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Gas chromatographic analysis of fatty acid salts

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ABSTRACT

Generally, the analysis of fatty acid salts is based on their treatment with a strong acid to remove the cation, extraction of the liberated fatty acids and their methylation with an appropriate reagent for the gas chromatographic (GC) analysis of the fatty acid methyl esters. Surprisingly, it was found that fatty acid salts can be reacted directly with a methylating agent, *e.g.*, boron trifluoride (BF_3)–methanol complex or dimethylformamide–dimethylacetal, without prior acidification and extraction. With BF_3–methanol, the fatty acid salt or salt mixture is reacted in a septum vial with excess of methanol and BF_3–methanol complex at 70°C for 30 min. After cooling, the reaction mixture can be injected directly into the gas chromatograph without any further preparation. By calibration, the contents of bonded and free fatty acids and the distribution of the individual fatty acids in the salt or salt mixture can be determined. The GC separation of the fatty acid methyl esters is carried out on a surface-bonded, cross-linked stationary phase (FS column) as usual. The analysis of metal stearate stabilizers and lubricants takes only 70 min and both the total and the distribution of the fatty acids, from lauric to behenic acid, can be calculated from a single analysis. For instance, the relative standard deviation was 2.66% for the content of free and bonded fatty acids in calcium stearate and 1.21% for the content of stearic acid.

INTRODUCTION

Metal salts of fatty acids (C_8–C_{18}) are widely used both as stabilizers and as lubricants for plastics. As commercially available batches vary in their chemical and physical characteristics and hence in their lubricant and stabilizer performance, it is necessary to characterize such technical-grade products chemically. Usually, the analysis of fatty acid salts is based on their reaction with a strong acid to liberate the fatty acids, which for their part are esterified, *e.g.*, with methanol in the presence of potassium hydroxide [1], perchloric acid [2], a cation-exchange resin [3] or boron trifluoride [4] and then analysed as their methyl esters by gas chromatography (GC). We have found that the liberation of the fatty acids from their salts and the subsequent extraction can be omitted as the fatty acid salts themselves can be reacted directly with strong methylating agents such as dimethylformamide dimethyl acetal or boron trifluoride–methanol complex to form the methyl esters. This reaction permits the salts to be converted directly to the methyl esters and these can be analysed to determine the content and the distribution of the individual fatty acid salts by injecting the reaction mixture into a gas chromatograph.

EXPERIMENTAL

Chemicals

Analytical-reagent grade chemicals were used unless indicated otherwise.

Methanol was obtained from Merck (Darmstadt, Germany). Boron trifluoride–methanol complex [14% (w/w) BF_3 dissolved in methanol) (Merck–Schuchardt) was of synthetic grade and the metal salts of fatty acids (zinc stearate, calcium stearate, magnesium stearate) were of technical grade from P. Greven Fettchemie (Bad Münstereifel, Germany). Fatty acids (myristic, palmitic and stearic acid) were of synthetic grade (>98%). N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) was obtained from Macherey, Nagel & Co. (Düren, Germany), toluene and light petroleum (b.p. 40–60°C) [Deutsches Arzneibuch No. 7 (DAB 7)] from Merck, diethyl ether (stabilized with ionone) (DAB 7) from Asid Bons (Böblingen, Germany) and sodium carbonate from Merck.

Materials

Crimp-seal vials N 20-5 (5 ml), septa (Teflon/silicone-rubber and aluminium crimp-on caps were purchased from Macherey, Nagel & Co. Syringes (5 μl) with removable needles (85 RN) were obtained from Hamilton (Bonaduz, Switzerland).

Chromatography

A Model 8500 gas chromatograph (DANI Analysentechnik, Mainz-Kastel, Germany) was equipped with a flame ionization detector, a temperature-programmed vaporizer and a Shimadzu Model C-R3A computing integrator. A 25 m × 0.32 mm I.D. fused-silica column coated with 0.2-μm DB-1 crosslinked and chemically bonded poly(dimethylsiloxane) (J & W Scientific, Folsom, CA, U.S.A.) was used with helium 4.6 [≥99.996% (v/v) purity] (Linde, Höllriegelskreuth, Germany) as carrier gas at 0.5 bar pressure, corresponding to a column flow-rate of *ca.* 0.7 ml/min at 50°C. The temperature of the flame ionization detector was 280°C and the splitting ratio was 1:20. The injector (temperature-programmed vaporizer) was programmed from 60 to 280°C within a few seconds and the column temperature was raised from 80 to 300°C at a rate of 10°C/min.

