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Stability of benzalkonium surfactants on hemimicelle-based solid-phase extraction cartridges

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Abstract

The capability of hemimicelle-based solid-phase extraction cartridges for the preservation of organic compounds after their concentration from water samples was investigated for the first time. The approach is illustrated by studying the stability of benzalkonium homologue (C_{12}, C_{14} and C_{16}) surfactants (BAS) on monolayers of dodecyl sulphate (SDS) hemimicelles formed on alumina. The stability study included storage of cartridges at room temperature, at 4 and −20 °C, during a period of up to 3 months. The influence of water matrix components was also investigated from parallel experiments using spiked distilled, river and wastewater samples. Complete recovery of BAS was obtained for all storage conditions tested. Recoveries were independent on the alkyl chain length of BAS homologues and water matrix. The SPE of BAS on the SDS hemimicelles had a strong stabilizing effect for the target compounds and their analysis can be accomplished after at least 3 months without the necessity of special storage conditions for cartridges. Because of the lack of data, an additional stability study was carried out for BAS in an aqueous matrix using traditional preservation methods such as acidification (pH 2)/refrigeration, addition of formaldehyde (5%)/refrigeration, and freezing (−20 °C). Only combination of chemical addition (e.g. nitric acid or formaldehyde)/refrigeration was found effective to preserve BAS in the short term (e.g. for a week), then losses up to 40% were observed for these target compounds after a month.

Keywords: Benzalkonium; Cationic surfactant; Admicelle; Hemimicelle; Stability; Storage; SPE

1. Introduction

Preservation of sample integrity during storage and transport constitutes an important issue in environmental monitoring programs. The preservation process encompasses both field and laboratory activities and includes a variety of techniques including chemical addition, temperature control and the choice of sampling containers [1]. Because trace enrichment is a necessary step for many pollutant analyses, an interesting alternative to traditional sample transport and storage has been to use on-site solid-phase extraction (SPE) of pollutants and stabilize organic compounds on the sorbent cartridge. In this way, environmental monitoring programs can be greatly simplified. Benefits of this strategy have been discussed for the extraction of a variety of pollutants (e.g. hydrocarbons [2], pesticides [3–7], phenols [8], dyes [9,10], non-ionic/anionic surfactants [11]) from environmental water samples, using different sorbent materials.

Hemimicelles and admicelles have been recently used as sorbent materials in SPE for the extraction of organic compounds [12–16]. Hemimicelles consist of monolayers of surfactants adsorbing head down on an oppositely charged mineral oxide surface (e.g. alumina, silica, titanium dioxide, ferric oxyhydroxide). Admicelles are surfactant bilayers formed from hemimicelles, under addition of more surfactant, by interaction of surfactant hydrocarbon chains. A main characteristic of these sorbents is their versatility. On the one hand, the outer surface of the hemimicelle and admicelle is hydrophobic and ionic, respectively, providing different mechanisms for retention of organics. On the other hand, the number of surfactants commercially available is very high, so both the degree of hydrophobicity and the charge of the sorbent can be easily modified according to the nature of ana-

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lytes. As a result, high extraction yields have been obtained for organic compounds of different nature such as hydrophobics [12,15], ionics [14] and amphiphilics [13,16]. Because the potential of hemimicelles and admicelles for the SPE of pollutants, their ability to preserve organic compounds after on-site extraction deserves to be researched.

This paper deals with the assessment of the performance of hemimicelles for the stabilization of benzalkonium surfactants (BAS) after their extraction from environmental water samples. These surfactants are used in large amounts as fabric softeners and disinfectants. The western European surfactants market is currently estimated at 2.2 M tonnes, of which about 9% are cationic (mainly ammonium quaternary salts) surfactants [17]. Most uses of BAS lead to their release to wastewater treatment systems where they adsorb strongly and rapidly to suspended solids and sludge [18]. As a result, levels of BAS in surface-water samples are in the low microgram-per-litre range which compels us to use a preconcentration step prior to chromatographic analysis [13,19].

