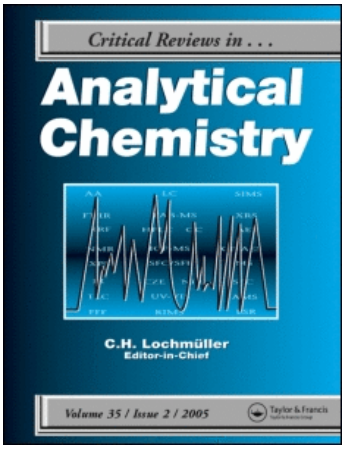

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Analysis of Nonionic Surfactants with Polyoxyethylene Chains by High-Performance Liquid Chromatography

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Analysis of Nonionic Surfactants with Polyoxyethylene Chains by High-Performance Liquid Chromatography

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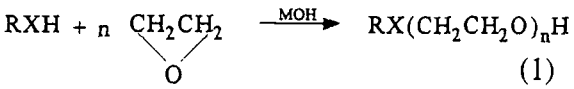
ABSTRACT: A critical review of HPLC methods for analysis of nonionic surfactants on normal and reversed phases, molecularx sieves and ion exchangers with UV, RI, FID, fluorometric, conductometric, MS and ELSD detection is presented.

KEY WORDS: alkylphenols, ethoxylated alcohols, gas liquid chromatography, hydrophobic reagents, nonionic surfactants, oxyethylene groups.

I. INTRODUCTION

Nonionic surfactants comprise, after their anionic counterpart, the most important class of surfactants. The reason for the use of polyoxyethylene nonionic surfactants in place of anionic surfactants is their good usage properties, appropriate biodegradability and low toxicity in aquatic environment. Nonionic surfactants are broadly used in industry and household. They usually contain one hydrophobic hydrocarbon chain and one hydrophilic group or block. Among nonionic compounds, surfactants having one or more polyoxyethylene groups are the most important. They are usually obtained in the reaction of various alcohols, alkylphenols, alkylamines, fatty acids and their amides, etc., with ethylene oxide according to the following reactions:



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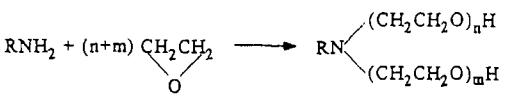

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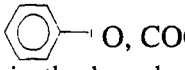
where X = O,  O, COO, S, S, etc. m and n changes in the broad range.

Thus the products contain several homologues with different length of the polyoxyethylene chain. Moreover hydrophobic reagents, e.g., alcohols, alkylphenols can consist of several components.

In the case of fatty acids ethoxylation, the ethoxylated acids (monoesters - ME) can react further with acids giving diesters - DE.

Ethoxylated compounds offer a real challenge to analytical chemists because they are

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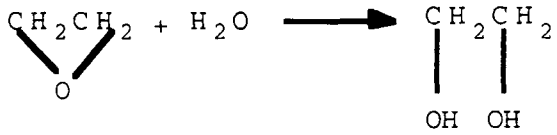
usually composed of complex mixtures of many compounds, reaching even a quantity of several dozen (polydisperse mixtures).

$$RCOO(CH_2CH_2O)_nH + RCOOH \longrightarrow RCOO(CH_2CH_2O)_nOCR + H_2O \quad (3)$$

Although these surfactants have been produced for a few dozen years the problem of their synthesis is still vivid. It is connected with their polydispersity and formation of undesired products, having too low and too high molecular mass which affect the physicochemical and usage properties of surfactants. Therefore new catalysts for ethoxylation have recently been proposed and narrow range distributed products manufactured [1-4].

Polyoxyethylene glycols, $HO(CH_2CH_2O)_nH$, are formed as unvaluable by-products. Ethylene glycol, formed from ethylene oxide in the presence of moisture, is the initiator of further addition of ethylene oxide.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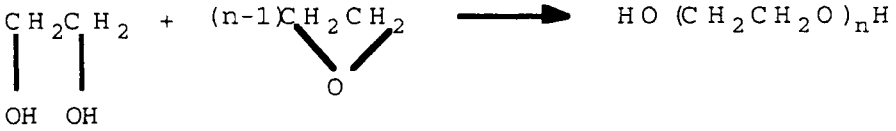

(5)

Nonionic surfactants with polyoxyethylene chains exhibit asymmetry and because of this, they can adsorb at different interfaces and can decrease surface and interfacial tensions. Thus, such compounds in systems containing an aqueous phase and an organic phase can (1) adsorb at the interface penetrating with their hydrophilic heads more or less deeply into the aqueous phase, or (2) dissolve better in the aqueous phase or in the organic phase. This behavior, as well as other properties of surfactants, depend on their affinity for the aqueous phase, which depends on the length and structure of their hydrophilic group, its polydispersity and/or the length and structure of the hydrophobic group.

Various systems have been proposed to correlate the properties of nonionic surfactants with their structure and so-called hydrophile-lipophile balance, which were broadly discussed in our previous reviews [5,6]. They include hydrophile-lipophile balance (HLB), emulsion inversion temperature (EIT), emulsion inversion point (EIP) and polarity parameters determined by inverse gas chromatography broadly discussed in our previous original papers [7-24]. They clearly demonstrate the importance of the structure of surfactants and their state of hydrophile lipophile balance which determine possible nonionic surfactant applications.

Thus, it is obvious that the determination of the composition of these complex mixtures of nonionic surfactants is decisive both in fundamental and applied research. As a result, various techniques have been used for the analysis of nonionic surfactants and several papers published on the subject.

Colorimetric determinations of ethoxylated nonionic compounds are rarely used because of their lack of selectivity and the dependence of color development upon the degree of polymerization of eth-

ylene oxide. Thus, chromatographic techniques occupy a very important place among analytical techniques of nonionic surfactants.

Gas-liquid chromatography was earlier used. Nonionic surfactants can be analyzed directly or after their derivatization into volatile derivatives. This method permits separation of the components of individual hydrophobes, i.e., containing only one alcohol, alkylamine, alkylphenol, etc. up to a homologue containing about 16 oxyethylene units. Thus, it does not concern the actual industrial systems in which complex mixtures of alcohols, alkylphenols, alkylamines, etc., are used as reagents.

The average content of the polyoxyethylene chain and the composition of hydrophobic reagents used for ethoxylation can be determined by gas chromatography after surfactant molecule degradation. It has been extensively reviewed by Cross in his monograph [25] and discussed in our previous papers [26-49].

Gas liquid chromatography thus permits the analysis of relatively simple models and products which can be transformed into volatile derivatives, i.e., having a relatively low molecular mass. As a result, other chromatographic techniques, including HPLC must be used to analyze commercial surfactants and to study their synthesis.

The following analytical problems can be important in surfactant analysis:

- Separation and determination of various homologues having different length of polyoxyethylene chain
- Separation and determination of hydrophobic precursors used for nonionic synthesis
- Simultaneous separation of nonionics according to the increasing length of the polyoxyethylene chain and various compositions of hydrophobes
- Determination of the total quantity of polyoxyethylene glycols
- Separation and determination of the polyoxyethylene glycol distribution

HPLC gives wide possibilities in surfactant analysis by a range of separation conditions including different stationary and moving phases. The following separation modes can be considered: normal phase, reversed phase, size exclusion, and ion exchange chromatography.

Various solvents and their mixtures with constant and changed in time compositions can be used. Aliphatic hydrocarbons with polar additives are used in normal phase mode. Water and organic polar additives are used in reversed phase mode. Usually individual solvents (water or tetrahydrofurane) are used with molecular sieves. The mixtures of acetonitrile and water or low molecular weight alcohol are used with ion exchange resins.

Thus, the separation conditions can be practically changed by an appropriate selection of stationary and moving phases which permits to obtain various types of separations to be obtained.

The next problem is connected with quantitative assessment of separated compounds. Various detectors can be used. UV, RI, FID, ELSD (Evaporative Light Scattering Detector), Fluorescent and Conductometric detector are among the most often applied.

Depending on the type of the detector, surfactants can be analyzed directly or after their derivatization.

II. SEPARATION MODE

A. Normal Phase Chromatography

In the early days of modern high performance liquid chromatography in 1970's, when packings with chemically bonded phases were not readily available, nonionic surfactants were analyzed by liquid-liquid partition chromatography (e.g., using PEG 400 as a stationary phase) and adsorption

chromatography on silica gels and diatomaceous earths [50-53]. Most of such determinations were not of the quantitative type due to unsatisfactory separation, detection systems and unavailability of appropriate standards. Using isocratic systems good enough separations were obtained for mixtures comprising only 5 to 7 components. More complex mixtures were eluted from a column either as a poorly separated 'umbrella type curve', or the Poisson's curve, without any separation into individual oligomers [54]. Application of a gradient elution proved to give much better results [53-57]. Some authors used 'weaker' gradients to separate adduct-oxirane mixtures having lower average ethoxylation degrees $\bar{n}$ and those with 'stronger' gradients for adducts with higher $\bar{n}$ [58]. To decrease adsorption on silica columns, ethoxylates of alcohols and alkylphenols were often converted into their less hydrophilic ester derivatives prior to analysis [53,59,60].

The performance of a non-modified silica is higher when ethanol instead of or together with propanol is used as a mobile phase together with a non-polar hydrocarbon [61].

The activity of the silica depends on the mobile phase water content and is observed to change in time [62]. Therefore, packings with chemically bonded phases, such as cyano -CN, diol -OH, or amino NH_2, replaced almost entirely the bare silica.

Mobile phases with modified silica are quite often used in the form of mixtures of hexane, 2-propanol and water [57,63-66], rather than chloroform and dichloromethane, as the latter cause the baseline to drift and may lower sensitivity in the case of UV detection and gradient elution.

Identification of ethoxylates is performed using either a mass or UV and IR spectrometer [67-70] or spiking with standards [71].

Chemically bonded diol and nitirile phases show regular retention behavior only with the mobile phases having a low propanol content. Using a gradient, it is possible to separate, in a reasonable time, only a small number of homologues containing no more than 6 to 8 oxyethylene groups in a molecule. Mobile phases that are rich in propanol tend to disturb the separation of the higher oligomers due to the presence of a mixed retention mechanism (partition, adsorption) which is responsible for a non-linear increment of log k′ (k′ - distribution factor) accompanying the growth of the polyoxyethylene chain. Regular retention behavior, even for higher homologues in the presence of a mobile phase with a high propanol content in a mixture with an n-alkane is shown by a chemically bonded amino phase. Ethoxylates are better separated on it than on the diol- and cyano phases, both under isocratic and gradient conditions. On the amino phases it is possible to predict capacity factors for the respective oligomers [61].

A *p*-nitrophenyl phase has particularly good properties favoring the separation of multicomponent mixtures of ethoxylated nonionic surfactants, when used with a heptane- dichloromethane- and methanol gradient [72]. It helps to obtain a good separation for ethoxylated C16-18 alcohols containing 1-80 oxyethylene groups in a molecule, and up to 60 such groups for ethoxylated *p*-nonylphenol.

Desbéne *et al.* [73,74] compared three columns: an amino, cyano and diol column. Satisfactory results (for distribution determination of surfactants) for 3 types of samples (ethoxylated C16-18 alcohol with low, medium and high average ethoxylation degrees), verified with the average ethoxylation degree, were obtained only using the diol column. Samples with low and medium average ethoxylation degrees could be separated by isocratic elution (heptane: CH_2Cl_2:CH_3OH). On the other hand, separation of a sample with a high ethoxylation degree requires application of a heptane/2-propanol gradient.

The sequence of elution on normal phases depends on the length of the polyoxyethylene chain, and retention time increases with the growth of the chain (Figure 1). Interactions

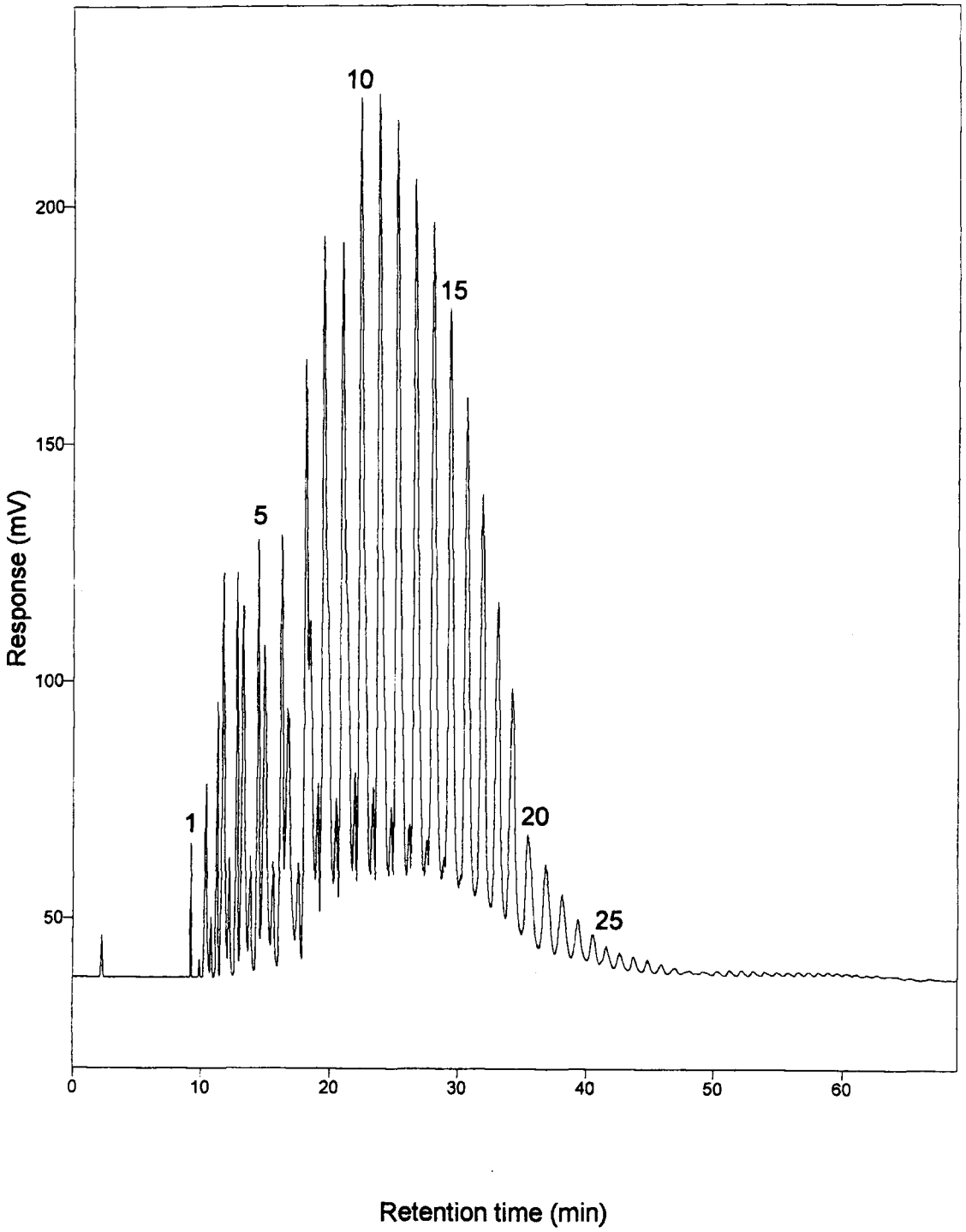


FIGURE 1. Separation of ethoxylated Lial 125 (mixture of oxo alcohols- isomers of C12,13,14,15) (average ethoxylation degree = 9) on normal phases according to hydrophile (polyethoxy) chain length (stationary phase: Hypersil APS 200 × 2.1 × 5; mobile phase: A-hexane, B-5% H_2O in 2-propanol, 0.3 ml/min; Gradient program: 0 → 60% B/55 min; ELSD - 50 mm N_2, 80°C).

between the alkylaryl and alkyl groups of ethoxylated alkylphenols, alcohols and acids, respectively, and the column packing are all much less important. For example, *p*-nonyl- and *p*-octyphenol are eluted as a single peak, just like their corresponding

ethoxylated *p*-octyl- and *p*-nonylphenols. Therefore, all oligomers with the same oligooxyethylene chain length have similar retention times under the same conditions, irrespective of the length of the alkyl and alkylaryl chain [58,60,63,75]. The distribution of PEGs can be determined during the same analysis on NH_2 column with *n*-hexane:2-propanol:water gradient when sufficiently narrow distributed ethoxylated alcohols and alkylphenols are analyzed. More polar PEGs start to elute from the column after the last surfactant has left it (Figure 2) [76].

