

Analysis of Glyphosate and AMPA in Environmental Water Samples by Ion Chromatography and On-Line Mass Spectrometry with Minimal Sample Preparation

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Overview

Purpose:

Development of a straight forward high-performance ion chromatography MS/MS method (IC-MS/MS) to determine glyphosate and AMPA (2-amino-3-(3-hydroxy-5-methylisoxazol-4-yl)propanoic acid) in surface and effluent water samples

Methods:

The separation method is based on anion exchange chromatography using a high capacity column so samples with a relative high ion concentration can be direct injected without dilution. The gradient of KOH is on-line electrolytically generated with the aid of an eluent generator. Prior to MS/MS and conductivity detection the eluent is on-line desalted by a self regenerating desalter.

Introduction

Glyphosate and AMPA are compounds widely used in weed prevention. As a consequence they occur in many parts of the environment. Several methods have been published. In order to reach the low detection and quantitation limits mostly laborious FMOC (Fluorenylmethyloxycarbonyl chloride) derivatization combined with LC-MS/MS (triple quadrupole) has been used.

Another LC approach explored is ion exchange chromatography which does not need derivatization of these components. These components are zwitterions so they can be separated by cation exchange [1] and anion exchange. Both approaches are explored and even in anion exchange a more complicated 2-dimensional method has been published [2]. We will present a straightforward IC-MS/MS approach in surface waters and effluents that will overcome the more complex technologies published.

Instrumentation

Ion Chromatography

All the glycans were separated using a Thermo Scientific™ Dionex™ ICS-2100 system with a Thermo Scientific Dionex AS-AP Autosampler, as shown in Figure 2.

Column: Thermo Scientific™ Dionex™ IonPac™ AG24/AS24 (2mm ID)
Gradient: 30 mM KOH (0 – 8 min)
30 – 40 mM (8 - 21 min) with EG
Flow Rate: 0.25 mL/min
Column temp: 30 °C
Desalter: Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor, 2-mm, external water 0.50 mL/min
Desalter current: 25 mA
Injection volume: 50 µl



FIGURE 1. Dionex ICS-2100 ion chromatography system.

Mass Spectrometry

MS analysis was performed with a Thermo Scientific TSQ Vantage Triple Stage Quadrupole Mass Spectrometer. IC-MS/MS used in the negative ion mode. The instrument was used in the SRM mode at unit mass resolution.

Software

Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System software and Thermo Scientific Xcalibur Software.

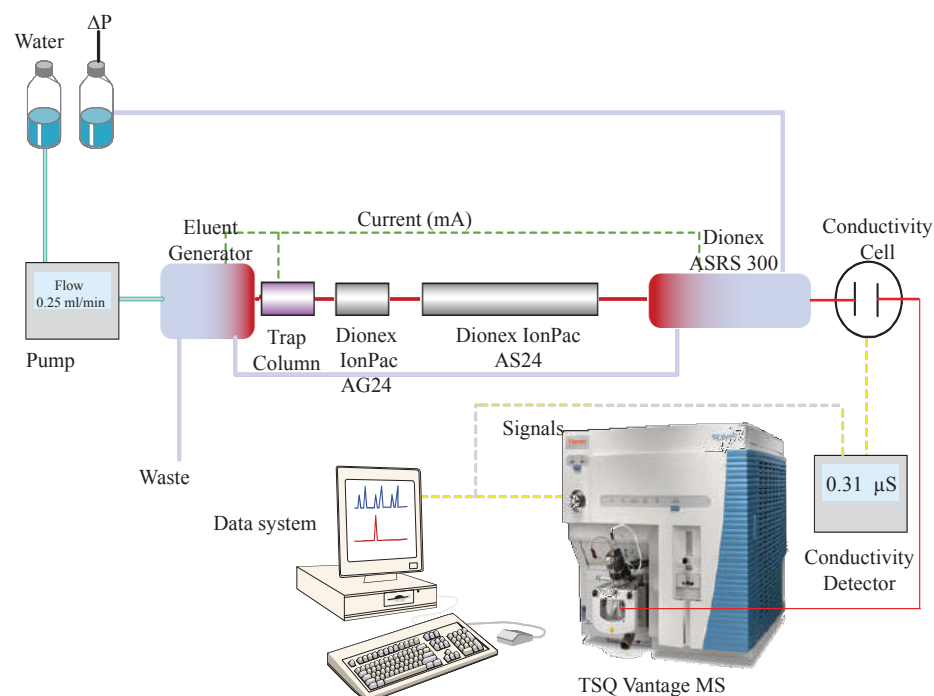


FIGURE 2. IC-MS/MS schematics.

Results and Discussion

Firstly a robust separation was developed. The retention behavior under isocratic conditions is shown in Figure 3. The final conditions for the separation are chosen in a way (i) that the major ions (chloride, sulfate, and nitrate) cannot interfere; (ii) and that the separation is robust in time.

