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Correction of predicted concentration in the use of solvent-based calibration lines for determining carbendazim, fuberidazole and thiabendazole in water after a SPE step

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Abstract

This paper addresses an attempt to overcome the deviation that results from the use of a solid phase extraction (SPE) procedure for extracting trace levels of three benzimidazole pesticides (carbendazim, fuberidazole and thiabendazole) from water samples, for their subsequent quantitative determination by spectrofluorimetry, using univariate calibration. The deviation is due to an attenuation effect originating in the C_{18} cartridge used in the SPE step. The approach developed is based on the calculation of a correction factor (fc) that is dependent on the signal measured after the SPE step. In order to calculate fc a study of the intermediate precision of two calibration graphs (with and without SPE) was performed. The fc was added to the predicted concentrations for the analytes using a calibration graph for pure solvent, built every time that the analysis is done. In addition, predictions were made using both average calibration graphs obtained from the intermediate precision study. In this study, the first of these three options was shown to improve the accuracy of predictions in the presence of matrix effects.

Keywords: Pesticides; SPE; Interferences correction

1. Introduction

The determination of compounds at trace levels is not a simple task and often the corresponding limit of detection is determined by the analytic instrumentation available. This instrumentation must clearly distinguish between a very small signal and one derived from a blank sample.

As important as achieving a low detection limit, is the capability to obtain good selectivity, i.e. to ensure that any variation in the measurement is caused exclusively by the amount of the substance to be determined in the sample. However, this circumstance is not always achieved. On numerous occasions, another substance or substances, or the matrix itself, affects the signal of the analyte being

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measured. If this effect is not accounted for, systematic errors will affect the result and cause bias [1]. This situation is described as a lack of selectivity or interference.

The interferences can affect the analyte response in two different ways: (i) some of the matrix components somehow modify the analyte signal; or (ii) some step of the sample treatment, such as the extraction or adsorption process, affects the response in a way that is not taken into account in the preparation of the calibration standards.

The above mentioned interferences can yield two types of systematic errors. Firstly, they may lead to relative systematic errors. The causal factors may be physical or chemical. They do not lead to a response as such, but rather affect the slope of the calibration line. The interferences that follow this behaviour can be identified by comparing the slopes of the calibration lines obtained with solvent-based standards and standards that undergo the sample treatment or matrix-matched standards [2–4]. Secondly, a lack of selectivity occurs when concomitant species have a response of their own which is additional to that of the analyte. This type of interference affects the blank and, if not corrected, would lead to a constant systematic error.

Various strategies are employed to resolve these problems [5]. One of them involves the use of the so-called matrix-matched calibration, and this method is used in several laboratories with excellent results [6–9]. Unfortunately, the procedure involves additional labour costs in the calibration step every time that the analysis is done.

In fact, a similar problem arises when transferring calibrations between instruments in order to avoid developing separate calibration models for each instrument. Several univariate procedures have been suggested to overcome the latter problem, such as the correction of the results by means of a linear regression function [10–12] or the approach proposed by Osborne and Fearn [13] to correct the constant systematic error for signals measured on different instruments. However, these simple univariate corrections of the predicted values are successful only when the signals are very similar to each other. In contrast, when dissimilar signals are measured, it is not normally possible to obtain satisfactory corrections of the values simply by fitting a straight line. To cope with these complex situations, different standardisation methods have been described [14].

The present paper describes the development of a method designed to overcome interference arising from the solid phase extraction (SPE) step in the determination of three pesticides (carbendazim, fuberidazole and thiabendazole) in water samples, using molecular luminescence spectroscopy. The approach developed is based on the correction of the results (predicted concentration) of the preconcentrated sample after quantitation using a calibration graph built using solvent standards. This correction factor (fc) is calculated from the results of an intermediate precision study of two calibration graphs (with and without SPE). Two additional approaches were also tested, in which predictions were made using the two average calibration graphs obtained from the intermediate precision study. A comparative study of the predictions obtained with the different options was carried out.

2. Theory

In order to correct the bias between signals with and without SPE, several procedures may be applied, in the same way as for intercalibration of different instruments [15]:

1) Transfer of spectra or signals, i.e. reproduction of the signals obtained using solvent-based standards on those obtained using SPE.
2) Transfer of calibration model, i.e. transformation of the regression model for solvent extraction to a model suitable for the use with SPE.
3) Correction of the results obtained using the solvent regression model for predicting preconcentrated samples.

