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GAS CHROMATOGRAPHY OF UNDERIVATIZED FATTY ACIDS ON POLYETHYLENE GLYCOL STATIONARY PHASES

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SUMMARY

A technique for preparing sorbents has been developed based on polyethylene glycols of different molecular weights and the solid support Chromaton N AW DMCS, which can be used for the gas chromatographic analysis of C_3–C_{20} free fatty acids. The technique includes temperature-programmed stabilization of the sorbent to a temperature of about 270°. The reproducibilities of the retention characteristics and peak areas were determined statistically. The weight loss of the stationary phases was evaluated using the weighing method and thermogravimetric analysis. The infrared spectra of the initial and stabilized polyethylene glycols are presented. The influence of the nature of the solid support on the retention and peak shape of free fatty acids has been studied.

INTRODUCTION

In the gas chromatographic (GC) determination of free fatty acids (FFA) a number of difficulties are encountered, the most important being the low volatility of the acids, necessitating operation at temperatures close to the maximal operating temperature of most known stationary liquid phases (SLP), the capacity of the acids for molecular association in the vapour phase and adsorption of the acids in the injector and separation column. In order to overcome these difficulties, more volatile derivatives, particularly esters[1–7], are often determined instead of the acids themselves. However, it is impossible to convert lower acids quantitatively into esters[8], and the direct analysis of these fatty acids is therefore desirable. This is achieved by using techniques involving selection of the sorbent[9–14], carrier gas[15,16] and modification of SLPs[11,17–19] and the solid support[19,20].

In this work, a method for analysing C_3–C_{20} FFA on polyethylene glycols (PEGs) of different molecular weight coated on to the silanized solid support Chromaton N AW DMCS without additional modification is proposed.

EXPERIMENTAL AND RESULTS

Apparatus

The experiments were conducted using a Shimadzu GC-5A chromatograph with a dual flame-ionization detector and glass spiral columns 0.35 and 1.5 m long and 3 mm I.D. Thermogravimetric analysis was carried out with a Paulik, Paulik and Erdey derivatograph. Alumina was used as the standard. Infrared (IR) spectral analysis was carried out with a Carl Zeiss Specord YR-75 spectrophotometer in the frequency range 400–4000 cm^{-1}.

Preparation of sorbent

To prepare the sorbents, PEGs with molecular weights of 1500, 20,000 and 40,000 in amounts of 3 and 10% of the support weight was dissolved in chloroform, then mixed with preliminarily injected Chromaton N AW DMCS with a grain size of 0.260–0.315 mm. The bulk of the chloroform was evaporated on a water bath for 1 h with constant agitation. Thereafter the sorbents were placed in a desiccator at 100°, where the remaining solvent was removed by periodic agitation for 2 h.

The columns, washed with acetone, were filled with the prepared sorbents using a microvibrator under the vacuum of a water-jet pump. The packed columns were stabilized under conditions of stepped heating under a current of nitrogen. Each step (there were three in all) consisted of linear temperature programming at a rate of 5°/min in the ranges 50–100°, 100–170° and 170–260° (270°), and an isothermal interval between each. The duration of isothermal heating at 100° and 170° was 1 h, that at 260° (270°) was 4 h. Stabilization of the sorbents under strictly controlled temperature conditions ensured the stability of the baseline during the analysis of acids under linear temperature programming conditions up to 230–280°.

Separation process

A mixture of C_3–C_{12}, C_{14}, C_{16}, C_{18} and C_{20} FFA in the form of a solution in chloroform was injected with a microsyringe directly into the column on to a sorbent layer. The content of each acid was 20–40 $\mu g/\mu l$ and the volume of sample injected was 10 μl. The temperature of the upper zone over the sorbent was 300°. The 1.5-m long glass column was heated under conditions of linear programming from 60° to 230°, or from 60° to 260°, depending on the amount of the SLP coated on the solid support at a rate of 4°/min. The flow-rates of the carrier gas (nitrogen), hydrogen and air were 40, 45 and 400 ml/min, respectively, and the duration of analysis was 35–50 min.

As can be seen from the chromatogram shown in Fig. 1, under the selected conditions the FFA peaks are symmetrical with complete resolution of all of the components.

The influence of the method of injecting the sample, and the influence of the column material on the asymmetry of the FFA peaks were studied. Injection of the sample through a steel injector, instead of directly into the column, and the use of stainless-steel instead of glass columns resulted in a sharp decrease in the chromatographic zones and a considerable (3–4-fold) increase in the asymmetry factor.

