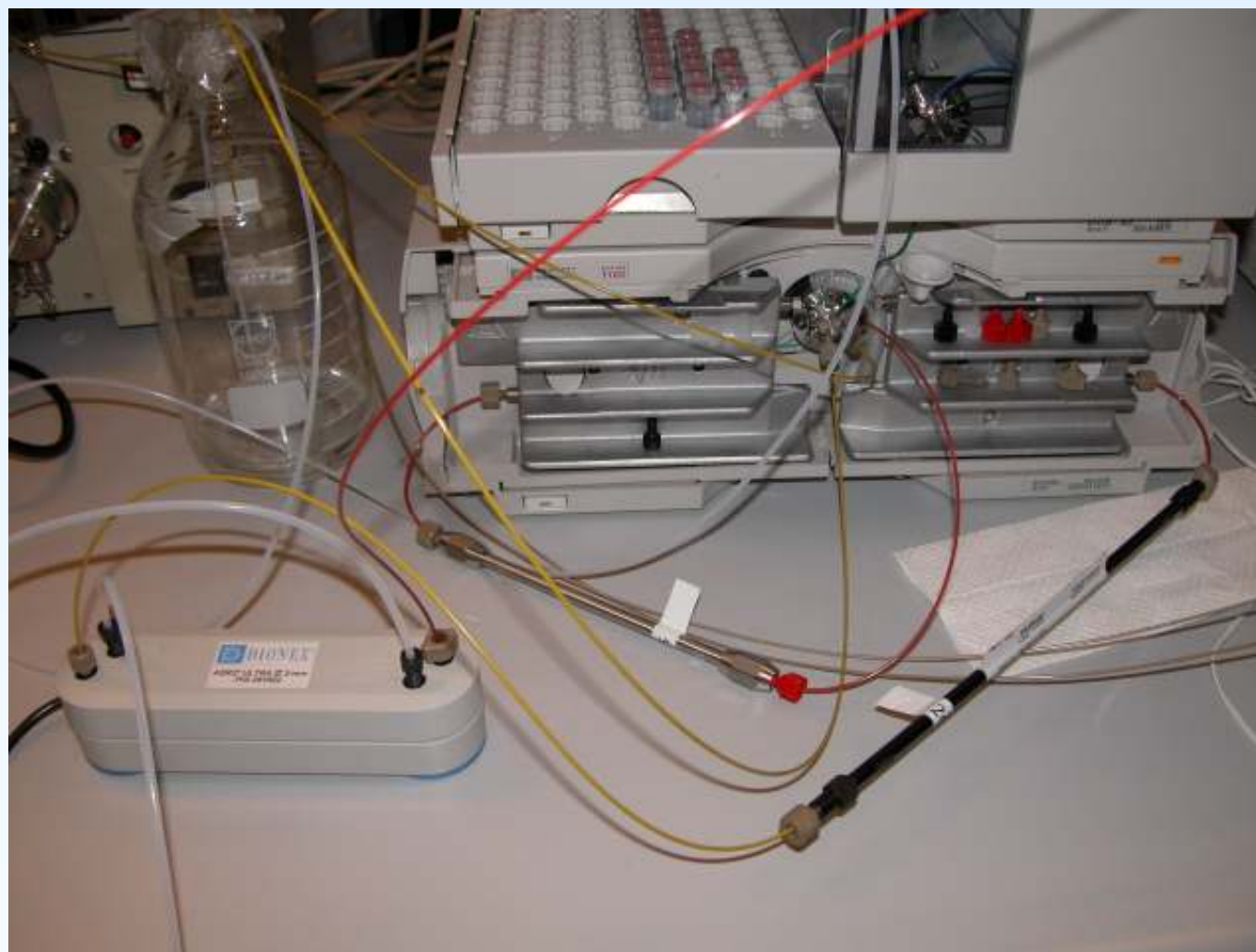
Clean up: PLRC-S (Polymer Laboratories)