The approach described in this paper corresponds to the third category and takes account of the intermediate precision study of regression models, i.e. the repeatability through time. It is

based on matching calibration graphs that are measured through time, with and without SPE. In both cases, equal concentration values are used to build the calibration lines. A bias correction term (bias due to constant and relative systematic errors) is computed to correct the predictions obtained when signals from the SPE procedure are used with a univariate model (or calibration graph) constructed with the solvent standard calibration procedure.

The correction factor consists of a univariate linear model obtained as follows:

a) Development of N_{SS} calibration lines based on solvent standards (SS), through time:

$$y_{SS} = a_{SS} + b_{SS}x \quad (1)$$

b) Development of N_{SPE} calibration lines based on SPE, through time:

$$y_{SPE} = a_{SPE} + b_{SPE}x \quad (2)$$

In this way, several sets of matched calibration lines from SS and SPE are obtained.

c) Calculation of a correction term fc using the above sets of calibration lines, given as the function:

$$\mathrm{fc}(y) = \frac{1}{N_{SPE}N_{SS}} \sum_{i=1}^{N_{SPE}} \sum_{j=1}^{N_{SS}} (\hat{x}_{SPEi}(y) - \hat{x}_{SSj}(y)) \quad (3)$$

$$\hat{x}_{SPE}(y) = \frac{y_{SPE} - a_{SPE}}{b_{SPE}} \quad (4)$$

$$\hat{x}_{SS}(y) = \frac{y_{SS} - a_{SS}}{b_{SS}} \quad (5)$$

where N_{ss} and N_{SPE} are the number of calibration lines built on SS and SPE, respectively, and $\hat{x}_{SPE}$ and $\hat{x}_{SS}$ represents the calculated concentration using the calibration graphs for SPE and SS, respectively. The index i and j in the above equations refers to the different calibration lines obtained through time using SS and SPE, and y represents the dependent variable.

In Eq. (3), N_{ss} and N_{SPE} introduce an average effect in the estimation of fc(y), which is used for correcting the bias due to the SPE step. In addition, the confidence intervals for each fc(y) can be easily calculated for a particular value of the analytical signal as the prediction interval for the dependent variable [16].

By using all the possible pairs of SS–SPE calibration lines obtained in the intermediate precision study, the highest variability in the system is accounted for.

Further improvements can be obtained by eliminating most dissimilar pairs of calibration lines.

Once fc has been obtained, it is used for correcting concentrations as follows:

a) Measurement of the signal for an unknown sample (y_{unkSPE}) after SPE, at the moment of analysis.
b) Recording the corresponding calibration graph using solvent based standards at the moment of analysis.
c) Prediction of the response (y_{unkSPE}) for the unknown sample signal obtained with SPE using the corresponding standard based calibration line ($\hat{x}_{unkSS}$).
d) Correction of the above result using the correction term, fc, calculated for the signal measured (y_{unkSPE}):

$$\hat{x}_{unkSPE} = \hat{x}_{unkSS} + \mathrm{fc}$$

In the light of this relation, it is clear that the uncertainty of the fc affects directly to the uncertainty of the estimated concentration, according to the error propagation criteria [16].

3. Experimental

3.1. Instrumentation and software

All spectrofluorimetric measurements were performed on an Aminco-Bowman Series 2 luminescence spectrometer (SLM Aminco, Rochester, NY, USA) equipped with a 150 W continuous xenon lamp. The instrument was interfaced by a GPIB card and drive with a PC Novo pentium

microcomputer supplied with the AB2 software, version 1.40, running under OS/2 2.0, for spectral acquisition and data analysis. The excitation and emission slits were both maintained at 4 nm. The scan rate of the monochromators was maintained at 2 nm s^{-1} in recording conventional spectra. All measurements were performed in a 10-mm quartz cell at 750 V in the emission domain.

A Büchi Vac V-500 (Switzerland) vacuum system, connected to an extraction manifold of Waters (Milford, USA), was used for preconcentration.

All computations were done using MATLAB version 5.3 (The Mathworks, Natick, MA) with programs developed by ourselves.

