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Analytica Chimica Acta 404 (2000) 131–139

ANALYTICA CHIMICA ACTA

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A flow-through solid phase UV spectrophotometric biparameter sensor for the sequential determination of ascorbic acid and paracetamol

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Received 6 May 1999; received in revised form 6 August 1999; accepted 3 September 1999

Abstract

For the first time, a continuous flow system with solid phase UV spectrophotometric detection (an optosensor) is described for the sequential determination of two analytes based on the alternate use of two carrier/self-eluting agents. The selective and sequential sorption of both on an active solid support (an anion exchanger gel placed in the detection zone into an appropriate quartz flow cell) is performed and their respective UV intrinsic absorbances monitored. Each carrier itself elutes the respective analyte from the solid support, so regenerating the sensing zone.

Ascorbic acid and paracetamol in concentrations ranging from 0.3 to 20 $\mu g\ ml^{-1}$ and from 0.4 to 25 $\mu g\ ml^{-1}$, respectively, could be determined with this UV flow-through optosensor using sodium acetate/acetic acid (pH 5.6) and 0.05 M NaCl (pH 12.5), respectively as carrier/self-eluting solutions and Sephadex QAE A-25 anion exchanger gel as solid phase placed in the inner of an 1 mm optical path length quartz flow cell. The RSDs % ($n = 10$) were lower than 1.3 (for ascorbic acid) and than 1.5 (for paracetamol). Detection limits (criterion 3σ) as low as 0.02 $\mu g\ ml^{-1}$ were achieved in both cases.

Application to the analysis of pharmaceutical samples (in addition to synthetic ones) testifies the utility of this sequential sensor, which tolerates amounts of the species usually accompanying the analytes much higher than those ones found in these samples. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Flow-through sensor; Solid phase spectroscopy; Ascorbic acid; Paracetamol

1. Introduction

Direct determination of analytes based on intrinsic absorbance measurements in the ultraviolet (UV) region usually shows problems arising from the non-specific absorption, interferences becoming too frequent and so limiting its application.

Recently, the use of solid phase spectroscopy (SPS) has made possible the direct UV spectrophotometric determination of analytes in the presence of other species also absorbing in this region and showing a strong spectral overlap without any prior separation and without suffering interference from them [1,2].

On the other hand, the combination of flow injection analysis (FIA) with SPS has made possible to automate SPS in both non-destructive spectroscopic techniques: spectrophotometry (also in the IR region [3]) and spectrofluorimetry [4,5]. This SPS–FIA integration, in which a surface (in this case an ion

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PII: S0003-2670(99)00693-5

exchanger) is surrounded by a flowing stream and its interaction with radiation is monitored, belongs to the so-called flow-through optosensors [6].

According to the number of analytes that a sensor can monitor from the same sample, sensors can be classified into two categories: (a) single-parameter sensors when they are sensitive to a single analyte or a family of chemical compounds (overall screening determination) and (b) multi-parameter sensors when they can respond to several analytes. Most photometric flow-through sensors developed up to date are single parameter (a)-type sensors [7–9]. A few multi-parameter sensors using a simple recognition element integrated with a photometric transducer have been developed (usually from compounds with similar chemical structure), but all of them either use multisignal handling capable transducer and processing the multisignal acquired by using a chemometric arrangement [10–12] or they operate in such a way that a previous on-line separation is used by means of a high resolution technique (e.g. HPLC) in order to allow the sequential arrival of the analytes to the sensor [13] thus carrying out their temporal discrimination. Nevertheless, there is no photometric multisensor described in bibliography for monitoring sequentially and directly more than one analyte showing different chemical structures. In this paper, we propose a new and simple photometric biparameter sensor based on the sequential retention on an active solid support and on-line solid phase detection of two analytes just by using two alternate carriers (at different pH values) in which the sample is sequentially injected, the carriers themselves being the regenerating agents of the solid support, respectively. That is, the same sensing solid phase zone responds each time to only one analyte in the sample after its previous conditioning by passing the appropriate carrier/self-eluting solution. So this paper contributes to the desired progress in the area of this type of flow-through sensors claimed by some authors [14].

