Quick Identification and Analysis of Plasticizers in PVC by Programmed-Temperature Gas Chromatography Using the Best Stationary Phases

DJELLOUL MESSADI and JEAN-MAURICE VERGNAUD, *Laboratory of Analytical Chemistry and Industrial Chemistry, U.E.R. Of Sciences, University of Saint-Etienne, 42100 France*

Synopsis

A quick and safe identification method is shown for plasticizers in PVC using programmed-temperature gas chromatography. Plasticizers were identified by their retention index values measured by using normal paraffins. Several stationary phases with quite different polarity are proposed: with silicone polymers (SE 30, OV 17, and QF 1) and a porous polymer such as Tenax. Operational conditions were optimized. The initial column temperature was chosen at a low value of 100°C with the first three phases and 180°C for the fourth. The best rate of temperature increase with time seemed to be 10°C/min. The calculation method for retention values (temperature, time, indices) was chosen just because it needed no approximation. Thermodynamic values for the solution of plasticizers were measured by using isothermal chromatography with all the stationary phases. Our method allows the analyst to optimize the operational conditions (solvent, percent, temperature) for chromatography, to solve his own problem by making use of a pocket computer. Quantitative analysis of plasticizers was obtained with good accuracy after a previous extraction and the addition of normal paraffin as internal standard.

INTRODUCTION

This work was done with the intent of realizing a quick, sure, and accurate method for the identification and quantitative analysis of the essential plasticizers in PVC. Identification methods such as infrared and nuclear magnetic resonance were suitable for a pure plasticizer, and they required preliminary separation of the mixture components, but gas phase chromatography is certainly the best separation method.

Several workers have used gas-phase chromatography working in isothermal conditions to obtain separation of PVC plasticizers. About 1960 and 1970, workers tried to reduce retention times of low volatile plasticizers. They worked with very short columns[1,2] or they put a low percent of solvent in stationary phases,[3,4] using sometimes a support made of glass beads.[5] Retention times were short enough, but the separation of plasticizer peaks was not so good. On the other hand, volatile plasticizers were separated with columns filled with stationary phases of higher solvent percent (silicon grease).[6,7] In some other works, two stationary phases with different polarity were used.[5,8] Some workers improved on the identification quality with the use of retention indices[5] or of an internal standard.[7,8] Unfortunately, isothermal gas chromatography could not permit the separation of all components in a plasticizer mixture the volatility of which was quite different.

Several workers used programmed-temperature gas chromatography to sep-

arate and identify some plasticizers. At one time, seven plasticizers were classified according to the dibutyl sebacate.[9] At another time, 15 plasticizers were classified using dioctyl phthalate as the internal standard.[10] Finally, some phthalate esters were separated,[11] and also some phosphate, adipate, and sebacate esters.[12–14] These latter works were the most valuable. However, these plasticizers were chromatographed in quite different operational conditions according to their acid function: initial temperatures of column, heating rates, heating rate changes during analysis. The solvent chosen was QF1, and it could be used at a high temperature.

To achieve separation of plasticizers and their indentification in one shot, our gas chromatography method had to have several characteristics:

1. At first, the method must be used whatever the volatility of plasticizers may be. So we chose a gas-chromatographic method with a temperature program. The initial temperature of the column at injection time must be low enough for a proper separation of the most volatile plasticizers. Stationary phases must be resistant to high temperature to be convenient for the less volatile plasticizers.

2. The method must allow for a reproducible retention time of solutes. Thus, we used retention indices[18,19] by simultaneously injecting plasticizers and normal paraffins. We used the fact that retention indices vary very little with operational conditions such as column temperature and mobile phase rate.

