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Forensic Science Applications of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS): II. Direct Analysis of Some Tablets, Capsule Powders, and Powders

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ABSTRACT: Fuller and Griffiths first demonstrated the feasibility of obtaining an infrared spectrum directly on an intact Empirin® tablet using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). We have found that several modifications of this method are necessary to obtain useful spectra for most other tablets. Applications of these modified procedures to the analysis of several tablets of forensic science interest are presented, and the results are compared to those obtained by conventional means. The direct analysis of some capsule contents and other powders is also presented and discussed.

KEYWORDS: criminalistics, spectroscopic analysis, reflectance, infrared, Fourier transform, diffuse reflectance, DRIFTS, tablet analysis, capsule analysis, powder analysis

Fuller and Griffiths, who performed most of the early studies in developing the technique of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), first demonstrated (1978) the feasibility of obtaining an infrared spectrum directly on a whole, intact Empirin® tablet using DRIFTS [*1,2*]. This Empirin tablet had an acetylsalicylic acid (aspirin), phenacetin, and caffeine compound (APC) formulation. Fuller and Griffiths also obtained DRIFTS spectra of this tablet after it had been ground to a fine powder, with this powder sampled neat (undiluted). The spectra obtained for these two sampling methods were similar, although Fuller and Griffiths observed some differences, which they attributed to particle size effects.

Since the initial report by Fuller and Griffiths, no other studies dealing with the direct analysis of tablets using DRIFTS have been published, despite the obvious advantages that this method provides. This can be attributed, in part, to the fact that diffuse reflectance accessories did not become commercially available until the early 1980s. A more important factor, however, may be some of the inherent difficulties with direct tablet sampling which were not fully addressed in the early feasibility study. Spectral results comparable to those demonstrated for Empirin, for example, generally cannot be obtained for most other tablets.

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In this study, we investigated the use of DRIFTS direct sampling for the analysis and identification of some tablets of forensic science interest. We found it necessary to use several modifications of the method described by Fuller and Griffiths to obtain good spectral results for a wide variety of tablets. We also investigated using DRIFTS for direct analyses of capsule powders and other powders.

Experimental Procedure

The Fourier transform infrared (FTIR) instrument and diffuse reflectance accessory used in this study have been previously described [*3*]. All of the DRIFTS spectra were referenced to a background of powdered KBr in a 4-mm cup collected at a gain of $4R$ where $R = \sqrt{2}$. The gains of the various samples were increased (if necessary) to adjust the baseline of the reflectance spectrum to approximately 100%; an adjustable attenuator comb placed in the sample beam was sometimes used along with this gain increase. For all of the DRIFTS spectra, 250 scans were collected for both the sample and reference. The normal scanning mode (5-cm^{-1} resolution) was used for all spectra, and the instrument housing was purged with dry nitrogen.

For the direct sampling of tablets, the surfaces of the tablets were positioned at the focal point of the reflectance accessory. The surface plane of the flat specular mirror of this accessory was used as a guide, and spacers were used to adjust the height of the tablet. All tablets were sampled using the focused (uncollimated) beam.

A Wig-L-Bug®, equipped with a stainless steel vial and ball-pestle (all from Cresent Dental Mfg. Co.), was used to produce finely ground powders. The Wig-L-Bug, which normally runs on a timer with a maximum time of 1 min, was modified to allow continuous operation.

The following materials were used: methocarbamol, *dl*-glutethimide, aspirin, *d*-methamphetamine hydrochloride, and potassium bromide (infrared [IR] grade), Sigma Chemical Co.; methyprylon, Roche Laboratories; methaqualone base, William H. Rorer, Inc.; *l*-cocaine hydrochloride, U.S.P.C., Inc.; ethinamate, Lilly Laboratories; meprobamate and mebutamate, Wallace Laboratories; phencyclidine base, San Diego Drug Enforcement Administration Laboratory; magnesium carbonate, J. T. Baker Chemical Co.; Doriden®, Robaxin®, Bufferin®, Bayers®, Equagesic® (newer formulation), Noludar®, Quaalude® 300, Equanil®, Miltown®, and Soma® (all tablets); and Noludar and Valmid® capsules, all purchased locally.

Results and Discussion

Tablet Analyses

Figure 1 is an illustration of direct analysis of a whole, intact tablet in which no sample preparation was required. A Doriden tablet (which weighs 650 mg and contains 500 mg of glutethimide) was positioned at the focal point of the DRIFTS accessory giving the reflectance spectrum shown in Fig. 1*b*. Low reflectances, as observed in this spectrum, are invariably obtained when tablets are sampled directly. Fuller and Griffiths circumvented this problem by expanding their Empirin reflectance spectrum, presenting at full ordinate scale the region between the highest and lowest points in the spectrum. As discussed previously [*3*], however, the pronounced scale compression occurring for the low reflectance regions in DRIFTS spectra tends to obscure much of the spectral information present in this region. Increasing the interferometer gain for these samples relative to the gain used for the background reference spectrum multiplies each reflectance value of the spectrum by a constant

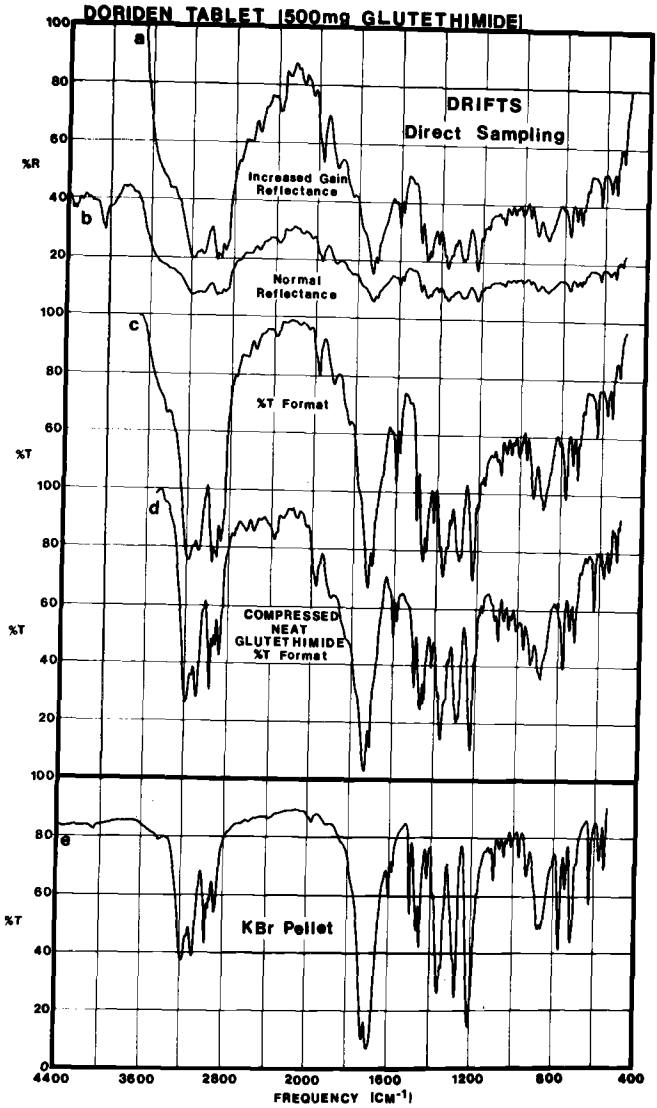

FIG. 1—(a) *Reflectance spectrum of a Doriden tablet sampled directly, gain 16.* (b) *Reflectance spectrum of above sample, gain 4*R. (c) %T *format of the above* (a) *spectrum.* (d) %T *format of the spectrum of sanded neat compressed glutethimide sampled directly, gain 32.* (e) *Absorption spectrum of glutethimide in a KBr pellet.*

(the gain increase factor) and serves to raise the entire spectrum.[2] Results of this gain increase for the Doriden tablet are shown in Fig. 1*a*.

Because of the lack of detail observed for the stronger absorptions in the reflectance spectrum, the percent transmittance (% T) format is useful for direct sampling [*3*]. The % T format of the Doriden (increased gain) spectrum is depicted in Fig. 1*c*; as may be observed, most of the spectral features are seen more clearly.

Comparison of this % T spectrum to the transmittance spectrum of glutethimide in a KBr pellet (Fig. 1*e*) indicates that although all of the glutethimide absorptions are present in the former, there are significant differences in some peak shapes, peak frequencies, and relative peak intensities. A much better agreement is obtained, however, when the Doriden spectrum (Fig. 1*c*) is compared to that obtained from the direct sampling of neat, compressed glutethimide (Fig. 1*d*). For this, pure glutethimide was pressed into a pellet (using the same procedure used for pressing KBr pellets) and the shiny face of this "tablet" was sanded lightly to simulate the surface of a Doriden tablet.

