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Fluorescence method using on-line sodium cholate coacervate surfactant mediated extraction for the flow injections analysis of Rhodamine B

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ABSTRACT

An on-line surfactant mediated extraction method in a flow injection analysis format with fluorescence detection was developed for the determination of Rhodamine B (RhB) in food condiments. The sample was extracted using the phase separation behavior exhibited by the bile salt surfactant, sodium cholate (NaC), upon addition of sodium dodecylsulfate (SDS) in the presence of acid at room temperature. The RhB in the sample was incorporated into the NaC/SDS coacervate phase which was then collected on a glass-wool packed mini column from which it was subsequently eluted using a 1.00 mol L^{-1} HCl solution. The inherent fluorescence (λ_{ex}=555 nm; λ_{em}=575 nm) of RhB was employed for detection. Good linearity (r^2=0.9933) was obtained over the concentration range 0.4–4794–479.0 μg L^{-1} RhB. The detection (LOD) and quantification (LOQ) limits were 0.12 and 0.40 μg L^{-1}, respectively. The method was successfully applied for analysis of RhB in food condiments and spiked samples. The average recoveries ranged from 95.3% to 118.9% at spiked concentration levels of 1.19 and 2.39 μg L^{-1}. Under optimized conditions, a throughput of 50 samples per hour was achieved. The proposed method may be a valuable tool not only for quality control of food condiments and similar food confectioneries but for the analysis of a variety of other RhB-containing samples as well.

1. Introduction

Synthetic xanthene dyes, such as Rhodamine, Rhodamine B ([9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride), etc. have been widely employed in textile applications as coloring dyes for fabrics and other materials as well as trace markers for a variety of agricultural agents (i.e., herbicides and pesticides) among others. They have also been employed as color adulterants in food products and beverages. Since rhodamines are considered to be neurotoxic, carcinogenic and mutagenic agents [1], there is a continuing need for new analytical methodology for their detection at trace levels. In most instances, a preconcentration or enrichment step is required prior to spectroscopic determination of rhodamine dyes in order to achieve the necessary sensitivity.

Rhodamine B (RhB) can exist in many different forms in aqueous solution that can be characterized by their absorption and fluorescent spectra [2,3]. The apparent pK_a for conversion of the zwitterion form to the protonated form, RhB^+, is reported to be 3.22 in water and 4.15 and 4.75 in the presence of nonionic surfactant Triton X-100 and anionic SDS micellar solutions, respectively [3]. Protonated rhodamines are expected to bind to anionic surfactant micelles due to favorable electrostatic as well as hydrophobic interactions. A binding constant of 34.6 L mol^{-1} has been reported for the binding of Rhodamine 123 to sodium cholate (NaC) surfactant micelles [4]. Likewise, stronger binding of the cationic form of RhB to anionic sodium dodecylsulfate (SDS) micelles has been observed relative to that seen with nonionic surfactant (Triton or Brij) micelles [3]. In general, the cationic form of RhB better binds micelles compared to its zwitterionic form [3,5]. This is why interaction and binding of RhB with anionic NaC micellar aggregates at low pH values is expected (Fig. 1). When bound to micelle aggregates, the fluorescence of RhB is intensified relative to that observed in aqueous solutions in their absence [2,3,6].

Surfactant mediated extractions (SME), also known as cloud point (CPE), coacervate, aqueous two phase surfactant or supramolecular

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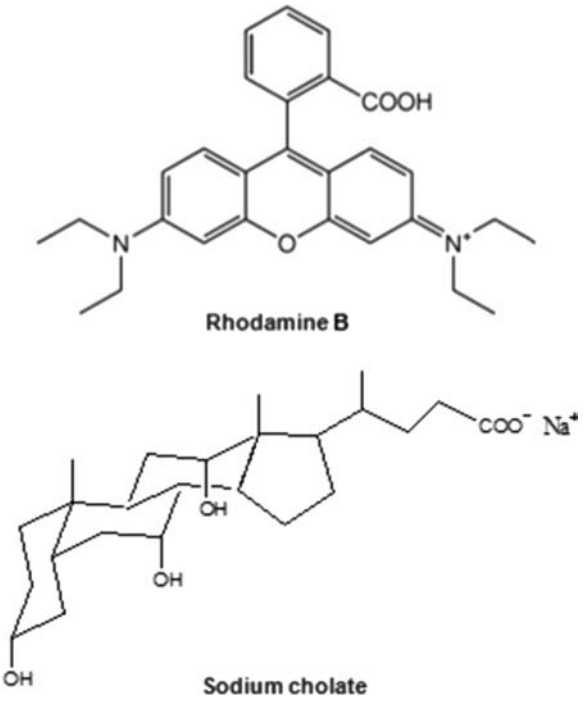