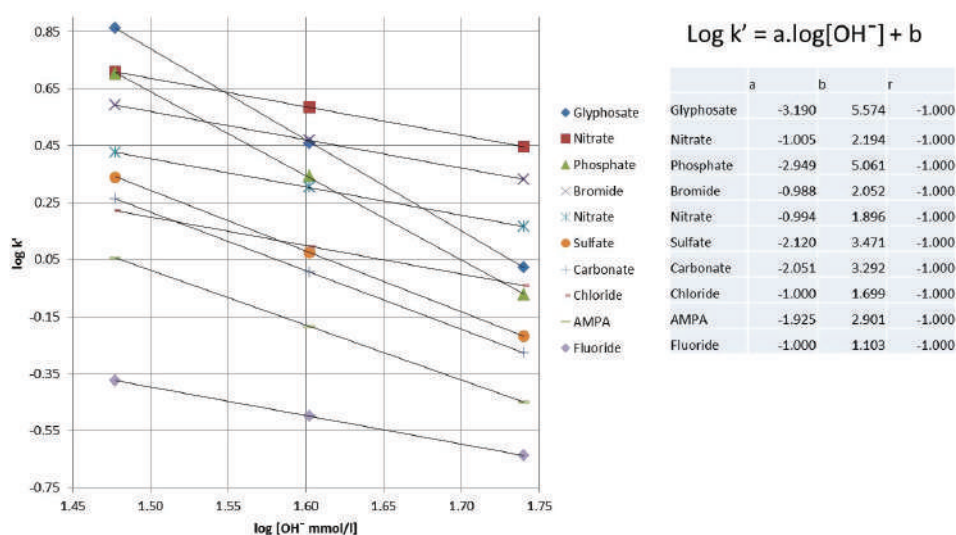


FIGURE 3. Retention behavior of anions under isocratic conditions

From the product spectra the masses are chosen for the SRM method, see Figure 4.

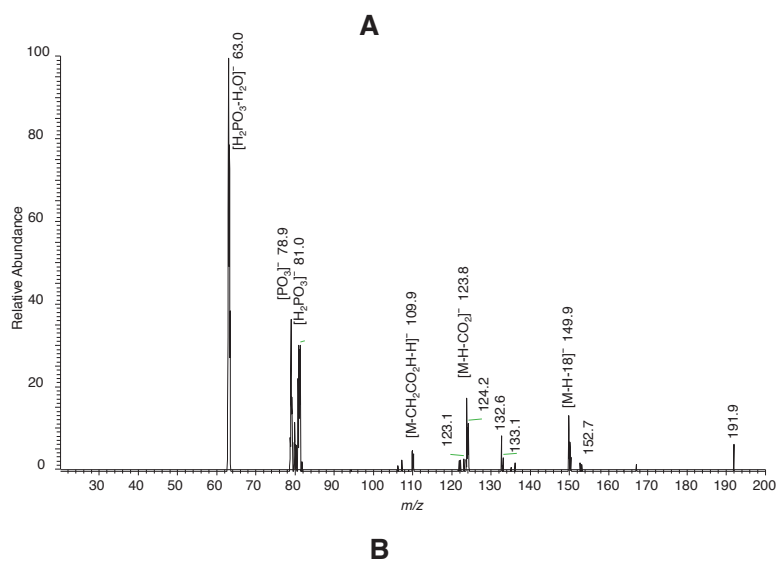
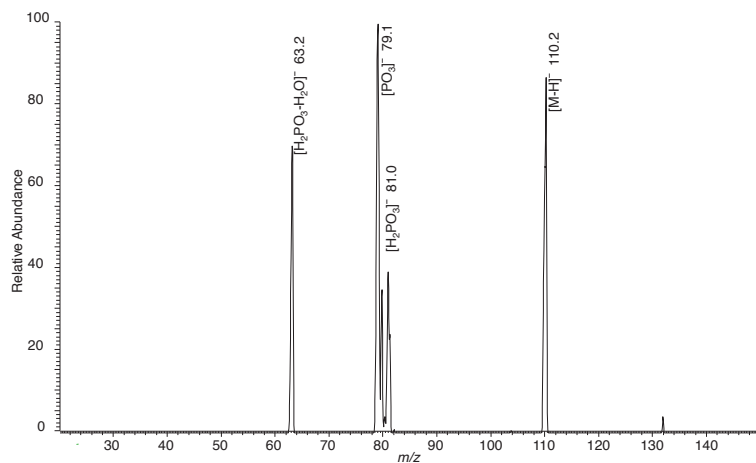


FIGURE 4. Product spectrum of AMPA (A) and Glyphosate (B)

Response in investigated from 1 to 50 $\mu\text{g/l}$ for Glyphosate as well as the AMPA and was linear for this range as shown in Figure 5.

