Journal of Chromatography, 368 (1986) 339–350
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 868

DETERMINATION OF THE COMPOSITION OF ETHOXYLATED ALKYLAMINES IN PESTICIDE FORMULATIONS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY USING ION-PAIR EXTRACTION DETECTION

R. H. SCHREUDER and A. MARTIJN
Plant Protection Service, P.O. Box 9102, 6700 HC Wageningen (The Netherlands)
and
H. POPPE* and J. C. KRAAK
Laboratory for Analytical Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)
(First received April 1st, 1986; revised manuscript received June 11th, 1986)

SUMMARY

A high-performance liquid chromatographic method for the characterization of the alkyl and ethylene oxide distribution of ethoxylated alkylamines in pesticide formulations has been developed. The method involves the separation of the samples on two different columns: a cyano-modified silica column to determine the alkyl distribution and an amino-modified silica column to determine the ethylene oxide distribution. The detection of the ethoxylated amines was performed with a post-column ion-pair extraction system, using 9,10-dimethoxyanthracene-2-sulphonate as pairing-ion and fluorimetric detection. The detection system behaves linearly over two decades. The detection limit for the ethoxylated alkylamines was determined to be 25 ng. The method is suitable for the determination of ethoxylated amines in the presence of ethoxylated alkylphenols, alcohols and esters, because these latter compounds do not respond to the applied ion-pair extraction detection system.

INTRODUCTION

Ethoxylated alkylphenols, alcohols, esters and alkylamines are widely used as surfactants. They are also extensively used in liquid pesticide formulations. Despite their relatively low content, *ca.* 2–10%, their influence on the physical and physico-chemical behaviour of these products is of paramount importance. It is therefore necessary to have information about the content and the identity of these compounds. Analytical procedures to check the complete composition of pesticide products are important in law enforcement. Gravimetry, colorimetry, several spectrometric methods and chromatography have been applied to the analysis of such products. The simpler of these methods, such as gravimetry and colorimetry, are suitable only for production control, when the chemical composition is known[1,2]. The degree of

0021-9673/86/$03.50

ethoxylation can be determined by the Zeisel method[3] or by hydrolysis with hydrobromic acid in acetic acid followed by gas chromatographic determination of the 1,2-dibromoethane formed[4]. For the acquisition of more detailed structural information, infrared and nuclear magnetic resonance spectroscopy have to be used. Although these techniques are very valuable they fail when more information about the distribution pattern is required. For more detailed studies, the complicated composition of technical products, in which both the alkyl and polyether chains may vary in length, necessitates the application of chromatography. Thin-layer chromatography (TLC) was introduced many years ago[5,6]. Gas chromatography has been shown to be a useful method for the identification and quantitation of compounds with low degree of polymerization. However, the applicability of gas–liquid chromatography (GLC) is limited to such cases, even after acylation or silylation[7–9].

High-performance liquid chromatography (HPLC) is an attractive method, because it combines high resolution with the possibility of precise quantitation and is generally applicable to this type of compounds. Several HPLC methods are available for the determination of ethylene oxide oligomer distribution. For instance alkylphenol ethoxylates have been separated on silicagel[10], alkylamine-modified silicagel[11–13], alkyl cyanide-modified silicagel[14] and with reversed-phase chromatography on octadecyl columns[15].

Ethoxylated alkylamines are prepared by reaction of alkylamines with ethylene oxide at increased pressure and temperature. The alkylamines are produced from natural products such as coconut oil, tallow oil or soya oil. The final product obtained from these sources consists of a mixture of alkylamines with different alkyl chains. Therefore we can expect a large variety of compounds when ethoxylating these alkylamine mixtures. The compounds have a general structure of:

$$\begin{array}{l} H(C_2H_4O)_n\text{–}N\text{–}(C_2H_4O)_mH \\ \qquad\qquad\quad | \\ \qquad\qquad\quad R \end{array}$$

