Designation: E 1642 – 00

Standard Practice for General Techniques of Gas Chromatography Infrared (GC/IR) Analysis[1]

This standard is issued under the fixed designation E 1642; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers techniques that are of general use in analyzing qualitatively multicomponent samples by using a combination of gas chromatography (GC) and infrared (IR) spectrophotometric techniques. The mixture is separated into its individual components by GC and then these individual components are analyzed by IR spectroscopy. Types of GC-IR techniques discussed include eluent trapping, flowcell, and eluite deposition.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 131 Terminology Relating to Molecular Spectroscopy[2]

E 168 Practices for General Techniques of Infrared Quantitative Analysis[2]

E 260 Practice for Packed Column Gas Chromatography[3]

E 334 Practice for General Techniques of Infrared Microanalysis[2]

E 355 Practice for Gas Chromatography Terms and Relationships[3]

E 932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers[2]

E 1252 Practice for General Techniques for Qualitative Infrared Analysis[2]

E 1421 Practice for Describing and Measuring Performance of Fourier Transform Infrared (FT-IR) Spectrometers: Level Zero and Level One[2]

E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs[3]

3. Terminology

3.1 *Definitions*—For definitions of terms and symbols, refer to Terminology E 131 and Practice E 355.

4. Significance and Use

4.1 This practice provides general guidelines for the proper practice of gas chromatography coupled with infrared spectrophotometric detection and analysis (GC/IR). This practice assumes that the chromatography involved in the practice is adequate to separate the compounds of interest. It is not the intention of this practice to instruct the user how to perform gas chromatography properly.

5. General GC/IR Techniques

5.1 Three different types of GC/IR technique have been used to analyze samples. These consist of analyte trapping, flowcell, or lightpipe, and direct eluite deposition and are presented in the order that they were first used.

5.2 The GC eluent must not be routed to a destructive GC detector (such as a flame ionization detector) prior to reaching the IR detector as this will destroy or alter the individual components. It is acceptable to split the eluent so that part of the stream is directed to such a detector or to pass the stream back to the detector after infrared analysis if such techniques are feasible.

5.3 *Eluent Trapping Techniques*—Analyte trapping techniques are the least elaborate means for obtaining GC/IR data. In these techniques, the sample eluting from the chromatograph is collected in discrete aliquots to be analyzed. In utilizing such techniques, it is essential that a GC detector be employed to allow definition of component elution. If a destructive detector is employed, then post-column splitting to that detector is required. GC fractions can be trapped in the condensed phase by passing the GC effluent through a solvent, a powdered solid, or a cold trap for subsequent analysis (see Practice E 1252) **(1)**.[4] Vapor phase samples can be trapped in a heated low-volume gas cell at the exit of the GC, analyzed, then flushed with the continuing GC effluent until the next aliquot of interest is in the gas cell when the flow is stopped again for analysis **(2)**. Since the analyte of interest is static when employing an analyte trapping technique, the spectrum

[1] This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and is the direct responsibility of Subcommittee E13.03 on Infrared Spectroscopy.

Current edition approved March 10, 2000. Published June 2000. Originally published as E 1642 – 94. Last previous edition E 1642 – 94.

[2] *Annual Book of ASTM Standards*, Vol 03.06.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] The boldface numbers in parentheses refer to a list of references at the end of the text.

can be recorded using a long co-addition time to improve the signal-to-noise (SNR) ratio. However, in analyte trapping, sample integrity can be compromised by slow decomposition. A spectrum should be obtained with a short co-addition time first, to create a reference spectrum to ensure the integrity of the spectrum obtained after long co-addition.

5.4 *Flowcell Detection of Vapor Phase Components*—The most common GC/IR technique is the flowcell or "light-pipe" technique. The GC eluent stream is monitored continuously in the time frame of the chromatography (real-time) by the IR spectrometer with the use of a specially designed gas cell called a light-pipe. In this design, the light-pipe is coupled directly to the GC by a heated transfer line. Individual components are analyzed in the vapor phase as they emerge from the transfer line. This technique typically yields low nanogram detection limits for most analytes **(3-5).** Instruments that include the IR spectrometer, the gas chromatograph, heated transfer-line, and light-pipe are commercially available.

5.4.1 The rapidity with which spectra of the individual components must be recorded requires a Fourier-transform infrared (FT-IR) spectrometer. Such instruments include a computer that is capable of storing the large amount of spectroscopic data generated for subsequent evaluation.

5.4.2 The transfer line from the GC to the light-pipe must be made of inert, non-porous material (normally fused silica tubing) and be heated to prevent condensation. The temperature of the transfer line is normally held constant during a complete analysis at a level chosen to avoid both condensation and degradation of the analytes. Typical working temperatures are about 100 to 300°C (normally 10°C higher than the maximum temperature reached during the chromatography).

5.4.3 The light-pipe is normally gold-coated on the interior to give maximum optical throughput and at the same time minimize decomposition of analytes. The light-pipe dimensions are typically optimized so that the volume accommodates the corresponding eluent volume of a sharp chromatographic peak at the peak's full width at half height (FWHH). The light-pipe is heated to a constant temperature at or slightly higher than the temperature of the transfer line. The maximum temperature recommended by the manufacturer should not be exceeded. In general, sustained light-pipe temperatures above 300°C may degrade the gold coating and the life of the coating drops quickly with successively higher temperatures. It should be pointed out that, if a chromatographic separation requires that the GC temperature be raised above this level, it may be necessary to temporarily raise both the temperature of the light-pipe and transfer line to maximum temperature of the chromatography to avoid condensation of the eluent. If this is the case, the temperature of the light-pipe should be reduced to a safe level as soon as possible. It must be noted that repeated temperature changes to the light-pipe and transfer line will cause a more rapid aging of the seals and may cause leaks.