3. Our identification method must be reliable. Therefore, we used several stationary phases, the polarity of which was quite different. Among all stationary phases tested, three were considered. The first two, SE 30 and OV 17, were silicone polymers. The third was a porous polymer called Tenax. A fourth stationary phase was proposed, QF 1, to solve the difficult separation of a plasticizer pair.
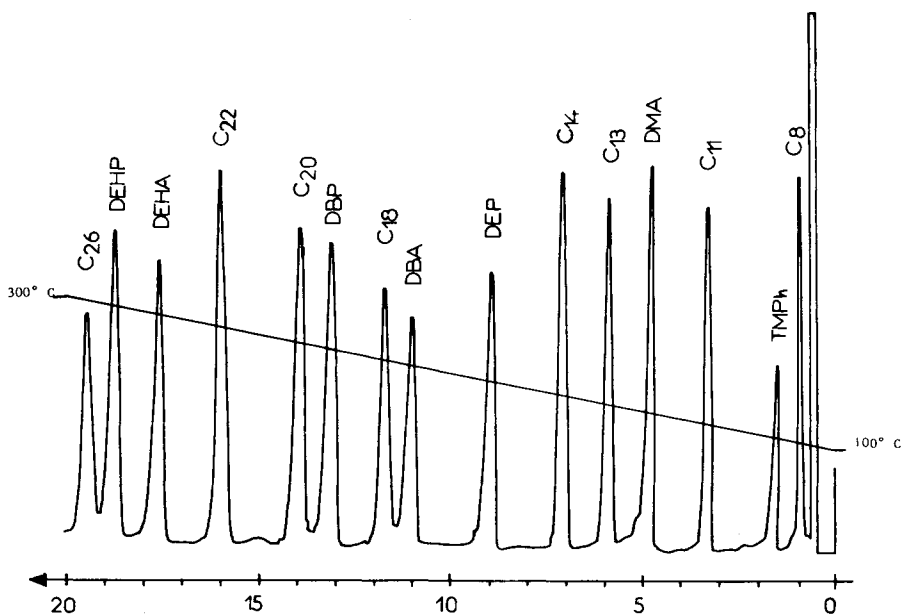

Fig. 1. SE 30 column. Chromatography with programmed temperature of plasticizers and alkanes: $b = 10°C/min$; $T_{init} = 100°C$; $T_{end} = 300°C$.

4. The method must allow for an accurate quantitative analysis whatever the additives in PVC may be. Our procedure was defined by two first steps such as extraction and addition of an internal standard.

Finally, we showed the thermodynamic vaporizing values for plasticizers in solution in the different stationary phases and a calculation method for the determination of retention values of plasticizers with the chromatographic parameters. This method and the thermodynamic values shown allowed to optimize the last operational conditions to solve any particular problem by using a pocket computer.

THEORETICAL

Certain conventional assumptions were made: (1) gas phase and solute vapors behave as ideal gases and obey Boyle–Mariotte's law; (2) vaporization enthalpy of solute varies little with temperature; (3) the temperature program is linear.

Retention Time with Isothermal Chromatography

At an abscissa x and time t, solute migration rate is defined by the well-known relation

$$\frac{dx}{dt} = U_x R_{fT} = \frac{L}{t_{rT}}$$

(1)

where U_x is the carrier gas velocity and R_{fT} the retardation factor of solute at temperature T.

