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# Quantitative analysis of polyethoxylated octylphenol by capillary supercritical fluid chromatography

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ABSTRACT

The rapid separation and quantitative determination of oligomers of polyethoxylated octylphenol surfactants was achieved using capillary supercritical fluid $CO_2$ chromatography. The oligomer distribution of all surfactants studied was graphically depicted, and the average ethylene oxide number of each individual surfactant was calculated. Temperature programming was investigated in combination with linear pressure programming to enhance long-chain surfactant analysis. The effect of the variable chromatographic parameters, including temperature, pressure programming ramp rate, and solvents used to prepare surfactant solutions, on the separation of polyethoxylated octylphenols are discussed. The capillary supercritical fluid chromatographic analysis results were validated by comparing them to the values obtained from C1 reversed-phase HPLC analyses.

## INTRODUCTION

Non-ionic surfactant polyethoxylated alkylphenols are used in a wide variety of applications, including liquid laundry detergents, wetting agents, emulsifiers, agricultural agents, biochemical research, and in institutional and industrial cleaners [1,2]. These surfactants are manufactured by the polymerization of ethylene oxide (EO) to alkylphenols. Consequently, these surfactants are complex mixtures in which the oligomer index, namely the number of EO units in each individual oligomer, varies over a considerable range.

The analysis of such complex samples is not trivial, and much research has been carried out in this area. It is possible to separate and identify oligomers of the Triton family of surfactants for which the EO units are relatively small (less than 5 units) by gas chromatographic (GC) analysis [3], although the prior formation of volatile derivatives of such surfactants is usually required [3–5]. High-temperature GC (oven temperature of about 400–430°C) has been shown to be applicable for the analysis of Triton X-100, a higher-average-molecular-mass member of that family [6,7]. Alternatively, Stephanou [8,9] reported the identification and determination of polyethoxylated alkylphenols and linear alcohols in untreated municipal wastewaters by GC–mass spectrometry (MS) using chemical ionization.

Normal-phase high-performance liquid chromatography (HPLC) coupled with UV detection and fluorescence has been used for the separation and measurement of ethoxy oligomers in polyethoxylated alkylphenols [10–16]. For example, Macomini and co-workers [17,18] and Ahel and co-workers [19,20] recently reported on reversed-phase HPLC methods for simultaneous quantitation of linear alkyl benzenesulfonates (LAS) and polyethoxylated alkylphenols (PEAP) in wastewater and other environmental samples. In their methods, all oligomers of PEAP eluted out as one or two peaks and the determination of individual oligomers required

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additional information from normal-phase HPLC. Allen and Rice [21] described a HPLC method for the separation of alkylphenol ethoxylate adducts of up to 9 or 10 EO units. Very recently, we reported on a rapid and simple approach for the separation and identification of polyethoxylated octylphenol surfactants that allows for the quantitative determination of the relative distribution of each oligomer using a C1 TMS (trimethylsilyl) column reversed-phase HPLC [22]. Polyethoxylated octylphenol oligomers up to 40 EO units (molecular mass up to approximately 2000) were satisfactorily separated and identified.

Parallel to the developments in high-temperature capillary GC, considerable progress has been achieved in supercritical fluid chromatography (SFC). The introduction of high-quality syringe pumps, narrow-bore capillary columns with immobilised stationary phase, density and pressure programming have made capillary SFC accessible for everyday chromatography. The high solvating power of supercritical fluid allows for the elution of high-molecular-mass components at much lower temperatures than in high-temperature GC. Capillary SFC was shown to be an effective means for the separation of ethoxylate adducts in polyethoxylated alcohol [23–25]. Knowles *et al.* [26] and colleagues recently published a review of polymer analysis by capillary supercritical fluid chromatography.

We are now reporting on a relatively simple, rapid and reproducible capillary SFC method for the separation and identification of polyethoxylated octylphenol surfactants, and on the determination of the ethylene oxide adduct distribution in each individual sample. The SFC analysis results are validated by comparing them to the values obtained from C1 reversed-phase HPLC analyses [22]. Work on the separation and the identification of polyethoxylated nonylphenols, by both capillary SFC and HPLC, will be presented elsewhere.

## EXPERIMENTAL

### *Materials*

All solvents were chromatographic grade and were used without further purification. The polyethoxylated octylphenol surfactant samples (Triton is a trade name for many of these surfactants) were purchased from Sigma (St. Louis, MO, USA) and Rohm & Haas (Philadelphia, PA, USA), and were used as is. The surfactant samples were dissolved in dichloromethane and methanol at concentrations ranging from 1.0 mg/ml to 10.0 mg/ml, depending on the average EO numbers and average molecular masses of the samples. A solution of *tert.*-octyl phenol was used as standard for the capillary SFC analyses.

### *Instrumentation*

The capillary supercritical fluid chromatograph was made up of a Brownlee microgradient fluid delivery system (Brownlee Labs., Santa Clara, CA, USA), and a Hewlett-Packard Model 5890 gas chromatograph (Hewlett-Packard, Avondale, PA, USA) equipped with a flame ionization detector operated at 350°C. SFC-grade carbon dioxide (99.99%) with helium backpressure in the tank (Matheson Gas Products, East Rutherford, NJ, USA) was used as the mobile fluid. The pump cylinder was filled with liquid carbon dioxide at a starting pressure of 2000 p.s.i. (1 p.s.i. = 6894.76 Pa).

A Model 7520 Rheodyne microinjector equipped with a 0.5-$\mu$l sample loop (Rheodyne, Cotati, CA, USA) was mounted above the oven of the gas chromatograph with the outlet stator flow-passage facing downward into the oven. The data were collected by a Hewlett-Packard integrator Model 3396.

The separation of surfactant oligomers was achieved using an isothermal linear pressure program for most of the samples investigated. A simultaneous linear pressure and temperature program was used for long-chain surfactant analysis to improve resolution, and especially to completely elute high-molecular-mass oligomers.

### *Column and restrictor*

A 5 m × 50 $\mu$m SB-Biphenyl-30 (30% biphenyl, 70% methylpolysiloxane) with 0.25 $\mu$m film thickness (Lee Scientific, Salt Lake City, UT, USA), equipped with a integrated on-column frit restrictor, was used. This type of restrictor resists plugging, allowing for fine tuning of the flow-rate. The outlet of the capillary

column was positioned into the flame ionization detector liner such that the restrictor end was even with the detector jet tip.

