APPLICATION OF INSTRUMENTAL METHODS FOR EVALUATING HIGHWAY MATERIALS

Third Progress Report: Pyrolysis Gas Chromatography

MICHIGAN DEPARTMENT OF STATE HIGHWAYS

APPLICATION OF INSTRUMENTAL METHODS FOR EVALUATING HIGHWAY MATERIALS
Third Progress Report: Pyrolysis Gas Chromatography

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ABSTRACT: A relatively new technique of combining pyrolysis (thermal decomposition) and gas chromatography has been used to produce characteristic identifying fragmentation patterns for many plastic and rubber materials which are used in highway construction and maintenance. In this report, pyrolysis gas chromatography has specifically been used to detect compositional or processing differences, or both, in preformed neoprene joint seals supplied by different manufacturers and between different width joint seals from the same manufacturer. Such differences are pertinent since joint seals whose pyrolysis components have long retention times generally have high tensile strength and higher recovery from compression tests than those having short retention times. Procedural details of the methods and equipment descriptions are included. Specific materials used in delineator buttons, electrical wire insulation, traffic cones, etc., would also be amenable to this type of analysis. It is recommended that: (1) other plastics and rubbers be characterized by pyrolysis gas chromatography, (2) the investigation of neoprene joint seals be continued, and (3) pyrolysis gas chromatography be applied to the analysis of bituminous materials and paints.

KEY WORDS: fragmentation, gas chromatography, joint sealers, neoprene, plastics, rubber, testing equipment, test methods.

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INTRODUCTION

Quality control of the plastic and rubber materials used in highway construction and maintenance, and evaluation of these new materials, have posed difficult problems almost since the inception of their use. These materials, by their very nature, do not lend themselves to simple methods of analysis. The plastics and rubbers used as highway materials are not simple chemical compounds (monomers) but are stable, finished products (polymers) with certain specified properties. To attain these desired properties, the raw material (monomer) has usually been subjected to various treatments such as: blending with other monomers; compounding with plasticizers, anti-oxidants, light stabilizers, fillers, and other additives; various thermal treatments, such as melting or extrusion; and combinations of the above.

The most commonly employed methods for analyzing plastic and rubber materials (physical testing, chemical analysis, and infrared spectroscopy), while valuable for many applications, often prove to be time consuming and inadequate. For example, physical testing does not identify the material or provide much information on chemical composition. Chemical methods are often slow and tedious and too specific for general applicability. Polymers (plastics and rubber) containing carbon black are difficult to identify by means of infrared spectroscopy since they transmit only a small amount of infrared energy. In view of the increased use of plastics and rubbers in highway construction and maintenance, and the inadequacy of present methods of characterizing these materials, a search for more rapid, easily performed, and generally applicable techniques was initiated. A search of the literature, and contacts with people in the chemical instrumentation and plastics fields, revealed a relatively new technique that successfully analyzes many polymers. This technique, commonly termed pyrolysis gas chromatography (PGC), combines pyrolysis (thermal decomposition) and gas chromatography. The utility of PGC as a means of rapidly identifying a broad variety of polymeric materials has been demonstrated by several researchers (1, 2, 3). Cole, et al, (4) describe a procedure for the identification and quantitative determination of polymers in compounded cured rubber stocks. Fisher and Neuman (5) have used

PGC to determine compositional differences between commercial automotive brake lining materials. This technique has also been used for the structural characterization and identification of bitumens (6) and pitch resins. (7).

In the light of this work, the decision was reached to investigate the applicability of PGC to the analysis of plastics and rubbers used in highway maintenance and construction. It was felt that the following objectives would serve the most immediate needs and interests of the Department:

1. Develop procedures whereby routine identification, i.e., "fingerprinting," could be performed for all plastics and rubbers having highway applications.

2. Develop techniques for detecting differences due to formulation or processing, or both, between comparable materials supplied by different manufacturers and correlating these relationships with performance, quality, and specification requirements for these materials. Such materials would include preformed neoprene joint seals, electrical cable insulation, delineator buttons, hazard warning flasher lenses, traffic cones, bridge bearing pads, water stops, etc.

3. Characterize common formulation ingredients of plastics and rubbers such as plasticizers, anti-oxidants, and light stabilizers. Ability to characterize these ingredients would allow for solvent-extraction and identification of similar additives from compounded products.

It was further decided that progress reports would be filed as the work progressed. This is the first of such reports and covers the following:

1. A general discussion of gas chromatography and pyrolysis gas chromatography.

2. A detailed description of the instrumentation employed.

3. The development of methods for the routine identification of many plastics and rubbers used as highway materials.

4. The development of a method for detecting differences in preformed neoprene joint seals supplied by different manufacturers.

Preformed neoprene joint seal was chosen to be the first material studied in detail because the large increase in use and accompanying increase in acceptance testing during the 1965 and 1966 construction seasons

stimulated interest in finding methods of test to supplement or replace physical testing.

The pyrolysis gas chromatographic work reported here was conducted with an electrical discharge pyrolyzer (described in detail later). Pyrograms[1] from other types of pyrolyzers may appear different due to differences in decomposition method.

EXPERIMENTAL PROCEDURES AND DISCUSSION

Method - Pyrolysis Gas Chromatography

Gas chromatography is a technique for separating the components of a volatilized sample, thus enabling identification and quantitation. As shown in the flow diagram (Fig. 1) the sample is introduced, usually by means of a hypodermic syringe, into a heated sample injection port where it is

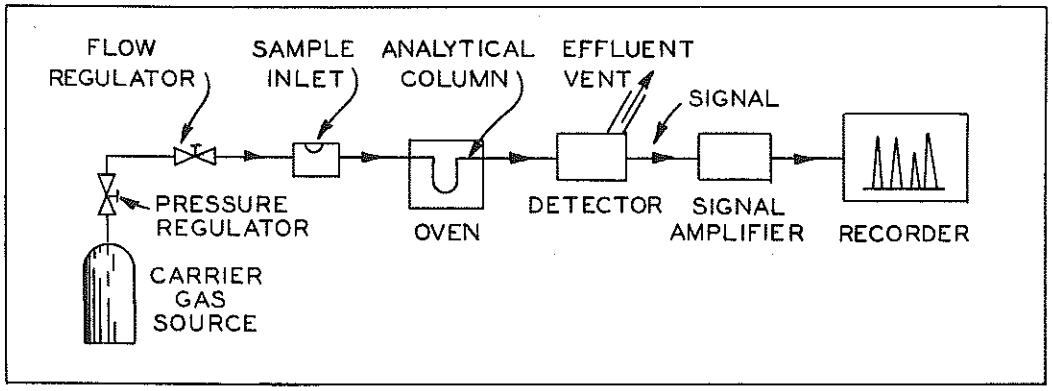

Figure 1. Simplified flow diagram of a gas chromatograph.

immediately vaporized. An inert carrier gas, usually helium, transports the vapor to the column and through it to the detector. While the vaporized sample is passing through the column, its components are separated by virtue of their differing chemical affinity for the column packing materials. Columns are usually small diameter tubes packed with low volatile liquids uniformly distributed over an inert solid material having a large surface area. Components having higher affinity for the column packing move more slowly and are retained longer. As each component passes

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[1] The terms chromatogram, fractogram, pyrogram and fragmentation pattern refer to the recorder trace which exhibits a peak for each component of the sample. Pyrogram and fragmentation patterns are used when the initial sample has been pyrolyzed to obtain volatile fragments.

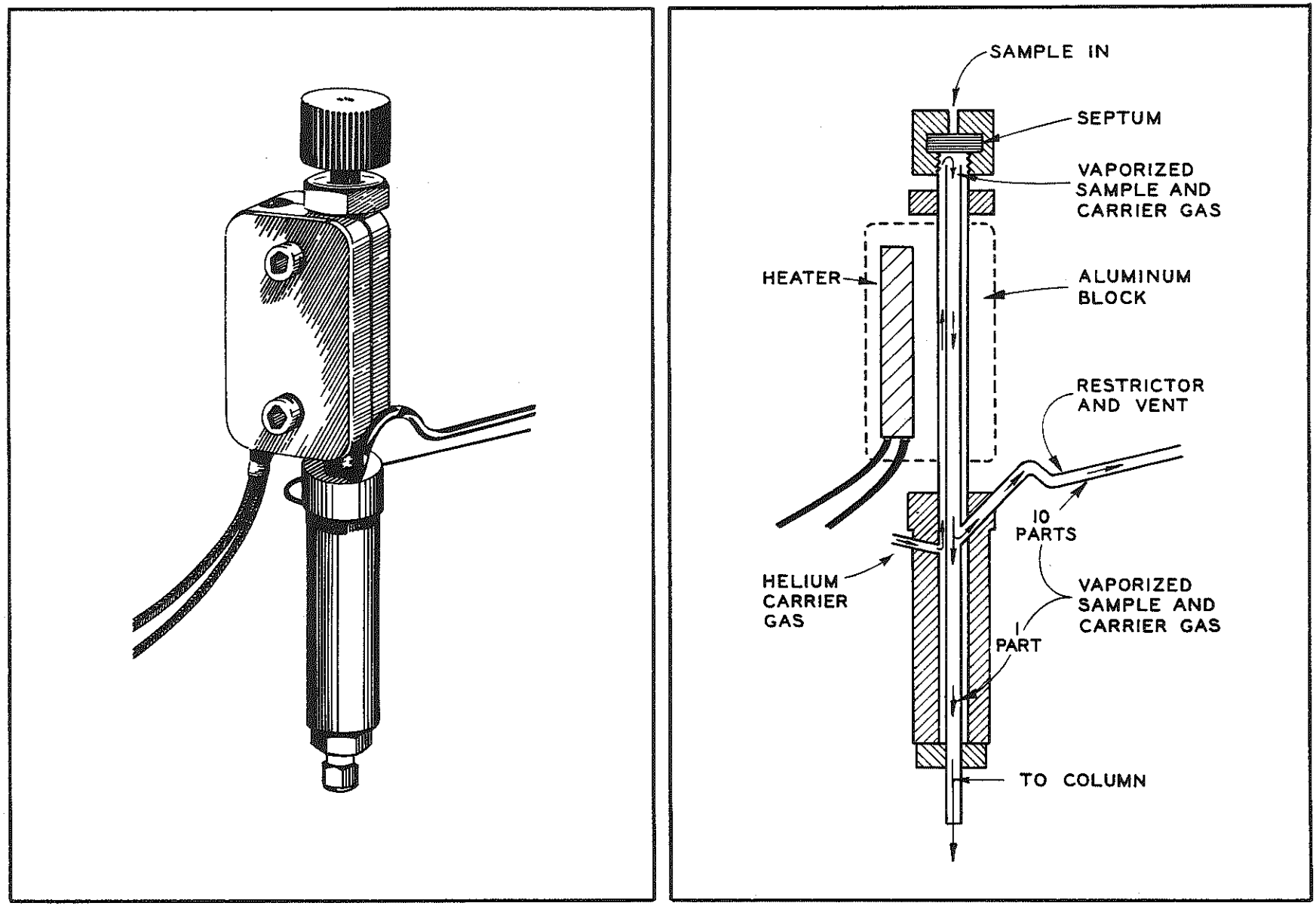


Figure 2. Stream Splitter Inlet.

through the detector, it creates an imbalance in the detector system which is amplified and transmitted to a recorder which traces a series of peaks called a chromatogram. The chromatogram serves as a characteristic pattern, or fingerprint, of the material for qualitative identification and gives an indication of the amount of each component present.

