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Forensic Science Applications of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS): III. Direct Analysis of Polymeric Foams

ABSTRACT: Many types of polymeric organic foams, which comprise items such as thermal insulation, packaging materials, furniture and garment fillings, carpet padding, and so forth, can be sampled directly using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Some of the advantages of direct DRIFTS sampling include: (1) no sample preparation is required, (2) the method is completely nondestructive, and (3) the method provides more spectral information for characterizing and individualizing particular substances than many alternative techniques do. Several examples illustrating the direct DRIFTS analysis of a variety of foam articles are presented and discussed.

KEYWORDS: criminalistics, spectroscopic analysis, reflectance, Fourier transform, diffuse reflectance, DRIFTS, forensic science applications, infrared spectrophotometry, polymeric foams, foams

Wiley [*1*] first demonstrated the ability of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to sample some bulk materials directly. Some of the items that were examined included paper, wool, and plant leaf. Fuller and Griffiths applied this direct sampling method to the analysis of an Empirin® tablet [*2,3*], while our previous paper [*4*] in this series extended this application to other tablets, capsule powders, and powders of forensic science interest. The latter work showed, however, that most tablets require some surface modification, or powdering, to minimize the effects of specular reflectance.

Direct DRIFTS analyses offer several significant advantages for forensic science examinations, including requiring no sample preparation, being totally nondestructive, and generally providing more spectral information [*4,5*] for characterizing and individualizing a particular substance. In view of these advantages, we have examined a wide variety of materials besides tablets to determine whether they are suitable for direct DRIFTS sampling. We found that good quality spectral data are obtained for many types of polymeric organic foams. These foams include a variety of articles such as thermal insulation, packaging ma-

terials, furniture fillings, garment fillings, carpet and other padding, floatation devices, sponges, filtration elements, and so forth.

One of the more widely used techniques for forensic science examination of foams and other polymeric materials is pyrolysis gas chromatography [6, 7]. This method usually provides a high degree of discrimination between different polymeric samples; it is limited, however, in its ability to distinguish [7] between materials comprised of the same polymer type but having different inorganic constituents (such as fillers, which are common in many foams). Infrared spectroscopy, in contrast, often provides a better discrimination between such samples, but conventional methods of sampling are usually not applicable for most foams. The pliable nature of many of these substances, for example, makes them difficult to sample using conventional KBr pellets; most would require grinding at liquid nitrogen temperatures to form a powder fine enough for this technique. The majority of foams are also insoluble in most solvents; representative cast films usually cannot be made, and unrepresentative spectra (for example, plasticizers) may result. The porous structures of these substances may render some of them unsuitable for sampling using attenuated total reflectance (ATR).

Two infrared methods that have been found to be useful for foams include Fourier transform infrared photoacoustic [8] spectroscopy (FTIR-PAS) and the use of a diamond anvil cell (DAC) accessory [9]. Like DRIFTS, the former method allows direct sampling, but does have several limitations [8, 10]. These include an inherent insensitivity which necessitates the use of long collection times. The DAC method, on the other hand, is quite sensitive, although the diamond absorptions may present a problem in some cases, and interference fringes and spectral distortions arising from pressure effects sometimes occur. None of these are a problem with DRIFTS, however. In this paper, the spectral results obtained for a variety of foam articles sampled directly using DRIFTS are presented. These results are compared to those obtained from conventional transmittance methods, primarily using the DAC.

Experimental Procedure

The FTIR and the diffuse reflectance and DAC accessories used in this work have been described previously [5]. All of the DRIFTS spectra were acquired using an uncollimated (focused) beam, and a reference of powdered KBr in a 4-mm cup was used. The majority of spectra were collected using a broadband mercury cadmium telluride (MCT) detector, although for a few spectra a narrow-band MCT detector was used. Reference gains of $4R$ and 1, respectively, where $R = \sqrt{2}$, were used for these two detectors. The gains of the various samples [4] 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 direct sampling, the surfaces of the foams to be examined were positioned at the focal point of the diffuse reflectance accessory.

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 normal scanning mode (5-cm^{-1} resolution) was used for most spectra, and the instrument housing was purged with dry nitrogen.

Samples of cross-linked polyethylene foam, Ensofoam® and Ensolite® (consisting of 23 different foams comprising a swatch package) were obtained from Uniroyal, Inc. (Mishawaka, IN). Samples of rigid polyurethane foams were obtained from General Plastics Manufacturing Company (Tacoma, WA). Along with these, numerous types of household and commercial foam articles were collected and sampled.

Results and Discussion

The reflectance spectrum obtained for the direct sampling of styrofoam is depicted in Fig. 1a; below (Fig. 1b) is shown this same data presented in the percent transmittance (%T) format [5]. As a comparison, the absorption spectrum of a polystyrene calibration film is shown in Fig. 1c and as may be observed, no significant specular reflectance distortions occur for the DRIFTS results.

Interestingly, the styrofoam samples were found to have higher baseline reflectances than
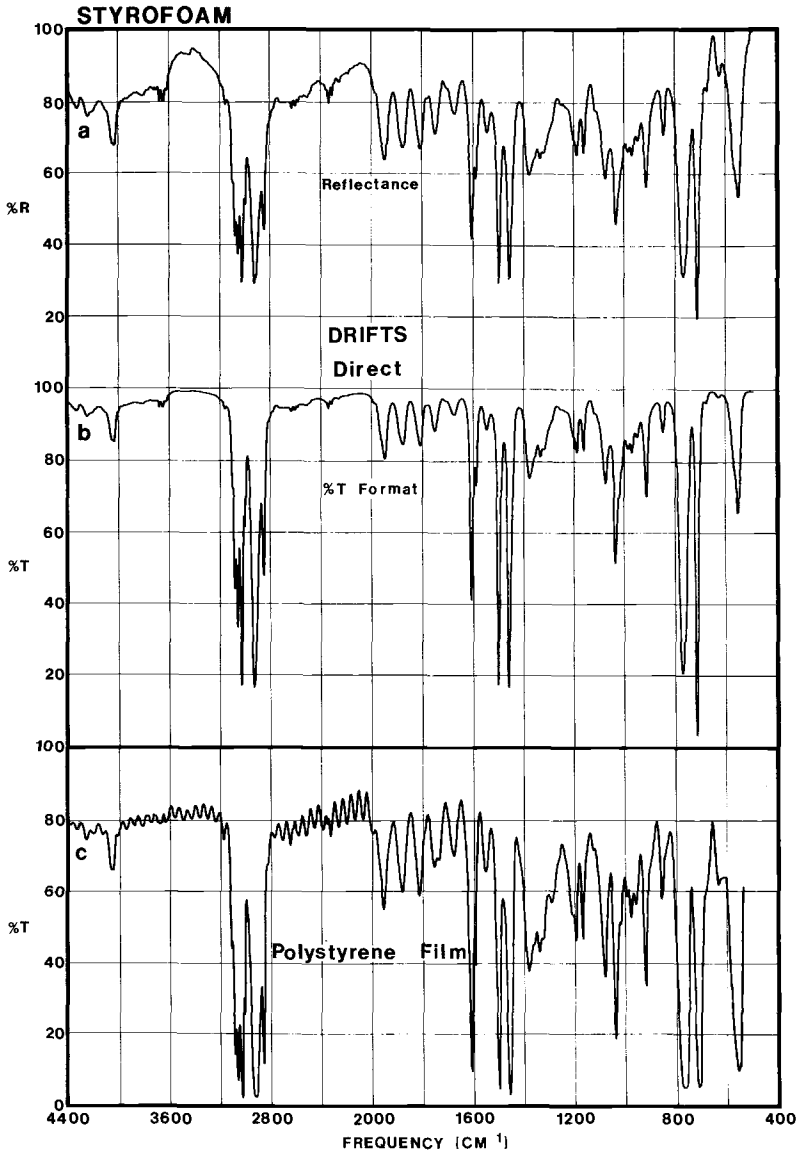

FIG. 1—(a) Reflectance spectrum of styrofoam sampled directly, gain 4R. (b) %T format of the above spectrum. (c) Absorption spectrum of a polystyrene calibration film.

the KBr references; this was compensated for by use of an attenuator comb placed in the beam. All of the other foam samples that were examined, in contrast, were found to have lower reflectances[2] than the references (which usually occurs for direct DRIFTS sampling—see Paper II [4] in this series). These differences in reflectances appear to correlate with the surface features of the various foams, with smooth surface samples generally having high reflectances and porous textured ones having lower reflectances. This probably reflects the effects of differences in the scattering coefficients and effective particle sizes for the different foams.

