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ANALYSIS OF FATTY ACIDS IN LUBRICATING GREASES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

A general method for the determination of fatty acids in soap-thickened lubricating greases is described. Saturated fatty acids, generally stearic and 12-hydroxystearic acids, are present in greases as metallic soaps of barium, calcium, lithium and other metals. The procedure involves the filtration of the crystalline soap from the mineral oil base, followed by conversion of the soap to the free acid. The fatty acid fraction is then analyzed directly by reversed-phase high-performance liquid chromatography with a mobile phase of tetrahydrofuran–0.1% aqueous trifluoroacetic acid (7:3) and refractive index detection.

INTRODUCTION

Lubricating greases are composed of a base fluid, either of mineral oil or synthetic type, and a thickening agent such as a metal soap, polyurea, bentonite clay or silica gel. In addition to the thickener, fillers and modifiers are often present, such as molybdenum disulfide, zinc oxide, graphite, polyethylene or PTFE, which serve to improve performance characteristics of the lubricant. This article details a method by which metallic soap gellants, which constitute the majority of grease thickeners, can be analyzed as their fatty acids using reversed-phase high-performance liquid chromatography (RP-HPLC). The procedure is useful for quality control purposes as well as for a qualitative examination of the soap-thickening agent in a used lubricant.

Since many agree with the thought that grease specifications should be based largely on functional tests rather than composition, a minimum of effort has been expended by most laboratories on the chemical analysis of greases[1]. Currently in this laboratory, wet chemical methods are employed to quantitate the soap portion of a grease while infrared (IR) spectrophotometry is used for identification[2–4]. Major improvements in grease testing in recent years are unknown to this author; the American Society for Testing and Materials (ASTM) method currently in use was originally issued in 1964[5].

The analysis of soap in greases has been previously approached in several ways. ASTM Test Method D 128 involves the decomposition of the sample, extraction to isolate the fatty acids and quantitation by titration. Alternatively, the Ford Labo-

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ratory Test Method AJ6-2 begins with light petroleum (b.p. 35–60°C) extraction and separation of insoluble materials. The insoluble soaps and fillers are separated by converting the soaps to acids, which are quantitatively analyzed gravimetrically. Consideration has been given to utilizing IR spectrophotometry as a quantitative tool for soap determinations[1,6], however this technique poses problems due to the non-uniformity of the crystalline structure of the soaps. Chromatographic methods for analyzing fatty acids appear to be a viable alternative for analyzing soaps in grease. They provide additional information about the identity of the acid and reduce analysis time. Gas chromatography with flame-ionization detection is acceptable for analyzing fatty acids after esterification[1,7,8]. Derivatization to the methyl ester yields compounds sufficiently volatile to be chromatographed at the expense of an additional step. RP-HPLC also offers a versatile mode of analysis for fatty acids[9–11]; application of HPLC to grease analyses is described in this paper.

EXPERIMENTAL

Materials and reagents

The greases used in this study contain lithium and barium soaps, both of which are multipurpose, long-life lubricants, frequently used in the automotive industry. A simulation of oxidative degradation is achieved by subjecting a grease to 110 p.s.i. of oxygen for 50 h at 100°C utilizing test equipment and sample sizes specified in ASTM D 942. Stearic acid from Fisher Scientific (Fair Lawn, NJ, U.S.A.) and 12-hydroxystearic acid from Sigma (St. Louis, MO, U.S.A.) were used as received. Acetic acid was from J. T. Baker (Phillipsburg, NJ, U.S.A.) and trifluoroacetic acid (TFA), tetrahydrofuran (THF) (HPLC grade) and all other solvents (reagent grade) were used as received from Fisher Scientific. Polytetrafluoroethylene membrane Millex-SR filters (0.5 μm) were from Millipore (Bedford, MA, U.S.A.).

Instrumentation

HPLC analyses were performed with a system from Waters Assoc. (Milford, MA, U.S.A.) consisting of a Model M45 solvent delivery system coupled with a WISP 710B autosampler. Manual injections were made with a Model U6K injector. For the separation, a Waters μBondapak C_{18} analytical column (30 cm × 3.9 mm I.D.) and a mobile phase of THF–0.1% TFA (7:3) were used. The detector was a Model R401 differential refractometer and chromatographic data were recorded by a Model 730 data module. A vortex mixer from Thermolyne (Dubuque, IA, U.S.A.) was used in the sample preparation.

