

Analysis of Chloroacetanilide and Other Acetamide Herbicide Degradates in Drinking Water by LC-MS/MS

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Key Words

- TSQ Quantum
- Pesticides

Introduction

Chloroacetanilide herbicide compounds in drinking water, specifically ethanesulfonic acid (ESA) and oxanilic acid (OA) degradates, may be found in water supplies near agricultural production areas and are used on various crops including corn and soybeans. Therefore, monitoring of these compounds is of interest to various regulatory agencies around the world.

The degradates of chloroacetanilide herbicide compounds are polar, making them ideal compounds for analysis by negative electrospray ionization mass spectrometry. This application note illustrates the direct analysis of drinking water spiked with chloroacetanilide herbicide compounds. Excellent linearity and reproducibility are demonstrated over the entire calibration range.

Experimental Conditions

Samples

The following chloroacetanilide herbicide compounds were purchased from Chem Service, Inc. (West Chester, PA): Acetochlor ESA, Alachlor ESA, Dimethenamid ESA, Flufenacet ESA, Metolachlor ESA, Propachlor ESA, Propachlor OA, Butachlor ESA, and Dimethachlor ESA. Stock solutions were prepared in methanol. Drinking water, purchased commercially, was spiked with these compounds prior to analysis and was used for all subsequent dilutions from stock solutions. Butachlor ESA, the internal standard for the analysis, was added to all samples at a concentration of 116 ng/mL. Dimethachlor ESA, the surrogate, was added to all samples at a level of 90 ng/mL. Calibrators were prepared over five levels, and the values are shown in Table 1.

Compound	Cal 01	Cal 02	Cal 03	Cal 04	Cal 05
Acetochlor ESA	180	90	18	9	3.6
Alachlor ESA	150	75	15	7.5	3
Dimethenamid ESA	90	45	9	4.5	1.8
Flufenacet ESA	158	79	15.8	7.9	3.16
Metolachlor ESA	112	56	11.2	5.6	2.24
Propachlor ESA	286	143	28.6	14.3	5.72
Propachlor OA	56	28	5.6	2.8	1.12
Butachlor ESA ISTD	116	116	116	116	116
Dimethachlor ESA SURR	90	90	90	90	90

Table 1: Actual concentrations for all analytes in the analysis. All concentrations are given in ng/mL (ppb).

LC Conditions

The gradient used in this experiment is shown in Table 2.

Instrument:	Thermo Scientific Accela pump
Autosampler:	Accela™ autosampler
Column:	Thermo Scientific Hypersil GOLD 50 x 2.1 mm, 3 μm
Column Temperature:	65 °C
Flow Rate:	0.25 mL/min
Injection Volume:	25 μL – Full Loop Mode
Mobile Phase A:	5 mM Ammonium Acetate in Water
Mobile Phase B:	Methanol

Time	% A	% B
0.0	90	10
7.0	80	20
10.0	75	25
18.0	75	25
20.0	20	80
25.0	20	80
25.1	90	10
40.0	90	10

Table 2: Gradient program used for the analysis. The flow rate was 0.25 mL/min using a Hypersil GOLD™ 50 x 2.1 mm 3 μm column heated to 65 °C.

MS Conditions

MS:	Thermo Scientific TSQ Quantum Discovery MAX
Source:	Heated-Electrospray (H-ESI)
Ionization:	Negative ESI
ESI Voltage:	3500 V
Sheath Gas:	30 units
Auxiliary Gas:	15 units at 300 °C
Capillary Temp:	300 °C

Precursor and product ions were optimized via direct syringe infusion. The optimized conditions for each compound are given in Table 3.

Compound	Precursor Mass	Product Mass	CE
Acetochlor ESA	314	80	31
Alachlor ESA	314	80	27
Dimethenamid ESA	320	121	25
Flufenacet ESA	274	121	22
Metolachlor ESA	328	121	26
Propachlor ESA	256	121	21
Propachlor OA	206	134	13
Butachlor ESA ISTD	356	80	31
Dimethachlor ESA SURR	320	121	25

Table 3: Optimized MS transitions for the compounds analyzed.

