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## A Novel Pyrolysis Technique for Micro Paint Analysis

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The recent advancement of highly specialized instrumentation and instrumental techniques has enabled the forensic scientist to analyze paint samples in the microgram and picogram ranges. The limiting factor is often the physical recovery of small samples for microchemical analysis. A number of chemical procedures have been employed for the microanalysis of paints. Both infrared spectrophotometry (IR) and pyrolysis-gas chromatography (PGC) are popular techniques for the identification and comparison of paints.

Several identification methods for the IR analysis of paints have been reported by several authors. Sample preparations have primarily been by KBr pellet techniques [1-7] or by diamond cell IR techniques [8,9]. The technique employed most widely by most scientists is the KBr pellet method. Cleverley has used both 13-mm macro KBr disks [4] with 250-mg samples and 1.5-mm micro KBr disks [2] with samples ranging from 10 to 50  $\mu\text{g}$ . Small-don [5] has employed KBr pellet techniques for the analysis of paint pyrolysis residues. May and Porter [6] have analyzed 30- $\mu\text{g}$  samples with Cleverley's 1.5-mm KBr techniques. Fox and Schuetzman [3] obtained KBr spectra with as little as 2 or 3  $\mu\text{g}$  of a fiber sample.

Pyrolysis-gas chromatography is also a well-established technique for the examination of 2- to 50- $\mu\text{g}$  samples of paints. The differentiating powers of PGC have been demonstrated by several authors [10-13]. Stewart [14], Wheals and Noble [15], and Gothard [8] have shown that PGC techniques are both reproducible and sufficiently characteristic to enable paints from motor vehicles of different manufacturers to be discriminated. Interlaboratory collaborative studies have been conducted by May et al [16], Stewart [17], and Coupe et al [18,19] and indicate the wide variety of PGC conditions employed for the analysis of paint samples. These reports also indicate the difficulties in interlaboratory standardizations. Small-don [5] and May and Porter [6] have demonstrated the use of PGC analysis of paints followed by KBr IR analysis of the remaining residues. May and Porter [6] have shown that for maximum discrimination between paint samples both inorganic and organic analyses are required. They have indicated that independent PGC and IR analyses can be employed on samples as small as 10 to 30  $\mu\text{g}$ . In addition, Gothard [8] has also shown the value of employing more than one experimental technique for discriminating paint samples.

The reported literature to date has indicated that PGC and IR analyses have been considered to be mutually exclusive analyses. In all of these situations it has been implied that the KBr pellet technique is a terminating analysis because of the contamination of the sample with KBr. We disagree with this hypothesis. We wish to introduce evidence that an IR analysis of a paint sample by KBr micro techniques is nondestructive. For

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the past year and a half, pyrolysis of 1.5-mm micro KBr pellets containing paint has been conducted in this laboratory. The same KBr pellet can be subsequently analyzed by PGC techniques to obtain further individualization of the paint sample. (Where necessary, emission spectrographic analysis could also be conducted on portions of the pellet.) This technique has now been refined to allow for the sequential IR-PGC analysis on a single 0.5-mm KBr pellet containing a paint sample.

## Instrumentation

### *Infrared Spectrophotometer*

A Perkin-Elmer 283 double-beam optical null filter-grating IR spectrophotometer was equipped with a  $\times 4$  all-reflective beam condenser and a reference beam attenuator. The spectrophotometer was employed over the scanning range of 4000 to 200  $\text{cm}^{-1}$  in the percentage of transmittance (%T) ordinate mode with a scanning time of 6 min, a response time of 1 s, and a slit program of 7. Both the ordinate expansion and abscissa expansion modes were in the normal positions ( $\times 1$  expansion).

### *Gas Chromatograph*

A Varian Model 2800 gas chromatograph equipped with dual flame ionization detectors was used. The columns were 1.8-m (6-ft) by 3.2-mm (0.125-in.) outside diameter stainless steel packed with a permanently bonded Carbowax 400 coating on an 80-100 mesh Porasil S solid support (Durapak 400). The detector temperature was 337°C and the injector temperature was 270°C. The carrier gas was nitrogen at a flow rate of 30 ml/min. The auto linear temperature programmer was programmed to operate between 75 and 195°C with a 10°C/min heating rate. The upper temperature of 195°C was held for the remainder of the program. The range was  $10^{-11}$  A/mV, and the attenuation was  $\times 4$ . A Varian A-25 single pen recorder was employed to record the pyrogram at a chart speed of 12.7 mm/min (0.5 in./min).

