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Note

Thin-layer chromatographic method for the identification of natural polyisoprene and synthetic polyisoprene rubber

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It has been reported^{1,2} that natural rubber can be determined both qualitatively and quantitatively by means of identification of β -sitosterol via thin-layer chromatography (TLC). Refs. 1 and 2 gave a TLC method for a relatively simplified system of compound ingredients. Our method was applied to more complex commercial compounds such as tire compounds, and automobile motor mounts. Furthermore, it was stated¹ "that relative concentration of β -sitosterol expressed as the spot area per gram of natural rubber was reasonably constant, irrespective of the natural rubber grade...". For the following natural rubber grades: No. 1 SSR, No. 3 SSR, No. 5 SSR, SMR Hevea crumb 5-50 etc., this statement is correct; however, SMR 20 or SIR 20 grade, natural gum stock had a β -sitosterol concentration of 1.7 times less than the others. (This is explained by the fact that this gum stock is prepared differently from other grades of natural rubber, and in turn shows different physical characteristics.) Our studies developed a two-stage solvent system, in one dimension, as well as utilizing a different visualization agent. The plates are high-efficiency plates, HETLC-GHL made by Analtech (Newark, DE, U.S.A., Cat. No. 56077). This type of plate is of utmost importance.

The solvent system is carbon tetrachloride followed by a mixture of 100 ml of chloroform and 5 ml of acetone; visualization agent, 3 g of cupric acetate in 100 ml of 10% H_3PO_4 . Blue-gray spots on a white background will appear for β -sitosterol, with no background interferences of other compounding ingredients. Fig. 1 shows a chromatogram of model compounds based on known and unknown tire compounds investigated by us. The spots above the β -sitosterol are the oils, antioxidants, anti-ozonants, waxes, accelerators, etc. The spots below are those of the different surfactants.

EXPERIMENTAL

Rubber compound samples of known composition (containing natural rubber), were thinly milled on a cold mill, then 5 g were analytically weighed and Soxhlet extracted for 16 h (overnight) with ACS-grade acetone. (All solvents used are ACS grade or better.) The acetone was evaporated on a low-heat hot-plate under the hood, and the last 10-ml portion of the acetone extractables were transferred carefully

