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Forensic Science Applications of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS): IV. Direct Analysis of Metallic Paints—Sampling Considerations

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ABSTRACT: Many metallic paints, which are commonly used for automotive finishes, can be sampled directly using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The density of metallic flakes used in a particular paint is the primary factor determining the applicability of this method. Specular reflectance, which often limits the usefulness of data obtained from direct DRIFTS sampling, can be mostly eliminated through selective changes in the geometry of the diffuse reflectance accessory. The nature of this direct sampling method depends on the density of the metallic flakes, and a Kubelka-Munk-type reflectance is not the only process involved. For paints having a high density of metallic flakes, spectra of chips as small as 0.5 by 0.5 mm can be obtained. Metallic paints having a basecoat/clearcoat finish can also be sampled using this method, but the clearcoat or primer layer must first be removed.

KEYWORDS: criminalistics, spectroscopic analysis, reflectance, Fourier transform, diffuse reflectance, DRIFTS, infrared spectroscopy, forensic science applications, metallic paints, paints, automotive paints

An infrared spectroscopic method requiring no sample preparation offers obvious advantages for the forensic science analyst. We therefore have been examining a wide variety of materials to determine whether they are suitable for direct sampling [1,2], using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). In Parts II and III of this DRIFTS study, applications of this direct sampling technique to the analysis of tablets [3] and polymeric foams [4], respectively, were examined. In the present work, presented in two parts, the analysis of some paints using this method is discussed.

Most paints could not be considered ideal materials for direct DRIFTS sampling in view of their smooth surfaces and relatively high absorption coefficients. Both of these factors tend to increase the amount of specular reflectance, which limits the usefulness of the resulting spectral data. Paint films having a low concentration of suspended particulates (such as many automotive paints) also are not strong scatterers of infrared radiation; even if no spec-

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ular reflectance occurred, collection of diffusely reflected radiation from thin² films of such materials would not be an especially efficient process.

These expectations are observed to be the case for many paints, as they tend to produce significant amounts of specular reflectance. We have found, however, that most metallic paints produce predominately diffuse reflectance when sampled directly. After observing this effect, it was learned that Chase et al. had previously (1982) used this feature in their study [8] of paint pigment photodecomposition. These investigators added metallic flakes to a paint vehicle containing the pigment under study. This permitted them to monitor the pigment decomposition in situ in dried films of the paint using direct DRIFTS sampling.

Metallic paints are used in many automotive finishes. Sixty-three percent of the paints comprising the Reference Collection of Automotive Paints through 1985, for example, are metallic. In line with this, two surveys [9,10] taken of vehicles on the road in the late 1970s, indicated that more than half of them had metallic finishes. DRIFTS could thus be useful for many forensic paint examinations. Unlike the diamond anvil cell (DAC) method, which is widely used in forensic science laboratories to obtain infrared data of paints [9,11-14], direct DRIFTS sampling requires no sample preparation and is completely nondestructive. The paint specimens, which often are limited in size, can thus be subject to further testing following a DRIFTS analysis. In this paper, the applicability, limitations, and other sampling considerations of direct DRIFTS sampling of metallic paints are discussed. Specific applications of this technique are presented in Part V of this series [15].

Experimental Procedure

The Fourier transform infrared (FTIR) instrument and the diffuse reflectance and DAC accessories used in this work have been described previously [7]. Most of the DRIFTS spectra were acquired using an uncollimated (focused) sampling beam, although a collimated beam was used for a few of the samples; unless indicated, the former was used. For direct sampling, the surfaces of the paints were positioned horizontally at the focal point of the reflectance accessory. The reflectance from the flat alignment mirror of this accessory was used as a reference for all of the DRIFTS spectra. A gain of $2R$ ($R = \sqrt{2}$) was used for this reference, with an attenuator screen placed in the beam. The gains of the various samples were increased (if necessary) to adjust the baselines of the reflectance spectra to approximately 100%; for some of the samples an adjustable attenuator comb was used to block a portion of the beam. Except where noted, the parabolic mirrors of the accessory were used in their normal (0° tilt) orientation.

For the DAC, a reference consisting of the empty cell itself, collected at a gain of $8R$, was used. For both DRIFTS and DAC spectra, 250 scans were collected for both the sample and reference, unless otherwise indicated.

The majority of samples examined were U.S. automotive paints. Most of these consisted of panels from the Reference Collection of Automotive Paints (Collaborative Testing Services, Inc.). These samples will be referred to by their coded designations; unless specified, they are not basecoat/clearcoat finishes.

²According to the Kubelka-Munk [5] equation $F(R_\infty) = (1 - R_\infty)^2/2R_\infty = k/s$, a low scattering (small s) sample actually *increases* the sensitivity of this method as $F(R_\infty)$, which is analogous to absorbance A , becomes larger. This is a result of the longer average pathlengths [6,7] that the sampling radiation experiences in low scattering samples (scattering tends to direct the radiation back to the sample surface before it can be absorbed). This only holds true, however, for samples which are effectively "infinite" in thickness.

Results and Discussion

Density of Metallic Flakes

The reflectance spectrum obtained for direct sampling of a typical nonmetallic automotive paint, Panel 74E0076, is shown in Fig. 1*b*. From a comparison to the DAC spectrum of the finish layer of this paint (Fig. 1*a*), it may be seen that a considerable amount of specular reflectance, manifested as attenuated or inverse peaks, is present. Interference fringes, occurring in the low-frequency region, are also observed. Metallic paints exhibit less specular