Sample preparation

A 100-mg sample of grease was dispersed in 5 ml of light petroleum using a vortex mixer. The suspension was filtered through a 0.5-μm Millex-SR filter affixed to a 10-ml syringe. The filter was washed three times with 2 ml each of light petroleum. The effluent, containing the base oil, was discarded or, if desired, retained for other analyses such as IR identification. The soap thickener, collected on the membrane, was converted to carboxylic acids and dissolved by passing 5 ml of a toluene–glacial acetic acid (7:3) solution through the filter. The effluent was collected and, to insure complete reaction and recovery of the fatty acids, the filter was rinsed

three more times with 2 ml each of the toluene–acid mixture. These rinses were combined with the filtrate and the membrane, containing the fillers and other modifiers, was discarded. The fatty acid fraction was washed with three 5-ml portions of water to remove the excess acetic acid and acetates. Evaporation of the toluene under a stream of air with gentle heating left the isolated fatty acids, which were dissolved in 2 ml of THF for HPLC analysis.

RESULTS AND DISCUSSION

A chromatogram of a standard solution of 12-hydroxystearic acid and stearic acid is shown in Fig. 1. The analysis is rapid and the compounds are well resolved. Fig. 2 displays three chromatograms of different grease samples. The lithium greases in Fig. 2a and c, contain a majority of the 12-hydroxystearic acid while the barium grease, Fig. 2b, contains nearly equal amounts of stearic and 12-hydroxystearic acids as well as an unknown component. The sample preparation for each was rapid and simple; the lithium grease which contained 15% polytetrafluoroethylene (Fig. 2c) caused no problems during filtration such as a pressure buildup. Table I compares the results of total fatty acid content obtained by HPLC and quantitated from the peak areas, and the Ford Laboratory Test Method AJ6-2. The values obtained by these two methods differ by less than 10%, while samples varied in concentrations

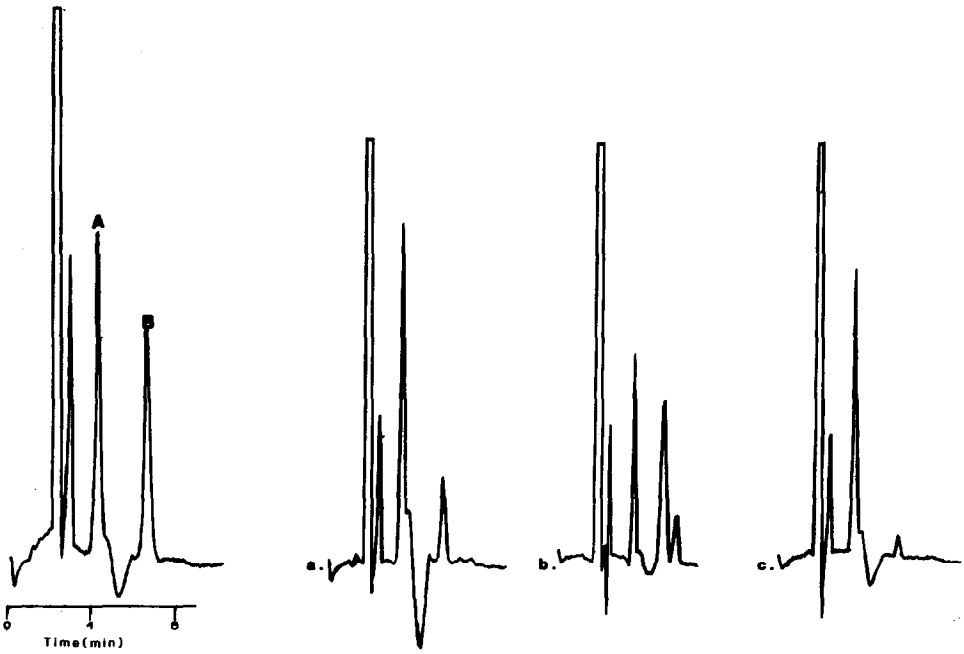

Fig. 1. Chromatogram of 1% solution of 12-hydroxystearic acid and stearic acid. Conditions: Column, μBondapak C_{18}; mobile phase, THF–0.1% aq. TFA (7:3); flow-rate, 1 ml/min; injection volume, 10 μl. Peaks: A = 12-hydroxystearic acid; B = stearic acid.

