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A flow-through fluorimetric sensing device for determination of α- and β-naphthol mixtures using a partial least-squares multivariate calibration approach

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Abstract

A single flow-through optosensor spectrofluorimetric system is proposed for the resolution of mixtures of α- and β-naphthol at μg 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 Sephadex QAE A-25 resin as an active sorbent substrate in the flow cell and the second derivative of the native synchronous fluorescence spectra of analytes as analytical signal. In the manifold, the solutions of naphthol (at pH 10.0) were injected in a carrier stream of KCl (0.15 M)/NaOH (10^{-2} M). Because of the strong spectral overlap, the mixture could not be resolved by conventional spectrofluorimetry. The non-additive behaviour of the fluorescence signals revealed an interaction in the system, which was not found by working in the solution only (without the sorbent support). This interaction, probably due to the environment of the analytes on the solid phase, made impossible their simultaneous determination. So, the use of synchronous fluorescence spectroscopy or even its derivative signal could not resolve satisfactorily the mixture. The simultaneous determination of both naphthol has been carried out by recording the signal of the second-derivative synchronous fluorescence ($\Delta\lambda = 170$ nm) spectra between 200 and 450 nm and a PLS multivariate calibration treatment. The optimum number of factors was selected by using the cross-validation method. After validating the proposed method, it was applied to the determination of these compounds in natural waters with different amounts of each chemical.

Keywords: α-Naphthol and β-naphthol determination; Flow-through sensor; PLS multivariate calibration

1. Introduction

Naphthalene derivatives are organic pollutants present in the environment as a result of various processes such as industrial, biogeochemical and

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as pesticide degradation products. α-Naphthol is a precursor of carbaryl, which is widely used as a pesticide because of its effectiveness and low mammalian toxicity. Commercially produced α-naphthol may contain β-naphthol as a by-product. Naphthalene derivatives with substituents at position 2 are usually more toxic than those at position 1. So, β-naphthol is capable of producing severe systemic intoxications. This is a compound of common use in the dyestuffs industry, in pharmacy and as cosmetic.

Therefore, the determination of α- and β-naphthol is of great importance in quality control and in environmental chemistry. Nevertheless, not so many simultaneous determination methods have been described.

A few procedures have been proposed which use chromatography (either high-performance liquid chromatography (HPLC) [1] or gas chromatography [2]) and spectroscopy (spectrophotometry and luminescence). Spectrophotometric methods involve preliminary precipitation and extraction steps [3,4], the formation of coloured derivatives [5] or kinetic approaches based on the differences in the rate of formation of some derivatives [6]. The scarce number of luminescence methods involves synchronous-derivative fluorimetry [7,8] or synchronous-derivative phosphorimetry [9].

Spectrophotometric methods are less sensitive and selective than luminescence ones, and so fluorimetry seems to be a very suitable technique. As the two analytes show native fluorescence signals, no derivative reaction is required.

In this paper, a flow-through sensor for the determination of α- and β-naphthol is proposed based on the combined use of (1) an FIA monochannel manifold, (2) a solid-phase fluorimetric transductor and (3) a partial least-squares (PLS) multivariate calibration approach from the second derivative of the native fluorescence spectra of the mixture when the analytes were retained on-line on the beads of Sephadex QAE A-25 anion exchanger gel in the detection zone itself.

The fundamentals of flow-through optical sensors were described elsewhere [10].

It was found that the system revealed a strong interaction in such a way that the fluorescence signal of the two analytes interfere with each other. So, conventional spectrofluorimetry, synchronous fluorescence spectroscopy or its derivative signal could not resolve satisfactorily the mixture due to the mutual interaction. Second-derivative synchronous fluorescence spectroscopy allowed the determination of the components but with a very low mutual tolerance level for the two components.

Therefore, a PLS multivariate calibration approach was performed using the second-derivative synchronous fluorescence spectra. The proposed determination is simple and fast. Moreover, it is very sensitive. The measurements are performed on the beads where the analytes are concentrated and retained from the sample plug injected so that sensitivity can be enhanced by increasing the sample volume injected.

