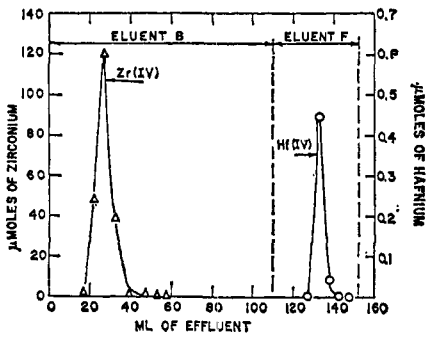

Figure 5. Separation of approximately 250 μmoles of zirconium and 0.5 μmole of hafnium on 1.4 × 50 cm. column

Eluent *F* is aqueous 1.0*M* sulfuric acid

as the hydroxides, ignited, and analyzed by our spectrographic laboratory. These analyses showed that the zirconium oxide contained less than 0.01% hafnium and that the hafnium oxide contained less than 0.01% zirconium.

Behavior of Other Cations. Experiments with single elements showed that molybdenum(VI), tin(IV), and zinc(II) are extracted into MIBK; these elements fail to breakthrough in 300 ml. when added to a 1.4 × 50 cm. column and eluted with eluent *B*. Although iron(III) is partly extracted, some iron breaks through in the 20- to 30-ml. fraction when eluted with eluent *B*. Behavior of several other elements can be predicted from the distribution ratios between MIBK and eluent *B* or aqueous 4*M* ammonium thiocyanate (see Table IV). The elements not extracted or only slightly extracted should accompany zirconium in the column separation. Cobalt(II) is strongly extracted and should stay on the column with hafnium(IV). Titanium(IV), which is approximately 35% extracted, may well appear partly in the zirconium and partly in the hafnium fraction.

Table IV. Distribution Coefficients for Batch Extraction of Various Elements from Aqueous Thiocyanate Solution into MIBK

Element	Distribution ratio: 4*M* NH_4SCN–0.2*M* $(NH_4)_2SO_4$	Distribution ratio: 4*M* NH_4SCN
Al(II)	~0	~0
Ca(II)	~0	~0
Cd(II)	0.02	~0
Ce(IV)	~0	~0
Co(II)	22.6	18.7
Cu(II)	0.06	0.05
Mg(II)	~0	~0
Mn(II)	~0	0.02
Pb(II)	...	~0
Nd(III)	~0	~0
Ni(II)	0.01	~0
Sm(III)	~0	~0
Th(IV)	0.03	...
Ti(IV)	0.54	0.51
V(IV)	0.03	~0

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Gas Chromatographic Separation and Determination of Pentaerythritol System by Trimethylsilyl Ether Derivatives

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▶ A new gas chromatographic method for analyzing the complete pentaerythritol system is presented. The method is based on the trimethylsilyl ether derivatives of these polyhydroxy compounds. This procedure is not only shorter and simpler than the best previous method but also makes possible a more detailed analysis of commercial grades of pentaerythritol. Using this method with an internal standard, mono-, di-, tri-, tetra-, and pentapentaerythritol can be detected under easily obtainable conditions with a conventional instrument equipped with a thermal conductivity detector. Other components that have been definitively detected are pentaerythritol dicyclic diformal, pentaerythritol cyclic monoformal, and pentaerythrose. Additional peaks, which were detected, were tentatively assigned to the following derivatives: bis(pentaerythritol) monoformal, dipentaerythrose hemiacetal, pentaerythritol-dipentaerythritol monoformal, tris(pentaerythritol) diformal, and bis(dipentaerythritol) monoformal.

EXCELLENT BACKGROUND for the synthesis and analysis of pentaerythritol (PE) is provided in the ACS Monograph of Berlow, Barth, and Snow (*2*). Accepted chemical methods, such as the benzal method for PE and the acetylation method for hydroxyl groups, have long been known to be nonspecific as applied to PE analysis. A selective technique such as gas chromatography could provide this specificity, but because of inherent thermal instability above the melting points, the PE system cannot be chromatographed directly. Volatile derivatives such as the acetate esters, on the other hand, have been chromatographed (*11*). The general applicability of this time-consuming acetate method is somewhat limited, however, by the greatly reduced sensitivity of even the tripentaerythritol (triPE) peak and the failure to detect any components with a higher retention time than triPE in spite of the use of extreme instrument conditions. Trimethylsilyl (TMS) ethers are advantageous derivatives for

studying many active hydrogen systems by gas chromatography (*3–5, 8–10, 12*).