Ascorbic acid (AA) and paracetamol (PCT) (two very used active principles either solely or in combination in commercial pharmaceutical preparations) are directly determined in this paper using a sequential photometric flow-through sensor with a dextran type anion exchanger resin as solid sensing zone and two alternate buffer solutions at pH 5.6 (for AA determination) and pH 12.5 (for PCT determination) as carrier/self-eluting solutions, respectively. Neither derivative reaction nor prior separation are necessary because of their intrinsic absorbance is used as analytical signal. Therefore, rapidity and simplicity are two characteristics of the sensor. The biparameter sensor shows both very good analytical features and excellent tolerance level to each analyte in the determination of the other one. Its successful application to the determination of these two active principles in pharmaceuticals as well as in synthetic samples has been demonstrated.

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade. Bidistilled water was used throughout the work for the dilution of samples and reagents. All solutions, the same as bidistilled water, were filtered through a 0.45 μm Millipore membrane filter.

Both $100\,\mathrm{mg\,l^{-1}}$ standard aqueous solution of L(+) ascorbic acid (Panreac) daily prepared, and paracetamol (Fluka), respectively, were used, the former being standardised by titration with indophenol [15].

The carrier/eluting solutions used consisted of:

a) Carrier A (C_a): A 0.04 M sodium acetate (NaAc)/acetic acid (HAc) buffer (Panreac) solution at pH 5.6, used as carrier/eluting solution for the determination of AA.
b) Carrier B (C_b): A 0.05 M NaCl solution at pH 12.5 (adjusted with NaOH solution), used as carrier/eluting solution for the determination of PCT.

Sephadex QAE A-25 (Aldrich) ion-exchanger gel 40–120 μm in the Cl^- form was used as solid support placed with the aid of a syringe inside a 1 mm Hellma 138-QS quartz flow-through cell (50 μl inner volume) with glass wool in the outlet to keep resin beads from movement.

2.2. Apparatus and procedure

All spectral measurements and real-time data acquisition of flow injection peaks were made with a Perkin Elmer Lambda-2 double-beam spectrophotometer controlled by means of a Mitac MPC 3000F-386

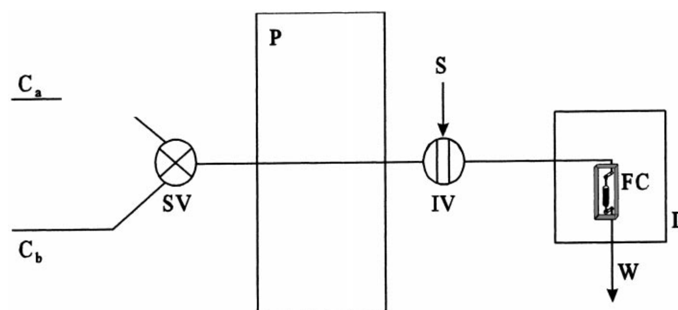

Fig. 1. Schematic diagram of the flow-through sensor system. C_a and C_b: carrier/self-eluting solutions; SV: selecting valve; P: peristaltic pump; S: sample; IV: injection valve; D: detector (tuned at 264 nm); FC: flow-through cell; W: waste.

personal computer, fitted with the software package PECSS 4.2 (from Perkin Elmer) for data processing.

A Gilson Minipuls-3 peristaltic pump with rate selector was used to generate the flow stream in the single manifold required for the system. Injections were carried out by using a Rheodyne Type 50 six-port rotary injection valve. The alternate selection of the carrier was also made by means of another Reodyne Type 50 rotary injection valve connected as a selecting valve. Other apparatus consisted of a Selecta (Barcelona, España) Model Ultrasons ultrasonic bath and a digital Crison Model 2002 pH meter fitted with a glass/saturated calomel electrode assembly and a temperature probe. Teflon tubing 0.8 mm. i.d. was also used.

A monochannel manifold (Fig. 1) having a very low residence time was used, as no derivative reactions were required, so the length coil between the injection valve and the detector was the minimum required (about 30 cm). NaAc/HAc carrier solution stream (C_a) was firstly pumped through a Teflon tube at a flow rate of $1.0\,ml\,min^{-1}$ and the sample containing AA y PCT was injected in it by means of the rotary injection valve (IV), fitted with the appropriate Teflon sample loop (300–600 or 1000 μl depending on the analyte concentration in the sample). The absorbance was monitored at a wavelength of 264 nm in the personal computer, and sent to the printer.

