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IDENTIFICATION OF ELASTOMERS BY HIGH-RESOLUTION PYROLYSIS–GAS CHROMATOGRAPHY AND MULTIPLE SELECTIVE DETECTORS

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SUMMARY

A pyrolysis–gas chromatographic method for the identification of rubbers is described. The simultaneous use of multiple and selective detectors and capillary columns provided satisfactory results for qualitative analysis. Examples of the identification of vulcanized rubbers and their pyrolysis products are given. The samples do not require preliminary treatments.

INTRODUCTION

Pyrolysis–gas chromatography (Py–GC) has been extensively used[1–5] for the identification of polymers through the main peaks of the volatile constituents obtained by thermal decomposition. This is the most popular analytical technique for vulcanized or cross-linked polymers, since the decomposition products can provide fingerprints of the raw material.

Our goal was to optimize the various steps in the procedure by using high-resolution and high-accuracy instrumentation, consisting of the pyrolysis chamber, chromatographic column, temperature-programmable column oven, detection system, recorder and integrator. We started by using a static pyrolysis system, a packed column, an ordinary precision temperature-programmable column oven, a single flame ionization detector and a limited capability of recording integration limits.

Under these conditions, it was quite difficult to solve problems of qualitative analysis because several limitations were encountered, especially when these results were compared with those obtained at later stage by an instrumentation improved in every single component, *i.e.,* dynamic pyrolysis unit, capillary column, accurate temperature-programmable column oven with sub-ambient capabilities, specific and multiple detection systems, multi-channel high-resolution recording–computing system with memory capability for future automation. This greatly extended the application of Py–GC, since it allowed discrimination between small compositional differences and gave greater reproducibility and specificity.

This paper reports the pyrograms obtained from several commercially available rubbers and blends and discusses the results.

METHODS

A Carlo Erba Strumentazione (Milan, Italy) Fractovap Model 2900 gas chromatograph, equipped with a sealed coolant circulation sub-ambient unit and flame ionization, nitrogen–phosphorus and electron-capture detectors, used simultaneously (the first two in series, and the last in parallel). Identification and integration of peak areas was accomplished with a Varian CDS 401 data system. A pyroprobe 100 (CDS) solids pyrolyzer was also used.

Column, 25 m × 0.32 mm I.D., glass wall-coated open tubular (WCOT) column, coated with JXR (methylsilicone), film thickness 1.3 μm (manufactured by MEGA, Milan, Italy, and available from Carlo Erba Strumentazione); temperature, isothermal at 5°C for 5 min, programmed from 5°C to 120°C at 3°C/min; carrier gas, helium, 4 ml/min, injection port temperature, 200°C; splitting ratio 1:5; detector temperature, 250°C; attenuation × 16; sample, <0.7 mg. The sample was placed inside the quartz capillary between two plugs of quartz wool. Commercially available rubber samples, vulcanized in our laboratory, were analysed.

RESULTS AND DISCUSSION

Figs. 1–9 show pyrograms of some commercially available vulcanized rubbers of different kinds, consisting of single polymers or blends.

Simultaneous recording of the signals from a single pyrolysis by three different detectors permits an immediate qualitative distinction. In most cases, electron-capture detection yields few and equivocal peaks, but it provides a great number of distinct signals when halogenated polymers are analyzed (chloroprene rubber, sulphochlorinated polyethylene). Nitrogen–phosphorus detection often gives peaks with
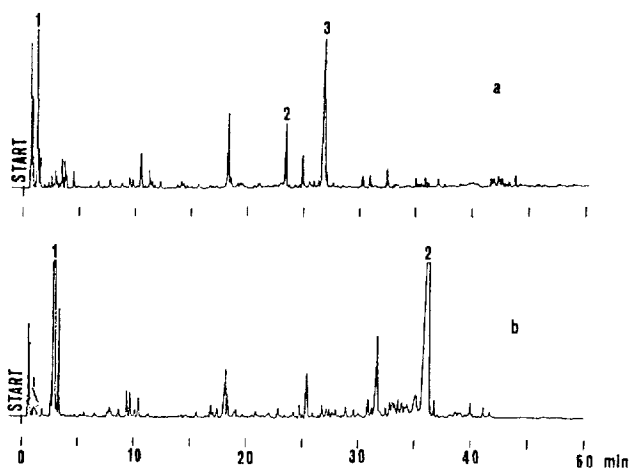

