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Use of the Cross-Section Technique Linked with Multivariate Calibration Methods To Resolve Complex Pesticide Mixtures

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The potential of the cross-section (CS) approach in combination with the partial least squares (PLS) and principal component regression (PCR) was assessed in the resolution of a complex pesticide mixture showing twelve overlapped components in High Performance Liquid Chromatography with Diode Array Detection (HPLC-DAD). Careful selection of the CS through the three-dimensional (3D) (*A*, *λ*, *t*) data matrix gave two-dimensional (2D) signals with the best sensitivity for the determination of each pesticide. In all cases, the application of the PLS method demonstrated a better quantitative prediction ability than that of the PCR method. The CS-PLS approach is a powerful analytical tool. Ten pesticides were well-resolved, while for the other two pesticides of the mixture prediction ability was poor, and they could not be determined, probably due to their low net analytical signal. The CS-PLS model was evaluated by predicting the concentrations of independent test set samples. Finally, the proposed model was successfully applied for the determination of these pesticides in groundwater.

Chromatographic techniques are among the most powerful tools available for qualitative and quantitative determination of the various components of a mixture. The idea is that each chromatographic peak corresponds to a single analyte of the mixture, and peak height or area could be used to quantify each analyte independently. However, such conditions are not always achieved, particularly in multicomponent mixture chromatograms.

Reversed-mode HPLC has frequently been employed for both analytical and preparative separation.[1−4] Optimization of HPLC separation methods is a difficult task, although there are numerous ways to optimize selectivity and improve resolution.[5] In practice, the problem is traditionally overcome by applying some gradient formation programming technique, such as solvent, flow, temperature, or stationary-phase (linked-column programming). The main disadvantage of any gradient is that it requires reconditioning, which takes a certain amount of time. As the importance of shortening the analysis time continues to be of interest, the requirement of baseline resolution becomes a less essential objective.

The capacity of different chemometric methods for resolving overlapped peaks in multicomponent chromatograms has recently received great attention. The main advantage of multicomponent analysis by using multivariate calibration is the speed with which components of mixtures are determined, avoiding a prior separation step that would otherwise be necessary because of overlapping signals. Multivariate chemometric methods based on factor analysis techniques[6−9] have frequently been used in quantitative analysis to obtain very selective information from unselective data. The PLS and PCR methods are two of the most widely used factor analysis techniques for quantitative determination, because of their ability to overcome problems such as collinearity and deviations from the Beer-Lambert law caused by different effects such as overlapping signals and component interaction.[7,10] These methods use a data vector as the response for each sample, so the same matrix effects and interference should be present in both the prediction and calibration samples.

Nowadays, second-order data are easily generated by hyphenated chromatographic methods in the analytical laboratory. For instance, the combination of HPLC with DAD allows analytical signals depending on two variables, wavelength and time, i.e., a matrix of data (*A*, *λ*, *t*) is obtained. These 3D matrixes or spectrochromatograms can be represented as a 2D matrix of absorbance intensity—a function of both elution time and wavelength. Standard spectra or chromatograms are cross sections (CS) of this matrix at fixed times or wavelengths, respectively, and they are employed in the majority of multivariate methods. In general, a single compromise detector wavelength is chosen to obtain chromatograms and to build up calibration models. The selection of this wavelength is quite difficult, especially in multicomponent mixtures with a large number of analytes having individual spectra that differ significantly. In this situation, to resolve the mixture more than one calibration model is neces-

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sary,[11] each one of them at the wavelength that maximizes the sensitivity of the determination of each analyte. Single spectra or chromatograms do not contain sufficient information to differentiate complex mixtures with a large number of analytes using only a calibration model.

A different tool recently proposed by the authors is the CS approach, based on the drawing of variable gradient linear trajectories through the 3D matrix data.[12−16] This technique allows choice of the optimum path by inspection of the contour plots, so that the CS goes through absorption maxima of the peak. If the chosen path is selective enough, each one of the straight portions allows the specific determination of one or more of the analytes, without interferences from the others, using univariate calibration. This option is especially useful when the analyzed multicomponent mixture is not very complex, as has been previously proven by the authors.[12,15−16]

However, when there are a great number of strongly overlapping analytes, it is virtually impossible to select a CS which will go through maximum intensity peaks but circumvent overlapping areas, i.e., where only one analyte of the mixture contributes to the signal with enough selectivity. In these cases, the sections, function of both wavelength and time, must be made as a balance between sensitivity and selectivity. In this way, the use of CS allows selection of the most useful information from the multivariate data in order to use it in multivariate methods, despite the fact that in complex mixtures this information lacks selectivity, i.e., it is not possible to obtain peaks that correspond to the signal of a compound without interference from the other compounds of the mixture. In addition, this approach avoids the application of more complicated algorithms[17−20] that work with second-order data and which, on the other hand, present some disadvantages because of their more severe constraints.[21]