Zeman [64] presented results of his research on the separation of ethoxylated alcohols, fatty acids and alkylphenols with a chemically bonded diol phase, using mobile phases with various strengths (hexane + isopropanol + H_2O + CH_3COOH) under isocratic conditions. Zeman noted the possibility of quantitative assessment of distribution for both ethoxylates and polyoxyethylene glycols on the same column. Ethoxylate homologues with lower polarities (i.e. compared with PEGs) are separated in the first analysis, using a less polar mobile phase (hexane + isopropanol + H_2O + CH_3COOH = 140:60:5:1), whereas polyoxyethylene glycols, having higher polarities, are separated as a single peak using the 'back flushing' technique. The homologues of PEGs are separated on the same column using the second mobile phase with higher polarity (hexane:isopropanol:H_2O + CH_3COOH = 105:95:10:1). The distribution of both ethoxylates and PEGs can also be obtained by combining HPLC method with Weibull's extraction method. Ethoxylates can be separated from PEGs by extraction, followed by their further separation into single peaks using eluents with the above-given compositions. Unfortunately, none of the ethoxylate sample analyses yielded a quite satisfactory separation performance, most probably because of isocratic mode of elution applied by the author.

Using appriopriate composition of *n*-hexane:2-propanol:water:acetic acid on diol column it is possible to obtain the distribution of PEGs present in ethoxylated fatty acids even using isocratic mode of elution. The elution order of the main components of such surfactant is fatty acid, diester, monoester and PEGs [64,65] (Figure 3). Depending on the polarity of the mobile phase monoester and diester can be obtained as two single peaks when more polar mobile phase is used and separated to appropriate homologues (oligomers) with less polar mobile phase [64]. Even in isocratic mode, homologues of PEGs present in above mixture can be separated fairly well [65].

It is also worthwhile to mention the effect of sterical shading of the polyoxyethylene chain by an alkylaryl hydrophobe present in ortho isomers of alkylphenol ethoxylates. The effect is manifested by partial overlapping of the peak of each *p*-alkylphenol homologue with the peak of the ethoxylated *o*-alkylphenol derivative that contains one more oxyethylene unit [77,78].

Data on separation on normal phases are presented in Table 1.

B. Reversed Phase Chromatography

As shown by comparison of the different reversed phases with various lengths of their alkyl substituents (C_2, C_4, C_6, C_8, C_{18}) using mixtures of methanol, acetonitrile, tetrahydrofurane, dioxane, acetone and 2-propanol with water as eluents, the C_{18} phase has the best performance, despite its quite long retention times. The C_8 packing gives somewhat shorter analysis times for surfactants with longer polyoxyethylene chains. With the other packings, separations are not satisfactory, especially for surfactants with shorter oligooxyethylene chains [79]. That is why C_{18} is the most preferable reversed phase in analyses of ethoxylated nonionic surface active agents.

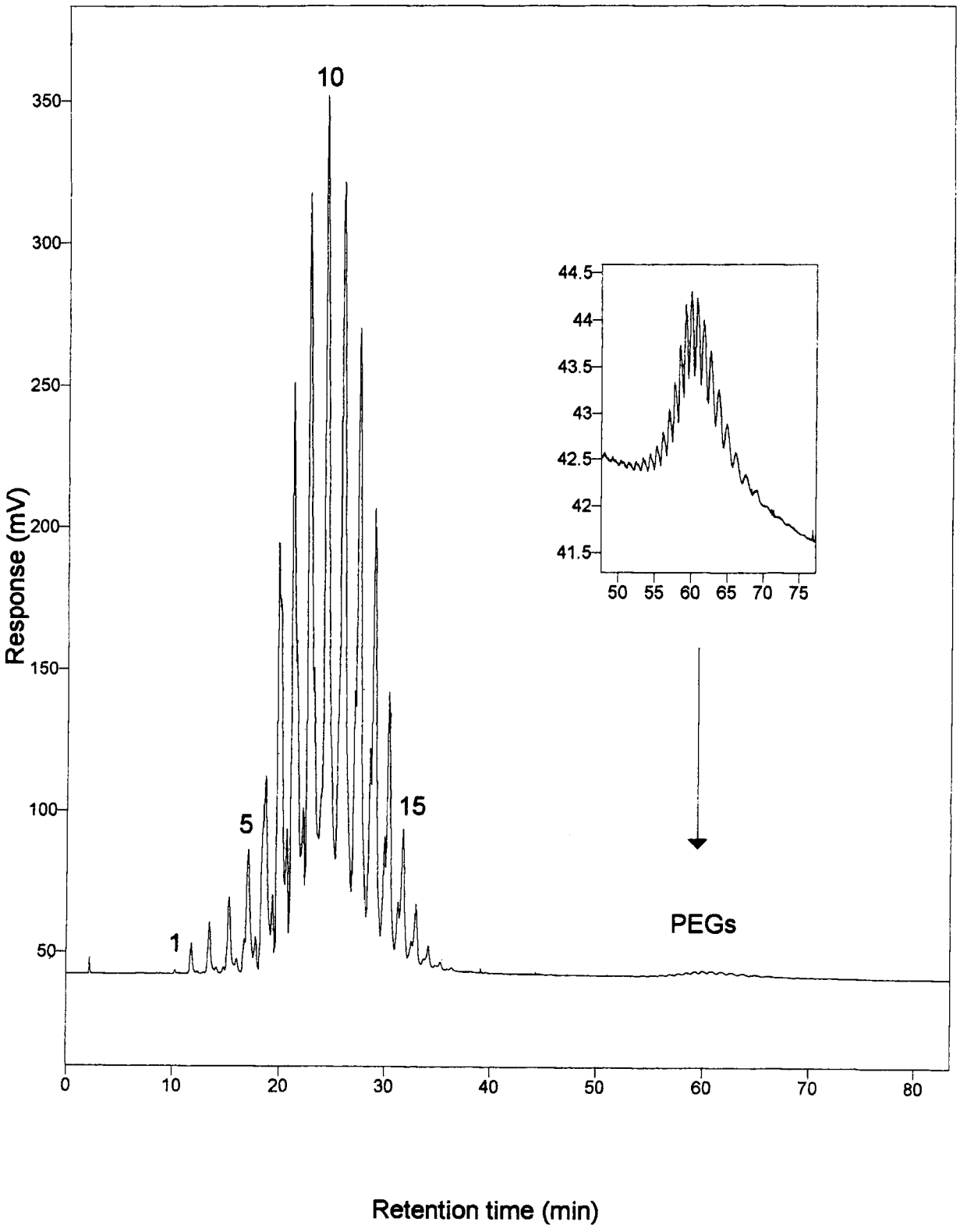


FIGURE 2. Discrete separation of PEGs from ethoxylated Lial 145 (mixture of oxo alcohols-isomers of C14,15 (average ethoxylation degree = 10) on normal phases (stationary phase: Hypersil APS 200 × 2.1 × 5; mobile phase: A-hexane, B-5% H_2O in 2-propanol, 0.3 ml/min; Gradient program: 0 → 60% B/55 min; ELSD - 50 mm N_2, 80°C)

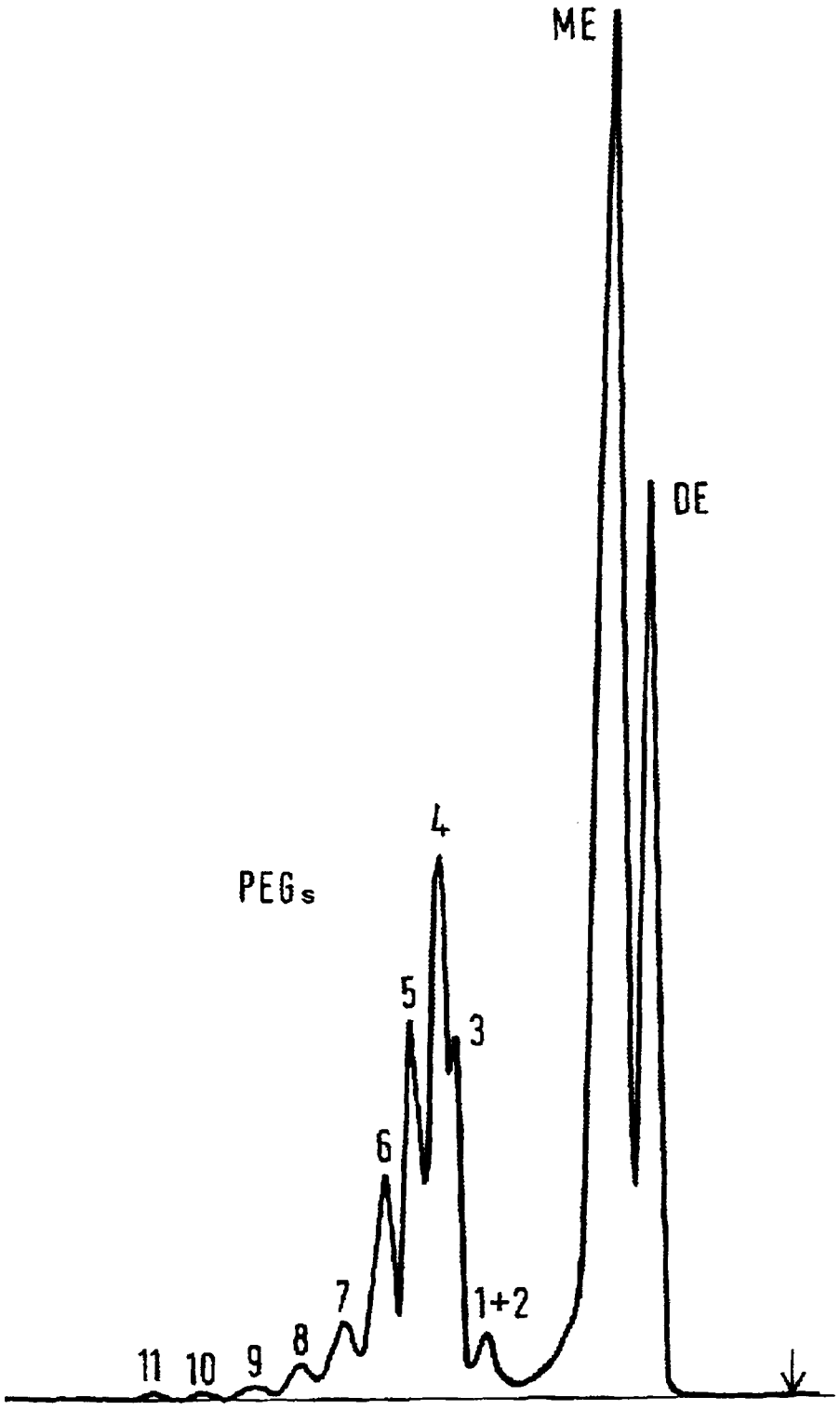


FIGURE 3. Separation of lauric acid ethoxylated by 20 mole EO on normal phases (stationary phase: LiChrosorb DIOL 250 × 4.61 × 7; mobile phase: C_6H_{14}/2-C_3H_8OH /H_2O/CH_3COOH (105:95:10:1 v/v), 1.0 ml/min, isocratic; RI); DE-fatty acid diesters, ME-fatty acid monoesters, PEGs-polyoxyethylene glycols [65] (From Zeman I., Šilha J., Bareš M., *Tenside Detergents*, 23, 4, 1986. With permission. © Tenside Surfactants Detergents.)

TABLE 1
Separation of Ethoxylated Compounds on Normal Phases

No 1	Type of surfactant (*) 2	Stationary phase (**) 3	Mobile phase 4	Isocratic/Gradient program and flow rate 5	Detector (parameters) 6	Quantification 7	Reference 8	Remarks 9
1	OPEO9.7	Silicic acid (1200 × 60) or (800 × 50)	A-$CHCl_3$, B-CH_3COCH_3	20%B/10l → 50%B/5l → 20%B/5l → 30%B/6l → 45%B/4l	Elution curves were created as follows: the eluate was taken in fractions, each fraction being either evaporated and weighed or evaporated to dryness, dissolved in chloroform and determined the absorption at 277 nm.	No	124	
2	Triton X-15, X-45 (OPEOn)	Corasil II (SiO2) (50 × 2.3 × 10)	95% n-hexane, 5% 2-C_3H_8OH	Isocratic, 0.75 ml/min	RI	No	51	
3	CmEOn, APEOn, fatty amines and alkanolamides ethoxylates	NaCl solution supported on cellulose put into a column (500 × 16)	$CH_3COOC_2H_5$	Isocratic	The eluate was taken in 10 ml fractions, each fraction being evaporated and weighed and then elution curves created.	No	91	Determination of PEGs in fatty alcohols, and alkylphenols, fatty amines and alkanolamides ethoxylates.
4	APEO3,5,7,9,14	Solid supports: silica (Spherosil, 1750A (270 × 2.7 × 2-5)), diatomaceous earth products (Hi-Flow Super Cell (270 × 2.7 × 5-10)) and (Kieselguhr (270 × 2.7 × 20-30)) Stationary phases: PEG-400 and 1,2,3-*tris*-(2′-cyanoethoxy)-propane	CCl_4; CCl_4/i-octane,1/1(w/w);i-octane; i-octane/CCl_4,2/1(v/v); i-octane/CCl_4,1/2(v/v);97.8% i-octane, 2.21%C_2H_5OH,0.084% H_2O (by weight)	Isocratic, 0.26 ml/min, 0.76 ml/min, 1.3 ml/min	UV (277 nm), RI	No	52	Identification based on MS spectrum of one peak and assumption that the others differ from each other by 1EO unit.
5	Arcopal N-040 (NPEO4), Arcopal N-060 (NPEO6), Arcopal N-090 (NPEO9)	Chezasorb coated with 15% PEG 400 (2500 × 2 × 60–80)	100% *n*-hexane	Isocratic, 0.45 ml/min	UV (254,285 nm)	Yes	104	Determination of non-ionic surfactants and mineral oil in waste waters.

TABLE 1 (CONTINUED)
Separation of Ethoxylated Compounds on Normal Phases

No	Type of surfactant (*)	Stationary phase (**)	Mobile phase	Isocratic/Gradient program and flow rate	Detector (parameters)	Quantification	Reference	Remarks
1	2	3	4	5	6	7	8	9
6	C12EO5, C12EO10, C12EO15, C12EO25, NPEO5, C12COEO10	Zorbax-SIL 250 × 2.1	A-*n*-hexane, B-CH_3COCH_3	25%B → 100%B/15 min	Moving wire detector	Yes	59	Distribution of ethoxylated alcohols and nonylphenols. Analyzed as acetylated derivatives — to decrease adsorption on a column. Retention time was directly proportional to an EO mole number.C.C.N.
7	CmCOEOn and mixture of CmCOEOn and CmEOn	μ-Porasil	A-*n*-heptane, B-$C_3H_5OC_2H_5$ (water saturated), C-THF, D-dioxane,E-2-C_3H_8OH,F-H_2O, G-CH_3COOH	10%B:0%C → 18%B:12%C; 10%B:0%D:0%E:0%F:0%G → 20%A:30%B:40%D:10%E:1%F: :0.5%G, 1.5 ml/min	Moving wire detector	No	109	Distribution of CmEOn and CmCOEOn.
8	Triton X-100 (OPEO9.5), Triton X-114 (OPEO7), Triton X-165 (OPEO16)	Porasil A(60) (8 ft. × 3/8 in. × 37–75), Porasil A(60) (2 ft. × 1/8 in. × 37–75)	A-$CH_3COOC_2H_5$:CH_3COOH:H_2O =100:32:30, B-$CH_3COOC_2H_5$	0%B → 100%B/100 min, 0.5 ml/min-for smaller column, 6.0 ml/min-for larger column	UV (280 nm), RI	No	53	Analyzed as acetate derivatives.
9	OPEOn	μBondapack NH2 (30 × 3.9 × 10)	A-*n*-hexane, B-10% H_2O, 90% 2-C_3H_8OH	2%B → 50% B/60 min, 1.0 ml/min	UV (280 nm)	No	57	
10	NPEO3, NPEO5, NPEO7, NPEO9, NPEO12	Micropak Si10	(1) A-*n*-hexane, B-$C_2H_5OC_2H_5$, C-CH_3OH (2) A-*n*-hexane, B-$CHCl_3$, C-CH_3OH	(1) 66.0% A 28.3% B 5.7% C, isocratic, 2.0 ml/min; (2) 5% B1% C → 5% B2% C/5 min: :5% B 2% C → 10% B10% C/5 min: :10% B10% C → 20% B20% C/10 min, 2.0 ml/min	UV (278 nm)	Yes	131	
11	NPEO10.5, C1012EOn, C12EOn, C1214EOn, C1218EOn	Two μ-Porasil	(1) A-$C_4H_8Cl_2$, B-2-C_3H_8OH-low-mol-adduct (2) A-CH_2Cl_2, B-2-C_3H_8OH-higher-mol-adduct	(1) 2% B → 32% B/60 min (2) 3% B → 18% B/60 min, 2–4 ml/min	UV (240 nm)	Yes	58	Analyzed as phenyl isocyanate derivatives. When large excess of phenyl isocyanate is used small amounts of double adducts of urea type can be formed which causes disturbances in elution times.
12	C10EO3, C14EO4,	Amino-Sil-X-I (250 × 26 × 10–13)	89.9% *n*-hexane 10.0% 2-C_3H_8OH 0.1% monoethanolamine	Isocratic, 0.3 ml/min	RI	Yes	133	Distribution. Individual standards were obtained in Williamson's