Pre / Analytical column, separation: AS4-AS

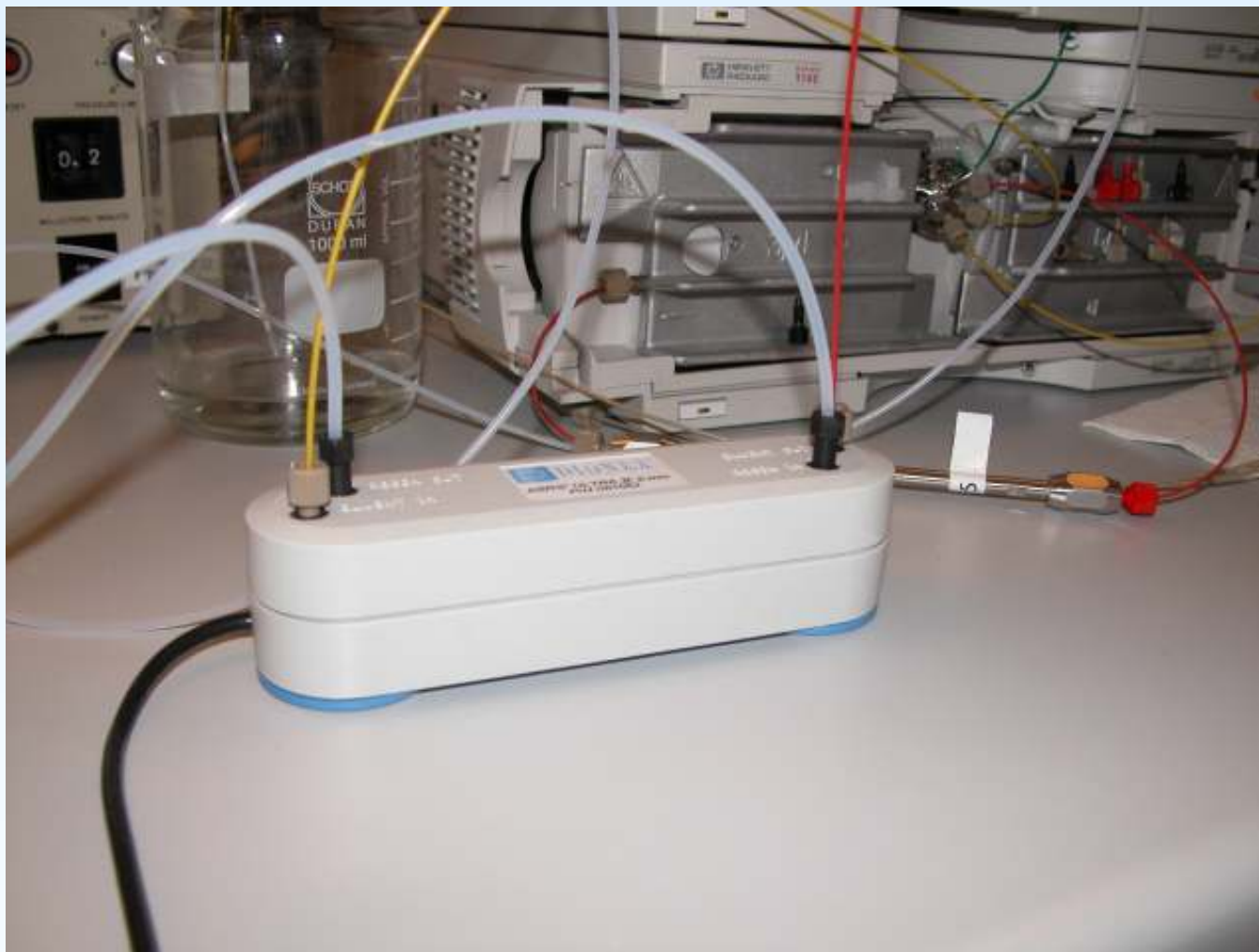


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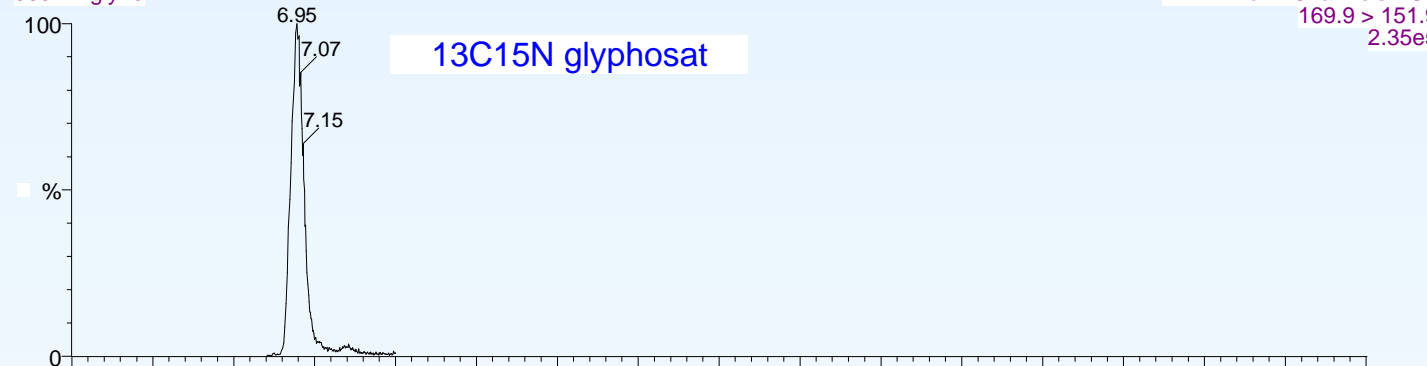


