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Dr. D. Puig and Dr. D. Barceló are at the Department Environmental Chemistry, CID-CSIC, c/Jordi Girona, 18-26, 08034 Barcelona, Spain.

Monitoring anionic surfactants (LAS) and their intermediate degradation products in the marine environment

E. González-Mazo*, A. Gómez-Parra
Cadiz, Spain

The determination of synthetic anionic surfactants and their degradation products in environmental samples is a complex problem. This complexity is even greater in seawater, especially from littoral zones, owing to the presence of numerous organic substances that may potentially interfere with the analysis of the samples; more common among these are naturally-occurring surfactant compounds.
Various stages are involved in the determination of linear alkylbenzene sulfonates (LAS), which are the surfactants most used commercially, and their degradation products (sulfophenylcarboxylic acids or SPC); successful completion of these analytical stages should result in the concentration of these compounds, their isolation, their quantification and, in cases where no reference standards are available, their structural identification. At the present time, some of these stages are still under development.

1. Introduction

Coastal ecosystems receive large quantities of surfactants, which are used as the principal constituents of commercial detergents. Among these, linear alkylbenzenesulfonate (LAS) (Fig. 1a), is the anionic surfactant most used in the formulation of detergents and other cleaning products, having a global production of 2.4×10^6 tonnes per year [1]. The environmental behaviour of LAS, as one of the most widely-used xenobiotic organic compounds, has aroused considerable interest and study. Particularly in the last decade, much research has been carried out to develop new analytical techniques for the quantification of this surfactant and its degradation intermediates (Fig. 1b) — sulfophenylcarboxylic acids (SPC). These have pursued the final objective of establishing the distribution of LAS among the various environmental compartments to which it gains access. Although there have been few studies of LAS in marine environments, its behaviour is known in a general way, since the question of the analysis of its different homologues and isomers has been resolved. The same cannot be said for its degradation intermediates, particularly those long-chain intermediates ($C > 7$) for which reference standards are not available, whose identification requires the use of spectroscopic techniques.

* Corresponding author.

0165-9936/96/$15.00
PII S0165-9936(96)00051-9

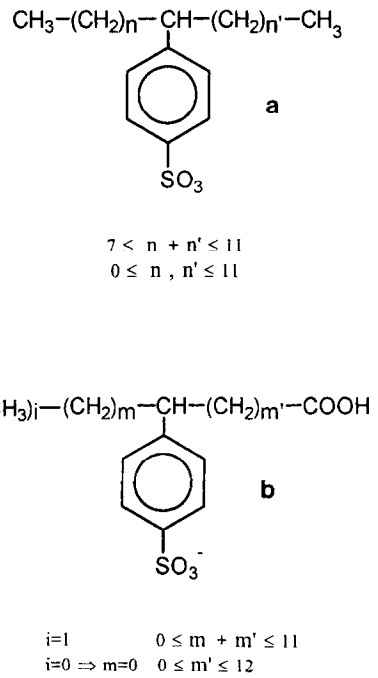

Fig. 1. General chemical structures of the linear alkylbenzene sulfonates (a) and the sulfophenyl carboxylate (b) compounds.

2. Preconcentration and prepurification

The complex composition of marine samples, especially those taken from littoral ecosystems, and the low concentrations in which the anionic surfactants are generally found, have made it necessary to perform an initial stage of concentration and purification of the analyte prior to its analysis. Among the various procedures used, the technique of solid-phase extraction (SPE) is currently considered the most appropriate for this purpose, in terms of its speed, selectivity and percentage of recovery. The hydrophobic and ionic nature of the LAS molecule has consolidated the use of minicolumns of the hydrophobic (C_8, C_{18}, C_2) and strong anionic exchange (SAX) types. However, the recommended order of utilization, as well as the physicochemical conditions under which the samples should be processed and subsequently eluted, differ from one author to another and depend largely on the origin of the samples (Table 1). For example, authors such as Kikuchi et al. [2], use minicolumns of octadecylsilica C_{18}; De Henau et al., [3], use first a SAX and then a C_8 column; Castles et al. [4], use first a hydrophobic type C_2, followed by a SAX; and, lastly, Di Corcia et al. [5], use a graphitized carbon black cartridge (CGB), acting as reversed-phase and anionic exchange at the same time.

