Detection of pesticides at 20 parts per trillion in drinking water by LC/MS/MS using direct injection with no sample pretreatment.

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Introduction

Pesticides are well known potential contaminants of drinking water supplies. As such water companies are required to screen water for contamination of pesticide classes such as organophosphate, organonitrogen, triazins, carbamates, acid herbicides and phenol urea pesticides. The required lower limit of quantitation for these pesticides is usually 100 ppt with a detection limit of 20 ppt and a CV of analysis of ideally 12% or below at the limit of detection.

Traditional methods usually use different sample pretreatments, e.g. solid phase extraction procedures, for each class of pesticide due to their differing polarities. This means that a multiple pesticide screen of one water sample is time consuming. This poster investigates the use of LC/MS/MS with high volume injections as a method to detect multiple classes of pesticides at the required limits of detection with no sample pretreatment.

Materials and Methods

A method was setup to screen for 50 pesticides from a selection of different classes in one period. For testing purposes standards from a selection of several different classes of pesticides were initially made up in methanol and then diluted into water. All mass spectrometry analysis was performed in positive electrospray mode

The pesticides included the urons isoproturon & MTBA, organonitrogen pesticides trietazin, propachlor & tebuconazole, triazine pesticides tebutylazine, atrazine, propazine, the organophosphate pesticide coumaphos, Chlorpyriphos-methyl & the carbamate carbendazim. All the 50 transitions were screened in one period using resolution settings of unit for Q1 and Q3 quadrupoles and dwell times of 60ms with a source temperature of 600 °C.

Compound	*Q1 (amu)*	*Q3 (amu)*
Propachlor	212	170
Tebuconazole	308	70
Tebutylazine	230	174
Atrazine	216	174
Propazine	230	146
Chlorpyriphos-methyl	322	125
Coumaphos	363	227
Isoproturon	207	72
MTBA	222	165
Carbendazim	192	160

Chromtagraphic separation was performed on a ACE C18 column 4.6 x 50 mm, 5µm using a gradient of water and methanol both containing 5mM ammonium acetate, 0.1% formic acid and a column temperature of 30 °C. Unless stated the injection volume was 500µl and the flow rate 1.5 ml/min directly into the TurboV™ source of an API 4000™ LC/MS/MS system. The Mobile phase was supplied by two LC-10AD*vp* ™ pumps from Shimadzu, and samples were injected using a SIL-HTc™ autosampler from Shimadzu fitted with a 2 mL sample loop. Data analysis was carried out using Applied Biosystems/MDS Sciex Analyst® 1.4.1 software.

Results

Calibration curves for all 10 test pesticides were obtained over the range 20 – 5,000 parts per trillion. The r value for these lines varied between > 0.98 using a Linear fit with 1/x weighting. An example of one such line is shown below in Figure 1 and an example of a typical chromatogram from a 100ppt standard is shown in Figure 2.

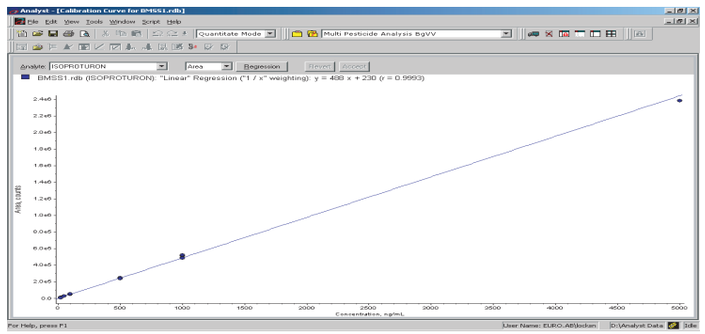

Figure 1. Calibration line for Isoproturon 20 – 5,000 ppt.

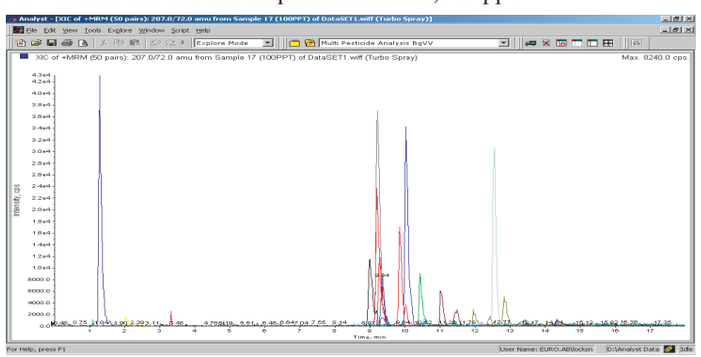

Figure 2. Chromtogram obtained from a 100ppt standard of 10 pesticides.

In order to gauge the effect of injection volume a comparison of a 50 and 500 µl injection of a 100ppt standard were compared. It can be seen in Figure 3 that by injecting 10 times the volume an increase by a factor of 10 is seen in intensity. 5 replicate 500 µl injections at 20, 50 and 1000 ppt gave CVs often below 12% as shown for Propachlor in Figure 4, even when an internal standard was not used.

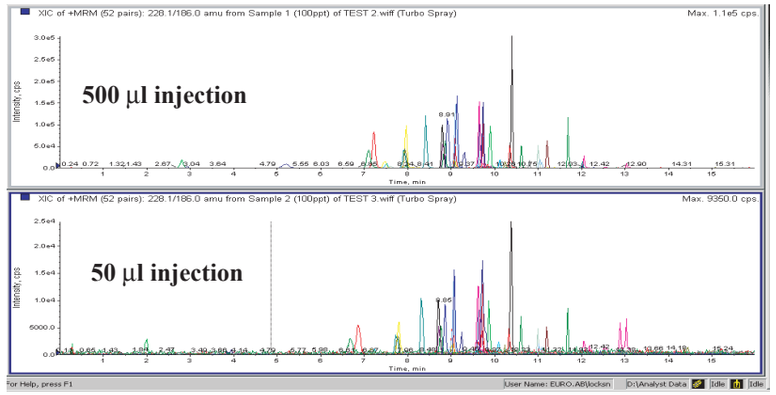

Figure 3. Comparison of a 50 and 500 µl injection of a 100 ppt standard containing 50 pesticides.

Propachlor Standards	20PPT	50PPT	1000PPT
Number Of Values Used	5 of 5	5 of 5	5 of 5
Data Point #1	19.335025	53.572137	1005.1902
Data Point #2	20.135466	49.867155	1031.625
Data Point #3	21.360955	48.45889	1011.3702
Data Point #4	18.86466	50.460645	1026.6069
Data Point #5	17.305656	49.805195	1064.9717
Mean	19.400352	50.432804	1026.8774
Low	17.305656	48.45889	1005.1902
High	21.360955	53.572137	1064.9717
Standard Dev.	1.505269	1.901734	21.040489
%CV	**7.758977**	**3.770828**	**2.048978**
Accuracy	97.001761	100.86561	102.68774

Figure 4. Comparison of CVs obtained from 500 µl injections of a 20, 50 & 1,000 ppt Propachlor standards.

Conclusions

From these results it can be concluded that pesticides are detectable & quantifiable in drinking water at the required limits by large volume injections on an API 4000 LC/MS/MS system, giving CVs of often <12% without internal standards. This methodology has been applied successfully to over 50 acid herbicides and organo-nitrogen, organo-phosphorus, triazins and uron pesticides routinely screened for in UK drinking water. With further development work ongoing, this method is currently being expanded to an increasing group of pesticides. With this approach separate sample preparation for each compound class has been eliminated greatly improving throughput in pesticide residue analysis of water

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