Rapid measurement of agrochemicals by PaperSpray mass spectrometry

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ABSTRACT

Purpose: A simplified analytical workflow for agrochemical measurement in food samples based on PaperSpray technology coupled to a triple quadrupole mass spectrometer, using minimal sample preparation.

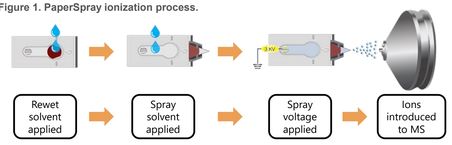
Methods: Agrochemicals (thiamethoxam, clothianidin, diphenylamine, imidacloprid, etc.) were analyzed in whole milk, olive oil, and leek homogenate using a simple spike-and-spot approach. Samples were analyzed using the Thermo Scientific™ VeriSpray™ PaperSpray Ion Source and Thermo Scientific™ TSQ Altis™ Triple Quadrupole Mass Spectrometer.

Results: Good linearity was achieved in all matrices. Linear ranges vary depending on the matrix, but typically extend to the low ng/mL.

INTRODUCTION

Food and crop samples are typically analyzed for agrochemical residues using extraction-based sample preparation methods such as QuEChERS followed by LC-MS/MS or GC-MS/MS. PaperSpray technology represents an alternative sample introduction approach, enabling MS/MS analysis of agrochemical compounds from food and crop matrices with minimal sample preparation and short analysis times, using a simple spike-and-spot workflow and a 1.1 minute analysis time.

Figure 1. PaperSpray ionization process.



PaperSpray ionization is an electrospray-derived ionization technique employing a paper substrate as both a sample holder and spray emitter. An aliquot of sample (spiked with a suitable internal standard) is applied directly to the paper substrate and dried. Typically little to no sample preparation is performed before the sample is applied to the paper. After drying, solvent and a high voltage are applied to the paper, extracting the analyte from the paper and ionizing it through generation of a plume of charged droplets from the pointed tip of the paper substrate.

The VeriSpray system incorporates PaperSpray technology to provide an integrated workflow for routine and research applications, combining automated sample introduction with the ease-of-use of PaperSpray. Up to 24 samples can be spotted on each VeriSpray sample plate, and the VeriSpray automated plate loader coupled to the VeriSpray ion source enables analysis of up to 10 plates (240 samples) without user intervention using Thermo Scientific™ Xcalibur™ software.

Figure 2. VeriSpray system coupled to the TSQ Altis mass spectrometer.

MATERIALS AND METHODS

Sample Preparation

Food matrices (organic whole milk, olive oil, and leek) were purchased from a local supermarket. For liquid matrices, a 970 µL volume of matrix was mixed with 30 uL of methanol containing isotopically labeled internal standard and target analytes to generate a calibration curve. The solid leek matrix was washed in warm water, dried, and homogenized using a laboratory blender. Leek homogenate was stored at -20 C. 500 mg of leek homogenate was mixed with 500 µL of methanol containing isotopically labeled internal standards and target analytes to generate a calibration curve. Samples were mixed thoroughly using a vortex mixer and spotted on VeriSpray sample plates in 10 uL aliquots. The spotted plates were allowed to dry for a minimum of 2 hours before analysis.

Test Method and Data Analysis

All samples were ionized using a spray voltage of 3800 V and an inlet temperature of 350 C. A blend of 90% methanol, 10% water, and 0.1% formic acid was used for both rewet and spray solvent. 10 uL rewet solvent and 120 uL spray solvent was used for all samples. Data was collected for 1.1 minutes per sample on a Thermo Scientific™ TSQ Altis™ mass spectrometer. The spray voltage was applied from 0.05 to 1.05 minutes. The distance from the paper tip to the inlet was approximately 4.5 mm. Data analysis was performed using Thermo Scientific™ Xcalibur™ software, version 4.2.

RESULTS

Leek Homogenate

Calibration curves for imidacloprid and boscalid in leek homogenate are shown in figures 3 and 4, below. Excellent linearity and precision was observed from 20 ng/g to 10 µg/g for imidacloprid and boscalid in leek homogenate. For analysis of concentrations above 10 µg/g, a greater concentration of internal standard is recommended.

Figure 3. Calibration curve for imidacloprid in leek homogenate, 20 ng/g – 10 µg/g.

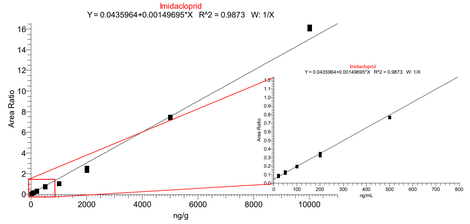
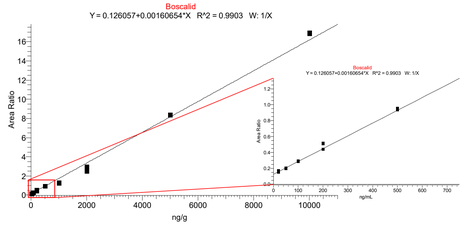


Figure 4. Calibration curve for boscalid in leek homogenate, 20 ng/g – 10 µg/g.



Olive Oil

Analysis of olive oil samples using PaperSpray technology requires no extraction or sample clean-up. Samples may be directly spotted on the paper in the VeriSpray sample plate and analyzed.

Calibration curves for diphenylamine (figure 5), clothianidin (figure 6) and thiamethoxam (figure 7) in olive oil are shown below. Excellent linearity and reproducibility were obtained from 10 ng/mL to 25 µg/mL (5 ng/mL to 50 µg/mL for diphenylamine).