The capillary column was connected to the microinjector by means of a splitter. A 70 cm × 15 μm fused-silica tubing was used as split restrictor to obtain an approximately 1:10 split ratio. The ratio can be modified by adjusting the length and the internal diameter of the split restriction tubing.

## RESULTS AND DISCUSSION

### *Supercritical fluid chromatography separation*

The solvating power of carbon dioxide is a function of its density, which in turn is dependent upon pressure. The elution of the various oligomers, for which volatility decreases as molecular mass increases, is accomplished by means of pressure programming. Non-ionic surfactant samples containing oligomers with EO units varying from 0 to 25 were investigated. Figs. 1 and 2 show SFC chromatograms of Triton X-102 and Triton X-100, respectively, using a linear pressure program (starting from 2000 psi with 2 min hold, and then 2000 to 5500 p.s.i. in 33 min). Twenty-three peaks and twenty peaks can be discerned for Triton X-102 and Triton X-100, respectively. The numbers assigned to the individual peaks in Figs. 1 and 2 represent the number of EO units for each oligomer. The retention times can be correlated to the molecular masses and to the boiling points of the oligomers in the samples, the shorter-chain-length oligomers being eluted first. The peaks representing oligomers with increasing EO units, are nearly equally spaced throughout the chromatograms. The EO (23) octylphenol and the EO (20) octylphenol eluted at approximately 30.7 and 27.4 min are the last peaks visible in the chromatograms 1 and 2, respectively.

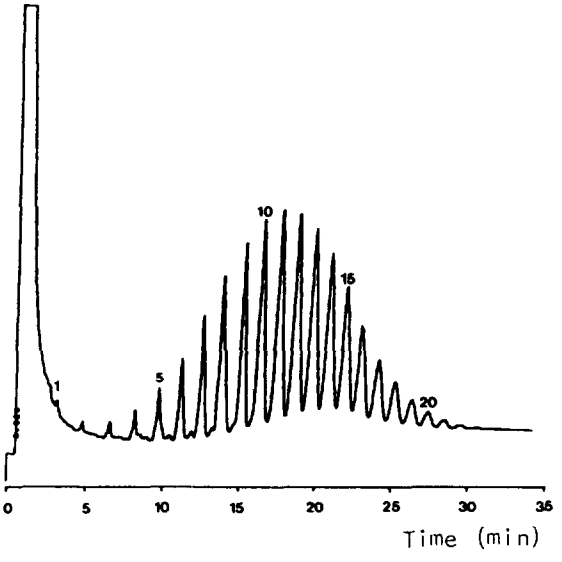


Fig. 1. Capillary SFC chromatogram of Triton X-102 (10.0 mg/ml) using a linear pressure program. Conditions: 5 m × 50 μm SB-Biphenyl-30 column; linear pressure program from 2000 p.s.i. with 2-min initial hold to 5500 p.s.i. in 33 min; $CO_2$ mobile phase at 100°C; FID at 350°C; integrator attenuation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

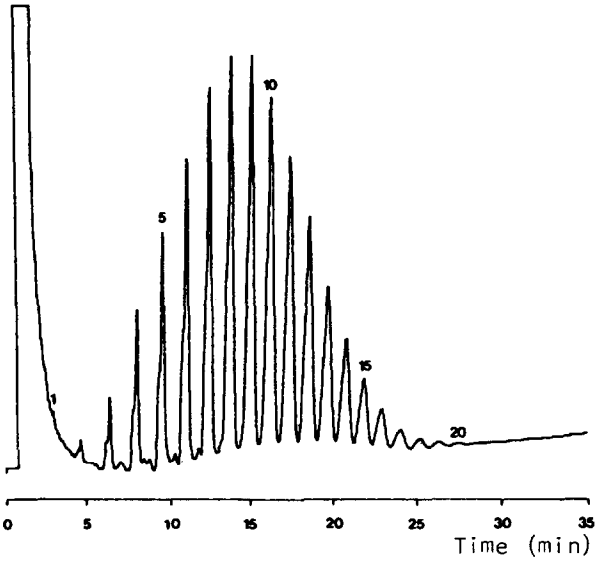


Fig. 2. Capillary SFC chromatogram of Triton X-100 (5.0 mg/ml) using a linear pressure program. Conditions are the same as those given in Fig. 1.

Because of the lack of single-EO-number octylphenol standards, the identification of these peaks was based on comparison of retention times with that of reference materials octylphenol (EO = 0) and Triton X-15 [its major component is EO (1) octylphenol], and on the assumption that they differ from each other by one EO unit; the rationale for this well-accepted assumption was presented elsewhere [16,22].

Figs. 1 and 2 show that there is a very slight

baseline drift as the pressure increases. The small shoulder eluted prior to the first oligomer peak (EO = 1) in Fig. 1 is the parent octylphenol remaining unconverted. The smaller intermediate peaks are thought to arise from alkyl groups of differing lengths but the same number of EO units as the main adjacent peak.

In capillary SFC, solute retention and its reproducibility is governed by a number of parameters such as the nature of the stationary and mobile phase, the pressure and/or density programming, the temperature, the injection technique and the mode of interfacing the capillary column to the valve. Under the chosen conditions (constant temperature and fixed fluid pressure program), the valve was manually actuated and good reproducibility for retention times and peak areas was achieved. Table I lists the average values of retention times and peak area percentages from typical 5 injections for the analysis of Triton X-100. Table I shows that the reproducibility is quite satisfactory with the relative standard deviations (R.S.D.) for the retention times of less than 0.5% and for peak area percentages below 4.0%. The work reported by Richter *et al.* [27] showed that the injection valve actuated by air or helium may give better precision and reproducibility.