For the characterization of the ethoxylated alkylamine mixture it is therefore necessary to obtain information about the various alkyl homologues and the ethylene oxide oligomers as well. This means that the mixture has to be completely separated. Although HPLC is a suitable technique, its separation power is too small to separate all compounds on one column type. We therefore decided to use two types of column: one that separates the compounds on basis of their alkyl part and another that separates the compounds on basis of the ethylene oxide (EO) part. Although detection is easy in the case of alkylphenol derivatives, where UV detection can be applied, the detection of non-UV-absorbing compounds, such as alkylamine ethoxylates studied in this work, presents serious difficulties. Refractive index detection[14] suffers from high detection limits. Pre-column derivatization has been applied to non-ionic ethoxylates using esterification of the terminal hydroxyl group with 3,5-dinitrobenzoyl chloride[10,16]. However, this approach may lead to artefacts as a result of partial and cross reactions. Also it is often preferable to separate the compounds as they are, *e.g.* when spectrometry is used to identify compounds in the collected fractions. Post-column reaction detectors can be designed, based on the extraction of the solute as ion-pair with a fluorescent counter-ion, as has been shown[17,18] for amine-containing

drugs and sulphonic acids[19]. Such a system is applicable to the ethoxylated amines under consideration. In this paper we report the results of such a detection approach using 9,10-dimethoxyanthracene-2-sulphonate (DAS) as the pairing ion reagent.

EXPERIMENTAL

Apparatus

The liquid chromatograph for the isocratic separations consisted of an Orlita pump (Orlita, Giesen, F.R.G.), an injection valve (a Rheodyne Model 7010, Berkeley, CA, U.S.A.) equipped with a 25-μl injection loop, a fluorimetric detector (Fluorichrom Varian, Palo Alto, CA, U.S.A.). For gradient elution a two-pump gradient system was used (Kipp, Delft, The Netherlands), and an injection valve (Rheodyne 7010) equipped with a 20-μl injection loop and fluorimetric detector (FS 950 Fluorimat, Kratos, Ramsey, NY, U.S.A.). The peak areas were determined with an integrator (Model HP 3390 A, Hewlett Packard, Avondale, PA, U.S.A.).

Detection system

The ion-pair extraction system used for the isocratic separations is schematically shown in Fig. 1a. The DAS was dissolved in the mobile phase and the organic extractant was added to the column effluent by means of a peristaltic pump (Technicon Pump III, Technicon, Tarrytown, NY, U.S.A.), which was also used to control the flow of organic solvent (dichloroethane) through the fluorimetric detector. Mixing

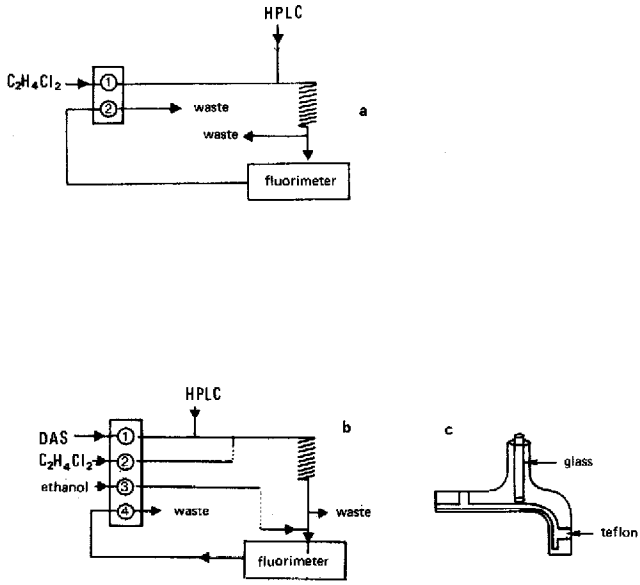

Fig. 1. Schematic representation of the post-column ion-pair extraction detection system. (a) System applied to isocratic reversed-phase separation; flow-rates: dichloroethane, 0.8 ml/min; through the cell, 0.6 ml/min; HPLC, 1 ml/min. (b) System applied to normal-phase gradient elution; flow-rates: DAS, 1.2 ml/min; dichloroethane, 1.6 ml/min; ethanol, 0.1 ml/min; through the cell, 0.6 ml/min; HPLC 1 ml/min. (c) Phase separator as applied to gradient elution; the glass tube was not needed in the case of isocratic elution.

