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Review

Separation and quantitative determination of non-ionic surfactants used as pesticide additives

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Abstract

The various chromatographic techniques suitable for the separation and quantitative determination of non-ionic surfactants in industrial and environmental samples are reviewed with special emphasis on the sample preparation methods. Techniques are classified (thin-layer, high-performance, supercritical fluid and gas–liquid chromatography) and discussed separately. The sophisticated gas chromatography–mass spectrometry and liquid chromatography–mass spectrometry techniques are the most suitable methods for the separation of non-ionic surfactants according to both the number of ethylene oxide groups per molecule and the character of the hydrophobic moiety.

Keywords: Reviews; Environmental analysis; Surfactants

Contents

1. Introduction

Pesticides are extensively used in up-to-date agrochemical practice [1]. The solubility of the majori-

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ty of pesticides is generally low in water [2], therefore, they are used as aqueous suspensions or emulsions. As the mechanical stability of such suspensions and emulsions is negligible, surfactants or surfactant mixtures (non-ionic, anionic and cationic surfactants) are added to enhance the stability of pesticide suspensions and emulsions [3]. Surfactants not only improve the application parameters of pesticide formulations but may also have advantageous or disadvantageous side effects. Thus, they increase the leaf retention of spray solutions [4], enhance herbicide effectiveness [5,6] and increase the adhesional forces of aqueous droplets on crop leaf surfaces [7]. However, it was found that Triton X-100 (polyethylene glycol *tert.*-octylphenyl ether) significantly increased time lags of naphthylacetic acid diffusion through isolated tomato (*Lycopersicon esculentum* Mill. cv. Pik Red) fruit cuticles [8]. A considerable portion of the surfactants present in pesticide formulations are in contact with the soil and pollute ground water by leakage, exerting various environmental effects.

Surfactants exert marked eye irritation potential [9,10], however, it has been revealed that non-ionic surfactants have a lower toxic effect than those of cationic, anionic and amphoteric surfactants [11,12]. Surfactants may have skin irritating capacity too [13,14]. Non-ionic surfactants can increase the absorption of xenobiotics in living organisms [15–17].

Non-ionic surfactants are amphipathic molecules consisting of a hydrophobic (alkylated phenol derivatives, fatty acids, long chain linear alcohols, etc.) and a hydrophilic part (generally ethylene oxide chains of various length). Although not as important commercially, tertiary amine and various sugar surfactants are also non-ionic surfactants. It has been established many times that the various biological activities and the toxicities of non-ionic surfactants depend on both the length of the polar ethylene oxide chain [18] and on the character of the hydrophobic moiety [19]. It has been found that the interaction between 2-(1-naphthyl)acetic acid and micelles of non-ionic surfactants (Triton X series) decreased with the logarithm of the length of the ethylene oxide chain [20] and that the more hydrophilic surfactants (>ethylene oxide number) had the smallest impact both on ethylene evolution and leaf growth of *Phaeolus vulgaris* L. [21].

The significant role of both the hydrophobic and hydrophilic parts of surfactants in the determination of biological activity and toxicity clearly shows that the separation of non-ionic surfactants according to the length of the polar ethylene oxide chain and according to the character of hydrophobic moiety is of paramount practical and theoretical importance. The growing awareness of environmental pollution problems and the stricter regulations require that there are not only highly accurate but also highly sensitive separation methods.

Although the separation of surfactant in both directions is an exciting challenge for chromatographers interested in this field, the number of papers dealing with the theoretical background of the separation is surprisingly low [22]. According to our knowledge, the effect of eluent composition on retention strength and selectivity, the relationship between the physicochemical parameters of eluent components and their retention characteristics and the impact of the various parameters of the support (surface pH, average pore diameter, quantity and quality of ligand bonded to the surface) have not been studied in detail. Practical results obtained in the analysis of alkylphenol ethoxylates and alcohol ethoxylates in the aquatic environment [23] and the chromatographic determination of alcohol polyethoxylates in the environment have been reviewed recently [24].

The objectives of this review are the enumeration and critical evaluation of the recent results obtained in the chromatographic separation and quantitative determination of non-ionic surfactants and the comparison of the efficacy of the various chromatographic techniques and procedures such as thin-layer chromatography (TLC), high-performance liquid chromatography (HPLC), supercritical fluid chromatography (SFC) and gas–liquid chromatography (GLC).

2. Sample preparation

The presence of a considerable quantity of impurities (mono-, oligo and polymeric carbohydrates, peptides, proteins, inorganic salts, humic acids, etc.) reduces the efficiency of any chromatographic separation, resulting in modified retention and distorted

peak shape (as TLC plates are disposable, sample preparation is generally less demanding than in the case of other chromatographic separation methods). As the efficacy of the pre-purification step has a considerable impact on the following chromatographic analysis, many methods have been developed for the separation of surfactants from liquid and solid accompanying matrices.

A wide variety of methods have been used for the pre-purification of surfactants from liquid media. Initially, various modifications of traditional liquid–liquid extraction procedures were used most frequently [25]. The disadvantage of liquid–liquid extraction is the formation of more or less stable emulsions, which cause a deterioration in phase separation. Modifying the ionic strength and pH of the solution to be extracted results in better phase separation. Thus, a typical extraction procedure used 300 ml of waste water with 5 ml of conc. HCl and 40 g of NaCl added to it. The sample was shaken, then 10 ml of dichloromethane were added, the sample was shaken again and the dichloromethane phase was separated [26]. Centrifugal partition chromatography (with water being the mobile and ethyl acetate being the stationary phase) has also been used for the extraction of nonylphenyl ethylene oxide oligomers from waste water [27]. In the gas stripping extraction procedure, a rising stream of gas (possibly nitrogen or helium) transfers the surfactants from an aqueous sample into the recycling layer of the organic phase (ethylacetate) [28]. This method has been successfully applied for the extraction of nonylphenol ethylene oxide surfactants from pulp and paper mill samples, with recovery varying between 45 and 100%, depending on the quantity of surfactants to be extracted and the composition of the sample [29]. Extraction was followed by the HPLC determination of surfactants using an octadecylsilica column [30]. In order to increase the recovery of surfactants from waste water, a continuous liquid–liquid extraction procedure was applied using 2 l of waste water and 300 ml of diethyl ether over a period of 5 h [31].