### *Oligomer distribution and its comparison with HPLC results*

In order for the method to be able to produce quantitative distributions, the flame ionization detection (FID) response factors for each individual oligomer should be known, in addition to acceptable separation of the components and the identity of the various ethoxylate peaks. Some authors have discussed FID response factors for quantitative analyses [28–32]. Single-EO-number octylphenols were not available to

TABLE I

REPRODUCIBILITY OF RETENTION TIME AND PEAK AREA PERCENTAGE OF TRITON X-100

| Peak | Retention time[a] | | | Peak area | | |
|---|---|---|---|---|---|---|
| | Average (min) | S.D. (min) | R.S.D. (%) | Average (%) | S.D. (%) | R.S.D. (%) |
| 1 | 3.18 | 0.018 | 0.56 | 0.114 | 0.004 | 3.58 |
| 2 | 4.79 | 0.014 | 0.28 | 0.420 | 0.015 | 3.48 |
| 3 | 6.577 | 0.030 | 0.46 | 1.411 | 0.049 | 3.45 |
| 4 | 8.233 | 0.035 | 0.43 | 3.311 | 0.043 | 1.29 |
| 5 | 9.794 | 0.037 | 0.38 | 5.354 | 0.056 | 1.04 |
| 6 | 11.254 | 0.042 | 0.37 | 7.206 | 0.044 | 0.62 |
| 7 | 12.635 | 0.045 | 0.36 | 9.425 | 0.076 | 0.80 |
| 8 | 13.938 | 0.048 | 0.34 | 11.396 | 0.079 | 0.69 |
| 9 | 15.193 | 0.047 | 0.31 | 12.433 | 0.052 | 0.42 |
| 10 | 16.383 | 0.061 | 0.37 | 12.184 | 0.029 | 0.24 |
| 11 | 17.538 | 0.046 | 0.26 | 10.788 | 0.064 | 0.59 |
| 12 | 18.659 | 0.057 | 0.31 | 8.761 | 0.072 | 0.82 |
| 13 | 19.724 | 0.058 | 0.30 | 6.532 | 0.050 | 0.76 |
| 14 | 20.788 | 0.080 | 0.39 | 4.496 | 0.034 | 0.75 |
| 15 | 21.839 | 0.056 | 0.26 | 2.851 | 0.025 | 0.88 |
| 16 | 22.912 | 0.085 | 0.37 | 1.669 | 0.035 | 2.10 |
| 17 | 23.977 | 0.085 | 0.36 | 0.901 | 0.027 | 2.95 |
| 18 | 25.08 | 0.083 | 0.33 | 0.451 | 0.013 | 2.90 |
| 19 | 26.23 | 0.082 | 0.31 | 0.204 | 0.008 | 3.87 |
| 20 | 27.43 | 0.082 | 0.30 | 0.082 | 0.003 | 3.68 |
| Average of total area (counts) | | 2 851 164 (S.D.: 117 768; R.S.D.: 4.13%) | | | | |
| Average EO number ($n$) | | 9.51 | | | | |

[a] S.D. = Standard deviation; R.S.D. = relative standard deviation (5 injections).

us, hence, the area percentage method was used to calculate the oligomer distribution and the sample molecular mass (see ref. 22 about the detailed discussion for the mathematical quantitation of the average EO number and average molecular mass). The accuracy of this method was evaluated by comparing the calculated results with the values obtained from the HPLC analysis of the same samples. It has been demonstrated that the octylphenol oligomers have nearly equal molar absorptivities at the selected UV wavelengths, and therefore the molar response factor for all oligomers can be taken as equal [16,22] in HPLC measurements.

Once each sample had been run and each peak representing a different oligomer had been identified, the peak areas were tabulated. Table II lists the peak area percentages for Triton X-102 oligomers from four repeated analyses. The average area percentage for each peak, standard deviations and relative standard deviations are also given in Table II. The average EO number for Triton X-102 was determined to be 11.67. As comparison, the corresponding value obtained from HPLC analysis was 11.61 [22]. Fig. 3 shows the oligomer distribution curves of Triton X-102 by SFC and HPLC analysis.

Table III lists the peak area percentages, standard deviations, relative standard deviations, and the average EO number for Triton X-15, Triton X-35 and Triton X-45. Their EO units range from 1 to 11. Similarly, Table IV gives the data for two other longer-chain polyethoxylated octylphenol samples (Triton X-114 and Triton X-165) with EO units ranging from 1 to 25. All statistical data given in Tables III and IV are

TABLE II

REPRODUCIBILITY OF PEAK AREA PERCENTAGE FOR THE ANALYSIS OF TRITON X-102

| Peak | Peak area (%) | | | | Average (%) | S.D. (%) | R.S.D. (%) |
|---|---|---|---|---|---|---|---|
| | Run 1 | Run 2 | Run 3 | Run 4 | | | |
| 1 | 0.148 | 0.174 | 0.158 | 0.160 | 0.160 | 0.011 | 6.69 |
| 2 | 0.214 | 0.251 | 0.229 | 0.231 | 0.231 | 0.015 | 6.69 |
| 3 | 0.352 | 0.402 | 0.367 | 0.355 | 0.369 | 0.023 | 6.22 |
| 4 | 0.821 | 0.702 | 0.690 | 0.728 | 0.735 | 0.059 | 8.07 |
| 5 | 1.469 | 1.463 | 1.409 | 1.464 | 1.451 | 0.028 | 1.95 |
| 6 | 2.332 | 2.303 | 2.301 | 2.314 | 2.313 | 0.014 | 0.61 |
| 7 | 3.670 | 3.649 | 3.826 | 3.606 | 3.688 | 0.096 | 2.60 |
| 8 | 5.751 | 5.666 | 5.654 | 5.669 | 5.685 | 0.044 | 0.78 |
| 9 | 7.817 | 7.727 | 7.687 | 7.658 | 7.722 | 0.069 | 0.90 |
| 10 | 9.552 | 9.543 | 9.438 | 9.409 | 9.486 | 0.073 | 0.77 |
| 11 | 10.803 | 10.840 | 10.673 | 10.668 | 10.746 | 0.089 | 0.82 |
| 12 | 11.117 | 11.215 | 11.117 | 10.994 | 11.111 | 0.091 | 0.81 |
| 13 | 10.707 | 10.801 | 10.745 | 10.725 | 10.745 | 0.041 | 0.38 |
| 14 | 9.547 | 9.631 | 9.618 | 9.552 | 9.587 | 0.044 | 0.46 |
| 15 | 7.862 | 7.931 | 7.940 | 7.950 | 7.921 | 0.040 | 0.50 |
| 16 | 6.055 | 6.110 | 6.236 | 6.285 | 6.172 | 0.107 | 1.74 |
| 17 | 4.344 | 4.382 | 4.454 | 4.469 | 4.412 | 0.059 | 1.34 |
| 18 | 3.050 | 2.949 | 3.128 | 3.113 | 3.060 | 0.081 | 2.66 |
| 19 | 1.899 | 1.881 | 1.917 | 2.046 | 1.936 | 0.075 | 3.87 |
| 20 | 1.206 | 1.172 | 1.186 | 1.281 | 1.211 | 0.049 | 4.01 |
| 21 | 0.733 | 0.690 | 0.701 | 0.755 | 0.720 | 0.030 | 4.13 |
| 22 | 0.366 | 0.340 | 0.351 | 0.377 | 0.359 | 0.016 | 4.55 |
| 23 | 0.182 | 0.173 | 0.175 | 0.189 | 0.180 | 0.007 | 4.05 |
| Total area (counts) | 4 835 871 | 4 809 275 | 5 241 771 | 4 558 626 | 4 861 386 | 282 679 | 5.81 |
| Average EO number ($n$) | 11.67 | | | | | | |

