

Liquid Chromatography / Mass Spectrometry

Authors:

Josh Ye, Feng Qin, Frank Kero, Craig Young,
Jason Weisenseel, Jamie Foss

PerkinElmer, Inc.
Downers Grove, IL

Matteo Maglioli, Ph.D.
Quebec, Canada

“No Dilute” Just Shoot: Robustness of a QSight LC-ESI-MS/MS for Low Level Pesticide Residue Analysis in Wine

Introduction

Traditional analysis by chromatography and mass spectrometry often requires sample cleanup to minimize matrix effects and to avoid contamination of the ion source in the mass spectrometer. However, sample preparation is usually labor intensive and requires trained analysts with specialized skills. Strategies to redesign the front end of mass spectrometers to minimize source

contamination and thereby avoid the need for extensive sample cleanup, led to the invention of a hot surface induced desolvation (HSID™) interface¹. The PerkinElmer QSight™ LC/MS/MS mass spectrometer contains the HSID interface coupled to a Laminar flow ion guide™, both of which prevent accumulation of contamination along the ion path making it a very sensitive and maintenance free instrument.

In this study, we used the QSight LC/MS/MS system to evaluate the potential of eliminating sample preparation for trace level pesticide analysis in a complex sample such as wine². We injected undiluted red and white wine samples into the mass spectrometer and studied reproducibility in analysis of the spiked pesticides over 200 injections. The instrument showed excellent reproducibility with minimal signal drift during the duration of the study (over a week), confirming the robustness of the QSight mass spectrometer.

What is the HSID Interface and How Does it Work?

The HSID apparatus is a multiorthogonal channel interface directly heated up to 300 °C that is present immediately after the sampling orifice in the source and connects the orifice to the Laminar flow ion guide of the QSight mass spectrometer. Unlike traditionally designed interfaces, the HSID with its multi-channels orthogonal to each other (Fig. 1) produces turbulent and Laminar flow and disrupts the free jet expansion of the sample ions. The orthogonal channels prevent neutrals from entering the mass spectrometer reducing chemical noise, and any solvated charged clusters entering the HSID are entrained and desolvated in the hot flow of gas, further contributing to reduction in chemical noise.

The ions from the HSID interface are gently transferred by gas flow to the Laminar flow ion guide™, which is not subject to the traditional axial fields, but is at zero potential. The ion guide has multiple pumping stages to generate several pressure regions from the sample interface to the mass analyzer. In these regions, pressure gradually drops, creating a well-defined flow pattern along the ion path enabling ions to be gently extracted into the analyzer. Both the HSID and laminar flow ion guide prevent accumulation of contamination along the ion path making the QSight maintenance free. Among many benefits of the HSID interface include high sensitivity due to an inherent reduction in chemical background (i.e. S/N, reduced N) and the ability to perform analysis at high LC flow rate (3 mL/min) without reduction in signal.

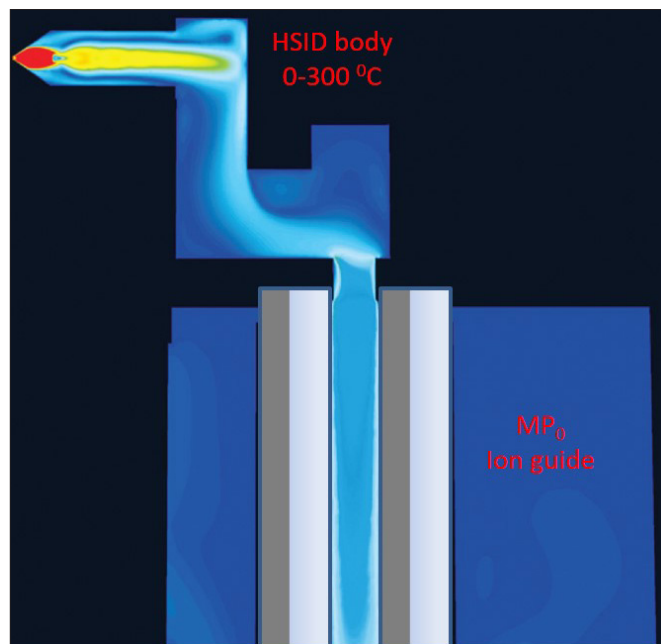


Figure 1. Schematic of an HSID interface for laminar flow tandem mass spectrometry.

Experimental

Hardware/Software

Chromatographic separation was conducted by a PerkinElmer Altus® A-30 UPLC® System and detection was achieved using a PerkinElmer QSight 220 MS/MS detector with a dual ionization source. All instrument control, data acquisition and data processing were performed using the Simplicity 3Q™ software platform. The mobile phase flow rate was at 0.5 mL/min.

