A NEW STRATEGY FOR THE DETERMINATION OF CAPTAN AND FOLPET IN FOOD MATRICES

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INTRODUCTION

Screening food samples for contaminants such as pesticides requires the use of GC-MS and LC-MS techniques. In order to cover a full suite of regulated compounds, several LC and GC methods are usually required that separately incorporate large suites of compounds, single residue methods, and “troublesome” compounds.

Of the troublesome compounds in the GC-MS suite of pesticide residues, the thiophthalimide fungicides, including captan and folpet, are amongst the most difficult to analyze. These compounds rapidly degrade in the GC inlet under normal splitless injection conditions used for multisite pesticide analysis methods. Captan and folpet lose the –SCl3 group to produce Tetrahydrothiophthalimide (THPI) and Phthalimide (PI), respectively. This degradation happens within as little as two injections making reproducible analysis nearly impossible. It is generally accepted that captan and folpet are GC compounds, although methods for their degradation products using APCI ionization using an LC-MS method have been reported.1

We assessed the possibility of developing an LC-MS/MS method to make the analysis of these compounds more robust and reliable. Electrospray ionization (ESI) and a novel LC-MS ionization technique (UniSpray or USI) were investigated to determine whether captan and folpet could be successfully analyzed with an LC-MS approach without the problems observed using GC analysis. The method evaluation was performed in challenging food matrices.

How Does UniSpray Work?

UniSpray is an novel atmospheric ionization technique that allows for multimode ionization of both polar and non-polar analytes in a single injection. A simplified diagram of how UniSpray ionization works is shown in Figure 2. The column effluent is nebulized in a grounded, heated probe and directed onto a stainless steel pin which is held under high voltage, creating smaller droplet sizes, which are ionized at impact on the grounded probe and directed onto a stainless steel pin which is held under high voltage, creating smaller droplet sizes, which are ionized at impact on the impedance and sampling efficiency.2,3

RESULTS AND DISCUSSION

GC analysis of pesticides like captan and folpet is often not repeatable as the pesticides degrade in GC splitless injections, as demonstrated in Figure 4 showing three consecutive GC injections of captan in matrix. Analysis using the LC-MS/MS methods developed using Electrospray and UniSpray (Figure 4) was shown to be repeatable (n=25 injections). Linearity in matrix was excellent with R2 values > 0.995 for all pesticides in each matrix in the range of 0.005 - 1.00 mg/kg. Limits of detection were well within the required EU maximum residue level (MRL) of 0.030 mg/kg in kale and 0.090 mg/kg in celery (Table 1).4,5 The methods proved to be robust as RSDs for 25 injections in matrix were < 10%. Figure 5 shows the trend of peak area and associated % RSD for folpet in 25 injections of kale. Although both LC-MS ionization techniques were robust, UniSpray ionization produced greater ionization, resulting in an increase of peak areas for all compounds. Figure 6 illustrates the peak areas for each compound normalized to UniSpray peak area in kale and celery matrix.

METHODS

LC Conditions: LC System: ACQUITY UPLC® I-Class MS System: Xevo TQ-MS Column: ACQUITY BEH C18 2.1 x 50 mm, 1.7um Column Temperature: 45°C Sample Temperature: 4°C Flow Rate: 0.45 mL/min Injection Volume: 10 µL Mobile Phase A: Water + 0.1% formic acid + 0.05% ammonium Mobile Phase B: Methanol + 0.1% formic acid + 0.05% ammonium Gradient: Time (min) Flow (mL/min) % A % B 0 0.45 100 0 5 0.45 0 100 8 0.45 90 10 MS Conditions: Electrospray Impactor Voltage: 3 kV Desolvation Temp: 300°C Desolvation Flow: 1.0 L/hr Cone Flow: 600 L/hr Electrostatics Capillary Voltage: 3 kV Desolvation Temp: 200°C Desolvation Flow: 1.0 L/hr Cone Flow: 600 L/hr

CONCLUSIONS

• An LC-MS/MS method was developed for the analysis of thiophthalimide fungicides captan and folpet as well as their degradation products THPI and PI.

• The LC-MS/MS analysis of captan and folpet was repeatable using both Electrospray and UniSpray ionization techniques. Compound degradation did not occur during sample analysis as compared to GC-MS analysis of the same compounds.

• Electrospray and UniSpray ionization produced very robust options for analysis methods of captan and folpet with RSDs < 10% in all matrices analyzed.

• The novel UniSpray ionization source provided enhanced ionization of all compounds studied when compared to Electrospray ionization.

• Limit of detection for captan and folpet in matrix were well below the regulated limits.

• The methods developed provide a viable alternative for analysis of thiophthalimide fungicides using LC-MS that is much more robust than GC-MS analysis.

REFERENCES


2. A. Lubin, S. Bajic, D. Cabooter, P. Augustijns, F. Cuyckens, 2016. Atmospheric pressure ionization and ionization techniques with associated RSD values. Red line indicates the mean, light blue shaded area represents +/- 2 standard deviations, dark blue shaded area represents +/- 3 standard deviations.


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