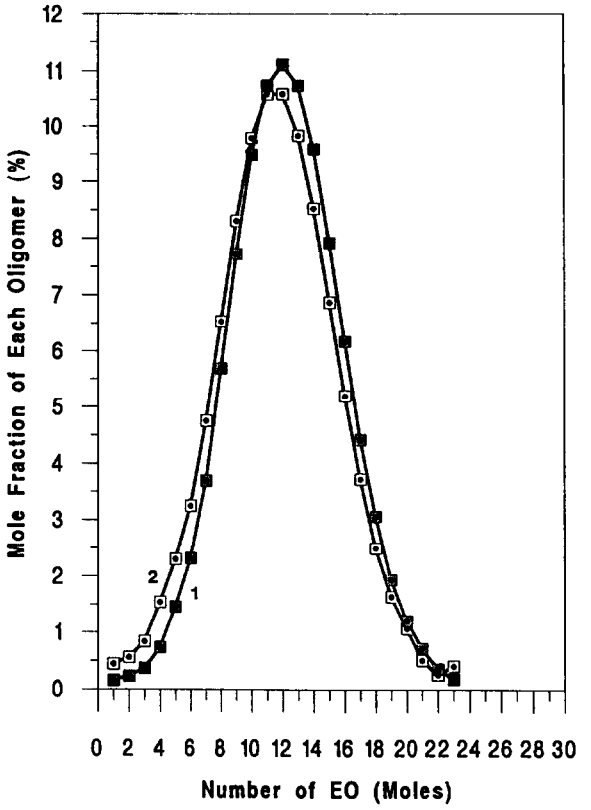


Fig. 3. Oligomer distribution curves for Triton X-102. (1) by capillary SFC; (2) by C1 reversed-phase HPLC.

obtained from four analyses for each sample. The average EO number for these six surfactants are determined to be 1.25, 3.23, 4.50, 7.63, 9.51 and 15.19, respectively. The corresponding values by HPLC measurement are 1.21, 2.99, 4.32, 7.43, 9.42 and 14.70.

Figs. 4 and 5 depict graphically the oligomer distribution as determined for samples given in Tables III and IV, respectively. For comparison purposes, Figs. 4 and 5 also present the oligomer distribution curves for Triton X-15, Triton X-35 and Triton X-45, and for Triton X-114, Triton X-100 and Triton X-165 from HPLC analyses. The Poisson distribution for samples having lower molecular masses and the Gaussian distribution for samples having higher molecular masses are obvious.

From Figs. 3 through 5, it is evident that the EO distributions obtained from SFC and from HPLC analyses are basically identical.

*Effect of temperature on separation of oligomers*

The influence of temperature on the separation of oligomers is illustrated in Fig. 6 and in Table V. In Fig. 6, chromatograms of Triton X-35 at four different temperatures (100, 110, 130 and 150°C) are shown. The pressure pro-

TABLE III

AREA PERCENTAGE AND AVERAGE EO NUMBER OF TRITON X-15, X-35 AND X-45

| Peak | Triton X-15 | | | Triton X-35 | | | Triton X-45 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Aver. area (%) | S.D. (%) | R.S.D. (%) | Aver. area (%) | S.D. (%) | R.S.D. (%) | Aver. area (%) | S.D. (%) | R.S.D. (%) |
| 1 | 76.659 | 0.759 | 0.99 | 5.304 | 0.103 | 1.94 | 0.901 | 0.012 | 1.33 |
| 2 | 21.501 | 0.659 | 3.06 | 28.921 | 0.537 | 1.86 | 11.367 | 0.139 | 1.22 |
| 3 | 1.84 | 0.17 | 9.24 | 30.089 | 0.595 | 1.98 | 21.501 | 0.300 | 1.40 |
| 4 | | | | 19.299 | 0.220 | 1.14 | 22.590 | 0.200 | 0.89 |
| 5 | | | | 9.298 | 0.464 | 4.99 | 17.262 | 0.205 | 1.19 |
| 6 | | | | 4.483 | 0.273 | 6.09 | 11.897 | 0.182 | 1.53 |
| 7 | | | | 1.681 | 0.200 | 11.90 | 7.192 | 0.094 | 1.31 |
| 8 | | | | 0.636 | 0.080 | 12.58 | 4.134 | 0.105 | 2.54 |
| 9 | | | | 0.289 | 0.025 | 8.65 | 1.927 | 0.071 | 3.68 |
| 10 | | | | | | | 0.876 | 0.031 | 3.54 |
| 11 | | | | | | | 0.354 | 0.021 | 5.93 |
| Total (%) | 100 | | | 100 | | | 100 | | |
| Average EO number | | 1.25 | | | 3.23 | | | 4.50 | |