and extraction took place in a 14-turns glass coil (2 mm I.D.). After phase separation the organic phase was monitored fluorimetrically (excitation 400 nm, emission 475 nm cut-off). Fig. 1b shows schematically the extraction detector as used for the gradient elution. The column effluent was first mixed with an aqueous solution of DAS and then segmented with 1,2-dichloroethane. Mixing and extraction took place in a 20-turns glass coil (2 mm I.D.). Phase separation was carried out with a Technicon phase separator provided with a piece of PTFE, and a glass capillary tube (*ca.* 10 mm × 1 mm I.D. × 1.8 mm O.D.) to accelerate the removal of the water phase to the polyethylene drain tubing (Fig. 1c). The organic phase was sucked through the fluorescence detector. The organic phase appeared to be slightly turbid. However, a clear organic phase was obtained by admixing a small amount of ethanol downstream of the phase separator. The DAS reagent solution, dichloroethane and ethanol were delivered by means of a peristaltic pump (mini-S8, Ismatex, Zürich, Switzerland), which was also used to control the flow of dichloroethane through the fluorimetric detector. As the precise conditions in the detector are highly dependent on the composition of the mobile phase, such details will be given in Results and Discussion.

Materials

The chromatographic columns (250 mm × 4.6 mm I.D.) used were of 316 stainless steel. The columns, filled with Hypersil APS (aminopropyl-modified silica) 5 μm and Polygosil 60 D-10 CN (alkylcyano-modified silica) were purchased from Chrompack (Chrompack, Middelburg, The Netherlands). The Hypersil SAS 5 μm (propyl-modified silica) was packed in the laboratory by a slurry method. Ethoxylated cocoamine (5, 10, 11, 15 EO), ethoxylated tallowamine (15 EO) and ethoxylated oleylamine (11 EO), as well as the precursory amines, were obtained from Servo (Delden, The Netherlands). Sodium 9,10-dimethoxyanthracene-2-sulphonate (DAS) was purchased from Fluka (Switzerland) and used without purification. The organic solvents used were of analytical reagent quality. Pure water was prepared by passing demineralized water through a Milli-Q system (Millipore, Bedford, MA, U.S.A.).

Procedure

The mobile phase for the isocratic elution was prepared by dissolving 34 mg of DAS in a mixture of 300 ml of methanol and 100 ml of dioxane, followed by adding 600 ml of a solution of 10 g/l magnesium chloride in water. The pH was adjusted to pH 2.5 (± 0.1) with 1 *M* hydrochloric acid, and the resulting solution was filtered through a 0.45-μm filter (Metricel, TCM-450, Gelman). Samples were dissolved in the mobile phase in concentrations from 1 to 1000 mg/l. The oligomer separations were made by a linear gradient between (A) *n*-hexane–tetrahydrofuran (7:3, v/v) and (B) 2-propanol–water (9:1, v/v). The solvent gradient was started at the injection point with 5% (v/v) B and than raised to 60% (v/v) B in 60 min. DAS reagent solution was made by dissolving 17 mg of DAS and 8 g of sodium dihydrogen phosphate in 1000 ml of water, and adjustment afterwards of the pH to 3.25 (± 0.1) with 1 *M* phosphoric acid. Samples were dissolved in solvent A in a concentration of 1–3 g/l.

RESULTS AND DISCUSSION

Separation of the alkyl homologues

Reversed-phase systems have been shown to be eminently suited for the separation of alkyl homologues. It is therefore obvious to apply this separation technique to the determination of the alkyl distribution in the ethoxylated alkylamines. For this purpose a short-chain-modified silica (Hypersil SAS) combined with water–methanol mixtures was tested first. From high-performance TLC experiments, on reversed-phase TLC plates, it was found that the presence of chloride in the developing liquid remarkably improved the shape of the spots of ethoxylated amines. For that reason 10 g/l of chloride (w/v), as magnesium chloride, was added to the mobile phases used in the HPLC experiments, and again led to improved results. Although a good separation was achieved on basis of the alkyl part in the ethoxylated amines (ranging from C_{10} to C_{18}), the phase system was not attractive from the point of view of detection. This was due to the relatively large methanol content (*ca.* 75%, v/v), needed to elute all compounds in a reasonable time. The mutual solubility of the mobile phase and the extraction solvent is therefore relatively large. This causes an increase in the unpaired DAS concentration in the extraction solvent and consequently leads to an unacceptable increase of the background noise. Moreover, the phase separation was very difficult. Some attempts to replace methanol by other organic modifiers such as acetonitrile, tetrahydrofuran (THF) and acetone did not improve the situation.

