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Discrimination of 1990s Original Automotive Paint Systems: A Collaborative Study of Black Nonmetallic Base Coat/Clear Coat Finishes Using Infrared Spectroscopy

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ABSTRACT: The 1990s saw the introduction of significantly new types of paint binder chemistries into the automotive finish coat market. Considering the pronounced changes in the binders that can now be found in automotive paints and their potential use in a wide variety of finishes worldwide, the Paint Subgroup of the Scientific Working Group for Materials (SWGMA) initiated a validation study to investigate the ability of commonly accepted methods of forensic paint examination to differentiate between these newer types of paints. Nine automotive paint systems typical of original equipment applications were acquired from General Motors Corporation in 1992. They consisted of steel panels coated with typical electrocoat primers and/or primer surfacers followed by a black nonmetallic base coat and clear coat. The primary purpose of this study was to evaluate the discrimination power of common forensic techniques when applied to the newer generation original automotive finishes. The second purpose was to evaluate interlaboratory reproducibility of automotive paint spectra collected on a variety of Fourier transform infrared (FT-IR) spectrometers and accessories normally used for forensic paint examinations. The results demonstrate that infrared spectroscopy is an effective tool for discriminating between the major automotive paint manufacturers' formulation types which are currently used in original finishes. Furthermore, and equally important, the results illustrate that the mid-infrared spectra of these finishes are generally quite reproducible even when comparing data from different laboratories, commercial FT-IR instruments, and accessories in a "real world," mostly uncontrolled, environment.

KEYWORDS: forensic science, criminalistics, automotive paint, collaborative study, infrared spectroscopy, binder discrimination, inter-laboratory reproducibility

The 1990s saw the introduction of significantly new types of paint binder chemistries into the automotive finish coat market. Al-

though high solids acrylic-melamine enamels still persisted, the number of suppliers to the original finish market had diminished to the "big three," Dupont, BASF, and PPG. PPG continued to offer waterborne base (color) coats and BASF joined the market with their version. Two of the three companies began to offer acrylic-urethane binders in their clear coat/base coat systems (previously targeted at only the refinish market), Dupont introduced their acrylic-melamine-silane clear coats, and PPG introduced their acrylic-melamine-epoxy clear coats. Company mergers and buy-outs resulted in a globalization of paint suppliers, with larger companies supplying original automotive paints in many different countries (North American, Asian, and European) and "foreign" nameplate vehicles being manufactured domestically.

Considering the pronounced changes in the binders that can now be found in automotive paints and their potential use in a wide variety of finishes worldwide, the Paint Subgroup of the Scientific Working Group for Materials (SWGMA) initiated a study to investigate the ability of commonly accepted methods of forensic paint examination to differentiate between these newer types of paint binders. For this study, black finishes without decorative flake were chosen because they cannot be easily distinguished from one another based on color and other microscopic characteristics. Such paints normally contain predominantly carbon black coloring pigments, which do not produce significant infrared absorption bands and are not detected by pyrolysis gas chromatography or elemental analysis methods unless they contain impurities. Differences in coloring pigment compositions therefore cannot serve as a basis for differentiation of these paints, and binder compositions assume a more important role in their characterization.

Obviously, this is also true for the corresponding clear coat layers, which normally lack significant quantities of pigments intended to absorb or scatter visible light. Primer system variations were also ignored, even though they typically provide substantial discrimination potential to forensic paint comparisons. Additionally, black base coat/clear coat finish systems may present somewhat of a challenging analysis using infrared spectroscopy because of the very thin base coats typically employed in the newer generation finishes along with the strong scattering and absorption effects induced by higher concentrations of carbon black pigment. These finishes therefore provide an appropriate and challenging subgroup for determining the degree to which newer binder formulations can be characterized and distinguished using infrared spectroscopy.

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Experimental

Nine automotive paint systems were acquired from General Motors Corporation in 1992. They consisted of steel panels coated with typical electrocoat primers and/or primer surfacers. The finish coat systems consisted of a clear coat over a black nonmetallic base coat. The coating system types as represented by General Motors are listed in Table 1. General Motors Corporation informed us that the paints supplied were either being used, had been used, or were going to be used on their 1990 to 1994 vehicle lines. Specific automotive model and manufacturing plant information was made available for corroboration but is considered confidential and is not presented herein.

The eight participating laboratories were asked to analyze both the clear coat and the black base coat for each of the nine samples via Fourier transform infrared (FT-IR) spectroscopy. This technique was targeted since it is the most common instrumental technique, aside from microscopy, used in forensic paint examinations in North American crime laboratories (results of an unpublished SWGMAT Paint Subgroup survey of 100 North American crime laboratories, Quantico, Virginia, November 1996). No instructions were given as to sample preparation or the infrared spectroscopic technique to be used. Thus, it was hoped that a clearer picture of normal discrimination potentials using a variety of instruments and techniques would be revealed. The participants inter-compared spectra to determine discrimination potential between the clear coats and the base coats. The types of instruments, accessories, and sample preparation methods are listed in Table 2. Six laboratories

used transmission techniques while two others used attenuated total reflection (ATR) techniques. The exercise also presented an opportunity to evaluate the reproducibility of infrared spectral data collected using these varieties of instruments and accessories in a "real world," mostly uncontrolled, environment.

Results and Discussion

Spectra from each of the eight participating laboratories were compiled using a standard format employing wavenumbers plotted from 4000 cm^{-1} to 200 cm^{-1} with an abscissa scale change at 2000 cm^{-1} . Spectra were plotted in percent transmittance (%T) to permit the simultaneous observation of both very weak and strong absorptions and to facilitate the viewing of fine details of absorption contours. To facilitate comparisons, spectra exhibiting significant baseline slopes were baseline corrected using a multiple point correction program performed on absorbance spectra. In particular, spectra of the black base coats usually required considerable baseline modification because of strong scattering effects. If baselines are corrected in transmittance, the resulting relative absorption intensities are inaccurate because the transmittance scale is not linear. This distortion is particularly pronounced when strongly sloping baselines, such as those for the black paints, are corrected in this manner. Each of the eight laboratory's corrected spectra were then visually inter-compared for reproducibility on each of the nine clear coats and nine base coats. Following this evaluation, the spectra for each of the nine clear coats and nine base coats were then inter-compared for discrimination potential.

TABLE 1—Typical 1990s clear coat over black base coat samples supplied by General Motors along with their designation as to the binder system types.

Sample	Supplier	Product (BC//CC)*	Type†
A	Dupont	706/707//RK-7103	acrylic-melamine base and clear
B	Dupont	541/542//RK-8010	acrylic-melamine base with acrylic-melamine-silane clear
C	Dupont	871/872//RK-7100	acrylic-melamine base with two-component urethane clear
D	BASF	E92/9//E126CD005	acrylic-melamine base and clear
E	BASF	E164/5//E126CD015	acrylic-melamine base with one-component urethane clear
F	BASF	E54/5//E10/N52CW022	waterborne acrylic base with two-component urethane clear
G	PPG	HBAL//DCT-1000	acrylic-melamine base and clear
H	PPG	NHUBC//DC-5000	acrylic-melamine base with one-component acrylic-epoxy clear
I	PPG	HWB//NCT-2	waterborne acrylic base with two-component acrylic-epoxy clear

* The codes refer to the paint manufacturer's formulation designation for the clear coat and the base coat.

† The listed binder types are those designations provided by the paint manufacturers and may not always reflect all of the functional group types of polymers evident in evaluation of the infrared spectra.

TABLE 2—Types of infrared spectrometers, accessories, and sample preparation methods used by the study participants.

Laboratory	FTIR	Resolution	Apodization	Sampling Accessory	Detector (Range)	Sample Mount	Sample Preparation
1	Nicolet 550	4 cm-1	Happ-Ganzel	Nic-Plan microscope	MCT A (4000–550)	micro-diamond ATR objective	thin peels
2	Nicolet 750	4 cm-1	Happ-Ganzel	Nic-Plan microscope	MCT A (4000–650)	low-press. diamond cell	thin peel compressed—run on one window
3	Digilab FTS-40	4 cm-1	triangular	UMA 300 microscope	MCT B (4000–450)	laid-on AgCl window	thin compressed peel
4	Nicolet 750	4 cm-1	Happ-Ganzel	Nic-Plan microscope	MCT A (4000–650)	laid on AgCl window	thin compressed peel
5	Digilab	4 cm-1	triangular	6 × beam condenser	DTGS (4000–220)	high-press. diamond cell	thin peel compressed—run on double windows with pressure backed off
6	Digilab FTS-7	4 cm-1	triangular	5 × beam condenser	DTGS (4000–220)	low-press. diamond cell	thin peel compressed—run on double windows
7	Perkin Elmer Spectrum 2000	4 cm-1	strong	I Series microscope	MCT A (4000–550)	laid-on KBr disk	thin compressed peel
8	Mattson Galaxy 5000	4 cm-1	triangular	Harrick Split Pea	MCT B (4000–450)		thin peel

Interlaboratory reproducibility is excellent for the transmission spectra of the clear coats. Even small shoulders and other minor features can be observed in the data obtained by each laboratory. The spectra of the acrylic-urethane clear coats of sample sets C and E for the six laboratories using transmission techniques are presented in Fig. 1a and 1b to demonstrate this stability from laboratory to laboratory. For example, not only are the overall patterns like one another for a given finish, but even the fine structure in the 1380 cm^{-1} to 1240 cm^{-1} region and the small peak at 1122 cm^{-1} (Fig. 1b) correspond from laboratory to laboratory.

