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GAS CHROMATOGRAPHIC AND MASS SPECTROMETRIC ANALYSIS OF A COMMERCIAL MIXTURE OF PHENYLALKANES (DETERGENT ALKYLATES)

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SUMMARY

Commercial phenylalkanes with a linear alkyl chain (C_9–C_{13}) were analyzed by gas chromatography and mass spectrometry. For the group separation of phenylalkanes from dialkylindanes and dialkyltetralins, liquid chromatography on silica gel was applied. All isomeric phenylalkanes could be separated or distinguished by gas chromatography on a capillary column coated with OV-101. The quantitative analysis of phenylalkanes was considerably influenced by dialkylindanes and dialkyltetralins present in the mixture being analyzed. The quantitative analysis of phenylalkanes, dialkylindanes and dialkyltetralins was verified by mass spectrometry using the molecular ion method.

INTRODUCTION

Phenylalkanes with a linear alkyl chain (C_9–C_{13}) (hereafter referred to as phenylalkanes) are important intermediates in the production of detergents, the biodegradability and other important characteristics of which depend on the structures of the alkyl chains[1]. The quality of the final product may also depend on the content of dialkylindanes and dialkyltetralins in detergent alkylates[2].

Commercial phenylalkanes are most often analyzed by gas chromatography, (GC) but it has been found that the resolving power of packed columns[3–7] is insufficient to separate all possible isomers. Difficulties have also been encountered on capillary columns[8–11] when 5- and 6-phenylalkanes had to be distinguished, and at present time 6- and 7-phenylalkanes cannot be separated. The best results were obtained using the silicone phase DC-550 (ref. 11). Gel chromatography[12] has also been used for the analysis of dialkylindanes and dialkyltetralins in detergent alkylates.

The identification, fragmentation and quantitative analysis of phenylalkanes have been studied by mass spectrometry (MS)[13–20]. Several commercial phenylalkanes have been analyzed by Ötvös *et al.*[8] using combined GC–MS.

The aim of this work was to study the problems that occur in the analysis of commercial phenylalkanes that have a high content of dialkylindanes and dialkyltetralins by GC–MS.

EXPERIMENTAL

Gas chromatography

The instrument used was a Fractovap Model 2300 gas chromatograph (Carlo Erba, Milan, Italy) equipped with a flame ionization detector (FID) and a stream splitter. Elution times and peak areas were measured with a digital Autolab integrator. The operating conditions are given in Table I.

TABLE I
OPERATING CONDITIONS

Conditions	*Stationary phase*	
	OV-101	*DEGS*
Column	Glass capillary	Stainless steel
Length (m)	50	90
Internal diameter (mm)	0.25	0.25
Column temperature (°K)	453	433
Carrier gas flow-rate (ml/min)	0.50	0.45
Injection block temperature (°K)	473	473
Splitting ratio	1/100	1/100
Carrier gas	N_2	N_2
Attenuation (A)	$8 \cdot 10^{-11}$	$8 \cdot 10^{-11}$

The elution dead time was determined with methane. Phenylalkanes were analyzed using 1-phenyltridecane as the internal standard. A capillary column coated with DEGS, was obtained from Perkin-Elmer (Norwalk, Conn., U.S.A.) (its efficiency for 2-phenyltridecane was 205,000 theoretical plates with a capacity ratio $k = 6.70$). A capillary column coated with OV-101 was obtained from the Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, Brno, Czechoslovakia (its efficiency for 2-phenyltridecane was 82,000 theoretical plates with a capacity ratio $k = 3.10$).

Liquid chromatography

Liquid chromatography on silica gel was used for the separation of dialkylindanes and dialkyltetralins from phenylalkanes. The sample of the commercial mixture (10 g) was chromatographed on a column (110 × 2 cm I.D.) of 0.05–0.1 mm silica gel PHH (Lachema, Brno, Czechoslovakia) which was activated at 150°C. Elution was carried out successively with *n*-hexane (300 ml), benzene (50 ml) and ethanol (20 ml). Fractions (20 ml) were collected and analyzed by GC–MS, GC on a capillary column and separately by MS. Mixed fractions were combined and re-chromatographed. Finally, a fraction (1.4 g) of dialkylindanes and dialkyltetralins free of phenylalkanes was obtained. Fractions of phenylalkanes (7 g) contained 2–5% of dialkylindanes and dialkyltetralins. The content of dialkylindanes and dialkyltetralins in other fractions was more than 15%, as shown by MS.

Gas–liquid chromatography–mass spectrometry

The presence of phenylalkanes and some dialkylindanes in the commercial mixture of phenylalkanes was determined using a Varian-MAT 111 instrument

equipped with a stainless-steel column (3 m × 2 mm I.D.) packed with 3% SE-30 on Chromosorb WHP (60–80 mesh), with temperature programming at 4°/min from 383 to 483 °K. Helium (15 ml/min) was used as the carrier gas. The mass spectra were measured at 80 eV at an ionizing current of 270 μA with an ion source temperature of 473 °K.