Solid-phase extraction (SPE) has been developed for the rapid extraction and enrichment of organic compounds from practically any accompanying matrices. As non-ionic surfactants readily adsorb on any surface, a wide variety of supports have been tested for their preconcentration, such as alkyl-bonded silica [32], graphitized carbon black [33] and macroreticular styrene–divinylbenzene resins [34,35]. SPE has also been used successfully for the preconcentration of sorbitan ester surfactants from salt–water prior to supercritical fluid chromatography [36].

Time-consuming and off-line extraction procedures can be replaced by on-line purification of the samples. Thus, it has been proven that the surfactant Triton X-100 can be successfully separated from proteins and analyzed in one run by using strong cation and anion-exchange HPLC guard columns. Proteins are retained on the column, while the surfactant elutes as one peak. This very rapid method is suitable for the quantitative determination of surfactants in protein solutions, however, it is not suitable for the separation of surfactants based on the length of the ethylene oxide chain [37].

Although non-ionic surfactant can come into contact with the soil and can adsorb on the surface of various inorganic soil components [38,39], the number of extraction procedures is surprisingly low. The extraction of ethoxylated tributylphenol derivatives from river sediment with methanol has been reported recently, but the recovery of the method was not determined [40]. According to our knowledge, up-to-date methods such as microwave extraction and sonication have never been used for the extraction of non-ionic surfactants from solid matrices.

3. Thin-layer chromatography

Although the sensitivity and separation capacity of the traditional TLC methods are lower than the similar parameters of HPLC, TLC has also been used for the separation and quantitative determination of surfactants, mainly prior to the wide-spread use of HPLC. The inherently low reproducibility of TLC resulted in the marked decrease of its application in the analysis of non-ionic surfactants. However, over the last decade, interest has been renewed in the use of TLC as a rapid and reliable analytical tool. This is probably due to the improved instrumentation and to automation of the various steps involved in TLC analysis (gradient and forced flow methods, centrifugal development, circular rotation planar chromatography, high-pressure planar liquid chromatography)

as well as coupled spectroscopic methods [TLC–UV–VIS, TLC–MS and TLC–Fourier transform infrared spectroscopy (FTIR)] [41].

3.1. Adsorption thin-layer chromatography

It has been recognized previously that adsorption TLC can successfully separate non-ionic surfactants according to the length of the polar ethylene oxide chain [42,43], but it is ineffective in separating them according to the character of the hydrophobic moiety. Ethoxylated nonylphenyl derivatives were separated on silica layers and were detected by iodine vapours [44].

A good example of the use of modern TLC instrumentation is the separation of polyoxyethylene glycerol trioleate derivatives on silica high-performance TLC plates [45]. Samples were applied using an ATS III unit (Camag), the dipping of the plates was carried out with TLC dipping fix (Baron, Germany) and the spots were evaluated by a Camag TLC Scanner II with CATS software. More than 25 fractions were separated under optimal conditions, proving the good separation capacity of the method (Fig. 1). The detection limit of the method was found to be 1.25 mg ml^{-1}, and the repeatability (relative standard deviation) was below 5%.

Nonylphenol ethylene oxide oligomer surfactants were separated on an alumina layer using acetonitrile–chloroform mixtures as eluents, and the different fractions were detected with a Shimadzu dual wavelength CS-930 TLC scanner operated at 275 nm [46]. It was assumed that the retention of surfactant fractions depends on the number of ethylene oxide groups in the molecule (n_e), and on the concentration of the stronger component in the eluent (C vol.%). The relationship between the parameters listed above was described by:

$$R_M = a + b_1 n_e + b_2 (n_e)^2 + b_3 C + b_4 C^2 \quad (1)$$

The inclusion of quadratic functions in Eq. (1) was motivated by the supposition that the ethylene oxide chains may be in a more or less folded state and that folding may depend on both the length of the ethylene oxide chain and on the concentration of the stronger component of the eluent. Surfactants with shorter ethylene oxide chain lengths were well separated in this TLC system (Fig. 2).

The optimum eluent composition was calculated for each neighbouring surfactant fraction and it was established that the greater the number of ethylene oxide groups in the surfactants to be separated, the higher the solvent strength has to be to achieve optimum separation. This finding emphasizes the need for gradient elution in the case of complicated surfactant mixtures and the limitations of TLC for solving such analytical problems. Another study

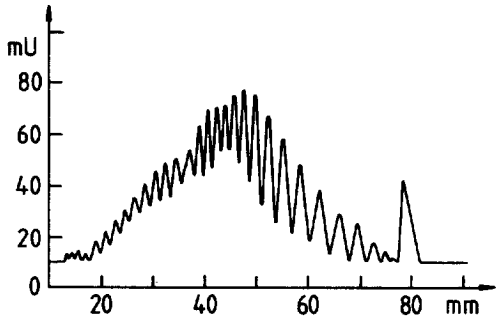

Fig. 1. Separation of polyoxyethylene glycerol trioleate derivatives on silica high-performance TLC plates. Eluent, methyl ethyl ketone–acetone–water (50:5:6, v/v/v). (Reprinted with permission from Ref. [45]).

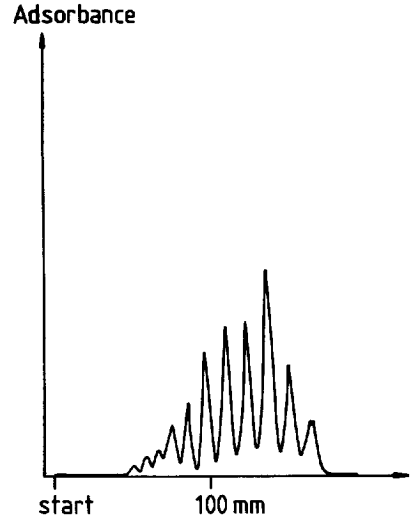

Fig. 2. Densitogram of commercial nonylphenyl ethoxylate (average number of ethylene oxide groups per molecule is six); eluent, chloroform–acetonitrile (7:3, v/v). (Reprinted with permission from Ref. [46])

using various eluent mixtures, and silica and alumina supports, separated the solvent strength and selectivity and calculated the relationship between chromatographic performance and the physicochemical parameters of eluent components [47]. The results clearly show that both solvent strength and selectivity depend significantly on the dielectric constant and the refractive index of the solvents; however, the relationships differed considerably and were markedly non-linear (Table 1).