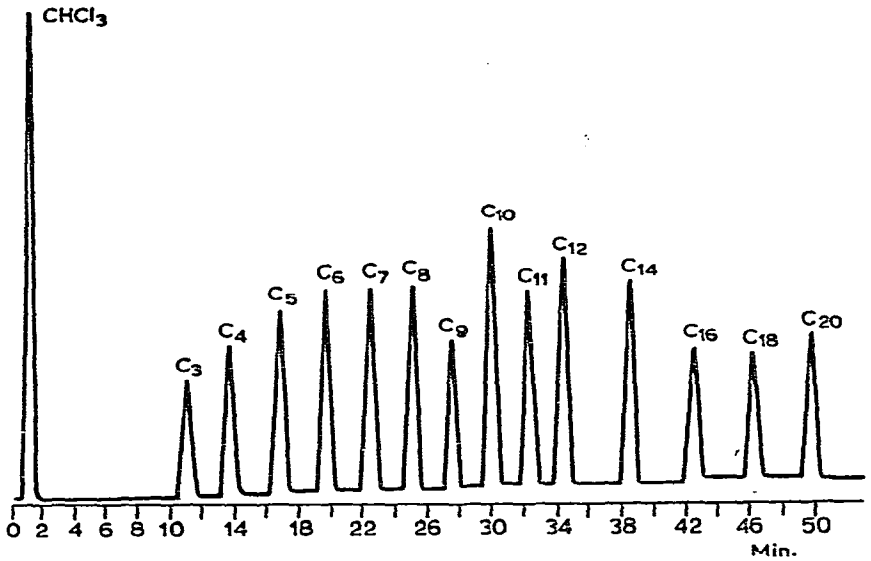

Fig. 1. Chromatogram of the mixture of C_3–C_{12}, C_{14}, C_{16}, C_{18} and C_{20} FFA with 10% of PEG 1500 as stationary phase on Chromaton N AW DMCS.

Evaluation of the suitability of the method for quantitative and qualitative analysis

In order to evaluate the suitability of the sorbents used for determining FFA, the following criteria were chosen: peak asymmetry factor ($K_a=a_1/a_2$), where a_1 and a_2 are the widths of the leading and rear fronts of the peak at half-height; the peak area (A), which was calculated by the triangle method using $A=hB_{1/2}$, where h is the peak height and $B_{1/2}$ is the peak width at half-height; and the relative retention time ($R_x=t_{R,K}/t_{R,st}$), where $t_{R,K}$ is the retention time of the corresponding acid (C_3–C_{20}) and $t_{R,st}$ is the retention time of the standard (propionic acid).

The reproducibility of the results was evaluated from the standard deviation (S_x), which was calculated using a Hewlett-Packard HP-65 microcomputer by a standard program corresponding to the equation

$$S_x = \sqrt{\frac{\sum_{i=1}^{n} x_i^2 - n\bar{x}^2}{n-1}}$$

where S_x is the standard deviation, Σx_i^2 is the sum of the squares of the measured values, $\bar{x}^2$ is the square of the arithmetic mean of the measured values and n is the number of measurements.

Standard deviations were calculated based on ten simultaneous experiments with each sorbent. As the duration of the simultaneous experiments never exceeded 48–72 h, randomization was not carried out. The standard deviations of the asymmetry coefficients, relative retention times and peak areas are shown in Tables I, II and III, respectively. Table II also gives the absolute retention time of propionic acid, and S_x values calculated on the basis of ten measurements for each of the sorbents studied.

TABLE I

ASYMMETRY COEFFICIENTS OF FREE FATTY ACID PEAKS

Acid	*PEG 1500*				*PEG 20,000*				*PEG 40,000*			
	3%		*10%*		*3%*		*10%*		*3%*		*10%*	
	K_c	S_x	K_a	S_x	K_a	S_x	K_a	S_x	K_a	S_x	K_a	S_x
C_3	0.41	0.13	0.80	0.05	0.47	0.04	0.80	0.06	0.80	0.02	0.90	0.03
C_4	0.65	0.09	0.86	0.05	0.73	0.06	0.87	0.05	0.90	0.05	1.00	0.01
C_5	0.95	0.07	1.02	0.04	1.00	—	1.19	0.13	0.99	0.02	1.00	—
C_6	1.28	0.06	0.96	0.05	1.00	0.03	1.10	0.11	0.99	0.02	1.00	0.02
C_7	1.50	0.07	1.02	0.04	1.00	0.04	1.03	0.05	1.00	0.02	1.00	—
C_8	2.01	0.12	0.99	0.02	1.14	0.03	1.28	0.12	1.02	0.06	1.05	0.04
C_9	1.67	0.16	0.95	0.06	1.00	0.03	1.11	0.08	0.98	0.03	0.96	0.04
C_{10}	2.11	0.08	1.00	0.03	1.07	0.05	1.19	0.06	1.03	0.05	1.00	0.01
C_{11}	2.04	0.09	0.98	0.04	1.04	0.06	1.12	0.09	1.01	0.04	0.95	0.03
C_{12}	2.07	0.11	1.03	0.05	1.15	0.06	1.27	0.06	1.06	0.08	0.95	0.03
C_{14}	1.91	0.11	1.00	0.05	1.17	0.07	1.46	0.10	1.00	0.04	0.90	0.04
C_{16}	1.87	0.09	0.87	0.03	1.02	0.05	1.35	0.07	0.95	0.04	0.67	0.04
C_{18}	2.00	0.06	0.74	0.04	0.94	0.03	1.49	0.07	0.95	0.05	0.67	0.06
C_{20}	2.25	0.08	0.79	0.07	1.00	0.03	1.74	0.12	0.98	0.02	0.77	0.06

In addition, confidence intervals for the actual values of the measured data and the mean relative measurement errors (δ) were selectively calculated.

