



An improved approach for flow-based cloud point extraction



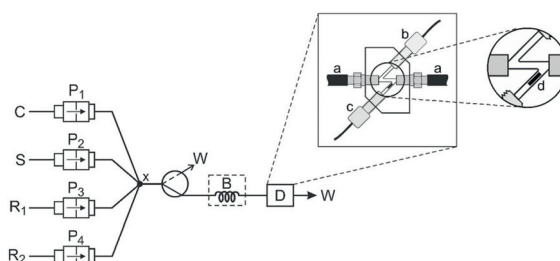
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HIGHLIGHTS

- Direct measurements in the surfactant-rich phase retained in the flow-cell.
- Avoid using organic solvents for elution.
- Improved mixing and heating by the pulsed flow.
- Retention and removal of the surfactant-rich phase by modifying the flow-rate.
- On-line neutralization reaction successfully exploited to induce the cloud point.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel strategies are proposed to circumvent the main drawbacks of flow-based cloud point extraction (CPE). The surfactant-rich phase (SRP) was directly retained into the optical path of the spectrophotometric cell, thus avoiding its dilution previously to the measurement and yielding higher sensitivity. Solenoid micro-pumps were exploited to improve mixing by the pulsed flow and also to modulate the flow-rate for retention and removal of the SRP, thus avoiding the elution step, often carried out with organic solvents. The heat released and the increase of the salt concentration provided by an on-line neutralization reaction were exploited to induce the cloud point without an external heating device. These innovations were demonstrated by the spectrophotometric determination of iron, yielding a linear response from 10 to 200 $\mu\text{g L}^{-1}$ with a coefficient of variation of 2.3% ($n=7$). Detection limit and sampling rate were estimated at 5 $\mu\text{g L}^{-1}$ (95% confidence level) and 26 samples per hour, respectively. The enrichment factor was 8.9 and the procedure consumed only 6 μg of TAN and 390 μg of Triton X-114 per determination. At the 95% confidence level, the results obtained for freshwater samples agreed with the reference procedure and those obtained for digests of bovine muscle, rice flour, brown bread and tort lobster agreed with the certified reference values. The proposed procedure thus shows advantages in relation to previously proposed approaches for flow-based CPE, being a fast and environmental friendly alternative for on-line separation and pre-concentration.

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1. Introduction

In 1978, cloud point extraction (CPE) was first exploited for analytical purposes by pre-concentration of zinc(II) after formation of an hydrophobic complex with 1-(2-pyridylazo)-2-naphthol [1]. Since then the approach has been widely explored as a green alternative to the conventional liquid–liquid extraction [2].

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In CPE, non-ionic surfactants above the critical micelle concentration (CMC) in aqueous solutions separate into two isotropic phases (a surfactant-rich phase (SRP) and an aqueous phase with surfactant concentration close to the CMC) when system is disturbed by increasing the temperature or by addition of salts. This phenomenon enables the extraction of hydrophobic species that are involved by the micelle aggregates, with potential for pre-concentration due to extraction with low volumes of surfactants. However, the steps usually involved in batch CPE (*i.e.* heating, centrifugation, phase separation and dilution of the SRP) make the procedure time-consuming and can affect reproducibility [3].

Coupling CPE to flow analysis circumvents time-consuming steps of batch procedures and minimize waste generation, without hindering the extraction efficiency [3]. However, induction of cloud point, retention of the SRP and detection of low amounts of analyte in the presence of high amounts of the surfactant are critical aspects. In relation to this last aspect, spectrophotometric measurements can be hindered by light scattering and FAAS or ICP OES detection can be impaired by changes in the nebulization efficiency.

Fang et al. [4] were the pioneers in the proposal of on-line CPE for determination of porphyrins in urine samples. Sample solutions, also containing the surfactant, were mixed by confluence with a saline solution ($(\text{NH}_4)_2\text{SO}_4$) to induce the cloud point (salting out effect), thus avoiding the use of an external heating system. The SRP was retained in a column packed with a filter material (*e.g.* cotton, glass wool or filter cigarettes). After elution with acetonitrile, the retained material was mixed with reagents aiming detection by chemiluminescence exploiting the peroxyoxalate system. In spite of the novelty, this procedure has some drawbacks such as addition of the surfactant to the samples before insertion into the FIA system and need for elution before detection, which causes inherent dilution and requires an organic solvent, thus diminishing the greenness of the procedure.