The analysis of pesticides in environmental samples by HPLC techniques requires the elution of a wide variety of analytes under the optimum conditions. However, it is difficult to avoid the overlapping peaks in the analysis of complex mixtures owing to their similar retention times or UV-spectrum properties. In such situations, it is advisable to check the capacity and possible limitations of traditional chemometric techniques for converting the data collected into useful information, as it has been demonstrated in the study of relatively simple mixtures.[22−29] In the same way, these techniques have been applied for the identification of coeluted analytes in gas chromatography/mass spectrometry.[30]

In this study, CS through the 3D data matrix of a mixture of twelve overlapped pesticides in HPLC-DAD is carried out in order to obtain new 2D profiles with the highest sensitivity for each. The latter profiles are obtained by projecting the absorption intensity of the CS on the wavelength or time domains. Afterward, the capacity of PLS and PCR methods was evaluated using the obtained analytical signals from the spectrochromatogram CS approach. The results obtained by the two models, CS-PLS and CS-PCR, were then critically compared by means of prediction errors for the calibration set.

The procedure was successfully applied to the simultaneous determination of these pesticides in groundwater at μg L^{-1} levels after liquid−liquid extraction.

EXPERIMENTAL SECTION

1. Chemicals and Solvents. Pesticide standards (Pestanal quality) of iprodione, procymidone, chlorothalonil, chlorfenvinphos, fenamiphos, malathion, parathion-methyl, parathion-ethyl, tebuconazole, triadimefon, triazophos, and vinclozolin were obtained from Riedel-de Haën (Seelze, Germany). Solid standards were dissolved and diluted in acetonitrile (AcN), where they were stable for several months. Analytical-reagent-grade solvents, AcN, acetone, and methylene chloride, obtained from Merck (Darmstadt, Germany), were also used. HPLC-grade water provided by a Millipore Milli-Q water filtration/purification system (Bedford, MA) was used.

2. Instrumentation and HPLC Procedure. A Waters (Milford, MA) model 990 liquid chromatographic system, equipped with a model 600 E constant-flow pump, a Rheodyne six-port injection valve with a 20-μL sample loop, a model 990 UV-vis photodiode-array detector, a printer/plotter, and a microcomputer using the Waters 991 software package, were used.

HPLC separations were performed on a Hypersil C_{18} column (100 × 0.46 mm i.d., 5-μm particle size). The mobile phase, under isocratic conditions, was AcN:water (60:40) v/v; this composition mobile phase was used to reduce the time of analysis and avoid too much peak dispersion. The solvents were filtered daily through a 0.45-μm cellulose membrane filter before use and degassed with helium before and during use. Twenty-microliter samples were injected at a solvent flow rate kept at 1 mL min^{-1}.

Photometric detection was performed in the 200−280 nm range with a spectral resolution of 1.4 nm, i.e., 57 variables in the spectral domain. Data were collected in 300 s with an integration period of 1.4 s per spectrum, i.e., 215 variables in the time domain.

3. Pesticide Calibration Mixtures. A random design calibration matrix was prepared with mixtures of the twelve pesticides, using a 35-sample set. The concentrations (Table 1) belonged to

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Table 1. Concentration Data (μg mL^{-1}) for the Mixtures in the Calibration Set[a]