There were two possibilities for solving these detection problems: (i) using mobile phases with a lower organic modifier content; (ii) dilution of the mobile phase with water before segmentation with the extraction solvent. The latter method was rejected because this would complicate the experimental set-up considerably. We therefore focused our efforts on developing a phase system with a lower organic modifier content in the mobile phase by using a more polar reversed packing, and so we investigated alkylcyano-modified (CN) silica. It seemed that on CN-silica, with 50% (v/v) of methanol in the mobile phase, the same retention was achieved as with 75% (v/v) of methanol on SAS-silica. However, the resolution of palmityl and oleyl was very poor, and in order to improve this we decided to add a second organic modifier to the mobile phase. Dioxane, THF and acetonitrile were tested. Of these three solvents, dioxane was found to improve significantly the resolution between palmityl and oleyl. By measuring the retention and selectivity at various methanol and dioxane contents, an optimum mobile phase composition for the separation of the ethoxylated amines on basis of their alkyl part could be determined. A mobile phase consisting of 10 g/l magnesium chloride hexahydrate in water–methanol–dioxane (60:30:10, v/v/v) adjusted to pH 2.5 with 1 *M* hydrochloric acid and 35 mg/l DAS seemed to be a good compromise. With this mobile phase compoisition a low background noise and a good phase separation were obtained. Fig. 2 shows the chromatograms of three products as obtained with the selected phase system and ion-pair extraction detection. This separation system discriminates the compounds only on the basis their alkyl part and not their EO content.

On reversed-phase systems a linear relationship is usually found between $\log k'$ of alkyl homologues and the number of methylene groups according to $\log k' = A + Bn$. This is also found with the ethoxylated amines used in this study (Fig. 3).

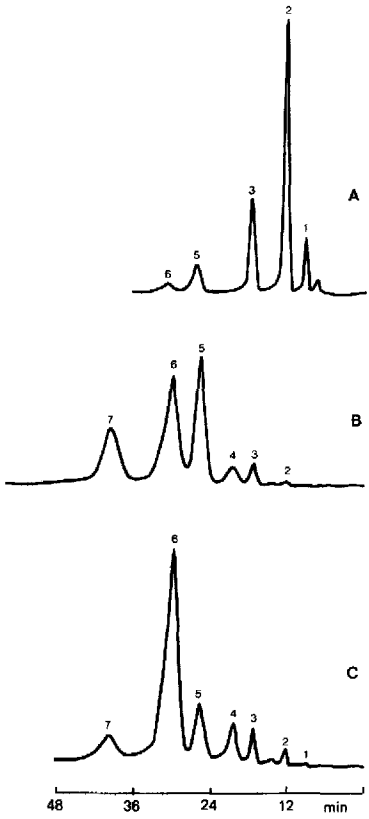

Fig. 2. Reversed-phase separation of ethoxylated amines, on basis of the alkyl part, on CN-silica; mobile phases, 10 g/l magnesium chloride hexahydrate in water–methanol–dioxane (6:3:1, v/v/v) plus DAS (34 mg/l), pH 2.5. (A) Cocoamine (10 EO); (B) tallowamine (15 EO); (C) oleylamine (11 EO). Peaks: 1 = C_{10}; 2 = C_{12}; 3 = C_{14}; 4 = $C_{16:1}$; 5 = C_{16}; 6 = $C_{18:1}$ and $C_{18:2}$; 7 = C_{18}.

Included in this figure are the k' factors of two unsaturated alkyl amines. Although only two solutes were available, the dependence of log k' on the methylene group increment (*e.g.* the slope) equals that of the saturated compounds, in agreement with earlier findings[20]. The linearity of the developed method was determined by injecting 0.25, 0.5, 2.5, 6.25, 12.5 and 25 μg of cocoamine (derived product) and measuring the peak area or peak height (correlation coefficient = 0.998; n = 6). The calibration curve is linear over two decades. For quantitative analysis the range 1–12 μg is the best. The detection limit, defined as three times the standard deviation (S.D.) of the baseline noise, was calculated to be 25 ng under these conditions. The S.D. of the method was determined by repeated injection of a solution of ethoxylated cocoamine (n = 6) and measurement of the peak area. The results of these measurements are given in Table I. The coefficient of variation was found to be 1.5% for C_{12} and C_{14} and 5–6% for C_{10}, which is quite acceptable for characterization purposes. The larger S.D. for C_{10} can be attributed to the lower concentration of C_{10} compounds in the sample compared with C_{12} and C_{14} (see Table II), which gives rise to a relatively small peak close to the detection limit of the method.

