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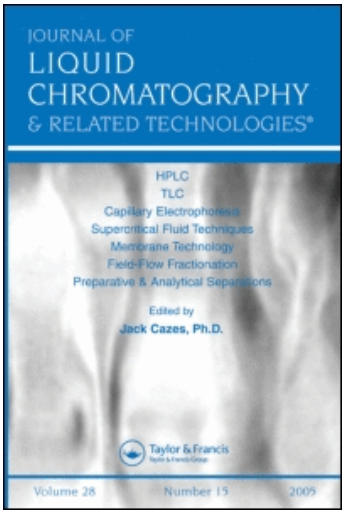

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AN HPLC METHOD FOR THE ANALYSIS OF GLYCEROL AND OTHER GLYCOLS IN SOAP

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ABSTRACT

A method has been developed to separate and quantitate glycerol (1,2,3 Propanetriol) in soap via HPLC using refractive index detection. The method has good reproducibility and accuracy, and can be achieved in 30 minutes or less, including sample preparation, and compares well with standard methods. The detection of other glycols common to the soap and cosmetics industry is also described.

INTRODUCTION

Soap manufacturers find it important to monitor the glycerol content of soap for several reasons. First, excessive glycerol may adversely affect production properties by causing soap to become too hydroscopic. Second, too little glycerol could reduce the plasticity of the soap and decrease the emollient and humectant qualities of glycerol, which is an important property in the soap and cosmetic industry.

Glycerol is a natural by-product from the saponification of triglycerides (Figure 1). The yield of glycerol is dependent upon the composition of the tri-

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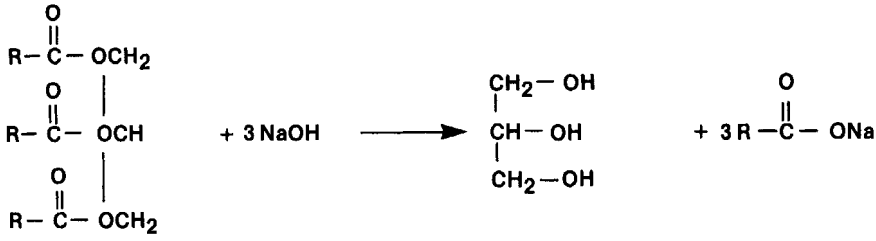
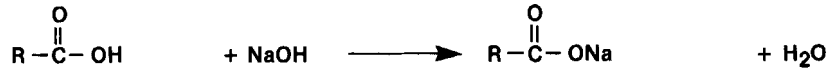
Figure 1

Triglyceride



Triglyceride Alkali Glycerol Soap

Fatty Acid



Fatty Acid Alkali Soap

glyceride mix and the amount of processing to recover glycerol from the soap making process. Typically, during the production of soap from Beef Tallow and coconut oil, the residual glycerol content in soap varies from 0.5% to 3.0%. When soaps are derived from fatty acids (Figure 1) rather than triglycerides, no glycerine is produced, however many manufacturers choose to add glycerol because of the benefits previously mentioned. Other glycols are used in the soap industry, such as Diethylene Glycol, Propylene Glycol, etc. for their plasticizing and cosmetic effects.

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There has been much investigation of glycerol and related compounds utilizing HPLC in various fields, but apparently not in the soap industry (1-5). Traditional wet method analysis (6,7) is tedious and time consuming, with the majority of time spent on sample preparation. The average time per analysis is two hours. Because of these drawbacks, we have developed and present here a rapid and accurate procedure for the determination of glycerol in soap via HPLC. We also present data on the detection of other glycols in various soap matrices.

EXPERIMENTAL

Materials

Glycerol 99.7% and 1,2,4 Butanetriol 95% were obtained from Aldrich Chemical Company. Commercial soap base (85:15 Sodium Tallowate: Sodium Cocoate), produced at Original Bradford Soap Works, was used throughout the study. All solvents were HPLC grade and were filtered through a 0.5u Millipore filter before use.

HPLC Apparatus

The apparatus consists of a constant delivery pump (Waters Associates, Milford, MA, model 6000A) fitted with a Septumless injector (Waters Associates model U6K) having a 2000 ul loop.