3.2. Reversed-phase thin-layer chromatography (RP-TLC)

Due to its low selectivity, RP-TLC has not been used for the separation of non-ionic surfactants based on the character of their hydrophobic parts. However, as theoretical studies have indicated, RP-TLC can be used as a pilot method for reversed-phase HPLC (RP-HPLC) [48,49], moreover, it can also be used to determine the hydrophobicity parameters of surfactants. Hydrophobicity is one of the physicochemical parameters frequently used in quantitative structure–activity relationship studies in the rational design of new bioactive compounds [50,51] and in the elucidation of the biochemical and biophysical processes influencing biological efficiency [52,53]. Hydrophobicity parameters can be determined by various liquid chromatographic techniques, such as RP-TLC [54,55] and RP-HPLC [56,57]. The hydrophobicity values determined by both RP-TLC and RP-HPLC generally showed good correlation [58]. The determination of hydrophobicity by RP-TLC offers considerable advantages: It is relatively rapid and simple, the compounds need not to be extremely pure and a very low amount can be used. The RP-TLC conditions required for determining the hydrophobicity of non-ionic surfactants have been extensively investigated [59]. It was established that the nature of the support [60], the impregnating agent [61] and the organic modifier [62] exert considerable influence on the determination of molecular hydrophobicity. For further structure–activity relationship studies, the chemical structure, lipophilicity (R_{M0}) and the specific hydrophobic surface area (SHSA) of some non-ionic surfactants are compiled in Table 2 Table 3, respectively. The data were taken from [63].

TLC has been further used for the separation of non-ionic surfactants from anionic and cationic ones with multiple development [64], for the quantitative determination of ethoxylated alkylphenol derivatives [65], for the assessment of the distribution of chain length in alkylpolyglucoside surfactants [66] and for the two-dimensional separation of ethoxylated alkylphenol carboxymethyl ethers [67].

Table 1
Parameters of the relationships between solvent strength (a) and selectivity (b_a) and the physicochemical characteristics of solvent

Parameter	No. of equation	
	I	II
A	3.99	4.84
B_1	$-2.62\cdot10^{-2}$	$-2.59\cdot10^{-2}$
S_{B1}	$5.82\cdot10^{-3}$	$2.69\cdot10^{-4}$
Path coefficient (%)	43.20	73.65
B_2	−4.66	−90.13
S_{B2}	1.71	26.09
Path coefficient (%)	27.56	26.35
B_3	−61.84	–
S_{B3}	19.72	–
Path coefficient (%)	29.24	–
r^2	0.4021	0.6509
$F_{calc.}$	11.43	48.47
$F_{99.9\%}$	8.01	8.01

I $a=A+B_1x_1+B_2(x_1)^2+B_3(\log x_2)^2$.
II $b_a=A+B_1(x_1)^2+B_2(\log x_2)^2$.
x_1 = dielectric constant.
x_2 = refractive index.
Results of stepwise regression analysis ($n=55$).
Reprinted with permission from [47].

4. High-performance liquid chromatography

Due to its high versatility and sensitivity, high-performance liquid chromatography (HPLC) has been extensively used for the separation and quantitative determination of non-ionic surfactants in both industrial products and various environmental matrices. Due to the different chemical structures of non-ionic surfactants, many methods were used or developed for their detection. The low sensitivity of refractive index (RI) detectors seriously limited their use in the analysis of surfactants. Surfactants with chromophores in the molecule (mainly ethoxylated alkylphenol derivatives) can be easily detected by a common UV detector. However, it has to be borne in

Table 2
Chemical structure of non-ionic surfactants General structure (Q= Hydrophobic moiety; ne=average number of ethylene oxide groups per molecule): $Q–O(C_2H_4O)_{ne}–H$

No. and common name	Q	ne
1. Tween 20	Sorbitan monolaurate	20
2. Tween 40	Sorbitan monopalmitate	20
3. Tween 60	Sorbitan monostearate	20
4. Tween 80	Sorbitan monooleate	20
5. Tween 61	Sorbitan monostearate	4
6. Tween 81	Sorbitan monooleate	5
7. Tween 65	Sorbitan tristearate	20
8. Tween 85	Sorbitan trioleate	20
9. Brij 30	Lauryl-alcohol	4
10. Brij 35	Lauryl-alcohol	23
11. Brij 56	Oleyl/cetyl-alcohol	10
12. Brij 76	Stearyl-alcohol	10
13. Brij 78	Stearyl-alcohol	20
14. Brij 96	Oleyl-alcohol	10
15. Arkopal N40	Nonylphenol	4
16. Arkopal N60		6
17. Arkopal N80		8
18. Arkopal N90		9
19. Arkopal N100		10
20. Arkopal N110		11
21. Arkopal N150		15
22. Arkopal N230		23
23. Arkopal N300		30
24. Sapogenate T40	Tributylphenol	4
25. Sapogenate T60		6
26. Sapogenate T80		8
27. Sapogenate T100		10
28. Sapogenate T110		11
29. Sapogenate T130		13
30. Sapogenate T180		18
31. Sapogenate T300		30
32. Sapogenate T500		50
33. Myrj 45	Stearic acid	8
34. Myrj 49		20
35. Myrj 51		30
36. Myrj 52		40
37. Myrj 53		50
38. Myrj 59		100
39. Span 80	Sorbitan monooleate	0

Reprinted with permission from [63].

Table 3
Lipophilicity (R_{M0}) and specific hydrophobic surface area (SHSA) of some non-ionic surfactants

No.	R_{M0}	SHSA
1	2.58	2.49
2	4.98	6.02
3	5.02	6.00
4	5.06	6.09
5	4.94	5.75
6	5.85	7.21
7	6.03	7.33
8	5.93	7.23
9	4.72	6.34
10	4.84	6.26
11	5.12	6.32
12	6.40	7.85
13	5.65	6.88
14	4.97	6.04
15	4.58	6.13
16	4.22	5.61
17	4.60	6.22
18	3.99	5.36
19	4.06	5.46
20	4.07	5.45
21	3.93	5.24
22	3.70	5.24
23	3.34	4.83
24	4.28	5.72
25	4.36	5.80
26	3.86	5.11
27	4.34	5.72
28	4.24	5.58
29	4.12	5.36
30	3.85	5.00
31	3.30	4.12
32	2.54	2.82
33	6.76	8.46
34	4.53	5.06
35	5.02	6.23
36	4.78	5.78
37	5.22	6.26
38	3.55	4.28
39	4.92	6.19

