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Analytical Methods

Evaluation of matrix effect on the GC response of eleven pesticides by PCA

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ABSTRACT

The components of seven matrices in the analysis of 11 pesticides by GC-ECD were analysed. The matrix effect was calculated based on the changing of chromatographic response of the analyte in the presence of co-extractives of the matrices in the organic phase obtained by solid–liquid and liquid–liquid extraction with partition at low temperature (ESL-PBT and ELL-PBT), in relation to the response of it in the pure solvent. It was used the Principal Component Analysis (PCA) in evaluating the results obtained for the percentages of the matrix effect. The tomato, grape and pineapple matrices caused greater matrix effect and were grouped. The other matrices such as apple, water and potato caused small matrix effect. For most pesticides the soil matrix caused negative matrix effect. The influence of pH of the samples on the matrix effect was also evaluated showing not to have a direct effect on the phenomenon.

1. Introduction

In chromatographic analysis of complex samples, the responses attributed to pesticides may undergo changes caused by matrix components. "Matrix effect" is the name given to these changes. This phenomenon is used to explain recovery rates of pesticides that exceed 100% and the low accuracy of results (Hajslová et al., 1998). Usually the matrix effect is observed when a significant difference in response is obtained between chromatographic standards prepared in solvent and those prepared in the matrix extract (Picó, Blasco, & Font, 2004). This effect can be positive, leading to an increase in chromatographic signal or negative, when there is a decrease of this signal. These changes are the result of adsorption of analytes and matrix components in both the injector and the detector and/or in chromatographic column (Hajslová & Zrostlíková, 2003).

When standard solutions are prepared in pure solvent and analysed by gas chromatography, the analytes can bind to the active sites of the inserter and a smaller amount of it is transferred to the chromatographic column and consequently detected. In the analysis of the matrix extract containing these analytes, the co-extractives "compete" with the analytes for the occupation of the sites, causing a larger amount of analyte is transferred to the chromatographic column than when prepared in pure solvent. When the detector response, attributed to the analyte, is compared with the response of standard solutions of the same analyte, there is an overestimation of the results (Pinho, Neves, Queiroz, & Silvério, 2009). Change in the chromatographic response of analytes can also be observed when the non-volatile components of the matrices accumulate in the inserter or in the chromatographic column, resulting in the formation of new active sites, in which analyte also connect, making a smaller amount be transferred to the chromatographic column, resulting in the decrease of the responses when compared to those prepared in pure solvent. This fact is often called induction of the decrease of the response by the matrix (Garrido Frenich, Martínez Vidal, Fernández Moreno, & Romero-González, 2009).

In order to try to minimise or even eliminate the matrix effect, several studies have been conducted, for example, the pre-cleaning of the extracts (Picó et al., 2004). This step consists of removing endogenous components to reduce the contamination of the chromatographic system. However, thorough cleaning of the extracts also reduces the percentage of extraction of analytes, thus making the methodology impracticable (Schenck & Lehotay, 2000) . The construction of the analytical curve in the same sample extract, free of pesticide residues, is also an alternative for assessing the matrix effect (Dömötörová, Kirchner, Matisová, & de Zeeuw, 2006; Erney, Gillespie, Gilvydis, & Poole, 1993; Menkissoglu-Spiroudi & Fotopoulou, 2004; Pinho et al., 2009). In this case, the active sites are occupied in the same way in both analysis of standards and analysis of samples reducing the matrix effect.

In the literature, several authors have been studying the matrix effect in chromatographic analysis. Menkissoglu-Spiroudi and Fotopoulou (2004) studied the effect of different plant components in the chromatographic response of a group of pesticides and

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observed recovery percentages greater than 200% for some pesticides. Erney et al. (1993) approached the study of the matrix effect on the analysis of organophosphates in milk and cream and high percentages of recovery were also observed (Erney et al., 1993). Jimenez, Bernal, del Nozal, Toribio, and Martín (1998) analysed the difference in chromatographic response for different pesticides in honey, finding for the pesticide captan recovery percentages greater than 1000% (Jimenez et al., 1998).

However, more comprehensive studies, which consider different types of matrices, different compounds and evaluate data from a multivariate way, are still needed, since the chromatographic analysis has become commonplace in many areas of knowledge.

In this sense, the aim of this study was to evaluate the effect of co-extractives of seven different matrices in the analysis of eleven pesticides by gas chromatography with electron capture detector and analyse the matrix effects obtained by principal component analysis (PCA).