sample	I	P	Ct	Cf	F	M	P−m	P−e	T	Td	Tz	V
C1	0	2	4	8	3	5	6	3	8	4	5	2
C2	5	0	3.5	7.5	3	5	5	3	8	4	4	2
C3	5	4	0	2	7.5	8	3	8	3	6	3	10
C4	2	4	6	0	7.5	8	3	8	3	6	3	9.5
C5	2	6	6	2	0	4	5	5	5	3	8	5
C6	6	6	3	4	6	0	5	5	5	3	8	5
C7	6	3	3	4	6	4	0	10	4	7	4	4.5
C8	4	3	8	7	5	5	7	0	4	6	4	4
C9	4	8	8	7	5	5	7	10	0	2	6	8
C10	8	8	2	3	2	8	4	8	7	0	6	8
C11	8	4	2	3	3	8	4	8	7	2	0	6
C12	3	5	7	5	4	7	6	4	4	7	5	0
C13	3	10	7	5	4	7	6	4	4	7	5	6.5
C14	2	10	10	2	7	3	8	6	6	5	8	7
C15	2	5	10	2	7	3	8	6	6	5	8	7
C16	7	5	5	6	6	9	4	7	8	6	3	3
C17	7	8	5	6	6	9	4.5	7	8	6	3	3
C18	4	8	4	10	3	5	5.5	3	10	4	4	5
C19	4	2	4	10	3	5	5.5	3	10	4	4	5
C20	6	2	7	3	8	6	8	4	5	10	6.5	4
C21	6	7	7	3	8	6	7.5	4	5	10	9	4
C22	2	7	5	6	1.5	10	3	8	8	6	8	7
C23	2	4	5	6	1.5	10	3	8	8	5	7.5	7
C24	8	4	8	8	5	6	6	3	4	3	4	5
C25	8	3	8	8	5	6	6	3	4	3	4	5.5
C26	5	3	3	5	5	8	10	5	7	3	6	8
C27	5	8.8	3	5	5.5	8	10	5	7	4	6	8
C28	7	6	6	4	6	3	7	7	5	5	5	4
C29	7	4	6	4	6	3	7	7	5	5	5	4
C30	3	4	8	7	7	4	5	4	3	9	3	3
C31	3	2	8	7	7	4	4	4	3	8	3	3
C32	10	2	4	3	4	7	3	3	8	5	4	6
C33	6	5	4	3	4	7	3	3	8	6	4	6
C34	6	5	2	6	8	5	7	6	6	7	5.5	5
C35	6	8	2	6	8	5	7	6	6	7	7	5

[a] I iprodione; P, procymidone; Ct, chlorothalonil; Cf, chlorfenvinphos; F, fenamiphos; M, malathion; P−m, parathion-methyl; P−e, parathion-ethyl; T, tebuconazole: Td, triadimefon: Tz, triazophos; V, vinclozolin.

Table 2. Concentration Data for the Mixtures in the Test Set and in the Spiked Groundwater Samples[a]

sample	I	P	Ct	Cf	F	P−m	P−e	Td	Tz	V
Test Set (μg mL^{-1})										
T1	4	8	7	5	5	8	5	4	5	6
T2	4	7	7	5	5	8	5	4	5	6
T3	5	7	4	4	3	4	6	8	10	4
T4	6	4	4	4	3	4	6	8	10	4
T5	6	3	6	7	4	4	6	6.5	7	8
Groundwater Samples (μg L^{-1})										
G1	2	2.5	4	4	3	3.5	6	5.5	5	3
G2	4	3.5	2	4	5	6	4	4.5	5.5	4
G3	5	4	6	8	2	3.5	5	7	5	8
G4	8	0	8	5	6	4	6	6	6	6
G5	6	5	5	6	4	5	8	6	8	4
G6	4	3.6	3	6	8	8	4	6	8	5
G7	6	4	8	3	5	6	6	8	6	8
G8	8	6	4	5	6	5	9	8	10	9
G9	4	5	3	5	4	8	4	4	6	5

[a] I, iprodione; P, procymidone; Ct, chlorothalonil; Cf, chlorfenvinphos; F, fenamiphos; P−m, parathion-methyl; P−e, parathion-ethyl; Td, triadimefon: Tz, triazophos; V, vinclozolin.

the linear range for the pesticides, the values for which were in the range 0.3−12 μg mL^{-1} for all of them except malathion and tebuconazole, which were between 2 and 15 μg mL^{-1}. Twenty-microliter volumes were injected into the HPLC system, and the spectrochromatographic data was collected.

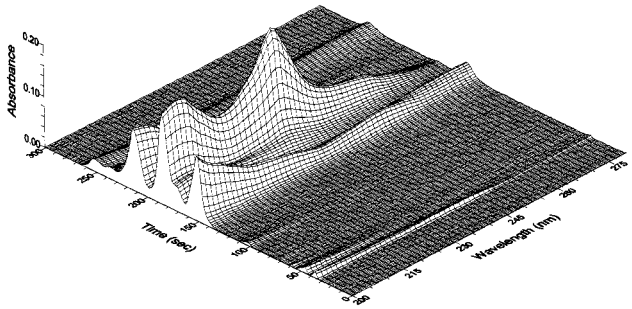

Figure 1. Three-dimensional plot of absorbance, wavelength, and time corresponding to a calibration set of a mixture of twelve pesticides.

