Achieving the Desired Prescribed Sensitivities of Selected Herbicides by Direct On-Column Aqueous Injection of Potable and Environment Samples Using the Agilent 6410BA LC/QQQ

Application Note

Environmental

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Abstract

Here we describe the analysis of 20 selected herbicides by direct on-column aqueous injection of environmental water samples of several matrices with little pretreatment. We demonstrate that this approach fulfills sufficient sensitivity requirements outlined by the UK Drinking Water Inspectorate. Precision data obtained were typically in the range of 2.2 to 7.0% and analyte recoveries were between 90.2 to 104.7%. Limits of detection were less than 10 ng/L (10 ppt) for all of the compounds in this suite.

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Introduction

Several sample preparation/analysis approaches are available for the determination of herbicides in water samples, typically LC/MS after solid phase extraction (SPE) and even LC/MS employing on-line analyte enrichment [1]. Solid phase extraction is time consuming and adds an expense to the method with consumable materials and additional man-hours. On-line enrichment [ibid], on the other hand, requires the purchase of additional hardware, such as switching valves and an additional LC pump. With the introduction of affordable, reliable and sensitive LC/QQQ instrumentation such as the Agilent 6410BA triple quadrupole LC/MS system, it is now possible to achieve prescribed analysis requirements by injecting aqueous samples directly onto the analytical column using conventional injection volumes of up to 100 µL.

The aim of this application note is to demonstrate a reliable and robust analytical method for the analysis of 20 selected herbicides in potable and environmental water samples, with a performance criteria of < 12.5% analyte precision, analyte recoveries in the range of 90 to 110%, and limits of detection < 10 ng/L (10 ppt).

The method presented here describes the analysis of a mixture of 20 acidic, neutral, and basic herbicides (Figure 1) in different water matrices by direct aqueous injection. An overview of the full validation data is summarized.