Results and Discussion

An example chromatogram for the lowest calibration level (Cal 05, Table 1) is shown in Figure 1. Two of the compounds, Acetochlor ESA and Alachlor ESA elute very closely together and are not baseline separated. Therefore, instead of using peak area to construct the calibration curve, peak height was used. Additionally, Dimethachlor, the surrogate compound for the experiment exhibited peak splitting. Both of the peak's areas were summed together for quantitation.

All of the compounds in this analysis were eluted in 22 minutes. Due to the clean nature of the samples, the chromatographic run time could be shortened to less than 40 minutes, including the time required to equilibrate the

column after the gradient. Furthermore, the Fast-HPLC capability of the Accela pump could be utilized along with a 1.9 μm particle size column to reduce the run time even more, while still providing adequate separation.

Excellent sensitivity was achieved for these analytes, even without any offline sample preconcentration.

The surrogate and internal standard compounds were used to illustrate the precision of the method. The %RSD for the surrogate compound, Dimethachlor ESA, was 2.0% for 25 injections, while Butachlor ESA's %RSD was 2.3%. Excellent linearity for all of the compounds was observed. The lowest R^2 factor was 0.9972 (Alachlor ESA), and the highest was 0.9999 (Metolachlor ESA).

Conclusion

This application note demonstrates the analysis of chloroacetanilide and other acetamide herbicide degradates using LC-MS/MS with no offline sample preparation. Significant time savings were achieved by bypassing offline solid phase extraction and preconcentration. There is the potential for even higher sensitivity and time savings in this method if the Thermo Scientific EQUAN automated solution for environmental and drinking water analysis is used.

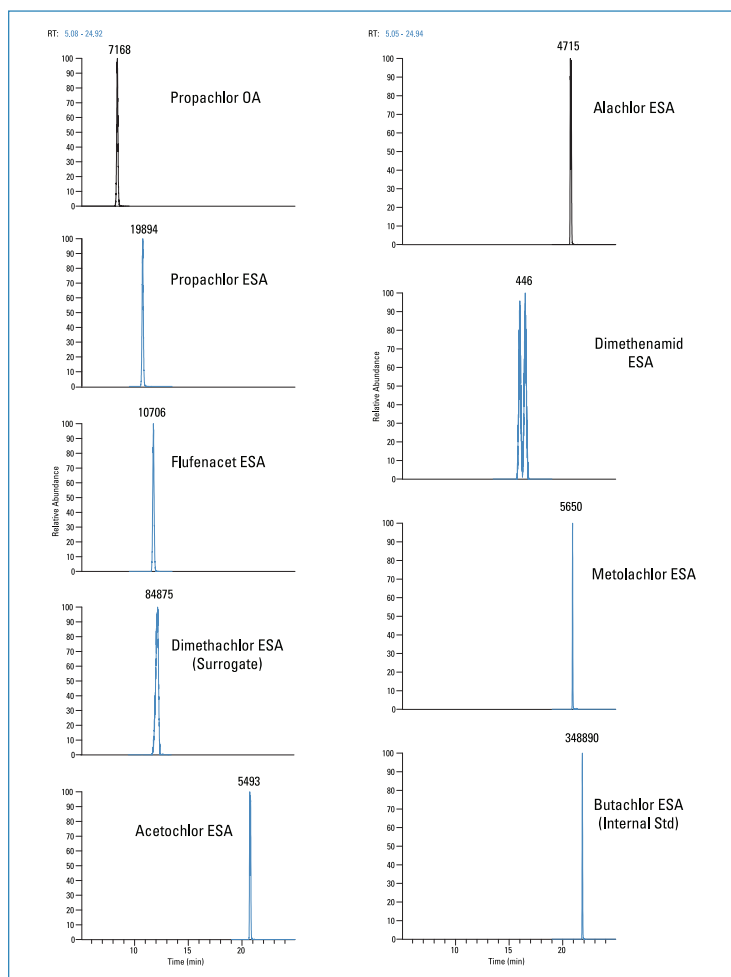


Figure 1: Chromatogram of the compounds at the lowest calibration level (Cal 05). The concentrations are given in Table 1.

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