2. Experimental

2.1. Apparatus and software

A Varian Cary-Eclipse Fluorescence Spectrofluorimeter (Varian Iberica, Madrid, Spain) was used to obtain the synchronous fluorescence measurements and spectra. The spectrofluorimeter was equipped with a xenon discharge lamp (75 kW), Czerny-Turner monochromators, two detectors (sample and 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 GRAMS/32 (from Galactic) software package, with the PLSplus/IQ application software [11] running in a 1 GHz PC was used for the statistical treatment of the data and the application of the PLS method.

The photomultiplier detector voltage was 700 V and the scan rate of the monochromators was maintained at 600 nm min^{-1} (a Savitzky-Golay [12] type smoothing with a filter size of 17 was used) to obtain the second derivative. The instrument's excitation and emission slits were set at 5 and 20 nm, respectively. An emission filter (295–1100 nm) was used in order to minimize the resin background signal at the excitation wavelength.

To obtain the flow stream, a four-channel Gilson Minipuls-3 peristaltic pump with rate

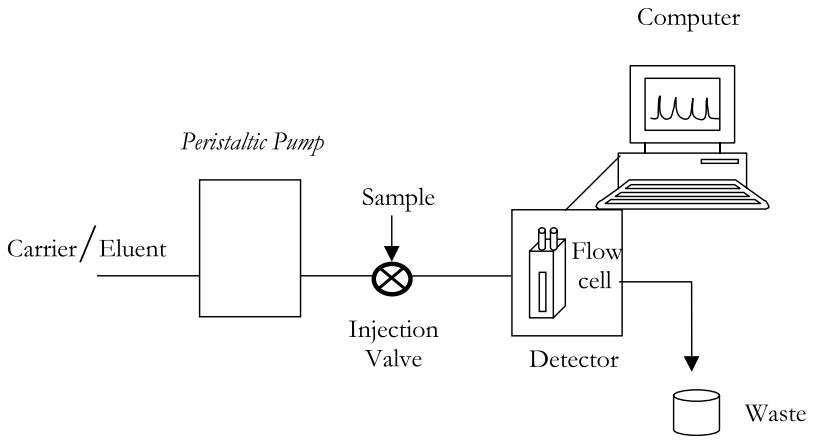

Fig. 1. Manifold.

selector was used. It was also utilized as a Rheodyne Model 5041 injection valve with variable sample loops and PTFE tubing of 0.8 mm ID.

A Hellma 176.052-QS quartz flow-through cell was used (light-path length of 1.5 mm), which was filled with Sephadex QAE A-25 resin. The resin was just placed in the complete light-path of the cell as an aqueous slurry with the aid of a syringe.

2.2. Reagents

All reagents were analytical reagent grade and deionized water was used to prepare all solutions.

Working solutions of α- and β-naphthol were daily prepared by suitable dilution of the stock solutions with deionized water. The concentration of these stock standard solutions of the analyte was 6.94×10^{-4} mol l^{-1} and they were prepared by dissolving the required amount of α-naphthol (Fluka, Madrid, Spain) and β-naphthol (Panreac, Barcelona, Spain) in deionized water. These solutions were stable for 4 days at about 5 °C.

KCl (0.15 mol l^{-1})/NaOH (10^{-2} mol l^{-1}) solution was used as carrier solution. The solid support used in this sensor was Sephadex QAE A-25 (Aldrich, Madrid, Spain), in the Cl^- form, as supplied, without any pre-treatment.

3. Procedure

Using a single-channel manifold (Fig. 1), the sample (100 μl at pH 10.0) containing between 0 and 20 μg l^{-1} of β-naphthol and, 10 and 20 μg l^{-1} of α-naphthol, was transported, inserted into the carrier stream (KCl 0.15 M/NaOH (10^{-2} M)) at a flow rate of 1.14 ml min^{-1}, through the flow cell. There, the analytes were sorbed on the solid support (Sephadex QAE A-25 resin) under their anionic form while synchronous spectra were being recorded between 200 and 450 nm, at stopped flow, in the peak maximum at a scan rate of 600 nm^{-1} and $\Delta\lambda = 170$ nm. From these spectra, the second derivative ones were obtained.