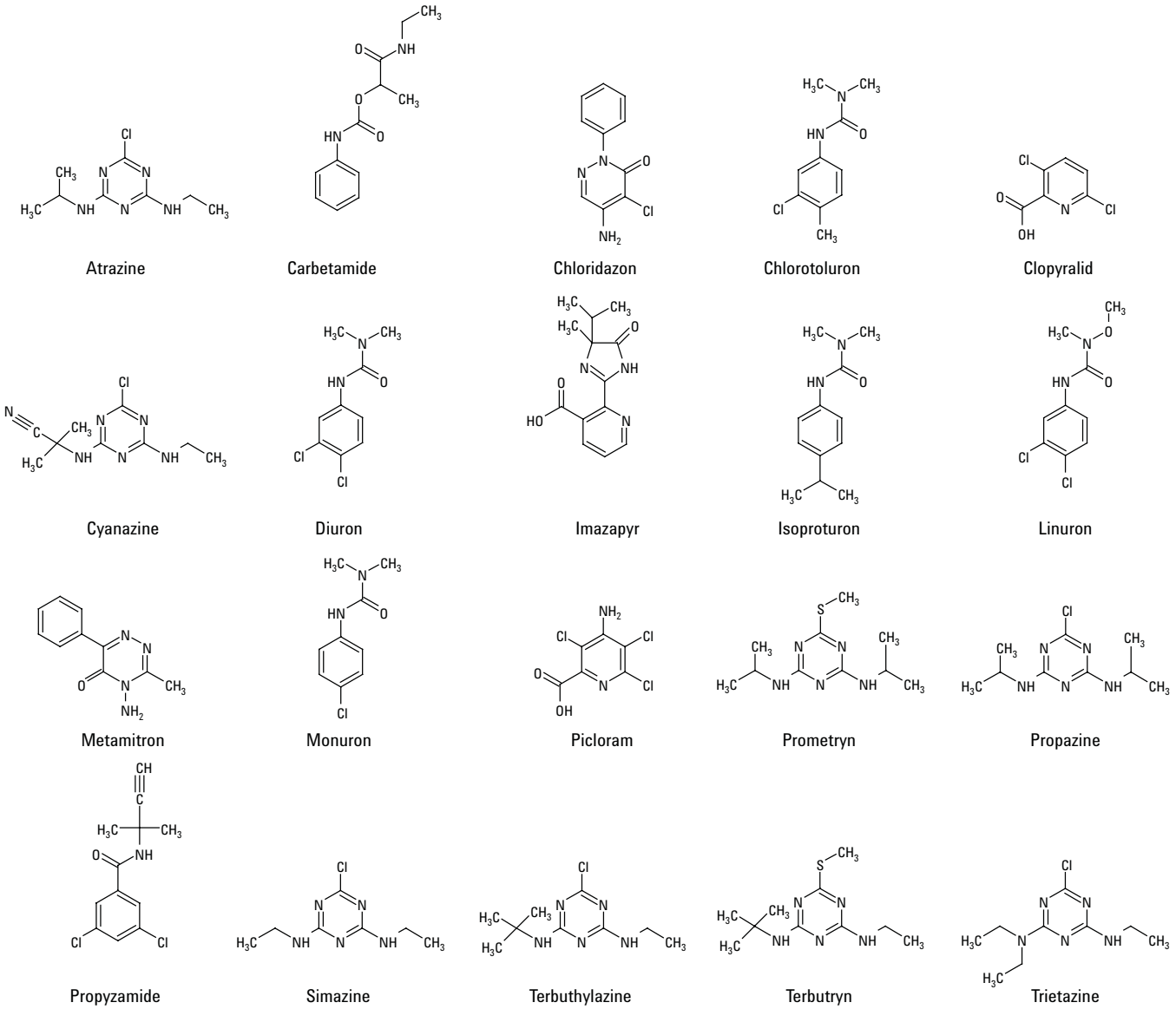

Figure 1. Suite of neutral, acidic, and basic herbicides.

Experimental

This analysis was performed using an Agilent LC/QQQ 6410BA mass spectrometer upgraded with a hotbox kit coupled to an Agilent 1200 Series LC system. The LC system consisted of a binary pump (G1312B), vacuum degasser (G1379B), automatic liquid sampler (G1367C), thermostatted column compartment (G1316B), and MassHunter data system. The hotbox upgrade kit (G2573A) comprised an additional MS turbo-pump with controller and replacement entrance and exit lenses for the collision cell.

Sample Preparation

Minimal sample preparation was required, which was simple acidification of all standards and samples. These were acidified to a concentration of 0.1% formic acid, which was used as the pH modifier.

Instrumentation

LC Conditions

Column:	Agilent ZORBAX SB-C18, 2.1 × 100 mm 1.8 µm thermostatted at 70 °C
Mobile phase	A: 0.1% formic acid in HPLC water B: methanol

Gradient program:

Time (min)	A (%)	B (%)	Flow rate (mL/min)
Initial	95	5	0.3
0.5	95	5	0.3
1.0	80	20	0.3
20.0	20	80	0.3
20.1	95	5	0.3

Injection volume:	100 µL
Total run time:	26.0 min

QQQ MS Conditions

Source Conditions

Electrospray AP-ESI:	Positive ionization polarity
Drying gas temperature and flow:	300 °C, 10 L/min
Nebulizer gas pressure:	40 psi
Capillary voltage:	3000 V
Fragmentor voltage:	See Table 1
MRM parameters:	See Table 1

MRM Parameters

Table 1. MRM Transitions for Herbicide Suite

Time seg	Time (min)	Delta EMV (V)	Compound	Precursor ion (*m/z*)	Product ions (*m/z*)	Fragmentor voltage (V)	Collision energy (V)	Dwell time (msec)
