PROTOCOL FOR THE USE OF EXTRACTIVE FOURIER TRANSFORM INFRARED (FTIR) SPECTROMETRY FOR THE ANALYSES OF GASEOUS EMISSIONS FROM STATIONARY SOURCES

1.0 INTRODUCTION

The purpose of this addendum is to set general guidelines for the use of modern FTIR spectroscopic methods for the analysis of gas samples extracted from the effluent of stationary emission sources. This addendum outlines techniques for developing and evaluating such methods and sets basic requirements for reporting and quality assurance procedures.

1.1 NOMENCLATURE

1.1.1 Appendix A to this addendum lists definitions of the symbols and terms used in this Protocol, many of which have been taken directly from American Society for Testing and Materials (ASTM) publication E 131-90a, entitled "Terminology Relating to Molecular Spectroscopy."

1.1.2 Except in the case of background spectra or where otherwise noted, the term "spectrum" refers to a double-beam spectrum in units of absorbance vs. wavenumber (cm^{-1}).

1.1.3 The term "Study" in this addendum refers to a publication that has been subjected to EPA- or peer-review.

2.0 APPLICABILITY AND ANALYTICAL PRINCIPLE

2.1 Applicability. This Protocol applies to the determination of compound-specific concentrations in single- and multiple-component gas phase samples using double-beam

absorption spectroscopy in the mid-infrared band. It does not specifically address other FTIR applications, such as single-beam spectroscopy, analysis of open-path (non-enclosed) samples, and continuous measurement techniques. If multiple spectrometers, absorption cells, or instrumental linewidths are used in such analyses, each distinct operational configuration of the system must be evaluated separately according to this Protocol.

2.2 Analytical Principle.

2.2.1 In the mid-infrared band, most molecules exhibit characteristic gas phase absorption spectra that may be recorded by FTIR systems. Such systems consist of a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption pathlength, an infrared detector, optical elements for the transfer of infrared radiation between components, and gas flow control and measurement components. Adjunct and integral computer systems are used for controlling the instrument, processing the signal, and for performing both Fourier transforms and quantitative analyses of spectral data.

2.2.2 The absorption spectra of pure gases and of mixtures of gases are described by a linear absorbance theory referred to as Beer's Law. Using this law, modern FTIR systems use computerized analytical programs to quantify compounds by comparing the absorption spectra of known (reference) gas samples to the absorption spectrum of the sample gas. Some standard mathematical techniques used

for comparisons are classical least squares, inverse least squares, cross-correlation, factor analysis, and partial least squares. Reference A describes several of these techniques, as well as additional techniques, such as differentiation methods, linear baseline corrections, and non-linear absorbance corrections.

3.0 GENERAL PRINCIPLES OF PROTOCOL REQUIREMENTS

The characteristics that distinguish FTIR systems from gas analyzers used in instrumental gas analysis methods (e.g., Methods 6C and 7E of appendix A to part 60 of this chapter) are: (1) Computers are necessary to obtain and analyze data; (2) chemical concentrations can be quantified using previously recorded infrared reference spectra; and (3) analytical assumptions and results, including possible effects of interfering compounds, can be evaluated after the quantitative analysis. The following general principles and requirements of this Protocol are based on these characteristics.

3.1 Verifiability and Reproducibility of Results. Store all data and document data analysis techniques sufficient to allow an independent agent to reproduce the analytical results from the raw interferometric data.

3.2 Transfer of Reference Spectra. To determine whether reference spectra recorded under one set of conditions (e.g., optical bench, instrumental linewidth, absorption pathlength, detector performance, pressure, and temperature) can be used to analyze sample spectra taken

under a different set of conditions, quantitatively compare "calibration transfer standards" (CTS) and reference spectra as described in this Protocol. (Note: The CTS may, but need not, include analytes of interest). To effect this, record the absorption spectra of the CTS (a) immediately before and immediately after recording reference spectra and (b) immediately after recording sample spectra.

3.3 Evaluation of FTIR Analyses. The applicability, accuracy, and precision of FTIR measurements are influenced by a number of interrelated factors, which may be divided into two classes:

3.3.1 Sample-Independent Factors. Examples are system configuration and performance (e.g., detector sensitivity and infrared source output), quality and applicability of reference absorption spectra, and type of mathematical analyses of the spectra. These factors define the fundamental limitations of FTIR measurements for a given system configuration. These limitations may be estimated from evaluations of the system before samples are available. For example, the detection limit for the absorbing compound under a given set of conditions may be estimated from the system noise level and the strength of a particular absorption band. Similarly, the accuracy of measurements may be estimated from the analysis of the reference spectra.

