Analytica Chimica Acta 932 (2016) 106–113

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Determination of the four major surfactant classes in cleaning products by reversed-phase liquid chromatography using serially connected UV and evaporative light-scattering detection

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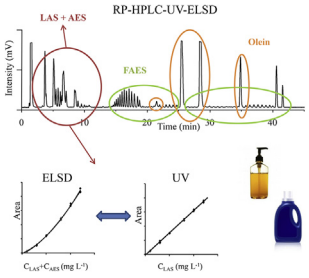
HIGHLIGHTS

- Single run LC determination of the four major surfactant classes in cleaning products.
- Serially connected UV and ELSD detection.
- Quantitation of coeluting LAS and AES in real commercial samples.
- Use of UV to correct ELSD predictions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 February 2016
Received in revised form
4 May 2016
Accepted 15 May 2016
Available online 24 May 2016

Keywords:
Evaporative light scattering detection
Fatty acids
Fatty alcohol ethoxylates
Alkyl ether sulphates
Linear alkyl benzenesulphonates
Olein
Cleaning products

ABSTRACT

A method for the simultaneous determination of the most frequently used surfactant families —linear alkyl benzenesulphonates (LAS), alkyl ether sulphates (AES), fatty alcohol ethoxylates (FAE) and oleins (soaps, fatty acid salts) — in cleaning products, has been developed. The common reversed phase octyl (C8), pentafluorophenyl and biphenyl columns were not capable of separating the anionic LAS and AES classes; however, since only LAS absorbs in the UV, these two classes were independently quantified using a C8 column and serially connected UV and ELSD detection. The best compromise to resolve the four surfactant classes and the oligomers within the classes was achieved with a C8 column and an ACN/water gradient. To enhance retention of the anionic surfactants, ammonium acetate, as an ion-pairing agent compatible with ELSD detection, was used. Also, to shift the olein peaks with respect to that of the FAE oligomers, acetic acid was used. In the optimized method, modulation of the mobile phase, using ammonium acetate during elution of LAS and AES, and acetic acid after elution of LAS and AES, was provided. Quantitation of the overlapped LAS and AES classes was achieved by using the UV detector to quantitate LAS and the ELSD to determine AES by difference. Accuracy in the determination of AES was achieved by using a quadratic model, and by correcting the predicted AES concentration according to the LAS concentration previously established using the UV chromatogram. Another approach also leading to accurate predictions of the AES concentration was to increase the AES concentrations in the samples by adding a standard solution. In the samples reinforced with AES, correction of the predicted AES concentration was not required. FAE and olein were quantified using also quadratic calibration.

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http://dx.doi.org/10.1016/j.aca.2016.05.022
0003-2670/

1. Introduction

Industrial and household cleaners mainly contain four major classes of surfactants, namely linear alkylbenzene sulfonates (LAS), alkyl ether sulfates (AES), fatty alcohol ethoxylates (FAE) and oleins or soaps, which are mixtures of salts of fatty acids [1,2]. LAS and AES are anionic at all pHs and FAE are non-ionic, whereas the olein components are ionized at pH values over pH = $pK_a \approx 5$. LAS is obtained as mixtures mainly containing the C10-C13 homologues. Each homologue comprises from four to six isomers which differ in the attachment point of the p-sulfonate phenyl group to the linear alkyl chain, starting from the second carbon atom. LAS is most frequently analyzed by HPLC-UV using C8 columns and ACN/water in the presence of an ion-pairing agent such as sodium perchlorate [3–7] or a tetraalkylammonium salt [4,8–10].

Both AES and FAE contain series of oligomers that differ both in the length of the hydrocarbon chain (the hydrophobic cut), and in the number of the condensed ethylene oxide (EO) units of the hydrophilic moiety. AES are the sulfuric acid esters of FAE, and then AES and FAE only differ in the nature of the terminal group of the hydrophilic tail, a sulfate and a hydroxyl, respectively. The separation of underivatized AES and FAE oligomers is most conveniently carried out using HPLC on C8 columns with an ACN/water gradient; however, an ion-pairing agent should be added to enhance retention of the oligomers of both LAS and AES [11]. Finally, the palm olein components (fatty acid salts) are also well resolved using the same chromatographic mode [12,13].

LAS are normally detected using UV [14], although fluorescence can be also used [15]. The olein components can be also detected using UV at a low wavelength, but their molar absorptivities are low. Instead of this, UV detection of AES and FAE requires previous derivatization. This can be achieved with anhydrides [16–23] and other reagents [17,18,24]; however, upon hydrolysis of the sulfate ester bond, AES gives rise to the same derivatives as FAE. For this reason, if these two classes should be independently characterized and quantified, separation of them before derivatization is mandatory. This can be achieved by ion-exchange on SPE cartridges [7,8]. Instead of derivatization followed by UV, mass spectrometry [24–28], evaporative-light-scattering (ELSD) [18,29] or charged-aerosol detection (CAD) [30–32] of the underivatized AES and FAE oligomers can be used. However, it should be noted that the non-ethoxylated FAE oligomers (the fatty alcohols) are too volatile to be detected in an evaporative detector, and that the mono-ethoxylated FAE oligomers, that are also fairly volatile, are underestimated. Underestimation of these oligomers results in a small systematic error, unless FAE standards having the same EO distribution as that in the samples would be used for calibration. This is not a problem in quality control of manufactured products, since the EO distribution of the samples is known, but requires correction according to the observed EO distribution when an unknown sample is analyzed [33].