After developing the analytical signal (due only to AA), the carrier itself eluted the analyte, so regenerating the ion-exchanger gel and the absorbance value returning to the baseline. Then, by rotating the selecting valve (SV) the second carrier/eluting solution C_b, (NaCl at pH 12.5) was pumped through the system and the sample containing AA and PCT was again injected. When the sample plug reached the detection area, the analytical signal at 264 nm (now due only to PCT) was acquired. The carrier itself also could elute PCT from the active sites of the resin, the signal coming back to the baseline. AA and PCT in the next sample could be measured in an inverse sequence with respect to the first one: firstly, PCT and then AA by pumping the NaAc/HAc carrier/eluting solution.

2.3. *Treatment of samples*

2.3.1. *Tablets and granular packs*

Weigh and finely powder 10 sample unites (tablets o granular packs). Transfer an accurately weighed amount of powder (equivalent to about 50–100 mg of the analyte(s)) into a glass baker, and dissolve in about 80 ml of distilled water by using an ultrasonic bath. Filtrate through a 0.45 μm pore size Millipore membrane filter and make up the filtrate to 100 ml. Use this clear solution as a stock solution and dilute appropriately before injecting in the flow system.

2.3.2. *Liquid preparation of PCT (Apiretal)*

Measure accurately a volume of drop sample equivalent to 50–100 mg of PCT and transfer into a 100 ml calibrated flask, making up to the mark. Dilute appropriately before injection.

2.3.3. *'Febrectal' (suppository)*

The sample, an accurately weighed amount containing 50–100 mg of PCT, is dissolved in 50 ml of CH_3Cl. Extract PCT by using four successive extractions with

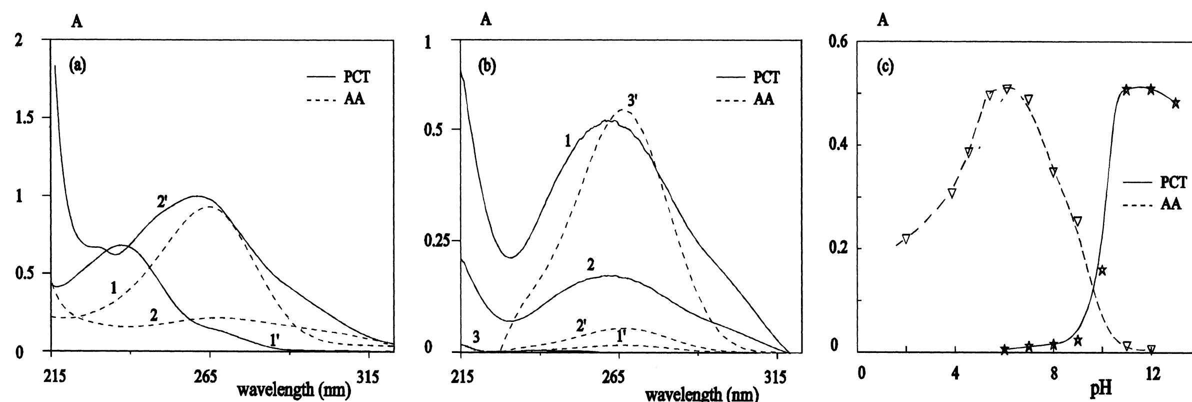

Fig. 2. Influence of the pH. (a) Spectra of aqueous solutions of AA and PCT at different pH values: pH = 6.0 (spectra 1 and 1′); pH = 12.0 (spectra 2 and 2′); [AA] = 10 μg ml^{-1}; [PCT] = 10 μg ml^{-1}. (b) Spectra of AA and PCT on the resin phase at different carrier pH values: pH = 12.0 (spectra 1 and 1′); pH = 10.0 (spectra 2 and 2′); pH = 6.0 (spectra 3 and 3′); [AA] = 5 μg ml^{-1}; [PCT] = 6 μg ml^{-1}; sample volume: 600 μl; flow-rate: 1.0 ml min^{-1}. (c) Sensor absorbance signal measured at 264 nm as a function of the carrier pH value.

25 ml of water at pH 8–9 adjusted with NaOH each time. Make up the aqueous phase to a final volume of 250 ml and dilute appropriately before injecting in the carrier stream.