The differences observed between the spectra obtained from direct DRIFTS sampling and KBr pellets arise from a number of factors. The most important of these is the specular reflectance components in the DRIFTS spectra. Specular reflectance, which tends to affect the stronger absorptions, causes a decrease in intensity for some absorptions, or inverse peaks in other cases. The "loss" in intensity of the 1700-cm^{-1} carbonyl peak (the strongest absorption in Fig. 1*e*) for the DRIFTS results, for example, undoubtedly arises from specular reflectance.

The second source of differences results from the fact that the intensity of peaks in a DRIFTS spectrum depends on both an absorption coefficient and a scattering coefficient. Yeboah et al. [*4*] studied the effects of pressure on the DRIFTS spectra of compressed powders, and found that the scattering coefficient is dependent on the pressure at which the powder was originally compressed. In particular, they observed relative peak intensity differences (and sloping baselines) when the reference material was compressed at a significantly different pressure than the sample. Since powdered KBr was used as the reference for the Doriden DRIFTS spectra, this effect may be responsible, in part, for the decreasing baseline in Fig. 1*b*. KBr pellets pressed at various pressures below that needed to form transparent disks were tested as reference materials, but these did not produce better spectra.

Another source of differences may arise from deviations from the Kubelka-Munk equation. Fuller and Griffiths [*5*] observed significant deviations from linearity for the Kubelka-Munk function with increasing sample concentrations. The concentrations occurring in tablets that contain relatively small amounts of excipients would certainly be expected to be in this nonlinear region; thus, some of the relative peak intensity differences could be due to these deviations. Because of these factors, it is clear that spectra of standards sampled in a matrix closely approximating that of the tablets should be used as a reference for comparisons.

Doriden was found to be one of the very few tablets that could be sampled directly with no sample preparation. Most other tablets produce significant amounts of specular reflec-

[2]For transmittance sampling, this gain increase is equivalent to a baseline adjustment linear in absorbance, and a "true" transmittance spectrum results. For reflectance spectra, assuming the Kubelka-Munk equation to apply, this procedure does not actually produce a baseline adjustment linear in Kubelka-Munk units. Comparisons of the Kubelka-Munk (absorbance format) spectra of data collected in this manner to those obtained without a gain increase, however, show insignificant distortions. Low reflectance spectral data may be subject to digitization noise; this becomes much less of a problem when this data is collected with an increased gain.

For FTIR instruments that do not permit a different gain to be used for the reference and sample, a baseline adjustment can be made after the data has been converted to the Kubelka-Munk form. The % T format of this adjusted data can then be obtained.

tance,[3] as illustrated in Fig. 2*a* and *b* for a Robaxin tablet (which weighs 776 mg and contains 750 mg of methocarbamol). Since the amount of specular reflectance is dependent on particle size and strong specular reflectance is generally associated with smooth surfaces, the tablet faces were sanded (with coarse sandpaper) to see if this would decrease or eliminate the specular components. The % T spectrum of the Robaxin tablet after sanding (Fig. 2*c*) indicates that the specular components are indeed decreased; that they are not completely eliminated, however, can be seen from a comparison of this spectrum to the absorption spectrum of Robaxin in a KBr pellet (Fig. 2*d*). Note that consistent with theory [*3,6*], specular reflectance can be seen to affect primarily the stronger absorptions of the sample.

For comparison purposes, pure methocarbamol was pressed into a "tablet," and its surface sanded. The reflectance and % T spectra obtained from direct sampling of this compressed methocarbamol are shown in Fig. 3*a* and *c*, respectively. Corresponding spectra for sanded Robaxin are also depicted (Fig. 3*b* and *d*). Note from these that *two* presentations of the spectral data are necessary to observe the details of all of the absorptions. As already mentioned, the stronger absorptions lack detail in the reflectance spectra but are observed more clearly in the % T formats. In contrast, the weaker features are seen clearly in the former, but only weakly (or hardly at all for the absorptions above 3600 cm^{-1} in this case) in the latter.

These weaker features, which generally are very weak or not observed at all in KBr pellet spectra (for example, see Fig. 2*d*), are due to the numerous overtone, combination, and difference bands. These can, in fact, be as characteristic as the fundamentals themselves in individualizing a particular compound[4] (an example illustrating this for some closely related compounds is presented later). These weaker absorptions also are not affected by specular reflectance distortions, and may be seen clearly in spectra of the unsanded samples (compare Figs. 2*a* and 3*b*). The presence of these weaker absorptions therefore provides more spectral data than available from other methods. This feature has previously [*3*] been shown to be quite useful in differentiating between some members of a homologous series.

For the stronger absorptions, a comparison of Figs. 2*c* and 3*d* (which represent spectra of two different Robaxin tablets taken from the same bottle) with Fig. 3*c* provides some indication of the reproducibility of the sanding method. It may be seen that for most absorptions, the method is quite reproducible. The areas where some irreproducibility occurs are precisely those where specular reflectance is prominant; these regions are easily identified from spectra of the unsanded tablets. When comparing spectra obtained in this manner, this factor should be kept in mind. More than offsetting this disadvantage, however, is the additional information provided by the numerous weaker absorptions.

In addition to specular reflectance, another reason for the sanding of tablets is readily evident in the case of coated tablets. Even for tablets that appear uncoated, however, inhomogeneous compositions may occur. Direct sampling of Bayer aspirin tablets (without sanding), for example, gives primarily a diffuse reflectance spectrum of aspirin having some in-

[3]The diffuse reflectance accessory used in this work has a feature designed to eliminate the specular reflectance component through rotation of the two off-axis parabolic mirrors of the accessory. This serves, however, only to eliminate specular reflectance from flat mirror-type surfaces. The specular reflectance from a tablet surface is actually "diffuse" in that it occurs in all directions. Rotation of these mirrors, therefore, did little to eliminate specular reflectance from these tablets.

[4]In many cases, the information provided by an overtone, combination, or difference band duplicates that provided by the fundamentals. The first overtones (which are generally the only ones observed in the mid-infrared region), for example, occur very near twice the frequencies of the fundamentals, while the binary combination bands (which also are the primary ones observed in this region) occur very near the sum of the frequencies of two of the fundamentals. In other cases, however, additional information may be provided by these bands. This occurs when a fundamental is not observed (because it is infrared inactive, too weak, or occurs outside of the region examined) but an overtone, combination, or difference band involving this fundamental is observed. Difference bands, in particular, involve the lower frequency (below 200 cm^{-1}) fundamentals which normally are not observed.

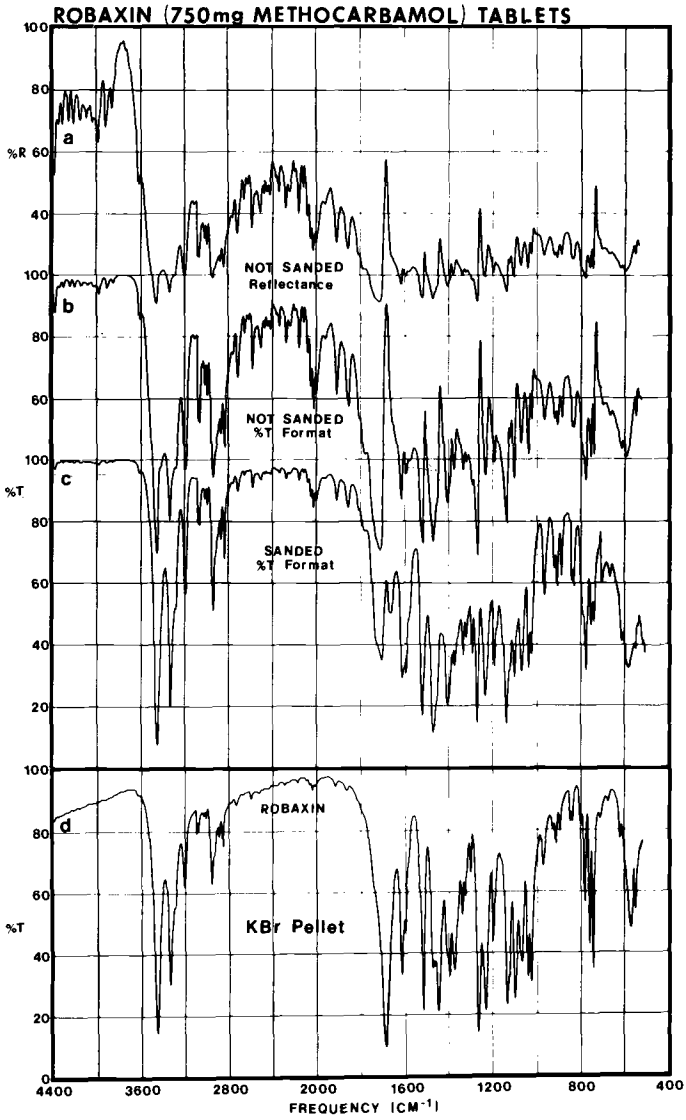

FIG. 2—(a) *Reflectance spectrum of a Robaxin tablet sampled directly without sanding, gain 8*R. (b) %T *format of the above spectrum.* (c) %T *format of the spectrum of a sanded Robaxin tablet sampled directly, gain 8*R. (d) *Absorption spectrum of Robaxin tablet scrapings in a KBr pellet.*

