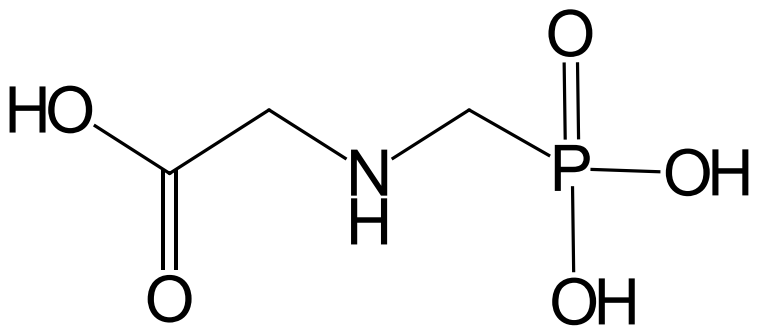
NIBIO
NORWEGIAN INSTITUTE OF
BIOECONOMY RESEARCH

Easy sample preparation of glyphosate in water with a new molecule imprinted polymer (MIP)

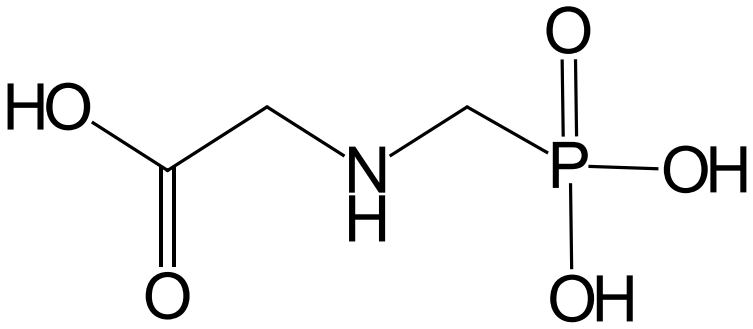
Marit Almvik



Glyphosate

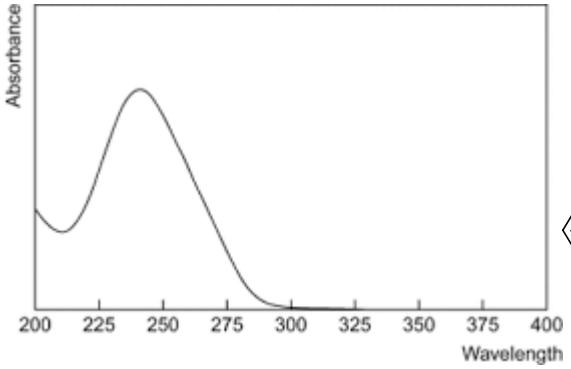
Introduced in 1971

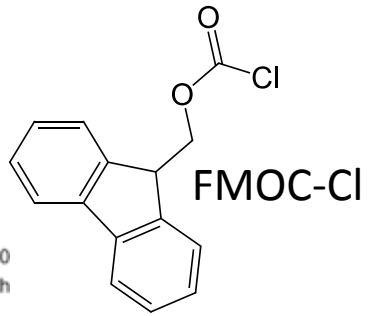
Sorbs to glass



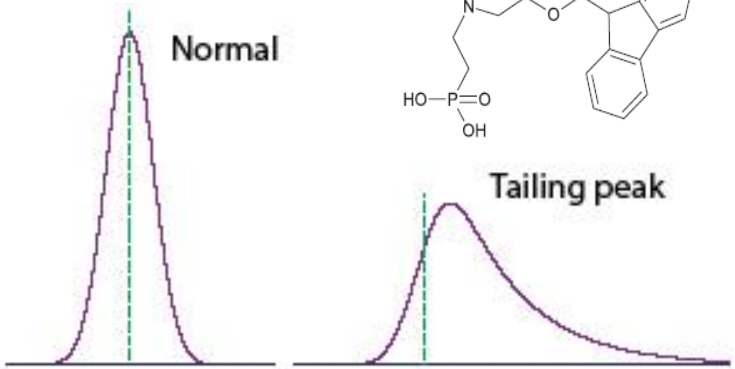