Slight differences in spectra can occasionally be seen between the laboratories that used diamond cell techniques versus microscopical techniques. An example can be found in the 1475 cm^{-1} region of the Sample B clear coat spectra as seen in Fig. 2. Absorptions in this spectral region are known to be prone to crystallinity effects in polyesters and will occasionally vary in intensity as a result of polymer chain orientation induced when smearing techniques are used to thin the specimen (1). Other slight ratio variations were occasionally encountered, such as that observed for the 1550 cm^{-1} and 1520 cm^{-1} doublet (melamine

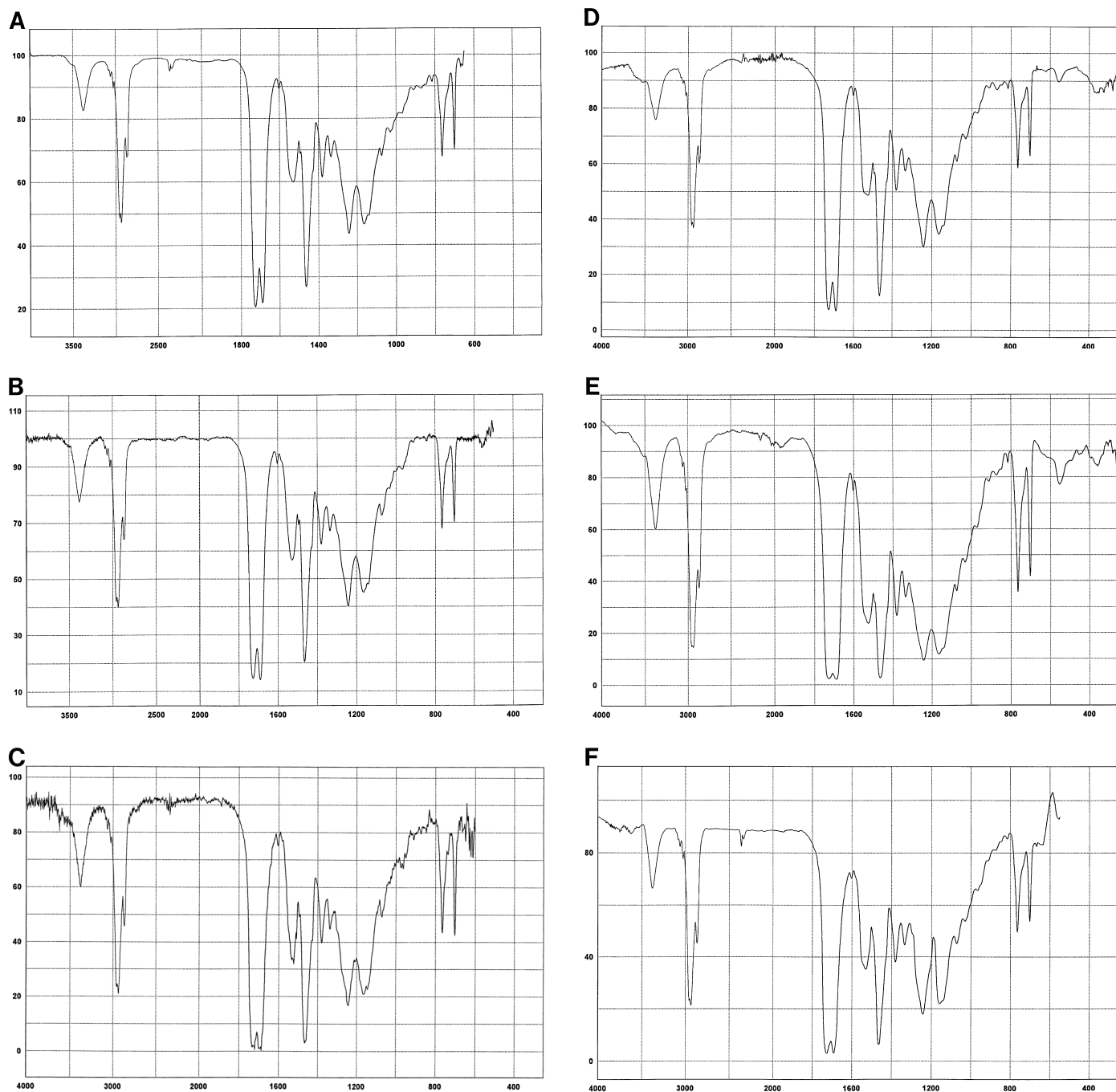


FIG. 1a—Infrared spectra of the Sample C clear coat acquired by the six laboratories using transmission techniques. (A) Sample C, Laboratory 2, (B) Sample C, Laboratory 3, (C) Sample C, Laboratory 4, (D) Sample C, Laboratory 5, (E) Sample C, Laboratory 6, (F) Sample C, Laboratory 7.

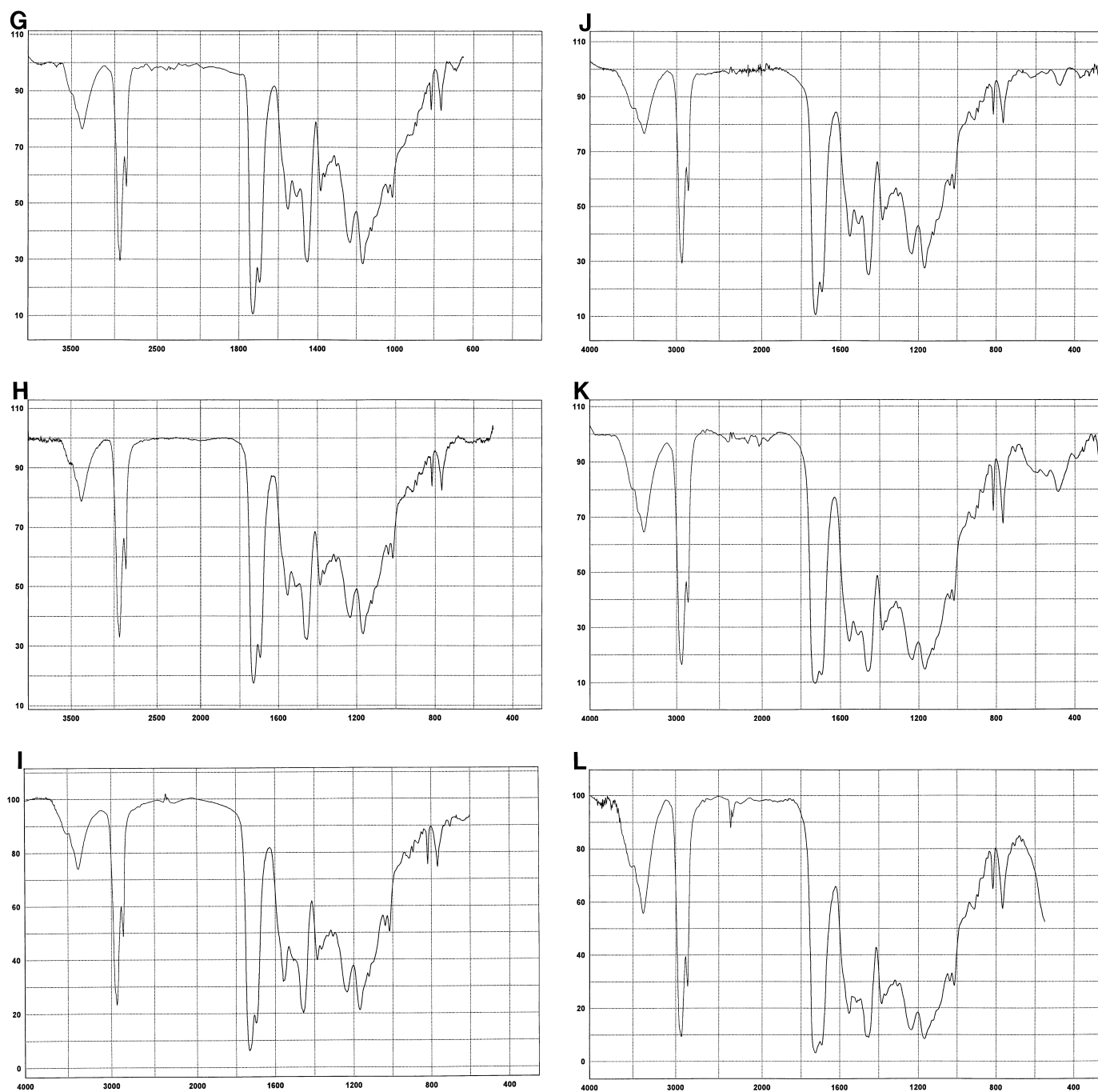


FIG. 1b—Infrared spectra of the Sample E clear coat acquired by the six laboratories using transmission techniques. (G) Sample E, Laboratory 2, (H) Sample E, Laboratory 3, (I) Sample E, Laboratory 4, (J) Sample E, Laboratory 5, (K) Sample E, Laboratory 6, (L) Sample E, Laboratory 7.

and urethane absorptions respectively) of Sample F in Fig. 3. Multiple runs will typically aid in evaluation of apparent discrepancies should such minor differences be observed in the comparison of otherwise similar spectra.

