# TECHNICAL NOTE

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# Pyrolysis-Gas Chromatographic Examination of Paints

**REFERENCE:** Cardosi, P. J., **"Pyrolysis-Gas Chromatographic Examination of Paints,"** *Journal of Forensic Sciences,* JFSCA, Vol. 27, No. 3, July 1982, pp. 695-703.

**ABSTRACT:** A pyrolysis-gas chromatographic technique for comparing paint samples is described. The problems encountered in switching to new equipment are discussed, and the advantages and disadvantages are compared.

**KEYWORDS:** criminalistics, chromatographic analysis, paints

The Illinois laboratory system had been using a pyrolysis-gas chromatographic method originally developed by Stewart [*1*] for the comparison of paints. This method used a Fisher gas chromatograph, a Fisher pyrolyzer, and a Fisher digital log electrometer. When the state laboratory system purchased new equipment, a Perkin-Elmer Sigma I gas chromatograph system and a Chemical Data System (CDS) Pyroprobe, it became necessary to convert our paint analysis method to that system. It was crucial that the new system give results comparable to those of the old system.

To minimize differences between the two systems, the same chromatographic column was used in both systems. While setting up the Sigma I-CDS Pyroprobe system, I decided to reproduce as closely as possible a chromatogram of a known standard that had been previously run on the old Fisher pyrolysis system (see Fig. 1).

The pyrolysis temperature of the CDS Pyroprobe using the coil-probe with a standard quartz boat had to be double the temperature required in the old system to adequately pyrolize the standard sample. This may be due to a heat transfer problem. In the Fisher pyrolysis unit the entire chamber heats up, while in the CDS Pyroprobe only the coils heat up. This heat has to be transferred through the quartz boat to the sample.

## Equipment

A CDS Pyroprobe with standard coil probe was used on Perkin-Elmer's Sigma I gas chromatographic system equipped with a flame ionization detector. CDS's standard quartz boat was used to hold the sample in the standard coil probe.

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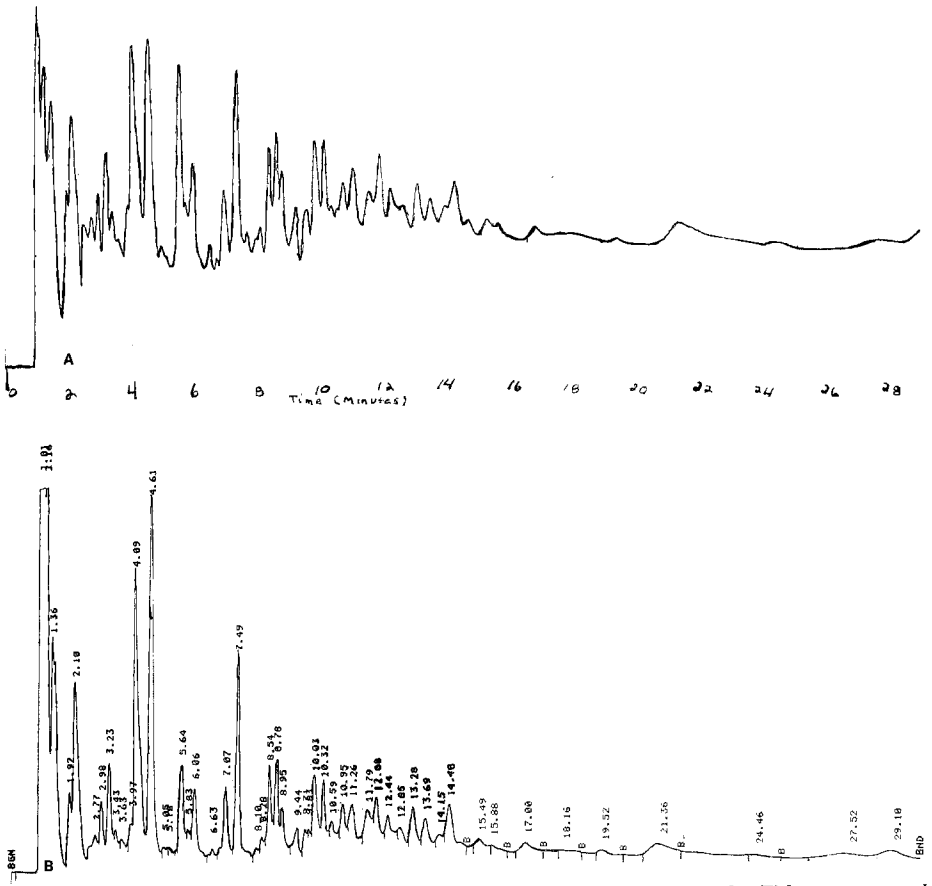


