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QUANTITATIVE DETERMINATION OF PENTAERYTHRITOL IN AQUEOUS SOLUTION

I. REPÁŠOVÁ, A. VANKO and J. DYKYJ
Research Institute of Petrochemistry, Nováky (Czechoslovakia)

SUMMARY

Mono-, di-, tri- and higher pentaerythritols are formed by aldol condensation of formaldehyde with acetaldehyde in alkaline medium, in addition to the formation of other organic compounds.

The conditions for the quantitative determination of monopentaerythritol in dilute aqueous solutions by gas–liquid chromatography were studied.

The method of silylation in aqueous solution was compared with the use of anhydrous reaction products. The greatest effects on the precision of the determination of pentaerythritol were caused by the silylation procedure and the presence and concentration of formaldehyde. A procedure for the elimination of the effect of formaldehyde on the precision and reproducibility of the determination of pentaerythritol was developed.

INTRODUCTION

In the application of gas chromatography to the analysis of organic compounds, the compounds must be sufficiently volatile and stable at high temperatures. It is therefore impossible to determine pentaerythritol as such and its four hydroxyl groups must be modified by acetylation or silylation[1–7]. The acetylation of the technical product proved to be convenient for chromatographic analysis[7] and Smith and Tullberg[8] evaluated both acetylation and silylation for this purpose. The advantages of silylation are the higher volatility of the products, a simpler and faster reaction and the possibility of using lower column temperatures. Suchanec[9] studied the composition of commercial pentaerythritol by the silylation method and found that pentaerythritol can include the pentaerythritol formals, higher pentaerythritols, pentaerythrose and dipentaerythrose hemiacetal. Weiss and Tambawala[10] extended the possibilities for the silylation of pentaerythritol in aqueous solution with simple silylating agents. In the present work, we used a modified silylation procedure for the study of the quantitative determination of monopentaerythritol in aqueous solution in the presence of formaldehyde and other condensation products with acetaldehyde.

EXPERIMENTAL

Apparatus

The work was performed on a Hewlett-Packard (Avondale, Pa., U.S.A.) research chromatograph, Model 5756 B, connected with an electronic integrator (Hewlett-Packard, Model 3370 A) and a printer.

Two stainless-steel columns, 220 cm long and I.D. 0.20 cm, packed with 3% (w/w) SE-30 on Chromaton N, AW DMCS, particle size 0.16–0.20 mm, were used. The instrument was equipped with a thermal conductivity detector. The carrier gas was pure helium at flow-rates of 52 and 62 ml/min in columns A and B, respectively. The column temperature was linearly programmed from 120 to 300° at the rate of 10°/min. The vaporizer was maintained at 230° and the detector was heated to 320°. The samples were introduced with a 10-μl Hamilton micro-syringe (Hamilton Bonaduz A.G., Switzerland).

Preparation of silylating agent

A small (*ca.* 1 ml) dry, heart-shaped flask, flushed with nitrogen, was closed with a plug of silicone rubber. One part of trimethylchlorosilane and two parts of hexamethyldisilazane were injected through the plug with separate dry syringes. The silylating agent thus prepared must be clear. The amount of silylating agent required is removed through the rubber plug with a syringe.

Preparation of internal standard solution

Dimethyl sulphoxide was used as the diluent. An appropriate amount was weighed into a dry flask and xylitol was added such that its concentration was about 1% (w/w).

Direct determination of pentaerythritol in aqueous solution

A 15-μl volume of aqueous pentaerythritol solution and 150 μl of internal standard (xylitol) in dimethyl sulphoxide were injected into the heart-shaped flask with a Hamilton micro-syringe, then 0.5 ml of silylating agent was added. The reaction mixture was shaken vigorously for about 1 min and then allowed to stand in order to separate into two layers. A sample for analysis was taken from the upper layer. The pentaerythritol concentration was determined by measuring the peak areas with the internal standard.