TABLE IV

AREA PERCENTAGE AND AVERAGE EO NUMBER OF TRITON X-114 AND X-165

| Peak | Triton X-114 | | | Triton X-165 | | |
|---|---|---|---|---|---|---|
| | Aver. area (%) | S.D. (%) | R.S.D. (%) | Aver. area (%) | S.D. (%) | R.S.D. (%) |
| 1 | 0.220 | 0.008 | 3.73 | 0.242 | 0.014 | 5.79 |
| 2 | 1.100 | 0.040 | 3.64 | 0.252 | 0.010 | 3.97 |
| 3 | 4.352 | 0.052 | 1.19 | 0.224 | 0.010 | 4.46 |
| 4 | 8.281 | 0.058 | 0.70 | 0.255 | 0.011 | 4.31 |
| 5 | 11.157 | 0.059 | 0.53 | 0.358 | 0.019 | 5.31 |
| 6 | 12.375 | 0.030 | 0.24 | 0.493 | 0.011 | 2.23 |
| 7 | 13.254 | 0.268 | 2.02 | 0.783 | 0.032 | 4.09 |
| 8 | 12.956 | 0.063 | 0.49 | 1.479 | 0.058 | 3.92 |
| 9 | 11.223 | 0.056 | 0.50 | 2.552 | 0.044 | 1.72 |
| 10 | 8.858 | 0.058 | 0.65 | 3.956 | 0.026 | 0.66 |
| 11 | 6.406 | 0.026 | 0.41 | 5.607 | 0.021 | 0.37 |
| 12 | 4.283 | 0.016 | 0.37 | 7.351 | 0.041 | 0.56 |
| 13 | 2.670 | 0.033 | 1.24 | 8.866 | 0.032 | 0.36 |
| 14 | 1.548 | 0.037 | 2.39 | 10.128 | 0.087 | 0.86 |
| 15 | 0.880 | 0.021 | 2.39 | 10.680 | 0.037 | 0.35 |
| 16 | 0.439 | 0.010 | 2.28 | 10.074 | 0.015 | 0.15 |
| 17 | | | | 9.102 | 0.038 | 0.42 |
| 18 | | | | 7.973 | 0.042 | 0.53 |
| 19 | | | | 6.134 | 0.077 | 1.26 |
| 20 | | | | 4.797 | 0.034 | 0.71 |
| 21 | | | | 3.320 | 0.060 | 1.81 |
| 22 | | | | 2.261 | 0.054 | 2.39 |
| 23 | | | | 1.678 | 0.046 | 2.74 |
| 24 | | | | 0.919 | 0.020 | 2.18 |
| 25 | | | | 0.518 | 0.012 | 2.32 |
| Total (%) | 100 | | | 100 | | |
| Average EO number | | 7.63 | | | 15.19 | |

gram was the same for all cases: 2 min at 2000 p.s.i., then a linear pressure ramp up to 5000 p.s.i. in 28 min, and then 5 min with pressure downward to 2000 p.s.i. The last peak was EO (9) octylphenol and eluted at 14.6, 15.2, 16.4 and 17.0 min for the four different temperatures, respectively.

Some peak splitting was observed in Fig. 6. The lower the temperature, the more pronounced the peak splitting. When temperature was increased to 150°C, no peak splitting was observed for those relatively low-molecular-mass ethoxy adducts.

Table V lists the retention times for the solvent and nine oligomers at four different temperatures. Table V shows that at lower temperature, a longer time was needed for the elution of the first oligomer and a shorter time, however, was needed for complete elution of all components.

Work has been reported on the theoretical aspects involved with temperature effects on the separation of compounds [33]. A combination of factors is responsible for the poor performance at relatively low temperature. First, a better separation of the lower-molecular-mass components can be achieved with GC-like conditions. This means that at the same pressure and at a higher temperature, the density of the mobile phase is lower and that the chromatographic conditions are more like those of GC, which leads to a more rapid diffusion and a higher efficiency. Secondly, lower temperature is unfavourable to mass transfer, as discussed by Novotny *et al.* [34] in a paper about the tempera-

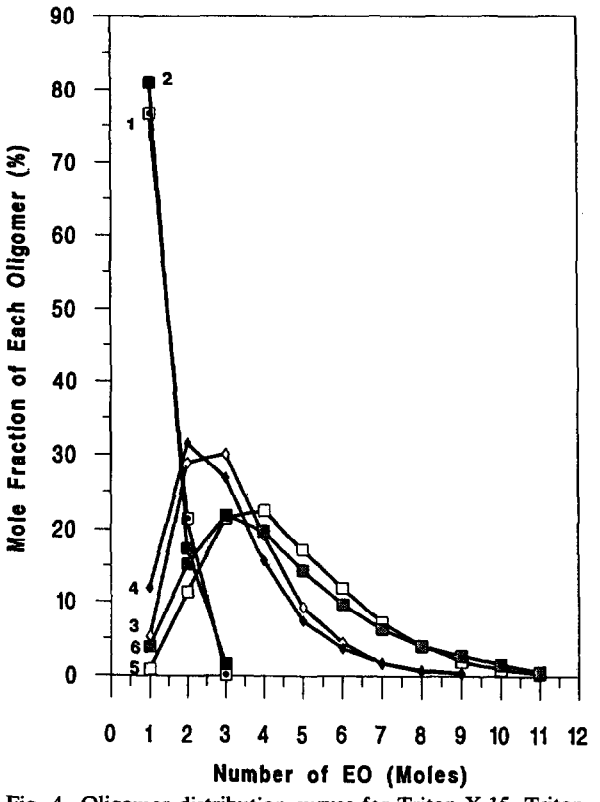


Fig. 4. Oligomer distribution curves for Triton X-15, Triton X-35 and Triton X-45. Triton X-15: (1) by capillary SFC; (2) by C1 reversed-phase HPLC. Triton X-35: (3) by capillary SFC; (4) by C1 reversed-phase HPLC. Triton X-45: (5) by capillary SFC; (6) by C1 reversed-phase HPLC.

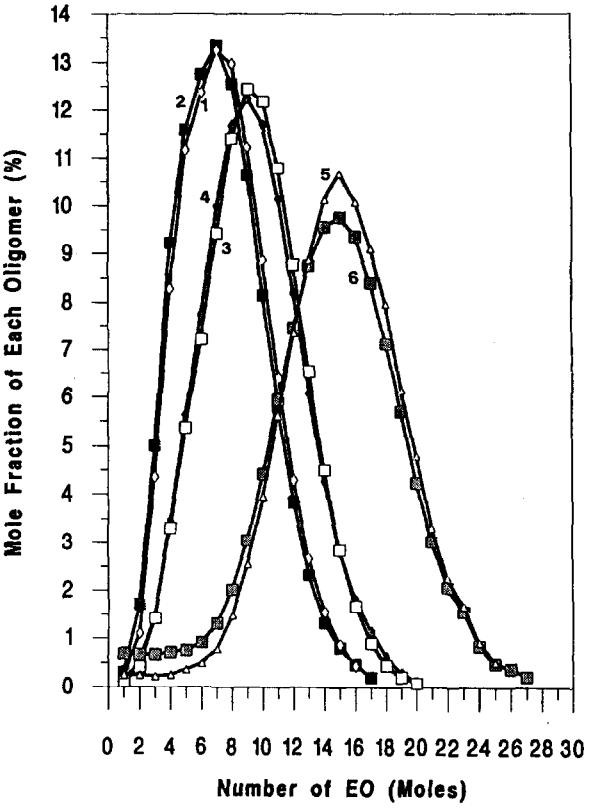


Fig. 5. Oligomer distribution curve for Triton X-114, Triton X-100 and Triton X-165. Triton X-114: (1) by capillary SFC; (2) by C1 reversed-phase HPLC. Triton X-100: (3) by capillary SFC; (4) by C1 reversed-phase HPLC. Triton X-165: (5) by capillary SFC; (6) by C1 reversed-phase HPLC.