Fig. 1. Chemical structures of the analyte and sodium cholate at the optimized pH value of the SME-FIA experiments.

extractions, among others, have become a popular approach to enrich and/or recover metal ions as well as organic and biological compounds from aqueous (or solid) matrices [7–11]. SME can be employed for samples with complex matrices due to the possibilities of manipulating and chemically modifying the matrix during the phase separation preconcentration step [12]. Previously, some batch SME methods had been employed for the preconcentration of different rhodamine dyes, including RhB, prior to spectroscopic detection [2,13–15].

Most SME are performed in the batch mode [7–12,16,17], although there have been some reports of their utilization in flow injection analysis (FIA) formats [18–24]. Batch mode SME typically involves several steps which can result in poor precision and lower enrichment factors [25,26]; in addition to the approach being time consuming and difficult to automate. In contrast, on-line FI-SME offers advantages in terms of greater sensitivity and precision as well as of a significant reduction of the amounts of the sample and reagents required and wastes generated [18,21,26]. SME was first incorporated within a flow injection format by Huie et. al., who utilized a cotton mini-column to collect the analyte-containing surfactant coacervate phase followed by elution of the analyte with an appropriate solvent [18]. Others have since reported similar designs with FI-SME configurations using non-ionic surfactants, such as Triton X-100, PONPE-7.5 and Triton X-114 [19–24]. In some of these applications, high temperature (30–70 °C) was required to induce phase separation [21,22,27]. However, elevated temperature, in addition to being experimentally complicated due to the necessity of a heating device, may affect the stability of thermally labile analytes [15].

Bile salts (BS) are biosurfactants that are synthesized from cholesterol in the liver. The BS molecule is concave with one side being hydrophobic (studded with methyl groups) while the other is hydrophilic (with hydroxyl and the carboxylate moieties) [28]. In common with traditional surfactant micelles, BS micelles, such as sodium cholate, have unique properties that can be exploited in chemical analysis and separation science applications such as the ability to solubilize solutes selectively, alter the rate and equilibria of chemical processes, modify the effective microenvironment (polarity, viscosity, and surface tension) of bound solutes, etc. [29]. However, in contrast to traditional surfactants (e.g., Triton X-110, Triton X-114, SDS), bile salt micellar solutions are much easier to work with since they foam and scatter light to a much lesser extent, which is beneficial in spectroscopic measurements [30]. The BS aggregation behavior is also different from that observed for conventional surfactants. Namely, they exhibit a sequential aggregation pattern and their micelle aggregation number is typically much less than that of conventional surfactant micelles. Moreover, their critical micelle concentration (CMC) is affected to a lesser extent by changes in experimental conditions (such as pH, ionic strength, and temperature) relative to that of traditional surfactants [30]. These features of BS simplify experimental procedures and offer greater flexibility in optimization of analytical protocols relative to that possible with conventional surfactant media [31].

BS surfactants reportedly serve as coacervate promoters when added to aqueous solution of nonionic surfactants [32,33]. In addition, aqueous solutions of BS, such as NaC, can form coacervate phases in the presence of additives such as quaternary ammonium surfactants, alcohols or acids [34–36].

This manuscript reports on the design and optimization of a FIA manifold coupled to a fluorescence detector for the on-line extraction and fluorimetric determination of Rhodamine B using a glass wool mini-column to collect the bile salt coacervate phase. The proposed method was successfully applied for determination of Rhodamine B in commercially available Argentinian food condiment samples.

2. Experimental section

2.1. Materials

The required materials, Rhodamine B dye (Fluka AG, Chemische Fabrik, Buchs SG, Switzerland), sodium dodecylsulfate (Tokyo Kasei Industries, Chuo-Ku, Tokyo, Japan), sodium cholate (Sigma Chemical Co., St. Louis, MO, United States) and absolute ethanol, HCl and acetonitrile (Merck, Darmstadt, Germany), were acquired as indicated and used as received without further purification. All other reagents employed in this study were of analytical grade quality.