In a recent paper, González-Mazo [6], has reviewed the methods proposed by the above authors and has put forward a scheme for purification and concentration by solid-phase extraction which shows good selectivity for LAS and a high recovery percentage over a wide range of concentrations. Designed specifically for samples of marine origin, this procedure keeps to the sequence suggested by Castles et al. [4] — first a hydrophobic type and then a strong anionic exchange (SAX) minicolumn — but substitutes the C_2 type sorbent with the C_{18}, which has been shown to have greater adsorption capacity [7]. The procedure described also optimizes the pH conditions of the samples and the polarity of the various eluents used. The recovery of the LAS in the solid-phase extraction stage is 96.5%±1.5%, a little higher than that obtained by Kikuchi et al. [2] and similar to that obtained by De Henau et al. [3]. However, the recovery of SPC is low, especially those of short chain. In tests carried out with synthetic SPC (C_2–C_5), it was determined that retention in the extraction cartridges is only 20%. Furthermore, Di Corcia et al. [8] demonstrated that when the samples contain appreciable

Table 1
Different methods for the isolation and concentration of LAS

Sample	Method	Ref.
Seawater, sediments, fish	SPE: C_{18}	[2]
Sludge, sewage, soil, river sediments	SPE: SAX + C_8	[3]
Sewage influent, final effluent, river water	SPE: C_2 + SAX	[4]
River water, sewage effluent, primary influent	SPE: graphitized Carbon black cartridge (CGB)	[5]
River water	SPE: C_{18}	[7]
Sea water	SPE: C_8 + SAX + C_8	[38]
Soil, sediment, municipal wastewater, sewage sludge	SFE	[9]
Sewage sludge	SFE	[10]

quantities of fulvic acids, this could have a considerable effect on the retention of the weak organic acids, which include SPCs. This mainly affects extracts derived from samples of sediment. As a solution to this problem, it has been suggested that the standards needed for the analysis should be subjected to the identical treatment as the environmental samples But this is obviously only possible when such standards are available.

The treatment of samples of sediment involves a prior phase of Soxhlet extraction, generally using methanol; the extract is evaporated and, when dry, is dissolved again and processed in the same way as the samples of water.

In addition, the use of supercritical fluid extraction (SFE) has recently been suggested to carry out the extraction of LAS from the original sample [9,10]. The technique which shows a high recovery percentage has been applied to soils, sediments, municipal wastewater and sewage sludge.

The handling to which the samples are subjected always carries with it the risk of contamination, particularly if one bears in mind that LAS is a frequently-used cleaning product in chemical laboratories. For this reason, it is advisable to process some blanks together with the samples; these should have the same ionic strength in the case of marine samples. In our case, the analysis of numerous samples of oceanic seawater and fossil seawater (taken from wells) shows, in many instances, traces of LAS (around 1 ppb); therefore environmental concentrations found of similar levels should be regarded with caution.

3. Separation

In parallel with the development of colorimetric methods and as a consequence of their low specificity, chromatographic techniques began to be applied to the determination — specific and individual — of the various surfactants. The problem of analyzing the different homologues of LAS in environmental samples has now been resolved, using techniques based on gas chromatography (GC) [11,12] and liquid chromatography (LC) [13–17], coupled to various detection systems. Due to their low volatility and anionic form, derivatisation of these compounds is necessary when GC-based analytical methods are used. This drawback is not encountered when LC-based methods are used. Furthermore, with LC the even more polar carboxylated transformation products (SPC) of the linear alkylbenzene sulfonates (LAS) compounds can be analyzed [13].

Currently, there are many possible choices in high-performance liquid chromatography (HPLC) methods, both for the stationary phase and for the mobile phase [18,6]. The quantification of the total concentration of LAS and of its individual homologues (eluting all the positional isomers of every homologue in a single peak) can be achieved using a C_8 column and working under isocratic conditions [5]. By using a C_{18} analytic column, the retention time is increased by a factor of 2.5 over that obtained with a C_8 column. Similarly, by increasing the polarity of the mobile phase, a better separation of the different homologues and isomers of the LAS is obtained. A complete separation of all the isomers and homologues of the LAS is obtained by using a long column (e.g. 250 mm × 4 mm I.D.) of octadecylsilica (C_{18}) with a particle size of 3 μm and applying a consistent elution gradient in two mixtures of acetonitrile and water in different proportions (A=33:67 and B=80:20) to which is added 10 g l^{-1} of sodium perchlorate [19,20]. The simultaneous determination of LAS and the alkylphenol polyethoxylates (APEO), which constitute the most commonly-used non-ionic surfactants, has been performed by means of elution gradients with water and acetonitrile [21].