3.3.2 Sample-Dependent Factors. Examples are spectral interferants (e.g., water vapor and CO_2) or the overlap of spectral features of different compounds and contamination

deposits on reflective surfaces or transmitting windows. To maximize the effectiveness of the mathematical techniques used in spectral analysis, identification of interferants (a standard initial step) and analysis of samples (includes effect of other analytical errors) are necessary. Thus, the Protocol requires post-analysis calculation of measurement concentration uncertainties for the detection of these potential sources of measurement error.

4.0 PRE-TEST PREPARATIONS AND EVALUATIONS

Before testing, demonstrate the suitability of FTIR spectrometry for the desired application according to the procedures of this section.

4.1 Identify Test Requirements. Identify and record the test requirements described in sections 4.1.1 through 4.1.4 of this addendum. These values set the desired or required goals of the proposed analysis; the description of methods for determining whether these goals are actually met during the analysis comprises the majority of this Protocol.

4.1.1 Analytes (specific chemical species) of interest. Label the analytes from i = 1 to I.

4.1.2 Analytical uncertainty limit (AU_i). The AU_i is the maximum permissible fractional uncertainty of analysis for the i^{th} analyte concentration, expressed as a fraction of the analyte concentration in the sample.

4.1.3 Required detection limit for each analyte (DL_i, ppm). The detection limit is the lowest concentration of an analyte for which its overall fractional uncertainty (OFU_i)

is required to be less than its analytical uncertainty limit (AU_i).

4.1.4 Maximum expected concentration of each analyte ($CMAX_i$, ppm).

4.2 Identify Potential Interferants. Considering the chemistry of the process or results of previous studies, identify potential interferants, i.e., the major effluent constituents and any relatively minor effluent constituents that possess either strong absorption characteristics or strong structural similarities to any analyte of interest. Label them 1 through N_j, where the subscript "j" pertains to potential interferants. Estimate the concentrations of these compounds in the effluent ($CPOT_j$, ppm).

4.3 Select and Evaluate the Sampling System. Considering the source, e.g., temperature and pressure profiles, moisture content, analyte characteristics, and particulate concentration), select the equipment for extracting gas samples. Recommended are a particulate filter, heating system to maintain sample temperature above the dew point for all sample constituents at all points within the sampling system (including the filter), and sample conditioning system (e.g., coolers, water-permeable membranes that remove water or other compounds from the sample, and dilution devices) to remove spectral interferants or to protect the sampling and analytical components. Determine the minimum absolute sample system pressure (P_{min}, mmHg) and the infrared absorption cell volume

(V_{SS}, liter). Select the techniques and/or equipment for the measurement of sample pressures and temperatures.

4.4 Select Spectroscopic System. Select a spectroscopic configuration for the application. Approximate the absorption pathlength (L_S', meter), sample pressure (P_S', kPa), absolute sample temperature T_S', and signal integration period (t_{SS}, seconds) for the analysis. Specify the nominal minimum instrumental linewidth (MIL) of the system. Verify that the fractional error at the approximate values P_S' and T_S' is less than one half the smallest value AU_i (see section 4.1.2 of this addendum).

4.5 Select Calibration Transfer Standards (CTS's). Select CTS's that meet the criteria listed in sections 4.5.1, 4.5.2, and 4.5.3 of this addendum.

Note: It may be necessary to choose preliminary analytical regions (see section 4.7 of this addendum), identify the minimum analyte linewidths, or estimate the system noise level (see section 4.12 of this addendum) before selecting the CTS. More than one compound may be needed to meet the criteria; if so, obtain separate cylinders for each compound.

4.5.1 The central wavenumber position of each analytical region shall lie within 25 percent of the wavenumber position of at least one CTS absorption band.

4.5.2 The absorption bands in section 4.5.1 of this addendum shall exhibit peak absorbances greater than ten times the value RMS_{EST} (see section 4.12 of this addendum)

but less than 1.5 absorbance units.

4.5.3 At least one absorption CTS band within the operating range of the FTIR instrument shall have an instrument-independent linewidth no greater than the narrowest analyte absorption band. Perform and document measurements or cite Studies to determine analyte and CTS compound linewidths.

4.5.4 For each analytical region, specify the upper and lower wavenumber positions (FFU_m and FFL_m, respectively) that bracket the CTS absorption band or bands for the associated analytical region. Specify the wavenumber range, FNU to FNL, containing the absorption band that meets the criterion of section 4.5.3 of this addendum.