Strategies similar to that proposed in the pioneer work (*i.e.* cloud point induced by salting-out, retention of the SRP in a cotton-packed column and elution to the detection system) were further exploited for determination of chromium by chemiluminescence with elution by a complexant solution containing Triton X-100 [5], mercury by spectrophotometry with elution by hot water [6], antimony speciation by ETV-ICP OES with elution by acetonitrile [7], and silver by FAAS with elution by tetrahydrofuran [8]. Other applications exploited FAAS for manganese determination with elution by $0.05 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ [9] or $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ [10] or metal ions with elution by $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ plus 50% acetone [11]. Some works have exploited a heating device for cloud point formation (*e.g.* determination of dysprosium in urine by ICP OES [12]) or to improve CPE in conjunction with salting-out effect [6,13]. CPE

was also exploited before chromatographic separation of HPAs extracted from soil, being the SRP retained in a column containing silica-gel and eluted by acetonitrile/water (7:3) [14]. In other works, exploiting detection by ETAAS, a knotted reactor replaced the column filled with cotton wool for pre-concentration of cobalt [15] or a column filled with silica gel was used for retaining the SRP followed by elution with acetonitrile for lead determination [16]. A novel approach was proposed to avoid dilution of the SRP before detection [17]: a column filled with cotton was placed in front of a photomultiplier aiming at the determination of total serum bilirubin by chemiluminescence.

This paper presents new strategies for flow-based CPE in a multi-pumping flow system (MPFS-CPE) in order to overcome the drawbacks usually found in literature works. Solenoid micro-pumps were employed to modulate the flow-rate and improve the mixing conditions in order to assist the formation of the cloud point. Sensitivity was increased by carrying-out the spectrophotometric measurements directly in the SRP, which was temporarily retained in the optical path. An on-line neutralization reaction was exploited to induce the cloud point, thus avoiding the use of an external heating device.

2. Experimental

2.1. Apparatus

The flow-based system comprised four solenoid micro-pumps (Biochem Valve Inc., Boonton, NJ, USA) of 11, 10, 13, and $8 \mu\text{L}$ (P_1 , P_2 , P_3 , and P_4 , respectively); one three-way solenoid valve (NResearch, West Caldwell, NJ, USA); transmission lines of 0.8 mm i.d. PTFE tubes and acrylic joint points.

The active devices were controlled by a Pentium I microcomputer equipped with a parallel interface through a power drive based on the ULN2803 integrated circuit. The control software was developed in Microsoft Visual Basic 6.0. Measurements were carried out with a CCD multichannel spectrophotometer (Ocean Optics, Dunedin, FL, USA; model USB2000) with data acquisition by the software provided by the manufacturer. Optical fibers were used for radiation transmission from a tungsten-halogen lamp (Ocean Optics, model LS-1) to a Z-shape flow-cell (20-mm path-length, PEEK material, Ocean Optics) and from the cell to the detector array. The cotton filter (*ca.* 1.0 mg) was introduced into output of the flow-cell (see the inset of Fig. 1) to retain the SRP at the optical path. The cotton filter was replaced once a week to avoid clogging and assure the effective retention of the SRP. The replacement was fast (took only *ca.* 1 min) and reproducible (response variations lower than 10%).

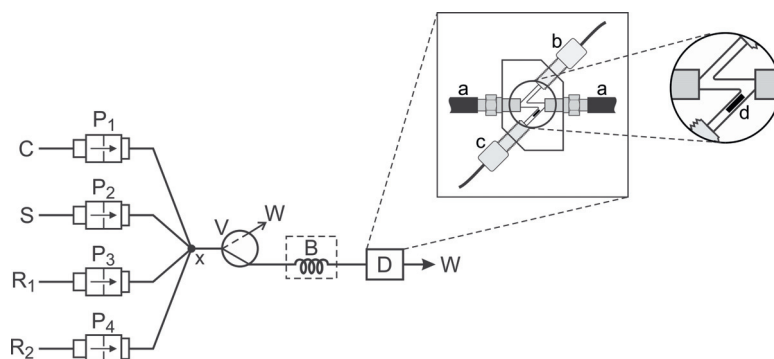


Fig. 1. Flow-based system for on-line cloud point extraction. P_1 – P_4 : solenoid micro-pumps; R_1 : chromogenic reagent ($800 \mu\text{mol L}^{-1}$ TAN + 1.5% (w/v) Triton X-114 in 0.5 mol L^{-1} acetate buffer, pH 5.5); B: 100-cm mixing coil; S: sample; V: three-way solenoid valve; D: Z-shape flow-cell (20 mm, $52 \mu\text{L}$ volume) coupled to a fiber-optic spectrophotometer (a: optical fibers; b: flow-cell input; c: flow-cell output; d: cotton piece); W: waste vessel. Flow system with external heating – C: water carrier; dashed lines indicate that the coil was heated at $(40.0 \pm 0.1)^\circ\text{C}$. System with on-line neutralization – R_2 : neutralizing solution (1.4 mol L^{-1} NaOH and 1.6 mol L^{-1} NaCH_3COO) and C: 0.1 mol L^{-1} NaCH_3COO .

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