

Short communication

Quantitative determination of mono- and dipentaerythritol in synthesis solutions by high-performance liquid chromatography

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Abstract

A rapid and reliable high-performance liquid chromatographic method for the quantitative determination of monopentaerythritol (MPE) and dipentaerythritol (DPE) in the synthesis solutions was investigated. The method involved sample preparation by using hydrogen peroxide to eliminate the effect of excess formaldehyde on the precision and reproducibility of the determination of MPE and DPE. The separation was carried out on a Shim-Pack CLC-ODS column with water as mobile phase. Determination was accomplished by a refractive-index detector. © 1997 Elsevier Science B.V.

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1. Introduction

A reasonable simple, fast and reliable method for determining mono- (MPE) and dipentaerythritol (DPE) and related by-products is required for routine use in the synthesis of MPE and DPE. Several gas chromatographic methods have been reported for the analysis of pentaerythritol and its by-products from reaction liquors [1–4]. Because of their inadequate volatility, it is necessary to convert these polyhydric compounds into lower-boiling derivatives by esterification, silylation and peralkylation. These methods of derivatization have the disadvantages of being time consuming and of introducing uncertainty through loss by incomplete conversion.

Direct high-performance liquid chromatographic determination should be well suited for the determination of MPE and DPE in synthesis solutions.

Callmer [5] has reported a quantitative HPLC method for determining pentaerythritol in industrial synthesis solutions on an ODS column. Drawbacks of this method, however, are the long elution times and the effect of excess formaldehyde in the synthesis solutions. Formaldehyde will severely interfere with the chromatographic separation of MPE unless a very low flow-rate of mobile phase is used. In addition, each hydroxyl group of mono-, di-, and higher pentaerythritols has the potential to form a hemiformal in the presence of formaldehyde under normal reaction conditions. Simon [4] confirmed that the formaldehyde reacted with PE and DPE to form hemiformals by using GC-MS. Therefore, if formaldehyde is not completely removed from the analytical samples, it is very difficult to accurately and rapidly determine MPE and DPE in the synthesis solutions.

In the present work, we successfully used hydrogen peroxide to remove the excess formaldehyde and

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the resulting hemiformal species from the synthesis solutions and we investigated the quantitative determination of MPE and DPE in aqueous solutions by HPLC.

2. Experimental

2.1. Apparatus

Quantitative HPLC was performed on a Shimadzu LC-6A chromatograph (Japan) equipped with a RID-6A refractive-index detector and a CR-3A data processor. A Shim-Pack CLC-ODS (150 mm×4.6 mm I.D.) column was used with water as mobile phase at a flow-rate of 0.8 ml/min. The column temperature was 50°C.

2.2. Reagents and solutions

Newly distilled water was used as eluent; degassing was accomplished by means of a water-ejector for 10 min. MPE and DPE standards of mono- and di-pentaerythritol were obtained from Shanghai Chemical Supply Co. (Shanghai, China). The hydrogen peroxide used was 30% solution (analytical-reagent grade). Synthesis solutions were made by aldol condensation of formaldehyde with acetaldehyde in a 1.0:5.0 mol ratio at 35°C followed by a Cannizzaro reaction in alkaline medium at 60°C.

2.3. Sample preparation

A 2-ml volume of synthesis solution was taken from the synthesis reactor, then 20 ml of distilled water and 0.5 ml of 30% hydrogen peroxide solution were added, the solution was heated gently to boiling for 5 min, then the solution was adjusted to pH 8~9 and diluted to 100 ml with distilled water. After dry filtering, a 5- μ l aliquot was injected onto the chromatographic column.

2.4. Standard solutions

1.0~5.0 mg/ml MPE and 0.2~1.0 mg/ml DPE solutions were prepared in distilled water. The

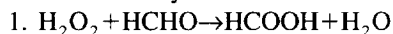
standard curves were obtained by injecting 5.0- μ l portions of the solutions. All quantitative analyses were made on the basis of peak-area measurement.