verse specular reflectance peaks. In contrast, direct sampling (without sanding) of Bufferin tablets give spectra similar to that depicted in Fig. 4*a* (which is the reflectance spectrum of an Extra Strength Bufferin tablet). A strong specular reflectance doublet at 1422 and 1486 cm^{-1} is observed that cannot be attributed to aspirin (Fig. 5*i*). A KBr pellet spectrum of the surface material of an Extra Strength Bufferin tablet is shown in Fig. 4*b*. It is clear that this surface material (which is comprised of only a very thin layer) is responsible for the observed specular reflectance doublet. The Bufferin bottle indicates that aluminum glycinate and magnesium carbonate are used as buffering agents. A KBr pellet spectrum of mag-

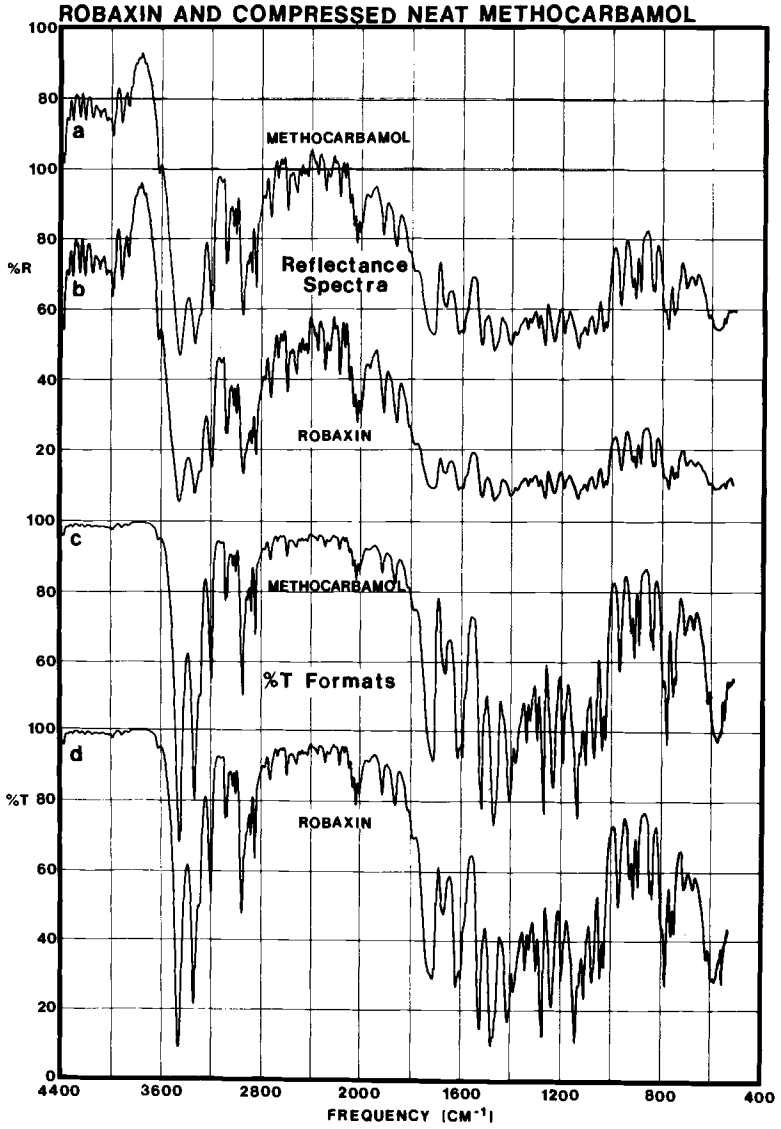

FIG. 3—(a) *Reflectance spectrum of sanded neat compressed methocarbamol sampled directly, gain 16.* (b) *Reflectance spectrum of a sanded Robaxin tablet sampled directly, gain 8*R. (c) *and* (d) %T *formats of the above two spectra, respectively.*

nesium carbonate is shown in Fig. 4*c*, and this material can be seen to be responsible for the specular reflectance doublet.

Reflectance spectra of an Extra Strength Bufferin tablet obtained after sanding and collected at two different increased gains are shown in Figs. 4*d* and *e*. Results for three different brands of aspirin tablets are shown in Fig. 5; the % *T* formats, obtained from reflectance spectra similar to Fig. 4*d*, are depicted along with portions of the reflectance spectra (obtained at a lower gain) above 3400 cm^{-1}. As a reference, the spectra of sanded, compressed aspirin and KBr (in a ratio of 3:1, which is similar to the relative amounts of aspirin in these tablets) are shown in Fig. 5*g* and *h*.

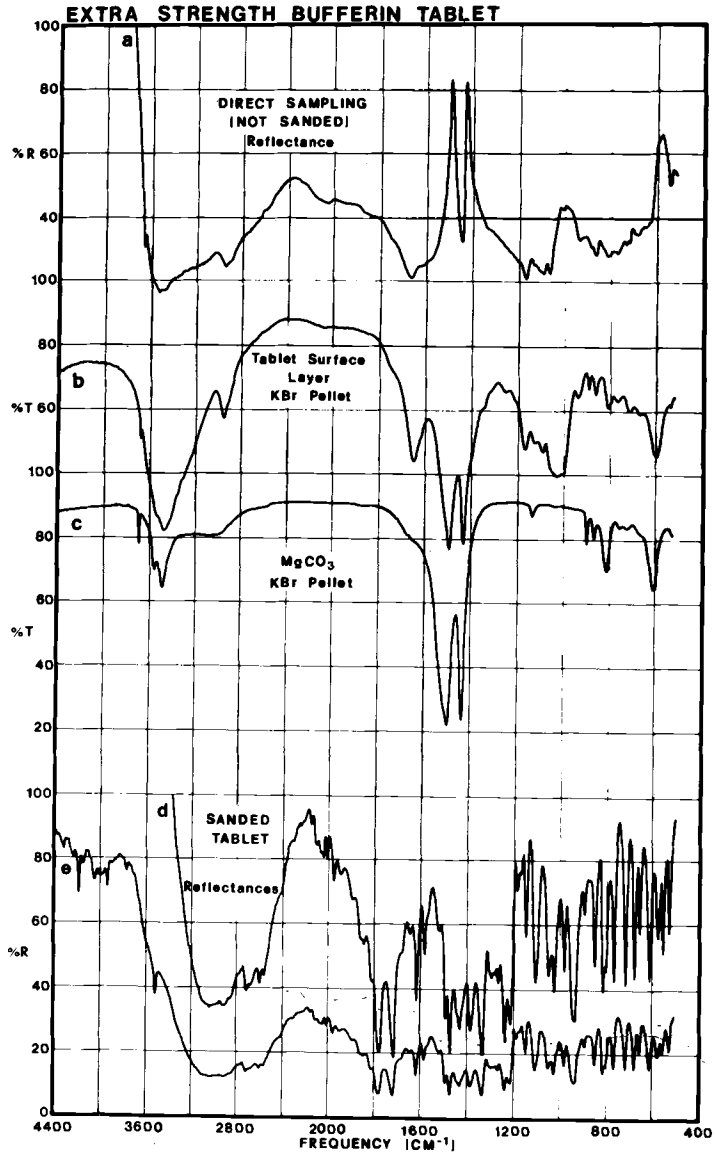

FIG. 4—(a) *Reflectance spectrum of an Extra Strength Bufferin tablet sampled directly without sanding, gain 16*R. (b) *Absorption spectrum of the surface material on an Extra Strength Bufferin tablet in a KBr pellet.* (c) *Absorption spectrum of magnesium carbonate in a KBr pellet.* (d) *Reflectance spectrum of a sanded Extra Strength Bufferin tablet sampled directly, gain 32*R. (e) *Same sample as* (d), *gain 16.*

Application of the sanding technique to the analysis of a Noludar tablet (which weighs 390 mg and contains 200 mg of methyprylon) is illustrated in Fig. 6. Note that although this tablet contains a relatively large amount of excipient (nearly half, by weight) the absorptions of methyprylon (Fig. 7*e*) are predominant in the spectrum.