Retention time is given[15] by

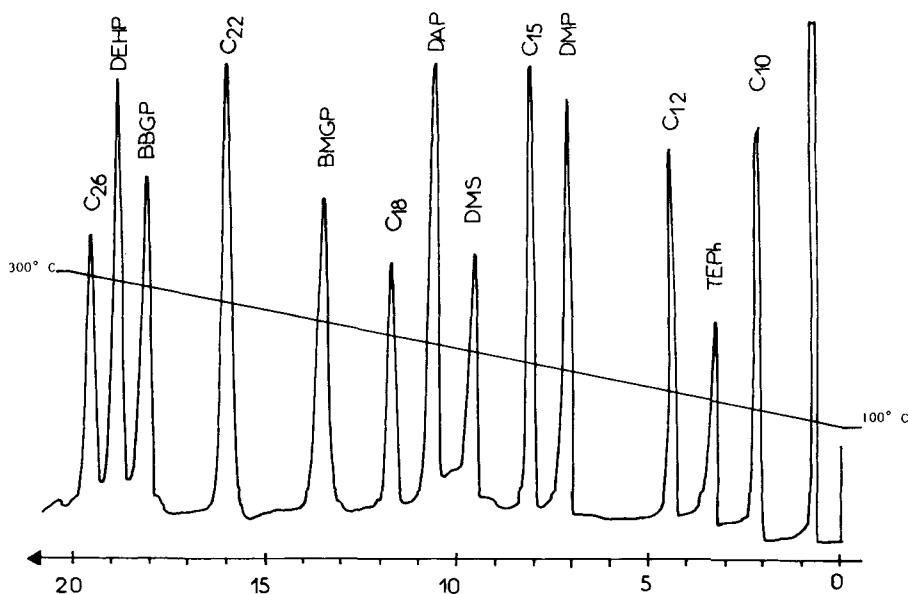$$\frac{t_r - t_g}{t_g} = A \exp \frac{\overline{\Delta H_v^0}}{RT}$$

(2)

Fig. 2. SE 30 column. Chromatography with programmed temperature of plasticizers and alkanes: $b = 10°C/min$; $T_{init.} = 100°C$; $T_{end} = 300°C$.

where $\overline{\Delta H_v^0}$ is the standard vaporization enthalpy of solute solution at temperature T, R is the ideal gas constant, t_g is the retention time of mobile phase, and A is given by

$$A = \frac{N_l}{N_g} \exp - \frac{\overline{\Delta S_v^0}}{R} \qquad (3)$$

$\overline{\Delta S_v^0}$ being the standard vaporization entropy of solute from the solution in the stationary phase. N_g is the mole number of gas phase situated in the column when the pressure is 1 atmosphere, and N_l is the mole number of solvent in the column. When the solvent is a polymer, N_l must be expressed differently.[20] But it does vary proportionally with the solvent weight.

Retention Time with Programmed-Temperature Chromatography

At time 0, when the solute is injected, the column temperature is T_0. Temperature programming is started, the rate of which is b:

$$b = \frac{dT}{dt} \qquad (4)$$

Relations (1) and (4) combined give the differential expression (5):

$$\int_0^L b\, dx = \int_{T_0}^{T_r} \frac{L}{t_{rT}} \cdot dT \qquad (5)$$

the integration limits of which are respectively 0 and column length L for abscissa x, and for temperature T_0 and solute retention temperature T_r.

This integral cannot be integrated by mathematical means. Several workers have used different approximate methods to obtain an approaching result.[17] We preferred to use a numerical method of integration[16] because it is more accurate and as quick as the previous one. The equation becomes

$$b\, t_g = \sum_{T_0}^{T_r} \left[1 + A \exp \frac{\overline{\Delta H_v^0}}{RT} \right]^{-1} \Delta T \qquad (6)$$

We had to calculate the upper limit of temperature T_r, step by step, with a convenient increment of temperature, ΔT. Calculation may be carried out by using a pocket calculator, and it does not take more than 1 min for one solute.

The solute retention time is then given by eq. (7) obtained from (4):

$$t_r = \frac{T_r - T_0}{b} \qquad (7)$$

Retention indices I_x of a solute X may be determined by using eq. (8):

$$I_x = 100 \left[n_A + (n_B - n_A) \frac{T_{r_x} - T_{r_A}}{T_{r_B} - T_{r_A}} \right] \qquad (8)$$

