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A green-analytical chemistry method for agrochemical-residue analysis in vegetables

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ABSTRACT

Ten agrochemicals, including fungicides, insecticides, herbicides and a plant growth regulator, were quantified at part per billion levels in complex matrices using a green-analytical chemistry (GAC) method. Liquid chromatography with dual UV/diode array (DAD) and fluorescence (FLD) detections was carried out in a single run, and the second-order DAD-elution time and FLD-elution time data obtained were treated with MCR-ALS (multivariate curve resolution/alternating least-squares) algorithm. In this way, while analytes are measured through their more appropriate (absorbance and/or fluorescence) signals, chemometric treatment of the corresponding matrices allows the resolution of total or partial overlapped bands, and to overcome the presence of interferences in real samples. In this work, FLD-elution time second-order data were obtained for the first time at two excitation wavelengths, improving the sensitivity of fluorescent analytes. The approach was successfully applied to in land cultivated vegetables, including mushroom, lettuce, alfalfa sprout, cucumber, and celery.

1. Introduction

The unquestionable benefits of the use of pesticides and growth activators in the agro-economy are contrasted with the disadvantages of the widespread human exposure to their residues in fruits and vegetables. Environmental agencies around the world have established legal directives to control their concentrations by defining suitable maximum residue levels (MRL), which refer to the highest level of a pesticide residue that is legally tolerated in or on food or feed when they are correctly applied [1].

Significant efforts have therefore been directed to the determination of residues in food, with special attention to the development of the so-called green analytical chemistry (GAC) methods [2]. The latter are based on green chemistry principles (e.g. minimizing reagent consumption and waste generation, using safer reagents and miniaturizing analytical systems) [3], and represent a real challenge for analytical chemists. There are a variety of resources to address and reduce environmental pollution caused by the different stages of the overall analytical process. The usual approach focuses on sample collection and preparation, separation, detection, and data evaluation [3].

In the present work, the simultaneous quantification of the fungicides thiabendazole (TBZ), fuberidazole (FBZ), carbendazim (CBZ) and fenarimol (FM), the herbicides dicamba, imazaquin (IMZQ) and norflurazon (NFZ), the insecticides carbaryl (CBL) and methiocarb, and the plant growth activator 1-naphthol (NAP) is attempted in vegetables samples. Table 1 shows structures, functions and dissociation constants of the studied compounds [4–11].

In complex systems such as the ones here investigated, it is usually difficult to develop a selective method without resorting to extensive preparation steps and comprehensive sample clean-up. In these cases, it is extremely useful to couple a chromatographic approach, carried out under isocratic conditions, with the chemometric analysis of second-order data. This allows to considerably simplify the sample pretreatment and to significantly reduce the analysis time [12]. Depending on the spectral properties of the analyzed compounds, either diode-array (DAD) [13–15] or fluorescence (FLD) [16,17] detectors are frequently employed. Recently, liquid chromatography (LC) with dual UV and fluorimetric detections was used for the chemometric determination of sex hormones in natural waters and sediments [18]. In the present work, for the first time, fluorescence emission-elution time second-order data are obtained by sequentially exciting the sample at two different excitation wavelengths during the chromatographic run. This procedure was carried out through the adequate control of the FLD software. Thus, in addition to take advantage of the simultaneous trace analysis of agrochemicals from different classes in a single run, we obtained better sensitivity in the fluorimetric detection by irradiating the analytes with optimal excitation wavelengths.

Both the LC-DAD and LC-FLD second-order data matrices were processed by multivariate curve resolution-alternating least-squares (MCR-

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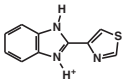
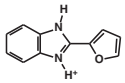
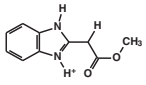
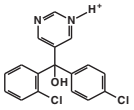
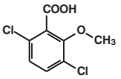
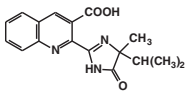
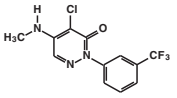
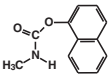
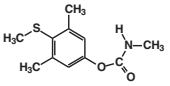
0026-265X/

Table 1
Chemical structures, activities and dissociation constants for the studied agrochemicals.