5.4.3.1 It should be noted that any metal surface inside the light-pipe assembly can react with, and sometimes destroy, some specific materials (for example, amines) as they elute from the GC. Consequently, it is possible to fail to identify the presence of such a compound in the mixture. This situation can be identified by comparing the response of the GC detector after the flowcell to that of a GC detector in the absence of a flowcell, or by comparing the GC/IR detector output to the results of a suitable alternate analytical technique.

5.4.3.2 The ends of the light-pipe are sealed with infrared transmissive windows. The optimum optical transmission is obtained by using potassium bromide windows, but this material is very susceptible to damage by water vapor. As the light-pipe is used, small amounts of water vapor will etch the window surfaces, and the optical throughput of the windows will drop. Eventually these windows will have to be changed. Users who expect to analyze mixtures containing water should consider using windows made of a water-resistant material such as zinc selenide, but this will result in a noticeable drop in optical transmission due to optical reflection properties of such materials.

5.4.3.3 Usage of the light-pipe at high temperatures may result in the gradual buildup of organic char on both the cell walls and end windows. As this occurs the optical throughput will drop correspondingly. Eventually the light-pipe assembly will have to be reconditioned (see 5.4.3.5).

5.4.3.4 As the temperature of the light-pipe is raised above ambient, the light-pipe emits an increasing amount of infrared radiation. This radiation is not modulated by the interferometer and is picked up by the detector as DC signal. The DC component becomes large at the normal working temperatures (above 200°C), and lowers the dynamic range of the detector. The result of this effect is that the observed interferometric AC signal is reduced in size as the temperature increases and the observed spectral noise level increases correspondingly. By raising the temperature from room temperature to 250°C, the noise level typically doubles; it is recommended that the user create a plot of signal intensity versus light-pipe temperature for reference purposes. As a consequence of this behavior, it may be advantageous to record data using relatively low temperatures for both temperature and transfer line for those GC experiments that only use a limited temperature ramp. Some instrument designs include a cold aperture between the light-pipe and the detector to minimize the amount of radiation reaching the detector (see Note 1) **(6,7)**.

NOTE 1—A cold aperture is a metal shield, maintained at room temperature, sited between the light-pipe and the detector. The infrared beam diverging from the light-pipe is refocused at the plane of the cold shield. The cold shield has a circular hole (aperture) of the same diameter as the refocused beam. After passing through the aperture and moving away from this focal point, the beam is again focused onto the detector element. This small aperture shields the detector from thermal energy emitted from the vicinity of the hot light-pipe.

5.4.3.5 The optical throughput of the light-pipe should be periodically monitored since this is a good indicator of the overall condition of the assembly. It is important that all tests be conducted at a constant temperature because of the effect of the emitted energy on the detector (see 5.4.3.4). It is recommended that records be kept of the interferogram signal strength, single-beam energy response, and the ratio of two successive single-beam curves (as appropriate to the instrument used). For more information on such tests, refer to Practice E 1421. These tests will also reveal when the MCT detector is performing poorly due to loss of the Dewar vacuum and consequent buildup of ice on the detector face. MCT

detectors, as discussed in this text later, are commonly used for these experiments as they provide greater detectivity and faster data acquisition.

5.4.3.6 Care must be taken to stabilize or, preferably, remove interfering spectral features resulting from atmospheric absorptions in the optical beam path of the spectrometer and the GC/IR interface. Best results will be obtained by purging the complete optical path with dry nitrogen gas. Alternatively, dry air can be used for the purge gas which will lead to interferences in the regions of carbon dioxide absorption (2500 to 2200 cm^{-1} and 720 to 620 cm^{-1}). Commercially available air scrubbers that remove water vapor and carbon dioxide also provide adequate purging of the spectrometer and GC interface. In some instruments, the beam path is sealed in the presence of a desiccant, but invariably interferences from both carbon dioxide and water vapor (1900 to 1400 cm^{-1}) will be found. If the purge is supplied to the interface when preparing to carry out a GC/IR experiment, the atmosphere must be allowed to stabilize before data collection commences. Atmospheric stability inside the instrument can be judged by recording the single-beam energy response and the ratio of two successive single-beam spectra.

5.5 *Direct Deposition GC/IR*—The direct deposition GC/IR technique can follow either of two methods, that of matrix isolation **(8)** or continuous subambient temperature analyte trapping **(9)**. In both of these methods, the gas chromatographic effluent is passed through a heated transfer line and is deposited onto a cold substrate. These methods permit detection as low as subnanogram amounts of material. The subambient temperature of the substrate necessitates the use of an evacuated chamber to avoid condensation of atmospheric gases. By freezing the eluite onto the cold substrate, the components of the sample are effectively stored there. It is possible, therefore, to analyze the sample after the GC/IR experiment has finished, as well as perform real-time analyses.

5.5.1 In the matrix isolation method, a small amount of argon is added to the helium carrier gas. The column effluent is directed onto a substrate maintained at a temperature of about 13K. Argon is condensed to form a solid matrix while the helium carrier gas is pumped away. It is important that any component eluting from the chromatograph is entrained in this argon matrix at a concentration (<0.2 %) sufficiently low such that each analyte molecule is surrounded by argon atoms and is isolated from other analyte molecules. An instrument has been devised in which the beam from the FT-IR spectrometer passes through the track of argon, is reflected from the gold surface, is transmitted a second time through the argon, and is finally focused onto the detector **(8)**. Additionally, other matrix isolation interface devices are available from vendors.

