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Short Communication

Quantitative determination of dehydroabietic acid methyl ester in disproportionated rosin

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ABSTRACT

A simple, rapid and accurate capillary gas chromatographic (GC) method for the quantitative determination of dehydroabietic acid in commercially disproportionated rosins was developed and tested. Dehydroabietic acid was converted into its methyl ester derivative and quantified by GC with flame ionization detection using a DB-1 column with methyl stearate as the internal standard. The method can also be applied to the quantitation of dehydroabietic acid in rosin or in other rosin derivatives.

INTRODUCTION

Dehydroabietic acid is the main component of disproportionated rosin, an important rosin derivative used industrially in paper sizing, in various coating compositions and synthetic resins and especially as an emulsifying agent in the manufacture of styrene–butadiene rubber. There are several commercial-grade disproportionated rosins available on the market containing between 30 and 65% dehydroabietic acid. Variations in disproportionation processes cause considerable variation in dehydroabietic acid content as a result of incomplete disproportionation of the conjugated diene acids, such as abietic, neoabietic and palustic acids. This reduces the overall stability to oxidation and the usefulness of the end product, hence the need for a method of quantitation of dehydroabietic acid.

Since the first application of gas chromatography to resin acid analysis in 1959 [1], a number of publications have appeared describing the GLC separation and characteristics of resin acids, evaluated first for packed columns with a variety of stationary phases [2–5] and later for capillary columns [6–10]. Zinkel and Han [11] reviewed the state of the art for both packed and capillary columns applied to resin acids analyses.

Most of the literature methods [1–11] were developed for the determination of resin acid composition in the matrix by normalizing total peak areas to 100%. Although this approach is adequate for many purposes, it is not fully quantitative in that detector responses for individual resin acids can vary by nearly 10%.

The need to find a simple, rapid, accurate and reproducible procedure for quantitative analyses of dehydroabietic acid in rosins and modified

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rosins from different industrial sources led us to the development of the present method using a capillary column with methyl stearate as the internal standard.

EXPERIMENTAL

Reagents and chemicals

Methanol, diethyl ether, methyl *tert.*-butyl ether and potassium hydroxide (Merck) were analytical-grade reagents. Diazomethane was generated from N-methyl-N-nitroso-*p*-toluenesulphonamide (Sigma) by a standard procedure [6–10].

Reference standards and standard solutions

Stearic acid (Sigma) and dehydroabietic acid (Helix-Biotech) were analytical-grade reagents; samples of rosin and disproportionated rosin were gifts from various companies.

An internal standard stock solution of methyl stearate in *tert.*-methyl butyl ether at a concentration of 1.0 mg ml^{-1} was used. The reference stock solution was prepared by accurately weighing about 50 mg of methyl dehydroabietate and dissolving with *tert.*-methyl butyl ether in a 50-ml volumetric flask. The reference solution for analysis of disproportionated rosin was prepared by measuring 2.0 ml of the reference stock solution and 3 ml of internal standard stock solution into a 10-ml volumetric flask and diluting to volume with *tert.*-methyl butyl ether.

To prepare standard solutions for the calibration graph, appropriate volumes were measured out of the reference solution, mixed with internal standard (3 ml) and diluted to 10 ml with *tert.*-methyl butyl ether. The calibration was carried out over a concentration range of 0.05–0.5 mg ml^{-1} for dehydroabietic acid as its methyl ester.

Apparatus

A Carlo Erba HRGC 5160 gas chromatograph equipped with a Spectra-Physics computer integrator Model SP 4270, flame ionization detector and a 15 m × 0.25 mm I.D. fused-silica column coated with a methyl silicone film (DB-1, J&W, Folsom, CA, USA) with a thickness of 0.10 μm was used for analyses. A 1-μl aliquot of the 10-ml methyl *tert.*-butyl ether solutions was used for the determination of methyl dehydroabietate content by capillary GC.

The split injection port of the instrument was adjusted to a split ratio of 1:100. Helium was used as the carrier gas at a flow-rate of 2 ml/min (68 cm/s) through the column with an inlet pressure of 65 (70) kPa. The column temperature was maintained at 195°C. The detector and injector port temperatures were set at 300°C and 275°C, respectively. Methyl dehydroabietate was quantified by comparing the peak areas of the detector response to injections of samples with known amounts of a standard of methyl dehydroabietate.

Esterification of standards and samples

About 50 mg of the sample dissolved in a mixture of diethyl ether and methanol (9:1) were esterified with excess diazomethane [11]. The esterification was complete when bubbles were no longer visible and the yellow colour of the solution was stable. Excess diazomethane was removed in a well ventilated fume cupboard under a nitrogen flow. After evaporation of the solvent, the sample was dried under vacuum, accurately weighed and stored at 4°C until GC analysis.