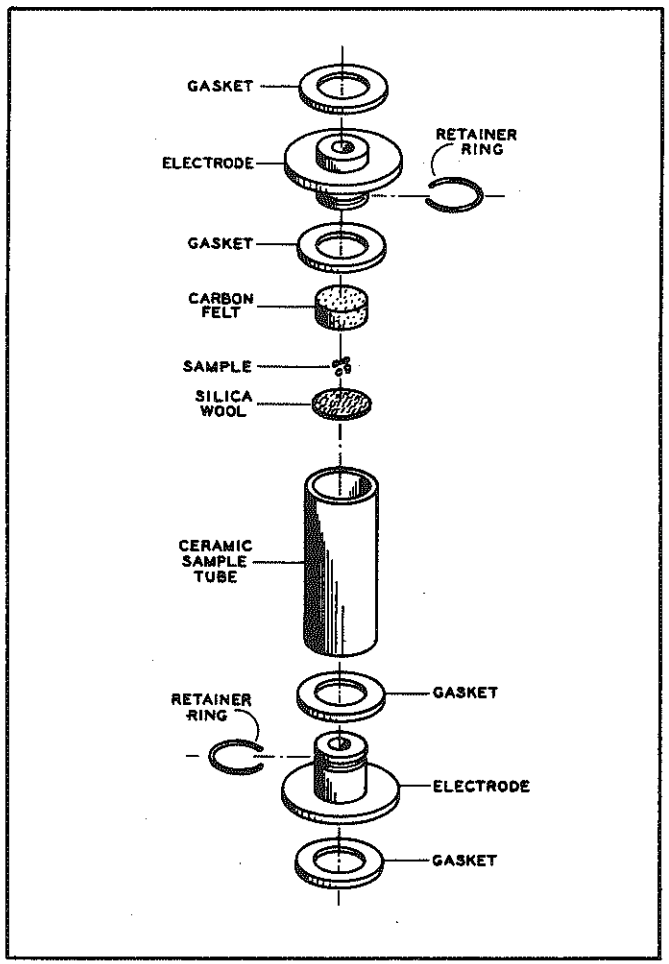
Gas chromatography is not usually directly applicable to the analysis of polymers since most of these materials have too low a vapor pressure, even at elevated temperatures, to pass through the column. Pyrolysis solves this problem by heating the sample to a sufficiently high temperature for thermal breakdown of the polymer into fragments having sufficient volatility to pass through the analytical column for analysis in the conventional manner. Pyrolysis can usually be applied directly to the sample, as received, so that little sample preparation is necessary.

Several methods have been used to pyrolyze and fragment samples. These include: (a) a heated filament, (b) a tube furnace, (c) induction heating, and (d) the electrical discharge method (8) used in this study. The first three techniques are somewhat similar in that they all employ controlled temperature pyrolysis in a reaction chamber, with the degradation products being swept from the chamber into and through the column by the carrier gas. The fourth technique, the electrical discharge method, employs a low current, high voltage electrical discharge to fragment the sample. This technique does not control pyrolysis temperature but maintains pyrolysis conditions by current control. The degradation products are carried to the column and detector in the conventional manner.

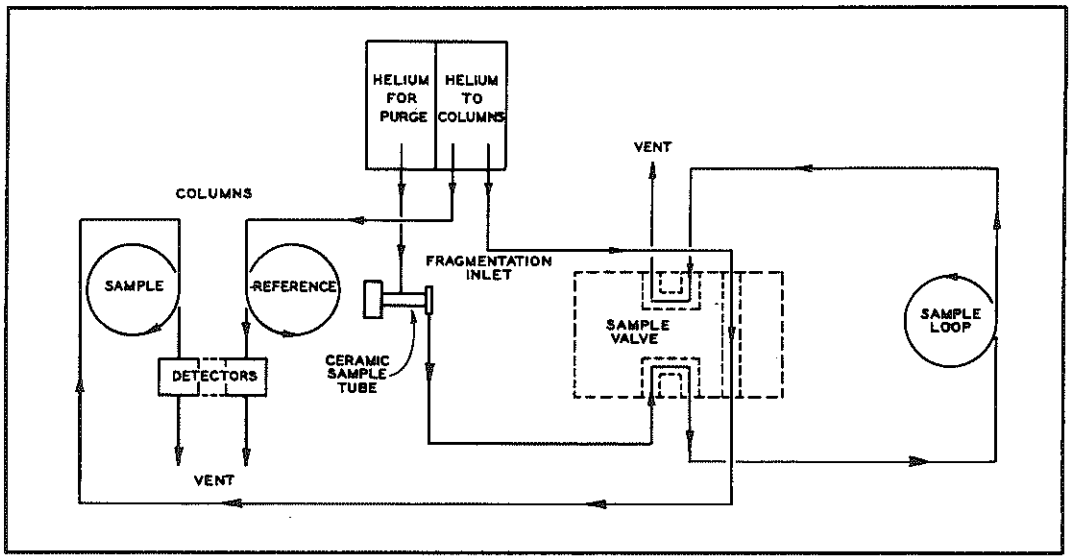
Equipment - Gas Chromatograph

The gas chromatograph used in this study is of the modular type, where selected modules or accessories may be added to the basic instrument to give the degree of sophistication desired. It can serve as a simple chromatograph for routine studies or as an instrument of complex research capabilities. The basic instrument consists of a cabinet with power supplies for all modules, voltage and temperature readouts of all heated areas, a column oven, and a column temperature controller. The modules and accessories used with the basic instrument in this study were as follows:

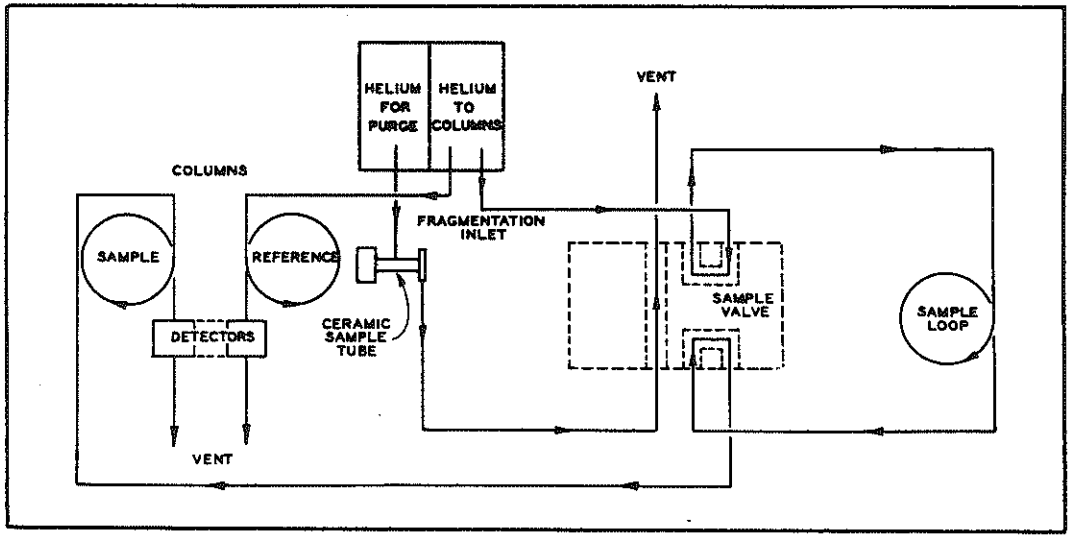
A. Stream Splitter Inlet This fixture (Fig. 2) permits the introduction of sample quantities too small to be accurately or reproducibly introduced by standard methods. The stream splitter accepts a larger sample volume, divides the stream of vaporized sample and carrier gas flow,



a. Exploded view of ceramic sample tube assembly.



b. Valve in collection position (with fragmentation products collecting in sample loop).



c. Valve in inject position (with fragmentation products from sample loop swept into column).

Figure 3. Fragmentation inlet, or pyrolysis accessory.

admits a precise sample volume to the column, and vents the excess. This inlet is constructed of two concentric stainless steel tubes encased in a heated aluminum block. The sample is injected with a hypodermic syringe through a silicone rubber septum directly into the center tube. Carrier gas (helium) sweeps up the outer tube, where it is preheated, then down the center tube, carrying the vaporized sample to the area where the gas stream is split in a predetermined ratio. The split ratio is controlled by the column pressure drop and a fixed restrictor on the vent side of the stream splitter. The split ratio of the fixed restrictor is 10 to 1 for 6-ft by 1/8-in. packed columns. One part is swept to and through the column for analysis and 10 parts are vented to the atmosphere.

B. Fragmentation Inlet or Pyrolysis Accessory This accessory (Fig. 3) utilizes a low-current high voltage discharge to break molecules down into components of lower molecular weight and thus higher volatility so they may be analyzed in the conventional manner. A solid sample, about 1 mg of rubber for example, is placed on a disc of graphite felt held in a ceramic sample tube (Fig. 3a). The sample tube is purged with a low helium flow (5-6 cc/min) to remove air from the reaction chamber and the balance of the system. The sample in the tube is then subjected to the arc discharge at some predetermined current for a prescribed time (about 90 ma for 30 sec for most solids). During fragmentation, the break-down products are collected in a sample loop (a 10cc stainless steel coiled tube, Fig. 3b). When fragmentation is complete, the products are introduced into the column by means of a switching valve (Fig. 3c).

C. Columns and Column Compartment The separating or analyzing ability of any gas chromatograph is based, primarily, on its columns. Column length, diameter, and packing material determine the resolution or separation, the analysis time at any temperature, and the size of sample that may be introduced. A typical column for the instrument used would be a 10-ft by 1/8-in. diam stainless steel tube packed with 5 percent SE-30 silicone gum rubber on 80-100 mesh Chromosorb W (inert high surface area solid support). This would be an excellent column for separating the breakdown fragments of polyethylene, for example. The columns are housed in a well insulated oven (Fig. 1) capable of being heated rapidly up to 500 C, and also rapidly cooled by means of an air dump which expels the hot air and introduces cool room air to return the oven to ambient temperature.