After developing the signal, the desorption of the analytes from the solid support in the flow cell was performed by the carrier itself, and so achieving the regeneration of the active ion-exchange gel microzone and allowing the signal value to return to the baseline, and so remaining ready for a new determination. For calibration, 20 synthetic mixtures of α- and β-naphthol were employed (see Section 5.2).

The concentration ranges were selected within the previously established linear calibration range for each compound. The optimized calibration model for PLS method was applied to spiked

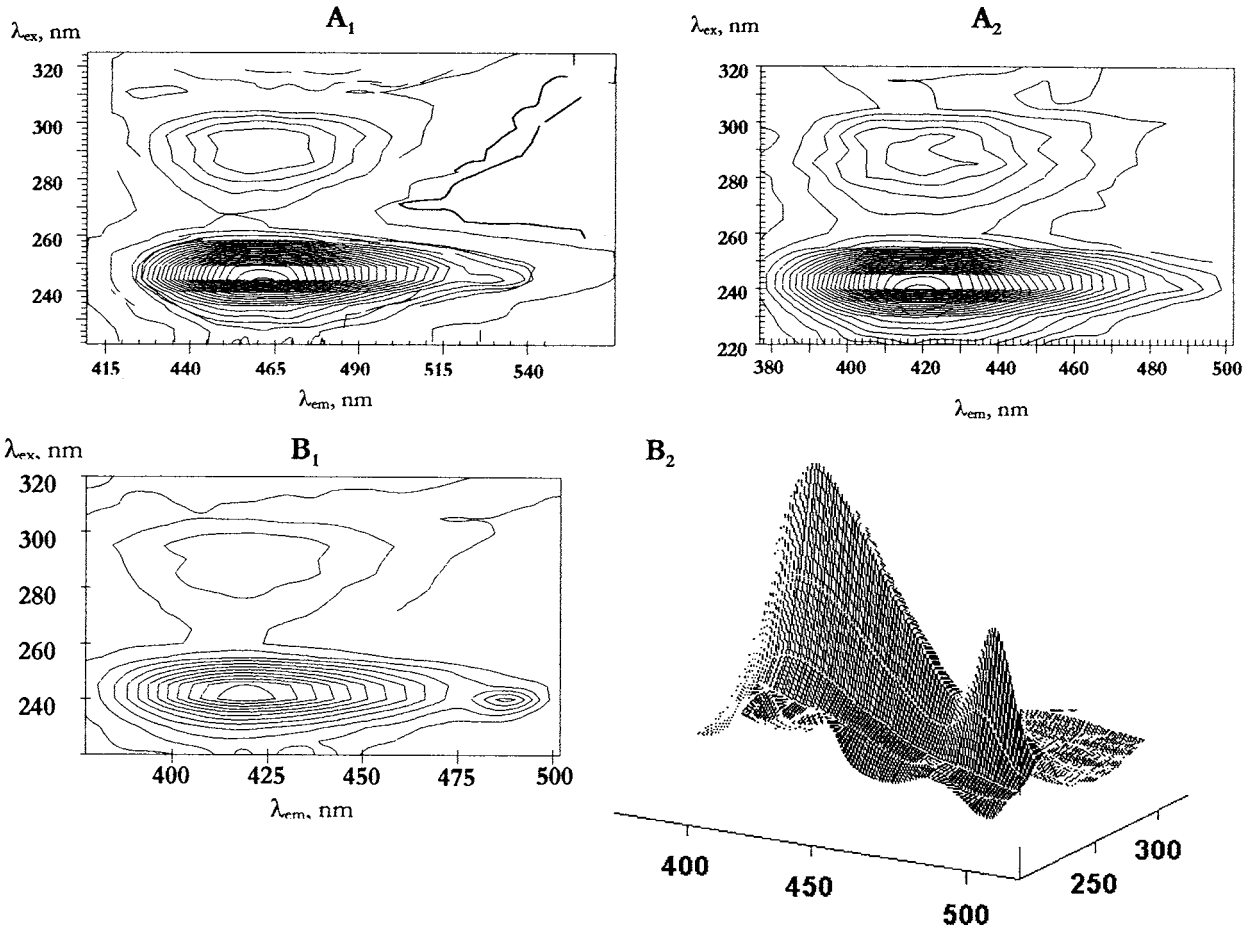

Fig. 2. A_1: Contour plot of α-naphthol; A_2: contour plot of β-naphthol; B_1, contour plot of the mixture; B_2: total luminescence spectrum of the mixture.

water samples to calculate the concentration of each chemical in the mixture.

