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Detection of malathion in food peels by surface-enhanced Raman imaging spectroscopy and multivariate curve resolution

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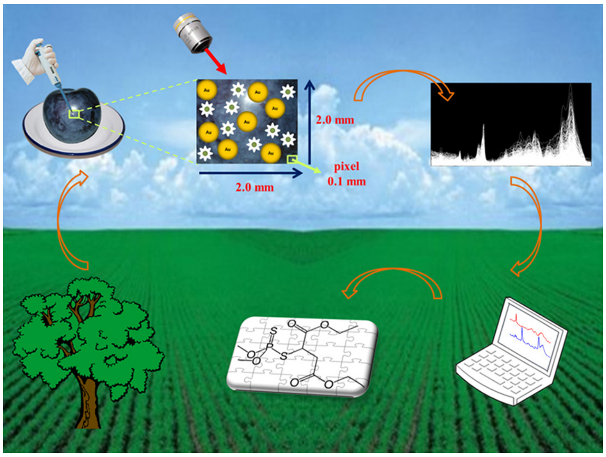
HIGHLIGHTS

- Methodology for in situ detection of malathion in tomato and Damson plum peels by SERS imaging.
- Multivariate curve resolution methods were used for malathion spectra recuperation.
- MCR-WALS allowed the spectra recuperation even in the presence of heteroscedastic noise.
- Detection on the order of 0.123 mg L^{-1}, which is below the maximum residue limit permitted for this pesticide.
- The proposed methodology is fast, efficient and does not require sample manipulation.

GRAPHICAL ABSTRACT



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ABSTRACT

An analytical methodology was developed for detection of malathion in the peels of tomatoes and Damson plums by surface-enhanced Raman imaging spectroscopy and multivariate curve resolution. To recover the pure spectra and the distribution mapping of the analyzed surfaces, non-negative matrix factorization (NMF), multivariate curve calibration methods with alternating least squares (MCR-ALS) and MCR with weighted alternating least square (MCR-WALS) were utilized. Error covariance matrices were estimated to evaluate the structure of the error over all the data. For the tomato data, NMF-ALS and MCR-ALS presented excellent spectral recovery even in the absence of initial knowledge of the pesticide spectrum. For the Damson plum data, owing to heteroscedastic noise, MCR-WALS produced better results. This methodology enabled detection below to the maximum residue limit permitted for this pesticide. This approach can be implemented for in situ monitoring because it is fast and does not require extensive manipulation of samples, making its use feasible for other fruits and pesticides as well.

1. Introduction

Malathion (Fig. 1) is an organophosphate insecticide widely used in agriculture, mainly to kill the boll weevil and fruit fly. According to the Environmental Protection Agency, this pesticide is classified as Class III, with suggestive evidence of carcinogenicity

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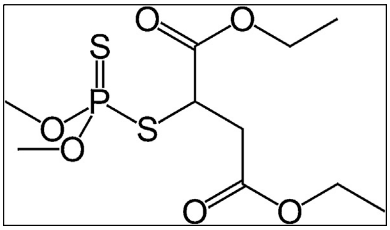

Fig. 1. Chemical structure of malathion.

[1]. The Food and Drug Administration has set the maximum residue limit (MRL) of this pesticide at 8 mg L^{-1} in foods [2]. Such concerns have led to several studies investigating malathion's safety, the majority of which used high-performance liquid chromatography (HPLC) [3–5]. However, this technique requires sample pretreatments, making the procedure laborious and time consuming.

Surface-enhanced Raman spectroscopy (SERS) has been spotlighted in recent years as a technique that enables detection of target molecules (analytes) in samples at low concentrations with excellent selectivity [6]. As a spectroscopic technique, SERS makes possible the development of analytical methodologies that are fast and require minimal sample manipulation. Many of the recent developments in SERS have been based on novel substrates with different morphologies [7–11]. Therefore, the architecture of nanoparticles has a significant effect on the observed SERS results [12]. These recent advances enable work in adverse environments and a variety of applications, such as the detection of complex biological structures and intracellular studies [8,9,13,14] and of pesticide and herbicide residues in foods [7,10]. Another important enhancement in SERS measurements is the ability to obtain additional spatial information on a sample by a procedure called SERS imaging [8,13–15]. In this technique, a sample area is delimited and a SERS spectrum is obtained at each point, called a pixel, on the surface of the sample area. Then, chemical information about the compounds present in the sample can be extracted from the mapped area. The main advantage of this approach is the possibility to achieve low detection limits. The bulk concentration in the monitored area can be low, but on the other hand, the concentration of a specific compound can be high in some pixels.