2. Experimental

2.1. Chemicals

Standard stock solutions of chlorothalonil (99.3% w/w), procymidone (99.9% w/w), iprodione (99.3% w/w), deltamethrin (99.7% w/w), azoxystrobin (99.9% w/w) purchased from Sigma Aldrich (Seelze, Germany), methyl parathion (99.0% w/w), chlorpyrifos (99.0% w/w), endosulfan (73.2% w/w), cypermethrin (92.4% w/w) purchased from Chem Service (West Chester, PA, USA), λ-cyhalothrin (86.5% w/w) and permethrin (92.2% w/w) purchased from Syngenta (São Paulo, Brazil) were prepared in acetonitrile at a concentration of 1000 mg L^{-1} and stored at 4 °C. From the dilution of stock, solutions were prepared containing the eleven pesticides at concentrations of 10 and 20 mg L^{-1} in the same solvent.

It was used as solvents ethyl acetate for trace analysis and HPLC grade acetonitrile both purchased from Vetec (Rio de Janeiro, Brazil). Anhydrous sodium sulphate with a purity superior to 99% was also purchased from Vetec. Florisil for residue analysis (0.150–0.250 mm) was obtained from Merck (Darmstadt, Germany).

2.2. Instruments

It was used a Shimadzu gas chromatograph (GC-2014) equipped with an electron capture detector (ECD), auto injector AOC – 20i and HP-5 capillary column from Agilent Technologies.

An ultrasonic bath from Unique (São Paulo, Brazil) was used to prepare the samples. The generator of this bath has an output of 150 W and a frequency of 25 kHz. It was also used a shaker table (Tecnal TE – 420, São Paulo, Brazil) and a Digimed pH metre. A Cintra GBC 20 spectrophotometer was used for spectrophotometric analysis.

2.3. Preparation of samples

The organic extracts of samples of tomato, potato, apple, pineapple, soil, grape and organic extracts from water samples were obtained from the method of solid–liquid extraction with partition at low temperature (SLE-PLT) and liquid–liquid extraction with partition at low temperature (LLE-PLT), respectively.

A certain amount of sample was transferred to a glass vial (22 mL) and then it was added to the extracting mixture consisting of acetonitrile, water and ethyl acetate. The system was subjected to homogenisation and cooled at −20 °C for 6 h. After this period, we obtained a biphasic system consisting of solid phase (freezing of the aqueous phase and the matrix) and the liquid phase (supernatant). This liquid was passed through 1.50 g of anhydrous sodium sulphate. The filtrate obtained (extract) was recovered in 10.0 mL volumetric flask with acetonitrile and the solution was stored in the freezer until the time of analysis by GC/ECD (Pinho, Silvério, Neves, Queiroz, & Starling, 2010).

2.4. Analysis by GC/ECD

The chromatographic separation of analytes was performed on a HP-5 capillary column from Agilent Technologies, stationary phase composed of 5% diphenyl and 95% dimethylpolysiloxane (30 m × 0.25 mm d.i., 0.1 mm film thickness), being nitrogen (99.999% purity) the carrier gas at a flow rate of 1.2 mL min^{-1}. The temperatures of split/splitless injector and detector were 280 and 300 °C, respectively. The column was initially placed at 150 °C for 2 min, heated at 40 °C min^{-1} up to 210 °C, remaining at this temperature for 2 min. and then heated at 20 °C min^{-1} up to 250 °C remaining at this temperature for 2 min. Finally it was heated at 10 °C min^{-1} up to 290 °C remaining at this temperature for 7 min. It was injected 1 mL of sample into the chromatograph at a divider ratio of 1:5. The total analysis time was 20.5 min.

2.5. Evaluation of matrix effect

In order to evaluate the influence of matrix components in the detector response, two sets of standard solutions containing the eleven pesticides at concentrations between 10 and 500 μg L^{-1} were prepared. The first series was obtained by diluting the working solution containing the pesticides at concentrations of 10 and 20 mg L^{-1} in pure acetonitrile (triplicate). The second series of standards was prepared by diluting the same working solution in organic extracts of the matrix (triplicate), obtained from the SLE-PLT samples of tomato, potato, apple, pineapple, grapes and soil free of pesticides and LLE-PLT for water free of pesticides sample. The quantification of analytes was performed by GC/ECD.

The evaluation of the influence of co-extractives on chromatographic responses of pesticides was performed by relating the areas of the analytes in pure solvent to areas obtained from organic extracts using the following equation:

$$\text{Matrix Effect } (\%) = \frac{X_1}{X_2} \times 100 \quad (1)$$

where X_1 is the average of the areas of analytical solution of each pesticide prepared in matrix extract and X_2 is the average of the areas of the solutions of these pesticides prepared in pure solvent.