3.2. Chemicals and solvents

Analytical standards (PESTANAL quality) of carbendazim (methylbenzimidazol-2-ylcarbamate), fuberidazole (2-(2-furyl)benzimidazole) and thiabendazole (2-(thiazol-4-yl)benzimidazole) were obtained from Riedel-de Haën (Seelze, Germany). Stock solutions of the fungicides were prepared by dissolving the reagent (99% purity) in methanol (HPLC grade), supplied by Panreac (Barcelona, Spain) at a concentration of 200 μg ml^{-1}. These solutions were stored in dark glass bottles at 4 °C. The working solutions, at 1 μg ml^{-1} for carbendazim and thiabendazole and at 0.01 μg ml^{-1} for fuberidazole, were prepared by dilution with methanol.

SPE was carried out using a cartridge containing 0.5 g of C_{18} stationary phase supplied by Waters (Milford, MA, USA).

3.3. Procedure for the analysis of target pesticides in groundwater samples

In order to measure the low pesticide concentrations found in drinking water, an extraction and concentration step was necessary prior to determination by spectrofluorimetry. Extraction of the pesticides from groundwater samples was carried out by SPE with C_{18} cartridges, previously conditioned by successive elution of 40 ml of methanol, 10 ml of a 1:1 (v/v) mixture methanol–water and 10 ml of Milli-Q water. All the solvents were passed by gravity throughout the cartridges. Then, a 200-ml aliquot of the water sample was aspirated through the cartridge under vacuum. The sample flow rate was controlled at approximately 8–10 ml min^{-1}. The cartridge was not allowed to dry completely during the extraction process. Before eluting the pesticides, the cartridge was dried by passing air for 15 min. Pesticides were eluted by gravity with 5 ml of methanol and the two-dimensional ($I_{fluorescence}$, $\lambda_{emission}$) data were obtained. Measurements were collected in the emission domain, from 325 to 370 nm for fuberidazole and thiabendazole and from 295 to 370 nm for carbendazim. The amount of pesticide was then determined from calibration lines based on solvent standards and then this predicted concentration of the preconcentrated sample was corrected with the fc.

4. Results and discussion

Methanol was used as solvent because this medium gives the highest fluorescence signals [17]; a blank of this solvent was subtracted in each experiment to eliminate the Raman interference of solvent.

4.1. Preliminary studies

First, the parameters needed for validation of the method were estimated in pure solvent. The results obtained are summarised in Table 1. Detection and quantitation limits (LOD and LOQ, respectively) were established according to the EURACHEM guidance [18], i.e. as the lowest concentration of analyte whose response is equivalent to the mean blank response plus three standard deviations for the LOD, and by measuring six replicates of a series of dilutions and setting the LOQ as the lowest concentration that gives a relative standard deviation (RSD) $\leq 5\%$. The LODs were less than 5 μg l^{-1} and LOQs were less than 10 μg l^{-1} for all pesticides.

The linear range for each pesticide was established between 10 and 100 μg l^{-1} for carbendazim, 0.1 and 1.0 μg l^{-1} for fuberidazole and 2.5 and 40.0 μg l^{-1} for thiabendazole. Good linearity was

Table 1
Statistic for carbendazim, fuberidazole and thiabendazole in the emission domain in pure solvent and taking into account the SPE step

Pesticide	$y=ax+b$	R^2	Lineal range ($\mu g\,l^{-1}$)	LOD ($\mu g\,l^{-1}$)	LOQ ($\mu g\,l^{-1}$)	[RSD (%)[a]]		
Pure solvent								
Carbendazim						*	**	***
286–303 nm	$y=0.80x+0.64$	0.9999	10–100	5	10	5.8	3.5	2.1
Fuberidazole								
306–340 nm	$y=34.07x+0.96$	0.9902	0.1–1.0	0.041	0.1	3.8	2.2	3.5
Thiabendazole								
300–340 nm	$y=2.08x-0.46$	0.9990	2.5–40	0.5	2.5	4.8	3.1	3.0
After SPE step								
Carbendazim						*	**	***
286–303 nm	$y=0.69x-5.78$	0.9999	0.250–2.500	0.125	0.250	6.4	3.3	1.8
Fuberidazole								
306–340 nm	$y=33.68x-4.51$	0.9982	0.002–0.025	0.001	0.002	4.7	3.7	4.1
Thiabendazole								
300–340 nm	$y=1.64x-3.52$	0.9999	0.062–1.00	0.012	0.062	3.5	2.6	2.8