Numbers refer to the non-ionic surfactants listed in Table 2.
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mind that the specific (molar) UV absorbance of alkylphenol ethoxylates markedly decreases with increasing length of the ethylene oxide chain, which has to be taken into consideration for the exact quantitative evaluation. Quantitative analysis is further hampered by the lack of pure standard, especially with longer ethylene oxide chains. Extrapolation of the absorption parameters used for quantitative analysis can result in a highly distorted distribution of fractions. Fatty acid and fatty alcohol derivatives absorb only at the low UV region, which restricts the use of solvents absorbing in the same region. Many detection methods have been developed to overcome this difficulty. Thus, non-ionic surfactants with ester groups were detected by postcolumn hydrolysation, following reaction with 2-nitrophenylhydrazine in

the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide. The violet colour of the hydrazide end product can be detected at 550 nm under alkaline conditions [68]. Evaporative light scattering detection (ELSD) has been used for the detection of various ethoxylated alkyl alcohols and their carboxylic acid derivatives and its efficacy was compared with those of RI and UV detection [69]. It has been found that ELSD is superior in signal-to-noise ratio as well as baseline drift (Fig. 3). Fluorescence detection has also been used in the HPLC analysis of non-ionic surfactants [70] and the detection limit for octylphenol ethoxylates was found to be 0.2 ng [71]. Various derivatising agents, such as phenyl isocyanate [72], benzoyl chloride, 3,5-dinitrobenzoylchloride [73,74], 1-anthroylnitrile [70] and 1-naphthyl isocyanate [75] have been successfully used in the HPLC analysis of non-ionic surfactants, as they increase sensitivity and selectivity. Liquid chromatography–mass spectrometry (LC–MS) offers a unique possibility for the analysis and identification of non-ionic surfactants [76]. These new hyphenated LC–MS techniques make possible the identification of surfactants according to both the isomerism of the hydrophobic moiety and the number of ethylene oxide groups [77].

A wide variety of supports have been tested for their capacity to separate non-ionic surfactants. The majority of analyses have been carried out on silica or modified silica supports with various (more or less apolar) ligands covalently bonded to the surface. Due to its higher stability at extreme pH values, alumina has been found to be a valuable substitute for silica [78]. A porous graphitized carbon (PGC) support was developed more than ten years ago as an inert support that can be used at any pH value [79,80]. PGC has been used for the effective separation of many polar and apolar compounds [81].

4.1. Separation of non-ionic surfactants according to the length of the ethylene oxide chain

Many different HPLC methods were developed for the separation of various non-ionic surfactants according to the length of the polar ethylene oxide chain. These methods usually use polar or moderately polar supports. As industrial non-ionic surfactants generally have a wide distribution of ethylene oxide units per molecule, they can be adequately separated only by using gradient elution. Silica has been used for the separation of various non-ionic surfactants. Ethoxylated alkylphenyl oligomers were separated

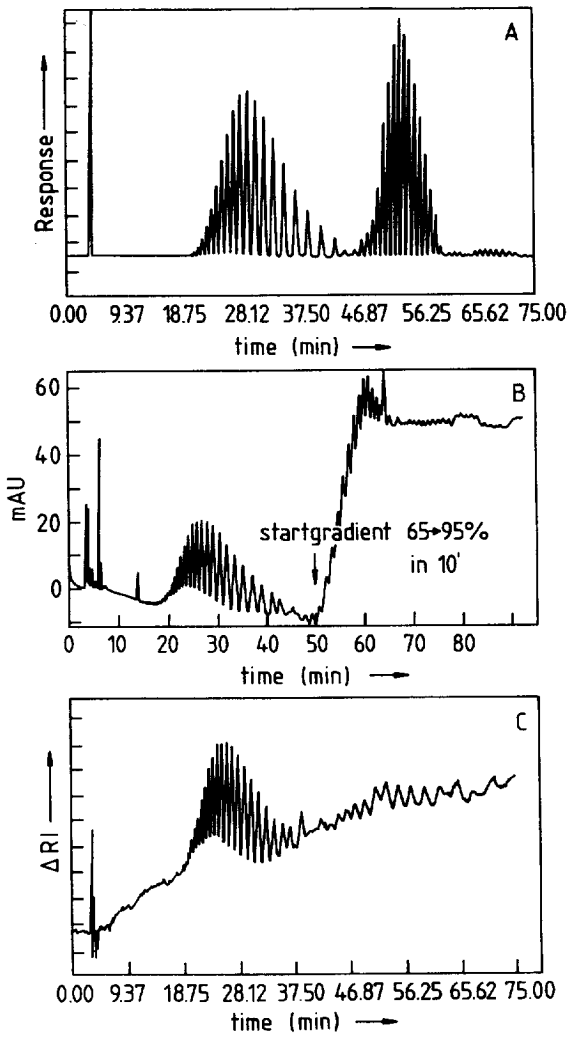

Fig. 3. Comparison of ELS (A), 190 nm UV (B) and RI (C) detection techniques for $C_{12}H_{25}$–O–$(C_2H_4O)_n$–H and $C_{14}H_{29}$–O–$(C_2H_4O)_n$–H. Column, 2×(250×4 mm I.D.) Nucleosil 120-5 C_{18}. Eluent: (A) 0.1% aqueous acetic acid; (B) acetonitrile. Gradient: 65% acetonitrile for 38 min then 90% acetonitrile for 10 min; at 75 min, back to 65% acetonitrile for 1 min. Flow-rate: 1 ml/min. Injection: 20 μl containing 1.2 mg of sample. (A) T_{neb}=100°C, 2.9 l/min carbon dioxide. (B) λ=190 nm (4 mm band width), λ_{ref}=500 nm (100 nm band width). (C) Isocratic separation at 65% acetonitrile, detector sensitivity setting=8. (Reprinted with permission from Ref. [69]).

using gradient elution consisting of mixtures of heptane–chloroform–methanol [82], or of mixtures of *n*-hexane–2-propanol and ethanol–water [83], in the UV detection mode (Fig. 4). An interesting application of silica as a cation exchanger for the separation of highly condensed non-ionic surfactants was also reported [84]. It was assumed that silica behaves as a weak cation exchanger at higher pH values and, therefore, that its separation capacity is different. The results entirely supported this assumption and a very good separation of surfactants according to the number of ethylene oxide groups was achieved (Fig. 5).

