

**Analysis of Captan, Folpet and Their Derivatives in
Water by APCI-LCMS™-8060**



■ Introduction

Captan and folpet are phytosanitary products belonging to the phthalimide family and are widely used as fungicides. Although folpet is not classified as one of the most toxic pesticides, it is one of the most widely used, particularly in vineyards and on wheat and tomato crops.

Captan is an active substance listed in Annex I to Directive 91/414/EEC by Directive 2007/5/EC (<https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:32007L0005>). This compound exhibits human toxicity with an acceptable daily dose (ADI) on the order of $0.01 \text{ mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$.

These compounds and their derivatives phthalimide and tetrahydrophthalimide are ecotoxic, in particular for aquatic organisms. Therefore, the aim of this study was the development of a quantification method for drinking and surface water. Taking advantage of the performance of the Shimadzu LCMS-8060 system with an APCI interface, a fast, sensitive method was developed, enabling analysis from a raw water sample without preparation by direct injection in a 6 min method.

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Method

This application describes the analysis of 4 compounds, captan, folpet, and their derivatives, in drinking water and surface water with a limit of quantification of 30 pg/mL. The captan and phthalimide were purchased from Wako, the folpet from Riedel-de Haën, and the tetrahydrophthalimide from TCI. The analytical system consisted of a Shimadzu LC and LCMS-8060. In this method, a triple quadrupole mass spectrometer with an APCI source was used. MRM transitions were optimized by using flow injection analysis (FIA) for all compounds. The source parameters were optimized to improve the ionization and desolvation 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 peak shape. Although no internal standards were used in the analyses described here, use is advisable in order to compensate for the possible matrix effect. Subsequently, the quantification analysis was carried out by spiking tap water sampled in Kyoto and surface water from the Tenjin River, also in Kyoto.

The optimized analytical conditions used in liquid chromatography and the mass spectrometer are shown in Table 1 and 2, respectively.

Table 1 Liquid Chromatography Conditions

Chromatography liquid	
System	: Nexera™ UHPLC system
Column	: Shim-pack Scepter™ C18 1.9 μm 30 × 2.0 mm
Temperature	: 40 °C
Injected volume	: Total 300 μL (stacked 3 × 100 μL)
Mobile phases	: Water + 10 mM ammonium acetate Methanol
Flow rate	: 200 μL/min
Analysis time	: 6 min

Table 2 Mass Spectrometry Conditions

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

Results and Discussion

A series of 10 calibration points prepared in pure acidified water were injected. The dynamic range was from 9 to 900 pg/mL. Solutions with concentrations of 27, 45 and 63 pg/mL were prepared 3 times. Solutions with the same concentration levels were prepared for both the drinking water and the river water for analysis as controls in order to verify the ability of the method to quantify the compounds in different types of water with a good repeatability.

Calibration Data

The calibration curves obtained with pure water are shown in Fig. 1. The regression of these curves is greater than 0.99%. The accuracy obtained for each solution is between 80 and 120%. Each compound is detected at 9 pg/mL, and the limit of quantification (LOQ) is therefore set at 27 pg/mL.

Repeatability

In order to estimate the repeatability of the method, the solutions with concentrations of 27, 45 and 63 pg/mL were prepared 3 times each in the 3 available kinds of water. The chromatograms at the LOQ obtained with the river water and the repeatability results are presented in Fig. 2 and Table 3, respectively, and show good repeatability below 12% for the 3 different levels, including the LOQ.