4. Results and discussion

4.1. Spectral characteristics

The contour plots were obtained from the total luminescence spectra (Fig. 2) and the spectral region for emission spectrum between 290 and 500 nm was recorded for 245 nm of excitation. α- and β-Naphthol showed highly overlapping fluorescence maxima at 460 and 420 nm, respectively (see Fig. 3a and b).

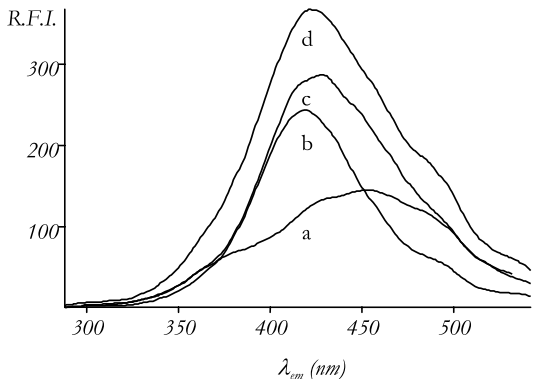

Fig. 3. Emission spectra at 245 nm as excitation wavelength: (a) α-naphthol; (b) β-naphthol; (c) real mixture; (d) arithmetic addition of (a, b).

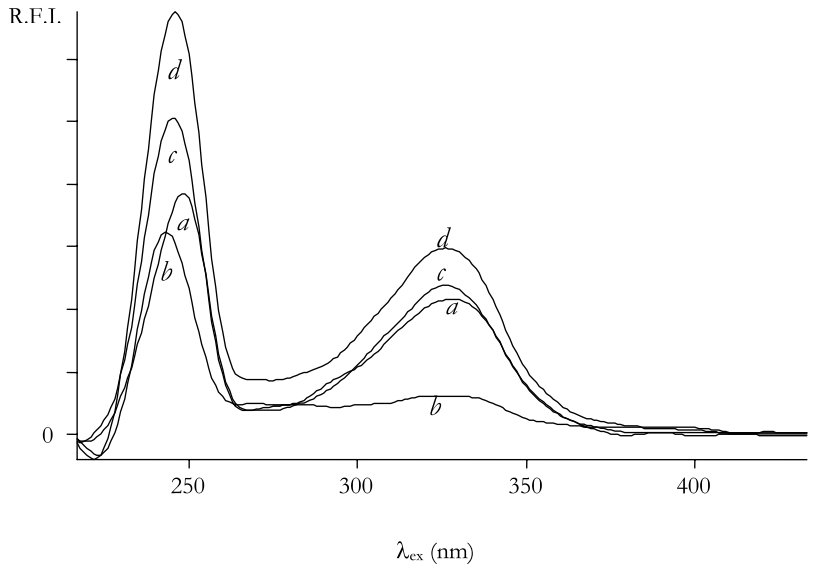

Fig. 4. Synchronous spectra ($\Delta\lambda = 170$ nm): (a) α-naphthol; (b) β-naphthol; (c) real mixture; (d) arithmetic addition of (a, b).

Therefore, conventional spectrofluorimetry cannot be applied satisfactorily to the resolution of the mixture. So, it was recorded the synchronous spectrum from 200 to 450 nm (see Fig. 4a and b). Previously, the optimal $\Delta\lambda$ was studied by varying this value from 50 to 230 nm with increase of 20 nm, and 170 nm was selected as working value, which allowed the best discrimination between the two analytes.

It could be proved, according to other authors [13], that the system α- and β-naphthol did not show an additive signal behaviour (see Figs. 3 and 4), and so the resolution of the mixtures could not be successfully performed by using synchronous spectrofluorimetry.

Fig. 5 shows the second derivative of the synchronous spectrum. "Zero-crossing" technique could be applied using the wavelengths indicated in this figure in order to resolve the mixture.