Amino-bonded silica supports have been also used for the separation of various non-ionic surfactants according to the length of the ethylene oxide chain [85]. Octylphenol derivatives were well separated using gradient elution (isooctane–2-propanol–2-methoxyethanol) [86]. Solid-phase microextraction combined with HPLC on an amino-bonded column or with GC after derivatization have been used recently for the determination of alkylphenol ethoxylate surfactants in water [87]. The detection limit of the individual surfactants was in the low μg/l range, or lower. The separation capacities of silica and amino-bonded silica have been compared recently and it was established that amino-bonded silica is more suitable for the separation of ethoxylated alkylphenyl derivatives than silica [82].

Diol columns have also found application in the separation of surfactants such as ethoxylated fatty acids using a mixture of *n*-hexane–2-propanol–water–acetic acid (105:95:10:1, v/v) as the eluent

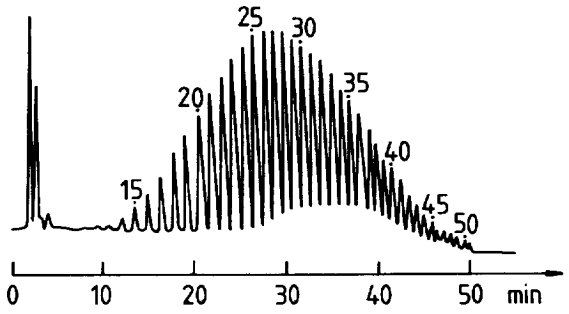

Fig. 4. Gradient elution of the oligomers from nonylphenol (ethylene oxide)$_{30}$. Eluent A, *n*-hexane–2-propanol (40:60, v/v); eluent B, ethanol–water (80:20, v/v). Gradient: 10–95% B in 45 min. (Reprinted with permission from Ref. [83])

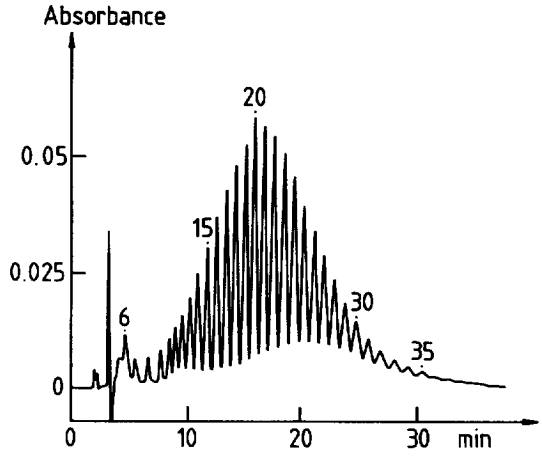

Fig. 5. Analysis of Brij 99 complexed with $5 \cdot 10^{-3}$ *M* CH_3COONa by ion-exchange chromatography. Stationary phase, ionized bare silica (particle size 5 μm, 150×4.6 mm); mobile phase, CH_3CN–water (92:8, v/v). Flow-rate, 0.7 ml/min. Temperature programming, initial temperature 25°C for 5 min, then 1.2°C/min to 45°C. (Reprinted with permission from Ref. [84]).

[88], fatty alcohols [89] and alkylphenols [90]. A comparative study established that the separation efficacy of the amino column was better than that of silica and diol-bonded silica columns [91].

A methylated silica support (C_1 TMS) has also been used for the separation of non-ionic surfactants according to the length of the polar ethylene oxide chain. An excellent separation of octylphenol ethylene oxide oligomers (Triton X series) was achieved using a C_1 column, as demonstrated in Fig. 6 [92].

The reproducibility of the quantitative evaluation was good, the relative standard deviation between the parallel determinations varied between 0.21–6.40%, even in the case of the most complicated surfactant sample. The use of a similar column, solid-phase extraction and mass spectrometry made possible the detection of ethoxylated alkylphenol surfactants in surface water. The recovery was approximately 100% and the detection limit was 50 ng, using fluorescence detection [93].

Nonylphenyl ethylene oxide oligomers were well separated on an alumina HPLC column using ethyl acetate–*n*-hexane mixtures as eluents. The capacity factor extrapolated to zero ethyl acetate concentration and the change in the capacity factor caused by a 1% change in the concentration of ethyl acetate

