Determination of Herbicide Degradates in Drinking Water on the Agilent 500 Ion Trap LC/MS (EPA 535)

Application Note

Environmental

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Abstract

The performance of the Agilent 500 Ion Trap LC/MS in EPA Method 535 is evaluated in terms of calibration and quantitative accuracy in a variety of matrices. The data reveals this instrument provides reliable quantitative data, even with the presence of highly concentrated surface water extracts.

Introduction

The Safe Drinking Water Act (SDWA) amended in 1996 requires the EPA to publish, every five years, a list of contaminants monitored in the nations public water supplies. On August 22, 2005, EPA proposed the design of the second Unregulated Contaminant Monitoring Rule (UCMR II) cycle [1]. This rule proposes monitoring 26 chemicals using nine different analytical methods between 2007 and 2011 for all large public water systems serving greater than 10,000, along with select small water systems.

EPA Method 535 is cited in the rule as the required method for monitoring ethanesulfonic acids (ESA) and oxanilic acid (OA) degradates of chloroacetanilide herbicides in drinking water [2]. These compounds are degradation products of parent acetanalides widely used for weed control on corn, soybean, and other crops [3]. Annual use for six of these compounds in total (Metolachlor, Alachlor, Acetochlor, Propachlor, Dimethenamide, and Flufenacet) between 1995 and 1998 was estimated to be 121 million pounds by the USGS [3]. The EPA is very interested in determining the degree of correlation between parent compound and degradate occurrence.

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Due to the polar nature of these degradates, LC/MS/MS was chosen for the analysis as it provided the necessary specificity required to quantitate them in matrices containing variable amounts of total organic carbon (TOC). LC ion trap mass spectrometry was used in the development of the method and is demonstrated as a reliable, quantitative technique for this analysis.

The performance of the Agilent 500 Ion Trap LC/MS in EPA Method 535 is evaluated in terms of calibration and quantitative accuracy in a variety of matrices. The surrogate standard (SS) Dimethachlor ESA (Figure 1) was used for matrix recovery and calibration experiments.
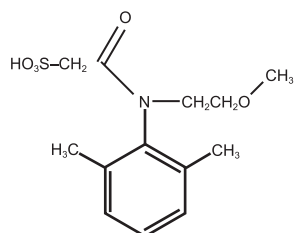

Figure 1.   Chemical structure of Dimethachlor-ESA.

Instrumentation

- Agilent 500 Ion Trap LC/MS, equipped with an electrospray ionization source (ESI) and built-in syringe pump

- Agilent ProStar 210 Binary Solvent Delivery Modules

- Agilent ProStar 420 AutoSampler

Materials and Reagents

10-20 mg each Dimethachlor-ESA (SS) and Butachlor ESA (internal standard-IS) were provided by the EPA National Environmental Research Laboratory in Cincinnati, OH. Methanol, HPLC and ACS grades provided by Fisher Scientific Co, Fair Lawn, NJ. Ammonium acetate, 99.99+ % purity, provided by Sigma-Aldrich, Milwaukee, WI. Solid Phase Extraction (SPE) with carbon type sorbents were used for this study.

Sample Concentration Unit: Agilent VacElut 20 Manifold, p/n 12234104 with large basin to accommodate 16 x 150 mm test tubes, with collection rack, (p/n 12234510).

Sample Preparation

Calibration Standards: Stock solutions of each analyte were prepared by weighing a small quantity of neat material into a volumetric flask and diluting with methanol. Substocks were then prepared at 100 ppm in methanol. Calibration standards were prepared in aqueous mobile phase (5 mM ammonium acetate) in which the concentration of the surrogate ranged from 10 ppb to 3000 ppb. Internal standard Butachlor ESA was added to all calibration standards and extracts.

Sample Matrix Preparation: Reagent water, finished tap water, and surface water were collected and preserved with ammonium chloride. The objective was to provide matrices that could be concentrated using the method sample preparation procedure, and then spiked to observe if quantitation accuracy and precision are maintained for SS-Dimethachlor-ESA. Using the following procedure as outlined in EPA 535, 250 mL of each water sample was extracted:

1. Rinse / clean the carbon cartridge with 20 mL 10 mM ammonium acetate in MeOH followed by 30 mL of reagent water, not allowing the cartridge to go dry in between these steps.

2. Extract the water samples at 10–15 mL/min, rinse with 5 mL reagent water, and dry under full vacuum for three minutes.