3. Results and discussion

3.1. Study of experimental variables

3.1.1. Selection of the solid support

Both AA and PCT are sorbed on anion exchange resins at appropriate pH values due to their anionic nature. We take advantage of it for the determination of these two analytes by direct measurement of their intrinsic absorbance when they are sorbed on an appropriate anion exchange resin placed in the flow-cell of a FI system. Anion exchangers with an aromatic matrix cannot be used for this purpose because of their very high background in the UV region. Therefore, resins with a styrene-divinyl-benzene (aromatic) matrix were discarded. Sephadex (dextran-type anions exchangers) QAE A-25 and DEAE A-25 were tested and the former was chosen due to the analytical signal obtained was about three times higher and the peak width was reduced by a quarter.

3.1.2. Influence of the pH of the carrier solutions

In homogeneous solution, AA and PCT show an extensive spectral overlap (Fig. 2a) which makes impossible the simultaneous determination of both analytes by conventional UV spectrophotometry. In resin phase, the maximum absorption wavelengths of the analytes are very close: 267 nm for AA and 262 nm for PCT, so they also show an extensive spectral overlap (Fig. 2b).

Nevertheless, AA is retained on the resin at pH values of the carrier solution between 2 and 10 adjusted with HCl or NaOH. Beyond pH 8, its fixation drastically decreases, probably due to the competition of the OH^- ions by the active sites of the ion exchanger. On the other hand, PCT is only retained from pH 8, reaching its maximum absorbance value from pH 11, as from this pH value its phenolic group is completely ionised. Therefore, from Fig. 2c it can be seen that it is possible to determine sequentially these two compounds by operating at two appropriately selected pH values: at pH 5.6, only AA is retained on the active solid sensing microzone, and at pH 12.5, only PCT is sorbed on the solid support. Therefore, these were the two working pH values chosen.

3.1.3. Selection of the carrier/eluting solutions

If the regeneration of the solid phase after developing the analytical signal is performed by the carrier itself, the sampling frequency is then drastically increased, the baseline is more stable and the solid phase life-time is also higher than that obtained in the case of using a regenerating solution in addition to the carrier solution. When the sample plug reaches the

active microzone, the analyte is retained by means of an ion exchange process. After this, the carrier solution reaches the resin containing the analyte retained and this is displaced by the anions (or cations) from the carrier solution, now actuating as eluting solution. In this way, the analytical signal developed is transient (the maximum corresponding to the end of the sample plug and the beginning of the elution process).

In order to achieve the above features, a carrier/self-eluting solution was selected for each analyte. For the determination of AA, several buffer solutions at pH 5.6 were tested (citric acid/citrate, acetic acid/acetate, succinic acid/succinate, maleic acid/maleate and dihydrogen orthophosphate/monohydrogen orthophosphate). The best results were obtained with a 0.04 M acetic acid/acetate buffer solution which, in turn, allowed the self-elution of the analyte.

For the determination of PCT, various NaOH solutions at pH 12.5 containing each time a 0.05 M solution of KCl, Na_2CO_3, K_2HPO_4, $Na_2B_4O_7$ or NaCl, respectively, were tested and the last one was found to be the most suitable as a higher signal and a more complete and quicker elution was achieved. In the absence of any salt in the carrier solution, PCT was very strongly sorbed and the self-elution by the carrier could not be performed. When the concentration of NaCl added to the carrier was varied from 0.01 to 0.50 M, the elution time decreased from 3 min 52 s to only 46 s but the absorbance signal also decreased a 52%. This can be explained by the displacement of PCT from the resin produced by the fixation of the anions of the carrier/self-eluting solution in the ion-exchanger, which is achieved in a more effective and quicker way as the concentration of NaCl is increased. In addition, the signal decreases due to the competition of the Cl^- ions (from the surrounding environment created by the carrier before the sample plug reaches the resin) for the active sites of the ion-exchanger. Therefore, a 0.05 M concentration of NaCl was chosen as a compromise.

3.1.4. *Effect of the flow rate*

The effect of varying the flow rate from 0.56 to 1.64 ml min^{-1} is shown in Fig. 3. From a flow rate value beyond 1 ml min^{-1}, the peak absorbances decrease in a significant way, so indicating that the fixation of the two analytes is not instantaneous. A flow rate value of 1 ml min^{-1} was chosen as a compromise

