Glyphosate and AMPA in tap water matrix

Branch 2: Water, waste water, environmental protection
Branch 11: Fertilizers, base materials, explosives

Keywords

IC / 850 / 858 / anions / Metrosep A Supp 7 – 250 / Metrosep A Supp 7 – 150 / herbicide / Roundup / Glyphosate / *N*-(Phosphonomethyl)glycine / AMPA / aminomethylphosphonic acid / branch 2 / branch 11

Summary

Analysis of glyphosate and AMPA was carried out in a tap water matrix using Metrosep A Supp 7 – 250 and an eluent containing sodium carbonate, sodium hydroxid, and acetone. Simultaneous determination of Oxyhalides, standard anions, glyphosate and AMPA was possible with this setting.

Glyphosate (*N*-(Phosphonomethyl)glycine) is a broad spectrum, non-selective herbicide. It is the main component of Roundup (from Monsanto). It causes plant's death by interfering with the production of certain amino acids. The glyphosate molecule mimics a part of the PEP (phosphoenolpyruvate) molecule and thereby blocks its action in a metabolic pathway that is specific to plants (the shikimate pathway).

Since animals are not capable of producing these amino acids, it was assumed that animals were not affected by glyphosate.

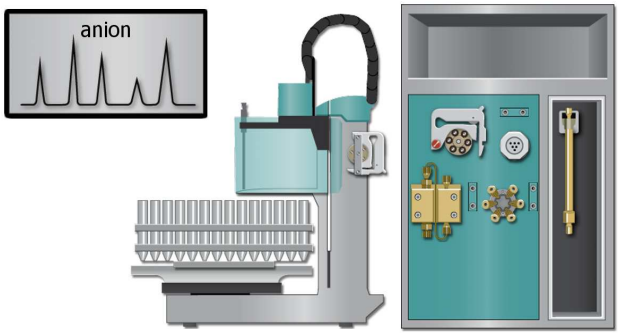
Glyphosate gets adsorbed by soil particles and biodegrades to AMPA (aminomethylphosphonic acid), the major metabolite of glyphosate.

Glyphosate and its degradation products are topics of ongoing environmental discussions. A negative impact on biodiversity has been reported, especially concerning the ecosystems of micro-organisms.

According to WHO, studies of acceptable daily intake describe a health-based value of 0.9 mg/L for AMPA alone or in combination with glyphosate of 0.3 mg/kg of body weight. In 2006, the US EPA set the maximum contaminant level (MCL) for glyphosate at 0.7 mg/L.

Apparatus and Accessories

850 Professional IC Anion – MCS	2.850.2030
858 Professional Sample Processor	2.858.0020
Rinsing Station for IC Sample Processor	6.2841.100
Metrosep A Supp 7 - 250	6.1006.630
Metrosep A Supp 4/5 Guard	6.1006.500



IC Reagents

(Ultra pure water, resistivity > 18 MOhm * cm (25 °C))

Anion Eluent:
3.0 mmol/L sodium carbonate
15.0 mmol/L sodium hydroxide
10% acetone

IC Suppressor solutions:
100 mmol sulfuric acid
ultrapure water

IC Parameters

Flow	0.8 mL/min
Sample Loop	20 µL
Pmax	15.0 MPa
Polarity	+
Temp. coefficient	2.3 %/°C
Recording time	57 min
MSM step after	20 min and 40 min
Column temperature	45°C

Sample

Glyphosate (*N*-(Phosphonomethyl)glycine 96%) and AMPA (aminomethyl-phosphonic acid 99%) from Sigma-Aldrich

Matrix

Artificial tap water matrix consisting of 10 ppm Cl^-, NO_3^-, SO_4^{2-} and 50 ppb F^-, BrO_3^-, ClO_2^-, ClO_3^-, Br^-, PO_4^{3-}.

Calculation

Automatic integration with MagIC Net 2.0™ software using peak area for all analytes.

Standards

[ppm (mg/L) in ultra pure water]

Standard	AMPA	Glyphosate
1	5	5
2	2	2
3	1	1
4	0.5	0.5
5	0.2	0.2
6	0.1	0.1
7	0.05	0.05

Comments

The goal of this setup was to measure oxyhalides, Glyphosate, and AMPA in one run in a tap water matrix. If the compounds of interest are Glyphosate and AMPA only, there are different (and faster) methods.