Mass spectrometry

For the quantitative analysis of the commercial mixture of phenylalkanes, an MS 902 S instrument (AEI, Manchester, Great Britain) equipped with an all-glass heated inlet system (473 °K) was used. The spectra were recorded at 8 eV at a trap current of 10 μA with an ionizing chamber temperature of 423 °K.

RESULTS AND DISCUSSION

Qualitative analysis

Although GC–MS analysis was carried out using a packed column that was incapable of separating all of the isomeric phenylalkanes, the identification of these substances could be successfully accomplished by taking the mass spectra of overlapping peaks. Phenylalkanes are known to give characteristic spectra from which their structures can be deduced[17]. As examples, the spectra of 3-phenyldecane (Fig. 1), 2-phenylundecane (Fig. 2) and 4-phenyldodecane (Fig. 3) are shown.

The presence of all isomeric phenylalkanes (except the 1-phenylalkanes, which are not present in detergent alkylates), was also determined by capillary GC. The separation of the commercial mixture of phenylalkanes at 453 °K on a capillary column coated with OV-101 is shown in Fig. 4. Although high-efficiency capillary chromatography was applied, some difficulties were encountered in the separation of 5- and 6-phenylundecanes and 6- and 7-phenyltridecanes. The identification of the peaks was based on GC–MS analysis, the known[21] elution indices and the recently published[22] results of the analysis of C_9–C_{14} secondary alcohols. The chromatogram of the fraction obtained by liquid chromatography (phenylalkanes containing 4% of dialkylindanes and dialkyltetralins) is shown in Fig. 5. A capillary column coated with OV-101 operating at 458 °K was used in this analysis. The retention times, separation factors, Kováts retention indices for phenylalkanes under these conditions and the structural increments of the phenyl group are given in Table II. It follows from the separation factors (α) that the separating power of packed columns is adequate for the separation of the isomeric 2-, 3- and 4-phenylalkanes. In order to separate 4- and 5-phenylalkanes, highly efficient packed columns are necessary. The isomeric 5- and 6-phenylalkanes are virtually inseparable on packed columns. As the number of carbon atoms in the alkyl chain of 5- and 6-phenylalkanes increases, their separation improves (α increases from 1.005 for 5- and 6-phenylundecanes to 1.03 for 5- and 6-phenyltridecanes). In order to separate 6- and 7-phenylalkanes, an extremely efficient capillary column must be used.

The Kováts retention indices were measured with a reprodicibility of $\pm$ 1 index unit. The structural increments were calculated according to the equation $H = I - I_H$, where I is the Kováts retention index of the phenylalkane and I_H is the Kováts retention index of the *n*-alkane that has the same number of carbon atoms as are present in the alkyl chain of the phenylalkane. The increment corresponding to the