Figure 5. Calibration curve for diphenylamine in olive oil, 5 ng/mL – 50 µg/mL.

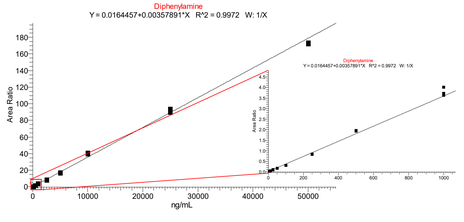


Figure 6. Calibration curve for clothianidin in olive oil, 10 ng/mL – 25 µg/mL.

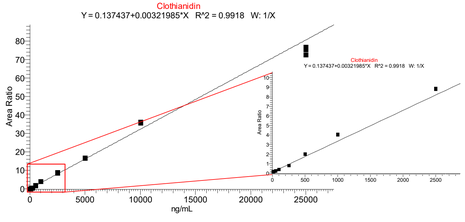
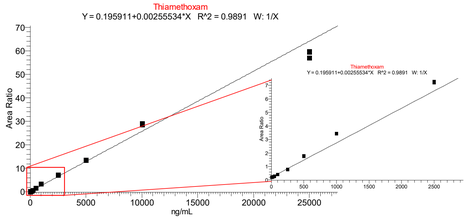


Figure 7. Calibration curve for thiamethoxam in olive oil, 10 ng/mL – 25 µg/mL.



Whole Milk

As for olive oil, whole milk samples can be analyzed using PaperSpray without sample clean-up, simply by spotting samples spiked with isotopically labeled internal standards on the VeriSpray sample plates, drying, and analyzing.

Calibration curves for atrazine (figure 8), thiamethoxam (figure 9), and imidacloprid (figure 10) are shown below. Good linearity and precision were obtained from 25 ng/mL up to at least 25 µg/mL for thiamethoxam and imidacloprid, and from 1 ng/ml to 50 µg/mL for atrazine.

Figure 8. Calibration curve for atrazine in whole milk, 1 ng/mL – 50 µg/mL.

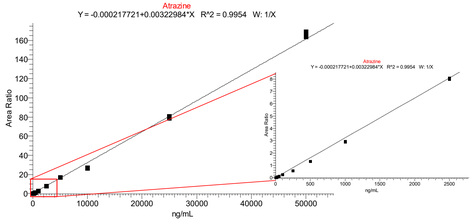


Figure 9. Calibration curve for thiamethoxam in whole milk, 25 ng/mL – 25 µg/mL.

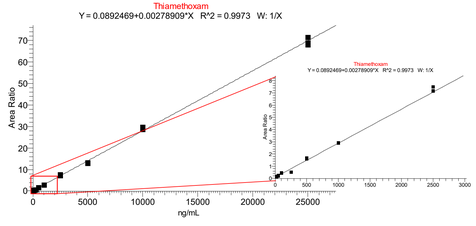
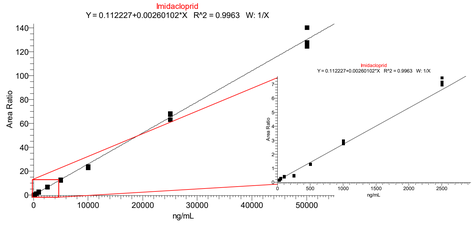


Figure 10. Calibration curve for imidacloprid in whole milk, 25 ng/mL – 50 µg/mL.



Summary

Linear and reproducible calibration curves were obtained for a variety of pesticides in leek homogenate, olive oil, and whole milk. Typical linear dynamic ranges obtained extended from the low ng/mL to the low µg/mL (the low ng/g to low µg/g for leek homogenate). The MS/MS transitions monitored for each compound are listed in Table 1, and the linear ranges and R^2 values obtained are summarized below.

Table 1. Transitions for analytes and internal standards

Analyte	Parent Mass	Product Mass	Internal Standard	IS Parent Mass	IS Product Mass
Atrazine	216	174	Atrazine-D_5	221	179
Boscalid	343	307	Boscalid-D_4	347	311
Clothianidin	250	169	Clothianidin-D_3	253	172
Diphenylamine	170	93	Diphenylamine-D_{10}	180	98
Imidacloprid	256	175	Imidacloprid-D_4	260	179
Thiamethoxam	292	211	Thiamethoxam-D_3	295	214

Leek Homogenate:

- Boscalid: 20 ng/g - 10 µg/g, R^2 = 0.9903
- Imidacloprid: 20 ng/g - 10 µg/g, R^2 = 0.9873

Olive Oil:

- Clothianidin: 10 ng/mL – 25 µg/mL, R^2 = 0.9918
- Diphenylamine: 5 ng/mL – 50µg/mL, R^2 = 0.9972
- Thiamethoxam: 10 ng/mL – 25 µg/mL, R^2 = 0.9891

Whole Milk:

- Atrazine: 1 ng/mL – 50 µg/mL, R^2 = 0.9954
- Imidacloprid: 25 ng/mL – 50 µg/mL, R^2 = 0.9973
- Thiamethoxam: 25 ng/mL – 25 µg/mL, R^2 = 0.9963

CONCLUSIONS

- PaperSpray simplifies the sample preparation process, requiring only mixing the internal standard with the sample, spotting the sample on the plate, and drying.
- Analysis of food liquids by PaperSpray is particularly advantageous as samples such as olive oil and whole milk can be analyzed without cleanup.
- Analysis of solid food samples using PaperSpray can be achieved using a simple homogenization and dilution strategy; alternatively, PaperSpray can also be coupled to established sample preparation workflows such as QuEChERS if desired.

TRADEMARKS/LICENSING

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