### *Pyrolyzer*

A Chemical Data System Model 190 Pyroprobe equipped with a 2-mm diameter quartz tube inside the platinum coil was employed. The pyroprobe was used directly in the injection port of the gas chromatograph. The pyrogram was obtained by using a pyrolysis temperature of 1000°C maintained for a 20-s period.

## Experimental Procedure

Samples of a 1970 Ford acrylic melamine formaldehyde paint standard (manufacturer's topcoat code No. X—dark blue) manufactured by Canadian Pittsburgh Industries were employed for this study. Samples (3 to 5  $\mu\text{g}$ ) of this paint were intimately ground with spectrographic-grade KBr powder (International Crystal Laboratory) with "spectranalyzed" methylene chloride as a solvent (Fisher-certified American Chemical Society). The samples were pressed into a 0.5-mm diameter opening centered in a 13-mm diameter stainless steel disk held within a Perkin-Elmer Ultra micro KBr die apparatus. The resulting pellets were pressed by employing a Carver hydraulic laboratory press. This technique produces a sample in a form that is easily analyzed by both IR and PGC.

An IR spectrum was obtained by placing the resulting disk in the  $\times 4$  beam condenser and recording the complete IR spectrum by employing normal techniques. The KBr suspended paint samples were then punched out of the stainless steel holder. The com-

plete 0.5-mm KBr disk was inserted into the quartz tube of the pyroprobe with the aid of microtweezers and a pointer. A pyrogram was subsequently obtained by employing standard pyrolysis techniques.

### Results and Discussion

Typical IR spectra of a 1970 Ford acrylic melamine paint employing both the 0.5-mm and the 1.5-mm KBr micro pellet technique are shown in Fig. 1. These spectra were obtained without employing the ordinate expansion capacity of the Perkin-Elmer 283 spectrophotometer or any other spectral enhancement process (such as computerization attachments). Both of these KBr sample sizes have been successfully used for further analysis by PGC.

Figure 2 illustrates the typical reproducibility of a series of twelve pyrograms obtained from the pyrolysis of 3 to 5  $\mu\text{g}$  of paint with this 0.5-mm KBr pellet technique. All twelve pyrograms were obtained sequentially. The PGC sample sizes employed were those used to obtain the 0.5-mm IR spectra in Fig. 1. It should be noted that sample sizes approximately half of that used for the pyrograms in Fig. 2 have produced reproducible pyrograms.

Although there were small differences in the amount of KBr used to produce the pyro-