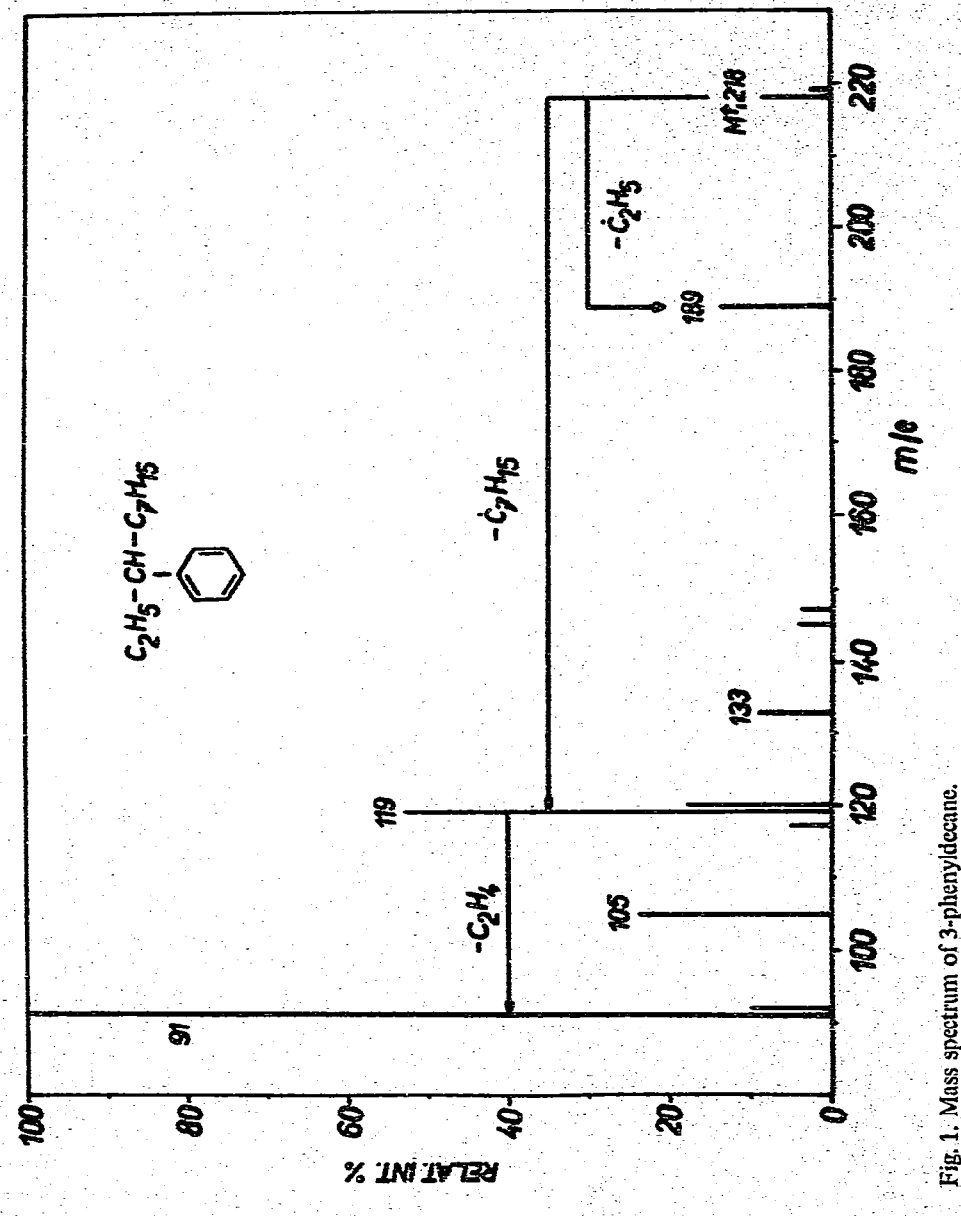

Fig. 1. Mass spectrum of 3-phenyldecane.

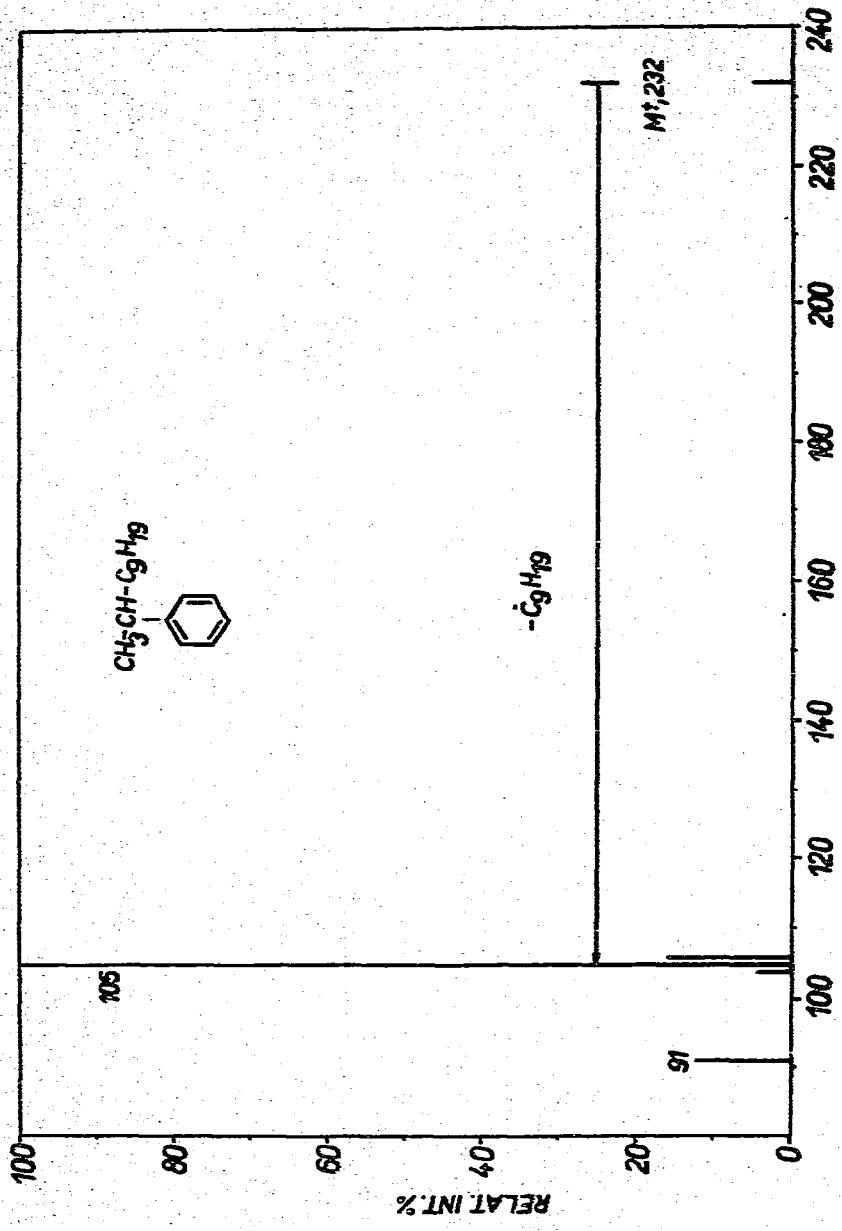

Fig. 2. Mass spectrum of 2-phenylundecane.