2.2. Instrumentation and apparatus

A Shimadzu RF-5301PC spectrofluorimeter (Shimadzu Corporation, Analytical Instrument Division, Kyoto, Japan), equipped with a Xenon discharge lamp was used for the fluorescent measurements. A 1.0 cm quartz cell was employed for the batch assays and a 12 μL LC flow cell unit (Shimadzu Corporation, Analytical Instrument Division, Kyoto, Japan) for the flow measurements. The RhB fluorescence measurements were carried out operating the spectrofluorimeter in the time-course mode (transient signals; λ_{ex}=555 nm; λ_{em}=575 nm, slits: 5/3 nm).

The FIA manifold (Fig. 2) consisted of a Rheodyne (Rohnert Park, CA) model-5020 six-port two-way rotary valve. The reagent and sample solutions were pumped through the FIA system with two Gilson (Villiers, France) Minipuls 3 peristaltic pumps connected to 1.3 mm i.d. Tygon tubing (Middleton, WI, USA).

A Model EA 940 pH-meter (Orion Expandable Ion Analyzer, Orion Research, Cambridge, MA, USA) equipped with a glass combination electrode was employed for all pH measurements.

2.3. Reagents and stock solutions

1.0×10^{-6} mol L^{-1} RhB stock solutions were prepared weekly by dissolution of suitable amounts of dye in ultrapure water.

Likewise, 0.020 mol L^{-1} standard solutions of NaC and SDS were prepared by dissolution of the required mass of the solid surfactant in ultrapure water. A 1.0 mol L^{-1} HCl solution was prepared by step-wise dilution of concentrated HCl with ultrapure water.

2.4. Samples and sample preparation

Samples of different Argentinian manufactured food condiments (i.e., *paprika*, *chimi-churri*, *rice* and *pizza spices*) were acquired in local shops. About 2.0 g of each condiment was dissolved in ultrapure water and homogenized for 5 min using a magnetic shaker after which they were filtered using filter paper (black ribbon). The samples were then transferred to a 100.0 mL volumetric flask and diluted to 100.0 mL with ultrapure water.

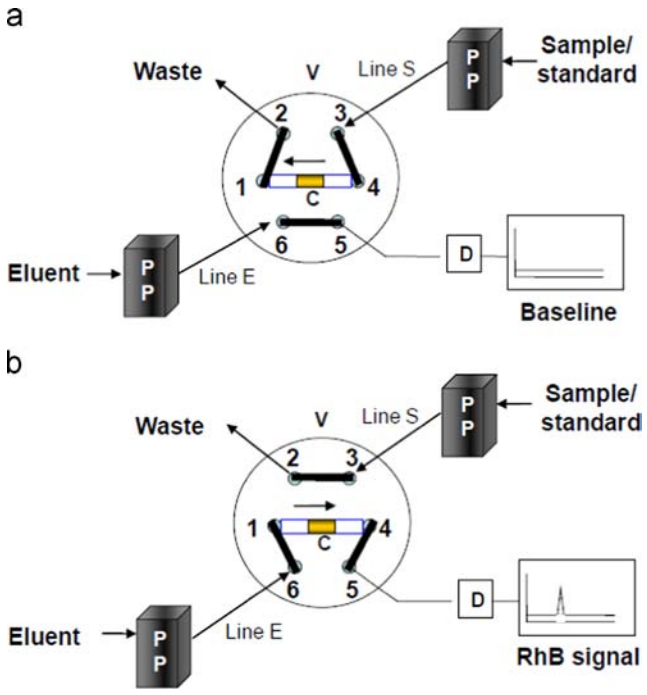

Fig. 2. Schematic diagram of the on-line SME/FIA system. mC, minicolumn; PP, peristaltic pumps; V, load/injection valve ((a) load position and (b) injection position); Line S, sample line; Line E, eluent line; and D, spectrofluorimeter.

2.5. On-line extraction and fluorescence monitoring protocol

To perform the on-line surfactant mediated extraction, 1.00 mL NaC (0.020 mol L^{-1}), 1.00 mL SDS (0.020 mol L^{-1}), 1.00 mL of analytical sample and 300 μL HCl (1.0 mol L^{-1}) were added into a 10.0 mL volumetric flask, and diluted to final volume with ultrapure water. The resulting RhB solution was immediately introduced into the FIA system for on-line extraction and subsequent spectrofluorimetric analysis. Long term storage of acidic SDS solutions should be avoided in order to prevent acid hydrolysis of SDS which results in formation of dodecanol [37].