The analytical separation was performed on a stainless steel reverse phase column, (Waters Associates Carbohydrate Analysis, 10 u, 3.9 mm IDX 30 cm)

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preceeded by an in-line precolumn filter (.45u). A differential refractometer (Waters Associates Model 401) was used to detect and quantitate the glycols.

HPLC Conditions

The optimum mobile phase consists of a 92.5:7.5 acetonitrile-water mixture. Flow rate was maintained at 1 ml/min. The injection size for the analysis was 50 ul for both the standard solutions and sample solutions. The level of glycerol in a given soap was calculated from the standard curves, based on internal standard techniques.

Sample Preparation

Standard Solutions for calibration work (1.0097-10.097 ug/ul) were made by dissolving glycerol in the mobile phase (92.5:7.5 acetonitrile:water).

Soap solutions for chromatography were prepared by adding 5 gms of soap to 50 ml of mobile phase, and blenderized for 10 minutes. The material was then filtered through a #541 Whatman paper, then clarified through a 0.45 u Acrodisc ^{R}-CR (Gelman) filter. This material was then mixed 1:1 with 6.200 ug/ul of 1,2,4, Butanetriol internal standard. This mixture is now ready for injection.

Soaps containing known amounts of glycerol were prepared by adding glycerol to an 85:15 tallow coconut fatty acid mixture, then neutralizing with sodium hydroxide. The resulting soap was air-dried then blenderized to insure uniformity.

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Soap solutions for standard methods analysis were prepared via ASTM [8] method D460.

RESULTS AND DISCUSSION

Preliminary investigation of optimum HPLC conditions was performed on a variety of columns using various mobile phases, as reported by other investigators (2,3,8). The types of columns ranged from silica, silica impregnated with amine modifiers and specialty columns. The mobile phases usually consisted of various mixtures of acetonitrile and water. One major problem we observed with these conditions was that the retention time of glycerol was very close to the void volume. Efforts to increase the retention time by changing operating parameters proved unsuccessful. We did observe, however, that a reverse phase "Carbohydrate Analysis" column provided excellent retention time and good peak symmetry using a 92.5:7.5 acetonitrile-water mobile phase (Figure 2).

Sample preparation was of prime consideration since glycerol and soap have mutual solubility characteristics, which could create interference problems. We discovered that when 5% soap solutions in water where injected under optimum conditions, (see HPLC conditions) the resulting chromatograph gave poor resolution, poor peak symmetry and an interference by the sample solvent. Other sample solvents were tried with no success. To circumvent this problem, the mobile phase was used as the sample solvent. Be-

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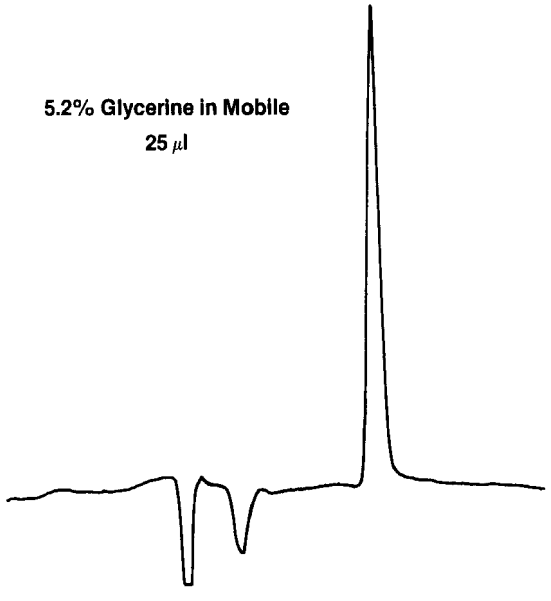
Figure 2

HPLC Chromatogram of Pure Glycerol
Using Stainless Steel Carbohydrate Analysis Column