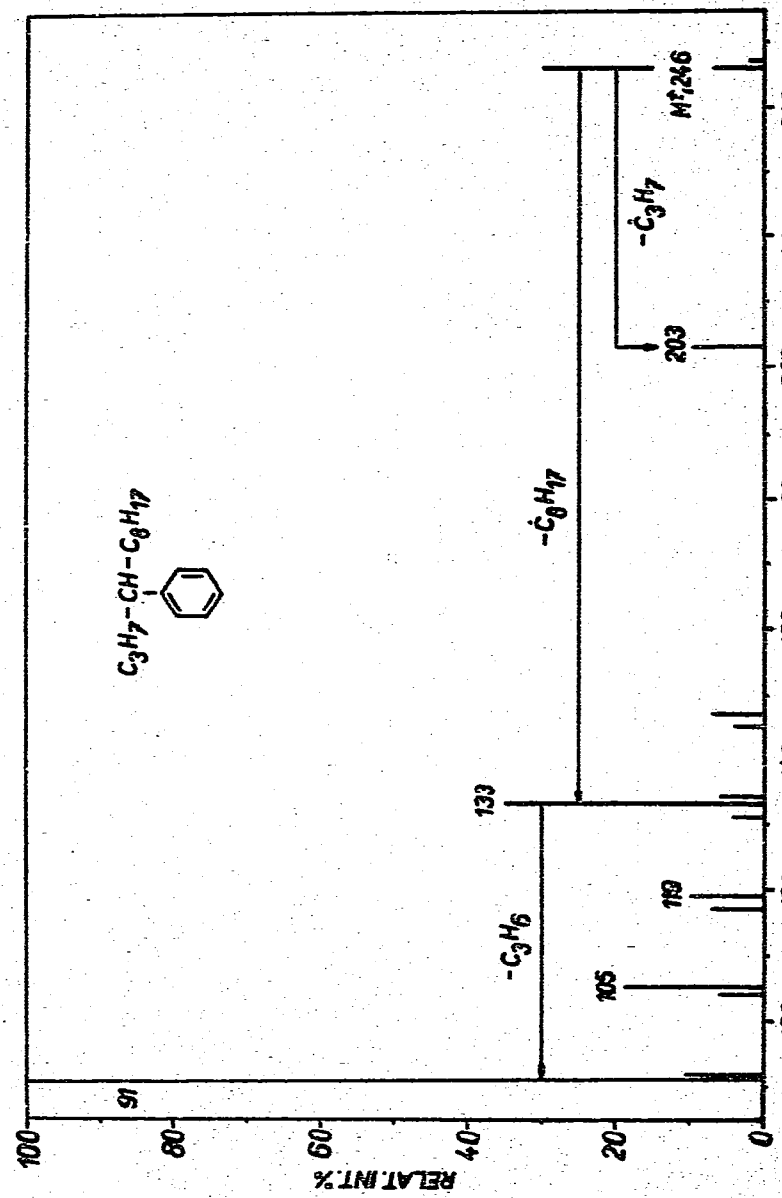

Fig. 3. Mass spectrum of 4-phenyldodecane.

