

Introduction

Automated on-line solid phase extraction (SPE) coupled with LC/Triple Quadrupole MS/MS is enabling low ppt level detection of target analytes in potable and environmental waters. The availability of improved polymeric sorbents including mixed bed and copolymers which retain both moderately hydrophilic and hydrophobic analytes^{1, 2, 3} provide a cost effective solution to the quantification of pesticides, personal care pharmaceutical products (PCPP) and emerging contaminants (EC). Major technological advances in mass spectrometer sample ionization, desolvation, and ion focusing provide improved sampling of ions resulting in a 5-10 fold increase in analyte detection limits. Reduced sample volume also results in substantial cost savings generally associated with water sample collection, transport and storage.

Analytical grade pesticide standard mixtures were purchased from the following suppliers for this study:

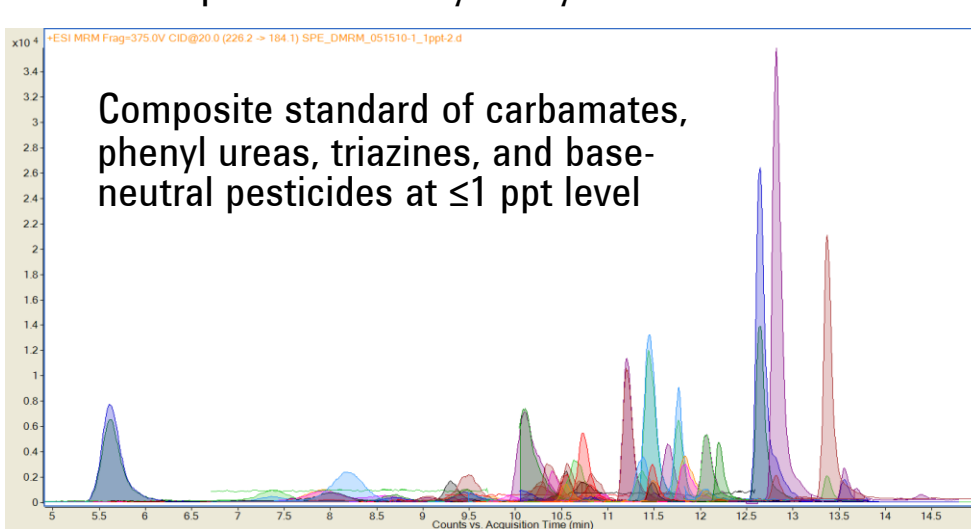
AccuStandard (New Haven, CT), Pesticide Mix 15, AE00024, 33 compounds

ChemService Inc. (West Chester, PA), Carbamate-Urea Pesticide Mix, CUP632-2JM, 20 compounds; Organophosphorous Pesticides Mixture-8140, OPP-8140JM, 20 compounds

Dr. Ehrenstorfer GmbH (Augsberg, Germany), Triazine Pesticide Mix 1, XA06190100AC, 11 compounds; Pesticide Mix 34, XA18000034AL, 27 compounds

Sigma-Aldrich (Saint Louis, MO) Herbicides Mix-1, 49136-U, 13 compounds)

