


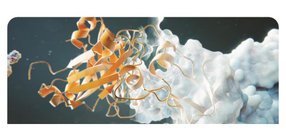


A Robust and Sensitive Method for the Direct Analysis of Polar Pesticides in **Environmental** Samples Without Derivatisation

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Introduction

The prevalence of multi-residue LC-MS/MS analyses for the quantification PPCP in environmental samples has been steadily increasing for many years, and they are now considered to be a minimum requirement of most laboratories working in these fields. Modern tandem quadrupoles are capable of detecting such regulated compounds at very low levels with minimal sample preparation, such as large volume injection without need of preconcentration. thereby enabling labs to process large numbers of samples for many analytes with a fast turnaround. However, some very polar compounds which are not amenable to the extraction procedure, chromatographic method or are poor ionizers require additional single-residue methods which involve time-consuming preparation and separation and often involve derivatization to improve detection.

Key Advantages Presented

- All analytes were well retained, allowing detection of the majority of background components which could otherwise interfere. Separation between the analytes was also sufficient to allow unambiguous identification, and retention times were reproducible. Sensitivity in spiked environmental waters was found to be similar to that in standards, and the target limit of detection of 20 ng/L was easily achieved with real drinking water samples.
- Matrix effects were largely eliminated in both the NofaLab method for food sample extracts and the modified method for direct injection of water samples. Use of QTRAP® is expected to confirm positive results by their full-scan MS/MS spectra, but future work will investigate different or additional clean-up.

Mass spectrometry: The SCIEX QTRAP 6500+ system was employed for its sensitivity and robustness. Optimized MRM transitions, detailed in Table 1, were selected and utilized for maximum sensitivity. Isotopically labelled target analytes (AMPA 13C15N, glyphosate 1,2-13C2 15N, fosetyl-aluminium D15) were utilized as internal standards for achieving the highest quality quantification. Note that AMPA 13C15ND2 was also used for the correction of glufosinate results. Details of ion source parameters can be found in table below.

Table 1. List of analytes with MRMs transitions and parameters.

Pesticide	Q1 m/z	Q3 m/z	RT (min)
AMPA 1	110	63	4.3
AMPA 2	110	79	4.3
AMPA IS	112	63	4.3
Glufosinate 1	180	63	4.4
Glufosinate 2	180	85	4.4
Glufosinate 3	180	95	4.4
Glufosinate IS	183	63	4.4
Fosetyl-Al 1	109	63	5.3
Fosetyl-Al 2	109	81	5.3
Fosetyl-Al IS	114	82	5.3
Glyphosate 1	168	63	8.4
Glyphosate 2	168	81	8.4
Glyphosate 3	168	150	8.4
Glyphosate IS	171	63	8.4

Table 2. Ion source parameters. Electrospray ionization (ESI) conducted in negative ion mode.

Parameter	Setting
Curtain Gas (CUR)	35 psi
Collision Gas (CAD)	9
Ion Spray voltage (IS)	-3500 V
Temperature (TEM)	700 °C
Nebulizer Gas (GS1)	55 psi
Heater Gas (GS2)	65 psi

Results

Environmental and drinking water samples varied widely in the degree of comprised particulate matter, which causes difficulties for LC injection and is detrimental to reproducibility. However, minimal sample preparation is desirable in a high throughput laboratory situation and SPE type clean-up would add significant time and financial cost. In order to overcome these challenges, a simple filtration step using Chromacol 17-SF-02 (RC) from 17 mm syringe filters was performed when transferring samples to the LC vials. Internal standards to a final concentration of 1ppb were added to samples and standards, and QC samples in tap water were prepared in a similar fashion. Experiments were also performed using standard addition to the samples to investigate any potential matrix effects.

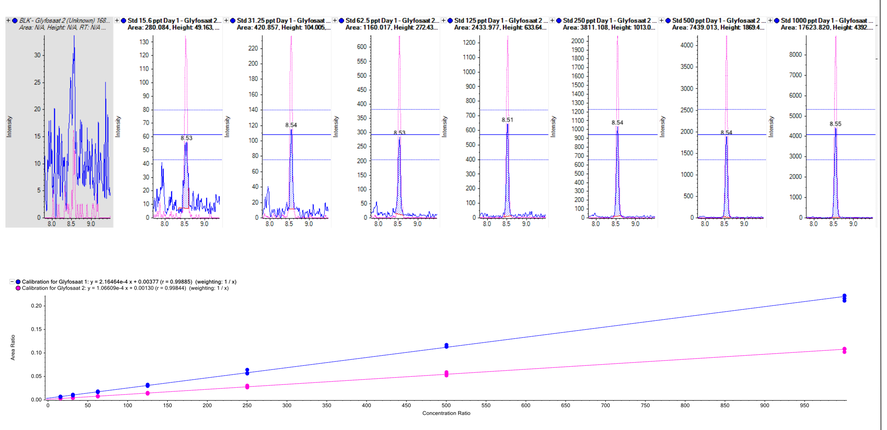

Figure 1. Method sensitivity and linearity of glyphosate. Calibration standards in concentrations from 15.6 to 1000 ng/L of glyphosate achieved using the modified method for water samples. Ion ratios were all well within the specified ±20% tolerance.