A second column [30 m × 0.25 mm I.D., fused-silica, coated with 0.50-μm Stabilwax DA chemically bonded poly(ethylene oxide)] from Restek (Bellefonte, PA, U.S.A.) was used with helium 4.6 as carrier gas at 0.7 bar pressure. The temperature of the flame ionization detector was 270°c and the splitting ratio was 1:15. The temperature-programmed vaporizer was programmed from 80 to 270°C within a few seconds and the column temperature was raised from 90 to 260°C at 10°C/min.

The third column was 25 m × 0.32 mm I.D. F.S., coated with 0.30-μm FFAP-CBDA (chemically bonded, for the determination of acids), from Chrompack (Middelburg, The Netherlands). The carrier gas was helium 4.6 at a pressure of 0.5 bar, the temperature of the flame ionization detector was 280°C and the splitting ratio was 1:20. The temperature-programmed vaporizer was programmed from 80 to 280°C and the column temperature was increased from 80 to 270°C at 8°C/min.

Procedures

A sample of *ca.* 100 mg of the fatty acid salt mixture was introduced into the

vial and weighed. After the addition of 2 ml of methanol and 1 ml of the boron trifluoride–methanol complex, the vial was sealed and heated for 30 min at 70°C. After cooling, the vial was unsealed, 200 mg of sodium carbonate were cautiously added (whilst wearing goggles) and the vial was resealed. Samples (1 μl) were withdrawn through the septum and injected into the GC apparatus. The separation was effected on both column 1 (Fig. 1) and column 2 (Fig. 2).

For quantification, the external standard method was applied. A synthetic mixture of myristic, palmitic and stearic acid, its composition corresponding approximately to the distribution of the fatty acids in the investigated metal salts, was reacted with boron trifluoride–methanol in the same way as above, and the counts per milligram of the respective fatty acid were used for the calculation of the content of the fatty acid in the metal salt.

Instead of the external standard method, an internal standard could also be used. However, when investigating various fatty acid salts, there is the risk of a general standard compound being coeluted with an impurity contained in a technical product.

It is well known that free fatty acids react with boron trifluoride–methanol. Therefore, in the course of the new direct reaction with the metal salts, not only the bonded but also the residual free fatty acids present as contaminants in the salts can react, and the total (bonded plus free) fatty acids will be found. However, the (low) content of free fatty acids can easily be determined separately as follows and subtracted from the total.

A 100 mg-sample of the metal salt of the fatty acid was extracted with toluene by ultrasonic treatment (30 min) and centrifuged. A 1-μl volume of the solution was injected into a gas chromatograph equipped with the FFAP-CBDA column, which was specially developed for the analysis of free fatty acids.

For comparison purposes, a conventional method for the investigation of metal salts of fatty acids was applied to the analysis of all three technical-grade stearates (calcium, magnesium and zinc stearate). A 10–20-g sample of the stearate was extracted with 250 ml of light petroleum, the solution containing free fatty acids and further soluble organic compounds was evaporated to dryness and the residual solid matter was vacuum dried and weighed. This solid residue was either methylated with boron trifluoride–methanol as already described or silylated as follows. A 0.1-mg sample was dissolved in 1 ml of toluene, silylated with MSTFA for 30 min at 70°C in a sealed vial to form the trimethylsilyl derivatives of the fatty acids and analysed under the same conditions as described under *Chromatography* to give the free fatty acid content and distribution.

The residue from the extraction, *i.e.*, the main constituent being insoluble in light petroleum, contained the fatty acid salts, free of fatty acids and other soluble organic compounds. A sample of 1–1.5 g was refluxed for 2 h with 5 *M* hydrochloric acid and after cooling, it was filtered, washed free from chloride, air dried and extracted with diethyl ether in a Soxhlet apparatus for 6 h. Finally, the solution was evaporated to dryness and the residue was weighed to yield the weight of bonded fatty acids. In order to obtain the proportion of each individual fatty acid (*i.e.*, the bonded fatty acid distribution), a sample of 0.1 g was dissolved in 1 ml of toluene and derivatized with MSTFA or methylated with boron trifluoride–methanol, then analysed as described above.

RESULTS AND DISCUSSION

From each of the technical-grade stearates (calcium, magnesium and zinc stea-
rate) three samples were reacted with boron trifluoride–methanol and, after being
allowed to cool, each reaction mixture was analysed seven times. Figs. 1 and 2 show
typical chromatograms.