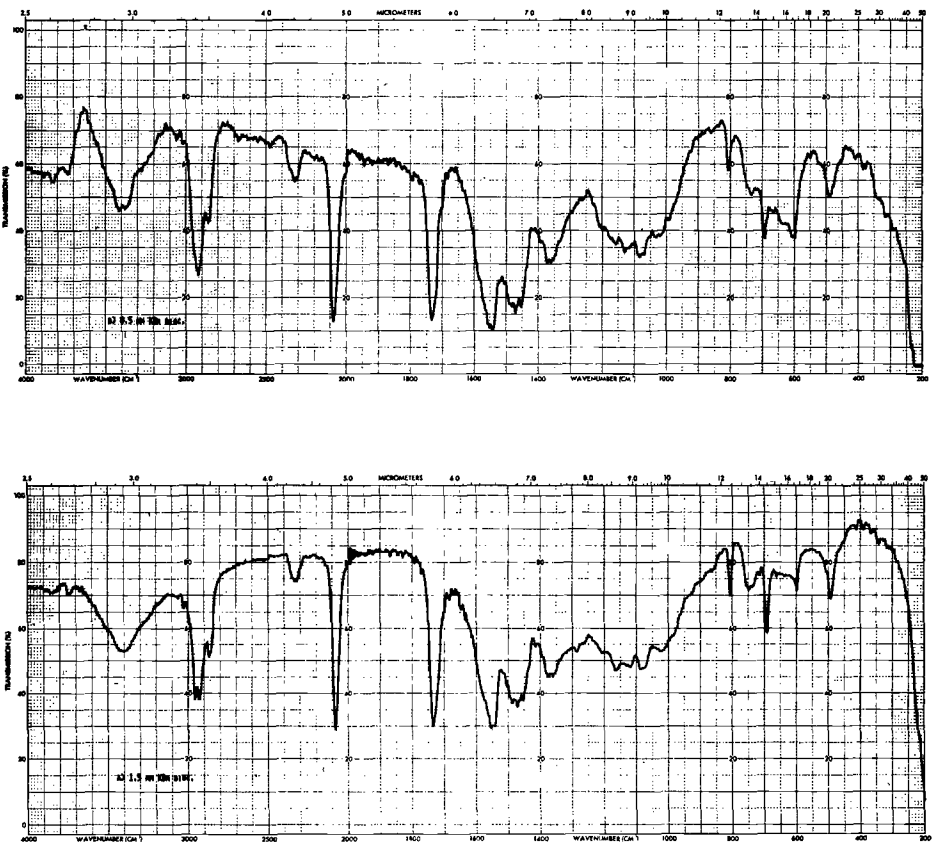


FIG. 1—Infrared spectra of 1970 Ford paint with (top) 0.5-mm and (bottom) 1.5-mm KBr techniques.

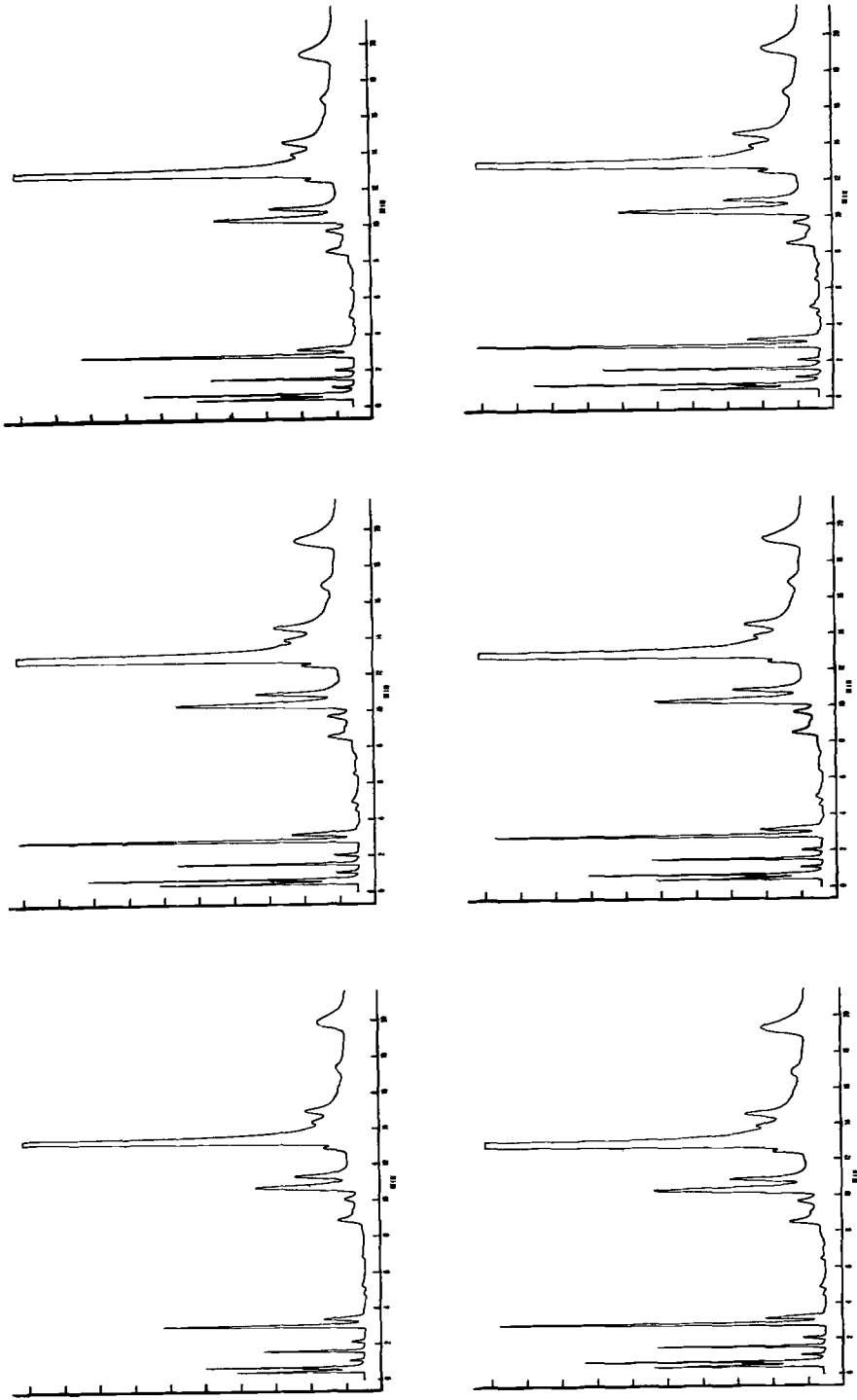


FIG. 2—Reproducibility of the pyrolysis of 0.5-mm KBr micropellets containing 3 to 5  $\mu\text{g}$  of paint.