One of the most useful applications of direct sampling is in the screening of unknown tablets. This application is illustrated in Fig. 8 for the analysis of suspected Quaalude. Al-

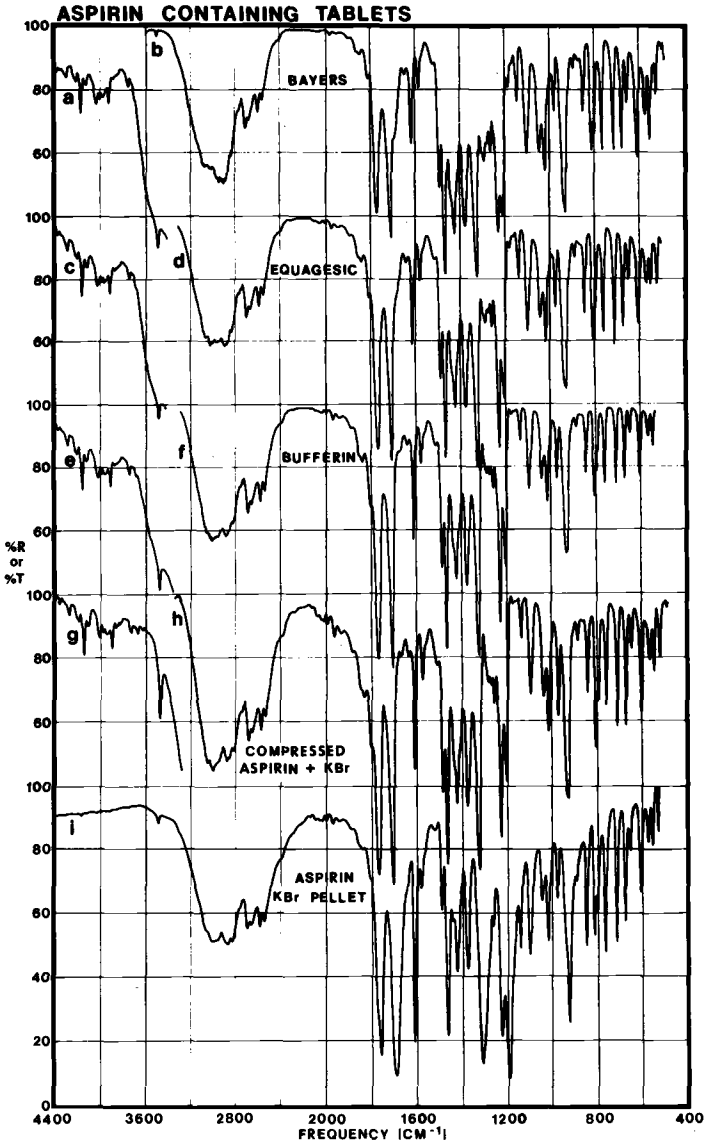

FIG. 5—(a), (c), *and* (e) *Portions of the reflectance spectra of sanded Bayers, Equagesic (aspirin layer), and Bufferin tablets, respectively, sampled directly, gain 16.* (b), (d), *and* (f) %T *formats for the above three samples, gain 32*R. (g) *Portion of the reflectance spectrum of sanded compressed aspirin and KBr (3:1 ratio) sampled directly, gain 16.* (h) %T *format for the above* (g) *sample, gain 32*R. (i) *Absorption spectrum of aspirin in a KBr pellet.*

though no longer manufactured, authentic Quaalude tablets are still encountered in some forensic science laboratories. More than likely, however, the "LEMMON 714" tablets received for analysis are counterfeit look-alikes.

The spectrum of a Quaalude 300 tablet that was sanded and sampled directly is depicted in Fig. 8*c* to *e*. Above (Fig. 8*a* and *b*), is shown the spectrum of sanded, compressed methaqualone base and KBr, mixed in a 300:370 ratio to give a methaqualone concentration simi-

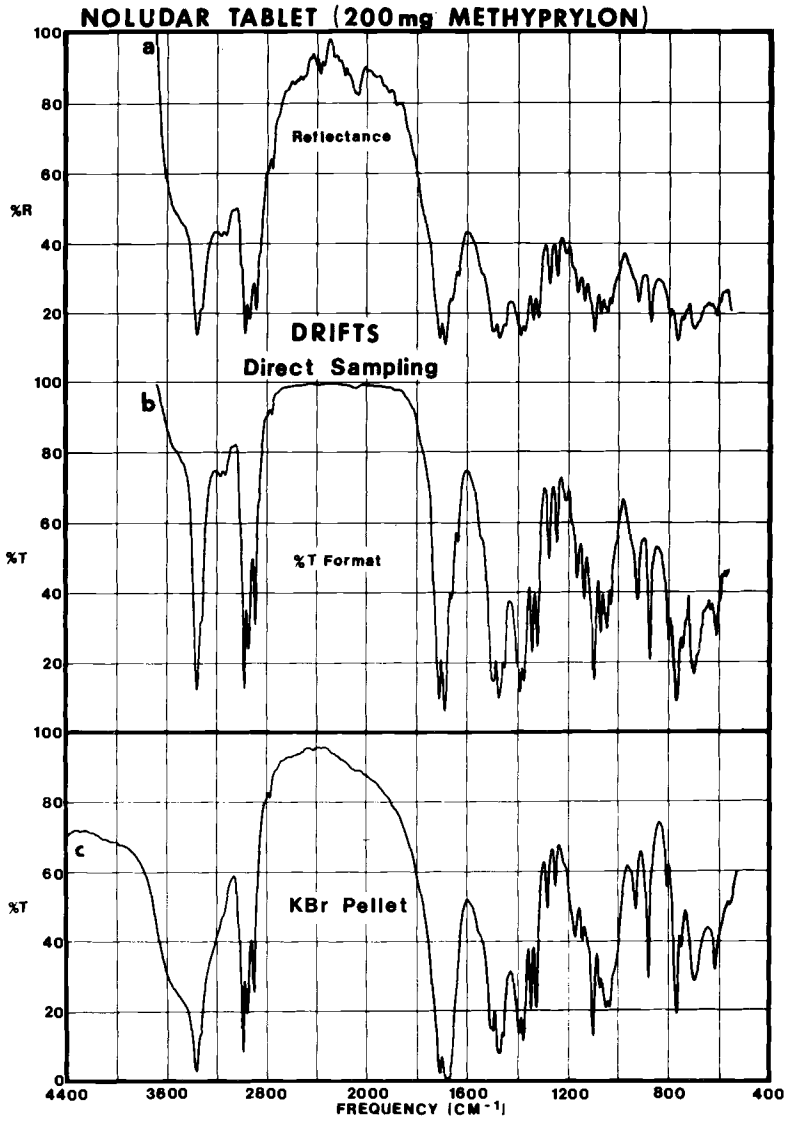

FIG. 6—(a) *Reflectance spectrum of a sanded Noludar tablet sampled directly, gain 32.* (b) %T *format of the above spectrum.* (c) *Absorption spectrum of Noludar tablets in a KBr pellet.*

lar to that occurring in Quaalude 300 tablets. Spectra of three different counterfeit "LEMMON 714" sanded tablets are shown in Fig. 8*f* to *o*. The first tablet (Fig. 8*f* to *h*) came from a bottle labeled "NITE-T-NITE" and had listed as ingredients: acetaminophen, 250 mg; salicylamide, 50 mg; and doxylamine succinate, 25 mg. The observed absorptions are primarily those of acetominophen, and this spectrum is very similar to those obtained for sanded Tylenol® and other acetaminophen tablets. The second tablet (Fig. 8*i* to *k*) contained mainly lactose, along with a small amount of diazepam. The last tablet was found to produce considerable specular reflectance distortions, as may be seen from a comparison of its spec-

