Analysis of Captan, Folpet and their derivatives in food with APCI-LCMS-8060

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1. Introduction

Captan and Folpet are phytosanitary products belonging to the phthalimide family and used as fungicides. Folpet is not classified as one of the most toxic, but it is one of the most widely used pesticides, particularly in vineyards and in wheat and tomato crops. Captan is an active substance listed in Annex I of Directive 91/414/EEC by Directive 2007/5/EC (https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:32007L0005). Currently, these compounds are mainly analyzed in GCMS. But this technique has weaknesses. Indeed, these compounds are showing a strong tendency to thermal degradation, thus generating the formation of tetrahydrophthalimide (THPI) and phthalimide (PI).

This thermal decomposition is highly dependent on the GCMS system used, especially regarding the liner and its inertness as well as the column head. This decomposition is difficult to control and increases over the injections. That's why the GCMS methods for the analysis of Captan and Folpet are weakly robust. (http://www.eurl-pesticides.eu/library/docs/srm/EurlSrm_Observation_Captan_Folpet_LC-V1.pdf) This study therefore presents an alternative with the use of the Shimadzu LCMS-8060 system and an APCI interface. A sensitive method is implemented for the food extract analysis. This method with a QuEChERS and dSPE sample preparation provides a good and robust alternative.

2. Method

This poster describes the analysis of 4 compounds Captan, Folpet and their derivatives, respectively Phthalimide and Tetrahydrophthalimide, in food matrices with a limit of quantification between 1 and 30 ng/mL. The Captan and Phthalimide were purchased from Wako, the Folpet from Riedel-de Haen and the Tetrahydrophthalimide from TCI. The analytical system used was a Nexera X2 HPLC and LCMS-8060 triple quadrupole (Shimadzu Corporation) with an APCI ion source. All MRM transitions have been optimized using flow injection analysis mode (FIA) for all compounds. The source parameters have been optimized to improve the ionization and desolvatation of these compounds and consequently to increase their sensitivity. The method was developed on distilled water acidified with 0.1% acetic acid. This acid helps to stabilize the compounds and to obtain a better chromatographic peaks shape.

Figure 1: UHPLC-MS/MS System

2.1 Analytical Conditions

Determination of the 4 compounds was realized under the optimized conditions resumed in the tables below:

Table 1: LC parameters

System	Nexera UHPLC system
Column	Scepter C18 1,9 µm 30 x2,0 mm
Temperature	40 °C.
Injected volume	10 µL
Mobile phases	water + 10 mM ammonium acetate Methanol
Flow rate	200 µL/min
Analysis time	10 min

Table 2: MS parameters

System	LCMS-8060
Interface	Atmospheric pressure chemical ionization (APCI)
Neb gas	3 L/min
Drying gas	3 L/min
Desolvatation line	150°C
Heat block	300°C
Interface	400°C

2.2 Calibration Curve Preparation

The calibration curves were prepared from 4 individual standard stock solutions at 1mg/mL in ACN + 0.1% acetic acid. Two intermediate solutions at 1 µg/mL and 10 ng/mL were prepared and further diluted to obtain 10 solutions at 0.5; 1; 2.5; 5; 10; 25; 50; 100; 500 and 1000 ng/mL. Then these solutions were diluted by 5 in water and 0.1% of acetic acid.

2.3 Calibration Curve Preparation

Four kind of food were analyzed, rice, apple, mikan and matcha tea. These samples were prepared following the norm EN 15662:2018. The main steps were described in Fig.2, with QuEChERS QSep EN and cleaning with dSPE PSA/C18 both from Restek.

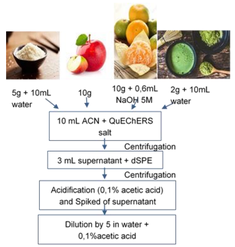

Figure 2: Sample preparation

2.4 Calibration data and LOQ tests

The results obtained are shown in Fig. 3. The regression factor is greater than 0.99%. The accuracies obtained are between 90 and 110%. The limit of quantification (LOQ) is 0.1 ng/mL in solvent.

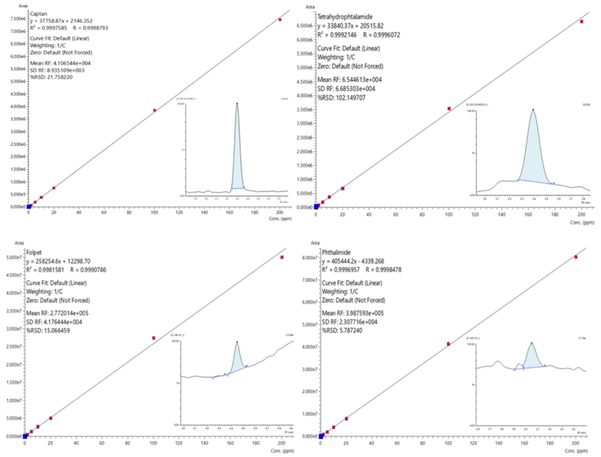

Figure 3: Calibration curves and chromatograms at 0.1 ng/ml

2.5 Limits of quantification

To set the limits of quantification (LOQs), each sample was extracted and spiked at different concentrations. The results obtained were shown in table 3 : LOQs between 0.1 and 30 ppb depending on the matrix and compound. The chromatograms obtained at LOQs were presented in Fig.4.

Repeatability

The area repeatability (RSD) were evaluated at the LOQs in matrix. Each sample was extracted 3 times. Whatever the matrix the Captan had RSD between 7 and 11%, Tetrahydrophthalimide between 2 and 11%, Folpet between 2 and 7% and Phthalimide between 1 and 8%.

Table 3: Limit of quantification in matrix

Limit of quantification (ppb)				
Matrix	**Captan**	**Tetrahydrophtalamide**	**Folpet**	**Phthalimide**
Solvent (ng/mL)	0.1	0.1	0.1	0.1
Tea	10	20	20	30
Rice	4	10	10	10
Mikan	1	5	5	10
Apple	1	5	5	5

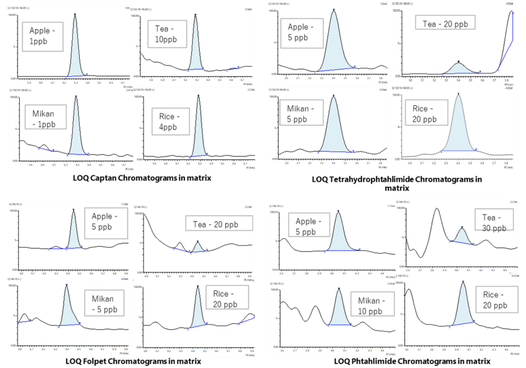

Figure 4: Chromatogram at LOQ in diffeent matrices

3. Summary and Conclusion

The Shimadzu LCMS-8060 allows the quantification of Captan, Folpet and their derivatives in food. A rapid method is set up with 10 min run. This sensitive method allows their quantification below the regulated limits whatever the matrix is. The robustness of this method allows to obtain a good repeatability of less than 11% even in difficult matrix like matcha tea. This LCMS method provides a good alternative to GCMS methods less robust.