2.6. Principal components analysis

A 7 × 11 matrix was constructed for the multivariate data treatment. The eleven pesticides were defined as variables and were therefore placed in the columns. The seven extracts were defined as samples and therefore were placed in rows. The response used as information of the matrix effect was the value of the percentage of the variation of the chromatographic response of the pesticide, calculated by Eq. (1). The data were imported by MATLAB 7 (The MathWorks, Inc.) software and treated using the PLS_Toolbox 6.5 (Eigenvector Research, Inc., USA). The matrix columns were autoscaled and then PCA was performed.

2.7. Influence of the pH of the samples on the matrix effect

In order to check the influence of pH on the extraction of pesticides, distilled water samples had their pH adjusted with glacial acetic acid solution to identical values to those of the more acidic matrices: grape (3.71), pineapple (3.64) and tomato (4.32). Water samples were submitted to LLE-PLT and the organic extracts were fortified with 11 pesticides at a concentration of 500 μg L^{-1}. The

chromatographic peak areas were compared with those of standards at the same concentration in pure solvent and matrix effect was calculated (Eq. (1)).

To check the influence of pH on the extraction of matrix components, organic extracts of tomato, pineapple and grape were obtained as described in Section 2.3. The same procedure was performed substituting water for the same volume of Na_2HPO_4 0.2 mol L^{-1} solution. The six organic extracts were analysed in a spectrophotometer in a range of 340–650 nm.

3. Results and discussion

3.1. Chromatographic analysis

The optimised chromatographic conditions for simultaneous analysis of 11 pesticides allowed a good separation of compounds as can be observed in the chromatogram presented in Fig. 1.

The identification of compounds in organic extracts of the matrices was performed by comparing the retention time (t_R) of each peak with the retention times of standard solutions of analytes in acetonitrile (Collins, Braga, & Bonato, 2006). The quantification of endosulfan, λ-cyhalothrin, permethrin, cypermethrin and deltamethrin compounds, which have more than one peak was performed by adding the peak areas related to the isomers of each one. Table 1 shows the retention times and the properties of each compound.

In the used concentration range between 10 and 500 μg L^{-1} of each of the pesticides in pure solvent, the detector response was linear with concentration, presenting coefficients of determination greater than 0.90.

3.2. Matrix effect

The presence of co-extractives in organic extracts of the samples causes changes in the baseline of the chromatograms and the responses of pesticides are also altered. However, no interference in the same retention time of pesticides was detected for all matrices.

The interference of the co-extractives on the chromatographic response can be evidenced by the different characteristics of the analytical curves of the same pesticide in pure solvent and in the extracts obtained from SLE-PLT. For each compound (chlorothalonil, methyl parathion, chlorpyrifos, procymidone, endosulfan, iprodione, λ-cyhalothrin, permethrin, cypermethrin, deltamethrin and azoxystrobin) analytical curves were obtained in pure solvent and in the extracts of the matrices (tomato, potato, water, apple, soil, pineapple and grape) in the concentration range from 10 to 500 μg L^{-1}. In all cases the coefficients of determination were above 0.90. The difference in the slopes of analytical curves (solvent × matrix) is attributed to a proportional systematic error, caused by matrix components (Cuadros-Rodríguez, García-Campaña, Almansa-López, Egea-González, & Cano, 2003; Cuadros-Rodríguez, Gámiz-Gracia, Almansa-López, & Bosque-Sendra, 2001). This effect can be positive when the slope of the standard curve in the organic extract is greater than in pure solvent. It can be negative when the slope of the standard curve in the organic extract is smaller than the standard curve in the pure solvent. When the slopes are similar but the curves differ in the intersection, the matrix effect causes a constant systematic error.

In this paper, the matrix effect was evaluated for all pesticides, by the relationship between the values of area of the analyte in the organic extract for each matrix and in pure solvent (Eq. (1)). According to Fig. 2, where the percentages of the matrix effect for chlorothalonil in different concentrations are related, one can observe that the matrix effect in the analysis of pesticides is more significant when they are in lower concentrations (Hajslová et al., 1998).

This occurs because when a standard solution of pesticides in pure solvent at a lower concentration is injected, a significant amount of the analyte is retained at the interface of the liner, thereby obtaining a lower chromatographic response. When the extracts in the same concentration are analysed, co-extractives of the matrices occupy the active sites of the inserter and only a negligible amount of the analyte is adsorbed, leading to a significant increase in the chromatographic response. It was also observed that for higher concentrations the values of the effects tend to equality. Similar results were observed for the other pesticides studied.