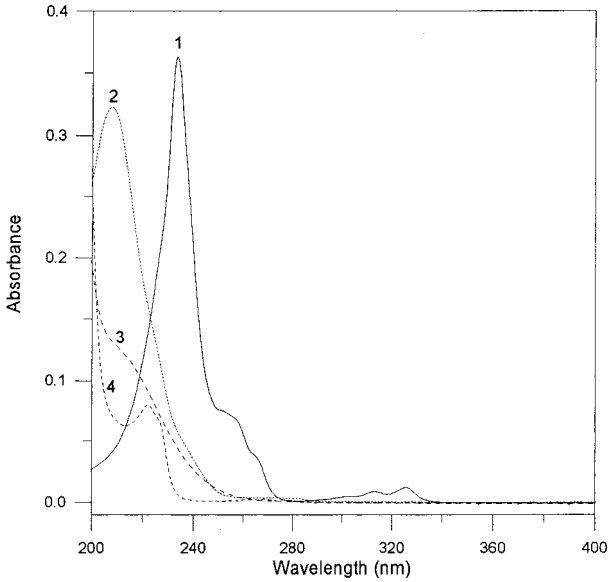

Figure 2. Absorption spectra of 4 μg mL^{-1} of: (1) iprodione, (2) chlorothalonil, (3) malathion, and (4) tebuconazole.

4. Software and Data Processing. The Surfer v.5 and Grapher v.2 software packages[31] were used for generating the CS and for obtaining the new profiles corresponding to the bidimensional data projection, $[A - f(\lambda)]$ or $[A - f(t)]$, respectively.

The Grams/386 software package with PLSplus v.2.1 G[32] was used for application of the PLS and PCR methods to the $[A - f(\lambda)]$ or $[A - f(t)]$ bidimensional data projections.

A CS was optimized on the contour plots, described by eight linear paths and defined by the initial and final coordinate (λ,t) pairs: (200, 280)−(206, 100) path I, (206, 100)−(218, 100) path II, (218, 100)−(222, 280) path III, (222, 280)−(242, 100) path IV, (242, 100)−(248, 280) path V, (248, 280)−(252, 100) path VI, (252, 100)−(272, 100) path VII and (272, 100)−(278, 280) path VIII, and applied to all calibration matrix samples. The optimized CS data was plotted on the wavelength domain to produce bidimen-

(31) Surfer, v.5 and Grapher, v.2; for Windows software packages version, Golden Software: Denver, CO, 1994. (htpp://www.goldensoftware.com/products/surfer/surfer.htm) and (htpp://www.goldensoftware.com/products/grapher/grapher.htm).

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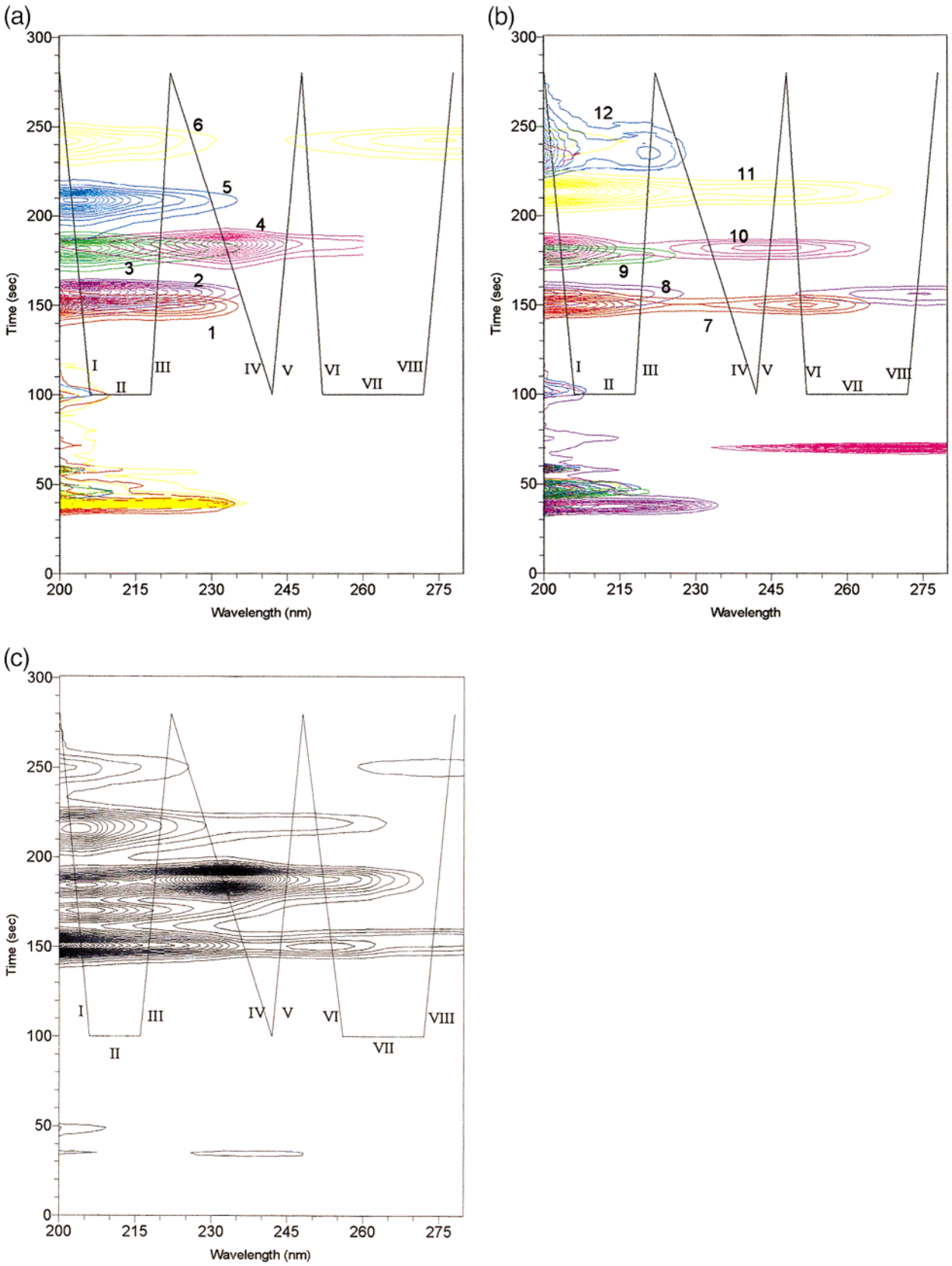

