

Screening of pesticides in water using SPE on line

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1. Introduction

Pesticides are widely used in agricultural products to protect crops from insect infestation during cultivation and product transport. The abuse of pesticides can cause important environmental pollution in different areas, especially at levels of lakes, rivers and aquifers. For this reason one of the most important and attractive application is the possibility to analyze pesticides in water and better if

it is without pretreatment of the sample. Shimadzu in cooperation with Arpa Asti (Italy) developed a system for injection of water samples using a triple quadrupole system using a Solid-Phase Extraction (SPE) on line. We injected water samples in a LCMS-8030 Shimadzu triple quadrupole instrument coupled Nexera UHPLC instrument in order to identify a mixture of 48 substances.

2. Materials and Methods

Several samples of water were analyzed using Shimadzu UFLC HPLC system coupled to a Shimadzu LCMS-8030 triple quadrupole mass spectrometer (Shimadzu Corporation, Japan). A standard mixture of pesticides was used for optimization of all MRM parameters. The chromatographic separation was performed using an SPE on-line column YMC Europe GMBH Guard cartridge C18 (2.1mmID x 20 mm) and a Shimapack XR-ODSII (2 mmID x 10mm, 2.2 µm) maintained at 40°C.

The system developed allows injection of different sample's volumes by mean a single autosampler:

- 2 mL of injection volume for analysis with SPE on-line for pre-concentration of the sample;
- 50 µL of injection volume for Ultra-Fast analysis.

The switch between the two loops is automatically and completely controlled by software LabSolution (Shimadzu Corporation, Japan).

Sample Preparation

The sample were previously filtered on 0.22 µm filter and then directly injected.

Analysis Condition

Mobile Phase A: Water + 3mM Ammonium Acetate + 0.1 Formic Acid

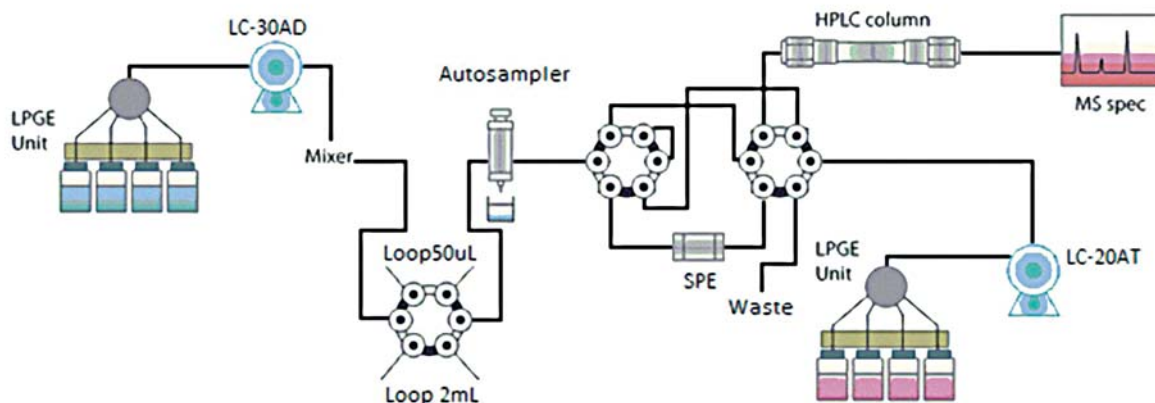
Mobile Phase B: Methanol + 3mM Ammonium Acetate + 0.1 Formic Acid

Loading Buffer SPE: Water / Methanol 99% / 1%

Flow: 0.3 mL/min

Gradient Program Solvent B: 1% (4.01 min) – 100% (14 min)

Total Run Time with SPE loading and equilibration: 35 min.