Method Parameters

MS settings are shown in Table 1 and Table 2, respectively. Source parameters including gas flows, source temperature and position settings were optimized for maximum sensitivity. The quadrupole peak widths (Q1 and Q2) were set at 0.7 amu. Example compound-dependent parameters for the partial list of MRM transitions are listed in Table 3.

Table 1. MS source settings.

ESI voltage	5000 V
Drying gas	120
HSID Temp	200 °C
Entrance voltage	30 V
Source Temp	325 °C
Nebulizer gas	350
Detection Mode	MRM Mode

Table 2. Optimized compound-dependent parameters for selected pesticides.

Name	Precursor	Fragment	Type	Collision Energy
Dimethenamid	276.1	244.0	Quantifier	18
Dimethenamid	276.1	168.0	Qualifier	30
Benthiavalicarb-isopropyl	382.1	180.0	Quantifier	38
Benthiavalicarb-isopropyl	382.1	197.0	Qualifier	24
Pyriproxyfen	322.0	96.0	Quantifier	22
Pyriproxyfen	322.0	185.0	Qualifier	30

Standards and Samples

Argentina wine samples, including a bottle of Cabernet Sauvignon (Cabernet) and a bottle of Pinot Grigio (Pinot), were purchased from a local grocery store. The samples were fortified to 10 ng/mL of pesticide mixed standards obtained from ULTRA Scientific® (North Kingstown, RI). Then, 10 µL of spiked samples (no further sample preparation and no dilution) were injected for robustness and reproducibility analysis. Linearity and LOQs of the analytes were also evaluated. Matrix-matched standards were prepared at 0.1, 1, 10, and 100 ng/mL levels by diluting the pesticide mix standards stock solution with blank Cabernet and Pinto wine samples.

Results and Discussion

Robustness Study

Commercial wine samples (Pinot and Cabernet) were fortified to 10 ng/mL with a pesticides mixed standard. These fortified samples were then tested with 200 repeat injections over the course of 7 days. Three pesticides (Dimethenamid, Benthiavalcarb-isopropyl and Pyriproxyfen) were selected to demonstrate the stability of the system. Summarized plot of peak area versus injection number for these analytes in spiked pinot and cabernet are presented in Figure 2. As observed, the trace remains flat across the 200 injections, and peak area reproducibility (CV, calculated as relative standard deviation) was ~5%, indicating excellent performance stability during analysis.

Comparison of Calibration Curves Before and After 200 Injection Study

Matrix-matched representative calibration curves for quantitative and qualitative ions for Benthiavalcarb-isopropyl, Dimethenamid, and Pyriproxyfen after the wine injection study was performed are shown in Figure 3 (Pinot) and 4 (Cabernet). The selected pesticides have a linear dynamic range of 0.5 to 100 ng/mL and are identical to the calibration curves generated prior to wine injections. Linear regression coefficients were obtained for all the pesticides with $R^2 > 0.992$. There is no maximum residue limit (MRL) of pesticides set for wine yet, according to the EU regulation. However, the limit of quantitation (LOQ) at level of low part per billion or less is considered sufficient.

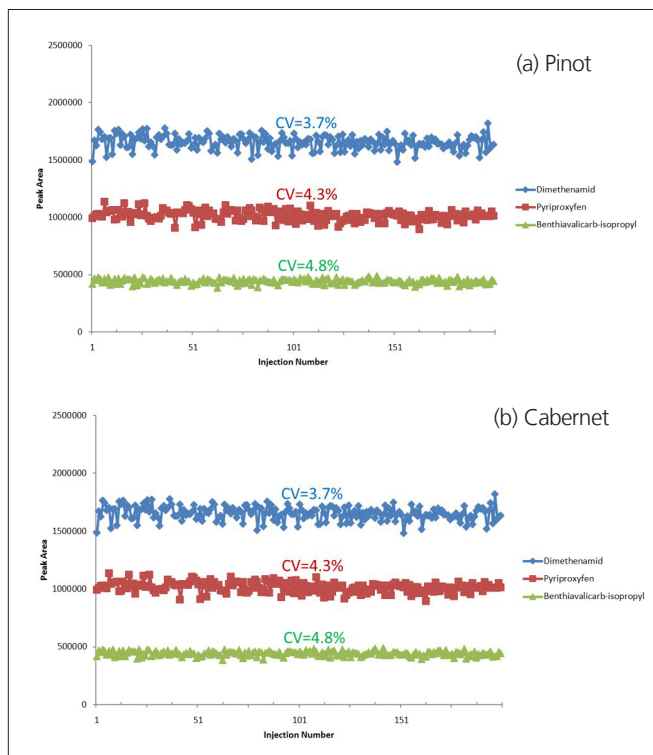


Figure 2. Peak area of three pesticides vs injection number for spiked (a) Pinot Grigio and (b) Cabernet Sauvignon samples.