Determination of pentaerythritol after evaporation of water

A 3-μl volume of aqueous pentaerythritol solution was injected into the heart-shaped flask with a Hamilton micro-syringe and 2 μl or more of 25% ammonia solution were added until the solution changed colour to blue. The flask was agitated and the mixture was dried under vacuum and at laboratory temperature for 5–10 min. Then 15 μl of xylitol or mannitol, dissolved in dimethyl sulphoxide were added to the dried sample, which was left to stand for about 10 min and then shaken in order to dissolve the sample. A 45-μl volume of silylating agent was added, the flask was closed with a plug and immersed in a water-bath at 80° for 15 min with shaking from time to time. It was then transferred by means of a 10-μl syringe into the capillary, which was then closed. After a short time, the mixture separated into two layers. The upper layer

contained silyl ethers, diluted with dimethyl sulphoxide and a small amount of silylating agent, and the lower layer contained silylating agent only. A 2-μl volume of upper layer was taken for analysis.

RESULTS AND DISCUSSION

Comparison of "wet" and "dry" methods with two internal standards

Two methods of silylation of aqueous pentaerythritol with a standard silylating agent, with mannitol and xylitol as internal standards, were examined.

Mannitol gives two peaks with retention times of $Mt_{R1} = 615$ sec and $Mt_{R2} = 640$ sec by direct silylation of the aqueous solution. Their ratio is dependent on the time of reaction with the silylating agent. Peak Mt_{R2} increases after a longer time in contact with the silylating medium (24 h). Xylitol gives one peak only under the same conditions and it is therefore impossible to obtain a correct analytical result with mannitol by the direct "wet" silylation. The silylation of mannitol by the "dry" method is unambiguous and it is possible to use it as an internal standard, as can be seen in Table I.

TABLE I

DETERMINATION OF MONOPENTAERYTHRITOL IN AQUEOUS SOLUTION AFTER EVAPORATION OF WATER USING MANNITOL AS INTERNAL STANDARD

Silylation No.	*Pentaerythritol (t_R = 368 sec)*		*Mannitol: t_R (sec)*	
	*mVsec**	*g/100 ml*	*Mt_{R1} = 615 mVsec**	*Mt_{R2} = 640 mVsec**
1	1053	11.25	—	639
2	1054	10.87	—	446
3		10.92		
4		10.86		
5		10.64		
6		10.93		
7		10.92		
Average		10.91		

* Integrated peak.

A comparison of both methods showed that mannitol is not quantitatively silylated in the aqueous solution. The results are more reproducible in the "dry" method. Xylitol is more advantageous as an internal standard. Its structure is more similar to pentaerythritol, does not coincide with those of other compounds, its elution is faster than that of mannitol and it gives more reproducible results.

The rate of silylation of aqueous solutions by the "wet" and "dry" methods must be determined in order to obtain quantitative results. It is very important to eliminate free hydroxyl groups and this is achieved by ensuring that a relatively large excess of silylating agent, compared with potential amount of reacting hydroxyl groups, is present. It is impossible to prevent an irregular course of the silylation reaction in the presence of different compounds. The results of the reproducibility of silylation with time are shown in Table II.

The silylation reaction is virtually completed within 5 min. The rates of reaction in both silylation methods are approximately the same. The results are lower with a greater fluctuation in the "wet" method, but the reason for this is not clear.

TABLE II

SILYLATION RATES IN THE "WET" AND "DRY" METHODS

Model aqueous solution containing 4.67% (w/w) of pentaerythritol (MPE). Silylation temperature = 80°.

Sample No.	*Silylation time (min)*	*"Dry" method*		*"Wet" method*	
		MPE (%, w/w)	*Mean (%)*	*MPE (%, w/w)*	*Mean (%)*
1	5	4.67	4.66	4.37	4.19
1a*	5	4.66		4.01	
2	10	4.65	4.63	4.43	4.43
2a*	10	4.62			
3	15	4.61	4.58	4.39	4.34
3a*	15	4.56		4.29	
4	30	4.56	4.56	4.28	4.28
4a*	30	4.57			
5	45	4.75	4.70	4.01	4.17
5a*	45	4.65		4.34	

* Parallel silylations with equal amounts of sample.