Figure 3. Optimized trajectories of the cross-section plotted across the contour plots of: (a) individual standards of (1) triadimefon, (2) iprodione, (3) procymidone, (4) chlorothalonil, (5) vinclozolin, and (6) parathion-ethyl; (b) individual standards of (7) fenamiphos, (8) parathion-methyl, (9) malathion, (10) triazophos, (11) clorfenvinphos, and (12) tebuconazole; and (c) a mixture of pesticides.

sional profiles that were used to optimize the calibration matrix by the PLS-1 and PCR methods. Only informative regions from these signals were used to apply the calibration methods, so the number of the variables was reduced from 831 to 400. The

optimized model was applied to analyze synthetic mixtures (Table 2) and to determine the concentrations of the pesticides.

5. Procedure for Determining Pesticides in Groundwater. Spiked groundwater samples (500 mL), Table 2, containing 50 mL of acetone were shaken with 50 mL of methylene chloride for 2 min each. Three extractions with methylene chloride were carried out. The combined organic phases were dried, by passing them through anhydrous Na_2SO_4, and evaporated using a rotary vacuum evaporator. The samples thus concentrated were dissolved with 1 mL of AcN, and the pesticides were determined as described above.

RESULTS AND DISCUSSION

Spectrochromatograms for Pesticide Separations. Many real samples often contain a great number of compounds that have to be determined simultaneously. Such is the case for most of environmental, industrial, or biological matrixes. Multivariate techniques are suitable for the analysis of these multicomponent systems. However, the highly complex HPLC-DAD mixture studied here, owing to both the large number of closely related analytes and the severe overlapping of their signals, led us to investigate the ability of the PLS and PCR methods to satisfactorily resolve these complex chromatographic cases.

Figure 1 shows the spectrochromatogram that corresponds to a sample of the twelve pesticides, selected for their great use in agriculture, where the substantial overlapping of the peaks can be seen. On the other hand, the analytes under study are highly absorptive substances in the UV region of the spectrum with absorption maxima located between 200 and 208 nm for iprodione, procymidone, vinclozolin, malathion, tebuconazole (223 nm), triadimefon (223 nm), chlorfenvinphos (250 nm), fenamiphos (250 nm), triazophos (250 nm), parathion-methyl (275 nm), and parathion-ethyl (275 nm) and at 233 nm for chlorothalonil. The wavelengths between parenthesis indicate a second absorption maximum, although in all cases the latter is less intense than the first at about 200 nm. It is worthwhile noticing that there are appreciable differences between their net signals, especially for the pesticides malathion and tebuconazole. This effect is clearly illustrated in Figure 2. Separate experiments were carried out for staying the linear range of each pesticide, which was found to be about six times less for malathion and tebuconazole than for the rest.

The contour plots of the individual standards of the pesticides are shown in figures 3a and 3b, for a better visualization of their elution profiles. As can be seen, the complexity of the mixture prevents their resolution either by conventional HPLC-DAD analysis (there is not a wavelength or a time for selective detection) or using a single multivariate calibration model evaluated with chromatograms at one compromise wavelength detector, whereas with the CS approach the best (A, λ, t) information can be achieved.

