Surfactants & Detergents Technical

Quantitative Determination of Glycerin In Soap by Capillary Gas Chromatography

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A simple and rapid procedure is described for the isolation, silylation and capillary gas chromatographic quantitation of the free glycerin content in soap. Free glycerin is determined by mixing the sample with dimethylformamide (DMF), filtering the mixture, silylating an aliquot with *bis*-trimethylsilyltrifluoroacetamide (BSTFA), and quantitating by capillary GC using flame ionization detection. Silyl derivatization and capillary gas chromatography provide for a quick and easy analysis which allows straightforward automated gas chromatographic analysis instead of the more tedious traditional periodate methods. This procedure also provides reliable quantitation for glycerin levels in soap lower than those measurable with the standard methods.

Traditional wet methods for determining free glycerin in soap (1,2) are tedious, time-consuming and subject to interferences from other glycols such as propylene glycol, sugars and sugar alcohols. Although other analytical methods, including redox titrations (3), gas chromatography (GC) (4,5), thin layer chromatography (6) and high performance liquid chromatography (HPLC) (7), have been reported in the literature for the analysis of glycerin in such substances as tobacco, meats, wines, polyesters, cosmetic products and others, the publication of George and Acquaro (8) was the only one which dealt specifically with soap analysis; their method involves extraction of the glycerin followed by reverse-phase HPLC using refractive index detection.

Recent advances in capillary GC technology have greatly enhanced capabilities for resolving complex volatile mixtures including flavors and fragrances; frequently, the resolving power of capillary columns can eliminate the need for extensive sample preparations or clean-ups. In this paper we report on a combined silyl derivatization-capillary GC method for determining free glycerin in soap bars and pellets adapted from the procedure of Goldstein, Molever and Lok (9). Silyl derivatization is used to enhance detectability and to increase chromatographic reproducibility; this method is especially well suited for use with an auto-sampling gas chromatograph.

EXPERIMENTAL

Instruments and conditions. Analyses were performed on a Hewlett-Packard Model 5890A gas chromatograph fitted with a capillary inlet system, flame ionization detector and Model 7671 auto sampler and connected to a Hewlett-Packard Model 3388A integrator. The column was a 12 m × 0.2 mm i.d. methyl silicone fluid coated Ultra fused silica capillary column supplied by Hewlett-Packard (No. 19091A-101). A glass split injection system (150:1) was used with helium carrier gas at head pressure of 12 psi and helium make-up gas.

The column temperature was held at 100 C throughout the entire 15 min run. Temperature programming was initiated at 15 min at a rate of 30 C/min to reach a temperature of 240 C to clean out the system for the next injection, only if late-eluting peaks from an earlier injection interfered. The inlet temperature was 200 C and the detector temperature was 260 C. A threshold value of 4 and attenuation of 64 were used. With these GC conditions, the retention time for silylated glycerin was about 8.7 min. For trace glycerin analysis, the threshold was set at 1 and the attenuation at 2.

Reagents and solutions. Glycerin standard (1,2,3-propanetriol), 99.5% purity, was from Aldrich Chemical Co., Milwaukee, Wisconsin; DMF (N,N-dimethylformamide), ACS reagent grade, from Sargent-Welch Scientific Co., Skokie, Illinois, and BSTFA (*bis*-trimethylsilyltrifluoroacetamide), silylation grade, from Regis Chemical Co., Morton Grove, Illinois.

Glycerin standard stock solution: About 0.1 g glycerin was accurately weighed (±0.0001 g) into a 200-ml volumetric flask, dissolved, and diluted to volume with DMF. Glycerin dilute stock solution (for use with samples containing trace level glycerin): Dilute 5.0 ml of the above solution to 100 ml with DMF. Silylated glycerin standards: 500 µl of the appropriate above stock solution was mixed with 250 µl BSTFA in a septum vial.

The stock solutions were prepared every few months and stored in a refrigerator. The silylated standards were prepared fresh for each day's use.