With complex matrices, it is sometimes not possible to obtain a SERS signal resulting only from the analyte; in such cases, multivariate curve resolution methods [15,16] have been successfully employed. Examples of this approach include investigation of drug distribution in tablets via SERS imaging [15] and the urinary quantification of nicotine in the presence of other interference compounds [16].

Among the several curve resolution methods, is possible to emphasize the multivariate curve resolution with alternating least squares (MCR-ALS) [17,18] and non-negative matrix factorization (NMF) [19]. However, a common limitation of these algorithms is that they assume that the error structure is homoscedastic, uncorrelated and independent, and identically distributed (i.i.d.) [20–22]. However, the measurements obtained from SERS imaging in complex samples presenting fluorescence can be heteroscedastic and/or affected by correlated noises [20,23]. These problems may appear as variations in the signal intensity with wavelength channel or as source intensity fluctuations, due to the inequality of the analyzed surface or common imperfections in the substrate/colloid and their nanostructures [12]. An alternative to overcome this situation is the use of MCR with weighted alternating least squares (MCR-WALS) [24], in which the algorithm addresses the structure of the error over all the data to find the best solution.

The goal of this work was to develop a fast and efficient analytical methodology for detection of malathion residues in food peels (specifically, those of tomatoes and Damson plums), without any sample pre-treatment, based on SERS imaging in conjunction with a multivariate curve resolution method. Because of the complex data structure, we also aimed to determine the most appropriate multivariate curve resolution method: NMF-ALS, MCR-ALS or MCR-WALS.

2. Algorithms

The multivariate curve resolution methods MCR-ALS, NMF-ALS and MCR-WALS are bilinear decomposition methods of a matrix (**G**) in scores (**T**), information about the samples and loadings (**P**), information about the variables (Eq. (1)), and an error matrix (**E**).

$$\mathbf{G} = \mathbf{T}\mathbf{P}^{\mathrm{T}} + \mathbf{E} \tag{1}$$

The dimension of **G** is $m \times n$, where m and n are the number of samples and variables, respectively. The dimension of **T** is $m \times r$ and the **P** is $r \times n$, where r is the rank, which can be determined by SVD, evolving factor analysis (EFA), or other methods [18]. These algorithms require an initialization from an estimate from **T** or **P** (concentrations or spectra). When this information is not available, a simple random initialization or a more accurate methods, such as PURE [17], SIMPLISMA [25] or the needle-search method [26], can be used.

2.1. Multivariate curve resolution alternating least squares (MCR-ALS)

In the MCR-ALS algorithm, firstly **T** is estimated from **G** (calculated by PCA from original data) and initial **P** by:

$$\hat{\mathbf{T}} = \mathbf{G}(\mathbf{P}^{\mathrm{T}})^{+} \tag{2}$$

In the next step, the estimated **T** matrix, obtained by Eq. (2), is used to reestimate **P**:

$$\hat{\mathbf{P}}^{\mathrm{T}} = \mathbf{T}^{+}\mathbf{G} \tag{3}$$

The procedure is repeated several times, estimating **T** and **P**, using the Eqs. (2) and (3), such that the error will be minimized as follows:

$$\min\|\mathbf{G} - \mathbf{T}\mathbf{P}^{\mathrm{T}}\| \tag{4}$$

Common problems in the MCR-ALS solution are the permutation ambiguity (no sorting order on the components), intensity ambiguity (different relative scales between the concentration profiles) or rotational ambiguity (range of feasible solutions). For this purpose, constraints such as non-negativity [17], closure [18] or others [27] can be used. For the non-negativity constraint [17], several methods are available to solve the problem of negative values, including simple methods to truncate these values or other robust solutions, such as non-negative least squares (NNLS) [28], fast NNLS (FNNLS) [29] or fast combinatorial NNLS (FCNNLS) [30].

2.2. Non-negative matrix factorization (NMF)

Non-negative matrix factorization (NMF) was primarily proposed by Lee and Seung for processing of facial images [31]. The main feature of this algorithm is that only positive values can be reached in the optimization process. The algorithm originally was implemented using the multiplicative update rule [31], although others algorithms can be used [32–33]. The ALS optimization [33], Eqs. (2) and (3), can be used for this task, and it was adopted in this

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