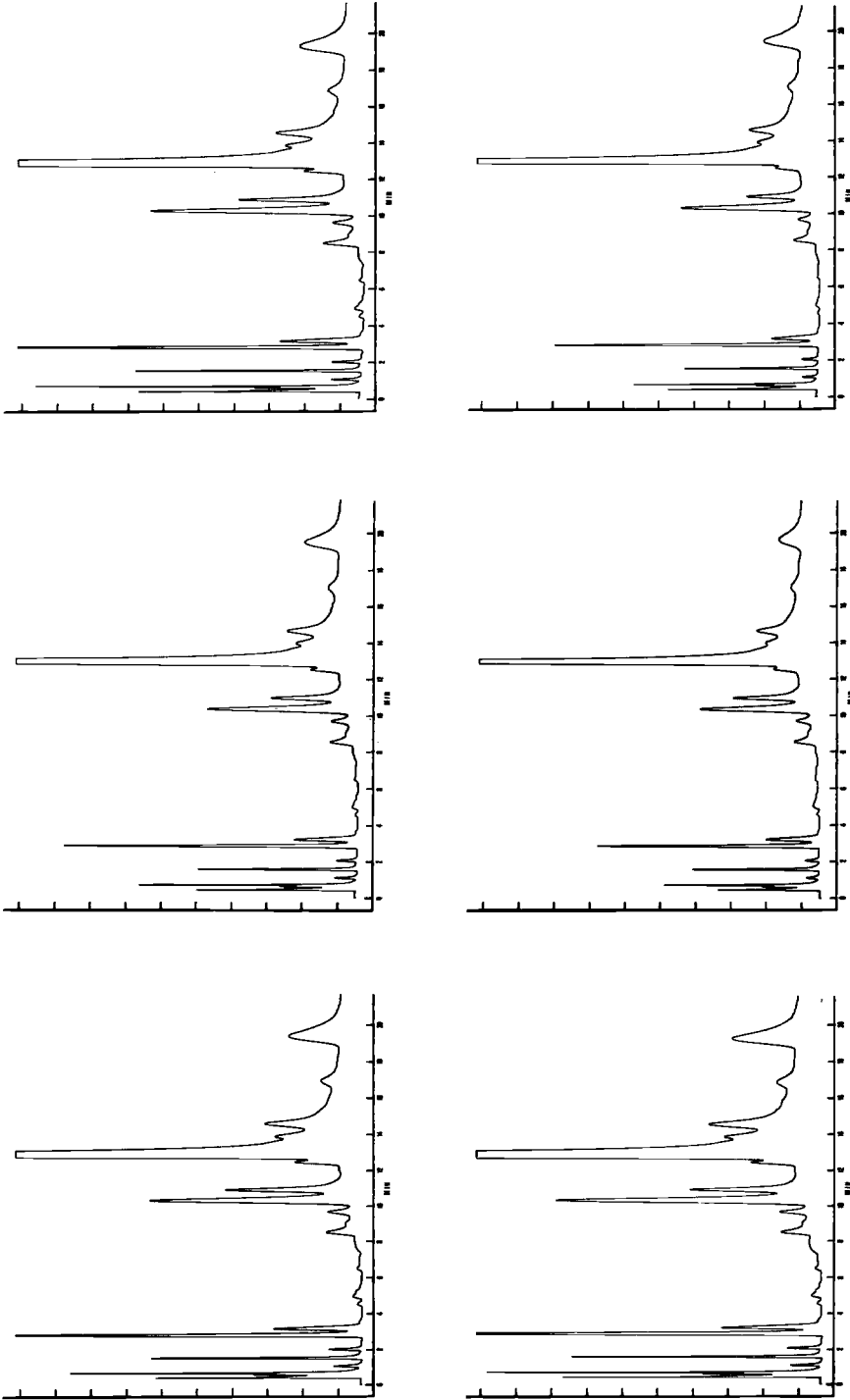


FIG. 2—Continued.

