Gas Chromatographic Determination of Biphenyl and Phenyl Ether in Oil

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ABSTRACT

Oils containing 0-100 ppm biphenyl and phenyl ether were analyzed by a new gas chromatographic method. Correlation coefficients (r) between gas chromatographic peak heights and biphenyl and phenyl ether concentrations were 0.99 and 0.98, respectively. As little as 5 ppm biphenyl and phenyl ether in oils could be determined rapidly and efficiently in 90 min by this new method.

INTRODUCTION

The most common heat transfer medium used in deodorization of oil is a mixture of biphenyl (73.5%) and phenyl ether (26.5%). The mixture of these 2 compounds is known as Dowtherm A. Deichman et al. (1) reported that biphenyl causes paralysis, central nerve system depression and convulsion in experimental animals. Phenyl ether has also been reported to be toxic and exposure of longer than 15 min at greater than 2 ppm concentration in air may cause irritation and nausea (2).

Sleeter (3) reported that heat transfer medium (Dowtherm A) may be present in soybean oil as a result of pinhole leaks in the heat exchanger or the deodorizer. Imai et al. (4) reported that a Japanese edible oil refinery shipped rapeseed oil contaminated with biphenyl and phenyl ether. This accident generated public attention on the safety of oil in Japan.

Takagi (5) analyzed Dowtherm A in oil by spectrometry and gas chromatography (GLC) after Dowtherm A was extracted and preliminarily separated by column chromatography. Takagi and Aoyama (6) analyzed Dowtherm A content in oil by a combination of unsaponifiable material extraction and a solvent partition method. Imai et al. (4) reported an analytical method which can determine the heat transfer media in rapeseed oil by a combination of steam distillation and GC.

All of the methods which require steam distillation or extraction to isolate heat transfer media in oil are complex, tedious and time-consuming, and may cause large, unnecessary experimental error. This paper reports a simple GC method which can be used to determine the heat transfer media in oil without prior time-consuming steam distillation or extraction.

EXPERIMENTAL

Isolation Apparatus

The apparatus used for the isolation of biphenyl and phenyl ether is shown in Figure 1. Two and one-half ft of GC quality aluminum tubing, 0.25-in. od, was bent into a U-tube and packed with 0.2 g of anhyd sodium sulfate, 0.1 g of silanized glass wool, 0.6 g of silanized glass wool, 0.2 g of potassium carbonate, and 0.15 g of silanized glass wool in sequence (Fig. 1). After packing, one side of the U-tube apparatus was connected to a nitrogen gas line (Fig. 1) and then the tube was lowered into a forced-air laboratory oven at 200 C. The oven was modified to accommodate the U-tube by cutting a 4 in. × 1 in. rectangular opening in the top of the oven. The tube was purged with nitrogen gas at 30 mL/min for 10 min at 200 C to remove contaminants.

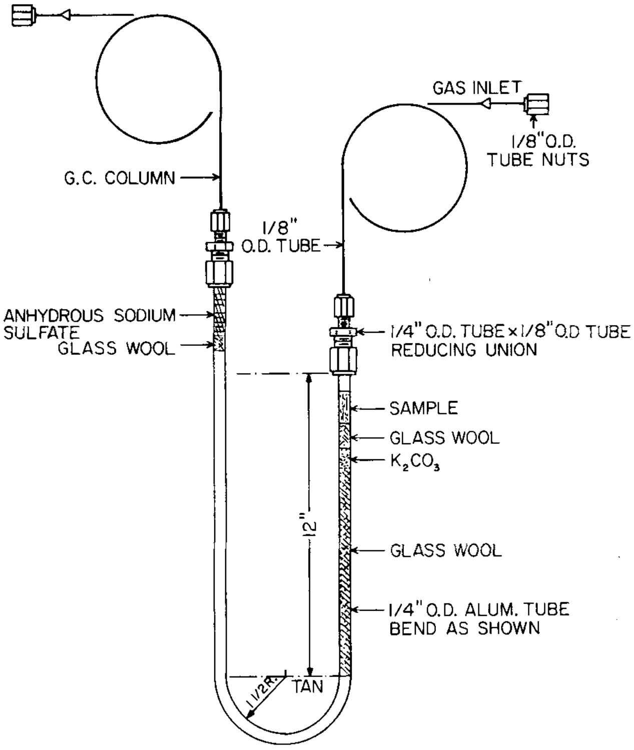

FIG. 1. The isolation apparatus of biphenyl and phenyl ether from oil.

After purging, the apparatus was removed from the oven and cooled to room temperature. The oil sample was placed in the cleaned U-tube apparatus for isolation of compounds as described later.