D. Temperature Programmer The function of the programmer is to provide a controlled, repeatable increase of column temperature throughout a sample run. The Temperature Programmer optically follows the

slope of a reflective program tape applied to a graduated clear plastic chart (Fig. 4). The chart is driven at a constant speed horizontally while the optical follower moves vertically along the contour of the program tape. The vertical position of the follower determines the temperature of the column compartment. Temperature programming offers distinct advantages over isothermal operation: viz., sample components can be analyzed in less time and shorter retention times of higher-boiling components reduces peak broadening to improve resolution.

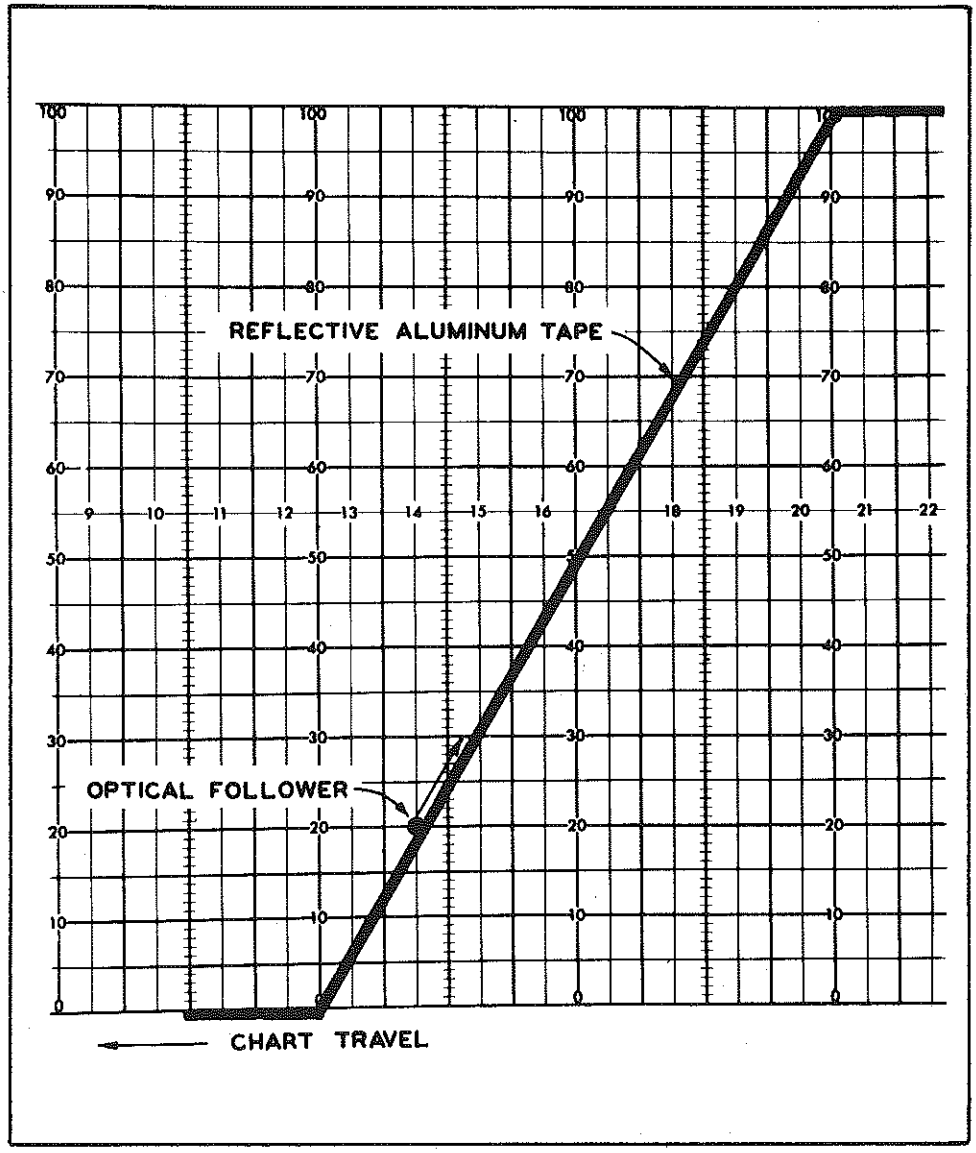


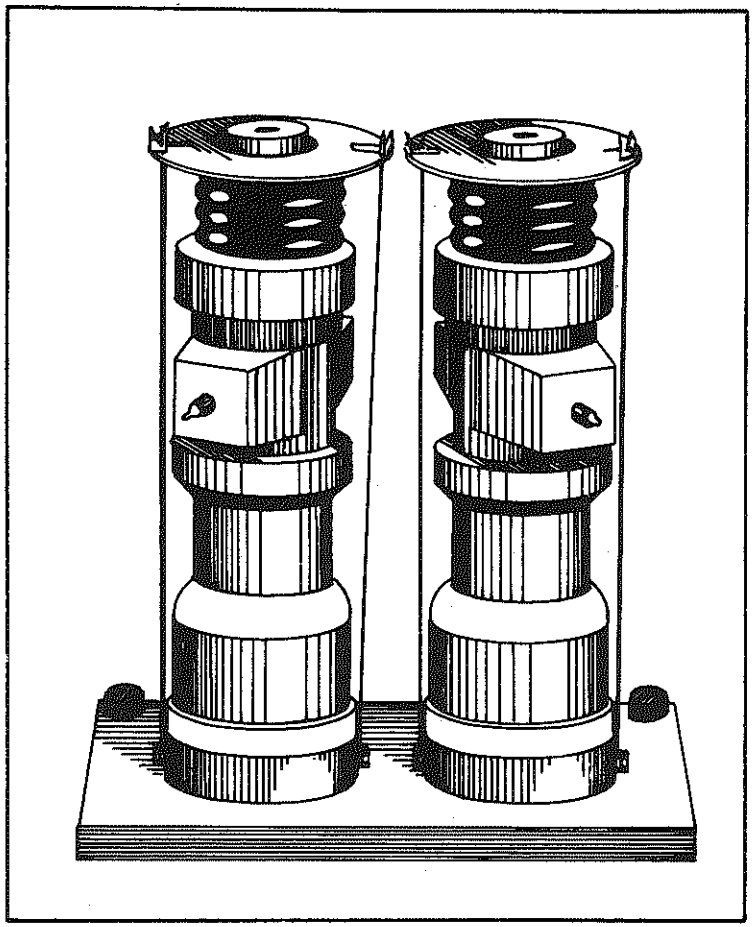
Figure 4. Temperature Program showing graduated plastic chart with reflective aluminum tape and optical follower

E. Detector A hydrogen flame detector (Fig. 5) was used in the present study. This detector utilizes a burner where the column effluent (components eluting from the column) passes through a hydrogen-air flame where it undergoes a complex ionization that frees electrons and positive ions (charged particles). The carrier gas transports these charged particles upward between polarized electrodes (two parallel flat metal plates). A 300-volt battery supplies the polarizing voltage. The electrical field between the electrodes causes the charged particles to migrate; electrons to the positive electrode, positive ions to the negative electrode. Thus, a small current flows between the plates. Normally, two burners are paired. Their outputs are opposed, and balanced, when each is receiving the effluent from separate identical columns with no sample present. This stabilizes the recorder baseline since both burners are equally affected by changing instrument conditions and column bleed (volatilization and discharge of column liquid phase) so that the net signal from the burner pair remains zero. When sample components pass through one of the burners, ions are generated and give rise to an unbalanced current flow in the system. This imbalance in signal is amplified and fed to a recorder which traces a chromatogram.

F. Fraction Collector The fraction collection system of the instrument allows the collection of high-purity volatile components from a complex sample. As a sample component is eluted from the column it is split by a 10:1 post stream splitter. One part goes to the detector and the balance is swept by carrier gas to a sample collection trap immersed in a coolant such as liquid nitrogen, where it condenses. The trapped fraction can then be subjected to further analysis by other instruments, such as an infrared spectrophotometer.

Procedures

Identification of Polymers The development of routine identification procedures for the many plastics and rubbers used in the highway field would, in effect, be the establishment of a reference file--a library of fragmentation patterns employing instrument conditions which would yield characteristic and repeatable patterns for the various materials. A literature search revealed very limited data on the analysis of plastics and rubbers by PGC employing an electrical discharge pyrolyzer. Sternberg and Litle (8) show fractograms of polyethylene, polypropylene, and poly-(methyl methacrylate) by this technique. Since it was obvious from the literature search that routine identification procedures could not be obtained from literature sources, reference fragmentation patterns for the materials



