



Standard Practice for General Techniques of Thermogravimetric Analysis (TGA) Coupled With Infrared Analysis (TGA/IR)¹

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1. Scope

1.1 This practice covers techniques that are of general use in the qualitative analysis of samples by thermogravimetric analysis (TGA) coupled with infrared (IR) spectrometric techniques. The combination of these techniques is often referred to as TGA/IR.

1.2 A sample heated in a TGA furnace using a predetermined temperature profile typically undergoes one or more weight losses. Materials evolved during these weight losses are then analyzed using infrared spectroscopy to determine chemical identity. The analysis may involve collecting discrete evolved gas samples or, more commonly, may involve passing the evolved gas through a heated flowcell during the TGA experiment. The general techniques of TGA/IR and other corresponding techniques, such as TGA coupled with mass spectroscopy (TGA/MS), as well as, TGA, used in conjunction with GC/IR, are described in the referenced literature (1-4).²

1.3 Some thermal analysis instruments are designed to perform both thermogravimetric analysis and differential scanning calorimetry simultaneously. This type of instrument is sometimes called a simultaneous thermal analyzer (STA). The evolved gas analysis performed with an STA instrument (5) is similar to that with a TGA, and so, would be covered by this practice. With use of a simultaneous thermal analyzer, the coupled method typically is labeled STA/IR.

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

1.5 *This statement 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 Spectroscopy³

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.

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² The boldface numbers in parentheses refers to the list of references at the end of this standard.

³ *Annual Book of ASTM Standards*, Vol 03.06.

E 168 Practices for General Techniques of Infrared Quantitative Analysis³

E 334 Practices for General Techniques of Infrared Microanalysis³

E 473 Terminology Relating to Thermal Analysis⁴

E 1131 Test Method for Compositional Thermal Analysis by Thermogravimetry⁴

E 1252 Practice for General Techniques for Qualitative Infrared Analysis³

E 1421 Practice for Describing and Measuring Performance of Fourier Transform Infrared (FT-IR) Spectrometers: Level Zero and Level One Tests³

3. Terminology

3.1 *Definitions*—For general definitions of terms and symbols, refer to Terminologies E 131 and E 473.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *evolved gas, n*—any material (or mixture) evolved from a sample during a thermogravimetric or simultaneous thermal analysis experiment. Materials evolved from the sample may be in the form of a gas, a vapor, an aerosol or as particulate matter. For brevity, the term “evolved gas” will be used throughout this practice to indicate any material form or mixture evolved from a sample.

3.2.2 *evolved gas analysis (EGA), n*—a technique in which the nature and amount of gas evolved from a sample is monitored against time or temperature during a programmed change in temperature of the sample.

3.2.3 *evolved gas profile (EGP), n*—an indication of the total amount of gases evolved, as a function of time or temperature, during the thermogravimetric experiment. In TGA/IR, this profile is calculated from the infrared spectroscopic data recorded by application of the Gram-Schmidt reconstruction (GSR) algorithm (6,7). Because the GSR was designed for use in gas chromatography coupled with infrared (GC/IR) analysis, the evolved gas profile has sometimes been erroneously called the evolved gas chromatogram.

3.2.4 *functional group profile (FGP), n*—an indication of the amount of gas evolved during the thermogravimetric experiment that contains a particular chemical functionality measured as a function of time or temperature. This profile is calculated from the infrared spectroscopic data recorded by

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

integration of the absorbances over selected spectral regions as the experiment progresses. Typically, a number of such profiles are calculated in real-time. Additional profiles (using different spectral regions) can often be calculated after the experiment from the stored spectroscopic data. Because the software used has similarities with that used for GC/IR analysis, the functional group profile has sometimes been erroneously called the functional group chromatogram.

3.2.5 *hit quality index (HQI)*, n —the numerical ranking of infrared reference spectra against that of an analyte spectrum through the use of search algorithms that measure a comparative fit spectral data.

3.2.6 *specific gas profile (SGP)*, n —a special type of functional group profile arises when the selected region of the spectrum contains absorbances due to a specific gas such as ammonia or carbon monoxide.

4. Significance and Use

4.1 This practice provides general guidelines for the practice of thermogravimetry coupled with infrared spectrometric detection and analysis (TGA/IR). This practice assumes that the thermogravimetry involved in the practice is proper. It is not the intention of this practice to instruct the user on proper thermogravimetric techniques. Please refer to Test Method E 1131 for more information.

5. General TGA/IR Techniques

5.1 Two different types of TGA/IR techniques are used to analyze samples. These consist of discrete evolved gas trapping and use of a heated flowcell interface. It should be noted that only the latter technique allows for the calculation of the evolved gas and functional group profiles.

5.2 *Evolved Gas Trapping Techniques*—Evolved gas trapping techniques are the least elaborate means for obtaining TGA/IR data. In these techniques, the evolved gas is collected from the TGA furnace in discrete aliquots that are then analyzed. In use of such techniques, it is essential to monitor the TGA weight loss curve to determine the time or temperature at which the effluent was captured. Vapor phase samples can be trapped in a heated low-volume gas cell at the exit of the TGA, analyzed, then flushed out by the TGA effluent. When the next aliquot of interest is in the gas cell, the flow is stopped again for analysis. This process can be made more convenient by designing the TGA temperature profile such that the temperature is held constant while a trapped sample is being analyzed (ramp-and-hold method). Alternatively, fractions can be trapped in the condensed phase by passing the TGA effluent through a solvent, a powdered solid, or a cold trap to yield condensed phase material for subsequent analysis (8). Infrared spectrometry is performed with either a monochromator, a filter spectrometer or a Fourier transform spectrometer. See also Practices E 334 and E 1252 for general techniques on microanalysis and qualitative practices.