Assay procedure and calculation. Ten g of chopped soap was weighed (±0.01 g) into a Waring blender jar. Two hundred ml of DMF was added and the contents thoroughly blended for 5 min. A portion of the mixture was filtered by gravity through Whatman No. 41 paper into a beaker. Five hundred µl filtrate was transferred to a septum vial and mixed with 250 µl BSTFA. One µl was then injected into the GC and compared to one µl injections of the appropriate silylated glycerin standard. Each was injected three times. Routine external standard type calculations are used to determine percent free glycerin:

$$\% \text{ Free Glycerin} = \frac{A_{sample} \times CONC_{std} \times 100}{A_{std} \times CONC_{sample}}$$

Where A_{sample} and A_{std} are the average peak areas of glycerin in the sample and standard, respectively, $CONC_{std}$ is the concentration of the appropriate glycerin standard stock solution before silylation (e.g. 0.1 g/200 ml for samples with normal glycerin levels or 0.0025 g/100 ml for samples with trace glycerin levels), and $CONC_{sample}$ is the sample concentration before silylation (e.g. 10 g/200 ml).

Smaller sample sizes should be used with samples containing more than about 2% free glycerin.

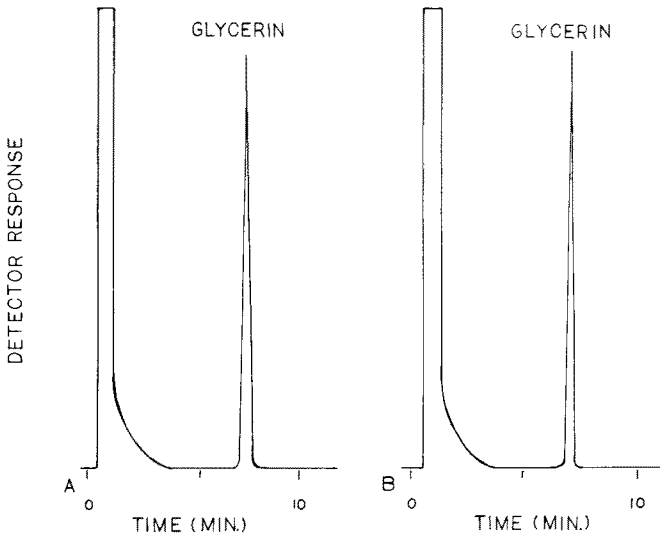

Fig. 1. Capillary gas chromatograms of: A, silylated standard glycerin, and B, silylated soap extract.

RESULTS AND DISCUSSION

Method development. The traditional periodate titration methods for determining free glycerin are quite labor intensive and lack accuracy at trace glycerin levels. Our goals were to develop a method that would require less operator time, be amenable to automated analysis, provide better specificity for glycerin, and provide reliable results for trace glycerin levels. Gas chromatography appeared to be able to meet all these requirements. It was decided to use silylation to obtain better, more reproducible chromatography than that which is obtained when underivatized glycerin is used with a column such as Tenax GC or Porapak. Capillary GC was chosen over packed-column GC to provide better resolution from perfume components or other materials which might be present in soap. The use of an internal standard such as a similar glycol, triol, or fatty alcohol was considered, but was deemed unnecessary, especially when using an automatic sampler.

Typical capillary GC curves for silylated standard glycerin and soap extracts are shown in Figure 1.

Accuracy and precision. Glycerin methodology validation studies were conducted in which soap bars of various compositions were analyzed by this method and by the traditional periodate titration method. Average glycerin levels compared to those obtained with the periodate method were 101.4%. Results are summarized in Table 1.

TABLE 1

% Free Glycerin Levels Obtained Using Different Methods

Sample	GC Method	AOCS Method #Da23-56
1	2.86	2.83
2	1.80	1.74
3	1.01	1.00
4	2.79	2.81

Additional verification was obtained by analyzing placebo bars spiked with glycerin. Bars spiked at 0.05 and 0.10% free glycerin and analyzed gave 97.1 and 100.3% recovery, respectively; bars spiked at higher levels gave similar results.

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