[a] The results are averages of six determinations at three levels concentration (*,**,***): 10, 50 and 100 $\mu g\,l^{-1}$ for carbendazim, 0.1, 0.52 and 1 $\mu g\,l^{-1}$ for fuberidazole and 2.5, 22 and 40 $\mu g\,l^{-1}$ for thiabendazole.

found in the above ranges, with correlation coefficients of more than 0.99 in all cases. The lower limit was the LOQ and the upper limit was the concentration for which the signal deviates from the linearity by 3–5%.

The precision of quantitative measurements was checked at three levels of concentration in the lineal range for each pesticide by measuring six replicate standard solutions at each concentration level. Table 1 summarises the results and shows that the precision was lower than 6%, for each of the concentrations. Accordingly, it is possible to quantify the pesticides at concentrations as low as 10, 0.1 and 2.5 $\mu g\,l^{-1}$ for carbendazim, fuberidazole and thiabendazole, respectively.

4.2. SPE studies

In order to determine the three pesticides at the trace levels, few $\mu g\,l^{-1}$, expected in water samples a SPE procedure using C_{18} cartridges was applied [17]. Emission spectra were registered on methanolic solutions of carbendazim, thiabendazole and fuberidazole and on spiked SPE extracts. An attenuation effect was found, due to the C_{18} cartridge background for all pesticides. In order to avoid this interference and the associated quantitation error, validation parameters were also estimated using aqueous solutions of the pesticides subjected to SPE. The results obtained are also summarised in Table 1. Calibration standards were prepared by spiking water with pesticides at concentrations of 0.250–2.500 $\mu g\,l^{-1}$ for carbendazim, 0.002–0.025 $\mu g\,l^{-1}$ for fuberidazole and 0.062–1.000 $\mu g\,l^{-1}$ for thiabendazole, and applying the SPE procedure. The linearity of the method was good with correlation coefficients of more than 0.99. The calibration lines drawn after the preconcentration step were compared with those obtained in pure solvent. Fig. 1 indicates the suppression effect of the analytical

Table 2
Recovery of carbendazim, fuberidazole and thiabendazole at different concentrations levels in reagent grade water using SPE

Pesticide	Added ($\mu g\,l^{-1}$)	Recovery (%)	RSD (%)
Carbendazim	10	99	1.4
	50	101	3.3
	100	98	1.8
Fuberidazole	0.1	109	4.7
	0.52	100	3.3
	1	104	4.1
Thiabendazole	2.5	102	4.2
	22	97	5.4
	40	101	2.1

The results are average of seven determinations.