5.2.1 Since the analyte of interest is static when employing an evolved gas trapping technique, the spectrum can be recorded using a long integration time or increasing scan co-addition to improve the signal-to-noise ratio (SNR). However, in vapor phase evolved gas trapping, the sample integrity can be compromised by slow decomposition or by deposition

on the cell walls. A spectrum should be obtained initially within a short co-addition time to create a reference spectrum to ensure the integrity of the spectrum obtained after long co-addition.

5.3 *Evolved Gas Analysis Using a Flowcell*—Another way to examine the gases evolved during a TGA/IR experiment is to use a specially designed flowcell. This flowcell is situated in the IR beam of the infrared spectrometer. IR monochromators and filter spectrometers are typically used to monitor a specific frequency range during the TGA experiment. If a full spectrum is to be obtained with these IR devices, the evolved gas is trapped via a stopped flow routine and the spectrometers are permitted to scan the infrared spectrum. In contrast, the Fourier transform IR spectrometer permits the acquisition of the complete IR spectrum in brief timeframes without impact upon the typical TGA experiment, that is, continuous spectral collection without interruption of evolved gas flow or sample heating.

5.3.1 In the typical TGA/IR experiment, the evolved gas is monitored in real-time by the IR spectrometer. The temporal resolution required during a TGA/IR experiment is on the order of 5–60 s/spectral data acquisition event. If the full IR spectrum is to be acquired, the rapidity of the TGA experiment requires a Fourier-transform infrared (FT-IR) spectrometer to maintain sufficient temporal resolution. Such instruments include a computer that is capable of storing large amounts of spectroscopic data for subsequent evaluation.

5.3.2 Some spectrometer data systems may have limited software, or data storage capabilities. Such instrument systems are capable of recording suitable spectra during the TGA/IR experiment, but may not be able to calculate the evolved gas and functional group profiles.

5.3.3 The flowcell is coupled directly to the TGA via a heated transfer line. Evolved gas components are analyzed as they emerge from the transfer line. This technique typically yields low microgram detection limits for most analytes (1). Instruments that include the IR spectrometer, data system, the thermogravimetric analyzer, heated transfer-line, and heated flowcell are commercially available.

5.3.4 It should be noted that any metal surface inside the TGA furnace, transfer line or flowcell assembly may react with, and sometimes destroy, specific classes of evolved gases, for example, amines. This can result in changes to the chemical nature of the evolved gas. Consequently, it is possible to fail to identify the presence of such compound in the mixture. This situation can sometimes be identified by comparison of the TGA weight loss profile with the evolved gas profile.

5.3.5 The infrared energy throughput of the flowcell should be periodically monitored since this indicates the overall condition of this assembly. It is important that all tests be conducted at a constant flowcell temperature because of the effect of the emitted energy on the detector (see 6.3.1). 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. If a mercury-cadmium-telluride (MCT) detector is being employed, these tests will also reveal degradation

of performance due to loss of the Dewar vacuum and consequent buildup of ice on the detector face. In general, when a loss of transmitted energy greater than 10 % of the total energy is found, cleaning of the flowcell is recommended.

5.3.6 Care must be taken to stabilize or, preferably, remove interfering spectral features that result from atmospheric absorptions in the IR beam path of the spectrometer. Best results will be obtained by purging the entire optical path of the spectrometer with dry nitrogen gas. Alternatively, dry air can be used as the spectrometer purge gas; however, this will lead to interferences in the regions of carbon dioxide absorption (2500 to 2200 cm^{-1} and 720 to 620 cm^{-1}) due to the presence of carbon dioxide in air. Further, commercially-available air scrubbers, that remove both water vapor and carbon dioxide, provide adequate purging of the spectrometer. In some instruments, the beam path is sealed in the presence of a desiccant, but interferences from both carbon dioxide and water vapor (1900 to 1400 cm^{-1}) may be found. Similarly, the TGA furnace, the transfer line and the gas cell interface are purged with a gas that does not absorb infrared energy. Typically, this TGA purge gas is inert (nitrogen or helium) and has a flow rate from 10 to 200 mL/min . Occasionally, oxidizing or reducing atmospheres, that is, oxygen or hydrogen respectively, are used with the TGA to promote specific chemical reactions. When preparing for a TGA/IR experiment, the atmospheres within the spectrometer and within the furnace and gas cell combination must be allowed to stabilize before spectral data collection and the thermal experiment commence to minimize spectral interferences. Atmospheric stability for the experiment can be judged by recording the single-beam energy response and the ratio of two successive single-beam spectra over a discrete time interval.