The use of HPLC in recent years for the analysis of SPCs has represented one of the most interesting applications of this technique to the study of the environmental behaviour of anionic surfactants. In this context, ion-pair chromatography [22], as well as that involving the 'ion suppression' effect [23] have enabled the separation of the SPCs.

4. Detection in HPLC

In the establishment of the ideal analytical conditions, the choice of the most suitable pretreatment stages and of the best chromatographic conditions are always allied to the search for the most sensitive and specific detection system. Kikuchi et al. [2] found by comparing the chromatograms obtained that detection by fluorescence is far more specific for LAS than by absorption in the ultraviolet. This opinion is shared by other authors [24,25] after finding that the use of octadecylsilica minicolumns as the purification stage was not sufficient to eliminate interferences when detection was performed with an ultraviolet detector.

The method shows a high reproducibility, expressed as the relative standard deviation of results: 6% for Marcomini and Giger [21]; 1.4–4% for Castles et al. [4]; 2–3% for González-Mazo [6]. However, the complexity of SPC mixtures and the lack of reference standards currently limit the applicability of HPLC with UV-fluorescence detection methods [26].

5. Identification

Mass spectrometry utilizing various ionization techniques has been applied for the identification of the SPCs for which no standards are available. Up to the present time, they had only been described in groundwater samples and in water from waste treatment plants using the NCI GC-MS technique [26]. In that study, the SPCs found were of a maximum chain length of 10 carbon atoms. Di Corcia et al. [27] used GC–MS according to the method developed by Trehy et al. [12] to identify the degradation products of LAS resulting from aerobic bioassays.

The development of LC–MS techniques has enabled the more accurate identification and quantification of pollutants in environmental samples. In earlier reports, the thermospray interface was mainly used [28,29], whereas in the recent past, a considerable number of new analytical methods have been published, based on the use of the API interfacing techniques [30,31]. With these techniques, better limits of detection, by approximately two orders of magnitude, were obtained. Also, more fragment ions can be generated with the API interfaces (APCI and ESP), making the confirmation of the unknowns possible [31]. Liquid chromatography coupled to mass spectrometry with the electrospray interface has been employed for the determination of non-ionic polyethoxylate surfactants, such as aliphatic ethoxylate alcohols (AEOs) and nonylphenol polyethoxylates [32]. In the case of LAS compounds, the use of LC–MS with the thermospray (TSP) interface has been reported [33].

The electrospray (ESP) interface, in particular, has been shown to be valuable when ionic compounds, e.g., quaternary ammonium compounds, need to be analysed. However, the major drawback of this interfacing system is the limited eluent flow-rates (< 10 µl/min). Modifications of the interface have been made in order to solve this problem. The so-called pneumatically-assisted electrospray or

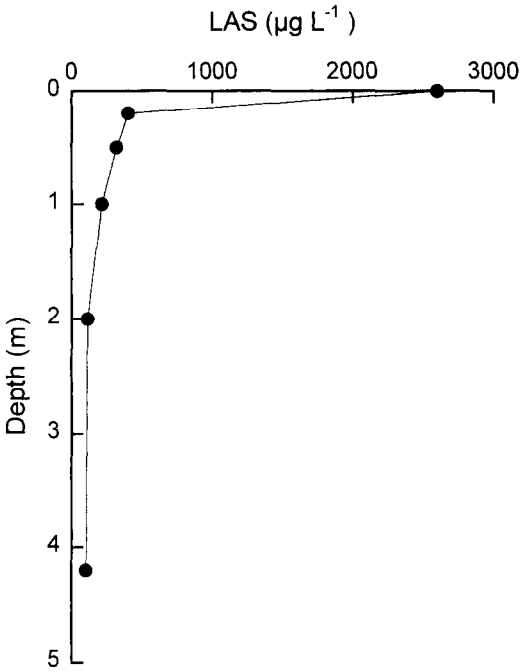

Fig. 2. Vertical distribution of LAS concentrations measured in water samples from one point in the bay of Cadiz.

ionspray (ISP) interface is a relevant example, although optimum flow-rates are still below 100 µl/min. Results have recently been reported with a newer version of this latter interface [34], using flow-rates up to 300 µl/min. In these reports, the main objective was the determination of carbamate and organophosphorus pesticides and their more polar transformation products.

Of particular interest from the analytical and environmental points of view is the ISP technique for the determination of the LAS compounds and the identification of their transformation products in water samples from the real environment. In this context, long-chain (C_7 to C_{13}) degradation intermediates of LAS, not described in environmental samples until now, have recently been unequivocally identified, by using liquid chromatography ionspray mass spectrometry [35].