3.3. Principal component analysis (PCA)

The principal component analysis was performed in order to find patterns in distributions of the eleven pesticides and verify the effect of matrices on each pesticide with the purpose to extract relevant information about this system.

The matrix effects calculated using Eq. (1) from the areas attributed to pesticides in the organic extracts and in pure solvent were obtained only for concentrations of 100, 150, 300, 400 and 500 μg L^{-1}, since these concentrations were common in analytical curves of the analytes. Positive values correspond to increased chromatographic response, in percentage, observed for an analyte in an extract in relation to the response in pure solvent. Negative values correspond to decreased chromatographic response for the analyte in the extract in relation to the response in the pure solvent.

Analysing the percentages of variance captured, it can be observed from that about 90% of the variance is captured with only two components for all sets, reaching an average of 96% of explained variance for three components. Since most of the information focused on the first two components, only these two were evaluated.

In order to visualise the data in two or three dimensions, the principal components (scores and loadings) are plotted together. Fig. 3 shows the graphics of PCA for the first two components, the five concentrations studied.

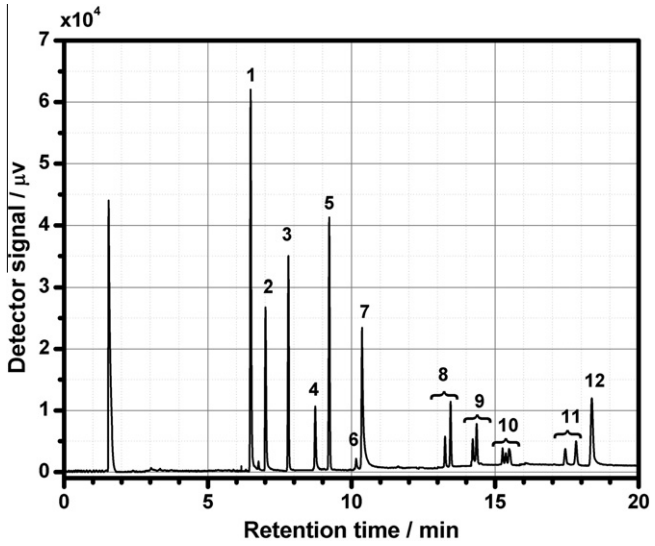
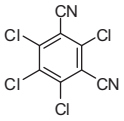
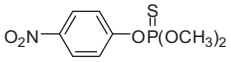
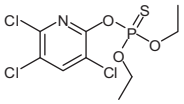
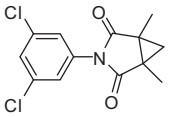
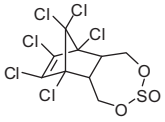
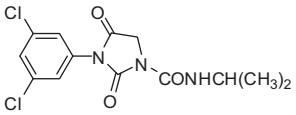
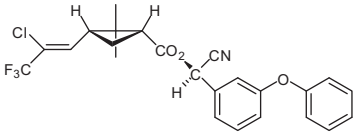
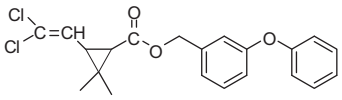
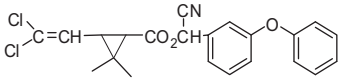
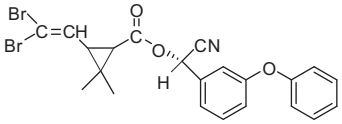
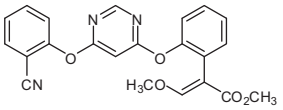


Fig. 1. Chromatogram of a standard solution of pesticides at 300 μg L^{-1} in acetonitrile: 1. chlorothalonil, 2. methyl parathion, 3. chlorpyrifos, 4. procymidone, 5. α-endosulfan, 6. β-endosulfan, 7. iprodione, 8. λ-cyalothrin, 9. permethrin, 10. cypermethrin, 11. deltamethrin, and 12. azoxystrobin.

Table 1
Physical and chemical properties of the compounds studied in this paper.