5.3.6.1 The spectral features of both carbon dioxide and, more importantly, water vapor depend upon the temperature at which they were measured. This can become an awkward problem in TGA/IR analysis, as many samples evolve these gases as they are heated. It may be necessary to identify these molecules in the heated flowcell when there is a possible background absorbance from molecules close to room temperature in the spectrometer and interface. It is particularly difficult to use spectral subtraction techniques (see Practice E 1252) to compensate for the presence of water vapor in the spectrum under these conditions. The significance of this problem is demonstrated by the attempt to identify the presence of a trace amount of a carbonyl compound when spectral features due to water vapor also are observed.

6. Component Design Considerations for TGA/IR Using a Flowcell

6.1 *Transfer Line*—A transfer line from the TGA to the flowcell must present an inert, nonporous surface to the evolved gas. Evolved gas transfer lines must be heated to temperatures sufficient to prevent condensation of the evolved gas species. Typically, the transfer line is constructed of a narrow-bore steel tube that has either a removable liner or is coated internally with silica. The temperature of the transfer line is normally held constant during an experiment at a level chosen to avoid both condensation and degradation of the evolved gases. Typical working temperatures have a range of

150 – 300°C . The flowcell usually is held at a slightly greater temperature, ca. 10°C higher, to avoid condensation of the evolved gas.

6.1.1 The use of a TGA/IR system to analyze complex materials, such as polymers or natural products, will result in carbonaceous material, high-molecular weight polymers and other high boiling materials accumulating in the transfer line and the flowcell. A periodic removal of these materials can be accomplished by passing air (or oxygen) through the hot line; however, the condensation of material will eventually yield a reduction in gas flow. At this point, it is necessary to clean out the line before it clogs completely. Flushing the transfer line with one or more solvents, such as acetone, pentane or chloroform may remove condensed materials. Alternatively, some commercial systems use a transfer line with a disposable liner that can be replaced.

6.2 *Design of the Infrared Flowcell*—The flowcell is optimized to give maximum optical throughput, to minimize decomposition and mixing of analyte gas stream, and to yield linear infrared absorption. The flowcell dimensions are optimized to accommodate a discrete volume and flow rate and provide sufficient optical pathlength for spectral data acquisition with reasonable temporal resolution. Preferably, the cell is heated to a constant temperature at or slightly higher than the temperature of the transfer line, ca. 10°C or higher; however, the maximum temperature recommended by the manufacturer should not be exceeded. It must be noted that repeated temperature changes to the cell and transfer line accelerate aging of the seals and may cause leaks.

6.2.1 The ends of the flowcell are sealed with infrared transmitting windows or window and mirror combinations. The optimum infrared transmission is obtained by using potassium bromide windows, but this material is very susceptible to damage by water vapor. As the flowcell is used, small amounts of water vapor etch the window surfaces and the optical throughput of the flowcell drops until a point is reached when these windows need to be replaced. Users who expect to analyze mixtures containing water should consider using windows made of a water-resistant material, such as zinc selenide (ZnSe); however, high refractive index windows, such as ZnSe, result in a noticeable drop in optical transmission due to the optical properties of such materials.

6.2.2 Use of the flowcell at high temperatures may result in the gradual buildup of organic char on both the cell walls and windows. As this occurs, the infrared throughput will drop correspondingly. Eventually, the flowcell assembly will have to be cleaned and reconditioned. It is suggested that, when infrared energy falls to 80 % of original intensity, the flowcell be cleaned and windows and mirrors be reconditioned.

6.3 Optical Interface

6.3.1 The flowcell may be positioned in the standard sample compartment of the infrared spectrometer. It is advantageous, however, to place the flowcell in a separate compartment to yield a dedicated optical interface. This interface can be designed to house the temperature controllers for the heated flowcell and transfer line, if so desired. There are several reasons for doing this:

6.3.1.1 A customized detector assembly can be used for

TGA/IR experiments (see 6.4.3 if using a DTGS detector);

6.3.1.2 The heat generated by use of the heated flowcell can be isolated from the main spectrometer optics and avoids degradation of spectrometer stability due to heat currents;

6.3.1.3 An optical aperture can be placed between the heated flowcell and the detector to act as a cold aperture (see 6.3.2 and Note 1); and,

6.3.1.4 The primary sample compartment then is available for routine IR spectroscopy needs without removal of the heated flowcell.

6.3.2 As the temperature of the flowcell is raised above ambient, it emits an increasing amount of infrared radiation. This radiation is not modulated by the spectrometer and is picked up by the detector as a DC signal. When the flowcell is at temperatures above 200°C, the DC portion of the signal is sufficient to lower the dynamic range of the detector. The result of this effect is that the observed AC signal is reduced and the observed spectral noise level is increased. For example, by raising the flowcell temperature from room temperature to 250°C, the noise level typically doubles. It is recommended that the user create a plot of interferogram intensity versus light-pipe temperature for reference purposes. Some instrument designs include a cold aperture between the flowcell and the detector to minimize the amount of unmodulated, extraneous infrared radiation reaching the detector.

NOTE 1—A cold aperture is a metal shield with a hole in it that is maintained at room temperature. The modulated infrared beam diverging from the flowcell is refocused at this cold aperture. The cold aperture has a diameter that matches the diameter of the refocused IR beam. The IR beam passing through the cold aperture diverges and is again refocused onto the detector element. This cold aperture shields the detector from the unmodulated thermal energy emitted from the heated flowcell.