Glyphosate

Poor solvent solubility



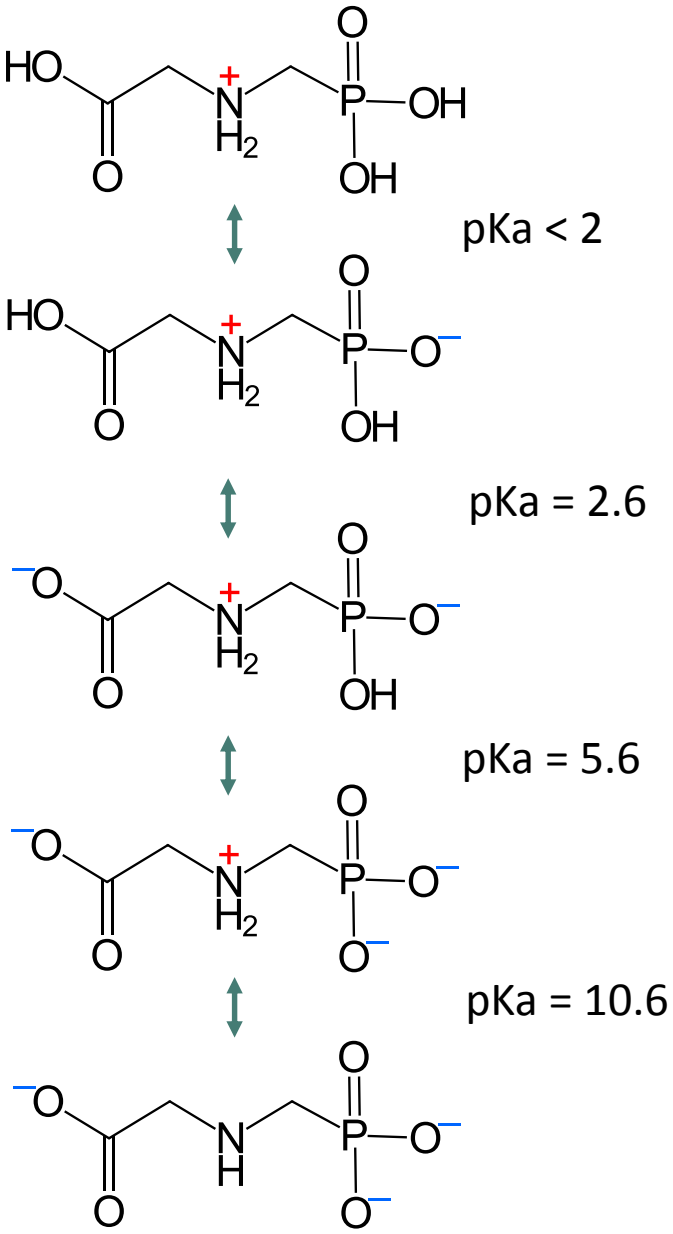


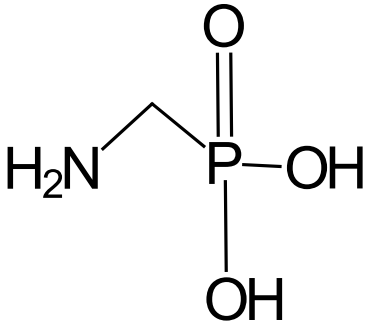
No chromophore/fluorophore



Sorbs to steel tubing in LC

The charm of a zwitterion

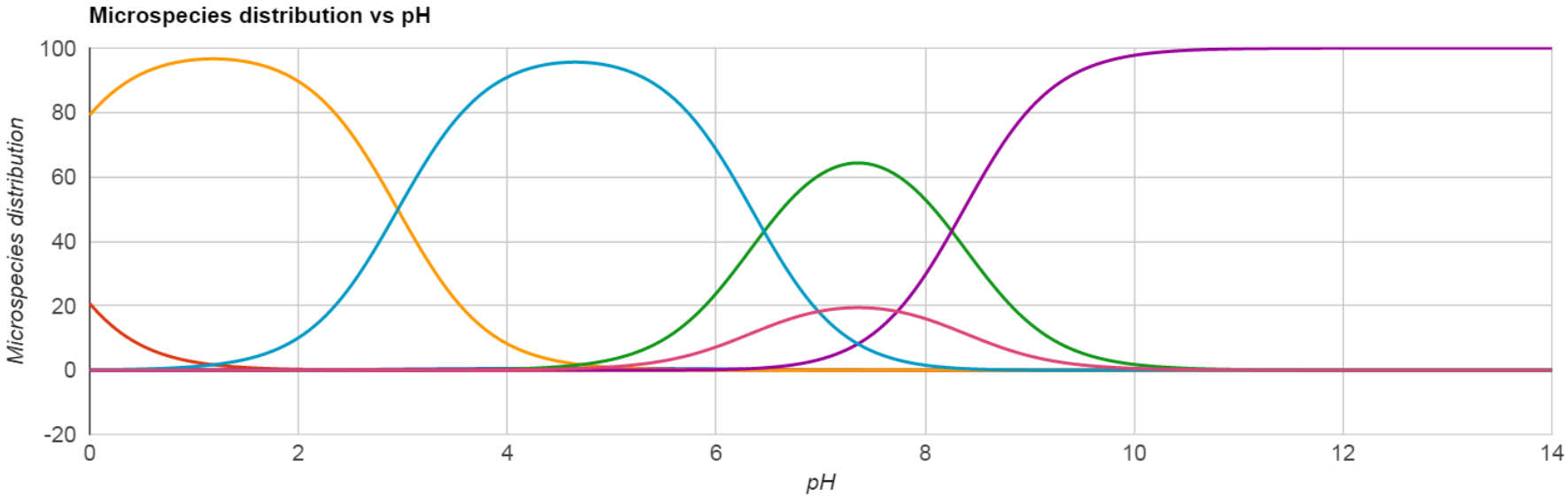


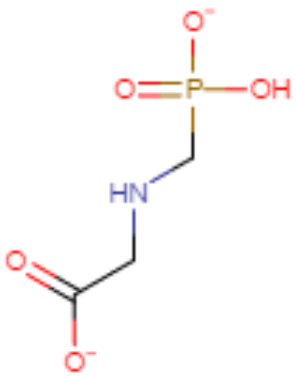


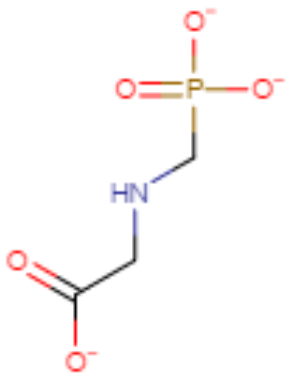
AMPA

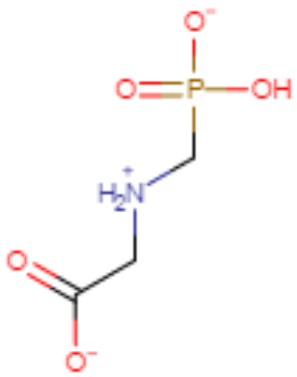
Sprankle et al. Weed Sci. 1975