								reaction of appropriate glycols with $C_QH_{1Q}OH$ and$C_{10}H_{21}OH$ that were used for determination of correction coefficients. Response of higher standards determined by extrapolation.
13	OPEO30, OPEO40 both of them PEGs free, obtained via the Weibull ethyl acetate extraction procedure	Zorbax-NH2 (250 × 4.6 × 6)	A-isooctane:CH_2Cl_2:CH_3OH = 95:5:3 B-isooctane:CH_2Cl_2:CH_3OH = 60:40:7.5	(1) 0% B → 50% B/30 min; (2) 0% B → 100% B/45 min (for higher condensates); 2.0 ml/min	UV (276 nm)	Yes	54	C.C.N.
14	Neodol 25-9 (C1215EO9), Neodol 23-6.5 (C1213EO6.5), Neodol 23-7.5 (C1213EO7.5)	μ-Porasil (1 ft. × 1/4 in.)	A-0.5% CH_3OH 4.5% CH_3COCH_3 95% *n*-hexane, B-10% CH_3OH 90% CH_3COCH_3, C-5% CH_3COCH_3 95% *n*-hexane, D-100 CH_3COCH_3	(1) 100% A:0% B → 0% A:100% B/40 min or 100% A:0% B → 0% A:100% B/45 min, (2) 100% C:0% D → 0% C:100% D/40 min or 100% C:0% D → 0% C:100% D/45 min; 2.0 ml/min for all gradients	Disc-flame ionization detector	Yes	60	Distribution of ethoxylated alcohols. Analyzed as acetylated derivatives. Response factors were calculated from experimentally determined response factors for C12EO(3) and C12EO(8)
15	APEOn	Hypersil-5 (250 × 4.6 × 5), Hypersil-5-CPS (250 × 4.6 × 5)	A-*n*-hexane, B-C_2H_5OH	0% B/10 min:0% B → 20% B/10 min: 20% B → 40% B/20 min:40% B → 80% B/10 min:80% B/10 min, 2.0 ml/min	UV (220 nm)	Yes	56	Distribution of ethoxylated alkylphenols. C.C.N.
16	Brij 92 (C18EO2), Brij 96 (C18EO10), Brij 98 C18EO20) — all with one unsaturated bond;	LiChrosorb SI-60 (250 × 4.6 × 10)	A-*n*-hexane, B-CH_3OH, C-2-C_3H_8OH	(1) 0% B:7% C - isocratic; (2) 0% B:7% C → 0% B:60% C/60 min; (3) 0% B:7% C → 10% B:42% C/20 min → 35% B:65% C/20 min; (4) 0% B:7% C → 0% B:15% C/5 min; 1.0 ml/min — for all gradients	UV (220 nm)	Yes	67	Distribution of ethoxylated fatty acids Based on peak area C.C.N. Identification made by CIMS; brominated AEO were also separated without a need to change elution conditions
17	Mapeg-200 (C18COEO4.5), Mapeg-400 (C18COEO(9)), Mapeg-600 (C18COEO(13.5)), Myo-2 (C18COEO2), Myo-10 (C18COEO10), G-5507 (C18COEO), G-2143 (C18COEO) — all acids are unsaturated with one double bone	LiChrosorb SI-60 (250 × 4.6 × 10)	A-*n*-hexane, B-CH_3OH, C-2-C_3H_8OH	0% B:7% C → 10% B:42% C/20 min → 35% B:65% C/20 min → 35% B:65% C/20 min; 1.0 ml/min	UV (220 nm)	Yes	68	Distribution of ethoxylated fatty acids based on peak area. C.C.N.;identification made by CIMS; brominated AEO were also separated without a need to change elution conditions

TABLE 1 (CONTINUED)
Separation of Ethoxylated Compounds on Normal Phases

No	Type of surfactant (*)	Stationary phase (**)	Mobile phase	Isocratic/Gradient program and flow rate	Detector (parameters)	Quantification	Reference	Remarks
1	2	3	4	5	6	7	8	9
18	NPEO9, OPEO10	LiChrosorb Si 60 (150 × 4 × 5)	A-*n*-hexane, B-C_2H_5OH:THF:H_2O = 60:40:1	0% B → 100% B/60 min, 2.0 ml/min	FSD (280 nm(ex)), 310 nm(em))	Yes	114	Determination of trace amounts of APEO. The presence of water should be avoided because silica gel was affected by H_2O and caused a *decrease in column* efficiency. C.C.N
19	Marlophen 83 NPEO3.15), Synperonic OP10 (OPEO10), OEO(1-4)	(1) LiChrosorb-NH2 (250 × 4.6 × 10), (2) Hypersil APS 60 × 4 × 3)	(1) A-*n*-hexane, B-50% *n*-hexane 50% 2-C_3H_8OH (2) A-*n*-hexane, B-85% *n*-hexane 15% 2-C_3H_8OH	(1) 2% B → 70 B/25 min, 2.0 ml/min; (2) 3% B → 25% B/10 min, 2.0 ml/min	UV (277 nm)	Yes	77	NP, NPEO(1) and NPEO(2) in samples from waste-water and sludge treatmen and aquatic environment. RF of NP NPEO(1), NPEO(2) with TMP as an IS were: 1.8, 2.6, 2.9 respectively; RF = (AsMn)/(AnMs); RF = = 0.34EO + 2.2 (R2 = 0.986) – for NPEO1 to NPEO5. RF for NP was significantly lower, indicating a higher specific absorbance.
20	NPEOn, OPEOn, CmEOn	Servachrom (250 × 4.6 × 5) (NH2)	A-20% THF 80% *n*-hexane, B-10% H_2O, 90% 2–C_3H_8OH;	2 B → 50% B/60 min, 1.0 ml/min	MS (EI,CI)	No	121	
21	Marlophen 83 (NPEO3.15), Synperonic OP10 (OPEO10), OEO(1-4)	(1) LiChrosorb-NH2 (250 × 4.6 × 10), (2) Spherisorb-NH2 (120 × 3 × 5) (3) Hypersil APS (100 × 4 × 3)	(1,2) A-10% *n*-hexane 90% 2-C_3H_8OH, B-90% 2–C_3H_8OH 10% H_2O (3) A-98% *n*-hexane 2% 2-C_3H_8OH, B-98% 2–C_3H_8OH, 2% H_2O	(1,2) 3% B → 63% B/60 min, 1,5 ml/min (3) 5% B → 50% B/20 min, 1.5 ml/min	UV (277 nm)	Yes	70	*Analysis of surfactant* products, municipal waste-waters and natural waters. Determination of RF of preparatively separated oligomers with TMP as an IS; RF = (AsMn)/(AnMs); RF = 0.3989 EO+ +2.0052 (R = 0.9976) for NPEO,

								RF = 0.3989 EO+ +1.9052 (R = 0.9976) for OPEO; the limits of detection: 1 µg/L for lower and 3 µg/L for highest oligomers.
22	C12COEO9,20	LiChrosorb Diol (250 × 4.6 × 7)	*n*-hexane: 2-C_3H_8OH: H_2O:CH_3COOH = 105:95:10:1	Isocratic, 1.0 ml/min	UV (210 nm), RI	No	65	Distribution of PEG and ethoxylates.
23	Nonidet P40 (OPEO8.5), Triton X-15 (OPEO1.5), Triton X-35 (OPEO3.5)	Zorbax NH2 (250 × 4.6), Partisil 5 PAC (250 × 4.6 × 5)	A-0.1% CH_3COOH in MTBE, B-0.1% CH_3OH in 95% CH_3CB 5% CH_3OH	0% B → 100% B/30 min, 2.0 ml/min	FSD (230 nm(ex), 302 nm(em))	Yes	115	Determination of OPEO in environmental samples. Gradient elution with MTBE, CH_3CN, CH_3OH allows the use of wavelengths down to 230 nm and increase sensitivity. Molar extinction coeff. for OPEO at 230 and 278 nm is ethoxylate chain independent of the length. OPEO(1) to OPEO(19) were confirmed by MS. Detection limit is 0.2 ng of individual oligomer.
24	Lutenso/AP-10 (NPEO4), OP-10 (NPEO5)	Silasorb-600 (250 × 4.6)	(1) 70% *n*-hexane 30% C_2H_5OH — for samples with av. ethox. degree < or = 5 (2) 50% *n*-hexane 50% C_2H_5OH — for samples with av. ethox. degree > or = 5	(1) isocratic, 0.5 ml/min (2) isocratic, 1.0 ml/min	UV (276 nm)	Yes	69	
25	C12EO6, C12COEO3,9,12,20, DPEO6, APEOn, fatty acid monoethanolamines	LiChrosorb Diol (250 × 4.6 × 10), LiChrosorb Diol (250 × 4 × 5)	Various ratios of *n*-hexane:2-C_3H_8OH:H_2O:CH_3COOH, (1) 75:125:10:1, (2) 90:110:10:1, (3) 105:95:10:1, (4) 120:80:10:1, (5) 125:75:10:1, (6) 140:60:5:1	Isocratic, 1.0 ml/min	UV (254 nm), RI	No	64	Distribution of PEGs and ethoxylates. Individual standards were preparatively separated (identified by UV and NMR) and used for identification. Application of back-flushing of the PEGs fraction.
26	C1315EO2.8	LiChrosorb Diol (250 × 4.6 × 10)	A-*n*-hexane, B-96% CH_2Cl_2 4% CH_3OH	15% B → 35% B/35 min	ELSD (t = 30°C)	No	136	

TABLE 1 (CONTINUED)
Separation of Ethoxylated Compounds on Normal Phases

No	Type of surfactant (*)	Stationary phase (**)	Mobile phase	Isocratic/Gradient program and flow rate	Detector (parameters)	Quantification	Reference	Remarks
1	2	3	4	5	6	7	8	9
27	KL 6 (C1618EO6)	LiChrospher Diol (250 × 4.6 × 5)	92% *n*-heptane, 5% CH_2CH_2, 3% CH_3OH	Isocratic, 1.0 ml/min	UV (235 nm)	Yes	73	Determination of total quantity of KL 6 (with unsaturated bone) in the presence of KM 11 (C1618EO11) and KM 20 (C1618EO20) and S 385 (ionic surfactant) found in the mixtures used for enhanced oil recovery. Studies on the partitioning of KL 6 in bi- and triphasic equilibria encountered during enhanced oil recovery.
28	KL6, KM11, KM20	Zorbax amino (250 × 4.6 × 7); Zorbax cyano (250 × 4.6 × 7); LiChrospher Diol (250 × 4.6 × 5)	(1) *n*-heptane:CH_2Cl_2:CH_3OH in various proportions (for amino, cyano and diol columns under isocratic mode); (2) A-97.5% *n*-heptane/ /CH_2Cl_2(95/5) 2.5% C_3H_8OH, B-70% *n*-heptane/CH_2Cl_2(95/5) 30% C_3H_8OH (for gradient with diol column)	Isocratic, 1.0 ml/min; gradient: 0% B → 100% B/40 min, 1.0 ml/min	RI, UV (254 nm)	No	74	Analyzed as 3,5-dinitrobenzoyl derivatives.
29	Marlophen 810 (NPEO(1-18), Marlophen 83, Synperonic OP10 (OPEO(2-15)), Imbetin-N7A (a mixture of NPEO1, NPEO2, NPEO3)	Hypersil APS (100 × 4 × 3)	A-*n*-hexane, B-85% *n*-hexane, 15% 2-C_3H_8OH	3% B → 25% B/10 min, 2.0 ml/min	UV (277 nm)	Yes	129	Quantitation of APEO in waste waters. C.C.N.
30	APEOn	μPorasil, Partisil 5 PAC, Zorbax NH2	(1) A-*n*-hexane, B-5% DMSO, 95% $CHCl_3$ (UV detection); (2) A-MTBE + 0.1% CH_3COOH, B-95% CH_3CN, 5% CH_3OH (0.1% CH_3COOH) (fluorescence detection)	0% B → 45% B/30 min, 3.0 ml/min (for UV detection); 0% B → 100% B/30 min:100% B/5 min, 2.0 ml/min (for fluorescence detection)	UV (280), FSD (230 nm(ex), 302 nm(em))	Yes	119	Comparison of UV and fluorescence detection; Identification confirmed by MS

31	BPEO4, BPEO6, BPEO8, BPEO10, BPEO13, BPEO15, BPEO18, BPEO50	Zorbax CN (250 × 4.6 × 10)	A-*n*-hexane, B-75% 2-methoxyethanol, 25% 2-C_3H_8OH	0% B → 50% B/50 min, 1.5 ml/min	UV (255 nm)	No	127	
32	NPEO4,6	HP-NH2 (200 × 4.6 × 10)	A-80% *n*-hexane, 20% THF, B-90% 2-C_3H_8OH, 10% H_2O	5 → 50% B/40 min, 1.0 ml/min	UV (280 nm)	Yes	71	Identification made with a trioxyethylene nonylphenol standard
33	NPEO8.5, Triton X-100 (OPEO9.5)	Hypersil APS (250 × 4.6 × 5)	A-70% *n*-hexane, 30% THF, B-90% 2-C_3H_8OH, 10% H_2O	5% B - › 50% B/60 min, 1.0 ml/min	UV (225 nm)	Yes	128	Determination of APEO in pesticidal emulsifiable concentrates after separation of emulsifiers from active ingredients. C.C.N
34	KL6(C16-18EO6), KM11(C16-18EO11), KM20(C16-18EO20)	LiChrospher Diol	A-*n*-heptane, B-CH_2Cl_2, C-2-C_3H_8OH	(1) 90% A 6% B 4% C — isocratic, 1.0 ml/min (2) 5% B 2.5% C → 3.5% B 30% C, 1.0 ml/min	UV (254 nm)	Yes	75	Analyzed as 3,5-dinitrobenzoyl chloride derivatives, C.C.N.
35	NPEO11, C1214EO5, C1214EO7, C1214EO11, C12EO12, C13EO7, C13EO11	Zorbax NH2 (250 × 4.6 × 5)	A-*n*-hexane, B-2-C_3H_8OH, C-H_2O	0% B 0% C → 60% 83% C/55 min, 1.0 ml/min	ELSD (45 p.s.i. N_2, t = 35°C)	Yes	63	
36	DPEO6, Slovafol 905 (NPEO5), Emulgator U 6 (NPEO6)	10 different Diol columns	*n*-hexane:2-C_3H_8OH:H_2O with slightly different composition for different laboratories	Isocratic and gradient, 0.5–1.0 ml/min	RI, UV	Yes	66	Distribution was checked by interlaboratory testing in ten laboratories. The statistical tests for differences between RI and UV detection with isocratic and gradient elution showed criteria without any significance
37	Neodol 25-9 (C1215EO9), Alfonic 1218-70 (C1218EO7)	μBondapack NH2 (300 × 3.9)	A-*n*-hexane:$C_2H_5Cl_2$ = 350:150, B-185CH3CN:2-C_3H_8OH (add 800 μl acetone per liter) = 185:65	0% B → 35% B/50 min, 3.0 ml/min	UV (235, 240 nm)	Yes	85	Analyzed as phenyl isocyanate derivatives. C.C.N.; the limit of quantification is 0.1 ppm
38	Arkopal N-20, Arkopal N-40, Arkopal N-60, Arkopal N-100, NPEOn	(1) Amino SIL-X-10 (250 × 4.6 × 5) (2) Lichrosorb-Diol (250 × 4.6 × 5)	(1) 95% *n*-hexane, 5% 2-C_3H_8OH (2) A-95% *n*-hexane 5% CH_2Cl_2, B-50% *n*-hexane, 40% CH_2Cl_2, 10% 2-propanol	(1) Isocratic, 1.0 ml/min (2) 30% B → 60% B/15 min, 1.0 ml/min	UV (275 nm)	Yes	105	Determ. of RF of preparatively separated oligomers NPEO(2)-NPEO(15) with TMP as an IS; RF = (HnCs)/(HsCn); RF = 0.3813 EO-0.01699 (R = 0.9976); the limits of detection for NPEO(2)(4)(6)(8)(10)(13)(15) were 51.0, 57.2, 63.8, 73.6, 84.7, 118.0, 132.1 ng