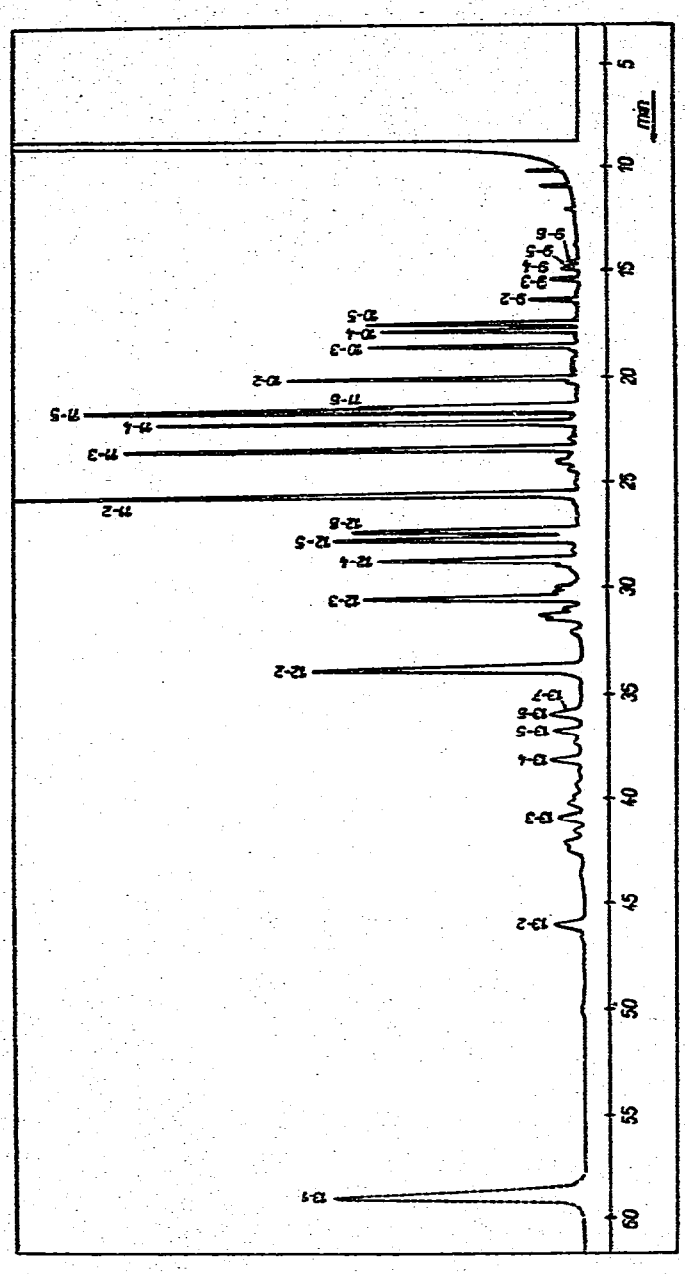

Fig. 4. Separation of the commercial mixture of phenylalkanes at 453 °K on a capillary column coated with OV-101. Peaks; the first numeral indicates the number of carbon atoms in the linear alkyl chain and the second numeral the position of the phenyl group on the chain. Broken peak 13-1 is the internal standard.

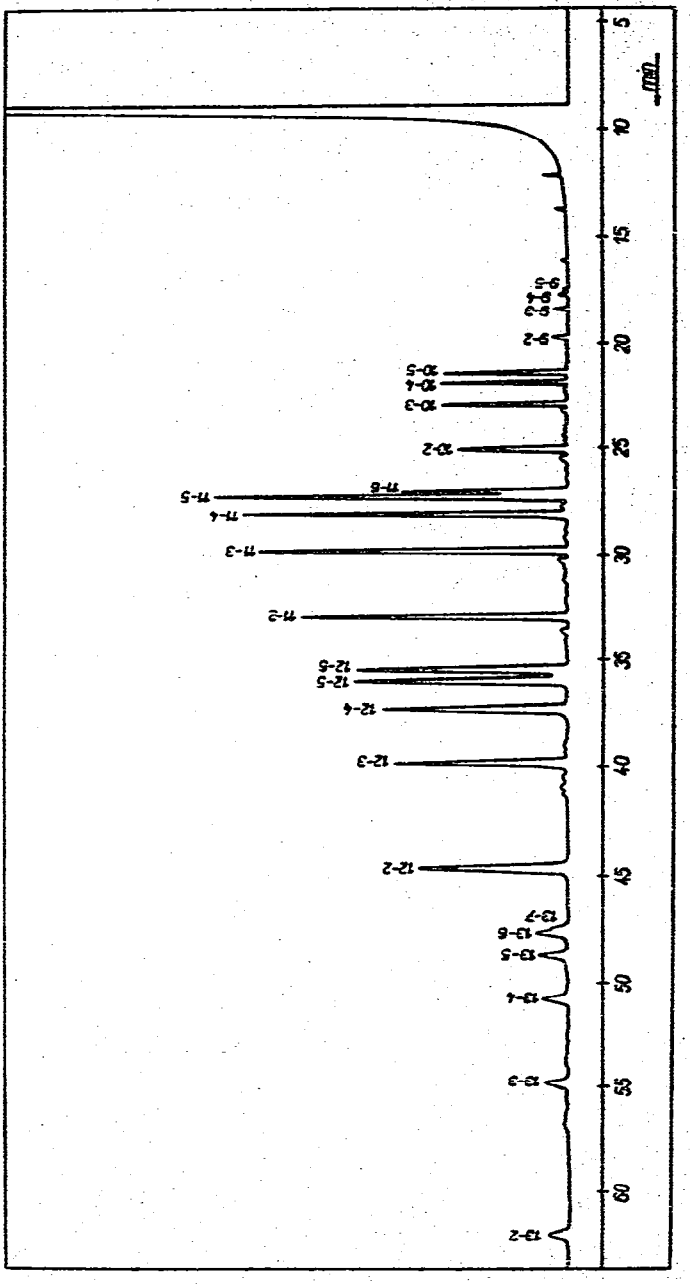

Fig. 5. Separation of the phenylalkane fraction at 458 °K on a capillary column coated with OV-101. Peak notation as in Fig. 4.

TABLE II

RETENTION TIMES (t'_R), SEPARATION FACTORS (α), KOVÁTS RETENTION INDICES (I) AND STRUCTURAL INCREMENTS OF THE PEHNYL GROUP (H) FOUND FOR PHENYLALKANES ON OV-101 AT 458 °K

$t'_R = t_R - t_M$; $\alpha = t'_{R,2}/t'_{R,1}$; $H = I - I_H$; $I_H = 100z$, where I = Kováts retention index, I_H = Kováts retention index for the linear alkyl chain and z = number of carbon atoms in the linear alkyl chain.