Different sorbent materials have been proposed for SPE of BAS [13,19,20]. The use of nonpolar silica sorbents (e.g C_{18}) is not recommended because the strong interaction of these cationic surfactants with the silanol groups which results in very broad elution bands. This problem can be solved using neutral polymeric sorbents, but BAS extraction recoveries are about 75% [19]. The use of sodium dodecyl sulphate (SDS) hemimicelles on alumina has proved to be a very convenient sorbent for these surfactants because both, the high BAS retention, derived from the formation of analyte:extractant mixed aggregates, and the easy BAS desorption, derived from the fast disruption of hemimicelles in the presence of organic solvents and the electrostatic repulsion between BAS and the positively charged alumina surface [13]. A similar approach, using dodecyl sulphate attached to an anion exchange resin has been recently proposed for extraction of BAS [20].

To our knowledge, no studies concerning the stability of BAS in SPE sorbents have been described. Known factors affecting BAS stability include adsorption on containers and microbiological degradation. Significant adsorption of BAS (around 90%) on glass, polypropylene and Teflon containers have been reported for filtered water samples stored at 4 °C [19], however, no BAS adsoption on glass containers at pH 2 [13] or under addition of acetonitrile to make a 25% solution [18] has been detected. Studies on aerobic biodegradability of BAS, using biodegradation tests, have proved that C_{12} and C_{14} BAS homologues undergo complete primary biodegradation in the first week and are ultimately biodegradable (i.e. mineralised) with >80% of CO_2 release on the 11th day [21]. On the other hand, the extent of primary biodegradation found for C_{16} BAS was only 30%, and non ultimate biodegradation was observed for this homologue [21]. Biodegradation of BAS in river water is considerably reduced by complexation with an anionic surfactant [22], and this behaviour is expected to be a stabilizing factor for BAS on SDS hemimicelle cartridges.

In this work, the storage stability of C_{12}, C_{14} and C_{16} BAS homologues on SDS hemimicelles-alumina cartridges was investigated during a period of 3 months at three different temperatures (−20, 4 °C and room temperature). The influence of light and matrix composition on BAS stability was also investigated. Because of the lack of data on the stability of BAS solutions treated with traditional preservation procedures, we also investigated the stability of BAS under acidification (pH 2)/refrigeration (4 °C), addition of 5% formaldehyde/refrigeration (4 °C), and freezing (−20 °C). The final goal of this research was to contribute to the knowledge of the ability of supramolecular sorbents to stabilize organic compounds and to establish preservation conditions for BAS in environmental water samples.

2. Experimental

2.1. Chemicals and materials

Benzyldimethyldodecylammonium bromide (BDDA), benzyldimethyltetradecylammonium bromide (BDTA), benzyldimethylhexadecylammonium chloride (BDHA) and sodium dodecyl sulfate (SDS) surfactants were supplied by Aldrich (Milwaukee, WI). Nitric acid, ammonia (30%, w/v), formaldehyde (35–40%, w/v) and HPLC-grade methanol were obtained from Panreac (Madrid, Spain). Formic acid was purchased from Merck (Darmstadt, Germany). Bond Elut Jr. cartridge columns filled with 500 mg of acid alumina (particle size 25 μm) were obtained from Varian (Victoria, Australia).

2.2. Stability studies

2.2.1. Sample preparation

Stability studies were carried out using spiked distilled water. For this purpose, stock standard solutions of BAS (60 mg/l) were prepared in methanol. Samples (0.25 l) in dark glass containers were spiked to obtain a final concentration of 48 μg/l of each surfactant. Then, they were treated with different preservation methods [hemimicelle-based cartridges, acidification (pH 2)/refrigeration (4 °C), addition of 5% formaldehyde/refrigeration (4 °C), and freezing (−20 °C)], and stored under different conditions. Duplicate samples were analysed for each experimental condition studied. Recoveries of BAS a time zero were established for each preservation method investigated and data on stability were normalised to these results. The matrix effect on the stability of BAS preconcentrated on hemimicelle-based cartridges was investigated using river and wastewater samples. River samples were taken from the Rabanales in Córdoba city. Treated sewage samples were collected from the wastewater treatment plant (WWTP) of Bailén in the south of Spain. Bailén WWTP receives ∼40–50% industrial effluents (mainly from brickworks, and ceramic and olive oil industries) mixed with ∼50–60% domestic wastewaters.