Tables I–III give the mean values of the contents of the individual C_{14}–C_{20}
saturated fatty acids (bonded + free) found with the proposed method. The standard
deviation and the relative standard deviation of the determinations are given, and
also the contents of the free fatty acids determined by injection of the toluene extracts
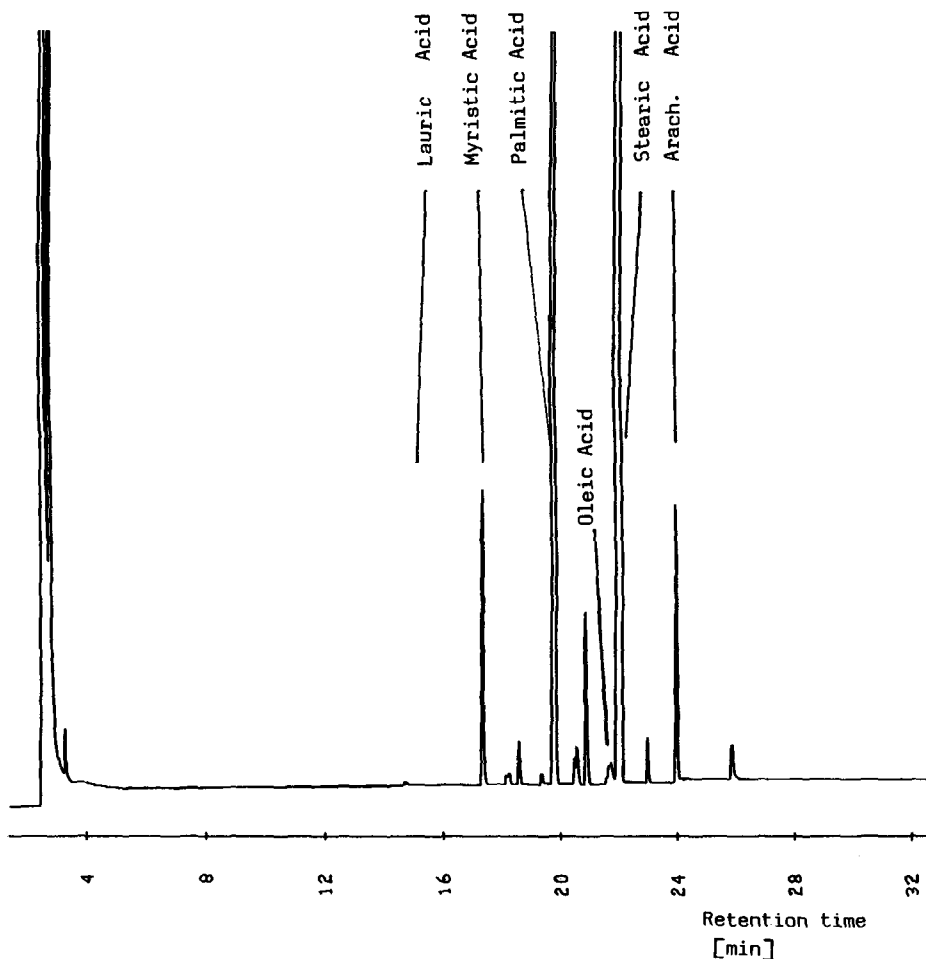of the salts without derivatization.

Fig. 1. Gas chromatogram of the methyl esters of fatty acids formed by the reaction of magnesium stearate
with BF$_3$–CH$_3$OH (non-polar liquid phase). Conditions: fused-silica column (25 m × 0.32 mm I.D.)
coated with DB-1, film thickness 0.20 μm. Temperature programmed from 80 to 300°C at 10°C/min.
Arach. = Arachidic.

TABLE I

DETERMINATION OF THE DISTRIBUTION OF FATTY ACIDS IN TECHNICAL-GRADE MAGNESIUM STEARATE

Parameter	Myristic acid	Pentadecanoic acid	Palmitic acid	Heptadecanoic acid	Stearic acid	Arachidic acid
$\bar{x}$ (%)[a]	1.69	0.74	30.97	1.82	63.73	1.38
s (%)[b]	0.18	0.14	0.72	0.21	0.65	0.24
$(s/\bar{x}) \cdot 100$ (%)[c]	10.65	18.92	2.32	11.54	1.02	17.39
Free fatty acid content (direct injection of the toluene extract) (%)	0.05	–	0.24	–	0.26	–
Content of bonded fatty acids (found by conventional method) (%)	1.8	0.5	29.6	1.4	65.4	1.1
Content of free fatty acids (found by conventional method) (%)	0.03	–	0.14	–	0.22	–

[a] Mean value of 21 determinations
[b] Standard deviation
[c] Relative standard deviation

For comparison, the values obtained with the described conventional determination of bonded and free fatty acids are presented. Acids at levels <0.1% are not reported.