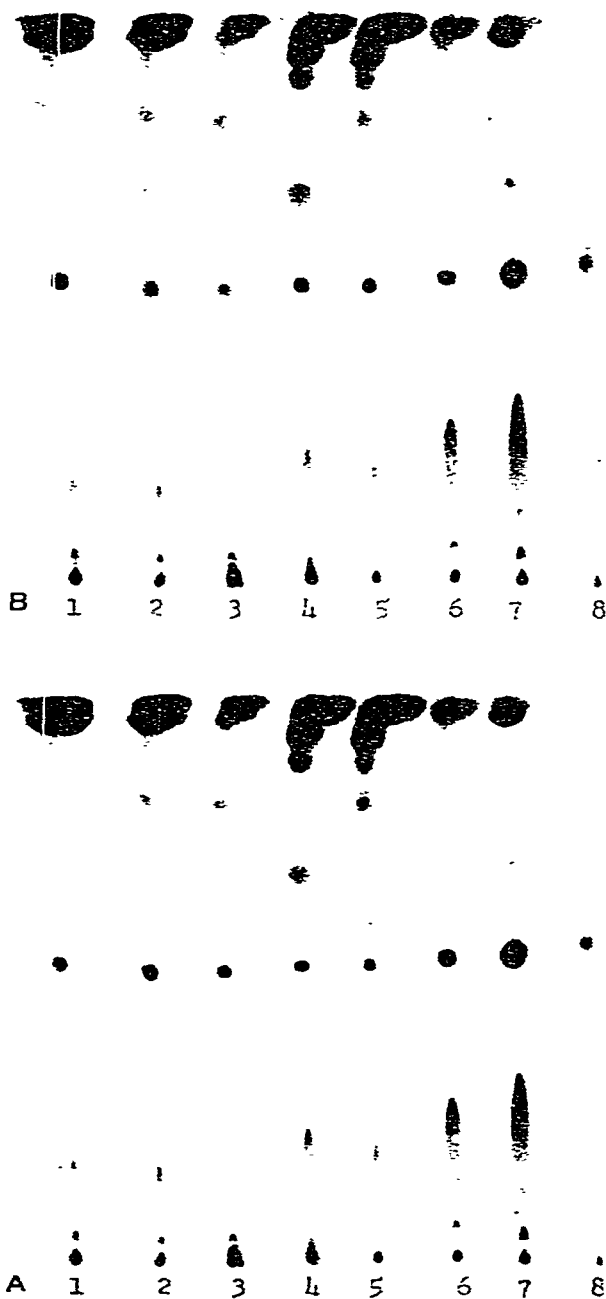


Fig. 1. A. Actual photocopy of plate, using bright light. B. Actual photocopy of plate, using intermediate light intensity (what the human eye actually sees on the plate). Spots: 1 = model based on No. 1 SSR rubber; 2 = Model based on No. 1 SSR different ratio of natural to synthetic; 3 = manufacturer No. 1, tire stock based on No. 1 SSR rubber; 4 = manufacturer No. 2, tire stock based on No. 1 SSR rubber; 5 = manufacturer No. 3, tire stock based on SMR 20 rubber; 6 = SMR 20; 7 = No. 1 SSR; 8 = β -sitosterol.

into a 20-ml glass vial and evaporated to complete dryness in an air oven at 75°C. The vial, after the acetone evaporation, was kept for 10 min at 105°C in the air oven. The vial was cooled, and exactly 5 ml of methylene chloride were added to the residue in the vial, the vial was capped, and then shaken to dissolve all the residue. Next, 2 μ l of the extracted methylene chloride solution were spotted onto the HETLC-GHL plate (10 \times 10 cm). This type of plate is one of the keys to the success of the analysis. The spotting is done 1 cm from the bottom of the plate, and at least 1.5 cm from the edge of the plate. We used TLC multi-spotter syringes (Analytical Instrument Specialties, Libertyville, IL, U.S.A.).

The plate is first developed in carbon tetrachloride. Let the solvent front reach the end of the plate. We always spot a pure β -sitosterol as a control. An efficiency developing chamber assembly, made by Analtech, Cat. No. 050A, was used. No saturating pads or filter paper were used, enough solvent was added so it just touched the bottom of the plates below the applied spots.

After the carbon tetrachloride reached the top of the plate, we removed the plate and let the solvent evaporate in an air oven at 105°C. We let the plate completely cool in the open air, and then developed the same plate in the same direction, in a solvent system consisting of 100 ml of chloroform and 5 ml of acetone mixed well and freshly prepared and introduced into the chamber 2 min prior to the insertion of the plate. After the solvent front reaches the top of the plate, the plate is removed and is dried in an air oven at 105°C. The plate, after cooling down enough to be handled by hand, is dipped for a few seconds, not sprayed, in a solution of 3 g of cupric acetate in 100 ml of 10% H_3PO_4 . The plate is heated in an air oven for 10 min at 125°C. Blue-gray spots on a white background will appear for the β -sitosterol.

RESULTS AND DISCUSSION

Fig. 2 shows the TLC plate obtained for SMR 20 and/or SIR 20 gum stock not compounded, and No. 1 SSR gum stock not compounded. The naked eye can see the difference in the size of the β -sitosterol. In our laboratory, we also photocopied the plate and with a planimeter measured the area of the β -sitosterol spot. We compared these results with the density counts obtained on the same spots by a Joyce Loebel scanning densitometer, and in both cases the No. 1 SSR rubber had a 1.7 factor bigger than that of the SMR 20 or SIR 20 for the β -sitosterol. Before further discussing the results, I would like to emphasize the importance of the plates we were using. They contain inert inorganic binder (not inert organic binder) which is the key to the good separation, and the dipping technique that gives it a uniform layer of visualization reagent, with no flaking or washing off of the TLC layer.