Samples were collected in dark glass containers. Immediately they were filtered through 0.45 μm filters (Whatman GF/F, Osmonics, France) in order to remove suspended solids, and then they were spiked to obtain a final concentration of 48 μg/l of each surfactant. Blank river and wastewater samples were analysed prior to spiking BAS.

2.2.2. *BAS preservation on hemimicelle-based SPE cartridges*

Fig. 1 shows the different steps followed to preserve BAS on hemimicelle-based SPE cartridges. Three kinds of experiments were designed to investigate the effect of using (a) different desiccation treatments, (b) dark conditions and (c) various temperatures, on BAS stability. The common protocol was as follows: spiked water samples were adjusted to pH 2 by the addition of nitric acid to avoid the adsoption of BAS on the wall of sample containers [13]. Bond Elut Jr. cartridge columns were conditioned with 5 ml of distilled water (pH 2). The hemimicelles were formed on the alumina by passing a 10 ml solution containing 12.5 mg of SDS at pH 2. The sorbent was not allowed to dry and then, 0.25 l of the spiked water samples were loaded on the hemimicelles using a vacuum pump (Eyela A35, Rikakikai Co., Tokyo), at a flow rate of 10 ml/min. Then, the percolated samples were subjected to the three kinds of experiments above specified: (a) Desiccation studies were carried out using the Eyela vacuum pump, for times ranging from 3 to 5 min (the time necessary to not observe water drops leaking out the cartridge) to 1 h. Wet cartridges (i.e. without drying) were also analysed at the same times. (b) Dark conditions were obtained by initially wrapping the cartridges up with aluminium foil. Drying of the percolated samples was stopped when not water drops were leaked out the cartridge. It took about 3–5 min. The cartridges containing the preconcentrated BAS were stored at room temperature for a period of 1 month and BAS concentrations were determined weekly. Non-covered cartridges were also analysed at the same times. (c) The effect of the temperature on BAS stability was studied by using non-covered