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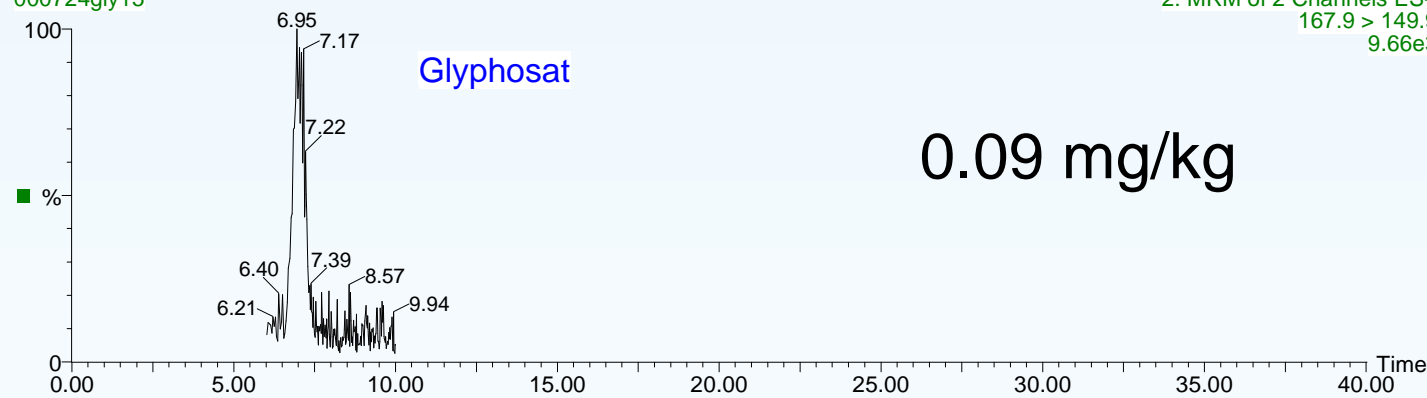
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2: MRM of 2 Channels ES-
169.9 > 151.9
2.35e5