For the calculation of confidence intervals, the tabulated values of the t criterion for a significance level of 0.05 were used, which is usually accepted in chromatographic analysis, and 9 degrees of freedom. The δ values for R_x and A did not exceed 2 and 5%, respectively.

TABLE II

RELATIVE RETENTION TIMES OF FREE FATTY ACIDS

Acid	*PEG 1500*				*PEG 20,000*				*PEG 40,000*			
	3%		*10%*		*3%*		*10%*		*3%*		*10%*	
	R_x	S_x	R_x	S_x	R_x	S_x	R_x	S_x	R_x	S_x	R_x	S_x
C_3	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—	1.00	—
	(4.22)*	0.23	(10.65)	0.14	(6.91)	0.18	(8.92)	0.10	(7.04)	0.22	(11.90)	0.03
C_4	1.54	0.03	1.24	0.01	1.38	0.04	1.29	0.01	1.39	0.22	1.22	0.01
C_5	2.23	0.04	1.54	0.02	1.84	0.04	1.64	0.01	1.83	0.03	1.49	0.01
C_6	2.89	0.04	1.80	0.02	2.27	0.05	1.96	0.02	2.25	0.04	1.74	0.02
C_7	3.50	0.05	2.07	0.02	2.65	0.06	2.26	0.03	2.63	0.06	1.96	0.02
C_8	4.08	0.07	2.31	0.03	3.06	0.06	2.56	0.03	3.00	0.07	2.19	0.02
C_9	4.61	0.09	2.54	0.03	3.42	0.08	2.83	0.03	3.35	0.08	2.40	0.02
C_{10}	5.17	0.10	2.77	0.03	3.78	0.08	3.11	0.04	3.70	0.09	2.61	0.02
C_{11}	5.67	0.11	2.98	0.04	4.11	0.09	3.16	0.04	4.04	0.10	2.80	0.02
C_{12}	6.16	0.12	3.19	0.04	4.45	0.10	3.61	0.05	4.34	0.10	2.99	0.03
C_{14}	7.05	0.15	3.56	0.05	5.06	0.12	4.07	0.05	4.92	0.11	3.35	0.04
C_{16}	7.89	0.16	3.94	0.06	5.63	0.12	4.51	0.05	5.46	0.13	3.70	0.04
C_{18}	8.71	0.18	4.29	0.05	6.16	0.14	4.91	0.06	6.00	0.14	4.00	0.04
C_{20}	9.50	0.19	4.62	0.06	6.69	0.15	5.32	0.06	6.49	0.15	4.31	0.04

* Absolute retention times (minutes) of propionic acid are shown in parentheses.

TABLE III

PEAK AREAS (A, mm²) OF FREE FATTY ACIDS

Acid	*PEG 1500*				*PEG 20,000*				*PEG 40,000*			
	3%		*10%*		*3%*		*10%*		*3%*		*10%*	
	A	S_x	A	S_x	A	S_x	A	S_x	A	S_x	A	S_x
C_3	81	5.66	72	3.02	62	3.00	90	3.41	116	4.16	134	3.72
C_4	104	4.82	102	2.75	94	7.13	137	3.40	152	4.26	179	3.95
C_5	119	3.32	119	2.77	138	4.74	168	3.34	177	5.59	181	2.50
C_6	121	5.48	132	2.98	169	3.41	182	3.33	201	6.88	198	3.71
C_7	120	4.47	133	2.91	177	2.79	185	3.54	208	6.49	203	2.84
C_8	139	5.85	136	2.92	188	6.32	189	3.88	212	5.37	205	3.68
C_9	108	4.00	94	3.13	142	7.69	157	3.69	157	4.13	157	4.24
C_{10}	147	5.83	163	4.13	198	3.46	212	2.63	255	4.92	225	3.41
C_{11}	135	7.97	129	3.53	170	4.98	187	4.01	196	4.30	172	2.83
C_{12}	157	6.30	141	3.67	184	3.28	209	4.84	234	3.82	195	5.98
C_{14}	151	7.61	124	3.60	173	4.41	250	4.51	223	3.27	197	4.28
C_{16}	125	3.30	73	3.28	122	6.82	218	4.15	168	3.63	180	4.34
C_{18}	146	4.21	85	4.08	108	6.28	222	5.97	168	6.21	210	5.26
C_{20}	174	6.29	114	3.16	123	8.61	294	5.24	237	5.44	281	6.86

As is evident from Tables II and III, the proposed technique ensures good reproducibility of both the retention times and of the FFA peak areas. Adsorption and dimerization of the acids did not occur with the sorbent used, which consisted of a highly polar SLP (polyglycol) on an inert support (silanized Chromaton), as demonstrated by the closeness to unity of the asymmetry coefficient (Table I), in addition to the constancy of the R_x and A values.

