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Note

Gas chromatographic determination of calcium stearate in polyethylene food packaging sheets

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Calcium stearate is widely used as both a stabilizer and lubricant for synthetic rubber and resin. One very important usage is in the production of high density polyethylene which is extensively used in Japan for the fabrication of packages containing milk. For use in various synthetic resins such as poly(vinyl chloride) (PVC), polystyrene, polypropylene, etc., in polyethylene packages for milk, calcium stearate levels must not to exceed 0.25%.

We have previously reported analyses of additives[1,2] such as antioxidants in food-grade polymers using gas chromatography (GC) or high-performance liquid chromatography (HPLC). However, direct analysis by chromatography has not been achieved for calcium stearate, because it is difficult to ensure total dissolution in an appropriate organic solvent. There are, moreover, no reports in the literature of the GC analysis of calcium stearate in synthetic resins.

In this paper, a method for determining the calcium stearate in polyethylene packages using GC and HPLC is discussed. An extract from the polyethylene packaging sheet is saponified, then the resulting acid is esterified to form a methyl ester[3] for the GC analysis, and the *p*-bromophenacyl ester, using 18-crown-6 as the catalyst, for the HPLC analysis[4–8]. To compare the efficacy of the two methods, they were used to determine calcium stearate contents and the results were found to be in reasonable agreement. The identification of calcium stearate was confirmed by GC–mass spectrometry (MS).

EXPERIMENTAL

Materials

Polyethylene sheets containing 0.15% of calcium stearate were prepared; the sheet thickness was 200 μm (similar to polyethylene packages for retail milk samples).

Calcium stearate was obtained from Tokyo Chemical Industries (Tokyo, Japan). The *p*-bromophenacyl bromide and 18-crown-6 were from Dojindo Laboratories (Kumamoto City, Japan) and Aldrich Chemical Company (Milwaukee, WI, U.S.A.) respectively. Filter paper No. 5C (9 cm in diameter) was from Toyo Roshi (Tokyo, Japan). The boron trifluoride–methanol complex was from Wako Pure Chemical Industries (Osaka City, Japan). Organic solvents were of analytical reagent grade.

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Preparation of standard

GC method. A stock solution of calcium stearate was prepared by dissolving 0.1 g in 10 ml of 0.5 *M* hydrochloric acid in chloroform. A 2.0-ml aliquot of this solution was transferred to an 100-ml round-bottom flask and evaporated to dryness.

HPLC method. The stock solution was prepared as above and the residue saponified with 10 ml of 0.5 *M* potassium hydroxide in methanol by refluxing for 10 min. A 2-ml aliquot of the cooled solution was transferred to an 100-ml round-bottom flask. As an internal standard, 1 ml of a margaric acid stock solution [0.01 g of margaric acid (*n*-heptadecanoic acid) dissolved in 10 ml methanol] was added to a round-bottom flask. The acids were neutralized with 0.5 *M* hydrochloric acid in methanol to the phenolphthalein endpoint[7]. The solution was evaporated to dryness and the residue was esterified (see below).

Preparation of sample

GC method. Polyethylene sheets were cut into narrow strips (*ca.* 1 cm × 0.2 cm). Samples of about 5.0 g were weighed accurately into an extraction thimble (100 mm × 28 mm) and extracted in a Soxhlet extraction apparatus with 180 ml chloroform for 4 h. The chloroform extract was discarded, and the samples (polyethylene) in the extraction thimble were transferred to a round-bottom flask and refluxed with 100 ml chloroform–10 ml hydrochloric acid (2:1) for 4 h. The extract was cooled and the chloroform layer transferred an 100-ml round-bottom flask. After the solvent had been evaporated to dryness at 35°C, the residue was esterified according to the following procedure.

HPLC method. Polyethylene sheets were extracted as above. The residue was prepared according to the preparation of the standard for HPLC.

Esterification procedure

GC method. To each residue of the standard and sample, in an 100-ml round-bottom flask, 4 ml of 0.5 *M* potassium hydroxide in methanol and 1 ml of a margaric acid stock solution (0.1 g of margaric acid dissolved in 10 ml *n*-heptane) were added. The solutions were refluxed for 10 min, through a condenser, 5 ml of the boron trifluoride–methanol complex were added and refluxed for 2 min. Moreover, to the solutions in the flask, 9 ml of *n*-heptane were added through a condenser and refluxed for 1 min.

The boiled solutions were allowed to cool to room temperature, and 30 ml of a saturated solution of sodium sulphate were added to the flasks. The flasks were capped and shaken for *ca.* 2 min. Again saturated sodium sulphate was added up to the neck of each flask. The solutions were allowed to stand until the phases had completely separated (about 30 min), and were then analyzed by GC.

HPLC method. To each residue of the standard and sample, in an 100-ml round-bottom flask, 5 ml of the alkylating reagent (0.4 g of *p*-bromophenacyl bromide and 0.2 g of 18-crown-6 dissolved in 100 ml of acetonitrile) were added. The flasks were heated at 80°C for 30 min. The solutions were filtered through filter-paper before HPLC analysis.

