Determination of Acidic Herbicides using an Agilent 6460 Triple Quadrupole LC/MS Equipped with Agilent Jet Stream Technology and Direct Aqueous Injection, for Potable and Environmental Samples

Application Note

Environmental

Authors

Neil Cullum
Anglian Water Services Laboratory
Huntingdon
Cambridgeshire
United Kingdom

Peter JW Stone
Agilent Technologies Inc
Stevens Creek Boulevard
Santa Clara, CA, 95051
USA

Abstract

The analysis of a suite of acidic herbicides by direct aqueous injection in several water matrices is presented, therefore negating the need for solid phase extraction. Standard deviations in the range of 2.5% to 6.6% for analyte precision and recoveries of between 91.5% and 105.1% were observed over 11 batches of samples. Limits of detection were less than 10 ng/L (10 ppt) for all the compounds in the suite thus meeting current industry standards.

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Introduction

Acidic herbicides cover a broad range of compounds which are widely used in crop protection and general weed control. Therefore, reliable and robust methods are required for their detection in potable and environmental waters. Currently, typical sample preparation and analytical techniques include solid phase extraction (SPE) followed by derivatisation for GC/MS or simply SPE for LC/MS analyses. Both methods are time consuming and the derivatising agents used in GC/MS techniques can be particularly hazardous.

Acidic herbicides are predominately ionized in negative ionization mode via LC/MS. They give a relatively low response when compared to other herbicides, such as the phenyl urea and triazine compounds that typically undergo positive ionization. Therefore, acidic herbicides traditionally require some form of sample enrichment before analysis. With the introduction of the new Agilent 6460 Triple Quadrupole LC/MS with Jet Stream Technology an increase in sensitivity of up to 5 to 10 times can be realized when compared to the Agilent 6410 Triple Quadrupole LC/MS. This increase in sensitivity allows the analysis of this class of compounds to be performed by direct aqueous injection, eliminating costly consumables such as SPE cartridges and other time-consuming sample preparation steps. [1]

The aim of this application note is to demonstrate a reliable and robust analytical method for the analysis of acidic herbicides in potable and environmental water samples, with an industry 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 acidic herbicides (Figure 1) in different water matrices by direct aqueous injection. An overview of the full validation data is summarized.

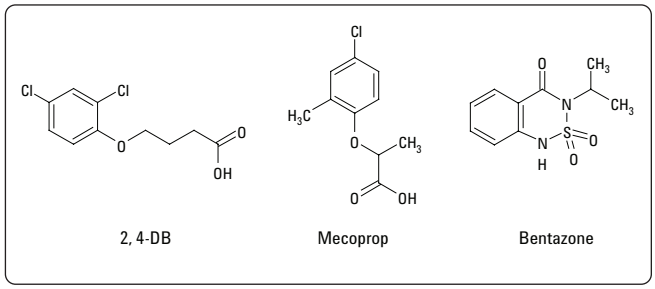

Figure 1. Molecular structures of selected acid herbicides.

Experimental

This analysis was performed using an Agilent 6460 Triple Quadrupole Mass Spectrometer 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.

Sample Preparation

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

Instrumentation

LC Conditions

Column:	Agilent ZORBAX SB C18, 2.1 mm × 100 mm, 1.8 µm, thermostatted at 60 °C
Mobile phase	A: 0.2% acetic acid in HPLC water B: acetonitrile

Gradient program:

Time (min)	A (%)	B (%)	Flow rate mL/min
Initial	95	5	0.3
0.5	95	5	0.3
8.0	68	32	0.3
20.0	35	65	0.3
20.1	95	5	0.3