2	0.2	600	Clopyralid	192.0	146.2	75	19	400
			Clopyralid	192.0	174.2 (q)*	75	6	100
3	6.4	600	Picloram	241.0	223.1	95	9	400
			Picloram	241.0	195.0 (q)*	95	18	100
4	7.6	400	Metamitron	203.1	175.1	115	14	90
			Metamitron	203.1	104.1 (q)*	115	22	90
			Imazapyr	262.2	234.3	130	14	90
			Imazapyr	262.2	217.2 (q)*	130	17	90
			Chloridazon	222.1	104.2	135	22	90
			Chloridazon	222.1	92.1 (q)*	135	27	90
5	10.0	400	Carbetamide	237.1	192.3	80	2	70
			Carbetamide	237.1	72.2 (q)*	80	22	70
			Monuron	199.1	72.2	105	16	70
			Monuron	199.1	126.1 (q)*	105	25	70
			Cyanazine	241.2	214.2	125	12	70
			Cyanazine	241.2	104.1 (q)*	125	31	70
			Simazine	202.1	132.2	125	16	70
			Simazine	202.1	104.1 (q)*	125	27	70
6	14.5	400	Chlorotoluron	213.1	72.2	110	21	250
			Chlorotoluron	213.1	140.2 (q)*	110	24	250
7	15.6	400	Diuron	233.1	72.2	110	22	90
			Diuron	233.1	160.3 (q)*	110	26	90
			Atrazine	216.2	174.2	120	15	90
			Atrazine	216.2	104.1 (q)*	120	32	90
			Isoproturon	207.2	72.2	110	22	90
			Isoproturon	207.2	165.3 (q)*	110	10	90
8	17.0	400	Prometryn	242.2	200.3	135	17	30
			Prometryn	242.2	158.2 (q)*	135	24	30
			Terbutryn	242.2	186.2	120	17	30
			Terbutryn	242.2	91.2 (q)*	120	30	30
			Linuron	249.1	182.1	105	18	100
			Linuron	249.1	160.3 (q)*	105	12	100
			Propazine	230.2	188.2	125	15	30
			Propazine	230.2	146.1 (q)*	125	24	30
			Terbuthylazine	230.2	174.2	110	15	30
			Terbuthylazine	230.2	104.1 (q)*	110	30	30
			Propyzamide	256.1	190.1	95	12	30
			Propyzamide	256.1	173.0 (q)*	95	22	30
9	19.6	400	Trietazine	230.2	202.2	130	18	250
			Trietazine	230.2	99.2 (q)*	130	24	250