Compound	Formula	Chemical group	Retention time (min)	Molar mass (g mol^{-1})	K_{ow} (pH 7.0 e a 20 °C)	Boiling point (°C)
Chlorothalonil		Isoftalonitrile	6.47	265.91	8.71×10^2	350.5
Methyl parathion		Organophosphorous	6.99	263.21	1.00×10^3	334.7
Chlorpyrifos		Neonicotinoid	7.76	350.89	5.01×10^4	375.9
Procymidone		Dicarboximide	8.70	284.14	2.00×10^3	477.9
Endosulfan		Clorociclodieno	9.18/10.11	406.93	5.62×10^4	449.7
Iprodione		Dicarboximide	10.4	330.17	1.26×10^3	—
λ-Cyhalothrin	 (*R*) (*Z*)-(1*S*)-*cis*	Pyrethroid	13.22/13.41	449.85	7.94×10^6	498.9
Permethrin		Pyrethroid	14.19/14.31	391.3	1.26×10^6	465.9
Cypermethrin		Pyrethroid	15.21/15.32/15.45	416.3	1.26×10^6	511.3
Deltamethrin		Pyrethroid	17.37/17.75	505.2	2.00×10^5	535.8
Azoxystrobin		Strobilurin	18.29	403.4	3.16×10^2	581.3

A convenient way to look at the graphics of the scores and loadings is using the biplot, which is a combined graphic of scores and loadings in a single graphic. It allows an easy interpretation of the variables responsible for the observed differences in the samples scores. Fig. 3 shows the PCA biplot graphics for the first two components, the five concentrations studied.

An analysis of *scores* indicates that the distribution of pesticides is not closely related to their physicochemical properties, such as retention time, boiling temperature or molar mass with the intensity of the matrix effect. It is observed, however, that some matrices (grape, pineapple and tomato) systematically cause a positive matrix effect. Other matrices such as soil, water and potato presents predominantly negative matrix effect.

Analysing the biplot graphics and observing the scores (○) and loadings (□) it is noted in Fig. 3 that the groups of pesticides and the influence of the matrices showed the same behaviour when varying the concentration of pesticides. The inversions of the graphics C, D and E in Fig. 3 in relation to graphics A and B, were due to reversal of effect (negative to positive or the opposite) when the concentration of some pesticides increased.

From an analysis of scores, it is observed that the first component separates the deltamethrin, permethrin and iprodione pesticides from other pesticides. The second component separates the deltamethrin, cypermethrin, λ-cyhalothrin, permethrin and iprodione pesticides from other pesticides. Analysing the *loadings* it is observed that the soil matrix was the only one that stood out from the rest. Similar results were found by Pinho et al. (2010). It was also seen that the pineapple, tomato and grape matrices separated from the other matrices by the second component.

This separation is due to the fact that higher percentages of matrix effect be obtained for this group of matrices (tomato, pineapple and grape), with a strongly acidity common feature of these

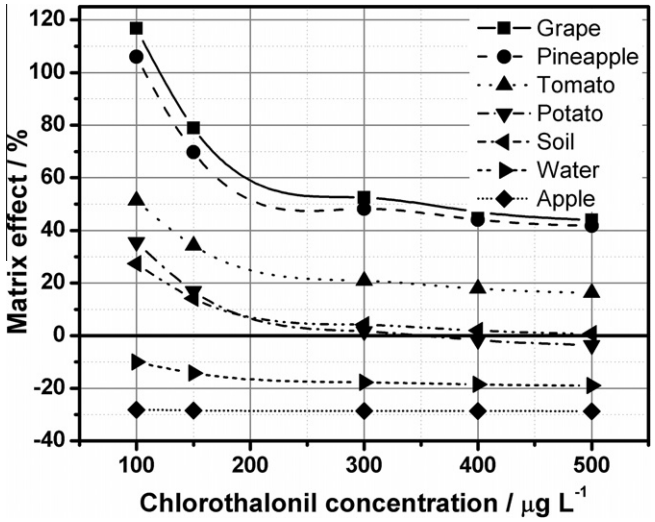


Fig. 2. Percentages of matrix effect for chlorothalonil in different concentrations in seven different samples.

matrices and to distinguish them from others. The soil matrix is rich in organic matter, presenting in its constitution compounds of high molecular weight that are sure to form new active sites on the *liner* to which the analytes can bind, causing a negative matrix effect for all pesticides and, for this reason, it is well separate from other matrices.

A second interpretation of the biplot graphics can be performed with the aid of Fig. 4.This figure graphically represents the matrix effect for the different samples (graphics A–G) on pesticides (*x* axis) at different concentrations (vertical bars).

Using Figs. 3 and 4 it is possible to analyse more thoroughly different systems. For the chlorothalonil and azoxystrobin pesticides a very similar behaviour was observed. It is noted that for most matrices these pesticides have experienced positive effect, except for soil and water. For potato these pesticides experienced negative effects when in high concentrations. In pineapple and tomato matrices chlorothalonil experienced a greater effect when at low concentrations. In the biplot graphic, chlorothalonil and azoxystrobin were located in the centre, because they showed positive and negative matrix effects.

