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Application News

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Liquid Chromatography Mass spectrometry

Analysis of Captan, Folpet, and their Derivatives in Food with APCI-LCMS™-8060

Captan, Folpet, and their derivatives are fungicides widely used in agriculture. In view of their toxicity and ecotoxicity, the concentration of these compounds is monitored in food.

For this, a sensitive and fast method has been developed using the Shimadzu LCMS-8060 system with an APCI interface. The samples were prepared by QuEChERS and dSPE following EN 15662:2018 norm.

This method allows the analysis of food extract with limits of quantification below the regulation, described in (EC) No 396/2005 or Joint FAO/WHO Meeting (https://apps.who.int/iris/bitstream/handle/10665/44064/9789241665230_eng.pdf?sequence=1&isAllowed=y).

This method ensures that good repeatability is obtained even in difficult matrix like matcha tea. This LC/MS method provides a good alternative to GC/MS methods that are considered less robust.

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Introduction

Captan and Folpet are phytosanitary products belonging to the phthalimide family and are 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 GC/MS, but this technique has weaknesses. Indeed, these compounds show a strong tendency toward thermal degradation generating the formation of tetrahydrophthalimide (THPI) and phthalimide (PI). This thermal decomposition is highly dependent on the GC/MS system, especially the liner and column head. This decomposition is difficult to control and increases over the injections. This is why the GC/MS 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 for 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.

Method

This application describes the analysis of 4 compounds –Captan, Folpet, and their derivatives, respectively, as well as Phthalimide and Tetrahydrophthalimide– in food 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 from Shimadzu Corporation with an APCI source. MRM transitions have been optimized using flow injection analysis (FIA) for all compounds. The source parameters have been optimized to improve the ionization and desolvation of these compounds and, consequently, to increase their sensitivity.

The method was developed in distilled water acidified with 0.1 % acetic acid. This acid helps stabilize the compounds and obtain a better chromatographic peaks shape. The optimized analytical conditions are described in Fig. 1.

Chromatography liquid

System	Nexera UHPLC system
Column	Shim-pack Scepter™ C18 1.9 µm 30 × 2.0 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

Mass spectrometry

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

Fig. 1 Analytical Conditions

Calibration Curve Preparation

The calibration curves were prepared from 4 individual solutions at 1 mg/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.

Samples Preparation

Four food types were analyzed, rice, apple, orange, and matcha tea. These samples were prepared following the norm EN 15662:2018. The main steps are described Fig. 2, with QuEChERS Q-Sep® EN and cleaning with dSPE PSA/C18, both from Restek.

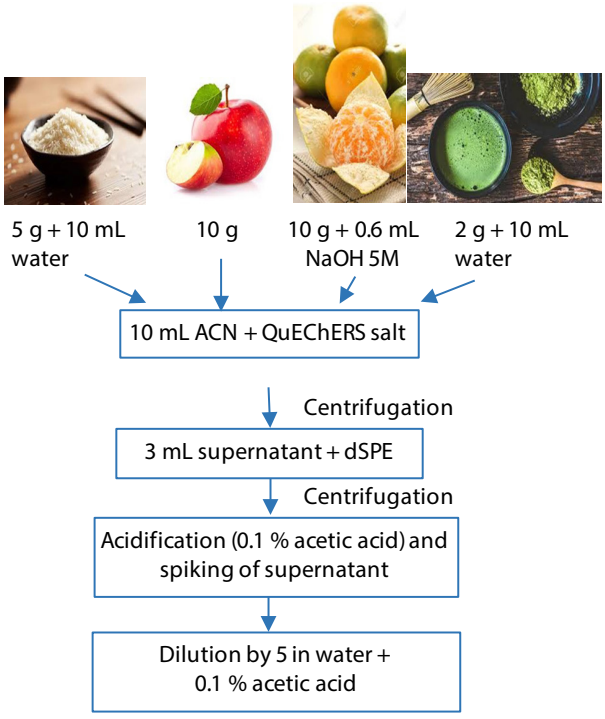

Fig. 2 Samples Preparation

Results and Discussion

Calibration Data

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.

Carry-Over and Interferences

To evaluate the carry-over, a solvent blank was injected after the highest calibration solution. No carry-over was observed. Then, the unspiked matrix extracts were injected to check the interferences. The analytical conditions allow interferences to be separated from the targets.

