

Determination of carbosulfan and its metabolites in oranges by liquid chromatography ion-trap triple-stage mass spectrometry[☆]

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Abstract

Liquid chromatography ion-trap mass spectrometry LC–MSⁿ has been successfully applied to identify and confirm carbosulfan and seven of its metabolites in oranges after pressurized liquid extraction (PLE) with dichloromethane. Mass spectra of carbosulfan and its metabolites were investigated using multiple stages of mass spectrometry. Although interpretation of the fragmentation pathways, based on mass spectra, enables structural elucidation and identification of these compounds, the proposed fragmentation pathways and ion structures need verification by exact mass measurements. The analytical method—PLE and LC–MS³—was validated: limits of quantification (LOQ) ranged from 0.01 to 0.07 mg kg⁻¹; at this level, recoveries were 55–90% with RSDs (five replicate analyses) from 8 to 19%. The degradation of carbosulfan was determined in a laboratory study carried out in mature oranges (Valencia Late) and tangerines (Clementine of Nules) already harvested. Main degradation products of carbosulfan were carbofuran, 3-hydroxycarbofuran, 3-ketocarbofuran and dibutylamine.

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1. Introduction

Pesticide determination in fruits and vegetables is a priority objective to evaluate food quality and to avoid possible risks for the human health. These compounds are widely used to pre- and post-harvest control of pests that affect agricultural crops. They can reach the human population via food-chain [1]. Analytical food laboratories, all over the world, carry out extensive research, monitoring, and screening of pesticide residues in fruits and vegetables. However, few studies have been managed on the identification and routine analysis of their main degradation products, which can be rather persistent and as hazardous as their parent compounds [2].

As an example, carbosulfan breaks down into carbofuran, 3-hydroxy carbofuran and 3-keto carbofuran, all of them toxic compounds [3,4]. This is a special case, in which a less toxic pesticide (carbosulfan) is transformed in a more toxic one (carbofuran) after its application. Carbosulfan has a temporary accept-

able daily intake (ADI) of 0–0.01 mg kg⁻¹ bw and a maximum residue limit (MRL) of 0.05 mg kg⁻¹ for the sum of carbosulfan, carbofuran and 3-hydroxy carbofuran in citrus fruits [5,6].

Photolysis, hydrolysis and microbial transformation of carbosulfan appear to be important degradation routes in the environment [7–14]. The dislodgeable residues of carbosulfan and its metabolites in oranges [3,4,15,16] and the kinetics of carbosulfan residue disappearance in peaches [17], sugarcane [18], and rice [19] have already been studied. As an example, the proposed metabolic pathways in plant materials are presented in Fig. 1 [4]. Most of these studies have been conducted using radiolabelled compounds, thin layer chromatography and gas or liquid chromatography with unspecific detectors. However, a serious weakness of all these methods is that they lack sufficient specificity for identification of the analyte in complex matrices such as fruits and vegetables by a certain pesticide [20,21]. Thus, mass spectrometry (MS) is a key element. Mass spectra of carbofuran and its major metabolites have only been investigated using electron impact mass spectrometry and verified by exact mass measurements and collision-induced dissociation (CID) [22]. In addition, most recent gas chromatography/mass spectrometry (GC/MS) and liquid chromatography (LC)/MS analyses identified 2-hydroxy-3-(3-methylpropan-2-ol) phenol as a product derived

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