TABLE 1 (CONTINUED)
Separation of Ethoxylated Compounds on Normal Phases

No 1	Type of surfactant (*) 2	Stationary phase (**) 3	Mobile phase 4	Isocratic/Gradient program and flow rate 5	Detector (parameters) 6	Quantification 7	Reference 8	Remarks 9
39	NPEO4, NPEO6, NPEO10	Silasorb-NH2 (62 × 2 × 5)	CH_3CN	*Isocratic, 02–200 µl/min*	UV (*278 nm*)	Yes	132	Changes of the run of lnk′ = f(n) for n = 6 – 7 and higher oligomers can be caused by conformational changes. Providing all the peaks are Gaussian type a method for distribution quantification with two parameters (Hn and its tr) was proposed. Correction coefficients taken from [77]
40	Triton type	Zorbax-NH2 (250 × 4.6); Supelcosil LC-NH2 (250 × 4.6)	A-isooctane, B-50% 2-C_3H_8OH 50% 2-methoxyethanol (for Zorbax); A-90% heptane, 10% 2-C_3H_8OH, B-90% 2-C_3H_8OH, 10% H_2O (for Supelcosil)	5% B → 30% b/30 min, 2.0 ml/min (for Zorbax), 25% B → 40% B/20 min, 1.5 ml/min (for Supelcosil)	UV (276 nm) LD/FT/ICR/MS	Yes	123	
41	C12EOn, APEO	Hypersil APS (250 × 4 × 5)	A-70% *n*-hexane, 30% 1,2-$C_2H_4Cl_2$, B-26% 2-C_3H_8OH, 74% CH_3CN	(1) 0% B → 30% B/40 min, 1.5 ml/min; (2) 10% B → 40% B/40 min, 2.0 ml/min	UV (240 nm), FSD (277 nm(ex), *298 nm (em)*)	No	106	Determination of traces of linear alcohol poly-*ethoxylates in surface* water. Analyzed as phenyl isocyanate derivatives. Impurities and reaction byproducts interfere if UV detection is used. C12EO(8) was used to identify the number of ethoxylate groups
42	*Brij 76 (C18EO10)*	*LiChrospher* 100 Diol (125 × 4 × 5)	A-*n*-hexane, B-98% $CHCl_3$, 2% 2-C_3H_8OH	10% B → 80% B/25 min, 1.0 ml/min	ELSD	No	62	Response with ELSD for ethoxylated products (waxy) in dichloromethane-methanol mixtures are similar and linear in log(s)/log(c) graph except for PEG 300 (liquid)

43	NPEO4, NPEO10, NPEO20, TBPEO13, TBPEO18	LiChrosorb Si 60 (250 × 4.6 × 10), Adsorbosphere NH2 (250 × 4.6 × 10)	(1) 70% *n*-heptane, 10% $CHCl_3$, 20% CH_3OH, (2) 80% *n*-heptane, 10% $CHCl_3$, 10% CH_3OH, (3) 85% *n*-heptane, 5% $CHCl_3$, 10% CH_3OH, (4) 90% *n*-heptane, 5% $CHCl_3$, 5% CH_3OH, (5 and 6) A-75% *n*-heptane, 10% $CHCl_3$, 15% CH_3OH, B-50% $CHCl_3$, 50% CH_3OH, C-90% *n*-heptane, 5% $CHCL_3$, 5% CH_3OH	(1) isocratic, 1.0 ml/min, (2) isocratic, 1.0 ml/min, (3) isocratic, 1.0 ml/min, (4) isocratic, 1.0 ml/min, (5) 0% B → 10% B/15 min, 1.0 ml/min (6) 100% C 0% B → 80% C 20% B/10 min, 1.0 ml/min	UV (270 nm)	No	140	Silica column exhibits good separation for low oligomers, and NH2 column is well suited . for the high ones; C.C.N
44	KM25 (C1618EO25) and Cetalox AT (C1618EO50); Igepal Co-720 (NPEO12), Co-890 (NPEO40),	Nucleosil *p*-nitrophenyl-bonded silica (250 × 3 × 5), Ultraspher cyano-bonded silica (250 × 4.6 × 5)	A-*n*-heptane, B-CH_2Cl_2, C-2-C_3H_8OH, C1-CH_3OH	(1) 85% A:7.5% B:7.5% C → 50% A: :25% B:25% C/40 min:50% A:25% B: 25% C/50 min (0.7 ml/min); (2) 85% A:7.5% B:7.5% C1 → 65% A: :17.5% B/17.5% C1/40 min; 65% A :17.5% B:17.5% C/30 min (0.7 ml/min);: (3) 90% A:5% B:5% C → 65% A:17.5% B::17.5% C/190 min:65% A:17.5% B:17.5% C/30 min (0.6 ml/min)	UV (254 nm), ELSD (121/min, t = 45°C)	No	72	Distribution of CnEOn and NPEOn. Analyzed as 3,5-dinitrobenzoyl derivatives. Increasing a temperature from 25 to 45°C it is possible to separate (on *p*-nitrophenyl column) 80 oligomers with constant resolution

Note: Ethoxylated alkylphenols: APEOn, BPEOn, TBPEOn, OPEOn, NPEOn, DPEOn — A, B, TB, O, N, D, denotes alkyl, butyl, tertbutyl, octyl, nonyl, and dodecyl groups, respectively; **n** denotes the average ethoxylation degree, given in parenthesis denotes the specific standard and number of oligomers when two numbers are separated by "-". Ethoxylated alcohols: CmEOn — **m** denotes the number(s) of carbon atoms in the alkyl group and **n** denotes the average ethoxylation degree, given in parenthesis denotes the specific standard and number of oligomers when two numbers are separated by "-". Ethoxylated fatty acids: CnCOEOm — **m** and **n** see above. Polyoxyethylene glycols: PEG600 — polyoxyethylene glycol with average molecular weight of 600. Three or two numbers given in parenthesis after the name of the column separated by ¥ sign denote length (mm) and diameter (mm) of the column and size of the separating material (mm) (length ¥ diameter ¥ size). **MTB,** methyl tertbutyl; **TMP,** 2,4,6-trimethylphenol; **TEA,** triethanolamine; **MEK,** methyl ethyl ketone; **RP,** response factor; **IS,** internal standard; **Mn, Ms,** amount of oligomer n and internal standard; **An, As,** peak area of oligomer n and internal standard; **Cn, Cs,** concentrations of oligomer n and internal standard; **Hn, Hs,** peak height oligomer n and internal standard; **FDMS,** field desorption mass spectrometry; **TSMS,** thermo spray mass spectrometry; **FABMS,** fast atom bombardment mass spectrometry; **LD/FT/ICR/MS,** laser desorption fourier transform ion cyclotron resonance mass spectrometry; **FSD,** fluorescent spectrometric detector.

In a molecule of ethoxylated alcohols and alkylphenols, both the hydrophobic and the hydrophilic parts interact with the column packing. The nature of the separation taking place depends on the type and strength of the organic modifier used, that is a proton donor and proton acceptor (e.g., CH_3OH) or a proton acceptor (e.g., CH_3CN, THF, CH_3COCH_3).

Reversed-phase separation with CH_3OH as an organic modifier (on a C18 packing) occurs only in accordance with the alkyl (alkylaryl) chain lengths [70,77,80-85]. From mixtures of ethoxylated octyl- and nonylphenols, owing to their weaker hydrophobic nature, ethoxylated octylphenols elute first and nonylphenols do next, as two separate peaks. Also mixtures of ethoxylated alcohols leave the column as separate single peaks of different ethoxylated alcohols. Retention time of ethoxylated alcohols and alkylphenols with different polyoxyethylene chain lengths and the same alkyl (alkylaryl) chain lengths is the same without even broadening of the width of peaks for ethoxylates with wider oligomer distribution — group separation (Figure 4).

In this system (reversed phases and CH_3OH as an organic modifier), interactions of the polyoxyethylene chains with the C_{18} are practically not observed at all, whereas elution itself depends only on the length of the hydrophobic chain of the original alcohol, alkylphenol and acid and is the better the longer the alkyl chain [76], that is, the longer the hydrophobic chain the longer retention time.

When sufficiently hydrophilic column is used (C1) also with methanol as a modifier of the mobile phase separation of the oligomers according to polyethoxylate chain length can be obtained [93]. In that case it is similar to normal phase separation mode, that is, longer retention times for longer polyethoxylate chains.

Contrary to ethoxylates, PEGs do not posses surface active properties and their total determination (without the assessment of their homologue distribution) in surface active products is of great importance from the practical point of view. Widely used Weibull method [86] is based on the extraction of PEGs from an ethyl acetate solution of surfactants with 5 N sodium chloride solution, followed by extraction of PEGs from the aqueous phase with chloroform and gravimetric determination of PEGs after evaporation of the solvent. Much less labor and time consuming is column chromatography, which provides more accurate results. Many methods with different stationary and mobile phases have been proposed [87-92].

PEGs are the most polar fraction and from C18 column with CH_3OH as an organic modifier they elute first as a single peak without separation to appropriate homologues (Figure 4). The more hydrophobic molecules of ethoxylates are retained on C18 phase for a longer time.

A system containing a mixture of acetonitrile and water as an eluent (e.g., 65% CH_3CN + 35% H_2O) under isocratic conditions on reversed phases enables also separation of polyoxyethylene glycols from ethoxylated alcohols (alkylphenols, acids). Being completely hydrophilic in their nature, polyoxyethylene glycols are eluted as a single peak with a constant retention time, irrespective of their molecular weights [87,94]. Their attraction to the mobile phase in this system is so strong that they do not interact with the stationary phase at all and their retention volume equals a column dead volume. On the other hand, hydrophilicity of ethoxylation products changes with polyaddition degree, being higher for those with more oxyethylene groups. This is caused by a depressed influence of the hydrophobic portion of the alcohol against a growing influence of the oligooxyethylene chain in the case of oligomers with higher molecular weights. Owing to their weaker interaction with the chromatographic column packing, the higher oligomers are sooner eluted; that

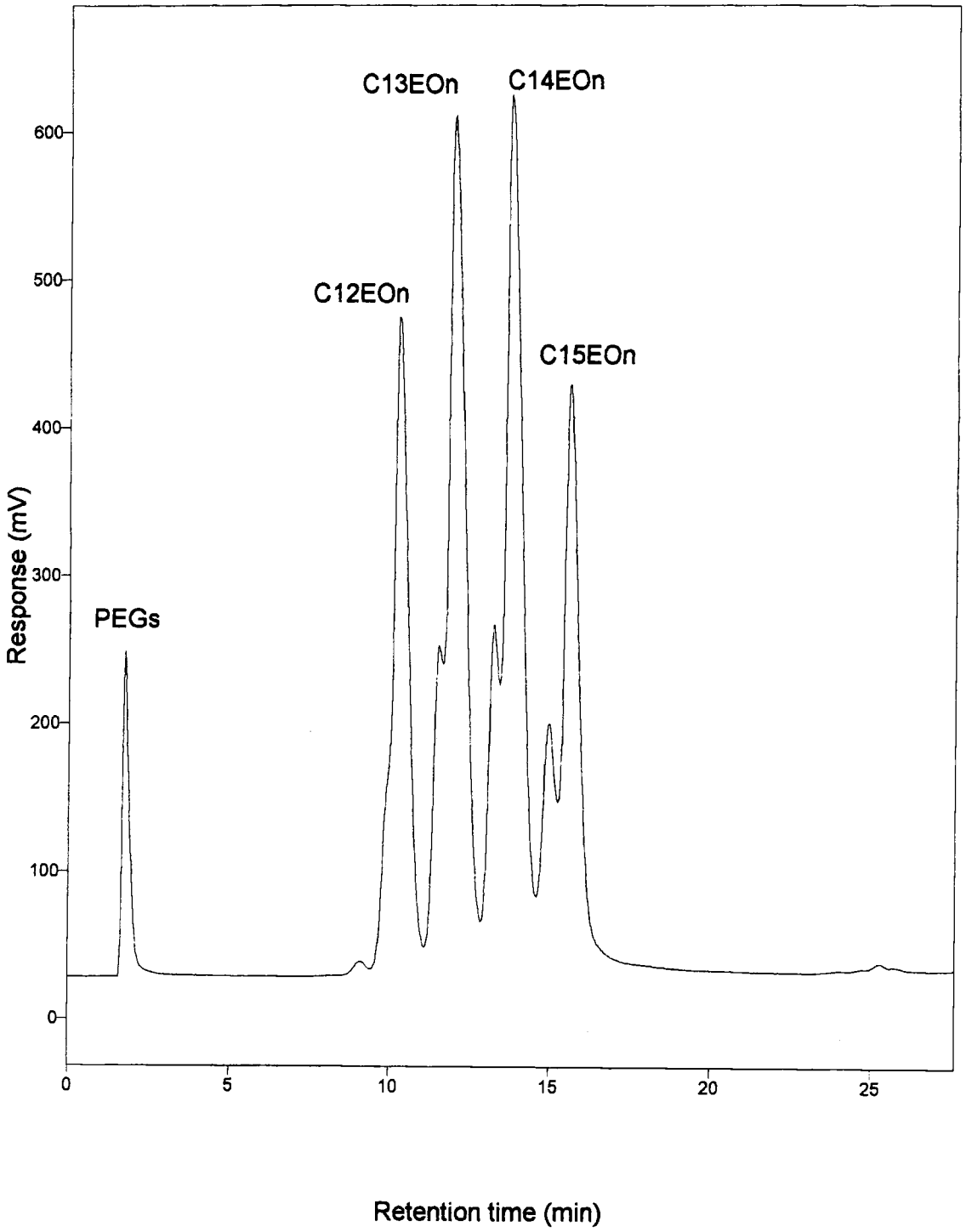


FIGURE 4. Separation of ethoxylated Lial 125 (mixture of oxo alcohols- isomers of C12,13,14,15) (average ethoxylation degree = 9) on reversed phases according to hydrophobe (alkyl) chain length (stationary phase: Hypersil ODS 200 × 2.1 × 5; mobile phase: A-H_2O B-CH_3OH, 0.3 ml/min; Gradient program: 80 → 100% B/30 min; ELSD - 50 mm N_2, 80°C); PEGs - polyethyleneglycols, C12EOn - ethoxylates of alcohols containing C12, C13EOn - ethoxylates of alcohols containing C13, etc.

means, they have shorter retention times which is shown in the chromatogram as shifting towards the PEGs peak [76,95] (Figure 5). Using an appropriate gradient of the eluent the ethoxylate mixture can be separated into single homologues with various numbers of oxyethylene groups (discrete separation).

In above mentioned isocratic mode using back-flush technique (after the elution of PEGs), group separation of ethoxylated acids can also be obtained with the following elution order: PEGs, ME, DE (Figure 6).

Application of a column with an octadecyl phase and additional cooling of the column enables satisfactory separation of a mixture of ethoxylated alcohols comprising thirty or more oligomers obtained from a single original hydrophobe (Figure 7). The number of components in a mixture which can be separated is greatly reduced in the case of mixtures of several hydrophobes. For ethoxylated alcohols with hydrophobe chain lengths which differ by two CH_2 group, the chromatogram shows 'space' for only 13 peaks of ethoxylated homologues with various lengths of their polyoxyethylene chains and the same lengths of hydrophobic chains (Figure 8).

It is worth mentioning that an increase of the strength of the eluent (increase of the concentration of CH_3CN in H_2O) obviously causes the decrease of the capacity factors of the homologues of a given hydrophobe, and reaches the point where the difference between their capacity factors equals zero. At that composition of the mobile phase the length of the hydrophile chain does not influence the retention time of the homologues. Above this point the inversion of elution order occurs and the difference in retention times begins again to increase. The inverse of elution order of compounds with polyoxyethylene (POE) chains is explained in terms of conformational changes of these chains. According to Melander *et al.* [96] a

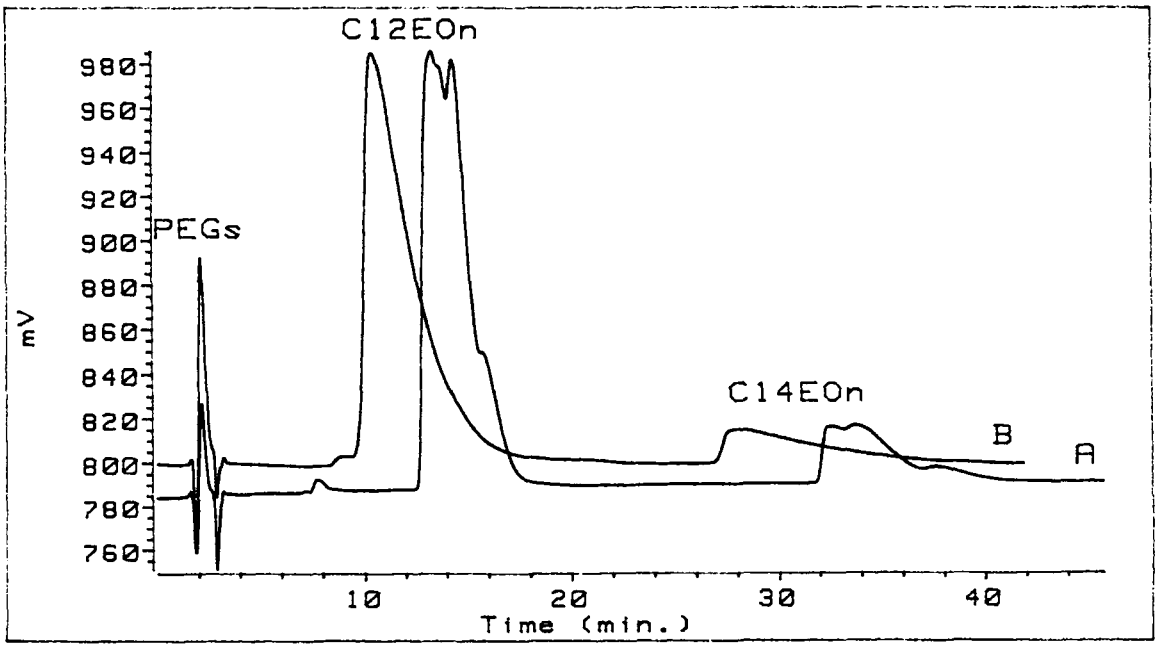


FIGURE 5. Separation of ethoxylated Alfol 1214 (mixture of C12 and C14 linear alcohols) (average ethoxylation degree A = 2 and B = 14) on reversed phases (stationary phase: Hypersil ODS 200 × 2.1 × 5; mobile phase: CH_3CN/H_2O (65/35 v/v), 0.3 ml/min, isocratic; RI). Notation is the same like in Figure 4.