EICs of 64 pesticides analyzed by on-line SPE-LCMS/MS

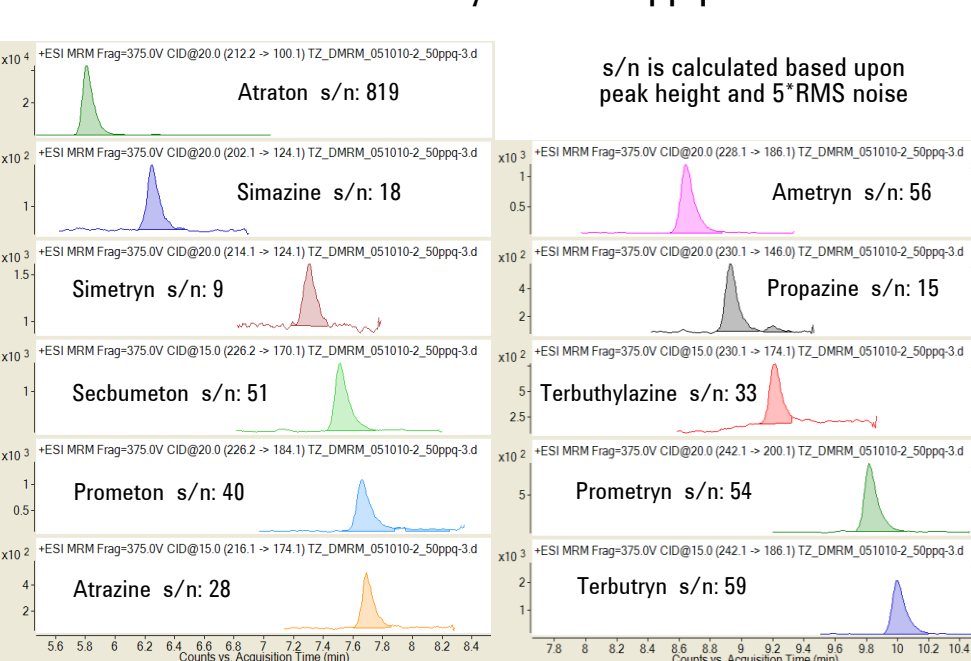


Experimental

2.3 ml water samples spiked with pesticides were loaded onto selected SPE polymeric cartridges at a flow rate of 1 ml/min utilizing an automated liquid sampler (ALS) with 900ul metering device and multi-draw capability, and a programmable 6-position selection valve. A second programmable 6 port/2 position valve was used to select between load or elute modes by directing liquid flow from either a quaternary pump used for transferring sample to SPE cartridges (also for conditioning/flushing cartridges) or a binary pump used to elute cartridges and provide an LC mobile phase gradient for an analytical column separation. LC/QQQ dynamic MRM methods were readily developed utilizing the Agilent Pesticide Database (G1733AA) consisting of over 750 pesticides. Data was acquired in dynamic MRM mode on a new G6490 triple quadrupole mass spectrometer with thermal gradient focusing technology and differentially-pumped dual ion funnels.