Results obtained for two other commonly encountered compositions of foams are presented in Figs. 2 and 3. A polyethylene foam packaging block (used as a shock-absorbing padding for shipping) gave the DRIFTS results shown in Fig. 2a and b and the DAC spectrum of c. The weaker absorptions above 3200 cm^{-1} and between 2800 and 1600 cm^{-1}, most of which are not observed in the DAC spectrum, are observed clearly in the reflectance spectrum (Fig. 2a). As discussed previously [4,5], these weaker features may, on occasion, be useful in distinguishing between closely related substances. The good agreement between the DRIFTS %T format spectrum (Fig. 2b) and the DAC spectrum (Fig. 2c) is again evident. In this case, however, a slight inverse specular reflectance peak is observed between the two C-H stretching absorptions for the DRIFTS results. The doublet of the 720-cm^{-1} DRIFTS absorption, on the other hand, is a real feature which is discussed later. Note also the low frequency interference fringes in the DAC spectrum (Fig. 2c), which can sometimes obscure the weaker absorptions of the spectrum.

Spectra of a sample of cross-linked polyethylene (obtained from Uniroyal) are shown in Fig. 3. Several diverse foam articles were found to give similar spectra, indicating this material to be a relatively common composition (it is worth noting that some of these materials have a gross appearance and texture quite similar to those of styrofoam). As in the case of the polyethylene spectrum (from which this cross-linked polyethylene spectrum is easily distinguished), the DRIFTS results display the 720-cm^{-1} doublet and a slight specular reflectance feature in the C-H stretching region.

Effects of Sampling Orientation

The majority of foam samples that were examined were observed, macroscopically and microscopically, to have an isotropic structure. For these materials, the orientation of the foam during sampling (that is, which surface of the piece was sampled) had no effect on the resulting spectra. Quite reproducible results are thus normally obtained for these materials.

A few foams, however, were observed to produce slightly different spectra depending on sampling orientation. Invariably for these cases, a nonisotropic structure for the foam was evident from a microscopic examination. An example of such a case is a polyethylene foam pipe insulation which, when sampled in three different orientations, gave the spectra (presented in %T formats) depicted in Fig. 4a, b, and c. This particular pipe insulation has a structure that can be roughly described as consisting of a collection of numerous narrow tubes running parallel to the length of the pipe. These tubes are divided into small cells. The outside of the pipe insulation has a relatively smooth, shiny surface. The differences in the
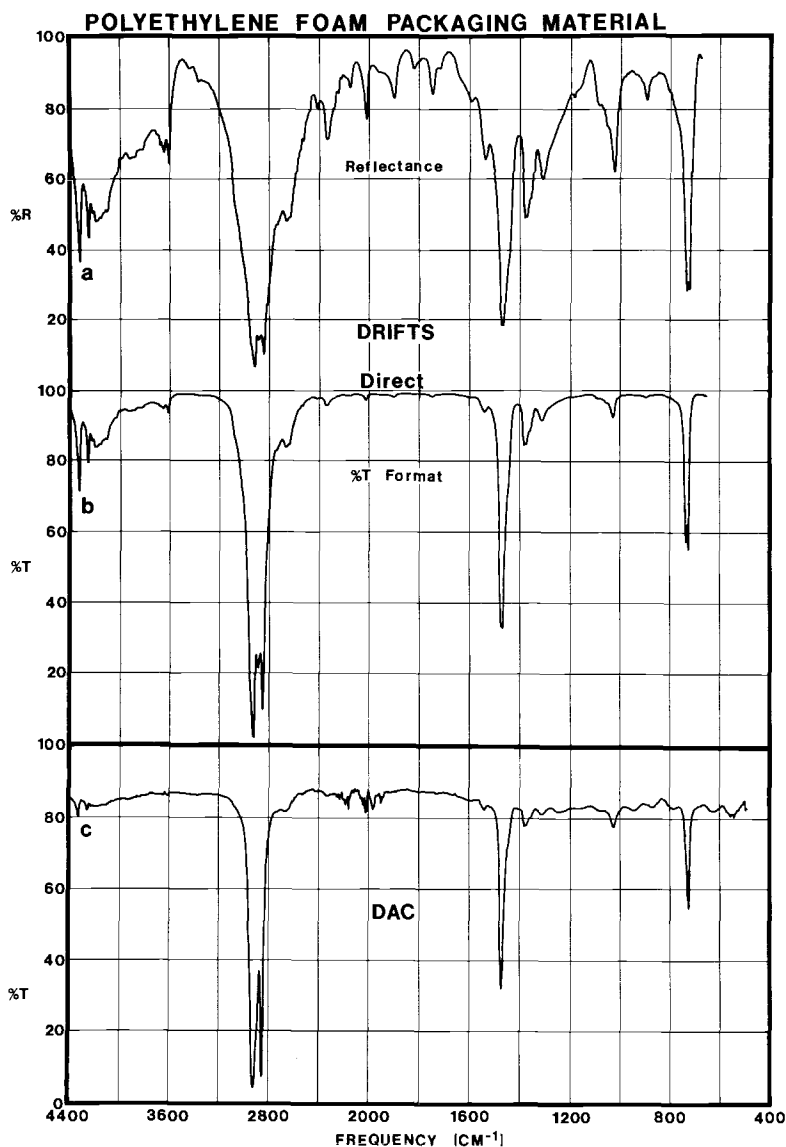
FIG. 2—(a) *Reflectance spectrum of a polyethylene foam packaging material sampled directly, gain 32.* (b) %T *format of the above spectrum.* (c) *DAC spectrum of this material.*

spectra (Fig. 4a–c) arise from the differing amounts of specular reflectance from the various surfaces. To illustrate better these differences, a higher resolution (3.2 cm^{-1}, obtained by using a boxcar apodization) was used for sampling this pipe insulation.