The tests were established for the analysis of water samples. For (diluted) soil samples, the set up might be equipped with an inline ultrafiltration.

The pH of the eluent is 11.8, hence a stronger/more alkaline eluent is not recommended (Metrosep A Supp 7 pH range 3 – 12). Any acceleration of glyphosate was always accompanied with a worse resolution of oxyhalides and standard anions.

The addition of organic modifiers higher than 10% increased the back pressure to ≥15 MPa (Metrosep A Supp 7 maximum pressure 15 MPa).

AMPA showed a poor peak which might be caused by decomposition of the substance during the separation process. Analysis with IC-MS confirmed this finding because abundance ratios of AMPA fragments changed at subsequent time points (see below).

Tests with Metrosep A Supp 7 – 150 and an eluent of 3.0 mmol/L sodium carbonate, 15.0 mmol/L sodium hydroxide, and 10% acetone resulted in shorter chromatogram times (30 min instead of >50 min). However, separation of oxyhalides was no longer possible. Changing the eluent to 2.5 mmol/L sodium carbonate, 15.0 mmol/L sodium hydroxide, and 8% acetone elongated the chromatogram time to ~40 minutes. It showed slightly better results, but the separation of bromated and chloride was not successful with Metrosep A Supp 7 – 150.

Appendix

Chromatograms, results, calibration curves, mass spectrum of AMPA

Date

October 28th 2009

Name

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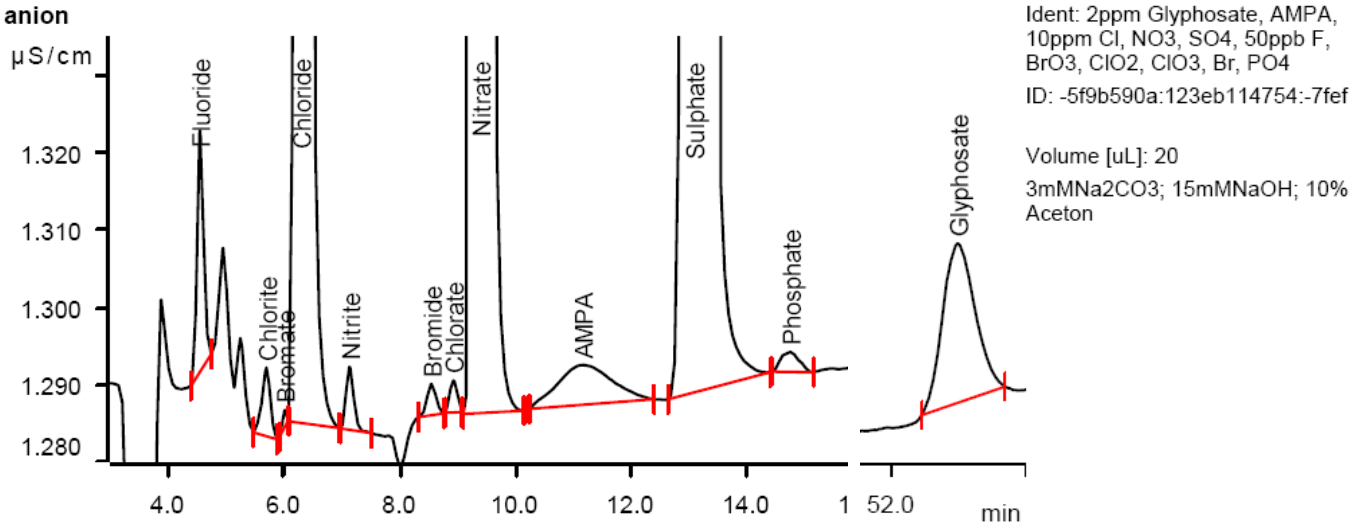
Metrohm International Headquarters

