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Environmental Water Samples Analysis of Pesticides by Means of Chemometrics Combined with Fluorimetric Multioptosensing

Ana Domínguez-Vidal · Pilar Ortega-Barrales · Antonio Molina-Díaz

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Abstract A single flow-through optosensor spectrofluorimetric system is proposed for the resolution of mixtures of three pesticides, α-naphthol, o-phenylphenol and thiabendazole, at $\mu g\, l^{-1}$ levels using a partial least-squares (PLS) calibration approach. The sensor was developed in conjunction with a monochannel flow-injection analysis system with fluorimetric detection using C_{18} silicagel as an active sorbent substrate in the flow cell. By using 20% methanol-water (v:v) solution as carrier solution, the multisensor responds linearly in the measuring range without requiring additional reagents or derivatization. First derivative emission spectra of the corresponding analytes recorded during the process of retention-elution were used to provide multivariate data. The different kinetic on the retention process of the analytes on the sensing zone allows the selection of a time matrix for each analyte providing best results in the PLS approach. Accurate prediction results were obtained for the three analytes with RMSEP values of 1.86%, 3.34% and 0.50% were obtained for α-naphtol, o-phenylphenol and thiabendazole respectively. In the analysis of environmental waters samples, a mean recovery of 103% was obtained.

Keywords Pesticide · FIA · Multisensing · PLS · α-naphthol · O-phenylphenol · Thiabendazole

A. Domínguez-Vidal · P. Ortega-Barrales · A. Molina-Díaz (✉)
Department of Physical and Analytical Chemistry,
Faculty of Experimental Sciences, University of Jaén,
Campus Las Lagunillas,
E-23071 Jaén, Spain
e-mail: amolina@ujaen.es

Introduction

With environmental protection high in the agenda of many countries, new rules and regulations are currently being set up for monitoring greater numbers of hazardous organic substances. Organic compounds present in environmental waters may be naturally occurring compounds, anthropogenic compounds or degradation products from agricultural activity and industrial and urban wastes [1]. Pesticides are a wide group of polluting compounds with anthropogenic origin that are used as herbicides, fungicides and insecticides. Their widespread use in modern agriculture together with the contribution to environmental contamination and health diseases makes imperative to develop high performance methods for their detection and quantification [1–3]. High-performance separation techniques [4, 5], mass spectrometry [6, 7] and immunochemical analytical techniques [8–11] are widely accepted for these purposes. Necessary additional steps as clean-up or preconcentration procedures are the main handicaps for these techniques [12].

Fluorescence spectroscopy is a versatile analytical tool regarded as simply, fast and greatly sensitive instrumental technique. However, it is moderately selective; one of the main difficulties can arise from multicomponent analysis due to the overlapping of the broad band spectra of structurally similar components. Despite chemical procedures as changes in solvent, pH etc. selectivity in the determination of pesticides can be improved through spectrofluorimetric strategies and preconcentration techniques [13, 14]. Solid phase spectroscopy (SPS) provides an enhancement on both selectivity and sensitivity due to the retention and preconcentration of the target species on an appropriate solid support placed in the detection zone [15]. On the other hand, flow systems are demonstrated to be powerful to meet the analytical requirements of environmental and agricultural analysis

in terms of automatization, monitoring, microsampling and sample handling [16]

Implementation of both the preconcentration on a solid support with the automatization of a flow system gives rise to the concept of flow through sensors [17] that has been widely developed improving speed and sensitivity as well as reducing reagents consumption [17–22]. Multioptosensors are those systems that allow the simultaneous determination of two or more analytes. Usually, this kind of systems are based on the different retention/elution processes of the analytes on a minicolumn packed with a solid support and placed before the detection zone [23–27]. It is also reported, for the simultaneous determination of two analytes, the possibility of using of an extra amount of solid support in the flow cell [21]. However, these methodologies are not always able to separate completely the analytes in their arrival to the sensing zone.