This paper is concerned with the formation and determination of TMS ether derivatives of the entire PE system including tetrapentaerythritol (tetraPE) and pentapentaerythritol (pentaPE), which have not been detected using the acetylation procedure. All the derivatives were formed quantitatively in 10 to 30 minutes depending on the amount of polypentaerythritols present in the sample; acetylation requires a 2.5-hour reflux even for monopentaerythritol (monoPE). In addition to having higher volatility, the TMS ethers are more thermally stable and are not easily hydrolyzed in the presence of excess reagent.

Formals of the PE system were also determined by this method, including a few having a longer retention time than triPE. Qualitative assignments were tentatively made where authentic samples were not available. These assignments were based upon such considerations as the possible component's molecular weight, theoretical number of available hydroxyl groups, relative probability of occurrence, and predicted peak temperature. Several grades of mono-, di-, and tripentaerythritol, and a synthetic blend of these components were analyzed. Precision and accuracy were determined for the analyses in the form of standard deviations and quantitative closures. A comparison was made of direct and by-difference analyses for the main sample component and results were related in some instances to other analytical data. Results show that through their TMS ether derivatives, commercial grades of the PE system and indeed any PE sample can be analyzed more easily and completely than previously.

EXPERIMENTAL

Apparatus. An F & M Model 300, 500, or 720 gas chromatograph was used. Each instrument was equipped with temperature programming, a thermal conductivity detector, and a Minneapolis-Honeywell recorder. A 4-foot analytical column was constructed from $^3/_{16}$-inch o.d. stainless steel (No. 316). The column was packed with 17 wt. % SE-30 silicone rubber liquid phase on 60- to 80-mesh Gas Chrom Z solid support. The column temperature was initially 125° C. The injection port and detector were maintained at 325° C. and the detector, which was equipped with W-1 filaments, was operated at 150 ma. Helium at 42 p.s.i. was used as the carrier at a flow rate of 100 ml. per minute. The sample size varied from 15 to 30 μl. The recorder (−0.2- to 1.0-mv. span, 1-second speed) was operated at varied sensitivities and a chart speed of 45 to 60 inches per hour.

Reagent. Mannitol (internal standard), $C_6H_{14}O_6$, m.p. 167° to 169° C. (Eastman Organic Chemicals Catalog No. 155), was used as received. Pyridine, reagent grade, b.p. 115° to 116° C. (Allied Chemical Co., General Chemicals Division, Code No. 2166), was dried over Molecular Sieve 5A before using. Trimethylchlorosilane (Silicone Division, Union Carbide and Carbon Corp., Code No. A-161) was carefully hydrolyzed with single drops of H_2O and mild swirling until rapid evolution of HCl subsided. The partially hydrolyzed reagent was distilled and the cut boiling at 57.7° C. was collected. Hexamethyldisilazane b.p. 125.0° to 125.6° C. (Applied Science Laboratories, State College, Pa.), was used as received.

Procedure. A 200-mg. sample of the PE mixture (100 mg. if large amounts of polypentaerythritols are expected) and 50 mg. of mannitol are weighed into a 50-ml. Erlenmeyer flask; 7 ml. of dry pyridine and 1 ml. of hexamethyldisilazane (HMDS) are added. The flask is placed on a hot plate in the hood and heated just under boiling for 10 minutes with intermittent gentle swirling. The flask and contents are cooled to at least 50° C. If the solution is not clear and free of solid particles, a few additional milliliters of pyridine are added and the flask is reheated and recooled. Two milliliters of distilled trimethylchlorosilane (TMCS) are added to the flask and the contents swirled for 2 to 3 minutes. This three- to fourfold excess of reagent minimized the possibility of partial etherification. The reaction mixture is then warmed to 70° to 80° C. on the hot plate, immediately removed and swirled for 1 minute, and allowed to cool to room temperature. The white precipitate of ammonium chloride and pyridinium chloride settles to the bottom of the flask where it does not interfere in sample transfer. With the chromatograph in operation and the column at 125° C., an aliquot of the etherified sample is introduced into the chromatographic column. The column temperature is programmed at a rate of 13° C. per minute to a maximum temperature of 326° C. and held isothermally for 3 minutes at 326° C. Other preferred program rates were 11° C. per minute (F & M Model 500) and 10° C. per minute (F & M Model 720). The peak areas are measured by triangulation (peak width at half-height is measured with an optical micrometer) and calibration factors are applied to obtain a weight % analysis.