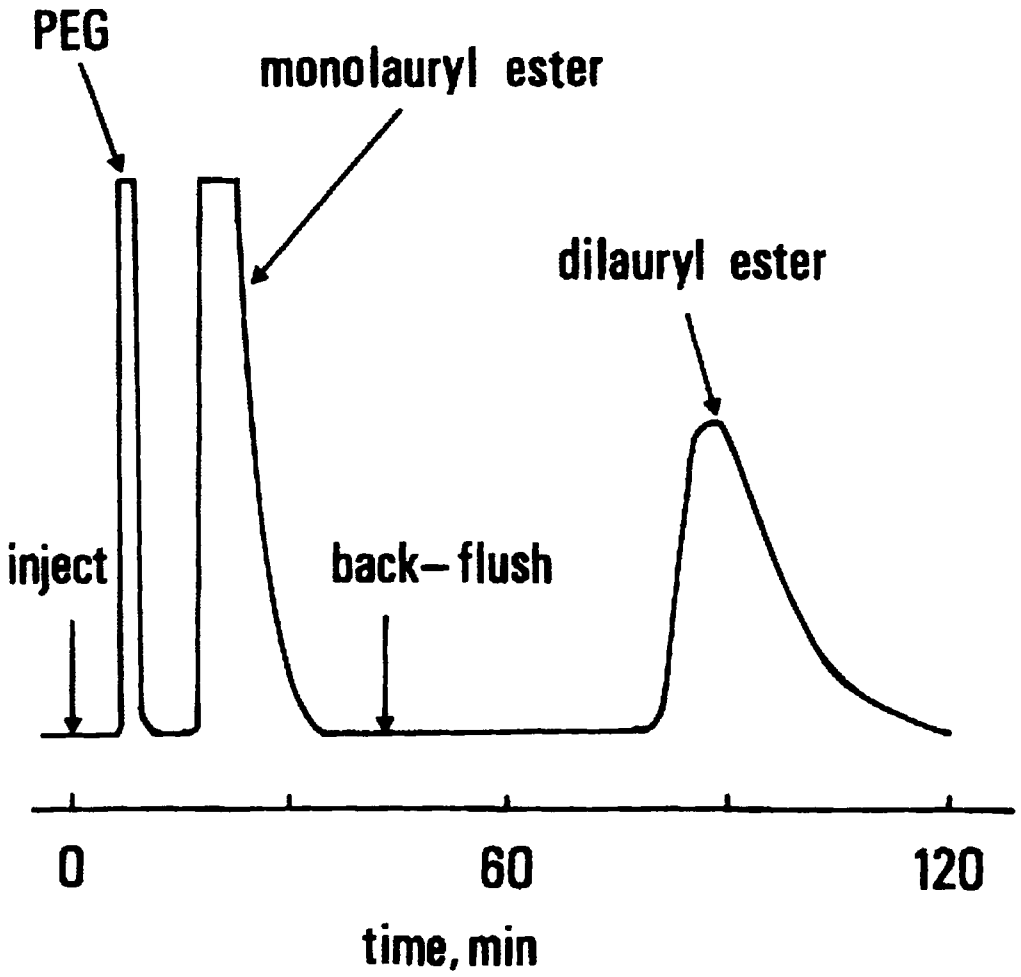


FIGURE 6. Typical chromatogram of lauric acid ethoxylate (average ethoxylation degree = 10) on reversed phases; (stationary phase: C18 500 × 20; mobile phase: CH_3COCH_3/H_2O (70/30 v/v), 10 ml/min, isocratic; RI [94]). (From Kudoh M., Kotsuji M., Fudano S., Tsuji K., *J. Chromatogr.*, 295, 187, 1984. With permission. © Elsevier Science.)

POE chain exists as a zig-zag and a helix form in a mobile phase (depending on its composition, temperature, and the length of the polyoxyethylene chain) and have different retention abilities.

A concept that enables the separation of complex mixtures of several ethoxylated alcohols and/or fatty acids on reversed phases, comparable to that obtained on normal phases is the application of a system comprising two or more steps, where separation is first made according to hydrophobe chains, and next according to hydrophilic chains [97]. The first step of such separation may be carried out using either a styrene-divinylbenzene column with CH_3OH/CH_3CN as an eluent or a C18 column with a CH_3OH/H_2O eluent. The second one can be applied on an ion-exchanger (Figure 9).

Mixtures of several ethoxylated alcohols and fatty acids may be separated using a system of connected C18 columns with weaker and stronger H_2O/CH_3CN gradients. To begin with, ethoxylated acids are separated from the alcohols by trapping the latter in a column where the eluent is too weak to elute them but strong enough to separate ethoxylated acids from ethoxylated alcohols.

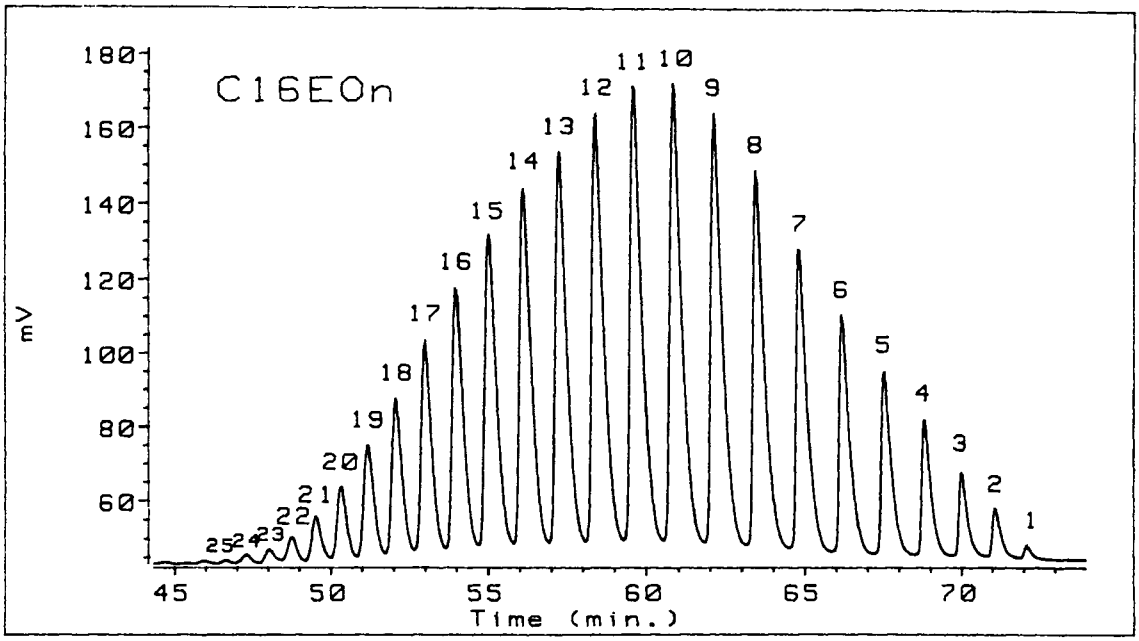


FIGURE 7. Separation of ethoxylated hexadecanol C16EO (average ethoxylation degree = 10) on reversed phases (stationary phase: Nucleosil 120-3 C18 (250 × 4); mobile phase: A-H_2O, B-CH_3CN, 1 ml/min; Gradient program: 46 →55% B/20 min, 55 →76% B/30 min, 76 →90% B/15 min; ELSD - 50 mm N_2, 110°C).

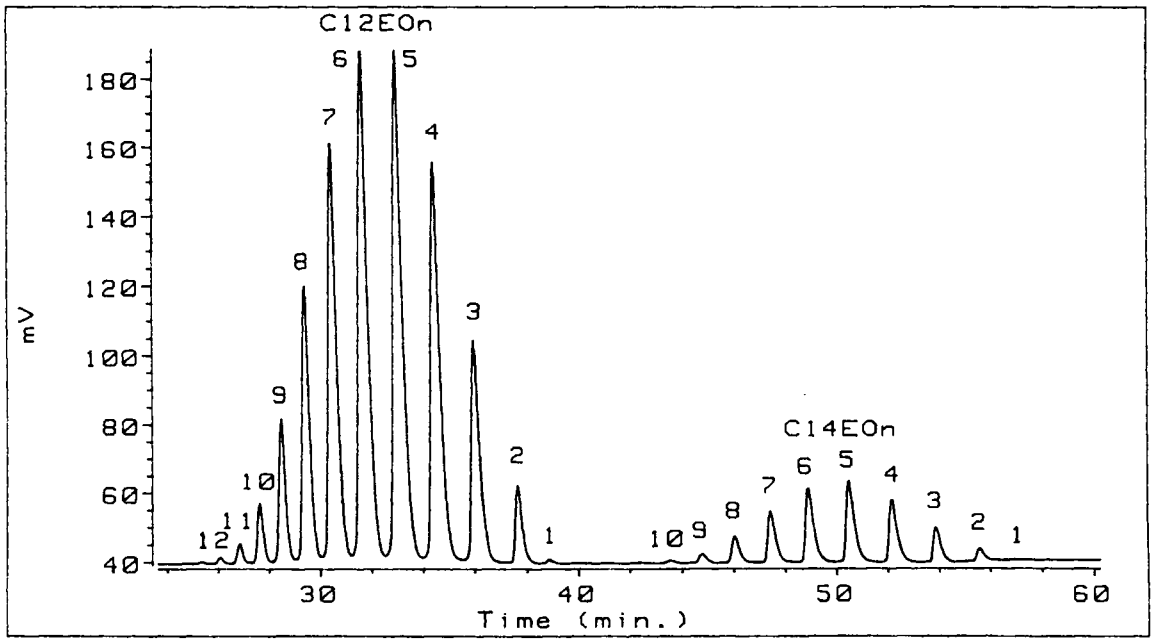


FIGURE 8. Separation of ethoxylated Alfol 1214 (mixture of C12 and C14 linear alcohols) (average ethoxylation degree = 6) on reversed phases; chromatographic conditions are the same as in Figure 7. Notation is the same as in Figure 4.

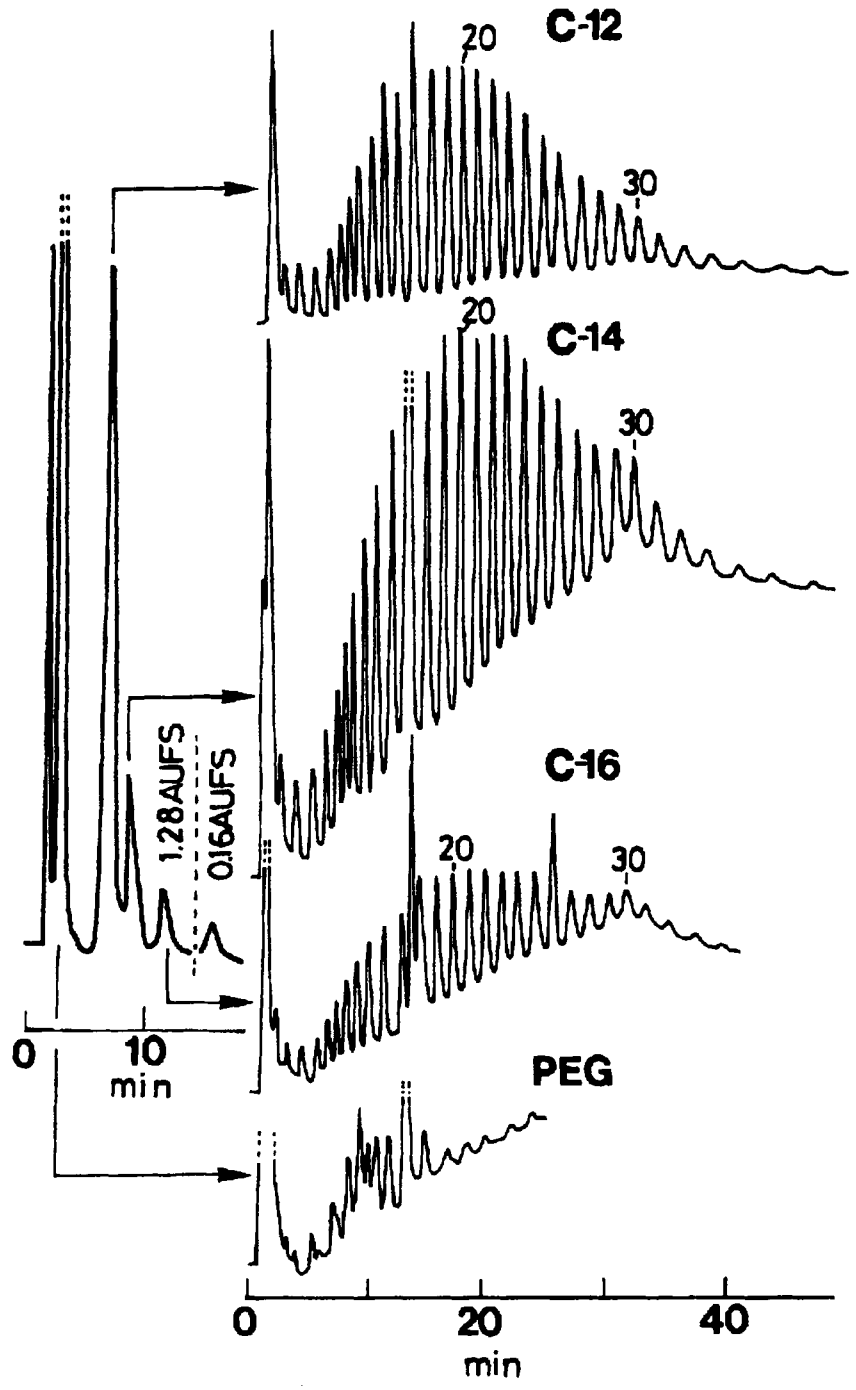


FIGURE 9. Separation of the dinitrobenzoyl derivative of ethoxylated dodecanol (Brij35) according to both the hydrophobic [MCI gel CHP-5C (150 × 4); CH_3CN-CH_3OH (1:5); UV (254 nm)] and hydrophilic chains length [TSK-gel IC-Cation-SW in the potassium form; (CH_3OH)/3 min: (CH_3OH → 7.5 m*M* KCl in CH_3OH)/30 min; UV (254 nm)] [97]. (From Okada T., *J. Chromatogr.*, 609, 213, 1992. With permission. © Elsevier Science.)

In the next step, the ethoxylated acids and alcohols are separated into single oligomers [95] (Figure 10).

In each case, separation of complex mixtures of various hydrophobes requires complicated analytical systems comprising several pumps and multiway valves.

Data on separation on reversed phases are presented in Table 2.

C. Size Exclusion Chromatography

Although Size Exclusion Chromatography, like adsorption chromatography on unmodified silica has been used as the first HPLC separation technique of ethoxylates it is not generally considered as a method of their analysis because it usually does not provide single oligomer separation obtained on Normal and Reversed Phase Chromatography. Separation is carried out in aqueous and non-aqueous solutions on silica, polystyrene and vinyl alcohol copolymer gels [50,98,99,138]. Separation of ethoxylates in SEC, when exclusion is the only separation mechanism, is usually much worse than in normal or reversed chromatography and does not provide complete oligomer resolution.