ture effect in SFC and by Schwartz *et al.* [35] in work on simulated distillation of high-boiling petroleum fractions by capillary SFC. Finally, a lower temperature results in a decrease in solubility for the non-volatile surfactant oligomers. Chromatographically, this brings about a decrease in peak heights and areas. Consequently, better resolution and higher sensitivity can be obtained at higher temperature (*e.g.* 150°C for Triton X-35). However, it must be noted that the optimum temperature for different samples is not the same. For the Triton family of surfactants, a lower temperature is preferred for samples containing relatively high-molecular-mass oligomers. Studies showed that 150°C was the optimal temperature for the separation of Triton X-15, Triton X-35, and Triton X-45, whereas 100°C was optimum for Triton X-114, Triton X-100, Triton X-102, and Triton X-165.

Temperature programming was investigated in combination with pressure programming in order to enhance the performance of longer-chain surfactant analysis. Fig. 7 shows the chromatogram of Triton X-165 using a simultaneous temperature-decreasing programming (5 min initial hold at 100°C, then to 88°C in 30 min at −0.4°C/min, and then 10 min for 88°C hold time) and pressure-increasing programming. Improved peak shape, better resolution and shorter analysis time for complete elution is achieved, compared with the chromatograms using varying simultaneous temperature-increasing and pres-

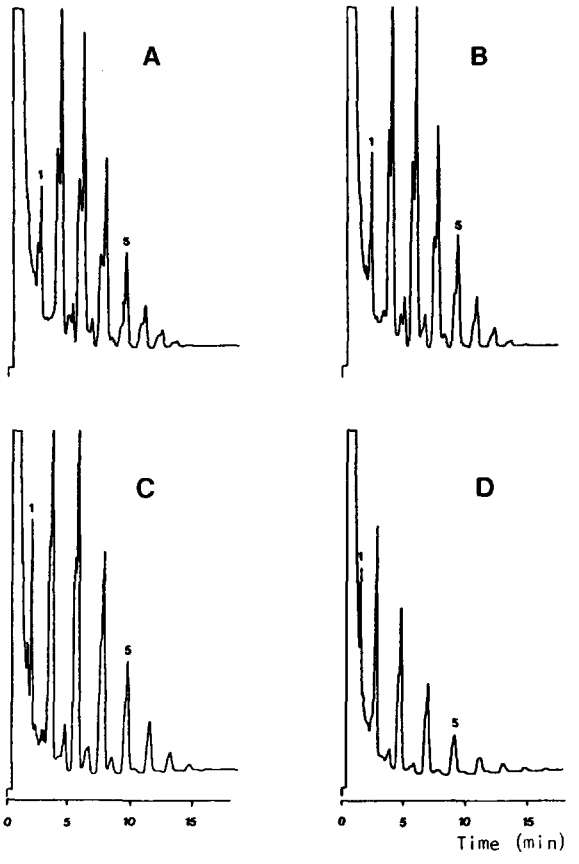


Fig. 6. Effect of temperature on the SFC separation of Triton X-35 oligomers. A, B, and C: isothermally at 100°, 110° and 130°C, respectively, and concentration of Triton X-35, 2.5 mg/ml. D: isothermally at 150°C; 1.0 mg/ml. Other conditions same as in Fig. 1.

sure-increasing programmings. This may be mainly because simultaneous temperature decrease and pressure increase lead to greater increase in fluid density and solvating power, resulting in an increased solubility of higher-molecular-mass components of Triton X-165 in the supercritical fluid.

It has been noticed that the data obtained from studying the influence of temperature on the separation of Triton surfactant oligomers are contrary to data already published by Later *et al.* [36] and Knowles *et al.* [26]. Their data show that enhanced resolution for some other polymers was obtained using a combination of positive temperature and pressure or density programming. More studies need to be done to find out the reasons for the discrepancies between these data.

TABLE V

EFFECT OF TEMPERATURE ON THE SEPARATION OF TRITON X-35 OLIGOMERS

| Peak No. | Retention time (min) | | | |
|---|---|---|---|---|
| | 100°C | 110°C | 130°C | 150°C |
| Solvent | 0.558 | 0.545 | 0.525 | 0.510 |
| 1 | 2.41 | 2.27 | | |
| | 2.66 | 2.44 | 1.99 | 1.61 |
| 2 | 3.98 | 3.89 | 3.46 | |
| | 4.38 | 4.21 | 3.69 | 2.98 |
| 3 | 5.74 | 5.80 | 5.54 | |
| | 6.19 | 6.17 | 5.81 | 5.02 |
| 4 | 7.51 | 7.60 | | |
| | 7.96 | 7.95 | 7.88 | 7.27 |
| 5 | 9.25 | 9.31 | | |
| | 9.63 | 9.61 | 9.85 | 9.53 |
| 6 | 10.82 | | | |
| | 11.16 | 11.14 | 11.66 | 11.56 |
| 7 | 12.24 | | | |
| | 12.57 | 12.58 | 13.39 | 13.50 |
| 8 | 13.52 | 13.94 | 14.94 | 15.30 |
| 9 | 14.62 | 15.24 | 16.44 | 17.00 |