3. Results and discussion

3.1. Separation of synthesis solution

Initially, we investigated the chromatographic separation of untreated synthesis solution (sample diluted 1:50 with distilled water, dry filtered, 5.0 μ l injected). Fig. 1a shows the chromatogram. The identification of the peaks in the chromatogram was made by retention times of known reference compounds. Pentaerythritols are manufactured by aldol condensation of acetaldehyde and formaldehyde followed by a Cannizzaro reaction in alkaline medium; the main products are MPE and DPE, the main by-products are sodium formate, tripentaerythritol (TPE), bispentamonfomal (PMF), cyclic pentamonofomal (CMF). At ambient temperature, MPE, DPE, CMF, PMF and sodium formate in the synthesis solution are soluble while TPE is practically insoluble. Therefore, TPE and other insoluble compounds in the solution must be removed by filtering before analysis. In Fig. 1a, peak 1 is due to sodium formate, and peak 3 to MPE; peak 2, which significantly interferes with the sodium formate peak and the MPE peak, is due to formaldehyde; peak 4 to CMF, peak 5 to DPE and peak 6 to PMF. Unfortunately, the elution positions of the hemiformal species can not be determined because they are reversible compounds and can only exist in solution and because there are several kinds of hemiformals for a single polyhydroxy compound.

The chromatograms in Fig. 1b were obtained from the same synthesis solution from which the excess formaldehyde and the resulted hemiformal species were completely removed by hydrogen peroxide. Fig. 1b shows that the formaldehyde peak and several small peaks have disappeared, and that completely separated and pure MPE and DPE peaks are obtained. The principal reactions of removing the excess formaldehyde and related hemiformals are:



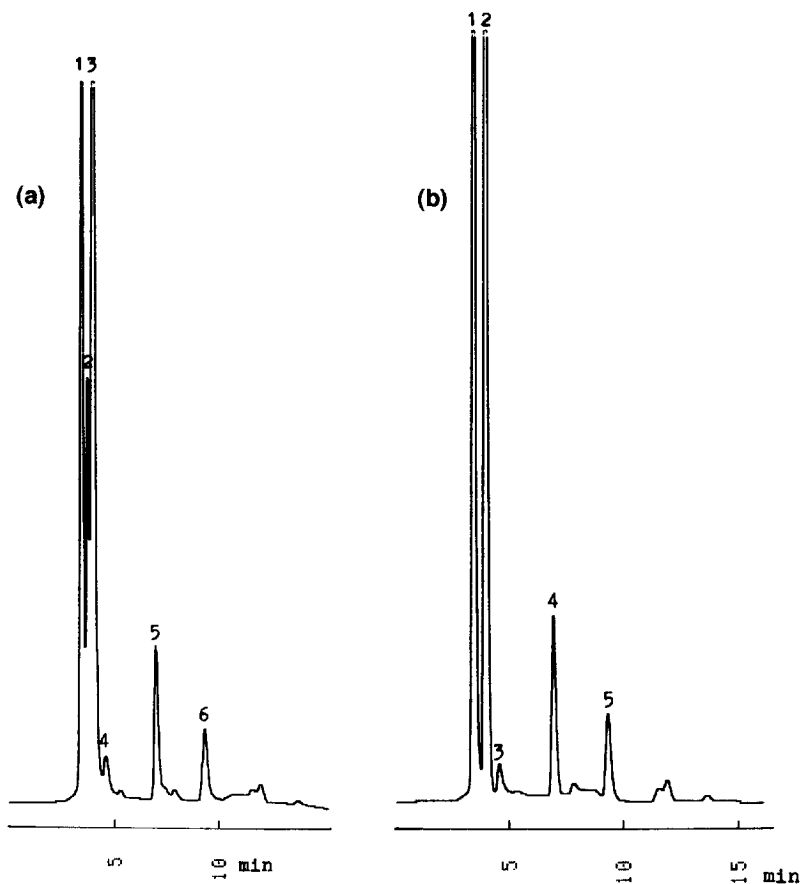
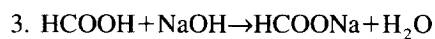
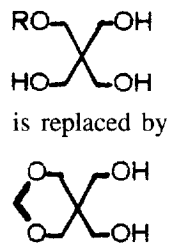
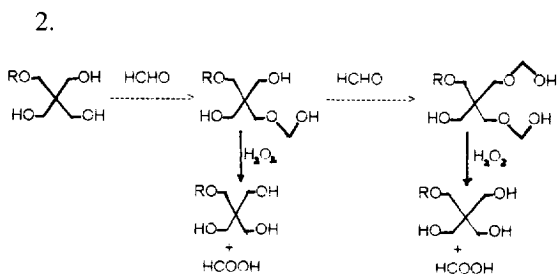