4.2. Optimization of procedure

Optimization studies were carried out for each individual constituent and optimum values of the experimental variables were selected. Different supports were tested under the same experimental conditions (Silica Gel C_{18}, and Sephadex DEAE A-25 and QAE A-25). Finally, the anionic exchange resin Sephadex QAE A-25 was selected providing an acceptable fluorescence background in working conditions. After above indicated, the variables influencing the system can be divided into three groups: instrumental, chemical and flow system variables.

4.2.1. Instrumental variables

The influence of the photomultiplier detector voltage was studied by varying from 400 to 750 V. It was selected as working voltage, 700 V, which allows to get a suitable sensitivity.

The scan rate of the monochromators was maintained at 600 nm min^{-1} (it is the standard value used by the instrument) since the analytical signal is not affected by this variable.

On the other hand, the study of the influence of instrument slits was also carried out. After checking different slit values, for excitation and emission, combined with different emission filters, 5 and 20 nm (for excitation and emission slit, respectively) were selected as working values and an emission filter from 295 to 1100 nm was used in

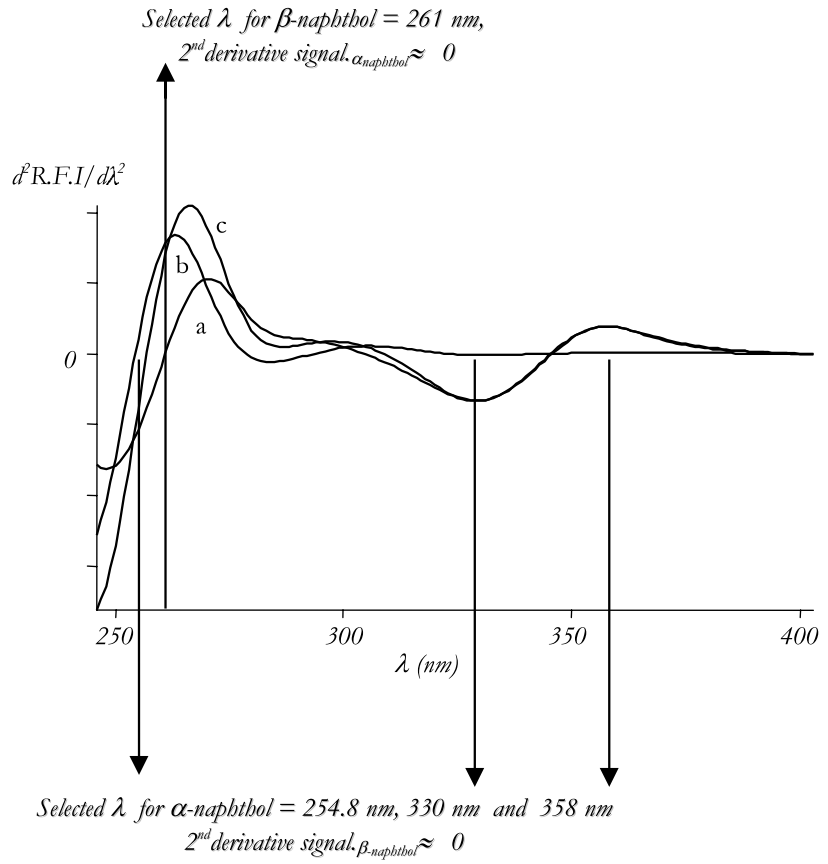

Fig. 5. Second derivative of the synchronous spectra: (a) α-naphthol; (b) β-naphthol; (c) real mixture.

order to minimize the resin background fluorescence.

4.2.2. Chemical variables

In order to optimize the self-eluting action of the carrier solution used, several electrolytes solutions at 0.15 M concentration were tested: NaCl, KCl, $NaNO_3$ and Na_2CO_3. KCl was selected because it gave a higher signal and a lower elution time. Next, the influence of its concentration was studied from 0.02 to 0.2 M. The increase of concentration decreased the signal (due to competition produced by the Cl^- ions) as well as the elution time (45 and 50%, respectively). As a compromise between a high sampling frequency and a high signal, 0.15 M was the concentration chosen. This concentration of electrolyte could also ensure the complete elution of the analytes from the resin after developing the peak signal without needing an additional eluting solution.