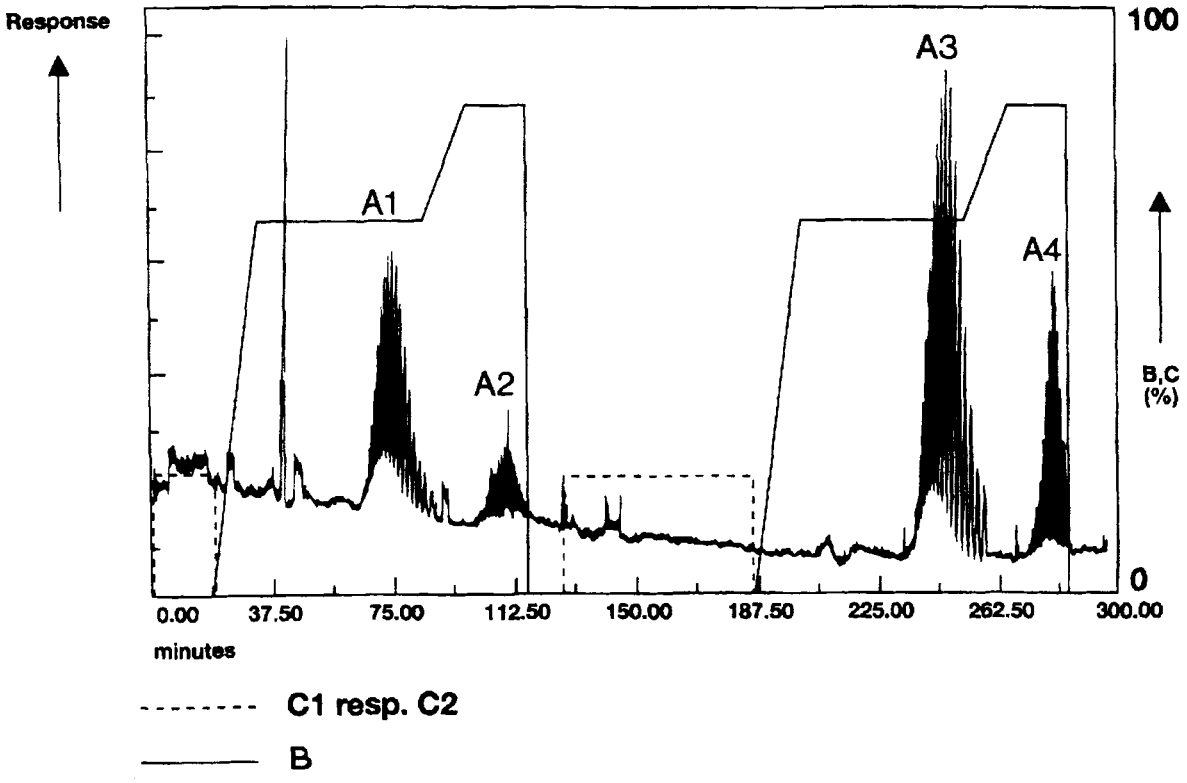


FIGURE 10. Separation of the ethoxylated alkyl alcohols (A3 and A4) and their carboxylic acid derivatives (A1 and A2) by automated column-switching HPLC. Sample size: 1.2 mg. Trapping column: 100 x 4 mm I.D. Nucleosil 120–5C_{18}. Separation columns: one 50 x 4 mm I.D. plus two (250 x 4 mm I.D.) Nucleosil 120–5C_{18}. Mobile phases: (A) 1% formic acid in water: (B) acetonitrile: (C1) 65% acetonitrile, 34% 50 m*M* ammonium bicarbonate: (C2) 82% acetonitrile, 18% 50 m*M* ammonium bicarbonate. Total mobile phase flow-rate: 1.0 ml/min. The trapping column is only eluted with mobile phase C; mobile phases A and B are introduced between the exit of the trapping column and the 4 ml mixing coil. Detector settings: nebulizer temperature 100°C; nebulizer gas flow 18.4 l/min helium [95]. (From Mengerink Y., de Man H. C. J., Van der Wal, Sj., *J. Chromatogr.*, 552, 593, 1991. With permission. © Elsevier Science.)

TABLE 2
Separation of Ethoxylated Compounds on Reversed Phases

No 1	Type of surfactant (*) 2	Stationary phase (**) 3	Mobile phase 4	Isocratic/Gradient program and flow rate 5	Detector (parameters) 6	Quantification 7	Reference 8	Remarks 9
1	C12EO4, C12EO12, C12EO25, C12EO50, C1618EO40, OPEO10, OPEO25, OPEO35, OPEO60, DPEO40	Bondapack C18/ /Corasil (2 ft × 2 mm)	65% CH_3CN, 35% H_2O	Isocratic, 1.0 ml/min	RI	Yes	87	Total PEGs determination in ethoxylates. The molecular weight of the PEGs in each sample is approximated using TLC. All PEGs oligomers elute as a single peak and their elution times are independent of their molecular weight. The precision of this method is 4% relative or better
2	Eumulgin B-3 (C16EO30)	Separon 40-S (250 × 8 × 25–30)	5% H_2O, 95% CH_3OH	Isocratic, 1.67 ml/min	RI	Yes	92	Determination of the total quantity of free PEGs in ethoxylates. All PEGs oligomers elute as a single peak and their elution times are independent of their molecular weight
3	Diethylene glycol monopelargonate, Tetraethylene glycol monopelargonate, Tetraethylene glycol monolaurate	μ-Bondapak-C10	80% CH_3OH, 20% H_2O	Isocratic	RI	Yes	135	Determination of diester content in diethylene glycol and tetraethylene glycol monoesters. C.C.N.
4	Lutensol ST 11(C12141618EO25), Lutensol ST 25 (C12141618EO25)	LiChrosorb RP 8 150 × 4.7 × 5)	90% CH_3OH, 10% H_2O	Isocratic	RI	No	81	
5	OPEOn, NPEOn, DPEOn	Bondapak C18/Corasil (120 × 2)	A-H_2O, B-CH_3OH	50% B/5 min:50% B → 100% B/10 min	MS (FD), UV (280 nm)	No	84	
6	C10EO7	LiChrosorb RP-2 (250 × 4 × 5)	40% H_2O, 60% CH_3CN	Isocratic, 0.8 ml/min	UV (254 nm)	No	108	Analyzed as 3,5-dinitrobenzoyl derivatives
7	CnEOn, OPEOn, ethoxylated amines	LiChroprep RP-18 (50 × 20)	55% CH_3COCH_3, 45% H_2O — for ethoxylated lauryl alcohols, octyl- and nonylphenols; 80% CH_3COCH_3 20% H_2O — for ethox cetyl, oleyl and stearyl alcohols; 60% CH_3COCH_3 40% H_2O for ethox alkylamines except stearylamine — 100% CH_3COCH_3	Isocratic, 9.0 ml/min	RI	Yes	126	Total PEG determination

TABLE 2 (continued)
Separation of Ethoxylated Compounds on Reversed Phases

No	Type of surfactant (*)	Stationary phase (**)	Mobile phase	Isocratic/Gradient program and flow rate	Detector (parameters)	Quantification	Reference	Remarks
1	2	3	4	5	6	7	8	9
8	C12EOn, C16EOn	Radialpak C18 (gradient), μ-Bondapak C18 (isocratic)	A-H_2O, B-CH_3OH	Isocratic: 80% B, 1.0 ml/min; gradient: 50 → 100% B/20 min, 1.0 ml/min	UV, RI, FDMS	Yes	83	Analyzed as 3,5-dinitro-benzoyl derivatives
9	C12EOn, C16EOn, C18EOn, C12POn, [C12PO3EOn, C12PO5EOn, C12PO10EOn-polyoxypropylene polyoxyethylene alkyl ethers], PEG 4000, PPG4000	Porous polymer gel (No. 3011; Hitachi, Japan) (250 × 4)	CH_3COCH_3/H_2O	Isocratic, 1.0 ml/min	RI	No	137	Examination of the retention behavior. Relation between log k' and the degree of polymerization of EO or PO adducts is linear
10	C12EOn, C16EOn, C18EOn	LiChrosorb RP-18, RP-8 and RP-2 and Hitachi gel No. 3053 (C18 type)	H_2O/CH_3COCH_3 with different conc. of org. modifier	Isocratic, 1.0 ml/min for 4 mm I.D., 2.0 ml/min for 8 mm I.D.	RI	No	80	
11	C12COEO10	LiChroprep RP-18 (500 × 20)	70% H_2O, 30% CH_3COCH_3	Isocratic, 10 ml/min	RI	No	94	Preparative determination of the total quantity of PEGs by gravimetry. Application of back-flushing of dilauryl ester; identification of PEGs, mono- and dialkyl esters in lauric acid ethoxylate by FD mass spectrometry
12	C12EO8, C10EO8	Hypersil ODS (150 × 6 × 3)	70% CH_3CN, 30% H_2O	Isocratic, 2.0 ml/min	FSD (395 nm(ex), 450 nm(em))	No	114	Determination of trace amounts of ethoxylates by FSD. Analyzed as antroylnitrile derivatives. The presence of water should be avoided because 1-antroylnitryle reacts with it. C.C.N.
13	Marlophen 83 (NPEO3.15), Synperonic OP10 (OPEO10)	RP-8 (250 × 3 × 10)	20% H_2O, 80% CH_3OH	Isocratic, 0.5 ml/min	UV (277 nm)	No	77	
14	Marlophen 83 (NPEO3.15), Synperonic OP10 (OPEO10), OEO(1-4)	RP-8 (250 × 3 × 10)	20% H_2O, 80% CH_3OH	Isocratic, 0.5 ml/min	UV (277 nm)	No	70	Analysis of surfactant products, municipal wastewaters, and natural waters
15	Marlophen 810 (NPEO(1-18), Marlophen 83, Synperonic OP10	LiChrosorb RP-8 (100 × 4 × 10)	A-H_2O, B-2-C_3H_8OH, C-CH_3CN:H_2O (45:55) + 0.02 *M* sodium perchlorate	5% B:55% C → 5% B:80% C/10 min	UV (225 nm); FSD (230 nm(ex), 295 nm(em))	Yes	129	Quantitation of APEO in waste waters. C.C.N.

	(OPEO(2-15)), Imbetin-N7A (a mixture of NPEO1, NPEO2, NPEO3)							
16	NPEO8.5, Triton X-100 (OPEO9.5)	LiChrosorb 10 RP-8 (250 × 4.6)	(1) 25% H_2O, 75% CH_3OH with 0.005 *M* tetramethyl-ammonium bromide (TMAB) — to separate dodecylbenzenesulfo-nates from OPEO; (2) A-35% H_2O, 65% CH_3OH with 0.01 *M* TMAB, B-15% H_2O, 85% CH_3OH with 0.01 *M* TMAB	(1) isocratic, 1.0 ml/min; (2) 40% B → 70% B/20 min, 1.0 ml/min	UV (225 nm)	Yes	128	Determination of APEO in pesticidal emulsifiable concentrates after separation of emulsifiers from active ingredients. C.C.N.
17	KL6, KM11, KM20 (C16EOn and C18EOn), unsaturated C18 chain in KL6	Nucleosil C4 (100 × 4.6 × 5), Nucleosil C6 (150 × 4.6 × 5), Ultraspher C18 (150 × 4.6 × 5), Nucleosil CN (150 × 4.6 × 7), Nucleosil phenyl (250 × 4.6 × 5), LiChrospher diol (250 × 4.6 × 7), Nucleosil C8 (250 × 4.6 × 5), LiChrosorb C2 (250 × 4.6 × 5)	Various ratios of H_2O and CH_3OH, CH_3CN, THF, dioxan, CH_3COCH_3 and 2-C_3H_8OH	Isocratic, 1.0 ml/min	UV (254, 340 nm), RI	Yes	79	Analyzed as 3,5-dinitrobenzoyl chloride derivatives. Peaks were identified by simultaneous elution of pur standards. Quantification based on the assumption (verified with preparatively obtained standards that, regardless of POE chain length, the molar absorptio is constant
18	Igepal CO 610	Novapak C18 (150 × 4.6)	85% CH_3CN, 15% H_2O	Isocratic, 0.5 ml/min	DAD (276 nm)	Yes	130	Determination of total quantity of surfactants in pulp and paper mill process samples. Surfactants had to be isolated from the sample matrixes by a gas stripping procedure, otherwise they were adsorbed onto the lignin retained on the column packing
19	Neodol 25-9 (C12-15EO9), Alfonic 1218-70 (C12-18EO7)	μBondapack C18 (300 × 3.9)	A-H_2O, B-CH_3OH	80% B → 100% B/30 min	UV (235 nm or 240 nm)	Yes	85	Analyzed as phenyl isocyanate derivatives. C.C.N.
20	Arkopal N-20, Arkopal N-40, Arkopal N-60 (NPEO)	HS-5 C18 (150 × 4.6 × 5)	H_2O:THF: *n*-hexane = 3:14:83	Isocratic, 1.0 ml/min	UV (275 nm)	No	105	
21	CnEOn, CnCOEOn, and ethoxylated amides	Octyl stationary phase (250 × 4.6)	CH_3OH, or mixtures of CH_3OH and H_2O	Isocratic, 1.0 ml/min	RI	No	82	Examination of the retention behavior
22	C12EO, C14EO, C12COEO, C14COEO	Nucleosil 120-5C18 (250 × 4 × 5) and (100 × 4 × 5)	A-0.1% CH_3COOH in H_2O, B-CH_3CN	65% B/38 min: 65 → 90% B/10 min: 90% B/27 min; 1.0 ml/min	ELSD (2.9 l/min CO_2:1 = 100°C	No	95	Comparison of UV, RI and ELSD; separation of mixture of ethoxylated fatty alcohols acids by automated column-switching HPLC

TABLE 2 (continued)
Separation of Ethoxylated Compounds on Reversed Phases

No	Type of surfactant (*)	Stationary phase (**)	Mobile phase	Isocratic/Gradient program and flow rate	Detector (parameters)	Quantification	Reference	Remarks
1	2	3	4	5	6	7	8	9
23	BC-7, BC-20, BC-30, BC-40 (C1618EO) and PEG400	Nucleosil C18 (150 × 4.6 × 5)	(1) 5% H_2O, 95% CH_3OH; (2) A-H_2O, B-CH_3CN	(1) isocratic, 1.0 ml/min; (2) 10% B → 90% B/30 min	ELSD	No	62	Response with ELSD for ethoxylated products in methanol-water mixtures are similar and linear in log(s)/log(c) graph
24	Ethonic 1214-6.5, Ethonic 1214-3 (both from Ethyl Corp. C1214EO6.5, C1214EO3) Liquid Tide Laundry Detergent (anionic, cationic, and nonionic surfactants	Nova Pak C18 (100 × 4.6)	92% CH_3OH, 7% H_2O, 1% glycerol, 0.005% TEA; pH adjusted to 4.5 with CH_3COOH	Isocratic, 1.0 and 1.2 ml/min (split to 10 µl/min	FRIT-FABMS	No	122	
25	Waste waters samples containing C8-C14EOn	Hypersil ODS (250 × 4 × 5)	A-CH_3OH, B-H_2O	(1) 80% B → 100% B/30 min, 2.0 ml/min; (2) 80% B/30 min :80% B → 100% B/30 min, 2.0 ml/min	UV (240 nm)	No	106	Determination of traces of linear alcohol polyethoxylates in surface water. Alcohol ethoxylates analyzed as phenyl isocyanate derivatives. The second gradient program was used to get a better resolution in the range from decanol to tetradecanol ethoxylates and to separate ethoxylates from interfering substances
26	Triton X-15, Triton X-35, Triton X-45, Triton X-100, Triton X-102, Triton X-114, Triton X-165, OPEO30	C1 TMS (150 × 4.6 × 5), Supelcosil LC-1 (150 × 4.6 × 5)	38–50% (0.02 g/l CH_3COONH_4 in H_2O) and 50–62% CH_3OH depending on the sample to be analyzed	Isocratic, 1.0 ml/min	UV (225 nm)	Yes	93	CH_3COONH_4 was added to improve baseline stability. Quantification based on the assumption that all oligomers have the same response at 225 nm; identification based on comparison of retention times with ethoxylated materials of which a major component was OPEO(1)
27	Marlipal 28/100 (C12-18EO10.2) — a mixture of even linear primary fatty alcohol polyethoxylates	LiChrospher 100 RP-18 (125 × 4 × 5)	H_2O/CH_3CN	Isocratic, 1.25 ml/min	UV (291 nm), FSD 229 nm(ex), 358 nm(em))	No	116	Analyzed as 1-naphtyl isocyanate derivatives
28	C11EOn, C13EOn, C1215EOn	Supelco LC 18 (250 × 4.6 × 5)	A-H_2O B-THF	Isocratic: 45% B, 0.7 ml/min	TSMS with postcolumn addition of CH_3COONH_4	Yes	120	

Note: Ethoxylated alkylphenols: APEOn, BPEOn, TBPEOn, OPEOn, NPEOn, DPEOn — A, B, TB, O, N, D, denotes alkyl, butyl tertbutyl, octyl, nonyl, and dodecyl groups, respectively; **n** denotes the average ethoxylation degree, given in parenthesis denotes the specific standard and number of oligomers when two numbers are separated by "-". Ethoxylated alcohols: CmEOn — **m** denotes the number(s) of carbon atoms in the alkyl group and **n** denotes the average ethoxylation degree, given in parenthesis denotes the specific standard and number of oligomers when two numbers are separated by "-". Ethoxylated fatty acids: CnCOEOm — **m** and **n** see above. Polyoxyethylene glycols: PEG600 — polyoxyethylene glycol with average molecular weight of 600. Three or two numbers given in parenthesis after the name of the column separated by × sign denote length (mm) and diameter (mm) of the column and size of the separating material (µm) (length × diameter × size). **MTB,** methyl tertbutyl; **TMP,** 2,4,6-trimethylphenol; **TEA,** triethanolamine; **MEK,** methyl ethyl ketone; **RP,** response factor; **IS,** internal standard; **Mn, Ms,** amount of oligomer n and internal standard; **An, As,** peak area of oligomer n and internal standard; **Cn, Cs,** concentrations of oligomer n and internal standard; **Hn, Hs,** peak height oligomer n and internal standard; **FDMS,** field desorption mass spectrometry; **TSMS,** thermo spray mass spectrometry; **FABMS,** fast atom bombardment mass spectrometry; **LD/FT/ICR/MS,** laser desorption fourier transform ion cyclotron resonance mass spectrometry; **FSD,** fluorescent spectrometric detector.