4.5.5 Associate, whenever possible, a single set of CTS gas cylinders with a set of reference spectra. Replacement CTS gas cylinders shall contain the same compounds at concentrations within 5 percent of that of the original CTS cylinders; the entire absorption spectra (not individual spectral segments) of the replacement gas shall be scaled by a factor between 0.95 and 1.05 to match the original CTS spectra.

4.6 Prepare Reference Spectra.

Note: Reference spectra are available in a permanent soft copy from the EPA spectral library on the EMTIC (Emission Measurement Technical Information Center) computer bulletin board; they may be used if applicable.

4.6.1 Select the reference absorption pathlength (L_R) of the cell.

4.6.2 Obtain or prepare a set of chemical standards for each analyte, potential and known spectral interferants, and CTS. Select the concentrations of the chemical standards to correspond to the top of the desired range.

4.6.2.1 Commercially-Prepared Chemical Standards. Chemical standards for many compounds may be obtained from independent sources, such as a specialty gas manufacturer, chemical company, or commercial laboratory. These standards (accurate to within ±2 percent) shall be prepared according to EPA Traceability Protocol (see Reference D) or shall be traceable to NIST standards. Obtain from the supplier an estimate of the stability of the analyte concentration. Obtain and follow all of the supplier's recommendations for recertifying the analyte concentration.

4.6.2.2 Self-Prepared Chemical Standards. Chemical standards may be prepared by diluting certified commercially prepared chemical gases or pure analytes with ultra-pure carrier (UPC) grade nitrogen according to the barometric and volumetric techniques generally described in Reference A, section A4.6.

4.6.3 Record a set of the absorption spectra of the CTS {R1}, then a set of the reference spectra at two or more concentrations in duplicate over the desired range (the top of the range must be less than 10 times that of the bottom), followed by a second set of CTS spectra {R2}. (If self-

prepared standards are used, see section 4.6.5 of this addendum before disposing of any of the standards.) The maximum accepted standard concentration-pathlength product (ASCPP) for each compound shall be higher than the maximum estimated concentration-pathlength products for both analytes and known interferants in the effluent gas. For each analyte, the minimum ASCPP shall be no greater than ten times the concentration-pathlength product of that analyte at its required detection limit.

4.6.4 Permanently store the background and interferograms in digitized form. Document details of the mathematical process for generating the spectra from these interferograms. Record the sample pressure (P_R), sample temperature (T_R), reference absorption pathlength (L_R), and interferogram signal integration period (t_{SR}). Signal integration periods for the background interferograms shall be $\geq t_{SR}$. Values of P_R, L_R, and t_{SR} shall not deviate by more than ± 1 percent from the time of recording {R1} to that of recording {R2}.

4.6.5 If self-prepared chemical standards are employed and spectra of only two concentrations are recorded for one or more compounds, verify the accuracy of the dilution technique by analyzing the prepared standards for those compounds with a secondary (non-FTIR) technique in accordance with sections 4.6.5.1 through 4.6.5.4 of this addendum.

4.6.5.1 Record the response of the secondary technique

to each of the four standards prepared.

4.6.5.2 Perform a linear regression of the response values (dependant variable) versus the accepted standard concentration (ASC) values (independent variable), with the regression constrained to pass through the zero-response, zero ASC point.

4.6.5.3 Calculate the average fractional difference between the actual response values and the regression-predicted values (those calculated from the regression line using the four ASC values as the independent variable).

4.6.5.4 If the average fractional difference value calculated in section 4.6.5.3 of this addendum is larger for any compound than the corresponding AU_i, the dilution technique is not sufficiently accurate and the reference spectra prepared are not valid for the analysis.

4.7 Select Analytical Regions. Using the general considerations in section 7 of Reference A and the spectral characteristics of the analytes and interferants, select the analytical regions for the application. Label them m = 1 to M. Specify the lower, center and upper wavenumber positions of each analytical region (FL_m, FC_m, and FU_m, respectively). Specify the analytes and interferants which exhibit absorption in each region.

4.8 Determine Fractional Reproducibility Uncertainties. Using appendix E of this addendum, calculate the fractional reproducibility uncertainty for each analyte (FRU_i) from a comparison of {R1} and {R2}. If $FRU_i > AU_i$ for

any analyte, the reference spectra generated in accordance with section 4.6 of this addendum are not valid for the application.

4.9 Identify Known Interferants. Using appendix B of this addendum, determine which potential interferants affect the analyte concentration determinations. Relabel these potential interferant as "known" interferants, and designate these compounds from k = 1 to K. Appendix B to this addendum also provides criteria for determining whether the selected analytical regions are suitable.