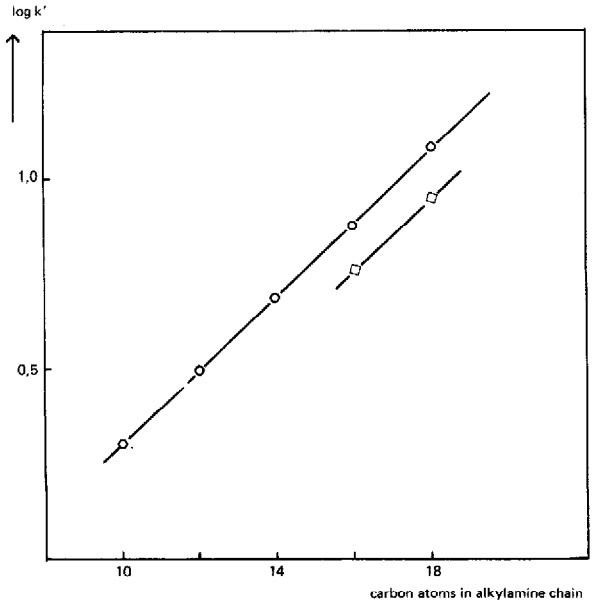

Fig. 3. Relationship between the logarithm of the capacity factor (k') and the number of carbon atoms in the ethoxylated alkylamines, on the CN-column. (○) Saturated compounds, (◇) unsaturated compounds. Mobile phase as for Fig. 2.

The developed method was applied to the determination of the alkyl distribution in a number of commercial ethoxylated alkylamines. The results were compared with those obtained for the precursor amines with capillary GC (25 m × 0.32 mm I.D. fused-silica Sil 5 column, Chrompack, the Netherlands; temperature, 200°C; split ratio, 1:50). As can be seen from Table II, there is good agreement between the results obtained by HPLC and by GC.

Separation of the ethylene oxide oligomers

So far we have described a HPLC method for determining the alkyl chain distribution in ethoxylated alkylamine samples. However, for a complete characterization of samples the EO distribution also has to be known. The determination of the EO distribution of ethoxylated amines is complicated because of the large number

TABLE I

REPRODUCIBILITY OF THE REVERSED-PHASE METHOD FOR DETERMINING THE ALKYL COMPOSITION IN ETHOXYLATED ALKYLAMINES

Injected amount of cocoamine (10 EO) (μg)	*Coefficient of variation*		
	C_{10}	C_{12}	C_{14}
2.5	4.97	0.83	1.74
6.25	6.58	1.5	0.96

TABLE II

ALKYL DISTRIBUTION (AS %, m/m) OF ETHOXYLATED ALKYLAMINES, PRODUCED FROM VARIOUS NATURAL PRODUCTS, AS DETERMINED BY GC AND HPLC

Carbon chain	*Cocoamine*		*Oleylamine*		*Tallowamine*	
	GC amine	*HPLC ethoxylated amine (10 EO)*	*GC amine*	*HPLC ethoxylated amine (11 EO)*	*GC amine*	*HPLC ethoxylated amine (15 EO)*
C_8	3.4	1.9				
C_{10}	7.0	8.8				
C_{12}	53.7	61.7	0.4	1.2	0.4	0.5
C_{14}	19.4	19.6	2.3	3.4	2.6	2.5
C_{16}	8.9	6.1	15.3	11.7	27.0	33.8
$C_{16:1}$	–	–	3.7	6.3	2.9	3.2
C_{18}	1.9	–	14.0	8.9	18.3	20.9
$C_{18:1} + C_{18:2}$	5.3	1.9	62.7	68.5	44.7	39.1
Total	99.6	100	98.4	100	95.9	100

of oligomers that can be formed during ethoxylation. Reversed-phase chromatography is apparently unsuitable for solving this separation problem because of its large selectivity towards alkyl groups, which would result in very complex and almost non-interpretable chromatograms. Hence we searched for a phase system that shows selectivity for the EO groups but not for alkyl groups. Normal-phase systems show such a behaviour and were therefore an obvious choice.