6.4 *Choice of Infrared Detector:*

6.4.1 Detectors typically used for TGA/IR are either mercury-cadmium-telluride (MCT) or deuterated triglycine sulfate (DTGS). Either detector is selected with regard to sensitivity, detectivity and speed requirements of the TGA/IR experiment. To achieve the highest signal-to-noise response (SNR), it is important that the detector element be filled with either the image of the cold aperture, the exit aperture of the flowcell or the IR source image depending on the optical design of the spectrometer and interface.

6.4.2 MCT photoconductive detectors range from narrow band detectors of high sensitivity that have a low limit of approximately 700 cm⁻¹ to broad band detectors of modest sensitivity that have a low limit of 400 cm⁻¹. MCT detectors are favored for TGA/IR experiments that show fast weight losses (occurring in seconds) or where exceptional sensitivity is required, such as when weight losses less than 1 % need to be studied in detail. An MCT detector should not be operated in a light saturating condition so as to maintain the linearity of signal response. If detector nonlinearity is present, it will severely limit the application of spectral subtraction routines. This restriction may mean that a narrow-band MCT is inappropriate for some TGA/IR instruments or applications. To determine if the MCT detector is operating in a nonlinear fashion, the single beam spectrum is examined below the detector's spectral range or "cutoff." If the values below the cutoff are non-zero, the detector is operating in a nonlinear

domain. It is recommended that the operational parameters of the spectrometer be adjusted to reduce energy throughput to the detector to prevent saturation and nonlinearity. While this typically occurs with MCT detectors, this phenomenon may also occur with DTGS detectors.

6.4.3 DTGS detectors are less sensitive and require slower scanning speeds; however, the DTGS detector is a good choice for general-purpose operation as the temporal resolution for acquisition of spectra in the TGA/IR experiment is on the order of 10 s or more and the gas evolution is sufficient to yield analyte concentrations to permit adequate detection of evolved species.

6.4.3.1 Because the DTGS detector is pyroelectric in operation, such a detector is sensitive to temperature changes in the instrument or the optical interface; hence, the spectrometer, the optical interface, and the detector must be in thermal equilibrium before spectra are acquired. In addition, a DTGS detector loses significant sensitivity at temperatures greater than 30°C as the DTGS element depolarizes. This problem can be avoided by using a detector equipped with a Peltier cooler or use of an appropriate cold aperture (shielding) prior to the detector.

7. Documentation of Significant Parameters for TGA/IR

7.1 The instrumentation used to conduct the TGA/IR experiment should be recorded properly within prescribed standard operating procedures (SOPs) or laboratory notebooks as necessary to meet requirements for laboratory practices. If the equipment is commercially available, the manufacturers' names and model numbers for the complete TGA/IR system, or the individual components, should be recorded. The various instrumental and software parameters that need to be recorded are listed and discussed in 7.2-7.4.5. In addition, any modifications made to a commercial instrument must be noted clearly particularly if they affect the instrument's performance.

7.2 *Instrumental Parameters (IR):*

7.2.1 *Flow Cell Temperature*—The flowcell is maintained at a constant temperature, such that condensation of analytes is minimized. The actual temperature of the cell should always be recorded.

7.2.2 *Window Material Used in the Flowcell*—The type of window material used in the flowcell must be recorded as its optical properties affect transmission of the infrared beam.

7.2.3 *Transfer Line Temperature*—The transfer line is typically held at a constant temperature. The actual temperature and the transfer line material must be recorded.

7.2.4 *Detector*—The type of detector should be specified. If an MCT detector is used, the detector cutoff frequency should be recorded.

7.3 *Instrumental Parameters (TGA)*—The success of the TGA/IR experiment is dependent on good thermogravimetric procedures. It is not the purpose of this to discuss TGA operational procedures in detail. For convenience, a list of the important TGA parameters to be recorded is listed below. Please refer to Test Method E 1131.

7.3.1 *TGA Temperature Profile*—The temperature profile should be specified in detail and include any initial delay or final hold times.

7.3.2 *TGA Purge Gas*—The atmosphere used during the

TGA experiment should be recorded, as well as the purge rate in mL/min. If the gas is switched during the run, the temperature and elapsed time at which this occurs should be noted.

7.3.3 Sample Weight—The sample weight at the beginning of the experiment must be recorded.

7.3.4 Description of Sample—A detailed description of the sample's characteristics should be recorded.

7.4 Software Parameters:

7.4.1 Apodization Function—For Fourier transform infrared spectrometers, it is recommended that an apodization function be applied to the interferogram before computation of spectral data. Suitable apodization functions include boxcar, triangular, Beer-Norton medium, Happ-Genzel, and cosine function. If acquired spectra are to be searched against spectral reference libraries, the apodization function of the acquired spectrum should match that of the reference spectra to improve spectral match quality.

7.4.2 Spectral Resolution—A compromise between the signal to noise ratio of a spectrum and its information content leads to an optimum spectral resolution for TGA/IR spectra of 4 cm^{-1} . If a rapid weight loss is expected, then 8 cm^{-1} resolution is recommended to permit faster spectral acquisition. Data for trapped samples normally are recorded at a resolution of 4 cm^{-1} . If collection method or time permits, it may be appropriate to acquire spectra at higher resolution, that is, 2 cm^{-1} or better, to identify components. This particularly is useful for those gases that exist as small molecules and give rise to spectra rich in rotational fine structure.