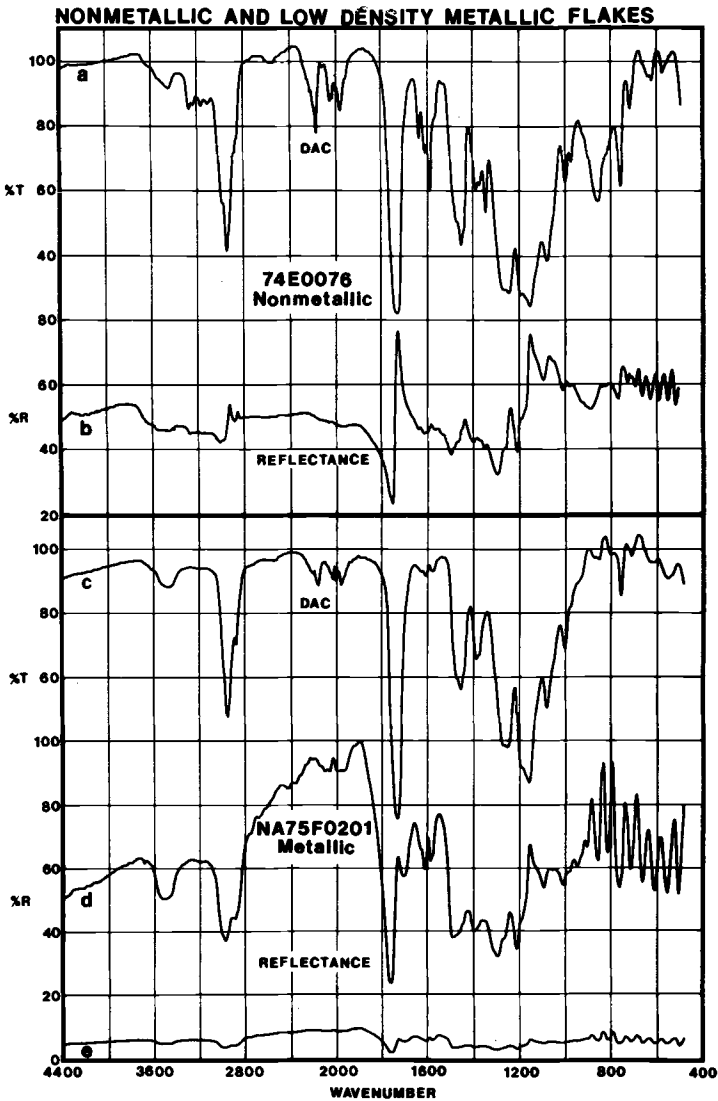


FIG. 1—Spectra of Reference Collection panel 74E0076: (a) DAC spectrum of the finish layer; (b) reflectance spectrum, sampled directly, gain 8. Spectra of NA75F0201: (c) DAC spectrum of the finish layer; (d) reflectance spectrum, sampled directly, gain 8; (e) same sample as (d), gain 2R (attenuator screen used).

reflectance than nonmetallic paints, but there is a fairly large variation in the relative amounts of specular reflectance observed for these. This can be seen from the reflectance spectra of three metallic paint panels—NA75F0201, NA79F0606, and 74K0087—shown in Figs. 1d, 2c, and 3c, respectively.

Decreasing amounts of specular reflectance are observed for these, as may be seen from comparisons to the corresponding DAC spectra of the finish layers (Figs. 1c, 2a, and 3a, respectively). This is especially evident by noting the differences between the distortions of the strong 1150-cm^{-1} absorption.

These differences in specular reflectance have been found to correlate strongly with the amounts and sizes of the metallic flakes used in these finishes. Stereomicroscopically, a wide

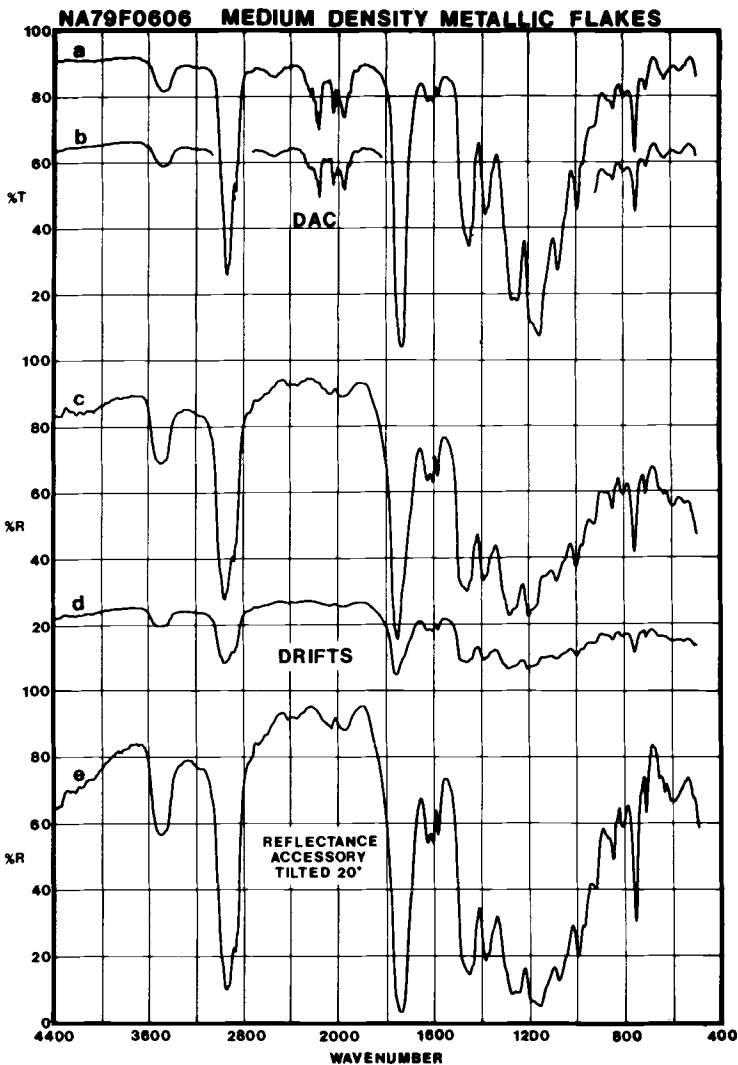


FIG. 2—Spectra of NA79F0606: (a) DAC spectrum of the finish layer, gain 16; (b) same sample as (a), gain 8R; (c) reflectance spectrum, sampled directly, gain 4R; (d) same sample as (c), gain 2R (attenuator screen used); (e) same sample as (c), accessory mirrors tilted 20° , gain 16R, 765 scans.