where n_A and n_B are the carbon numbers of the successive normal paraffins A and B chosen so that X is between them. All the T_r are retention temperatures of indexed solutes.
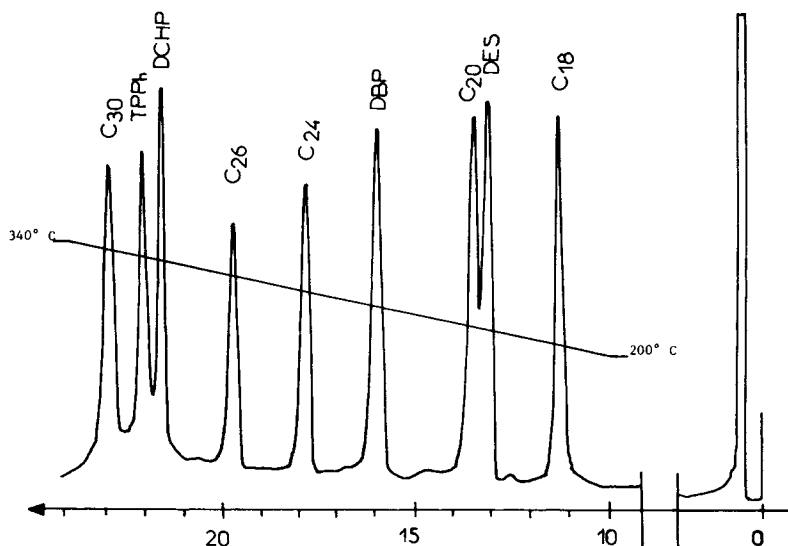
Fig. 3. OV 17 column. Chromatography with programmed temperature of plasticizers and alkanes: $b = 10°C/min$; $T_{init} = 100°C$; $T_{end} = 340°C$.

EXPERIMENTAL

Apparatus

An F7 gas chromatograph (Perkin–Elmer) and an IGC 16 one (Intersmat) equipped with temperature programming and fitted with a FID detector; a potentiometric two-channel Recorder Servotrace (SEFRAM) (the first channel for the chromatogram, the second for temperature); and a stainless steel column 2 m long, 3 mm internal diameter were used.

The characteristics of stationary phases are shown in Table I. It is shown that $4\eta L^2/3K$, a parameter in which there is gas viscosity η and column permeability K. $N_g°$, is the gas mole number in the column while pressure is 1 absolute atmosphere. Silicone SE-30 is a methyl silicone (General Electric, U.S.A.); silicone OV-17 is a 50% phenyl, methyl silicone; silicone QF-1 is a 50% trifluoropropyl, methyl silicone (Dow Corning, U.S.A.); Tenax is a porous polymer based on 2,6-diphenyl-p-phenylene oxide (AKZO) (Holland). Carrier gas is Nitrogen U (Air Liquide, France).

Heating rate is $b = 10°C/min$. A preliminary study showed that the heating rate value permits at first to obtain a linear relation between the carbon number of paraffins and their retention temperature, and on the other hand to chromatograph all the plasticizers, the retention time of which is less than 30 min with all the columns.

TABLE I
Characteristics of Stationary Phases

Liquid phase	Solid support	Stationary phase weight,	$4\eta L^2/3K$ at 25°C, atm, sec	$N_g°\times10^3$, moles
SE 30 1.5%	Chromosorb Q 60–80 mesh	10.58 g	23.2	4
OV 17 2.5%	Chromosorb Q 60–80 mesh	9.55 g	16.67	4.9
Tenax 100%	Tenax	1.84 g	8.92	8.4

Initial temperature of columns: $T_0 = 100°C$ for SE30, OV 17, and QF 1; T_0 = 180°C for Tenax. These initial temperature values are suitable to allow the separation of higher volatile plasticizers.

Extraction Method of Plasticizers for PVC Compounds

PVC was prepared without solvent by a mass process (Lucovyl, Rhone Poulenc, France).

PVC–plasticizers mixtures were made by using the mixing apparatus. Plastograph (Brabender), at 130°C for 10 min. Then, the couple of forces was constant for the mixing motor. These mixtures were flattened into a 0.6-mm thin leaf, by using a laboratory calender (Camil, France), the two rollers of which were heated to 140°C.

Extraction method of plasticizers was as follows: (1) Solution of PVC + plasticizers mixtures by using an equivolume solution of acetone and carbon disulfide. (2) Precipitation of PVC alone by addition of methanol, while plasticizers remained in solution. (3) Separation of the remaining solution, evaporation of solvent, and new solubilization of plasticizers in benzene. Addition of convenient weights of internal standards (normal paraffins).