Dual Hydrogen Flame Detector Burners

Simplified Diagram of Detector Burner

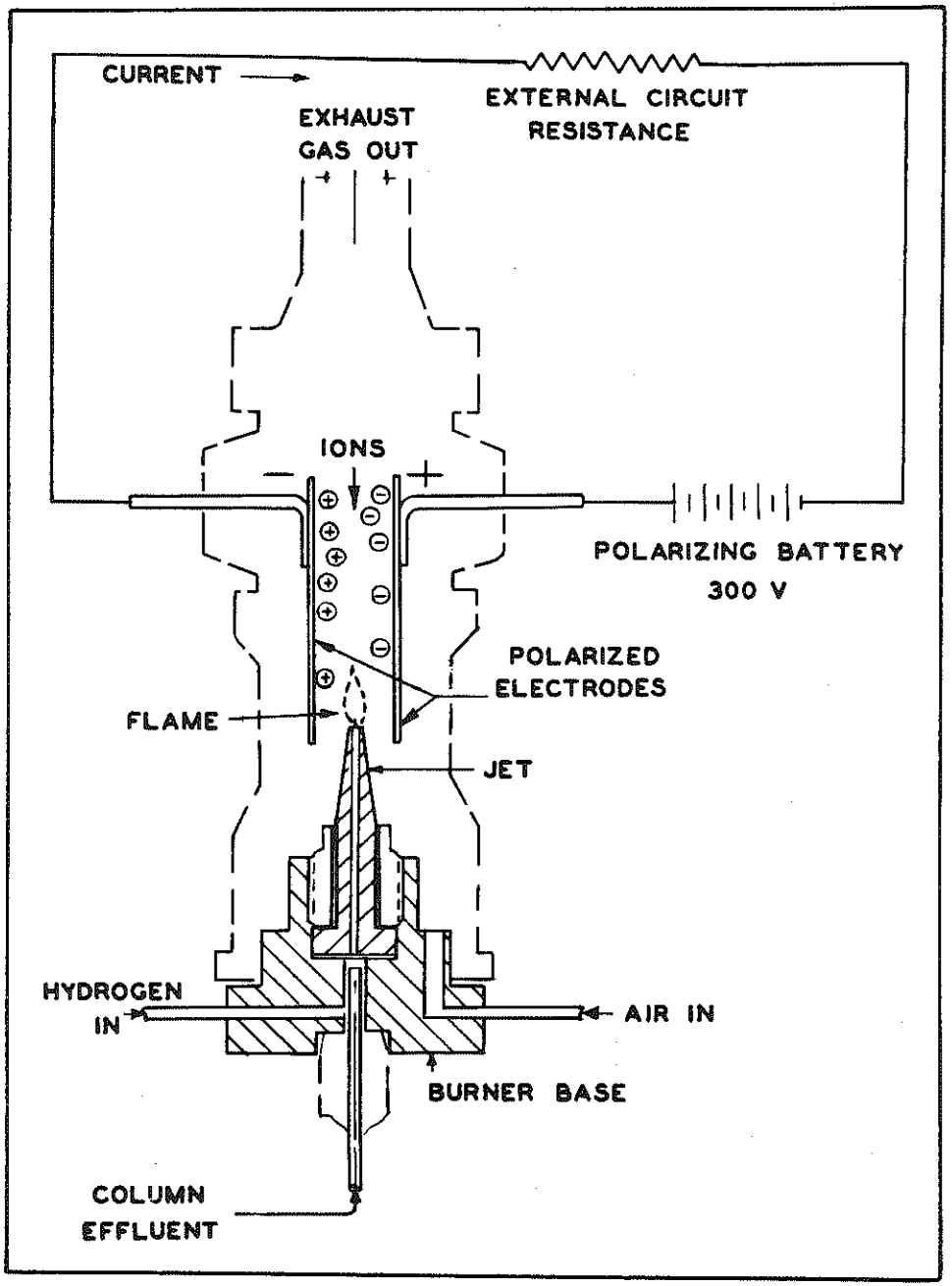
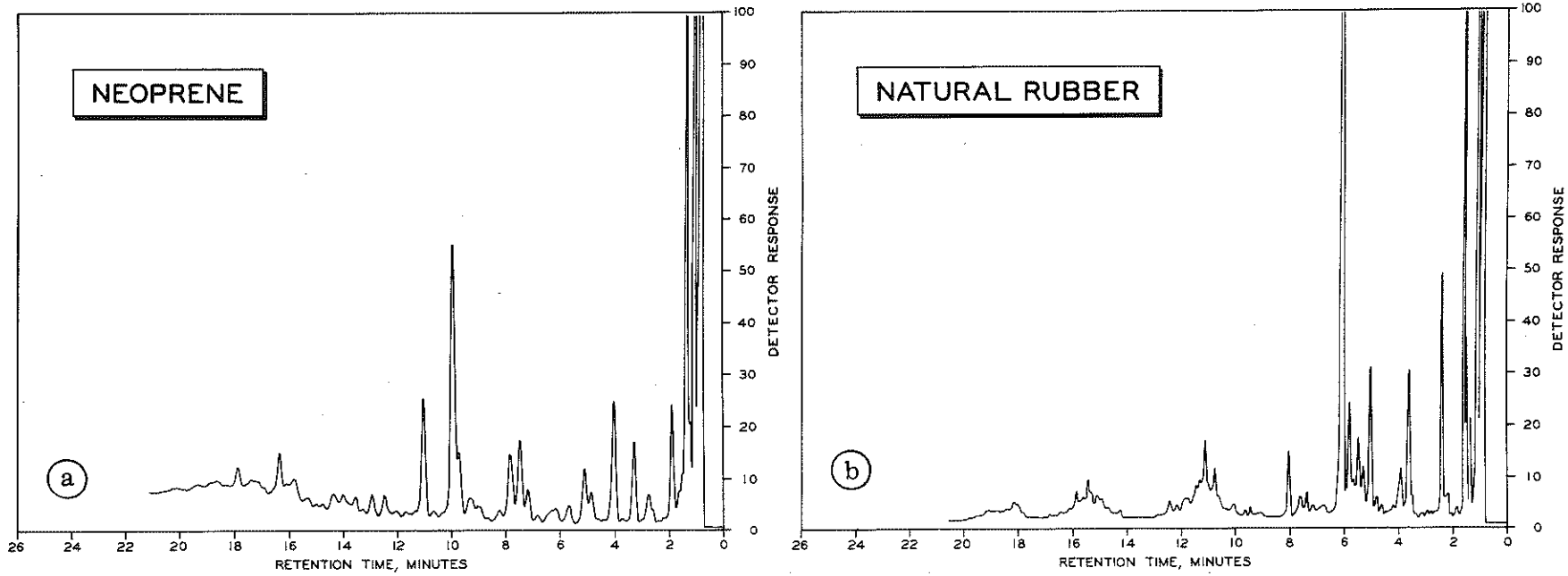


Figure 5. Hydrogen Flame Detector.

of interest were prepared. The polymers used in the study were uncompounded commercial resins (no pigments or additives) obtained from various manufacturers and included the following: polyethylene, polypropylene, polystyrene, polycarbonate, polyurethane, poly-(vinyl chloride), poly-(methyl methacrylate), terpolymer of acrylonitrile butadiene and styrene (ABS), nylon, natural rubber, styrene-butadiene rubber, polyisobutene (butyl rubber), and neoprene. Approximately 0.5 mg samples of the solid polymers were weighed to the nearest 0.01 mg with an electrobalance and fragmented under the proper instrument conditions, column arrangements, and sampling techniques necessary to produce repeatable and definitive pyrograms for each material. The resulting pyrograms (Figs. 6, 7, and 8) indicate that each of the polymers has its own characteristic fragmentation pattern. Similar materials, such as the polyolefins: (Fig. 7) polyethylene, polypropylene, and polyisobutene (butyl rubber)--while showing definite distinguishable differences from one another--all display an interesting regularity of pattern not usually noted in other materials. This regularity is indicated by the repeating three and four peak groupings in polypropylene and polyisobutene and the long series of symmetrical peaks in polyethylene. Polymers containing styrene (Fig. 8): styrene butadiene rubber, polystyrene, and acrylonitrile butadiene styrene (ABS) all have a common peak at four minutes retention time. This common peak is probably styrene monomer resulting from breakdown by reversal of the polymerization process and indicates that styrene could probably be determined quantitatively in these materials. Some polymers, such as nylon, show a few large peaks within the first two or three minutes retention time and only very minor ones beyond four minutes. This probably indicates that nylon breaks down into low molecular weight fragments.

This collection of fragmentation patterns will greatly facilitate the characterization of many plastic and rubber materials used for highway purposes by serving as a basis of comparison for known materials, and as a means of identifying unknowns.

Preformed Neoprene Pavement-Joint Seals The development of a PGC method for detecting differences in preformed neoprene joint seals supplied by different manufacturers, and correlating these differences with quality, necessitated the development of a reproducible procedure with sufficient sensitivity to detect minor differences in formulation or processing. This involved a long sequence of experiments aimed at finding optimum operating parameters. When it was felt that satisfactory sensitivity and reproducibility had been attained, approximately 0.5 mg samples were cut from joint seals supplied by three different manufacturers, weighed to the nearest 0.01 mg, and pyrolyzed.



INSTRUMENT CONDITIONS: for preparing a and b
COLUMN: 10-ft by 1/8-in. stainless steel packed with 5 percent W-98 (methylsilicone gum rubber) on 100/200 mesh Chromosorb W
COLUMN TEMP: programmed 2 min isothermal at 60 C, then to 230 C at 11.3 deg/min
FRAGMENTATION: 30 sec at 90 ma
INLET TEMP: 280 C
DETECTOR TEMP: 400 C
VALVE COMPARTMENT TEMP: 270 C
CARRIER FLOW RATE (HELIUM), COLUMN: 40 cc/min
MAKE-UP FLOW RATE (HELIUM): 55 cc/min
FRAGMENTATION PURGE FLOW RATE (HELIUM): 6 cc/min
HYDROGEN FLOW RATE: 55 cc/min
AIR FLOW RATE: 300 cc/min

INSTRUMENT CONDITIONS: for preparing c and d
COLUMN: 6-ft by 1/8-in. copper packed with 10 percent Carbowax 20 M on 42/60 mesh Chromosorb W

Other conditions are the same as for a and b

INSTRUMENT CONDITIONS: for preparing e, f, and g
COLUMN: 10-ft by 1/8-in. stainless steel packed with LAC 2-R-446 (diethylene glycol adipate polyester) on 60/80 mesh Chromosorb W
COLUMN TEMP: programmed 2 min isothermal at 60 C, then to 200 C at 9.3 deg/min

Other conditions are the same as for a and b

Figure 6. Reference pyrograms of highway plastics and rubbers.