Although the general absorption band patterns are quite similar, some significant deviations in both peak intensities and absorption frequencies can be observed when comparing the microscopic ATR technique demonstrated by Laboratory 1 with the six laboratories using transmission techniques (Laboratories 2,3,4,5,6,7). This is not surprising for uncorrected ATR spectra. ATR infrared spectroscopy results in the longer wavelength

(lower frequency) absorption bands having increased relative intensities compared with those obtained in transmission methods, since the penetration depth of the sampling beam is proportional to the wavelength in this reflection technique. The longer wavelengths penetrate deeper into the sample and undergo more interaction with the sample components. Laboratory 1, therefore, used a commonly available mathematical correction routine to adjust the ATR absorption intensities so that they are comparable to those produced using the transmission method. An example of Laboratory 1's uncorrected ATR spectra and corrected spectra are presented in Fig. 4. Even after using the correction routine, sig-

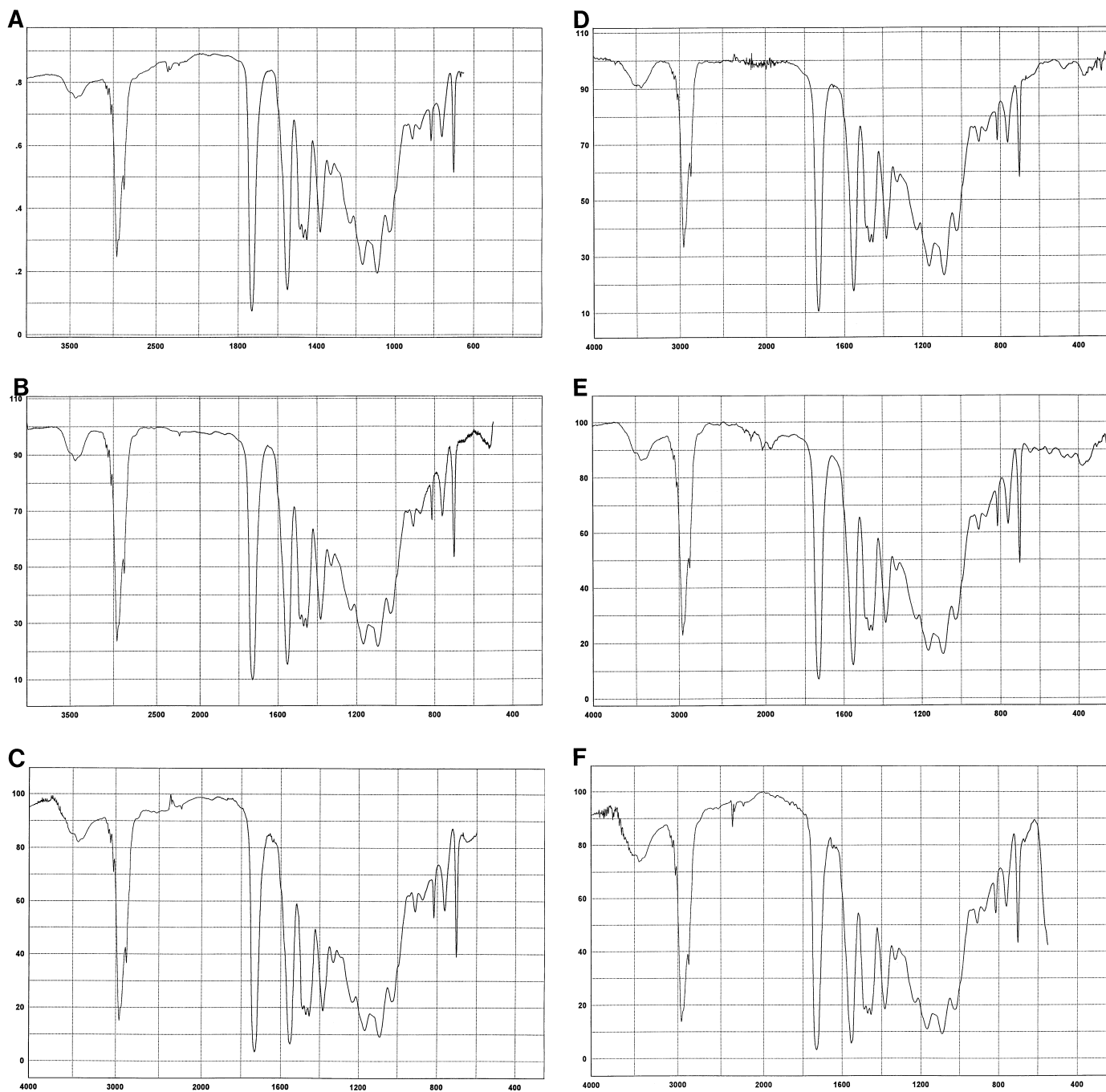


FIG. 2—Infrared spectra of the Sample B clear coat obtained by those laboratories using diamond compression cells versus those using microscope accessories demonstrating slight differences in the 1475 cm^{-1} region of spectra. (A) Sample B, Laboratory 2, (B) Sample B, Laboratory 3, (C) Sample B, Laboratory 4, (D) Sample B, Laboratory 5, (E) Sample B, Laboratory 6, (F) Sample B, Laboratory 7.

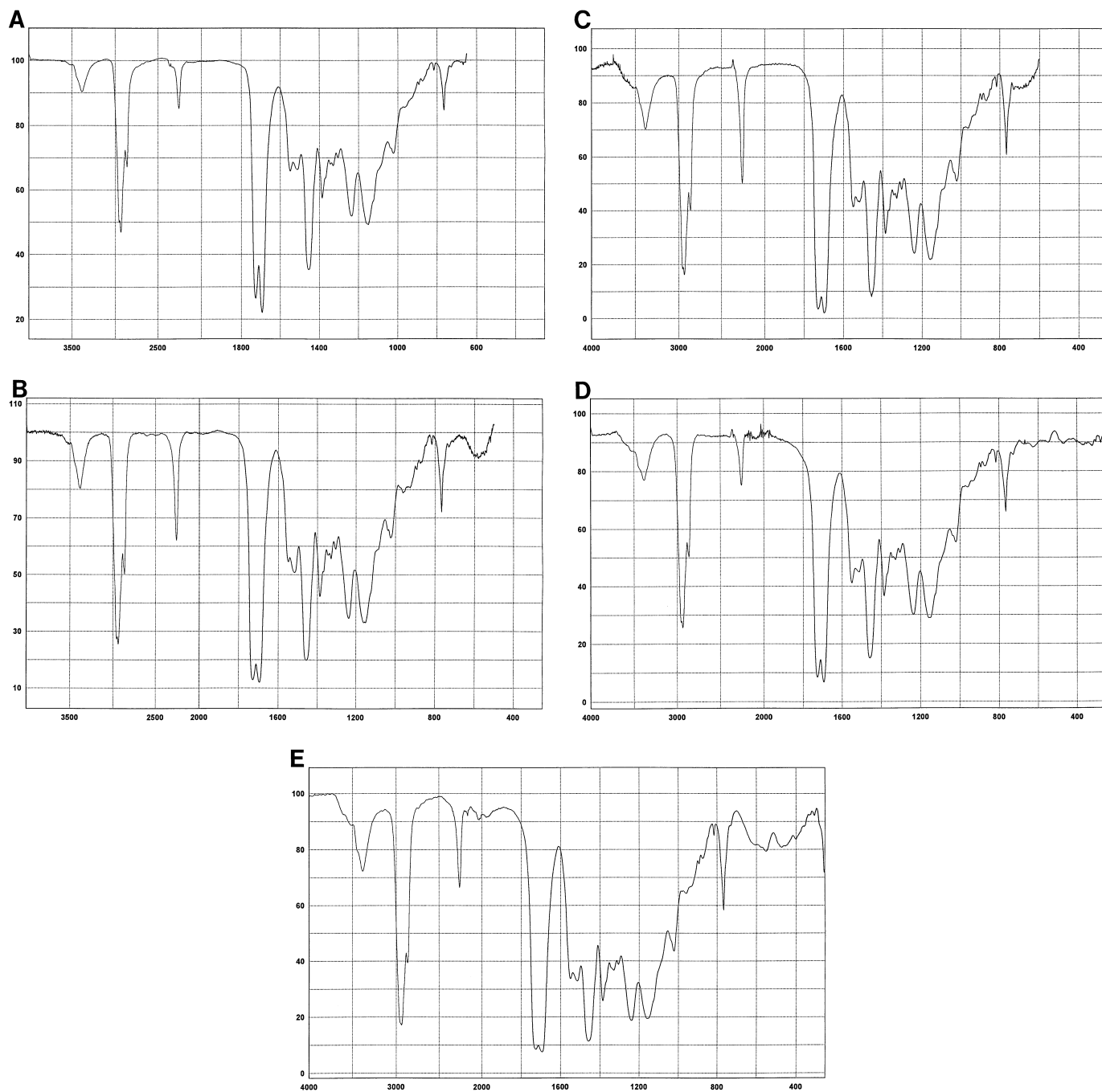


FIG. 3—Slight variations observed in the intensity of the 1550 cm^{-1} and 1520 cm^{-1} doublet (melamine and urethane absorptions, respectively) for the Sample F clear coat spectra. (A) Sample F, Laboratory 2, (B) Sample F, Laboratory 3, (C) Sample F, Laboratory 4, (D) Sample F, Laboratory 5, (E) Sample F, Laboratory 6.