*(q) = Qualifier ion

Results and Discussion

The total ion chromatogram (TIC) for a 0.5 µg/L (500 ppb) standard consisting of this 20 herbicide suite is shown in Figure 2, which also illustrates the positioning of the time segmentation.

Five levels of calibration standards were used to prepare the calibration curves over the concentration range of 0.0, 0.05, 0.10, 0.30, and 0.50 µg/L. Selected and representative calibration curves are shown in Figures 3a through 3c.

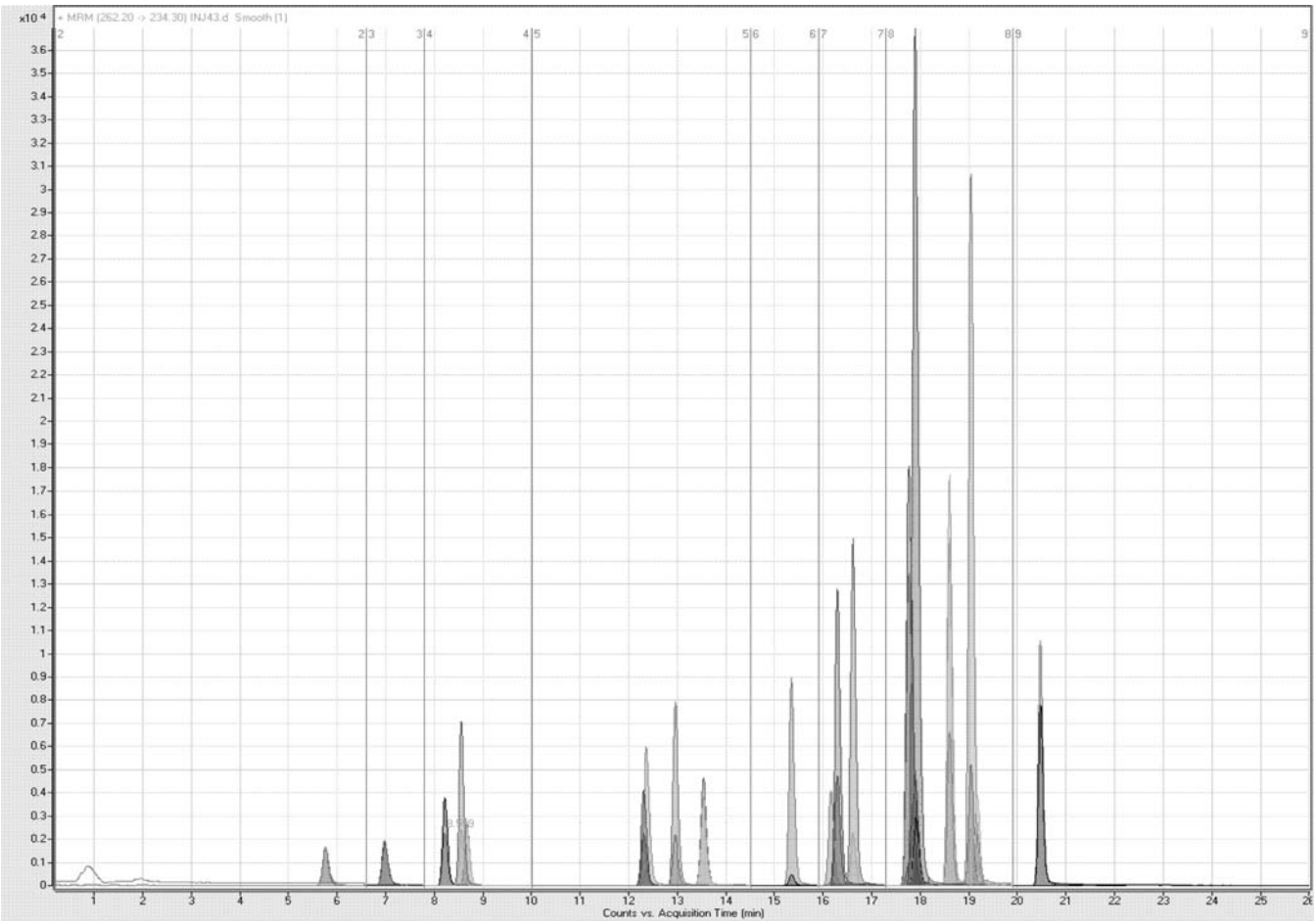

Figure 2. MRM overlay showing 20 herbicides from 0.5 µg/L standard.

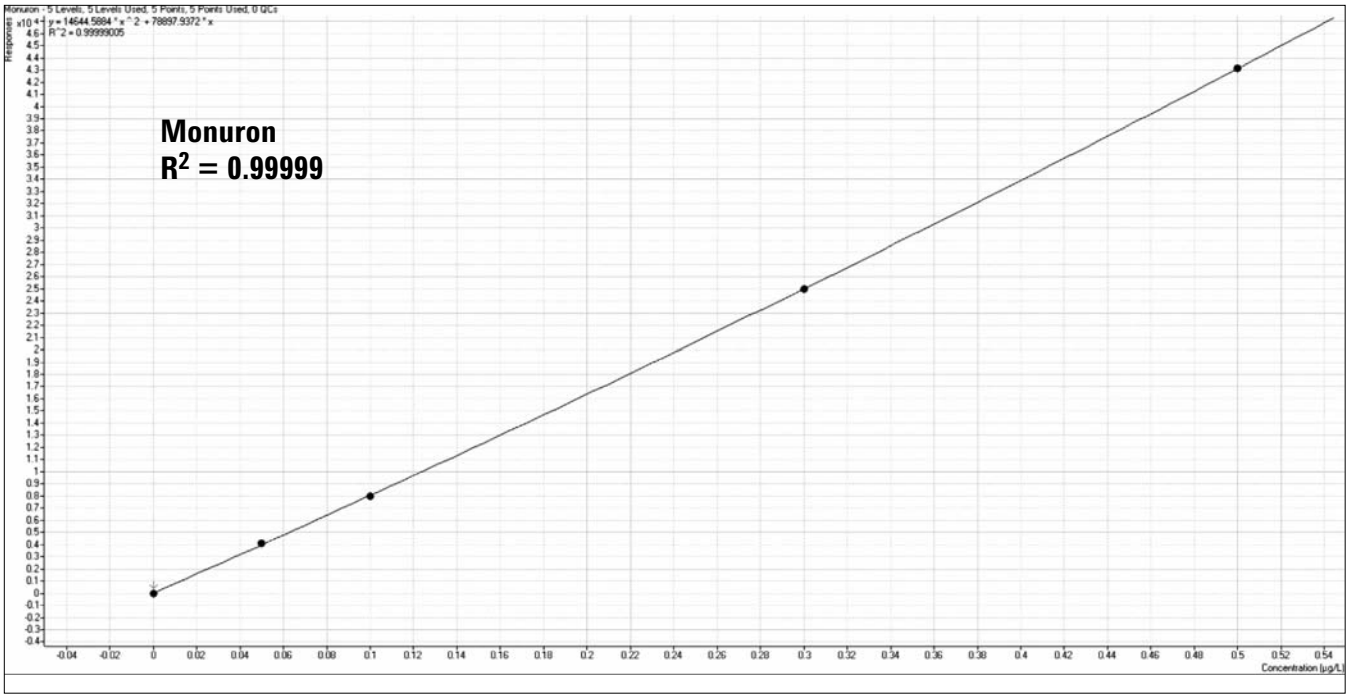

Figure 3a. Monuron calibration curve.