The influence of temperature on silylation was studied at 50, 80 and 150°. The results are comparable and a temperature of 80° is sufficient for the silylation to proceed quantitatively. The composition of the silylating agent is suitable. The use of higher silylation temperatures is reasonable, with the occurrence of di- and higher pentaerythritols and other compounds formed by condensation.

Effect of formaldehyde on the determination of pentaerythritol in aqueous solutions

The study of the effect of formaldehyde was carried out with an aqueous solution of pure pentaerythritols with gradual additions of formaldehyde. The results are shown in Table III.

The explanation of the complicated effect of formaldehyde on the pentaerythritol concentration lies in the chemical properties of formaldehyde.

The aqueous formaldehyde solutions are mixtures of different compounds. Monomeric formaldehyde reacts with water to give methylene glycol, which is able to react with other formaldehyde molecules[11]. Formaldehyde is stabilized with methanol. It reacts with methanol to give pentaerythritol hemiformal. All these reactions are reversibile, so that in formaldehyde solutions, stabilized with methanol, anhydrous formaldehyde, its hydrate, hemiformal and polyoxymethylene derivatives formed by condensation with more formaldehyde molecules coexist. The concentration of the components is dependent on the formaldehyde and methanol concentration in the aqueous solutions, and on temperature and pH.

TABLE III

EFFECT OF FORMALDEHYDE ON THE DETERMINATION OF PENTAERYTHRITOL

*Sample No.**	*Amount (%, w/w)***					
	Added formaldehyde	*MPE*	*$MPEx_1$*	*$MPEx_2$*	*$MPEx_3$*	*$MPEx_4$*
S-1	0.0	4.68	—	—	—	—
S-2	2.0	4.02	0.29	0.12	—	—
S-3	5.0	3.35	0.82	0.29	—	—
S-4	7.5	2.37	1.18	0.64	0.05	—
S-5	10.0	0.82	1.11	1.12	0.77	0.45
M-1	0.0	4.96	—	—	—	—
M-2	2.0	4.70	0.17	—	—	—
M-3	5.0	4.24	0.64	—	—	—
M-4	7.5	2.94	1.58	0.21	—	—
M-5	10.0	2.84	1.58	0.27	—	—

* S = "dry" silylation method; M = "wet" silylation method.

** MPE = pentaerythritol; $MPEx_{1-4}$ = products of reaction of pentaerythritol with formaldehyde.

The course of the reaction of pentaerythritol with formaldehyde is analogous. The reaction products are more varied, because pentaerythritol contains four hydroxyl groups, and pentaerythritol mono-, di-, tri- and tetrahemiformals can be formed. The hemiformals can be formed not only with methylene glycol, but also with polyoxymethylene glycols, or both hydroxyl groups can react with one or two pentaerythritol molecules.

The hemiformals are reversibile compounds; they can exist only in solution and are stable only in equilibrium with other molecules.

Of course, the silyl ethers are stable compounds and their chromatographic separation is possible. They appear in the spectra as defined chemical compounds. This phenomenon is typical for reaction solutions containing formaldehyde and is characterized in both the "wet" and "dry" silylation methods. It can also be seen that the presence of water retards the rate reaction of pentaerythritol with formaldehyde, or silylation reactions, but does not interfere in them. The consecutive growth of by-product peaks and the pentaerythritol peak indicates an increasing molecular weight with a constant dependence on the ratio of the concentrations of pentaerythritol and formaldehyde.

A more detailed explanation of this phenomenon will be given later. It can be said that it is impossible to achieve quantitative results for the determination of pentaerythritol in aqueous solutions without the elimination of formaldehyde.

Blocking of pentaerythritol reaction with formaldehyde in quantitative analysis

It is known that formaldehyde reacts very rapidly with ammonia in aqueous solutions to give hexamethylenetetramine. We have studied the effect of ammonia on the determination of pentaerythritol in aqueous solutions in the presence of formaldehyde. The results are shown in Table IV and Fig. 1.

The results confirmed the favourable effect of ammonia on the determination

TABLE IV

EFFECT OF AMMONIA ON THE DETERMINATION OF PENTAERYTHRITOL IN THE PRESENCE OF FORMALDEHYDE

Model aqueous solution containing 4.1% (w/w) of pentaerythritol and 10% (w/w) of formaldehyde.