Specular reflectance, seen as an inverse spike occurring between the two C-H stretching absorptions, is greatest when the shiny surface of the insulation is sampled (Fig. 4c; compare to 4d). It is least (Fig. 4a) when the surface perpendicular to the length of the pipe is examined. Note that the latter orientation would not be expected to present much surface area facing the incident sampling beam. This particular orientation also produced spectra having the lowest overall reflectance (which was compensated for by using a higher gain). The sur-
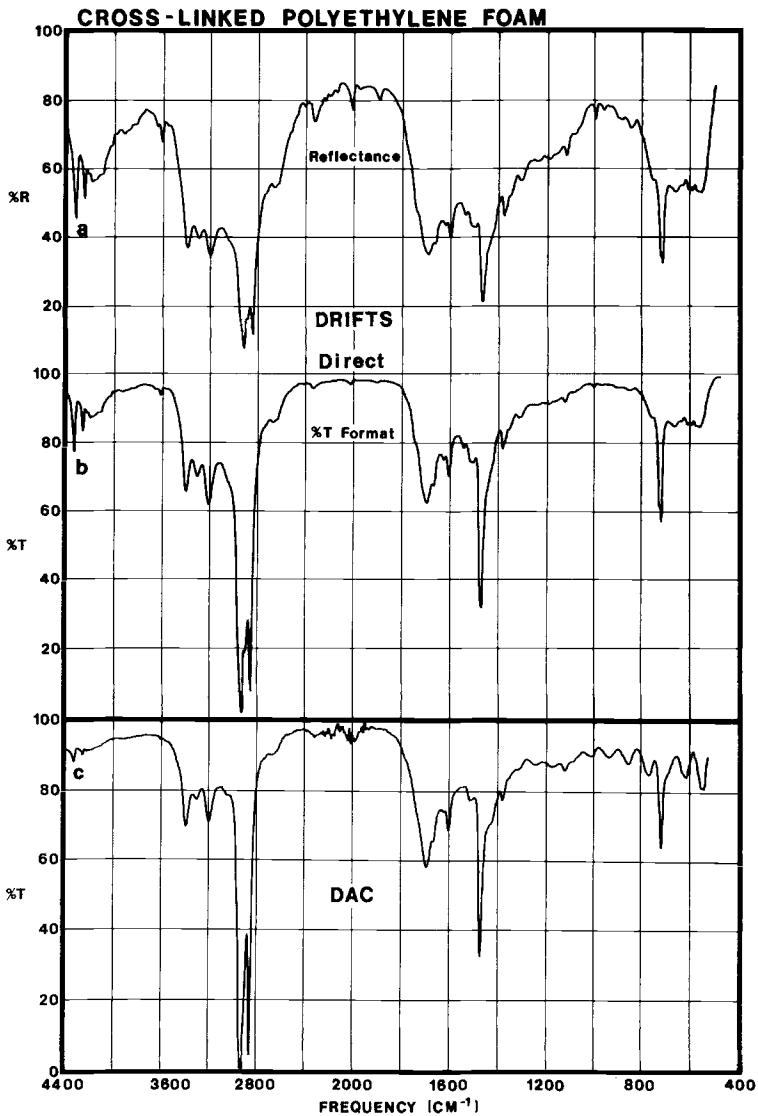
FIG. 3—(a) *Reflectance spectrum of Uniroyal cross-linked polyethylene foam sampled directly, gain 8R.* (b) *%T format of the above spectrum.* (c) *DAC spectrum of this material.*

face resulting from slicing of the foam through a plane containing the pipe axis produced an intermediate amount of specular reflectance (Fig. 4*b*), which is also consistent with the nature of that surface.

Because of spectral dependence on sampling orientation, it is important that this feature be considered when examining nonisotropic foams. While this dependence (and deviation from the "true" absorption spectrum) might be considered a drawback of the sampling technique, it is actually providing more information about the surface characteristics of the sample.
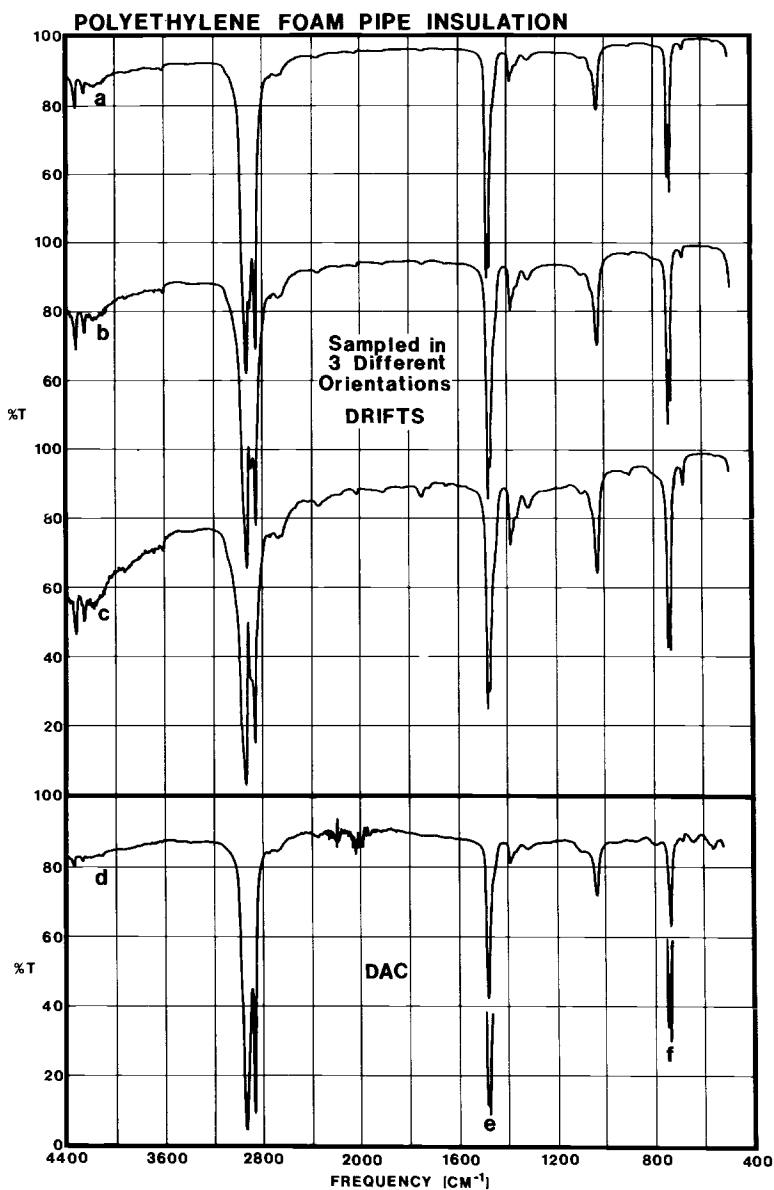
FIG. 4—%T *format spectra of a polyethylene foam pipe insulation sampled directly in three different orientations:* (a) *surface perpendicular to pipe axis, gain 16*R; (b) *surface containing pipe axis, gain 16*R; (c) *exterior surface of insulation, gain 16; 765 scans were collected for all of these.* (d) *DAC·spectrum of this insulation.* (e) *and* (f) *Portions of the direct transmittance spectrum of a thin section of this insulation. A boxcar apodization (3-cm⁻¹ resolution) was used for all of the above spectra.*

For the polyethylene and cross-linked polyethylene foams previously discussed, the 720-cm^{-1} DRIFTS peaks (Figs. 2b and 3b, respectively) appeared as doublets. These doublets are much more evident in the pipe insulation spectra (Fig. 4a–4c) which were collected at a higher resolution; doublets for the 1470-cm^{-1} peak are also observed for these. While a higher resolution was also used for the corresponding DAC spectrum (Fig. 4d), no splittings

are observed. They are observed, however, in direct transmission spectra[3] of thin sections of the pipe insulation (Fig. 4c and d). These doublets arise from the crystallinity of polyethylene [13] and are not due to specular reflectance. Their absence in the DAC spectra reflects a pressure-induced effect such as disordering or other [14] lattice changes.

Another feature in the pipe insulation spectrum worth noting is the presence of two weak nonpolyethylene peaks at 1019 and 670 cm^{-1}. These are due to a talc filler used in this particular foam. A talc filler is also present in the polyethylene foam packaging block (Fig. 2), although there is less present than in the pipe insulation (compare Figs. 2c and 4d). A DRIFTS examination of a second, different polyethylene foam pipe insulation indicated that it contained no detectable talc. The presence and relative amount of talc, as well as other fillers, can thus be quite useful in distinguishing between certain similar foams.