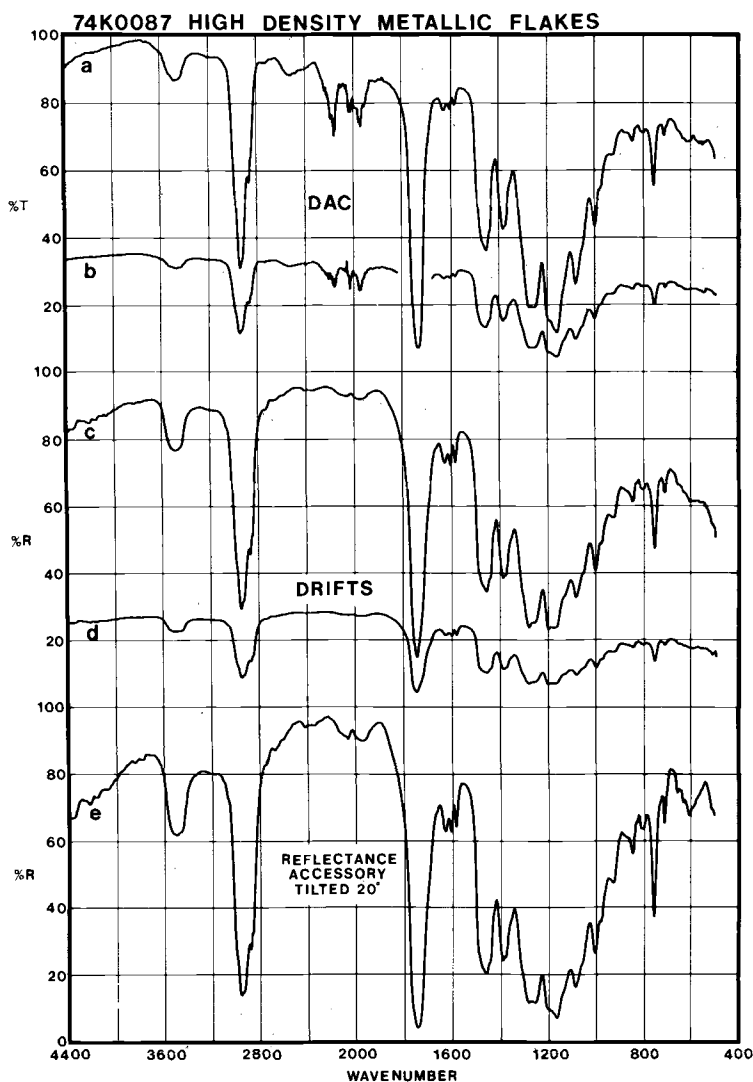


FIG. 3—Spectra of 74K0087: (a) DAC spectrum of the finish layer, gain 32; (b) same sample as (a), gain 8R; (c) reflectance spectrum, sampled directly, gain 2R; (d) same sample as (c), gain 2R (attenuator screen used); (e) same sample as (c), accessory mirrors tilted 20°, gain 8R, 510 scans.

range in these amounts and sizes is observed for the numerous metallic paints of the Reference Collection. The three panels discussed above, for example, were observed microscopically to have increasing amounts of metallic flakes present.

Two complementary methods have been used to measure the relative amounts of metallic flakes present in various finishes more accurately. The first is comparison of the "normal" throughputs for the DAC spectra of films of paints having similar thicknesses. Because of the opaqueness of the flakes, these throughputs will vary, depending upon the concentra-

tions and sizes of the flakes used. The combined effects³ of these two factors, with regard to their tendency to block the passage of light, will be referred to as the density of the metallic flakes.

Figures 1c, 2b, and 3b depict the throughput scans for the above three finishes. NA75F0201, which was observed to have the lowest concentration of flakes, has the highest throughput. Portions of this scan (Fig. 1c), in fact, are above 100% transmittance (%T). This results from more of the incident sampling beam being lost through reflection (from the faces of the diamond anvils) when the DAC is empty. Note that the throughput for this metallic paint is only slightly less than that of a nonmetallic paint (Fig. 1a). NA79F0606 and 74K0087, which were observed to have higher densities of metallic flakes, have lower throughputs (approximately 65 and 35%, respectively, at 4400 cm⁻¹). The DAC spectra of these two paints shown in Figs. 2a and 3a were obtained using increased instrument gains [3] to compensate for the low throughputs.

Along with throughput, the relative reflectances of these paints provides another measure of the density of metallic flakes present. For this, gain increases were not used and the depicted spectra for the three panels (Figs. 1e, 2d, and 3d) are reflectances relative to a mirror used for the background. As expected, the highest reflectance is observed (Fig. 3d) for that finish (74K0087) having the lowest throughput in transmittance and visually observed to have a high density of flakes; the lowest reflectance (Fig. 1e) is observed for the low-density finish.

It is clear that the “optical density” of the metallic flakes—that is, their ability to reflect light or block its passage—has a pronounced effect on the spectra obtained through direct sampling. It seems reasonable that the specular reflectance component, which depends on compositional and surface characteristics [7, 16], should be similar for the above three paints (which are all acrylics). The greater reflectances observed for finishes having higher densities of metallic flakes therefore must be due to the “diffuse” component, and the apparent decrease in specular reflectance really reflects an increase in the contribution of the “diffuse” component. For other paints to be discussed, high, medium, and low density will refer to metallic finishes having throughputs or reflectances similar to those presented above.

Reflectance Accessory Geometry

For high-gloss paints, the specular reflectance component may approach a mirror-type behavior. The Analect reflectance accessory that was used in this work allows a tilting of the parabolic mirrors to remove mirror-type specular reflectance. The effects of tilting these mirrors on the reflectance spectra of metallic paints sampled directly were thus examined.

Figure 4a and b depicts spectra of NA75F0201, which has a low density of metallic flakes, obtained with the reflectance accessory mirrors tilted by 15 and 20°, respectively. This data is presented in the %T formats [7]. The reflectance spectrum for the latter sampling is shown in Fig. 4d. By comparing these spectra to that obtained without tilting (Fig. 1d), one can see that this procedure does eliminate most of the specular reflectance component. Only a slight specular reflectance distortion, manifested as a spiked tip for the carbonyl peak in Fig. 4b, is observed for the 20° results (compare to Figs. 1c and 4a). For some low-density metallic paints, significant specular reflectance features remain, even with the accessory mirrors tilted by more than 20°.