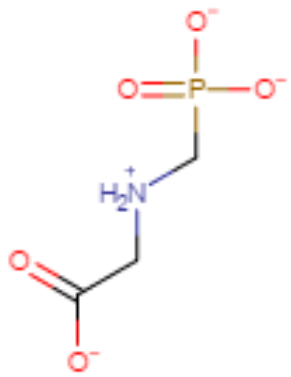
In silico predicted pK_a *(chemicalize.org)*:











Limit of quant. (LOQ) 0.05 µg/L wanted

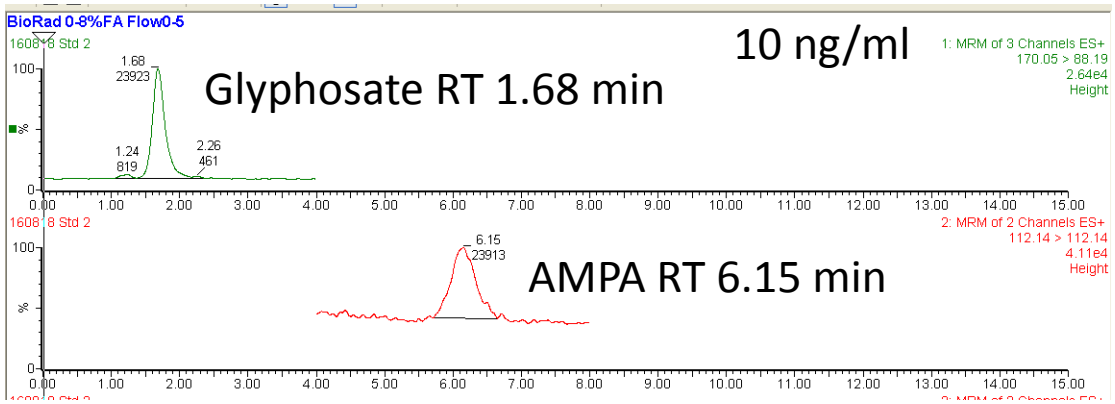
- Agricultural streams in Norway show mean glyphosate concentrations of 0.15 µg/L and maximum 4 µg/L
- Our current water method, with FMOC-derivatization, dichloromethane clean-up and LC-MS/MS analysis has an LOQ of 0.05 µg/L