Calibration and Calculation. The purest grade of commercial monoPE was used to obtain the response factor of PE. Sublimed fractions of dipentaerythritol (diPE) and triPE from impure mixtures were acetylated and the acetate esters were extracted with petroleum ether and fractionally recrystallized from acetone. The diPE hexaacetate and triPE octaacetate thus obtained were heated on a steam bath in an anhydrous methanol–sodium methoxide solution in a sealed tube. The cleaved polyhydric alcohols precipitate from the solution and can be filtered and washed with small portions of cold water and then with anhydrous methanol. The resulting diPE and triPE were heated in a 60° C. oven for 1 hour. The melting points of the final materials were 217° to 224° C. and 240° to 245° C., respectively. (There were a few crystals in both even at 264° C., probably due to traces of monoPE.) A sample of high purity reagent diPE was also used to corroborate the response factor assignments for mono-, di-, and tripentaerythritol, which were 0.91, 1.18, and 1.40, respectively. Pentaerythritol cyclic monoformal (PEMF) and pentaerythritol dicyclic diformal (PEDF) were synthesized by reacting PE with different amounts of formaldehyde under acid conditions. The products were isolated by recrystallization from acetone. Pentaerythrose (m.p. 127° to 128° C.), which was synthesized from tris(hydroxymethyl) acetic acid, was obtained from C. A. Armour, University of London (*1*).

Some of the other products associated with the PE system are difficult to isolate in large enough quantities to determine their retention times and factors directly. Their retention times can be estimated, however, by almost linear correlation between molecular weight and peak temperature of the known constituents. In addition, through the use of a series of simultaneous equations of the type

$$\left[\sum(\text{Area} \times F)_{\text{component}} = \text{Area}_{\text{mannitol}} \times \left(\frac{\text{weight}_{\text{sample}}}{\text{weight}_{\text{mannitol}}}\right)\right]$$

where $F_{\text{component}}$ is the only unknown, the contributions of any component to the weight of any sample as a whole can be estimated. The (Area × F) contribution of those components whose response factors were individually determined can be subtracted directly from the right side of the equation above leaving only those minor components whose response factors are truly unknown.

The absence of components known to elute above the last detectable impurity in a given sample was used as indirect assurance of the absence of nonvolatile matter which would be a source of error in calculating the response factors via the simultaneous equation route—e.g., a sample containing no tetraPE is not likely to contain any pentaPE. The response factors obtained in this way for these components were felt to be more realistic than those obtained by merely assigning factors of 1.00 to them. The actual identity of a particular minor peak determined in this way is tentative at best and may be in error—e.g., trisPE-DF may be the 307° C. or the 314° C. peak.

Also to be taken into consideration is the utilization of peak temperatures as an absolute value. Such assignments will necessarily require calibration when different equipment or operating conditions are employed. Synthetic blends and commercial samples were analyzed using the internal stand-

ard method. These analyses corroborated the response factor assignments which are listed in Table I. Different ratios of the PE components did not appear to alter these assignments and the factors could be used to convert peak area to weight %.

Response factors for mono-, di-, and triPE were also determined independently by making and isolating large quantities of their TMS ethers, which were then weighed directly. The monoPE derivative is a clear, colorless liquid at room temperature (b.p. 128° C. at 6 mm.). The derivatives of mannitol (b.p. 147° C. at 2 mm.) and triPE (b.p. 193° C. at 2 mm.) are also liquids, whereas the diPE derivative is a white crystalline solid (m.p. 47.0° to 49.8° C.). In using the TMS derivatives as standards, a conversion factor of the molecular weight of parent polyol divided by the molecular weight of its TMS derivative must be applied to the sample weight to determine the free polyol.