The effects of tilting for finishes having medium and high densities of flakes are shown in Figs. 2e and 3e, respectively. Although not as pronounced as the low-density case, these spectra also exhibit less specular reflectance distortions, especially for the 1150-cm⁻¹ ab-

³Although they may have similar densities as defined above, a finish having a low concentration of large flakes and one having a higher concentration of smaller flakes do not always produce similar effects—see, for example, footnote 4.

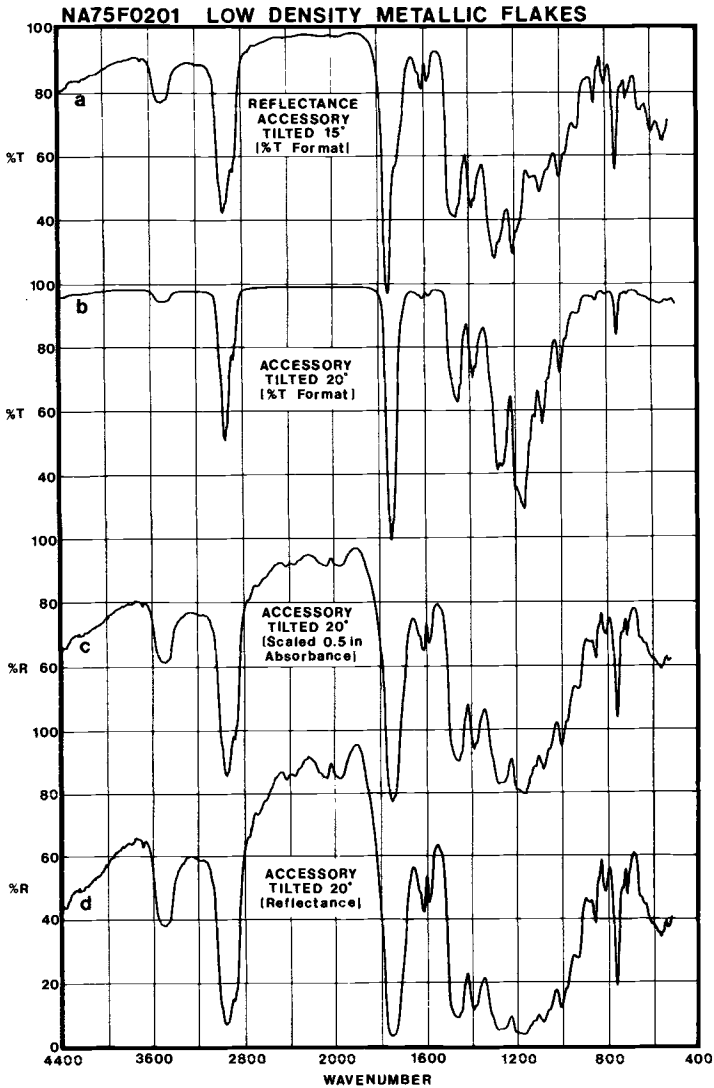


FIG. 4—Spectra of NA75F0201 sampled directly: (a) %T format, accessory mirrors tilted 15°, gain 16, 510 scans; (b) %T format, accessory mirrors tilted 20°, gain 64, 1020 scans; (c) reflectance spectrum (see below) scaled 0.5 in absorbance; (d) reflectance spectrum, same sample as (b).

sorptions. Figure 5c and d shows the tilting changes for 74L0022, an acrylic melamine enamel having a medium density of metallic flakes. In this case, only a small change occurs, with slight relative increases in intensities for peaks at 1170 cm^{-1} (compare this to the adjacent 1380- cm^{-1} peak in Fig. 5b, c, and d) and 2930 cm^{-1} (the lower frequency member of the doublet, see Fig. 5a).

Along with a decrease in the specular reflectance component, the overall reflectances also decrease with tilting, especially for paints having low densities of metallic flakes. Increased gains are thus used for these samples (gains of 8 and 64 were used to obtain the spectra depicted in Figs. 1d and 4d, respectively), and longer collection times may be necessary.

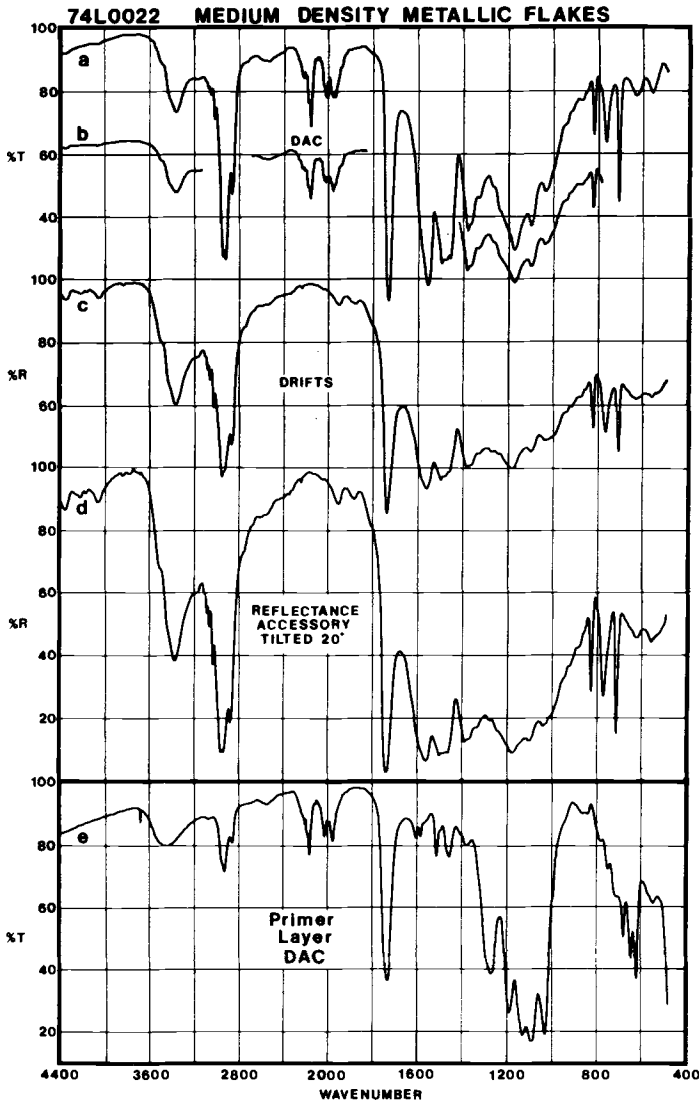


FIG. 5—Spectra of 74L0022: (a) DAC spectrum of the finish layer, gain 16; (b) same sample as (a), gain 8R; (c) reflectance spectrum, sampled directly, gain 4R; (d) same sample as (c), accessory mirrors tilted 20°, gain 16; 510 scans; (e) DAC spectrum of the primer layer.