Chromatograms

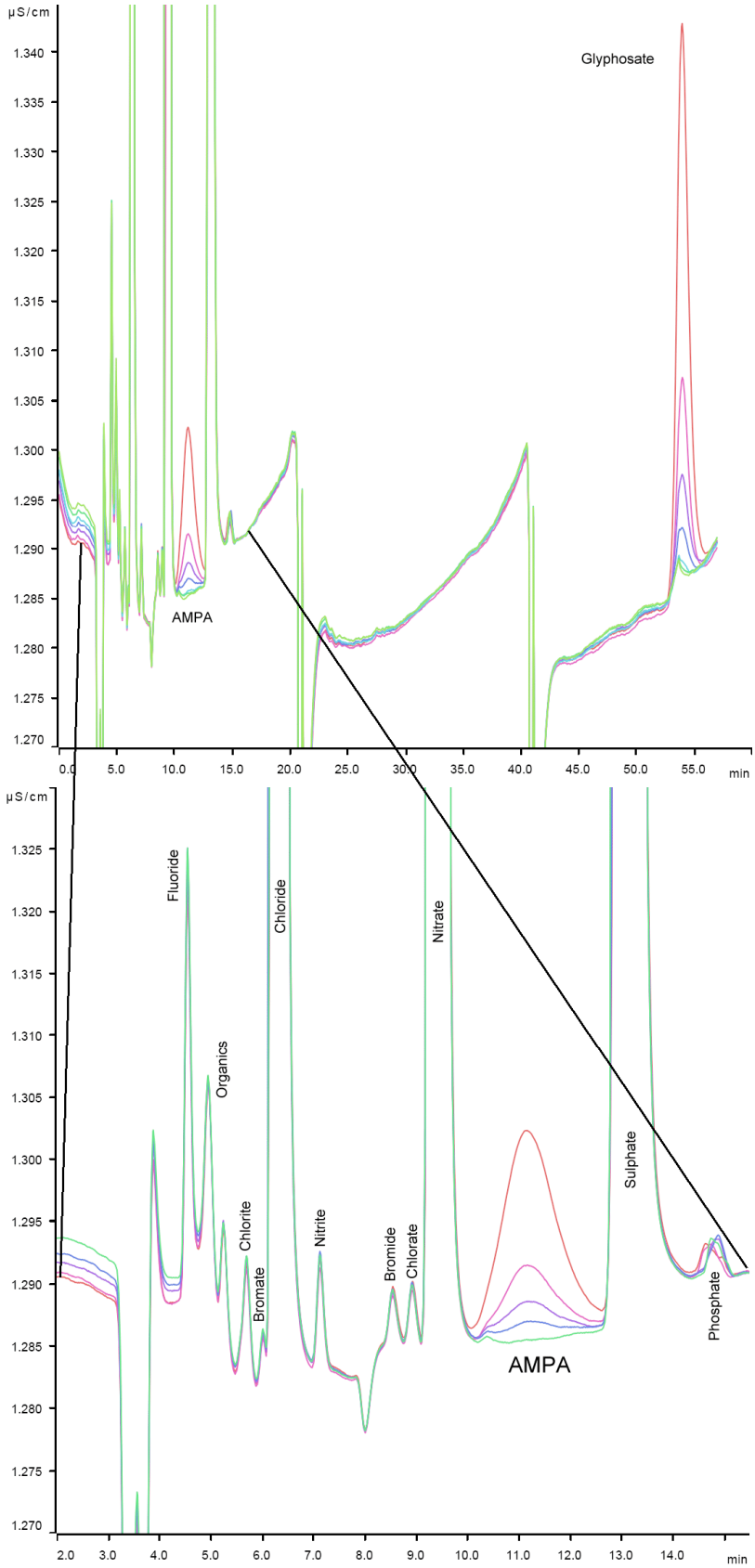
Glyphosate and AMPA (2 ppm each) in an artificial tap water matrix. Under these conditions, the retention time of AMPA was in between those of nitrate and sulfate. Glyphosate elutes after 54 minutes.



anion

Peak number	Retention time min	Height µS/cm	Area (µS/cm) x min	Resolution	Component name
1	4.56	0.029	0.004	4.738	Fluoride
2	5.67	0.008	0.001	1.608	Chlorite
3	5.99	0.002	0.000	1.991	Bromate
4	6.51	0.060	0.518	2.266	Chloride
5	7.23	0.002	0.001	4.635	Nitrite
6	8.53	0.004	0.001	1.425	Bromide
7	8.92	0.004	0.001	2.006	Chlorate
8	9.61	0.088	0.286	1.768	Nitrate
9	11.30	0.005	0.006	1.999	AMPA
10	13.51	0.034	0.478	1.949	Sulphate
11	14.77	0.002	0.001	34.247	Phosphate
12	53.93	0.021	0.023	invalid	Glyphosate