Fig. 1. (a) Products from the pyrolysis of styrene–butadiene rubber: 1 = butadiene; 2 = vinylcyclohexene; 3 = styrene. (b) Products from the pyrolysis of natural rubber: 1 = isoprene; 2 = dipentene.
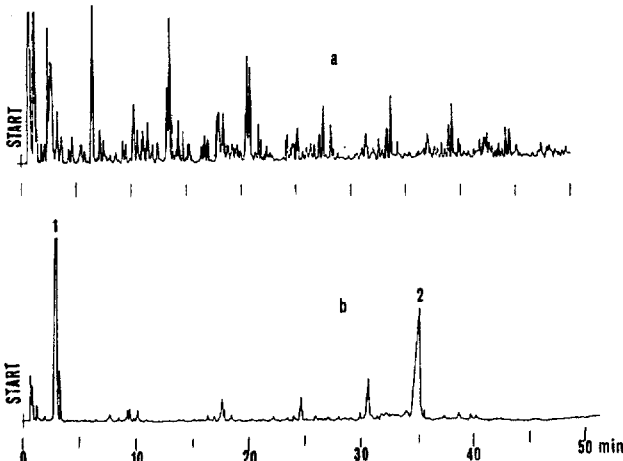
Fig. 2. (a) Pyrolyzate chromatograms of ethylene–propylene-diene rubber. (b) Pyrolyzate chromatograms of polyisoprene: 1 = isoprene; 2 = dipentene.
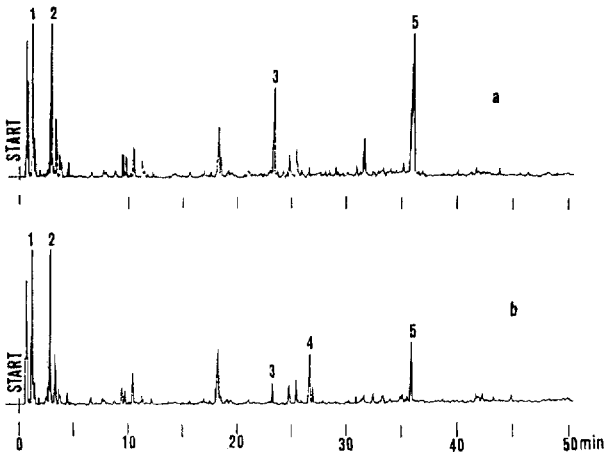
Fig. 3. Pyrograms of polybutadiene–natural rubber blend (a) and styrene–butadiene–polybutadiene–natural rubber blend (b). Peaks: 1 = butadiene; 2 = isoprene; 3 = vinylcyclohexene; 4 = styrene; 5 = dipentene.

the same retention time as in flame ionization detection, but its signal intensity is totally different, demonstrating the presence of nitrogen-containing polymers by specific and very high peaks (Figs. 7 and 8). For instance, the presence of nitrile rubber + poly(vinyl chloride) (PVC) blends can be immediately recognised by the simultaneous use of electron-capture and nitrogen–phosphorus detectors (Fig. 9). Thus, it may be assumed that samples not yielding significant peaks with these detectors do not contain heteroatoms in the polymer structure. In these cases the chromatogram obtained by flame ionization detection generally permits identification of the components through the recognition of the main peaks (characteristic peaks) with
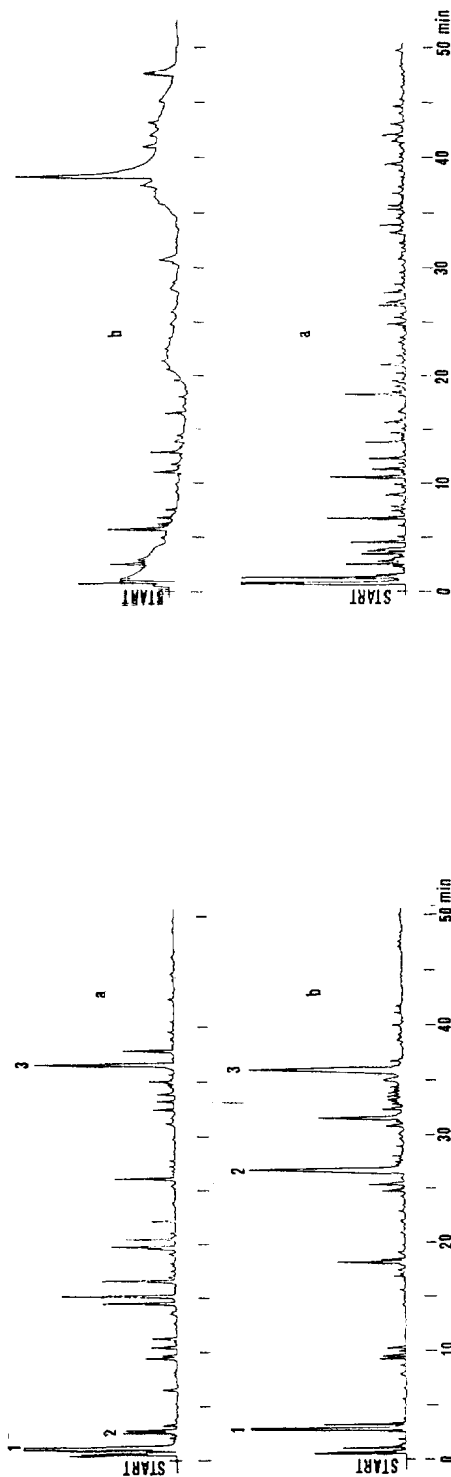
Fig. 4. (a) Pyrogram of isobutylene–isoprene rubber: 1 = isobutylene; 2 = isoprene; 3 = dipentene. (b) Pyrogram of styrene–isoprene–styrene rubber: 1 = isoprene; 2 = styrene; 3 = dipentene.