All of the above data were taken using an uncollimated sampling beam. Although the reflectance accessory was designed for use with a collimated beam, we had previously [7] found it to work as well (except for microsampling) using an uncollimated beam. Interestingly, for elimination of the specular reflectance component through tilting of the accessory mirrors, the uncollimated beam seems to work much better than the collimated beam. This may be due, in part at least, to the differences in sampling areas for these two beams. As discussed below, the orientations of the metallic flakes are important in DRIFTS sampling. The larger area covered by the uncollimated beam would be expected to include more flakes

exhibiting favorable orientations for DRIFTS sampling than produced by the collimated beam.

Nature of the Sampling Process

Chase et al. [8] presented all of their paint pigment DRIFTS data in the Kubelka-Munk format. These investigators thus assumed the Kubelka-Munk model to be valid for this sampling process. The results of the present study suggest, however, that two different types of sampling processes are occurring simultaneously and that the density of metallic flakes determines which of these is dominant.

For paints having a relatively high density of metallic flakes, the sampling process depicted schematically in Fig. 6a appears to be the main one occurring. Note that although the incident sampling beam for our accessory converges onto the sample [7] from a tilted cone (having a conical angle of approximately 40°), the incident sampling beam in Fig. 6 is shown at only one angle for clarity. Because of low inter-flake scattering in these matrices, radiation penetrating the sample surface is more likely to encounter a metallic flake than be back-scattered from within the matrix. Since the flakes typically have dimensions greater⁴ than the infrared wavelengths, they act as mirrors (which indeed is their intent—for visible radiation—to confer a metallic appearance). The exiting radiation, which occurs in all directions, is comprised of a number of individual “double-pass transmittance reflection” samplings having somewhat variable pathlengths.

Evidence supporting this non-Kubelka-Munk sampling is shown in Fig. 7. For this, DB81B0817, which has a very high density of metallic flakes, was sampled with the accessory tilted 20° to eliminate mirror-type specular reflectance. The resulting reflectance spectrum was then transformed to both an absorbance format (Fig. 7b) and the Kubelka-Munk for-

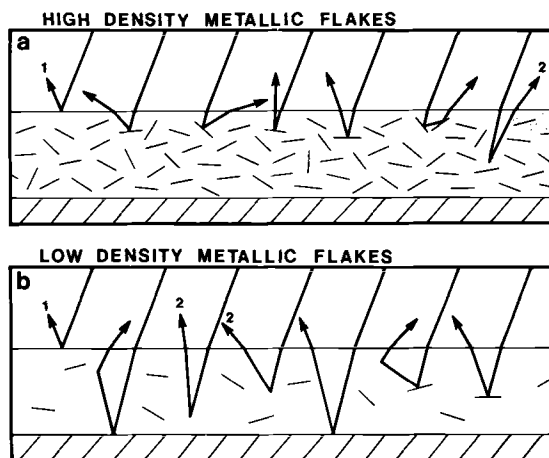


FIG. 6—Schematic representation of some of the types of reflections involved in direct DRIFTS sampling of metallic paints having relatively high (a) and low (b) densities of metallic flakes present. Mirror-type specular reflectance is depicted by rays labeled 1, while Kubelka-Munk reflectance from the paint matrix is depicted by rays labeled 2.

⁴For some finishes, the dimensions of the smaller metallic flakes are similar to the wavelengths of the far infrared region (the wavelength of 500 cm^{-1} is 0.02 mm), and some diffraction occurs. Diffraction appears to be responsible, in part at least, for a low-frequency drop in the baseline observed in some DRIFTS spectra (compare, for example, Figs. 2a and 2c).

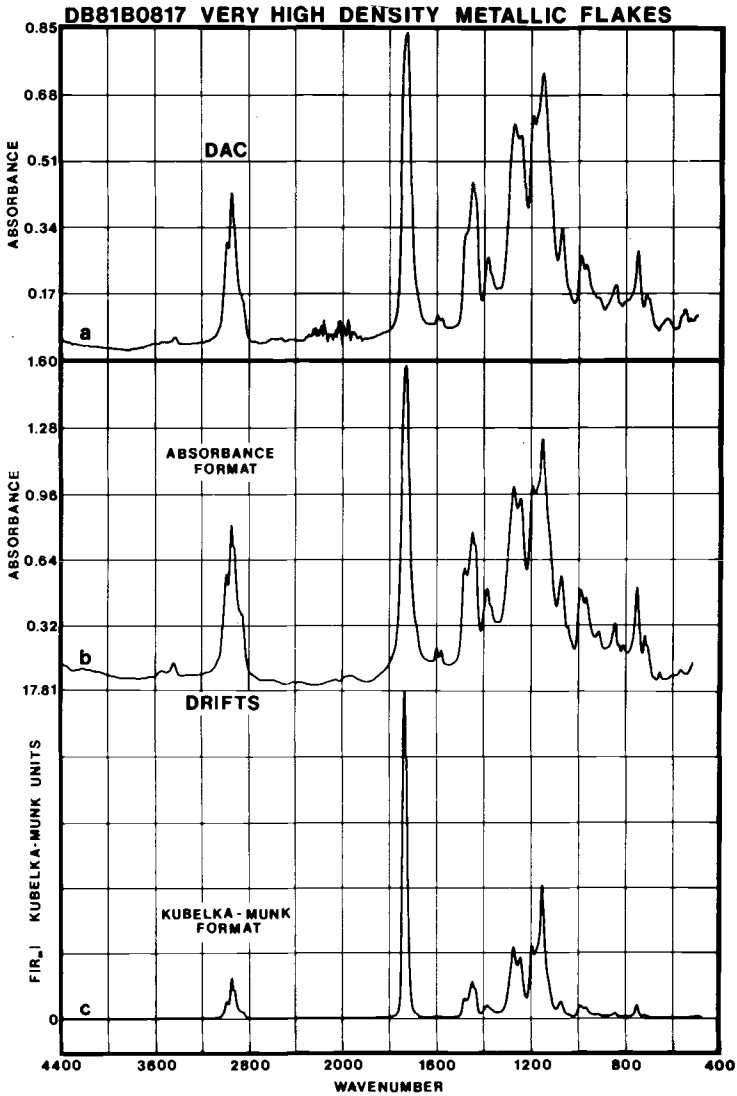


FIG. 7—Spectra of DB81B0817: (a) DAC spectrum of the finish layer, presented in absorbance, gain 32R; (b) sampled directly, accessory mirrors tilted 20°, gain 8R, presented in absorbance; (c) same data as (b) presented in the Kubelka-Munk format.