RESULTS

We successively established the values of solution thermodynamics constants of plasticizers in our different stationary phases; the values of retention temperatures and retention indices of plasticizers when chromatographed with our method; and finally, we determined the relative error in our quantitative analysis results made for several mixtures.
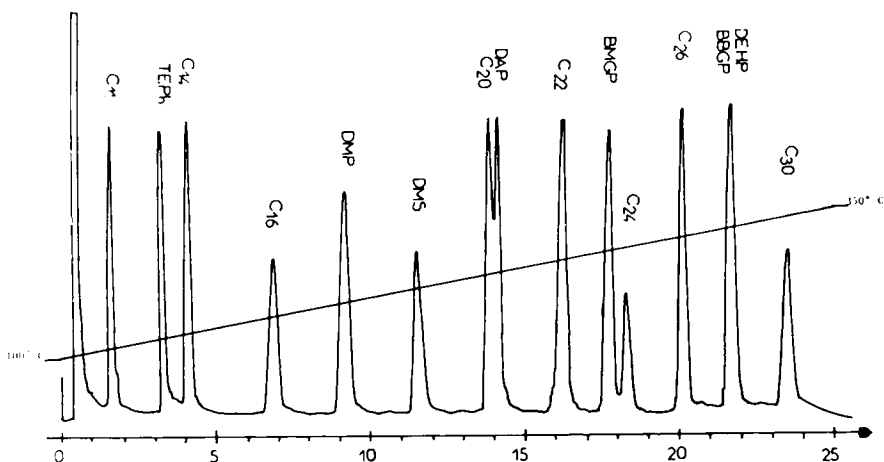

Fig. 4. OV 17 column. Chromatography with programmed temperature of plasticizers and alkanes: $b = 10°C/min$; $T_{init} = 100°C$; $T_{end} = 340°C$.
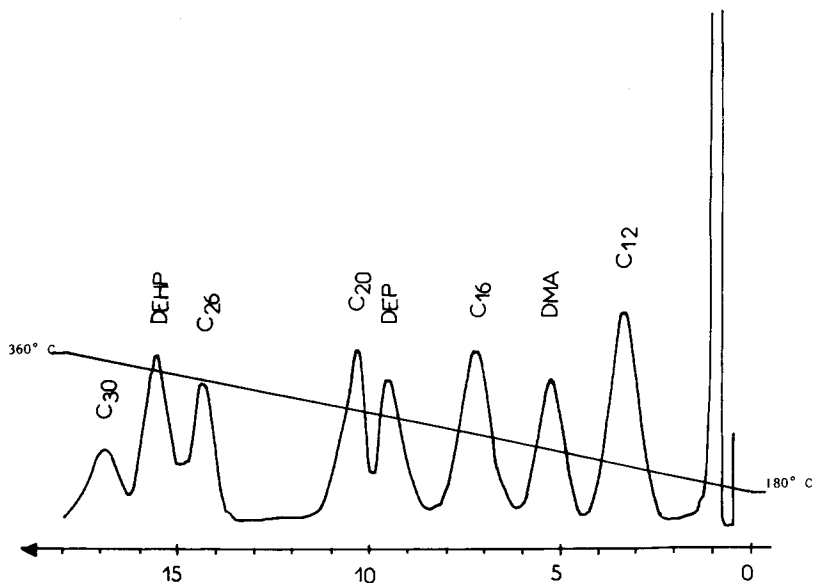
Fig. 5. Tenax column. Chromatography with programmed temperature of plasticizers and alkanes: $b = 10°C/min$; $T_{init} = 180°C$; $T_{end} = 360°C$.