In this system, the effect of pH on the fluorescence intensity has been studied for both the carrier solution and the sample. The influence of the carrier solution pH was studied using HCl or NaOH solutions from 1.9 to 13.0. The sorption of naphthol only occurred at alkaline pH values, as expected, as its pK values are 9.34 and 9.51 for α- and β-naphthol, respectively. So, the peak signal increases up to its maximum at a pH value of 12.0 in which, the analytes are completely in their anionic form and they are strongly retained. Beyond this value, the fluorescence signal decreases probably due to the competition of the OH^- group by the active sites of the solid support. So, pH 12.0 was selected as the carrier solution pH value.

Table 1
Calibrations

Calibration line	α-Naphthol		β-Naphthol ($\lambda = 261$ nm)
	$\lambda = 254.8$ nm	Peak-to-peak measurements (358–330 nm)	
Intercept	−0.20	0.29	1.09
Slope	(−)0.20	(−)0.03	1.34
Correlation coefficient	(−)0.996	(−)0.999	0.999

On the other hand, the influence of the sample pH was studied by varying in the range 2.0–13.0. The signal is almost constant from 2.0 to 9.0 and a slight increase (about 8%) is achieved between 9.0 and 10.0. Higher values also produce a decrease in the signal, similarly at the effect of the carrier solution pH. Therefore, pH 10.0 was selected as the sample pH value.

4.2.3. FIA variables

The flow-injection variables studied were the sample volume (which influenced the sensitivity of the method and the sampling frequency), and the flow rate, which determines both the residence time and the rate at which the analyte can be eluted. As the flow rate decreased, both the signal and the elution time increased (hence, wider peaks were obtained). A value of 1.16 ml min^{-1} was chosen as a compromise between sensitivity and a good sampling throughput.

On the other hand, we can increase the sensitivity by increasing the sample volume, because the signal increases linearly with the increase in the sample volume from 40 to 800 μl for the two analytes according to the equations: $d^2RFI/d\lambda^2 = -1.08$ to 7.32×10^{-3} V ($r = (-)0.990$; at 254.8 nm) and $d^2RFI/d\lambda^2 = -0.4 + 7.1 \times 10^{-5}$ V ($r = 0.992$; peak-to-peak measurement (358–330 nm)) for α-naphthol; and $d^2RFI/d\lambda^2 = 2.6 + 9.0 \times 10^{-3}$ V ($r = 0.994$) for β-naphthol (volume in μl). The increase is not linear for sample volumes higher than 800 μl. Moreover, increasing sample volumes resulted in decreasing sampling frequency; so, 100 μl was chosen as working volume to get an optimal sampling frequency.

5. Determination of α- and β-naphthol

5.1. Calibration for α-naphthol

The calibration of α-naphthol was carried out (working at optimum conditions), registering the second-derivative synchronous spectra and taking signal dates at 254.8 nm and peak-to-peak measurements (358–330 nm; Table 1). The signal was found to be linearly related to the analyte concentration in the range 10–100 μg l^{-1} of α-naphthol using 100 μl as sample injection volume.

In order to test the tolerance of the proposed procedure to the presence of β-naphthol, three calibrations graphs were constructed for α-naphthol in the presence of 10, 5 and 2 μg l^{-1} of β-naphthol, respectively (for every wavelength). The significance of differences between the slope values in the presence and absence of β-naphthol, respectively, were evaluated by using the *t*-test (see Table 2).

According to these results, it can be seen that up to 2 μg l^{-1} of β-naphthol was tolerated in the determination of α-naphthol taking the measurement at 254.8 and up to 5 μg l^{-1}, using the peak-to-peak procedure (358–330 nm).

5.2. Calibration for β-naphthol

In this case, the calibration was carried out in the same way as α-naphthol, measuring at 261 nm Fig. 5. The linear response was found between analytical signal and β-naphthol concentrations in the range 5–20 μg l^{-1} (100 μl as sample volume, see Table 1).