Modern multivariate methods [28] constitute a very attractive alternative for the resolution of complex systems. Partial least squares (PLS) and principal component regression (PCR) are the most extensively used multivariate calibration methods in chemometrics and they have been discussed in more detail elsewhere [28–30]. They can resolve overlapping signals and reduce interference problems as well as background noise [31]. PCR [32, 33] and PLS [2, 22, 31, 34–37] approaches are increasingly being used in conjunction with flow injection (FIA) analysis techniques.

Therefore, this work, proposes a straightforward flow-through spectrofluorimetric multisensor for the simultaneous determination of three pesticides, o-phenylphenol (OPP), thiabendazole (TBZ) and α-naphthol (NFT) as hydrolysis product from carbaryl. The application of a PLS approach exploits the different kinetic behaviour in the retention–elution process onto the solid support by choosing the time values which provide the most different behaviour of the target species. An enhancement of the native fluorescence signal due to the retention of the analytes on the solid microbeads in the detection zone itself is also provided.

Experimental

Reagents

Analytical-reagent grade chemicals were used for all the experiments. Standard solutions of 10 μg ml^{-1} of α-naphthol (Fluka, Madrid, Spain), o-phenylphenol (Fluka, Madrid, Spain) and thiabendazole (Sigma, Madrid, Spain) were prepared by dissolution of the appropriate amounts in a solvent mixture of 50% methanol-deionized water (v:v). Solutions stability was demonstrated for at least 4 days at 5°C and darkness. Work solutions were prepared daily by dilution with deionised water. 20% (v:v) aqueous methanol (MeOH) (Panreac, Barcelona, Spain) was used as carrier solution.

C_{18} silica gel (Waters, Milford, USA) with average particle size of 55–105 μm was used as solid support in a Hellma 176.052-QS flow-through cell (1.5 mm optical path length).

Apparatus

All spectral measurements and real-time data acquisition of flow injection peaks were made with a Varian Cary-Eclipse Fluorescence Spectrofluorimeter (Varian Iberica, Madrid, Spain). The spectrofluorimeter was equipped with a xenon discharge lamp (75 kW), Czerny-Turner monochromators, two detectors (sample and internal reference), an R-928 photomultiplier tube which is red-sensitive (even 900 nm) with manual or automatic voltage controlled using the Cary-Eclipse software for Windows 95/98/NT system.

The TQ-Analyst Professional Edition (from Thermo Nicolet) version 6.1 software running in a 4.5 GHz PC was used for the statistical treatment of the data and the application of PLS-1 algorithm.

A Gilson Minipuls-3 (Villiers le Bell, France) peristaltic pump was used to generate the flow stream in the single manifold (Fig. 1) required for the system. Injections were carried out by using a Rheodhyne type 50 six-port rotary injection valve (Cotati, USA). Teflon tubing 0.8 mm i.d. was also used.

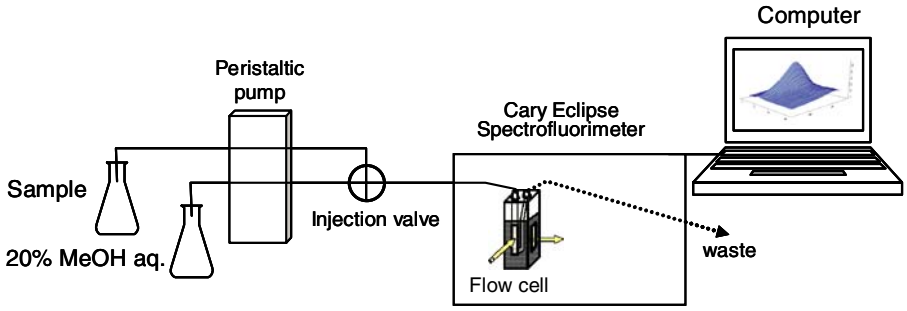

Fig. 1 Flow injection manifold for the simultaneous determination of NFT, OPP and TBZ

