Analytica Chimica Acta 814 (2014) 23–30

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Determination of five pesticides in juice, fruit and vegetable samples by means of liquid chromatography combined with multivariate curve resolution

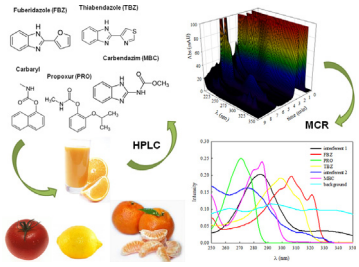
Valeria Boeris, Juan A. Arancibia, Alejandro C. Olivieri *

Departamento de Química Analítica, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario e Instituto de Química Rosario (IQUIR-CONICET), Suipacha 531, S2002LRK Rosario, Argentina

HIGHLIGHTS

- Five pesticides were determined in juice, fruit and vegetable samples.
- Liquid chromatography was coupled to diode array detection.
- Chromatographic-spectral matrices were analyzed by multivariate curve resolution.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 November 2013
Received in revised form 4 January 2014
Accepted 10 January 2014
Available online 18 January 2014

Keywords:
High-performance liquid chromatography
Diode array detection
Multivariate curve resolution
Pesticides
Vegetable samples

ABSTRACT

The aim of this work was to quantify five commonly used pesticides (propoxur, carbaryl, carbendazim, thiabendazole and fuberidazole) in real samples as: tomato, orange juice, grapefruit juice, lemon and tangerine. The method used for the determination of these analytes in the complex matrices was high-performance liquid chromatography with diode array detection. In order to work under isocratic conditions and to complete each run in less than 10 min, the analysis was carried out applying multivariate curve resolution coupled to alternating least-squares (MCR–ALS). The flexibility of this applied multivariate model allowed the prediction of the concentrations of the five analytes in complex samples including strongly coeluting analytes, elution time shifts, band shape changes and presence of uncalibrated interferents. The obtained limits of detection (in $\mu g\,L^{-1}$) using the proposed methodology were 2.3 (carbendazim), 0.90 (thiabendazole), 12 (propoxur), 0.46 (fuberidazole) and 0.32 (carbaryl).

1. Introduction

Although the use of pesticides provides unquestionable benefits in providing a plentiful, low-cost supply of high-quality fruits and vegetables, their incorrect application may leave harmful residues, which involve possible health risk [1]. The concentration of pesticides is regulated in many samples such as drinking waters, vegetables, juices, etc., by the European Commission [2] and the Food and Drug Administration [3], among other agencies. Traditionally, the instrumental techniques employed to determine these compounds involve fluorescence, gas or liquid chromatography [4–8]. Specifically, the determination of benzimidazolic pesticides (carbendazim, thiabendazole and fuberidazole) and/or carbamates (carbaryl, propoxur and carbendazim) in fruits and vegetables have been carried out by various approaches, such as supramolecular solvent-based microextraction followed by high-performance

Abbreviations: HPLC, high-performance liquid chromatography; DAD, diode array detection; MCR–ALS, multivariate curve resolution coupled to alternating least-squares; PRO, propoxur; CBL, carbaryl; MBC, carbendazim; TBZ, thiabendazole; FBZ, fuberidazole.

* Corresponding author. Tel.: +54 3414372704; fax: +54 3414372704.
E-mail addresses: olivieri@iquir-conicet.gov.ar, aolivier@fbioyf.unr.edu.ar (A.C. Olivieri).

0003-2670/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.aca.2014.01.034

liquid chromatography (HPLC) with fluorescence detection [9], gas chromatography coupled to mass spectrometry and selected ion monitoring [10], enzymatic immunoassay using antibodies [11–13] or electrochemical methods [14,15].

The analysis of mixtures of pesticides using methods based on HPLC sometimes results in complex separations and overlapped peaks [16,17]. Nevertheless, complex multicomponent mixtures can in many cases be qualitatively and quantitatively resolved by means of chemometrics. Depending on their nature, data can be arranged in a two-way structure (a table or a matrix), as in the case of collecting the absorbance spectra for many samples, or in a three-way structure, e.g., in HPLC with diode array detection (DAD), where spectra are recorded at several elution times for each sample. Such data arrangements in three- or higher way arrays can be handled using multi-way methods of analysis [18,19].

Collection of multi-dimensional chromatographic information, and data processing by advanced chemometric algorithms constitute a fruitful combination of techniques, recently applied to diverse research areas [20–22]. Chemometrics is required whenever perfect separation of the various sample components cannot be achieved by the employed chromatographic system, leading to overlapping peaks in the elution time mode. In these cases, selectivity may be mathematically restored by applying multivariate data analysis [23]. In particular, the so-called second-order advantage can be achieved, a property which is inherent to matrix instrumental data, and implies that analytes can be quantified in samples containing potential interferences [21]. Signals arising from coeluting analytes or foreign components can be modeled by powerful second-order multivariate algorithms.

The combination of chemometrics to HPLC presents additional advantages in relation to traditional methods: since chemometrics allows resolving coeluted peaks, it is possible to reduce the duration of the chromatographic run, allowing not only processing more samples but also reducing the solvent consumption, saving time and money. Moreover, several authors report that gradient of solvents was required to achieve resolution of the analytes [24–26]: this requirement may be avoided using isocratic conditions and resolving the peak by applying chemometrics.