Three normal-phase packings, bare silica (Si 60, Merck), a CN-modified silica (Polygosil 60 D-10 CN) and an NH_2-modified silica (Hypersil APS), were investigated as stationary phases in combination with various organic solvent mixtures as mobile phase. Although bare silica, with chloroform–methanol (*ca.* 10–20%, v/v), could separate the lower oligomers, it was not further investigated, as bad reproducibility was observed when gradients were applied in order to elute higher oligomers. Results with CN-modified silica, with mixtures of chloroform or dichloroethane with 3-methoxyethanol or methanol, and 3-aminopropanol, indicated very poor separations, in contrast to literature reports[14].

We have previously used NH_2-modified silica for the separation of ethoxylated alkylphenol using gradient elution[13]. The gradient starts with a mobile phase composition of hexane–THF (7:3, v/v) and is linearly mixed, from 5% to 60% (v/v), with a mixture of propanol–water (9:1, v/v). Because this gradient system was found to be very effective in separating ethoxylated alkyl phenols we decided to apply it to the ethoxylated amines as well. After optimization of the shape of the gradient we finally succeeded in separating the ethylene oxide oligomers. Fig. 4 shows the chromatograms of three ethoxylated amines samples with different degrees of ethoxylation. As can be seen from this figure the degree of ethoxylation is clearly visualized. The chromatogram also shows that the phase system has some selectivity towards the alkyl groups as well. From Fig. 5 it is clear that each amine shows a specific pattern,

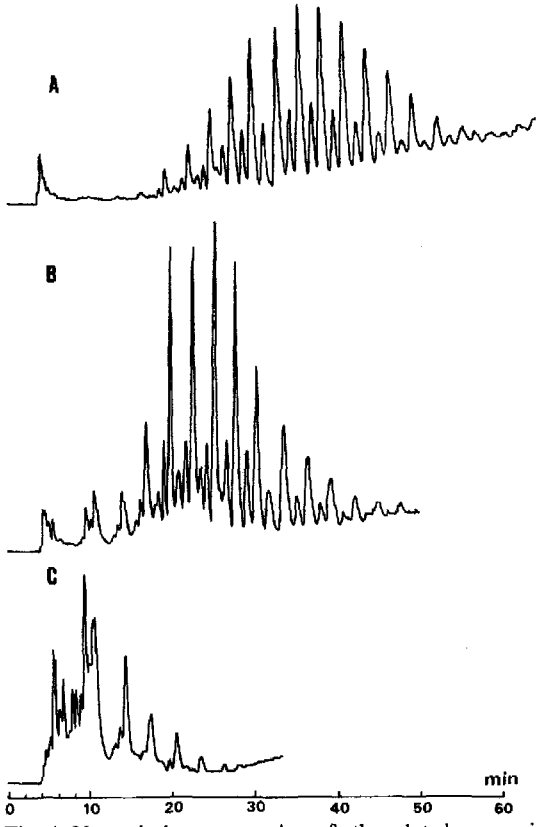

Fig. 4. Normal-phase separation of ethoxylated cocoamine on an NH_2 column; conditions as in Fig. 5. (A) 15 EO/mol; (B) 10 EO/mol; (C) 5 EO/mol.