5.5.2 In the case of the continuous subambient temperature trapping method, the sample is deposited directly onto an infrared transmissive plate maintained at the temperatures sufficient to condense analytes from the eluent. The temperature of this substrate is maintained by Peltier cooling or with liquid nitrogen. The transmissions mode of infrared analysis is used to obtain the spectroscopic data.

5.5.3 Direct deposition techniques provide the advantage of greater sensitivity for real-time measurements. Additionally, extended co-addition of spectra post-run permits further improvement of the signal-to-noise ratio of spectral results. However, slow sublimation of the analyte recrystallization of the sample or ice formation, or both, may occur with direct deposition techniques. It is prudent to obtain a spectrum with a short co-addition time initially to create a reference spectrum. This will ensure the integrity of the spectrum obtained after longer co-addition times.

6. Significant Parameters for GC/IR

6.1 Where the instrumentation used is commercially available, the manufacturer's name and model numbers for the total GC/IR system, or the individual components, should be given. The various instrumental and software parameters which need to be recorded are listed and discussed in this section. In addition, any modifications made to a commercial instrument that affect the instrument's performance must be clearly noted.

6.2 *Instrumental Parameters (IR)*:

6.2.1 *Detector*—The detectors typically used for GC/IR are the mercury-cadmium-telluride (MCT) narrow band photodetectors of high sensitivity, that have a lower frequency limit of approximately 700 cm^{-1}. It is possible to measure spectra to frequencies lower than 700 cm^{-1} by using an MCT detector that has a broader band spectral response, but the sensitivity of such detectors is significantly lower. The MCT detector should not be operated in a light saturating condition so as to maintain linearity of signal response. Nonlinear response is found as a non zero signal intensity below the detector cut-off point in the single beam spectrum.

6.2.1.1 *Flowcell Temperature*—For flowcell GC/IR, the gas cell or light-pipe is usually maintained at a constant temperature between 200 and 300°C (ca. 10 degrees above maximum temperature of the chromatographic separation) such that condensation of analytes does not occur. See 5.4.3 for more details. The actual temperature of the cell should always be noted with the spectrum.

6.2.1.2 *Deposition Conditions*—For direct deposition GC/IR, the temperature of the deposition surface and the speed of its motion should be noted. In the case of matrix-isolation GC/IR, the ratio of argon gas to helium carrier gas should be given, or preferably, for a particular sample spot the ratio of sample to argon matrix should be given (if known). Spot size of the deposit is directly determined by the diameter of the capillary restriction end and the distance separating the restriction end from the deposition surface. If these distances are known, they should be noted appropriately.

6.2.2 *Transfer Line Temperature*—The temperature of the transfer line should be noted. This should always be higher than the highest temperature achieved by the GC oven during the experiment (see 5.4.2), but at or slightly below that of the light-pipe.

6.3 *Instrumental Parameters (GC)*—The success of the GC/IR experiment is dependent on good chromatographic practices. It is not the purpose of this practice to discuss those practices in detail, but for convenience, a list of the important GC parameters to be noted is also given. Refer to Practices E 260, E 355, and E 1510 for proper measurement and reporting of these parameters.

6.3.1 *Chromatographic Column*—The length and internal

diameter of the column, along with the type and thickness of column coating (stationary phase) employed, must all be noted.

6.3.2 *Temperature Profile*—The temperature profile should be specified in detail, including any initial delay or final hold time.

6.3.3 *Carrier Gas*—The type of carrier gas used (normally helium) should be noted. More importantly, the flow rate of the carrier gas must be recorded with its measurement at a specified oven temperature (normally room temperature) and the light-pipe and transfer line at working temperature. The linear velocity of the carrier gas through the column is also a useful parameter to note. In addition, some GC ovens are equipped with pressure programming, in order to maintain a specified flow rate as the oven temperature increases. This feature maintains the resolution of the chromatographic peaks as the GC oven temperature is varied, and its presence (or absence) should be noted.

6.3.3.1 Proper care should be taken to be certain that the carrier gas is clean, that is, free of moisture, carbon dioxide and other molecular contaminants. This is particularly important in the use of the direct deposition GC/IR method as carrier gas contaminants will co-deposit with the eluite and lead to contamination of spectral information.

6.3.4 *Injection*—The sample size; solvent matrix; solvent dilution factor (if appropriate); injection temperature; and type of injection employed, that is, split (with split ratio), splitless, or on-column, are all critical parameters that must be recorded.

6.3.5 *Chromatographic Detector Employed*—If a chromatographic detector is employed, in addition to the IR analysis, then the following information should be listed: type of detector, scale expansion on the integrator, and whether the detector is serial (after) the light-pipe, or parallel to it by side-splitting (in which case the split ratio should be specified).

6.4 *Software Parameters*:

6.4.1 *Apodization Function*—For Fourier transform infrared spectrometers, it is recommended that an apodization function be applied to the interferograms before computation of spectral data. Suitable apodization functions include triangular, Beer-Norton medium, Happ Genzel, and cosine.

6.4.2 *Spectral Resolution*—A compromise between the SNR of a spectrum and its information content leads to an optimum resolution for GC/IR spectra of 8 cm^{-1} if recorded in real time, and 4 cm^{-1} if recorded subsequently on a trapped sample (see Note 2).