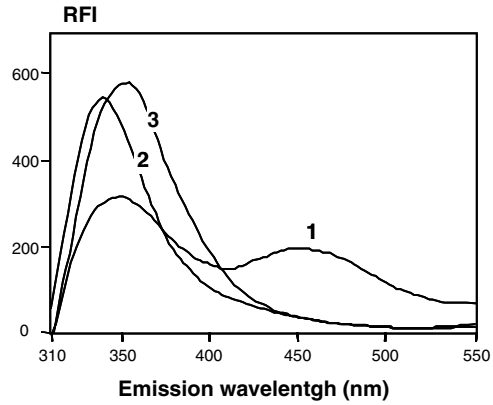

Fig. 2 Emission spectra of NFT (1), OPP (2) and TBZ (3), at 0.5 μg l^{-1}, made at stopped flow and sorbed on C_{18} silica gel

Experimental procedure

500 μl of the sample solution containing of NFT (2–1040 μg l^{-1}), OPP (2–400 μg l^{-1}) and TBZ (2–450 μg l^{-1}), were inserted into the carrier solution, MeOH-water, 20% (v:v), and pumped through the system (Fig. 1) using a flow rate of 1.55 ml min^{-1}. Spectra were recorded while sample plugs were passing through the flow cell where the analytes were transitorily retained on the solid support (C_{18}). Emission spectra were recorded in the region of 325–435 nm using an excitation wavelength of 290 nm. A spectrum was registered each *ca*. 5 s.

Results and discussion

Preliminary exploration of the three dimensional fluorescence spectra of the analytes was performed at stopped flow in solution as well as retained on C_{18} silica gel. 290 nm was selected as excitation wavelength and emission spectra (Fig. 2) recorded in the region of 325–425 nm. As it can be seen, they were highly overlapped; therefore, conventional spectrofluorimetry cannot be applied to solve this mixture.

As it was explained above, partial least squares regression has the powerful capability of discriminating complex mixtures, fact that together with the different behaviour of the analytes on the solid support can be exploited for the simultaneous determination of NFT, OPP and TBZ.

Study of experimental variables

Experimental variables in flow-through sensors are usually divided in four main groups, related to the retention-detection unit, chemical variables, flow system variables and instrumental variables. Each individual constituent was solely optimized and compromise values of the experimental variables were selected.

Retention-detection unit

The support in the flow cell has to be carefully selected in order to retain temporally the analytes while improving the fluorescence signal. For this, several supports of different nature (Sephadex QAE A-25, Sephadex SP- C-25 and C_{18} silica gel) were tested. The non-polar silicagel C_{18}, was chosen for further studies. This support was demonstrated to present the best interaction with the three pesticides increasing their signals comparing with those obtained in solution. 55–105 μm was selected as particle size obtaining good compactness without increasing too much the background absorbance and the possible high pressure troubles.

The amount of C_{18} silica gel in the flow cell was fixed to avoid both the measurement in solution and the retention of the analytes above the detection zone due to their rapid fixation on the top of the support.

Chemical variables

pH of the carrier solution and samples was studied by adjusting them at various pH values HCl or NaOH (for the 2–12 pH region). No significant influence was found in both cases. Then a water-organic solvent mixture was selected to act as carrier. Ethanol, methanol and acetone ranged from 0 to 100% (v:v) were tested. The most appropriate carrier was the methanol-water mixture 20% (v:v). Furthermore, 50% methanol-water (v:v) was selected to completely regenerate the sorbent after a each daily session.