Simpler analysis method

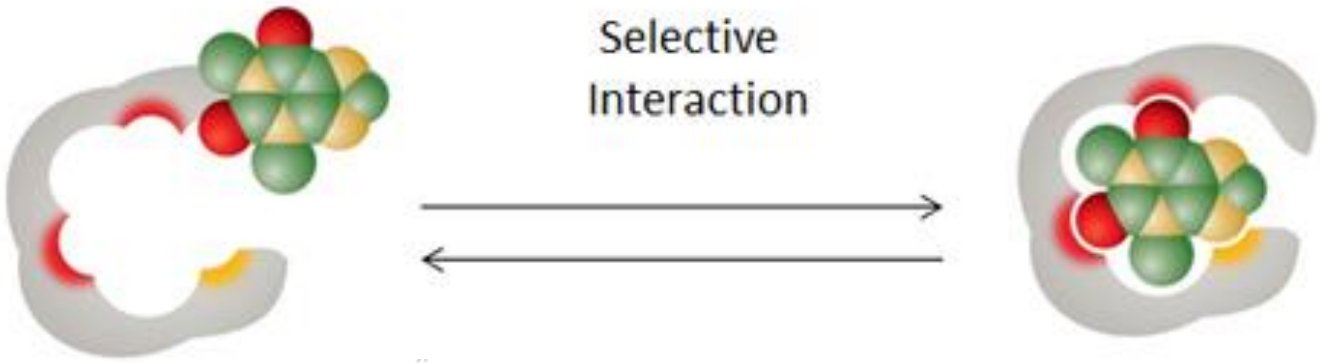
- Separate glyphosate and AMPA on a Bio-Rad cation (H+) guard column (3 cm)

  (Marek & Koskinen 2014; Jensen et al. 2016)

- Detect in ESI-Positive (Glyphosate: 170>88/60, AMPA: 112>112) using 0.8% formic acid (pH 2.25) at 0.5 ml/min as mobile phase. Column temp. 50°C.



Molecule imprinted polymer (MIP):