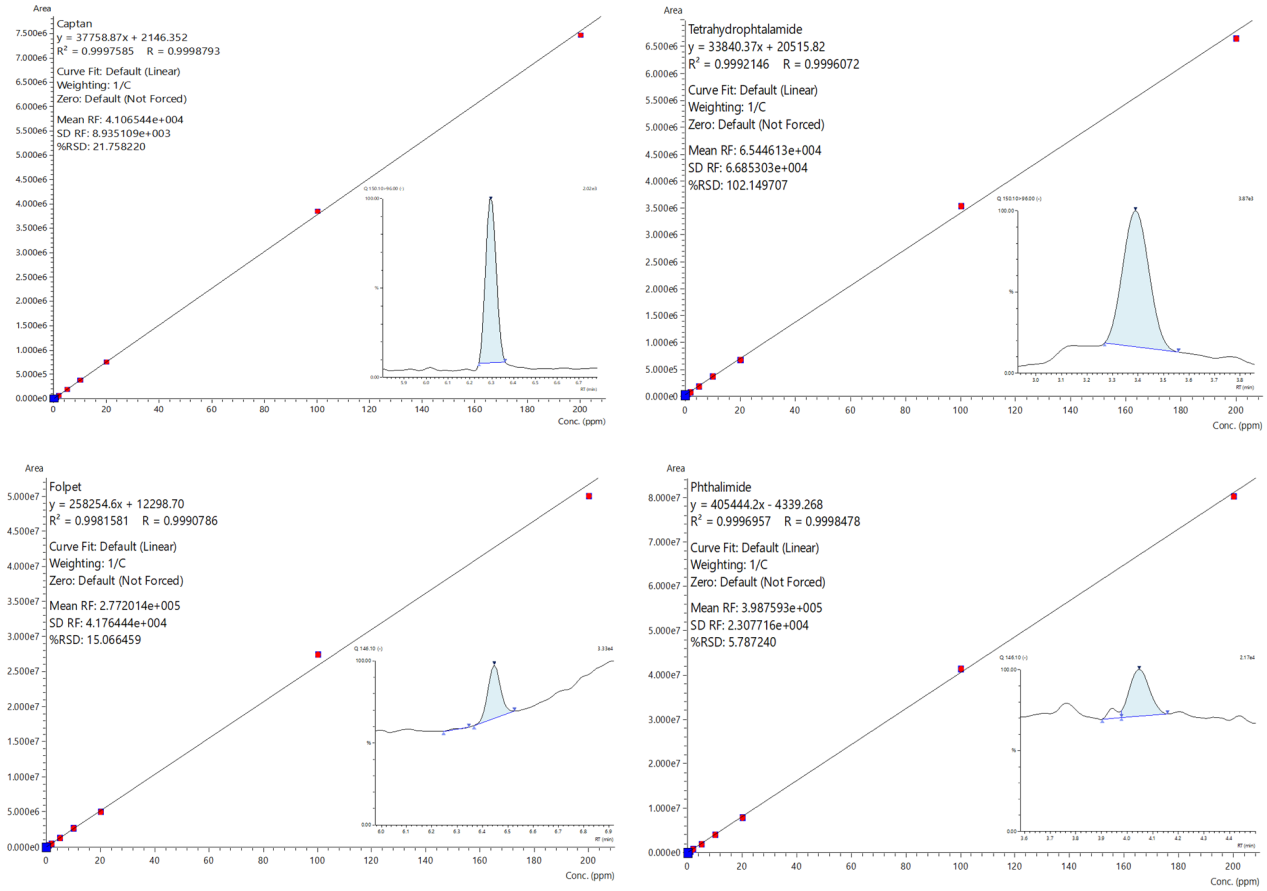

Fig. 3 Calibration Curves and Chromatograms at 0.1 ng/mL

Table 1 Limit of Quantification in Matrix

Limit of quantification (ppb)				
Matrix	**Captan**	**Tetrahydrophthalimide**	**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