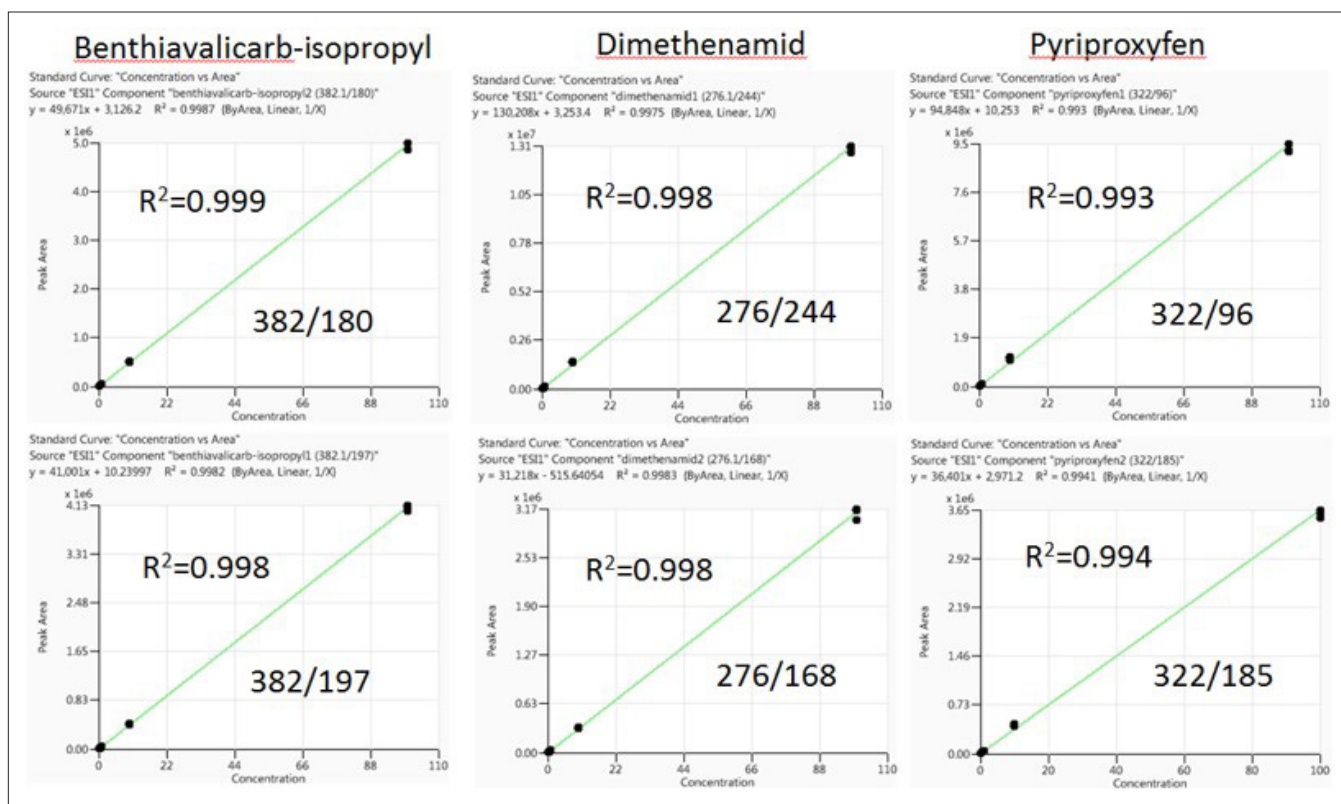


Figure 3. Pinot matrix-matched calibration curves for Benthiavalcarb-isopropyl, Dimethenamid, and Pyriproxyfen.

