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SEPARATION AND QUANTITATIVE DETERMINATION OF TRIMETHYLOLPROPANE AND PENTAERYTHRITOLS IN INDUSTRIAL SYNTHESIS SOLUTIONS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

Technical synthesis solutions have been analyzed for their contents of trimethylolpropane and mono- and di-pentaerythritols by means of high-performance liquid chromatography. By using water as eluent, trimethylolpropane solutions were successfully chromatographed on four different columns, namely, Corasil II, Merckosorb SI 60, Cyano Sil-X-I and μBondapak C_{18}. Pentaerythritol solutions were chromatographed on a μBondapak C_{18} column with water as mobile phase. Detection was accomplished by a refractive-index monitor. The methods have been applied to the direct determination of trimethylolpropane, monopentaerythritol and dipentaerythritol in technical synthesis solutions, no sample treatment (except for dilution with distilled water) being necessary. The methods are rapid, accurate, reproducible and easy to perform; they represent a considerable saving in time and labour in comparison with gas chromatographic methods now in use.

INTRODUCTION

Trimethylolpropane (TMP) and mono- and di-pentaerythritols (MPE and DPE, respectively) are important starting materials for the manufacture of plastics. everal chromatographic methods have been proposed for the analysis of technical ynthesis solutions containing these and other types of polyhydric alcohols, as well s their derivatives[1]. Gas chromatography has been widely used, especially for the nalysis of pentaerythritols[2–5], but also for that of TMP[6]. Because of their low olatility, it is necessary to convert the polyhydric compounds into lower-boiling ters or ethers by acetylation or silylation; this method of determination has the sadvantages of being time-consuming and of introducing uncertainty through loss incomplete conversion.

A direct assay of technical synthesis solutions of TMP and MPE was desired. odern high-performance liquid column chromatography (HPLC) should be well ited to this purpose because of its speed and high resolution capability. Liquid olumn chromatography has been applied to the separation of various types of polyydric alcohols[7], among them TMP[8] and erythritol[9–12]. Preferred methods are adsorption chromatography on silica[8,9] and partition chromatography using ion-exchange resins[10–12]. Drawbacks of the latter method, however, are the long elution times and high temperatures that are generally required. Paper and thin-layer chromatography have also been used for the separation of a number of polyhydric alcohols[13,14], but these methods are less suited to quantitative analysis.

In the present work, quantitative HPLC of TMP and pentaerythritols in technical synthesis solutions has been performed on two types of columns, *viz.*, adsorption columns containing silica (Corasil II and Merckosorb SI 60) and partition columns with chemically bonded stationary phases (Cyano Sil-X-I and μBondapak C_{18}). Although all of the columns were suitable for the analysis of the TMP synthesis solution, only the C_{18} column gave sufficient resolution of the compounds present in the pentaerythritol synthesis solution. In all instances, water was used as mobile phase, and the substances were monitored by a refractive-index detector.

EXPERIMENTAL

Apparatus

A Varian 4100 liquid chromatography pump was used throughout the investigation. The detector was an LDC (Laboratory Data Control) Refractomonitor of the Fresnel type.

Columns

Corasil II (Waters Ass., Frankfurt/M, G.F.R.) was dry-packed in precision-bored columns (0.5 m × 2.6 mm) according to the procedure described by Kirkland[15]. Two such columns were connected by means of low-dead-volume unions. Silica gel (Merckosorb SI 60; 10-μm particles; E. Merck, Darmstadt, G.F.R.) was packed in a 0.2 m × 2.6 mm precision-bored stainless-steel column by a balanced-density-slurry packing technique as described by Majors[16]. The Cyano Sil-X-I column (0.5 m × 2.6 mm; 13 μm particles; Perkin-Elmer, Norwalk, Conn., U.S.A.) and the μBondapak C_{18} (0.3 m × 4.2 mm; 10 μm particles; Waters Ass.) were delivered pre-packed from the manufacturers.

Reagents, standards and samples

Distilled water was used as eluent; de-gassing was accomplished by means of a water-ejector for 15 min. The standards and the synthesis solutions of TMP and pentaerythritol were obtained from Perstorp AB (Perstorp, Sweden); the purity of the standards was 96–99% and they were used without further purification.

Conditions and procedure

The column parameters and performance are shown in Table I.

Standard solutions (2–7 mg/ml) of TMP and pentaerythritols were made up in distilled water, and the standard curves were obtained by injecting 3–5-μl portions of the solutions. All quantitative analyses were made on the basis of peak-height measurement in order to simplify the procedure.

The TMP synthesis solution was diluted 1:25 with distilled water, and 3-μl portions of this solution were injected on to the columns. For the determination of MPE, the pentaerythritol synthesis solution was diluted 3:50 with distilled water,

TABLE I

COLUMN PARAMETERS AND COLUMN PERFORMANCE

Column	*Flow-rate (ml/h)*	*Linear velocity (cm/sec)*	*Pressure drop (kp/cm²)*	*Capacity factor, k'_{TMP}*	*HETP (mm)*
Corasil II (1.0 m × 2.6 mm)	20	0.3	20	0.3	0.50
Merckosorb SI 60, 10 μm (0.2 m × 2.6 mm)	10	0.1	20	0.4	0.14
Cyano Sil-X-I, 13 μm (0.5 m × 2.6 mm)	20	0.2	45	0.7	0.44
μBondapak C_{18} (0.3 m × 4.2 mm)	20	0.06	20	2.2	0.04

and 4 μl of this solution was injected on to the μBondapak C_{18} column. For the determination of DPE, the synthesis solution was injected directly on to the column without prior dilution. All analyses were performed at ambient temperature (23 ± 2°).