The precise trajectory of the CS through the data matrix was determined by trial and error so that it would traverse as near as possible to the different wavelength maximums of all the pesticides, to maximize the sensitivity and, in as far as possible, the selectivity in the analysis. In this way, not more than three designs were required, taking not more than 3 min for each trial. The linear trajectories of the selected CS are indicated on the contour plot of a mixture (Figure 3c), being described by eight linear paths

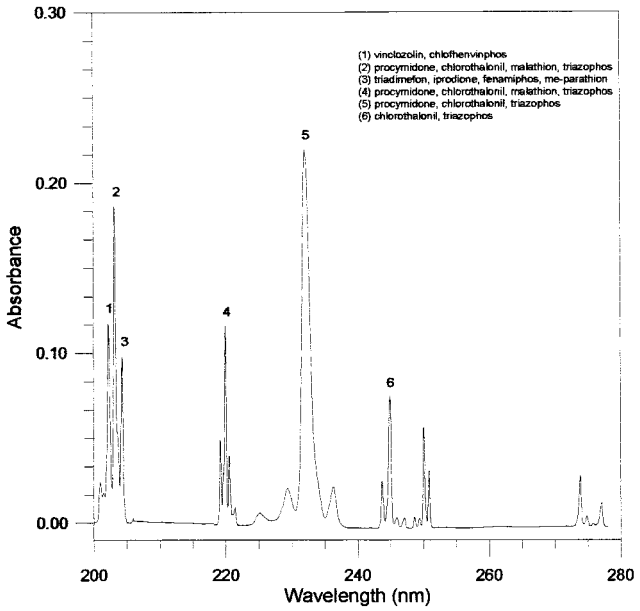

Figure 4. Profile produced from Figure 3c by plotting absorbance versus wavelength.

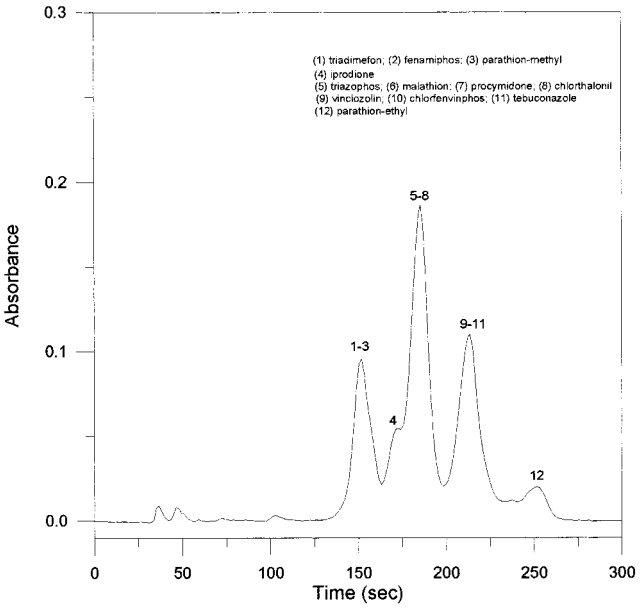

Figure 5. Chromatogram at 205 nm of the same sample plotted in Figure 1.

based on the initial and final coordinate (λ, t) pairs. In fact, paths II and VII did not add any information and were only defined for visual connectivity.

The bidimensional projection on the wavelength domain generated by the selected CS through the data matrix is represented in Figure 4. Although the generated analytical signal seems quite complex, a detailed visualization in Figure 3 may help to understand how it was obtained. The new profile is different from a conventional chromatogram (Figure 5) or spectrum, but it represents the best bidimensional information for resolving this mixture. It is evident that the information contained in Figure 4 is improved with regard to that in the chromatogram (Figure 5), because it contains a greater amount of information and the discrimination between signals is more favorable. However, in this case it was not possible to select an interference-free CS through

the twelve pesticides that allows use of a univariate calibration, as may be deduced from figures 3a and 3b. Besides, in Figure 4 it can be checked that each of the main peaks shows contribution from several pesticides. These nonselective signals were used in combination with the PLS and PCR methods to resolve the twelve-pesticide mixture.

Obviously, the new bidimensional profiles generated contained a higher number of variables than a conventional spectrum or chromatogram, and therefore the uninformative regions were not taken into account in building up the calibration models.

Calibration. A calibration set of 35 samples was taken with concentrations belonging to the linear range of the analytes. The optimized CS was applied to all calibration-set samples and projected on the wavelength domain to produce the corresponding bidimensional profiles. In a first step, the bidimensional signals generated were used for evaluating centered PLS and PCR models. The computational time was 2 min for building up the optimum PLS model and somewhat less (1.3 min) for the PCR model.

The selection of the number of factors is one of the most difficult tasks in the optimization of the PLS and PCR models. This number must be less than the number of samples in the calibration set and always greater than the number of components in the calibration. A good first guess is to use as maximum a number which is half the number of calibration samples; in our case that is 17 or 18 factors.

