[TECHNOLOGY BRIEF]

Using Large Volume Injections to Increase Sensitivity for Pesticide Detection in Water Samples

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GOAL

To demonstrate the increase in sensitivity afforded by performing a larger volume injection using Waters® Pesticide Screening Application Solution with UNIFI®.

BACKGROUND

Ever-decreasing detection limits due to advances in mass spectrometry have led to numerous studies on trace-level contaminants in the environment and food. Typically, tandem quadrupole MS is preferred for sub-ppb level contaminant level analysis, but uses a targeted approach. Using Waters® Xevo® G2-S QTof, screening for both known and unknown compounds in the ppb range is easily achievable. However, by increasing the volume of injected sample, significant increases in sensitivity can be attained. When combined with the excellent mass accuracy (<3 ppm) of the Xevo G2-S QTof, the ability to perform screening experiments at such low levels is of great utility to many environmental analyses, where unknown or large numbers of contaminants make relying on MS/MS alone not ideal.

THE SOLUTION

A 100-µL extension loop was installed on to the ACQUITY UPLC® I-Class System to allow the increased sampling volume. Two different water samples, one bottled drinking water and local tap water, were used for this study.

Using a 100-µL injection volume of water matrices, the sub-ppb range LODs and LOQs are achievable for spiked pesticides.

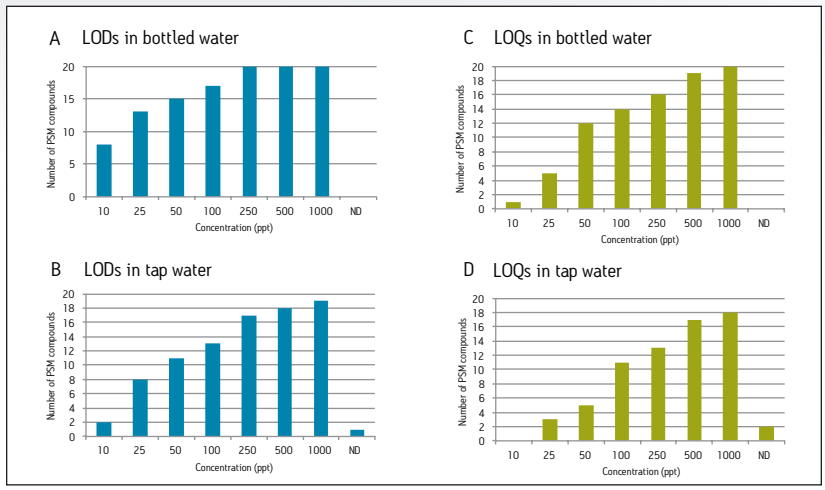

Figure 1. Number of pesticide screening mix (PSM) compounds that are found to have LODs (A and B), and LOQs (C and D) at the specified concentrations for bottled water (A and C), and a local tap water source (B and D).

A calibration series, composed of 7 points ranging from 10 to 1000 ppt, was prepared by addition of the Waters Pesticide Screening Mix (PSM). This certified standard mix contains 20 pesticides of varying polarities and chemical classes. Tap water samples were filtered through a 0.45-µm PTFE filter prior to injection. The bottled drinking water was injected with no cleanup, due to its previously observed cleanliness and lack of matrix effect on the pesticides studied here. In a previous experiment not displayed here, the PTFE filter was found to be an appropriate filter for these compounds, based on results that assessed retention on the filter by comparing the pre- and post-filter spike response of the pesticides

in matrix. Limits of detection (LODs) and limits of quantification (LOQs) were calculated for all 20 pesticides, Figure 1, and were based on peak to peak signal-to-noise (S/N) ratios of 3 and 10, respectively. As shown in Figure 1, sensitivity of the 20 pesticides was better in bottled water than tap water, most likely because of the increased complexity of the tap water matrix. Figure 2 shows the S/N calculation in UNIFI for the pesticide chlortoluron. Linearity was also investigated for those compounds which had at least 5 points of the calibration series over the LOQ. These results are displayed in Table 1.

SUMMARY

The use of Waters Pesticide Screening Application Solution with UNIFI with larger injection volumes has been shown to be effective in the analysis of trace contaminants in water samples.

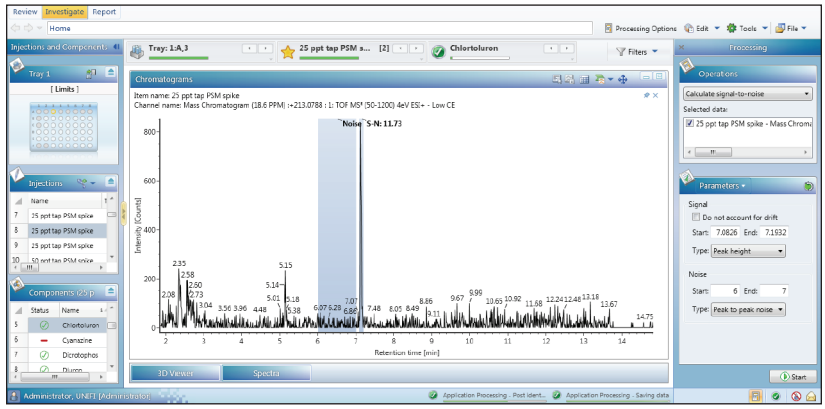

Figure 2. The determination of S/N in UNIFI for chlortoluron at 25 ppt in tap water; the S/N >10 makes this the experimentally determined LOQ for chlortoluron in the tap water sample.

	Bottled water			Local tap water		
	R^2	LOD (ppt)	LOQ (ppt)	R^2	LOD (ppt)	LOQ (ppt)
Acephate	NA	250	500	NA	250	500
Atrazine	NA	25	100	NA	25	100
Atrazine-desethyl	0.994	25	50	NA	50	100
Buprofezin	0.996	25	50	NA	1000	ND
Chlortoluron	0.998	10	25	0.995	10	25
Cyanazine	NA	50	100	NA	500	1000
Dicrotophos	0.999	10	10	NA	250	500
Diuron	0.998	10	25	0.998	25	25
Fenpropimorph	NA	250	1000	NA	ND	ND
Hexazinone	0.997	10	25	NA	25	100
Linuron	0.999	25	50	NA	50	100
Methamidophos	NA	100	250	NA	250	500
Methomyl	NA	100	500	NA	250	500
Metobromuron	0.998	10	50	0.991	25	50
Metolachlor	0.999	10	50	0.986	25	50
Metoxuron	0.999	10	25	0.999	10	25
Monolinuron	NA	50	250	NA	50	250
Sebuthylazine	0.998	10	50	NA	25	100
Simazine	NA	250	500	NA	100	250
Terbuthylazine	0.998	25	50	NA	100	100

Table 1. Analysis performance for 20 pesticides in bottled and tap waters. R^2 values are listed here for the compounds in the PSM which had at least 5 points above the LOQ as observed for both water types. Generally, very good linearity (R^2>99) was observed, although fewer pesiticides with 5 data points above the LOQ were observed in tap water because of matrix effects.

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