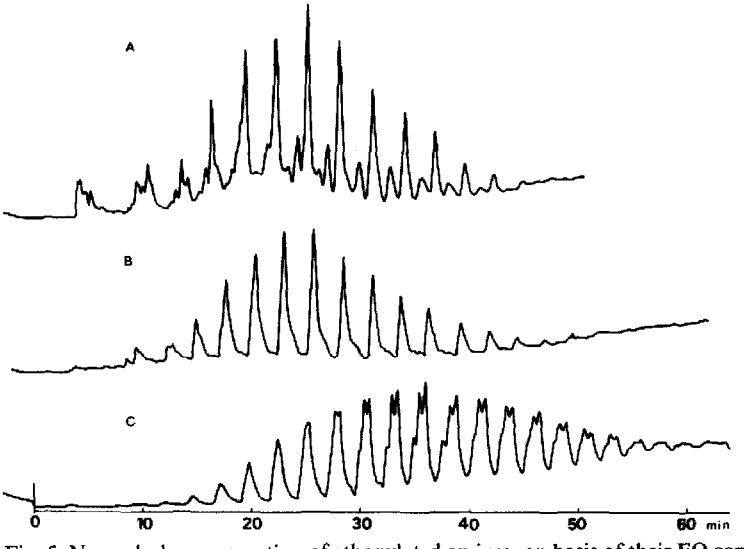

Fig. 5. Normal-phase separation of ethoxylated amines, on basis of their EO content, on an NH_2 column. Mobile phase: A = hexane–tetrahydrofuran (7:3, v/v); B = 2-propanol–water (9:1, v/v); linear gradient from A plus 5% (v/v) B to A plus 60% (v/v) B in 60 min. (A) Ethoxylated cocoamine (10 EO); (B) ethoxylated oleylamine (11 EO); (C) ethoxylated tallowamine (15 EO).

which can be used for identifying the type of alkyl group. Note that the ion-pair detection system works well up to 60% (v/v) of B. This means that the method is suitable up to a mean EO content of 15 moles EO/mol.

Identification of the oligomers by mass spectrometry

To calculate the molar average ethoxylated number of the oligomer, the ethoxymer peaks in the chromatogram had to be identified. For this reason one peak was isolated from an HPLC separation of the oligomers of cocoamine by trapping 20 times. After concentration and removal of the DAS anion by means of a disposable microcolumn filled with quaternary amine-modified silica, the resulting residue was analysed by field desorption mass spectrometry. The found figure of 605 gives, after correction for the sodium ion, a molecular mass of 582. This agrees with dodecylamine with an EO number of 9. Starting with the identified peak, each peak preceding or following this peak is consecutively given a lower or higher ethoxylate number, respectively. The peak areas of the ethoxylated oligomers are independent of the ethoxylated chain length and are therefore directly proportional to the mole percent of the compounds. The average ethoxylate number was calculated according to Rothman[12].

The results were compared with those obtained by NMR and GLC (Table III). Hydrolysis and GLC were carried out according to the method presented by Slagt *et al.*[4]. The NMR data were obtained by using the ratio of the integrated peak intensities of ethyleneoxy protons to the protons of the three carbon atoms directly connected to the nitrogen atom.

Analysis of commercial pesticide formulations

The developed two-column HPLC system was applied to determine the ethoxylation degree and content of ethoxylated amines in some commercial pesticide formulations. These commercial formulations also contained ethoxylated alkylphenols and small amounts of ethylene glycol. For the analysis on the NH_2 column the samples were first purified over a disposable anion-exchange column in order to remove anions that might be retained strongly on the NH_2 column. The degree of ethoxylation was determined on the NH_2 column by comparison of the EO distribution in the samples with those of standard samples with known EO distribution.

TABLE III

THE DEGREE OF ETHOXYLATION OF VARIOUS SAMPLES AS DETERMINED BY GC, NMR AND HPLC

Amine	*Degree of ethoxylation (mol EO/mol)*			
	Declaration	*GLC after hydrolysis with hydrogen bromide*	*NMR*	*HPLC*
Cocoamine	10	9.2	9.5	10.1
Oleylamine	11	10.4	12.0	11.1
Tallowamine	15	14.4	13.2	14.9

Then the content of ethoxylated amines in the samples was determined on the CN column. Chromatograms of samples did not differ from that of the standard, because the active ingredients and inert materials did not respond to the fluorimetric detector. The results of the analysis of these formulations are given in Table IV. For some formulations the values found with HPLC agree very well with the declared values. However, for one formulation (A2) the declared values seem to be incorrect. These results show that the ethoxylated amines can be very well determined by HPLC in samples containing other types of ethoxylated compound, such as alkylphenols.