7.4.2.1 When employing post-TGA run data acquisition with stopped flow or trapping methods, data normally are collected at a higher resolution, such as 4 cm^{-1} if in the condensed phase or at least 2 cm^{-1} for the vapor phase, to increase the information content of the spectra.

7.4.3 Temporal Resolution—The time taken for each co-added spectrum acquisition should be noted, as well as the number of scans co-added.

NOTE 2—During real-time data acquisition, it is advantageous to co-add several scans per time increment to improve the signal to noise ratio (SNR) of the result. The actual number of co-added scans depends on the spectrometer's optimal scanning speed and spectral resolution. Typical spectrometer operation would permit co-addition of four to ten scans before the data is stored. More extensive spectral co-addition may be performed with post-run spectral collection and data manipulation routines.

NOTE 3—Gas evolution from the sample often occurs over extended periods of time. Coaddition of scans then can be extended to higher levels, for example, 100 scans/spectrum, to further improve the signal-to-noise of the spectrum without significant loss of resolution on the time axis. This greatly reduces the amount of data stored and speeds up post-run data treatment; however, it is important to remember that the spectral acquisition should be set to accommodate the fastest weight loss or gas evolution and the minimum time increment of the complete experiment.

7.4.4 Data Storage Threshold—This function must be recorded if used (see 8.2).

7.4.5 Additional Processing—If any smoothing functions, baseline correction algorithms or spectral subtractions are applied to the data, this must be documented. It should be pointed out that some commercial TGA/IR instruments give the operator only a limited control over these functions and the instrument may be operating with these functions automati-

cally. The operator should investigate as to whether the instrument software does include such operations.

8. Software Treatment of Infrared Data

8.1 Gram-Schmidt Reconstruction—As each interferogram is recorded, a method, called Gram-Schmidt reconstruction (6, 7), quickly determines the information content of the interferogram is applied. In this method, sets of interferograms are typically recorded once the sample has been placed in the TGA, the TGA purge gas has been stabilized and before the TGA run is started. These interferogram sets are used to create a series of basis vectors that represent the experiment's TGA/IR baseline profile. During the experiment, each new interferogram is used to generate a similar vector. Comparison of this new vector and subsequent vectors against the reference vector set by orthogonalization yields a measure of the change in total infrared energy and in the amount of material evolving from the TGA. The resulting plot of vector magnitude (intensity) versus time is representative of how the total infrared energy at any given time changes during the experiment. This is called the Gram-Schmidt reconstruction (GSR) profile, or more appropriately for TGA/IR, the Evolved Gas Profile (EGP). This profile is similar in appearance to the first derivative of the weight loss profile from the TGA experiment. The EGP normally is displayed on the computer screen during the experiment and is an important tool in the subsequent analysis of the data.

8.2 Data Storage Threshold—With older computing systems, the large number of spectra recorded during a typical TGA/IR experiment can exceed the digital storage capacity of the computer. Because of this, some software programs monitor the GSR information and only record spectral data when the intensity change exceeds a preset threshold value. It is possible that, if a minor component is not detected during the experiment, no spectral data are stored. With current digital storage capacities a data storage threshold is rarely used as the typical TGA/IR file sizes are easily accommodated.

8.3 Functional Group Profiles—As each interferogram is recorded, it may be transformed to a spectrum in real-time. Absorptions at selected spectral regions may be integrated and displayed with the evolved gas profile. Commonly selected regions of the infrared spectrum and properly assigned functional groups that may be monitored are as follows:

Unsaturated/Aromatic C-H stretch: $3150\text{ to }3000\text{ cm}^{-1}$
Saturated C-H stretch: $3000\text{ to }2850\text{ cm}^{-1}$
C-O stretch: $1800\text{ to }1650\text{ cm}^{-1}$
C-O stretch: $1300\text{ to }1000\text{ cm}^{-1}$

8.3.1 It should be noted that these absorption band assignments do not correspond to all possible functional groups that may absorb in these or other spectral regions. Absorption band assignments should be verified with appropriate reference materials.

8.4 Specific Gas Profiles—A special type of functional group profile arises when the selected region of the spectrum contains absorbances from only one particular gaseous species. This profile is called the specific gas profile (SGP). Judicious selection of frequency windows allows the operator to monitor the evolution of several important gases independently. It must be pointed out, however, that the expected gases and their

specific absorption frequencies must be well understood for this approach to be completely successful. Useful spectral regions for specific gases include:

Carbon Dioxide: 2300 to 2200 cm^{-1}
 Carbon Monoxide: 2200 to 2050 cm^{-1}
 Water Vapor: 1950 to 1800 cm^{-1}

8.4.1 It should be noted that these absorption band assignments do not correspond to all possible specific gases that may absorb in these spectral regions. Absorption band assignments should be verified with proper reference materials. The ability to use SGP's results from the fact that many TGA experiments lead to the evolution of small molecule gases, such as sulfur dioxide, ammonia, and the nitrogen oxides, in addition to the gases listed in 8.4.