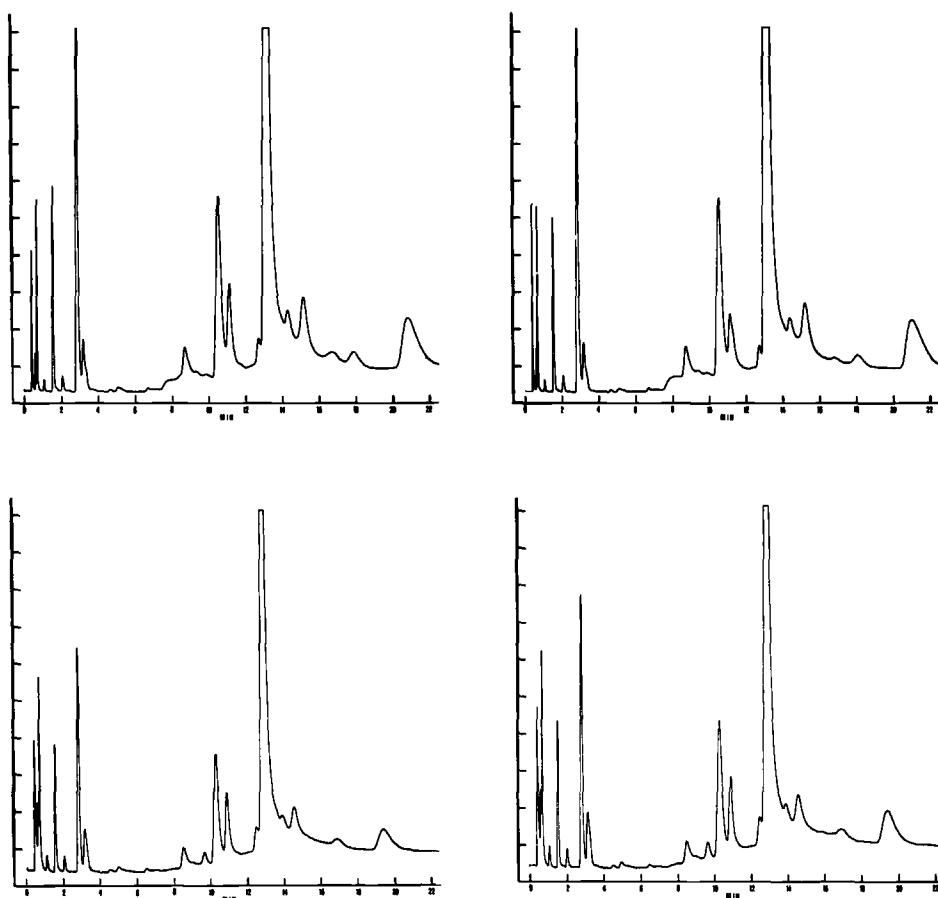


FIG. 3.—Analysis by PGC of 3 to 5  $\mu\text{g}$  of paint without (top) and with (bottom) KBr matrix.

grams in Fig. 2, the pyrograms in Fig. 3 adequately illustrate the effect KBr has on the pyrolysis of paint samples. These pyrograms were again obtained on 3 to 5- $\mu\text{g}$  samples. The normal pyrogram (without KBr) was obtained by simply inserting the paint sample into the quartz tube of the pyroprobe and pyrolyzing. Alterations in retention times of the heavier components and some intensity ratios did occur with KBr as a support matrix. However, the pattern alterations found did not hinder the PGC analysis of the paint. It is completely feasible to obtain two distinctly different types of analysis on the same sample when only very small quantities of paint are available.

### Summary

The analysis by IR and PGC of paint samples has normally been assumed to be mutually exclusive. The introduction of the use of both techniques enables the forensic chemist to obtain a complete IR spectrum of a paint sample while leaving the sample in a form easily handled and readily analyzed by PGC. With sufficient sample size, the remaining KBr pelletized sample could possibly be subjected to analysis by emission spectroscopic techniques. The results of these analyses, therefore, demonstrate that IR analysis of microgram-size samples of paint with KBr techniques is nondestructive. This technique enables the same sample to be analyzed structurally and chemically by distinctly different

techniques before the sample is finally destroyed. By analyzing a paint sample for its elemental composition by such nondestructive techniques as X-ray fluorescence or energy dispersive X-ray analysis prior to employing destructive techniques the forensic chemist could maximize the discrimination between paint samples with a minimum amount of sample.