RESULTS AND DISCUSSION

Separation of trimethylolpropane on silica

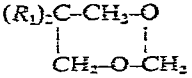
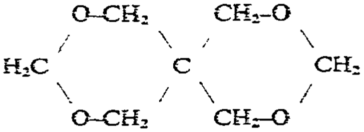
Silica gel is predominantly used as stationary phase in liquid chromatography in combination with eluents that are non-polar or of medium polarity. In combination with polar solvents such as ethanol and water, silica gel provides a fairly non-selective system. For the adsorption of polar molecules, *e.g.*, polyhydric alcohols, on to a hydroxylated silica surface, the only important adsorption sites are surface hydroxyl groups[17], which interact with adsorbed molecules by hydrogen bonding. Three different types of surface hydroxyl groups are usually distinguished, namely bound, free, and reactive hydroxyl groups, with the site strength increasing in the order mentioned. On severe deactivation of silica by water, all reactive hydroxyl groups are selectively covered[17], thus leaving a surface of bound and free hydroxyl groups, which give little contribution to the retention. In a system with silica as stationary phase and water as mobile phase partition of the adsorbate between the aqueous mobile phase and the adsorbed water may also contribute to the retention.

TMP is manufactured by condensation of butyraldehyde with formaldehyde. The main impurities in the synthesis solution are sodium formate, neopentyl glycol (NPG), di-TMP and TMP-monoformal (TMF)[18]; the structures of these solutes are shown in Table II. Fig. 1 shows the chromatogram obtained for a TMP-synthesis solution on a 1-m column of Corasil II; the peaks were identified against the retention imes of known reference compounds. Peak 1 is due to sodium formate, and peak 2 o TMP. Peak 3, which slightly interferes with the TMP peak, is due to NPG, peak 4 o di-TMP, and peak 5 probably to TMF (unfortunately, a reference sample of TMF as not available for identification). At a flow-rate of 20 ml/h, the HETP was 0.50 mm Table I), and no significant change in column performance was observed during a eriod of about 5 months, during which 500 injections were made on the column. n Table III, the variations in HETP, retention time and asymmetry factor (A_s) of he peak for TMP are listed as a function of the injection number.

To check the purity of the TMP peak, it was repeatedly collected, and the esulting solution was gently evaporated and injected on to three other columns

TABLE II

STRUCTURES OF SOME COMPOUNDS PRESENT IN SYNTHESIS SOLUTIONS OF TMP AND MPE

Compound	*Structure*	*Radicals*
Trimethylolpropane (TMP)	$CH_3CH_2C(R_1)_3$	R_1: $-CH_2OH$
Bis-trimethylolpropane (di-TMP)	R_2-O-R_2	R_2: $-CH_2C(R_1)_2CH_2CH_3$
TMP-monoformal (TMF)	$R_2-O-CH_2-O-R_2$	
Neopentyl glycol (NPG)	$CH_3C(R_1)_2CH_3$	
Monopentaerythritol (MPE)	$C(R_1)_4$	
Dipentaerythritol (DPE)	R_3-O-R_3	R_3: $-CH_2C(CH_2OH)_3$
Tripentaerythritol (TPE)	$R_3-O-CH_2C(R_1)_2CH_2-O-R_3$	
Bis-pentamonoformal (PMF)	$R_3-O-CH_2-O-R_3$	
Cyclic pentamonoformal (CMF)		
Cyclic pentadiformal (CDF)		

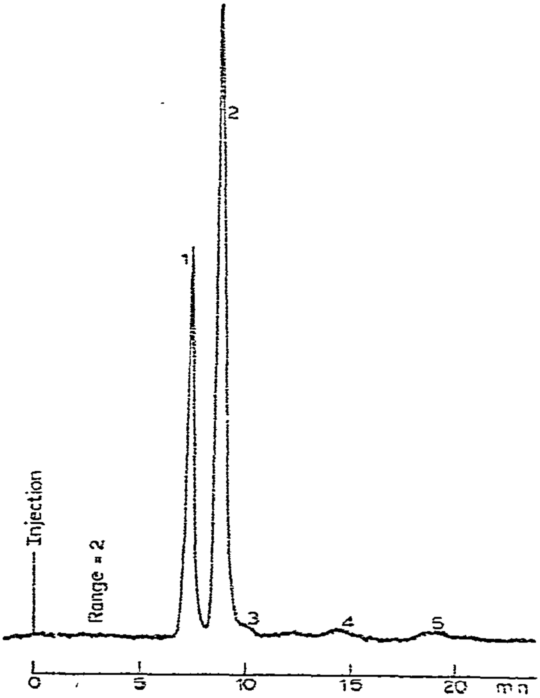


Fig. 1. Separation of components in a TMP-synthesis solution. Column: Corasil II, 1 m × 2.6 mm. Mobile phase: water (20 ml/h). Injected sample diluted 1:25 with water. Peak identity: 1 = sodium formate; 2 = TMP; 3 = NPG; 4 = di-TMP; 5 = unknown.