These factors for mono-, di-, and tripentaerythritol and mannitol are 0.322, 0.371, 0.394, and 0.294, respectively.

Table I. Components of Pentaerythritol System Assignments of Peak Temperatures and Response Factors

Component	Short-form abbreviation	TMS derivative, mol. wt.	No. of hydroxyls per molecule	Peak temp., ° C.	Response factor *F*
Pentaerythritol diformal (dicyclic)	PEDF	160.1	0	155–6	2.76
Pentaerythritol monoformal (cyclic)	PEMF	292.2	2	180–5	1.53
Pentaerythrose		350.3	3	188–90	1.42
Pentaerythritol	PE	424.4	4	193–6	0.91
Mannitol		620.6	6	239–43	1.00
Dipentaerythritol	DiPE	686.6	6	256–9	1.18
Bispentaerythritol monoformal[a]	BisPE-MF	716.6	6	263–6	1.20[b]
Dipentaerythrose hemiacetal[c]		700.6	6	275–6	1.30[b]
Tripentaerythritol	TriPE	948.8	8	300–3	1.40
Pentaerythritol-dipentaerythritol monoformal[a]	PE-DiPE-MF	978.8	8	307–9	1.45[b]
Trispentaerythritol diformal[a]	TrisPE-DF	1008.8	8	314–5	1.60[b]
Tetrapentaerythritol[d]	TetraPE	1211.0	10	326+	1.70[b]
Bisdipentaerythritol monoformal[a]	BisdiPE-MF	1227.0	10	326++	1.80[b]
Pentapentaerythritol[d]	PentaPE	1473.2	12	326+++	2.00[b]

[a] Assigned by mol. wt., no. of hydroxyl groups, and peak temperature.
[b] Assignments by simultaneous equation approximations.
[c] Pentaerythrose impurity (*1*).
[d] Assigned by extrapolation.

DISCUSSION

HMDS and TMCS are the reagents normally used together for the trimethylsilization reaction in the presence of pyridine as solvent. Some authors have tried these reagents separately or with other companion reagents. During the present study, the reagents used separately were less effective than when used together in etherifying even monoPE. Also, lower recoveries sometimes occurred if the TMCS was added to the sample before the HMDS. These lower recoveries were traced to impurities in the TMCS, particularly dimethyldichlorosilane (DMDCS), which is more reactive than TMCS. This results in lower response factors—e.g., 0.70 instead of 0.91 for monoPE—probably because of the formation of derivatives involving two hydroxyls and one DMDCS. The internal standard, mannitol, at times produced two peaks due to this phenomenon.

The DMDCS can be detected by a gas chromatographic (G.C.) analysis of the TMCS (*6*). If present, the DMDCS can be removed by careful hydrolysis (*7*) followed by distillation of the TMCS. The hydrolysis products, which would otherwise produce extraneous reagent-blank peaks, remain in the pot residue. TMCS pretreated in this way was used throughout the analytical procedure outlined above. The final method was checked on three different G.C. instruments with no apparent discrepancies detected in the results. All of the figures and most of the tabular data, however, pertain to the F & M Model 300 instrument. The chosen 13° C. per minute program from 125° to 326° C. gave the necessary resolution of component peaks and made a 20-minute analysis possible. Although at lower programming rates components would elute at nominally lower temperatures, unnecessarily long analysis times

Table II. Weight % Composition of Different Grades of Pentaerythritols via Single Gas Chromatographic Analysis