Injection volume:	100 µL
Total run time:	26.0 min

Triple Quadrupole MS Conditions

Spray chamber conditions:	Electrospray interface (Positive ionization):	
	Gas temperature:	275 °C
	Drying gas:	Nitrogen 8 L/min
	Nebulizer pressure:	45 psig
	V_{cap} voltage:	3500 V
	Sheath gas temp:	300 °C
	Sheath gas flow:	Nitrogen 11 L/min
	Nozzle voltage:	500 V
	Electrospray interface (Negative ionization):	
	Gas temperature:	250 °C
	Drying gas:	Nitrogen 8 L/min
	Nebulizer pressure:	45 psig
	V_{cap} voltage:	2000 V
	Sheath gas temp:	300 °C
	Sheath gas flow:	Nitrogen 11 L/min
	Nozzle voltage:	500 – 1000 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 ion (m/z)	Product ions (m/z)	Fragmentor voltage (V)	Collision energy (V)	Dwell time (msec)
1	0.0	400	Aminopyralid +ve ion	206.8	161.0	75	15	500
2	2.8	500	Clopyralid +ve ion	192.0	146.2	65	19	500
3	4.9	500	Picloram +ve ion	241.0	195.0	75	18	500
4	7.0	300	Imazapyr +ve ion	262.2	234.3	95	14	500
5	9.0	0	Quinmerac +ve ion	222.0	204.0	75	6	500
6	11.1	500	Bromacil +ve ion	261.1	205.1	85	11	100
			Fluroxypyr +ve ion	255.0	209.1	90	9	300
			Benazolin +ve ion	244.0	170.0	90	20	100
			Bentazone +ve ion	241.1	199.2	80	6	100
7	13.8	400	Bromoxynil -ve ion	275.9	79.0	130	40	100
			2,4-D -ve ion	219.1	161.0	80	7	300
			MCPA -ve ion	199.2	141.1	90	7	100
8	15.3	400	Ioxynil -ve ion	369.9	127.0	135	50	125
			Triclopyr -ve ion	254.1	196.1	65	6	125
			2,4,5-T -ve ion	253.1	195.1	75	7	125
			Dichloroprop -ve ion	233.1	161.0	75	5	125
			Mecoprop -ve ion	213.2	141.1	80	9	125
9	17.3	400	2,4-DB -ve ion	247.1	161.0	65	7	300
			MCPB -ve ion	227.2	141.1	65	0	300
10	18.6	400	Propyzamide -ve ion	254.2	228.2	125	9	500

Results and Discussion

The TIC MRM chromatogram for a 0.5 µg/L (500 ppt) standard consisting of this acidic herbicide suite is shown in Figure 2 which also illustrates the positioning of the time segmentation.