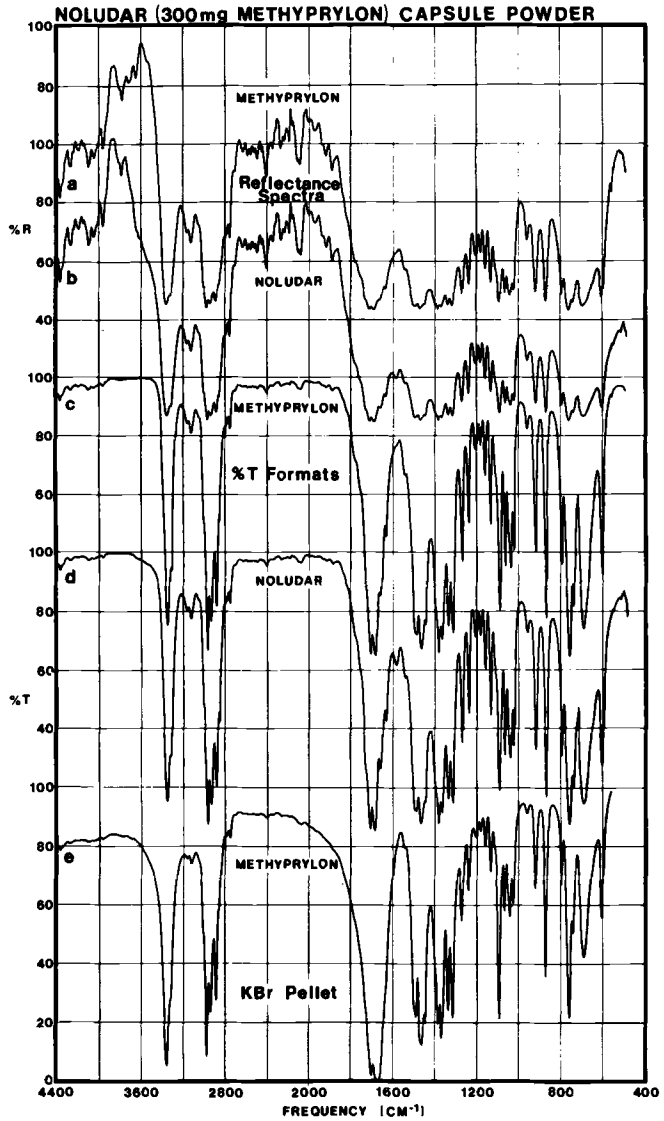

FIG. 7—(a) *Reflectance spectrum of neat methyprylon powder, gain 8*R. (b) *Reflectance spectrum of the powder from a Noludar capsule sampled neat, gain 8.* (c) *and* (d) %T *formats of the above two spectra, respectively.* (e) *Absorption spectrum of methyprylon in a KBr pellet.*

trum (Fig. 8*l* to *n*) to a portion of the absorption spectrum obtained for a KBr pellet (Fig. 8*o*). Even with these distortions, however, the value of direct sampling for the screening of tablets is evident.

A second example of a screening application involves tablets suspected of containing meprobamate. When such tablets are sampled directly with no sanding, a spectrum comprised predominantly of specular reflectance peaks is obtained (see Fig. 2*a* and *b* in Part I of this paper [*3*]). Soma tablets, which contain 350 mg of carisoprodol (a compound closely related to meprobamate), produce a somewhat similar spectrum (also comprised primarily of specular reflectance peaks) when sampled directly without sanding.

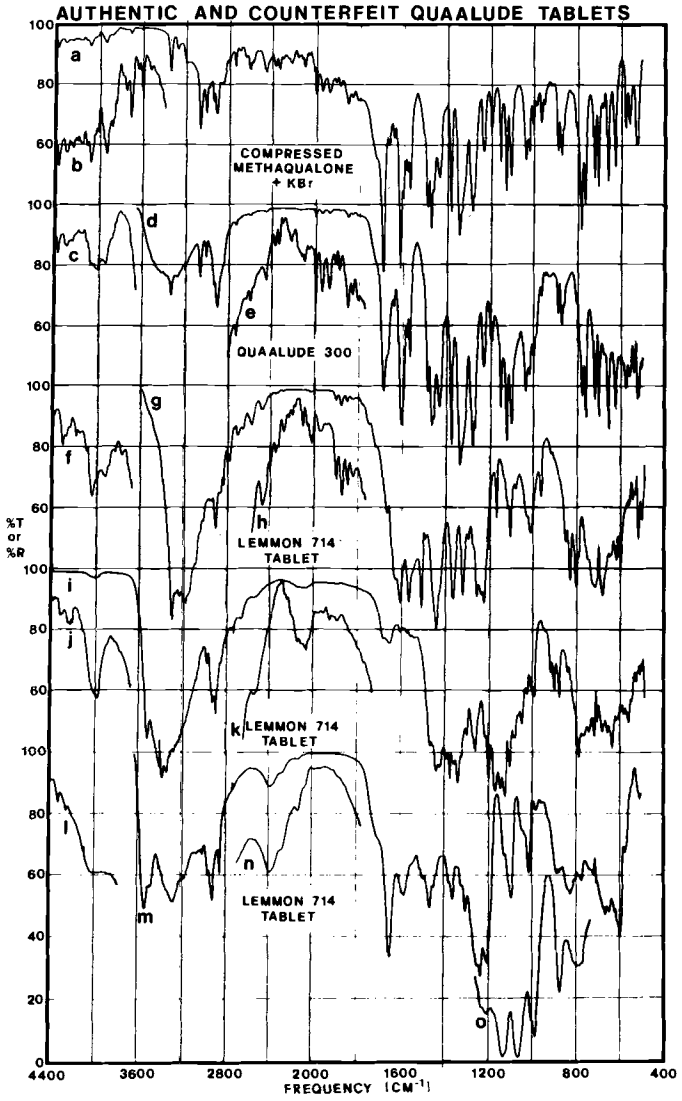

FIG. 8—(a) %T *format of the spectrum of sanded compressed methaqualone base and KBr (300:370 ratio) sampled directly, gain 16.* (b) *Portion of the reflectance spectrum of the above sample.* (c), (e), (f), (h), (k), (l), *and* (n) *Portions of the reflectance spectra of three counterfeit Quaalude tablets that were sanded and sampled directly.* (g), (i), *and* (m) %T *formats for the three counterfeit Quaalude tablets.* (o) *Portion of the absorption spectrum of the third counterfeit Quaalude tablet in a KBr pellet.*

The prominant specular reflectance peaks observed when such tablets are sampled directly arise from the fact that meprobamate and carisoprodol are relatively strong infrared absorbing compounds. This was also the case for the specular reflectance peaks observed for the coated Bufferin tablets—inorganic compounds generally are much stronger infrared absorbers than organic compounds [7]. Even with sanding, these tablets still exhibit fairly strong inverse peaks. For such cases, grinding the tablet to a fine powder and sampling this powder neat produces much better results (the amount of specular reflectance is dependent

not only upon the absorption coefficient of the sample, but also upon particle size; decreasing the latter decreases [6] specular reflectance).

The reflectance and %*T* spectra of an Equanil tablet (which weighs 460 mg and contains 400 mg of meprobamate) which was ground in a Wig-L-Bug for 5 min and sampled neat are shown in Fig. 9*b* and *d*, respectively. Analogous spectra for meprobamate powder that was ground in a Wig-L-Bug for 2 min are also presented (Fig. 9*a* and *c*), along with a KBr pellet

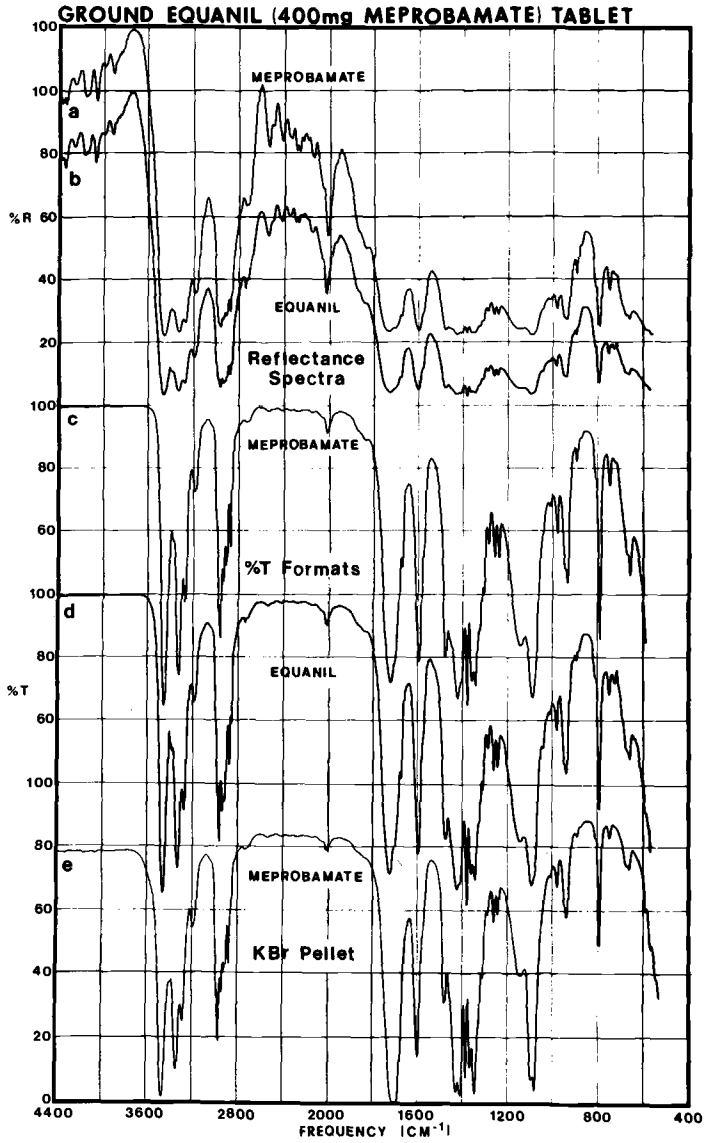

FIG. 9—(a) *Reflectance spectrum of meprobamate powder ground for 2 min and sampled neat, gain 8.* (b) *Reflectance spectrum of an Equanil tablet that was ground for 4 min and sampled neat, gain 8*R. (c) *and* (d) %T *formats of the above two spectra, respectively.* (e) *Absorption spectrum of meprobamate in a KBr pellet.*