4.10 Prepare Computerized Analytical Programs.

4.10.1 Choose or devise mathematical techniques (e.g, classical least squares, inverse least squares, cross-correlation, and factor analysis) based on equation 4 of Reference A that are appropriate for analyzing spectral data by comparison with reference spectra.

4.10.2 Following the general recommendations of Reference A, prepare a computer program or set of programs that analyzes all of the analytes and known interferants, based on the selected analytical regions (section 4.7 of this addendum) and the prepared reference spectra (section 4.6 of this addendum). Specify the baseline correction technique (e.g., determining the slope and intercept of a linear baseline contribution in each analytical region) for each analytical region, including all relevant wavenumber positions.

4.10.3 Use programs that provide as output [at the

reference absorption pathlength (L_R), reference gas temperature (T_R), and reference gas pressure (P_R)] the analyte concentrations, the known interferant concentrations, and the baseline slope and intercept values. If the sample absorption pathlength (L_S), sample gas temperature (T_S), or sample gas pressure (P_S) during the actual sample analyses differ from L_R, T_R, and P_R, use a program or set of programs that applies multiplicative corrections to the derived concentrations to account for these variations, and that provides as output both the corrected and uncorrected values. Include in the report of the analysis (see section 7.0 of this addendum) the details of any transformations applied to the original reference spectra (e.g., differentiation), in such a fashion that all analytical results may be verified by an independent agent from the reference spectra and data spectra alone.

4.11 Determine the Fractional Calibration Uncertainty. Calculate the fractional calibration uncertainty for each analyte (FCU_i) according to appendix F of this addendum, and compare these values to the fractional uncertainty limits (AU_i; see section 4.1.2 of this addendum). If $FCU_i > AU_i$, either the reference spectra or analytical programs for that analyte are unsuitable.

4.12 Verify System Configuration Suitability. Using appendix C of this addendum, measure or obtain estimates of the noise level (RMS_{EST}, absorbance) of the FTIR system. Alternatively, construct the complete spectrometer system

and determine the values RMS_{Sm} using appendix G of this addendum. Estimate the minimum measurement uncertainty for each analyte (MAU_i, ppm) and known interferant (MIU_k, ppm) using appendix D of this addendum. Verify that (a) $MAU_i < (AU_i)(DL_i)$, $FRU_i < AU_i$, and $FCU_i < AU_i$ for each analyte and that (b) the CTS chosen meets the requirements listed in sections 4.5.1 through 4.5.5 of this addendum.

5.0 SAMPLING AND ANALYSIS PROCEDURE

5.1 Analysis System Assembly and Leak-Test. Assemble the analysis system. Allow sufficient time for all system components to reach the desired temperature. Then, determine the leak-rate (L_R) and leak volume (V_L), where $V_L = L_R\ t_{SS}$. Leak volumes shall be ≤4 percent of V_{SS}.

5.2 Verify Instrumental Performance. Measure the noise level of the system in each analytical region using the procedure of appendix G of this addendum. If any noise level is higher than that estimated for the system in section 4.12 of this addendum, repeat the calculations of appendix D of this addendum and verify that the requirements of section 4.12 of this addendum are met; if they are not, adjust or repair the instrument and repeat this section.

5.3 Determine the Sample Absorption Pathlength. Record a background spectrum. Then, fill the absorption cell with CTS at the pressure P_R and record a set of CTS spectra {R3}. Store the background and unscaled CTS single beam interferograms and spectra. Using appendix H of this

addendum, calculate the sample absorption pathlength (L_S) for each analytical region. The values L_S shall not differ from the approximated sample pathlength L_S' (see section 4.4 of this addendum) by more than 5 percent.

5.4 Record Sample Spectrum. Connect the sample line to the source. Either evacuate the absorption cell to an absolute pressure below 5 mmHg before extracting a sample from the effluent stream into the absorption cell, or pump at least ten cell volumes of sample through the cell before obtaining a sample. Record the sample pressure P_S. Generate the absorbance spectrum of the sample. Store the background and sample single beam interferograms, and document the process by which the absorbance spectra are generated from these data. (If necessary, apply the spectral transformations developed in section 5.6.2 of this addendum). The resulting sample spectrum is referred to below as S_S.

Note: Multiple sample spectra may be recorded according to the procedures of section 5.4 of this addendum before performing sections 5.5 and 5.6 of this addendum.