The number of factors in the PLS and PCR models was selected by cross-validation[9,33] which has become standard in multivariate calibration. It is a practical and reliable way to test the statistical significance of each new added factor, i.e., to determine when factors start to be insignificant. Using this procedure, the right number of factors is determined as the lowest number for which the prediction error sum of squares (PRESS) does not significantly differ from the minimum. Significance was determined by the *F*-statistic.[7]

To evaluate the effectiveness of the models in predicting concentrations in unknown samples, the root-mean-square prediction error (RMSE) and the error total of prediction (ET), both based on cross-validation, were calculated as

$$\mathrm{RMSE\ (f)} = \left(\sum_{i=1}^{n}\frac{(x_i - \hat{x}_{i(f)})^2}{n}\right)^{0.5}$$

$$\mathrm{ET(f)} = \left(\sum_{i=1}^{n}(x_i - \hat{x}_{i(f)})^2\right)^{0.5}$$

where n is the total number of calibration samples, $\hat{x}_{i(f)}$ represents the estimated concentration of the ith component using a model with f factors, and $\hat{x}_i$ is the reference concentration.

The optimum number of factors and the statistical results obtained for the PLS and PCR methods, using cross-section signals (CS-PLS and CS-PCR), are summarized in Table 3. It may be observed that in all cases the best prediction error values were obtained by the PLS method, in spite of the fact that for chlorothalonil, malathion, and tebuconazole the differences were not significant, and therefore only this method was applied to the analysis of the pesticide mixture. Moreover, it is worth pointing out that RMSD and ET results reported by both methods were much too high for malathion and tebuconazole. The poor results obtained for malathion and tebuconazole were probably caused by their lower net analytical signals compared with those of the other pesticides. Hence, the proposed PLS model enabled the simultaneous determination of 10 of the twelve pesticides of the mixture.

Table 3. Statistical Parameters of the PLS and PCR Models

	CS−PLS model		CS−PCR model	
pesticide	RMSE[a]	ET(%)[b]	RMSE	ET (%)
iprodione	0.12 (10)	0.68	0.15 (13)	0.86
procymidone	0.30 (10)	1.77	0.42 (13)	2.47
chlorothalonil	0.22 (4)	1.31	0.23 (13)	1.35
chlorfenvinphos	0.39 (12)	2.32	0.75 (13)	4.31
fenamiphos	0.55 (16)	2.71	0.68 (13)	4.05
malathion	2.21 (10)	13.06 [12.84]	2.12 (13)	12.54
parathion-methyl	0.25 (12)	1.51	0.53 (13)	3.11
Parathion-ethyl	0.33 (15)	2.01	0.84 (13)	4.97
tebuconazole	1.90 (5)	11.16 [11.05]	1.91 (13)	11.27
triadimefon	0.36 (14)	0.14	0.49 (13)	2.87
triazophos	0.32 (16)	1.87	1.03 (13)	6.11
vinclozolin	0.32 (16)	1.92	0.45 (13)	2.64

[a] (): number of optimum factors. [b] [ ] ET values for standardized models.

To improve the malathion and tebuconazole results, models with standardized data were constructed to give all variables the same variance, i.e., the same chance to influence analyte estimation. This produced slightly better prediction errors, but the models still were unable to predict malathion and tebuconazole. Therefore, the previous CS-PLS model with centered data was selected as the optimum model.

To test the performance of the proposed CS-PLS model, a set of five synthetic mixtures of the twelve pesticides was prepared with concentrations within its linear range, and predictions were made (Table 4). The proposed CS technique in conjunction with the PLS method was successful in the resolution of the synthetic pesticide mixtures, with predictions ranging between 82.5 and 122.6%, except for malathion and tebuconazole.

Determination of the Pesticides in Groundwater. The proposed CS-PLS model was employed for the determination of the mixture of pesticides in groundwater, as described in the Experimental Section. Samples were spiked between 0.0 and 10.0 μg L^{-1}, and recoveries were calculated. Three replicates were performed for each sample. Table 5 shows the results obtained with recoveries ranging from 70 to 124.7% and RSD values ranging from 3.9 to 7.1%. These results are in the range expected after a preconcentration step[34−36] and confirm the suitability of the method for this purpose.