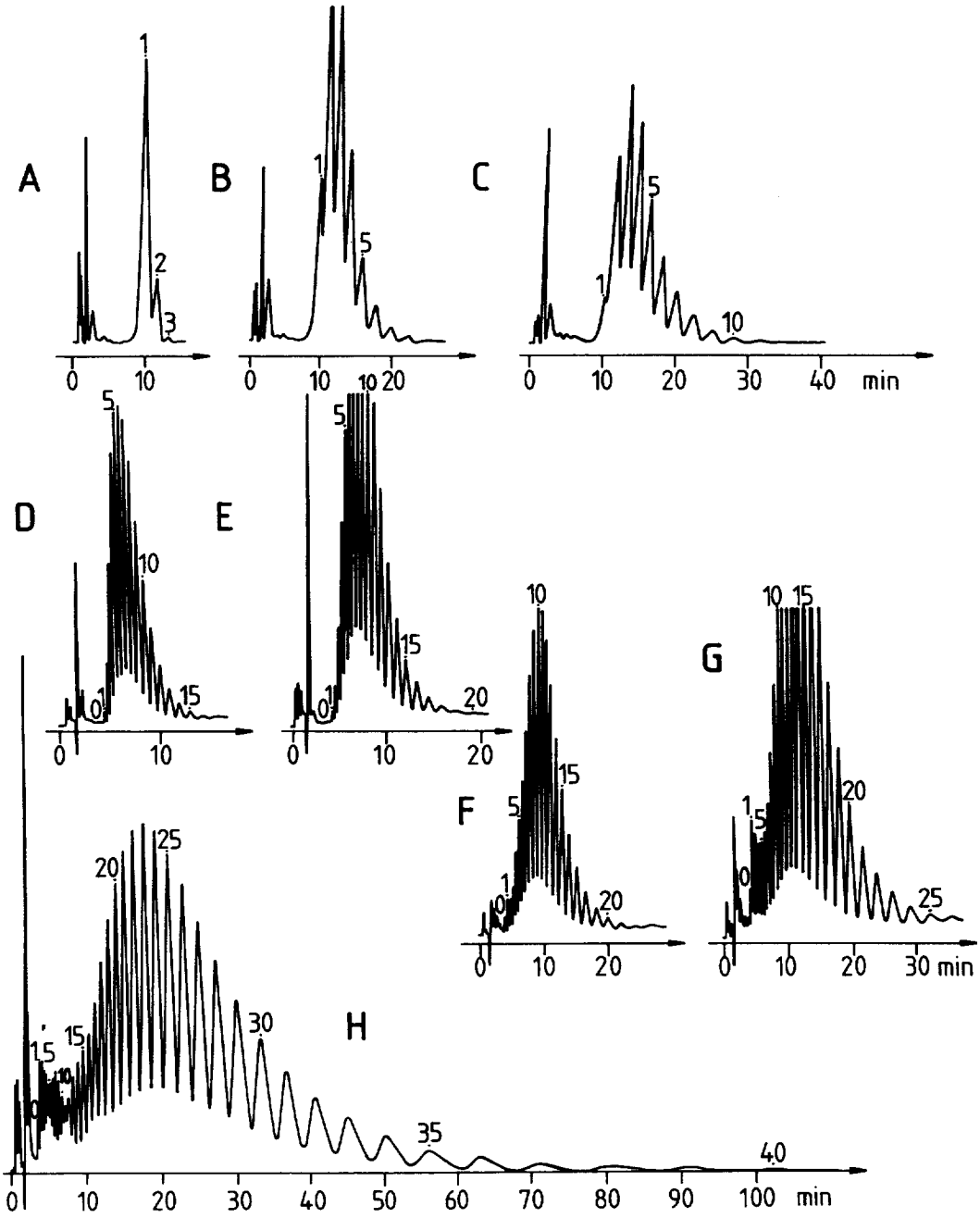

Fig. 6. HPLC of non-ionic surfactants of polyethoxylated octylphenol. (A) Triton X-15 (0.02 mg/ml); (B) Triton X-35 (0.1 mg/ml); (C) Triton X-45 (0.1 mg/ml); (D) Triton X-114 (0.2 mg/ml); (E) Triton X-100 (0.2 mg/ml); (F) Triton X-102 (0.5 mg/ml); (G) Triton X-165 (0.8 mg/ml); (H) POE (30) octylphenol (1.0 mg/ml). Conditions: CSC-C1 TMS column; temperature, 22±1°C; mobile phase, methanol–water [(A)–(C) 53:47, v/v; (D)–(H) 60:40, v/v]; elution mode, isocratic; flow-rate, 1.0 ml/min; UV detection at 225 nm. The numbers assigned to the individual peaks represent the number of ethylene oxide units in the oligomers; O represents the parent *tert.*-octylphenol. The integrator attenuation was set at 3, 4 or 5, depending on the intensities of the peaks. (Reprinted with permission from Ref. [92]).

in the eluent were calculated. It was established that both retention parameters linearly increased with an increasing number of ethylene oxide groups in the surfactant molecule [94]. The relationship between the physicochemical parameters of the stronger eluent component and their retention characteristics on an alumina column was studied in more detail. The retention strength and selectivity of dichloromethane, dioxane, tetrahydrofuran, chloroform and ethyl acetate were calculated using nonylphenyl ethylene oxide oligomers as solutes. Calculations indicated that the separation of the solutes can be easily influenced by changing the bulkiness, dielectric constant and the dipole moment of the stronger component in the eluent. It has also been found that each solvent has a different impact on the chromatographic parameters, with only the bulky solvents, dioxane and tetrahydrofuran, showing some similarity. This result emphasizes the considerable role of molecular dimensions in the determination of eluent characteristics [95].

4.2. Separation of non-ionic surfactants according to the character of the hydrophobic moiety

Due to the considerably lower number of fractions, the separation of non-ionic surfactants according to the character of the hydrophobic moiety seems to be easier than their separation based on the number of ethylene oxide groups. This consideration is true when the hydrophobic moieties differ only in the length of the alkyl chain, which can be separated in many RP-HPLC systems. In these cases, the length of the ethylene oxide chain does not influence the separation because the various ethylene oxide oligomers containing the same hydrophobic moiety elute as one compact peak. However, in many cases, linear and variously branched alkyl chains of identical carbon number or other structural isomers can occur in the same surfactant mixture, making the RP-HPLC separation tedious or impossible. Thus, it was reported that the sorbitan ester surfactants could be separated into sorbitan mono-, di-, tri- and tetra-ester fractions using RP-HPLC with an octadecylsilica column, however, neither the ester isomers nor the esters with high molecular mass were well separated [96]. The retention characteristics of various RP-HPLC supports (C_1, C_2, C_6, C_8, C_{18}, polyethylene-coated silica, polyethylene-coated alumina and alumina-based C_{18}) have been compared using the ethylene oxide oligomers of nonylphenol [97], 1,1,3,3-tetramethylbutylphenol [98] and tributylphenol [99]. The efficacy of separation and the retention of surfactants increased with increasing length of the alkyl chain covalently bonded to the surface of silica (Fig. 7). Calculations indicated that not only the retention strength but also the retention selectivities of RP-HPLC columns differ markedly.It was assumed that the length of the hydrophobic alkyl chain, the character of the apolar polyethylene coating and the original adsorption characteristics of the support may have a similar influence on the selectivity. The successful separation of alkylglycosides, based on the length of the alkyl substituent using C_8-, C_{18} and phenyl-bonded silica supports, was also reported [100]. A C_8 column was used for the simultaneous determination of linear alkylbenzenesulphonates (LASs) and alkylphenol polyethoxylates (APEOs) from treated and untreated municipal waste waters. Recovery was over 80% and the detection limit was below 20 and 4 $\mu g\ l^{-1}$ for LASs and APEOs, respectively [101]. A C_{18} column was used for the separation of LASs, APEOs and their biotransformation products (sulphophenyl carboxylates and nonylphenoxy carboxylates, respectively) using both UV and fluorescence detection [102]. SPE combined with thermospray LC–MS (C_{18} column) has also been used for the enrichment of alcohol ethoxylates from ground and waste waters [103]. It was stated that the detection limit of the method for the individual alcohol ethoxylates varied between 60 ppt and 2.17 ppb.