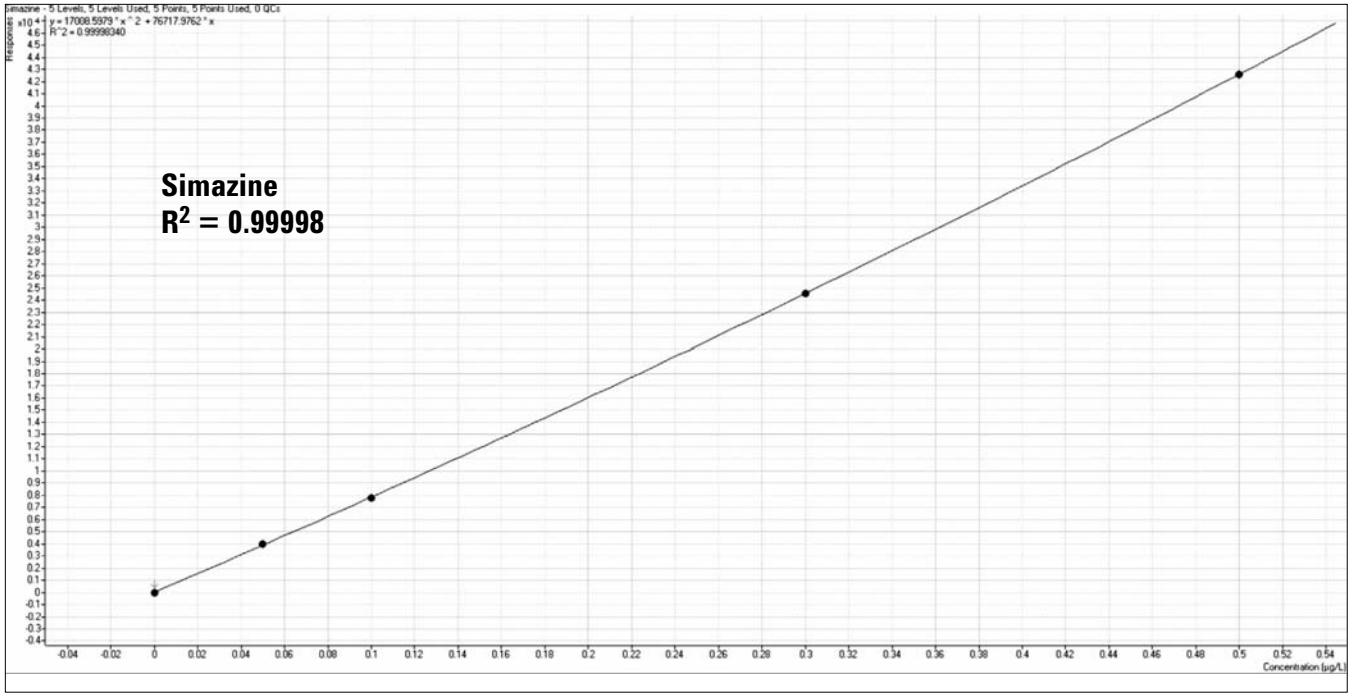

Figure 3b. Simazine calibration curve.