FIG. 1—*Comparison of pyrograms of Rez. Chromatogram A was run on the Fisher system and Chromatogram B was run on the Sigma I-CDS Pyroprobe.*

The column used was a combination of a 2.4-m (8-ft.) by 3.3-mm (⅛-in.) stainless steel column packed with 15% Carbowax 20M on 80-100 Supelcoport followed by a 0.9-m (3-ft) by 3.2-mm (⅛-in.) stainless steel column packed with 10% DC200 on 80-100 Supelcoport. A stainless steel union and stainless steel fittings joined these columns.

## Method

CDS's instructions regarding installation of the coil probe were followed for adjusting the depth of penetration of the probe [*2*]. After trying a number of settings on the CDS Pyroprobe electronics module, I found the following conditions reproduced fairly well the pyrogram of the standard, a sealer containing alkyd resin (Rez), which had been previously run on the Fisher pyrolysis system. The CDS Pyroprobe conditions were these:

Ramp: off
Interval: 10 s
Final temperature: 800°C

The Sigma I analyzer conditions were these:

Air pressure: 207 kPa (30 psi)
Carrier gas: nitrogen
Inlet A carrier pressure: 475 kPa (69 psi)
Injector temperature: 200°C
Detector zone: 225°C
Carrier gas flow rate: 25 mL/min
Initial oven temperature: 60°C
Initial temperature hold: 2 min
Program rate: 15°C/min
Final temperature: 180°C
Final temperature hold: 20 min
Range: 100
Attenuation (actual): 1
Area sensitivity: 100
Base sensitivity: 10
Chart speed: 13 mm/min

A weighed sample was placed in a clean boat and pyrolyzed under the above conditions. The range and attenuation used produce a good chromatogram with 0.05-mg samples. Increasing the instrument sensitivity by changing the attenuation to less than 1 makes column bleeding more prominent. For routine work the 0.05-mg sample level is probably the most satisfactory for the column since column bleeding becomes more prominent as the attenuation is changed to detect smaller samples.

**Discussion**

Reproducibility on the CDS Pyroprobe appears to be affected by the following conditions:

(1) sample location in the quartz boat,
(2) sample size and weight,
(3) sample contact with the boat, and
(4) cleanliness of the boat.

The best location for the sample appears to be in the center of the sample boat with the sample located directly over a coil or several coils; otherwise, pyrolysis may not be complete or reproducible. To determine if you have reproduced the sample location in the boat, count the number of coils from the first or last coil to the sample. This should be done for each sample and standard being compared to ensure consistent sample location.

For best reproducibility at a given range and attenuation, the samples should be weighed and the particle sizes of each sample kept the same; in addition, the sample should be in contact with the boat. One must remember that the heat is transferred from the coil to the sample through the quartz boat.

For good contact the boat should be clean—no charred material from old samples still in the boat. Clean the boat in detergent and water and rinse it in water, then distilled water, then methanol, and then hexane. Immediately before using the boat, heat it in air (in the coil probe) at approximately 950°C with a 5-s interval. Check the heated boat for cleanliness with a blank run. After the blank has been run, handle the boat with forceps to prevent contamination from hands.