Fig. 5. Pyrograms of polyethylenechlorosulphonate obtained by flame ionization (a) and electron-capture detection (b).
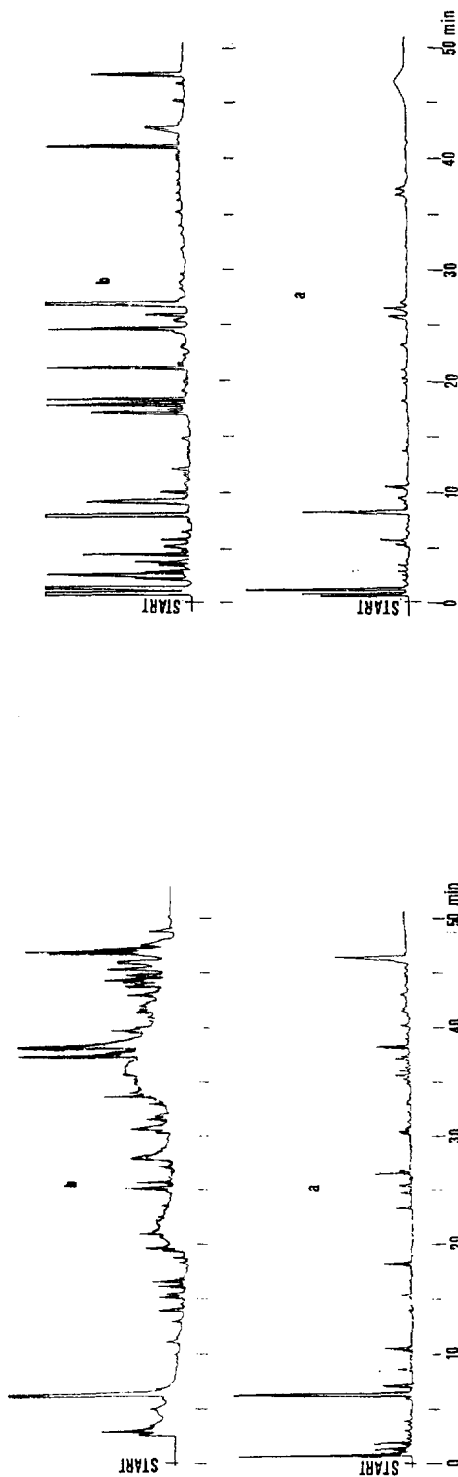
Fig. 6. Pyrograms of polychloroprene rubber obtained as in Fig. 5.