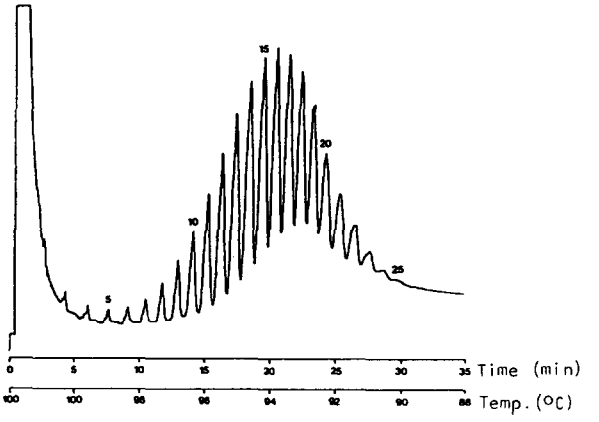


Fig. 7. Capillary SFC chromatogram of Triton X-165 (10.0 mg/ml) using a simultaneous linear pressure/temperature program. Linear pressure program from 2000 p.s.i. (2 min initial hold) to 5500 p.s.i. in 33 min; linear temperature programmed simultaneously from 100°C (5 min initial hold) to 88°C at −0.4°C/min. Other conditions are the same as in Fig. 1.

*Effect of solvent on separation of oligomers*

Two solvents —methanol and dichloromethane— were used to prepare solutions of polyethoxylated octylphenol samples. All samples tested can readily be dissolved in these two solvents. It is interesting to note that the chromatograms obtained from solutions which were made from the same surfactant at the same concentration, but with different solvents, are quite different. Fig. 8 shows the typical chromatograms of Triton X-114 under identical SFC conditions.

There are three differences between Fig. 8A and B: (1) the baseline of Triton X-114 in methanol is much better, and all components are completely resolved to the baseline. (2) The peak profiles in Fig. 8A are much better, the peak width is smaller and the sensitivity is higher. (3) The elution time is different. For the methanol solution, it ranges between 3.89 to 21.96 min, whereas it ranges from 4.60 to 22.57 min for dichloromethane solution.

The non-aqueous surfactant solution is a very complex system [37]. The microstructure of surfactant micelle may be different in different solvents with different physical and chemical properties (for example, the boiling point and the Hildebrand solubility parameter of methanol are 64°C and 14.4, and 40°C and 9.7 for dichloromethane, respectively), which could result in different chromatographic behaviour. Another possible reason for such phenomena may be that the diffusion of the analyte varies with the solvents used. Prior to injection, all components are equally dissolved in solvents. However, right after injection, a much faster evaporation of the dichloromethane at the top of capillary column, combined to a constant transfer rate onto the column, lead to an analyte concentration gradient, resulting in wider peaks and incomplete resolution of the oligomers.

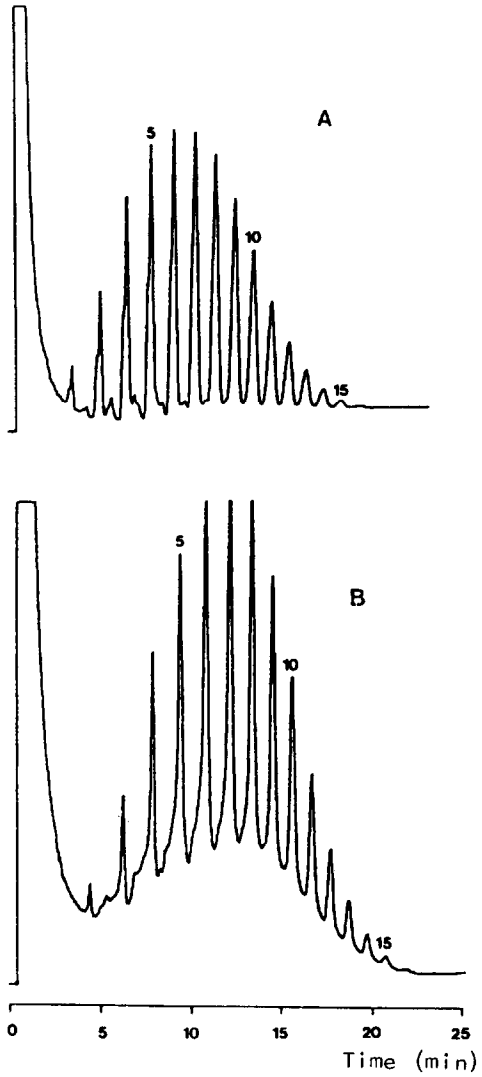


Fig. 8. Effect of solvent on the SFC separation of Triton X-114 (5.0 mg/ml) oligomers under identical SFC conditions as Fig. 1. The upper trace, chromatogram of Triton X-114 methanol solution, integrator attentuation at 2; the lower trace, chromatogram of Triton X-114 dichloromethane solution, integrator attentuation at 1.

*Effect of pressure programming ramp rate*

In order to optimize the SFC condition, the analyst must use conditions which maximize diffusion of analytes into the mobile phase. The most important parameters which affect analyte diffusion are temperature and pressure. When the analysis is performed isothermally at 100°C, the retention and resolution will strongly depend on the pressure programs used. Fig. 9 shows the chromatogram of Triton X-102 in 0–35 min using the chromatographic conditions identical to those used in Fig. 1 except for using a low-pressure programming ramp rate —starting from

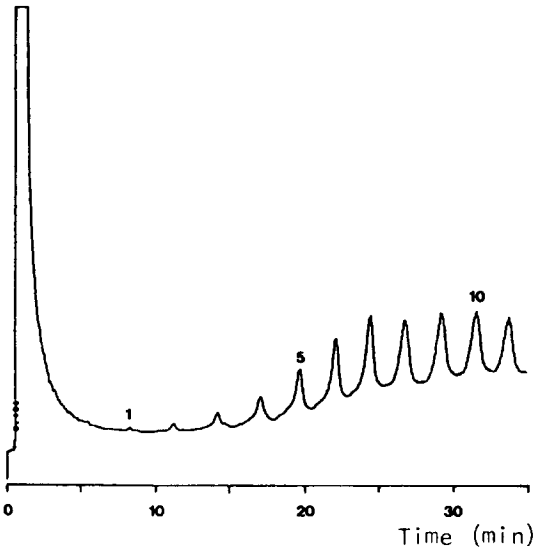


Fig. 9. Capillary SFC chromatogram of Triton X-102 using identical conditions as Fig. 1 but approximately half that of the pressure program ramp used in Fig. 1 (pressure ramp rate starting from 2000 p.s.i. and 2 min initial hold, and then linear pressure ramp to 5000 p.s.i in 58 min, instead of 33 min).