*Sample No.**	*Amount (%, w/w)*		*Notes*
	Ammonia solution	*Pentaerythritol*	
S-1	10	4.07	
S-2	20	4.05	
S-3	30	4.09	
S-4	40	4.08	
S-5	50	4.13	
S-6	60	4.26	
S-7	100	4.22	
S-8	100	4.05	Solution without formaldehyde
M-1	10	4.08	
M-2	20	3.98	
M-3	30	4.38	
M-4	40	4.18	
M-5	50	4.34	Solution is yellow
M-6	60	4.37	Solution is yellow
M-7	100	8.05	Solution is yellow
M-8	100	6.21	Solution without formaldehyde double peak of xylitol

* S = "dry" silylation method; M = "wet" silylation method.

of pentaerythritol and the existence of pentaerythritol hemiformals under equilibrium conditions in aqueous solution. All the formaldehyde bonded with pentaerythritol is released by changing the equilibrium by the rapid reaction of formaldehyde with ammonia, and pentaerythritol can be determined quantitatively. This is a "dry" method. Considerable fluctuations in the results were observed in the "wet" method

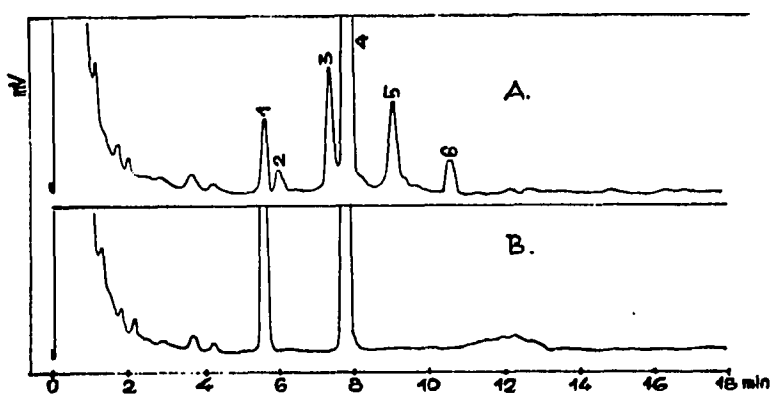

Fig. 1. Typical chromatogram of aqueous pentaerythritol solution in the presence of formaldehyde. Silylation by "dry" method: A, without ammonia; B, with ammonia. 1 = Pentaerythritol (MPE); 2 = $MPEx_1$; 3 = $MPEx_2$; 4 = xylitol (internal standard); 5 = $MPEx_3$; 6 = $MPEx_4$.

and in the presence of a large excess of ammonia there are indefinite results (xylitol with two peaks). The anomaly produced by the large excess of ammonia is not observed in the "dry" method. It can be explained by the vaporization of free ammonia.

Reproducibility of the method

The reproducibility of the "dry" method was calculated by determination of the sensitivity factor for pentaerythritol according to the procedure of the "dry" method described above. The results are shown in Table V.

TABLE V

REPRODUCIBILITY OF SENSITIVITY FACTOR (SF) FOR PENTAERYTHRITOL

Run	*SF*	$\Delta SF \cdot 10^{-3}$	$(\Delta SF)^2 \cdot 10^{-6}$	$\pm \sigma$	$\pm$ % *(relative)*
1	0.829	−6	36		
2	0.825	−2	4		
3	0.820	+3	9		
4	0.826	+3	9	$1.3 \cdot 10^{-3}$	0.15
5	0.821	+2	4		
6	0.820	+3	9		
7	0.825	−2	4		

CONCLUSIONS

Gas–liquid chromatography can be used for the determination of monopentaerythritol in aqueous solutions, after evaporation of water under vacuum and at room temperature, by silylation at room temperature or 80° in the presence of high-molecular-weight compounds. Reproducible and quantitative results are obtained after the addition of ammonia in the presence of formaldehyde. Xylitol is a suitable internal standard.

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