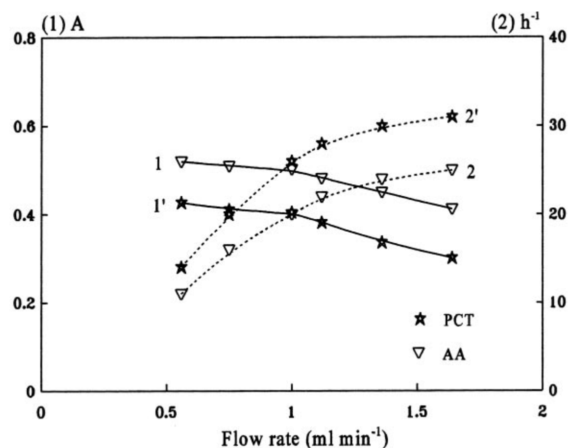

Fig. 3. Effect of the flow rate: (1) on peak absorbance signal and (2) on sampling frequency. [AA] = [PCT] = 5 μg l^{-1}; sample volume: 600 μl.

because it gave a high sampling frequency in both cases and only a slight decrease in the signal was observed (about 4%) with respect to the minimum flow rate value tested.

3.1.5. *Influence of sample volume*

The effect of using different sample volumes was tested for each analyte in the above established conditions. A continuous and strong increase in the peak height was found in both cases until a sample volume of 1000 μl (AA) or 800 μl (PCT) was injected. Beyond these values, the increase in absorbance was not so strong probably due to the pH value in the detection zone was not held at its optimum value during the complete pass of so large sample plugs and also due to not very high distribution ratios. These results are usual in this type of continuous flow solid phase systems [4]. It follows the interesting advantage of analysing samples in a large range of concentrations by simply varying the sample volume used, previous calibration of the SPS–FIA system and without any previous preconcentration or dilution process being necessary. Three different sample volumes were used in this paper which allowed to reach a calibration range from 0.4 to 20 μg ml^{-1} for AA and from 0.4 to 25 μg ml^{-1} for PCT. Fig. 4 shows, as an example, the fiagram corresponding to the calibration of the sensor for a sample volume of 600 μl.

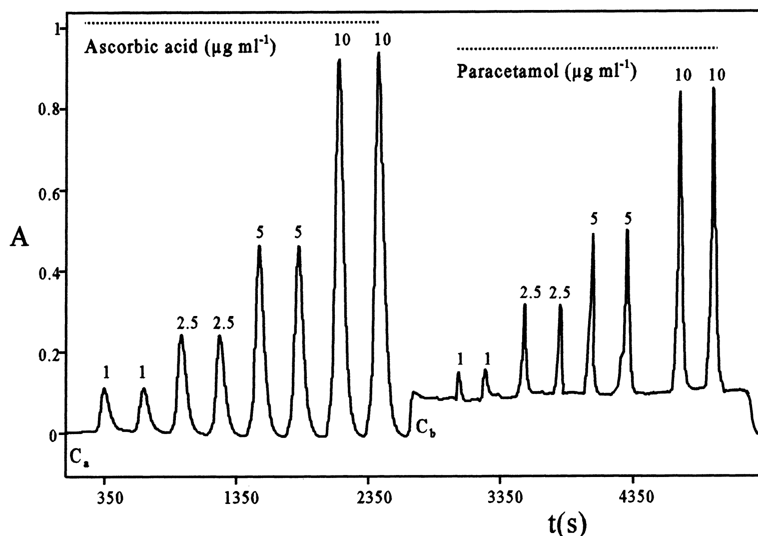

Fig. 4. Fiagram obtained in the calibration of the sensor for a sample volume of 600 μl. The higher baseline in the calibration (and determination) of PCT with respect to AA is due to the compaction of the solid support beads when C_b carrier is flowing through the system.

Table 1
Analytical features of the biparameter sensor

Parameter		Ascorbic acid			Paracetamol		
		Volume of sample injected (μl)			Volume of sample injected (μl)		
		300	600	1000	300	600	1000
Calibration line	Intercept (a.u.)	0.022	0.008	0.011	0.033	0.003	0.020
	Slope $\times 10^2$ (ml μg^{-1})	5.58	9.79	15.6	3.91	8.14	9.95
	Correlation coefficient	0.9998	0.9999	0.9998	0.9996	0.9999	0.9995
Sensitivity[a] (l mol^{-1} cm^{-1})		9.83×10^4	1.72×10^5	2.75×10^5	5.93×10^4	1.23×10^5	1.50×10^5
Linear dynamicrange (μg ml^{-1})		1–20	0.5–10	0.3–6	1.0–25	0.5–12	0.4–10
Detection limit (μg ml^{-1})		0.045	0.040	0.018	0.075	0.045	0.025
Quantification limit (μg ml^{-1})		0.15	0.013	0.06	0.25	0.15	0.08
RSD % ($n=10$)		1.06	1.23	0.88	1.23	1.41	1.09
Sampling frequency (h^{-1})		23	20	18	30	26	24

[a] Expressed as apparent molar absorptivity.