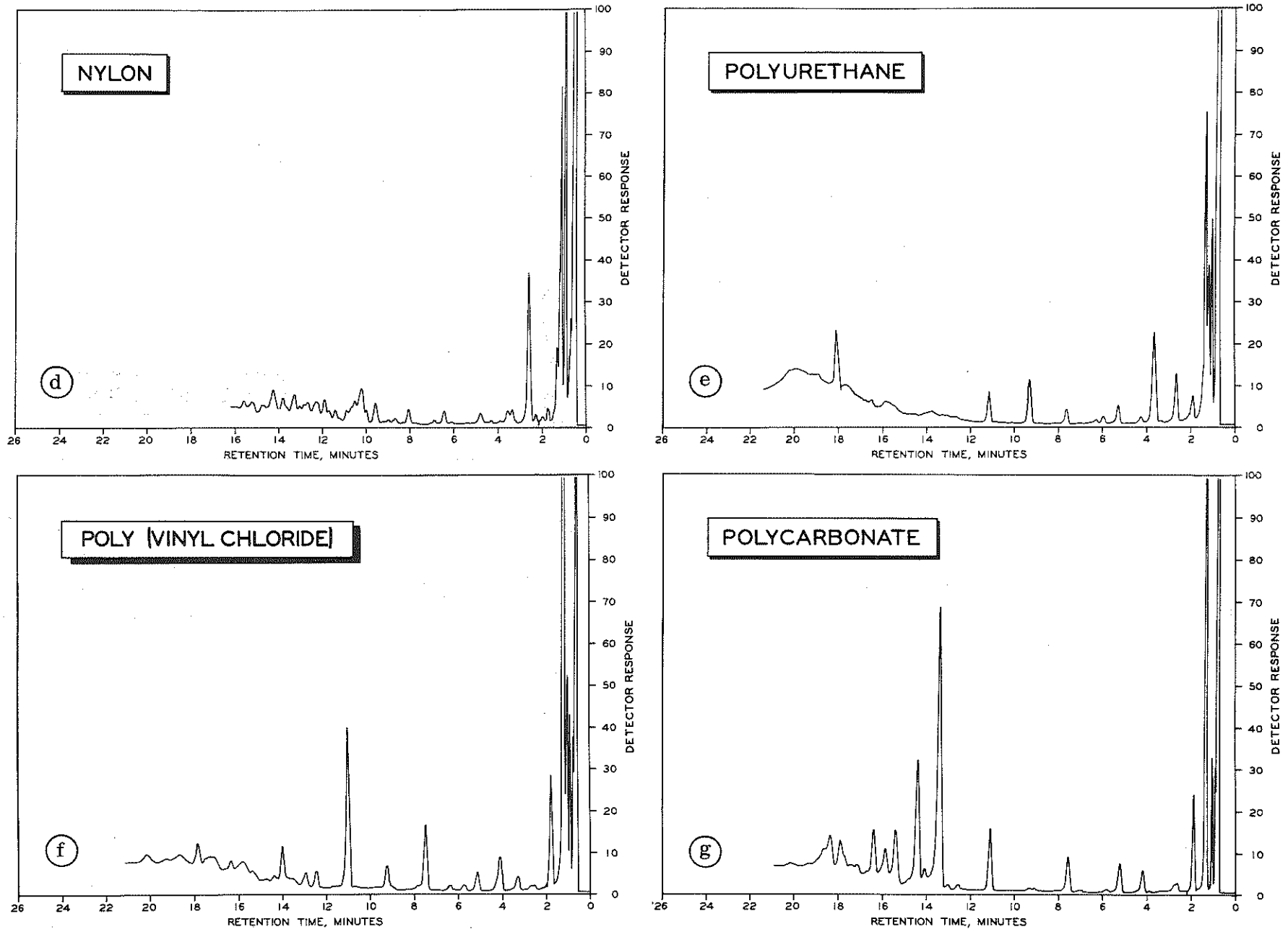
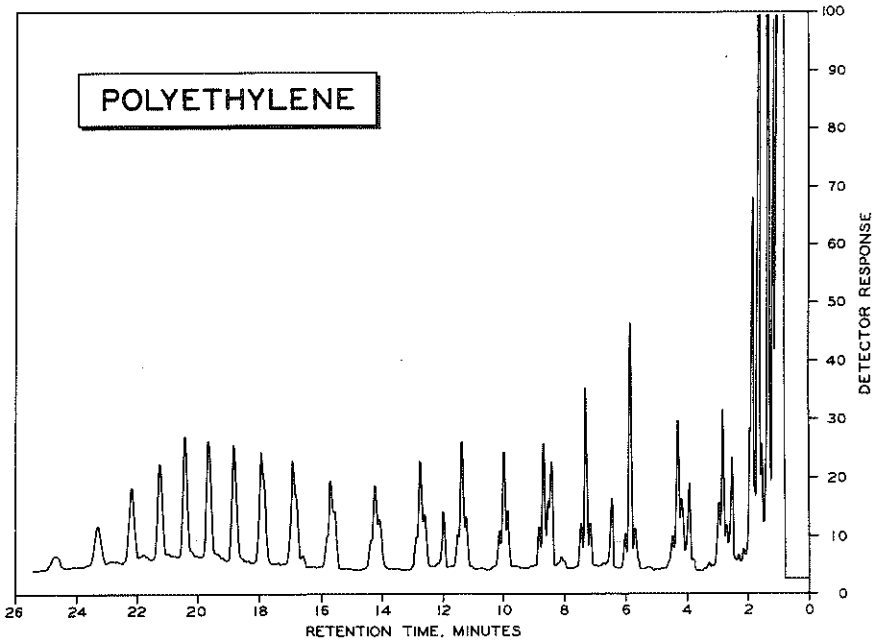
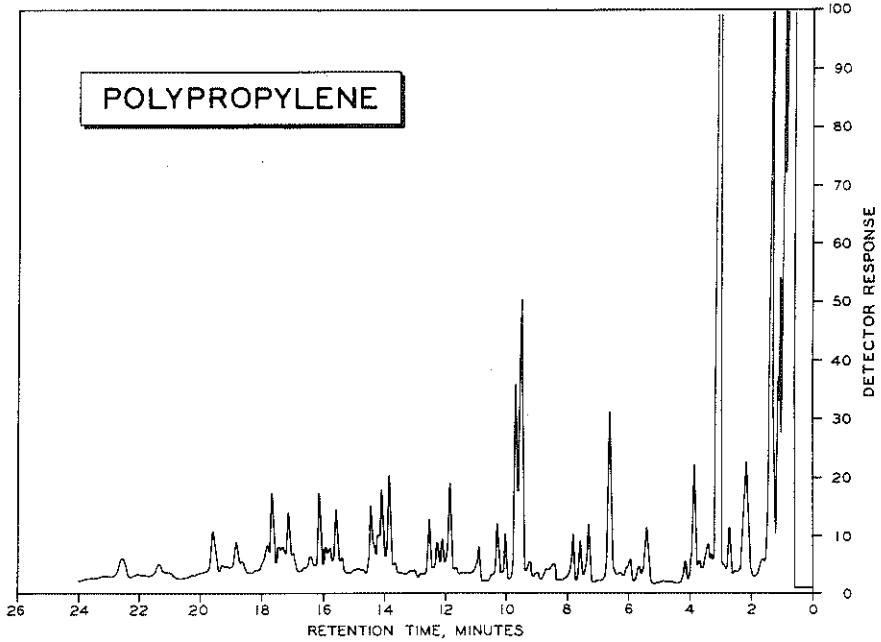


Figure 6 (cont.). Reference pyrograms of highway plastics and rubbers.





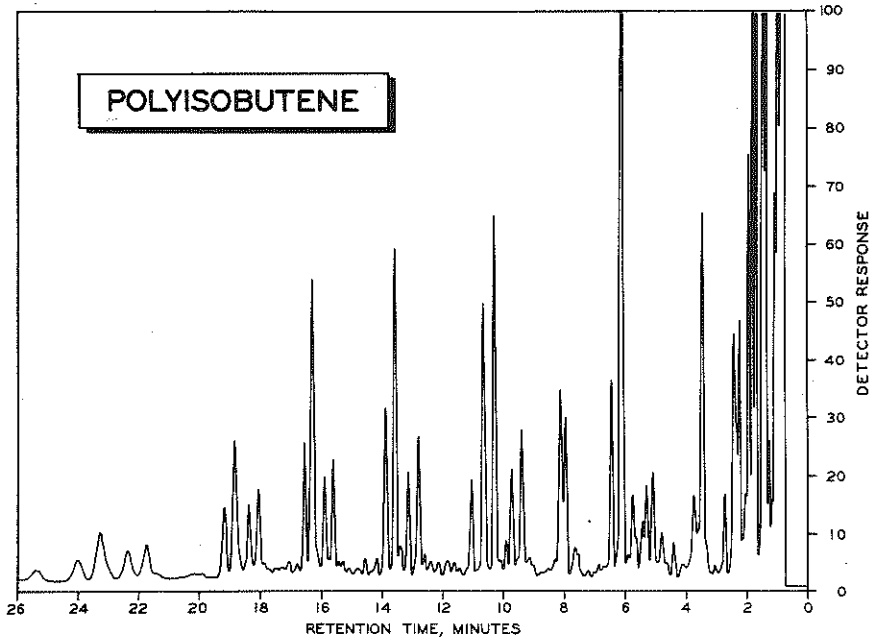
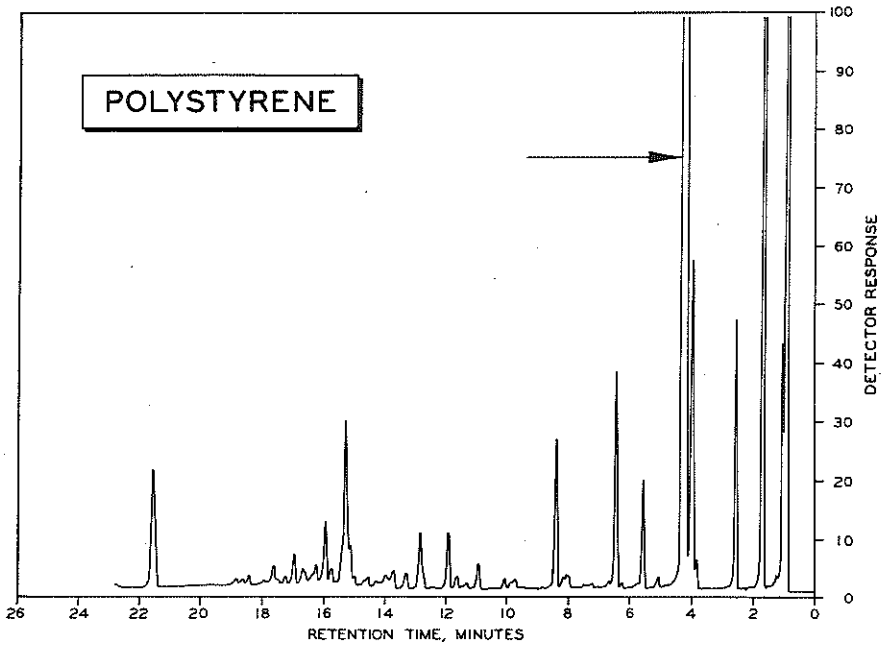
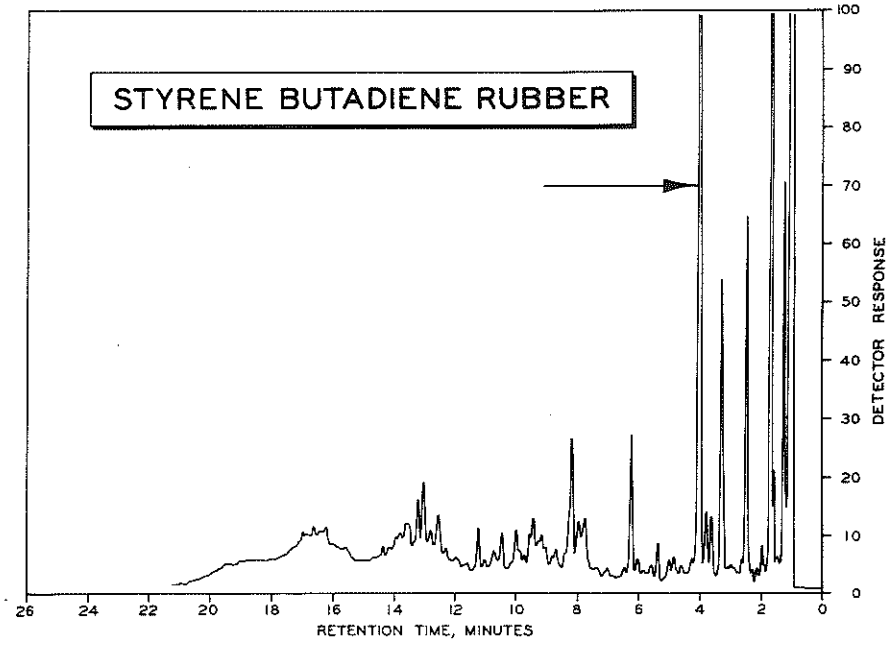


Figure 7. Polyolefin polymers. Note regularity of patterns and repeating groups of peaks in polypropylene and polyisobutene. Instrument conditions are the same as a and b of Figure 6.





