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A method for distinguishing different types of processed rubber by gas-liquid chromatographic analysis of their volatile emanations

The analysis of volatile matter evolved from a material has been widely used in practice as a guide for identification of the material itself and also as a qualitative measure of the chemical processes taking place in the material under atmospheric conditions. Gas–liquid chromatography (GLC) has been the method of choice in most cases. The application of GLC to the analysis or identification of elastomeric polymers is well known but in almost all cases the polymer was subjected to a process of complete breakdown or pyrolysis, and the products of pyrolysis were analysed by GLC[1–7]. It is true that the products of pyrolytic fission will bear some relation to the initial structure and properties of the polymer used, but in practice these polymeric substances will rarely be used at temperatures as high as 500–700°.

However, even under conditions such as those under which these polymers are normally used in practice, that is at low temperatures often not exceeding 150–200°, volatile matter is continually evolved and the processes of destruction or degradation are taking place. The present work is a preliminary attempt to investigate any relationship that may exist between the volatile matter and the properties of different varieties of natural rubber under conditions that the rubber will experience during processing. Work carried out during the specification analysis of rubber indicates that the major part of the volatile matter is water. However, it is believed that there should be other substances present because it is noticeable that the odour of a sample of rubber, even under atmospheric conditions, varies with the method of production and sometimes the type of clone from which it originated. We report here preliminary work carried out on the volatile emanations from four different preparations of natural rubber.

Experimental

A Varian Aerograph Model 90-P3 gas chromatograph was used for the analysis with a thermal conductivity detector and helium as the carrier gas. The analysis of the head-space over small amounts of rubber in a closed container did not give satisfactory results owing to technical problems in transferring the head-space into the injector of the chromatograph. Accordingly, two different techniques of studying the volatiles were adopted.

In the first method, the rubber was cut into small pieces of about 4 mm^3 in volume and packed into a glass column 10 in. × 1 in. I.D. Then steam was passed through the column for 1 h and the steam distillate was cooled and extracted with diethyl ether, hexane and *n*-butyl acetate using only one solvent at a time. The extract was concentrated and analysed by GLC. The same procedure was repeated with different varieties of rubber, *viz.* pale crepe, smoked sheet, scrap rubber and crumb rubber.

In the second method, a system was assembled to heat the rubber in a cylindrical glass column, through which air was passed. The temperature inside the column was maintained at 110–120° and the gaseous products were absorbed in a glass container containing a small volume of carbon disulphide solution. The container was