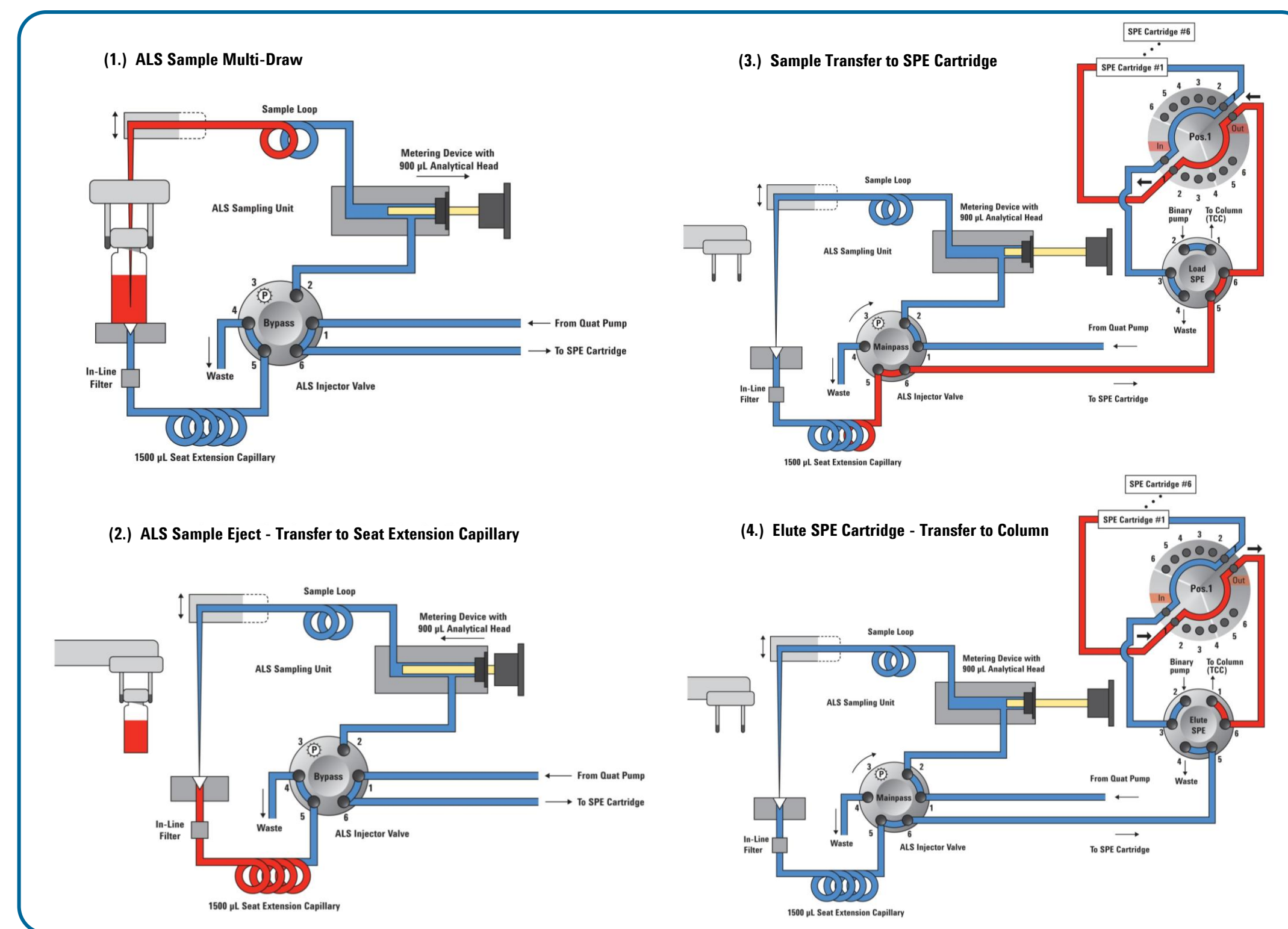
Various chemical classes of pesticides in a water matrix were analyzed in replicates by automated on-line SPE LCMS/MS utilizing several sorbent cartridge types in order to evaluate their retentive properties and suitability for quantitative analysis. PLRP-S, a macroporous reverse phase PS-DVB copolymer retains most base-neutral pesticides, Macroporous hydrophilic-hydrophobic copolymeric sorbents with high specific surface areas (e.g. Oasis-HLB and SampliQ-OPT) provide better selectivity and retention for a larger subset of analytes, however, highly polar compounds such as acid herbicides are often subject to breakthrough. A new triple quadrupole mass spectrometer with improved ionization and ion sampling/focusing capabilities was used to detect a number of pesticide analytes at low ppt to sub-ppt levels. Linear calibrations of three orders of magnitude were obtained for many analytes.