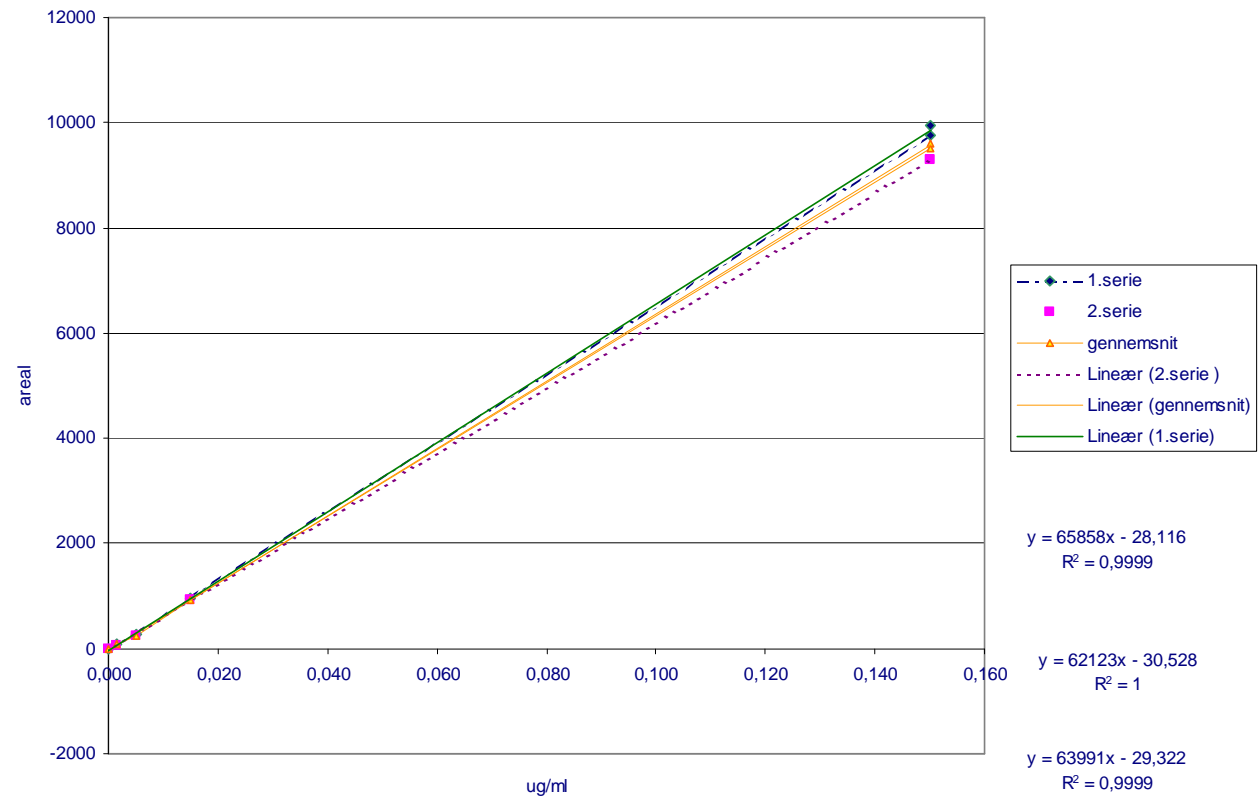
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2: MRM of 2 Channels ES-
167.9 > 149.9
9.66e3



0.09 mg/kg

20/7-00 glyphosate in barley standards



Conclusions

- A specific and sensitive LC-MS/MS method for analysis of glyphosate in cereals.
- The short analysis time due to automatic cleanup and no concentration steps makes the method suitable for routine control.
- The method is environmentally friendly, not using organic solvents or chemicals apart from NaHCO_3 for the eluent.
- The detection limit is 0.02 mg/kg (well below the MRL, except for babyfood).
- Recovery is $93 \pm 9\%$ (n=10).

Future work

- Exchange mobile phase (without Na⁺),
 - ➔ exclude membrane suppressor
 - ➔ Include AMPA in the analytical method
- Collaborative study on Glyphosate in collaboration with EU-CRL Single residue methods