Tap water matrix with different concentrations of AMPA and Glyphosate (upper scheme 5 ppm, 2 ppm, 1 ppm, 0.5 ppm, 0.2 ppm, 0.1 ppm, 0.05 ppm; lower scheme 5 ppm, 2 ppm, 1 ppm, 0.5 ppm, 0.1 ppm).



Results

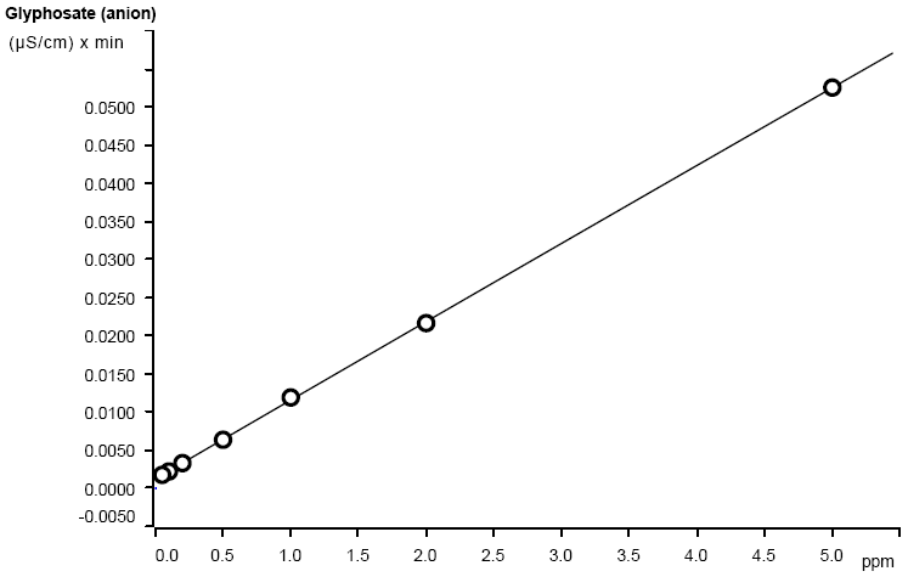
A mix of 10 ppm Cl^-, NO_3^-, SO_4^{2-} and 50 ppb F^-, BrO_3^-, ClO_2^-, ClO_3^-, Br^-, PO_4^{3-} was exemplarily used as artificial tap water, and spiked with different concentrations of AMPA and glyphosate:

Artificial tap water	AMPA [ppm]	Glyphosate [ppm]
...spiked with 0.05 ppm	-	0.049
...spiked with 0.1 ppm	-	0.099
...spiked with 0.2 ppm	-	0.202
...spiked with 0.5 ppm	0.308	0.497
...spiked with 1 ppm	0.926	1.078
...spiked with 2 ppm	1.781	2.021
...spiked with 5 ppm	4.092	5.03

Recoveries of AMPA and glyphosate in “tap water”:

Recoveries [%]	AMPA	Glyphosate
Spiked with 0.05 ppm	-	98
Spiked with 0.1 ppm	-	99
Spiked with 0.2 ppm	-	101
Spiked with 0.5 ppm	62	99
Spiked with 1 ppm	93	108
Spiked with 2 ppm	89	101
Spiked with 5 ppm	82	101

