

Analysis of Epoxidized Soybean Oil by Gas Chromatography

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A fast and cost-effective procedure to quantitate epoxidized soybean oil by means of an external standard method is reported. This procedure is applicable to commercial epoxidized oils, polymer additive packages and polymers—polyvinyl chloride (PVC)—containing epoxidized oils. The epoxidized soybean oil is converted into fatty acid methyl esters with tetramethylammonium hydroxide, and analyzed by capillary gas chromatography with flame-ionization detection. In PVC samples, the epoxidized soybean oil was extracted with toluene and followed by derivatization prior to analysis. The methyl esters of monoepoxyoctadecanoic, diepoxyoctadecanoic and triepoxyoctadecanoic acid were separated with a short capillary column.

KEY WORDS: Capillary GC, derivatization, epoxidized soybean oil, epoxy fatty acid methyl esters, extraction, PVC, quantitation.

Epoxidized vegetable oils are widely used as additives in plastics. Epoxy soybean oil (ESO) forms the base of this class of compounds due to its economics and availability. Regardless of the popularity of ESO as plasticizer, its analysis in an additive package or in polyvinyl chloride (PVC) has not been straightforward. Literature references include normal-phase high-pressure liquid chromatography with refractive index detection (1), size-exclusion chromatography at elevated temperature (2) and capillary gas chromatography (GC) (3). The capillary GC method is the most specific and sensitive reported so far, but the need of a commercially unavailable internal standard two-stage derivatization and double evaporation of sample to dryness made it unattractive.

In this paper, we report a single-step transesterification to generate the epoxidized fatty acid methyl esters (EFAME) from the ESO with a commercial reagent to analyze an additive package sample. For PVC samples, a one-step extraction with toluene, followed by direct EFAME derivatization, is used.

EXPERIMENTAL PROCEDURES

Reagents. ESO was purchased from Chem Service (West Chester, PA); tetramethylammonium hydroxide (TMAH; 25 wt% in methanol) was obtained from Aldrich (Milwaukee, WI) and toluene (reagent-grade) was from Mallinckrodt (Paris, KY).

Instruments and conditions. A Hewlett-Packard gas chromatograph (model 5890; Hewlett-Packard, Avondale, PA) equipped with split/splitless injection port and flame-ionization detector and fitted with a 5 M × 0.5 mm WCOT Ultimet HT SimDist CB column (Chrompack, Middelburg, The Netherlands) with 0.15- μ m film was used. The injection port temperature was 250°C, and the detector temperature was 300°C. The oven temperature was programmed from 100 to 240°C at 10°C/min. The carrier gas was helium at 5 mL/min. The split ratio was 25:1 for PVC samples and 40:1 for additive samples containing high levels of ESO.

Sample preparation for ESO and additive package. Weigh 50 mg of sample into a 4-dram vial, and add 10 mL toluene. Add 0.2 mL of TMAH, shake well and wait for 5–10 min. Add 4 mL of water, and shake gently. Dry the toluene layer by passing through a Pasteur pipette packed with anhydrous sodium sulfate. Inject 1 μ L of the toluene layer into the chromatograph.

A standard of ESO (Chem Service) is prepared and analyzed the same way as the additive package. Routine external-standard calculations are applied to obtain the response factor of ESO and to calculate the weight percent of ESO in samples.

Preparation of PVC sample. Weigh about 0.50 g of PVC into a 3-dram vial, and add 3.0 mL toluene. Cap the vial and extract with sonication for approximately 30 min, and let stand overnight. Remove the PVC pellets carefully, and add 0.1 mL TMAH. Shake well and wait 5–10 min. Add 5 mL H₂O and shake gently. Wait for phase separation, and analyze the toluene (a clear solution) layer without the drying step.

RESULTS AND DISCUSSION

The ESO in two PVC samples and two additive package samples from different suppliers were converted into the EFAME by TMAH prior to GC analysis. This single-step derivatization method provided reproducible results as shown in Table 1.

PVC samples were extracted with numerous solvents. However, toluene was the solvent of choice for two reasons—it extracted the ESO from PVC effectively and it is a convenient solvent for the preparation of methyl esters of fatty acids from the ESO. Hexane, a good solvent for ESO, failed to extract ESO from the PVC pellets. The levels of ESO found in PVC samples are listed in Table 1. A second extraction of the PVC pellets did not yield any additional amount of ESO.

The structures of the EFAME were confirmed by GC/mass spectrometry by using a chemical ionization technique (NH₃ as reagent). As shown in Figure 1, the C16, C18, monoepoxy C18, diepoxy C18 and triepoxy C18 are well separated, so that the quantitation of each component is possible when needed. The results in Table 1 are the total of ESO (sum of all EFAME peaks).

TABLE 1

Determined Level of Epoxidized Soybean Oil (ESO)

Sample	wt% ESO	
	Determination 1	Determination 2
Additive 1	73.9	73.4
Additive 2	70.5	70.4
PVC ^a 1	0.72	0.74
PVC 2	0.013	0.016
PVC 3	0.016	0.017

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^aPolyvinyl chloride.

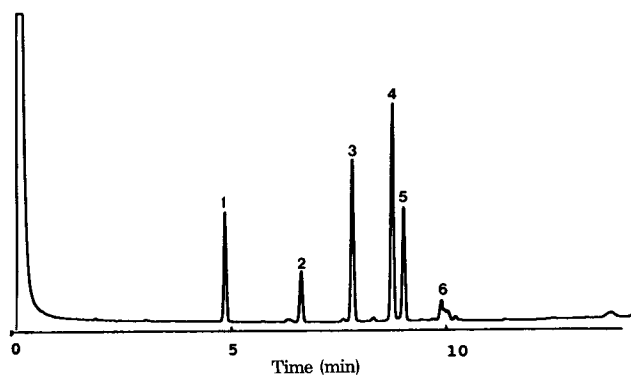


FIG. 1. Typical chromatogram of methyl esters of epoxidized soybean oil on a 5 M \times 0.5 mm WCOT Ultimet HT SimDist CB column: 1, C16; 2, C18; 3, mono-epoxy-C18; 4 and 5, di-epoxy-C18; 6, tri-epoxy-C18. Column from Chrompack (Middelburg, The Netherlands).

The short WCOT metal capillary column with thin film (0.15 micron) provided sufficient separation, and all EFAME could be eluted at a relatively low temperature (240°C), which ensures the integrity of the epoxidized

species. Other high-boiling compounds, present in the additive package or in the PVC, can be cleaned easily from the column by ramping up the temperature. Elution of the EFAME from polar columns (cyanopropyl polysiloxane), which are routinely used for the FAME analysis, was incomplete. Elimination of the high-molecular weight compounds in PVC was extremely difficult when a conventional polar column was used.

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