Flow injection variables

The flow rate in a flow injection system determines both the residence time and the rate at which the analytes can be eluted from the solid support. When flow rate decreased, both the signal and the elution time increased, hence, wider peaks were obtained. On the other hand, the

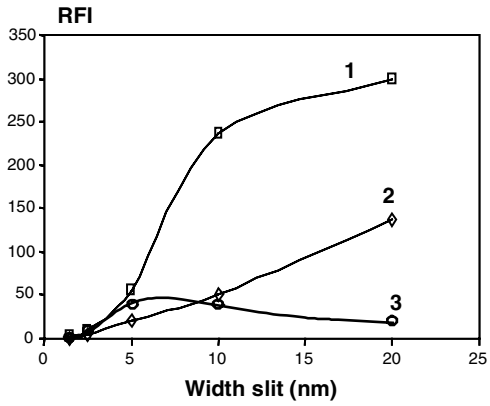

Fig. 3 Width slits study for thiabendazole. Excitation slit: (1) analyte plus background and (3) net signal for the analyte. Emission slit (2)

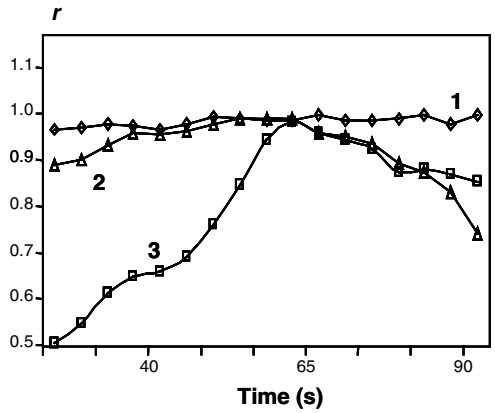

Fig. 4 Correlation coefficients for the different times. (1) α-naphtol, (2) o-phenylphenol and (3) thiabendazole

injection volume influences the sensitivity of the method and the sampling frequency. The relative fluorescence intensity (RFI) increases linearly with the increase in the sample volume from 40 to 750 μl for α-naphthol (RFI = 70 + 0.125v, r = 0.987) and to 1000 μl for the other two analytes (OPP, RFI = 42 + 0.213v, r = 0.9952 and TBZ, RFI = 34 + 0.314 v, r = 0.9963; v, μl). As a compromise between sensitivity and a good sampling throughput, 1.55 ml min^{-1} and 500 μl were the selected values flow rate and injection volume, respectively.

Instrumental variables

Excitation and emission width slits have to be optimized in order to obtain the maxima analyte signal/background ratio. Relative fluorescence intensity increased when the width slits increased. For the emission slit width the increasing intensity was mainly ascribable to the samples; however the drastic increment obtained for the excitation slit was tested to be mainly due to the background signal. This effect was found to appear for the three analytes; therefore net analyte signal was calculated by subtraction before chosen the width slit. Fig. 3 shows the study for thiabendazole. 5 nm and 20 nm width slits were selected for excitation and emission respectively.

PLS treatment of spectrofluorimetric data

Multivariate calibration methods can obtain selective and reliable analyte quantifications from spectral data where the analyte and the matrix composition are varying. Partial least squares (PLS) regression, a flexible full spectra method, was used. In this method, a few latent variables should be optimized to produce the best correlation between the information contained in the fluorescence spectra and the sample concentration.

The first step in constructing the PLS model was defining a calibration set of 25 samples and a validation set of 15 samples. Samples concentrations of both sets were established within the linear range obtained for each individual component, which were 2–1000 μg l^{-1}, 2–400 μg l^{-1} and 2–440 μg l^{-1} for NFT, OPP and TBZ respectively. Samples containing every analyte solely were also included.

Each one of these samples was inserted in the system following the above described experimental procedure, which means, emission spectra were continuously recorded while the sample plug was passing the sensing zone. In this way, 30 spectra were taken, for each sample, from the injection moment till the complete elution of all the analytes. The different behaviour of the analytes on the silicagel C_{18} suggested that a study at different times could enhance the discrimination between analytes. Spectra before the analytes reached the detection zone and those after the elution were disregarded. Therefore, 17 matrices were built with the recorded spectra during the FIA peak. First derivative spectra were treated during the PLS procedure.