AFFINIMIP® SPE Glyphosate - AMPA

Extraction of Glyphosate and AMPA

AFFINIMIP® SPE Glyphosate - AMPA - 3mL- 50/box

Reference : FS113-03

For more information

Add to cart

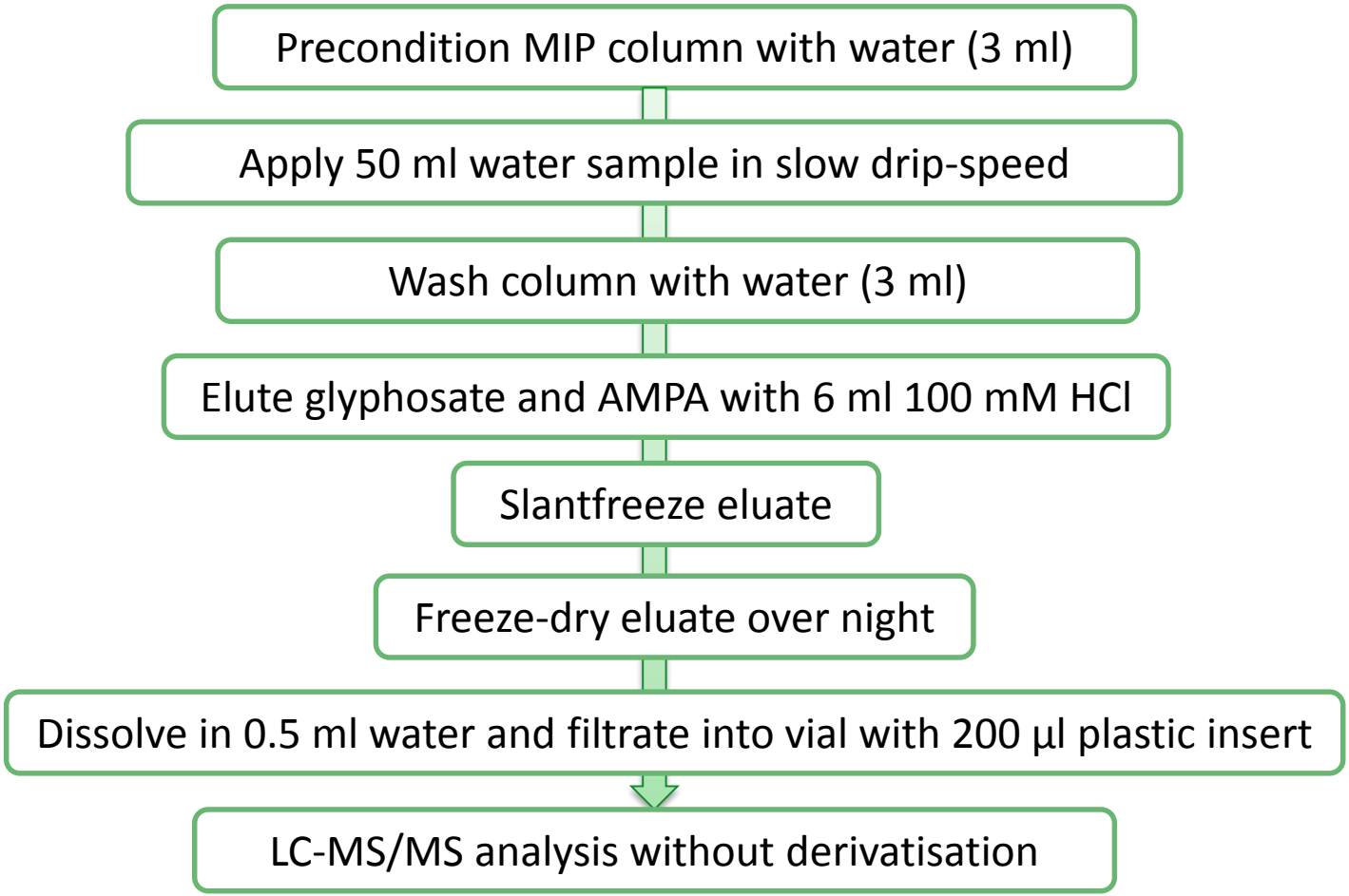
Affinisep.com


1
2
3
4
5
4
Bl.


SARSTEDT
1
4
2
5
3


VACUUM
COLLECTOR
0.010 mBar
-102C
AUTO
MAN
VACUUM
MENU
SELECT
LABCONCO
VACUUM
TEMP
ALARM

Simpler method:



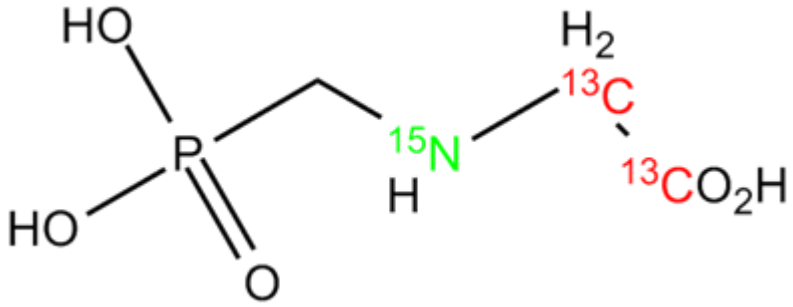
Recovery (at 0.05-4 µg/L, 3-ml MIP):

	Glyphosate	AMPA
3 ml ultrapure water	78 %	NA
50 ml ultrapure water	60 %	42 %
50 ml pond water	70 %	60 %
100 ml pond water	48 %	31 %