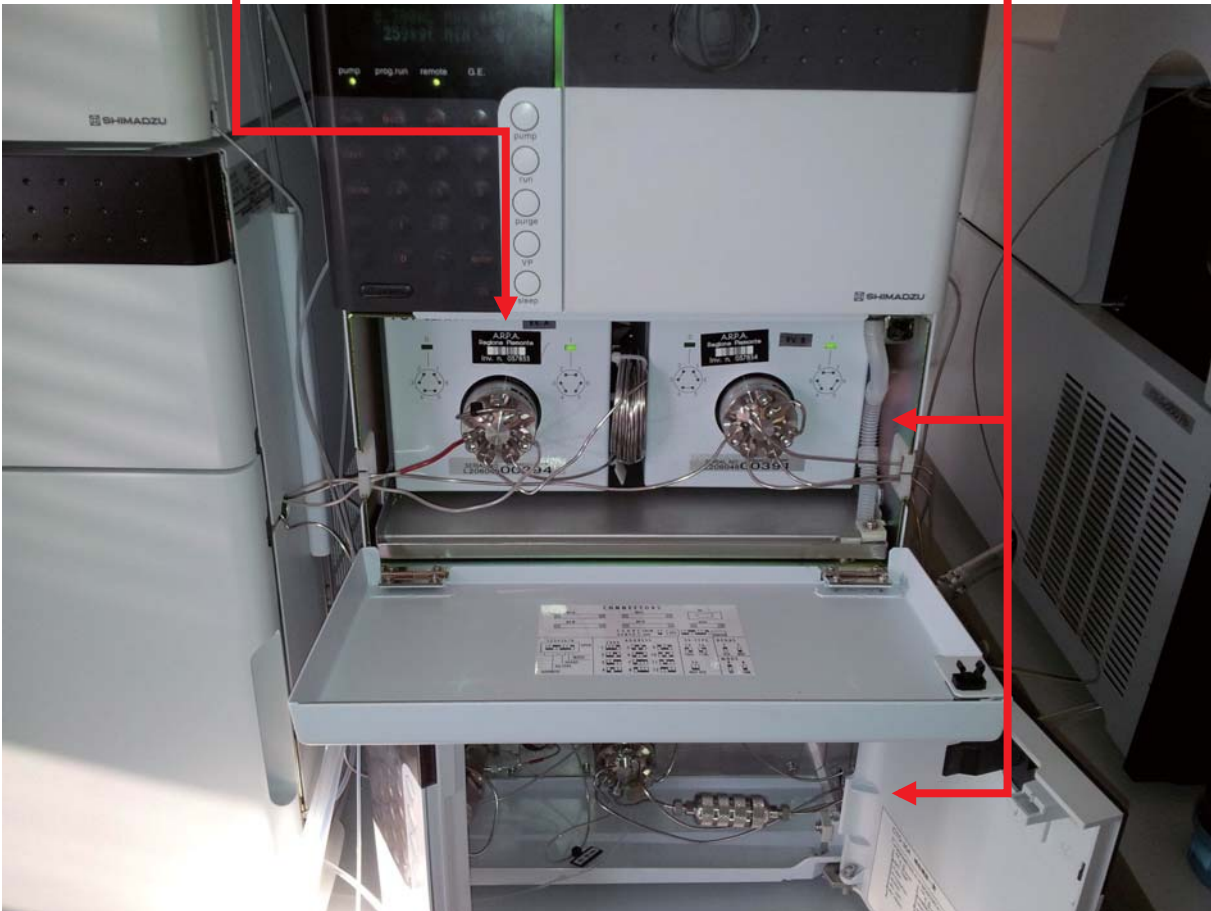
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Key feature of LCMS-8030 triple quadrupole mass spectrometer

- * ultra fast polarity switching of 15msec
- * ultra fast scan speed of up to 15,000 u/sec
- * UFsweeper™ technology dramatically minimizes cross talk
- * excellent linearity with wide dynamic range

Switch between two loops

Switch between UFLC system mode and SPE system mode

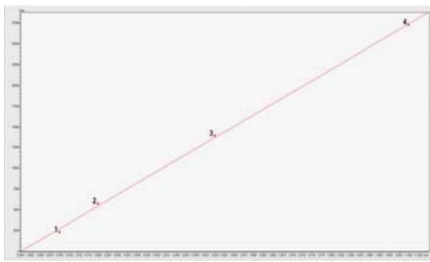


Screening of pesticides in water using SPE on line

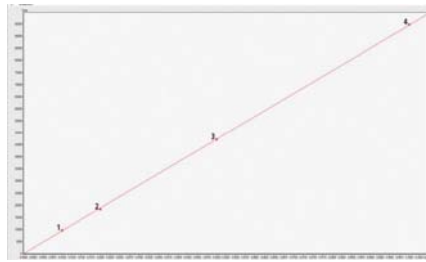
3. Results

Before analysis we checked the correct volumes of aspirations and injections of the autosampler with both loops. We developed calibration curves for 48 compounds

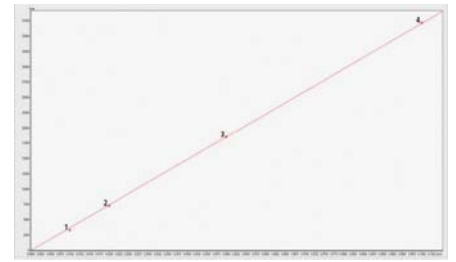
spiked in 1mL of water, ranging from 0.002 µg/L to 0.100 µg/L.



