Designation: E1642 – 00 (Reapproved 2005)

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

This standard is issued under the fixed designation E1642; 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 standard. No other units of measurement are included in this 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:*[2]

E131 Terminology Relating to Molecular Spectroscopy
E168 Practices for General Techniques of Infrared Quantitative Analysis
E260 Practice for Packed Column Gas Chromatography
E334 Practice for General Techniques of Infrared Microanalysis
E355 Practice for Gas Chromatography Terms and Relationships
E932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers
E1252 Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis
E1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests
E1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs

3. Terminology

3.1 *Definitions*—For definitions of terms and symbols, refer to Terminology E131 and Practice E355.

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,

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

Current edition approved Sept. 1, 2005. Published September 2005. Originally approved in 1994. Last previous edition approved in 2000 as E1642 – 00. DOI: 10.1520/E1642-00R05.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

a powdered solid, or a cold trap for subsequent analysis (see Practice E1252) (**1**).[3] 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 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

[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.

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 E1421. 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 E260, E355, and E1510 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