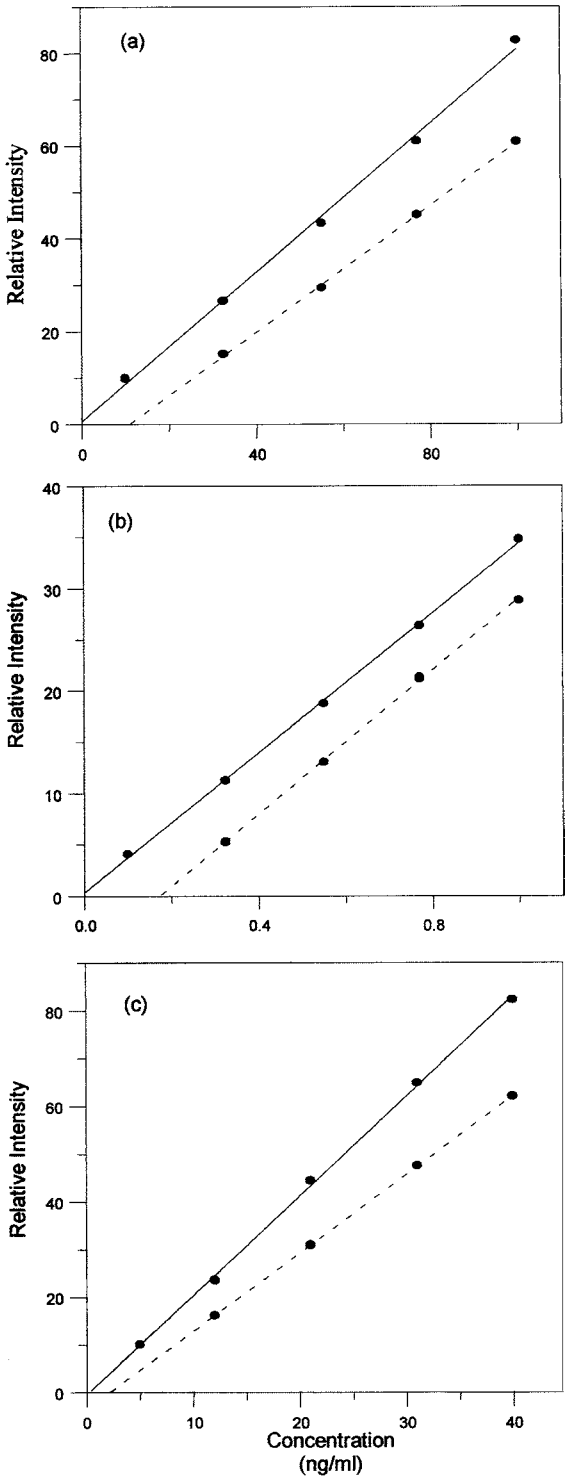

Fig. 1. Calibration graphs for carbendazim (a), fuberidazole (b) and thiabendazole (c) in pure solvent (solid lines) and after the SPE step (dotted lines).

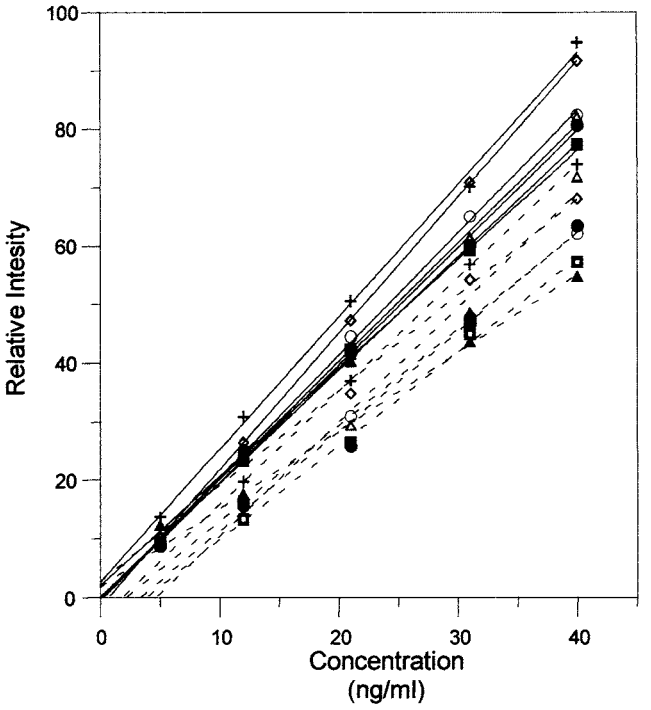

Fig. 2. Calibration graphs through time for thiabendazole in pure solvent (solid lines) and after the SPE step (dotted lines).

signal for the three pesticides, which was both compound- and concentration-dependent.

The LOD and LOQ were calculated and are shown in Table 1. The values obtained for LOD varied from 0.001 to 0.125 $\mu g\, l^{-1}$, were sufficiently low to determine pesticide residues in water samples within the limits established by EU legislation [19].

To assess the efficiency of the SPE method [17], recovery and precision studies were performed at three concentration levels (low, medium and high) for each pesticide in reagent-grade water. Satisfactory results were obtained in all instances using the calibration graphs constructed taking into account the SPE step with recoveries ranged from 97.0 to 109.0% and RSD values associated ranging from

Table 3
Recoveries at three concentration levels, after eliminating the 5, 10, 15 and 20 most dissimilar calibration graphs for estimating fc

