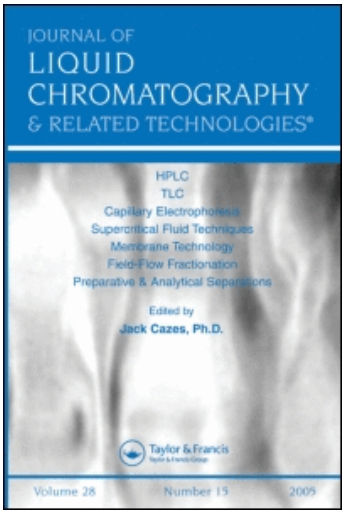


Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

HPLC Analysis of the Products of the Reaction Between Glycoluril and Formaldehyde

M. Poskrobko[a]; M. Dejnega[a]
[a] Institute of Heavy Organic Synthesis, "Blachownia", Kędzierzyn-Koźle, Poland

To cite this Article Poskrobko, M. and Dejnega, M.(1998) 'HPLC Analysis of the Products of the Reaction Between Glycoluril and Formaldehyde', Journal of Liquid Chromatography & Related Technologies, 21: 17, 2725 — 2731
To link to this Article: DOI: 10.1080/10826079808003419
URL: http://dx.doi.org/10.1080/10826079808003419

J. LIQ. CHROM. & REL. TECHNOL., 21(17), 2725–2731 (1998)

HPLC ANALYSIS OF THE PRODUCTS OF THE REACTION BETWEEN GLYCOLURIL AND FORMALDEHYDE

M. Poskrobko, M. Dejnega

Institute of Heavy Organic Synthesis, "Blachownia"
ul. Energetyków 9
47-225 Kędzierzyn-Koźle, Poland

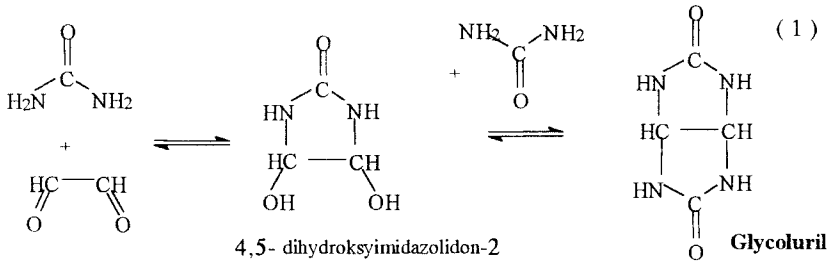
ABSTRACT

Conditions have been developed for the liquid chromatography analysis (HPLC) which make it possible to control formaldehyde concentrations in glycoluril derivatives which are responsible for the emissions of free formaldehyde from cellulose fabric treatment formulations.

INTRODUCTION

Cellulose textiles have for many years been subjected to mechanical and chemical treatment to make them shrinkproof and creaseproof. The Petersen's[1] study on the relation between chemical structures of finishing agents and their ability to release formaldehyde showed advantages of hydroxymethyl- and methoxymethyl-derivatives of glyoxalurea (4,5-dihydroxy-imidazolidon-2). Within this group, the products obtained in the reaction of glyoxal with urea and formaldehyde have found commercial applications.[2,3]

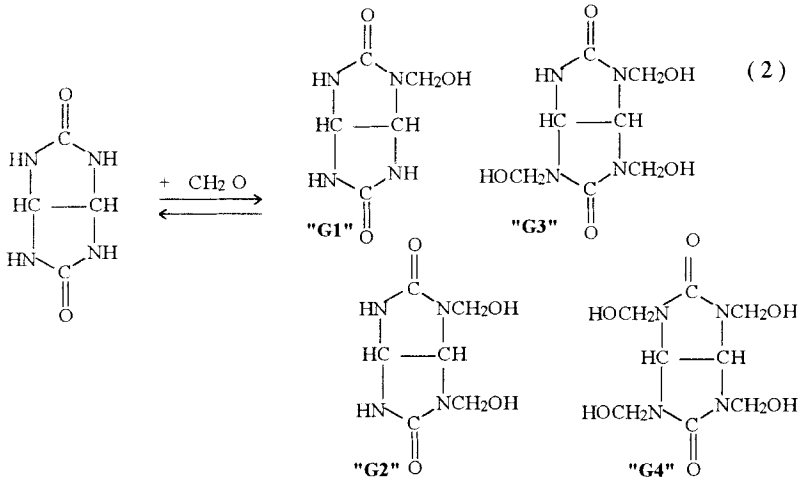
As per Valk's[4] investigations, the reactions of glyoxal and urea are equilibrium reactions. In the aqueous system, glyoxalurea can be accompanied by glycoluril [496-46-8] which is shown in Scheme 1.



(1)

Scheme 1

Glycoluril has reactive hydrogens at the nitrogen atoms and hence addition of from one to four formaldehyde molecules is easy (2); this yields a mixture of products and the composition is not dependent on the amount of formaldehyde reacted.