Figures 2 through 7 are chromatograms of metallic brown paints from the National Bureau of Standards (NBS) reference collection of automotive paints (NBS F0283 and

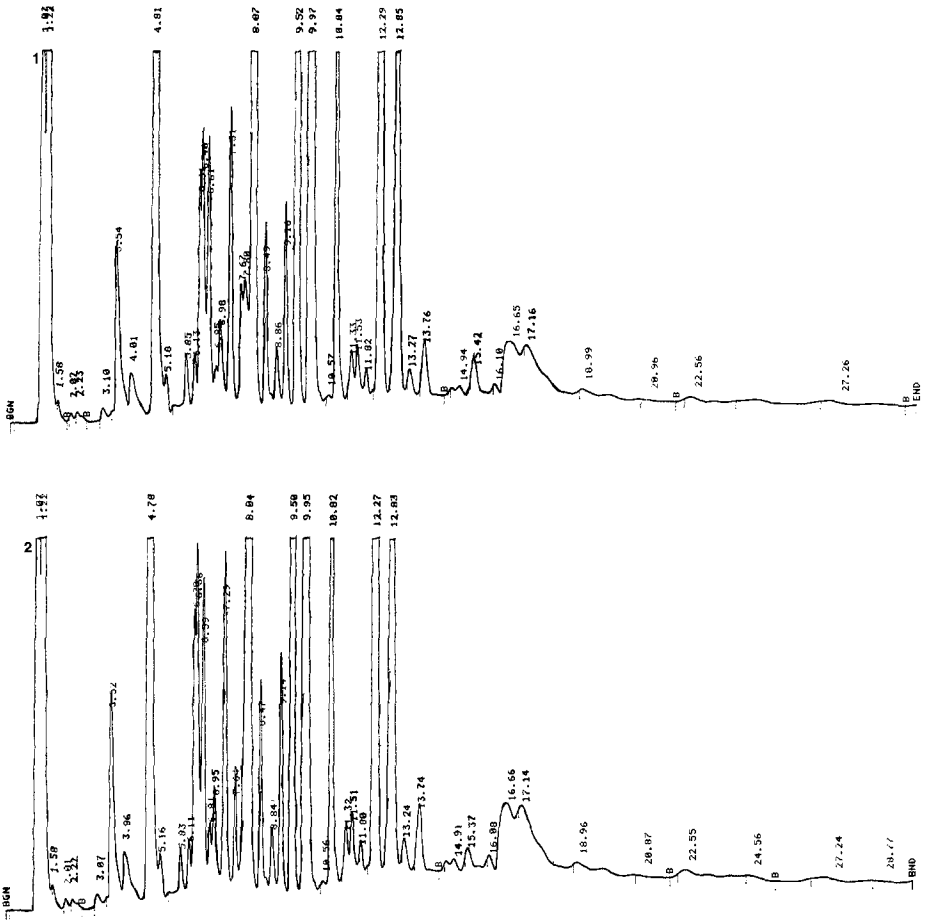

FIG. 2—*Two chromatograms of NBS FN77F0283 (Runs 1 and 2).*

F0167). These paints are from different paint manufacturers and were used by American Motors. Our paint collection has samples from three suppliers for Color F0283 and three for Color F0167. Note that NBS FN77F0283 (supplier, Ford), BN77F0283 (supplier, Canadian Pittsburgh Industries [CPI]), and LN78F0283 (supplier, Canadian Industries, Ltd. [CIL]) can be distinguished from each other by careful examination of the chromatograms. Duplicate samples of each were run and both runs are shown in Figs. 2, 3, and 4.

Color CN75F0167 (supplier, Jones-Dabney) can be distinguished from PN76F0167 (supplier, PPG) and BN76F0167 (supplier, CPI). BN76F0167 and PN76F0167 are extremely close, but they show some small differences. Check the relationship of peaks 5.18 (5.13) to 6.12 (6.05), and 6.83 (6.73) to 6.97 (6.90) in the first run of these paints. Duplicate runs of these paints are shown in Figs. 5, 6, and 7.