Effects of Foam Density

Some foams can occur in a wide range of densities. Since the relatively low densities of foams are undoubtedly a large factor in their suitability for direct DRIFTS sampling, the effects of foam density on spectra were examined. For this, four different rigid polyurethane foams having similar compositions and densities of 0.03, 0.06, 0.15, and 0.30 g/mL were sampled (as a comparison, various styrofoam samples were found to have densities of 0.01 to 0.03 g/mL).

The reflectance, %T format, and KBr pellet spectra for the lowest density (0.03 g/mL) foam are shown in Fig. 5b, a, and e, respectively; corresponding spectra for the highest density foam (0.30 g/mL) are given in Fig. 5d, c, and f, respectively. The pellet spectra for the four foams (two of which may be seen in Fig. 5e and f) are fairly similar. The DRIFTS spectra, however, exhibit increasing amounts of specular reflectance as the foam density increases, as might be expected. This is evident from the greater distortions (which result in narrower absorptions) that are observed for the peaks of Fig. 5c relative to those of Fig. 5a. The overall reflectance also decreases with increasing density (compare Fig. 5b and d; the same gain was used for both samples).

A further confirmation of this trend was obtained from examination of a second rigid polyurethane foam used as a thermal insulation sheath. DRIFTS spectra of this foam, which had a density of 0.02 g/mL, exhibited less specular reflectance than the 0.03-g/mL foam (Fig. 5a).

Ensolite Foams

A large line of different foams encompassing a wide variety of uses and products is produced by Uniroyal and marketed as Ensolite. Most of these foams are comprised of a vinyl-nitrile composition, but a few are based on a polyethylene/ethylene-vinyl acetate (EVA) blend. DRIFTS (%T format) and DAC spectra of one of the latter type (Product PE308S) are shown in Fig. 6e and h, respectively; portions of the reflectance spectrum showing the weaker absorptions are also depicted (Fig. 6f and g). Spectra of a Uniroyal non-Ensolite polyethylene/EVA foam (known as Ensofoam), which has a somewhat different composition, are shown in Fig. 6a to d. Only very slight specular reflectance distortions in the DRIFTS spectra of these two foams can be seen (Fig. 6a and e) for the most intense C-H stretching absorption.

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[3]Because of the opacity of this black foam, a substantial gain increase was used for this transmittance scan. Note that the relative intensities of the two peaks comprising the 1470- and 720-cm^{-1} doublets in the four spectra (Fig. 4a, b, c, e, and f) vary somewhat. This is probably caused by the fact that the intervals between data points for this spectrometer are too far apart to allow faithful representation of these relatively narrow peaks; specular reflectance or anisotropy of the crystallinity of the polyethylene may also contribute to this.
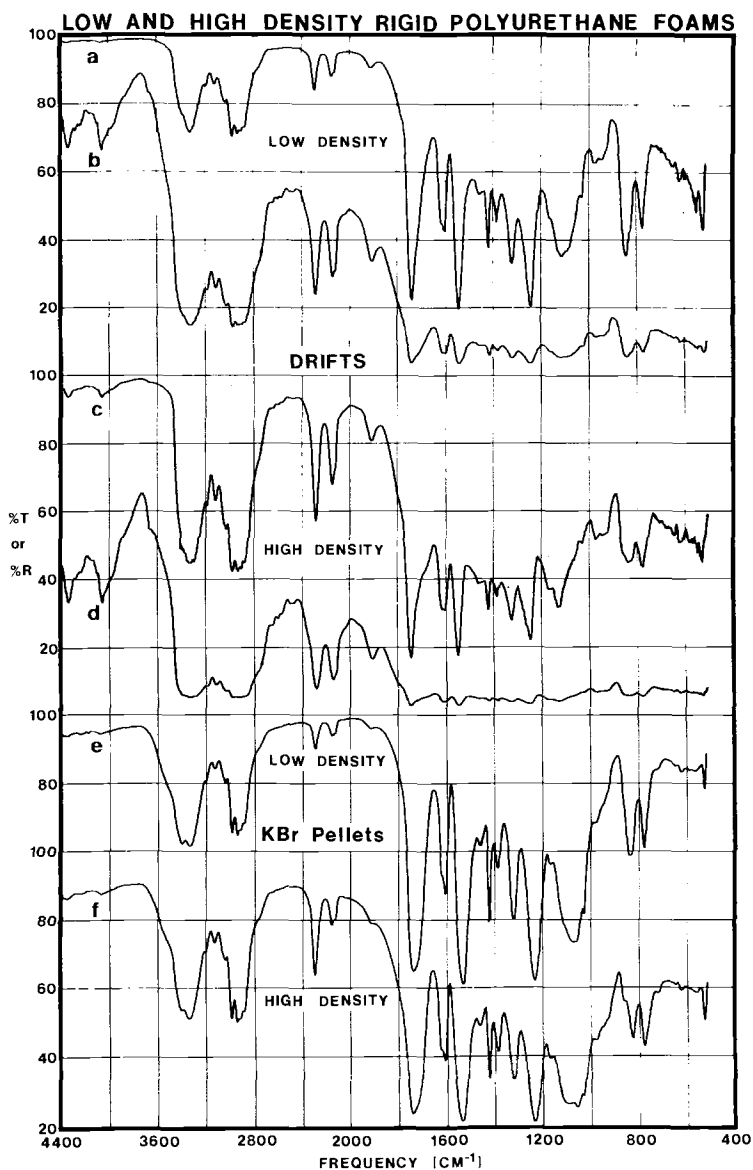
FIG. 5—(a) *and* (b) %T *format and reflectance spectra, respectively, of a piece of low density rigid polyurethane foam sampled directly, gain 8R.* (c) *and* (d) %T *format and reflectance spectra, respectively, of a piece of high density rigid polyurethane foam sampled directly, gain 8R.* (e) *and* (f) *KBr pellet spectra of the above two samples, respectively.*

Spectra of some Ensolite vinyl-nitrile foams are shown in Figs. 7 and 8. A general composition for the vinyl-nitrile foams was provided[4] by Uniroyal and is given below:

40% poly(vinyl chloride) (PVC),
20% nitrile-butadiene rubber (of which approximately 34% is acrylonitrile),
20% fillers (such as calcium carbonate [$CaCO_3$] or titanium dioxide [TiO_2]),