4.3. Separation of non-ionic surfactants based on the character of the hydrophobic moiety and the length of the ethylene oxide chain

As the biological activity, decomposition rate and surface activity of surfactants depends both on the length of the polar ethylene oxide chain and the character of the hydrophobic moiety, many efforts have been devoted to the separation of non-ionic surfactants in both directions. Traditional methods separate surfactants containing various hydrophobic moieties on an RP-HPLC column, then determine the distribution of surfactant fractions according to the

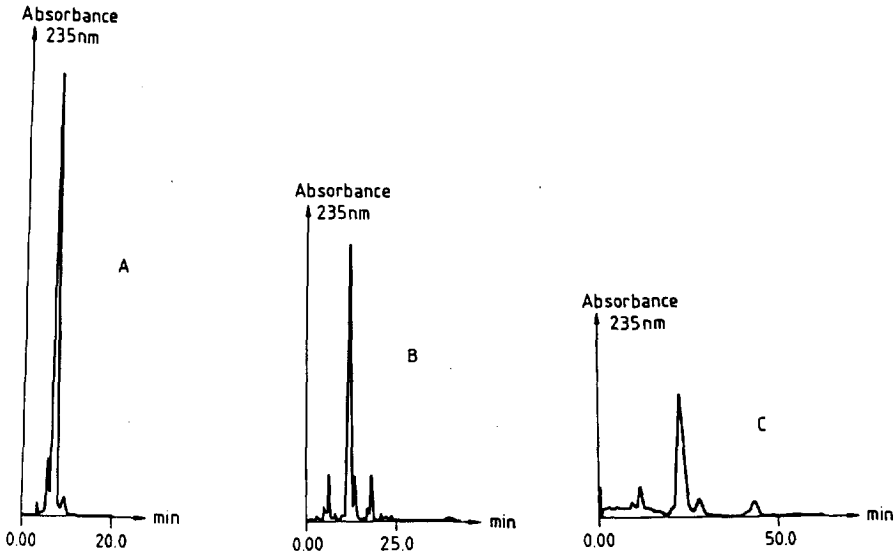

Fig. 7. Separation of tributylphenol ethylene oxide surfactant (average number of ethylene oxide groups=4) on C_1- (A), C_6- (C) and C_{18}-bonded silica (D). Eluent, methanol–water (8:2, v/v); flow-rate, 0.5 ml/min; detection wavelength, 235 nm. (Reprinted with permission form Ref. [99]).

number of ethylene oxide groups per molecule on a polar column, and assume that the distribution of ethylene oxide groups is the same in each fraction separated by RP-HPLC. This is true in practice, but is theoretically incorrect. The unambiguous solution to the problem is the use of the column-switching technique: The fractions separated on a RP-HPLC column can be further separated according to the length of the ethylene oxide chain on another column. An excellent example of this type of analysis is the two-dimensional separation of the non-ionic surfactant Brij 35 (mainly ethoxylated laurylalcohol containing an average of 23 ethylene oxide groups per molecule). It was separated on polystyrene–divinylbenzene copolymer gel, according on the hydrophobic moiety, and on K^+-form cation-exchange resin using the column switching technique, according to the ethylene oxide chain length [104]. The system firstly separates the surfactants according to the length of the fatty alcohol chain and then according to the number of ethylene oxide groups per molecule (Fig. 8).The column-switching technique is a very powerful technique in the analysis of non-ionic surfactants in terms of both ethylene oxide number and hydrophobic moiety. However, it needs complicated instrumentation and considerable expertise in chromatographic separation techniques. The ideal solution may be the use of a support that will separate the surfactants in both directions in a single step. Promising results were achieved in the separation of tributylphenyl ethylene oxide oligomers using alumina and PGC columns. A typical chromatogram of tributylphenyl ethylene oxide oligomers on an alumina column is shown in Fig. 9 [105]. The fractions were clustered in groups of three peaks. It was assumed that each 'triade' represents tributylphenol derivatives with an identical ethylene oxide number, and that the three members of the triad represent the possible structural isomers of the tributylphenol moiety. Steric considerations make it probable that the sterically less hindered 2,4,6-tributylphenol isomers are the most prevalent in the sample, followed by 2,4,5- and 2,3,5-tributylphenol isomers. Unfortunately, the fractions were not identified by mass spectrometry or by another method. Similar results were achieved using a PGC column, however, the separation of fractions was less good than on an alumina column (Fig. 10) [106].

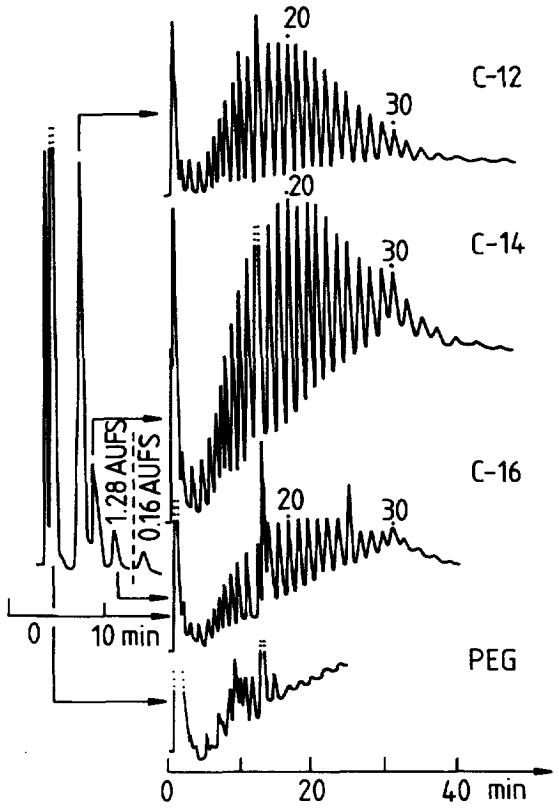

Fig. 8. Results of analysis of Brij 35 (mainly ethoxylated laurylalcohol containing an average of 23 ethylene oxide groups per molecule). (Reprinted with permission from Ref. [104]).