Although BN77F0283 (supplier, CPI) and PN76F0167 (supplier, PPG) are visually slightly different metallic brown colors, they appear to be indistinguishable by this method. The color difference is difficult to see on microscopic particles of these paints. Since CPI is a subsidiary of PPG, it is conceivable that CPI and PPG organic paint systems are so close that they can-

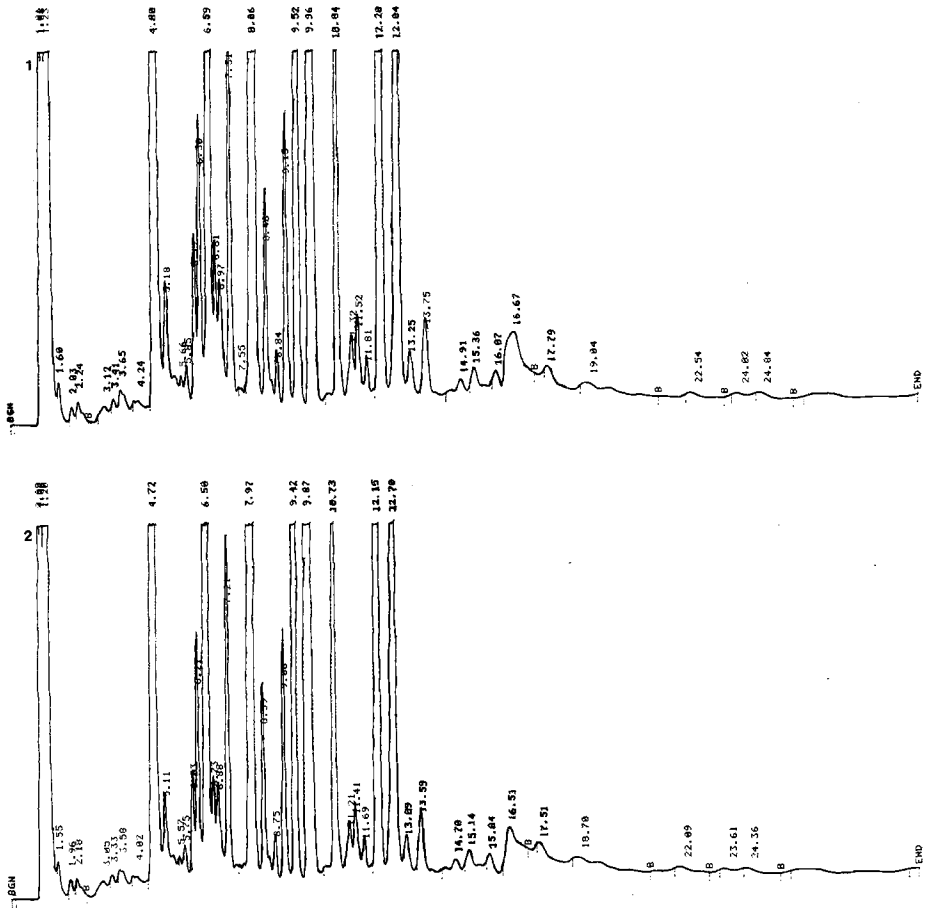

FIG. 3—*Two chromatograms of NBS BN77F0283 (Runs 1 and 2).*

not be distinguished from each other by this method. Further analysis by comparison of the inorganic components may show differences that would distinguish the paints.

The linear electrometer on the Sigma I system is more sensitive than the Fisher digital log electrometer, allowing the analyst to use less sample than with the Fisher digital log electrometer. This is an important factor when only trace amounts of paint are available for testing.

In addition to the chromatogram printed out with the Sigma I system, a printout of the concentration of the components is obtained. This is especially helpful in comparing the peaks that go off scale on the chromatogram.

## Conclusion

The Sigma I-CDS coil Pyroprobe system appears to differentiate paints as well as the Fisher system previously used by our laboratory system. Each system has its advantages and disadvantages for sample handling.