[4]Uniroyal, Inc., Plastics Products Division, Mishawaka, IN, private communication, July 1984. Published here with permission.
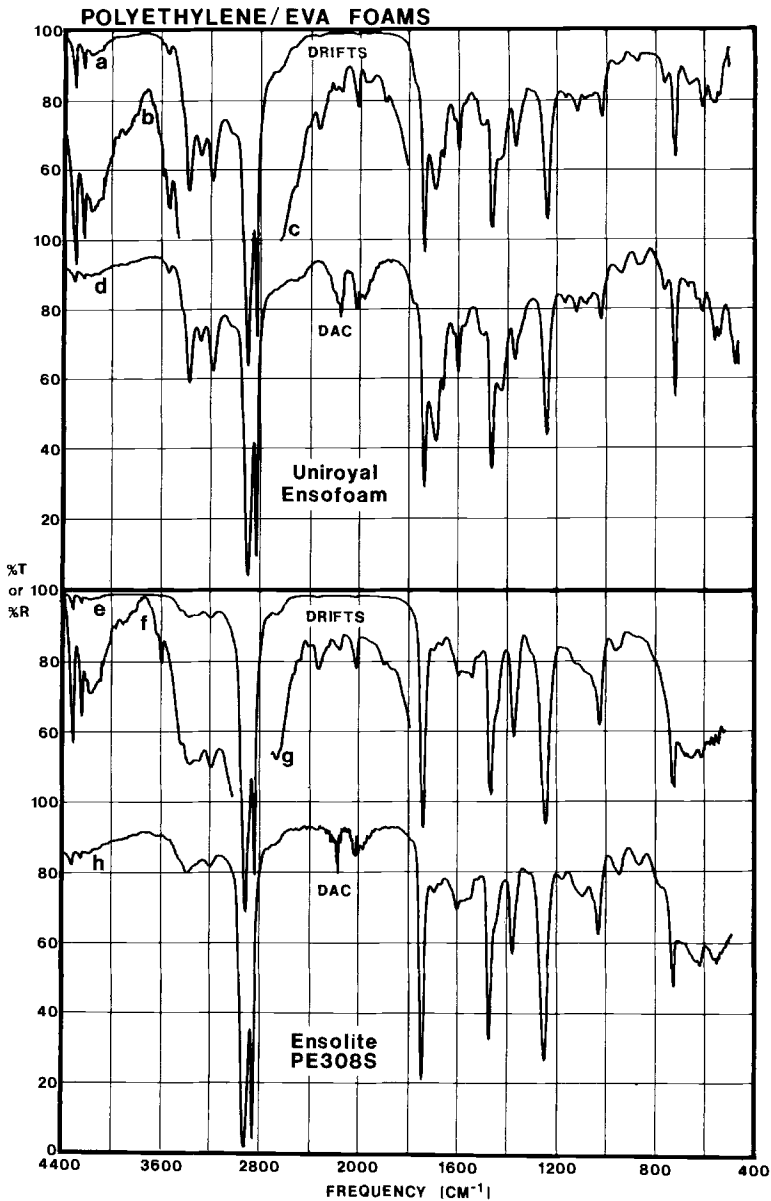
FIG. 6—*Spectra of Uniroyal polyethylene/EVA Ensofoam:* (a) *%T format and* (b) *and* (c) *portions of the reflectance spectra, sampled directly, gain 16;* (d) *DAC spectrum. Spectra of polyethylene/EVA Ensolite Foam PE308S:* (e) *%T format and* (f) *and* (g) *portions of the reflectance spectra, sampled directly. gain 8;* (h) *DAC spectrum.*

10% plasticizers (pthalates, and so forth), and
10% miscellaneous.

Most of the strong absorptions observed for the spectra depicted in Fig. 7a and b are due to the PVC component. Prominent carbonyl absorptions, arising from plasticizers or other nonbinder components, are also evident. The 2240-cm^{-1} nitrile absorption, which is highly
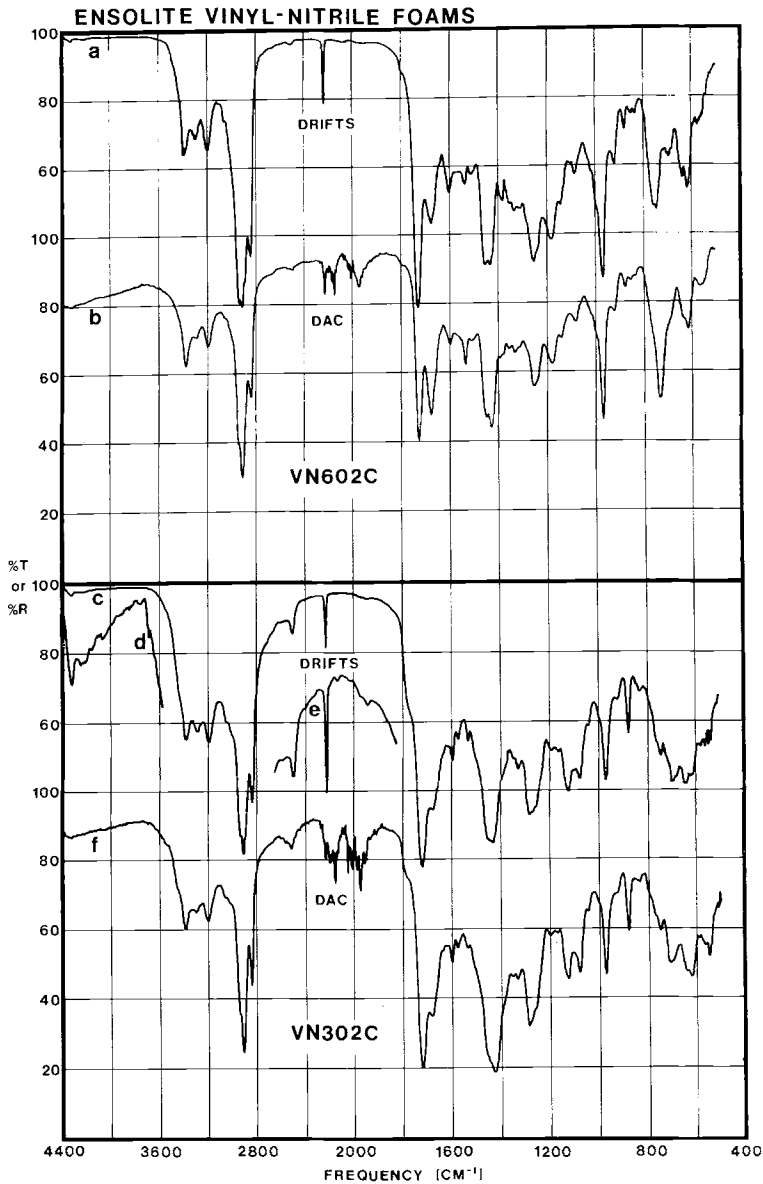
FIG. 7—*Spectra of Uniroyal Ensolite vinyl-nitrile Foam VN602C:* (a) *%T format spectrum, sampled directly, gain 8;* (b) *DAC spectrum. Spectra of Ensolite vinyl-nitrile Foam VN302C:* (c) *%T format and* (d) *and* (e) *portions of the reflectance spectra, sampled directly, gain 8;* (f) *DAC spectrum.*

characteristic of the Ensolite vinyl-nitrile foams, is relatively weak but can be observed in all of the DRIFTS spectra (Figs. 7a, 7c, 8a, and 8e). This absorption cannot be clearly discerned from the background noise in the DAC spectra (Figs. 7b, 7f, 8d, and 8h), however, as this is the region where the diamond anvils absorb strongly.

