

Supplementary Information

MS/MS of PEN and BIX on LTQ

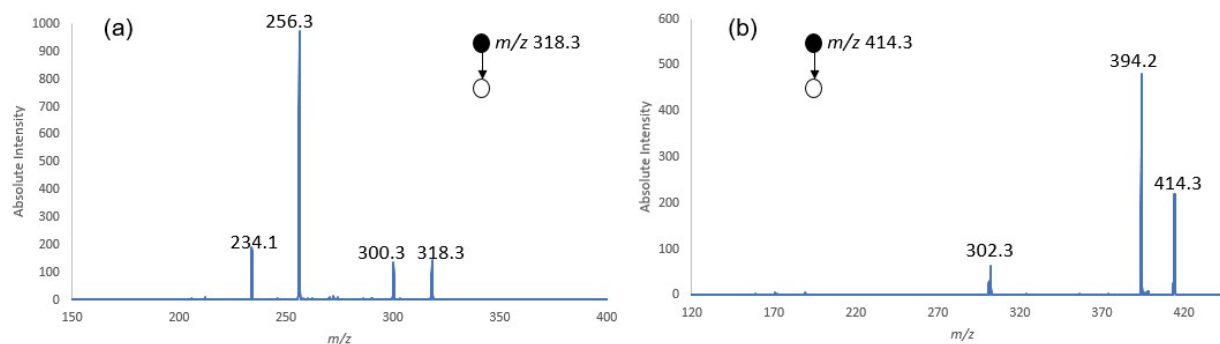


Figure S 1. MS/MS spectra of (a) PEN and (b) BIX obtained using LTQ. m/z 256.3, m/z 300.3 in (a) and m/z 302.3 in (b) were from background.

LC-MS/MS of wine 4

The experiments were performed using an established method (X.-z. Chen, B.-q. Xia, F.-z. Huang, J. Cheng, Y. Shen, and C. Han, *Journal of Instrumental Analysis*, 2015, **34**, 1311-1314.). The sample was first diluted with ultrapure water, then cleaned up with HLB SPE. The separation was performed using an Agilent ZORBAX C18 column (Agilent, Santa Clara, CA, USA) and the analytes was determined by ESI MS/MS using an API 4000 (AB Sciex, Concord, ON, Canada) in MRM mode.