NOTE 2—Most conventional light-pipe GC/IR instruments are optimized to record a spectrum at 8-cm^{-1} resolution in approximately 1 s. This allows for adequate sampling of the spectral data as a chromatographic peak flows through the light-pipe. Thus, the optimal SNR is obtained for spectral data with minimal loss of chromatographic resolution.

When examining samples by cryogenic deposition GC/IR, real-time data are again optimally collected at 8-cm^{-1} resolution for the above reason. When employing post-run signal averaging, however, data are normally collected at a better resolution (such as 4 cm^{-1}) to increase the information content of the spectra, and also to match the resolution of available spectral libraries suitable for solid-phase samples.

6.4.3 *Spectral Co-addition*—During real-time data acquisition it is normally advantageous to co-add several scans per time increment (generally, a 1-s time frame) to improve the SNR of the result. The actual number of co-additions depends on the selected scanning speed and spectral resolution. Typical instrumental operation would permit co-addition of four to ten scans during each time increment, that is, a discrete infrared spectrum is stored approximately every second. Spectral averaging may be performed during post-run data processing. Here, the SNR improvement is limited to the total elution time of an analyte.

6.4.4 *Data Storage Thresholding*—This function must be recorded if used (see 7.2).

6.4.5 *Additional Processing*—If any smoothing functions, baseline correction algorithms, or spectral subtractions are applied to the spectral data either during acquisition or with post-run data manipulation, these must be reported. It should be pointed out that most commercial GC/IR instruments provide the operator only a limited control over these functions and that these functions may be operating automatically. The operator should investigate as to whether an instrument's operational software includes such functions and is configured properly for data acquisition.

7. Software Treatment of Infrared Data

7.1 *Gram-Schmidt Reconstruction*—As each interferogram is recorded during the chromatographic separation, a method called the Gram-Schmidt Reconstruction **(10, 11)** quickly determines the information content of the interferogram. In this method, a set of scans is recorded before the sample is injected into the GC. These interferograms are used to create a series of basis vectors that represent the instrument background profile. During the experiment, each stored interferogram is used to generate a similar set of vectors, and a comparison of these new vectors against the reference set is performed (generally in real-time) to give a measure of the presence, or absence, of material eluting from the GC, and its relative concentration. The resulting plot of vector intensity versus time indicates how the total infrared absorbance (across the spectral range being measured) changes during the experiment. This is called the Gram-Schmidt reconstructed chromatogram and, is similar in appearance to the response from a flame-ionization or thermal conductivity detector. This chromatogram is normally displayed on the computer screen or the plotter.

7.2 *Data Storage Thresholding*—With older instruments the very large amounts of spectra recorded during a typical GC/IR experiment are more than can be stored with the available computer. Because of this, some software sets monitor the signal strength of the infrared data (by using the Gram-Schmidt reconstructed chromatogram), and will only store spectral data when a peak from the GC exceeds a preset threshold value, that is, discontinuous spectral storage. It is possible that, if a minor component is not detected during elution, no spectral data are stored for it. With current computer data storage capabilities, data storage thresholding is largely ignored, as the typical GC/IR files sizes (up to 30MB) are easily accommodated.

7.3 *Functional Group Chromatograms*— As each interferogram is recorded, it may be converted to a spectrum in real-time. In this case, a useful operation is to integrate selected regions of the spectrum immediately, and to present these to the screen display or plotter, along with the GramSchmidt reconstructed chromatogram. Commonly selected regions of the infrared spectrum, and some selected functional groups that

can be monitored in this way are as follows:

Saturated Hydrocarbon: 3000 to 2850 cm^{-1}
Carbonyls: 1800 to 1650 cm^{-1}
Ethers and Esters: 1300 to 1000 cm^{-1}
Unsaturated and Aromatic Hydrocarbons: 3150 to 3000 cm^{-1}
Unsaturated Hydrocarbons: 850 to 700 cm^{-1}

7.4 *Spectral Searching*—The normal purpose of the GC/IR experiment is to identify the individual species that are separated by the GC experiment. In order to do this, absorbance spectra of each component are generated, either automatically or with operator attention. These spectra are then compared individually to a library of pure compound spectra that is stored on the computer disk. The computer uses one of several algorithms to correlate which library spectra match the sample spectrum most closely, and to rank these in order of their match quality.

7.4.1 It should be stressed that the results of a computer search cannot be relied upon to always give the correct answer. Potential problems that the user should consider include incorrect library entries, differences between the temperatures at which the library and unknown spectra were recorded, differences in the phase of sample from which the spectrum was recorded, absence of the relevant spectrum from the library, low SNR of the measured spectrum, and similarity between the reference spectra of members of a homologous series. The analyst should therefore always verify the computer result by visually comparing the spectrum of the best matches to the spectrum of each sample.

7.4.2 An important parameter to be considered when utilizing spectral searching is the search algorithm being employed. Some algorithms, such as the Euclidean algorithm, match the spectrum point by point with each entry in the database. This method takes into consideration the relative intensity, shape, and frequency of each spectral feature, but places the heaviest importance on strong, broad features. If the derivative of the spectrum is compared to the derivative of each library entry, however, emphasis is placed instead on the peak frequencies of sharp bands. Any shifts in peak frequencies between the spectra of the sample and standard will therefore lead to poor matches when using the derivative algorithm. When considering which algorithm to use, the sharpness of spectral features and similarity in physical conditions of the sample and database standards should be taken into account. As several search algorithms are available, it is important to understand how each one operates upon the spectral data and library databases to obtain effective use of spectral searching.

7.4.3 It is common practice for users to generate their own libraries containing spectra of samples that they expect to analyze on a routine basis. These spectra can then be obtained under identical conditions to those used for the GC/IR experiment. Recommendations for the generation of reference data in spectral libraries are available (see Note 3) **(12)**.