Many of the Ensolite vinyl-nitrile foams have spectra similar, with small to moderate differences, to that depicted in Fig. 7a and b; several, however, have distinct differentiating features. Spectra of three of the latter are shown in Fig. 7c to f, and Fig. 8. The differentiat-
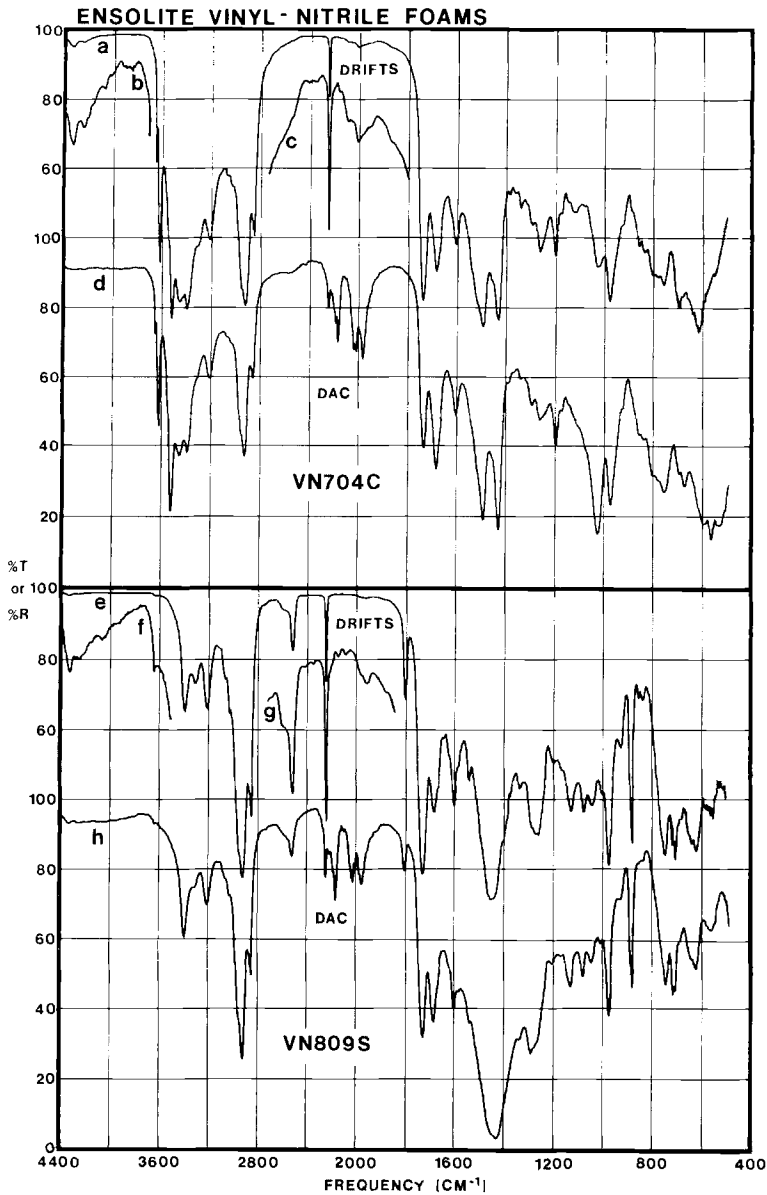
FIG. 8—*Spectra of Uniroyal Ensolite vinyl-nitrile Foam VN704C:* (a) %T *format and* (b) *and* (c) *portions of the reflectance spectra, sampled directly, gain 16;* (d) *DAC spectrum. Spectra of Ensolite vinyl-nitrile Foam VN809S:* (e) %T *format and* (f) *and* (g) *portions of the reflectance spectra, sampled directly, gain 8R;* (h) *DAC spectrum.*

ing features are due primarily to the presence of inorganic fillers. Absorptions of calcium carbonate (1430, 875, and 713 cm^{-1}, see Fig. 12c) and titanium dioxide (broad absorption from 800 to 500 cm^{-1}), for example, are observed in the first of these (Fig. 7c to f, Product VN302C). Distinctive absorptions of magnesium carbonate (3649, 1488, and 1425 cm^{-1}, see Fig. 4c in Paper II [4] in the series) are evident in the second foam (Fig. 8a and d), while the third foam (Fig. 8e and h) contains a considerable amount of calcium carbonate.

From a comparison with the DAC spectra, the absorption intensities for some of the DRIFTS peaks can be seen to be partially attenuated. This is particularly true for the 1430-cm^{-1} calcium carbonate absorption in Fig. 8e. As discussed previously [4,5], inorganic compounds, because of their higher absorption coefficients and indices of refraction, tend to produce more specular reflectance than organic compounds. The form of the inorganic constituent may also affect this attenuation as will be discussed later.

Flexible Polyurethane Foams

Flexible polyurethane foams are used for a variety of common household articles such as furniture filling, carpet padding, foam mattresses, constituents of toys, and so forth. Most of the numerous such polyurethane articles that were examined gave spectra similar to those depicted in Fig. 9.

The flexible foams are quite porous and tend to produce low reflectances; fairly large gain increases were thus necessary for these. The reflectance spectra for these foams also display strong absorptions, and a pronounced scale compression effect [5] is evident for the peaks below 10% relative reflectance in Fig. 9a (this also occurs for the rigid polyurethane foams—especially the higher density ones—as may be seen in Fig. 5b and d). As a result of this compression, the details of the absorption peaks are not apparent, although they are observed clearly for the %T format display (Fig. 9b).

Spectra of four other types of less commonly encountered flexible polyurethane foams are shown in Figs. 10 and 11. All of the DRIFTS spectra exhibit weak absorptions (which appear much stronger in the reflectance spectra) between 2300 and 2200 cm^{-1} arising from residual isocyanate groups. Again, these absorptions are obscured in the DAC spectra. This spectral region, however, can be important in distinguishing between two different foams as may be seen by comparing the spectra depicted in Fig. 9 to those shown in Fig. 10e through h. The latter DRIFTS spectrum has an absorption at 2242 cm^{-1} not observed[5] for the former, but otherwise the two spectra are similar.

All of the flexible polyurethane foam DRIFTS spectra, with the possible exception of that depicted in Fig. 11e, display significant specular reflectance attenuations for some of the peaks. The most intense absorptions are usually the ones affected, although this is not always the case. This specular reflectance is probably due to the relatively strong absorptions of the polyurethane foams. As discussed previously [4,5], direct DRIFTS sampling of intact meprobamate tablets produces predominantly specular reflectance. Meprobamate contains two carbamate groups which is also the type of linkage used in polyurethanes; this moiety thus appears to be responsible for producing these strong absorptions.

Limitations

For the various types of foams that have been examined, it is clear that the best DRIFTS spectra are obtained for those foams having relatively low infrared absorption coefficients (such as the hydrocarbon compositions including polyethylene and polystyrene), low densities, or both. Specular reflectance distortions may become significant as deviations from

[5]The relative intensities of the two peaks comprising the 2274/2242-cm^{-1} doublet (Fig. 10g) remain constant in all of the spectra taken for different portions of this foam. This is also true for the high frequency shoulders to the isocyanate peaks of Figs. 10c and 11c. This was *not* observed to be the case, however, for the high density rigid polyurethane foam whose spectra are shown in Fig. 5c and f. The 2280-cm^{-1} peak of this foam exhibits considerable variation in intensity depending on which portion of this material was examined (using KBr pellets, direct DRIFTS sampling, and DRIFTS spectra of this foam ground with excess KBr). In some spectra this absorption has an intensity slightly less than half that of the adjacent 2140-cm^{-1} peak, while for others, it is more than twice as intense. An inhomogeneous composition for this foam (which consisted of a rectangular block 5 by 8 by 1 in. [13 by 20 by 2.5 cm]) is thus apparent. The possibility of such inhomogeneities should thus be considered when comparisons involving this type of foam are encountered.
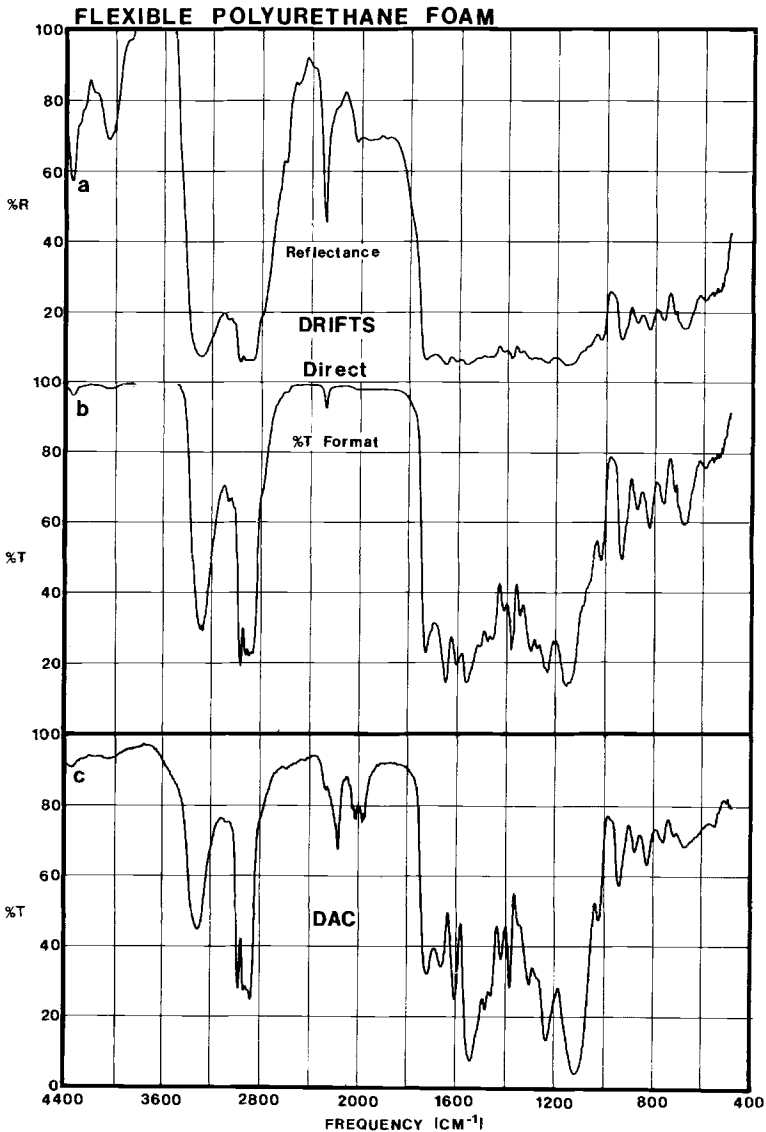
FIG. 9—(a) *Reflectance spectrum of a flexible polyurethane foam sampled directly, gain 16*R. (b) %T *format of the above spectrum.* (c) *DAC spectrum of this material.*