Procymidone, chlorpyrifos, endolssulfan, methyl parathion pesticides were the pesticides that presented less matrix effects. It is also noted that the chlorpyrifos and procymidone pesticides have showed more negative effects, but both experienced positive effects on apple extract and chlorpyrifos in the tomato extract. These behaviours have caused these pesticides to be located in the quadrant of the matrices that showed more negative effects, i.e., soil, potato, water and apple. These pesticides have presented both negative and positive effects, but as both were low, these pesticides were closer to the centre in the biplot graphic.

The λ-cyhalothrin showed significant positive effects from pineapple, grape and tomato. Apple and water had little influence and potato and soil presented a negative effect on this pesticide. Therefore, the reason for the λ-cyhalothrin to be, in the biplot graph, along with the matrices that had more positive effects, i.e., pineapple, grapes and tomatoes is clear.

The cypermethrin and deltamethrin pesticides presented greater influences of the components of pineapple, grape and tomato matrices, making them to remain located in the same quadrant of these matrices, as shown in Fig. 3. Deltamethrin however, presented more positive matrix effects than cypermethrin for the apple, pineapple, grape and tomato matrices. The cypermethrin showed negative matrix effect for potato and water matrices, while deltamethrin, for these matrices, had a positive effect. This made the cypermethrin be located closest to the centre of the biplot graphic and deltamethrin closer to the tomato, pineapple and grape matrices. It is important to emphasise that the behaviour of delta-