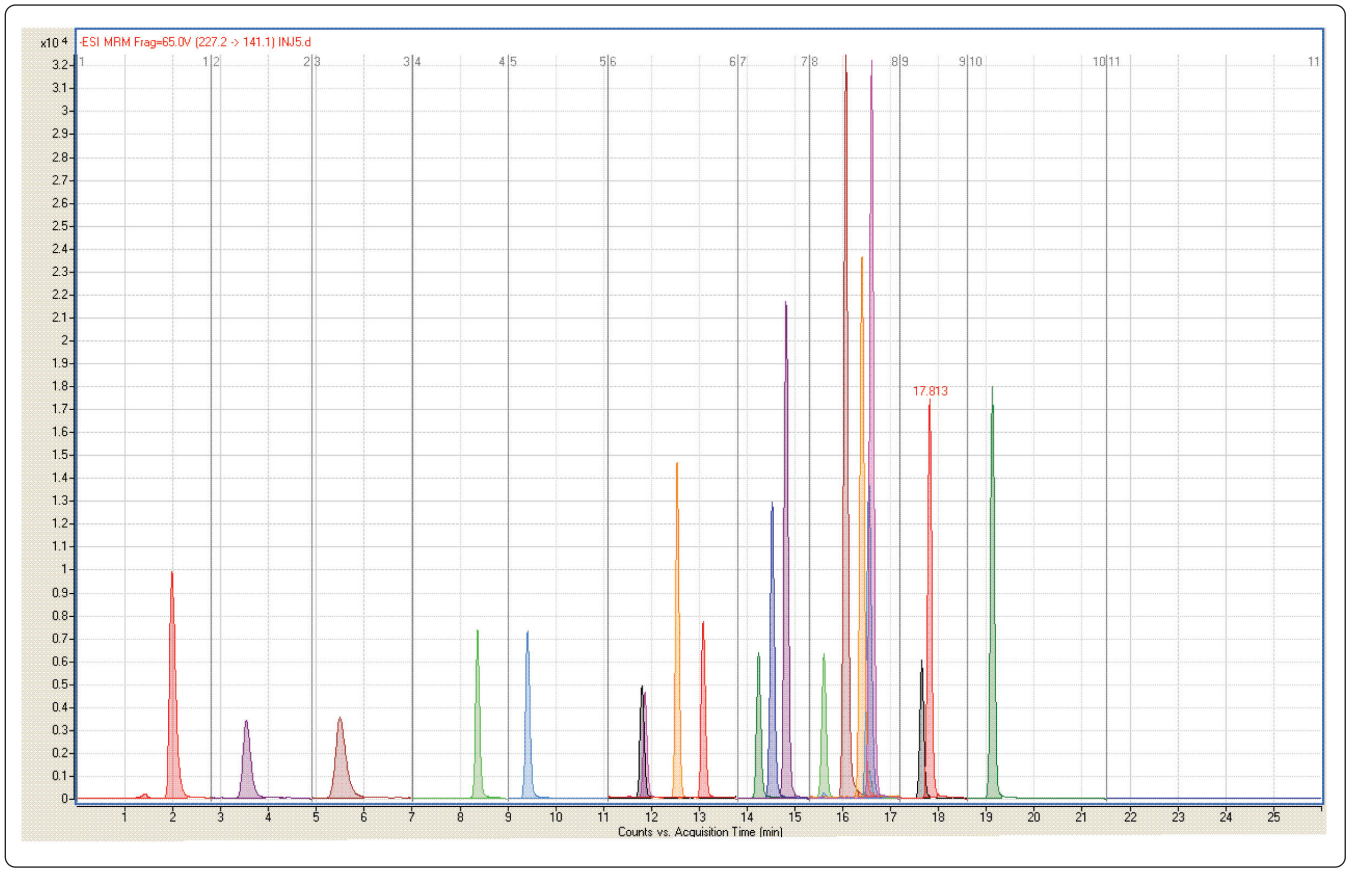

Figure 2. Total ion MRM chromatogram of 0.5 µg/L standard.

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 (ppb). Selected and representative calibration curves are shown in Figures 3a through 3c.