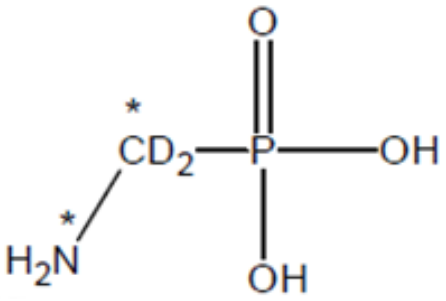
For sample volumes > 50 ml: use 6-ml MIP cartridges

Recovery of internal standards (IS):

50 ml volume on MIP	IS Glyphosate	IS AMPA
Ultrapure water	70 %	37 %
Pond water	58 %	45 %
Drainage water	52 %	47 %



Glyphosate-13C$_2$-15N



AMPA-13C,15N,methylene-D2

IS-adjusted recovery:

50 ml sample to MIP	Glyphosate	AMPA
Ultrapure water	115 %	97 %
Pond water	118 %	118 %

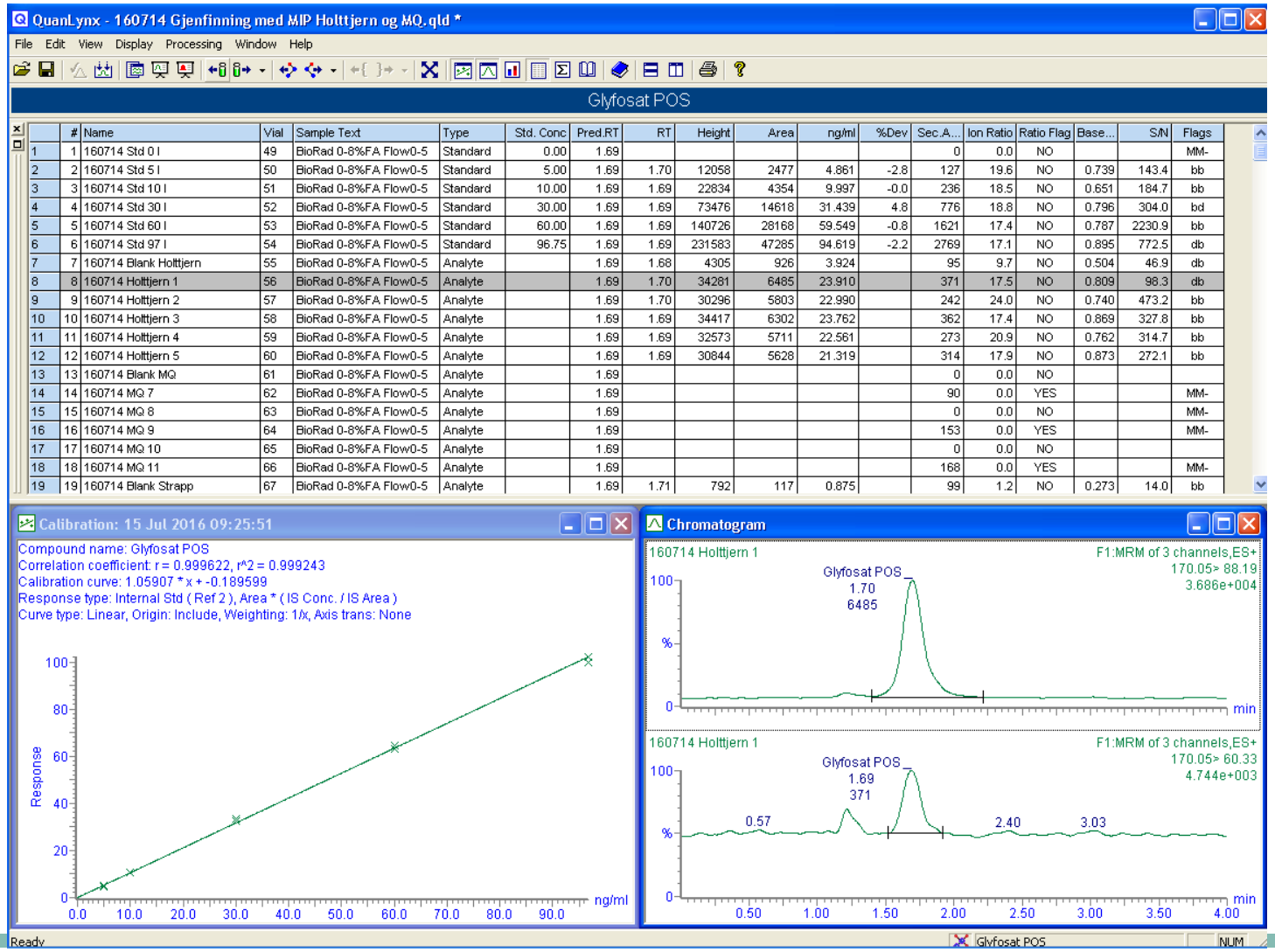
Analysis of real drainage water samples:

Sample no.	Glyphosate		AMPA	
	NIBIO	Other lab.*	NIBIO	Other lab.*
13-04	8.2	8.2	0.37	0.40
13-07	0.92	2.10	0.27	0.47
13-10	1.40	0.89	0.28	0.29

*Other lab: different analysis method, with derivatisation

A larger round robin study is necessary to verify test results

Pond water (0.10 µg/L)

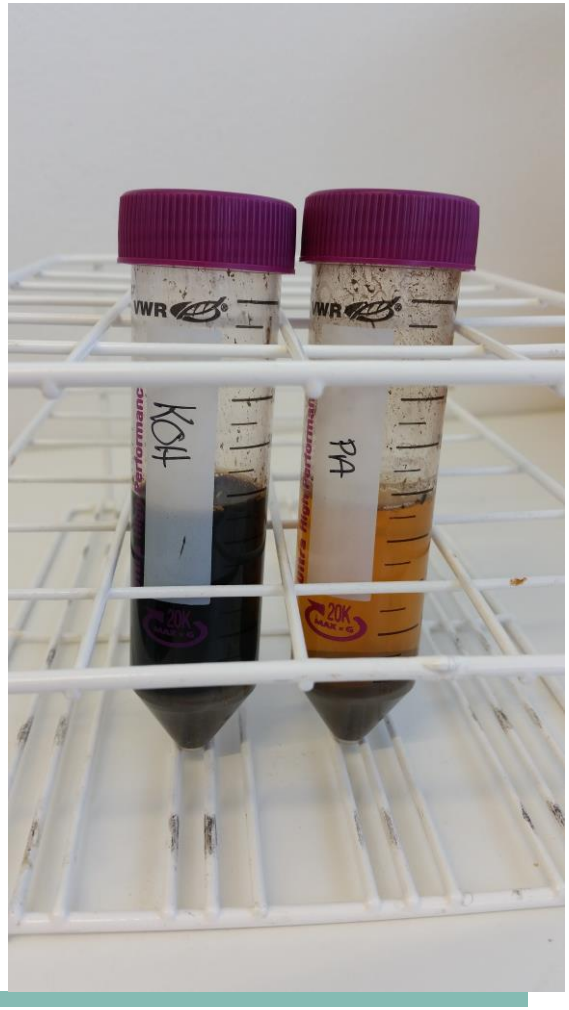


	#	Name	Vial	Sample Text	Type	Std. Conc	Pred.RT	RT	Height	Area	ng/ml	%Dev	Sec.A...	Ion Ratio	Ratio Flag	Base...	S/N	Flags
1	1	160714 Std 0 l	49	BioRad 0-8%FA Flow0-5	Standard	0.00	1.69						0	0.0	NO			MM-
2	2	160714 Std 5 l	50	BioRad 0-8%FA Flow0-5	Standard	5.00	1.69	1.70	12058	2477	4.861	-2.8	127	19.6	NO	0.739	143.4	bb
3	3	160714 Std 10 l	51	BioRad 0-8%FA Flow0-5	Standard	10.00	1.69	1.69	22834	4354	9.997	-0.0	236	18.5	NO	0.651	184.7	bb
4	4	160714 Std 30 l	52	BioRad 0-8%FA Flow0-5	Standard	30.00	1.69	1.69	73476	14618	31.439	4.8	776	18.8	NO	0.796	304.0	bd
5	5	160714 Std 60 l	53	BioRad 0-8%FA Flow0-5	Standard	60.00	1.69	1.69	140726	28168	59.549	-0.8	1621	17.4	NO	0.787	2230.9	bb
6	6	160714 Std 97 l	54	BioRad 0-8%FA Flow0-5	Standard	96.75	1.69	1.69	231583	47285	94.619	-2.2	2769	17.1	NO	0.895	772.5	db
7	7	160714 Blank Holttjern	55	BioRad 0-8%FA Flow0-5	Analyte		1.69	1.68	4305	926	3.924		95	9.7	NO	0.504	46.9	db
8	8	160714 Holttjern 1	56	BioRad 0-8%FA Flow0-5	Analyte		1.69	1.70	34281	6485	23.910		371	17.5	NO	0.809	98.3	db
9	9	160714 Holttjern 2	57	BioRad 0-8%FA Flow0-5	Analyte		1.69	1.70	30296	5803	22.990		242	24.0	NO	0.740	473.2	bb
10	10	160714 Holttjern 3	58	BioRad 0-8%FA Flow0-5	Analyte		1.69	1.69	34417	6302	23.762		362	17.4	NO	0.869	327.8	bb
11	11	160714 Holttjern 4	59	BioRad 0-8%FA Flow0-5	Analyte		1.69	1.69	32573	5711	22.561		273	20.9	NO	0.762	314.7	bb
12	12	160714 Holttjern 5	60	BioRad 0-8%FA Flow0-5	Analyte		1.69	1.69	30844	5628	21.319		314	17.9	NO	0.873	272.1	bb
13	13	160714 Blank MQ	61	BioRad 0-8%FA Flow0-5	Analyte		1.69						0	0.0	NO			
14	14	160714 MQ 7	62	BioRad 0-8%FA Flow0-5	Analyte		1.69						90	0.0	YES			MM-