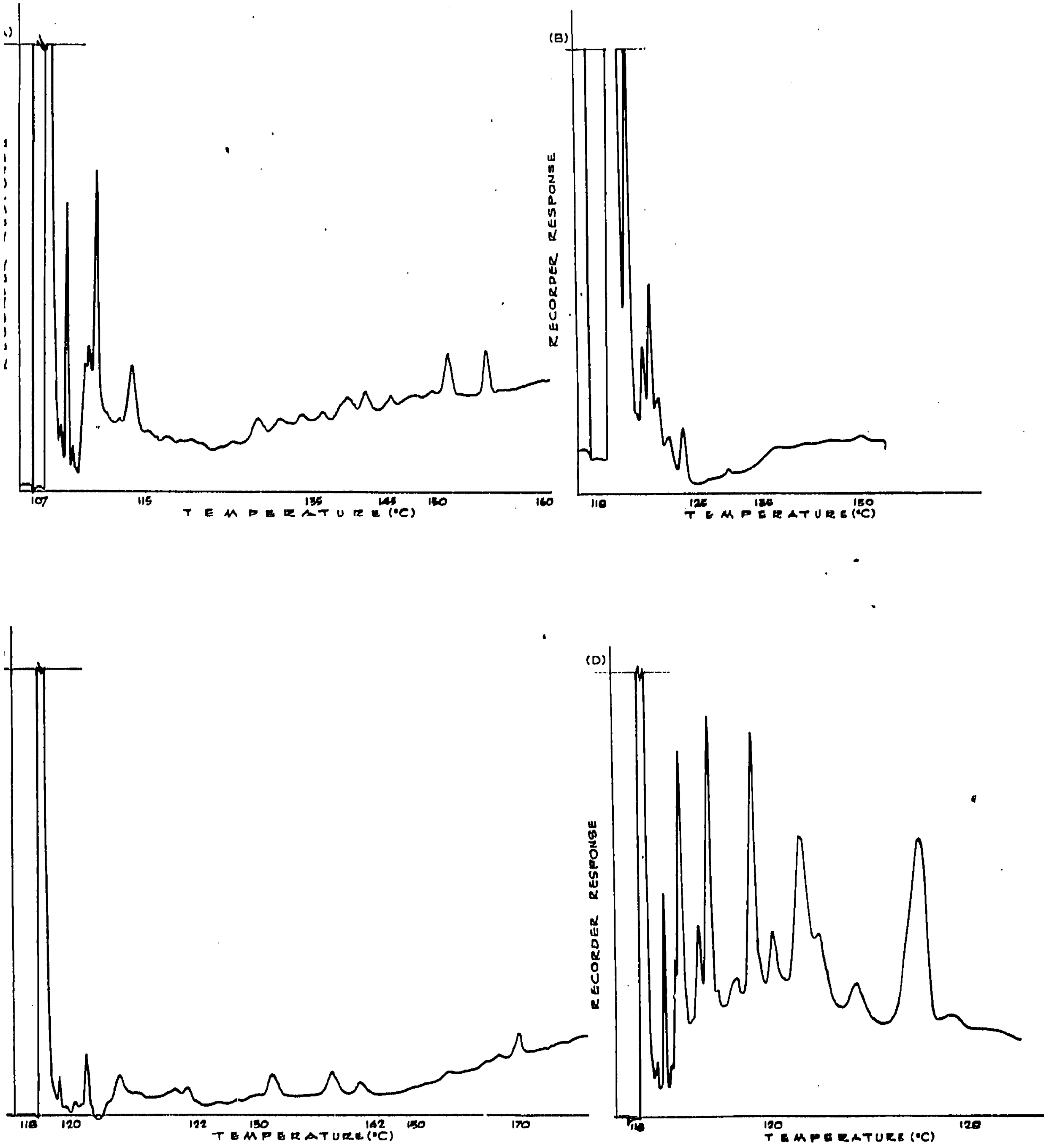
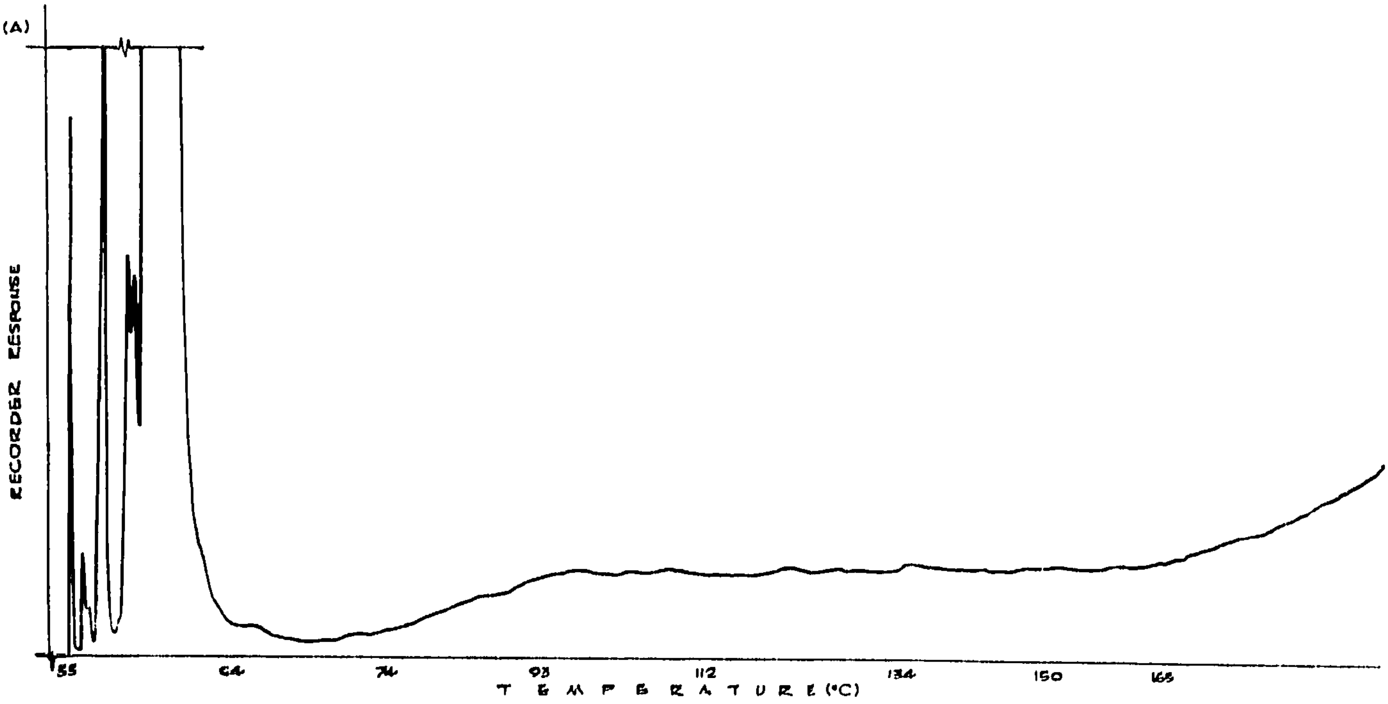