Pesticide	Concentration ($\mu g\, l^{-1}$)	[Number of calibration graphs eliminated at each extreme]				
		[0]	[5]	[10]	[15]	[20]
Carbendazim	10	97 (5.4)	96 (5.3)	97 (5.2)	98 (5.0)	97 (4.8)
	55	92 (2.4)	91 (2.6)	91 (2.6)	93 (2.4)	93 (2.2)
	100	95 (5.3)	94 (5.3)	92 (5.3)	94 (5.2)	95 (4.6)
Fuberidazole	0.1	107 (2.1)	105 (3.2)	102 (4.6)	106 (5.0)	107 (5.0)
	0.55	95 (2.5)	94 (3.1)	94 (3.1)	96 (3.2)	96 (3.2)
	1.00	103 (4.6)	102 (5.2)	102 (5.3)	103 (4.6)	104 (4.8)
Thiabendazole	2.5	98 (3.1)	95 (3.8)	97 (4.1)	96 (4.2)	98 (4.1)
	21	98 (4.7)	97 (5.5)	97 (5.5)	98 (4.7)	99 (4.2)
	40	97 (4.8)	96 (5.2)	96 (5.6)	97 (4.8)	97 (4.8)

Values in parenthesis correspond to RSD ($n = 3$).

Table 4
Recoveries (%) obtained in the water samples

Pesticide	Concentration ($\mu g\,l^{-1}$)	[Calibration lines]			
		[5]	[7]	[12[a]]	[17]
Carbendazim	10	107 (5.4)	107 (5.5)	102 (5.6)	98 (5.6)
	55	97 (2.6)	97 (2.6)	94 (2.6)	91 (2.6)
	100	94 (5.3)	94 (5.3)	94 (4.6)	92 (5.3)
Fuberidazole	0.1	105 (5.0)	103 (4.8)	104 (4.8)	102 (4.0)
	0.55	95 (0.9)	95 (2.9)	94 (3.0)	94 (3.1)
	1	102 (5.5)	102 (5.5)	99 (5.6)	102 (5.3)
Thiabendazole	2.5	92 (4.2)	97 (4.2)	98 (4.1)	96 (4.3)
	21	96 (5.5)	96 (4.9)	98 (5.5)	97 (5.5)
	40	96 (5.3)	96 (4.3)	96 (5.6)	96 (5.6)

The results in parenthesis correspond to RSD (%) values ($n = 3$).
[a] Optimum approach (approach 1).

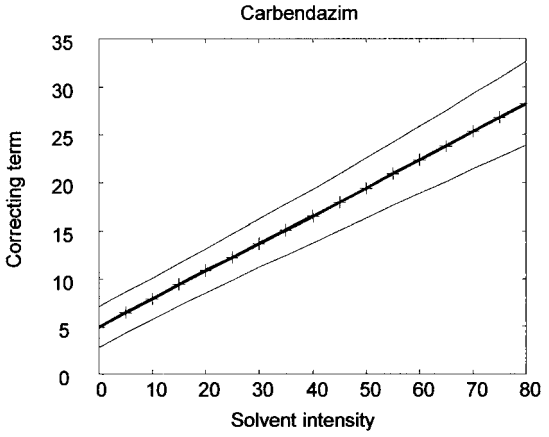

Fig. 3. Corrected term, fc, for the carbendazim pesticide (solid lines) indicating the confidence intervals (dashed lines).

1.4 to 5.4% (Table 2). From the particular behaviour of each pesticide in the SPE process (Fig. 1), it is evident the largest source of quantification error introduced in the case of predicting the concentration of the preconcentrated samples by using the calibration lines obtained with solvent standards (prepared directly spiking solvent).

4.3. Univariate correction of the predicted values

Matched calibration graphs (SS–SPE) were registered every day for the 1st week, twice a week for the next 4 weeks and once at week for the last 2 weeks. In this way, 17 pairs of calibration lines were obtained during the experimental study for each pesticide, and all possible combinations of them, i.e. $17^2 = 289$ combinations were used to calculate the correction term, fc, using Eq. (3). Fig. 2 shows, as an example, the range of variability of the slopes and intercepts in both calibration graphs, with and without SPE. To obtain more reliable results, this situation was taken into account in the calculation of the correction term. In order to determine the influence of the most dissimilar pairs of calibration graphs, i.e. those with the most dissimilar slopes with respect to the average, we studied the effect of eliminating 5, 10, 15 and 20 pairs of calibration lines from all combinations, at each extreme. New fc values were thus calculated eliminating 10, 20, 30 and 40 pairs of calibration lines, respectively, from the original $17^2 = 289$ combinations. Each new fc value was then used to correct the predicted concentrations of each the three pesticides at three concentration levels, by adding it to the predicted concentrations from preconcentrated water samples using calibration lines prepared in pure solvent that day. Table 3 shows that slightly better results were obtained when the number of calibration lines eliminated was higher than 10 at each extreme. In addition, this elimination step has some influence on the confidence intervals ob-