Data pretreatment consisted in "*mean centering*" the spectra to eliminate common spectral information. To assess the fitting of the model, the root mean square error of calibration (RMSEC) and the correlation coefficient between actual and predicted value for the calibration set (r) were calculated for these 17 matrices. Results (Fig. 4) concluded that α-naphthol is well modeled by all the proposed matrices, with a

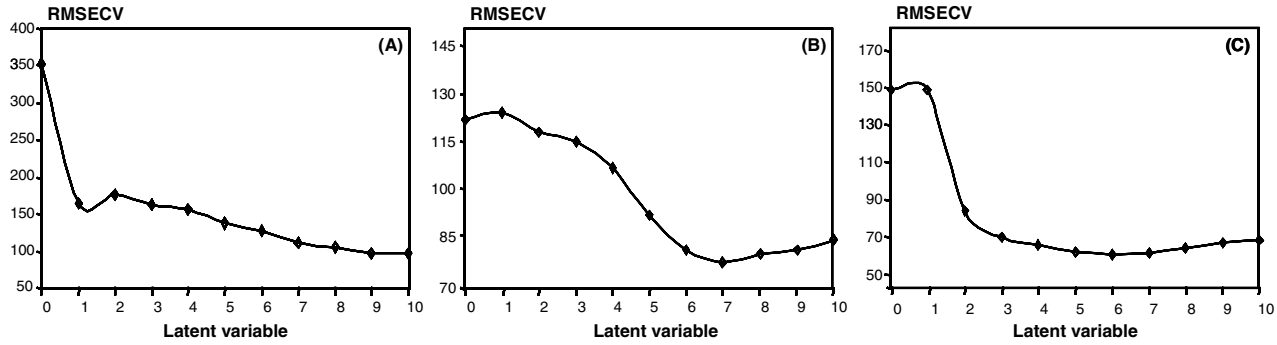

Fig. 5 RMSECV values for t = 96 s (A) α-naphtol, and t = 62.4 s for (B) o-phenylphenol and (C) thiabendazole

Table 1 Validation set

Sample	α-Naphthol (μg l^{-1})		o-Phenylphenol (μg l^{-1})		Thiabendazole (μg l^{-1})	
	C added	C found	C added	C found	C added	C found
1	85	92	230	219	250	254
2	360	382	200	215	140	138
3	2	—	120	132	100	105
4	400	414	150	144	15	17
5	475	463	180	157	40	45
6	250	231	275	266	90	102
7	600	611	210	217	300	278
8	700	684	110	126	275	261
9	32	34	250	239	230	246
10	105	97	300	282	320	287
11	60	64	15	22	80	102
12	6	6	80	88	150	156
13	9	8	30	29	120	126
14	65	70	2	1	130	134
15	80	88	5	2	180	172

maximum *r* for time equals to 96 s. The different spectral features of α-naphtol comparing to the other two pesticides are the responsible of this effect. In the cases of o-phenylphenol and tiabendazole, the correlation coefficients are completely related to the retention elution process in the active microzone. Then, *r* increases up to time = 62.4 s, which corresponds to the maximum of FIA peak, where the differences between the spectra of the three analytes are enhanced. After this time value, the correlation decreases, due to the autoelution process. Hence, these two matrices (t_1 = 62.4 s and t_2 = 96s) were used to model the system.

The optimum number of latent variables for the model was selected based on the root mean square error of cross-validation (RMSECV), which should be minimized. The RMSECV was calculated using the leave-one-out approach. This parameter is a measurement of how well a particular model fits the concentration data. Fig. 5 shows the obtained RMSECV for the selected matrices considering 10 maxima latent variables.

6 latent variables were chosen to model thiabendazole and 7 for modelling both α-naphtol and o-phenylphenol.