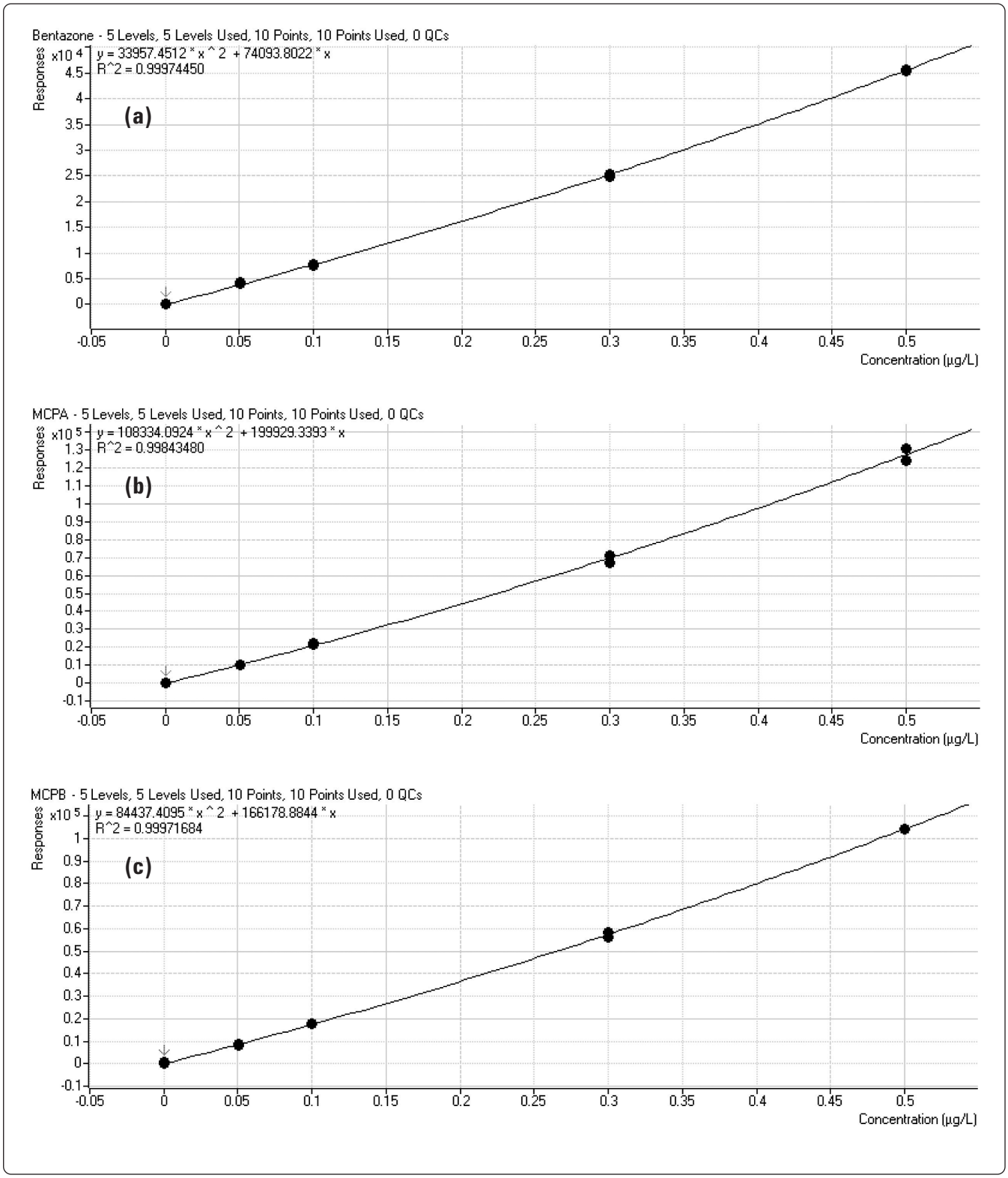

Figure 3. Calibration curves of (a) Bentazone, (b) MCPA and (c) MCPB.

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 µg/L (10 ppt) and 0.10 µg/L (100 ppt). Deionized water was spiked at three levels with Aqc material at 0.01 µg/L, 0.10 µg/L 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 × sw) of the deionized water spiked at 0.01 µg/L. Recoveries for the groundwater, potable water and river water were calculated using each respective 0.1 µg/L (100 ppt) matrix spike.

The overall experimental and validation results are shown in Table 2.

Table 2. Validation data – %Recovery, ± %RSD and the Limit of Detection (LOD)

Compound	Borehole %Rec	Tap Water %Rec	River Water %Rec	LOD (ug/L)
Clopyralid	96.6, ± 4.6	91.5, ± 3.4	91.9, ± 6.6	0.004
Picloram	102.1, ± 3.5	105.1, ± 2.5	99.9, ± 4.5	0.003
Benazolin	97.0, ± 5.1	95.2, ± 3.4	96.2, ± 5.3	0.005
Fluroxypyr	100.0, ± 6.3	96.9, ± 3.5	97.3, ± 4.0	0.003
Bromacil	99.0, ± 3.6	94.9, ± 3.6	92.3, ± 4.7	0.003
Bentazone	99.2, ± 4.4	97.1, ± 3.7	96.6, ± 3.3	0.004
Bromoxynil	99.0, ± 4.4	97.1, ± 5.8	94.8, ± 4.4	0.005
2,4-D	96.9, ± 3.9	96.9, ± 3.9	96.4, ± 2.9	0.005
MCPA	97.7, ± 4.1	94.4, ± 4.4	95.8, ± 3.7	0.004
Triclopyr	97.8, ± 5.0	94.9, ± 5.4	97.0, ± 4.0	0.006
Ioxynil	99.7, ± 4.8	101.3, ± 4.7	98.6, ± 3.7	0.004
Dichloroprop	98.3, ± 4.9	96.6, ± 3.1	96.7, ± 3.0	0.002
Mecoprop	97.4, ± 3.4	97.6, ± 3.5	96.2, ± 2.5	0.003
2,4,5-T	96.2, ± 4.5	95.1, ± 4.6	96.3, ± 3.4	0.004
2,4-DB	100.0, ± 4.0	98.1, ± 3.5	97.2, ± 3.5	0.004
MCPB	98.5, ± 4.1	97.1, ± 3.4	97.4, ± 3.1	0.003
Propyzamide	99.2, ± 4.2	99.0, ± 2.5	99.8, ± 3.0	0.002
Overall Suite	98.5, ± 4.4	97.0, ± 3.8	96.5, ± 3.9	0.004

Aminopyralid, imazapyr and quinmerac are included in the suite but for screening analysis only.