Solution Thermodynamic Constants of Plasticizers

The solute retention times were expressed for isothermal chromatography by eq. (2) in terms of thermodynamic constants of solution. By measuring the retention time at different temperatures, we could easily obtain the standard molar partial enthalpy of solution $\overline{\Delta H_v^0}$ and the values of A expressed by eq. (3). Both of these thermodynamic values were quite constant throughout the temperature range between 100° and 330°C. These values are shown in Table II for the different stationary phases.

Remember that according to eq. (3), A varies proportionately with the mole number of the solvent and consequently with the solvent weight deposited in the column. The A values were measured for the values of solvent weights gathered in Table I. Equation (3) is suitable when the solvent percentage is between 1% and 10%.

The relative error enthalpy values $\overline{\Delta H_v^0}$ is generally less than 4%, and it is less than 7% for A.

Retention Values for Plasticizers with our Method

The main characteristics of our chromatography method with programmed temperature are described in the experimental section.

Retention temperatures of plasticizers were calculated by using (6) and a pocket calculator, and the solution thermodynamic values are shown in Table II. Retention indices were determined with the help of eq. (8). The calculated retention indices coincided with the experimental values, with a relative error of less than 0.9% for SE 30 and OV 17 and 1.7% for Tenax.

We summarized in Table III the retention temperature and retention index values measured by using our method. For the different plasticizers, the relative error of the retention indices was better than 0.6% for SE 30 and OV 17 and 1%

TABLE II
Solutions' Thermodynamic Values for Plasticizers

Solute	Symbol	Boiling temperature, °C		SE 30		OV 17		Tenax		QF 1	
				ΔH°_v, cal/mole	$A \times 10^6$	ΔH°_v, cal/mole	$A \times 10^6$	ΔH°_v, cal/mole	$A \times 10^7$	ΔH°_v, cal/mole	$A \times 10^7$
Trimethyl phosphate	TMPh	196	(21)	9,100	8.19	9,400	17.30	13,500	3.00		
Triethyl phosphate	TEPh	215	(21)	10,600	4.15	11,300	6.76	18,900	0.11		
Dimethyl adipate	DMA			10,400	12.00	11,700	7.70	15,100	7.37		
Dimethyl phthalate	DMP	280	(23)	11,400	9.35	12,800	5.13	16,500	6.19	13,300	19.20
Diethyl phthalate	DEP	296	(23)	11,900	9.38	13,900	2.74	18,700	1.06	14,200	9.59
Dimethyl sebacate	DMS	290	(23)	12,700	4.07	14,100	2.09	18,800	0.89	14,900	4.60
Tributyl phosphate	TBPh	180_{20}	(23)	12,600	4.90	13,900	2.67	18,400	1.01	15,400	3.31
Diallyl phthalate	DAP	290		12,900	4.67	14,800	1.71	22,200	0.09	15,200	5.14
Dibutyl adipate	DBA	150_{14}	(22)	13,400	2.80	14,600	1.53	20,100	0.29	14,800	7.40
Diethyl sebacate	DES	305	(23)	13,900	1.85	14,800	1.37	19,200	0.74	15,000	5.47
Dibutyl phthalate	DBP	325	(23)	14,300	2.22	15,800	1.27	20,200	0.74		
Bis(methyleneglycol) phthalate	BMGP	235_{20}	(22)	14,800	1.44	16,500	0.79	21,000	0.59		
Triphenyl phosphate	TPPh	260_{20}	(23)	15,900	0.16	18,100	0.49				
Dioctyl adipate	DOA	250_{20}	(22)	16,300	1.03	18,800	0.13	23,800	0.05		
Bis(butyleneglycol) phthalate	BBGP	250_{20}	(22)	15,900	1.81	18,800	0.32	21,300	1.48		
Dicyclohexyl phthalate	DCHP	225_4	(22)	16,600	1.11	19,800	0.15	21,300	2.06		
Dioctyl phthalate	DOP	265_{20}	(22)	16,900	0.89	21,100	0.19	21,000	1.00		
Dioctyl sebacate	DOS	284_4	(23)	18,700	0.29	18,800	0.37				

TABLE III
Retention Temperature and Retention Indices with Programmed Temperature