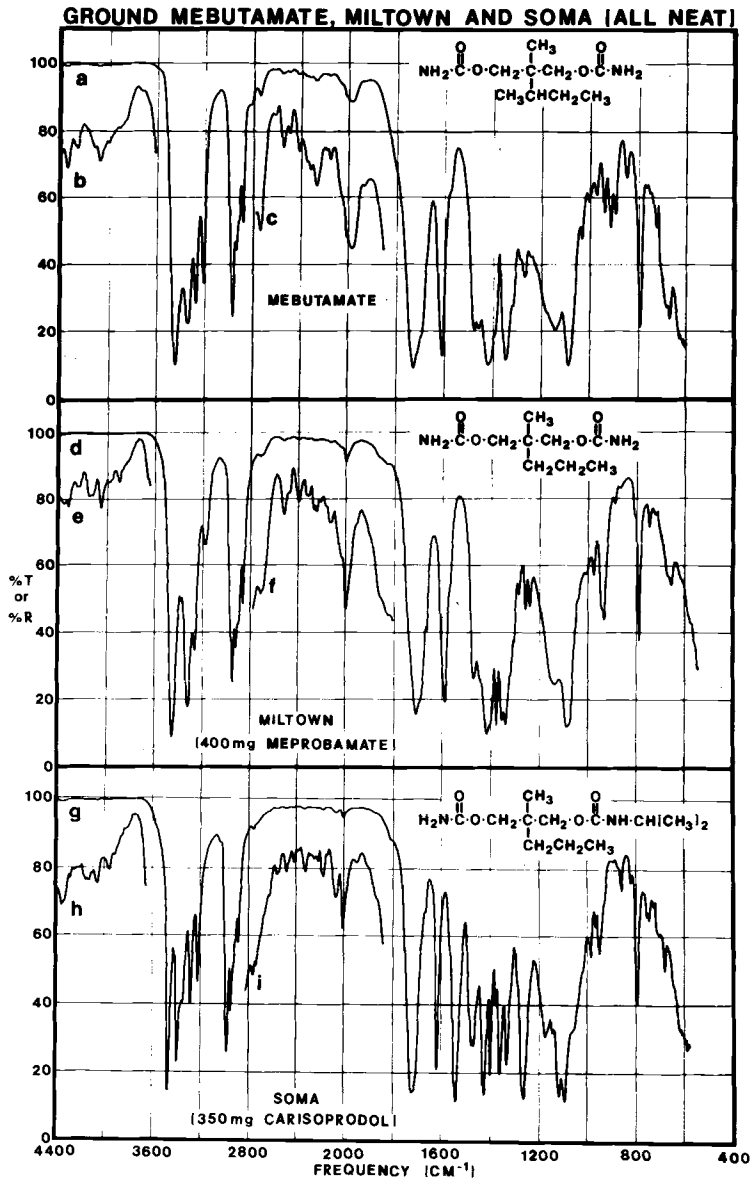

FIG. 10—(a) %T *format of the spectrum of neat mebutamate powder that was ground for 2 min and sampled neat, gain 8.* (b) *and* (c) *Portions of the reflectance spectrum of the above sample.* (d) %T *format of the spectrum of a Miltown tablet that was ground for 5 min and sampled neat, gain 8.* (e) *and* (f) *Portions of the reflectance spectrum of the above* (d) *sample.* (g) %T *format of the spectrum of a Soma tablet that was ground for 5 min and sampled neat, gain 8.* (h) *and* (i) *Portions of the reflectance spectrum of the above* (g) *sample.*

spectrum of this powder (Fig. 9*e*). Results for a second tablet, Miltown, are depicted in Fig. 10*d* to *f*.

A comparison of the Miltown spectrum to the spectra of two compounds closely related to meprobamate is shown in Fig. 10. For this, mebutamate powder and a Soma (carisoprodol) tablet were ground in a Wig-L-Bug for 2 and 5 min, respectively, and sampled neat. This comparison can provide some indication of the specificity of this analysis and as may be observed, the three spectra have many distinguishing features. Note that this is also true for the weaker absorptions observed in the reflectance spectra (Fig. 10*a, c, e, f, h*, and *i*).

Capsule Powders

The direct analysis of powder straight from a capsule is illustrated in Fig. 7 for Noludar 300 (the powder from which weighs approximately 318 mg and contains 300 mg of methyprylon). This powder was poured into a 4-mm sample cup and sampled neat giving the reflectance and % *T* spectra depicted in Fig. 7*b* and *d*, respectively. Spectra of methyprylon powder sampled neat are shown in Fig. 7*a* and *c*, while the absorption spectrum of methyprylon in a KBr pellet is shown in Fig. 7*e*. The DRIFTS % *T* spectra (Fig. 7*c* and *d*) are quite similar in appearance to the KBr pellet results, except for the two specular reflectance inverse peaks on the low frequency side of the strongest carbonyl absorption. Note the similarity of these features to those observed for the Noludar tablet (Fig. 6*b*).

As expected, the intensities of these two inverse peaks, as well as those comprising the carbonyl doublet itself, are dependent on sample particle size. The inverse peaks are weaker, or not observed at all, for capsule powders that have been ground before sampling. The methyprylon powder as received from Roche Laboratories, on the other hand, was observed microscopically to be comprised of particles significantly larger than those observed in Noludar. Neat sampling of this powder produced spectra having more pronounced inverse peaks; thus, this standard powder was ground slightly (by hand) until particle sizes comparable to those occurring in Noludar were obtained. This ground sample was used to obtain the results depicted in Fig. 7*a* and *c*.

The reproducibility of this neat sampling method was tested by examining a number of capsules from the same bottle, and also by sampling from a second bottle containing capsules manufactured from a different lot. In general, the method was found to be quite reproducible and only a slight variability, primarily in the relative intensities of the two carbonyl peaks, was observed. No significant variations between capsule powders from the two lots were evident from their spectra or from microscopic examinations. All of the capsule powder particles exhibit a fairly large range of sizes.

For most other capsules, neat sampling of the powder directly from the capsules results in significant amounts of specular reflectance. This is illustrated in Fig. 11*a* for Valmid, which contains approximately 550 mg of powder containing 500 mg of ethinamate. The effects of particle size on specular reflectance can be seen from a comparison of this spectrum to those depicted in Fig. 11*b* and *c*. The latter were taken of Valmid capsule powders that were ground for 30 s and 10 min in a Wig-L-Bug, respectively, and sampled neat.

The spectrum obtained after 5 min of grinding (Fig. 12*b* and *d*) shows little difference from that obtained after 10 min of grinding; hence, no significant further decrease in specular reflectance occurs after the powder has been ground for approximately 5 min. As a comparison, the spectrum of ethinamate powder that was ground for 3 min in the Wig-L-Bug and sampled neat, is also shown (Fig. 12*a* and *c*).