The specific FIA protocol was as follows: a glass wool minicolumn, mC, (comprised of a 1.5 mm i.d. by 3.0 cm long glass tube filled with 25 mg of glass wool), was loaded with the RhB standard (or sample) solution prepared as just noted, (Line S) with valve V in load position (Fig. 2a), allowing for the retention of the surfactant-rich coacervate phase containing the analyte, while the filtrate was sent to waste. Simultaneously, the mobile phase (1.0 mol L^{-1} HCl solution) flowed through the eluent line (Line E) to the detector to record the baseline fluorescence. During this step, 1.0 mL of the RhB standard/sample was loaded at a flow rate of 2.0 mL min^{-1} into the mC (Fig. 2a). After this loading step, valve V was switched to the injection position (Fig. 2b), so that the mobile phase flowed through the mC (2.0 mL min^{-1}) and the retained coacervate phase was eluted (in the opposite direction

Table 1
Summary of the different additives examined for their effectiveness in inducing phase separation in aqueous solutions of sodium cholate containing Rhodamine B[a].

Coacervate inducer	Volume range examined (mL)
$CaCl_2$ (1.0 mol L^{-1})	0–0.5
KI (1.0 mol L^{-1})	0–0.5
NaCl (1.0 mol L^{-1})	0–0.5
SDS (0.020 mol L^{-1})	0.5–1.5
HCl (1.0 mol L^{-1})	0–0.5

[a] NaC (1.0 mL, 0.020 mol L^{-1}); RhB (250 μl 1.0×10^{-6} mol L^{-1}).

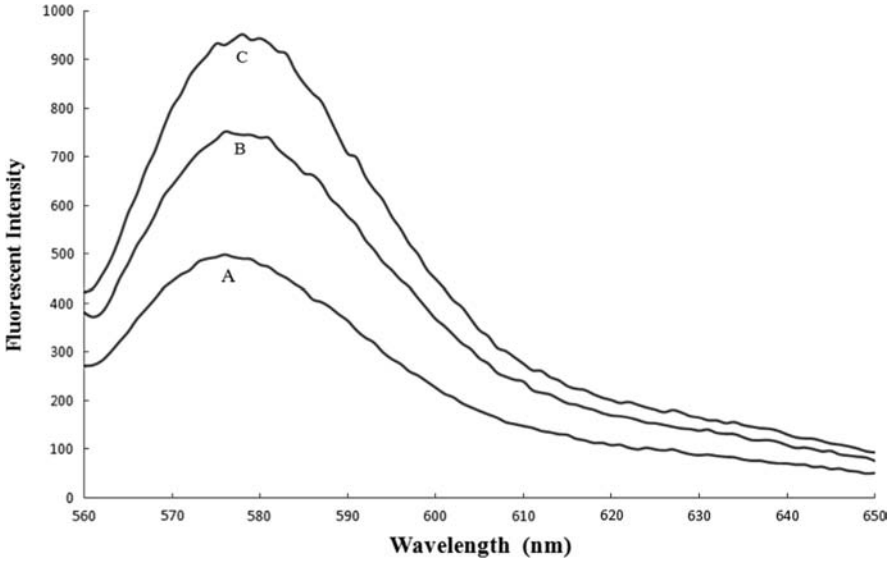

Fig. 3. Emission spectra of RhB ($1 \times 10-8$ mol L^{-1}) in water and micellar media. (A) aqueous solution; (B) NaC (2×10^{-3} mol L^{-1}); and (C) NaC (2×10^{-3} mol L^{-1})/SDS (2×10^{-3} mol L^{-1}); λ_{ex}=555 nm and λ_{em}=575 nm with excitation and emission slit widths equal to 5 nm and 5 nm, respectively.

