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A multicommuted stop-flow system employing LEDs-based photometer for the sequential determination of anionic and cationic surfactants in water

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ABSTRACT

It has been developed an automatic stop-flow procedure for sequential photometric determination of anionic and cationic surfactants in a same sample of water. The flow system was based on multicommutation process that was designed employing two solenoid micro-pumps and six solenoid pinch valves, which under microcomputer control carry out fluid propelling and reagent solutions handling. A homemade photometer using a photodiode as detector and two light emitting diodes (LEDs) with emission at 470 nm (blue) and 650 nm (red) as radiation sources, which was tailored to allow the determination of anionic and cationic surfactants in waters. The procedure for anionic surfactant determination was based on the substitution reaction of methyl orange (MO) by the anionic surfactant sodium dodecylbenzene sulfonate (DBS) to form an ion-pair with the cetyl pyridine chloride (CPC). Features such as a linear response ranging from 0.35 to 10.5 mg L^{-1} DBS ($R = 0.999$), a detection limit of 0.06 mg L^{-1} DBS and a relative standard deviation of 0.6% ($n = 11$) were achieved. For cationic surfactant determination, the procedure was based on the ternary complex formation between cationic surfactant, Fe(III) and chromazurol S (CAS) using CPC as reference standard solution. A linear response range between 0.34 and 10.2 mg L^{-1} CPC ($R = 0.999$), a detection limit of 0.05 mg L^{-1} CPC and a relative standard deviation of 0.5% ($n = 11$) were obtained. In both cases, the sampling throughput was 60 determinations per hour. Reagents consumption of 7.8 μg MO, 8.2 μg CPC, 37.2 μg CAS and 21.6 μg Fe(III) per determination were achieved. Analyzing river water samples and applying *t*-test between the results found and those obtained using reference procedures for both surfactant types provide no significant differences at 95% confidence level.

1. Introduction

Nowadays, surfactants comprise a set of chemical compounds widely used for several purposes and among the usual products one could cite detergents, shampoos, soaps, cosmetics, etc. [1–3]. The surfactants consumption has been increased with the economical development of the populations, therefore, contributing to increase the pollution of tap water

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sources. Intending to prevent water pollution, governmental agencies involved with control of water quality have been established normative indicating the maximum concentration that could be acceptable [4,5]. In this sense, the water source for human consumption such as rivers, lakes and dams must be monitored in order to assure that surfactant concentration does not surpass the tolerated limits.

Spectrophotometric methods for cationic surfactant determination are frequently based on the formation of ion-pairs with anionic dyes such as disulfine blue, bromophenol blue and methylene blue [6–8]. These procedures require an extraction step with organic solvents such as chloroform, which undergoes environmental restriction due to its toxicity for living organisms.

The reference method for anionic surfactant determination in water is based on liquid–liquid extraction involving several sample processing steps carried out manually [9], thus requiring a long time to perform analysis and generating a big volume of organic waste. These disadvantages were surpassed employing a procedure based on multicommutation process, where improvement of throughput and drastic reduction on consumption of organic solvent were achieved without any significant loss of sensitivity [10]. Albeit the use of less organic solvent could be considered as an advantage, chloroform presents an environmental lifetime very long, thus requiring laborious and careful waste management. In this sense, analytical procedures without using organic solvents should be useful. This requirement was achieved employing methods based on flow injection analysis (FIA) [11–13].

Analytical procedures employing adsorption on silica gel with detection by spectrophotometry, and potentiometric titration with ion selective electrodes have been also proposed [14,15]. These procedures do not use organic solvents, but involve tedious manual processing. This drawback could be surpassed adopting procedures based on flow injection analysis [16–18]. Employing this methodology throughput improvement could be easily attained, nevertheless the continuous pumping of the reagents solutions could imply in the generation big volumes of wastes. This effect could be considered as an inherent feature of the classical FIA process, which could be minimized designing the manifold of the flow system based on sequential injection analysis [19,20] or multicommutation process [21,22].

The core of the flow system network based on multicommutation is constituted by a set of solenoid valves, which are designed to work as independent commutation units. The flow system manifold is controlled by a microcomputer in order to insert reagent solution slugs into the analytical path following an intermittent pattern, thus affording a significant reduction of reagent consumption as well as waste generation [23,24].

Peristaltic pump has been the most widely employed device to displace solutions in the flow systems presenting as main features the stability of the selected flow rate, which is an essential condition to assure a good performance of the flow systems. The solenoid micro-pumps were introduced 4 years ago as an alternative to fluid propelling in flow system to replace peristaltic pumps [25]. The flow system based on micro-pumps has been designed employing one propelling device for each solution, which were controlled by microcomputer, thus permitting that solutions flow rates could be individually varied by software. Exploiting these features analytical procedures for analytes determination in different matrices have been proposed providing low reagent consumption [26–29]. Analytical procedures based on multicommutation process have been implemented by employing flow system manifolds designed utilizing three-way solenoid valves. The flow systems have been designed employing either a single pumping channel to handle the solutions [30,31] or one pumping channel for each solution [32]. In the first case, solutions are displaced through the analytical path by suction (pumping-pull mode), while in the other one they are pumped (pumping-push mode). When sample processing steps such as extraction with organic solvent or chemical conversion using enzymes immobilized on glass beads were incorporated to flow system, the pumping-push mode is preferred [33,34]. In both cases, the flow systems have been designed employing three-way solenoid valves, albeit in the procedures designed to displace solutions in the pumping-pull mode, these valves have been assembled to work as a single input/output device. This working condition could be obtained using pinch solenoid valves, which present a simplest function structure than that of the three-way solenoid valves [35].

In the earlier works proposed for the determination of cationic and anionic surfactants, the micro-pumps were assembled to work at the solution pumping-push mode, thus requiring a pumping device to propel each solution [28,29]. In this sense, to perform the solutions handling each flow system was assembled employing four micro-pumps. The photometric detection was carried out using diode array spectrophotometer. In the present work, the flow system was designed based on multicommutation process [21–24] employing solenoid micro-pumps to propel solutions and solenoid pinch valves to control the solutions handling. These devices were assembled to afford facilities to allow the determination of both analytes sequentially in a same sample. The detection unit using a homemade LED-based photometer was designed to allow the assembling of photodiode, radiation sources ($\lambda = 470$ and 650 nm) and flow cell to comprise a compact setup. Attention was given to develop a downsized equipment aiming to reduction of reagent consumption and waste generation, presenting also low energy requirement to permit its use in the field condition.

2. Experimental

2.1. Reagents and samples

All solutions were prepared with analytical grade chemicals. Purified water presenting conductivity less than 0.1 $\mu S\,cm^{-1}$ was used throughout.

A 1.0×10^{-3} mol L^{-1} DBS ($C_{18}H_{29}NaO_3S$) stock solution was prepared by dissolving 0.0436 g of solid (purity 80%) from Sigma–Aldrich in 100 mL of water. Working standard solutions with concentration within the range of 1.0×10^{-6} to 3.0×10^{-5} mol L^{-1} (0.35–10.5 mg L^{-1}) DBS were prepared daily by dilution of the stock solution with water.

A 1.0×10^{-3} mol L^{-1} hexadecylpyridiniun chloride monohydrate (CPC) ($C_{21}H_{38}ClN$) stock solution was prepared by dissolving 0.034 g of solid (purity 99%) from Sigma–Aldrich