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

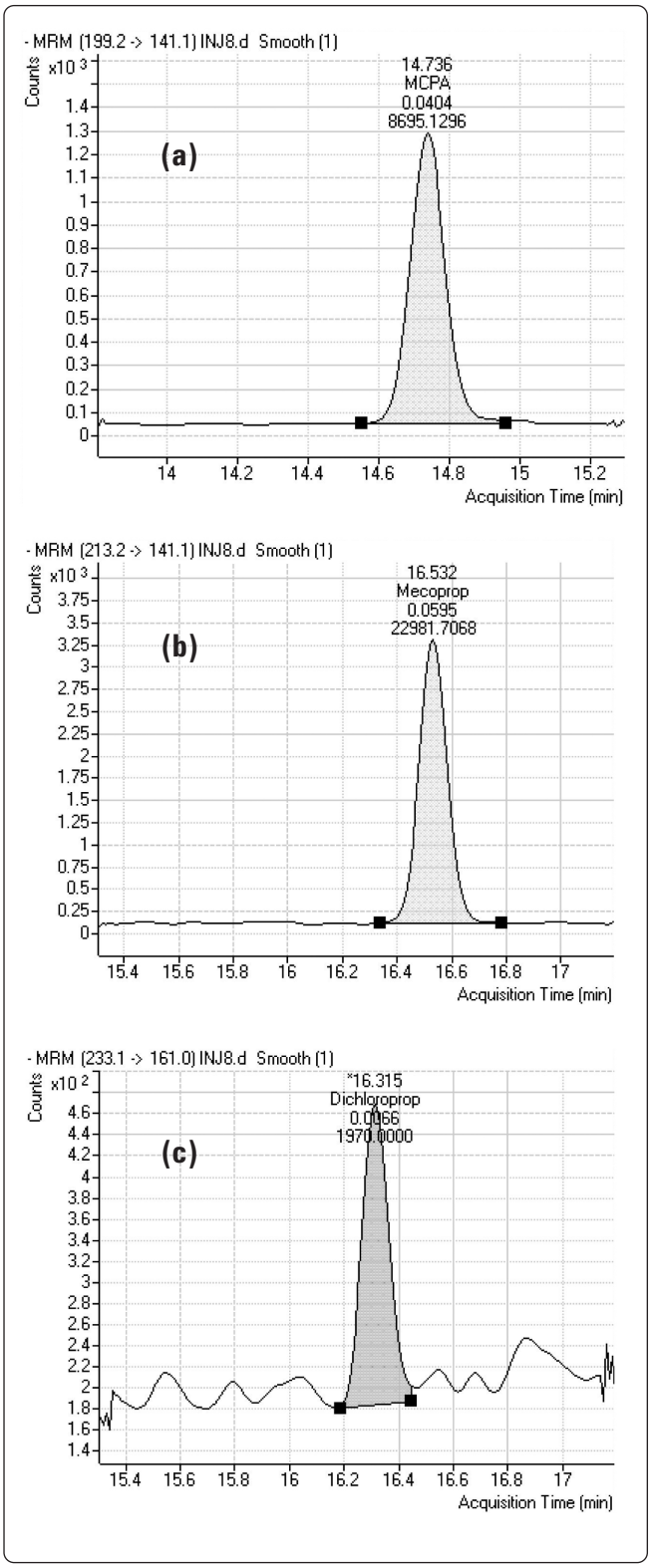

Figure 4. MRM chromatogram (EIC) of (a) MCPA in river water; (b) mecoprop in river water; (c) dichloroprop in river water.

Conclusions

The data show that this method is capable of a sensitive and quantitative analysis for the acidic herbicides in a single analytical suite by a direct aqueous injection of 100-µL sample volumes onto the analytical column. This can be achieved without a need for SPE sample preparation; only sample acidification was undertaken as a preparation stage. All of the current industry method performance criteria are met, which include ≤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 analytical method performance levels, through sensitivity increases and selectivity with the Agilent 6460 Triple Quadrupole LC/MS instrumentation equipped with Agilent Jet Stream Technology. The net benefits of such an approach to this methodology are direct and significant cost reduction in consumable items (solid phase cartridges), which are no longer required and significant labor reductions with minimal sample preparation necessary.

References

1. "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," Agilent Technologies publication 5990-3762EN.

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

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