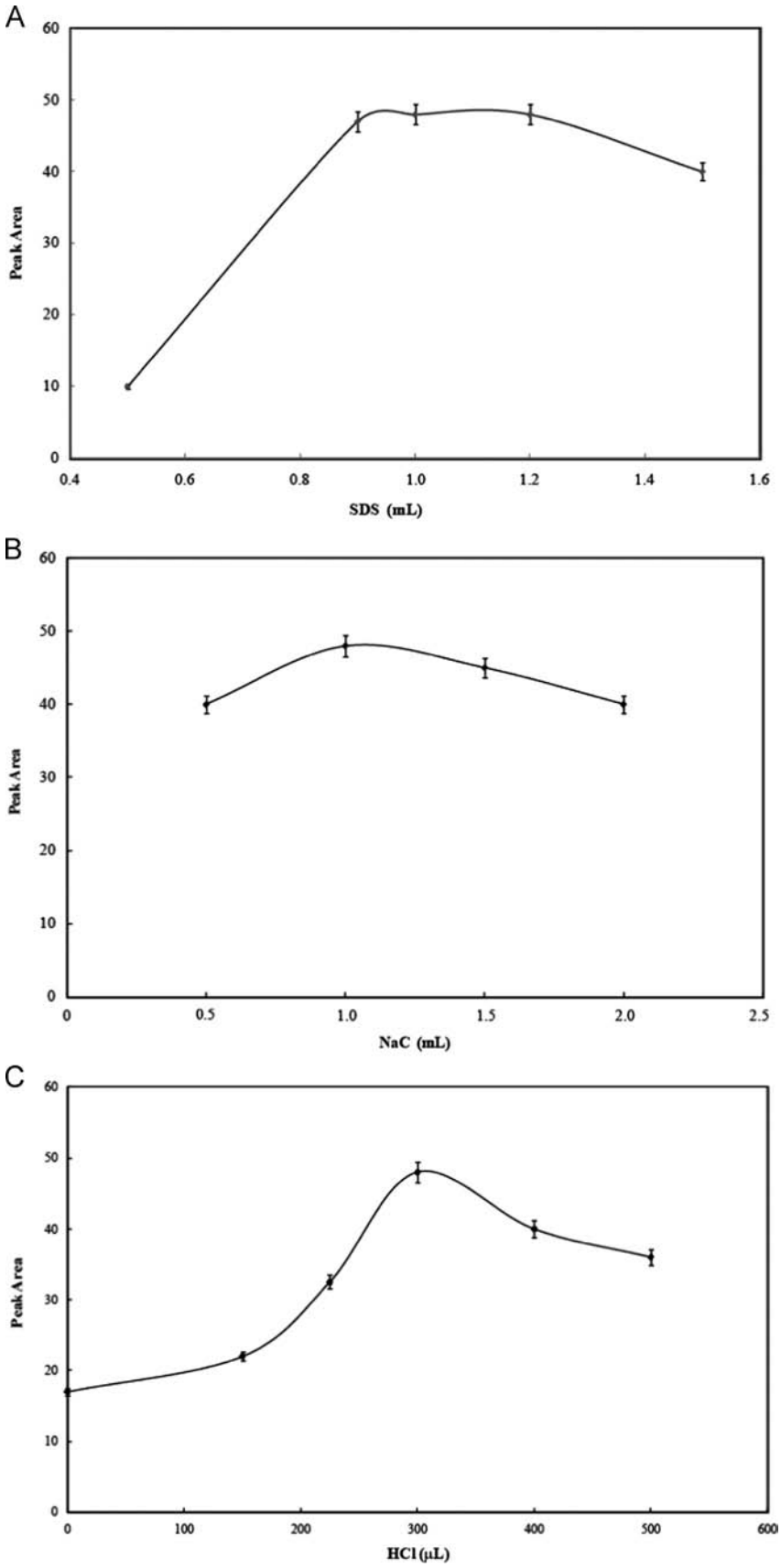

Fig. 4. Effect of variation of the amount (volume) of (A) SDS; (B) NaC; and (C) HCl upon the fluorescence intensity. [Conditions: (A) 0.020 mol L^{-1} SDS (HCl = 3×10^{-2} mol L^{-1}, NaC = 2×10^{-3} mol L^{-1}); (B) 0.020 mol L^{-1} NaC (SDS = 2×10^{-3} mol L^{-1}, HCl = 3×10^{-2} mol L^{-1}); and (C) 1.0 mol L^{-1} HCl (NaC = 2×10^{-3} mol L^{-1}, SDS = 2×10^{-3} mol L^{-1})].

from which it was initially loaded in order to minimize analyte dispersion effects) to the flow cell of the fluorescence detector (Fig. 2b). Afterwards, valve V was switched to load position and the sequence started again for the next sample.

3. Results and discussion

The method presented in this work is based on the on-line preconcentration/separation of RhB via surfactant mediated extraction using NaC as the coacervate agent at room temperature. NaC is an anionic surfactant and its CMC value in water has been reported to be in the 5.0–9.0 mM range [29,38].