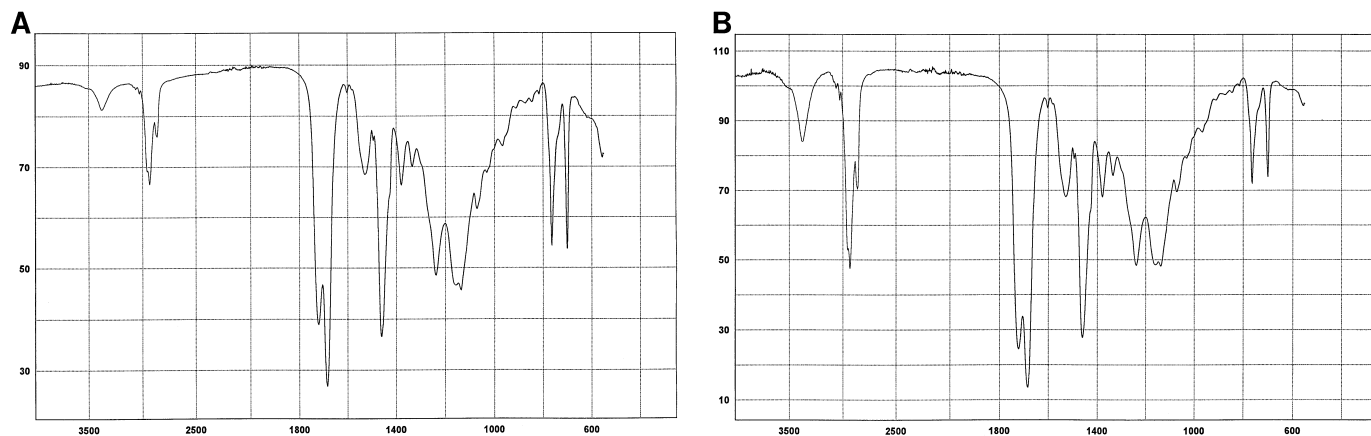


FIG. 4—An example of Laboratory 1's uncorrected ATR spectrum of the Sample C clear coat (A) and its mathematically corrected spectrum (B), intended to simulate a transmission spectrum.

nificant differences were noted between the ATR spectra and the transmission spectra. A typical example can be seen in Fig. 5 when comparing the 1730 cm^{-1} carbonyl absorption intensity with that of the 1690 cm^{-1} urethane absorption intensity in the Sample C clear coat corrected spectra of Laboratory 1 versus those laboratories using transmission techniques (Laboratories 2, 3, and 5). Secondly, examples of absorption maxima wavenumber differences are presented in Table 3. Differences as great as 12 cm^{-1} can be seen in the more intense absorption bands, such as in the C-O stretching region of the spectra. It has been reported that when using a diamond ATR internal reflection element, the infrared beam is focused into a small crystal, which can give rise to a wider angular spread of the incident beam (2). Dispersion effects become more pronounced as the incident light gets closer to the critical angle of the small internal reflection element (3). This may result in absorption maxima differences for strongly absorbing bands compared to those acquired by transmission techniques. Deviations of this magnitude are of concern if ATR absorption band maxima are used to qualitatively classify paint binders based on criteria established using transmission techniques, such as those in Rodgers, et al. and Ryland (4,5). Contrasting the microscopic ATR technique (Laboratory 1) with the Split Pea ATR technique (Laboratory 8) also disclosed marked differences in some of the spectra. Laboratory 8's data are uncorrected, as can be seen by the intensity of the methyl/methylene stretching absorptions relative to the carbonyl absorption, and they should therefore be compared with Laboratory 1's uncorrected data. Examples of the variations can be found in Fig. 6. The differences occur primarily as intensity variations in the 1000 cm^{-1} to 1200 cm^{-1} C-O stretch and the 600 cm^{-1} to 800 cm^{-1} out-of-plane C-H bending on aromatic and heterocyclic ring regions of the spectra. Such differences are to be expected when using internal reflection techniques, since the absorption intensities depend on the differences in indices of refraction between the refractive element and the sample, the angle of incidence, and the degree to which the sample has made contact with the element (6). On the other hand, Laboratory 1's and Laboratory 8's ATR spectra for Samples C, E, F, H and I are quite similar overall. Some intensity differ-

ences, although not inversions, can be noted between the 1720 cm^{-1} and 1690 cm^{-1} carbonyl absorption bands of the Sample C and E spectra. It is worthy of note, however, that despite the differences between ATR spectral data and transmission spectral data, discrimination between samples can be accomplished by observing the same general pattern differences in the same regions of the spectra. This supports the viability of using the ATR technique for comparison purposes.

All eight participants easily differentiated between the clear coats in Samples B, C, E, F, H, and I. Thus, Dupont's acrylic-melamine-silane clear coat is easily distinguished from PPG's one- and two-component acrylic-melamine-epoxy clear coats, and Dupont's acrylic-urethane clear coat is easily distinguished from BASF's one- and two-component acrylic-urethane clear coats. An example is given in Laboratory 5's data as seen in Fig. 7. Discrimination between the acrylic-melamine enamel clear coats in Samples A, D, and G (Dupont, BASF, and PPG) is not so straightforward. The similarity of their spectra can be observed in the data from each of the eight laboratories. Again, an example is given in Laboratory 5's data as can be seen in Fig. 8. Slight differences were noted between samples A and G in their absorption intensities in the 1350 to 1280 cm^{-1} and 1000 to 800 cm^{-1} regions of the spectra. For those laboratories using extended range techniques (such as Laboratory 5), further differences were noted in the 480 cm^{-1} region of the spectra, most likely due to differences in the amount of silica extender present. Spectra of samples A and D are virtually indistinguishable except for some very slight intensity differences (shoulders) in the 1350 to 1280 cm^{-1} region and in the ratio of the 760 cm^{-1} to the 706 cm^{-1} bands. Interlab reproducibility of these differences is demonstrated; however, the magnitude of the differences is such that most would find it very difficult to unequivocally conclude the two were different from one another based on the infrared spectra alone. To illustrate the value of employing alternate techniques to further evaluate perceived similarities, the three samples were subjected to comparison by pyrolysis gas chromatography (PGC). The improved ease of differentiating the three manufacturers' acrylic-melamine clear coats (Samples A, D, and G) is evident in the pyrograms from Laboratories 2, 3, and an additional