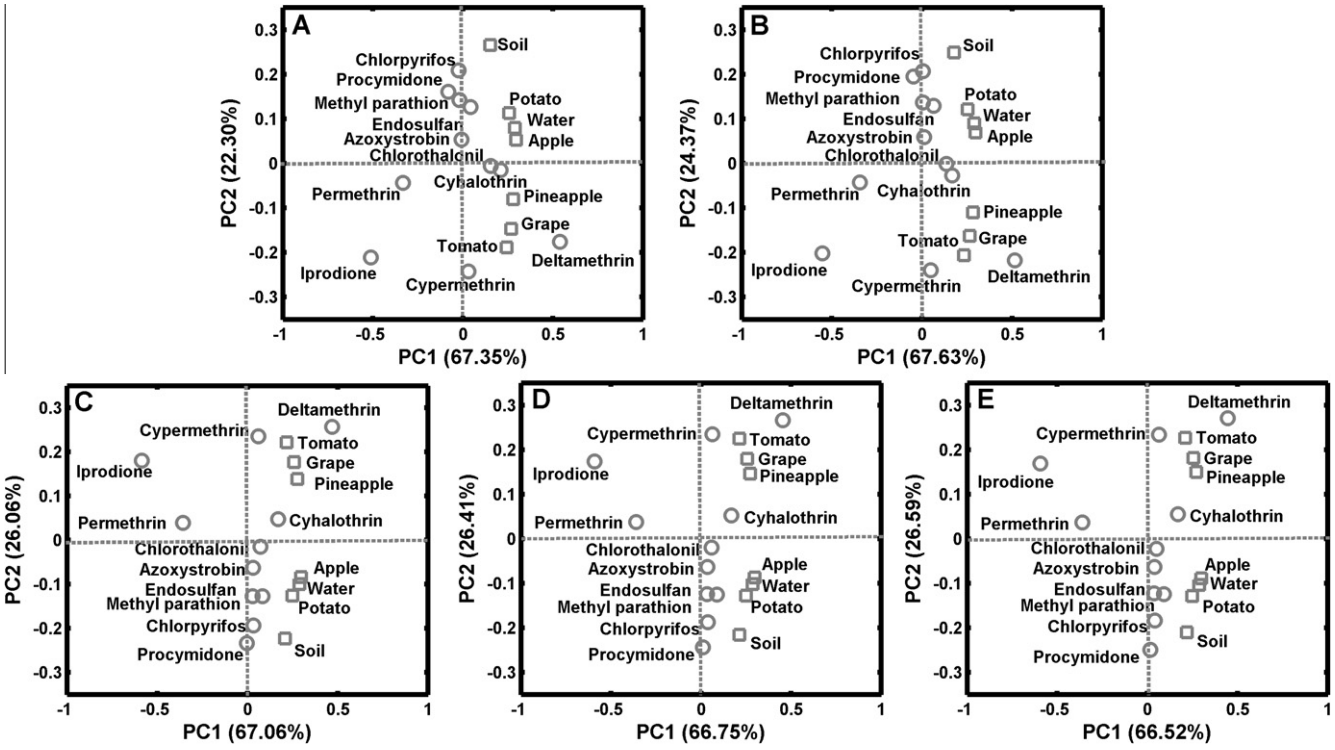


Fig. 3. PCA analysis using the biplot from matrix effects of seven different samples – *loadings* (□) over eleven pesticides – *scores* (○) in five concentrations (A) 100 μg L^{-1}, (B) 150 μg L^{-1} (C) 300 μg L^{-1}, (D) 400 μg L^{-1}m and (E) 500 μg L^{-1}.

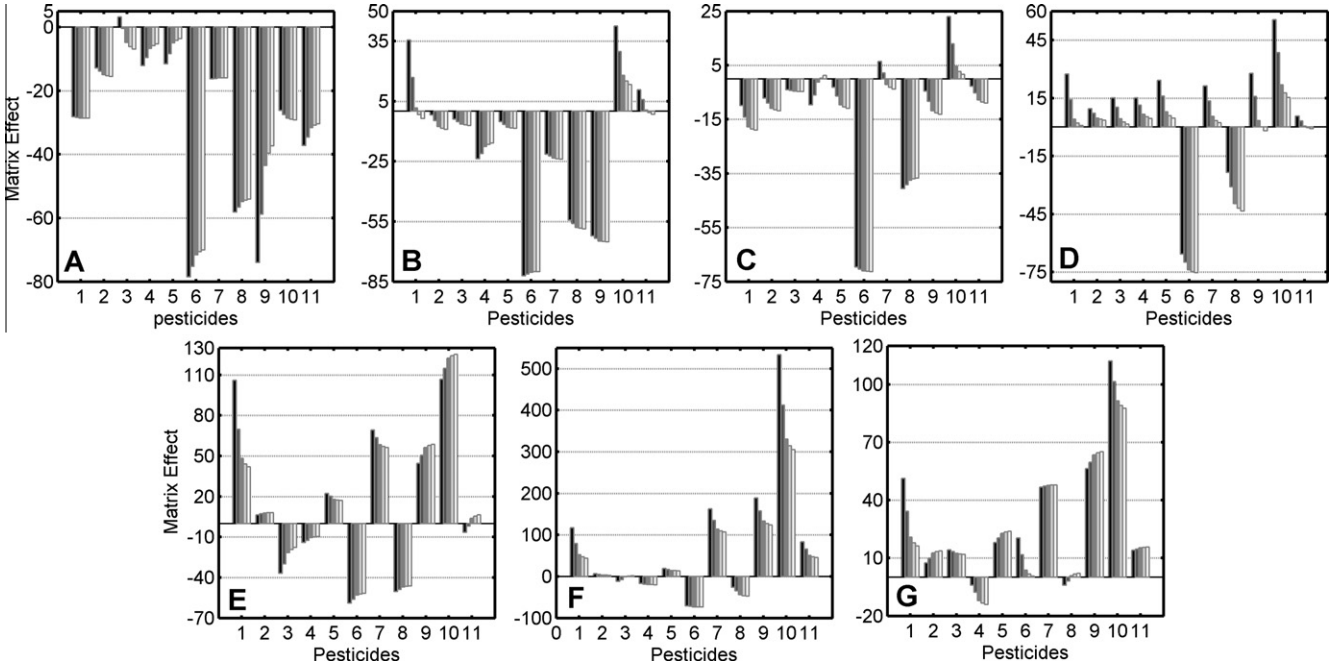


Fig. 4. Matrix effects for matrices soil (A), potato (B), water (C), apple (D), pineapple (E), grape (F), and tomato (G). Pesticides are 1-chlorothalonil, 2-methyl parathion, 3-chlorpyrifos, 4-procymidone, 5-endosulfan, 6-iprodione, 7-cyhalothrin, 8-permethrin, 9-cypermethrin, 10-deltamethrin, and 11-azoxystrobin. The darker bar is the less concentration and the clearer bar the highest concentration.

methrin for the potato, water, apple, grape and tomato matrices was more significant at lower concentrations of the analyte.

The iprodione and permethrin pesticides have shower negative effects for all matrices for tomatoes. The negative matrix effects presented were very significant, thus justifying the position in the biplot graphic in the same quadrant of tomato, pineapple and grape matrices when analysing the second component.