Table 5
Recoveries obtained in the prediction of water samples using the approaches 2 and 3

Pesticide	Calibration graph ([a]/[b])	Concentration (ng ml^{-1})	Approach 2	Approach 3
Carbendazim	$y = 0.73x + 2.91 / y = 0.67x - 3.36$	10	97 (4.5)	96 (4.7)
		55	88 (2.1)	86 (2.2)
		100	86 (5.0)	85 (4.9)
Fuberidazole	$y = 31.21x + 2.34 / y = 30.85x - 4.65$	0.1	98 (2.7)	101 (2.9)
		0.55	93 (2.6)	93 (2.6)
		1	104 (4.7)	104 (4.7)
Thiabendazole	$y = 2.10x - 2.07 / y = 1.67x - 4.07$	2.5	92 (3.3)	91 (3.2)
		21	92 (4.8)	91 (4.8)
		40	90 (5.3)	89 (5.3)

[a] Pure solvent (approach 2).
[b] SPE (approach 3).

tained for the correction factor fc, because the confidence interval decreases as more calibration lines are eliminated. Therefore, as a compromise solution, the 10 most dissimilar pairs of calibration lines were eliminated in all of the following experiments.

In order to establish the minimum number of lines required in the calibration series obtained through time, we studied the effect of taking the first five, seven and 12 calibration lines and using them to estimate the fc for each (i.e. with 5^2, 7^2, 12^2 and 17^2, combinations, respectively). The best results were obtained using the first 12 calibration graphs. This correction term was added to the concentrations predicted using calibration lines prepared in pure solvent that day. Table 4 shows the results obtained from preconcentrated samples using this approach (approach 1). Satisfactory predictions were obtained with values ranging from 91 to 107% and RSD values of less than 6%. Fig. 3 shows, for the carbendazim compound, the correction term fc obtained in the selected conditions, accompanied by its confidence intervals.

In addition, in order to take advantage of the intermediate precision study, two new approaches for predicting preconcentrated samples were tested. Approach 2 used the fc estimated with all combinations of the first 12 calibration graph pairs. Quantitation of the preconcentrated samples was achieved using the average calibration graph obtained in pure solvent calculated using the 12 individual calibration lines. Approach 3 predicted the samples using the average calibration graph with SPE that was also estimated by considering the first 12 calibration lines. Both approaches yielded acceptable results (Table 5), with recoveries ranging from 85 to 104% and precision values better than 6%. However, more accurate predictions were obtained by quantifying with a calibration graph performed on the same day (approach 1), as indicated in Table 4.

Table 6
Recoveries (and RSD values) obtained in spiked real groundwater samples

Pesticide	Added (μg l^{-1})	Approach 1	Approach 2	Approach 3	Solvent calibration	SPE calibration
Carbendazim	20	93 (6.8)	83 (7.4)	84 (9.1)	49 (9.1)	89 (7.9)
	80	95 (6.0)	89 (6.5)	90 (7.0)	83 (7.8)	90 (6.8)
Fuberidazole	0.4	101 (6.5)	103 (7.7)	107 (8.6)	45 (7.9)	105 (6.6)
	0.8	98 (5.9)	97 (6.8)	94 (7.5)	73 (6.4)	97 (6.2)
Thiabendazole	10	102 (6.9)	82 (7.8)	88 (7.9)	50 (7.2)	90 (7.2)
	30	96 (6.1)	91 (6.8)	90 (7.0)	70 (7.0)	96 (7.9)

4.4. Application: Determination of the pesticides in groundwater samples

In order to test the feasibility of the approaches in real samples, they were applied to the determination of the pesticides in spiked real groundwater samples from The 'Campo de Dalías', Almería (Spain). In addition, the predictions obtained using both pure solvent and SPE calibration lines prepared the same day of the analysis have been presented. The results obtained are summarised in Table 6. Satisfactory results were found with the three approaches and using SPE calibration standards, with recoveries ranging from 82 to 107% and RSD values lower than 10%. Again, the more accurate results were obtained with approach 1. However, very poor results were obtained when the predictions were performed using solvent calibration curves, above all at low concentration levels.