8.5 *Spectral Searching*—The normal purposes of the TGA/IR experiment is to identify, or at least classify, the various species that are evolved in the TGA experiment. It must be realized, however, that a TGA/IR experiment usually generates a number of components. These components often evolve as one or several overlapping groups. It is desirable that the temperature profile used for the thermal analysis leads to well-resolved weight losses. It is very common for the evolved gases to include many members of a homologous series, or a number of spectroscopically indistinct species, such as hydrocarbons. In this case, the most information that can be obtained is an identification of key functional groups found in the mixture of evolved gases.

8.5.1 For spectral searching, absorbance spectra are selected by examination of the EGP, FGPs, and SGPs. Spectra are compared individually, using one or several search algorithms, to a library or database of reference spectra. These databases typically reside in a digitized format on the computer disk. The spectral comparison algorithms yield a list of potential identities that match the sample spectrum most closely and rank these identities in order of their match quality. Additionally, some search algorithms allow a comparison of specified regions of the spectrum, instead of the complete spectrum. In this fashion, spectral interferences due to contaminant species in other regions of the sample spectrum do not unduly influence the search results.

8.5.2 It should be stressed that the results of a computer search cannot be relied upon to always give the correct answer. This is a general caveat for infrared spectroscopy, but it is very important for the practitioner of TGA/IR to understand because of the large number of co-evolving gases to be expected. The search always will present the spectrum of a single compound as its best match, especially, if a library of the spectra of vapors is used. For example, when a polymer, such as polybutadiene is studied, the complex mixture of evolved gases yields an "average" spectrum. The spectral search software may report that the best hit may be 1-butene, but this may not be the predominant species present. This situation can be identified by examination of the hit quality index (HQI) reported for the first few matches. These will be found to be very similar and indicate a poor confidence in the result.

8.5.3 Other potential problems that influence spectral searching include: library spectra that have errors or spectral interferences, temperature differences between the sample and

reference spectra, physical state differences between sample and recorded reference spectra, absence of a relevant sample from the library, and low SNR of the measured spectrum. The analyst should always verify the search result by visually comparing the spectra of the best matches to each sample spectrum.

8.5.4 An important parameter to be considered when performing a spectral search is the search algorithm. Selection of the search algorithm is dependent upon the sharpness of spectral features in the sample spectrum and database reference spectra. As several search algorithms are available, it is important to understand how each one operates upon the sample and database spectra to obtain effective use of spectral searching.

8.5.4.1 Search algorithms, such as the Euclidean algorithm, match the spectrum, point by point, with each entry in the database. The Euclidean algorithm takes into consideration the relative intensity, shape, and frequency of each spectral feature, but places the heaviest importance on strong, broad features. In the TGA/IR experiment, the Euclidean algorithm is useful when relatively large molecules are expected in the evolved gases.

8.5.4.2 If the derivative of the spectrum is compared to the derivative of each library entry, emphasis is placed on the peak frequencies of sharp bands. Any shifts in peak frequencies between the spectra of the sample and references will lead to poor matches when using the derivative algorithm; however, this type of algorithm can be extremely sensitive when the evolved gases include gases that are small molecules, since a number of these, for example, methane, ethene, hydrogen cyanide, and hydrogen chloride, exhibit sharp peaks in their spectra.

8.5.5 It is common practice for users to generate their own libraries containing spectra of samples that they expect to analyze on a routine basis. Spectra can be obtained under identical conditions to those used for the TGA/IR experiment. Of most importance are those gases that are small molecules, such as water vapor. Their spectra are particularly sensitive to temperature and so better databases will include spectra of these gases recorded at a specified flowcell temperature (9), usually that used during the majority of the TGA/IR experiments.

NOTE 4—Libraries of spectral data are available from commercial sources. For vapor phase TGA/IR, the most suitable libraries are those that contain spectra recorded using gaseous samples. It should be realized, however, that these spectra were recorded at the most suitable temperature available to the library maker. This normally is room temperature for volatile species, but compounds having low vapor pressure may have been studied in a heated cell to increase the analyte absorbance to an acceptable level. Condensed phase TGA/IR data generally are matched against spectra recorded for condensed phase samples. For evolved gas trapping yielding condensed phase analytes, it is often possible to use the much larger libraries of condensed-phase reference spectra, where the samples have been collected using sampling methods such as KBr disks, mineral oil mulls or some other technique.

8.6 *Spectral Subtraction*—This mathematical tool is used to improve the quality of the sample spectrum. It is useful particularly with gas species that evolve in an overlapping

fashion. Here, overlapping evolved species must exhibit differential concentrations that can be discerned via inspection of multiple spectra across a discrete experiment timeframe. Subtraction of spectra judiciously selected may yield the spectrum of the analyte with minimal interferences from the other evolved species. In this manner, a more representative spectrum of a single evolved analyte may be obtained; however, this procedure should only be used with great care. It should be cautioned that invalid results could be obtained from improper subtraction, especially if the recorded spectrum is of low intensity.