The fluorescence emission spectrum of RhB in aqueous solution alone and in anionic surfactant NaC and SDS solutions was determined (Fig. 3). The fluorescence signal was greater in NaC compared to water and still greater in the mixed NaC/SDS surfactant system. This probably reflects the altered microenvironment experienced by RhB (relative to that in water alone) upon its binding to the NaC surfactant or mixed NaC/SDS surfactant aggregate system. NaC and SDS are known to form mixed micellar aggregates with the CMC value for 1:1 NaC–SDS systems reported as 8.0 mM [38,39]. The presence of bulky hydrophobic ions, like protonated RhB, is known to diminish such CMC values and/or lead to formation of pre-micellar aggregates; and such is probably the case here.

3.1. Optimization of experimental variables

Experiments were conducted in order to optimize the experimental conditions so that the best sensitivity and reproducibility for RhB determination as well as stable and quantitative extractant coacervate phase retention were achieved. In addition, the FIA parameters (such as sample loading time, mobile phase composition and flow rate) were optimized using univariate analysis.

3.1.1. Coacervate formation

The ability of different substances to induce phase separation and coacervate formation in aqueous solutions of sodium cholate at room temperature was surveyed. Namely, variable amounts of calcium chloride, potassium iodide, sodium chloride, and sodium dodecylsulfate (SDS), both in the absence and presence of hydrochloric acid, were added to aqueous solutions of NaC containing RhB (Table 1) and the solutions assessed for signs of coacervate (or precipitant) formation as well as the degree of partitioning of the RhB into the coacervate phase. Although all of the noted additives were effective in terms of inducing NaC coacervate (or precipitate-like) formation, the features of the NaC coacervate formed upon addition of SDS/HCl were optimal considering the aggregate size. It should be noted that aqueous solutions of NaC/SDS mixed micelles have been frequently employed as the run buffer in electrokinetic chromatographic separations and that the interactive properties of these mixed micelles is different from that of the individual NaC or SDS micelles alone [40]. Such mixed NaC/SDS micellar surface may provide ideal binding sites for the protonated RhB analyte.

Some batch studies were conducted in order to determine the optimal volumes (concentrations) of SDS and HCl required for retention of the formed coacervate on the glass wool in the mC (as gauged by its physical appearance) and for obtainment of the maximum RhB fluorescence signal. The influence of HCl volume on the coacervate formation of solutions containing RhB was evaluated in the range 0.0–0.5 mL. The results (such as the fluorescence profiles shown in Fig. 4) indicate that the optimal amounts were 1.0 mL of 0.020 mol L^{-1} SDS, 1.0 mL of 0.020 mol L^{-1} NaC and 0.30 mL of 1.0 mol L^{-1} HCl. This corresponds to the following molar concentrations of these reagents in the sample mixtures: 0.0020 mol L^{-1} SDS; 0.0020 mol L^{-1} NaC and 0.030 mol L^{-1} HCl. All subsequent experiments were conducted using these conditions.

3.1.2. Eluent composition and concentration

Different solvents, such as water, ethanol, acetonitrile, aqueous HCl solutions, and mixtures thereof, were tested as eluents to achieve complete release of the RhB analyte from the NaC/SDS coacervate with adequate analytical signal. Weak fluorescence signals (peak area) were obtained when water, ethanol, acetonitrile, water:ethanol or water:acetonitrile mixtures were employed as the eluent solvent system. However, satisfactory elutions were achieved when aqueous solutions of HCl were employed as the eluent. Consequently, HCl was selected as eluent for the subsequent experiments. Next, the effect of HCl concentration over the range from 1.0 mmol L^{-1} to 1.0 mol L^{-1} was examined. The