NOTE 3—Libraries of spectral data are available from commercial sources. For light-pipe GC/IR the most suitable libraries are those which contain spectra recorded using gaseous samples. Condensed phase GC/IR data are generally matched against spectra recorded for solid phase samples. Similarly for matrix-isolation GC/IR, a library of matrix isolation reference spectra should be used. For subambient temperature analyte trapping, it is often possible to use the much larger libraries of condensed-phase reference spectra where the samples have been prepared either as KBr disks or mineral-oil mulls. If the library available was recorded for a different phase, then problems can be minimized by setting the computer search to ignore data above 2000 cm^{-1}.

7.5 *Spectral Subtraction*—With the advent of Fourier-transform spectrometers, this mathematical tool may be used to improve the quality of match before performing a spectral search and has proven very useful in resolving analytes eluting as overlapping chromatographic peaks. Additionally, the spectrum of a reference material, in absorbance, may be subtracted by computer from the absorbance spectrum of a mixture until the contribution of that reference spectrum is removed from the spectrum of the mixture. In this manner the spectrum of the pure sample can be obtained. *However, this procedure should only be used when poor results are obtained in its absence. It should be cautioned that invalid results can be obtained from improper subtraction, especially when the spectrum recorded was of low intensity*.

7.5.1 When performing a GC/IR experiment, it is often possible to generate a reference spectrum of an interferent (for example,“ column bleed”) by examining the spectra collected close to the elution time of the eluite peak. Typically, regions of the chromatogram where no analytes have eluted are selected to obtain a reference spectrum of the carrier gas and contaminants such as column bleed. However, it should be pointed out that the use of the thresholding algorithm (see 7.2) during data collection will generally mean that absorbance spectra of baseline regions cannot be generated for this purpose since no data were stored at that time.

7.5.2 If the absorbance spectra generated contain significant spectral interferences from atmospheric water vapor or carbon dioxide, then a reference spectrum of one or both of these compounds may be subtracted from the spectrum of each peak. Typically, these interferences will be observed also in the spectra of the baseline (where no analytes are eluting), so that a reference spectrum may easily be generated close to the elution time. It is sometimes possible to have the software automatically remove spectral contributions from both of these components.

7.5.3 If the chromatographic peak of interest is close to or overlapping the strong peak due to the eluting solvent, then spectral subtraction should be employed to remove contributions from the solvent in the spectrum of that peak.

7.5.4 The spectra of chromatographic peaks should be inspected for the contamination of the eluent by “column bleed,” especially towards the latter part of the experiment when the oven is the hottest. Typically, this bleed is made up of silicones, that show a sharp, strong infrared absorption band close to 1260 cm^{-1}, with broader, very intense absorptions in the region of the spectrum between 1200 and 1000 cm^{-1}, and a weaker band near 800 cm^{-1}. If such evidence is observed, then a suitable reference spectrum may normally be generated from the neighboring baseline and be subtracted from the spectrum corresponding to each peak. Similar problems can also arise from “septum bleed” when using on-column injection; it is possible to avoid these by using a septum-free, “duck-bill” injector.

7.5.5 On occasions, two chromatographic peaks will elute at similar times, so that they overlap each other. Since the width

of each individual peak is typically several seconds, it is often possible to generate separate spectra of the leading edge and trailing edge of the overlapped region. Depending on the difference in elution times between the two peaks, these two spectra may represent the two pure compounds, or mixtures of both. In the latter case, variable-ratio subtraction of the spectrum of the trailing edge from that of the leading edge will give the spectrum of the pure compound that elutes first, and *vice versa*.

8. Standard Samples

8.1 A standard test solution should be used on a regular basis to test the instrument response and indicate when problems have occurred with either the IR spectrometer or the GC. The parameters discussed in Section 6 need to be reproduced exactly each time. The actual sample, and concentration of the test mixture used will depend on the type of analysis being performed. The test procedure involves calculation of the SNR of the GC/IR spectrum of the test sample, recorded on-the-fly. During this procedure the SNR may be calculated in terms of either peak-to-peak noise or root-mean-square noise, but the method used to generate the SNR must be specified. The user is also referred to the instrument documentation supplied by the equipment manufacturer.

8.1.1 The recommended standard sample for a vapor-phase GC/IR system is a dilute solution of dodecane in hexane. A typical test mixture is made by adding 2.6 µL of dodecane to 100 mL hexane solvent, and then injecting a 1-µL sample of the mixture using splitless or on-column injection. This gives an injection of 20 ng of dodecane. A typical GC column is a 30-m DB-5 column, having 0.32-mm internal diameter (ID) and 0.25-µm coating thickness. A helium flow rate of 6 mL/min is recommended. The GC/IR light-pipe and transfer line should be maintained at 250°C. The oven temperature should be held at 40°C for 1 min after injection, then ramped at 25°C per minute to 240°C, and held at this temperature for 3 min. Under these conditions the dodecane will elute after about 7 min. The noise level in the region of the infrared spectrum between 2000 and 2200 cm^{-1} should be ratioed to the peak height of the 2930-cm^{-1} band of the dodecane, and this value for signal-to-noise ratio recorded. Under normal conditions, the peak absorbance near 2930 cm^{-1} will be about six milli-absorbance units (dependent on the light-pipe dimensions).