Compound	t'_R *(sec)*	α	I	H
5-Phenylnonane	512		1437	537
		1.03		
4-	526		1443	544
		1.08		
3-	566		1460	560
		1.14		
2-	644		1492	592
5-Phenyldecane	745		1528	528
		1.04		
4-	774		1538	538
		1.09		
3-	841		1560	560
		1.15		
2-	966		1595	595
6-Phenylundecane	1090		1625	525
		1.005		
5-	1094		1628	528
		1.05		
4-	1053		1638	538
		1.09		
3-	1251		1659	559
		1.16		
2-	1449		1696	596
6-Phenyldodecane	1596		1718	518
		1.01		
5-	1616		1722	522
		1.05		
4-	1699		1734	534
		1.10		
3-	1866		1758	558
		1.16		
2-	2157		1797	597
7-Phenyltridecane	2318		1818	518
		1.007		
6-	2336		1819	519
		1.03		
5-	2403		1825	525
		1.05		
4-	2519		1838	538
		1.10		
3-	2771		1866	566
		1.16		
2-	3204		1906	606

phenyl group and to its location in the alkyl chain is given by H. The value of H decreases with the shift of the phenyl group to the middle of the alkyl chain and for a given location in the alkyl chain it increases as the number of carbon atoms increases. For instance, H for the 2-phenylalkanes, from 2-phenylnonane to 2-phenyltridecane increases from 592 to 606.

Although the use of capillary columns coated with polar stationary phases results in improved separations of 5- and 6-phenylalkanes, owing to solvent–solvent polar interactions, 2-phenylalkanes are eluted together with those which have an alkyl chain that is one carbon atom longer. An example is shown in Fig. 6, where the separation of a mixture of phenylalkanes on a capillary column coated with DEGS at 436 °K is illustrated. It can be seen that 2-phenylalkanes are eluted close to the 4-phenylalkanes that have an alkyl chain that is one carbon atom longer.

The dialkylindane–dialkyltetralin mixtures were analyzed by combined GC–MS and capillary chromatography. Interpretation of the spectra confirmed the presence of 1-ethyl-3-pentylindane, 1-ethyl-3-hexylindane and 1-ethyl-3-heptylindane

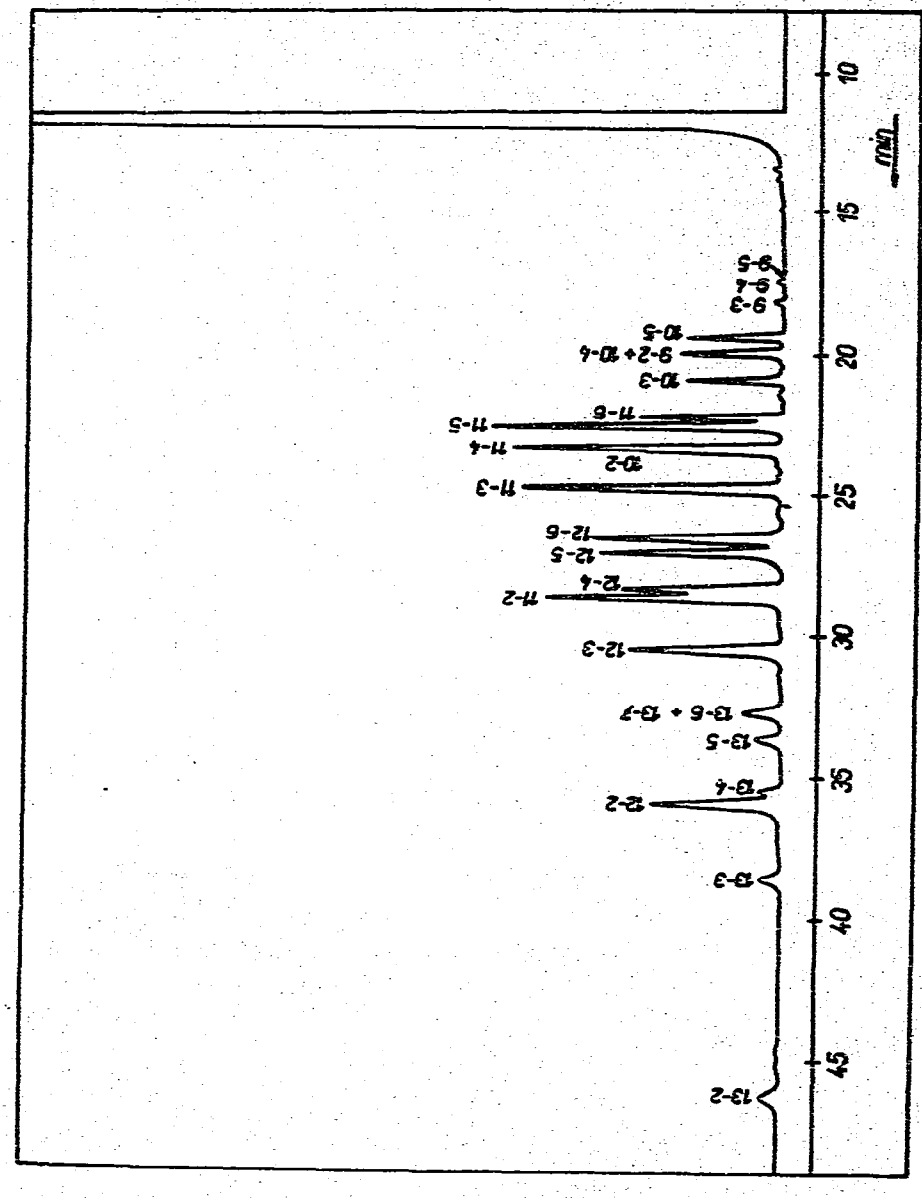

Fig. 6. Separation of the phenylalkane fraction at 436 °K on a capillary column coated with DEGS. Peak notation as in Fig. 4.