The best results, *i.e.*, symmetrical peaks, the absence of tailing, and minimal standard deviations of the R_x, A and K_a values, were obtained with Chromaton H AW DMCS coated with 10% of PEG 1500.

The proposed technique was used for the qualitative analysis of FFA. The retention temperature (T_R), equal to the column temperature at the moment of separation of a given component, was used as a retention characteristic. Fig. 2 shows the dependence of the difference $T_R - T_0$, where T_0 is the temperature at the start of the programme, on the number of carbon atoms (n) in the molecule for the homologous series of n-carboxylic acids in a column packed with 3% and 10% of PEG 20,000. It is evident that the dependences are almost linear and can be used for identification of the acids.

Determination of the removal of stationary phase

In the temperature-programmed stabilization of sorbents, the temperatures used (up to 260–270°) exceeded the maximal operating temperatures known from the literature (175–200° for PEG 1500 and 225–250° for PEG 20,000[21,22]), and it was therefore interesting to determine experimentally the extent of the removal of these SLPs under the given temperature conditions.

For determining the extent of removal of the SLPs during stabilization of the sorbents, the weighing method was used, based on determining the weight loss of SLP by the sorbents with 10% of PEG 1500 and 20,000 under conditions of stepped

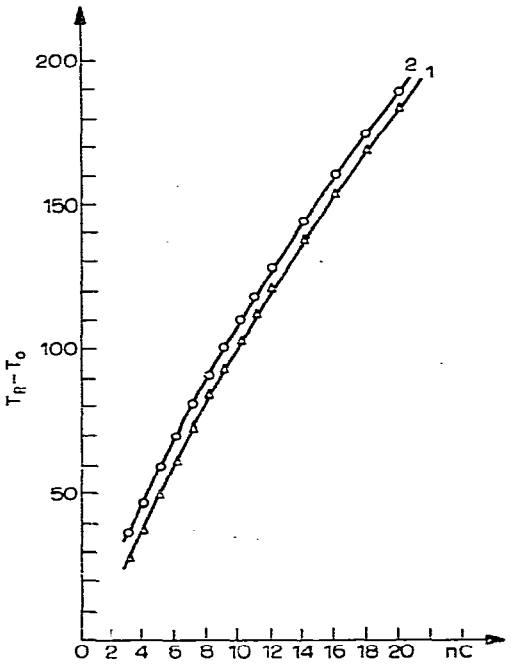

Fig. 2. Dependence of retention temperature (minus the initial temperature) on the number of carbon atoms for C_3–C_{20} FFA on 3% (w/w) (1) and 10% (w/w) (2) of PEG 20,000.

heating under a current of nitrogen. In order to achieve this, the columns were subjected to a three-stage heating programme by the technique described above.

This part of the investigation resulted in the determination of the total decrease in the mass of the sorbent, $\Delta m'_{sorb.}$, during temperature-programmed stabilization. To determine the contribution of the solid support, $\Delta m_{supp.} = \Delta m^*_{supp.} + \Delta m_{DMCS}$, to $\Delta m_{sorb.}$ Chromaton N AW DMCS was also subjected to a three-stage heating programme under similar conditions. The $\Delta m^*_{supp.}$ values were obtained during the stabilization of non-silanized Chromaton N. The true value of the extent of removal of SLP was determined by using the difference between $\Delta m_{sorb.}$ and $\Delta m_{supp.}$ The decreases in the mass of the inert supports were compared with the literature data using $\Delta m^*_{supp.}$.

TABLE IV

EXTENT OF REMOVAL OF SLP DURING TEMPERATURE-PROGRAMMED STABILIZATION OF PEG 1500 (10%) ON CHROMATON N AW DMCS

	$M_{sorb.}$ (g)	$m_{sorb.}$ (g)	$m^*_{supp.}$ (g)	m_{DMCS} (g)	$m_{supp.}$ (g)	m_{SLP} (g)
Starting sorbent	3.9276	—	—	—	—	—
Step 1	3.8045	0.1231	0.0243	0.0424	0.0667	0.0564
Step 2	3.7195	0.0850	0.0067	0.0029	0.0096	0.0754
Step 3	3.5637	0.1558	0.0014	0.0138	0.0152	0.1406
Total removal	—	0.3639	0.0324	0.0591	0.0915	0.2724