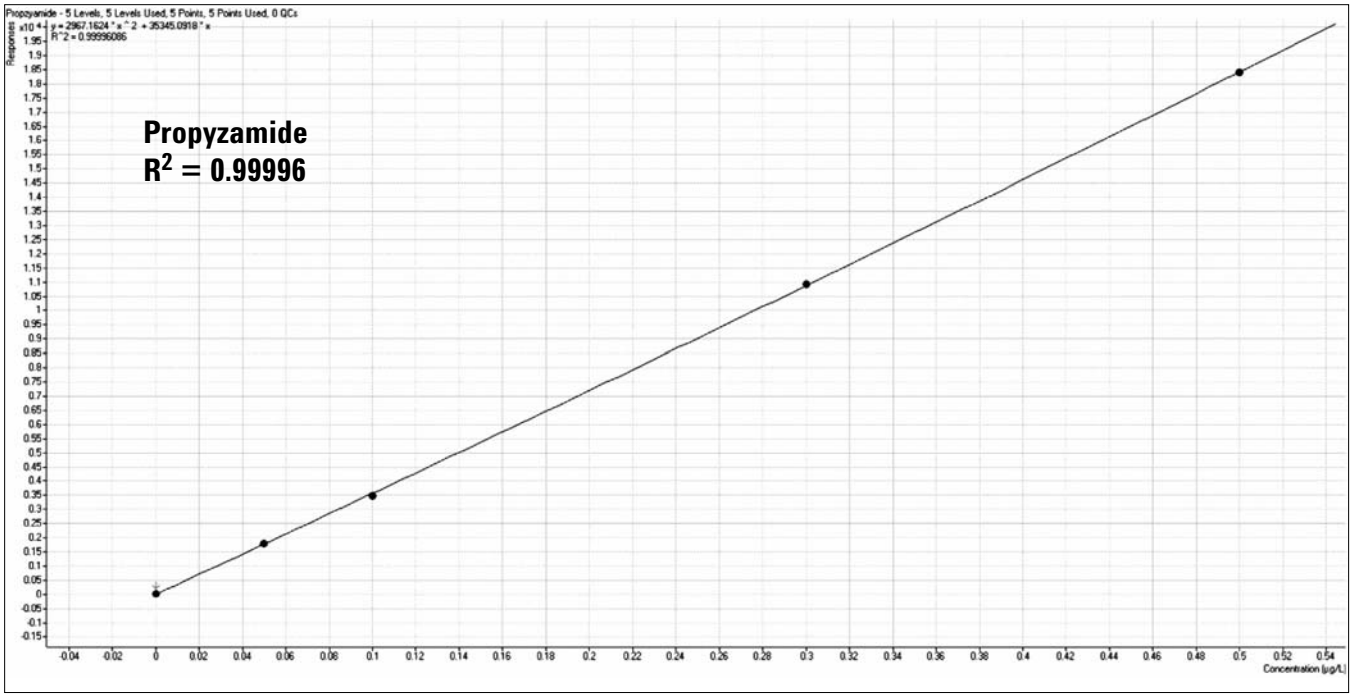

Figure 3c. Propyzamide calibration curve.

Validation of the method was carried out on 11 batches of samples. Borehole groundwater, potable water (which was from a surface water source), and river water were spiked at two levels (0.01 and 0.10 µg/L). Deionized water was spiked at three levels with analytical quality control material at 0.01, 0.10, and 0.40 µg/L. Each batch of samples was analyzed in duplicate and in a random order. The limit of detection (LOD) for each herbicide was calculated from the within-batch standard deviation (5 x sw) of the deionized water spiked at 0.01 µg/L. Recovery for the groundwater, potable water, and river water was calculated from the 0.1 µg/L spike.

Experimental results are shown in Table 2.

Table 2. Validation Data: %Recovery, ±%RSD, and Limit of Detection (LOD)

Compound	Borehole groundwater %Rec	Potable water %Rec	River water %Rec	LOD (µg/L)
Clopyralid	100.8 ± 5.7	104.7 ± 5.7	101.4 ± 7.0	0.007
Picloram	99.7 ± 4.0	94.2 ± 4.0	94.3 ± 5.5	0.005
Metamitron	100.5 ± 4.3	96.2 ± 3.9	97.1 ± 3.4	0.003
Imazapyr	101.7 ± 3.4	97.9 ± 3.2	97.3 ± 3.9	0.005
Chloridazon	99.7 ± 3.5	93.0 ± 4.5	92.9 ± 4.5	0.004
Carbetamide	98.0 ± 5.2	90.2 ± 4.7	93.8 ± 3.9	0.009
Monuron	99.8 ± 3.3	92.5 ± 3.8	90.8 ± 3.5	0.005
Cyanazine	99.4 ± 4.5	91.0 ± 4.5	92.7 ± 3.2	0.004
Simazine	100.1 ± 2.9	98.9 ± 2.9	98.2 ± 3.1	0.004
Chlorotoluron	99.5 ± 3.2	99.9 ± 3.8	99.7 ± 3.7	0.003
Diuron	98.3 ± 3.7	100.2 ± 5.0	98.9 ± 5.3	0.006
Atrazine	99.4 ± 2.2	99.4 ± 2.9	100.5 ± 3.5	0.002
Isoproturon	99.1 ± 3.8	99.7 ± 3.7	99.0 ± 3.9	0.003
Prometryn	99.7 ± 2.9	100.1 ± 3.0	100.5 ± 3.5	0.003
Terbutryn	99.0 ± 2.9	99.1 ± 3.4	99.7 ± 3.3	0.002
Linuron	99.3 ± 5.8	100.2 ± 3.3	102.4 ± 6.4	0.003
Propazine	99.6 ± 3.2	99.9 ± 3.3	99.4 ± 2.9	0.002
Terbuthylazine	99.8 ± 3.8	99.0 ± 3.0	100.6 ± 2.9	0.003
Propyzamide	101.4 ± 4.4	99.4 ± 3.3	99.8 ± 3.8	0.004
Trietazine	99.9 ± 2.8	100.0 ± 2.7	101.0 ± 2.5	0.002
Overall suite	**99.7 ± 3.8**	**97.8 ± 3.7**	**98.0 ± 4.0**	**0.004**

Selected and representative examples of MRM chromatograms derived from real sample matrices are shown in Figure 4.