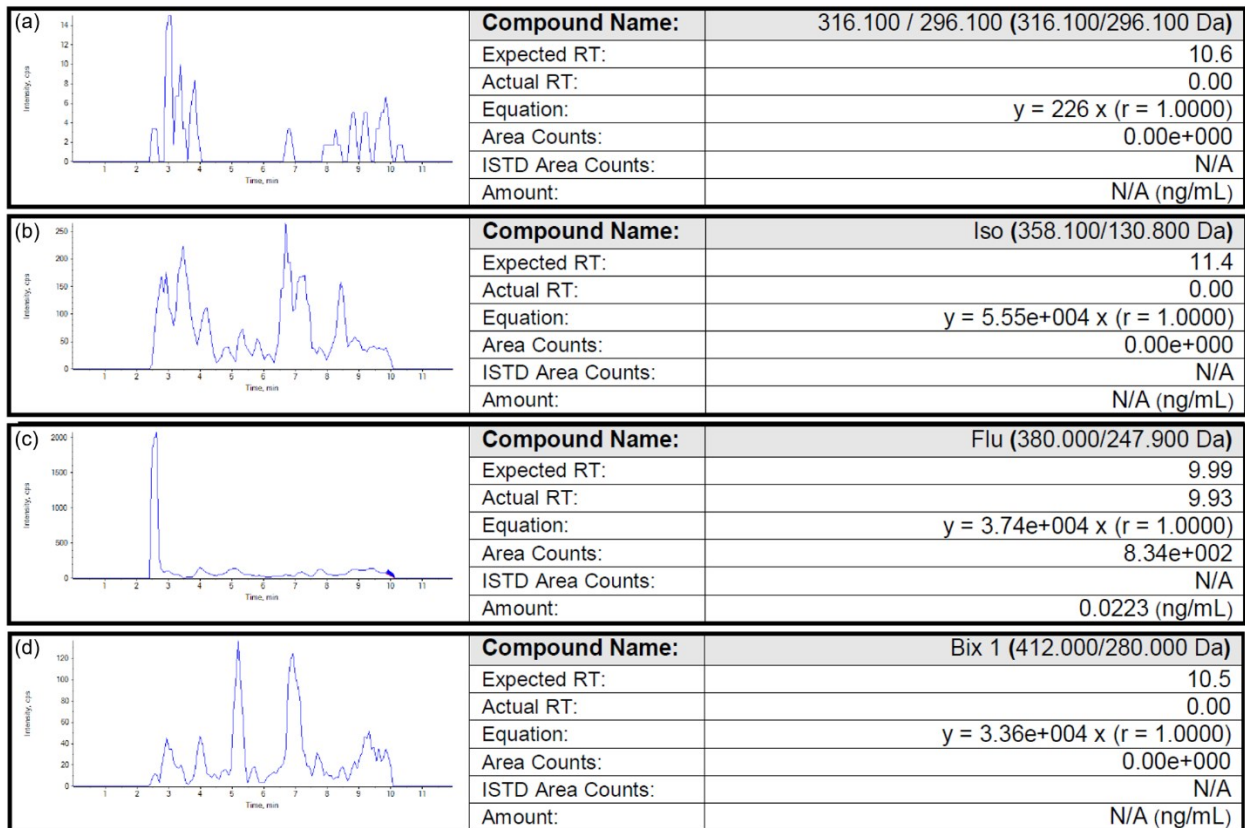


Figure S 2. LC-MS/MS MRM chromatograms of (a) PEN, (b) ISO, (c) FLU and (d) BIX in wine 4.

Calibrations curves obtained using paper capillary spray

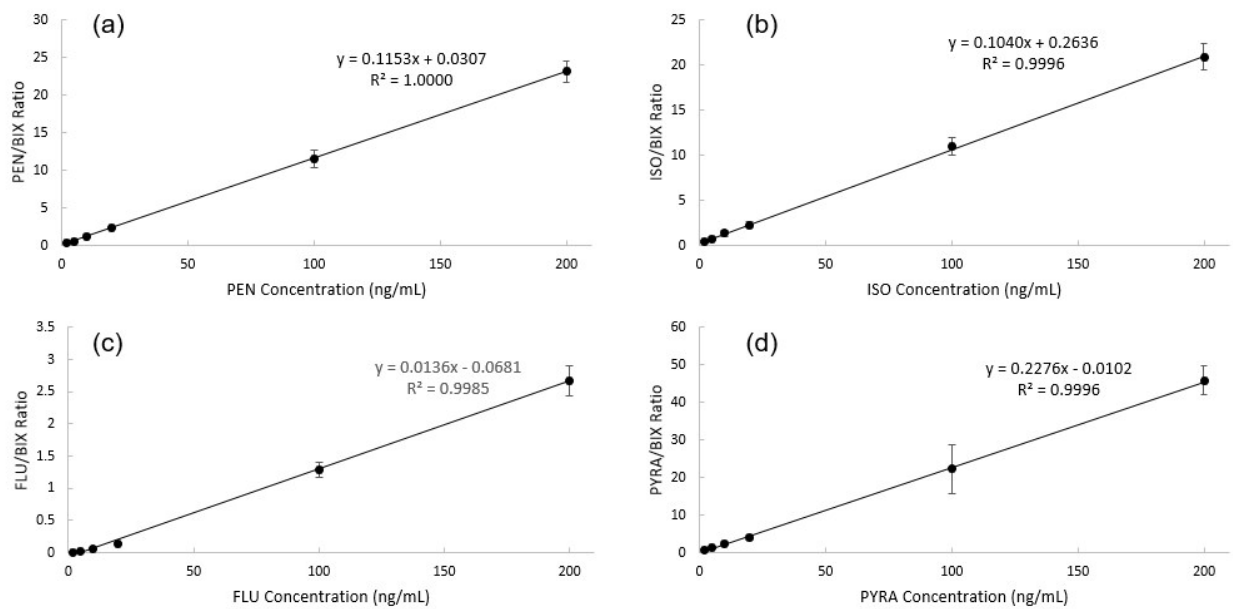


Figure S 3. Calibration curves of (a) PEN, (b) ISO, (c) FLU and (d) PYRA with paper capillary spray mass spectrometry.