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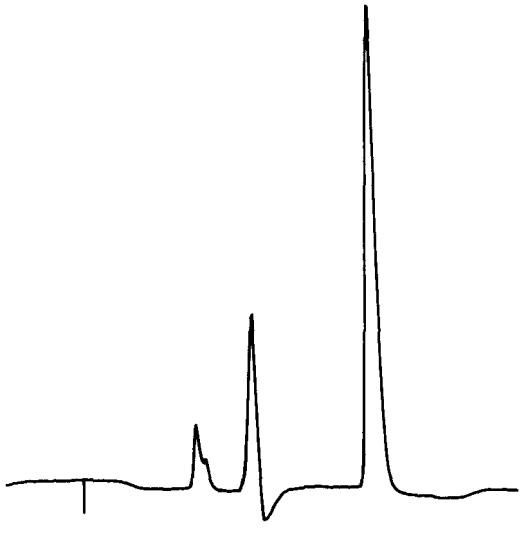
cause of the poor solubility of soap in acetonitrile, we developed a blending technique to extract the glycerol which is soluble in low concentrations in acetronitrile, from the soap into the mobile phase. This blending operation produces a loose paste-liquid which is easily filterable. The blender should be large enough and have sufficient mechanical action to disintegrate the soap in the mobile phase, facilitating the extraction of the glycerol. This technique enabled us to eliminate any interferences

Figure 3

HPLC Chromatogram of Glycerol in Soap
Extracted by Blender Method



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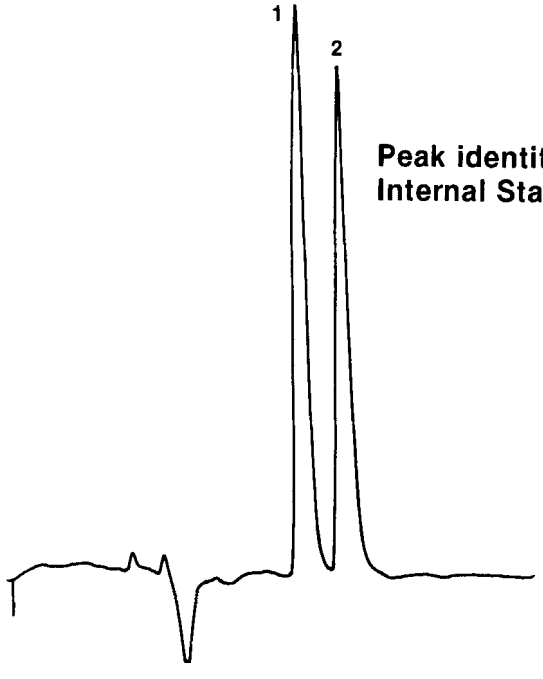
from the soap and sample solvent resulting in a good chromatograph (Figure 3).

An internal standard was employed for quantitation to minimize operator and sample preparation error. 1,2,4 Butanetriol was a suitable internal standard since it was stable in the solvent system, did not interfere with any other compounds of interest and exhibited good detector response (Figure 4).

To determine the precision and accuracy of the procedure, we established a calibration curve resulting from

Figure 4

HPLC Chromatogram of Pure Glycerol with Internal Standard



Peak identities: (1) 1,2,4 Butanetriol Internal Standard (2) Pure Glycerol

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injecting various concentrations of glycerol with the internal standard. The ratio of sample peak area to standard peak area was measured (Table I) and plotted (Figure 5). Spiked samples were prepared by adding known amounts of glycerol to soap. These spiked samples were analyzed by this new HPLC procedure with excellent results, as shown in Table II. A comparison study was undertaken involving the new HPLC procedure and the standard method (ASTM D460), with soaps of known glycerol content. The

Table 1
Calibration Table of Standard Mixtures

Sample No.	Amount Injected (μg)	Peak Area Ratio x 10
1	10.0970	15.913
2	9.0873	15.399
3	8.0776	13.659
4	7.0676	12.069
5	6.0582	10.293
6	5.0485	8.641
7	4.0388	6.891
8	3.0291	5.245
9	2.0194	3.440
10	1.0097	1.768