Calibration curves

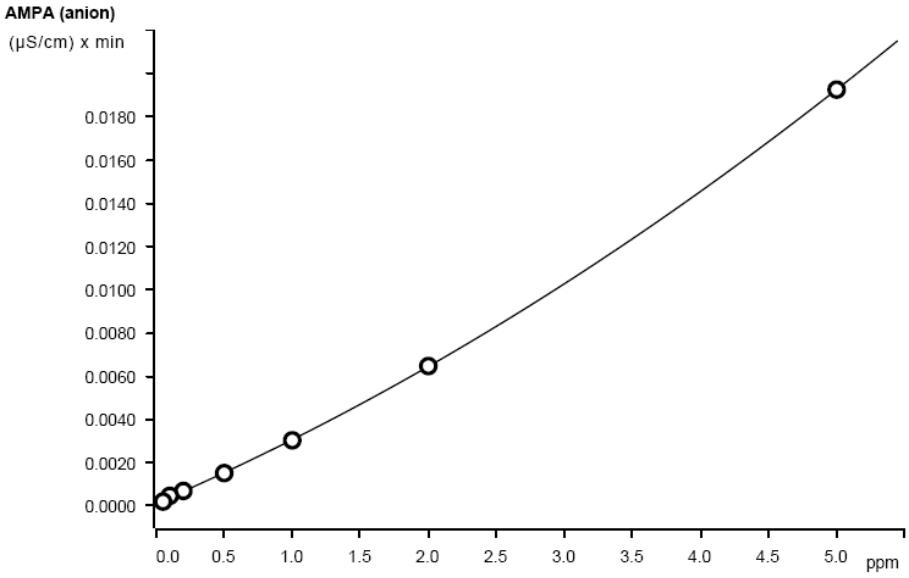


Function: . . . . . *A = 1.25437E-3 + 5.16408E-4× Q - 3.80559E-8× Q²*

Relative standard deviation . . . . . *1.421232 %*

Correlation coefficient *0.999959*

Sample type	Index	Conc.	Volume	Area	Ident	Date	Used
Standard 2	1	2.000	20.0	0.022	2ppm Glyphosate, AMPA	2009-09-23 13:32:16 UTC+2	used
Standard 1	1	5.000	20.0	0.053	5ppm Glyphosate, AMPA	2009-09-23 14:31:21 UTC+2	used
Standard 3	1	1.000	20.0	0.012	1ppm Glyphosate, AMPA	2009-09-23 15:30:32 UTC+2	used
Standard 4	1	0.500	20.0	0.006	0.5ppm Glyphosate, AMPA	2009-09-23 16:30:34 UTC+2	used
Standard 5	1	0.200	20.0	0.003	0.2ppm Glyphosate, AMPA	2009-09-23 17:30:38 UTC+2	used
Standard 6	1	0.100	20.0	0.002	0.1ppm Glyphosate, AMPA	2009-09-23 18:30:39 UTC+2	used
Standard 7	1	0.050	20.0	0.002	0.05ppm Glyphosate, AMPA	2009-09-23 19:31:07 UTC+2	used



Function: . . . . . *A = 1.18337E-4 + 1.36087E-4× Q + 5.53034E-7× Q²*

Relative standard deviation . . . . . *1.122309 %*

Correlation coefficient *0.999982*

Sample type	Index	Conc.	Volume	Area	Ident	Date	Used
Standard 2	1	2.000	20.0	0.006	2ppm Glyphosate, AMPA	2009-09-23 13:32:16 UTC+2	used
Standard 1	1	5.000	20.0	0.019	5ppm Glyphosate, AMPA	2009-09-23 14:31:21 UTC+2	used
Standard 3	1	1.000	20.0	0.003	1ppm Glyphosate, AMPA	2009-09-23 15:30:32 UTC+2	used
Standard 4	1	0.500	20.0	0.002	0.5ppm Glyphosate, AMPA	2009-09-23 16:30:34 UTC+2	used
Standard 5	1	0.200	20.0	0.001	0.2ppm Glyphosate, AMPA	2009-09-23 17:30:38 UTC+2	used
Standard 6	1	0.100	20.0	0.000	0.1ppm Glyphosate, AMPA	2009-09-23 18:30:39 UTC+2	used
Standard 7	1	0.050	20.0	0.000	0.05ppm Glyphosate, AMPA	2009-09-23 19:31:07 UTC+2	used

The following plot shows a typical mass spectrum of an AMPA peak. Two fragments were detected (m/z 110 = AMPA anion; m/z 63 = degradation product). In the front part of the peak, m/z 110 was more abundant, in the peak's tail m/z 63 was more abundant (displayed a spectrum from AMPA's peak tail). This shift of abundance probably indicates that the decomposition already occurred during chromatographic separation. That observation may explain for the broad and poor peak of AMPA.