(2)

G1 - monohydroksymethylglycoluril
G2 - dihydroksymethylglycoluril
G3 - trihydroksymethylglycoluril
G4 - tetrahydroksymethylglycoluril

The presence of hydroxymethyl derivatives of glycoluril in textile finishing formulations is disadvantageous due to formaldehyde released therefrom. The share of these components can be lowered by selecting and adjusting parameters for the reaction between glyoxal and urea and formaldehyde or by final etherification of hydroxymethyl groups.

The purpose of this work was to develop the analytical method for the control of the presence of formaldehyde-derivatives of glycoluril, and in particular of derivatives with three and four formaldehyde molecules (tri- and tetra-hydroxymethylglycoluril) which have good water solubility. Having considered low volatility and thermal instability of the compounds studied, liquid chromatography (HPLC) was selected for the investigations.

Despite numerous application references for glycoluril[5-8] as a component of various auxiliaries, there are few reports on analytical procedures available for the determination of its content or the content of its derivatives.

Valk[2] employed thin layer chromatography for the identification of the reaction products obtained from urea and glyoxal, and potentiometric titration in an anhydrous medium for the quantitative determinations. Baloniak and Blaszczak[9] identified the presence of glycoluril in allantoine through its derivatives.

EXPERIMENTAL

An L-7100 isocratic pump (Merck Hitachi), metering valve (Knauer) with a 20 mL loop and refractometric detector HP 1047A (Hewlett Packard) was employed in the study. The detector signal was processed by a PC computer equipped with GRAMS/386 for Chromatography (Galactic) software.

Distilled water, additionally purified with HP 661A Water Purifier (Hewlett Packard) and ultrasonically out-gassed was used as eluent and methanol for HPLC (Merck) was utilized. Ambient temperatures were applied throughout analyses.

As there were no pure standards available for hydroxymethyl-derivatives of glycoluril which could be used in identifying components and in evaluating chromatographic separation efficiency, standard samples were prepared by condensing glyoxal and urea at molar ratio of 1:2, at pH value of 2 (glycoluril), and then condensing the product with formaldehyde at molar ratios of 1:1 (G+1F), 1:2 (G+2F) and 1:4 (G+4F), at pH value of 8 and at 70°C.

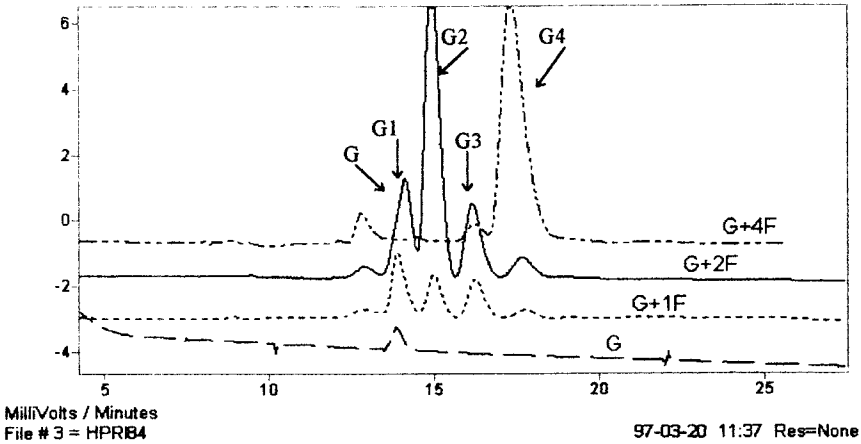


Figure 1. Chromatograms for standard samples for products obtained in the reaction of glycoluril and formaldehyde. (Refer to the body of the paper for symbols used)

In search of the best separation conditions, the following chromatographic columns were tested (tests involved eluents: water and water with about 10 vol. % methanol):

Lichrosorb RP2, 250 x 4,6 mm (packed within our own means)
Hypersil MOS 5 mm, 200 x 4,6 mm (Hewlett Packard)
Nucleosil 10d-7 C_6H_5, 125 x 4,6 mm (Bischoff)
Hypersil APS-2 5 mm, 250 x 2,1 mm (Alltech)
Nucleosil 120-7OH, 250 x 4 mm (Macherey Nagel).

RESULTS AND DISCUSSION

The best separation of sample components were obtained for the column MOS 5 μm 200 x 4,6 mm with the use of 100 % water eluent.

Figure 1 compares chromatographic profiles for glycoluril with those for samples obtained by condensing glycoluril with formaldehyde at various molar ratios. It was found from the comparison of molar ratios employed and from peak areas in the chromatograms obtained that the peak at the retention time of about 13.9 min. corresponded to the mixture of unreacted glycoluril (G) and its derivative G1. The peak at the retention time of about 15.0 min. corresponded to derivative G2, peak at about 16.3 min. to G3, and peak at 17.6 min. to G4.