In liquid chromatographic runs, elution time shifts and band shape changes usually occur from sample to sample: in these cases, a useful alternative is to analyze the data with flexible algorithms, which allow a given component to present different time profiles in different samples, such as parallel factor analysis 2 (PARAFAC2) or multivariate curve resolution coupled to alternating least-squares (MCR–ALS) [27]. Recent work from our laboratory indicated better performance with MCR–ALS in the case of multi-analyte quantification in the presence of high overlapping of elution profiles and uncalibrated interferences, mainly because of the possibility of building a more constrained model in MCR–ALS in comparison with PARAFAC2 [22].

In the present report, we selected MCR–ALS as the algorithm of choice for processing HPLC–DAD data, and discuss its behavior towards the quantification of the following five pesticides in fruit and vegetable samples: propoxur (PRO), carbaryl (CBL), carbendazim (MBC), thiabendazole (TBZ) and fuberidazole (FBZ) (Fig. 1). The presence of benzimidazoles, carbamates and their degradation products in waters or food products is potentially harmful for humans due to their proven toxicity. This is the cause of the continued interest in the development of analytical methods for monitoring these families of compounds. Previous chromatographic analysis of the presently studied compounds required up to 35 min [28,29]. The aim of this work is to quantify these analytes in complex matrices under HPLC isocratic conditions and in less than 10 min.

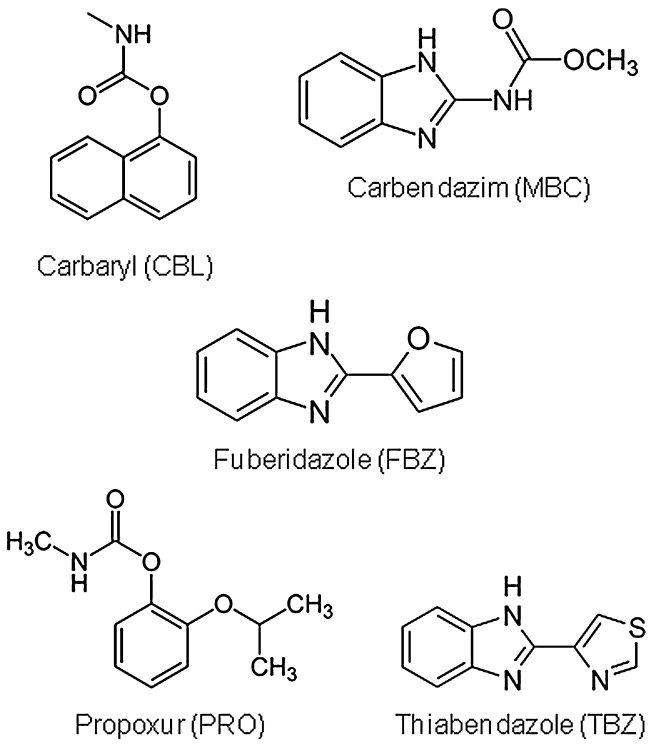


Fig. 1. Chemical structures of the five assayed pesticides.

2. Theory

The bilinear model assumed by MCR methods is analogous to the generalized Lambert–Beer's law, where the individual responses of each component are additive. In matrix form, this bilinear model is expressed as:

$$\mathbf{D} = \mathbf{C}\mathbf{S}^{\mathrm{T}} + \mathbf{E} \tag{1}$$

where $\mathbf{D}$ (size $J \times K$) is the matrix of experimental data (J is the number of elution time data points and K is the number of absorption wavelengths), $\mathbf{C}$ (size $J \times N$) is the matrix whose columns contain the concentration profiles of the N components present in the samples, $\mathbf{S}^{\mathrm{T}}$ (size $N \times K$) is the matrix whose rows contain the component spectra and $\mathbf{E}$ (size $J \times K$) is a matrix collecting the experimental error and the variance not explained by the bilinear model of Eq. (1).

The first step in MCR–ALS studies is to obtain a rough estimation of the number of components, which can be simply performed by visual inspection of singular values or principal component analysis (PCA) [30,31].

The resolution is accomplished using an iterative ALS procedure, initialized using an initial estimation of the spectral or concentration profiles for each intervening species. Different methods are used for this purpose, such as evolving factor analysis [32] or the determination of the purest variables [33]. If the initial estimations are the spectral profiles, the unconstrained least-squares solution for the concentration profiles can be calculated from the expression:

$$\mathbf{C} = \mathbf{D}(\mathbf{S}^{\mathrm{T}})^{+} \tag{2}$$

where $(\mathbf{S}^{\mathrm{T}})^{+}$ is the pseudoinverse of the spectral matrix $\mathbf{S}^{\mathrm{T}}$ [34]. If the initial estimations were the concentration profiles, the unconstrained least-squares solution for the spectra can be calculated from the expression:

$$\mathbf{S}^{\mathrm{T}} = \mathbf{C}^{+}\mathbf{D} \tag{3}$$