The results in Tables I–III show that the direct derivatization of fatty acid salts with boron trifluoride–methanol proceeds completely with all C_{14}–C_{20} fatty acids

TABLE II

DETERMINATION OF THE DISTRIBUTION OF FATTY ACIDS IN TECHNICAL-GRADE CALCIUM STEARATE

Parameter defined as in Table I.

| Parameter	Myristic acid	Pentadecanoic acid	Palmitic acid	Heptadecanoic acid	Stearic acid	Arachidic acid
$\bar{x}$ (%)	1.84	0.59	31.30	1.86	63.58	1.19
s (%)	0.07	0.06	0.61	0.17	0.77	0.06
$(s/\bar{x}) \cdot 100$ (%)	3.80	10.17	1.95	9.14	1.21	5.04
Free fatty acid content (direct injection of the toluene extract) (%)	0.09	–	0.36	–	0.59	–
Content of bonded fatty acids (found by conventional method) (%)	2.2	0.5	31.0	1.5	63.5	1.0
Content of free fatty acids (found by conventional method) (%)	0.03	0.07	0.08	–	0.12	–
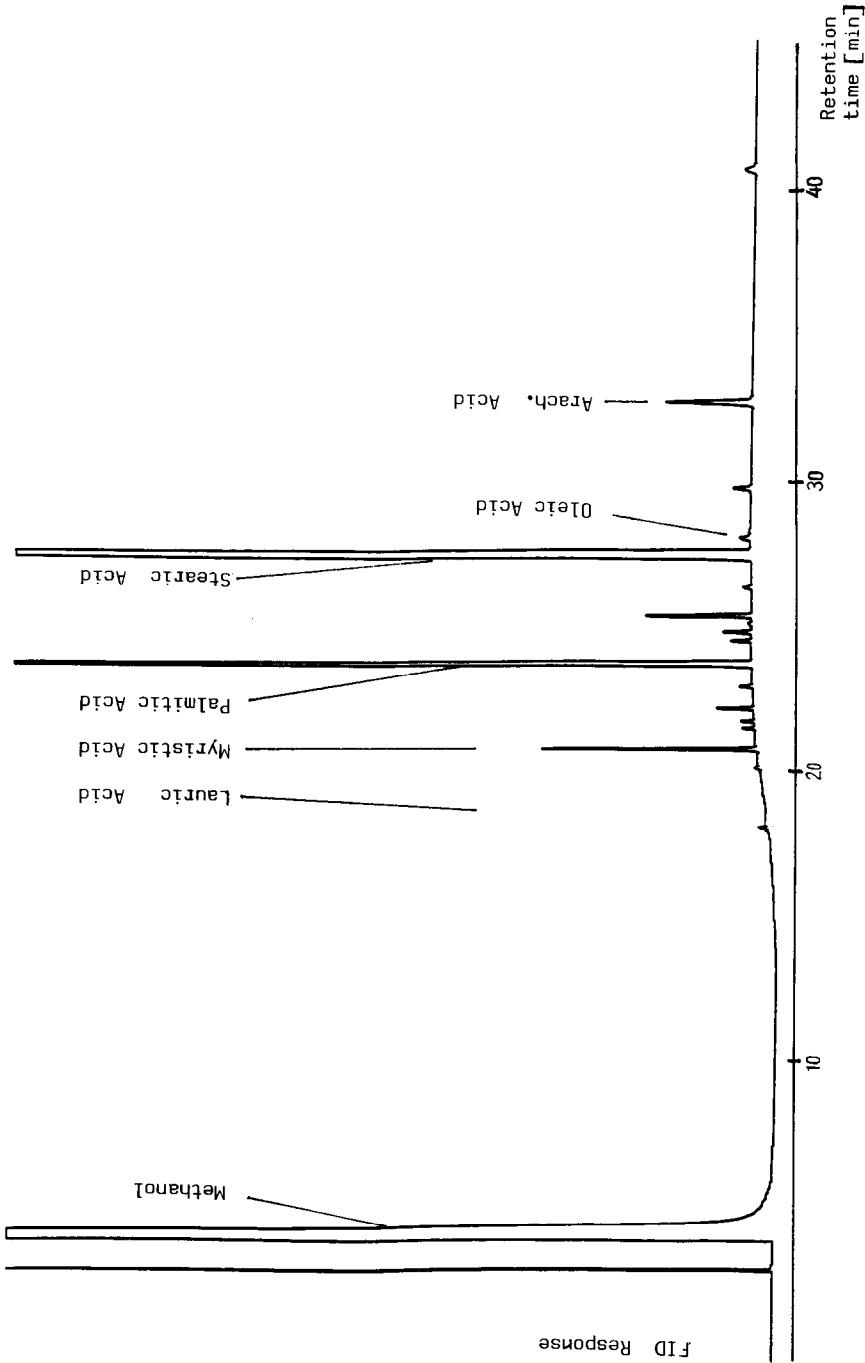
Fig. 2. Gas chromatogram of the methyl esters of fatty acids formed by the reaction of magnesium stearate with BF_3-CH_3OH (polar liquid phase). Conditions: fused-silica column (30 m × 0.25 mm I.D.) coated with Stabilwax DA, film thickness 0.50 µm. Temperature programmed from 90 to 260°C at 10°C/min. Arach. = Arachidic.