Fig. 1. (a) Separation of components in the untreated synthesis solution. Sample diluted 1:50 with water, 5.0 μ l injected. Column: Shim-Pack CLC-ODS (150 \times 4.6 mm I.D.); Column temperature: 50°C; Mobile phase: Water (0.8 ml/min); Peaks: 1=sodium formate; 2=formaldehyde; 3=MPE; 4=CMF; 5=DPE; 6=PMF. (b) Separation of components in the treated synthesis solution. The aqueous sample was treated with hydrogen peroxide, sample diluted 1:50 with water, 5.0 μ l injected. Column: Shim-Pack CLC-ODS (150 \times 4.6 mm, I.D.); Column temperature: 50°C; Mobile phase: water (0.8 ml/min); Peaks: 1=sodium formate; 2=MPE; 3=CMF; 4=DPE; 5=PMF.



R=H-, MPE;

R=(HOCH_2)₃ CCH₂-, DPE;

R=(HOCH_2)₃ CCH₂ OCH₂-, PMF.

For CMF, the

The use of hydrogen peroxide for sample preparation has several advantages, especially since this treatment eliminates the excess formaldehyde and the resulting hemiformal species in the synthesis solution and does not introduce new compounds into the analytical samples.

Table 1
Results of quantitative determination of MPE and DPE in synthesis solutions

Sample No.	Compound	Determined conc. (mg/ml)	Relative standard deviation (%), $n=5$
1	MPE	108.2±1.1	0.6
	DPE	32.1±0.5	1.1
2	MPE	107.4±0.6	0.6
	DPE	33.5±0.6	0.9
3	MPE	111.5±1.0	0.7
	DPE	32.5±0.4	1.2

Column: Shim-Pack CLC-ODS (150×4.6 mm, I.D.). Column temperature: 50°C; Mobile phase: water (0.8 ml/min); RID detector.

Water has been proved to be the best eluent for the chromatographic separation of pentaerythritols. Its low refractive index, relatively high value of viscosity and heat capacity contribute to good detector sensitivity and excellent baseline stability. It also provides adequate solubility for pentaerythritols and related by-products.

The column efficiency did not change significantly for more than 10 months under the conditions of our research.

3.2. Quantitative determination

All quantitative determinations (Table 1) were based on peak-area measurements. The calibration graphs for the determination of MPE and DPE were constructed by analysing a series of standards of known concentration. Significant linear relationships between peak area and solute concentration were found. The correlation coefficients (r) were 0.9999 for MPE and 0.9998 for DPE. We also examined the recovery of this method. The average recoveries of added known amount of MPE and DPE in analytical samples are 101.8% and 99.1%, respectively.

4. Conclusions

We conclude that HPLC can be used for the quantitative determination of MPE and DPE in aqueous synthesis solutions using a sample preparation procedure which involves the use of hydrogen peroxide to remove the excess formaldehyde and the resulting hemiformals. It proved to be a simple, fast and reliable method in terms of accuracy and reproducibility.

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