The predictive ability of the model was also taken into account using the root mean square error of prediction [38] (RMSEP) for the validation set. RMSEP percentage values of 1.86, 3.34 and 0.50 were obtained for α-naphtol, o-phenylphenol and thiabendazole respectively. Table 1 summarizes the added and predicted concentrations obtained for each analyte showing the success in the prediction of the concentrations.

Applications

The proposed method has been used in the simultaneous determination of α-naphtol, o-phenylphenol and thiabendazole

Table 2 Applications

Sample	α-Naphthol (μg l^{-1})			o-Phenylphenol (μg l^{-1})			Thiabendazole (μg l^{-1})		
	C added	C found	Rec ± σ_r (%)	C added	C found	Rec ± σ_r (%)	C added	C found	Rec ± σ_r (%)
1	—	—	—	150	145.0	103 ± 4	—	—	—
2	80	85.3	94 ± 4	—	—	—	75	81.5	92 ± 6
3	275	288.0	95 ± 5	275	261.1	105 ± 4	50	49.2	102 ± 7
4	—	—	—	—	—	—	15	13.1	114 ± 4
5	125	115.0	109 ± 2	50	44.4	113 ± 3	—	—	—
6	5	4.6	108 ± 6	3	2.6	117 ± 7	35	36.5	96 ± 2
7	50	49.6	101 ± 2	—	—	—	—	—	—
8	—	—	—	20	24.2	82 ± 3	300	299.8	100 ± 2
9	500	472.0	106 ± 3	350	352.5	99 ± 2	150	131.3	114 ± 2

Samples 1–3: Tap water from Jaén (Spain).

Samples 4–6: "Pantano Rumblar" (Baños de la Encina, Jaén, Spain).

Samples 7–9: "Rio Grande" (La Carolina, Jaén, Spain).

C, concentration, Rec, recovery.

in spiked natural water samples. Samples from *Pantano Rumbla*" (reservoir in Baños de la Encina, Jaén, Spain), *Grande River* (La Carolina, Jaén, Spain) and drinkable water from tap (Jaén, Spain) were analyzed (Table 2). The determination was carried out by applying the proposed procedure to samples containing either only one compound or binary and ternary mixtures. The results obtained and the percentages of recovery with respect to the added amounts are shown in table 4. The mean recovery percentage was found to be around 103%. In some cases, errors were higher than 10% probably due to matrix effects which were not present in the calibration standards. Nevertheless, the results can be considered satisfactory taking into account that calibration standards were prepared in deionized water and a unique calibration was used for the different environmental samples.

Conclusions

The combination of chemometrics and fluorimetric detection on flow through multisensors has been demonstrated to be an interesting technique for the determination of pesticides. Simplicity, sensitivity, low cost and flexibility are provided by the proposed method. The employment of a solid support placed in the flow cell increases both the sensitivity and selectivity of the detection. Furthermore the different kinetic on the retention-elution process is exploited by powerful PLS approach which allows the discrimination between analytes.