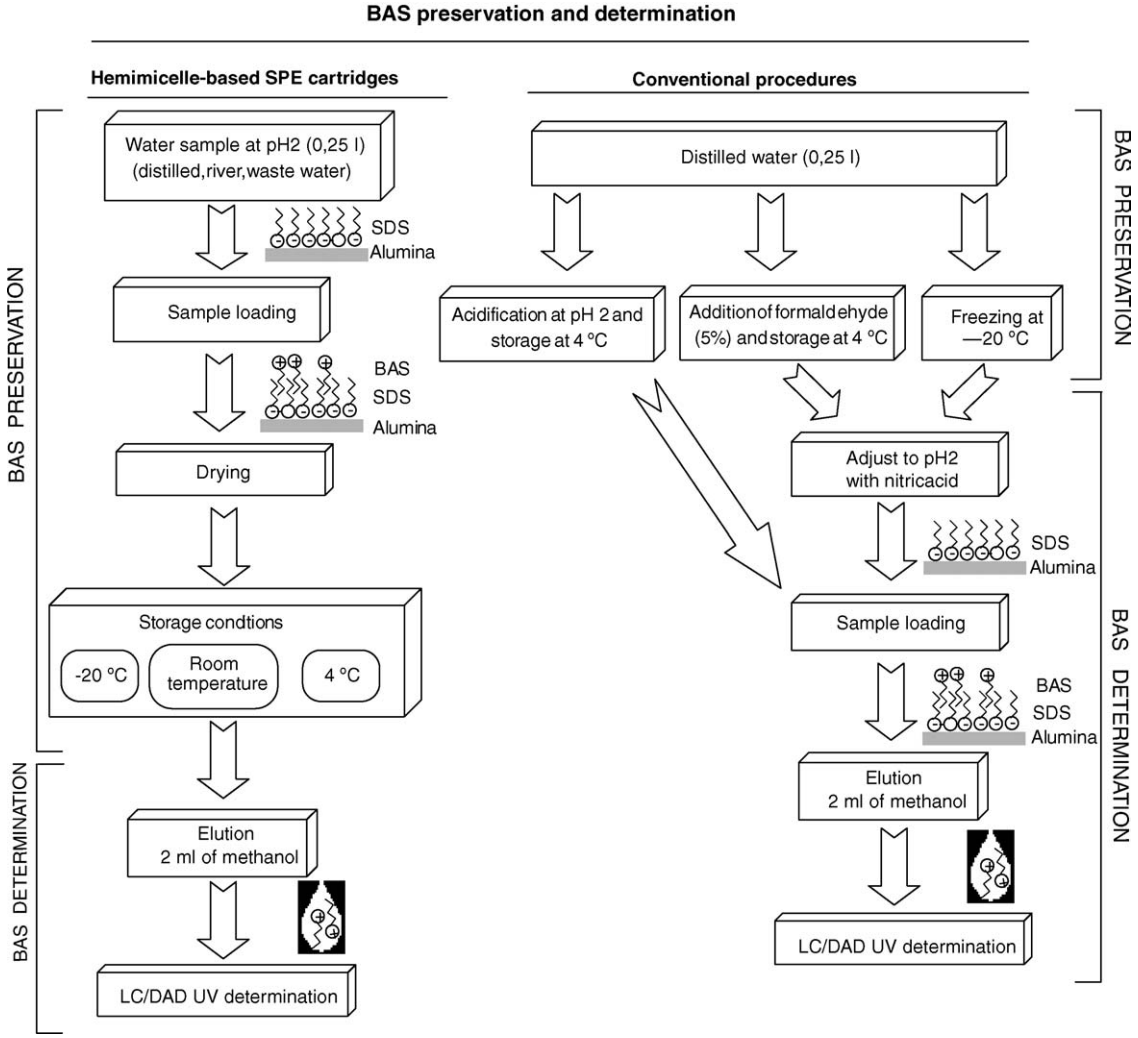

Fig. 1. Scheme of the different steps followed for the preservation/determination of BAS using hemimicelle-based cartridges and conventional procedures for storage of samples.

cartridges. After drying the percolated samples for 3–5 min, the preconcentrated BAS were stored at −20, 4 °C and room temperature for a period of 3 months. BAS concentrations were analysed after 0.25, 0.5, 0.75, 1, 2 and 3 months. The cartridges at 4 °C and −20 °C were brought to room temperature for 15 min and 1 h, respectively, prior to the determination of BAS.

2.2.3. BAS preservation using conventional procedures

The stability of spiked distilled water samples (0.25 l), contained in dark glass bottles, was also studied according to the following conventional procedures (see Fig. 1):

- They were adjusted to pH 2 by the addition of concentrated nitric acid and stored at 4 °C.
- Formaldehyde was added to make a final concentration of 5% and then, the samples were stored at 4 °C.
- Samples were frozen at –20 °C.

Stability measurements were performed at time zero and at each week for a month.

2.2.4. BAS determination

The sequence followed for BAS determination, after their storage under different conditions, is depicted in Fig. 1. BAS stored on hemimicelle cartridges were eluted with 2 ml of methanol and aliquots of the eluate (typically 20 μl) were injected into a LC/DAD UV system. Samples preserved by conventional procedures were adjusted at pH 2 and preconcentrated on SDS hemimicelles-based cartridges according to the procedure previously described (Section 2.2.2). Then, elution with 2 ml of methanol and injection of an aliquot in the chromatograph was performed.

Liquid chromatographic analysis was made using a Waters 616 multisolvent pump and a 717 autosampler. The stationary-phase column was a 10-cm BDS Hypersil C_{18} column with 4.6 mm i.d. and 3 μm particle diameter (ThermoQuest, San José, CA, USA). The mobile phase consisted in an isocratic mixture of 50 mM ammonium formate at pH 3.5 (5%) and methanol (95%), at a flow rate of 0.4 ml/min. The time required to complete the chromatogram was 20 min. Measurements were performed at 210 nm using a 996 diode array detector. External calibration was used for quantitative determination. Linearity was obtained for BAS concentrations between 2 and 40 mg/l.