Type of a solvent used as a mobile phase with hydrophobe columns is not critical and does not influence the separation selectivity, provided that size exclusion is the only mechanism of separation. Nonylphenol and alcohol ethoxylates are usually soluble in short chain alcohols, chloroform toluene and THF. Hydrophobe columns can not be used with alcohols as they cause their swelling and degradation. Chloroform is rarely used because it is more viscous and has a higher volatility than THF and toluene which are often used as eluents in SEC. The elution order of ethoxylates takes place according to decreasing molecular weight. Polystyrene standards as most often used standards in SEC can be safely used in calibrating curve construction for determination of the MW of the surfactants, but correction coefficient has to be applied to take into account the differences in the relationship between the molecular weight and the hydrodynamic volume of polystyrene and ethoxylate chain [138]. The molecule of the latter one is known to form a ball, which in effect gives smaller gyration radius (and hydrodynamic volume) than the coresponding former one.

In the case of aqueous solutions using hydrophilic columns, ethoxylated alkylphenol surfactants are also eluted in order of decreasing molecular weight, without changing the order of elution for the full range of water:organic solvent ratios. Separation performance on hydrophilic gel columns largely depends on the strength of the mobile phase used. With low concentrations of an organic modifier (i.e., 0 to 30 % CH_3CN in H_2O) interactions between the surfactants and the stationary phase are so strong that elution of the surfactants is either extremely delayed or it does not occur at all. With slightly stronger mobile phases (i.e., 30 to 60 % CH_3CN in H_2O) separation is effected mainly by hydrophobic interactions between the gel and alkylaryl groups and, to a lesser degree, as a result of size-exclusion. It can be assumed that hydrophobic interactions and size-exclusion occur more readily for the alkylaryl part of the ethoxylate with a longer alkyl substitute. On the other hand, longer polyoxyethylene chains are merely a larger steric hindrance for hydrophobic interactions. Therefore, the steric hindrance and hydrophobic interactions effects account for the delayed elution of ethoxylates with shorter oligooxyethylene chains. With still higher CH_3CN concentrations in H_2O (60 to 100%), where the hydrophobic interaction is much weaker and there occurs only size exclusion according to the size of the molecules, separation occurs in the same order, that is in order of lowered molecular weights, but is much poorer.

The hydrophobic interaction between the gel and alkylaryl (alkyl) groups is the principal mechanism of separation; the gel has too weak hydrophobic properties to cause effective interaction with oligooxyethylene groups. Longer oligooxyethylene chains are only a steric hindrance to the interactions of the gel and alkylaryl (alkyl) groups.

Data on separation on molecular sieves are presented in Table 3.

D. Ion Exchange Chromatography

Okada has separated an ethoxylated alcohol according to the oligooxyethylene chains on an ion exchanger, using metal cation complexing by oligooxyethylene chains on an ion exchanger in a K^+ form with methanol as a mobile phase [100,101]. The method was based on the phenomenon of 7/2 helix complexes formation by oligooxyethylene chains with Lewis acids, such as metal cations, as is the case with cyclic crown ethers [25]. The potential of the method can be increased by using a temperature gradient [102] which enables effective separation of ethoxylated dodecanol with an average ethoxylation degree of $\bar{n} = 25$. The technique allows separation of more than 40 oligomers, although it is limited in the

TABLE 3
Separation of Ethoxylated Compounds on Ion Exchangers and Molecular Sieve Resins

No. 1	Type of surfactant (*) 2	Separation mode 3	Stationary phase (**) 4	Mobile phase 5	Isocratic/Gradient program and flow rate 6	Detector (parameters) 7	Quantification 8	Reference 9	Remarks 10
1	Triton X-45	Size exclusion	Styragel, 500 A, (160 ft × 3/8 in)	THF	Isocratic, 0.4 ml/min	RI	No	134	
2	Triton X-45	Size exclusion, adsorption	100 A Poragel (4 ft × 2 3/8 in.), Porasil 60 (4 ft. × 1 in.)	THF for Poragel and 5% H_2O in MEK	Isocratic, (17.5–64.0 ml/min)	RI	No	50	Application of recycle
3	Triton X-45, X-100	Size exclusion	Styragel 60 A, 100 A and 500 A	100% THF or 100% toluene	Isocratic	RI, UV	No	99	
4	Ethylene glycol, propylene glycol, glycerol	Cation exchange	Hamilton HC-75 HC-75, Ca^{++} form	40% CH_3CN, 60% H_2O	Isocratic, 1.0 ml/min	RI	No	139	Selectivity depends on the metal ion chosen
5	APEO7, APEO10	Ion exchange	Partisil PXS 10/25 SCX	25% CH_3CN, 100% THF 50% CH_3OH or 1% CH_3OH in 0.2 *M* CH_3COONa buffer, pH 4.0	Isocratic, 1.0 ml/min	RI	Yes	125	C.C.N. The first peak contains AP and APEO(1)
6	OPEOn, NPEOn	Size exclusion	Asahipack GS-310 (500 × 7.6 × 9) — vinyl alcohol copolymer gel	H_2O/CH_3CN with different concent. of org. modifier	Isocratic, 1.0 ml/min	RI, UV (280 nm)	No	98	
7	C12EO9, PEG400, PEG1000	Cation exchangw	TSK-gel IC-Cation-SW (50 × 4.6 × 5) (silica-based cation exchange resin)	(1) 0.4 m*M* KI in CH_3OH (2) 0.4 m*M* in 25% CH_3OH, 75% CH_3COCH_3	(1,2) isocratic, 1.0 ml/min	RI, conductometric detector	Yes	101	Distribution of AIEO and PEGs. Quantification based on the assumption that the mobility of the POE-K^+ complex is the same for oligomers with different hydrophilic chains (valid for narrow range distribution).
8	C12EO6, C12EO8, PEG282, NPEO7.7, NPEO10, NPEO15, NPEO18, NPEO20	Cation exchange	TSK-gel IC-Cation-SW (50 × 4.6 × 5) (silica-based cation exchange resin)	(1) 100% CH_3OH (2) A-CH_3OH, B-5 m*M* KCl in CH_3OH (3) A-CH_3OH, B-5 m*M* KCl in CH_3OH	(1) Isocratic (2) 0% B/7 min:0% B → 100% B/25 min (3) 0% B/10 min:0% B → 100% B/25 min; 1.0 ml/min	RI, UV (280 nm)	No	100	Distribution of AIEO, PEGs, and NPEO. Separation is based on a difference in the complexation of POEs with K^+ in the stationary phase (the retention increases with an increase in oxyethylene units)

9	C12EO9, C12EO21, NPEO7.5, NPEO20, PEG400, PEG1000	Cation exchange	TSK-gel IC-Cation-SW (50 × 4.6 × 5) (silica-based cation exchange resin) in K+, Rb+, Cs+ form	100% CH_3OH	Isocratic, 1.0 ml/min	RI, UV(280 nm), conductometric detector	No	102	Influence of the temperature on the chromatographic resolution
10	KM 25, Brij99 (C1618EOn)	Cation exchange	Nucleosil Silica (150 × 4.6 × 5)	92% CH_3CN, 8% H2O, pH = 7.4, sodium acetate (5 m*M*)	Isocratic, 0.7 ml/min	RI, UV(235, 254 nm)	No	103	Application of gradient of temperature (25–50°C)
11	C12EO9, C16EO20, C18EO10, C18EO20, Brij 35 (C12EO23)	Cation exchange	MCI gel CHP-5C (Mitsubishi Kasei) (150 × 4 × 5) (styrene-divinylbenzene copolymer gel — separation according to hydrophobic chain length); TSK-gel IC-Cation-SW (50 × 4.6 × 5) (silica based cation exchange resin — separation according to POE chain length)	(1) (20–25%) CH_3CN and (75–80%) CH_3OH — for separation in terms of hydrophobic chain length; (2) A-CH_3OH, B-7.5 m*M* KCl in CH_3OH — for separation in terms of hydrophilic chain length	(1) Isocratic (2) 0% B/3 min:0% B → 100 B/30 min	UV (254 nm)	Yes	97	Analyzed as 3,5-dinitro-benzoyl chloride derivatives. Application of automated system for separation in terms of hydrophobic and polyethoxylated chain lengths
12	Makon 4, Makon 6, Makon 8, Makon 10, Carsonon 4, Carsonon 8, Carsonon 30, Alkasurf 4, Alkasurf 6, Alkasurf 8, Alkasurf 40, Siponic 9, Siponic 40, Emulgen 35 (numbers indicate av. ethox. deg.)	Size exclusion	A PLgel mixed-C (300 × 7.5 × 5) (MW 10^3–10^7); A Ultrastyragel 100 A (300 × 7.8) (MW 10^2–10^3)	THF 100%	Isocratic, 1.0 ml/min	RI	No	138	

Note: Ethoxylated alkylphenols: APEOn, BPEOn, TBPEOn, OPEOn, NPEOn, DPEOn — A, B, TB, O, N, D, denotes alkyl, butyl, tertbutyl, octyl, nonyl, and dodecyl groups, respectively; **n** denotes the average ethoxylation degree, given in parenthesis denotes the specific standard and number of oligomers when two numbers are separated by "-". Ethoxylated alcohols: CmEOn - **m** denotes the number(s) of carbon atoms in the alkyl group and **n** denotes the average ethoxylation degree, given in parenthesis denotes the specific standard and number of oligomers when two numbers are separated by "-". Ethoxylated fatty acids: CnCOEOm — **m** and **n** see above. Polyoxyethylene glycols: PEG600 — polyoxyethylene glycol with average molecular weight of 600. Three or two numbers given in parenthesis after the name of the column separated by × sign denote length (mm) and diameter (mm) of the column and size of the separating material (μm) (length × diameter × size). **MTB,** methyl tertbutyl; **TMP,** 2,4,6-trimethylphenol; **TEA,** triethanolamine; **MEK,** methyl ethyl ketone; **RP,** response factor; **IS,** internal standard; **Mn, Ms,** amount of oligomer n and internal standard; **An, As,** peak area of oligomer n and internal standard; **Cn, Cs,** concentrations of oligomer n and internal standard; **Hn, Hs,** peak height oligomer n and internal standard; **FDMS,** field desorption mass spectrometry; **TSMS,** thermo spray mass spectrometry; **FABMS,** fast atom bombardment mass spectrometry; **LD/FT/ICR/MS,** laser desorption fourier transform ion cyclotron resonance mass spectrometry; **FSD,** fluorescent spectrometric detector.

case of components containing from 6 to 14 oxyethylene groups and impossible in the case of homologues with 1 to 6 oxyethylene groups due to the fact that lower oligomers have no complexing abilities. Having optimized the system with respect to the type of stationary phase, type and concentration of the complexed cation and its counter-ion, pH of the aqueous phase, and separation temperature, Desbéne *et al.* [103] achieved separation of as many as 60 homologues (Figure 11).

The retention of ethoxylates increases with the increase of the oligooxyethylene chain. This suggests that the separation is based on a difference in the complexation ability of the different oligooxyethylene chains with K + in the stationary phase. Ethoxylates with the same polyoxyethylene chain and different hydrophobe chain length show similar retention only with slight differences concerning the hydrophobe chains. Namely, for such ethoxylates retention increases in the following order: a dodecyl ether, *p*-nonylphenyl ether, *p*-isooctylphenyl ether, PEG, which is reversed than predicted from hydrophobicity [100]. This observation together with the fact that there is no retention of ethoxylates on cation exchangers without complexing cations proves that hydrophobic interactions between polyoxyethylene chains and sulfonic groups is absent. Thus the differences in retention between compounds with the same polyoxyethylene chain and different hydrophobe chain length is connected with the complexation ability of the entire molecules.

Data on separation on ion exchangers are presented in Table 3.

III. DETECTION

For reasons beyond discussion, the most frequently used detector in analyses of ethoxylated alkylphenols is the UV detector (DAD). It was originally assumed that molar UV absorption was the same for all the homologues. Consequently, the mer content

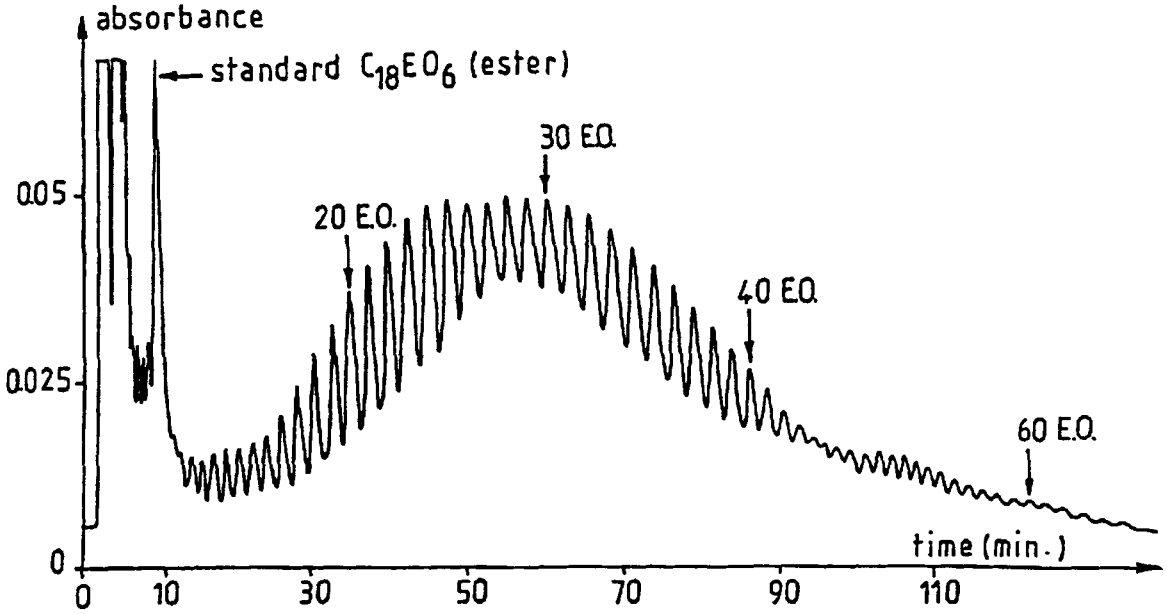
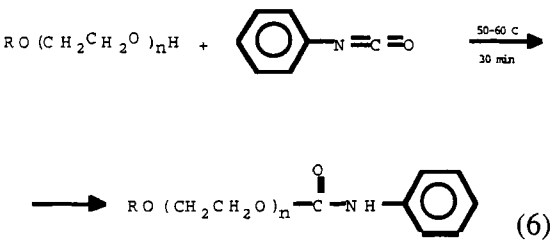


FIGURE 11. Separation of KM 25 3,5-dinitrobenzoyl ester complexed by $5 * 10^{-3}$ M CH_3COONa by ion exchange chromatography (stationary phase: ionized bare silica (150 × 4.6 × 5); mobile phase: CH_3CN/H_2O (92/8 v/v), 1 ml/min; Gradient of the temperature: initial temperature 21°C for 7 min, then 0.3°C/min to 50°C and isothermal at 50°C for 90 min) [103]. (From Desmazieres B., Portet, F., and Desbéne, P. L., *Chromatographia*, 36, 307, 1993. With permission.)

was found from the respective peak areas by standardization [54,56,104]. Only after the respective mers of ethoxylated nonylphenol were preparatively separated, the aromatic ring contribution to the value of UV absorption was found to decrease with the growing number of oxirane molecules added [77,105]. Therefore, quantitative analysis must allow for correction coefficients which grow proportionally to the length of the oligooxyethylene chain and also depend on UV wavelength. Detection of ethoxylated alcohols can also be performed using a UV detector provided that the compounds are converted into their derivatives having absorption in the UV range of electromagnetic spectrum.