these criteria increase. Sample surface texture, which can be viewed as a factor somewhat analogous to particle size for powdered samples [5], also affects the amount of specular reflectance.

Even with some specular reflectance distortions, the DRIFTS spectra of most foams provide very useful information, especially if such data is to be used primarily for comparative purposes. Since the amount of specular reflectance depends on both the surface and compositional properties of the sample, the resulting distortions give, in effect, more information about the sample than just the absorption characteristics. As a practical matter, this is true provided that these effects are not too great, and also, that they are reproducible.
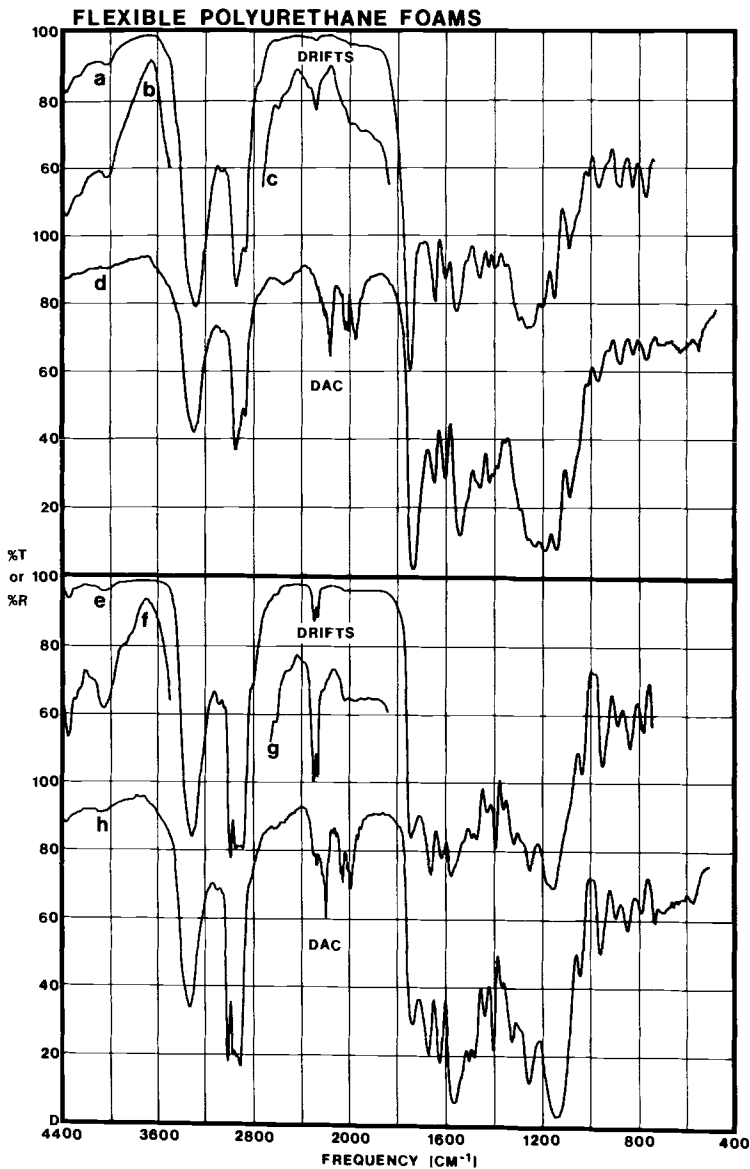
FIG. 10—*Spectra of a flexible polyurethane foam:* (a) %T *format and* (b) *and* (c) *portions of the reflectance spectra, sampled directly, gain 2R, narrow-band detector;* (d) *DAC spectrum. Spectra of a second flexible polyurethane foam:* (e) %T *format and* (f) *and* (g) *portions of the reflectance spectra, sampled directly, gain 4, narrow-band detector;* (h) *DAC spectrum.*

When specular reflectance is significant, as may be the case for the spectrum shown in Fig. 11a, much of the detail for the peaks is lost (compare to Fig. 11d). For most foams, with the exception noted for nonisotropic structures, quite reproducible results are generally obtained with DRIFTS. Reproducibility may become a problem, however, when specular reflectance is significant. For such samples, direct DRIFTS spectra can still be useful for providing information about the weaker absorptions (which are largely unaffected by specular reflectance) or observing peaks in the regions where the DAC absorbs.
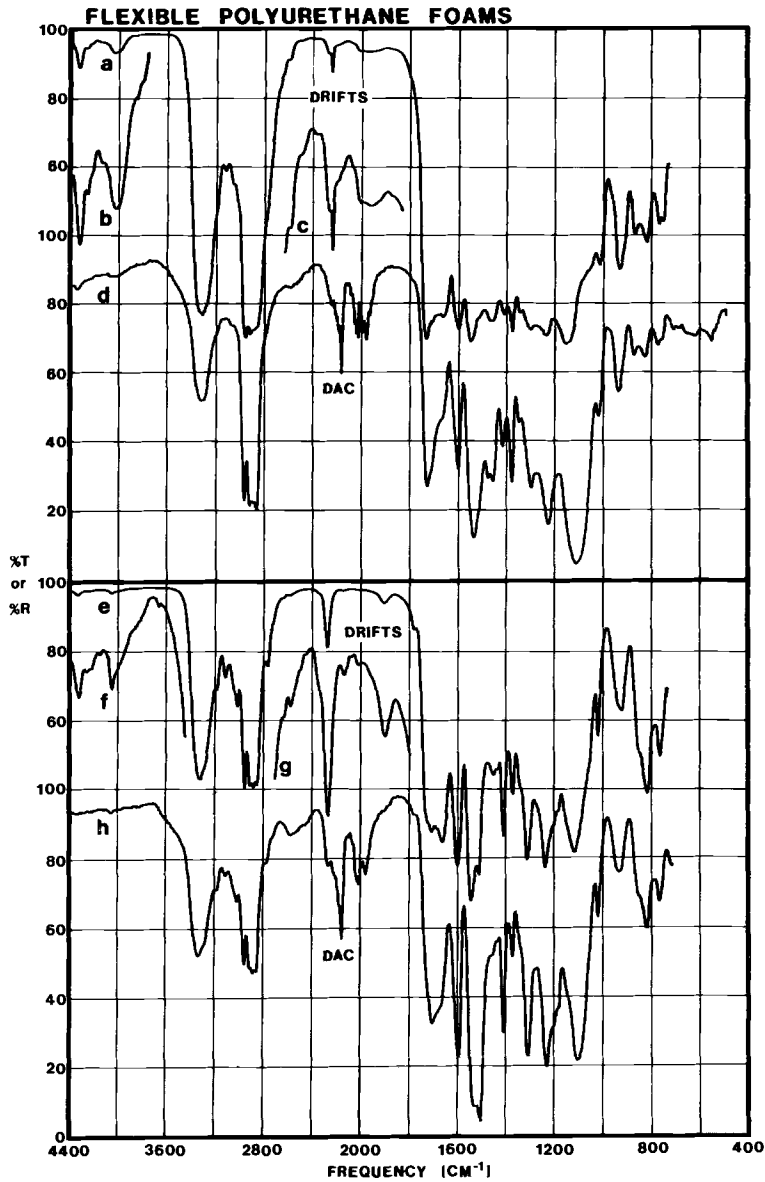
FIG. 11—*Spectra of a flexible polyurethane foam:* (a) %T *format and* (b) *and* (c) *portions of the reflectance spectra, sampled directly, gain 4, narrow-band detector;* (d) *DAC spectrum. Spectra of a second flexible polyurethane foam:* (e) %T *format and* (f) *and* (g) *portions of the reflectance spectra, sampled directly, gain 4, narrow-band detector;* (h) *DAC spectrum, narrow-band detector.*