TABLE III

VARIATION IN PERFORMANCE OF CORASIL II COLUMN

The column was operated with a flow-rate of 20 ml/h and a linear velocity of 0.26 cm/sec.

Month	*Run No.*	t_R *(sec)*	*HETP (mm)*	*Asymmetry factor* (%)*
Sept.	23	542	0.51	71
Sept.	65	550	0.49	71
Oct.	163	547	0.51	72
Nov.	220	540	0.51	67
Nov.	330	535	0.51	69
Dec.	410	540	0.50	70
Jan.	500	540	0.51	70

* This factor (A_r) is given by the expression $100a/b$ %, where a and b are the distances (at a height of $h/10$ from the baseline) from the vertical line through the peak max. to the front and back lines of the curve, respectively.

(Merckosorb 10 µm, Cyano Sil-X-I and µBondapak C_{18}); no peaks except the one corresponding to TMP were obtained on any of the chromatograms, thus indicating that the separation on Corasil II was sufficient for quantitative assay.

The use of water as eluent has several advantages, especially in combination with a refractive-index detector. The low refractive index of water provides good detector sensitivity, while the relatively high values of viscosity and heat capacity contribute to excellent baseline stability, both short-time noise and long-range drift being minimal. Other solvents were also tested as mobile phase, *e.g.*, methanol, methanol–water, diethyl ether, acetone and ethyl methyl ketone–water–acetone (85:10:5), but none gave satisfactory results as regards baseline stability and sensitivity.

A separation of the compounds in the TMP-synthesis solution equally as good as on Corasil II was achieved on a 0.2-m micro-particle silica column (Merckosorb SI 60, 10 µm). Although this column was tested during a period of only 3 weeks, the stability should be similar to that of the Corasil II column; the HETP was determined to be 0.14 mm at a linear velocity of 0.1 cm/sec (Table I).

Retention of the compounds in the TMP-synthesis solution on the silica column is probably due to a combination of adsorption and partition. TMP, for nstance, has three hydroxyl groups that can interact with the surface hydroxyl groups of silica. Partition of the solutes between the aqueous mobile phase and adsorbed water probably contributes to the retention, although the adsorbed water does not xist as a distinct liquid boundary phase, but rather as a gradient of more or less trongly held water molecules.

onded-phase chromatography

Cyano Sil-X-I column. This column contains a polar stationary phase hemically bonded to a modified silica support; the polar groups are nitrile groups. The chromatogram of the TMP solution is shown in Fig. 2, from which it can be seen that separation between TMP and sodium formate is better on this column than on silica, partly because of the increased retention of TMP ($k' = 0.7$, Table I). The

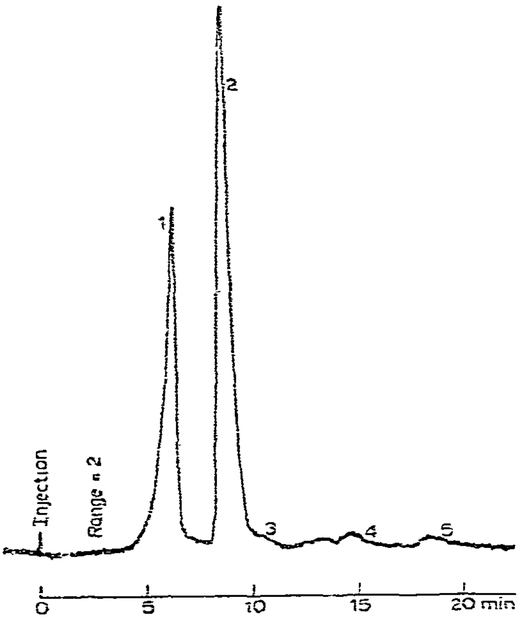


Fig. 2. Separation of components in a TMP-synthesis solution. Column: Cyano Sil-X-I, 0.5 m × 2.6 mm. Mobile phase: water (20 ml/h). Injected sample diluted 1:25 with water. Peak identity: 1 = sodium formate; 2 = TMP; 3 = NPG; 4 = di-TMP; 5 = unknown.

elution order is the same as on the silica columns, *i.e.*, sodium formate, TMP, NPG and di-TMP.

μBondapak C_{18}. This is a packing material consisting of porous micro-particles with a chemically bonded, non-polar stationary phase. It has been used for the separation of a wide variety of both polar and non-polar compounds[19]. Fig. 3 shows typical chromatograms of the TMP-synthesis solution with water as mobile phase; it can be seen from Fig. 3a that NPG does not interfere with the peak for TMP, as it did on the silica columns (Fig. 1). The increased retention of the solutes on the non-polar stationary phase is noteworthy considering their high solubility in water. Partition effects of the non-polar part of the TMP molecule and adsorption effects between the solute and the surface layer of the packing material may contribute to the retention.