	Direct analysis of all components							
	Pentaerythritol		Dipentaerythritol				Tripentaerythritol	
Components detd.	Mono	Technical	Crude	Commercial	Cleaved hexaacetate	Reagent	Commercial	Cleaved octaacetate
PEMF	n.d.[a]	0.73	1.27	0.84	n.d.	n.d.	n.d.	n.d.
MonoPE	99.50	86.80	8.01	4.90	1.75	0.20	0.42	0.29
DiPE	0.46	10.55	69.60	84.90	94.00	96.60	3.26	0.49
BisPE-MF	n.d.	n.d.	n.d.	n.d.	2.00	n.d.	n.d.	n.d.
[b]	n.d.	0.14	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TriPE	n.d.	1.90	14.31	7.70	2.13	4.40	71.80	94.90
PE-DiPE-MF	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.52
TrisPE-DF	n.d.	n.d.	1.36	0.69	n.d.	n.d.	n.d.	n.d.
TetraPE	n.d.	Trace[c]	2.97	1.20	n.d.	n.d.	19.45	3.82
BisdiPE-MF	n.d.	n.d.	1.84	0.33	n.d.	n.d.	6.46	n.d.
PentaPE	n.d.	n.d.	0.42	n.d.	n.d.	n.d.	n.d.	n.d.
Wt. % recovery	99.96	100.12	99.78	100.56	99.88	101.20	101.39	101.02
	By-difference analysis of main component							
MonoPE	99.54	86.68	...	...	...	...	...	...
DiPE	...	...	69.82	84.34	94.12	95.40	...	...
TriPE	...	...	...	...	...	...	70.41	93.88

[a] Limit of detection = 0.05%.
[b] Dipentaerythrose hemiacetal.
[c] >0.05% but <0.10%.

would also result—e.g., at 4.6° C. per minute, the TMS derivative of triPE would elute in 35 minutes at 285° C.

The derivative of pentaerythrose, which elutes between PEMF and monoPE, is stable for only a few hours. It is, however, the only markedly unstable component in the pentaerythritol system, probably because of its available aldehyde functionality. Although pentaerythrose does not appear to be a common impurity, based on the samples analyzed, it can nevertheless be detected if the sample is analyzed within the first hour after making the TMS ethers. The loss in the pentaerythrose derivatives due to this instability is 18% after 1 day, 34% after 2 days and 58% after 1 week.

Concurrent with the loss of the 189° C. parent peak is a rise in a 266° to 269° C. peak which is in the region of the chromatogram corresponding to six hydroxyls per molecule. This new entity is similar to the diPE derivative, indicating the occurrence of some type of dimerization, but it has not as yet been isolated to confirm its structure because it is not a normal impurity but a product of the derivative.

An extrapolated plot was made of the log of the molecular weight of mono-, di-, and triPE as a function of the air-bath peak temperature during a special program from 125° to 364° C. The upper temperature limit of the column was purposely extended to obtain a peak temperature for a component of commercial triPE tentatively assigned as tetraPE. This measured peak temperature agreed exactly with the extrapolated value (334° C.) for tetraPE. During the normal program, this peak is referred to as $326^{+\circ}$ C. because it is the first peak off the column after the isothermal hold has been reached.

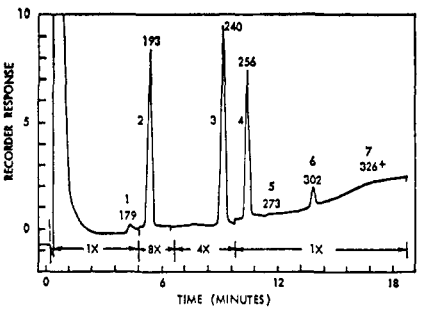

Figure 1. Analysis of technical pentaerythritol

TMS derivatives of:
1. Pentaerythritol cyclic monoformal
2. Monopentaerythritol
3. Mannitol
4. Dipentaerythritol
5. Dipentaerythrose hemiacefal
6. Tripentaerythritol
7. Tetrapentaerythritol

A second impurity in this sample eluted at 344° C. Its peak has been designated $326^{++\circ}$ C. during the normal run and has been ascribed to bisdiPE-MF. In addition to these two impurities, a sample of crude diPE contained a component which eluted at 361° C., the extrapolated peak temperature for pentaPE. This peak has been designated as $326^{+++\circ}$ C. during the normal run and has been ascribed to pentaPE. This peak has not been found, however, in any commercial PE samples. Its absence was used as an indirect assurance of the completeness of the TMS analysis under study and the absence of higher nonvolatile polyols in the sample.