TABLE V

EXTENT OF REMOVAL OF SLP DURING TEMPERATURE-PROGRAMMED STABILIZATION OF PEG 20,000 (10%) ON CHROMATON N AW DMCS

	$M_{sorb.}$ (g)	$m_{sorb.}$ (g)	$m^*_{supp.}$ (g)	m_{DMCS} (g)	$m_{supp.}$ (g)	m_{SLP} (g)
Starting sorbent	2.7294	—	—	—	—	—
Step 1	2.6649	0.0645	0.0169	0.0295	0.0464	0.0181
Step 2	2.6433	0.0216	0.0047	0.0020	0.0067	0.0149
Step 3	2.6015	0.0418	0.0010	0.0096	0.0106	0.0312
Total removal	—	0.1279	0.0226	0.0411	0.0637	0.0642

The weighing was carried out after each stabilization stage using an analytical balance with a precision of up to 0.1 mg. Before each weighing the glass column (0.35 m × 3 mm I.D.) with a sorbent or support was maintained in a thermostat at 25° for 25 min. The experimental results are reported in Tables IV and V.

The residual content of PEG 1500 with a correction for $\Delta m_{supp.}$ was 2.4%. The results of a similar experiment in which Tsvetochrom-1 was used as the solid support were as follows: $\Delta m_{sorb.} = 0.1910$ g ($M_c = 4.4289$); $\Delta m_{supp.} = 0.0053$ g; residual PEG 1500 content = 5.8%. The residual content of PEG 20,000 with a correction for $\Delta m_{supp.}$ was 7.4%.

According to the experimental results, the decrease in $\Delta m_{supp.}$ for chromaton N AW DMCS was 0.9% of its mass, while for Tsvetochrom-1, with $\Delta m^*_{supp.} = \Delta m_{supp.}$, it was 0.13%, which almost coincides with the value in the literature[23], indicating that the decreases in the mass of diatomic supports during heating within the range 200–300° are 0.1–0.6%.

The results of the thermogravimetric analysis of the sorbent (Chromaton N AW DMCS coated with 10% of PEG 1500) are presented in Fig. 3. The temperature range was 22–500°, the heating rate 5°/min and the amount of sample 780 mg. Curve 1 (Fig. 3b) was recorded in an atmosphere of air, curve 2 in an atmosphere of helium and curve 3 refers to PEG 1500 without a solid support in an atmosphere of helium (this curve was recalculated on the basis of an experiment with an amount of sample of PEG 1500 of 180 mg). The removal of SLP starts at 120–140° and proceeds more readily in an atmosphere of air. The slow removal of pure PEG 1500 may be dependent on kinetic effects.

At the final stabilization temperature (260°), the residual amount of PEG 1500 on the Chromaton was 1.2%. Three characteristic peaks are observed on the DTA curve for the sorbent heated in an atmosphere of helium (Fig. 3a), one of the peaks (I) corresponding to the boiling point of PEG 1500 (65°). The presence of the other two peaks, exothermic (II) with a maximum at 165° and endothermic (III) at 285°, may be associated with two processes taking place concurrently in the column, *viz.*, formation of volatile products resulting from the destruction of polymer molecules and transition of these products from the SLP into the gas phase, respectively. For the sample heated in an atmosphere of air, the area of the exothermic peak (II) increases sharply, indicating more profound SLP decomposition processes in the presence of oxygen. On the DTA curve for pure PEG 1500 without the solid support, the areas of peaks II and III are similar which indicates that the solid support produces a particular effect on the removal of SLP.

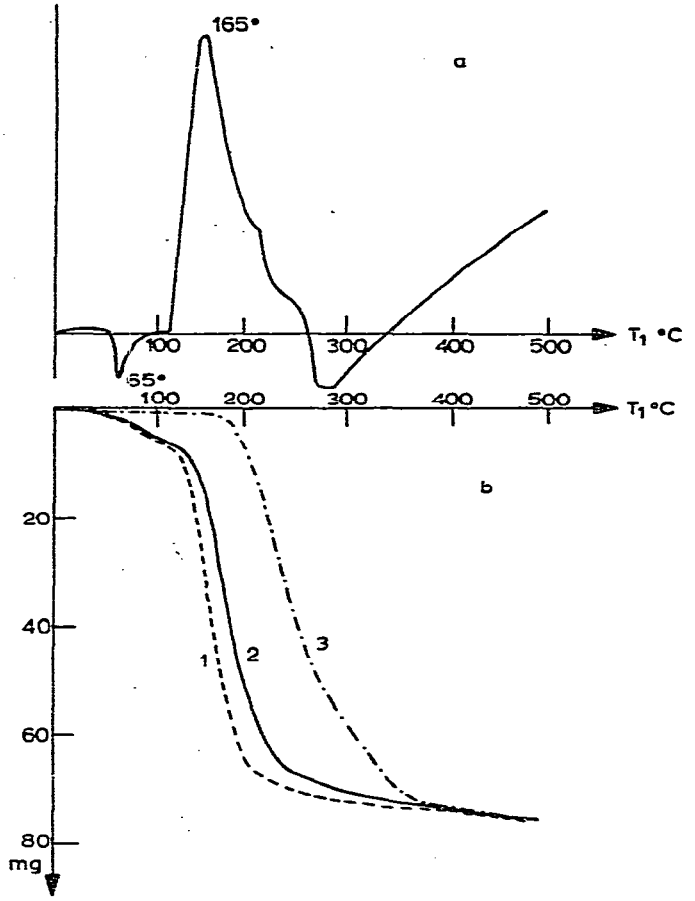

Fig. 3. Curves for (a) differential thermal and (b) thermogravimetric analysis of the sorbent samples.