The distorted band shape ($A_s \approx 20\%$) of the peak for TMP can be avoided by adding a few percent of methanol to the mobile phase, which would also cause a decrease in retention and thereby shorten the time of analysis. However, the tailing did not affect the quantitative measurements, as the chromatogram was very reproducible and repeated injections of the TMP standard gave exactly the same peak height. In order to investigate whether or not a second compound was present in the peak for TMP, repeated TMP fractions were collected and, after evaporation, the solution was chromatographed on the other columns. No indication of the presence of other compounds was found.

Care should be taken when applying this system to the analysis of TMP solutions, as di-TMP is not eluted from the column (Table IV). As the concentration of di-TMP was very low in this instance and the column capacity was high, the

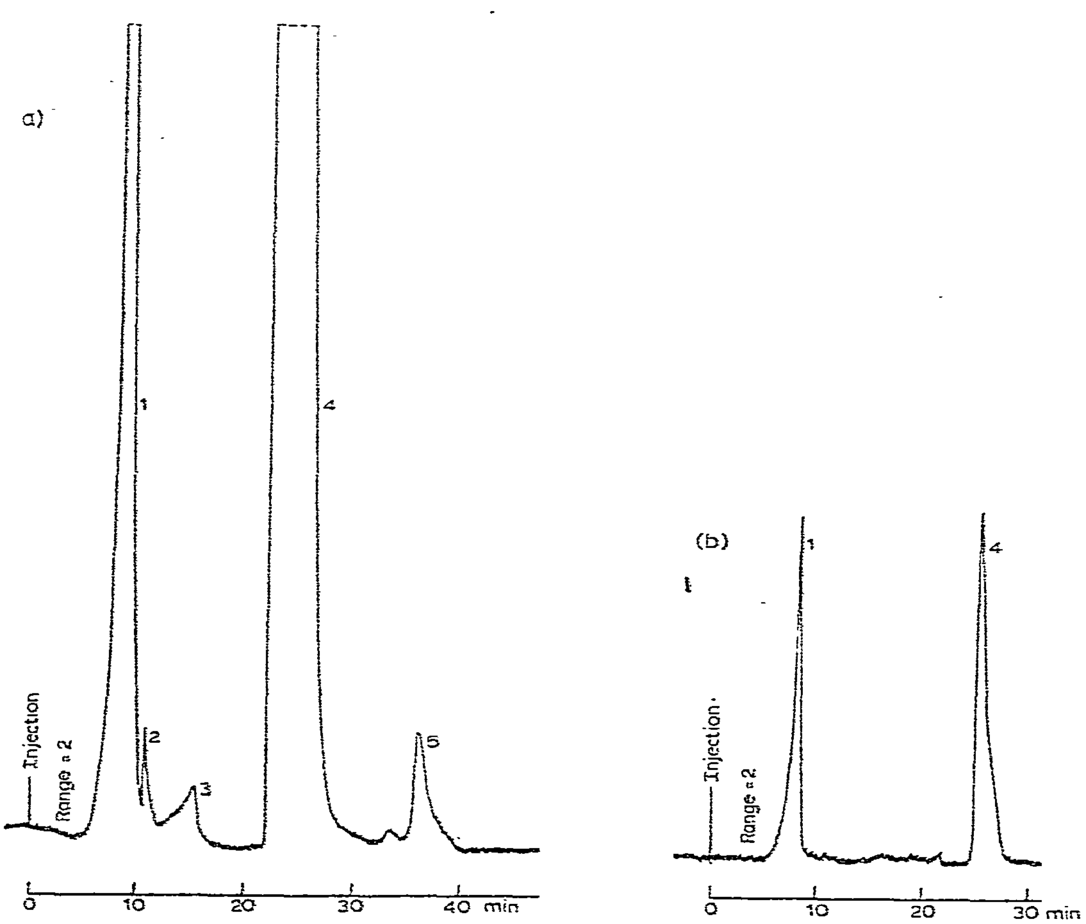


Fig. 3. Separation of components in a TMP-synthesis solution. Column: μBondapak C_{18}, 0.3 m × 4.6 mm. Mobile phase: water (20 ml/h). Peak identity: 1 = sodium formate; 2 = and 3 unknown; 4 = TMP; 5 = NPG. (a), No sample dilution, 3 μl injected; (b), sample diluted 1:25 with water, 3 μl injected.

c lumn performance was not affected during the course of this work. Should a change i column performance be observed, which could be due to non-eluted di-TMP or milar retained compounds, the column could easily be regenerated (for example, using a stronger eluent, such as methanol). Column efficiency was excellent, as is own in Table I, the HETP being 0.04 mm under the prevailing conditions.

The μBondapak C_{18} system was also successfully used for the separation of mpounds in pentaerythritol-synthesis solutions. Fig. 4 shows a chromatogram obned for a prepared mixture of some of these components. Pentaerythritols are nufactured by alkaline condensation of acetaldehyde and formaldehyde; the main -products are DPE, tripentaerythritol (TPE), bispentamonoformal (PMF), cyclic ntamonoformal (CMF) and cyclic pentadiformal (CDF) (see Table II). Depending the choice of reaction conditions, the main product, MPE, will become more or s contaminated with by-products. The chromatograms in Fig. 5, for instance, were