By comparison, the acetates of mono-, di-, and triPE eluted at 217° C., 300° C., and 350° C., respectively, under the conditions of the same special run. A plot similar to that for the TMS derivative gave a straight line extrapolation of 390° C. and 423° C. for the acetates of tetra- and pentaPE, respectively. These higher elution temperatures for tetra- and pentaPE would explain their not being detected by the G.C. method using the acetylation procedure.

Qualitative assignments of all the detected peaks in the PE system are presented in Table I. Included are short form abbreviations for the components which appear to elute from the column according to the molecular weight of their TMS derivatives. Dipentaerythrose hemiacetal (*1*) appears to be the only exception. Structural considerations of its eight-member ring are thought to be the reason. Trends are also noted in the number of hydroxyl groups per molecule and the relative response factors.

Table II illustrates the scope of analyses possible with typical single analyses of different grades and types of PE. All the components are not found in any one sample. In fact, neither PEDF nor pentaerythrose have been detected (<0.05%) in any sample in large enough concentrations to really be certain of their presence. The total recovery of the sample components presented in Table II appears to justify the response factor assignments listed in Table I, and an inspection of the mono-, di-, and triPE ranges covered reveals the near independence of these response factors from concentration. As expected the largest deviations in recovery occur in the higher polyol samples. The main component in each sample was also determined by subtracting the impurities from 100%. These by-difference values are also noted for each sample in Table II, and usually compare favorably with the direct analysis results.

Table III. Precision of Gas Chromatographic Analysis of Pentaerythritols

Components detd.	Mono pentaerythritol A Wt. %	σ	Mono pentaerythritol B Wt. %	σ	Synthetic blend[a] of pentaerythritols Wt. %	σ	Technical pentaerythritol Wt. %	σ	Commercial dipentaerythritol Wt. %	σ	Reagent dipenta-erythritol Wt. %	σ	Commercial tripenta-erythritol Wt. %	σ
Direct analysis of all components														
PEMF	n.d.		n.d.		0.10	0.00	0.59	0.07	0.80	0.05	n.d.		n.d.	
MonoPE	98.20	0.50	99.07	0.60	89.92	0.67	86.17	0.40	4.82	0.10	0.10	0.05	0.42	0.05
DiPE	0.74	0.07	Trace	...	8.40	0.60	10.89	0.33	84.96	0.40	95.14	1.24	3.41	0.17
[b]	0.18	0.04	0.65	0.17	0.10	0.00	0.12	0.03	n.d.		n.d.		n.d.	
TriPE	0.25	0.09	Trace	...	0.85	0.05	1.78	0.07	7.30	0.30	4.71	0.26	71.35	0.96
TrisPE-DF	n.d.		n.d.		n.d.		n.d.		0.70	0.07	n.d.		n.d.	
TetraPE	n.d.		n.d.		n.d.		Trace		1.20	0.15	n.d.		19.08	0.55
BisdiPE-MF	n.d.		n.d.		n.d.		n.d.		0.30	0.05	n.d.		5.83	0.60
Wt. % recovery	99.37		99.72		99.37		99.55		100.08		99.95		100.09	
No. of detn.	6[c]		6[c]		6[d]		7[d]		5[c]		6[d]		5[d]	
By-difference analysis of main component														
MonoPE	98.83	0.14	99.34	0.15	90.55	0.61	86.42[e]	0.33	...		...		...	
DiPE	...		...		...		...		84.88	0.60	95.19	0.23	...	
TriPE	...		...		...		...		...		...		71.30	0.97

[a] Theoretical composition: MonoPE 90–91%, DiPE 8–9%, TriPE <1%.
[b] Dipentaerythrose hemiacetal.
[c] Aliquots of single weighing from single lot.
[d] Replicates of separate weighings from single lot.
[e] 0.20% H_2O also present; all others contain <0.1% H_2O.