11 triazine herbicides analyzed at 50 ppq level in water



Results and Discussion

(1, 2) The ALS injector is programmed to successively draw and eject two 700 μ l sample aliquots into a 1500 μ l retention volume (i.e. seat extension capillary). Then an additional 900 μ l sample is drawn and the ALS injector valve is switched to mainpass (3.) to allow the quaternary pump to transfer the sample to a selected SPE sorbent cartridge via a 2-position selection valve (load or elute).



Agilent 1200 Series LC modules consisted of the following: G1379B Micro Vacuum Degasser, G1311A Quaternary Pump, G1329A Standard ALS with Extended Injection Volume option (020) and Multi-Draw Kit (021), G1330B ALS Thermostat, G1158A 2-position/6-port valve, G1159A 6-position selector valve, G1312B Binary Pump SL and G1316B TCC.

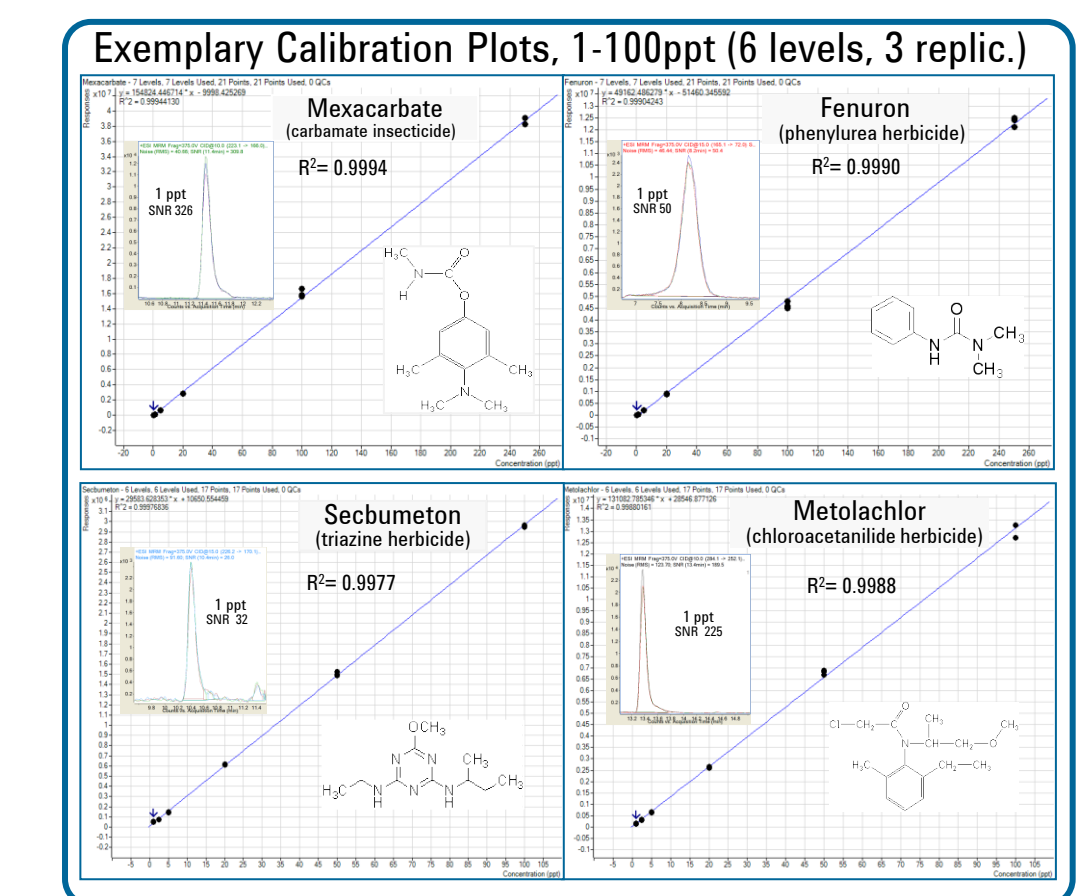
At 1 ml/min sample loading, quat pump backpressure for polymeric SPE cartridges is typically <math>< 15</math> bar. Finally, the SPE cartridge is back-flushed (4.) and analytes are eluted by the gradient generated by the binary pump and analyzed on an 2.1 x 150mm EclipsePlus C18 column, 3.5 μ m with a 5 μ m column guard of the same type.

The LC modules were configured with either a G6460 QQQ or G6490 QQQ Lab Prototype (dual ion funnel technology). Both quadrupole mass analyzers (MS1 and MS2) were tuned to unit mass resolution (0.7 Da FWHM).

Mass Hunter Acquisition SW: B.03.01 SP1 with control for external valves G1158A and G1159A was used to acquire data.

Results and Discussion

The success of on-line SPE-LCMS/MS analysis largely depends upon sample complexity (analyte isolation from matrix) and the availability/selectivity of polymeric SPE sorbents capable of quantitatively retaining the analytes. Although polymeric SPE sorbents and particularly the balanced hydrophobic-hydrophilic interaction types offer a number of advantages over silica-based sorbents, namely wide pH range, high sample loading capacities (surface areas up to 1200 m²/gm) and loading rates (1 ml/min), they are often limited by their inherent mechanical stability to use up to a maximum of 300 bar. This makes their use in on-line SPE-LCMS/MS applications less tenable since the analyst must tailor the LC system pumps and chromatography (columns, flow rates, solvents - typically H₂O/ACN) to match the operational pressure of the SPE cartridge. This is where off-line SPE has some distinct advantages, especially when the off-line SPE sample prep is highly automated. Moreover, the use of UHPLC combined with sub-2 micron analytical columns can result in greater sensitivities, high chromatographic resolution and/or extremely rapid analysis times. .



Organophosphorus and organothiophosphorus pesticides were the most problematic of the various classes of pesticides analyzed by on-line SPE-LCMS/MS. A number of analytes are highly polar and are thermally labile as well. Their analysis requires careful selection of SPE sorbent materials and attention to optimizing ion source conditions.

The use of 6 ml sample vials allows for sample volumes up to 5.4 ml if the 1500 μ l seat extension capillary is exchanged for a 5 ml capillary. Pre-slit septa reduced septa coring and maintenance of the in-line prefilter below the capillary seat

A new triple quadrupole mass spectrometer with improved ionization and ion sampling/focusing capabilities was used to detect pesticide analytes at low ppt to sub-ppt levels. Linear calibrations of three orders of magnitude were obtained for many analytes.

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References

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- 3.] D. Bratkowski, et al., J. Chromatogr., A, Vol. 1217, 19 (2010) 3238-3243. Hydrophilic hypercrosslinked polymeric sorbents for the solid-phase extraction of polar contaminants from water.

Conclusions

- Low PPT to sub-PPT level detection of pesticides in water by on-line SPE-LCMS/MS utilizing improvements in MS hardware designs.
- Highly polar pesticides are not always quantitatively retained on commercially available SPE sorbents. There is a great need to develop SPE sorbents for on-line use which are applicable to a wide class of analytes.