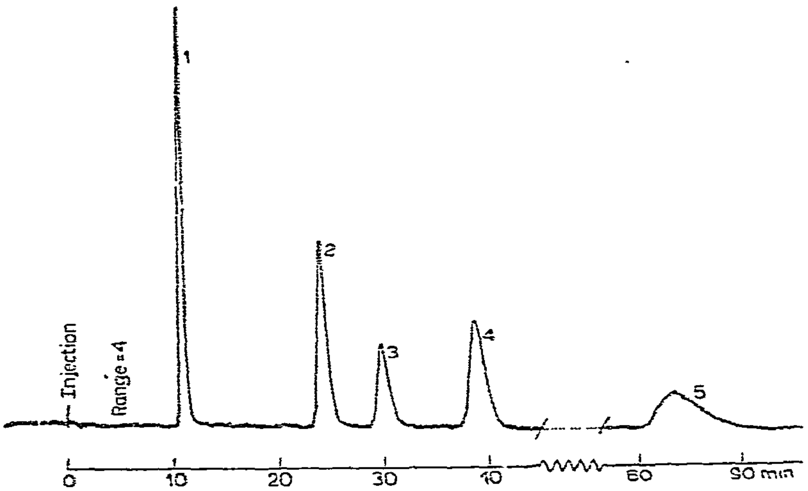


Fig. 4. Separation of a mixture of some products formed in the manufacture of MPE. Column: µBondapak C_{18}, 0.3 m × 4.6 mm. Mobile phase: water (20 ml/h). Peak identity: 1 = MPE; 2 = CMF; 3 = DPE; 4 = PMF; 5 = CDF.

obtained from a technical synthesis solution for which the conditions were chosen to give the maximum amount of MPE without regard to the amount of by-products formed. The chromatograms in Fig. 6, on the other hand, were obtained from a technical solution where the main interest was to obtain MPE free from DPE. This, of course, affects the yield. The identification of the peaks in the chromatograms was only made by retention times; as many other by-products are formed in the process, the identification is somewhat uncertain. For instance, the relatively high peak (No. 4), which in Fig. 6 has been ascribed to acetaldehyde, may be due to an unknown by-product.

In Table IV, relative retention values for the compounds are summarized for the four different HPLC systems. For the pentaerythritols, there is a correlation between solubility in water and retention on µBondapak C_{18}. The solubilities of MPE and DPE at 20° are 7.2 and 0.22 g/100 g of water, respectively[20], while TPE is practically insoluble at ambient temperature (0.5 g/100 g of water at 100°). The relative retention increases with decreasing solubility. This correlation, however, is not applicable to CMF and PMF, which are very soluble in water ($>$30 g/100 g water at ambient temperature), but are quite strongly retained on the column, and, in spite of the high solubility of TMP in water (70 g/100 g), this solute is retained on the column much more than is MPE. This can be explained by the presence of the alkyl chain in the TMP molecule, which may contribute to retention by partition effects. In the MPE molecule four hydroxymethyl groups symmetrically surround the central carbon atom, thus leaving little possibility for non-polar interaction with the stationary phase.

There is no general agreement concerning the retention mechanism in bonded-phase chromatography, although it has been discussed by several authors[21–25]. Thus, Snyder and Kirkland[22] suggested that the retention on the Du Pont bonded phase (Permaphase) involved liquid–liquid partition between the mobile phase and a sol-