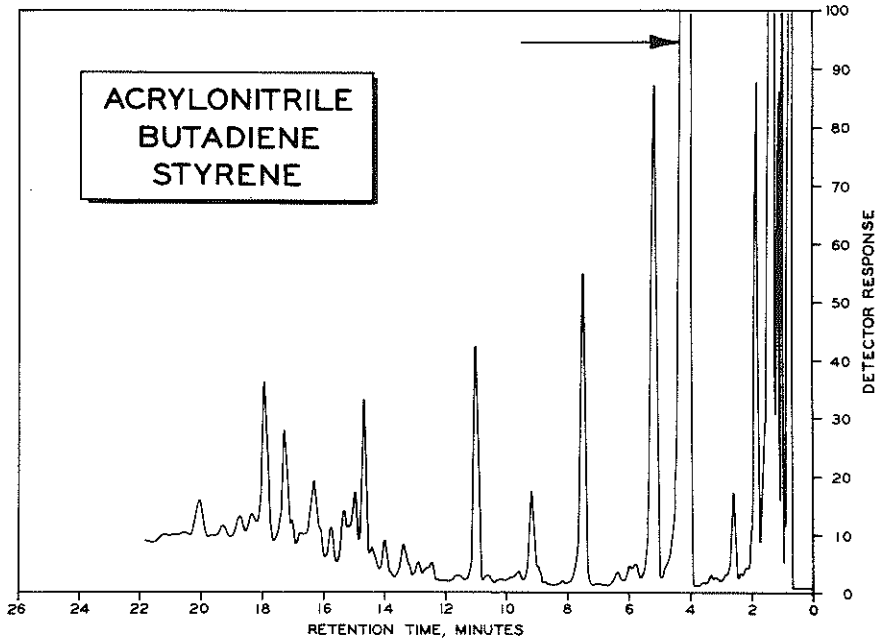
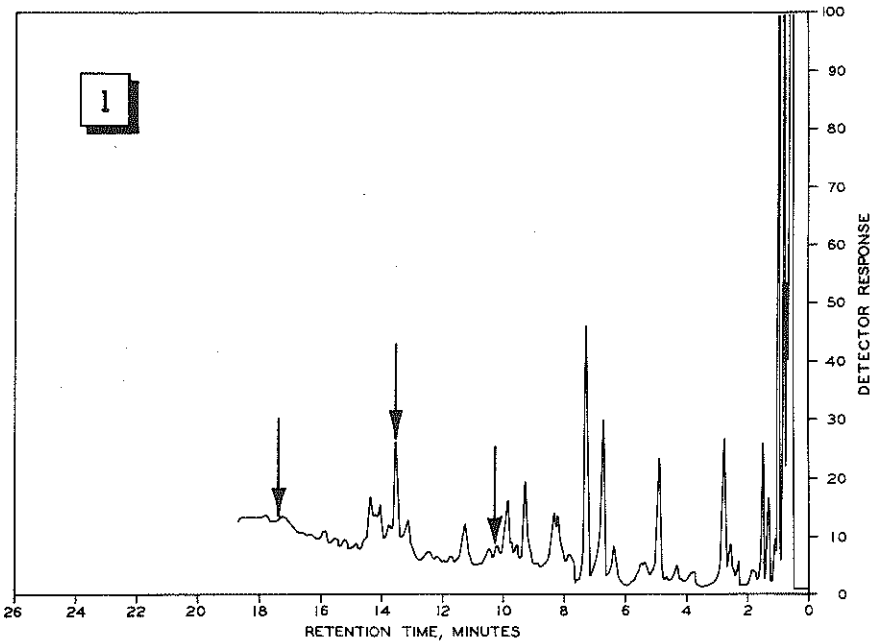
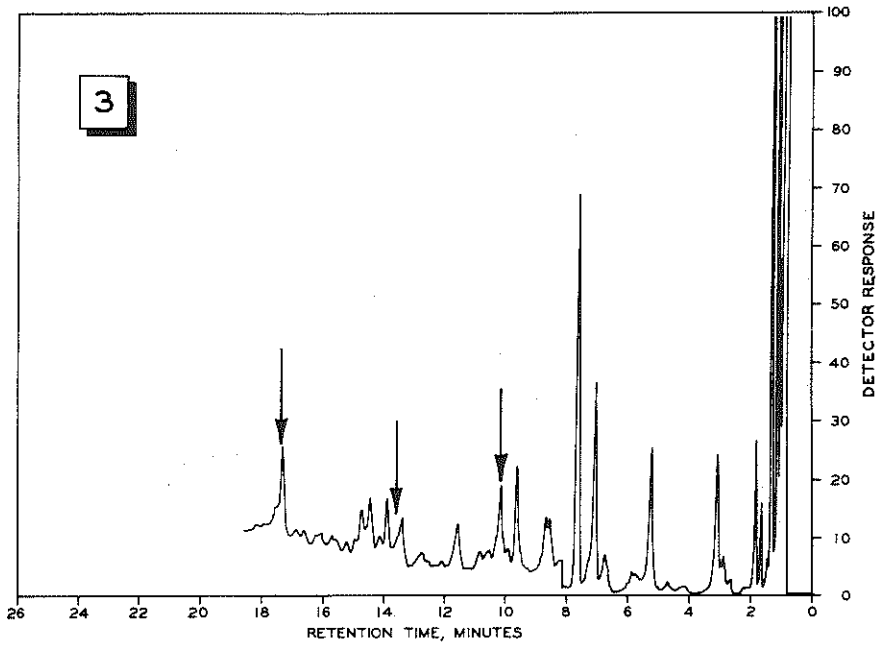
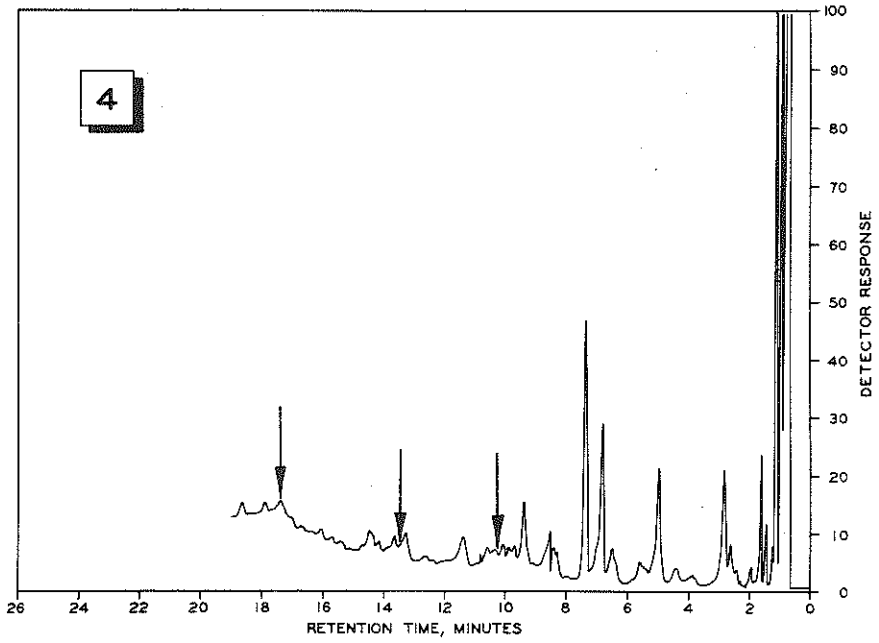


Figure 8. Styrene containing polymers. A common major peak is apparent at 4 min retention time (arrow). Instrument conditions are the same as a and b of Figure 6.







INSTRUMENT CONDITIONS:
- COLUMN: 10-ft by 1/8-in. stainless steel, packed with 5 percent SE-30 (silicone rubber) supported on 42/60 mesh Chromosorb W
- COLUMN TEMP: programmed 2 min isothermal at 60 C, then to 260 C at 13.3 deg/min
- FRAGMENTATION: 30 sec at 90 ma
- INLET TEMP: 270 C
- DETECTOR TEMP: 400 C
- VALVE COMPARTMENT TEMP: 270 C
- CARRIER FLOW RATE (HELIUM), COLUMN: 50 cc/min
- MAKE-UP FLOW RATE (HELIUM): 55 cc/min
- FRAGMENTATION PURGE FLOW RATE (HELIUM): 6 cc/min
- HYDROGEN FLOW RATE: 55 cc/min
- AIR FLOW RATE: 300 cc/min

Figure 9. Fractograms of neoprene joint seal from different manufacturers. Note differences in peak heights 10.2, 13.5, and 17.4 min retention time (arrows).

The resulting pyrograms revealed minor differences between the various suppliers' products (Fig. 9). These differences are apparent in the eight- to eighteen-minute retention time range where variations can be noted in several peak heights and peak ratios. The most obvious differences are in the peaks at 10.2, 13.5, and 17.3 minutes retention as indicated by the arrows. Differences between joint seals from the same manufacturer that failed specification requirements during acceptance testing, and those that did not fail, were not noted. Since the differences noted above were not pronounced, the procedure was altered to include a preliminary solvent extraction step and minor parameter changes, as follows: (1) Extract approximately one gram (accurately weighed) of finely divided joint seal with 100 ml of acetone-chloroform azeotrope (32 percent acetone, 68 percent chloroform, constant boiling mixture) for four hours in a Soxhlet extractor. (2) Decant the solution and evaporate to dryness, finishing in a vacuum oven at 60C. Weigh the residue and calculate percent solubles. (3) Dissolve the dried soluble fraction in a known amount of the extraction solvent (1 ml for each 1 percent of the solubles). (4) Inject a 25-μl aliquot of the resulting solution directly onto the carbon felt in a ceramic sample tube (Fig. 3) and heat in a 60 C vacuum oven for one hour to remove all solvent. (5) Pyrolyze the sample, employing the same instrument conditions as with the solid whole material, except: reduce valve compartment temperature to 200 C, fragment for 15 sec at 30 ma, and start temperature program at 100 C and increase at 14.4 deg/min to 230 C.

This revised technique produced pyrograms revealing definite repeatible differences between the various suppliers' joint seals (Fig. 10 a, b, c). The differences are apparent in the eight- to twenty-minute retention time range. The overlay (Fig. 10 d) of the three pyrograms clearly shows no matching of retention times between any of the component peaks present in any of the pyrograms. This indicates the presence of different materials and suggests differences in formulation or processing, or both, between the seals. Differences are also noted between joint seals of different widths from the same supplier (Fig. 11). The overlay of these pyrograms clearly shows differences in retention times between the component peaks. This would seem to indicate only minor, but detectable, differences in formulation or processing or both, between neoprene joint seals of different widths from the same supplier. Again, for a given supplier, no differences were found between joint seals that met specifications and those that failed during acceptance testing.