mat (Fig. 7c). Comparison of these to the DAC absorbance spectrum of the finish layer (Fig. 7a) makes it clear that the absorbance format (Fig. 7b) is a much better representation. Note in particular the diminished intensities of the weaker absorptions in the Kubelka-Munk spectrum (true Kubelka-Munk sampling produces a distinct enhancement of the relative intensities of the weaker absorptions [3, 4, 6, 7]).

Further support for this double-pass reflection process is evident from the fact that paints having high densities of metallic flakes exhibit significantly greater overall reflectances than powdered KBr. A mirror, rather than KBr, is thus used as a reference for metallic paints. The reflectance spectra themselves, rather than the %T formats, are presented since they

are, in effect, "transmittance" spectra. It should be remembered, however, that Beer's Law is not strictly obeyed for the overall process since variable pathlengths⁵ are involved. The average pathlength, and hence the intensity of a particular reflectance spectrum, depends on the concentration of metallic flakes; a nonrandom distribution of either the concentration or orientation of flakes may also affect this pathlength.

For paints having low concentrations of metallic flakes (Fig. 6*b*), scattering within the matrix itself becomes more likely and the Kubelka-Munk (diffuse reflectance) sampling increases. This can be seen from the DRIFTS results for NA75F0201. The reflectance spectrum for the 20° sampling (Fig. 4*d*) is shown scaled by 0.5 (linear in absorbance and presented in transmittance) in Fig. 4*c*, while the %T format (obtained from the Kubelka-Munk function) is shown in Fig. 4*b*. In this case, the %T format spectrum more closely resembles the DAC results (Fig. 1*c*) than does the scaled reflectance spectrum. In particular, the relative intensities of the weaker absorptions (for example, the weak aromatic doublet near 1600 cm⁻¹) match the DAC results better for the %T format presentation (alternatively, the enhancement of the weaker features in Fig. 4*d* might arise from greater attenuations of the stronger features as a result of deviations from Beer's Law, but DAC spectra of thick films of this sample indicate that this is not a major factor).

Since nonmetallic paints generally do not produce spectra comparable to that depicted in Fig. 4*d* (with the accessory mirrors tilted), it is clear that double-pass reflection also contributes significantly to the sampling for low-density finishes (this was also suggested from the observations with the collimated beam). Combined processes, such as reflection from a flake followed by scattering by the matrix, may also occur (Fig. 6*b*) along with processes involving reflection from the bottom of the finish layer. For convenience, the data obtained for all metallic paints will be referred to as DRIFTS spectra, even though a Kubelka-Munk type diffuse reflectance is not the only process—or necessarily the dominant process—occurring.

Sampling Depths

The fringes observed for the nonmetallic paint (Fig. 1*b*) and low-density metallic paint (Fig. 1*d*) result from interference between radiation specularly reflected from the sample surface and radiation reflected from the bottom of the finish layer. Although these fringes are usually more prominent for panels in which there is a metal substrate and no primer, they also occur for panels having primers and for finish layers sampled alone. For the low-density metallic finish, it is thus clear that sampling occurs to the bottom of the finish layer. This is also evident from the pronounced increase in intensities for the absorptions of this panel following tilting of the accessory mirrors (compare Figs. 1*d* and 4*d*). Some of this increase results from elimination of specular reflectance, but longer effective pathlengths are also clearly involved.

When the accessory mirrors are tilted, fringes are less likely to be observed since most of the specular reflectance component is not collected, but considerable radiation is probably still reaching the bottom of the finish layer for these low-density metallic paints. Because these samples are not "infinitely thick" and double-pass reflection also occurs, the Kubelka-Munk function (which assumes an infinite thickness) is not entirely valid. It is still a useful approximation for low-density metallic paints, however, as the %T format spectra (for example, Fig. 4*b*) indicate.

For finishes having higher densities of metallic flakes, shorter pathlengths (Fig. 6*a*) are expected and fringes are not observed (see, for example, Figs. 2*c*, 3*c*, and 5*c*). The pathlengths for these samples also appear to increase with tilting (compare Figs. 2*c* and 2*e*,

⁵For sufficiently small incident beam (such as may be produced by an infrared microscope accessory), reflection from an individual flake is possible. Assuming that this flake has the proper orientation and is large enough so that diffraction is not a problem, a double-pass sampling obeying Beer's Law occurs. It should be possible to "adjust" the intensity of the spectrum (within limits) through proper choice of flakes.

3c and 3e, and 5c and 5d); in this case of mostly non-Kubelka-Munk sampling, the incident angle changes increase the distance from the sample surface to the metallic flakes. This may arise from the preference of the metallic flakes in these paints to assume [17,18] more of a horizontal orientation (this preference can be seen by viewing cross sections of such finishes—the lighter-colored ones are easier to see—using dark-field epi-illumination microscopy). It is possible that part of this increase may also be due to an increased amount of total internal reflectance. In any case, these finishes are effectively “infinitely thick” for DRIFTS sampling, and subcoats or primers are not sampled. This can be seen from examination of the various spectra (Fig. 5) of 74L0022, which has a medium density of metallic flakes. Note that significant absorptions of the primer (Fig. 5e) are not evident in the reflectance spectra (Fig. 5c and d) of this panel.