Gas chromatography

An Hewlett-Packard Model 5890A instrument equipped with a flame ioniza-

tion detector was used. The inlet system used was split injection. A 25 m × 0.2 mm I.D. fused-silica capillary column was coated with 0.33 μm a cross-linked methyl silicone gum phase (Hewlett-Packard Part No. 19091A-102). The nitrogen carrier gas flow-rate was 25 cm/s measured at 200°C, the nitrogen make-up gas flow-rate was 30 ml/min and the air and hydrogen flow-rates for the flame were 400 and 30 ml/min, respectively. The injection temperature was 250°C, and the detector temperature, 300°C. The column oven was held at 200°C for 0.5 min and then programmed to 270°C at 10°C/min. Integration of peaks and processing of chromatograms was carried out by the Hewlett-Packard 3392A automation system.

High-performance liquid chromatography

The chromatographic system consisted of a Model L-4000 pump (Yanagimoto Manufacturing, Kyoto, Japan), a M-315 UV detector (Yanagimoto) operated at 254 nm and a Rheodyne 7125 valve injector. A 250 mm × 4.6 mm I.D., 5 μm reversed-phase column (Nucleosil $5C_{18}$; Macherey-Nagel, Düren, F.R.G. protected by a 50 mm × 4.6 mm I.D., 10 μm guard column (Unisil Q C_{18}; Gasukuro Kogyo, Tokyo, Japan) was used. Operating conditions: mobile phase, 90% acetonitrile (HPLC grade, Wako) in water; flow-rate, 1 ml/min; column temperature, 40°C; injection volume, 10 μl. Data were collected and analyzed with the Hewlett-Packard 3392A automation system.

RESULTS AND DISCUSSION

A method for the determination of calcium stearate in polyethylene sheets by GC has been developed. Separation times were less than 10 min per sample.

After extractions of the glycerine fatty acid esters and stearic acid in polyethylene by chloroform, chloroform in the presence of hydrochloric acid was chosen as the extraction solvent because calcium stearate was completely dissolved in this solvent. Zinc salts present in polyethylene were estimated by atomic absorption analysis.

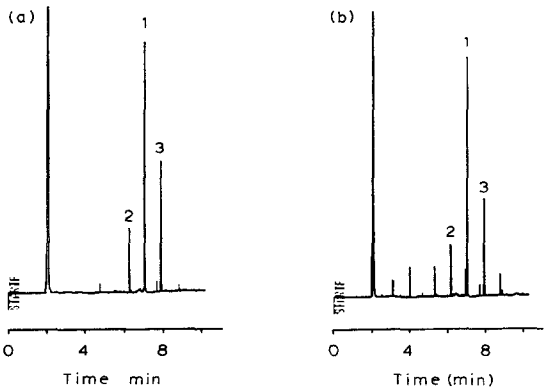

Fig. 1. Gas chromatograms of (a) standard fatty acid methyl esters from calcium stearate and (b) fatty acid methyl esters of an extract from a polyethylene food packaging sheet. Peak identification: 1 = margarate (internal standard); 2 = palmitate; 3 = stearate.

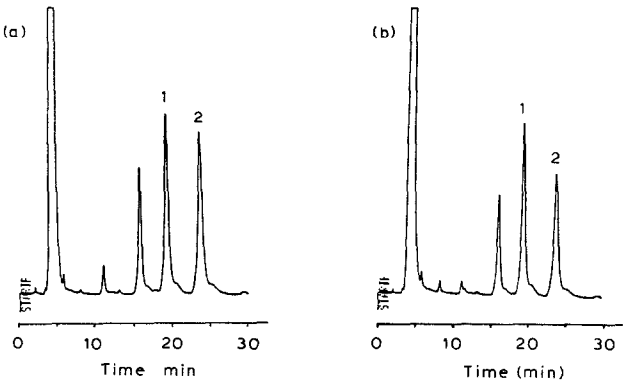

Fig. 2. HPLC chromatograms of (a) standard fatty acid *p*-bromophenacyl esters from calcium stearate and (b) fatty acid *p*-bromophenacyl esters of an extract from a polyethylene food packaging sheet. Peak identification: 1 = margarate (internal standard); 2 = stearate.

Margaric acid was used as the internal standard so that the sample esterification yields could be monitored relative to a single standard. Typical chromatograms obtained by GC and HPLC are shown in Figs. 1 and 2. For polyethylene with a known addition of 0.15% calcium stearate, the mean level (n = 10) was found by GC to be 0.16% (C.V. = 1.5%) and by HPLC was 0.15% (C.V. = 2.0%). Duplicate analyses of calcium stearate agreed reasonably well.

Finally, the practical use of the method was demonstrated. Calcium stearate from polyethylene sheets was analyzed.

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