6. Strategy for environmental sampling

In addition to the remaining problems involved in the actual analysis of LAS, consideration must be given to other problems, caused by its physicochemical properties, which can make it difficult to obtain representative samples from the sampling

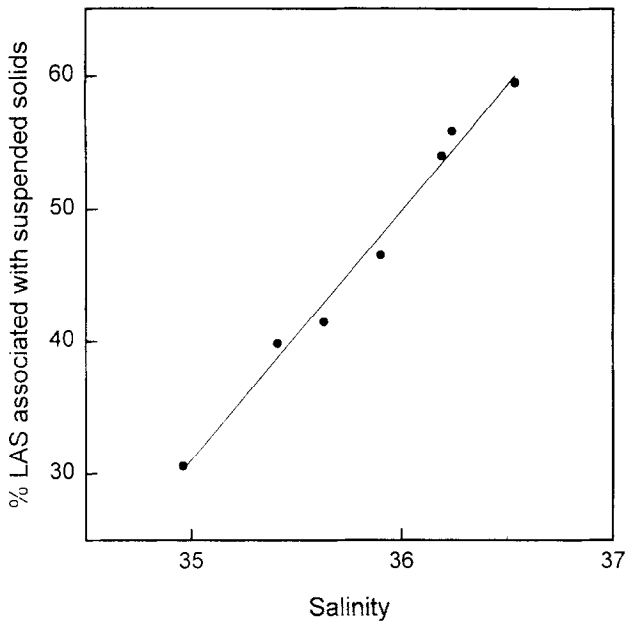

Fig. 3. Variation in % LAS associated with suspended solids with salinity. The percentage of LAS was calculated after measuring its concentration in the particulate and dissolved phases. Both phases were separated by continuous centrifugation at 12000 rpm of a volume of 50–70 l of sea water.

site. The surfactant nature of LAS results in the tendency for it to accumulate first on the surface of the aqueous medium into which it is discharged. This affects the way it disperses and also influences which environmental compartments experience an accumulation of LAS.

Fig. 2 shows the vertical profile of the concentration of LAS measured at a point close to the discharge outlet (300 m) of untreated urban effluent in the Bay of Cádiz. It can be seen that there is a steep vertical gradient and that the concentration in the topmost surface layer (1–3 mm) is greater by almost an order of magnitude compared to that found below 20 cm. The reason for this is that the dilution of the residual waters, which are less dense and rise to the surface, in the sea water is still incomplete.

Since the vertical gradient of salinity found there is not at all steep, the surfactant property of the compound must make a considerable contribution to causing the observed distribution. In fact, at greater distances from the urban effluent outlet (5–6 km), a certain vertical gradient is still found, even though there is a reduction in the differences in concentration at different depths.

LAS demonstrates a notable capacity for adsorption by sediments and by matter in suspension, both in continental ecosystems [36] and in the marine medium [37]. This affects the transport mechanisms involved in the dispersion of LAS. In Fig. 3, it can be observed that in coastal waters, LAS is associated with particulate matter to a very considerable extent; up to 60% of total LAS. Also, the magnitude of adsorption is closely correlated with the ionic strength of the medium, which agrees with the results obtained in adsorption tests with marine sediments [37].

This fact has important consequences: if one wishes to avoid serious default errors in the quantification of LAS, one must ensure the effective desorption of LAS from the solids in suspension before or during the pretreatment of the samples.

In this respect, Di Corcia et al. [17] propose, among other procedures, adding a specific volume of methanol to the sample before the extraction stage to encourage the desorption of the LAS. Another procedures, that they suggest is to filter the sample and analyze the LAS in two phases. This could be useful for samples taken from sewage treatment plants, but for environmental samples it involves processing large volumes of water to obtain a sufficient quantity of solids from which the LAS can be extracted; this could be somewhat tedious and could considerably complicate the sampling. Furthermore, during the sample handling, the risk of contamination of the samples would be greatly increased.

As a final point, it is well-known that the way LAS disperses, together with its rate of degradation, depend to a large extent on the environmental conditions, principally on the salinity, temperature and, above all, on the concentration of oxygen. This implies that, in the course of field studies to establish the behaviour of LAS, all these variables must be monitored, especially concerning the sediments.

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Dr. Eduardo González-Mazo and Professor Abelardo Gómez-Parra are at the Departamento de Química Física, Facultad de Ciencias del Mar, Universidad de Cádiz, 11510 Puerto Real, Cadiz, Spain.