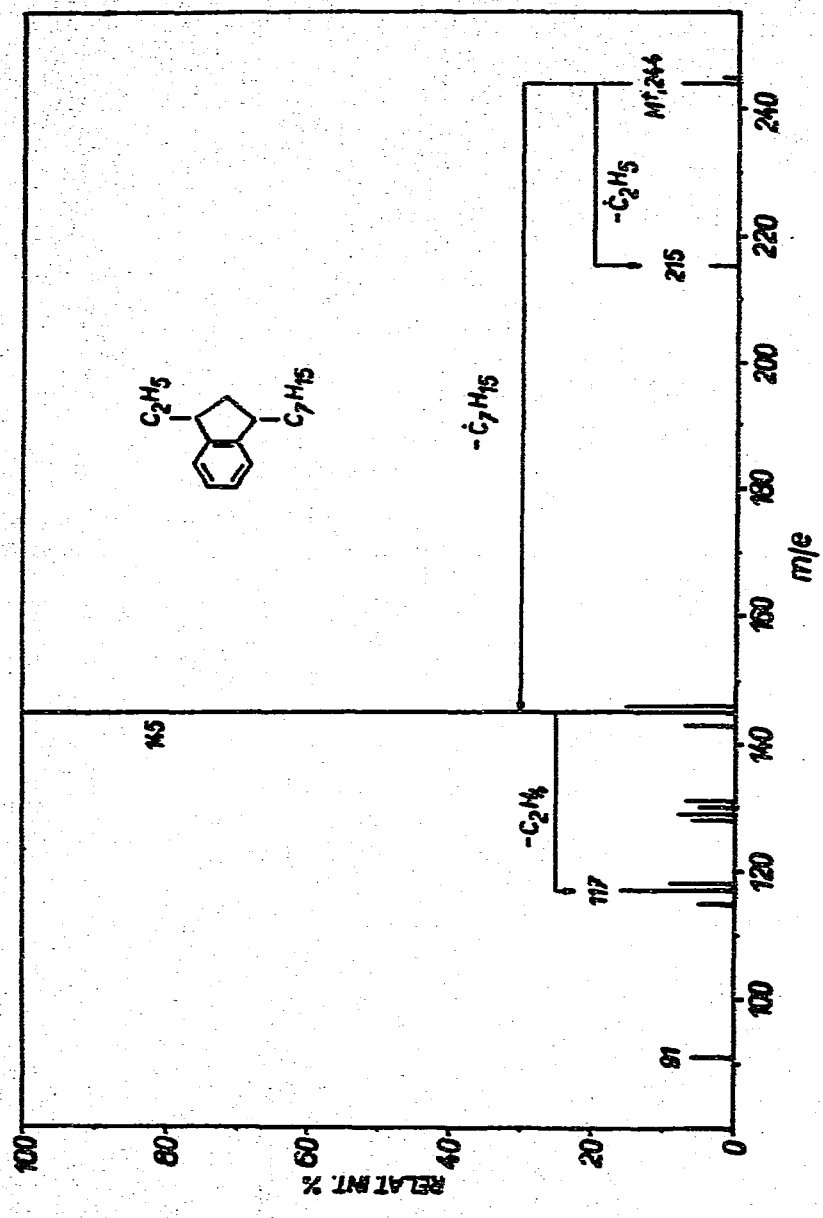

Fig. 7. Mass spectrum of 1-ethyl-3-heptylindane.