No direct correlation has been found between gas chromatographic data and field performance of neoprene joint seals. However, it has been noted that samples from two producers which have pyrolysis fragments, from

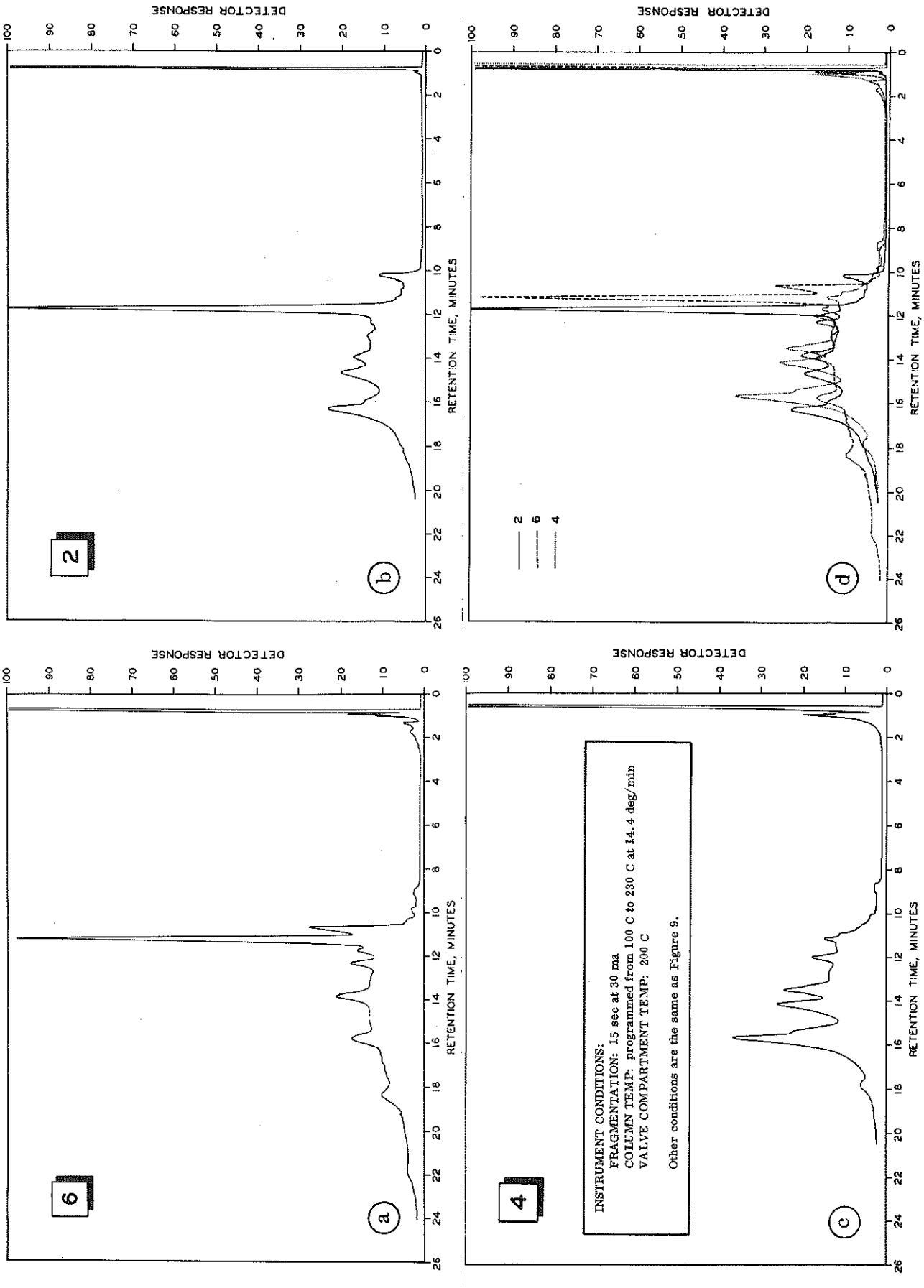


Figure 10. Fractograms of the soluble fraction of neoprene joint seals from different manufacturers. Differences occur in the 8 to 20 min range. Overlay (d) clearly shows no matching of retention times between component peaks.

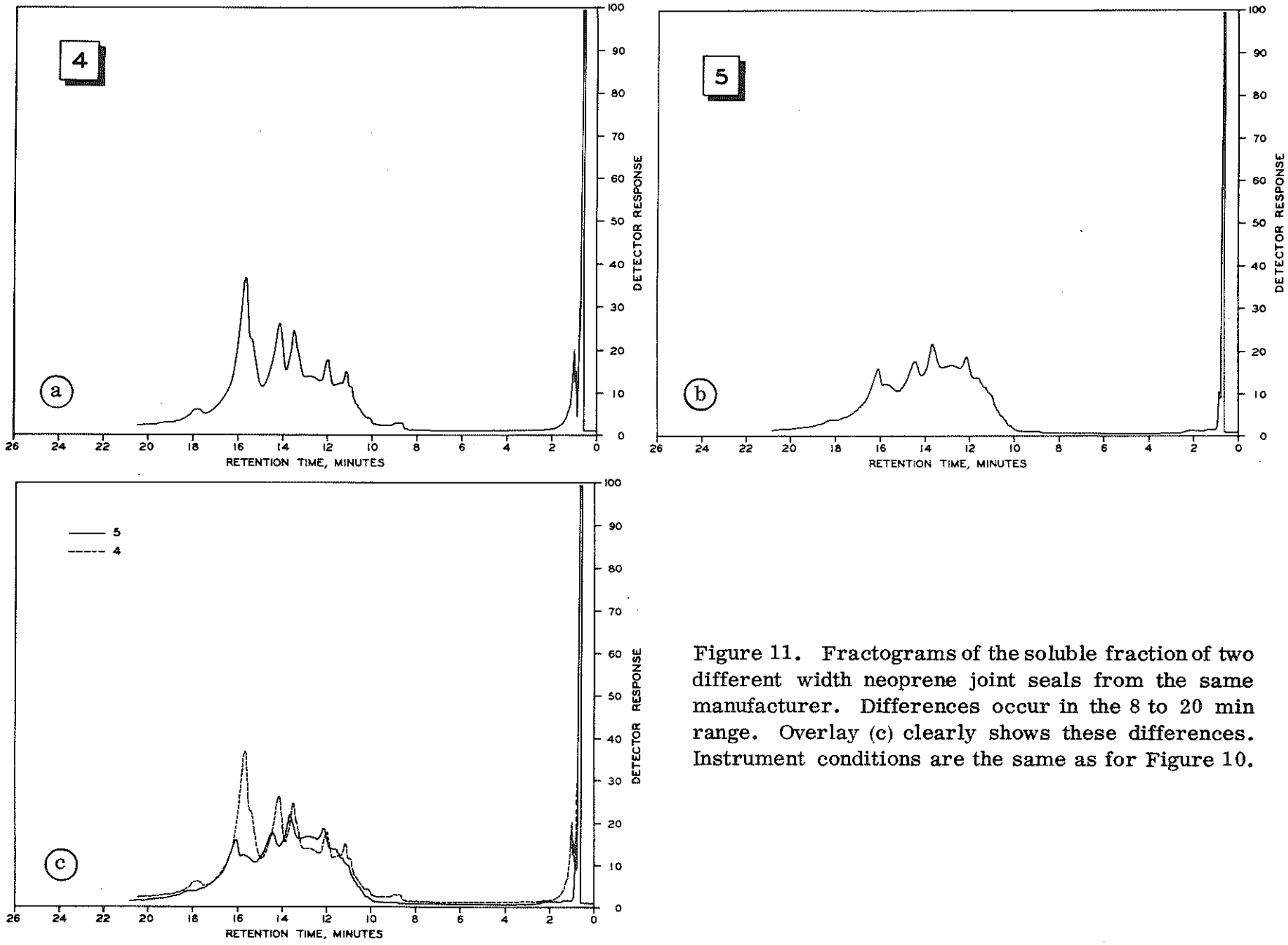
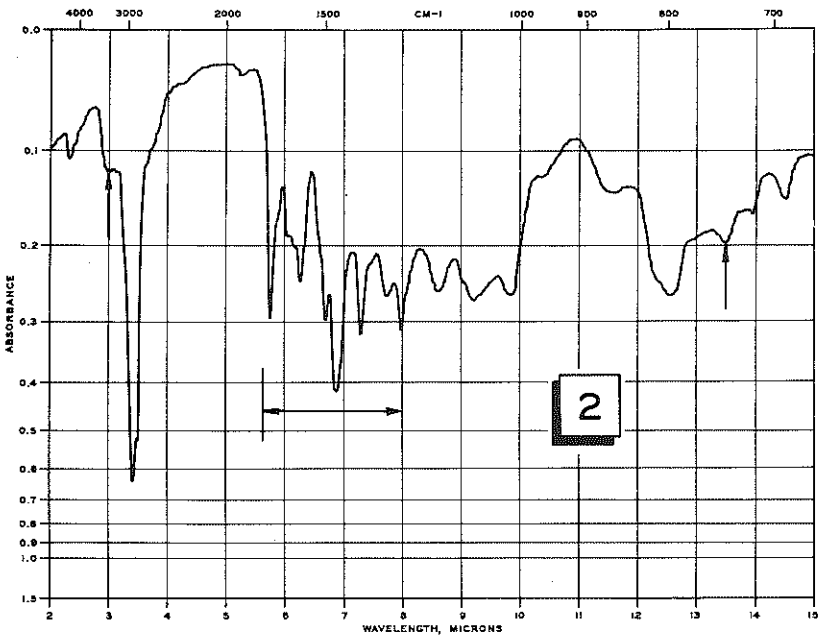
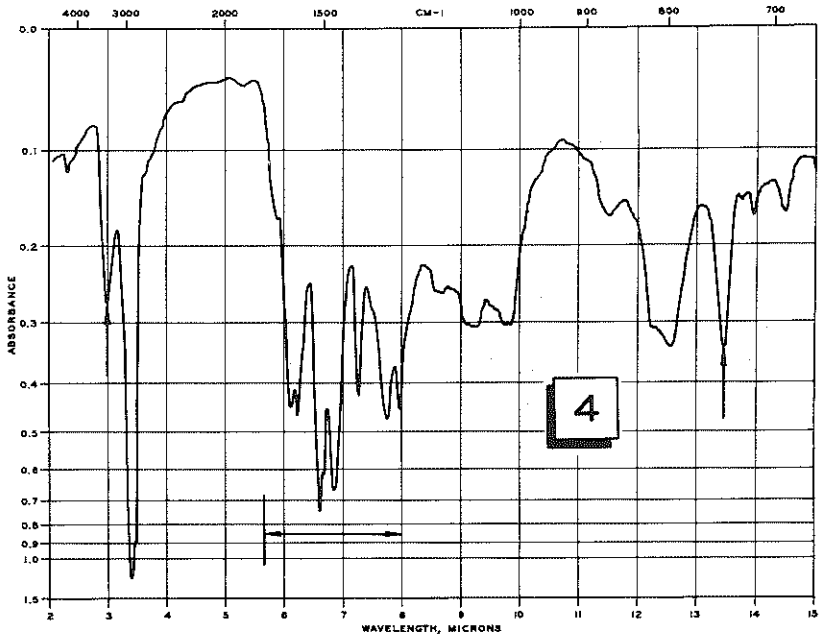


Figure 11. Fractograms of the soluble fraction of two different width neoprene joint seals from the same manufacturer. Differences occur in the 8 to 20 min range. Overlay (c) clearly shows these differences. Instrument conditions are the same as for Figure 10.