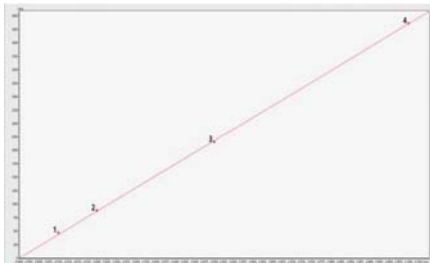
Chloridazon R² 0.999



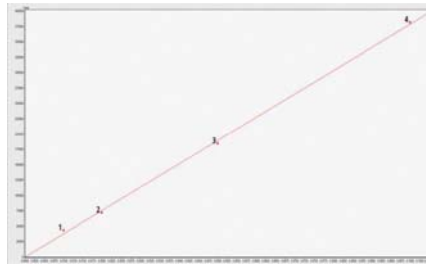
Cinosulfuron R² 0.999



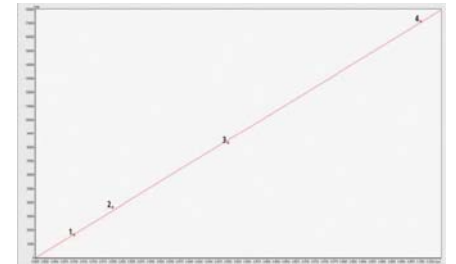
Bromacil R² 0.999



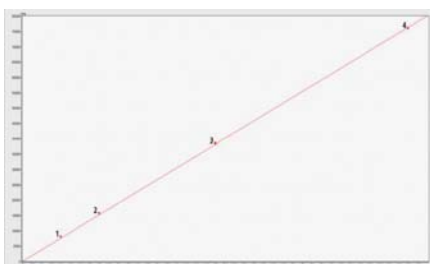
Azimsulfuron R² 0.999



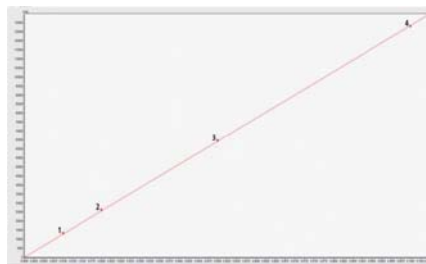
Isoproturon R² 0.998



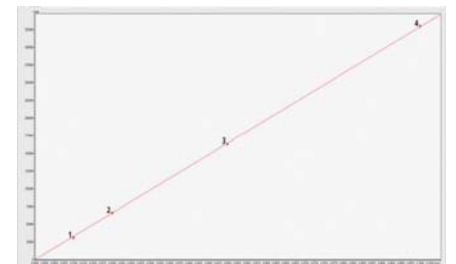
Diuron R² 0.998



Azoxystrobin R² 0.999



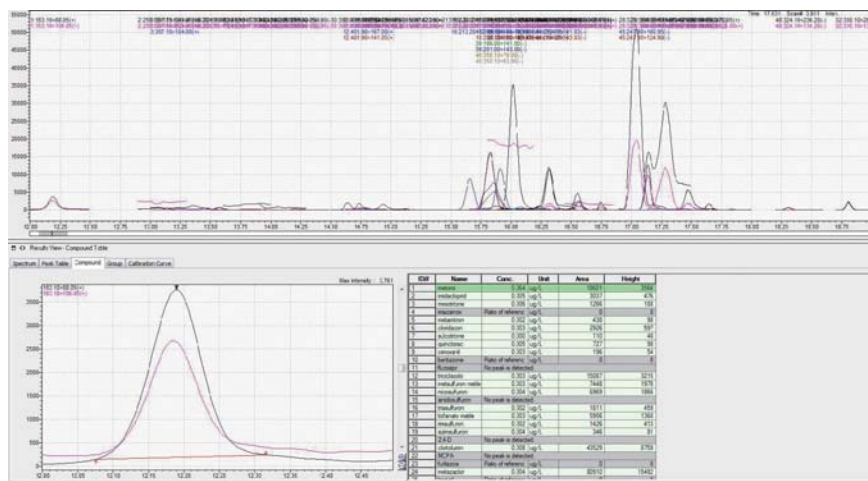
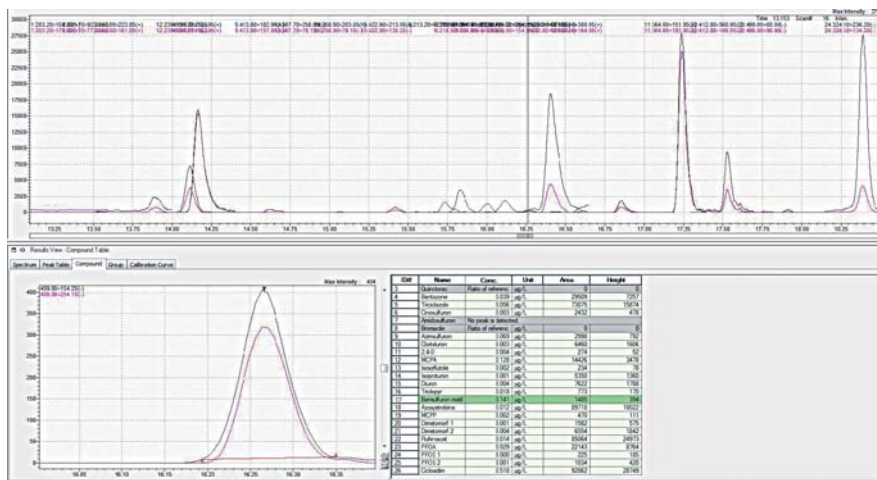
Nicosulfuron R² 0.999



Tralkoxydim R² 0.999

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Example of real samples injected using SPE on line.



4. Conclusion

The data reported shows that the configuration developed allows to use of a single autosampler to perform both Ultra Fast analysis that using SPE on-line in order to reduce cost

and complexity of the system. LabSolution Software (Shimadzu Corporation, Japan) enables the automatic control of the entire fluidics set up.