



Determination of Herbicides in Drinking Water by LC-MS/MS Using Solid Phase Extraction and Modified USEPA 525.3

Application Note ENV0113

Keywords

USEPA (United States Environmental Protection Agency, SPE (Solid Phase Extraction), Residues, Herbicides, Drinking Water, Maximum Contamination Level Goals (MCLG), Simazine, Atrazine, Alachlor

Introduction

In 1974, the Safe Drinking Water Act was passed by the United States Congress. This law is enforced by the USEPA to make certain that there are Maximum Contamination Level Goals (MCLG) set for contaminants as an indicator to the public that when tested at or below this level, there are likely to be no harmful health effects in the drinking water supply^{1,2,3}. In this application, three commonly used herbicides were tested following Solid Phase Extraction (SPE) concentration of drinking water samples: Simazine, Atrazine, and Alachlor.

Materials & Methods

Materials

- Solid Phase Extraction Cartridges:
 - ASPEC Silica 6 mL, 1 g
 - Gilson PN: 54350506



Solid Phase Extraction Steps

1. **Condition 1:** 5 mL of MeOH@ 10 mL/min
2. **Condition 2:** 5 mL of MeOH@ 10 mL/min
3. **Condition 3:** 5 mL of H₂O @ 10 mL/min
4. **Condition 4:** 5 mL of H₂O @ 10 mL/min
5. **Load:** 10 mL of drinking water @ 5 mL/min
6. **Wash 1:** 5 mL of H₂O @ 10 mL/min
7. **Wash 2:** 5 mL of H₂O @ 10 mL/min
8. **Elute 1:** 3 mL of Acetone @ 3 mL/min
9. **Elute 2:** 3 mL of Acetone @ 3 mL/min

Sample Reconstitution

- Sample fractions were evaporated at 25°C for 30 minutes with nitrogen
- Evaporated fractions were reconstituted with 1 mL of reconstitution solution composed of H₂O/ACN (60/40).

Chromatographic Conditions

- **Mobile Phase:** 1.000 mL/min
 - **A:** 1mM ammonium formate in (ACN/Water, 10/90), 0.1% Formic acid
 - **B:** 1mM ammonium formate in (ACN/Water, 90/10), 0.1% Formic acid

GRADIENT			
Time (min)	MPA (%)	MPB (%)	Flow (mL/min)
0.00-0.20	60	40	1.000
0.21-1.00	20	80	1.000
1.01-3.00	60	40	1.000

- **Column:** 3.0 x 30 mm C18, 2.5 µm @ 23 °C
- **MS Splitting Flow:** 0.30 mL/min
- **Detector:** Sciex API 3000
 - **Turbo Ion Spray Heater Gas Flow:** 8000 cc/min
 - **Turbo Ion Spray Heater Temperature:** 375 °C, ESI⁺, MRM SCAN
- **Injection Volume:** 10 µL



Results

Analysis of drinking water samples for presence of Simazine, Atrazine, and Alachlor demonstrated adequate response from 1 ng/mL through 100 ng/mL. Blank drinking water samples were absent of each main compound. The ion suppression effect was at 2% for each compound, indicating that the SPE process to cleanup and concentrate drinking water samples did not impact overall quantitation.

Recovery results for Atrazine show a range of 83-85% recovery for six samples varying from 1 ng/mL to 100 ng/mL levels. Simazine shows similar recovery ranges. Recovery results for Alachlor show a range of 67-72% recovery for six samples varying from 1 ng/mL to 100 ng/mL levels (Table 1).

Figure 1: LC-MS/MS Results and Ion Suppression Results of Simazine, Atrazine, and Alachlor