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References

1. Hennion MC, Scribe P (1993) In: Barceló D (ed) Enviromental analysis. Techniques, aplications and quality assurance, 1a edn. Elsevier, Amsterdam, pp 23–77
2. Piccirilli G, Escándar G (2006) Partial least-squares with residual bilinearization for the spectrofluorimetric determination of pesticides. A solution of the problems of inner-filter effects and matrix interferents. Analyst 131(9):1012–1020
3. Santos Delgado MJ, Rubio Barroso S, Toledano Fernandez-Tostado G, Polo-Diez LM (2001) Stability studies of carbamate pesticides and analysis by gas chromatography with flame ionization and nitrogen-phosphorus detection. J Chromatogr A 921(2):287–296
4. He Y, Lee HK (2006) Continuous flow microextraction combined with high-performance liquid chromatography for the analysis of pesticides in natural waters. J Chromatogr A 1122(1–2):7–12
5. Tse H, Comba M, Alaee M (2004) Method for the determination of organophosphate insecticides in water, sediment and biota. Chemosphere 54(1):41–47
6. Sadao N, Shigeki D (2005) Simultaneous determination of 64 pesticides in river water by stir bar sorptive extraction and thermal desorption-gas chromatography-mass spectrometry. Anal Bioanalytical Chem 382(1):99–107
7. Richardson SD (2006) Environmental mass spectrometry: emerging contaminants and current issues. Anal Chem 78(12):4021–4046
8. Lee N, Kennedy IR (2001) Environmental monitoring of pesticides by immunoanalytical techniques: validation, current status, and future perspectives. J AOAC Int 84(5):1393–1406
9. Zhi ZL (1999) Flow-injection immunoanalysis, a versatile and powerful tool for the automatic determination of environmental pollutants. Lab Robotics Automat 11(2):83–89
10. Schobel U, Barzen C, Gauglitz G (2000) Immunoanalytical techniques for pesticide monitoring based on fluorescence detection. Fresenius' J Anal Chem 366(6):646–658
11. Jeanty G, Wojciechowska A, Marty L, Trojanowicz M (2002) Flow-injection amperometric determination of pesticides on the basis of their inhibition of immobilized acetylcholinesterases of different origin. Anal Bioanalytical Chem 373(8):691–695
12. Georgiou PP, Liapis KS, Miliadis GE, Siskos PA (2006) Solid-phase extraction cleanup of tomato samples for the determination of pesticide residues by gas chromatography-electron capture detection. Int J Environ Anal Chem 86(1–2):69–76
13. Martinez-Calatayud J, Golcalves deAscensao J, Albert-Garcia JR (2006) FIA-fluorimetric determination of the pesticide 3-indolyl acetic acid. J Fluoresc V16(1):61–67
14. Mohammad MK, Chi WJ, Hyun SL, Seikh MA, Sang HL, Jong HC, Seung OJ, Ajoy KD (2006) Simultaneous determination of acetylsalicylic acid and caffeine in pharmaceutical formulation by first derivative synchronous fluorimetric method. J Fluoresc V16(5):713–721
15. Ortega-Barrales P, Fernandez de Cordova ML, Molina-Diaz A (1998) Microdetermination of vitamin B1 in the presence of vitamins B2, B6, and B12 by solid-phase UV spectrophotometry. Anal Chem 70(2):271–275
16. Miro M, Frenzel W (2004) What flow injection has to offer in the environmental analytical field. Microchimica Acta 148(1):1–20
17. Valcárcel M, Luque de Castro MD (1994) Flow through (bio)chemical sensors. Elsevier, Amsterdam
18. Dominguez-Vidal A, Ortega-Barrales P, Molina-Diaz A (2002) Fast flow-injection fluorimetric determination of amiloride by using a solid sensing zone. Talanta 56(6):1005–1013
19. Diaz-Garcia J, Costa-Fernandez JM, Bordel N, Pereiro R, Sanz-Medel A (2003) Energy transfer – room temperature phosphorescence for the optosensing of transition metal ions. Anal Chim Acta 486(1):1–10
20. Dominguez-Vidal A, Ortega-Barrales P, Molina-Diaz A (2002) Determination of triamterene by transitory retention in a continuous flow solid phase system with fluorimetric transduction. J Pharmaceut Biomed Anal 28(3–4):721–728
21. Garcia-Reyes JF, Llorent-Martinez EJ, Ortega-Barrales P, Molina-Diaz A (2004) Continuous-flow separation and pre-concentration coupled on-line to solid-surface fluorescence spectroscopy for the simultaneous determination of o-phenylphenol and thiabendazole. Anal Bioanalytical Chem 378(2):429–437
22. Ortega-Algar S, Ramos-Martos N, Molina-Diaz A (2003) A flow-through fluorimetric sensing device for determination of [alpha]- and [beta]-naphthol mixtures using a partial least-squares multivariate calibration approach. Talanta 60(2–3):313–323
23. Ortega Barrales P, Dominguez Vidal A, Fernandez de Cordova ML, Molina Diaz A (2001) Simultaneous determination of thiamine and pyridoxine in pharmaceuticals by using a single flow-through biparameter sensor. J Pharmaceut Biomed Anal 25(3–4):619–630
24. Llorent-Martinez EJ, Dominguez-Vidal A, Ortega-Barrales P, de la Guardia M, Molina-Diaz A (2005) Implementation of multicommutation principle with flow-through multioptosensors. Anal Chim Acta 545(1):113–118
25. Dominguez-Vidal A, Ortega-Barrales P, Molina-Diaz A (2003) Simultaneous determination of paracetamol, caffeine and