TABLE IV

ANALYSIS OF ETHOXYLATED ALKYLAMINE CONTENT AND DISTRIBUTION IN SOME COMMERCIAL PESTICIDE FORMULATIONS BY THE TWO-COLUMN HPLC SYSTEM

Sample	*Type of alkylamine (EO)*	*Degree of ethoxylation determined by HPLC (mol EO/mol)*	*Assay determined by HPLC (%, m/m)*	*Declared value (%, m/m)*
A1	Oleylamine	14.4	8.4	8.2
A2	Cocoamine	5	<0.1	1.25
B	Tallowamine	14.0	16.4	15

CONCLUSIONS

The main results of this study can be summarized as follows.

(1) Ethoxylated alkylamines can sensitively and selectively be detected in HPLC by applying an ion-pair extraction detection system, using DAS as a fluorigenic pairing-ion.

(2) Alkylphenols, alcohols and esters do not respond to the ion-pair extraction detection system.

(3) The determination of the alkyl distribution in ethoxylated alkylamines can be very well performed by reversed-phase HPLC on a CN-modified silica as reversed-phase packing.

(4) The EO oligomer distribution, and thus the degree of ethoxylation, can best be determined by normal-phase HPLC on an NH_2 column with gradient elution.

(5) The content of ethoxylated alkylamines in commercial pesticide formulations can be determined by analysing the sample successively on the normal and reversed-phase systems.

(6) The HPLC and detection system described might be useful for the determination of ethoxylated amines in other materials, such as antistatics, corrosion inhibitors and cosmetic materials. Determinations in surface waters will require preconcentration techniques.

ACKNOWLEDGEMENTS

The authors thank Prof. Dr. N. M. M. Nibbering and Mr. R. H. Fokkens for performing the mass spectrometric analysis.

REFERENCES

1 M. J. Rosen and H. A. Goldsmith, *Systematic Analysis of Surface-Active Agents*, Wiley, New York, 2nd ed., 1972.
2 G. F. Longman, *The Analysis of Detergent and Detergent Products*, Wiley, London, 1977.
3 S. Siggia, *Quantitative Organic Analyses*, Wiley, New York, 1963.
4 C. Slagt, J. M. H. Daemen, J. Dankelman and W. A. Sipman, *Fresenius' Z. Anal. Chem.*, 264 (1973) 401.
5 H. K. Mangold and R. Kammereck, *J. Am. Oil Chem. Soc.*, 39 (1962) 201.
6 K. Bey, *Fette, Seifen, Anstrichm.*, 67 (1965) 217.
7 B. Stancher, L. Favretto Gabrielli and L. Favretto, *J. Chromatogr.*, 111 (1975) 459.
8 H. Szewczyk, J. Szymanowski and W. Jerzykicwicz, *Tenside Deterg.*, 19 (1982) 5.
9 R. Gnauck, *J. Chromatogr.*, 284 (1984) 87.
10 H. Brüschweiler, *Mitt. Geb. Lebensm. Hyg.*, 68 (1977) 46.
11 F. P. B. van der Maeden, M. E. F. Biemond and P. C. G. M. Janssen, *J. Chromatogr.*, 149 (1978) 539.
12 A. M. Rothman, *J. Chromatogr.*, 253 (1982) 283.
13 R. H. Schreuder and A. Martijn, *Proceedings Pesticide Formulation Analysis*, Collaborative International Pesticides Analytical Council Limited, Harpenden, 1981.
14 *HPLC of Surfactants*, Du Pont Liquid Chromatography Technical Report, Du Pont, Wilmington, DE, 1980.
15 W. R. Melander, A. Nahum and Cs. Horváth, *J. Chromatogr.*, 185 (1979) 129.
16 O. Nozawa and T. Ohnuma, *J. Chromatogr.*, 187 (1980) 261.
17 J. F. Lawrence, U. A. Brinkman and R. W. Frei, *J. Chromatogr.*, 171 (1979) 73.
18 R. J. Reddingius, G. J. de Jong, U. A. Th. Brinkman and R. W. Frei, *J. Chromatogr.*, 205 (1981) 77.
19 F. Smedes, J. C. Kraak, C. F. Werkhoven-Goewie, U. A. Th. Brinkman and R. W. Frei, *J. Chromatogr.*, 247 (1982) 123–132.
20 E. Tomlinson, H. Poppe and J. C. Kraak, in E. Reid (Editor), *Blood Drugs and other Analytical Challenges*, Ellis Horwood, Chichester, Vol. 7, 1978, p. 207.