8.6.1 In the performance of post-run data manipulation, elimination of spectral interferences in analyte spectra due to contaminating species is possible. A reference spectrum of the contaminant for use in spectral subtraction may be obtained by examining spectra collected at various times on the evolved gas profile. If the contaminant component does not change in intensity as the run progresses, for example, a constant level of water vapor in the purge, the reference spectrum may be obtained at a point in the experiment where no evolved gases are present in the flowcell (see Note 5). If it is suspected that a component species evolves after a weight loss has begun, then this might be observed by subtracting spectra from the beginning of the weight loss event from those later in the event. This subtraction technique requires skill in data manipulation, as well as, an understanding of thermal analysis and the potential chemistry that may be occurring to yield results properly.

NOTE 5—It should be pointed out that the use of the data storage threshold algorithm (see 8.2) during data collection will generally mean that absorbance spectra of baseline regions cannot be generated for subtraction purposes, since no data were stored at that time.

8.6.2 If the analyte spectra contain significant interferences from atmospheric water vapor or carbon dioxide, then a reference spectrum of either one or both of these interfering species may be subtracted (see Note 6). Typically, these interferences will be observed also in the TGA/IR baseline, so that a reference spectrum may easily be generated close to the time of analyte gas evolution. Some software programs permit automatic removal of spectral contributions due to these species.

NOTE 6—It is important to be able to distinguish whether the water vapor giving contributions to the spectra is near room temperature, that is, in the instrument purge or a part of the evolved gases, in which case it will be at the temperature of the flowcell. As discussed in 5.3.6.1, the spectrum of water vapor is temperature sensitive, and attempts to subtract a reference spectrum recorded at a different temperature will lead to poor results.

8.6.3 When heating a sample, complex gas mixtures are often evolved. This is especially true when heating under an inert atmosphere. Even for a single weight loss, as shown by a symmetric peak in the derivative of the weight loss, the gases evolving may change during the weight loss. This can be caused by a number of factors, such as back-reaction of the gases with the sample, and may give important information to the practitioner. To investigate this event, subtraction of spectra, taken at different times during the weight loss event, should be carried out.

9. Standard Samples

9.1 A standard test sample should be used on a regular basis to test the instrument response and indicate when problems have occurred with either the IR spectrometer, the TGA or the optical interface. This test will also determine if the transfer line is obstructed, or if the gas flow has been interrupted in some other way. The parameters discussed in Section 7 must be reproduced exactly each time. The actual sample and concentration of the test mixture used will depend on the type of analysis being performed. It is useful to choose one “manufacturer’s” test sample that can be recorded during installation of the instrument and also a “customer’s” test sample that is selected from materials commonly examined by the laboratory.

9.1.1 The “manufacturer’s” test sample typically is a simple substance that shows several well-resolved weight losses over the temperature range of the TGA. Common test samples are calcium oxalate, copper sulfate pentahydrate, and calcium carbonate. This type of sample can be tested in a reasonable amount of time and can be used to check the TGA balance noise level, the IR signal to noise ratio, the carrier gas flow, and measure the delay time observed between the weight loss derivative curve and the EGP.

9.1.2 The “customer’s” test sample typically is a material that can be obtained easily in reproducible form when needed. In addition to those mentioned in 9.1.1, one material that has proven useful for this application is zinc stearate.

9.1.3 The TGA/IR analysis of zinc stearate (5,9), heated under nitrogen, shows unusual behavior. The material melts at about 120°C and releases a small amount of water vapor. The weight loss may not be sufficient to be recorded on the TGA curve, but should show observable infrared absorbance. This weight loss and gas evolution can serve as a sensitivity test. As the experiment continues, two major weight losses are observed, near 380°C and 440°C. Both are due to the loss of stearic acid (leaving zinc oxide residue), but the spectra of the two weight losses differ. In a TGA/IR system having an efficient, heated transfer of the evolved gases, the first weight loss is stearic acid vapor, whereas the second weight loss has additional amounts of stearic acid as an aerosol. These species give rise to infrared carbonyl absorptions at 1780 cm⁻¹ and 1717 cm⁻¹, respectively. A system having a problem with a cold region in the transfer line will not show the spectral features at 1717 cm⁻¹, since the aerosol condenses within the transfer line.

9.1.4 The test procedure should allow collection or calculation of the following: the signal-to-noise ratio of the infrared spectrum, spectra of the test sample recorded in the real-time mode, the signal-to-noise ratio of the TGA weight loss curve, the time difference between the peak in the derivative of the weight loss and the EGP, and a comparison of the width of the derivative and EGP peaks.

10. Sampling Criteria

10.1 The sampling criteria for the various TGA/IR techniques depend on the application of the analysis. The advantages and disadvantages of each sampling technique are discussed previously (see Section 5). These must be taken into consideration when determining the best method of combined

separation and identification for a particular analysis.

10.2 The action of loading the sample onto the TGA pan may require that the pan be removed from the furnace and balance. This allows for atmospheric gases (water vapor and carbon dioxide) to enter into the furnace, balance head, and the transfer line. If these vapors are to be studied during the TGA/IR experiment, then a suitable time of purging will be needed before the atmosphere in the TGA, transfer line, and sampling interface will be free of these gases. Because of this, the TGA temperature program should allow for a suitable delay time, for example, 10 min, before the temperature ramp commences.