CONCLUSIONS

In this paper the CS technique is employed to select the best quantitative information for the determination of a complex

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Table 4. Predictions (%) Obtained in Synthetic Mixtures by the PLS Model[a]

pesticide	mixture 1	mixture 2	mixture 3	mixture 4	mixture 5
iprodione	100.5(2.8)	102.2(3.1)	92.0(3.0)	101.8(3.6)	97.7(3.4)
procymidone	103.4(3.8)	104.0(3.6)	112.3(3.6)	98.0(4.0)	90.1(4.3)
chlorothalonil	103.1(4.3)	101.4(3.6)	105.7(3.2)	106.7(3.4)	106.5(3.3)
chlorfenvinphos	104.8(4.0)	106.2(4.4)	95.5(4.6)	94.5(4.1)	122.6(4.5)
fenamiphos	112.7(5.4)	121.8(5.1)	90.0(4.9)	94.3(5.0)	90.3(4.6)
parathion-m	98.2(3.6)	96.4(4.0)	99.7(3.2)	105.0(3.5)	115.0(3.9)
parathion-e	98.0(3.9)	98.2(3.8)	85.0(4.1)	89.3(4.3)	93.7(4.9)
triadimefon	121.7(4.8)	118.2(4.6)	93.4(3.7)	99.6(3.5)	83.8(3.8)
triazophos	112.8(4.1)	104.6(3.8)	91.9(3.6)	87.4(4.1)	84.9(4.5)
vinclozolin	99.3(3.2)	94.5(3.1)	82.5(4.1)	95.7(3.8)	102.6(4.2)

[a] Results are average of three determinations with RSD values in parentheses

Table 5. Recoveries (%) for the Pesticide Mixture in Groundwater Using the Proposed PLS Model[a]

pesticide	sample 1	sample 2	sample 3	sample 4	sample 5	sample 6	sample 7	sample 8	sample 9
iprodione	107.5(3.9)	77.5(4.3)	86.4(4.5)	87.6(4.7)	87.7(4.9)	99.0(4.4)	80.3(5.0)	89.8(5.1)	99.5(4.2)
procymidone	82.8(4.3)	101.7(4.0)	72.3(4.8)	106.6(5.1)	97.2(4.2)	91.1(5.7)	90.0(5.2)	100.7(4.7)	92.8(4.9)
chlorothalonil	83.0(5.1)	86.0(4.9)	79.3(5.4)	83.5(4.7)	82.8(4.2)	97.3(4.1)	78.7(5.2)	90.7(4.4)	90.3(4.8)
chlorfenvinphos	97.2(4.5)	70.0(5.7)	79.8(5.9)	85.0(5.3)	88.8(5.0)	95.3(4.4)	95.3(4.8)	108.8(5.4)	105.2(5.7)
fenamiphos	89.7(6.0)	78.5(6.9)	108.0(5.8)	74.8(5.4)	86.7(6.3)	99.4(5.6)	95.4(5.5)	90.7(6.3)	121.2(6.4)
parathion-m	103.1(5.1)	75.5(5.5)	89.1(6.0)	90.2(5.6)	94.4(4.2)	93.1(5.2)	81.8(5.2)	103.6(4.4)	91.5(4.9)
parathion-e	95.7(4.9)	93.5(5.1)	79.6(5.8)	98.3(4.3)	91.6(5.3)	123.7(6.2)	94.0(5.9)	88.1(5.7)	118.2(5.3)
triadimefon	117.6(6.8)	124.7(7.1)	76.8(6.0)	105.3(5.1)	95.5(5.4)	118.3(6.1)	77.7(6.5)	70.2(6.5)	124.5(6.0)
triazophos	99.0(5.2)	82.0(5.8)	91.6(4.9)	102.3(5.3)	91.1(6.0)	97.4(5.6)	94.3(5.7)	80.5(6.2)	95.2(5.7)
vinclozolin	82.3(4.9)	94.7(5.3)	79.1(6.3)	87.5(5.9)	98.2(4.5)	120.0(5.8)	119.8(5.9)	87.3(4.7)	94.2(5.0)

[a] Results are averages of three determinations with RSD values in parentheses.

pesticide mixture with overlapping HPLC-DAD chromatographic signals. With this technique, new 2D profiles are obtained, functions of the wavelength or time, with the best determination sensitivity and from which multivariate calibration models are obtained.

It has been demonstrated that PCR method predictions are worse than those of the PLS method, probably because this latter algorithm is more suitable to overcoming the existence of problems such as the presence of random linear baseline variations or deviations from Beer's law caused by component interactions and overlapping signals. This is not surprising considering the different ways in which the two methods decompose the independent-variable matrix.

From these results, it may be concluded that this methodology is especially useful for multicomponent analysis because the obtained signals simultaneously contain the best information from the time and wavelength domains. In this way, the need of evaluating a different calibration model, at the absorption-maximum wavelength of each pesticide, to perform the analysis at the optimum wavelength is avoided. Although two pesticides in the mixture were not resolved, this would seem to be due to their low net signals rather than to a lack of capacity of the CS-PLS method for resolving mixtures containing more than 10 analytes.

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