

QUANTIFICATION OF GLYPHOSATE AND AMINOMETHYLPHOSPHONIC ACID IN WATER USING SPE-LC-MS/MS

Irene HANKE, Heinz SINGER

Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland, email: irene.hanke@eawag.ch

Motivation and Background

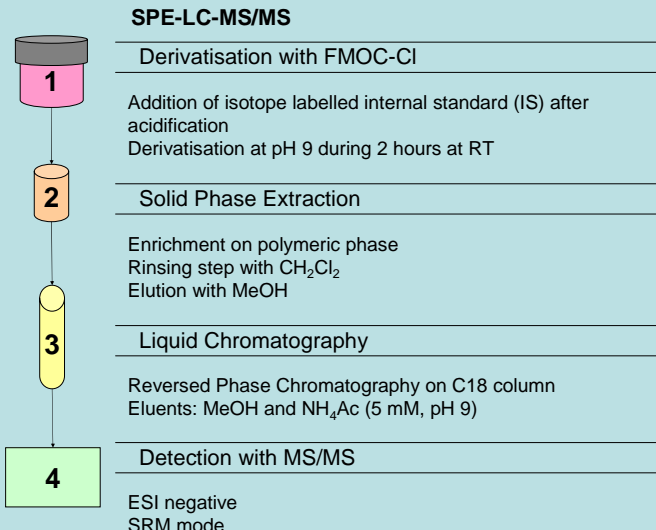
Glyphosate is one of the most important herbicides worldwide. Despite the high use of glyphosate there are comparatively few environmental data available. This is mainly due to the difficult trace level determination in water and the limited robustness of some of the existing methods.

Objective

The goal of our work was to develop an improved analytical method for the quantification of glyphosate and its major metabolite aminomethylphosphonic acid (AMPA) at the low ng/L level in surface and groundwater and to analyse different waters in Switzerland.

Different parameters were examined in order to better understand the derivatisation reaction, to avoid complexation with metal ions and to allow the removal of interfering matrix during sample preparation.

Analytical Method



Method Optimisation

Derivatisation		1
Concentration of FMOCl.....	65 mM	
Content of organic modifier (ACN).....	10%	
Duration of reaction.....	2 h	
Inhibition of metal complexes		
Acidification of the sample and addition of EDTA after derivatisation		
Enrichment step		2
Evaluation of different SPE materials → Strata-X		
Amount of SPE material.....	200 mg	
Removal of undesirable by-products		
Rinsing of the SPE cartridge with dichloromethane after enrichment		
Limit of detection LOD (glyphosate)		
Nanopure water.....	0.4 ng/L	4
Groundwater.....	0.5 ng/L	
Surface water.....	0.2 ng/L	

Environmental Water Samples

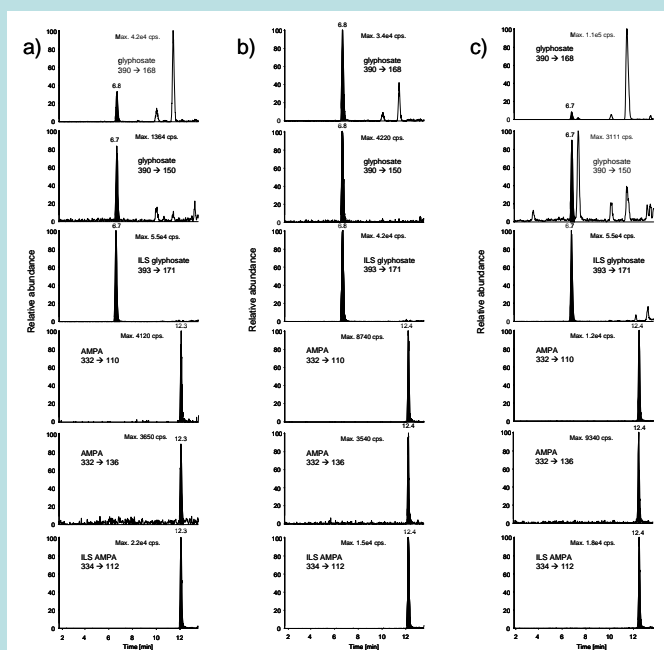


Val Roseg is a remote alpine valley that is situated in the southeast of Switzerland, whereas the Lake of Zurich is located in the densely populated Swiss plateau.

Performance

LC-MS/MS chromatograms for spiked surface water samples (Val Roseg) with a concentration of 1 ng/L (a) and 10 ng/L (b) for glyphosate and AMPA and a sample of Lake Zurich with a concentration level of 5 ng/L for glyphosate and 15 ng/L for AMPA (c).

Both transitions and the quantifier of the corresponding isotope labelled standard are shown.



Conclusions

A larger sample volume, a complete FMOCl-CL derivatisation, a minimized complexation with metal ions, a removal of derivatisation by-products and optimisation of the LC and MS conditions led to an excellent method performance:

- ⇒ Limit of detection in environmental water samples is between 0.2 and 0.5 ng/L
- ⇒ the recovery of spiked analyte amounts in surface water and groundwater is in the range of 97% - 103%

Literature:

I. Hanke, H. Singer, and J. Hollender, Ultratrace-level determination of glyphosate, aminomethylphosphonic acid and glufosinate in natural waters by solid-phase extraction followed by liquid chromatography-tandem mass spectrometry; performance tuning of derivatization, enrichment and detection. *Analytical and Bioanalytical Chemistry*, 2008. 391(6): p. 2265-2276.