10.3 For the same reason as in 10.2, the initial infrared background spectrum should not be recorded until these interfering gases have been purged from the TGA, transfer line, and sampling device. If insufficient time is allowed, the spectra recorded during the experiment will show negative absorbances due to water and carbon dioxide as the TGA purge gas becomes purer.

10.3.1 One common use of TGA/IR is for the measurement of residual or entrapped solvents, such as water and volatile organic solvents. In this case, the purge time specified in 10.2 should not be allowed, because as soon as the furnace is sealed around the sample, the volatile vapor will start to evolve from the sample. The background spectrum should be recorded using a purged system before the sample is loaded onto the pan and the TGA/IR experiment is started as soon as the sample has been loaded.

10.4 The amount of sample required for a study of evolved gases depends on a number of factors, most importantly the furnace volume and the weight loss of the vapors of interest.

10.4.1 The TGA balance is typically sensitive to weight losses in the microgram range, whereas the FT-IR spectrometer can detect amounts of vapor 10–100 times smaller than that. Because of this, the TGA/IR technique is so sensitive that evolved gases can sometimes be detected by careful examination of the infrared spectra even though the TGA does not record a weight loss.

10.4.2 For very small weight losses, the TGA pan can be filled loosely to capacity if sensitivity to low levels of volatiles is required.

10.4.3 If a weight loss of more than a few percent is to be studied, a relatively small amount of sample should be utilized. This gives an adequate signal-to-noise ratio for both the TGA and the FT-IR instruments, but avoids putting too much volatile and semi-volatile products through the transfer line, where they may condense and cause obstruction of the transfer line.

11. Qualitative Information

11.1 In TGA/IR, the infrared spectrometer acts as an evolved gas detector. When using a FT-IR spectrometer, several different profile representations may be obtained during the on-line data collection to assist the analysis. The evolved gas profile, which resembles the derivative of the weight loss curve, can be used for locating spectroscopic data files having spectra of each component. Similarly, the functional group profile can detect selectively a compound having a specific functional group. Since different functional groups absorb infrared light at different frequencies, functional group profiles,

generated at different frequency ranges, may indicate and separate the evolution of multiple components.

11.2 Spectral identification by database searching is a recommended step in the TGA/IR analysis. Best results will be obtained when the physical state of the reference compounds used to create the database matches that of the analyte, that is, vapor phase reference spectra are compared to a vapor phase analyte spectrum. In particular, vapor phase TGA/IR spectra should be compared to spectra from a database recorded for gaseous reference materials and ideally, at similar temperatures. Similarly, the best search results for condensed phase analytes will be obtained using a condensed phase reference database.

11.3 For a more reliable validation of the identity of a thermogravimetric peak, a suitable reference sample or compound can be examined by TGA/IR using identical conditions. In this procedure, it is not important that the evolution times match, as the purpose of the experiment is to have the reference material pass through the optical interface at the same temperature as the unknown. Alternatively, other analytical techniques, for example, solvent extraction of the analyte, can be used for verification of the identity of the unknown sample.

12. Quantitative Information

12.1 The evolved gas composition and concentration vary appreciably during the measurement and may result in distorted spectra. Reasonably accurate quantitative information can be obtained by flowcell TGA/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 (10,11).

12.2 The amount of a species evolving from the sample can be ascertained from the weight loss profile generated by the TGA if only a single component is being evolved during a weight loss.

12.3 The various evolved gas profiles, especially the SGP, can be used to obtain quantitative information on components evolving from the sample. This requires careful calibration of the instrument's IR response function (the area under the specific gas profile) using standard samples. This is particularly useful when the weight loss is complex, and more than one species is being evolved simultaneously.

12.4 Quantification via other sampling methods correspond to standard techniques and should be performed in accordance with Practices E 168. Integration across the appropriate spectral region (peak area), or simply measurement of peak height, also can be used for some applications. As sample temperature can influence the peak area or height of infrared spectra, sample spectra recorded at a specified temperature must be used for quantitation purposes to produce repeatable results.

12.5 When using evolved gas 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 re-crystallization in the condensed phase.

13. Record of the Data

13.1 It is recommended that the raw spectroscopic data, that

is, interferograms, be stored if physically possible; otherwise the transformed spectra should be saved.

13.2 Storage of Raw Data—All current TGA/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. Ideally, the raw data should be stored on a magnetic or optical media such as a hard drive, tape backup or a compact disk system capable of read and write operations. In this case, the relevant background single-beam spectrum, vectors calculated for Gram-Schmidt reconstruction, and the functional group and evolved gas profiles should all be stored with the TGA/IR data set. 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 7, but also a record of the sample identity and a description of any sample preparation.

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

13.4 Spectral Interchange—A universally compatible for-

mat for digital storage of data has been developed called JCAMP-DX (12). This protocol generally is useful for transferring individual spectra between instruments of different manufacturers. It is not likely that the large raw data files of a TGA/IR experiment 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.

13.5 Information to Appear With the Spectrum—The sample identification and source of the sample, if known, should appear with the spectrum. An indication of the quantity of sample should be given, together with the pathlength, volume, shape, and temperature of the cell or sample substrate. The sampling method should also be given. The make and model of the spectrophotometer should be recorded, as well as the model name or number of the TGA/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 also should be given.

14. Keywords

14.1 infrared spectroscopy; TGA/IR; thermogravimetry

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