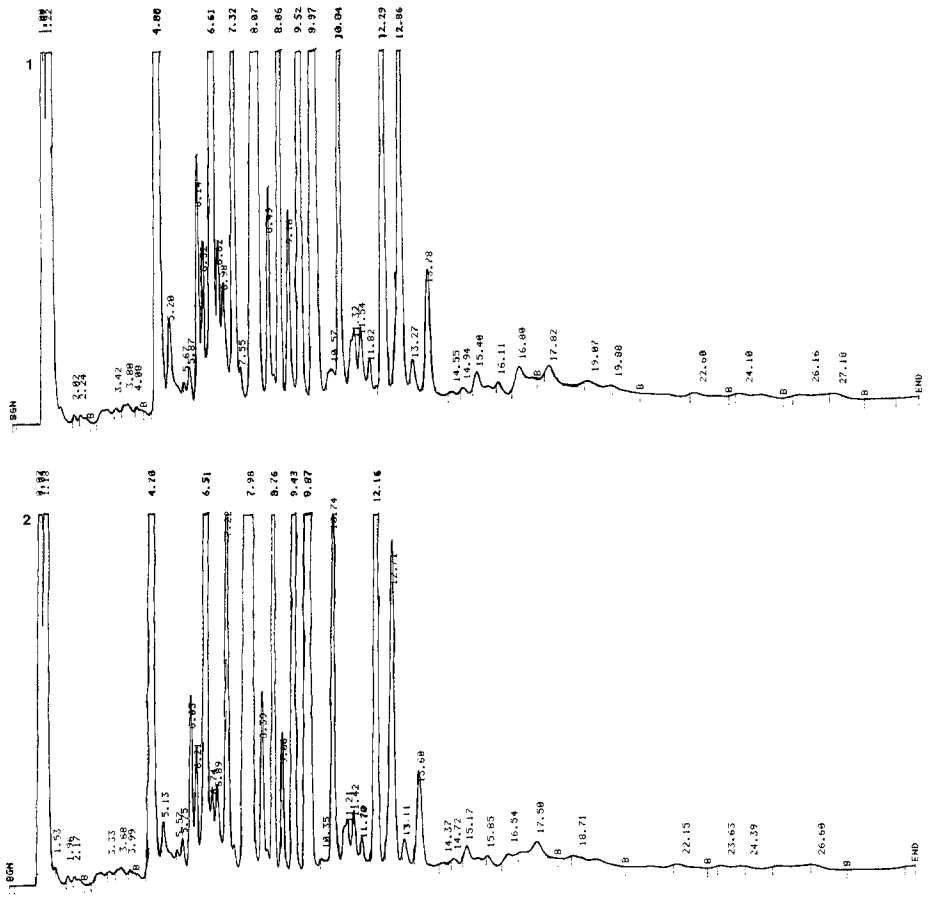

FIG. 4—*Two chromatograms of NBS LN78F0283 (Runs 1 and 2).*

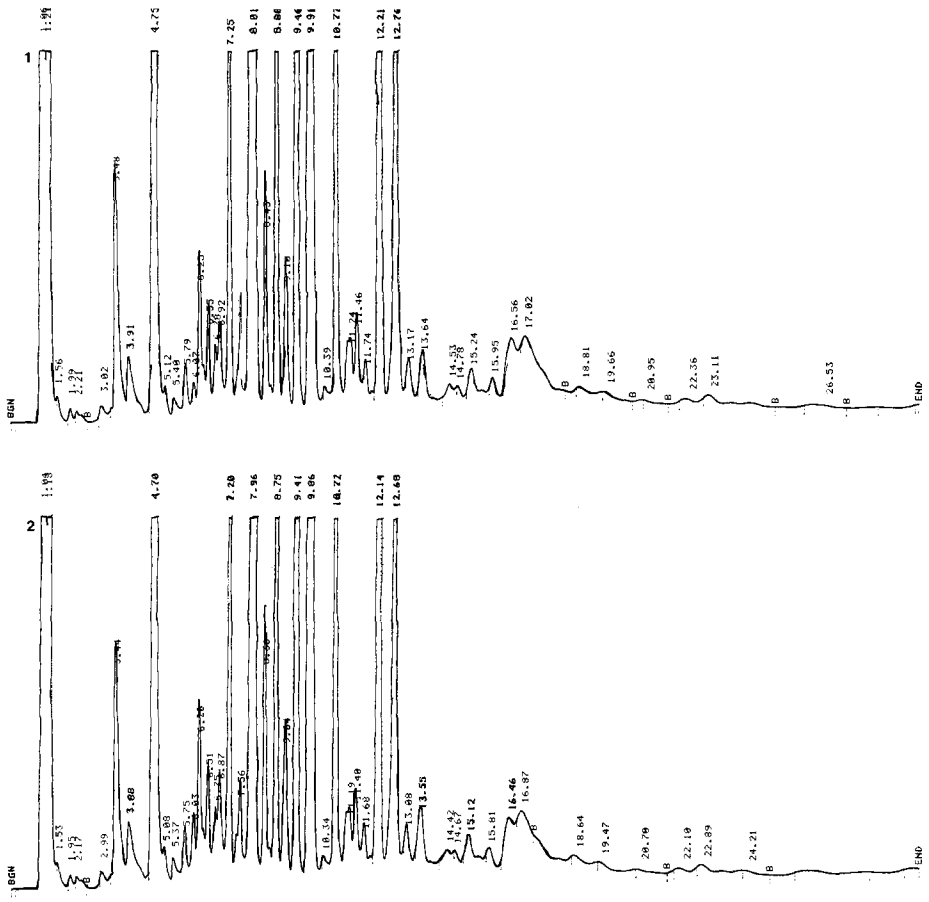


FIG. 5—*Two chromatograms of NBS CN75F0167 (Runs 1 and 2).*

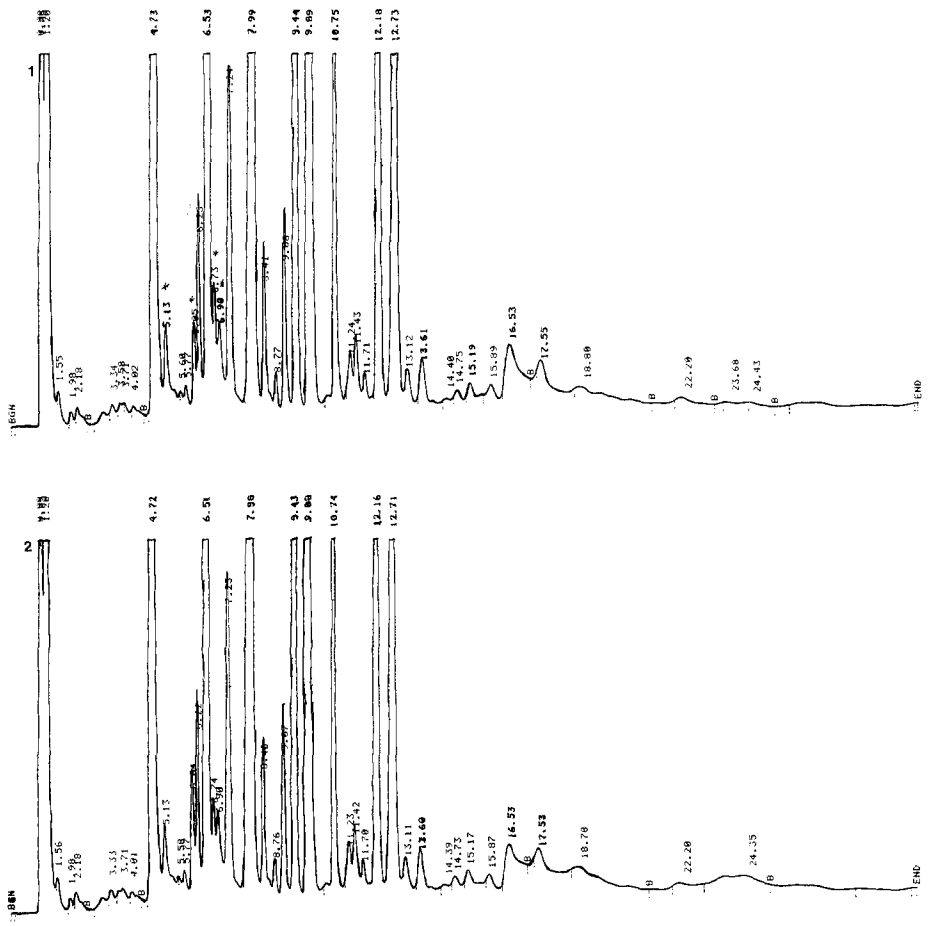