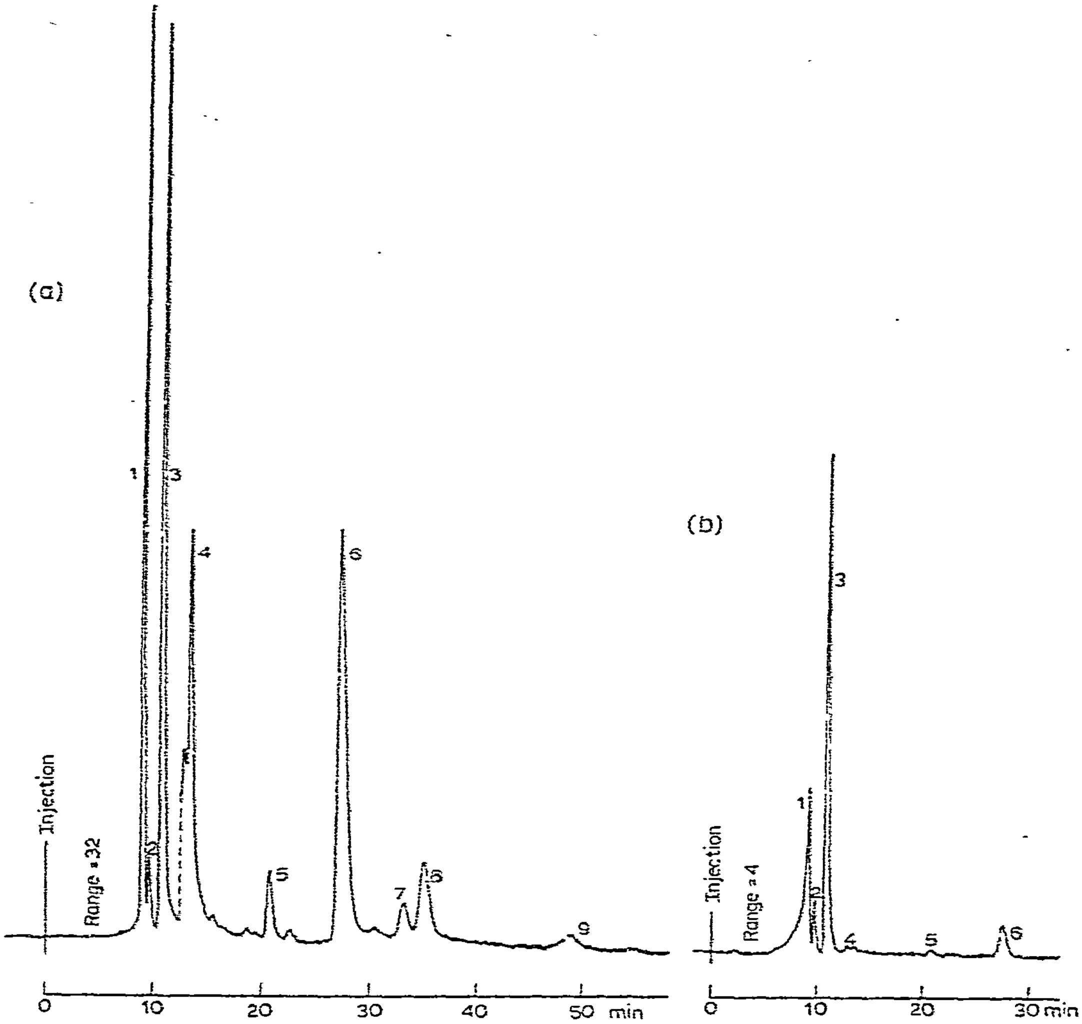


Fig. 5. Separation of components in technical pentaerythritol solution (TP-1165). Column: μBondapak C_{18}. Mobile phase: water (20 ml/h). Peak identity: 1 = sodium formate; 2 = formaldehyde: 3 = MPE; 4 = acetaldehyde; 5 = CMF; 6 = DPE; 7 = unknown; 8 = PMF; 9 = unknown. (a), no sample dilution, 4 μl injected; (b), sample diluted 3:50 with water, 4 μl injected.

ted gel network, which functions as the stationary phase. However, adsorption fects can play a role in some systems. Telepchak[23] proposed a separation mechanism volving reversed-phase adsorption chromatography on a chemically bonded hydro-rbon phase (Sil-X-II R.P.). Locke[24] claimed that chemically bonded phases should considered as highly modified adsorbents and that selectivity was primarily deter-ined by the solvent, while Pryde[25] preferred to call this kind of chromatography quid–solid partition chromatography, as the interactions resemble those found in quid–liquid partition chromatography. As residual Si–OH groups may remain on e surface of the support, ordinary adsorption effects can contribute to retention[26].