Since the presence of inorganic fillers may be important in distinguishing between certain similar foams, the limitations arising from specular reflectance of these constituents are worth discussing. For all of the foams that have been examined which contain low to moderate concentrations of inorganic constituents, little or no specular reflectance peak attenuations are apparent. This can be seen for foams containing talc (Figs. 2 and 4), calcium carbonate (Fig. 7c to f), magnesium carbonate (Fig. 8a to d), and titanium dioxide (Figs. 6e to

h and *7c* to *f*). Because of the significant amounts of specular reflectance that occur when most inorganic compounds are sampled neat (see below), it is evident that the inorganic fillers used in these foams are finely ground and evenly dispersed in the foam matrix. Supporting this, microscopic examinations of the above foams showed either no particles, or very fine particles.

When the concentration of the inorganic material becomes significant, increasing amounts of specular reflectance may occur as seen for the foam whose spectrum is depicted
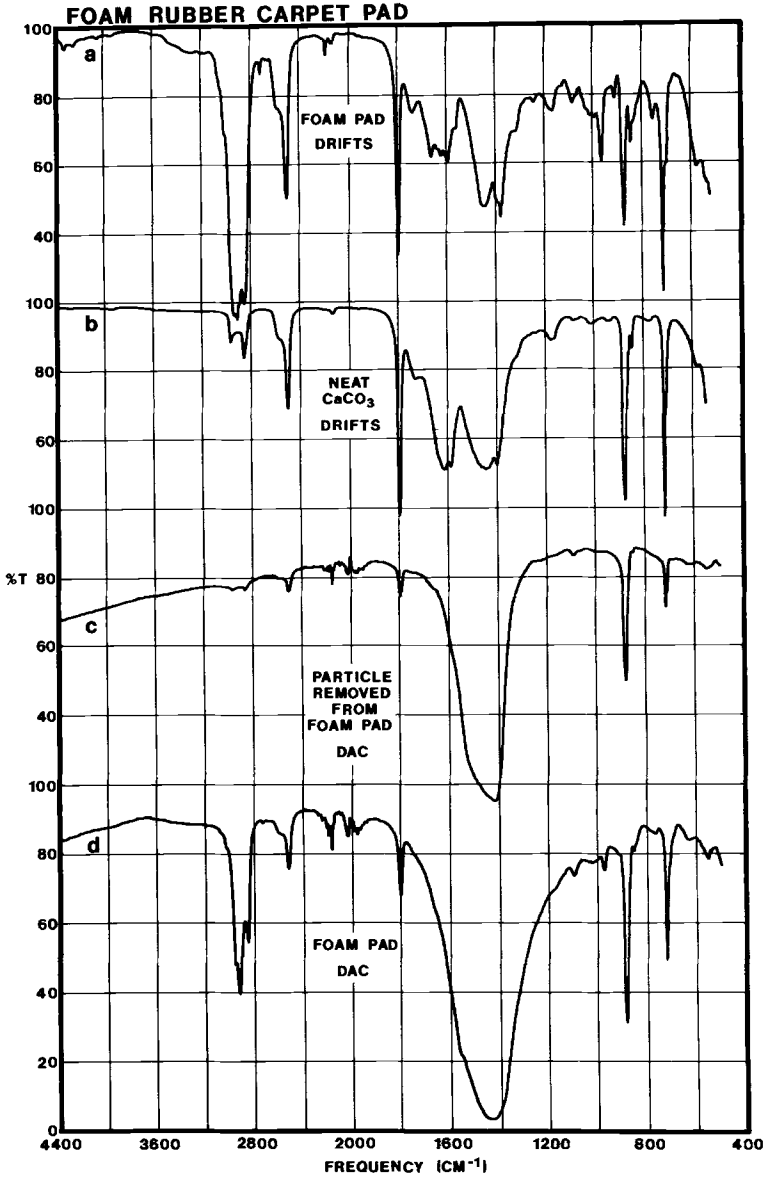

FIG. 12—(a) %T *format spectrum of a foam rubber carpet pad sampled directly, gain 8*R. (b) %T *format spectrum of ground calcite (CaCO₃) sampled neat using DRIFTS, gain 8.* (c) *DAC spectrum of a particle removed from the foam rubber carpet pad.* (d) *DAC spectrum of carpet pad.*

in Fig. 8e through h. A more dramatic example of this is shown in Fig. 12. A foam rubber carpet pad was examined and as its DAC spectrum (Fig. 12d) indicates, this sample contains a large quantity of a carbonate. A microscopic examination of this foam revealed numerous exposed particles, some as large as 0.3 mm. The DAC spectrum (Fig. 12c) of one of these, as well as other examinations, indicated the particles to be calcium carbonate. The direct DRIFTS spectrum (%T format) of this foam (Fig. 12a) has severe specular reflectance distortions, especially for the strongest carbonate peak at 1430 cm^{-1}. This peak is very strongly attenuated and as a consequence, the two weak carbonate nonfundamentals at 2515 and 1797 cm^{-1} assume unusual proportions (compare the relative intensities of these three peaks in Fig. 12c to those in 12a). A totally unrecognizable spectrum results from these effects.

The distortions observed for the DRIFTS foam spectrum are similar to those seen in DRIFTS spectra of calcium carbonate powder sampled neat (Fig. 12b). For the latter, these distortions are strongly dependent on the particle sizes; the spectrum shown (Fig. 12b) is for this powder ground to particle sizes similar to those observed on the foam rubber. Foams observed to have significant amounts of relatively large particles on their surfaces may therefore not be suitable for direct DRIFTS sampling.

As discussed previously [4], the amount of specular reflectance for a particular sample is dependent on the geometry of the diffuse reflectance accessory used [15]. The spectra depicted here may not, therefore, be exactly the same as those obtained on other instruments or accessories. This was observed to be the case for a few of the foams discussed here, which were also run on the Nicolet 5DXB FTIR using a Barnes DRIFTS accessory. Small to moderate differences in specular reflectance attenuations were observed for some of these.

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