In Fig. 1, we show the TLC plate of several tire compounds being manufactured by several different companies. We have determined the ratios of natural to synthetic polyisoprene in the rubber. The procedure was confirmed by the analysis via TLC of model compounds and comparing it to known formulations, using both No. 1 SSR stock and SMR 20 stock rubber. It should be mentioned that those model compounds as well as the unknown, contained natural rubber, synthetic polyisoprene, polybutadiene and SBR blends. The composition of the models were obtained using thermal gravimetric analysis (TGA), which gave us percent volatiles, percent polymer and percent carbon black and ash. The ratio of the polymer types was

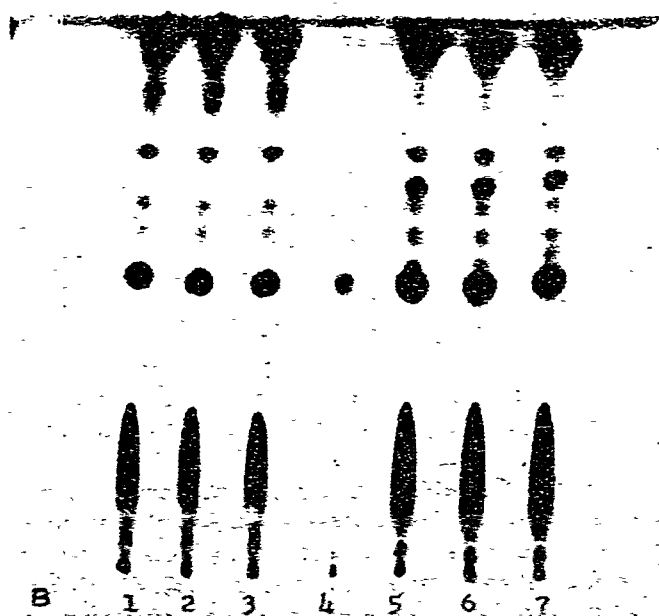
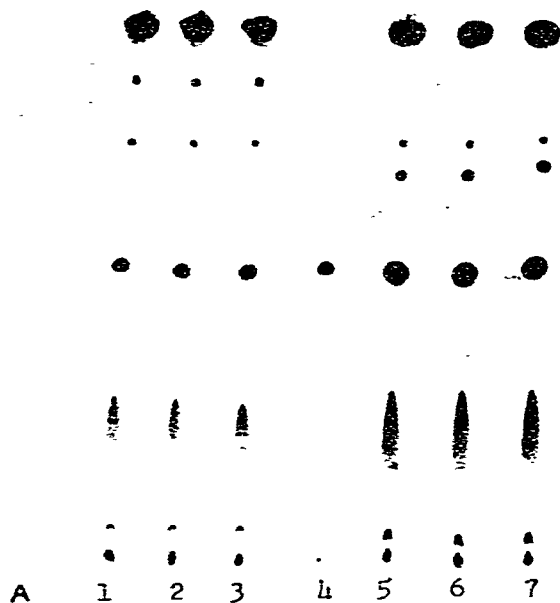


Fig. 2. A, Actual photocopy of plate, using bright light. B, Actual photocopy of plate, using intermediate light intensity (what the human eye actually sees on the plate). Spots: 1, 2, 3 = $2 \mu\text{l}$ of 5 g SMR 20 stock rubber extract in 5 ml of methylene chloride; 4 = $2 \mu\text{l}$ of 0.5% (w/w) β -sitosterol in methylene chloride; 5, 6, 7 = $2 \mu\text{l}$ of 5 g No. 1 SSR stock rubber extract in 5 ml of methylene chloride.

obtained using infrared analysis. Within the model, we have changed the ratio of natural polyisoprene to synthetic polyisoprene. Figure 1 shows extractables in the model (based on the unknowns). A typical formulation was found to be: natural polyisoprene; polybutadiene and SBR; carbon black; paraffinic type oil; paraffin wax; Santocure (an accelerator); Flectol-H (an antiozonant); Wingstay 300 (an antiozonant); stearic acid and rosin acid.

The model compounds were the basis for a calibration curve via β -sitosterol measurements. This paper emphasizes the qualitative aspect of the separation, but when the square root of the intensity of the spots obtained for β -sitosterol on the TLC plates was plotted *versus* \log_{10} of the concentrations of natural rubber to synthetic, a straight line was obtained³. A Joyce Loebbl densitometer was utilized to determine the intensity of the TLC spots. A TLC scanner utilizing our method no doubt will give better results for the quantitative measurement of natural rubber as a function of its β -sitosterol content.

ACKNOWLEDGEMENT

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REFERENCES

- 1 J. R. Davies, *J. Chromatogr.*, 28 (1967) 451.
- 2 A. Gomoryova, *Plaste Kaut.*, 20 (1973) 1.
- 3 Z. Ronen, unpublished results.