## References

- [1] Heilman, W. R., "Nondestructive Infrared Analysis and X-Ray Diffraction Analysis of Paints and Plastics," *Journal of Forensic Sciences*, Vol. 5, No. 3, July 1960, pp. 338-345.
- [2] Cleverley, B., "Comparison of Plastic Materials and Paint Films Using Infrared Spectroscopy," *Medicine, Science and the Law*, Vol. 7, 1967, pp. 148-152.
- [3] Fox, R. H. and Schuetzman, H. I., "The Infrared Identification of Microscopic Samples of Man-Made Fibers," *Journal of Forensic Sciences*, Vol. 13, No. 3, July 1968, pp. 397-406.
- [4] Cleverley, B., "The Identification of Motor Body Fillers," *Journal of the Forensic Science Society*, Vol. 10, No. 2, 1970, pp. 73-76.
- [5] Smalldon, K. W., "The Identification of Paint Resins and Other Polymeric Materials from the Infrared Spectra of Their Pyrolysis Products," *Journal of the Forensic Science Society*, Vol. 9, Nos. 3 and 4, 1969, pp. 135-140.
- [6] May, R. W. and Porter, J., "An Evaluation of Common Methods of Paint Analysis," *Journal of the Forensic Science Society*, Vol. 15, No. 2, 1975, pp. 137-146.
- [7] Gothard, J. A., "Evaluation of Automobile Paint Flakes as Evidence," *Journal of Forensic Sciences*, Vol. 21, No. 3, July 1976, pp. 636-641.
- [8] Tweed, F. T., Cameron, R., Deak, J. S., and Rodgers, P. G., "The Forensic Microanalysis of Paints, Plastics and Other Materials by an Infrared Diamond Cell Technique," *Forensic Science*, Vol. 4, 1974, pp. 211-218.
- [9] Rodgers, P. G., Cameron, R., Cartwright, N. S., Clark, W. H., Deak, J. S., and Norman, E. W. W., "The Classification of Automobile Paint by Diamond Window Infrared Spectrophotometry. Part I: Binders and Pigments," *Journal of the Canadian Society of Forensic Science*, Vol. 9, No. 1, 1976, pp. 1-14.
- [10] Jain, N. C., Fontan, C. R., and Kirk, P. L., "Identification of Paints by Pyrolysis-Gas Chromatography," *Journal of the Forensic Science Society*, Vol. 5, 1965, pp. 102-109.
- [11] Levy, R. L. and Barney, J. E., "High Resolution and High Sensitivity Pyrolysis Gas Chromatography (PGC) for the Identification of Paints," in *Proceedings of the Second National Symposium on Law Enforcement and Technology*, Chicago, 16-18 April 1968, pp. 325-331.
- [12] Wheals, B. B. and Noble, W., "Application en Expertise Legale de la CG des Produits de Pyrolyse," *Chromatographia*, Vol. 5, 1972, pp. 553-557.
- [13] Schultz, B. W. and Perros, T. P., "Pyrolysis Gas Chromatographic Analysis of Black Paints," *Journal of the Association of Official Analytical Chemists*, Vol. 58, No. 6, 1975, pp. 1150-1153.
- [14] Stewart, W. D., "Pyrolysis-Gas Chromatographic Analysis of Automobile Paints," *Journal of Forensic Sciences*, Vol. 19, No. 1, Jan. 1974, pp. 121-129.
- [15] Wheals, B. B. and Noble, W., "The Pyrolysis Gas Chromatographic Examination of Car Paint Flakes as an Aid to Vehicle Characterization," *Journal of the Forensic Science Society*, Vol. 14, No. 1, 1974, pp. 23-32.
- [16] May, R. W., Pearson, E. F., Porter, J., and Scothern, M. D., "A Reproducible Pyrolysis Gas-Chromatographic System for the Analysis of Paints and Plastics," *Analyst*, Vol. 98, 1973, pp. 364-371.
- [17] Stewart, W. D., "Pyrolysis-Gas Chromatographic Techniques for the Analysis of Automobile Finishes: Collaborative Study," *Journal of the Association of Official Analytical Chemists*, Vol. 59, No. 1, 1976, pp. 35-41.
- [18] Coupe, N. B., Jones, C. E. R., and Perry, S. G., "Precision of Pyrolysis-Gas Chromatography of Polymers. A Progress Report," *Journal of Chromatography*, Vol. 42, 1970, pp. 291-296.
- [19] Coupe, N. B., Jones, C. E. R., and Stockwell, P. B., "Precision of Pyrolysis Gas Chromatography of Polymers. Part III. The Standardization of Fingerprinting—Assessment of the Third Correlation Trial," *Chromatographia*, Vol. 6, No. 11, 1973, pp. 483-488.

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