



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. No other units of measurement are included in this 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.*

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.

2. Referenced Documents

2.1 *ASTM Standards:*³

E 131 Terminology Relating to Molecular Spectroscopy

E 168 Practices for General Techniques of Infrared Quantitative Analysis

E 334 Practices for General Techniques of Infrared Microanalysis

E 473 Terminology Relating to Thermal Analysis and Rheology

E 1131 Test Method for Compositional Thermal Analysis by Thermogravimetry

E 1252 Practice for General Techniques for Qualitative Infrared Analysis

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

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

³ 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.

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 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