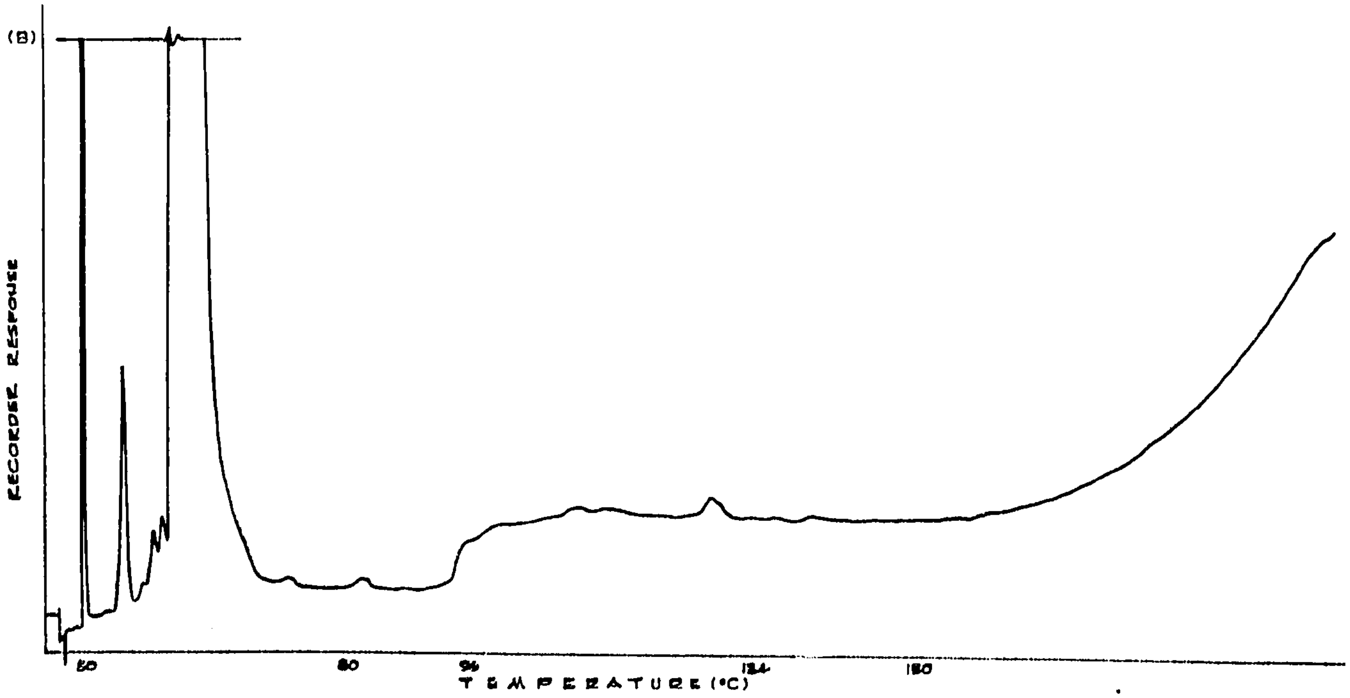