The increase in retention of and resolution between polyhydric alcohols when

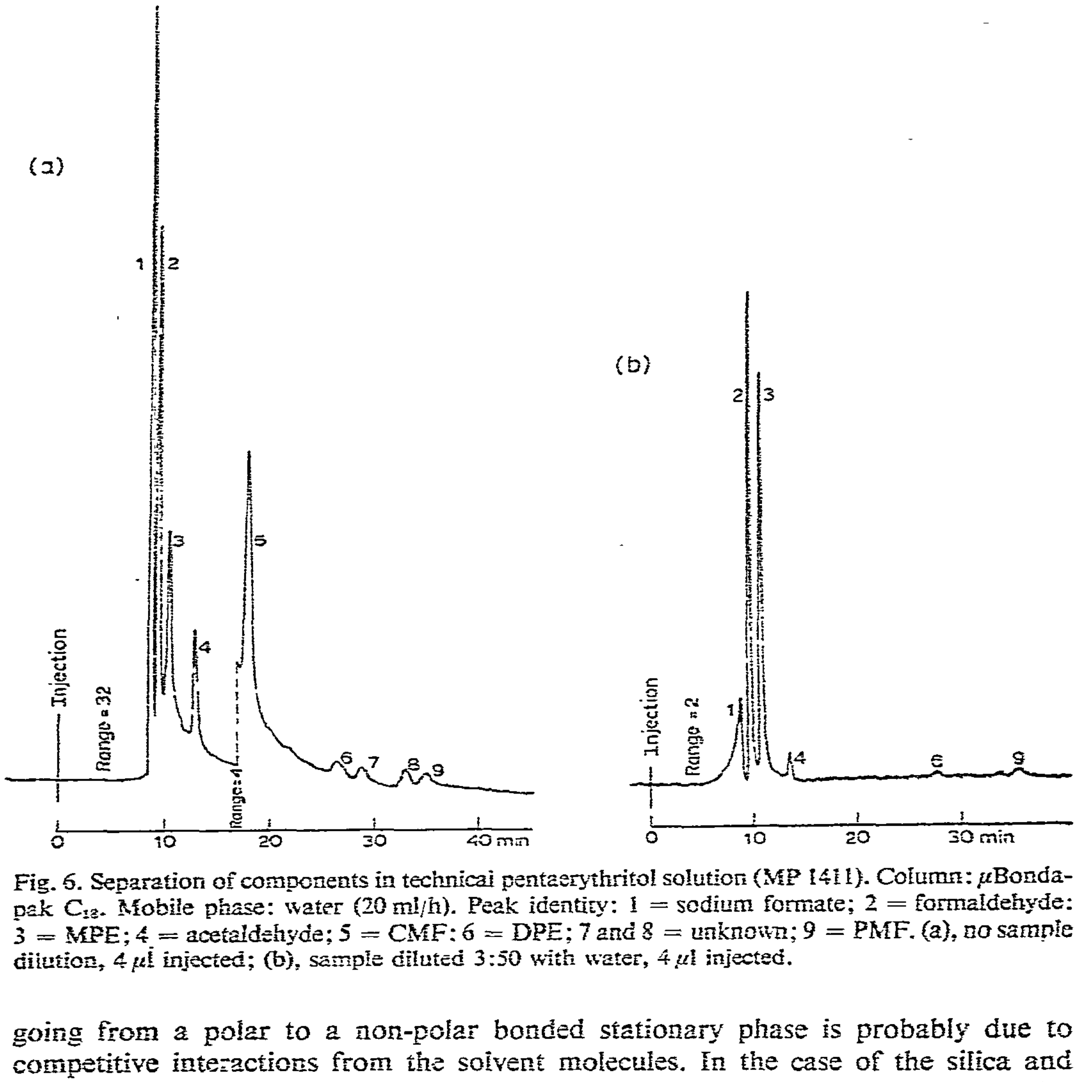


Fig. 6. Separation of components in technical pentaerythritol solution (MP 1411). Column: μBondapak C_{18}. Mobile phase: water (20 ml/h). Peak identity: 1 = sodium formate; 2 = formaldehyde: 3 = MPE; 4 = acetaldehyde; 5 = CMF: 6 = DPE; 7 and 8 = unknown; 9 = PMF. (a), no sample dilution, 4 μl injected; (b), sample diluted 3:50 with water, 4 μl injected.

going from a polar to a non-polar bonded stationary phase is probably due to competitive interactions from the solvent molecules. In the case of the silica and nitrile phases, which interact with the solute molecules with predominantly polar forces[27], the mobile phase (water) competes with the solute molecules for the active polar sites, thus leaving few contributions for solute retention. Assuming that the non-polar stationary phase interacts with predominantly dispersive forces, there will be no similar competition from the solvent molecules, *i.e.* the main part of the dispersive forces can be exploited for retention of the solutes. This results in stronger retention and improved selectivity compared with the polar stationary phases. The molecular size plays an important role in the retention of the solutes, *viz.* for similar compounds the retention increases with increasing molecular size. This holds good for the components in the chromatograms in Figs. 4–6.

Quantitative determinations

All quantitative determinations were based on peak-height measurements.

TABLE IV

RELATIVE RETENTION VALUES OF SOME COMPOUNDS PRESENT IN SYNTHESIS SOLUTIONS OF TMP AND MPE

*Solute**	*Column***			
	μBondapak C_{18}	*Corasil II*	*Merckosorb SI 60*	*Cyano Sil-X-I*
TMP-synthesis solution				
Sodium formate	0.7–0.8	0.89	0.89	0.86
Trimethylolpropane (TMP)	2.37	1.09	1.13	1.18
Neopentyl glycol (NPG)	3.12	1.13	1.25	1.37
Bis-trimethylolpropane (di-TMP)	∞	1.88	1.90	2.22
MPE-synthesis solution				
Formaldehyde	0.90	—	—	—
Monopentaerythritol (MPE)	1.00	1.00	1.00	1.00
Acetaldehyde	1.20	—	—	—
Cyclic pentamonoformal (CMF)	2.32	1.08	1.13	1.18
Dipentaerythritol (DPE)	2.88	1.03	1.03	1.01
Bis-pentamonoformal (PMF)	3.74	1.01	1.02	1.01
Cyclic pentadiformal (CDF)	7.88	—	—	—
Tripentaerythritol (TPE)	∞	—	1.07	1.12

* For the structures of the compounds, see Table II.

** For the column conditions, see Table I.

This method gave reproducible results with syringe injection, provided that the column pressure did not exceed 25–30 kp/cm^2. This condition was fulfilled for the Corasil II, Merckosorb, and μBondapak C_{18} columns under the conditions used (see Table I). To obtain reproducible quantitative results on the Cyano Sil-X-I column with syringe injection, it would be necessary to decrease the pressure by decreasing the flow-rate. This is possible without seriously increasing the analysis time.

Trimethylolpropane. The quantitative determinations of TMP were primarily performed on the Corasil II column and to some extent on the μBondapak C_{18} column. The standard curve for TMP on the Corasil II column was rectilinear, with good correlation within the range investigated (3–200 μg, Fig. 7). The accuracy and precision of the method for prepared mixtures of sodium formate and TMP are shown in Table V.

In Table VI are shown the results obtained on Corasil II from 10 different c terminations of TMP in a technical synthesis solution; the analyses were evenly s read over a period of 5 months. The mean value for TMP was 133.0 mg/ml with a standard deviation of 1.4 mg/ml. Two determinations of TMP on the μBondapak C$_8$ column gave the result 131.0 ± 0.2 mg/ml. This value is 1.5% lower than the r an value obtained on the Corasil II column. Unfortunately, the true value is u known, as there is no other reliable method available for the determination of T IP. As the separation on the μBondapak C_{18} column is better, it is believed that t s value is the most representative, and that the higher value on the Corasil II c umn arises from the interference of NPG, Fig. 1.