3.4. Influence of pH

According to the results obtained in the PCA, it is clear that the matrices that caused an increase in the chromatographic response for most pesticides were tomato, pineapple and grape, which are acidic matrices. This suggests that pH is a variable that deserves to have its effects studied. Thus, to check the influence of pH on the matrix effect, all matrices studied had the pH determined. The values obtained were tomato (4.32), potato (5.74), water (6.65), apple (6.73), soil (6.76), pineapple (3.64), and grape (3.71).

Water samples at pH 6.65 were adjusted to 4.32 (tomato pH), 3.64 (pineapple pH), and 3.71 (grape pH) and submitted to LLE-PLT. In addition, organic extracts of tomato, pineapple and grape were obtained by SLE-PLT as described in Table 1. Standard solutions of pesticides were prepared at a concentration of 500 $\mu g\ L^{-1}$ in these six extracts and in pure solvent and analysed by GC-ECD. It was observed that water acidification promoted a reduction in pesticides chromatographic response similar to the results found for samples of pure water. This behaviour was also observed for the other pesticides studied. Thus, the pH of the samples does not influence the properties of pesticides in the organic phase, and therefore the pH is not the directly responsible factor for the higher matrix effect observed for the more acidic samples.

On the other hand, the increasing of the pH of the extracting mixture caused by the use of Na_2HPO_4 0.2 mol L^{-1} solution replacing the water used in SLE-PLT technique for samples of tomato, pineapple and grape, affected the extraction of the matrix components. Fig. 5 depicts the absorption spectra of organic extracts of the three matrices in two pH values. The spectra have the same characteristics,

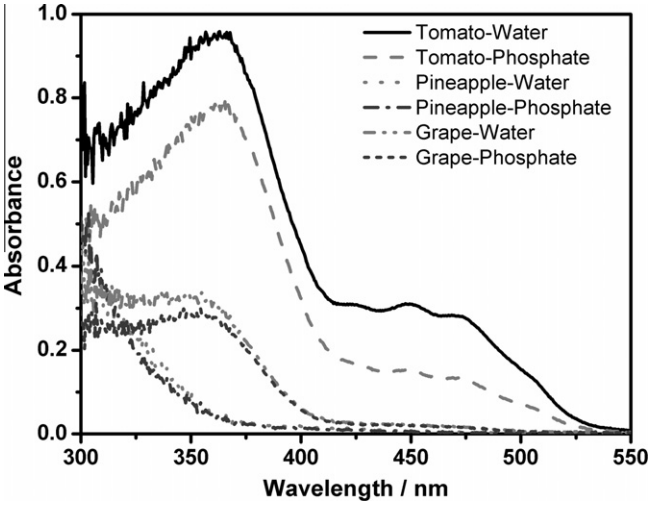


Fig. 5. Absorption spectra of organic extracts of tomato, pineapple and grape prepared with distilled water and Na_2HPO_4.

showing only that the organic extracts of these samples using pure water in the extracting mixture (<pH) have a higher absorbance.

For tomato samples, the organic extracts presented more intense staining and the extraction of these co-extractives is significantly affected by pH. At lower pH values a greater presence of lipophilic co-extractives from the sample can be observed, such as pigments (Prestes, Friggi, Adaime, & Zanella, 2009). For the organic extracts of grape the same behaviour is observed, but there is less variation in absorbance related to pH, since this extract has a lighter colour than the tomato extract. For the pineapple extracts this difference is quite small, since the extract obtained is very limpid. Based on these results we can conclude that the pH affects the extraction of the co-extractives of the samples, showing that the pineapple, tomato and grape matrices that have low pH values, presented higher matrix effects.

4. Conclusions

The chemometric analysis using PCA proved to be a useful tool in studying the effect of co-extractives of seven matrices in chromatographic response of eleven pesticides. The co-extractives of the tomato, grape and pineapple matrices caused a positive matrix effect in the analysis of the pesticides and were grouped. The apple, potato and water matrices caused small matrix effect. The soil matrix caused a negative matrix effect for most pesticides and was well separated from other matrices by principal component analysis. The influence of pH on the matrix effect was also evaluated. Organic extracts obtained from water samples with low pH led to a reduction in the chromatographic response of pesticides. The reduction was of the same order of magnitude of pure water samples, showing that the pH of the samples does not directly influence the matrix effect. However, by increasing the pH of the more acidic samples, less co-extractives are extracted to the organic phase. Thus it was concluded that pH influence the matrix effect favoring or not the extraction of the co-extractives of the samples not interfering directly in the properties of pesticides.

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