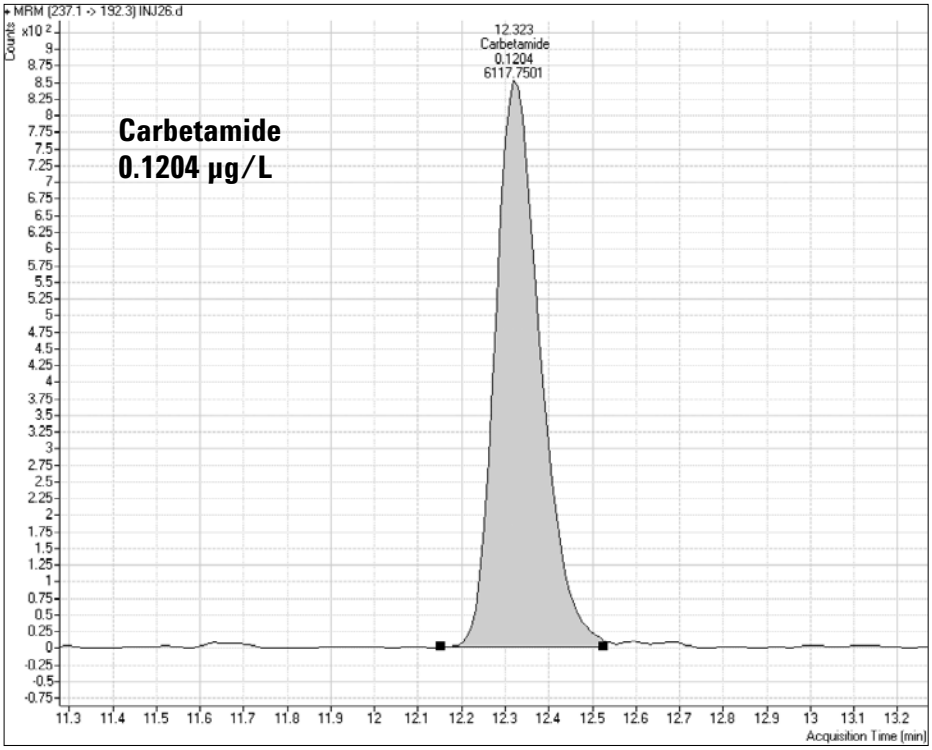

Figure 4a. MRM chromatogram of carbetamide (river water matrix).