Other Powders

Neat sampling using DRIFTS can be quite useful for the screening of unknown powders, and for those cases where the sample is fairly pure, it can be used for identification. Three

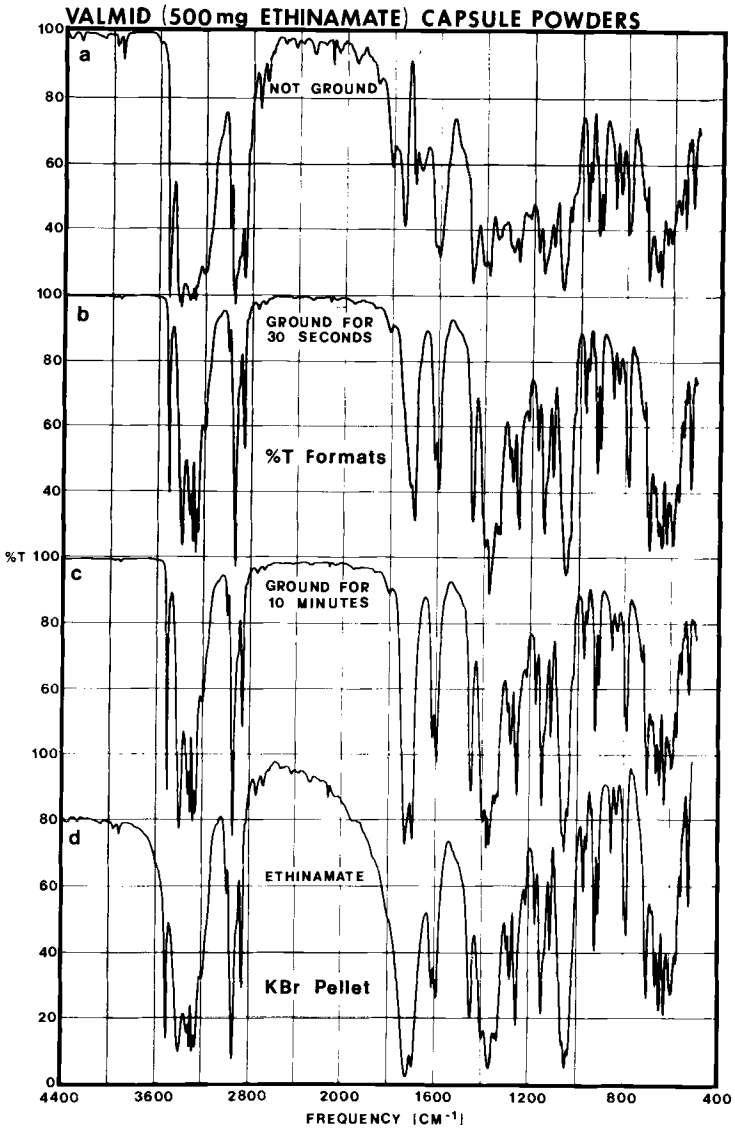

FIG. 11—(a) %T *format of the spectrum of Valmid capsule powder sampled neat, gain 16.* (b) %T *format of the spectrum of Valmid capsule powder ground for 30 s and sampled neat, gain 8*R. (c) %T *format of the spectrum of Valmid capsule powder ground for 10 min and sampled neat, gain 8*R. (d) *Absorption spectrum of ethinamate in a KBr pellet.*

examples of the latter are shown in Figs. 13, 14, and 15 for the analysis of powders that were received in our laboratory. These samples were found to contain cocaine hydrochloride, phencyclidine base, and methamphetamine hydrochloride, respectively, and as may be seen from comparisons to spectra of the standards, all three were relatively pure.

For these analyses, the standard powders were all ground in a Wig-L-Bug for 1 min, while the case powders were all ground by hand using a mortar and pestle. The latter were ground to approximately the same extent as normally used to produce KBr pellets; as may be seen by

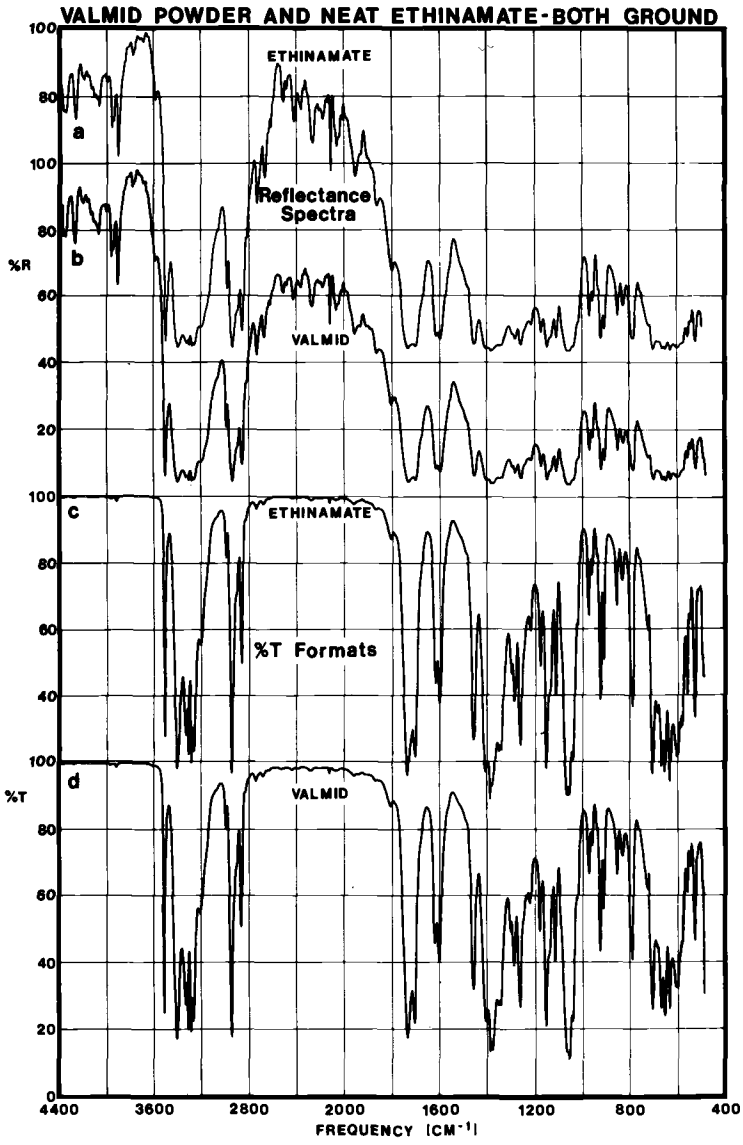

FIG. 12—(a) *Reflectance spectrum of neat ethinamate powder ground for 3 min, gain 8*R. (b) *Reflectance spectrum of Valmid capsule powder ground for 5 min and sampled neat, gain 8*R. (c) *and* (d) %T *formats of the above two spectra, respectively.*

comparisons to the standard spectra, this produces results comparable to those obtained using the Wig-L-Bug.

Comparison of the DRIFTS data (in % *T* format) to the corresponding KBr pellet spectra shows them to be very similar; this is especially true for phencyclidine and methamphetamine (note also the conspicuous lack of scattering effects—evident in the sloping baselines of the pellet spectra of these two—for the DRIFTS spectra). In general, we have found that

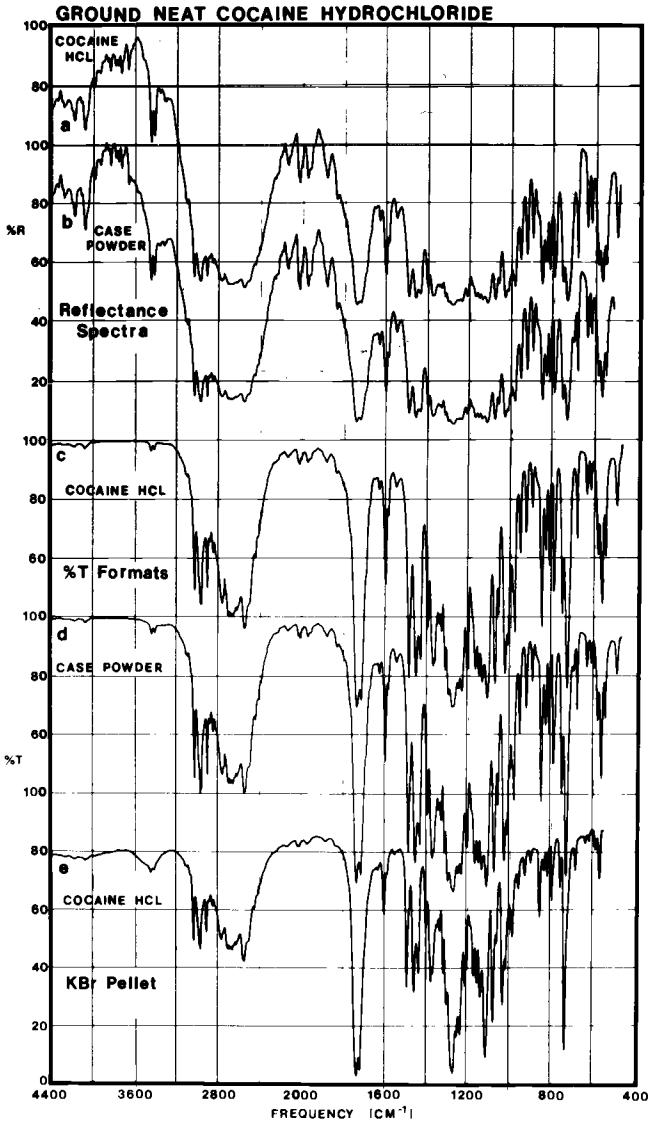

FIG. 13—(a) *Reflectance spectrum of l-cocaine hydrochloride ground for 1 min and sampled neat, gain 8.* (b) *Reflectance spectrum of a white powder ground by hand and sampled neat, gain 8.* (c) *and* (d) *%T formats of the above two spectra, respectively.* (e) *Absorption spectrum of* l-*cocaine hydrochloride in a KBr pellet.*

when relatively weak infrared absorbing compounds are ground to fine powders and sampled neat, their % T format spectra closely resemble those obtained for KBr pellets. This strongly suggests that specular reflectance is the primary factor producing differences between these two methods.