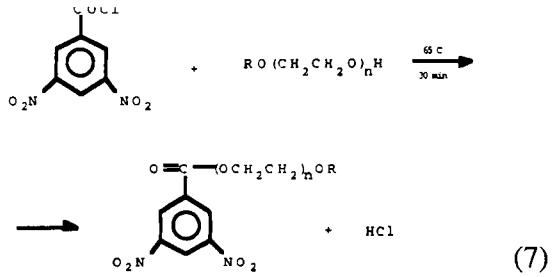
Literature offers two derivatization methods, applicable with ethoxylated alcohols that do not absorb the UV radiation. The method of Allen *et al.* [58,85,97,106,107] is described by the following reaction with phenyl isocyanate at a temperature in the range of 50-60°C:



(6)

Detection is performed at 240 nm.

The other method is based on esterification of ethoxylated derivatives with 3,5-dinitrobenzoyl chloride in the presence of pyridine at a temperature of 65°C according to the reaction below [108]:



(7)

Detection is performed at 254 nm.

In the opinion of the authors, the molar absorption of these derivatives is virtually the same in either of the two methods above, so the polyoxyethylene chain lengths can be obtained straight from the diagram (following peaks integration), without making any additional corrections.

The near ultraviolet (220 nm range) is also suitable for detecting unsaturated ethoxylated alcohols and fatty acids or their brominated derivatives. An irregular shape of the baseline, which is often the case at such electromagnetic wave lengths, when gradient is used, can be corrected by addition of traces of anthracene [68,70].

Detection in isocratic systems may also be performed with an RI detector, suitable for determining the homologue distribution of relatively simple mixtures (i.e., comprising up to 10 components) [64], as well as for determining total contents of polyoxyethylene glycols which, being more hydrophilic compared with ethoxylated alkylphenols, alcohols and acids, are eluted as a single peak at the beginning of the chromatogram [87,94]. The RI detector is also useful for determining the contents of dialkyl esters in ethoxylated fatty acids which are eluted as a single peak next to polyoxyethylene glycols and monoalkyl esters on reversed [94] and before them on normal phases [64,65].

Yet another type is a transport flame-ionization detector (transport-FID). Quite complicated but useful for gradient analyses, the FID detector has not become popular due to its poor reproducibility of results, although it seemed a very promising tool still in 1980s [60,109]. It also lacked sensitivity as the majority of the eluate is not retained for detection. There were models with rotating wires, chains, tapes and disks introduced straight into the flame of the FID. In some versions of such detectors, nonvolatile organics remained after the eluent evaporation were first subjected to pyrolysis of which the products were placed in the detector using an inert gas or hydrogen stream.

Quite interesting is a version developed by Scott and Lawrence [110], where organic compounds on a carrier are converted into methane which is detected by the FID. The signal obtained is directly proportional to the quantity of carbon. For compounds with similar carbon contents in a molecule, such model is a mass detector. At present, these detectors are practically not mentioned in literature at all.

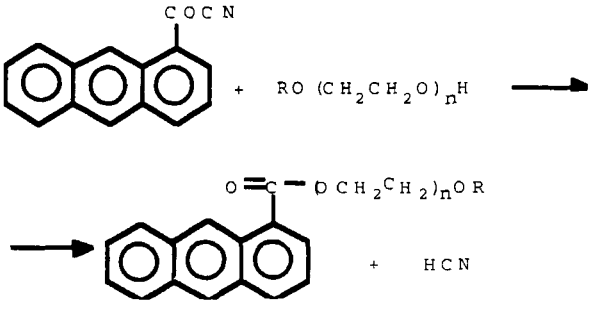
Although now practically sunk into oblivion due to its poor reproducibility of results, the FID detector has had some role in analysis of substances which show no absorption in the UV range. Correction coefficients for ethoxylated alcohols have been determined experimentally only for a few commercially available standards. For oligomers for which commercial standards are not available the values of correction coefficients have been computed based on the assumption that the contribution of every additional oxyethylene group to the value of the correction coefficient of any ethoxylate is the same [60].

Another detector, useful for ethoxylated alcohols, which does not need derivatization, is the Evaporate Light Scattering Detector (ELSD). For the time being, it seems the most promising detector in liquid chromatography.

The ELSD was marketed a few years ago. Compared with the RI detector, it offers the possibility of using an eluent gradient for separations of mixtures under analysis. Unlike the UV detector, the ELSD enables analysis of chemical compounds which show no absorption in the UV range, even with the use of a gradient [62,63,95,111]. The principle of its operation is introduction of an eluent from the HPLC column onto the top of a heated diffusion tube, followed by spraying it by a stream of gas, usually N_2, CO_2, or He. When passing through the diffusion tube, the sprayed beads are evaporated so the mist formed in the nebulizer contains only nonvolatile particles of the substance under examination, which leave the column together with the eluent used for separation. The particles are introduced onto a light beam and scatter it. Measured at a constant angle [112,113], the scattered light is proportional to the concentration of the substance under analysis (Figure 12). The ELSD detector is inexpensive and user friendly.

The nebulizing gases most frequently used for analyses of surfactants are CO_2, N_2, air, or helium. At similar flowrates, the thermal conductivity of helium is five time as high as that of the other spraying gases above, which allows for decrease of the eluent evaporation temperature; this in turn, permits analysis of more volatile substances, that is homologues with shorter oligooxyethylene chains. Besides, helium gives a much higher response than does e.g. CO_2 when used at the same flowrate [95]. However, from our experience, the ELSD detector is not reliable in determinations of ethoxylates with few oxyethylene groups, especially unconverted alcohols [76].

Traces of ethoxylated alcohols and alkylphenols are also determined using a fluorescent detector [114,115]. Alkylphenol ethoxylates can be determined without derivatization but ethoxylated alcohols with no fluorescent groups in a molecule need conversion into their appropriate derivatives according to the following reaction (with 1-anthroylnitryl):



The detection limit is 0.05 ppm for such derivatives and 0.2 ppm for ethoxylated alkylphenols. For analysis of alkylphenol ethoxylates, Kudoh et al. [114], used the

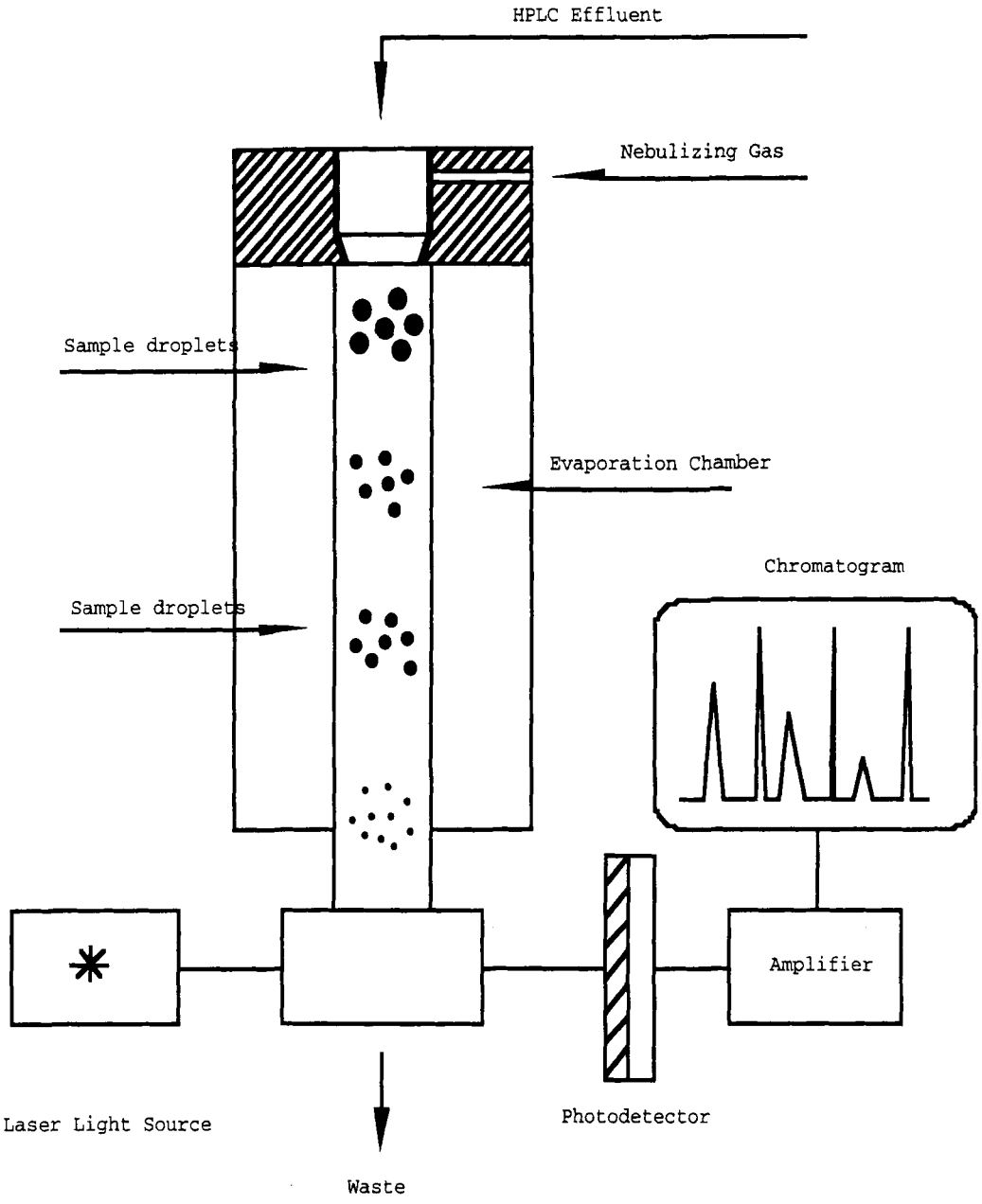


FIGURE 12. Schematic diagram of ELSD.

following gradient A:*n*-hexane, B:ethanol-THF-water (60:40:1); 0 min: 0%B; 60 min: 100%B on silica column (5 mm LiChrosorb Si 60 - Merck, Darmstadt, F.R.G.). The column effluent was monitored at an excitation wavelength of 280 nm and emission wavelength of 310 nm (maximum response determined for nonylphenol ethoxylate with 5 oxyethylene units). Changing the above gradient to one with MTBE, acetonitrile and methanol it was possible to use excitation wavelength down to 230 nm and hence increase the degree of sensitivity. The minimum level of detection of individual homologues is 0.2 ng [115]. Separation of ethoxylated alcohol derivatives carried out on 3 mm Hypersil ODS column (Shandon, Cheshire, U.K.) and acetonitrile-water (7:3) as a mobile phase were monitored at an excitation wavelength of 395 nm and an emis-

sion wavelength of 450 nm. The other derivatizing agents include 1-naphtyl isocyanate [116,117] and naphtoyl chlorides [118]. Because of its very low detection limit (high sensitivity) fluorescent detector is very often used in analysis of waste water samples (environmental analysis).

On line HPLC-MS is a very powerful technique used in ethoxylate analysis. It can be used both in identification [52,67,68,119] and quantification [83,120] of ethoxylated compounds. It can also provide information both on the distribution of homologues and the presence of impurities. MS detector allows to resolve the overlapping sub-bands (C18, CH_3OH/H_2O) because it simulates the effect of having thousands of compound specific detectors on line simultaneously. The MS method is also very useful in studies of biodegradation of nonionic surfactants.

Different (both "hard" and "soft") ionization techniques are used in on line HPLC-MS analysis of nonionics. The most popular ones are Electron Impact (EI) [121], Chemical Ionization (CI) [121], Field Desorption (FD) [83,84], Fast Atom Bombardment (FAB) [122], and Laser Desorption (LD) [123]. Soft techniques produce relatively little fragmentation of the parent ion and tend to simplify the interpretation. On the other hand, although the hard ionization techniques (EI) are difficult to interpret, the rich fragmentation patterns provide a wealth of structural information.

Although the molecular ion of EI spectrum of alkylphenol ethoxylates is clearly discernible, the EI spectra of alcohol ethoxylates are dominated, in the lower mass range, by unspecific ions of the general formula $[(CH_2CH_2O)_nH]^+$ and have no molecular ion [121]. This technique allows to distinguish linear from branched nonylphenol ethoxylates because the upper mass range (of the branched ones) is dominated by a fragment at m/z 311 formed by loss of hexyl radical.

The CI mass spectra of alkylphenol- and oxoalcohol ethoxylates with isobutane as the reagent gas are dominated by protonated molecules, while for all lower homologues with up to six oxyethylene units an abundant fragment formed as a result of loss of nonene or octene (the former for nonyl- and the later for octylphenol ethoxylate) is observed. The CI mass spectra of higher homologues show a fragment formed by cleavage of the C-O bond in the second oxyethylene unit (m/z 291 for nonyl- and m/z 277 for octylphenol ethoxylate) [121].

Thermospray LC/MS spectra (with postcolumn addition of ammonium acetate solution) are dominated by molecular ions of the type $[M + NH_4]^+$ and $[M + H]^+$ and only by $[M + NH_4]^+$ ions for some lower molecular weight compound ($C_{11}EO_2$-$C_{15}EO_2$. This method, proposed by Evans *et al.* [120], can quantify concentrations of linear primary alcohol ethoxylates at levels of 25 to 100 ppb for total alcohol ethoxylates and less than 3 ppb for individual homologues. In the absence of individual ethoxylated alcohols, C12-15EO9 and C11EO9 were used as standards, which were well characterized by LC/GC separation analysis. The chromatographic separation used by the authors (C18; 55%water + 45%THF) prevents ^{13}C and ^{14}C isotopic mass overlap interferences.

Field Desorption Mass Spectrometry (FD) can be applied to the identification and quantification of ethoxylated alcohols at trace levels in natural waters, because it is a useful tool for identifying and quantifying relatively high molecular weight and thermally unstable organic compounds. In contrast to the ethoxylated alkylphenols (molecular ions), it produces for ethoxylated alcohols $[M + H]^+$, $[M + \text{cation}]^+$ and cluster ions of the type $[M_1 + M_2 + H]^+$ and is mainly affected by emitter current, sample loading amount and the presence of metal salts. Tetradeuterioocta(oxyethylene) dodecyl ether is used as an internal standard in quantification of ethoxylated alcohols. Optimum sample size for determination is from 3 to 5×10^{-6} g to 10^{-8} g [83].

A relatively little fragmentation of the parent ion is obtained, in FRIT-FAB (FRIT–Fast Atom Bombardment), and the mass spectra yield pseudo-molecular ions derived from protonation of molecules. Consequently, FAB mass spectrum is relatively easy to interpret. But even these spectra may contain structurally significant fragment ions like, for example, diagnostic for ethoxylated compounds protonated polyoxyethylene glycol fragments $[CH_2CH_2O]_nH^+$ (n = 3, 4, 5, etc.). They cannot be observed in the spectrum taken early in the band where little fragmentation of short polyoxyethylene chain is evident, but the fragment peaks are strong in the spectrum taken late in the band where the polyoxyethylene chain is long (C18; water/methanol) [122].

For high molecular weight surfactants (>2000 u) which HPLC can not resolve, to individual oligomers Laser Desorption Fourier Transform ion cyclotron resonance mass spectrometry (LD/FT/ICR/MS) provides a simple and accurate measure of molecular weight distributions. This method is based on a single-shot laser pulse measurement of a few seconds duration. Because this ionization gives minimal fragmentation, it offers a reliable measure of the relative content of the oligomers, even without prior chromatographic separation of the compounds. In addition, the LD/FT/ICR/MS mass spectrum shows a low-abundance distribution of polyoxyethylene glycols [123].

Compounds that have an oligooxyethylene group in their molecules are known to form complexes with alkali metals, alkaline earth metals and transition metals. Conductivities of salt solutions decrease in the presence of oligooxyethylene chains because their metal complexes, larger and with higher microviscosities [141,142], are less mobile than is the ion metal itself. This feature is utilized in indirect conductometric detection of complexes separated on an ion exchanger in a K^+ form with methanol as a mobile phase. Detection limits were 3 to 4 times lower than that of RI detection [100,101].

IV. CONCLUSIONS

The discussion above shows there has been a great progress in analysis of nonionic surfactants over the past few years. Application of high-performance liquid chromatography offers the following advantages:

- Component separation according to the hydrophobe group,
- Component separation according to the hydrophile group,
- Component separation according to both the hydrophobe and hydrophile groups, with complete separation in the case of less complex mixtures,
- Group separation of polyoxyethylene glycols from ethoxylates,
- Separation of polyoxyethylene glycols from ethoxylates with a simultaneous separation into single homologues.

A properly selected system, that is a stationary and mobile phase, provides information needed to study processes with new catalysts, as well as for developing new technologies to obtain ethoxylates with average ethoxylation degrees that have practical applications.

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