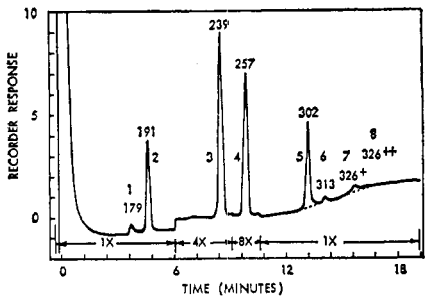

Figure 2. Analysis of commercial dipentaerythritol

TMS derivatives of:
1. Pentaerythritol cyclic monoformal
2. Monopentaerythritol
3. Mannitol
4. Dipentaerythritol
5. Tripentaerythritol
6. Trispentaerythritol diformal
7. Tetrapentaerythritol
8. Bisdipentaerythritol monoformal

Whereas a single diPE impurity peak is detected in a typical sample of monoPE, the sample of technical PE shown in Figure 1 contains four measurable impurities, of which the major is diPE. Figure 2 shows the chromatogram of a typical sample of commercial diPE. In this sample, triPE is the major impurity and the total number of impurities is six. Figure 3 shows the chromatogram of a typical commercial triPE. Four impurities are detected, the major being tetraPE (326+° C.). Mono- and diPE are also present, along with a peak attributed to bisdiPE-MF (326++° C.).

Except for Table II, the qualitative behavior of the TMS derivatives of the PE system has been emphasized to this point. Before general applicability can be claimed, the quantitative reproducibility of the method must be considered. These results, in the form of average weight percentages and standard deviations for the components of several types of PE, are presented in Table III. Data are presented for the analysis of six aliquots of two separately weighed samples of monoPE whose analyses by the benzal method indicated the two lots to be similar—i.e., 98.3% and 98.4%, respectively. The subtle differences between these samples, as revealed clearly by gas chromatography, involve low concentrations of diPE, dipentaerythrose hemiacetal, and triPE. By determining these impurities on a large sample and a large injection volume, meaningful by-difference values of monoPE can be calculated. As the monoPE concentration drops, so does the σ on an absolute basis.

Composition of a synthetic blend of monoPE and commercial diPE, as determined by direct analysis of six separately weighed samples, agrees well with the theoretical concentrations of mono-, di-, and triPE. PEMF and dipentaerythrose hemiacetal were also detected in this blend. As the concentration and number of impurities increases, as with the technical PE, the by-difference and direct methods tend to give similar results for the major component. This point is also illustrated by the five aliquots of a commercial diPE sample which were analyzed. At the higher concentration levels of diPE, the standard deviation of a direct analysis reflects not only the higher response factor of the diPE, but also the instrument and measurement parameters inherent in any direct gas chromatographic analysis. Commercial triPE also reflects this effect of a much higher response factor for a major component.

An overall comparison of the data in Table III indicates that the main component in the various samples can be determined with almost equal accuracy directly or by difference if enough mutiple analyses are done. If the main component alone is desired, a sample weight equal to that of the internal standard is advantageous, with both peaks being at the same attenuation. The impurities, on the other hand, are more accurately determined by using a larger sample, compared with the internal standard, and injecting a larger volume. With the usually lower standard deviation for the main component in the resulting by-difference analysis, fewer analyses are necessary.

As long as the low level of impurities in a sample is well defined, a by-difference analysis will have greater accuracy and precision. Our experience has been that the gas chromatographic analysis of the TMS ether derivatives, by virtue of their selectivity and reproducibility, offers a qualitative and quantitative method for determining the impurities in any PE sample. This method has been in use in three company laboratories for the past year.

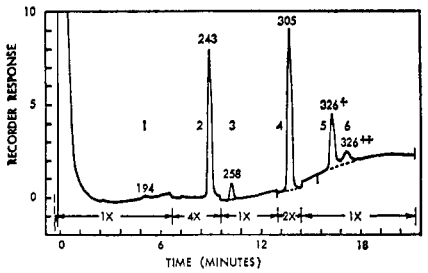

Figure 3. Analysis of commercial tripentaerythritol

TMS derivatives of:
1. Monopentaerythritol
2. Mannitol
3. Dipentaerythritol
4. Tripentaerythritol
5. Tetrapentaerythritol
6. Bisdipentaerythritol monoformal

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