8.1.2 An alternative standard solution is isobutylmethacrylate in hexane. However, it should be noted here that isobutylmethacrylate suffers two drawbacks as a standard material. It is subject to polymerization over time, and so it is advisable to use a fresh solution if possible, as even under refrigeration the solution is good for only about one month. Secondly, it is a toxic, lachrymatory substance that should only be handled in its pure form and always with suitable precautions. This alternative standard is prepared using 2.2 µL of isobutylmethacrylate in 100 mL of hexane (20 ng μL^{-1}). In this case the observed noise level in the spectrum between 2000 and 2200 cm^{-1} should be ratioed to the peak intensity at about 1740 cm^{-1}. A 1-µL splitless injection is made. The suggested GC column is a 30-m SE54 column having 0.32-mm inside diameter and 0.25-µm coating thickness. The GC/IR light-pipe and transfer line should be maintained at 180°C. The oven temperature should be held at 60°C for 5 min after injection, then ramped at 30°C/min to 150°C and held at this temperature for 5 min. Under these conditions the isobutylmethacrylate will elute after about 4 min. The noise level in the region between 2000 and 2100 cm^{-1} should be ratioed to the peak height of the 1740-cm^{-1} ester band of the methacrylate, and this value for signal-to-noise ratio recorded. Under normal conditions, the peak absorbance near 1740 cm^{-1} will be about four milli-absorbance units (dependent on the light-pipe dimensions).

8.1.3 For the cryogenic deposition systems a more complex mixture of three components is recommended. These compounds should have a range of polarities, have their strongest infrared absorptions in different regions of the infrared spectrum, and be well resolved chromatographically. A suggested mixture is isobutylmethacrylate, 3-ethyl phenol, and dodecane made by dissolving 1 µL of each component in 250 mL of hexane. This mixture should be stored and handled in accordance with 8.1.2. A test mixture of 1.8 µL is injected using a split ratio of 30:1, to give approximately 270 pg of each component for the analysis. A15-m DB-5 column with 0.25-mm inside diameter and 0.25- µm coating thickness is used. The injection temperature is 250°C. The oven is held at 90°C for 2 min, then ramped at 20°C/min up to 160°C. All components will typically elute in less than 8 min under these conditions. The observed absorbance will depend on the deposition method being employed.

9. Sampling Criteria

9.1 The sampling criteria for the various GC/IR techniques depend on the application of the analysis. The advantages and disadvantages of each sampling technique are discussed (see Section 5) and these must be taken into consideration when determining the best method of combined separation and identification for a particular analysis.

10. Qualitative Information

10.1 In the GC/IR analysis the infrared spectrometer acts as a GC detector. When using an FT-IR spectrometer there are several different chromatographic representations that may be obtained from the on-line data collection in order to assist the analysis. The Gram-Schmidt reconstructed chromatogram (see 7.1), which resembles the traditional GC detector chromatogram, can be used for location of spectroscopic data files having the spectrum of each component. Infrared functional group chromatograms (see 7.3) can selectively detect compounds having desired functional groups, or separate data for compounds that elute together.

10.2 Spectral identification by data base searching is a recommended step in the GC/IR analysis. Best results will be obtained when the physical state of the standards used to create the data base matches that of the analyte. In particular, vapor phase GC/IR should be used in conjunction with a data base recorded for gaseous standards, where the standards were held at elevated temperatures, if available. Matrix isolation GC/IR results should be used in conjunction with a database recorded for standards deposited in a similar fashion using the same instrument type, temperature Ar/He ratio, of the analyte deposition. Similarly, the best results for subambient temperature depositions is to use a reference database collected in the same

fashion as the analyte deposition or use a condensed phase spectral database.

10.3 For a more reliable validation of the identity of a chromatographic peak, a suitable reference sample should be examined by GC/IR using identical conditions. In this procedure, it is important that the chromatographic retention times be matched, as well as the spectra of the unknown and the reference. Alternatively, other analytical techniques can be used for verification of the identity of the unknown sample.

11. Quantitative Information

11.1 Quantitation of data obtained by light-pipe GC/IR has been a concern in the past. The infrared beam passing through a light-pipe may undergo a number of reflections inside the path, and thus have an indeterminate pathlength. However, it has been shown **(7)** that the off-axis rays are severely attenuated and so the effective pathlength of a light–pipe is almost exactly equal to its length. It has also been shown **(13)** that when the volume of the light-pipe is equal to the FWHH, (that is, the usual GC/FT-IR criterion), the maximum quantity of sample in the light-pipe is less than 80 % of the injected quantity, and the concentration changes rapidly with time (see Note 4). Because the sample concentration varies appreciably during the measurement for the vapor phase GC/FT-IR sampling, it may result in spectra that have a low accuracy of frequency and relative absorbance for some bands. Even so, reasonably accurate quantitative information can be obtained by light-pipe GC/IR, and measured values within 10 % of the actual quantities are attainable with careful reproduction of experimental parameters. In order to obtain quantitative results, comparison should be made to standard samples examined under identical conditions.

NOTE 4—To maintain quantitative results for GC/IR data obtained by this technique, the volume of the light–pipe would have to be greater than 4 times the full width of the GC peak at half its peak concentration (FWHH). This would ensure that all of the known injected amount of sample is in the light–pipe during the measurement, but would severely degrade the chromatographic resolution.

11.2 The amount of each material present in the mixture can be ascertained from a GC chromatogram generated from detectors other than the GC/IR detector. In this case, the quantity of each analyte can be calculated from the GC parameters (that is, flow rate, injected sample quantity, etc.) and the peak area from the GC integrator if a standard sample is available to calibrate the GC response. Quantification by other detection methods is described by Practices E 168 and should be performed in accordance with that practice.