At the present time, HPLC-MS has become the preferred technique for the analysis of surfactants in industrial and environmental samples [15,34,35] because of its specificity, high capacity for identification of homologues and ethoxymers and capability of determining different surfactants at the same time [36,37]. Another powerful tool which is gaining more importance in the analysis of cleaning product samples, due to the elevated amount of components of different nature that these samples contain, is two-dimensional HPLC (2D-HPLC) [33,38,39]. However the development of HPLC-MS and 2D-HPLC methods, requires expensive instrumentation, which is not affordable for a big range of small industries and quality control laboratories. Instead of this, traditional and cheaper detection methods, such as UV–vis and ELSD, can still be used for quality control of raw materials and industrial samples, where high sensitivity is not required as occurs for environmental samples.

Therefore, in this work, a cheap, practical and simple method capable of determining the four major surfactant classes mainly used in all types of cleaning products (LAS, AES, FAE and oleins) all in a single chromatographic run using UV-ELSD detection, has been developed. The best separation was achieved with a single C8 column with modulation of the concentrations of ammonium acetate (NH_4AcO), used as an ELSD compatible ion-pairing agent [40] and acetic acid (HAcO) in the mobile phase. Using RP-HPLC, and in the presence of an ion-pairing agent, anionic surfactants elute first, followed by FAE and oleins. We have not found any RP system capable of separating the LAS and AES classes; however, in this work, we present an alternative method to HPLC-MS [37] for the independent evaluation of these two classes. First, using the UV chromatogram the LAS concentration was established, followed by the subtraction of this concentration from the sum of the LAS and AES concentrations obtained using ELSD, to finally obtain the AES concentration. The difficulties derived from the non-linear nature of the ELSD signal were overcome by using two different strategies which consisted in performing a quadratic calibration and the addition of an excess of AES to the samples. On the other hand, the olein peaks also overlap with the peaks of a few FAE oligomers; however, the successive FAE oligomers were well resolved, following a highly regular distribution pattern that made possible the accurate prediction of the areas of the overlapped peaks. Using this procedure, the high cost in instrumentation or the required time to make successive extractions of the different surfactant classes, using SPE protocols [7,8] and further derivatization can be avoided.

2. Experimental

2.1. Reagents, samples and standard solutions

The following analytical grade reagents were used: acetic acid (HAcO), methanol (MeOH), acetonitrile (ACN) (Scharlab, Barcelona, Spain) and ammonium acetate (NH_4AcO, Riedel de Haën, Seeltze, Germany). The industrial surfactants Dehydol LT-7 (fatty alcohol ethoxylates, FAE, with n = 12, 14, 16 and 18 carbon atoms in the hydrophobic tail, and an average EO number of 7, Cognis, Monheim, Germany), Lutensol AO7 (FAE with n = 13 and 15 and an average EO number of 7, BASF, Germany), alkyl ether sulfates (AES, sodium salts, with $12 \leq n \leq 18$ and average EO number of 3, Limsa, Barcelona, Spain), lineal alkylbenzenesulfonates (LAS, mixture of the $10 \leq n \leq 13$ homologues, Fluka, Steinheim, Germany) were used. Palm olein and other components of cleaning products were kindly supplied by Químicas Oro (San Antonio de Benagéber, Valencia, Spain). In Table 1, the structure and specifications of the used standards can be observed. Stock standard solutions of 10 g L^{-1} of LAS and AES, and 5 g L^{-1} of FAE, were prepared in water. A stock standard solution of 5 g L^{-1} of palm olein was prepared by dissolving the proper amount with a NaOH solution in methanol, followed by dilution with water. Dilutions of the stock standard solutions were made with water. Samples of liquid detergents and dishwashers, supplied by Químicas Oro, were prepared in ca. 1 kg batches according to the full formulations of 6 different commercial products including laundry cleaners, handwashers and dishwashers. These formulations are constituted, by one or more surfactants and other components including water, boric acid, sodium chloride, triethanolamine, ethylenediaminetetraacetic sodium salt, alkyl phosphonate sodium salts, colorants, fragrances, opacifiers and preservatives. Portions of these samples were weighed and diluted with water. Deionized water (Barnstead deionizer, Sybron, Boston, MA) was used in all cases. Identification of the olein