Analysis of Glyphosate in cereals

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**Glyphosate**

![Zwitterion structure](image)

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

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Usage

Glyphosate (N-phosphonomethyl glycine) (Round up) is used worldwide 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 0.1 p*.
Analytical method

Glyphosate
- Extraction with water
- HPLC, anion exchange column
- On-line ion suppression to remove Na⁺
- Quantification by MS/MS (ESI-)
- ISTD: $^{13}$C$^{15}$N-glyphosate

MRM transitions:
- 168 → 150 (quantification)
- 168 → 124 (qualification/verification)
- 170 → 152 (2-$^{13}$C-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

- Milling
- Weighing, 3g + 25 ml Water
- Ultrasonication, 10 min
- Centrifuge, 10 min
- Ultrasonication, 10 min
- Centrifuge, 10 min
- Filtrating
- LC-MS/MS
Glyphosate, pH dependency


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Schematic set up of columns

Columns
Clean up: PLRC-S (Polymer Laboratories)
Pre / Analytical column, separation: AS4-AS
24-JUL-2000
10:59:34

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

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

0.09 mg/kg
20/7-00 glyphosate in barley standards

\[ y = 62123x - 30,528 \]
\[ R^2 = 1 \]

\[ y = 63991x - 29,322 \]
\[ R^2 = 0.9999 \]

\[ y = 65858x - 28,116 \]
\[ R^2 = 0.9999 \]
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 NaHCO₃ for the eluent.
- The detection limit is 0.02 mg/kg (well below the MRL, except for babyfood).
- Recovery is 93 ± 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