11.3 It should be noted that the direct deposition techniques were designed for low detection limits with small sample quantities. If increasingly large sample quantities are injected and absorbance values exceed 1 au for any spectral band, deviations from Beer's Law may occur. While detection limits differ substantially between direct deposition and other GC/IR methods, the linear range is approximately equal, that is, two to three orders of magnitude. Proper care in the selection of GC column capacities and separation parameters is necessary to ensure correct detection flowcell GC/IR methods. Additional descriptions on quantification via GC/IR are found in the literature (**14,15**).

11.4 When using analyte trapping techniques, estimates of sample quantities can be complicated by the possibilities of sample condensation or degradation in the vapor phase, or by sample sublimation or recrystallization in the condensed phase.

11.5 Integration across the appropriate spectral region or simply measurement of peak height from the Gram-Schmidt reconstructed chromatogram can also be used for quantitation. These methods can yield values of good precision and accuracy and are similar to quantitation of GC data **(11)**.

12. Record of the Data

12.1 It is recommended that the raw spectroscopic data be stored if physically possible; otherwise the computed spectra should be saved.

12.2 *Storage of Raw Data*—All current GC/IR technology is based on rapid scanning FT-IR spectrometers. Some of these instruments store the raw data as interferograms while the others store computed (and ratioed) spectra in absorbance or transmittance format. These raw data may be as much as 30 megabytes, or even more, depending on the data format, computer word length, and length of the chromatography experiment. Ideally, the raw data should be stored on a magnetic or optical media such as a hard drive, tape backup or read/writable compact disk. In this case, the relevant background single-beam spectrum, vectors calculated for Gram-Schmidt Reconstruction, and the Functional Group and Gram-Schmidt chromatograms should all be stored with the data. These extra files may be required by the software to reanalyze the raw data files. It is very important to store an information file that contains not only the instrumental parameters, as in Section 6, but also a record of the sample identity, solvent matrix, and any treatment carried out on the sample.

12.3 *Storage of Computed Spectra*—In addition to the raw data, as discussed in 12.1, the GC/IR experiment will result in a series of infrared spectra corresponding to some, or all of the chromatographic peaks. These spectra occupy a substantially lower amount of storage space than the raw data, and can often easily be saved on a more convenient medium, such as a floppy disk. Again, all instrument parameters, sample identity information, and so forth, should also be stored on the same medium. These spectra are then readily available for subsequent plotting, searching, or other use. It may also be useful to store them with the raw data, in accordance with 12.1.

12.4 *Spectral Interchange*—A universally compatible format for digital storage of data, JCAMP-DX, has been developed **(16)**. This protocol is generally useful for transferring individual spectra between instruments of different manufacturers, but it is not likely that the very large raw data files will be transferable in this way due to limitations of storage space and RS232 transfer speed. All instrument manufacturers have provided or are in the process of producing provisions for converting digitally stored data in their own software formats to that of the universally transportable JCAMP-DX. It is recommended that data be handled in accordance with each instrument manufacturer's specification that would allow for conversion into JCAMP-DX for maximum versatility.

12.5 *Information to Appear With the Spectrum*—The sample identification and source of the sample, if known, should appear with the spectrum. The solvent matrix and any

sample preparation should also be noted. An indication of the quantity of sample should be given, together with the path-length, volume, shape, and temperature of the cell or sample substrate. The sampling method should also be given. If flow-through GC/IR techniques are used, the half width of the GC peak (in seconds), the carrier gas flow rate (in cm^3s^{-1}) at the analyte retention time, and the data acquisition time (in seconds) should be stated. The make and model of the spectrophotometer should be recorded, as well as the model name or number of the GC/IR interface. For spectra measured on dispersive spectrometers all changes of gratings and filters should be recorded, together with the wavenumbers at which they occur. The date on which the spectrum was measured should also be given.

13. Other Techniques (17)

13.1 In general, any sampling technique that is normally used in conjunction with gas chromatography is applicable to GC/IR analysis. These sampling techniques, such as headspace, pyrolysis, and thermal desorption sampling greatly extend the types of samples that can be studied by GC/IR from the normal solution and gaseous samples to include some solid samples. This allows GC/IR analysis to be utilized for a broad area of applications. These alternate techniques would follow the same fundamentals for obtaining good infrared spectra as described herein and assume that the operator is able to perform good practices for the alternate part of the application.

13.2 *Headspace GC/IR*—This involves the study of volatiles that are found in the vapor phase above a condensed phase sample. The actual sample can be a solution or a solid matrix, but will not be a pure material. The sample is sealed into a small vial fitted with a septum cap, and allowed to equilibrate at a constant temperature, commonly above ambient. A vapor-phase aliquot is then withdrawn by syringe, and injected into the GC. A typical injection volume is 1 mL. The relative concentrations of the analyte(s) in the matrix and the headspace will be governed by the normal thermodynamic partition coefficient, and thus by the temperature. Because of this, the concentration of a particular analyte, with reference to the matrix material, may be two to three orders of magnitude higher in the headspace than in the condensed phase matrix, that leads to a significant increase in sensitivity to that analyte.

13.2.1 In the case of a solution, the polarity of the solvent will govern the behavior of each analyte in a headspace analysis. Analytes with the same polarity as the solvent will be predominantly retained in the solution, whereas those analytes with opposing polarities will preferentially move to the headspace. Thus, the increase in sensitivity using headspace analysis will be greatest for polar analytes in non-polar solvents (for example alcohols in gasoline), and non-polar analytes in polar solvents (such as hydrocarbons in water). In general, increase in temperature will increase the headspace concentration of both analyte and solvent, and the relative increase is a function of the volatility of each component.