Pentaerythritols. For the quantitative determination of MPE in technical synt sis solutions, the samples were diluted with distilled water and injected on to the μ ondapak C_{18} column. For the determination of DPE, the sample was injected

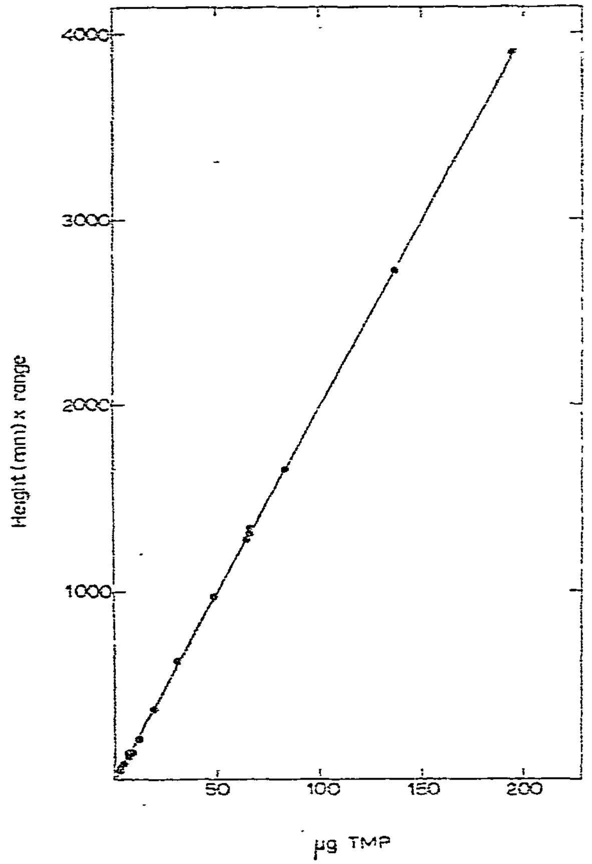


Fig. 7. Standard curve (peak height *vs.* amount injected) for TMP. Column: Corasil II. Mobile phase: water (20 ml/h). Pressure: 10 kp/cm^2.

TABLE V

QUANTITATIVE DETERMINATION OF TMP IN PREPARED MIXTURES ON A CORASIL II COLUMN

Actual conc. (mg/ml)	*Determined conc. (mg/ml)*	*Error (%)*	*Relative standard deviation (%)*	*Number of injections*
5.557	5.558	±0.0	0.9	5
8.274	8.370	+1.2	1.1	6
4.936	4.909	−0.6	0.5	4

without prior dilution. Table VII shows the results obtained for MPE and DPE in the two solutions (Figs. 5 and 6). For comparison, the manufacturer's results (obtained by gas chromatography) are included. In the technical solution TP-1165 (Fig. 5) the DPE concentration is high enough to allow accurate determination by means of a standard curve. In the technical solution MP-1411 (Fig. 6), however, the DPE concentration is very low and, although a standard-addition method based on peak-area measurement was used in this instance, the accuracy of determination is

TABLE VI

QUANTITATIVE DETERMINATION OF TMP IN TECHNICAL SYNTHESIS SOLUTION ON A CORASIL II COLUMN

Run No.	*Correlation for standard curve*	*TMP conc.* (mg/ml)*
1	0.999	134.6
2	0.999	132.3
3	0.999	134.0
4	0.999	135.7
5	0.997	133.6
6	0.999	131.5
7	0.997	131.9
8	0.998	131.7
9	0.998	132.0
10	0.997	133.0
		Mean 133.0 ± 1.4

* Mean of at least three injections.

TABLE VII

QUANTITATIVE DETERMINATION OF MPE AND DPE IN MANUFACTURED SYNTHESIS SOLUTIONS ON A μBONDAPAK C_{18} COLUMN

Batch	*Compound*	*Determined conc. (%)*	
		*This method**	*GC method*
TP 1165	MPE	7.87 ± 0.03	7.11
	DPE	1.13 ± 0.01	1.06
MP 1411	MPE	6.51 ± 0.06	6.60
	DPE	0.2–0.4	0.27

* Mean of three injections.

not satisfactory. As the HPLC values were obtained 4 months later than the gas chromatographic results, and as the solutions are unstable, complete agreement between the two sets of values cannot be expected.

CONCLUSIONS

HPLC has been used for the quantitative determination of TMP, MPE and DPE in technical synthesis solutions. TMP was successfully chromatographed on our different columns with water as mobile phase, while MPE and DPE were sepaated and determined on a μBondapak C_{18} column with water as mobile phase. Detection was by means of a refractive-index detector, which, in combination with water as mobile phase, provides excellent sensitivity and baseline stability. Quantiative determinations were based on peak-height measurements and standard curves. he relative standard deviation in the determination of TMP in technical solutions was 1.1%, while the mean relative error for prepared mixtures was ± 0.6%. Results or the determinations of MPE in technical solutions were in good agreement with those of a conventional gas chromatographic method. The proposed HPLC methods are rapid, accurate, easy to perform and suitable for routine analysis of TMP and MPE in synthesis solutions.

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