The tolerance of the proposed method to the presence of α-naphthol was tested calibrating with

Table 2
Influence of the presence of an analyte in the determination of the other one

Influence of the presence of β-naphthol in the slope value for α-naphthol calibration line			
α-Naphthol solely	α-Naphthol with 10 μg l^{-1} β-naphthol	α-Naphthol with 5 μg l^{-1} β-naphthol	α-Naphthol with 2 μg l^{-1} β-naphthol
(−)0.20[a] ± 0.03	(−)0.37 ± 0.03	(−)0.30 ± 0.06	(−)0.23 ± 0.03
(−)0.030[b] ± 0.002	(−)0.035 ± 0.003	(−)0.033 ± 0.002	(−)0.29 ± 0.003
Influence of the presence of α-naphthol in the slope value of β-naphthol calibration line			
β-Naphthol solely	β-Naphthol with 20 μg l^{-1} α-naphthol	β-Naphthol with 10 μg l^{-1} α-naphthol	
1.09 ± 0.11	1.46 ± 0.06	1.20 ± 0.03	

$P = 0.05$. α-Naphthol tolerance level: 10 μg l^{-1}.
[a] $\lambda = 254.8$ nm, β-naphthol tolerance level: 2 μg l^{-1}.
[b] Peak-to-peak measurements (358–330 nm), β-naphthol tolerance level: 5 μg l^{-1}.

two levels of this analyte and with the same evaluating criterion above described concluding that up to 10 μg l^{-1} α-naphthol was tolerated in the determination of β-naphthol (see Table 2).

As can be seen, the resolution of the mixture by means of the second-derivative synchronous signal shows a low tolerance level to the analytes in this mixture. This is due to the shift of the "zero-crossing" wavelengths chosen as the α/β-naphthol concentration ratio's change which can be attributed to the interaction between the analytes in the solid support environment.

6. PLS treatment of spectrofluorimetric data

In order to achieve a more satisfactory resolution of the mixture, a PLS treatment was performed.

We used the second-derivative synchronous spectra to develop this method. The signal data from a calibration set of 20 standard samples (see Table 3) were taken between 200 and 450 nm. The maximum concentration tested was 20 μg l^{-1} because the strong interaction showed by the system above this value made the PLS algorithm to reject the corresponding spectral date. Also, for concentrations below 10 μg l^{-1} of α-naphthol the spectral date were rejected.

The PLS algorithm that performed the PLS analysis one component at a time has been selected to perform the determination.

6.1. Selection of the optimum number of factors and statistical parameters

To select the number of factors, in order to model the system without overfitting the concentration data, a cross-validation method, leaving out one sample at a time, was used [14]. Cross-validation consists of systematically removing one of the observations in turn and using the remain-

Table 3
Calibration matrix

Sample	α-Naphthol (μg l^{-1})	β-Naphthol (μg l^{-1})
1	10	10
2	10	12
3	10	15
4	10	1
5	10	20
6	10	2
7	10	4
8	10	5
9	10	8
10	10	–
11	12	12
12	12	1
13	12	20
14	12	2
15	12	4
16	15	15
17	15	3
18	20	10
19	20	4
20	20	5

Table 4
Statistical parameters

Analyte	R^2	RMSD	REP (%)	AIC
α-Naphthol	0.9513	0.789	6.3	23.06
β-Naphthol	0.9710	1.064	14.0	37.07

ing observations for construction of latent factors and their regression. PLS calibration was performed on the 20 calibration spectra set: 19 spectra were used and from there, the concentration of the analytes in the sample left out once during this calibration process was predicted. This process was repeated 20 times until each calibration sample had been left out once and its concentration predicted. The predicted concentration of the analytes in each sample was then compared with the known concentration of them in the respective sample and the prediction error sum-of-squares (PRESS) calculated. This parameter was calculated each time adding a new factor to the model. PRESS is a measurement of how well a particular model fits the concentration data.

To select the optimum number of factors, the criterion of Haaland and Thomas [14,15] was taken into account. According to this, rather than the selection of the model which yields a minimum in PRESS that usually leads to some overfitting, the model to be selected is the one with a minimum number of factors that provides a PRESS value not significantly greater than the minimum one. Haaland and Thomas empirically determined that an F-ratio probability of 0.75 was a good choice. Therefore, the number of factors for the first PRESS value showing an F-ratio probability below 0.75 was selected as the optimum. The maximum number of factors tested was selected at 11 (half of the number of standards plus 1). It was found that the optimum number of factors for the PLS algorithm was 3 for β-naphthol and 7 for α-naphthol.