Sample for analysis

The sample solution was prepared by accurately weighing about 50 mg of the esterified sample and diluting with methyl *tert.*-butyl ether in a 50-ml volumetric flask. The injection solution was prepared by accurately measuring 2 ml of the sample solution, mixing with 3 ml of internal standard stock solution and diluting with methyl *tert.*-butyl ether in a 10-ml volumetric flask.

RESULTS AND DISCUSSION

A capillary GC method that does not require time-consuming purification steps prior to analysis has been developed for the rapid and accurate determination of dehydroabietic acid as its methyl ester in commercially disproportionated rosins. Derivatization to the methyl ester, carried out in diethyl ether–methanol (9:1) [11], was chosen since it leads to clean, fast and

complete reactions, no sample purification being required; consequently, losses involved in the procedure are minimized.

In spite of the many industrial uses of disproportionated rosin, which is superior to rosin for many applications, the only two relevant publications are those describing reversed-phase partition chromatography of disproportionated rosin [12] or a colorimetric method comparing the colour intensity of the violet solution with permanganate solutions of different concentrations [13].

An internal standard method was employed, with methyl stearate as the internal standard. Upon application of the analytical procedure to commercially disproportionated rosins, the separation of the critical pair of peaks 2 and 3 (Fig. 1) was achieved through adjustment of temperature and flow-rate at the expense of a slightly increased analysis time (*ca.* 9.5 min).

A bonded methyl silicone, DB-1 capillary fused-silica column having 15 m length, 0.25 mm internal diameter and a film thickness 0.10 μm, was used. This column was previously tested for resin acids analysis [11] and proved to have good resolution and short analysis time.

The linearity of the detector response to variations in concentration was determined by constructing a calibration graph of peak area *versus* concentration over the range of 0.05–0.5 mg ml^{-1} methyl dehydroabietate. For each concentration, replicate determinations ($n = 5$) with five injections were made and the average values of peak area were plotted. The slope, the intercept and the correlation coefficient were, respectively, 0.3731, −0.0304 and 0.9991 ($n = 5$) for peak area measurements and were obtained by linear regression analysis.

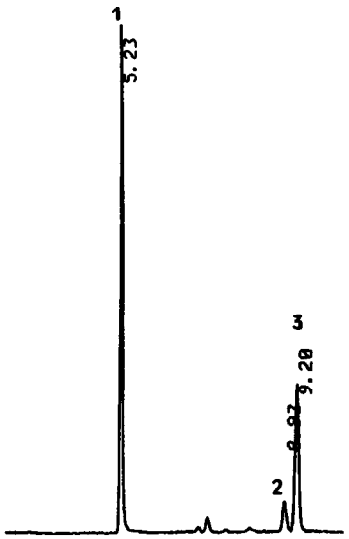

Fig. 1. Chromatogram of a sample of commercially disproportionated rosin. Peak 1 is methyl stearate (internal standard, 0.3 mg ml^{-1}) and peak 3 is methyl dehydroabietate (0.20 mg ml^{-1}). Values at peaks are retention times in min.

The repeatability and reproducibility of the method were tested with replicate ($n = 5$) analysis of samples ($n = 5$) corresponding to the average weight of samples with an average concentration of dehydroabietic acid. The results show a 0.82–1.73% R.S.D. between the analysis and the low value of the overall R.S.D. between the analysis and the low value of the overall R.S.D. (1.31%).

The precision of the method was determined using two methyl dehydroabietate standard solutions with concentrations 1.662 μg ml^{-1} and 2.216 μg ml^{-1}, each injected five times. The method is accurate for the above concentrations with a 99% confidence level (Table I).

For commercial disproportionated rosin, the results were in agreement with state levels. This method can be applied to the quantitation of minor amounts of dehydroabietic acid in gum rosin, provided a high enough mass of sample is used to work within the calibration graph limits.

The method is simple, specific, exact and reproducible and therefore can be applied to various commercial modified rosins.

TABLE I

CALIBRATION DATA FOR ANALYSIS

St. conc. = standard concentration; $\bar{x}$ = arithmetic mean; σ_x = standard deviation; t = Student's constant; n = number of measurements.

St. conc., X (μg ml^{-1})	$\bar{x}$	σ_x	$(X - \bar{x})$	$t\sigma_x/\sqrt{n}$
1.662	1.636	0.022	0.026	0.045
2.216	2.106	0.215	0.110	0.443

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