Solute	SE 30		OV 17		Tenax		QF$_1$	
	T_r, °C	I_r	T_r, °C	I_r	T_r, °C	I_r	T_r, °C	I_r
TMPh	107	854	124	1110				
TEPh	125	1091	143	1285				
DMA	140	1205	160.5	1426	200	1384		
DMP	165	1425	189	1705	234	1842	172	1971
DEP	181.5	1558	205.5	1884	240.5	1928	183	2110
DMS	186	1619	205	1863	239.5	1884	184	2106
TBPh	186.5	1623	204	1865	237	1865	193.5	2195
DAP	195	1708	215	2022	255	2091	194	2242
DBA	199	1731	206.5	1942	244.5	1955	195	2225
DES	200	1759	211.5	1962	246.5	1998	193	2221
DBP	218	1930	232.5	2201	265	2312		
BMGP	219.5	1954	244.5	2352	282	2481		
TPPh	258	2359	283	2841	Remains in column			
DOA	260.5	2382	261	2543	285	2526		
BBGP	265	2438	281	2856	319	2985		
DCHP	268.5	2472	291	2919	330	3126		
DOP	272.5	2519	280	2807	299	2732		
DOS	294	2778	297	2995				

for Tenax. The peak width, expressed in terms of retention index units, was about 25 for SE 30 and OV 17 and 90 for Tenax.

Thus, all plasticizers shown in Table II were completely separated by using the three stationary phases each in turn (Table IV). Both the plastizers dimethyl sebacate and tributyl phosphate could not be separated by using any one of the three stationary phases SE30, OV 17, and Tenax. We used a fourth stationary phase with 2.5% silicone, polymer QF1, to obtain the separation of both plasticizers and under the same operational conditions ($T_0 = 100°C$, $b = 10°C/$ min).

Solute	Retention index, retention index units
Dimethyl sebacate	2106
Tributyl phosphate	2195
Peak width	25

To illustrate our results, we showed several chromatograms corresponding to the first three stationary phases: SE30, OV17, and Tenax. With the last one, we could find the separation of dimethyl sebacate and tributyl phosphate obtained by using the fourth stationary phase with QF 1.

TABLE IV
Nonseparated Plasticizers when Using the Three Stationary Phases

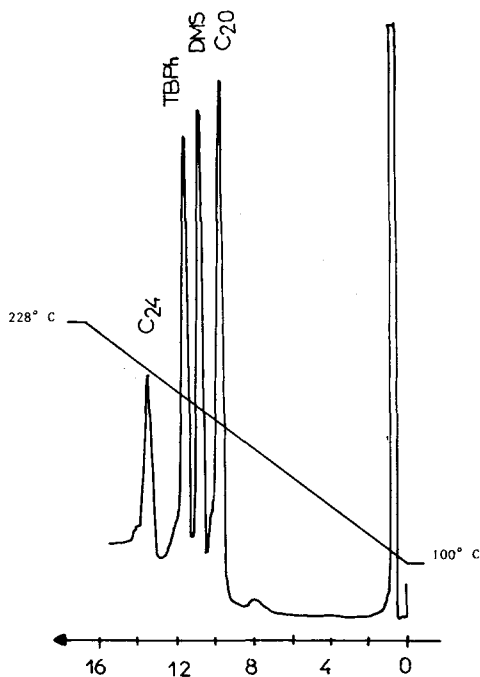| Stationary phase	Retention index	Plasticizers
SE 30	1619–1623	dimethyl sebacate and tributyl phosphate
OV 17	1863–1865	dimethyl sebacate and tributyl phosphate
Tenax	1884–1865	dimethyl sebacate and tributyl phosphate

Fig. 6. QF 1 column. Chromatography with programmed temperature of plasticizers dimethyl sebacate, tributyl phosphate, and alkanes: $b = 10°C/min$; $T_{init} = 100°C$.

Quantitative Analysis of Plasticizers from PVC Compounds

Plasticizers were analyzed by using our chromatographic method and our own extraction method with an internal standard whose retention is about that of the plasticizer.