Fig. 2. Chromatograms of greases. (a) Lithium grease No. 404082; (b) barium grease No. 710174; (c) lithium grease No. 601056 containing 15% PTFE. HPLC conditions as in Fig. 1.

TABLE I

QUANTITATION OF TOTAL FATTY ACID CONTENT

Values are in wt.-% in grease.

Sample	*HPLC analysis*				*Ford Laboratory Test Method AJ6-2*
	12-Hydroxy-stearic acid	*Stearic acid*	*Unknown**	*Total*	*Total*
Lithium No. 600966 Multipurpose	3.0	N.D.	N.D.	3.0	2.9
Lithium No. 504773 Wheel bearing	6.4	0.4	N.D.	6.8	7.1
Barium No. 710174 Multipurpose	4.1	6.9	1.0	12.0	13.0
Lithium No. 601272 15% PTFE	0.9	.4	2.8	6.1	5.5

* Unknown is calculated using the detector response of stearic acid. N.D. = not detected.

from 2 to over 10%. For purposes of comparison, the assumption that the detector response for the unknown compound is similar to that of stearic acid, is made. Although total acid concentrations for samples are similar, the chromatographic method provides the analyst with additional information regarding the acid composition, which may be useful in characterizing greases. The fatty acid distribution of an unknown grease could possible be used to identify its source.

The analyses of the oxidized grease samples are shown in Fig. 3. Both samples exhibited an almost complete loss of hydrolyzable stearate soap, while the 12-hydroxystearate soap appears to be more stable under oxidative conditions. Sample preparation of the oxidized sample was more difficult than that of the virgin material;

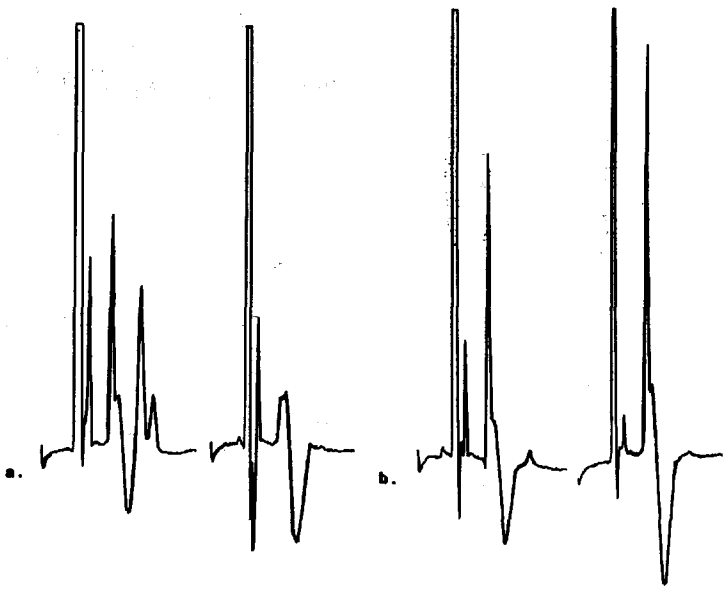

Fig. 3. Chromatograms of greases before (left) and after (right) oxidation. (a) Barium grease; (b) lithium grease. HPLC conditions as in Fig. 1.

a significant backpressure developed during filtration due to clogging of the membrane by tarry by-products. A reduction in sample size to 50 mg helped but did not eliminate this problem. Further investigation is required to determine whether rinsing the membrane filler with better solvents would help. Even so, the procedure is a valuable qualitative analysis of oxidized greases.

Future studies of the analysis of grease by HPLC will include a wider range of samples, such as aluminum complex soaps, which are reportedly difficult to convert to their acids, samples subjected to shear conditions as well as used greases from actual applications. In addition to an assessment of precision, continuing correlation studies between chromatographic and wet methods will be performed.

CONCLUSIONS

The method described herein is well suited for the analysis of soaps in greases, and is providing more information with a reduction in analysis time when compared to classical wet methods.

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