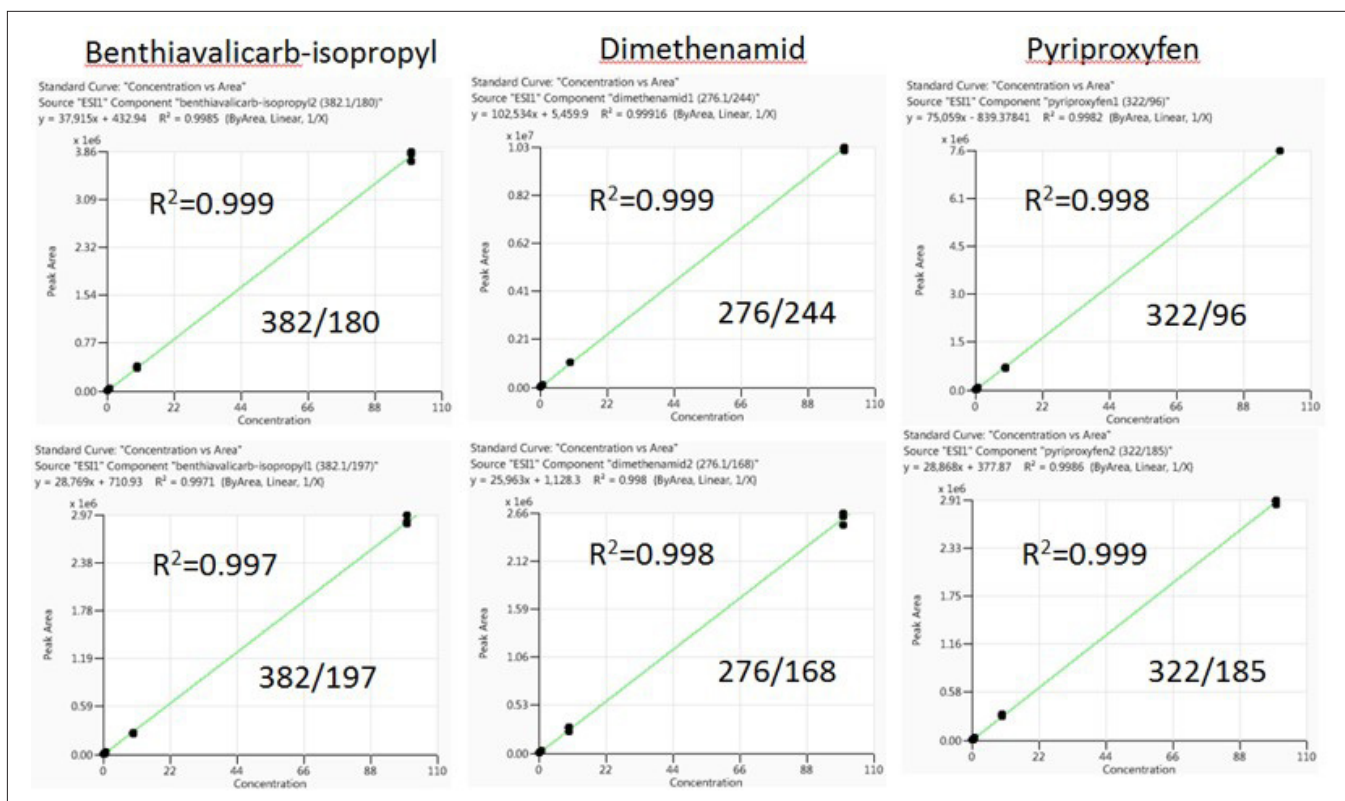


Figure 4. Carbernet matrix-matched calibration curves for Benthiaivalcarb-isopropyl, Dimethenamid, and Pyriproxyfen.

Conclusion

A "no-dilute-just-shoot" approach was presented in this study to demonstrate the advantages of an HSID interface on a PerkinElmer QSight 220 LC/MS/MS system. The orthogonal design of the interface, and the turbulent and laminar flows used for ion transportation provide maximum protection for the MS instrument from being contaminated. Over the two matrix variables x200 continuous injections of wine samples without any cleanup steps, the instrument performance remained consistent. Peak area CVs are ~5%, and peak shape and height are nearly the same. Linearity and LOQs of the calibration curves for all analytes using matrix-matched standards was found to be maintained after >200 injections. This study suggests that it is possible to increase the lab productivity and reduce cost on QSight LC/MS/MS system by injecting samples that are prepared with minimal cleanup steps.

References

1. Flow Characteristics of a Laminar Flow Interface for LC-MS/MS. PerkinElmer Tech Note 0129893.
2. Meglioli M, Kero F, Ye J, Young C, Reddy S "No dilute" just shoot LC-ESI-MS/MS : feasibility and robustness of a maintenance-free source for applications in low-level pesticide residue analysis "The Proceedings of the 64th ASMS Conference on Mass Spectrometry and Allied Topics, San Antonio, TX, June 2016.