5. Supercritical fluid chromatography

Capillary SFC combines the advantageous separation characteristics of GC and HPLC. Due to its high separation capacity, it has been successfully used for the separation of various non-ionic surfactants, based on the length of the ethylene oxide chain [107,108]. Thus, a 5-m×50 μm SB-Biphenyl-30 column (30% biphenyl, 70% methylpolysiloxane) with a film thickness of 0.25 μm was used for the separation of polyethoxylated octylphenol derivatives, as demonstrated in Fig. 11. [109].It was stated that the separation capacity of SFC is similar to that of HPLC and it can be easily used for the separation and quantitative analysis of surfactants without chromophores in the molecule. A similar SFC method was used for the separation of ethoxylated nonylphenols and was compared with the results of HPLC

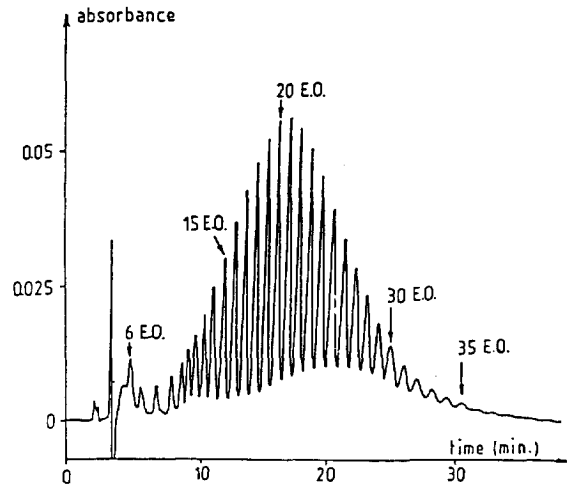

Fig. 9. Separation of tributylphenol ethylene oxide oligomer surfactants on an alumina column. Eluent, ethyl acetate–*n*-hexane (1:1, v/v); flow-rate, 1 ml/min; room temperature, 22±2°C; detection wavelength, 275 nm. (Reprinted with permission from Ref. [105]).

separation [110]. Also, in this instance, the efficacy of the SFC separation was superior to that of HPLC. The propoxylated and ethoxylated derivatives of dimethylpyrazole were also separated using capillary

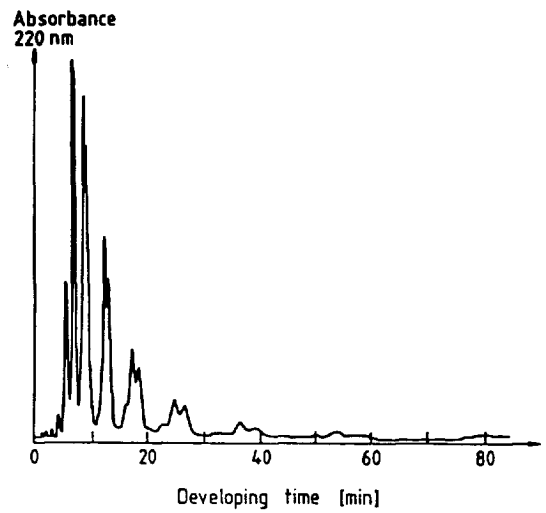

Fig. 10. Chromatogram of ethoxylated tributylphenol oligomers with an average ethylene oxide unit number of four on a PGC column. Eluent, methanol–distilled water (85:15, v/v). Detection wavelength, 220 nm. Flow-rate, 1 ml/min. (Reprinted with permission from Ref. [106]).

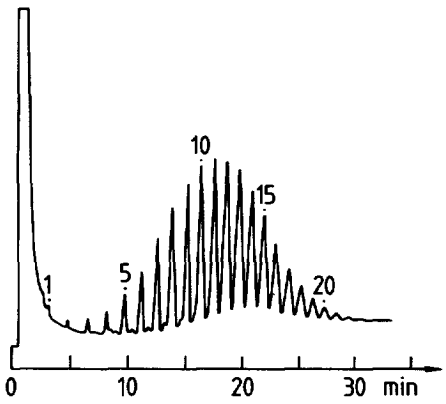

Fig. 11. Capillary SFC chromatogram of Triton X-102 (10.0 mg/ml) using a linear pressure program. Conditions: 5 m×50 μm SB-Biphenyl-30 column; linear pressure program from 2000 p.s.i. with a 2-min initial hold to 5500 p.s.i. in 33 min (1 p.s.i.= 6894.76 Pa); CO_2 mobile phase at 100°C; FID at 350°C; integrator attenuation at 2. The numbers assigned to the individual peaks represent the number of ethylene oxide units in the oligomers. (Reprinted with permission from Ref. [109]).

supercritical fluid chromatography interfaced with chemical ionization mass spectrometry [111].

6. Gas chromatography

The inherent low volatility of non-ionic surfactants hampered the application of gas chromatography for their analysis. Only surfactants with a low number of ethylene oxide groups per molecule can be separated without derivatization [112]. Many efforts have been devoted to the development of suitable derivatization procedures and the subsequent GC analysis of surfactants. Various derivatization processes, such as acylation [113] and silylation [114], have been used to increase the volatility of the non-ionic surfactants, however, the time-consuming derivatization and the low volatility of surfactants, even after derivatization, limited the application of these methods to surfactants with a maximum of twenty ethylene oxide units [115].

As the most common decomposition pathway of non-ionic surfactants is the cleavage of the ethylene oxide chain, the resulting free alkylphenols, fatty acids and fatty alcohols can be toxic [116] and can cause environmental pollution [117]. Capillary GC–MS offers ideal conditions for the analysis of such decomposition products. Thus, the GC–MS analysis of 4-nonylphenol as the acetyl derivative has been reported recently [118]. The recoveries from waste water and sludge were 93%, with a relative standard deviation below 5%, and the detection limits were 0.1 μg/l of waste water and 0.1 μg/g of sludge.

7. Conclusions

The production and the world-wide use of non-ionic surfactants is continually growing. As surfactants in soil and in ground water cause environmental pollution, monitoring them becomes more and more important. Various chromatographic techniques, especially hyphenated methods (GC–MS and HPLC–MS) offer a unique opportunity to separate and to sensitively determine these surfactants. Column switching makes the separation of surfactants possible, based both on the length of the ethylene oxide chain and on the character of the hydrophobic moiety. It is fairly difficult to point out which is the best chromatographic technique for the separation of non-ionic surfactants. It depends on the type of surfactants and on the instrumentation available to the chromatographer, which is usually the limiting factor. At present, HPLC–MS methods combined with the column-switching technique offer an excellent choice for the solution of such analytical problems. The high separation power of capillary zone electrophoresis and supercritical fluid chromatography has not been entirely explored in this intricate field of analysis, but their future use in the area of surfactant analysis is expected. The development of new, more selective adsorbents for the solid-phase extraction of surfactants, the use of microcolumns and new supports to enhance the efficacy of separation and to further reduce the detection limit, will be the exciting challenges in the future for chromatographers.

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