Separation was achieved using a Shimadzu Nexera UHPLC system comprising LC-30AD pumps, a SIL-30AC autosampler fitted with a 500µL loop and a CTO-20A column oven. An injection volume of 500µL was employed in a chromatographic method similar to that used for the food samples. During verification of the method, the primary focus was on achieving stable peak shapes and retention times for all analytes. Loop size (irrespective of injection volume), initial conditions, gradient and pH of the mobile phase had very significant effects, so the final optimized method should be fixed, and fresh mobile phases prepared regularly.

Method verification was performed with real drinking water samples, testing for both AMPA and Glyphosate, a LOQ of 20ng/L could be reached.

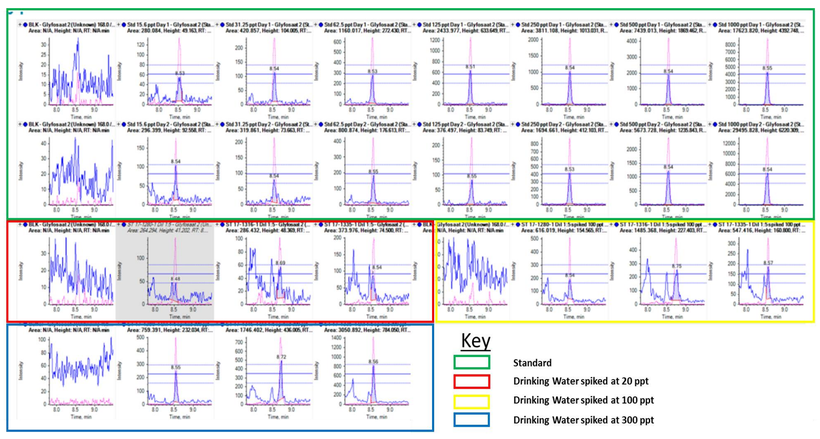

Figure 2. Example chromatography from drinking water samples using the modified water method

Sensitivity in spiked environmental waters was found to be similar to that in standards, and the target limit of detection of 20 ng/L was easily achieved with real drinking water samples. In order to verify the results, analyses with standard addition of the target compounds were also performed.

Accreditation results

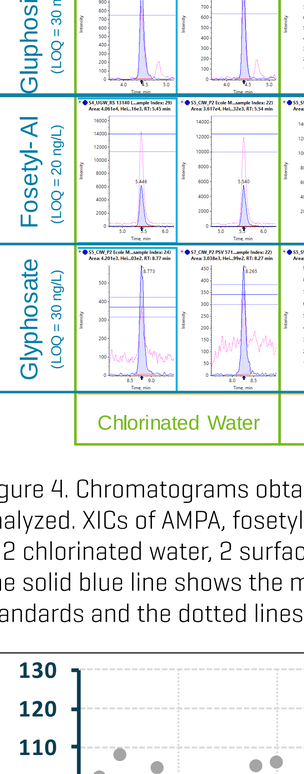

Figure 3. Common structure of the analytical series done for accreditation.

Figure 4. Chromatograms obtained at LOQ levels for the 3 water types analyzed. XICs of AMPA, fosetyl-Al, glufosinate and glyphosate at LOQ level in 2 chlorinated water, 2 surface water and 2 underground water samples. The solid blue line shows the mean ion ratio calculated among the standards and the dotted lines a tolerance of 20%.

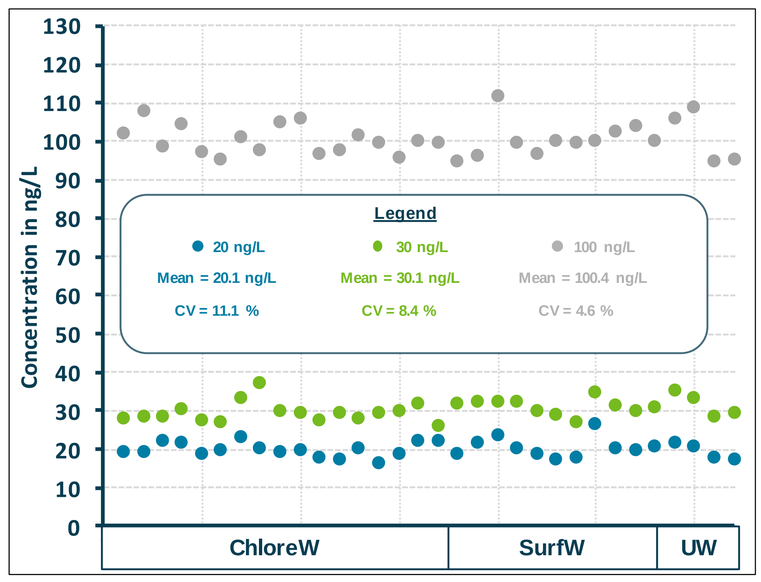

Figure 5. Calculated concentration of glyphosate in 3The methods were found to be considerably more robust and sensitive than other approaches described in various publications and have achieved the target limits of detection 2 water samples Calculated concentration of glyphosate from 16 water samples (8 chlorinated, 6 surface and 2 underground waters) in duplicate spiked with 20, 30 and 100 ng/L of glyphosate. Results for 400 ng/L spiking are not shown for scale reasons (Mean = 408.4 ng/L; CV = 4.7 %).

Conclusions

The methods were found to be considerably more robust and sensitive than other approaches described in various publications and have achieved the target limits of detection

The very good stability of retention time and signal intensity observed during 3 months of analyses in a non-dedicated SCIEX QTRAP 6500+ System demonstrates the robustness of both the method and instrument and also the ease of use and flexibility of the modified NofaLab / SCIEX method for polar pesticides in a routine laboratory.