3. Elute the cartridge with 15 mL 10 mM ammonium acetate in MeOH at very low vacuum into a 16 × 150 mm test tube.

4. Evaporate the extract to dryness with a gentle stream of nitrogen gas at 70 °C using a hot block.

5. Dilute up to 1 mL with the mobile phase. Spike the extract with the internal standard Butachlor-ESA and a low, mid, or high concentration of SS-Dimethachlor-ESA.

Concentrations chosen for the experiment were starting aqueous concentrations of 0.2 and 2.0 µg/L, equivalent to final extract concentrations of 50 and 500 ppb.

HPLC Conditions

Column	Agilent Polaris C18A, 50 × 2 mm, 5 μm (Agilent p/n A2000-050 × 020)			
Solvent A	5 mM ammonium acetate			
Solvent B	methanol			
LC program	Time (min:sec)	%A	%B	Flow (mL/min)
	00:00	95	5	0.4
	02:00	75	25	0.4
	05:00	40	60	0.4
	10:00	20	80	0.4
	12:00	0	100	0.4
	15:00	95	5	0.4
Injection volume	20 μL			

MS Parameters

	SS-Dimethachlor-ESA	IS-Butachlor-ESA
Ionization mode	ESI negative	ESI negative
Transition	300 → 121 m/z	356 → 121 m/z
Needle	–2100 V	–2300 V
RF storage	m/z 99.1	m/z 78.4
API drying gas temp	400 °C	400 °C
API drying gas pressure	35 psi	35 psi
Shield	–600 V	–600 V
Waveform	Resonant	Resonant
Scan range	119–123 m/z	119–123 m/z

Results and Discussion

The LC method used faster gradient conditions with a shorter column to reduce the total analysis time and increase sample turn-around. This is possible with the Enhanced Charge Capacity (ECC) which provides the Agilent 500 Ion Trap LC/MS with the capability to reliably quantitate contaminants in complex samples. Calibration data in Figure 2 for SS-Dimethachlor- ESA shows an excellent correlation factor (r2) value over the calibration range studied (0.01 to 3 ppm).

The results obtained for the spiked matrices (Table 1) demonstrated excellent accuracy over the concentration ranges studied and the complexity of samples. As an example, the finished tap water extract was light brown in color, the surface water sample was much darker indicating a high dissolved organic content, likely from naturally occurring fulvic and humic acids to cause potential strong interfering effects.

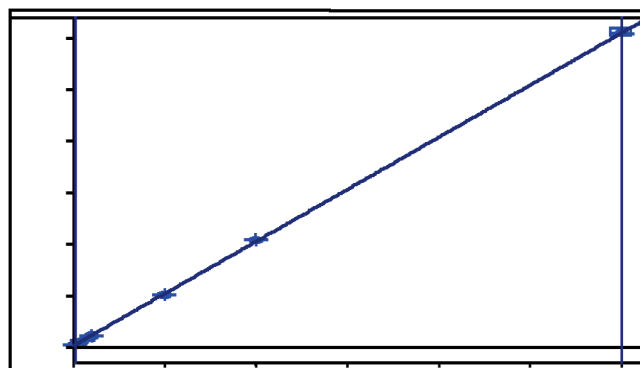Recovery criteria (70–130%) were in agreement with the EPA 535 method.

Figure 2.   Standard calibration curve for SS-Dimethachlor-ESA on 500-MS, (r^2) = 0.9999.

Table 1:   Average and % Recovery in Matrices, (n = 3 α each concentration) on the Agilent 500 Ion Trap LC/MS.

Final extract concentration, ppm	Surface water	Tap (Ground) water	Reagent water
0.05	0.048–96%	0.059–118%	0.05–100%
0.50	0.48–95%	0.44–87%	0.37–74%

Conclusion

The data clearly demonstrates that the Agilent 500 Ion Trap LC/MS provides excellent reliable quantitative data, even with the presence of highly concentrated surface water extracts. Surrogate recoveries met method specifications at all of the concentrations studied. Future work will include the entire validated procedure when target analytes of known and acceptable quality are available. The Agilent 500 Ion Trap LC/MS is proven to be the instrument of choice for this method and is a versatile tool for other environmental laboratory applications.

References

1   40 CFR Part 141, Unregulated Contaminant Monitoring Regulation (UCMR) for Public Water Systems Revisions; Proposed Rule

2   J. A. Shoemaker, M. V. Bassett, Method 535: Measurement of Chloroacetanalide and Other Acetamide Herbicide Degradates in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), Version 1.1, April 2005

3   United States Geological Survey (USGS), national maps: http://ca.water.usgs.gov/pnsp

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