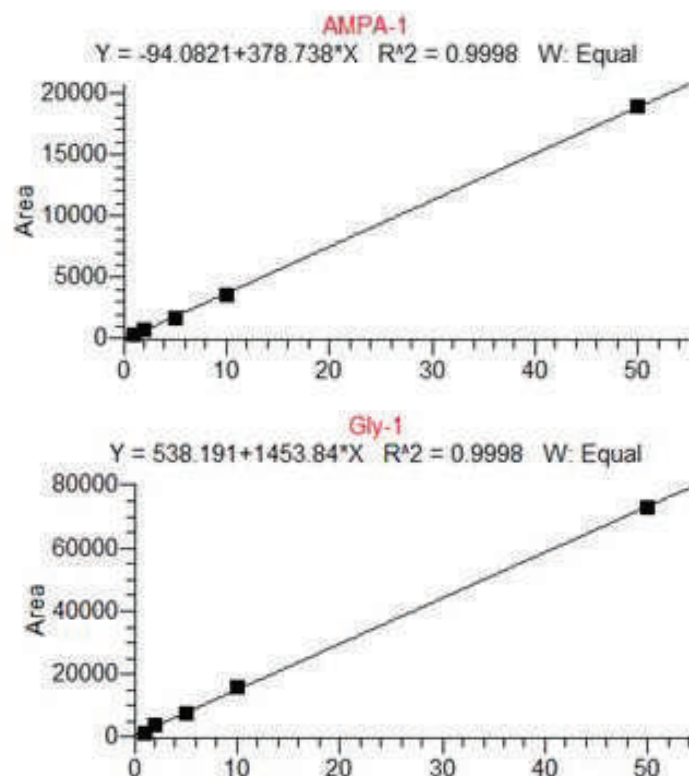


FIGURE 5. Calibration plots of AMPA and glyphosate

Figure 6 shows the result of a surface water where 2 $\mu\text{g/l}$ of AMPA and glyphosate were added. This concentration level was below the LOD of the conductivity detector, while it easily could be measured by the mass spectrometer in SRM mode.

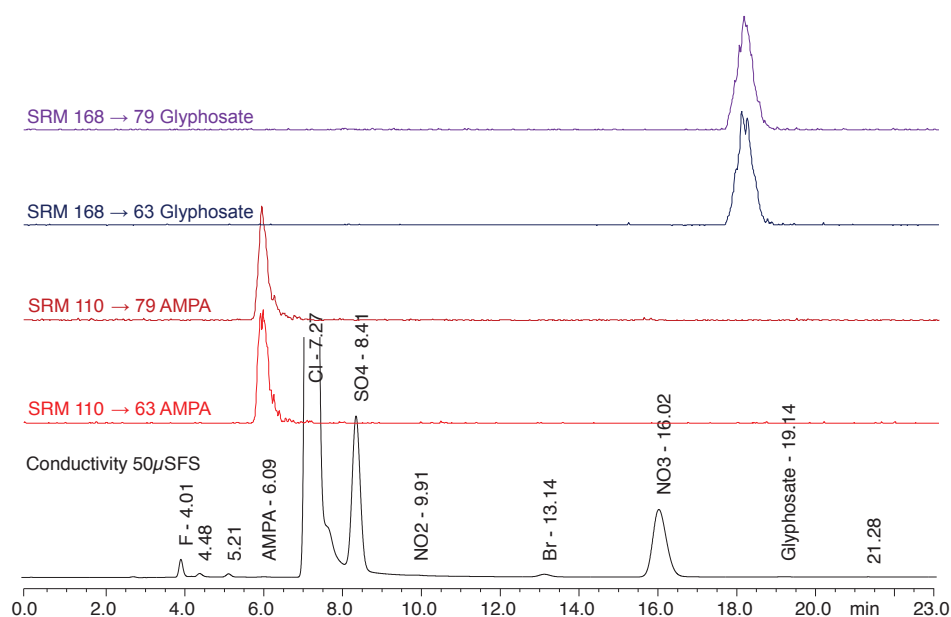


FIGURE 6. Surface water sample 2 $\mu\text{g/l}$ addition of Glyphosate and AMPA

Conclusions and Future Work

The method meets the objectives and was easy to set up and thus we can conclude that IC is compatible with mass spectrometry. We will work to obtain even lower limits of detection for the application in drinking water samples. Other metabolites should also be included in the method.

References

1. You, J.; Koropchak, J. A. Condensation nucleation light scattering detection with ion chromatography for direct determination of glyphosate and its metabolite in water *J of Chromatogr.* **2003**, *989*, 231–238.
2. Yang, C.; Henday, S.; Wang, L.; Schnute, B. Analysis of Glyphosate and AMPA in Environmental Water by Ion Chromatography Electrospray Tandem Mass spectrometry (IC-ESI-MS/MS); Application note 491, **2010**; Thermo Fisher Scientific Inc.

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