The spectral data presented here will not, in all cases, be identical to those obtained on other instruments. Since the geometries of diffuse reflectance accessories vary, the specular

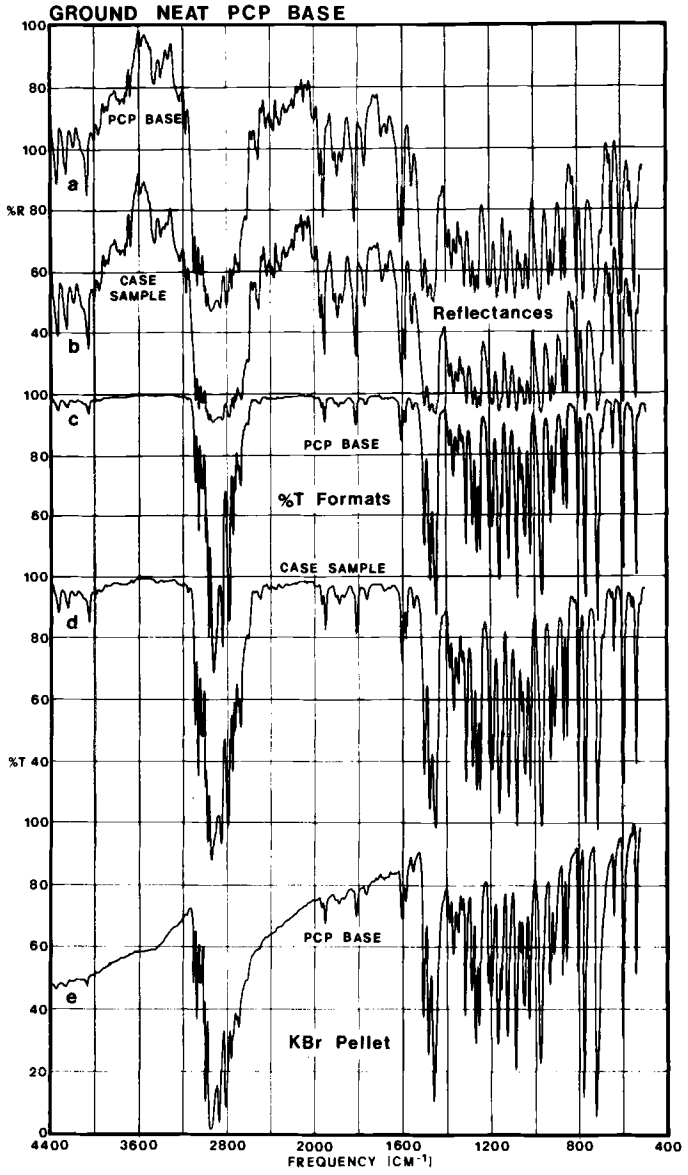

FIG. 14—(a) *Reflectance spectrum of phencyclidine base ground for 1 min and sampled neat, gain 8.* (b) *Reflectance spectrum of a white powder ground by hand and sampled neat, gain 8.* (c) *and* (d) %T *formats of the above two spectra, respectively.* (e) *Absorption spectrum of phencyclidine base in a KBr pellet.*

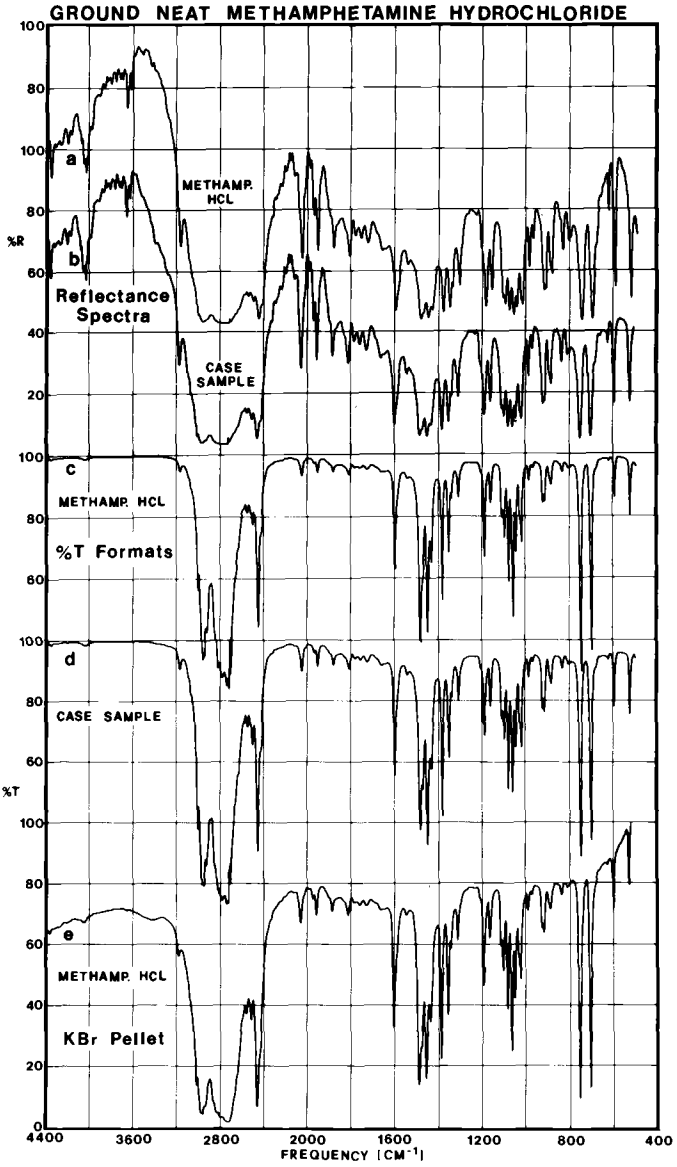

FIG. 15—(a) *Reflectance spectrum of* d-*methamphetamine hydrochloride ground for 1 min and sampled neat, gain 8.* (b) *Reflectance spectrum of a white powder ground by hand and sampled neat, gain 8.* (c) *and* (d) %T *formats of the above two spectra, respectively.* (e) *Absorption spectrum of* d-*methamphetamine hydrochloride in a KBr pellet.*

reflectance components will, to some extent, depend on the particular system used.[5] Because of this, it is important that reference spectra for this type of sampling be collected on the individual instruments used.

Previously, Fuller and Griffiths demonstrated that for dilute samples mixed with finely ground potassium chloride (KCl), the maximum penetration depth in DRIFTS sampling is approximately 3 mm [7]. Samples at least this thick are thus required to meet the criteria of "infinite thickness" according to the Kubelka-Munk model [8] of diffuse reflectance. In our work, sampling of neat powders having various thicknesses (placed over KBr) indicated that no further increase in band intensities was observed for samples more than approximately 1 mm thick. The penetration depth is thus significantly reduced in neat sampling, and as a consequence, smaller sample volumes than that needed to fill a sample cup can be used.

Summary

Fuller and Griffiths first demonstrated the feasibility of obtaining an infrared spectrum directly on an Empirin tablet using DRIFTS. Several modifications of this technique, including sanding of tablet surfaces, use of differential interferometer gains, presentation of the spectral data in two formats, and grinding the tablet to a fine powder, have been found to be necessary to obtain useful data for most other tablets. Specular reflectance, which produces a decrease in absorption intensity or inverse peaks, is the primary reason for these modifications. Direct analysis has been found to be particularly useful for the screening of unknown tablets. For identification purposes, this method provides more spectral data than obtainable by other techniques, as very weak overtone, combination, and difference bands are observed. Capsule powders and other powders can also be sampled directly, but they usually require grinding. The spectra of weak infrared-absorbing compounds, when ground to a fine powder and sampled neat, are very similar to those obtained for KBr pellets.

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[5]This was confirmed by some preliminary work. For this, our Analect reflectance accessory was tested on both a different model of an Analect instrument (an AQS-20 FTIR) and a Nicolet 5DXB FTIR; a Barnes reflectance accessory was also tested on the latter instrument. For all of the ground neat powders and sanded tablets that were examined, DRIFTS spectra very similar to those obtained on our instrument were produced for these three configurations. For tablets run directly without sanding (such as Doriden), no differences were observed using the AQS-20. Some differences were observed for these, however, using our accessory on the Nicolet instrument, and the Barnes accessory produced considerably more specular reflectance.

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