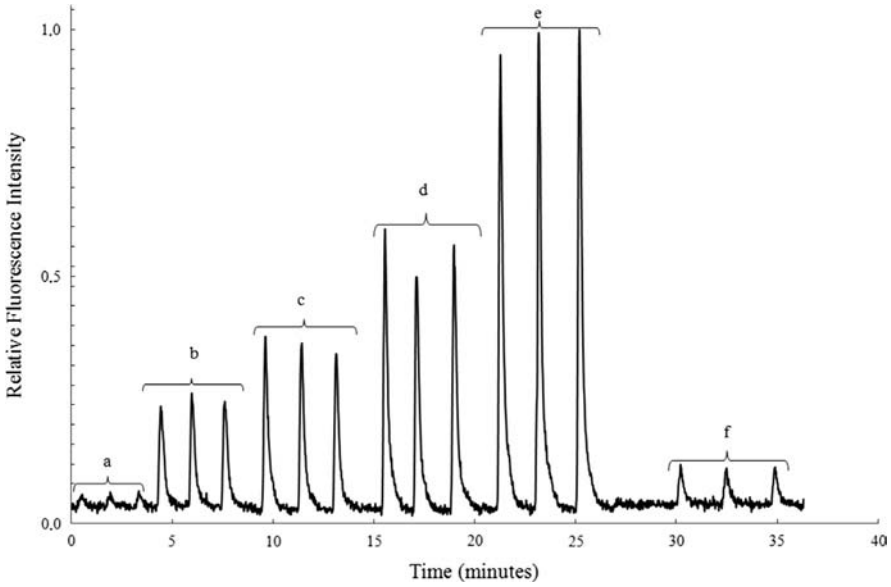

Fig. 5. Calibration and sample signal traces. (a) reagent blank; standard solutions of RhB; (b) 5×10^{-10} mol L^{-1}; (c) 1.0×10^{-9} mol L^{-1}; (d) 2.5×10^{-9} mol L^{-1}; (e) 5.0×10^{-9} mol L^{-1}; and (f) real sample (chimichurri). [Conditions: λ_{ex}=555 nm and λ_{em}=575 nm; with excitation and emission slit widths equal to 5 nm and 3 nm, respectively. Injection time: 30 s].

optimal concentration considering the quantitative elution of RhB was found to be 1.0 mol L^{-1} HCl.

3.1.3. Optimization of FIA system and flow conditions

The variables influencing the performance of the FIA method were examined one-at-a-time in order to determine the conditions necessary for an optimal fluorescence signal and best reproducibility. Column design, packing material and packing conditions were experimentally evaluated (data not shown) by measuring the RhB fluorescence signal in the waste line (filtrate) as a function of the parameter being varied. Results led to the design of the FIA manifold shown in Fig. 2 and indicated that a mC filled with 25 mg of glass wool was sufficient for quantitative retention of the NaC/SDS coacervate containing the RhB and subsequent stripping of the analyte RhB allowing for maximal signals and reproducible (and symmetric) elution peaks.

3.1.3.1. Sample loading rate. The sample flow rate through the mini-column is a compromise parameter related to (i) the time of contact between the NaC/SDS coacervate phase and glass wool solid support and (ii) the total time of analysis [41]. The effect of sample flow rate on the preconcentration efficiency was evaluated using loading flow rates between 0.5 and 2.5 mL min^{-1}. It was found that the analytical signal decreased slightly upon increasing the sample flow rate above 2.0 mL min^{-1} presumably because of incomplete coacervate retention. Therefore, a sample flow rate of 2.0 mL min^{-1} was selected as optimal.

3.1.3.2. Eluent flow rate. The effect of eluent flow rate on the analytical response was studied at flow rates between 1.0 and 3.0 mL min^{-1}. In general terms, it was observed that the analytical signal increased with the eluent flow rate. However, despite the benefit of greater speed of analysis, flow rates greater than 3.0 mL min^{-1} generated large and undesirable back-pressures. Therefore, an elution flow rate of 2.0 mL min^{-1} was selected as optimal because it allowed for a reasonable analysis time and acceptable mini-column backpressure.

Reports indicate that better sensitivity is obtained if the elution flow is in an opposite direction to that of sample loading onto a packed column [42]. The impact of the direction of the elution flow upon the analytical signal was examined and indeed the best results in terms of sensitivity and peak shape (i.e., symmetry, sharpness) were obtained when the elution was performed in a countercurrent manner (Fig. 2).

Table 2
Analytical figures of merit for the FIA on-line SME – fluorimetric determination of Rhodamine B.

Parameter	Value (μg L^{-1})
LOD	0.12
LOQ	0.40
LOL	0.40–479.0
r^2	0.9933

3.2. Analytical performance

Fig. 5 shows the transient responses (FIAgram) obtained for the blank, standards and a real sample analyzed using the recommended optimized procedure. The calibration plot of FIA fluorescence peak area vs. RhB concentration was linear over the concentration range (limit of linearity, LOL) of 0.4–479.0 μg L^{-1} RhB (r^2=0.9933). The limits of detection (LOD) and quantification (LOQ) were calculated in the usual manner [2], using the relation k (SD)/m where k=3 for LOD and 10 for LOQ and SD represents the standard deviation from 15 replicate blank responses and m is the slope of the calibration curve. Table 2 summarizes the analytical figures of merit for this method for determination of RhB.