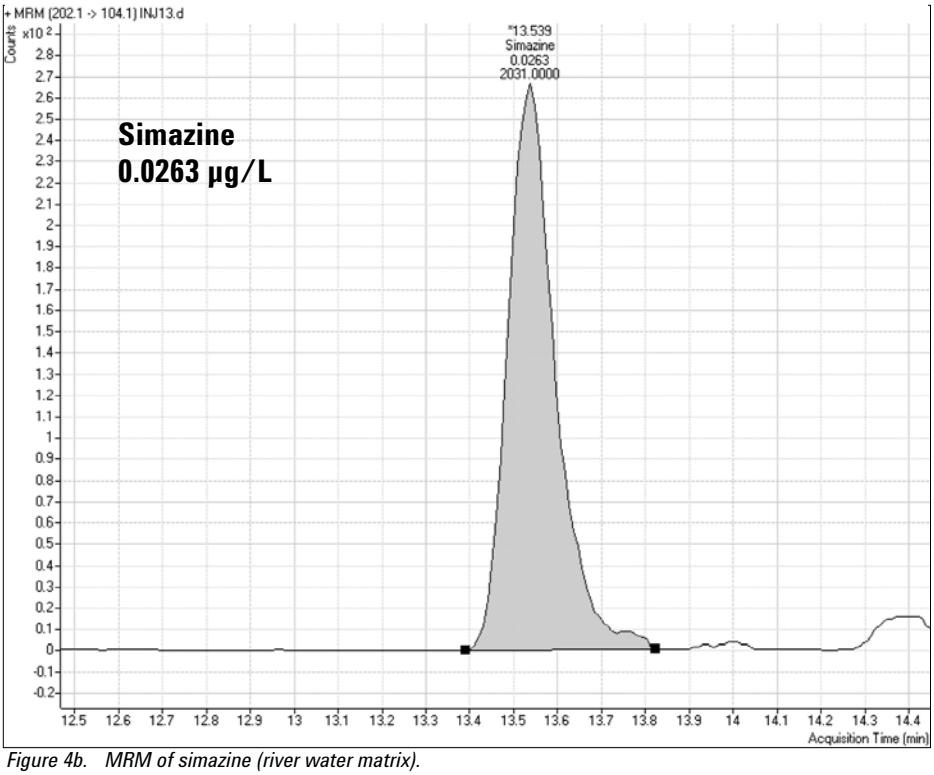

Figure 4b. MRM of simazine (river water matrix).

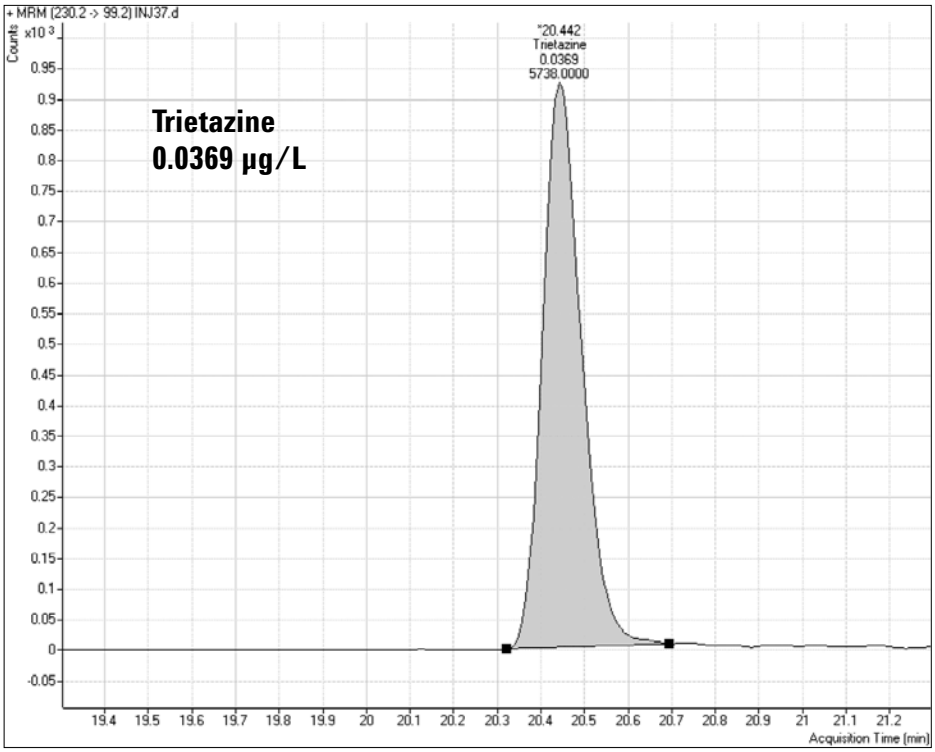

Figure 4c. MRM of trietazine (river water matrix).

Conclusions

The data show that the method herein presented is capable of sensitive and quantitative analysis for the 20 herbicides in a single analytical suite by a direct aqueous injection of 100 µL sample volumes onto the analytical column. Only sample acidification was undertaken as a preparation stage. All the method performance criteria are met, which are < 12.5% analyte precision, recoveries in the range of 90 to 110%, and limits of detection < 10 ng/L (10 ppt).

We demonstrate in this application note that direct aqueous injection of 100 µL samples onto the analytical column achieves the required method performance levels and is possible due to the sensitivity and selectivity of the Agilent LC/QQQ 6410BA instrumentation. The net benefit of such an approach to this methodology is a direct cost reduction in the form of consumable items (solid phase cartridges), which are no longer required, together with significant man-hour cost reductions since only minimal sample preparation is undertaken (acidification).

Reference

1. "Determination of Phenyl Urea and Triazine Herbicides in Potable and Groundwaters by LC/MS Using AP-ESI Selective Ion Monitoring and Direct Large Volume Aqueous Injection," Agilent Technologies publication 5989-0813EN.

For More Information

For more details concerning this application note, please contact Neil Cullum at Anglian Water Services Laboratory, Huntingdon, Cambridgeshire, UK.

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