Modification of characteristics of the stationary phase during sorbent stabilization

It was assumed that, as a result of preparing the sorbents for an analysis of FFA, all of the SLP (PEG 1500) undergoes chemical changes, and separations on such a sorbent occur not on the initial phase, but on the products of its chemical changes formed on the surface of the solid support during temperature-programmed stabilization under controlled temperature conditions (250–270°).

In order to confirm this assumption, FFA were analysed on unstabilized sorbents. The results were presented in the form of a graph of the absolute retention time, t_R, of the FFA (C_3–C_7) on the amount of PEG 1500 coated on the solid support (Fig. 4). Using this dependence, the residual SLP content of the stabilized sorbent was determined (by the absolute t_R of FFA obtained with the stabilized sorbent), which was 3.8–4.5% (w/w). By comparing these data with those obtained by the weighing method and using thermogravimetric analysis [1.2–2.4% (w/w)], one can make a hypothetical conclusion that such a large difference between the results (these results should virtually coincide, provided that the residual SLP was PEG) is caused by different interactions of FFA with the stabilized and starting sorbents, which may finally indicate that on the starting sorbent separation takes place on the PEG itself,

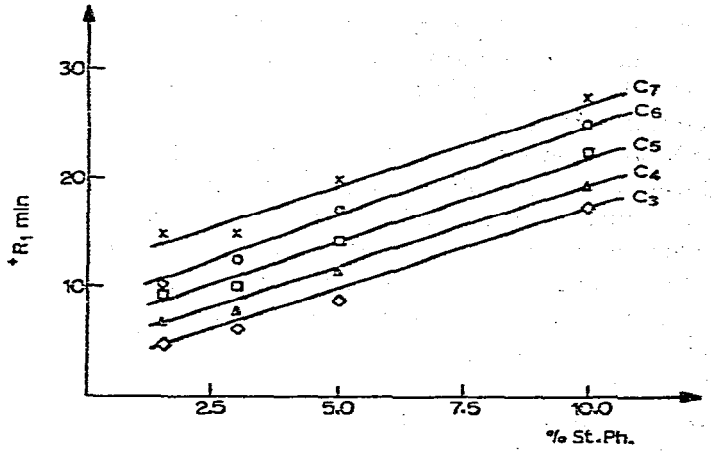

Fig. 4. Dependence of the absolute retention times, t_R, of C_3–C_7 FFA on the amount of PEG 1500 coated on Chromaton N AW DMCS (sorbent unstabilized).

whereas on the stabilized sorbent it takes place on the products of its chemical transformations.

IR spectral results are also indicative of the change in molecular structure of the starting SLP. For IR spectral analysis, the SLP was washed out of the stabilized and unstabilized sorbents with carbon tetrachloride at room temperature for 24 h, because the main absorption bands (AB) in the IR spectra of SLP and Chromaton N AW DMCS overlap. From the solutions obtained 25-μm layers were prepared and IR spectra were recorded with a Specord IR-75 spectrophotometer in the frequency range 400–4000 cm^{-1}. The IR spectra of the stabilized and unstabilized samples (Fig. 5) differ in the frequency ranges 1700 cm^{-1} (oscillations of C=O groups), 1180 cm^{-1} (oscillations of C–O groups), 3300–3500 and 1640 cm^{-1} (oscillations of the OH group). The IR spectrum of unstabilized PEG is characterized by the presence of two AB bands at 1710 and 1740 cm^{-1}, while that of stabilized PEG is characterized by only one AB band at 1740 cm^{-1}. The absorption band at 1710 cm^{-1} results from the oscillations of C=O groups in acids and aldehydes, and the AB band at 1740 cm^{-1} from oscillations of C=O groups in the complex ester groups. The AB bands with absorption maxima at 3350 cm^{-1} in both spectra differ in their intensities.