Sample Size Requirements

All of the reflectance spectra that have been discussed were taken of intact panels, 25 by 40 mm in size, using an uncollimated sampling beam. To determine the minimum sample sizes needed to obtain usable DRIFTS spectra, we cut a high-density metallic paint panel, NW79B0605, into 1- by 1-mm and 0.5- by 0.5-mm squares with most of the metal backing removed. A collimated beam, which produces a sampling area approximately 1 mm in diameter, was used for sampling these chips, which were positioned using a laser alignment beam as a guide. The reflectance spectra obtained for these are shown in Fig. 8b and a, respectively. The spectrum of the entire panel (also obtained using a collimated beam) is shown in Fig. 8c, while the DAC spectrum of the finish layer is shown in Fig. 8e.

Comparisons of the spectra obtained for the two chips and the entire panel indicate that the effective sampling area is approximately 3 mm², or nearly 2 mm in diameter, rather than 1 mm. The spectrum for the 0.5- by 0.5-mm chip (Fig. 8a) thus represents results obtained for samples covering less than one tenth of the incident beam area.

Figure 8d depicts this spectrum with the region between 100 and 80 %T shown at full ordinate scale. This presentation,⁶ rather than an expansion linear in absorbance, appears to produce more faithful spectra for small samples. This situation is analogous to a transmittance sampling in which the sample covers only a portion of the incident beam. All of that fraction of the light not sampled reaches the detector and a distorted spectrum results. For these samples, a better representation of the spectral data is obtained by viewing that portion of the spectrum corresponding to the fraction sampled (for example, 100 to 75 %T when the sample covers one fourth of the beam). By analogy, the above expansion is used for the reflectance data.

The accessory mirrors were not tilted for these samples, and medium- or low-density metallic paints will give spectra having some specular reflectance distortions. Since elimination of these requires the use of an uncollimated beam and tilting of the mirrors, samples considerably larger than 0.5 by 0.5 mm would be required. The analysis of small chips is thus limited to finishes having relatively high densities of metallic flakes.

Basecoat/Clearcoat Finishes

The vast majority of metallic paints in the Reference Collection through 1985 are not basecoat/clearcoat (bc/cc) finishes. In the past few years, however, bc/cc finishes for metallic paints have become more common [17,19] for U.S. automobiles (79 new metallic paint colors were added to the 1985 Reference Collection; 42 of these [53%] had bc/cc finishes).

The reflectance spectrum obtained from the direct DRIFTS sampling of a metallic bc/cc

⁶The software of the Analect FX-6200 FTIR used in this work does not permit an ordinate expansion of the spectral data between two arbitrary %T values. The results depicted in Fig. 8, although collected on an FX-6200, were replotted using an Analect AQS-20 FTIR instrument.

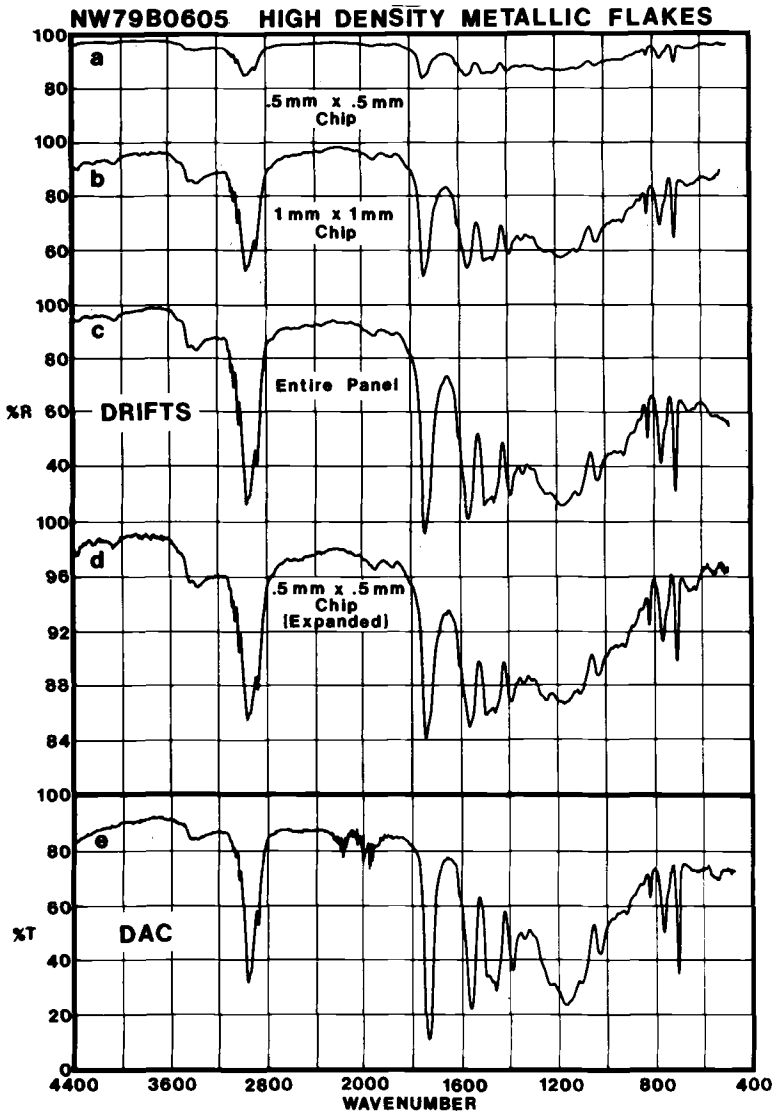


FIG. 8—Spectra of NW79B0605: (a) reflectance spectrum of a 0.5- by 0.5-mm chip sampled directly, gain 2R, 510 scans; (b) reflectance spectrum of a 1.0- by 1.0-mm chip sampled directly, gain 2R; (c) reflectance spectrum of the entire panel, gain 2R; all of the above were collected using the collimated sampling beam; (d) spectrum (a) expanded; (e) DAC spectrum of the finish layer, gain 16R, 510 scans.

panel, CC77F0360, is shown in Fig. 9d. This spectrum is typical of those observed for bc/cc finishes, which invariably give spectra with strong absorptions having little detail present, even after conversion of such data to the %T formats. This undoubtedly arises from the clearcoat layers being thicker than the corresponding basecoats [20]; most of the strong absorptions observed in the DRIFTS spectrum (Fig. 9d) are due to the clearcoat layer, whose DAC spectrum is shown in Fig. 9c.