Compound Isolation

A 10-ft × 1/8 in. stainless steel column packed with 80/100 mesh Tenax GC coated with 10% polymetaphenoxylene (Applied Science Laboratories, State College, PA) was connected to the side of the isolation U-tube apparatus which did not contain the glass wool as seen in Figure 1. One mL of oil sample was introduced onto the top of the glass wool in the U-tube apparatus which was connected to a 1/8-in. nitrogen gas inlet tube. The apparatus containing the oil sample was lowered into a 160 C forced-air oven. Only the aluminum portion of the apparatus was in the oven, and the reducing unions were outside of the oven. The sample in the isolation apparatus was purged for 15 min by nitrogen gas at 30 mL/min. The compounds thus isolated from the oil were collected on the Tenax GC coated with polymetaphenoxylene. The GC column was then disconnected from the U-tube apparatus and connected to the gas chromatograph to separate the isolated compounds.

Gas Chromatography

A Hewlett-Packard 5880A gas chromatograph with an electronic integrator for GC peak area calculation, equipped with flame ionization detector, was used. The initial column temperature was maintained at 140 C for 2 min and then programmed at 6 C/min to 250 C and held at 250 C for 20 min. The flow rate of nitrogen was 40 mL/min.

Materials and Sample Preparation

Fresh, deodorized, whole soybean oil was obtained from Capital City Products, Columbus, OH. Reagent-grade biphenyl and phenyl ether were purchased from Aldrich Chemical Company, Inc., Milwaukee, WI. Soybean oil samples containing 0, 25, 50, 75 and 100 ppm (w/w) of biphenyl and phenyl ether were prepared to obtain a range of biphenyl and phenyl ether concentrations.

RESULTS AND DISCUSSION

To determine the reproducibility of the isolation and separation of the heat transfer medium from oil, biphenyl was added at 50 ppm concentration (w/w) to fresh, deodorized soybean oil, and the sample was analyzed 6 times. The mean value of GC peak heights for the 6 trials was 7.45 cm with a standard deviation of 0.16, and the coefficient of variation was 2.1%.

Methyl octanoate in ether (0.3%) was used as an external standard to monitor the daily variation in gas chromatograph sensitivity. Because extraction and derivatization steps were not included in the analyses of heat transfer media in oil, and good reproducibility of isolation, separation, and quantitation of biphenyl and phenyl ether were obtained, an internal standard was unnecessary. We have not experienced the need for internal standards in the quantitative analyses of biphenyl and phenyl ether in oil using the apparatus shown in Figure 1.

Gas chromatograms of oil containing different levels of biphenyl and phenyl ether are shown in Figure 2. Oil without added biphenyl or phenyl ether gave an almost flat baseline. As the concentrations of biphenyl and phenyl ether were increased from 0 to 100 ppm, the GC heights and peak areas increased.

The linear regression equation for predicting the biphenyl content in oil was $y = 13.35x - 0.1335$, where y is the predicted biphenyl concentration in ppm and x is the peak height in cm. The correlation coefficient (r) was 0.99 which suggests that the biphenyl content in oil can be accurately determined by measuring the height of the GC peak. Similarly, the linear regression equation for predicting the phenyl ether content in oil was $y = 10.834x - 0.0975$. The correlation coefficient (r) between concentration of phenyl ether in oil and GC peak height was 0.98, which suggests that the phenyl ether in oil also can be accurately determined by measuring the gas chromatographic peak height of phenyl ether.

The analysis time for this method takes 90 min, including preparation of U-tube, isolation of compounds and separation of the isolated biphenyl and phenyl ether. The used aluminum U-tube is thrown away after one use. It was later found that it is better to mix K_2CO_3 with sodium sulfate and place the mixture where the sodium sulfate is placed in the tube (see Fig. 1).

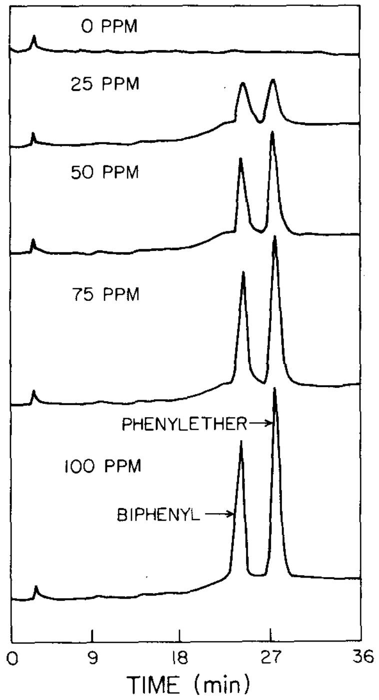

FIG. 2. Gas chromatograms of different levels of biphenyl and phenyl ether in oils.

To determine the lowest limits of detection of biphenyl and phenyl ether in oil, limited studies were conducted with samples containing 0, 0.5, 2.5, 5 and 10 ppm of biphenyl or phenyl ether. The results indicated that the method can measure as little as 5 ppm of biphenyl or phenyl ether in oil. It may be possible to increase the sensitivity of measurement by improving the GC conditions to produce sharper and narrower peaks.

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