5.5 Quantify Analyte Concentrations. Calculate the unscaled analyte concentrations RUA_i and unscaled interferant concentrations RUI_K using the programs developed in section 4 of this addendum. To correct for pathlength and pressure variations between the reference and sample spectra, calculate the scaling factor, R_{LPS} using equation

A.1,

$$R_{LPS} = (L_R P_R T_S) / (L_S P_S T_R) \quad \textbf{(A.1)}$$

Calculate the final analyte and interferant concentrations RSA_i and RSI_k using equations A.2 and A.3,

$$RSA_i = R_{LPS} RUA_i \quad \textbf{(A.2)}$$

$$RSI_k = R_{LPS} RUI_k \quad \textbf{(A.3)}$$

5.6 Determine Fractional Analysis Uncertainty. Fill the absorption cell with CTS at the pressure P_S. Record a set of CTS spectra {R4}. Store the background and CTS single beam interferograms. Using appendix H of this addendum, calculate the fractional analysis uncertainty (FAU) for each analytical region. If the FAU indicated for any analytical region is greater than the required accuracy requirements determined in sections 4.1.1 through 4.1.4 of this addendum, then comparisons to previously recorded reference spectra are invalid in that analytical region, and the analyst shall perform one or both of the procedures of sections 5.6.1 through 5.6.2 of this addendum.

5.6.1 Perform instrumental checks and adjust the instrument to restore its performance to acceptable levels. If adjustments are made, repeat sections 5.3, 5.4 (except for the recording of a sample spectrum), and 5.5 of this addendum to demonstrate that acceptable uncertainties are obtained in all analytical regions.

5.6.2 Apply appropriate mathematical transformations (e.g., frequency shifting, zero-filling, apodization, smoothing) to the spectra (or to the interferograms upon

which the spectra are based) generated during the performance of the procedures of section 5.3 of this addendum. Document these transformations and their reproducibility. Do not apply multiplicative scaling of the spectra, or any set of transformations that is mathematically equivalent to multiplicative scaling. Different transformations may be applied to different analytical regions. Frequency shifts shall be less than one-half the minimum instrumental linewidth, and must be applied to all spectral data points in an analytical region. The mathematical transformations may be retained for the analysis if they are also applied to the appropriate analytical regions of all sample spectra recorded, and if all original sample spectra are digitally stored. Repeat sections 5.3, 5.4 (except the recording of a sample spectrum), and 5.5 of this addendum to demonstrate that these transformations lead to acceptable calculated concentration uncertainties in all analytical regions.

6.0 POST-ANALYSIS EVALUATIONS

Estimate the overall accuracy of the analyses performed in accordance with sections 5.1 through 5.6 of this addendum using the procedures of sections 6.1 through 6.3 of this addendum.

6.1 Qualitatively Confirm the Assumed Matrix. Examine each analytical region of the sample spectrum for spectral evidence of unexpected or unidentified interferants. If found, identify the interfering compounds (see Reference C

for guidance) and add them to the list of known interferants. Repeat the procedures of section 4 of this addendum to include the interferants in the uncertainty calculations and analysis procedures. Verify that the MAU and FCU values do not increase beyond acceptable levels for the application requirements. Re-calculate the analyte concentrations (section 5.5 of this addendum) in the affected analytical regions.

6.2 Quantitatively Evaluate Fractional Model Uncertainty (FMU). Perform the procedures of either section 6.2.1 or 6.2.2 of this addendum:

6.2.1 Using appendix I of this addendum, determine the fractional model error (FMU) for each analyte.

6.2.2 Provide statistically determined uncertainties FMU for each analyte which are equivalent to two standard deviations at the 95 percent confidence level. Such determinations, if employed, must be based on mathematical examinations of the pertinent sample spectra (not the reference spectra alone). Include in the report of the analysis (see section 7.0 of this addendum) a complete description of the determination of the concentration uncertainties.

6.3 Estimate Overall Concentration Uncertainty (OCU). Using appendix J of this addendum, determine the overall concentration uncertainty (OCU) for each analyte. If the OCU is larger than the required accuracy for any analyte, repeat sections 4 and 6 of this addendum.

7.0 REPORTING REQUIREMENTS

[Documentation pertaining to virtually all the procedures of sections 4, 5, and 6 will be required. Software copies of reference spectra and sample spectra will be retained for some minimum time following the actual testing.]

8.0 REFERENCES

A) Standard Practices for General Techniques of Infrared Quantitative Analysis (American Society for Testing and Materials, Designation E 168-88).

B) The Coblentz Society Specifications for Evaluation of Research Quality Analytical Infrared Reference Spectra (Class II); Anal. Chemistry 47, 945A (1975); **Appl. Spectroscopy 444, pp. 211-215, 1990.**

C) Standard Practices for General Techniques for Qualitative Infrared Analysis, American Society for Testing and Materials, Designation E 1252-88.

D) "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards," U.S. Environmental Protection Agency Publication No. EPA/600/R-93/224, December 1993.