2000 p.s.i. pressure with 2 min hold, then applying a linear pressure ramp to 5000 p.s.i. in 58 min, approximately one-half of the pressure ramp rate used for data presented in Fig. 1.

The most striking difference observed between Figs. 1 and 9 is that using the low-pressure ramp rate programming, the highest oligomer eluted in 35 min was the one with EO number = 11, and in contrast, the highest oligomer using the high-pressure ramp rate programming was the one with EO number = 23. In addition, the peaks were largely broadened, the sensitivity was much decreased, and the first two oligomers in the early part of the chromatogram were barely distinguished from the baseline, which can be clearly seen from Fig. 9. In general, if optimal resolution is achieved, the higher pressure programming rate would be preferred so as to shorten the analysis time and to increase the analysis sensitivity.

## CONCLUSIONS

In this paper, a method for the analysis of non-ionic surfactant polyethoxylated octylphenols using capillary supercritical fluid chromatography has been described. The validity of the capillary SFC methods was examined and demonstrated by comparing the SFC results with corresponding data obtained from HPLC analysis. The advantage of the HPLC method is its simplicity because all oligomers of polyethoxylated alkylphenols have nearly equal molar absorptivities, and therefore the response factor of all oligomers can be considered equal. However, its applicability is limited to the compounds containing UV-absorbing chromophores. Compared with GC, the capillary SFC–FID system operates at a relatively low temperature. It provides another effective, convenient and economic means for the analysis of non-ionic surfactants. It is expected that reasonable results may be obtained for the analysis of more complex and higher molecular-mass surfactant oligomers and components using supercritical fluid chromatography coupled with a universal detection method such as FID.

## REFERENCES

1 P.L. Layman, *Chem. Eng. News*, January (1984) 17.
2 P.L. Layman, *Chem. Eng. News*, January (1986) 21.
3 H.G. Nadeau, D.M. Oaks, Jr., W.A. Nichols and L.P. Carr, *Anal. Chem.*, 36 (1964) 1914.
4 F.J. Ludwig, Sr., *Anal. Chem.*, 40 (1968) 1620.
5 L. Gildenberg, and J.R. Trowbridge, *J. Am. Oil Chem. Soc.*, 42 (1965) 69.
6 S.R. Lipsky and M. L. Duffy, *LC·GC*, 4 (1986) 898.
7 P. Sandra, F. David, F. Munari, G. Mapelli and S. Trestianu, in R.M. Smith (Editor), *Supercritical Fluid Chromatography*, The Royal Society of Chemistry, London, 1988, p. 153.
8 E. Stephanou, *Chemosphere*, 13 (1984) 43.
9 E. Stephanou, *Int. J. Environ. Anal. Chem.*, 27 (1985) 41.
10 P. Rudewicz and B. Munson, *Anal. Chem.*, 58 (1986) 674.
11 F.P.B. Van der Maeden, M.E.F. Biemond and P.C.G.M. Janssen, *J. Chromatogr.*, 149 (1978) 539.
12 M.S. Holt, E.H. McKerrell, J. Perry and R.J. Watkinson, *J. Chromatogr.*, 362 (1986) 419.
13 J.A. Pilc and P.A. Sermon, *J. Chromatogr.*, 398 (1987) 375.
14 *Separating Homologs and Polymers by HPLC, HPLC Bulletin 796D*, Supelco, Bellefonte, PA, 1988.
15 M.C. Allen and D.E. Linder, *J. Am. Oil Chem. Soc.*, 58 (1981) 950.

16 J.F.K. Huber, F.F.M. Kolder and J.M. Miller, *Anal. Chem.*, 44 (1972) 105.
17 A. Marcomini and W. Giger, *Anal. Chem.*, 59 (1987) 1709.
18 A. Marcomini, S. Capri and W. Giger, *J. Chromatogr.*, 403 (1987) 243.
19 M. Ahel and W. Giger, *Anal. Chem.*, 57 (1985) 1577.
20 M. Ahel and W. Giger, *Anal. Chem.*, 57 (1985) 2584.
21 C.F. Allen and L.I. Rice, *J. Chromatogr.*, 110 (1975) 151.
22 Z. Wang and M. Fingas, *J. Chromatogr.*, 637 (1993) 145.
23 P.R. Geissler, *J. Am. Oil Chem. Soc.*, 66 (1989) 685.
24 A.E. Johnson, Jr., P.R. Geissler and L.D. Tally, *J. Am. Oil Chem. Soc.*, 67 (1990) 123.
25 *SFC Columns & Accessories*, Lee Scientific, 1991.
26 D.E. Knowles, L. Nixon, E.R. Campbell, D.W. Later and B.E. Richter, *Fresenius' Z. Anal. Chem.*, 330 (1988) 225.
27 B.E. Richter, D.E. Knowles, M.R. Andersen, N.L. Porter, E.R. Campbell and D.W. Later, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 29.
28 A.H. Silver and H.T. Kalinoski, *J. Am. Oil Chem. Soc.*, 69 (1992) 599.
29 J.T. Scanlon and D.E. Willis, *J. Chromatogr. Sci.*, 23 (1985) 333.
30 R.G. Ackman, *J. Gas Chromatogr.*, 6 (1968) 497.
31 R.G. Ackman, *J. Gas Chromatogr.*, 2 (1964) 173.
32 J.C. Sternberg, W.S. Gallaway and D.T.L. Jones, in N. Brenner, J.E. Callen and M.D. Weiss (Editors), *Gas Chromatography*, Academic Press, New York, 1962, Ch. XVIII.
33 D. Leyendecker, in R.M. Smith (Editor), *Supercritical Fluid Chromatography*, The Royal Society of Chemistry, London, 1988, Ch. 3.
34 M. Novotny, W. Bertsch and A. Zlatkis, *J. Chromatogr.*, 61 (1971) 17.
35 H.E. Schwartz, R.G. Brownlee, M.M. Boduszynski and Fu Su, *Anal. Chem.*, 59 (1987) 1393.
36 D.W. Later, E.R. Campbell and B.E. Richter, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 65.
37 K.L. Mittal (Editor), *Solution Chemistry of Surfactants*, Vols. 1 and 2, Plenum Press, New York, 1979.