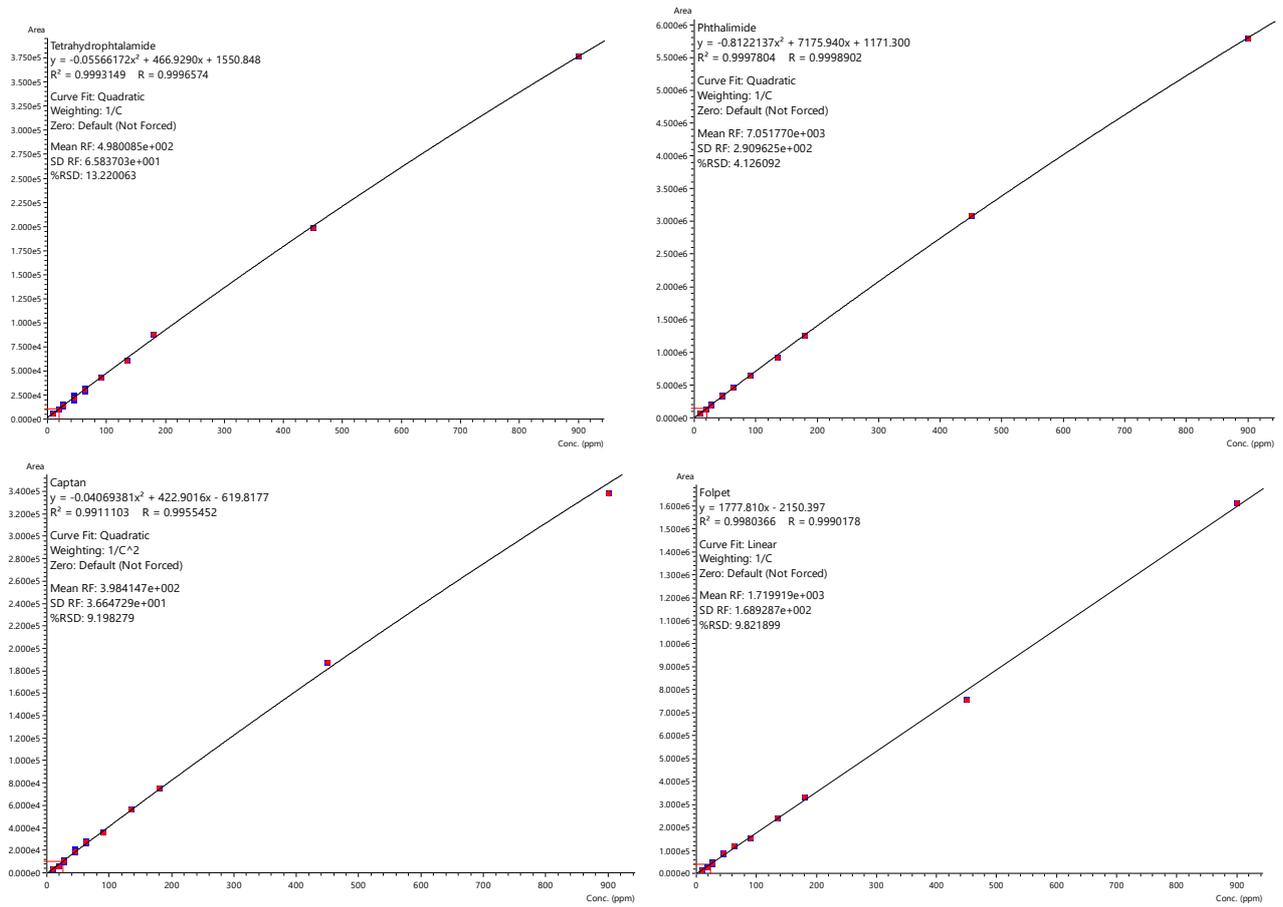


Fig. 1 Calibration Curves

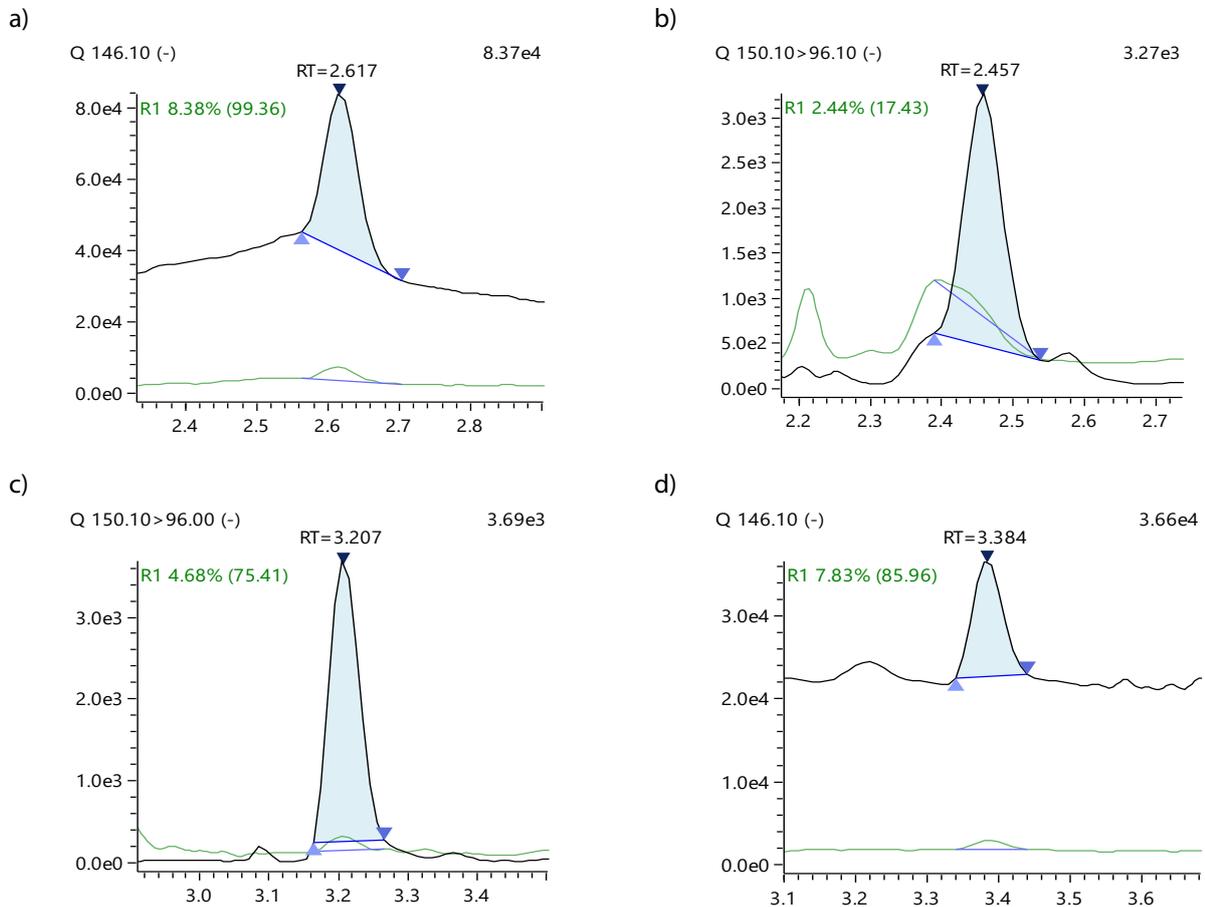


Fig. 2 Chromatograms of River Water (Concentration: 27 pg/mL)
 a) Folpet, b) Tetrahydrophthalimide, c) Captan, d) Phthalimide

Table 3 Repeatability

Compounds	Solutions	RSD (%) distilled water	RSD (%) Tap water	RSD (%) River water
Captan	27 pg/mL	11	10	8
	45 pg/mL	7	2	5
	63 pg/mL	3	4	10
Tetrahydrophthalimide	27 pg/mL	4	4	8
	45 pg/mL	10	6	2
	63 pg/mL	6	1	1
Folpet	27 pg/mL	9	11	3
	45 pg/mL	3	2	2
	63 pg/mL	2	1	4
Phthalimide	27 pg/mL	3	4	3
	45 pg/mL	2	5	3
	63 pg/mL	1	6	7

Table 4 Accuracy

conc. pg/mL	Folpet			Tetrahydrophthalimide		
	Pure water Accuracy (%)	Tap water Accuracy (%)	River water Accuracy (%)	Pure water Accuracy (%)	Tap water Accuracy (%)	River water Accuracy (%)
9	94	96	83	101	104	89
18	89	90	89	96	98	76
27	107	79	94	96	84	89
45	114	111	86	107	87	80
63	109	97	79	92	77	81
90	98	89	89	100	80	83
135	101	78	77	95	81	84
180	105	84	77	105	86	88
450	95	103	75	99	83	88
900	101	102	84	100	86	89

Accuracy

The accuracy of the method has been established at all concentration levels. Drinking and river water were quantified as controls with the calibration curve established with distilled water. The results presented in Table 4 show good accuracy of between 75 and 120% for all 3 waters. Although this was determined by external calibration, these values could be further improved by using internal standards, which would correct the matrix effect.

conc. pg/mL	Captan			Phthalimide		
	Pure water Accuracy (%)	Tap water Accuracy (%)	River water Accuracy (%)	Pure water Accuracy (%)	Tap water Accuracy (%)	River water Accuracy (%)
9	108	118	115	99	92	76
18	82	92	92	97	75	79
27	106	85	103	101	91	87
45	101	107	90	106	92	77
63	106	93	91	102	79	86
90	96	84	97	101	80	86
135	102	77	76	97	84	76
180	102	85	76	99	91	76
450	104	107	75	101	96	88
900	97	108	89	100	91	84

Summary and Conclusion

The Shimadzu LCMS-8060 with an APCI source allows the quantification of captan, folpet and their derivatives in drinking water and surface water. A rapid method with a 6 min run without sample preparation was established. This sensitive method allows quantification of these compounds with a limit of at least 30 pg/mL, and its reliability is shown by the good repeatability and accuracy values.

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First Edition: Apr. 2020



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