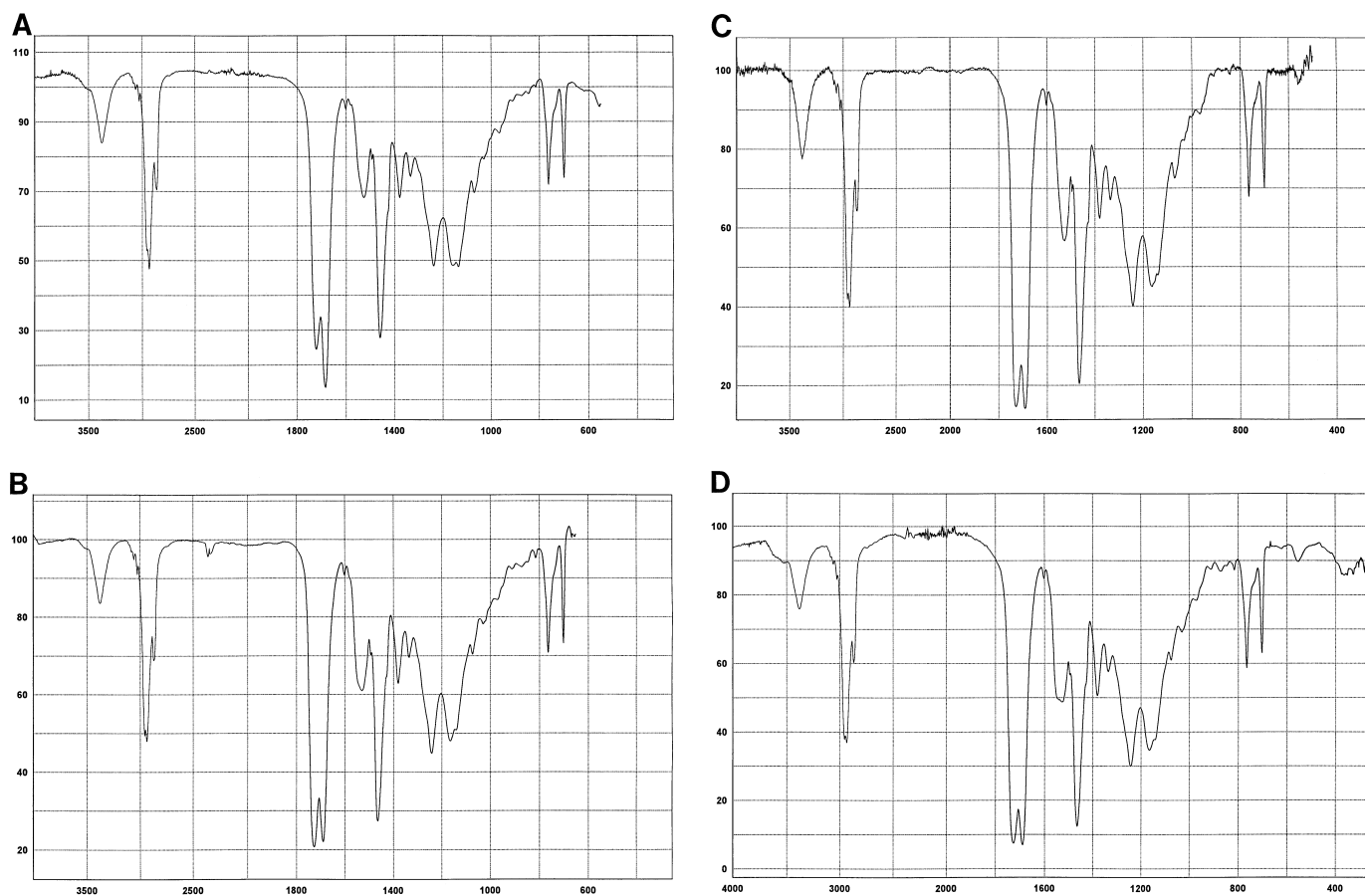


FIG. 5—A typical example of the absorption band intensity differences encountered when comparing corrected ATR spectra and transmission spectra, as seen in the ratio of the 1730 cm^{-1} carbonyl absorption and the 1690 cm^{-1} urethane absorption in the Sample C clear coat spectra. (A) Laboratory 1 corrected ATR spectrum and the transmission spectra of (B) Laboratory 2, (C) Laboratory 3, and (D) Laboratory 5.

TABLE 3—Observed differences in the absorption maxima of the more intense absorption bands between laboratories using the ATR technique* versus the transmittance technique.†

Laboratory	Sample A 1730 cm^{-1} Carbonyl (cm^{-1})	Sample A 1550 cm^{-1} Melamine (cm^{-1})	Sample A 1095 cm^{-1} C-O Stretch (cm^{-1})	Sample C 1690 cm^{-1} Urethane (cm^{-1})	Sample A 815 cm^{-1} Melamine (cm^{-1})
Laboratory 1*	1727	1545	1083	1684	814
Laboratory 2†	1732	1551	1094	1690	815
Laboratory 3†	1732	1550	1094	1691	815
Laboratory 4†	1733	1552	1094	1692	815
Laboratory 5†	1731	1551	1094	1690	815
Laboratory 6†	1732	1552	1095	1690	815
Laboratory 7†	1731	1552	1093	1690	815
Laboratory 8*	1728	1548	1085	1687	815

laboratory (which was not one of the eight participating laboratories). An example can be seen in Fig. 9.

Although instances may arise in forensic paint investigations where only the clear coat is available for examination, the normal situation involves multilayer transfers of fragments which will include at least the base coat and the clear coat, if not the primer systems as well. In evaluating the results of the eight laboratories with respect to the black base coats, differentiation of all nine samples

was again possible. As can be seen in Fig. 10, differences between the Sample A, D, and G acrylic-melamine base coats were more recognizable than those in the clear coats. Just as in the clear coats, variations were seen in the 1350 to 1280 cm^{-1} and 800 to 1000 cm^{-1} regions of the spectra, but they were more pronounced. Furthermore, Samples A and G appear to have some iso-phthalate modification, as evidenced by the presence of a 730 cm^{-1} absorption band, while Sample D's 730 cm^{-1} band is obscured by a

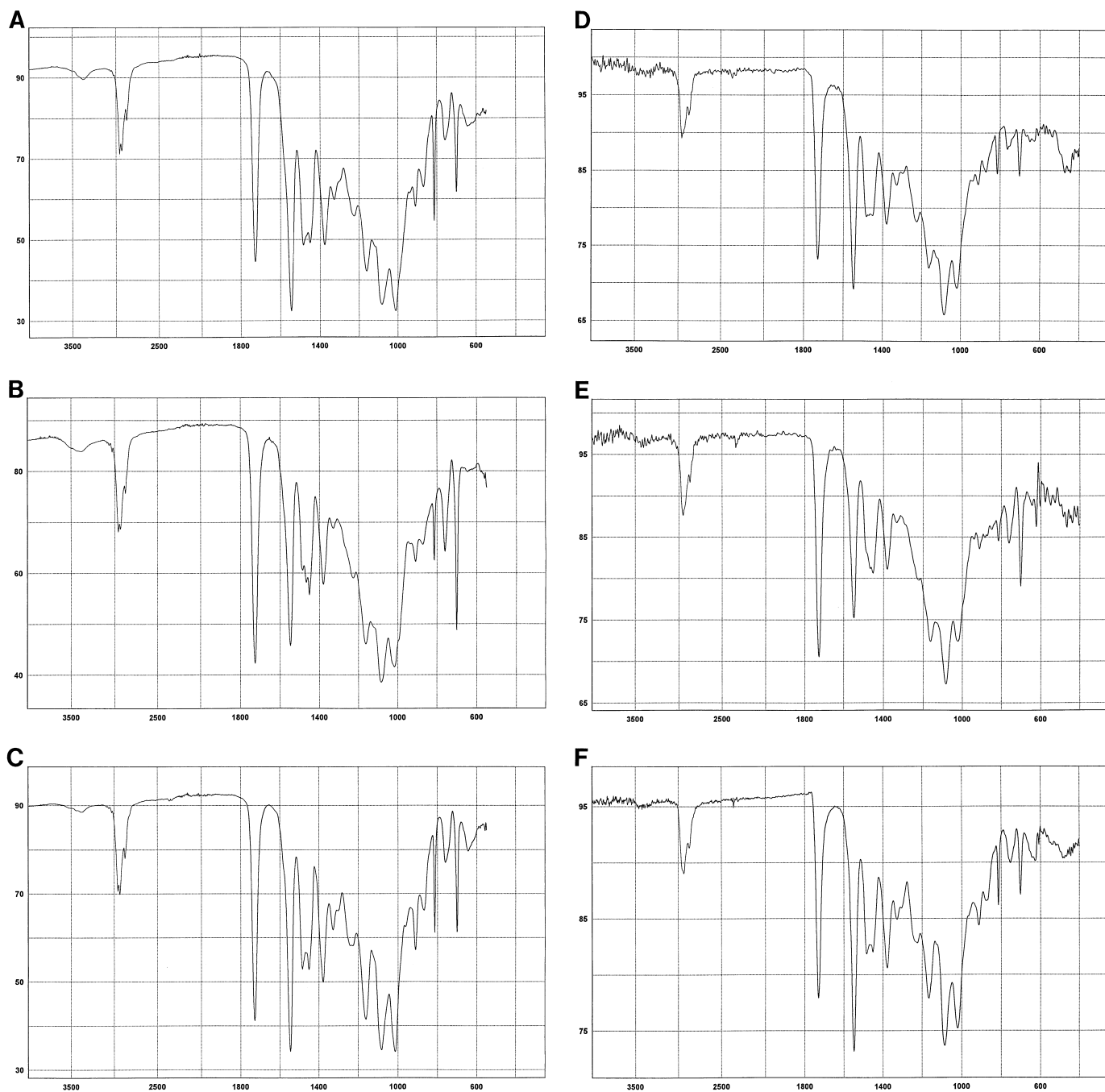


FIG. 6—Comparison of clear coat infrared spectra collected using the diamond ATR objective in a microscope accessory with those collected using the split pea ATR accessory in the main sample compartment for (A) Sample A, Laboratory 1, (B) Sample B, Laboratory 1, (C) Sample G, Laboratory 1, (D) Sample A, Laboratory 8, (E) Sample B, Laboratory 8, and (F) Sample G, Laboratory 8.