Quantitation using paper spray for a comparison

Similar quantitation experiments were performed with paper spray for comparison and validation. Grade 1 chromatography paper was cut to triangles with 8 mm base and 15 mm height. The sample load was smaller than that for paper capillary spray, at 5 μL ; and the elution and spray solvent was 40 μL . All other parameters were kept the same (distance between the sharp of the paper to MS inlet was kept at 10 mm). The calibration curves (Figure S4) and the quality control data (Table S1) were summarized in the supplementary information. Linear ranges were 2-200 ng/mL for PEN and ISO, and 5-200 ng/mL for FLU and PYRA, respectively, with R^2 value above 0.99 for all four fungicides. Quality control experiments showed that similar levels of accuracy and precision to paper capillary spray was achieved.

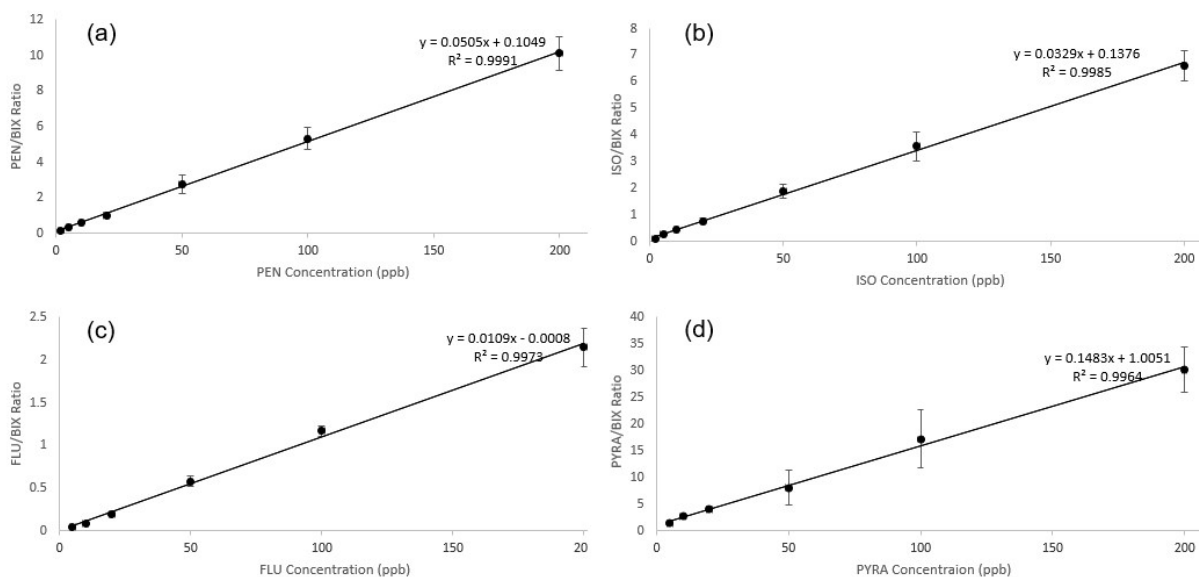


Figure S 4. Calibration curves of (a) PEN, (b) ISO, (c) FLU and (d) PYRA with paper spray mass spectrometry.

Table S 1. Quality control data, paper spray, n=3*

Compounds	Nominal Concentration (ng/mL)	Accuracy (%)	Precision (RSD %)
Penflufen	2	89.2	8.6
	10	115.9	3.3
	100	109.1	13.3
Isopyrazam	2	82.2	4.2
	10	112.7	6.4
	200	102.9	8.5
Fluxapyroxad	10	83.9	6.8
	50	102.2	13.1
	100	100.4	9.2
Pyraclostrobin	10	91.8	4.0
	50	108.9	31.5
	200	117.2	13.2

*Marked bold indicates not meeting the recommended requirements.