TABLE III

DETERMINATION OF THE DISTRIBUTION OF FATTY ACIDS IN TECHNICAL-GRADE
ZINC STEARATE Parameters defined as in Table I.

Parameter	Myristic acid	Pentadecanoic acid	Palmitic acid	Heptadecanoic acid	Stearic acid	Arachidic acid
$\bar{x}$ (%)	2.03	0.55	30.97	1.82	62.96	1.77
s (%)	0.05	0.05	0.60	0.06	0.62	0.19
$(s/\bar{x}) \cdot 100$ (%)	2.46	9.09	1.94	3.30	0.98	10.73
Free fatty acid content (direct injection of the toluene extract) (%)	0.12	–	0.33	–	0.68	–
Content of bonded fatty acids (found by conventional method) (%)	2.1	0.4	29.6	1.2	64.8	1.4
Content of free fatty acids (found by conventional method) (%)	0.01	–	0.11	–	0.12	–

salts from magnesium to zinc, and that the standard deviation is very good, considering that technical-grade salts were reacted. With two exceptions, the coincidence with conventionally obtained values was fairly good. One exception, the difference between the content of stearic acid in magnesium stearate and zinc stearate found with both methods, may be explained by the errors of both methods, and the other discrepancy, the distinctly lower values of free acids (e.g., 0.01, 0.11 and 0.12% for zinc stearate) found with the conventional method compared with the direct underivatized determination (0.12, 0.33, and 0.68%) could be a result of the tedious and multi-stage sample preparation in the conventional method.

As the usual gravimetric determination of the total content of bonded fatty acids (extraction of a 1–2-g sample to remove all organic compounds except bonded fatty acids, boiling of the extraction residue with hydrochloric acid, washing of the liberated fatty acids, extraction, evaporation to dryness and weighing) is very tedious and error prone, we tried to quantify the boron trifluoride–methanol reaction with respect to the determination of the total content of fatty acids by applying an external standard method (a sample of weighed pure fatty acids was reacted in the same way as the fatty acid salt and the respective peak areas were related to the corresponding peak area obtained with the true, weighed sample). In Table IV, the values obtained with the boron trifluoride–methanol reaction are compared with those given by the gravimetric method. The results are considered to be satisfactory, especially with regard to the fact that in the derivatization method fatty acid at levels <0.1% were not taken into consideration and that with the gravimetric method the values for the free fatty acids must be too high because the extraction includes not only fatty acids but also fatty alcohols and hydrocarbons. Nevertheless, more thorough investigations are planned to confirm the applicability of the direct derivatization of metal salts of fatty acids.

TABLE IV

DETERMINATION OF THE TOTAL CONTENT OF FATTY ACIDS IN METAL STEARATES

Parameter	Magnesium stearate	Calcium stearate	Zinc stearate
$\bar{x}^a$	89.93	90.17	89.46
$s\ (\%)^b$	0.37	2.40	1.62
$(s/\bar{x}) \cdot 100\ (\%)^c$	0.41	2.66	1.81
Free fatty acids (GC) (%)	0.55	1.04	1.13
Bonded fatty acids (gravimetric) (%)	91.41	91.40	90.03
Free fatty acids (gravimetric) (%)	0.74	1.15	1.58

[a] Mean value of two reactions with BF_3–CH_3OH and four injections each (free + bonded fatty acids).
[b,c] See Table I.

Regarding the residue within the injection port, caused by the metal content and the boron trifluoride reaction products of the injected sample, as a guide the number of injections into the gas chromatograph should be limited to twenty, then the injector should be purified (replacement of the glasswoll or glass/quartz liner).

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