Quantitative analyses were made with several plasticizer PVC compounds which contained different additives: stabilizer (Sandovar, VSU), lubricating wax PA 130 (Hoechst), chalk, carbon black such as Regal SRF and Monarch 1300 (Cabot), and pigment such as Lexrot G (Bayer).

Experiments done on dioctyl phthalate from the different mixtures showed that it was possible to find the percentage of introduced plasticizers with a relative error less than 2% from plasticizer mixtures, 3% from plasticizer–PVC compounds, and 3% from plasticizer–additive–PVC compounds.

CONCLUSIONS

Our chromatographic method allows the separation and identification of the different plasticizers from PVC compounds. This method involves a chromatography with programmed temperature, the initial value of which is low enough (100°C), working with three stationary phases of quite different polarity. By using the retention indices with the help of normal paraffins, we obtained an accurate identification, despite variation of experimental parameters, such as temperature and gas speed.

We introduced a calculation method for retention temperatures and retention indices which requires only a small pocket calculator. We presented the values of solution thermodynamics for plasticizers according to the different stationary phases.

Thus, by using this quick and accurate calculation method, and our own values of solution thermodynamics for plasticizers, one can easily carry out a preliminary calculation to obtain the best operational conditions for resolving his own problem concerning plasticizers.

References

1. S. J. Lewis and H. W. Patton, in *Gas Chromatography*, V. J. Coates, H. J. Noebbels, and I. S. Fagerson, Eds., Academic, New York, 1959.
2. C. D. Cook, E. J. Elgood, E. S. Schaw, and D. H. Solomon, *Anal. Chem.*, **34**, 1177 (1962).
3. J. C. Courtier, Chromatogr. Method. Immed. Sep. Prod. Meeting, Athens, 1965.
4. Y. Hoshi, S. Tani, G. Akazomand, and K. Murai, *Yukagaku*, **17**, 461 (1968).
5. F. J. Zulaica and G. Guiochon, *Bull. Soc. Chim. Fr.*, 1242 (1963).
6. S. Dal Nogare and L. W. Safranski, *Anal. Chem.*, **30**, 894 (1958).
7. G. Norwitz and J. B. Apatoff, *J. Chromatogr. Sci.*, **9**(11), 682 (1971).
8. D. T. Burns, W P. Hayes, and P. Steele, *J. Chromatogr.*, **103**, 241 (1975).
9. G. G. Esposito, *Anal. Chem.*, **35**, 1439 (1963).
10. A. Krishen, *Anal. Chem.*, **43**, 1130 (1971).
11. L. Veres, *Kunststoffe*, **59**(4), 13 (1969).
12. P. J. Bloom, *J. Chromatogr.*, **72**, 35 (1972).
13. P. J. Bloom, *J. Chromatogr.*, **75**, 261 (1973).
14. P. J. Bloom, *J. Chromatogr.*, **115**, 571 (1975).
15. M. H. Guermouche and J. M. Vergnaud, *J. Chromatogr.*, **58**, 169 (1971).
16. W. E. Harris and H. W. Habgood, *Programmed Temperature Gas Chromatography*, Wiley, New York, 1966.
17. K. Abdeddaim, R. Granger, and J. M. Vergnaud, *J. Chromatogr.*, **89**, 139 (1974).
18. H. W. Habgood and W. E. Harris, *Anal. Chem.*, **36**, 663 (1964).
19. E. Kovats, *Helv. Chim. Acta*, **41**, 1915 (1958).
20. S. A. Taleb-Bendiab and J. M. Vergnaud, *J. Chromatogr.*, **107**, 15 (1975).
21. H. Guinot, *Solvants et Plastifiants*, Dunod, Paris, 1948.
22. B. A. S. F., *Der Weichmacher*, Ludwigshafen, R. F. A., 1957.
23. J. Jousset, *Matieres Plastiques*, Vol. 1, Dunod, Paris, 1968.