3.2. *Analytical features of the method*

Table 1 summarises the analytical parameters of the SPS–FIA procedure developed for the UV sequential determinations of both analytes.

It can be seen that the sensitivity of the procedure, expressed as the slope of the calibration line or the apparent molar absorptivity (l mol^{-1} cm^{-1}), increases drastically as the sample volume is increased: the slope ratios are $m_{1000}/m_{300}=2.80$ (AA) and $m_{1000}/m_{300}=2.54$ (PCT), the subscripts being the sample volumes (μl) injected.

The detection and quantification limits, calculated by using the 3σ [16] and 10s [17] criteria, were established by using the peak absorbance signal from ten different injections of blank solutions in every case. The solid support lifetime in the flow cell allows, at least, 300 and 200 determinations of AA and PCT, respectively.

Table 2
Study of interferences

Foreign species	Tolerance level ($\mu g\, ml^{-1}$) ([interfering species]/[analyte])	
	Ascorbic acid	Paracetamol
Saccharose, Glucose, Lactose	>500[a]	>200[a]
Ephedrine	>50[a]	>50[a]
Glutamic acid	30	20
Paracetamol	20	–
Ascorbic acid	–	>20[a]
Caffeine	20	1
Acetylsalicylic acid	20	1
Codeine	15	10
Citric acid	6	5
Salicylamide	5	2
Salicylic acid	5	1
Saccharin	1.5	1

[a] Maximum ratio interfering species/analyte tested.

3.3. Interference study

A study of the influence of potentially interfering species on the analytical response of the biparameter sensor was carried out for the determination of $5\,\mu g\, ml^{-1}$ of each analyte contained in the same solution by injecting $600\,\mu l$ of this. A total of fourteen different species usually accompanying the analytes in pharmaceuticals were tested. The tolerance limit was taken as the maximum concentration in the solution that caused a relative error of ±5% in the signal in comparison with the average signal either of AA or PCT, respectively.

As can be seen in Table 2, where the results are summarised, excellent tolerance levels towards these species usually accompanying the analyte(s) in pharmaceuticals are achieved. It should be noted that these amounts tolerated (including the interfering species showing the lowest limit of tolerance) are usually much higher than those ones found in pharmaceuticals. Therefore, the sensor allows the determination of AA in the presence of amounts of caffeine and codeine up to 200 and 750 times higher, respectively, than those ones found in pharmaceuticals. In the case of the determination of PCT the tolerance level to those species is up to 20 and 500 times higher, respectively. This high selectivity is due to both the fixation of the analytes, respectively, on the active solid support and the exclusion from it of the coexisting species in working conditions.

Table 3
Calibration graph for each analyte in the presence of various amounts of the other one

[PCT] ($\mu g\, ml^{-1}$)	Calibration graph (AA)	Correlation coefficient
0	$A=0.008+0.0979c$	$r=0.9999$
5	$A=0.009+0.0980c$	$r=0.9998$
10	$A=0.008+0.0977c$	$r=0.9996$
20	$A=0.008+0.0975c$	$r=0.9997$
[AA] ($\mu g\, ml^{-1}$)	**Calibration graph (PCT)**	**Correlation coefficient**
0	$A=0.003+0.0814c$	$r=0.9999$
5	$A=0.004+0.0820c$	$r=0.9995$
10	$A=0.003+0.0807c$	$r=0.9998$
20	$A=0.005+0.0803c$	$r=0.9998$

The independence of the signals of an analyte from the presence of the other one was also tested by calibrating each one in the presence of various amounts of each other (Table 3). A test [18] did not show significant difference at a probability level of 5% between the slopes of the calibration lines in these conditions compared with those respective ones when the analytes are solely.