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Figure 5

Calibration Curve

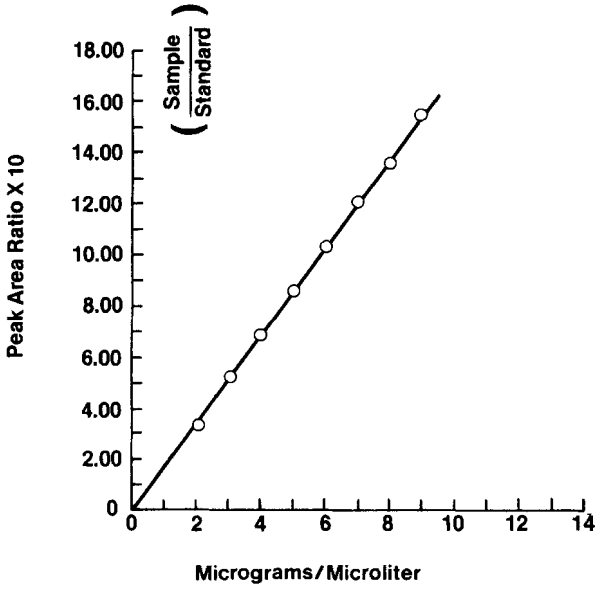


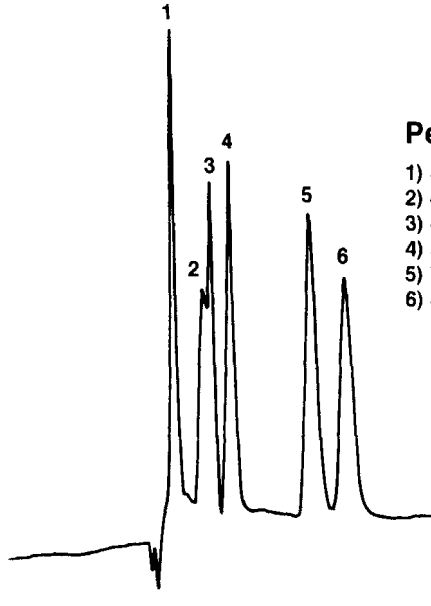
Table 2
Recovery Data*

Sample No.	Amount Added (%)	Amount Recovered (%)	% Recovery
1	0.66	0.64 0.68	97.0 103.0
2	1.50	1.44 1.48	96.0 98.7
3	3.02	2.96 3.00	98.0 99.3
4	4.41	4.16 4.32	94.3 98.0
5	5.82	5.92 5.76	101.7 99.0
6	8.57	8.20 8.40	95.7 98.0
7	9.66	10.12 10.08	104.8 104.3

*Duplicate injections of each sample

Figure 6

HPLC Chromatogram of Various Glycols



Peak Identities:

1) 36.5 - Hexylene Glycol
2) 44 - 1,3-Butylene Glycol
3) 46.5 - Propylene Glycol
4) 51 - Diethylene Glycol
5) 71.5 - 1,2,4-Butane Glycol
6) 80.5 - Glycerol

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Table 3
Comparative Analysis

Sample No.	% Glycerol (HPLC)	% Glycerol (Std. Method)	% Actual
1	1.55	1.53	1.42
2	3.32	3.46	3.28
3	5.36	5.34	5.67
4	6.65	6.67	6.81
5	9.50	9.42	9.42

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results shown in Table III demonstrate good correlation between the two methods.

We examined other types of leading soap products on the market, including liquids, powders, and gels by this new procedure, again with good agreement with standard methods.

We also examined other glycols common to the soap and cosmetic industry such as hexylene glycol, propylene glycol, and diethylene glycol (Figure 6). These compounds could be monitored alone or in combination during routine quality control analysis.

Conclusion

This study has demonstrated the use of reverse phase HPLC as an alternate method of analyzing glycerol and other glycols in soap products. After establishing calibration c rves, the method is applicable to routine analysis, since only 15 minutes is required for sample preparation and 15

minutes for the LC analysis. The short preparation time, combined with the precision and accuracy of the LC analysis, provides an analytical method for quality control of the glycols. Since HPLC has grown considerably over the last few years, many labs possess HPLC capabilities in their quality control programs. Therefore we believe this new method is attractive in terms of speed, accuracy, and precision over current standard methods.

ACKNOWLEDGEMENTS

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