Fig. 7. Products from the pyrolysis of polyurethane obtained by flame ionization (a) and nitrogen–phosphorus detection (b).
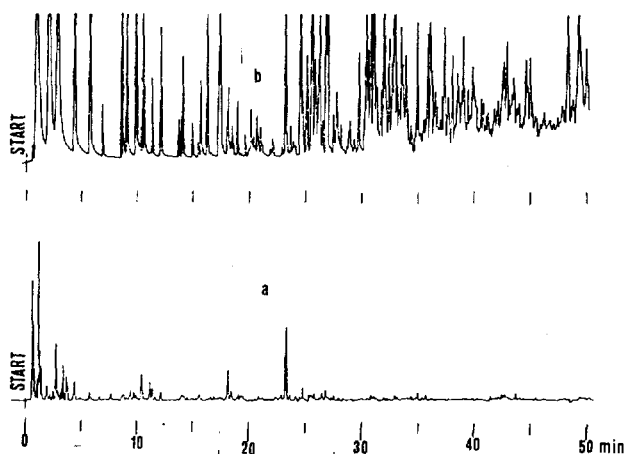
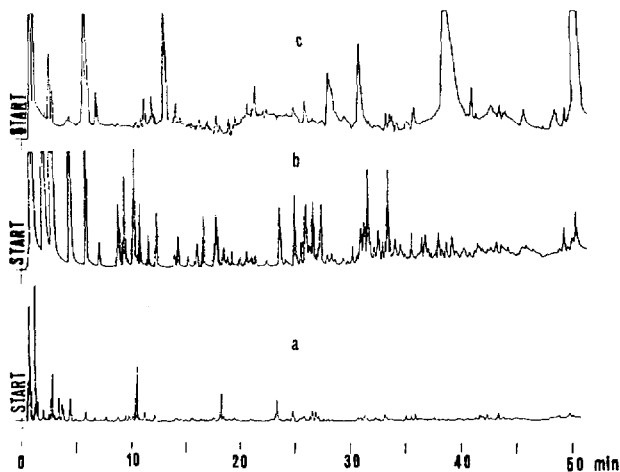Fig. 8. Products from the pyrolysis of nitrile rubber obtained as in Fig. 7.

Fig. 9. Pyrolyzate chromatograms of a nitrile rubber–poly(vinyl chloride) blend obtained by flame-ionization (a), nitrogen–phosphorus (b) and electron-capture detection (c).

retention times that are sufficiently reproducible, even when the copolymers are different.

The main pyrolysis products have been identified in some cases by injecting reference standards under the same operating conditions. The standard deviation of the retention time is within 0.8%. Taking into account the high resolution of the capillary column, the observed deviation seems adequate for automatic identification of the main monomeric units, based on the retention times of the main peaks. The standard deviation results from different causes: inhomogeneous samples, fluctuations of oven and pyrolyzer temperature, flow variations and small differences in the integration procedure.

A prompt check of retention times can be made by comparing the parallel

pyrogram of the nitrogen–phosphorus detector: the retention times of the characteristic peaks should match the corresponding ones from the flame ionization detector within a tolerance of 0.01 min.

In some cases, a rapid characterization of the composition of the blends can be obtained by comparing the area ratio of the characteristic peaks. The analysis of some styrene–butadiene rubber + butadiene rubber blends gives an average peak area ratio, calculated from the pyrograms, of 0.44, while the theoretical value calculated on the basis of the blend composition (1:1) is 0.45.

We believe that satisfactory quantitative results, suitable for routine analysis, could be obtained by proper calibration with blends of known composition. For the identification of polymers having similar chemical structures, a larger number of peaks must be taken into consideration. The combined use of capillary columns and dedicated chromatographic instrumentation provides a great deal of information, useful for establishing a fingerprint of the sample. Of course, this imposes some stringent requirements also on the computing/integration unit, which should be capable of storing a large number of peaks, besides integrating them properly, as does the Varian CDS 401.

CONCLUSIONS

The combined use of multiple detectors, operated simultaneously, and capillary columns, coupled to a dynamic pyrolysis unit, provided satisfactory results for the qualitative and, semiquantitative analysis of commercially available rubbers, either singly or in blends. Selective detectors allowed the prompt identification of nitrogen- or halogen-containing polymers.

Other polymers could be identified by flame ionization detection, either through the presence of characteristic peaks or by comparison of different series of peaks. The reliability and sensitivity characteristics of the proposed analytical instrumentation permit the use of this method for routine control. In this case, the "fingerprint" method does not require a knowledge of the composition of the pyrolysis products and their relation to the structure understudy.

REFERENCES

1 K. V. Alekseeva, *J. Anal. App. Pyrol.*, 2 (1980) 19.
2 B. Groten, *Anal. Chem.*, 36 (1964) 1206.
3 H. M. Cole, D. L. Petterson, V. A. Sljaka and D. S. Smith, *Rubber Chem. Technol.*, 39 (1966) 259.
4 V. G. Berezkin, V. R. Alishoyev and I. B. Nemirovskaya, *Gas Chromatography of Polymers*, Elsevier, Amsterdam, 1977, pp. 159–193.
5 C. E. R. Jones and C. A. Cramers (Editors), *Analytical Pyrolysis*, Elsevier, Amsterdam, 1977.