propyphenazone in pharmaceuticals by means of a single flow-through UV multiparameter sensor. Microchimica Acta 141(3):157–163
26. Llorent-Martinez EJ, Garcia-Reyes JF, Ortega-Barrales P, Molina-Diaz A (2005) Flow-through fluorescence-based optosensor with on-line solid-phase separation for the simultaneous determination of a ternary pesticide mixture. J AOAC Int 88(3):860–865
27. Ruedas Rama MJ, Ruiz Medina A, Molina Diaz A (2002) Use of a solid sensing zone implemented with unsegmented flow analysis for simultaneous determination of thiabendazole and warfarin. Anal Chim Acta 459(2):235–243
28. Martens H, Naes T (1989) Multivariate calibration, 7a edn. John Wiley & Sons Ltd., Chichester
29. Geladi P, Kowalski BR (1986) Partial least-squares regression: a tutorial. Anal Chim Acta 185:1–17
30. Beebe KR, Pell RJ, Seasholtz MB (1998) Chemometrics. A practical guide, 1st edn. John Wiley & Sons, New York
31. Picón-Zamora D, Martínez-Galera M, Garrido-Frenich A, Martínez-Vidal JL (2000) Trace determination of carbendazim, fuberidazole and thiabendazole in water by application of multivariate calibration to cross-sections of 3-dimensional excitation-emission matrix fluorescence. Analyst 125(6):1167–1174
32. Saurina J, Hernandez-Cassou S (1999) A comparison of chemometric methods for the flow injection simultaneous spectrophotometric determination of aniline and cyclohexylamine. Analyst 124(5):745–749
33. Saurina J, Hernandez-Cassou S (1995) Simultaneous determination of several amino acids with multivariate calibration methods by using a continuous-flow system. Analyst 120(2):305–312
34. Ayora-Cañada MJ, Pascual-Reguera MI, Molina-Diaz A, Apitan-Vallvey LF (1999) Solid-phase UV spectroscopic multisensor for the simultaneous determination of caffeine, dimenhydrinate and acetaminophen by using partial least squares multicalibration. Talanta 49(3):691–701
35. Capitán-Vallvey LF, Kalil M, Deheidel A, de Orbe I, Avidad R (1999) Application of partial least squares multivariate calibration for the determination of mixtures of carbaryl and thiabendazole in waters by transmitted solid phase. Analyst 124(1):43–56
36. Ruiz Medina A, Fernandez de Cordova ML, Molina-Diaz A (1999) Simultaneous determination of paracetamol, caffeine and acetylsalicylic acid by means of a FI ultraviolet pls multioptosensing device. J Pharmaceut Biomed Anal 21(5):983–992
37. Teixeira L, Costa A, Garrigues S, de la Guardia M (2002) Flow-injection solid phase partial least-squares spectrophotometric simultaneous determination of iron, nickel and zinc. J Brazil Chem Soc 13(1):54–59
38. Danzer K, Otto M, Currie LA (2004) Guidelines for calibration in analytical chemistry. Multispecies calibration. Pure Appl Chem 76(6):1215–1225