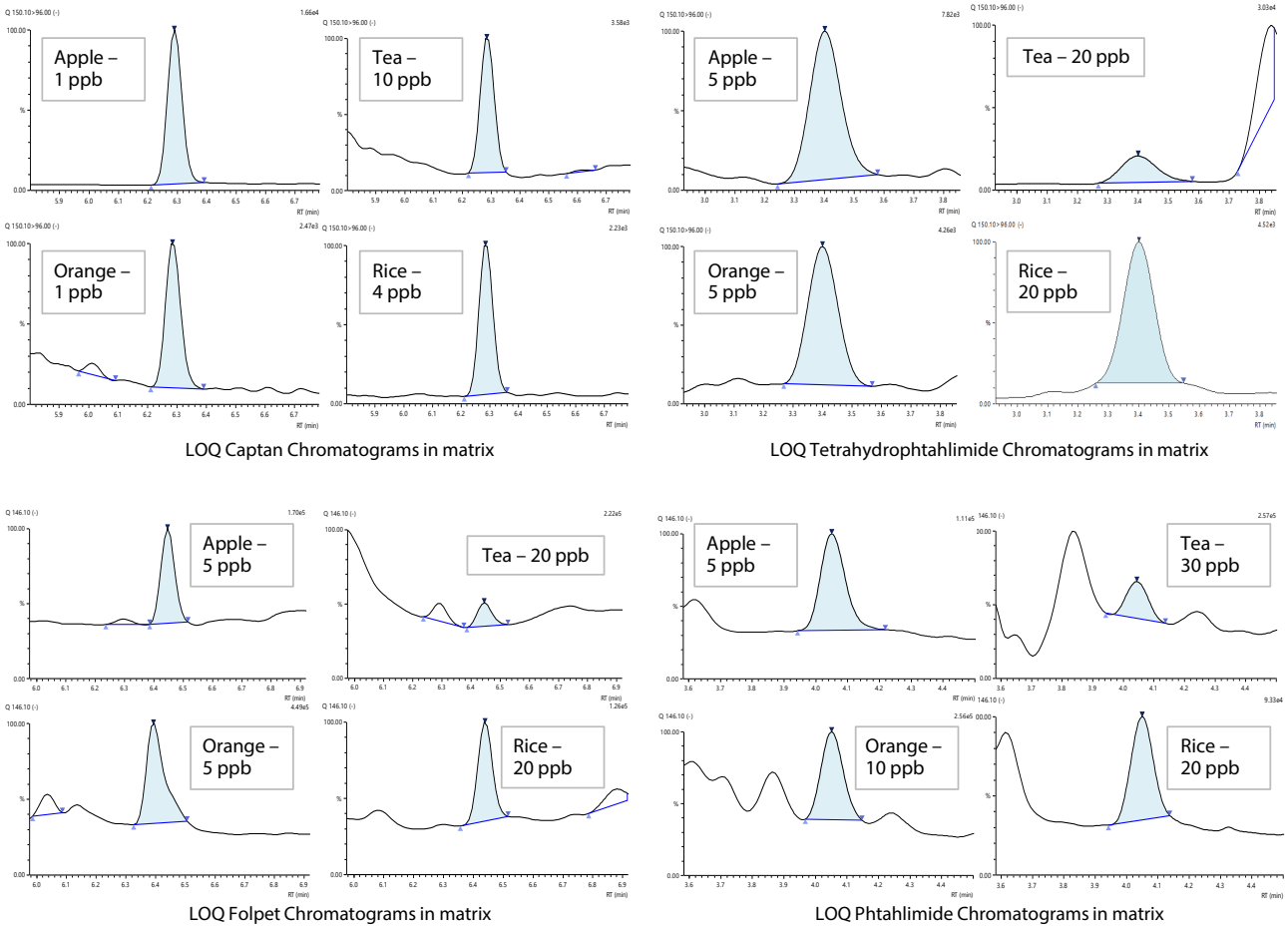

Fig. 4 LOQs Chromatograms in Matrix

Limits of Quantification

To set the limits of quantification (LOQs), each sample was extracted and spiked at different concentrations. The results obtained are shown in Table 1: LOQs between 1 and 30 ppb depending on the matrix and compound. The chromatograms obtained at LOQs are presented in Fig. 4.

Repeatability

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

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 a 10 minute run.

This sensitive method allows their quantification below the regulated limits, regardless of the matrix.

The robustness of this method allows good repeatability of less than 11 % to be obtained even in difficult matrix like matcha tea.

This LC/MS method provides a good alternative to GC/MS less robust methods.

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