Name	Activity	Structure	Dissociation constant	Ref
TBZ	Fungicide		p*K*a1 ~ 0.5 p*K*a2 = 4.8 p*K*a3 = 11.3	[4]
FBZ	Fungicide		p*K*a1 = 5.0 p*K*a2 = 11.7	[4]
CBZ	Fungicide		p*K*a1 = 4.3 p*K*a2 = 10.8	[4]
FM	Fungicide		p*K*a1 = 1.67 p*K*a2 = 11.23	[5]
Dicamba	Herbicide		p*K*a = 2.4	[6]
IMZQ	Herbicide		p*K*a = 3.8	[7]
NFZ	Herbicide		No dissociation in pH range 1–12	[8]
CBL	Insecticide		p*K*a = 12.02	[9]
Methiocarb	Insecticide		p*K*a = 12.16	[10]
NAP	Plant growth regulator		p*K*a = 9.4	[11]

ALS) [19] algorithm, which allows us to obtain reliable results in the analysis of the studied agrochemicals in spiked vegetable samples.

2. Experimental

2.1. Reagents and solutions

TBZ, CBL and NAP were purchased from Sigma Aldrich Co. (St. Louis, MO, USA). CBZ, dicamba, IMZQ, NFZ, FM, and methiocarb were obtained from Fluka (Buchs, Switzerland). FBZ was provided by Riedel-de Haën (Seelze, Germany). Acetonitrile (ACN), methanol, phosphoric acid and sodium dihydrogen phosphate monohydrate were obtained from Merck (Darmstadt, Germany). Milli-Q water (Millipore, Bedford, USA) was used in all experiments. Stock solutions of all analytes of about 1000 μg mL^{-1} were prepared in methanol. From these solutions, more diluted methanol solutions (around 5 μg mL^{-1}) were obtained. Working solutions were prepared immediately before their use by taking appropriate aliquots of diluted methanol solutions, drying the solvent under nitrogen and adding mobile phase (see below) to the desired concentrations.

2.2. Apparatus

Chromatographic runs were performed on an HP 1200 liquid chromatograph (Agilent Technologies, Waldbronn, Germany) consisting of a quaternary pump, a manual injector fitted with a 20 μL loop, a DAD, an FLD, and the HP ChemStation software package for instrument control, data acquisition and data analysis. A C18 Poroshell 120 EC (4.6 × 100 mm, 2.7 μm particle size) column (Agilent Technologies, Santa Clara, CA, USA) was employed.

2.3. Chromatographic procedure

The selected mobile phase was a 60:40 (v/v) mixture of ACN and 0.01 mol L^{-1} phosphate buffer (pH 2.8), delivered at a flow rate of 0.6 mL min^{-1} with a chromatographic system operating under isocratic mode.

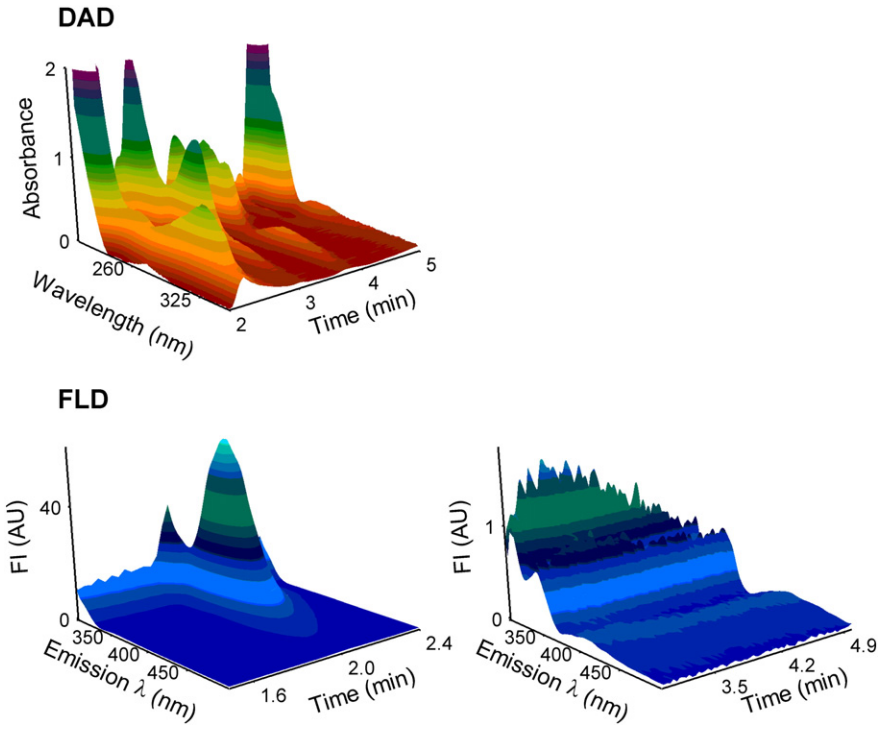


Fig. 1. Three-dimensional profiles obtained with DAD and FLD for a synthetic sample containing the ten studied agrochemicals dissolved in mobile phase at part-per-billion concentrations. For clarity, FLD data were split in two plots.