For a quantitative evaluation of the differences found in the above IR spectra,

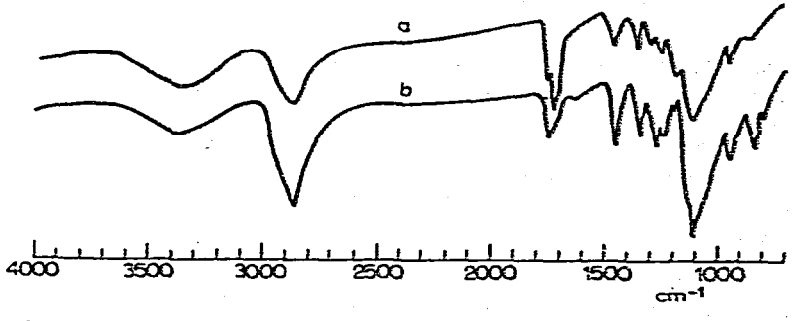

Fig. 5. IR spectra of SLPs washed out of (a) unstabilized sorbent and (b) stabilized sorbent.

absorbances of the 1710, 1740 and 3350 cm^{-1} AB bands were calculated with respect to the 1465 cm^{-1} AB band (deformation oscillations of CH_2 groups) selected as a reference (Table VI). The reference band was slected in order to eliminate the influence of the thickness of the sample layer.

It can be seen from Table VI that the amounts of C=O and OH groups in the stabilized PEG are lower than those in the unstabilized PEG. As was indicated above, the difference in the molecular structures of the stabilized and unstabilized samples was detected by the absorption bands of the C=O (1710–1740 cm^{-1}), C–O (1180 cm^{-1}) and OH groups (1640, 3300–3500 cm^{-1}). The intensities of these bands, and their absorbances, are lower in the IR spectrum of the stabilized sample.

TABLE VI

ABSORBANCES OF AB BANDS OF UNSTABILIZED AND STABILIZED PEG

Absorption band (cm^{-1})	*Absorbance*	
	Unstabilized sample	*Stabilized sample*
1710	3.17	—
1740	1.94	0.854
3350	1.33	0.565

These differences in the molecular structure of the sample may be due to the separation of the OH end-group at high temperatures (250–270°) on SLP during sorbent stabilization. This is also indicated by the change in the 3300–3500 cm^{-1} AB band: in the stabilized sample it widens and has a blurred maximum in comparison with the unstabilized sample. Apart from this, in the stabilized sample the intensity of the 1640 cm^{-1} AB band is higher, which may be caused by the appearance of double bonds during dehydration of the stabilized SLP (PEG 1500).

Investigation of the possibility of using other supports to analyse FFA

In order to study the possibility of using untreated diatomic supports to analyse FFA, preliminarily stabilized sorbents [10% of PEG 1500 coated on the solid supports Spherochrom-1 (0.250–0.300 mm), Tsvetochrom-1 (0.250–0.315 mm) and Tsvetochrom-2 (0.315–0.460 mm)] were used to analyse an artificial mixture of

TABLE VII

PHYSICO-CHEMICAL AND STRUCTURAL CHARACTERISTICS OF SOLID DIATOMIC SUPPORTS

Support	*Bulk density (g/cm^3)*	*Specific surface area (m^2/g)*	*Mechanical strength (% abrasion in boiling layer)*	*Catalytic activity (% of cyclohexene formation)*	*Adsorption activity (ml)*	*Total volume of pores (cm^3/g)*	*Effective radius of pores (μm)*
Spherochrom-1	0.43	1.06	1.75	5.2	45	0.65	1.0
Tsvetochrom-1	0.55–0.65	2.0–3.0	—	—	—	1.5–2.0	—
Tsvetochrom-2	0.6 –0.7	1.3–1.5	—	—	—	2.0–2.5	—
Chromaton N	0.24	1.0	—	—	—	1.3–1.4	6.0
Chromosorb W	0.33	1.25	19.8	0.70	47	1.8	2.0

C_3–C_7 FFA. Simultaneously, C_3–C_7 FFA were analysed on PEG 1500 coated on Silochrom C-80, Chromaton N AW DMCS and Chromosorb W HP. The physicochemical and structural characteristics of these supports are reported in Table VII[24].

In addition to the above solid supports, the silicone adsorbent Silochrom C-80 (0.250–0.350 mm) was also used with a total volume of the pores of 1.2 cm^3/g, specific surface area 80 m^2/g and mean volume of pores 2.5 μm.

A mixture of C_3–C_7 FFA (1–4 μl) was injected with a microsyringe on to the sorbent layer. The temperature of the upper zone of the column over the sorbent was 250°. The 1.5-m glass columns were heated under conditions of linear temperature programming from 60 to 150–190° at a rate of 4°/min.

It can be seen from the chromatograms in Fig. 6 (a–d) that adsorption and dimerization of FFA on the sorbents occurred (solid supports Spherochrom-1, Tsvetochrom-1, Tsvetochrom-2 and Silochrom C-80), this being indicated by blurring of the chromatographic zones, formation of tails and a sharp increase in the asymmetry of the peaks. It is also worth noting that when using the above supports, it is impossible to achieve reproducibility of the quantitative separation of FFA from the column. Hence these supports are unsuitable for analysing even the C_3–C_7 FFA. The application of Chromaton N AW DMCS as the solid support made it possible not