Fig. 1. (A) Scrap rubber steam distillate in diethyl ether. (B) Crumb rubber steam distillate in diethyl ether. (C) Pale crepe rubber steam distillate in diethyl ether. (D) Smoked sheet rubber steam distillate in diethyl ether.

kept at a low temperature by the use of a mixture of dry ice and acetone in a Dewar flask. The condensate was then analysed by GLC. The same procedure was again repeated with the above varieties of rubber.

Spectro-grade solvents were used and were injected into the chromatograph prior to the solution in order to identify the peaks produced by the solvent itself.





Results and discussion

Figs. 1A–D represent the tracings of typical chromatograms obtained with the four different types of rubber by the first technique. Figs. 2A–D are similar tracings obtained with the second technique.

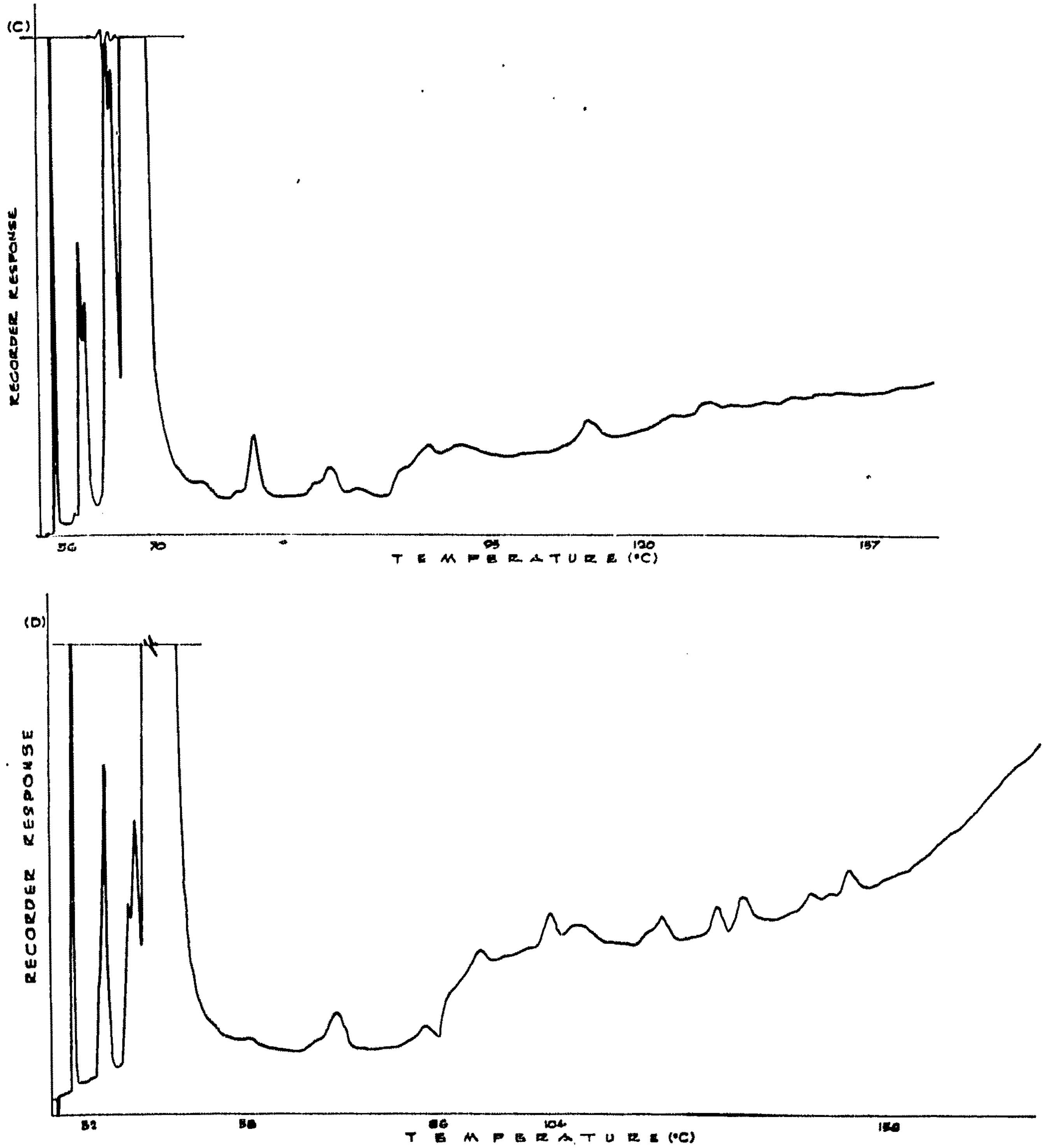


Fig. 2. (A) Condensate of scrap rubber volatiles in carbon disulphide. (B) Condensate of crumb rubber volatiles in carbon disulphide. (C) Condensate of pale crepe rubber volatiles in carbon disulphide. (D) Condensate of smoked sheet rubber volatiles in carbon disulphide.

In both methods, the sample size was 6 μl, detector temperature 200°, recorder range 2.5 mV and chart speed 20 in./h. In the first method, the column consisted of 3% of SE-30 on A.W. Chromosorb, 5 ft. × 1/4-in. O.D. The temperature was linearly programmed from 115° to 150° at 4°/min. The injector temperature was 200° and the carrier gas flow-rate was 50 ml/min. In the second method the column consisted of 15% of Apiezon L on A.W. Chromosorb, 5 ft. × 1/4-in. O.D. The temperature was linearly programmed from 55° to 170° at 4°/min. The injector temperature was 150° and the carrier gas flow-rate was 40 ml/min.

It was noticeable that the chromatographic profiles obtained were characteristic of each type of rubber and were consistently reproducible. Small variations in the GLC operating parameters did not alter the over-all results. As expected, the smoked sheet gave the largest number of peaks while the pale crepe displayed only a few low-boiling constituents.

Identification of the constituents of the steam volatile fractions of the various natural rubbers is in progress. It is conceivable that the GLC profiles will be useful as a guide for assessing the quality and condition of processed rubbers.

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