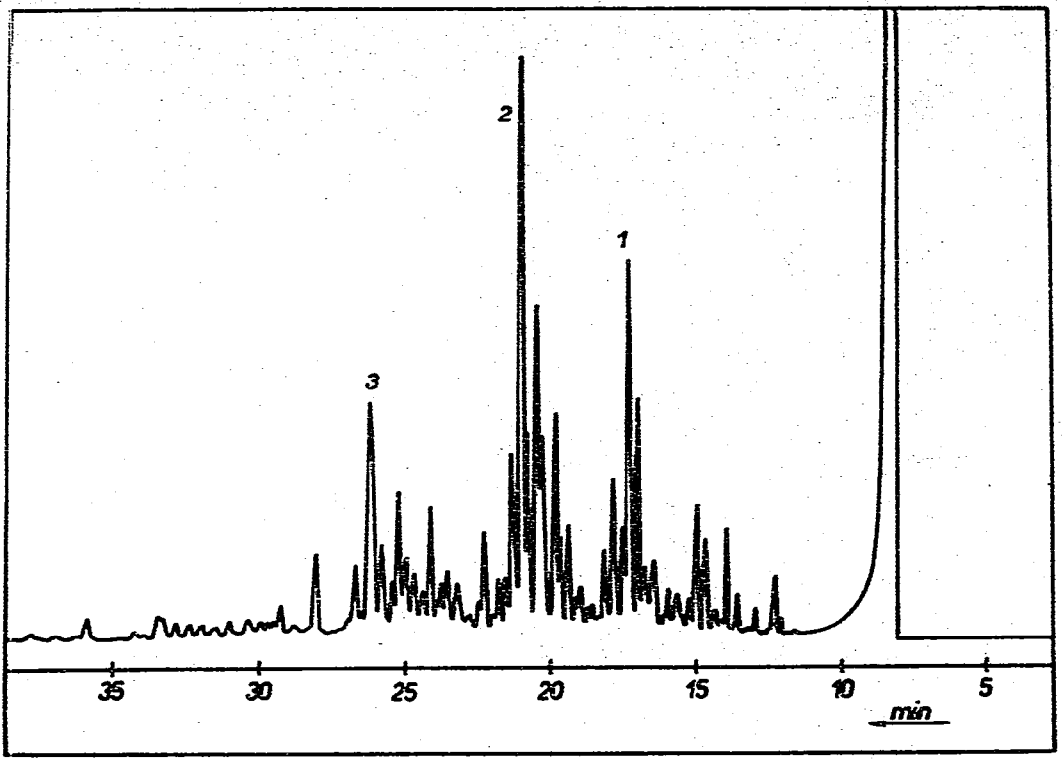

Fig. 8. Separation of the dialkylindane–dialkyltetralin fraction at 473 °K on a capillary column coated with OV-101. Peaks: 1, 1-ethyl-3-pentylindane; 2, 1-ethyl-3-hexylindane; 3, 1-ethyl-3-heptylindane.

TABLE III

QUANTITATIVE GC ANALYSIS OF PHENYLALKANES IN THE COMMERCIAL MIXTURE OF DETERGENT ALKYLATES

Compound	*W (%)*	*Compound*	*W (%)*
5-Phenylnonane	0.32	6-Phenyldodecane	5.16
4-	0.33	5-	5.15
3-	0.41	4-	4.75
2-	0.53	3-	5.20
		2-	8.15
5-Phenyldecane	2.22	6- and 7-phenyltridecane	1.55
4-	2.17	5-	1.19
3-	2.60	4-	1.32
2-	3.69	3-	1.00
		2-	1.65
6-Phenylundecane	3.55		
5-	6.94		
4-	6.46		
3-	7.48	Total	82.58
2-	10.76		

(Fig. 7). The dialkylindane–dialkyltetralin fraction is a complex mixture of substances (Fig. 8). The work on its detailed analysis is in progress and will be published later.

Quantitative analysis

The commercial mixture of phenylalkanes was quantitatively analyzed on a capillary column using 1-phenyltridecane as the internal standard and by MS. The results obtained are given in Table III.

As sufficiently pure isomeric standard materials, which are needed for the calibration of the FID response factor, were not available, correction factors were determined, taking into account the number of effective carbon atoms in the phenylalkane molecule. The quantitative analysis was effected according to the results of capillary chromatography on OV-101 (Fig. 4) using the equation $W(\%) = fAn_s/A_s n$, where W(%) is the weight percentage, $f = 19/z$ (z is the number of effective carbon atoms in a molecule of the phenylalkane), A is the area of the peak of the isomer, A_s is the area of the peak of the internal standard (1-phenyltridecane), n is the weight of the commercial phenylalkane mixture and n_s is the weight of the internal standard. The results given are mean values obtained from three consecutive analyses run, with a relative standard deviation of $\pm$ 3%. Owing to the considerable amounts of dialkylindanes and dialkyltetralins present in the commercial mixture (Fig. 4), the results of the analysis with respect to the amount of phenylalkanes are distorted by the amount of substances eluted together with phenylalkanes.

The results of the GC analysis (total content of phenylalkanes in the detergent alkylates) were checked by MS applying the molecular ion method. The relative abundances of the monoisotopic phenylalkane and dialkylindane–dialkyltetralin molecular ions, according to the number of carbon atoms, are given in Fig. 9. The calibration was carried out using the fractions of phenylalkanes and dialkylindane–dialkyltetralins obtained by liquid adsorption chromatography. The analysis by MS showed that the commercial mixture contained 80% of phenylalkanes and 20% of dialkylindane–dialkyltetralins. The mean relative error of the measurement, found from the series of the measurements, was $\pm$ 2.5%.

The fractions obtained by liquid chromatography were also analyzed quantitatively by MS. The total content of phenylalkanes found in the mixture was 77.8%, that of dialkylindane–dialkyltetralins was 20.2%, and the losses amounted to 2%.

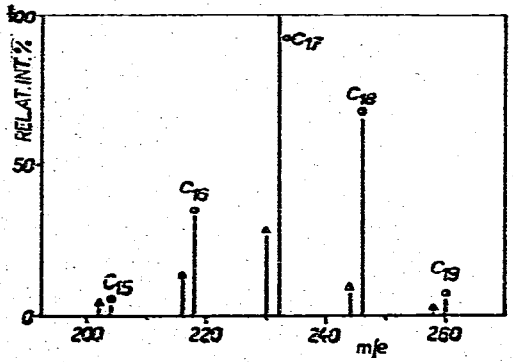

Fig. 9. Relative abundances of the monoisotopic molecular ions of phenylalkanes (○) and dialkylindane–dialkyltetralins (▲) according to the number of carbon atoms in the molecule.

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