3. Results and discussion

3.1. Analytical performance

Combination of SDS hemimicelle-based SPE with liquid chromatography/electrospray ionization in positive ion mode/ion trap mass spectrometry has been previously proposed by our research group for the quantification of BAS at the levels found in environmental waters (i.e. low μg/l) without interference of the major surfactants (i.e. anionic and non-ionic) and electrolytes [13]. Recoveries of BAS homologues from SDS hemimicelles were found quantitative and independent of the alkyl chain length under a wide range of experimental conditions. The strong retention of BAS was a consequence of their hydrophobic and electrostatic interactions with the surfactant coating the mineral oxide.

A simpler technique (i.e. liquid chromatography/UV detection) was used in this work to control the stability of BAS in SDS hemimicelles since its performance was enough for this purpose. BAS were monitored at 210 nm because of this wavelength provided the best signal to noise ratio in the range 210–250 nm. Recoveries of BAS from distilled water, river water and wastewater, spiked with 48 μg/l of each homologue, was nearly 100% and no interference was detected from the components of the different matrices using this detection system. No clean-up steps were required to determine benzalkonium surfactants in the environmental water samples analysed.

Calibration curves obtained for BAS homologues were linear in the concentration range 2–40 mg/l. These calibrations covered the whole concentration range in which the stability study was carried out taking into consideration the possibility of diminution of the concentration of BAS due to degradation. The instrumental detection limits were calculated from blank determinations by using a signal-to-noise ratio of 3. They ranged between 0.8 and 1.2 mg/l. The precision of the method was evaluated by extracting 11 independent spiked (48 μg/l) distilled water samples. The relative standard deviation was always between 4 and 6%.

3.2. Stability studies

3.2.1. Stability of BAS in water samples

The ability of traditional stabilization procedures to preserve BAS at the levels found in environmental water samples was assessed. In order to decrease microbiological degradation the strategies tested always included the use of refrigeration or freezing (see Fig. 1). Adjustment of the pH solution at 2, to decrease BAS adsorption on the glass container, and addition of formaldehyde, a typical stabilizing agent for organic compounds, were used in combination with refrigeration. All experiments were carried out under dark conditions.

Fig. 2 shows the results obtained for the study of the stability of BAS in spiked (48 μg/l) distilled water samples, for a period of a month, using the three conventional procedures specified in Fig. 1. Combination of both chemical addition (i.e. nitric acid or formaldehyde) and decrease of the temperature was the only effective way to preserve BAS in the short term (i.e. for a week). Then progressive losses of these cationic surfactants, which were higher as the alkyl chain length increased, were found. Therefore, chemical addition/refrigeration is not a useful strategy for preservation of BAS in the medium-long term. Freezing of samples did not improve the stability of BAS suggesting that adsorption on containers was an important issue for the loss of these cationic surfactants.

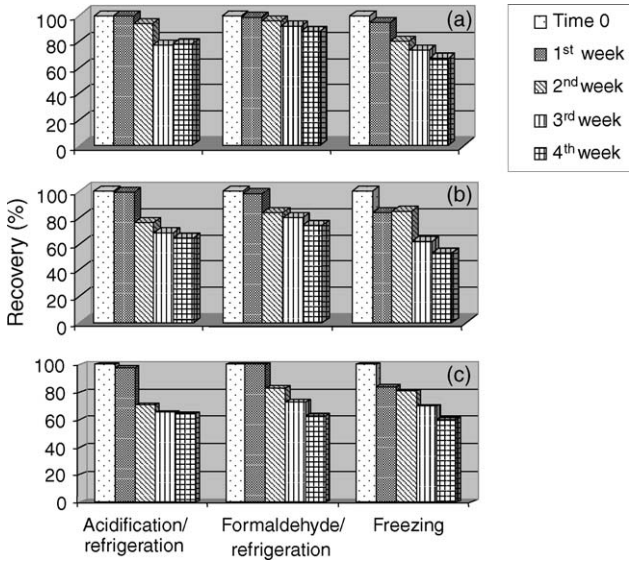

Fig. 2. Recovery of (a) benzyldimethyldodecylammonium; (b) benzyldimethyltetradecylammonium and (c) benzyldimethylhexadecylammonium surfactants from spiked (48 μg/l) distilled water after storage under different conventional preservation methods.