The statistical results obtained for the matrix are summarized in Table 4. The values of the root mean square difference (RMSD), the square of the correlation coefficient obtained when plotting actual versus predicted concentration (R^2), the Akaike [16] information criterion (AIC) and the relative error of prediction (REP) for each component are included in order to give an indication both of the average error in the analysis and the quality of fit of all data to a straight line.

In view of the obtained results, it is possible to determine under the conditions of the proposed method the two analytes with an acceptable relative error of prediction ranging from 6.3 to 14.0% depending on the respective analyte.

As can be seen, the tolerance levels to determination of the analytes have been substantially increased with respect to the use of derivative treatment:tolerance ratio (w:w) β-naphthol:α-naphthol up to 2 in the determination of α-

Table 5
Validation set

Sample	α-Naphthol ($\mu g\,l^{-1}$)			β-Naphthol ($\mu g\,l^{-1}$)		
	C_{added}	$C_{recovered}$[a]	$\%R \pm \sigma_m t$	C_{added}	$C_{recovered}$[a]	$\%R \pm \sigma_m t$
1	–	–	–	5	4.7	94±3
2	20	20.6	103±2	–	–	–
3	10	10.5	105±2	10	11	110±5
4	10	10.9	109±5	–	–	–
5	10	11	110±4	20	22	110±5
6	10	11	110±3	5	5.4	108±4
7	15	15.1	101±2	15	13.9	93±3
8	15	13.7	91±3	–	–	–
9	20	20.8	104±2	10	8	80±5
10	10	10.9	109±4	8	8.9	111±5

[a] Mean of three determinations.

Table 6
Analytical applications

Sample	α-Naphthol (μg l^{-1})			β-Naphthol (μg l^{-1})		
	C_{added}	$C_{recovered}$[a]	$\%R \pm \sigma_m t$	C_{added}	$C_{recovered}$[a]	$\%R \pm \sigma_m t$
Paraná river	10	10.3	103±2	10	9.0	90±3
	10	8.5	85±5	5	5.1	102±3
	15	12.0	80±5	15	10.5	70±5
Guadalquivir river	10	10.9	109±3	–	–	–
	15	18.0	120±4	15	13.6	91±4
	15	15.8	105±3	–	–	–
"Pozo del Hierro" (water well)	10	12.0	120±5	10	11.0	110±2
	–	–	–	20	21.2	106±4
	20	16.0	80±5	–	–	–

[a] Mean of three determinations.

naphthol and tolerance ratio (w:w) α-naphthol:β-naphthol up to 20 in the determination of β-naphthol.

6.2. Validation set

In order to test the performance of the proposed method, it was applied to the triplicate determination of artificial mixtures containing various concentrations of the two compounds at μg l^{-1} levels. The above-mentioned model was used to predict the concentration of the analytes in 10 synthetic mixtures. Results are summarized in Table 5. As can be seen, the amounts added and found were consistent for most of the mixtures tested. The results can be considered satisfactory keeping in mind the strong interaction showed between α- and β-naphthol sorbed on the solid-phase sensing support.

7. Applications

The proposed method has been used in the simultaneous determination of the two analytes in spiked natural water samples, two river waters and well water (Table 6). Known amounts of the analytes were added at μg l^{-1} level. The determination was then carried out by applying the proposed procedure to the sample containing either only one of the analytes or two of them.

Although the relative prediction errors are higher than those obtained with the validation set, it can be said that the PLS flow-through sensing device proposed shows a good prediction, if we take into account the matrix effect, which is not present in the calibration standards.

8. Conclusions

The continuous flow-through solid surface fluorescence system developed has proved to be useful for the simultaneous determination of α- and β-naphthol at μg l^{-1} level. The system is based on the measurement of their native fluorescence signal when they are sorbed on-line on the beads of a strongly acidic ion exchanger, and so no derivative reagents are needed, the system being sensitive and inexpensive. The solid support provides improvement on sensitivity (due to the preconcentration of the analytes just in the detection microzone) and the PLS treatment of the second-derivative synchronous spectra signal contributes to resolve the mixture at a more satisfactory way than the "zero-crossing" technique does, as the system suffers a very strong mutual interaction between the analytes.

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