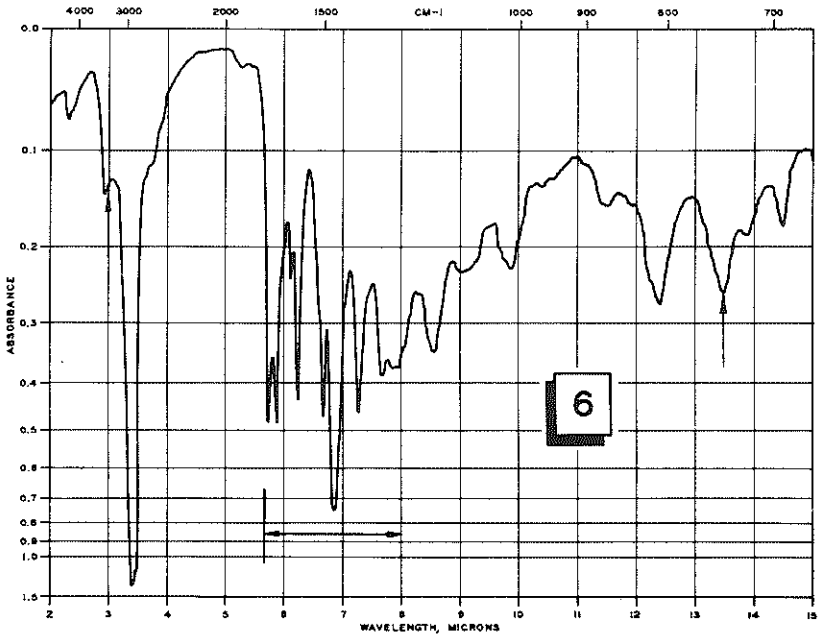


Figure 12. Infrared spectra of soluble fraction of neoprene joint seals from different manufacturers. Differences in spectral intensity are marked at 3.0, 5.7 to 8.0, and 13.4 microns.

the acetone-chloroform soluble extract, eluting at 10-12 min retention time (Fig. 10 a & b) had lower tensile strength and poorer recovery from a compression test than a third producer sample which did not exhibit such peaks in the pyrogram of the soluble extract (Fig. 10 c). The fragments eluting at 10-12 min were cold-trapped and identified by infrared spectrophotometry as compounds used as plasticizers in rubber formulation. The presence of such peaks in joint seal pyrograms could alert personnel performing acceptance tests to expect less than optimum physical properties from the samples.

Infrared spectra of the soluble fraction of the extracted joint seals also revealed differences between the various suppliers' products (Fig. 12), and differences between samples taken from different widths of joint sealer from the same supplier (Fig. 13). These differences are indicated by spectral variations such as those at 3.0 microns, in the 5.7 to 8.0 micron range and at 13.4 microns (as shown by the arrows). Other spectral differences are present but they are not specifically discussed since they add little to the case. As previously shown in the pyrograms (Fig. 11), the spectral differences noted for different width seals from the same supplier are not pronounced, suggesting rather minor differences in formulation and/or curing for the different width seals.

Conclusions

Based on these data, pyrolysis gas chromatography has the capability of becoming a very useful technique for analysis of a broad variety of highway materials. Presently, we can identify various polymers in products and compare samples from different batches or suppliers to detect changes in composition or methods of processing. In the future, after experience with many more samples, it may be possible to predict performance characteristics directly from instrumental data.

RECOMMENDATIONS FOR FURTHER WORK

1. Prepare characteristic identifying pyrograms for other plastics and rubbers having highway applications or potential highway applications.

2. Continue the PGC Investigation of neoprene joint seals as a possible method for determining neoprene content. Attempt to identify and quantitate joint seal formulation ingredients such as plasticizers and antioxidants. The ability to quantitate noeprene and other formulation ingredients would permit the inclusion of such items in specifications for premolded joint seals.

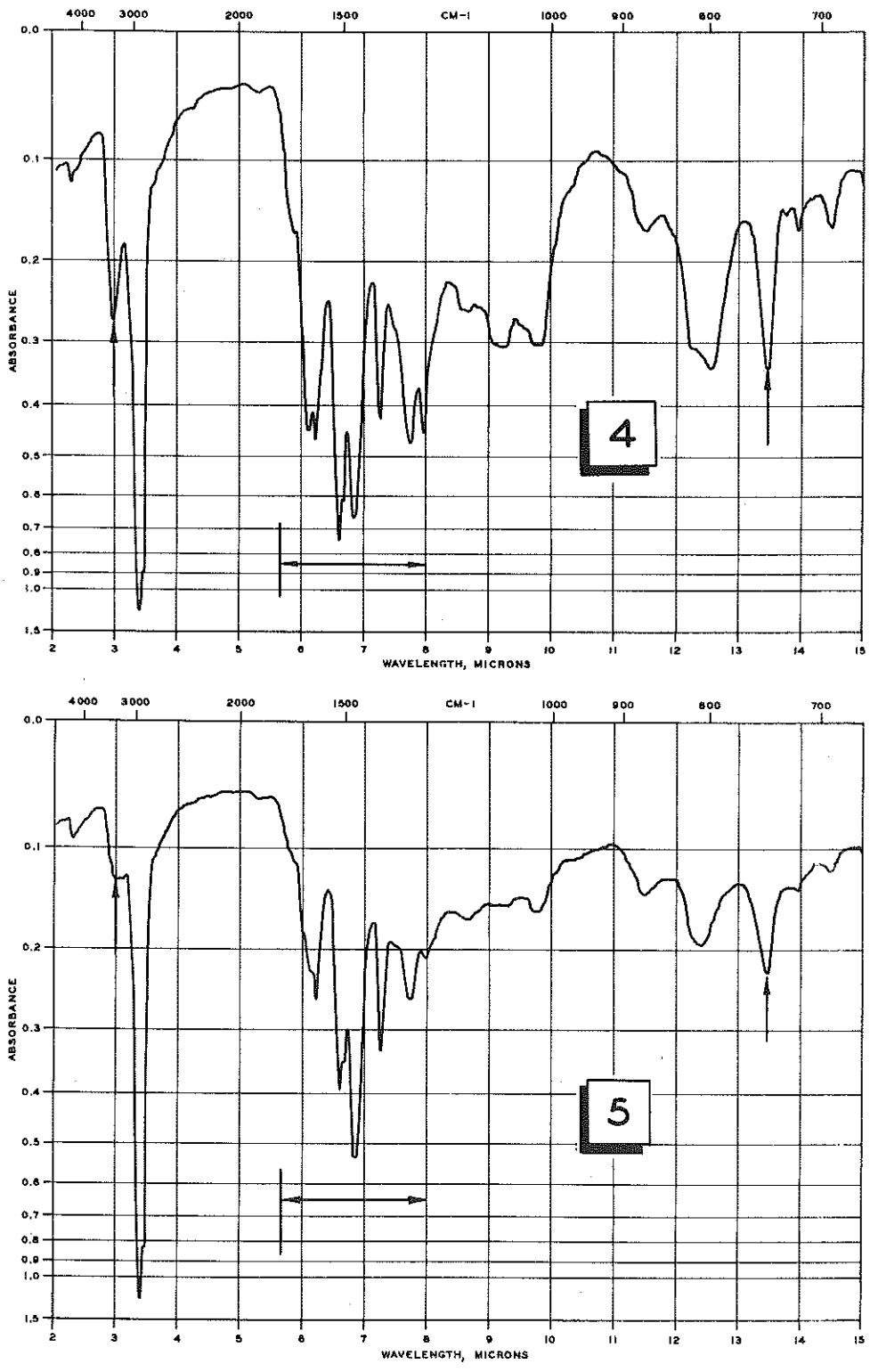


Figure 13. Infrared spectra of the soluble fraction of two different width neoprene joint seals from the same manufacturer. Differences in spectral intensity are marked at 3.0, 5.7 to 8.0, and 13.4 microns.

3. Apply PGC to the analysis of plastic and rubber materials such as electric cable insulation and delineator buttons.

4. Apply gas chromatography and PGC to the analysis of bituminous materials and paints.

The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the Bureau of Public Roads.

REFERENCES

1. Radell, E. A. and Strutz, H. C., "Identification of Acrylate and Methacrylate Polymers by Gas Chromatography," Analytical Chemistry, Vol. 31, 1959, p. 1890.

2. Nelson, D. F., Yee, J. L., and Kirk, P. L., "Identification of Plastics by Pyrolysis and Gas Chromatography," Journal of Microchemistry, Vol. 6, 1962, p. 225.

3. Barlow, A., Lehrle, R. S., and Robb, J. C., "Polymer Degradation by Gas Chromatography," Polymer, Vol. 2, No. 1, 1961, p. 27.

4. Cole, H. M., Petterson, D. L., Slayaka, V. A., and Smith, D. S., "Identification and Determination of Polymers in Compounded Cured Rubber Stocks by Pyrolysis and Two-Channel Gas Chromatography," Rubber Chemistry and Technology, Vol. 39, March 1966, p. 259.

5. Fisher, G. E. and Neerman, J. C., "Identification of Brake Lining Constituents by Pyrolysis Gas Chromatography," Industrial Chemistry and Technology, Vol. 5, Sept. 1966, p. 288.

6. Knotnerus, J., "Constitution of Asphaltic Bitumen," Industrial Chemistry and Technology, Vol. 6, March 1967, p. 43.

7. Karr, C., Jr., Comberiati, J. R., and Warner, W. C., "Comparison of Pitch Resins from Different Sources by Combined Pyrolysis and Gas Liquid Chromatography," Analytical Chemistry, Vol. 35, 1963, p. 1441.

8. Steinberg, J. C. and Litle, R. L., "Electrical Discharge Pyrolyzer for Gas Chromatography," Analytical Chemistry, Vol. 38, 1966, p. 321.