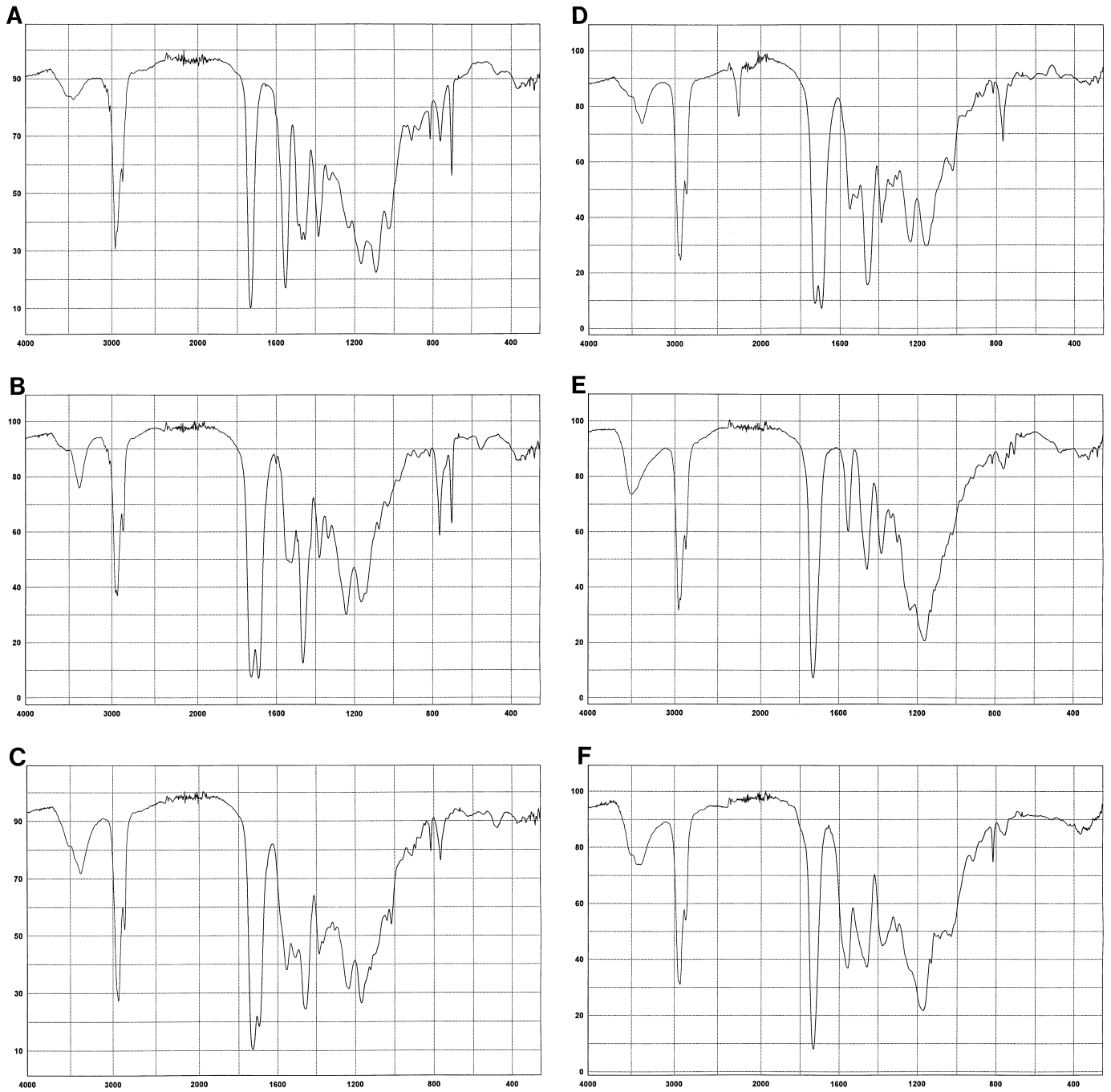


FIG. 7—Differentiation between the clear coats in Samples B, C, E, F, H, and I as demonstrated by Laboratory 5's transmission infrared spectra. (A) Sample B, Laboratory 5, (B) Sample C, Laboratory 5, (C) Sample E, Laboratory 5, (D) Sample F, Laboratory 5, (E) Sample H, Laboratory 5, (F) Sample I, Laboratory 5.

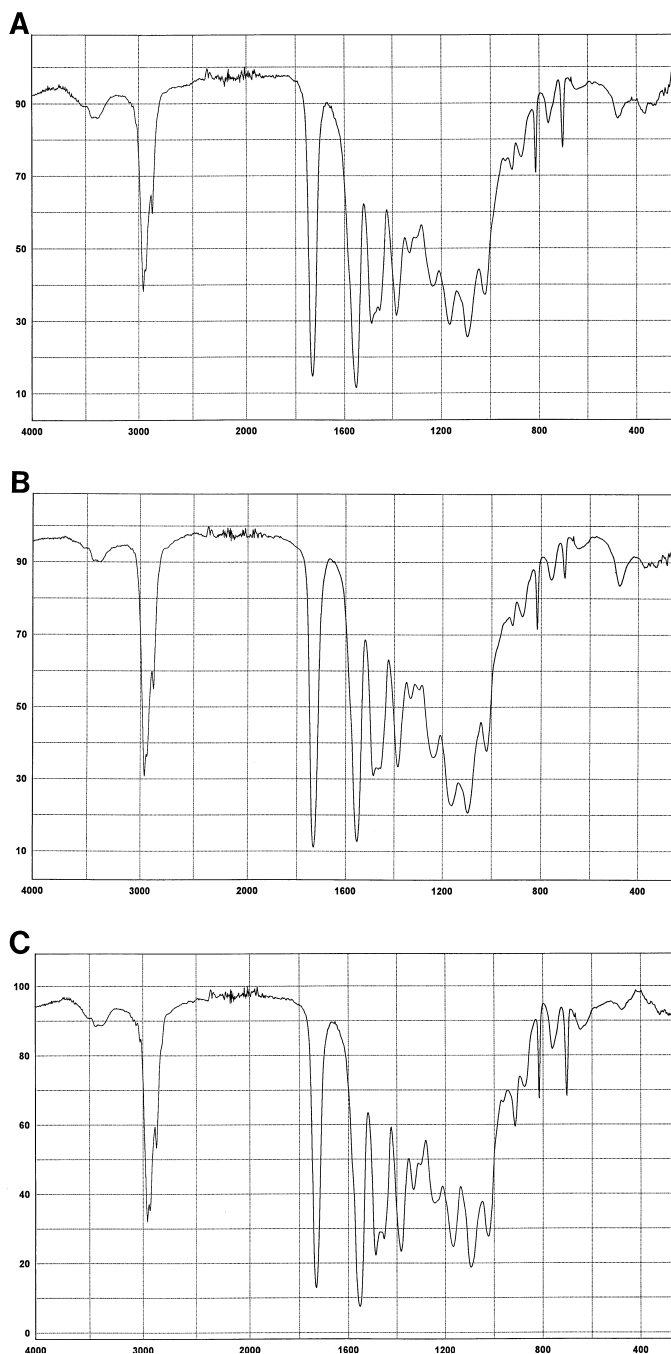


FIG. 8—The similarity of the acrylic-melamine clear coat spectra of Samples A, D, and G (Dupont, BASF, and PPG) as demonstrated by Laboratory 5's transmission infrared spectra. (A) Sample A, Laboratory 5, (B) Sample D, Laboratory 5, (C) Sample G, Laboratory 5.

styrene 750 cm^{-1} absorption. Sample G is further discriminated by the presence of a small 1130 cm^{-1} absorption band. Consequently, differentiation of Samples A, D, and G can be definitively accomplished by FT-IR spectroscopy alone if the base coats were present in the transfer.

Variations in spectral detail between laboratories were much more pronounced in the base coats than in the clear coats. This is not surprising considering the difficulties that may arise when analyzing the thin newer generation base coats (typically only 12 to 20 μm thick), particularly black ones. These thin base coats will con-

tinue to be encountered, however, since they permit universal application of the same colored finish coat over a variety of substrate materials, e.g., vehicle panels. Changing the chemistry of the 30-to-50- μm -thick clear coat then controls the overall physical performance of the finish coat system. As noted, black base coats strongly absorb and scatter light, which may result in pronounced sloping baselines and reduced throughputs. Furthermore, for those laboratories that physically isolated the thin base coats, it was necessary to exclude any of the adjacent clear coats and under coats. This often results in smaller sample sizes and subsequent reductions in signal to noise. Laboratories that sequentially analyze individual layers of a cross section, on the other hand, face a potential problem with diffraction-produced stray light and small sample sizes for the relatively thin base coat layers. Although an overwhelming majority of the sample spectra were reproducible, such as those depicted for Sample A in Fig. 11, more severe variations, like those presented for Sample H in Fig. 12, were occasionally noted.

A comparison of the binder classifications obtained by interpretation of spectral data with the paint supplier's nomenclature for these same finishes reveals some interesting observations. Although the manufacturer describes the samples A, (Fig. 11), B, G (Fig. 10), and H (Fig. 12) base coats as acrylic-melamine enamels, they also have apparent iso-phthalate polyester modification as indicated by the 1240 cm^{-1} , 1305 cm^{-1} , and 730 cm^{-1} absorption bands. The sample F base coat is described as a waterborne acrylic

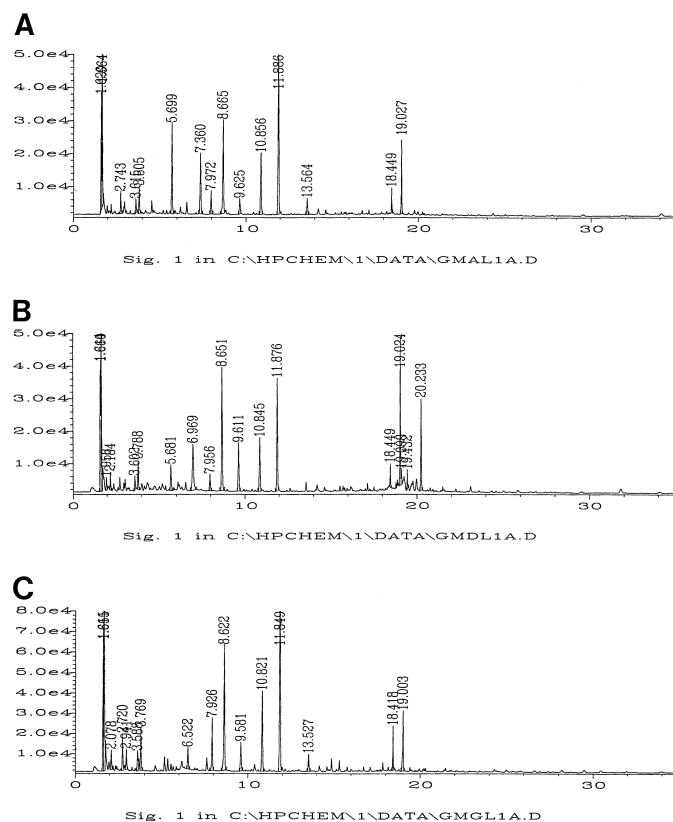


FIG. 9—The ease of differentiating the sample A, D, and G acrylic-melamine enamel clear coats by pyrolysis gas chromatography as demonstrated by Laboratory 3's pyrograms. The Signal 1 column is a 25 m by 0.32 mm (ID) fused silica column coated with a 1.0 μm film thickness of high polarity free fatty acid phase (Quadrex Corporation). (A) Sample A, high polarity column, (B) Sample D, high polarity column, (C) Sample G, high polarity column.