This study indicates that, before using traditional preservation procedures for monitoring campaigns involving BAS, additional research should be developed to ensure that the integrity of these target compounds is kept. Because of the convenience of using SPE cartridges to preserve pollutants in terms of transportation costs and simplicity, we focused in this research on the stability of BAS in hemimicelles and we did not try to find the optimal preservation conditions for BAS using conventional procedures.

3.2.2. Stability of BAS on hemimicelle-based SPE cartridges

3.2.2.1. Effect of water removal and dark conditions on BAS stability. Residual water surrounding the sorbent after sample filtration has been described to cause hydrolysis of susceptible compounds [23]. So, different desiccation treatments have been proposed to enhance the stability of analytes stored on SPE cartridges or disks [3–11]. The effect of water removal after percolation of the sample on the stability of BAS was assessed by drying the cartridges with a vacuum pump for times ranging between 3 min and 1 h. BAS recoveries decreased about 4–5% after their storage in wet cartridges at room temperature for 1 day. Partial drying of cartridges stabilized the target compounds and recoveries were quantitative after their storage at room temperature for at least a week. No effects of the drying time on BAS stability were observed. So, drying of cartridges for 3–5 min after percolation of the sample was proposed.

The storage of cartridges under dark conditions (i.e. using aluminium foil wrapped cartridges) was not necessary to achieve BAS stability. Recoveries obtained for the target compounds from aluminium foil wrapped cartridges (Table 1) and non-covered ones (top of Table 2), stored at room temperature for a month, were similar. Therefore, natural illumination in the lab (i.e. that from sunlight) did not affect BAS stability and further experiences were carried out using non-covered cartridges.

Table 1
Mean recoveries (%) of benzalkonium surfactants after storing the SDS-hemimicelles aluminium foil wrapped cartridges at room temperature

Storage time (week)	BDDA (%)	BDTA (%)	BDHA (%)
0	100	100	100
1st	100	98	97
2nd	106	96	96
3rd	98	105	96
4th	103	95	102

Adjustment of the pH of samples at 2 prevented the adsorption of BAS on the wall of the materials used in the analytical process, as it can be derived from the quantitative recoveries obtained for the target compounds under the different experimental conditions investigated.

3.2.2.2. Effect of the cartridge storage temperature on BAS stability. For this study, hemimicelle-based SPE cartridges loaded with spiked distilled water were analysed during a 3-month period. After preconcentration, the cartridges were dried and then stored at −20, 4 °C and at room temperature, respectively. Before elution, cartridges at −20 and 4 °C were kept at room temperature for a period varying between 5 min and 5 h in order to defrost the sample and/or avoid variability problems. It was found that sorbents should be kept at room

Table 2
Mean recoveries (%) of benzalkonium surfactants after storing the SDS-hemimicelles cartridges at different temperature values

Storage conditions	Storage time (week)	BDDA (%)	BDTA (%)	BDHA (%)
Room temperature	0	100	100	100
	1st	96	97	98
	2nd	97	101	97
	3rd	94	97	99
	4th	96	101	94
	8th	101	97	94
	12th	104	99	97
4 °C	0	100	100	100
	1st	102	98	100
	2nd	105	104	105
	3rd	114	103	98
	4th	97	103	103
	8th	103	98	96
	12th	99	97	98
−20 °C	0	100	100	100
	1st	105	100	94
	2nd	101	98	94
	3rd	94	97	94
	4th	95	95	95
	8th	96	96	95
	12th	94	94	95