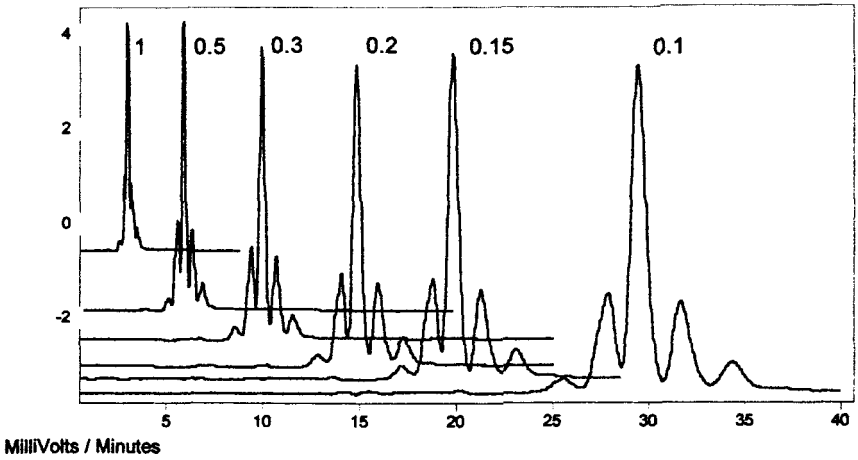


Figure 2. Comparison of chromatograms for sample G+2F at eluent flows of from 0.1 to 1 mL/min.

Table 1

Resolution for G2 andG3 Peaks and Retention Times for G4 Peak at Eluent Flows Studied

Flow (mL/min)	1	0.5	0.3	0.2	0.15	0.1
Resolution	<0.7	0.82	1.12	1.13	1.13	1.19
R_tG4 (min)	3.53	6.95	11.6	17.6	32.1	34.3

The eluent flow was optimised with the use of the G+2F sample. Chromatograms for this sample at various flows were compared in Figure 2. Table 1 provides resolution for G2 and G3 peaks calculated as the difference in retention time values divided by the sum of half-value widths, for the eluent flows studied, and retention times G4 as important parameters for the duration of analysis. Having considered satisfactory resolution of 1.13 and reasonable time needed for an individual analysis, the optimum flow of 0.2 mL/min. was selected from this study. The analytical conditions selected in this way were adopted for the samples studied; these were introduced directly or in a 2 % aqueous solution, depending on the expected concentrations of the components present.

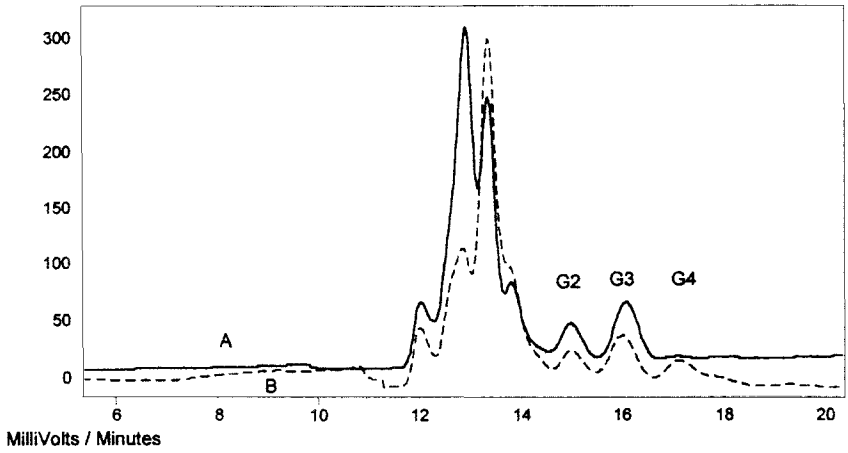


Figure 3. Chromatograms for typical samples A and B taken from the products of the reaction between glyoxal, urea and formaldehyde.

Figure 3 presents the comparison of chromatograms for exemplary two samples of the products obtained in the reaction of glyoxal with urea and formaldehyde. Percentages for components G2, G3, and G4 were calculated with the normalization method and they amounted to 6.0; 9.1; 4.7 for the sample A and 5.6; 8.9; 0.6 for the sample B.

The peaks with poor separation and retention times below 14 minutes represent unreacted raw materials, glyoxalurea, glycoluril and mono-hydroxymethylglycoluril (G1).

The analytical method developed allows for the quick and simple control of the amounts of di-, tri- and tetrahydroxymethylglycoluril in the samples under analysis.

This method has been utilized in practice for a few months and no deviation was found in the separation of the components analysed. After a few tens of analytical runs the column was washed with methanol as a preventive treatment to remove any possible higher components present in the samples.

ACKNOWLEDGMENT

Financial support provided by the state Committee for Scientific Research within the Research Project 3 T09B 089 09 is gratefully acknowledged.

REFERENCES

1. H. Petersen, Melliand Textilberichte, **2**, 155 (1976).

2. US patent specification, 4.016.335 (1977).

3. US patent specification, 6.304.880 (1984).

4. G. Valk, K. Schlieffer, Anal. Chem., **245**, 149-154 (1969).

5. Patent specification, DE 4142207 (1993).

6. Patent specification, EP 565924 (1993).

7. Patent specification, EP 604980 (1994).

8. Patent specification, JP 07157694 (1995).

9. S. Baloniak, H. Blaszczak, Acta Pol. Pharm., **40(2)**, 249-50 (1983).

Received October 22, 1997
Accepted November 22, 1997
Manuscript 4656