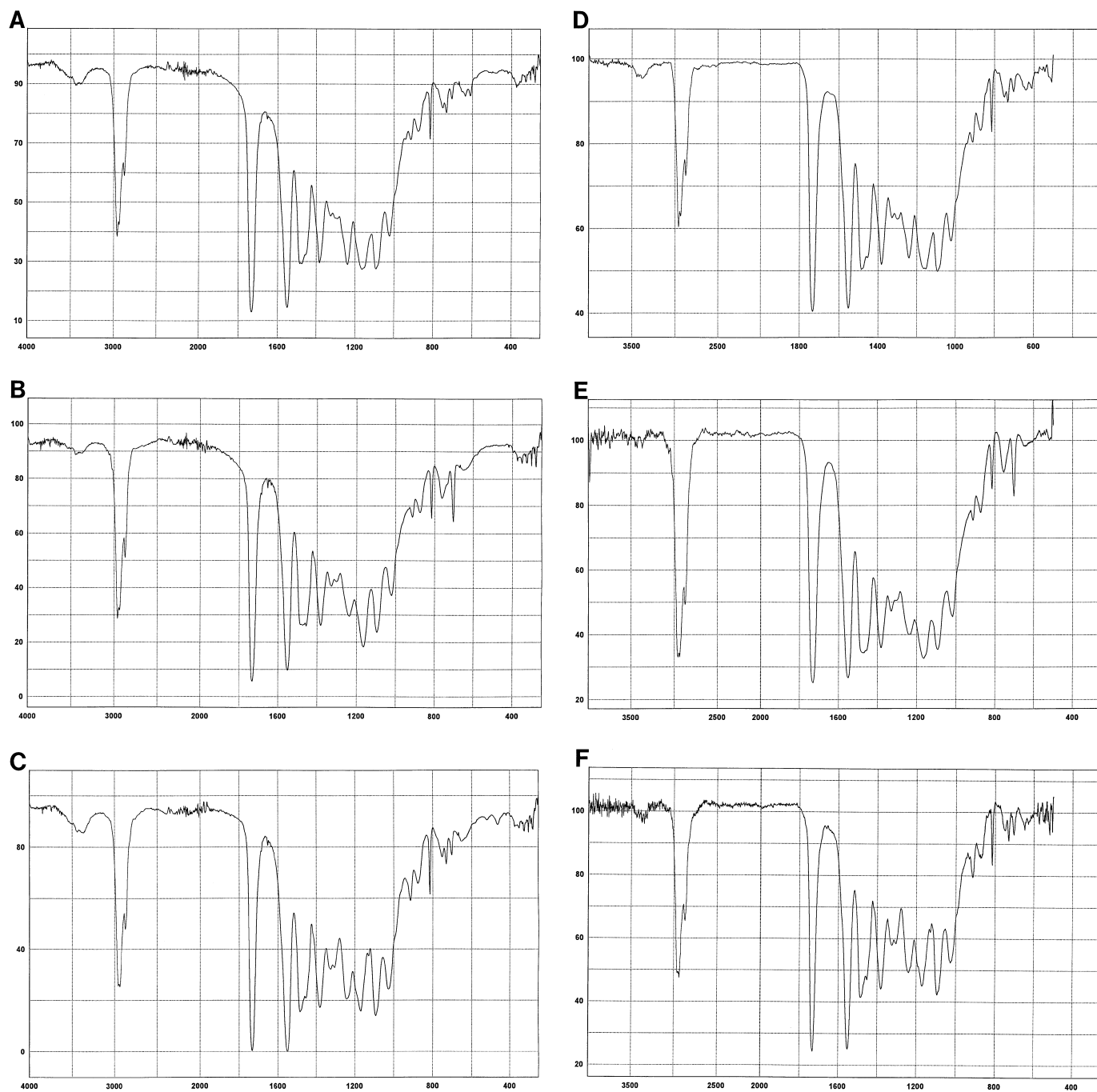


FIG. 10—Reproducible differentiation of the Sample A, D, and G black acrylic-melamine base coats as demonstrated by two of the laboratories' infrared spectra. (A) Sample A, Laboratory 5, (B) Sample D, Laboratory 5, (C) Sample G, Laboratory 5, (D) Sample A, Laboratory 3, (E) Sample D, Laboratory 3, (F) Sample G, Laboratory 3.

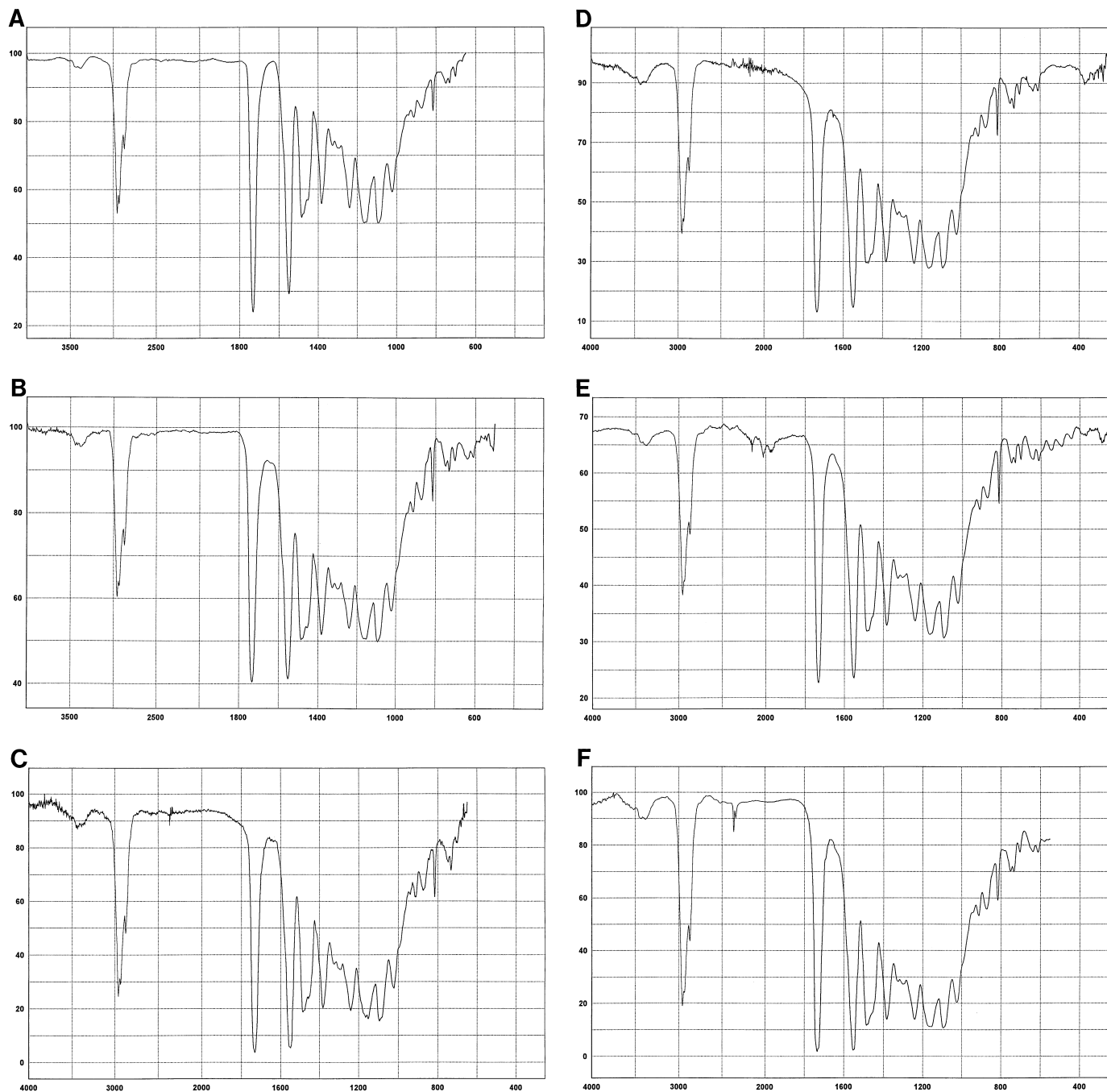


FIG. 11—Infrared spectra of the Sample A black base coat acquired by the six laboratories using transmission techniques. (A) Sample A, Laboratory 2, (B) Sample A, Laboratory 3, (C) Sample A, Laboratory 4, (D) Sample A, Laboratory 5, (E) Sample A, Laboratory 6, (F) Sample A, Laboratory 7.