15	15	160714 MQ 8	63	BioRad 0-8%FA Flow0-5	Analyte		1.69						0	0.0	NO			MM-
16	16	160714 MQ 9	64	BioRad 0-8%FA Flow0-5	Analyte		1.69						153	0.0	YES			MM-
17	17	160714 MQ 10	65	BioRad 0-8%FA Flow0-5	Analyte		1.69						0	0.0	NO			
18	18	160714 MQ 11	66	BioRad 0-8%FA Flow0-5	Analyte		1.69						168	0.0	YES			MM-
19	19	160714 Blank Strapp	67	BioRad 0-8%FA Flow0-5	Analyte		1.69	1.71	792	117	0.875		99	1.2	NO	0.273	14.0	bb

Clean-up of *soil extracts* with MIP?

Conclusion: *No*

KOH-extracts are too complex, no retention of glyphosate on MIP



Clean-up of *wheat extracts* with MIP?

To be tested

Weigh 3g. + 2x25 ml water

Ultrasonication 2x10 min.

Centrifuging 2x10 min.

Filtration

Apply on MIP

Freeze-dry eluate over night

Dissolve in 0.5 ml water and filtrate into vial with 200 µl plastic insert

LC-MS/MS analysis without derivatisation

Conclusion

- MIP provide a simple and selective method for the cleanup and preconcentration of water/water extracts
- 50 ml sample → 0.5 ml extract
- No need for dichloromethane cleanup
- Recoveries >60 % (adjusts to 97-118 % with IS)
- Repeatability < 6 %
- LOQ for glyphosate: 0.05 µg/L (using 50 ml water)
- LOQ for AMPA: 0.3 µg/L (will be improved with optimization of analysis method)
- Method can be combined with a micro-derivatisation

References

Marek, L. J.; Koskinen, W. C. Simplified Analysis of Glyphosate and Aminomethylphosphonic Acid in Water, Vegetation and Soil by Liquid Chromatography-Tandem Mass Spectrometry. *Pest. Manag. Sci.* **2014,** *70,* 1158-1164.

Jensen, P. K.; Wujcik, C. E.; McGuire, M. K.; McGuire, M. A. Validation of Reliable and Selective Methods for Direct Determination of Glyphosate and Aminomethylphosphonic Acid in Milk and Urine Using LC-MS/MS. *J Environ Sci Health B* **2016,** *51,* 254-259.

Koskinen, W. C.; Marek, L. J.; Hall, K. E. Analysis of Glyphosate and Aminomethylphosphonic Acid in Water, Plant Materials and Soil. *Pest. Manag. Sci.* **2016,** *72,* 423-432.

NIBIO

NORWEGIAN INSTITUTE OF
BIOECONOMY RESEARCH