3.4. Analytical applications

In order to check the accuracy of the proposed biparameter sensor, it was applied to the analysis of both

Table 4
Analytical applications: synthetic samples

Ratio (PCT : AA)	Recovery mean ± RSD[a] (%)	
(w : w)	PCT	AA
1 : 10	99.2 ± 0.8	101.1 ± 0.7
1 : 5	101 ± 1	100.2 ± 0.3
10 : 1	99.0 ± 0.5	99.8 ± 0.5
5 : 1	100 ± 1	99.1 ± 0.6
5 : 5	99.5 ± 0.2	100 ± 1
2 : 7	100.2 ± 0.4	100.7 ± 0.9

[a] Mean of three determinations.

a) a series of synthetic samples of PCT and AA and b) seventeen commercial formulations including tablets, packs and a solution containing either one of the analytes solely or in combination.

3.4.1. Synthetic samples

Six synthetic samples containing both AA and PCT in different ratios AA : PCT (w : w) ranging from 10 : 1 to 1 : 10 were sequentially analysed for the two analytes. Results, summarised in Table 4, show a very good recovery.

3.4.2. Commercial formulations

Table 5 shows the results obtained in the application of the sensor to different pharmaceuticals. In the formulations containing the two analytes together, the analyses were carried out sequentially by using two successive injections from the same sample. Results show good agreement with the composition indicated by the supplier. In addition, a recovery study was performed by adding the respective analyte by triplicate at two different concentration levels (100 and 200 mg per unit) for each formulation containing both analytes. Mean recovery values (±RSD) ranged from (98.7 ± 0.9) to (100.5 ± 0.5) for AA and from (99.1 ± 0.7) to (100.0 ± 0.3) for PCT. These good results found in all cases confirm the applicability of the proposed sensor.

Table 5
Determination of AA and PCT in pharmaceutical preparations

Sample[a]	Labelled amount (mg per unit)		Recovery mean ± RSD[b] (%)	
	PCT	AA	PCT	AA
Algidol	650	500	100.7 ± 0.8	100.4 ± 0.9
Veganin	250	–	99.3 ± 0.7	–
Febrectal	300[c]	–	101 ± 1	–
Frenadol	650	250	99.6 ± 0.5	103 ± 1
Fludeten	500	–	99 ± 1	–
Fiorinal	300	–	101.4 ± 0.8	–
Rinomicine	400	300	100.4 ± 0.2	101.4 ± 0.6
Apiretal	100[d]	–	98 ± 1	–
Propalgina Limón	500	–	98.8 ± 0.8	–
Duorol	500	–	100.3 ± 0.7	–
Termalgin	500	–	98.9 ± 0.6	–
Saldeva	500	–	98 ± 1	–
Analgilasa	500	–	101.1 ± 0.5	–
Cortafriol	500	250	100.6 ± 0.8	100.7 ± 0.6
Redoxón	–	1000	–	99.7 ± 0.4
Citrovit	–	1000	–	101.1 ± 0.8
Cebión 500	–	500	–	99.2 ± 0.5

[a] Algidol: codeine phosphate 10 mg, saccharin 2.5 mg; Veganin: acetylsalicylic acid 250 mg, codeine phosphate 10 mg; Frenadol: caffeine citrate 30 mg; Fludeten: codeine phosphate 30 mg; Fiorinal: acetylsalicylic acid 200 mg, caffeine 40 mg; Rinomicine: salicylamide 200 mg, caffeine 30 mg; Apiretal: sodium saccharin 5 mg ml^{-1}; Duorol: sodium saccharin 20 mg, caffeine 50 mg; Analgilasa: caffeine 30 mg, codeine phosphate 10 mg; Redoxon: sodium saccharin 20 mg; Cebion 500: sodium saccharin 7 mg.

[b] Mean of three determinations.

[c] Standard addition method.

[d] Per ml.

4. Conclusions

Solid phase spectroscopy has been integrated with FIA to develop, for the first time, an UV optosensor that responds alternately to two analytes. The use of two different carriers also actuating as the respective eluting agents has allowed the selective sequential retention (and subsequent elution) of each analyte in the solid phase and it is the key of the working of the biparameter sensor. The solid support, in turn, provides the selective retention and concentration of each analyte in the detection area and the excellent tolerance levels showed by the integrated sensor. Finally, a noticeable feature of the proposed sensor, that makes it very versatile, is the possibility of working in a wide range of concentrations (for both analytes) just by changing the sample loop connected to the injection valve, as its sensitivity is a function of the sample volume injected.

Acknowledgements

Authors are grateful to Dirección General de Enseñanza Superior e Investigación Científica for financial support (Project PB97–0849).

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