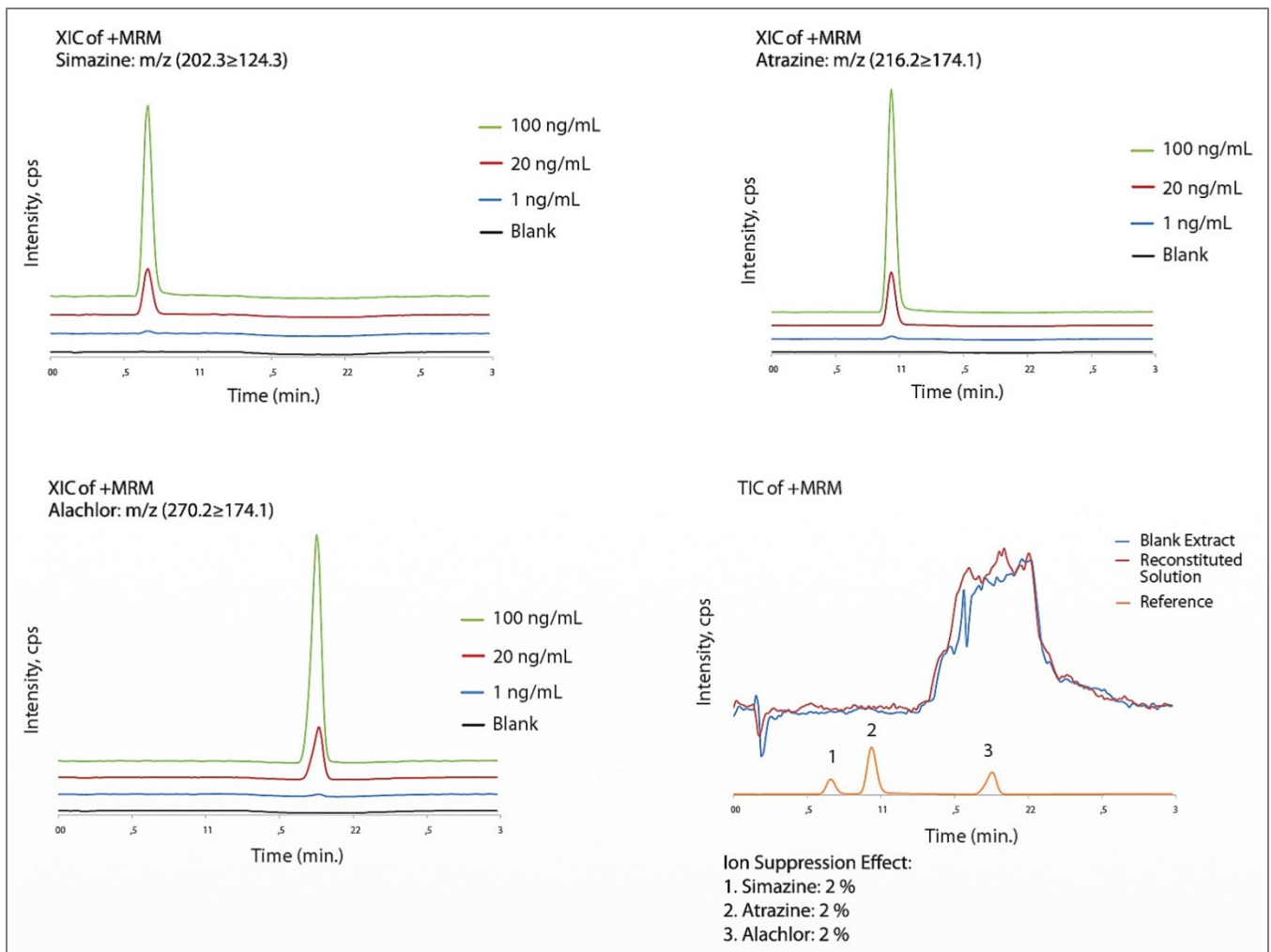




Table 1: LC-MS/MS Recovery Results of Simazine, Atrazine, and Alachlor in Drinking Water

HERBICIDES MEAN RECOVERY with Relative Standard Deviation (RSD)			
Pesticides	Fortification Levels (ng/mL)	Recovery (% for N=6)	RSD (%)
Atrazine	1	83	6
	20	84	3
	100	85	2
Simazine	1	85	7
	20	84	2
	100	83	2
Alachlor	1	72	7
	20	70	2
	100	67	3

Conclusion

Drinking water recoveries from LC-MS/MS analysis were obtained for 1, 20, and 100 ng/mL fortification levels. Recovery results were lower for Alachlor compared to Atrazine and Simazine recovery values. This application demonstrated that with only 10 mL of drinking water, ion suppression could be removed and lower level detection limits of 1 ng/mL were detectable and quantifiable without interferences. Results from this SPE application with Gilson ASPEC Silica cartridges shows no ion suppression impact.

References

1. Environmental Protection Agency (2012). Basic Information about Simazine in Drinking Water. <http://water.epa.gov/drink/contaminants/basicinformation/simazine.cfm>
2. Environmental Protection Agency (2012). Basic Information about Atrazine in Drinking Water. <http://water.epa.gov/drink/contaminants/basicinformation/atrazine.cfm>
3. Environmental Protection Agency (2012). Basic Information about Alachlor in Drinking Water. <http://water.epa.gov/drink/contaminants/basicinformation/alachlor.cfm>