Table 3
Recoveries (%) of benzalkonium surfactants from spiked environmental water samples after storing the SDS-hemimicelles cartridges at 4 °C for a month

Time (week)	Waste water (effluent)			River water		
	BDDA (%)	BTDA (%)	BHDA (%)	BDDA (%)	BTDA (%)	BHDA (%)
0	100	100	100	100	100	100
1st	96	100	96	98	102	94
2nd	104	104	100	100	96	101
3rd	101	102	95	106	97	101
4th	103	101	94	103	105	104

temperature before elution for at least 15 min and 1 h when they are brought from storage conditions involving 4 and −20 °C, respectively, in order to obtain quantitative and high precision results. So, these times were used through the whole experiment.

Table 2 shows the recoveries obtained for the three BAS homologues under study at the three temperatures examined. SDS hemimicelles had a high stabilizing effect on BAS; the integrity of the target compounds was kept for the whole period of time investigated, independently on the temperature used for storage of cartridges. No differences of recoveries were found for the three homologues, despite C_{12} and C_{14} are known to be more easily biodegradable than C_{16} [20]. The high stability afforded by BAS after formation of mixed aggregates with SDS is in agreement with the biodegradation reduction observed for cationic-anionic surfactant complexes in natural environments [22]. The fact that BAS are stable at room temperature for at least 3 months is an outstanding feature of the stabilizing strategy here proposed since it will permit an easy transportation of the samples preconcentrated on the cartridges to laboratories for analysis.

3.2.2.3. Effect of the water matrix on BAS stability. In order to validate the preservation technique we have to take into account the character of samples since matrix components can degrade the stability of the target compounds. In previous studies using SDS hemimicelle-based SPE [13], no interference has been found for BAS determination from alkylbenzenesulphonates and nonylphenol/alcohol ethoxylates, at the concentration level found in sewage (mg/l), or from other matrix components. The stability of sorbed BAS was investigated using river and wastewater (effluent) samples. Since both kinds of samples contain non-ionic [16] and anionic [24] surfactants and other organic components (e.g. humic material), they were considered appropriate to this purpose. The concentration of BAS was undetectable because the practical detection limit of LC/UV (about 10 μg/l) was superior to the concentrations usually found in these samples (e.g. between 0.1 and 6 μg/l [13,19]). So, spiked samples were used. The loaded cartridges were kept at room temperature and 4 °C for a month. Measurements were carried out weekly for a month. The results obtained (Table 3) indicated that matrix components had not influence on the stability of BAS homologues, thus confirming the high resistance of SDS:BAS aggregates to degradation.

4. Conclusions

From the results reported in this study, it can be concluded that SDS-hemimicelles onto alumina is a valuable sorbent to stabilize BAS after preconcentrating them from environmental samples. The recovery of BAS was found quantitative and independent of the alkyl chain length under the range of temperatures examined (from room temperature to −20 °C) for a period of 3 months. No complete removal of water after percolation of the sample was required for stabilization of BAS; drying the cartridges for 3–5 min with a vacuum pump achieved the stabilization. Storage of cartridges under dark conditions was not required; natural illumination in the lab (i.e. sunlight) did not affect BAS stability.

On the contrary, conventional stabilization procedures, based on chemical addition/refrigeration, were only effective to stabilize BAS in the short term (e.g. for a week). So, the use of hemimicelle-based cartridges presents clear advantages over traditional stabilization methods. In addition to the easy shipping of the disposable SPE pre-columns and their easy storage in the laboratory, the high stability of BAS on the SDS hemimicelles makes possible to analyse the samples after several weeks without special storage conditions.

The results obtained open the possibility of using hemimicelles/admicelles as stabilizing agents in environmental monitoring programs thus extending the applicability of SPE for this purpose. Because of the high ability of these sorbents to concentrate a variety of organic compounds on the basis of different interaction mechanisms, the study on their capacity to stabilize the concentrated compounds is especially interesting in order to use them to integrate different steps of the analytical process, namely, concentration/transport/preservation/clean up. Research on this topic is being carried out by our group at the present.

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