5. Conclusions

The procedure developed in this paper allows the determination of a correction factor, which is added to the concentration obtained using a solvent calibration line from a SPE sample. This avoids the need for constructing a separate SPE calibration each time that a new sample has to be analysed, as well as the additional labour costs that would otherwise be required to calibrate each time the analytical method is used. Accordingly, it is highly appropriate for routine analysis. From the different approaches tested it can be concluded that the results obtained does not vary significantly from one method to another, although the most accurate predictions were obtained with the approach 1.

Although the strategies proposed have been applied to a particular example dealing with the fluorimetric determination of carbendazim, fuberidazole and thiabendazole in water samples after SPE extraction, they could be extended to other cases using other sample treatments (clean-up, adsorption etc.) or matrix components that show matrix effects. In spite of the importance of this issue, there are no references in the bibliography addressing the subject of the present paper.

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References

[1] D.L. Massart, B.G.M. Vandeginste, L.M.C. Buydens, S. de Jong, P.J. Lewi, J. Smeyers-Verbeke. Handbook of Chemometrics and Qualimetrics: Part A, Elsevier, Amsterdam, (1998) 463.
[2] K.S. Boolsh, B.R. Kowalski, Anal. Chem. 66 (1994) 782.
[3] I.E. Bechmann, L. Norgaard, C. Ridder, Anal. Chim. Acta 304 (1995) 229.
[4] P. Campíns Falcó, J. Verdú Andrés, F. Bosch-Reig, C. Molíns-Legua, Anal. Chim. Acta 302 (1995) 323.
[5] F.J. Schenck, S.J. Lehotay, J. Chromatogr. A 868 (2000) 51.
[6] M. Martínez Galera, T. López López, M.D. Gil García, J.L. Martínez Vidal, J. Chromatogr. A 918 (2001) 79.
[7] D. Ronald Erney, T.M. Pawlowski, C.F. Poole, J. High Resol. Chromatogr. 20 (1997) 375.
[8] P.D. Johnson, D.A. Rimmer, R.H. Brown, J. Chromatogr. A 765 (1997) 3.
[9] K.A. Barnes, R.J. Fussell, J.R. Startin, M.K. Pegg, S.A. Thorpe, S.L. Reynolds, Rapid Commun. Mass Spectrom. 11 (1997) 117.
[10] M. Forina, M. Casolino, Quim. Anal. 18 (1999) 49.
[11] E. Bouveresse, C. Hartmann, D.L. Massart, I.R. Last, K.A. Prebble, Anal. Chem. 68 (1996) 982.
[12] J.A. Jones, I.R. Last, B.F. MacDonald, K.A. Prebble, J. Pharm. Biomed. Anal. 11 (1993) 1227.
[13] B.G. Osborne, T. Fearn, J. Food Technol. 18 (1983) 453.
[14] O.E. De Noord, Chemom. Intell. Lab. Syst. 25 (1994) 85.
[15] M. Forina, M. Casolino, Quim. Anal. 18 (1999) 61.
[16] D.L. Massart, B.G.M. Vandeginste, L.M.C. Buydens, S. De Jong, P.J. Lewi, J. Smeyers-Verbeke. Handbook of Chemometrics and Qualimetrics: Part A, Elsevier, Amsterdam, (1997) 195.
[17] D. Picón Zamora, M. Martínez Galera, A. Garrido Frenich, J.L. Martínez Vidal, Analyst 125 (2000) 1167.
[18] Eurachem Guidance Document No. 1 WELAC Guidance Document No. WGD 2: Accreditation for chemical laboratories: Guidance on the interpretation of the EN 45000 series of Standards and ISO/IEC Guide 25.
[19] Commission of the European Communities EEC Drinking Water Guidelines, 80/779/EEC No. L229/11-29, EEC, Brussels, August 30th 1980.