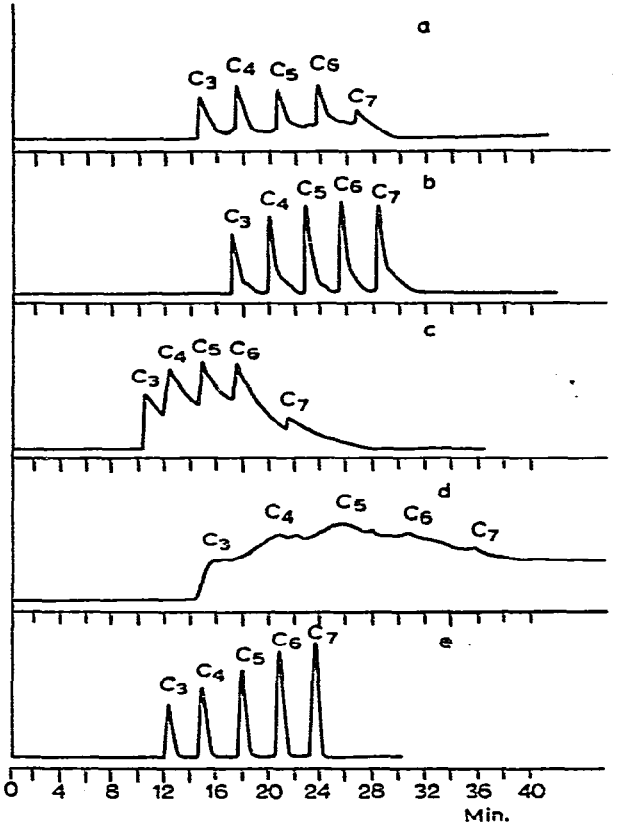

Fig. 6. Chromatograms of C_3–C_7 FFA mixture using 10% (w/w) of PEG 1500 on various solid supports: (a) Spherochrom-1; (b) Tsvetochrom-1; (c) Tsvetochrom-2; (d) Silochrom C-80; and (e) Chromaton N AW DMCS.

only to separate the mixture of C_3–C_7 FFA (peak asymmetry coefficient 0.95–1.10) (Fig. 6e), but also to separate a multi-component mixture of C_3–C_{22} acids (T_c = 60–270°) (Fig. 7a). As can be seen from the chromatogram in Fig. 7b, a complete separation of the mixture of C_3–C_{18} acids was also achieved when using Chromosorb W HP as the solid support: according to calculations, the δ values for R_x and A were 2–5%; the K_a values of the peaks increased by 30–40% in comparison with the K_a values for Chromaton N AW DMCS.

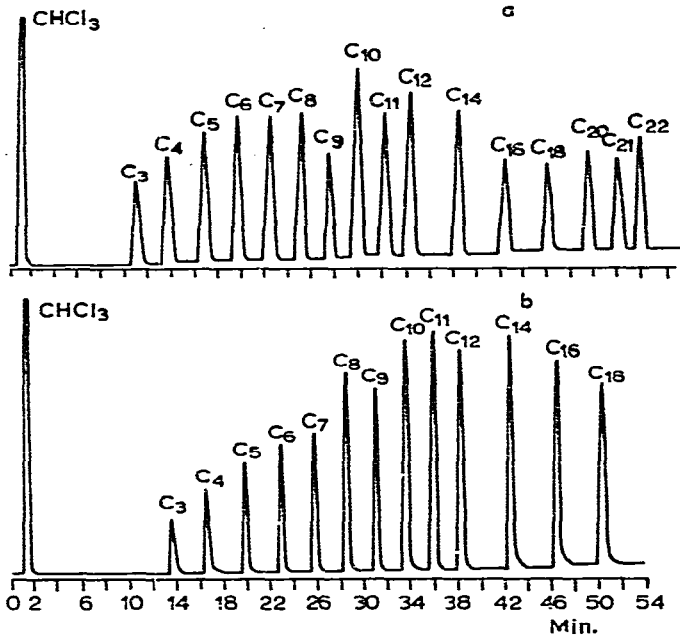

Fig. 7. Chromatograms of C_3–C_{22} and C_3–C_{18} FFA mixture with 10% (w/w) of PEG 1500 coated on (a) Chromaton N AW DMCS (0.260–0.315 mm) and (b) Chromosorb W HP (60–80 mesh).

CONCLUSIONS

A gas chromatographic method for analysing FFA in which polyethylene glycols coated on Chromaton N AW DMCS as the SLP are used has been developed. The relative error of the determination of retention times and peak areas did not exceed 2 and 5%, respectively, permitting the method to be used for studying a broad FFA fraction.

The extents of removal of PEG 1500 and 20,000 during the preparation of the sorbents for the analysis of FFA have been determined. It has been found that during the stabilization of the sorbents under controlled temperature conditions (up to 250–270°), a change in the molecular structure of the SLP (PEG 1500) occurs, which may be due to dehydration of the end-groups.

It has been established that untreated diatomic supports Spherochrom-1, Tsvetochrom-1 and Tsvetochrom-2 in combination with polyethylene glycol SLP cannot be used for the separation of FFA.

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