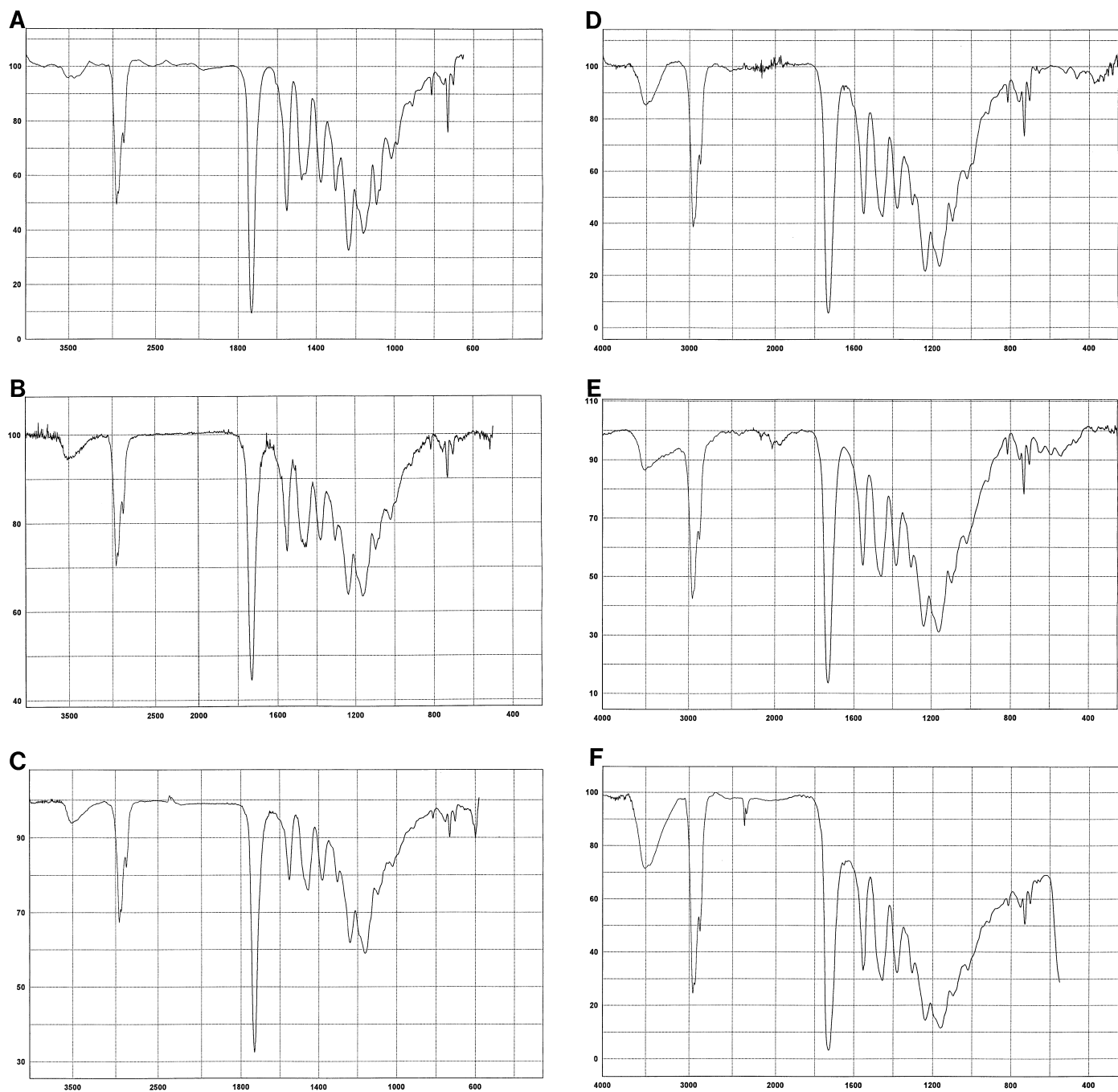


FIG. 12—Infrared spectra of the Sample H black base coat acquired by the six laboratories using transmission techniques. (A) Sample H, Laboratory 2, (B) Sample H, Laboratory 3, (C) Sample H, Laboratory 4, (D) Sample H, Laboratory 5, (E) Sample H, Laboratory 6, (F) Sample H, Laboratory 7.

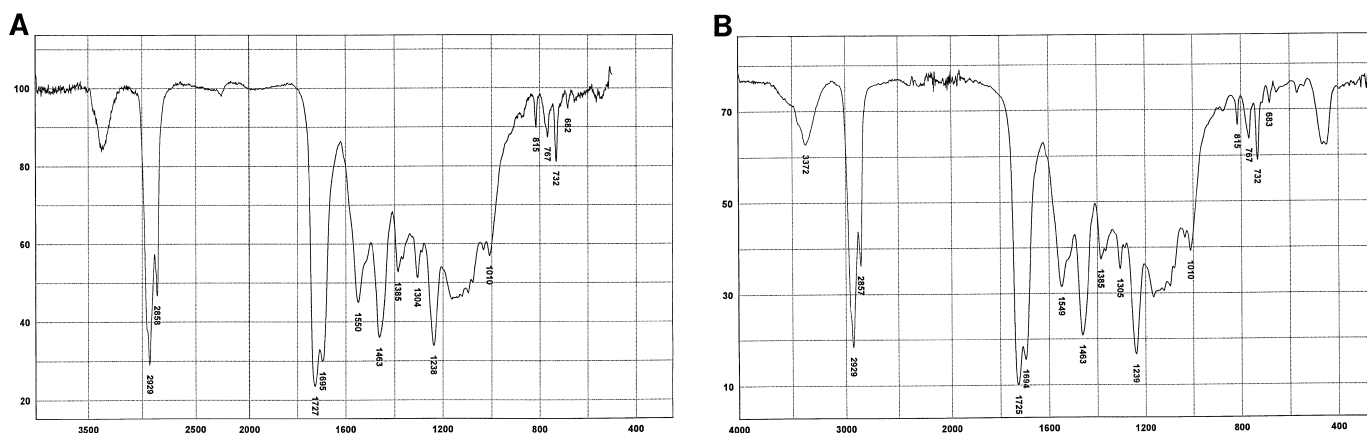


FIG. 13—Infrared spectra of the Sample F black base coat acquired by (A) Laboratory 3 and (B) Laboratory 5.

base coat, yet, as can be seen in Fig. 13, it contains absorption bands attributable to urethane (1695 cm^{-1} and 1520 cm^{-1} shoulder), acrylic (1165 cm^{-1}), polyester (1240 cm^{-1} , 1305 cm^{-1} , and 732 cm^{-1} , 1070 cm^{-1} , and 1095 cm^{-1}), and melamine (1550 cm^{-1} and 815 cm^{-1}) components. These observations underscore the fact that a manufacturer's nomenclature for a particular product is not always totally reflective of its chemical composition.

Summary and Conclusions

The primary purpose of this study was to evaluate the discrimination power of common forensic techniques when applied to the newer generation original automotive finishes. Finish systems for which microscopic characteristics and pigment compositions could not easily serve as a basis for differentiation were chosen for this study to isolate binder formulation as the main factor under consideration. Nine black nonmetallic base coat/clear coat finishes representative of automotive original paints used in the 1990s and produced by DuPont, BASF, and PPG were examined by eight forensic laboratories using infrared spectroscopy. Although spectra of three of the clear coats were difficult to distinguish, these three acrylic-melamine paint systems were easily differentiated when considering spectra of both the clear coats and the base coats. Furthermore, the three different manufacturers' acrylic-melamine clear coats, which were difficult to distinguish using infrared spectroscopy, were easily differentiated by pyrolysis gas chromatography. All other finish systems were easily discriminated by infrared spectroscopy of the clear coats alone.

The second purpose of the study was to evaluate interlaboratory reproducibility of automotive paint spectra collected on a variety of FT-IR instruments and accessories normally used for forensic paint examinations. The spectra obtained in this study demonstrated that for the most part, reproducibility is generally quite good, even for relatively small details. Some minor absorption peak intensity variations were noted, with the most pronounced of these occurring in spectra of the thin base coats. These thin layers tend to present difficulties, as might be expected. Typically, when a severe variation did occur, it was observed in the results of only one of the laboratories, with the rest of the laboratories' results being quite similar to one another. Detailed inter-comparison of corrected attenuated total reflection spectra with transmission spectra is quite tenuous owing to absorption band intensity differences and absorption maxima frequency shifts. Inter-comparison of ATR spectra obtained with an ATR accessory for an infrared microscope with those acquired using a Split Pea internal reflection accessory demonstrated major absorption band intensity variations in at least

four of the nine clear coats. The use of ATR accessories for forensic paint examinations is thus better suited for comparative analyses, and caution should be exercised when comparing such spectra with those acquired using transmission techniques.

This study demonstrates that infrared spectroscopy is an effective tool for discriminating between the major automotive paint manufacturers' formulation types which are currently used in original finishes. Furthermore, and equally as important, the study illustrates that the transmission spectra of these finishes are generally quite reproducible even when comparing data from different laboratories, commercial FT-IR instruments, and accessories in a "real world" mostly uncontrolled environment.

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