13.2.2 One particularly important use for headspace GC/IR is in the analysis of non-polar species in water. Water is a difficult solvent for analysis by GC, and is especially troublesome for GC/IR, for two reasons. Firstly, water has an intense IR spectrum, and even small amounts of solvent interference will swamp the spectrum of an analyte. Secondly, the optimum window material for the GC/IR light-pipe, in terms of optical throughput, is potassium bromide, which is immediately damaged by the passage of a significant amount of water vapor. Water can be handled by GC/IR if the light-pipe windows are constructed of zinc selenide, but these reduce the optical throughput, and thus, the signal-to-noise ratio of the results by a factor of two.

13.2.3 The headspace concentration of non-polar analytes above a polar solvent (in particular water) can be greatly increased by the addition of an ionic salt to the solution. This technique is known as “salting out” the analytes.

13.2.4 Analytes in samples that are a solid matrix, such as soil or a polymer, can be examined by headspace analysis. This technique is therefore useful for the observation of volatile organics in such samples, without the necessity for solvent extraction.

13.3 *Thermal Desorption GC/IR*—This is a similar technique to headspace GC/IR. An adsorbent material, conveniently sold in a sorbent tube, is used to adsorb volatile species from a gas stream (normally air). The sorbent tube is then sealed, and then heated to release the volatiles. The resulting vapor phase is then injected into the GC for analysis. This technique is very useful for monitoring air for hazardous components at very low levels, since the sorbent material concentrates the volatiles from many litres of air into a volume of a few millilitres.

13.4 *Pyrolysis GC/IR*—This is an extension of the common pyrolysis GC method for analysis of polymers. The pyrolysis may be performed by simply “flash” heating the sample; more sophisticated pyrolysis accessories allow for more control of the heating rate, by the use of pulsed heating or programmed heating. Pyrolysis by programmed heating is generally used to study materials at a faster rate than can be accomplished by using thermogravimetric analysis infrared spectroscopy (TGA/IR) (see Practice E 334), but at a slower rate than the flash heating **(3)**.

13.4.1 Some polymers, such as poly(ethyl methacrylate) **(3)**, degrade to give relatively simple mixtures of monomeric fragments. On the other hand, when complex materials such as polymer blends are pyrolyzed, the resulting chromatograms (often called pyrograms) can be very rich. Because of this, the analysis often involves the comparison of pyrograms from a series of related materials such as polymers having different degrees of crosslinking.

14. Keywords

14.1 gas chromatography; GC/IR; infrared spectroscopy

REFERENCES

(**1**) Willis, H. J., van der Maas, J. H., and Miller, R. G. J., *Laboratory Methods in Vibrational Spectroscopy*, 3rd Edition, Wiley and Sons, Chichester, UK, 1987, pp. 327–362.

(**2**) Rossiter, V., *American Laboratory*, Vol 14, No. 2, 1982, pp. 144–152.

(**3**) Herres, W., *HRGC-FTIR: Capillary Gas Chromatography—Fourier Transform Infrared Spectroscopy: Theory and Applications*, Huthig, 1987.

(**4**) White, R., *Chromatography/Fourier Transform Infrared Spectroscopy and Its Applications*, Marcel Dekker, Inc., 1990.

(**5**) Griffiths, P. R., and de Haseth, J. A., *Fourier Transform Infrared Spectroscopy*, Wiley Interscience, 1986.

(**6**) Brown, R. S., Cooper, J. R., and Wilkins, C. L., *Analytical Chemistry*, Vol 57, 1985, pp. 2275–2279.

(**7**) Henry, D. E., Giorgetti, A., Haefner, A. M., Griffiths, P. R., and Gurka, D. F., *Analytical Chemistry*, Vol 59, 1987, pp. 2356–2361.

(**8**) Reedy, G. T., Ettinger, D. G., Schneider, J. F., and Bourne, S., *Analytical Chemistry*, Vol 57, 1985, pp. 1602–1609.

(**9**) Haefner, A. M., Norton, K. L., Griffiths, P. R., Bourne, S., and Curbelo, R., *Analytical Chemistry*, Vol 60, 1988, pp. 2441–2444.

(**10**) deHaseth, J. A., and Isenhour, T. L., *Analytical Chemistry*, Vol 49, 1977, pp. 1977.

(**11**) Sparks, D. T., Lam, R. B., and Isenhour, T. L., *Analytical Chemistry*, Vol 54, 1982, pp. 1922–1926.

(**12**) Kalasinsky, K. S., Griffiths, P. R., Gurka, D. F., Lowry, S. R., and Boruta, M., *Applied Spectroscopy*, Vol 44, No. 2, 1990, pp. 211–215.

(**13**) Griffiths, P. R, *Applied Spectroscopy*, Vol 31. No. 4, 1977, pp. 284–288.

(**14**) Diehl, J. W., and DiSanzo, F. P., *Anal. Chem.*, 67, 2015 (1995)

(**15**) Diehl, J. W., Finkbeiner, J.W., and DiSanzo, F. P., *Anal. Chem.*, 65, 2493 (1993).

(**16**) McDonald, R. S., and Wilks, Jr., P. A., *Applied Spectroscopy*, Vol 42, No. 1, 1988, pp. 151–162.

(**17**) McClure, G. L.," General Methods of Sample Preparation for Infrared Hyphenated Techniques," Chapter 7 in *Practical Sampling Techniques for Infrared Analysis*, Coleman, P. B., Ed., CRC Press, Boca Raton, 1993, pp. 165–215.