DRIFTS spectra of the metallic basecoat alone can be obtained by first removing either the clearcoat or primer layer. For the above panel, which consisted of a cardboard substrate

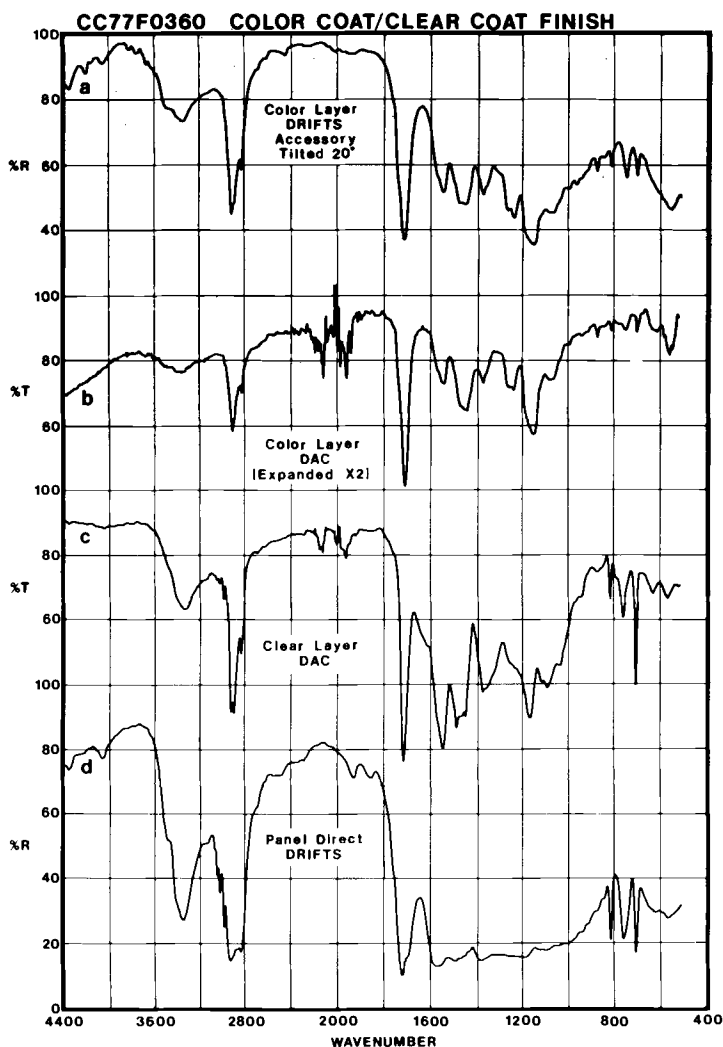


FIG. 9—Spectra of CC77F0360 (which has a metallic basecoat/clearcoat finish): (a) reflectance spectrum of the basecoat layer of a chip 2.5 by 3.0 mm (prepared by removing the cardboard backing from the panel) sampled directly, accessory mirrors tilted 20° , gain 8R; (b) DAC spectrum of the basecoat layer, expanded by a factor of 2, gain 32, 510 scans; (c) DAC spectrum of the clearcoat layer, gain 8R; (d) reflectance spectrum of the panel sampled directly, gain 2R.

without a primer, all of the substrate was removed, exposing the bottom of the basecoat; this surface was sampled giving the reflectance spectrum shown in Fig. 9a. As a comparison, the DAC spectrum (which was expanded linear in absorbance by a factor of 2) of the basecoat is shown in Fig. 9b.

The DRIFTS sample consisted of a chip 2.5 by 3 mm in size, and the uncollimated beam was used with the accessory mirrors tilted by 20° . Although this basecoat had a very high density of metallic flakes, some specular reflectance attenuation of the strong 1150-cm^{-1} absorption is apparent (compare Fig. 9a and b; note also the low-frequency diffraction effects in the former). This attenuation may reflect the fact that the surface resulting from

removal of the substrate was not entirely smooth, thereby decreasing the effectiveness of rotation of the accessory mirrors on eliminating mirror-type specular reflectance.

Because a considerable amount of sample preparation is usually required for bc/cc finishes, the advantages of DRIFTS are largely lost on such samples. DRIFTS may be a useful alternative, however, for some bc/cc finishes having very high densities of metallic flakes. We have found the metallic basecoats of some of these to be quite difficult to sample using the DAC because they are so thin and have such high densities of metallic flakes. DAC samples having thicknesses necessary to produce desired absorption intensities are usually too opaque to obtain usable spectra (spectra of these basecoats can be obtained, in some cases, by using thinner samples and expanding the spectrum—see, for example, Fig. 9b).

Summary

The density of metallic flakes used in a particular finish is the dominant factor determining the various characteristics involved in direct DRIFTS sampling. For finishes having relatively high densities of metallic flakes, this sampling consists primarily of diffuse double-pass reflections from the flakes, and the resulting reflectance spectrum is very similar to conventional transmittance results. For finishes having lower metallic flake densities, this process also occurs along with increased amounts of Kubelka-Munk reflectance. Because reflection from the metallic flakes is a much more efficient process than Kubelka-Munk reflectance, the "diffuse" component is greater for higher-density finishes. Consequently, the relative amount of specular reflectance (which appears to be independent of the metallic flake density) is greater for lower-density finishes.

With the Analect reflectance accessory used in this work, collection of the specular reflectance component may be minimized by tilting the accessory mirrors. Relatively distortion-free spectra are possible using this technique, although longer collection times may be required for low-density metallic finishes. The average sampling pathlengths also increase with tilting, especially for low-density metallic finishes.

Since DRIFTS works best for high-density metallic finishes, it is a useful complement to conventional infrared transmittance techniques. As a result of the opaqueness of the metallic flakes, the spectra obtained using these transmittance methods may exhibit very low throughputs for high-density metallic finishes.

As discussed previously [3,4], direct DRIFTS spectral distortions may vary with the type of reflectance accessory used due to differences in specular reflectance [21,22]. Although we did not examine any panels using other accessories, this would certainly be expected to be the case for metallic paints. In particular, some accessories may not allow a geometry change to exclude mirror-type specular reflectance; others may be specifically designed to achieve this without a change. It may thus not be possible to obtain usable spectra for low-density finishes on every system.

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