FIG. 6—*Two chromatograms of NBS PN76F0167 (Runs 1 and 2).*

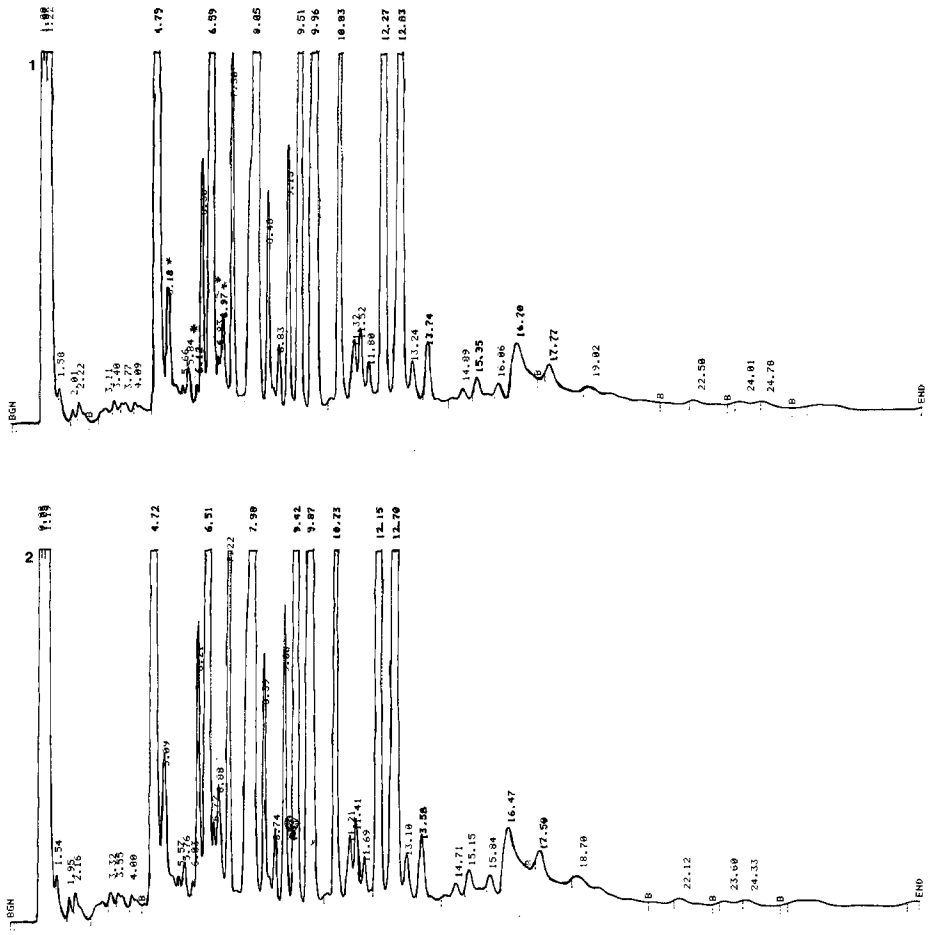

FIG. 7—*Two chromatograms of NBS BN76F0167 (Runs 1 and 2).*

## References

[1] Stewart, W. D., Jr., "Pyrolysis Gas Chromatographic Analysis of Automobile Paints," *Journal of* Forensic Sciences, Vol. 19, No. 1, Jan. 1974, pp. 121-129.

[2] Chemical Data Systems, Inc., "Pyroprobe 100 Series Solids Pyrolyzer Operating and Service Manual," Chemical Data Systems, Inc., Oxford, PA.

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