A comparison of the sensitivity of this method relative to reported methods in the literature [2,14,15,43–49] is presented in Table 3. Many of the published methods require a number of steps (such as heating, centrifugation, cooling, dilution of the extractant phase (lower sensitivity)), or the need to specially synthesize the solid phase extraction material [2,14,15,45–49]. In contrast, no such manipulations or steps are required in the proposed methodology. In addition, the method is sensitive, simple, convenient and rapid offering high sample throughput (50 samples per hour).

3.3. Applications

RhB's use as a food colorant is illegal in many countries due to its toxicity towards humans and animals [1,24]. In Argentina, there is no official regulation regarding the use of RhB in food stuffs. It is very important to achieve RhB quantification in foods owing to health risks derived from its consumption. Hence, the developed methodology was applied to different food condiment samples in order to determine their RhB content. The results (Table 4) indicate that all four of the condiment samples contained RhB (in the concentration range of 0.7–1.49 μg L^{-1}). The recovery achieved from spiked samples was also satisfactory (Table 4).

Table 3
Comparison of the sensitivity of the proposed method to published methods for the extractive determination of Rhodamine B.

Detection system	Preconcentration method	LOD	Ref.
UV–visible spectrophotometry	CPE (with TX-100)[a]	1.3 μg L^{-1}	[14]
Spectrofluorimetry	SME[b]	0.014 μg L^{-1}	[2]
Mass spectrometry	CPE–LC (with TX-114)[c]	30 μg kg^{-1}	[15]
Spectrofluorimetry	None	0.24 μg L^{-1}	[43]
UV–visible spectrophotometry	SPE[d]	3.14 μg L^{-1}	[44]
Spectrofluorimetry	Micro SPE	1.0 μg L^{-1}	[45]
UV–visible spectrophotometry	SPE–LC	250 μg L^{-1}	[46]
Mass spectrometry	SPE–LC	0.36 μg kg^{-1}	[47]
UV–visible spectrophotometry	LLE[e]–LC	5 μg kg^{-1}	[48]
UV–visible spectrophotometry	DLLME[f]	1.05 μg L^{-1}	[49]
Spectrofluorimetry	CPE (with NaC/SDS)	0.12 μg L^{-1}	Proposed method

[a] CPE refers to cloud point extraction; TX-100 refers to Triton X-100 as surfactant.
[b] Surfactant mediated extraction with the surfactant PONPE-7.5.
[c] Triton X-114 as surfactant.
[d] Solid phase extraction.
[e] Classical liquid–liquid extraction (with acetone/hexane).
[f] Ionic liquid based dispersive liquid–liquid microextraction; ionic liquid was 1-hexyl-3-methylimidazolium hexafluorophosphate.

Table 4
Determination of RhB in different food condiment samples.

Sample	RhB added ($\mu g\ L^{-1}$)	RhB found $\pm$ $\pm$ CV($\mu g\ L^{-1}$)	Recovery (%, $n=3$)	RhB found (ng/g)[a]
Paprika	–	1.06 ± 0.01	–	530
	1.19	2.33 ± 0.02	106.6	
	2.39	3.41 ± 0.01	98.4	
Chimi churri	–	1.49 ± 0.03	–	745
	1.19	2.84 ± 0.02	113.3	
	2.39	3.80 ± 0.02	96.7	
Rice spice	–	0.70 ± 0.01	–	350
	1.19	1.88 ± 0.04	99.2	
	2.39	3.10 ± 0.07	100.2	
Pizza spice	–	0.75 ± 0.02	–	375
	1.19	2.16 ± 0.03	118.9	
	2.39	3.03 ± 0.05	95.3	

[a] RhB contained in 1 g of sample.

These results indicate that the proposed method can be successfully employed for the determination of RhB in different food stuffs.

4. Conclusions

An on-line surfactant mediated extraction method using NaC/SDS as the coacervate extractant phase with fluorimetric detection for determination of trace amounts of RhB in food condiments has been developed. The method is safe, convenient, simple, economic and rapid as well as sensitive. The proposed methodology offers a viable alternative to the conventional methods for determination of RhB in food stuffs. The same general methodology should be applicable for the analysis of RhB content in a variety of other products as well. In addition, this method presents the first report on the utilization of a bile salt surfactant (NaC) in a surfactant mediated extraction application.

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