

**PROTOCOL FOR FTIR MEASUREMENTS OF
FLUORINATED COMPOUNDS IN
SEMICONDUCTOR PROCESS TOOL EXHAUST**

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**Dr. William Reagen
3M Company
St. Paul, MN 55144**

PREFACE

The semiconductor industry and the United States Environmental Protection Agency have reached a voluntary agreement (memorandum of understanding, MOU) to reduce the emission of perfluorocompound (PFC) gases during microelectronics manufacturing. Industry groups are pursuing four general activities to reach the emission reduction objectives stated in the MOU. The four emission reduction activities include; (1) using new manufacturing processes based on alternative gases, (2) optimizing current manufacturing processes, (3) recovering and recycling PFCs from exhaust streams, and (4) abatement of PFC exhaust through combustion. Feasibility testing and development of these options will require gas sampling and test methods which provide information on the composition of various exhaust streams.

The Protocol For FTIR Measurements Of Fluorinated Compounds In Semiconductor Process Tool Exhaust provides information on an emissions monitoring method which can provide accurate assessments of the gases listed in the MOU. Therefore, this protocol should prove valuable to the semiconductor industry's emissions reduction activities.

This document was prepared by Dr. Bill Reagen of 3M Company with assistance from Dr. Grant Plummer of Rho Squared Inc. (their biographies follow this Preface) for the Technical Working Group on Sampling and Measurement Methodologies headed by the National Institute of Standards and Technology (NIST). The NIST Technical Working Group was part of a subcommittee created during the Motorola Sponsored PFC Emissions Measurement Workshop, and the Semiconductor PFC Workshop, "A Partnership for PFC Emissions Reductions", co-sponsored by: Semiconductor Safety Association (SSA), SEMATECH, and the Semiconductor Industry Association (SIA), February 7-8, 1996. The goal of the NIST Technical Working Group was to guide the development of standard PFC emissions sampling protocols.

This FTIR protocol is modeled after three earlier protocols: SEMATECH document 95123039A-TR, S68 Final Report: Template Methodology and Lessons Learned for Sampling and Analyzing Tool Effluents, SEMATECH document 95012695A-ENG, Global Warming Studies: Sampling/Test Plan Template; and USEPA document Protocol For The Use Of Extractive Fourier Transform Infrared Spectrometry For The Analyses Of Gaseous Emissions From

Stationary Sources (U.S. EPA Emission Measurement Center; available on-line from the Emission Measurement Technical Information Center Bulletin Board System, telephone 919-541-5742).

This FTIR protocol is also based on method validation tests performed by 3M at semiconductor production facilities, during beta testing of new manufacturing processes. In order to perform these tests, 3M and MIDAC Corporation, Irvine CA generated quantitative infrared reference spectra for the MOU listed gases following EPA protocol requirements. As a result, the reference spectra for the MOU listed gases are now commercially available. Using this FTIR protocol as a guide, process emissions containing multicomponent gas mixtures of the MOU listed compounds (CHF_3 , CF_4 , C_2F_6 , C_3F_8 , SF_6 , and NF_3) were simultaneously identified, quantified and displayed on site, during testing of new CVD chamber cleaning processes. In addition to the MOU listed compounds, the FTIR protocol can be used to simultaneously measure other process emissions including SiF_4 , COF_2 , WF_6 , CO_2 , CO and HF .

The FTIR protocol has been used by 3M to support development of new semiconductor manufacturing processes, to support optimization of current manufacturing processes, to support recovery and recycling efforts, and to support PFC abatement programs. The FTIR protocol is one example of how 3M is actively participating in the technical developments needed to attain the PFC emission reduction objectives outlined in the MOU. Through similar commitment, support and participation 3M will continue to provide valuable solutions to semiconductor manufacturers, gas distributors, equipment manufacturers, and other partners in the semiconductor industry.

Larry Zazzera, Ph.D.
3M Company
St. Paul, Minnesota
December 12, 1996

BIOGRAPHIES

William Reagen - received degrees in chemistry from the University of North Dakota (B.S., 1982, Ph.D. Inorganic Chemistry 1987), where he specialized in organometallic and inorganic synthesis. He received a one-year 3M post-doctoral fellowship in 1988 and filled a position at the 3M Environmental laboratory. From 1989-1990, he worked in the area of olefin polymerization catalysis for Phillips Petroleum, where he developed a series of new ethylene trimerization catalysts resulting in 13 issued U.S. & international patents. From 1991-1992, he worked in the area of fiber optic sensor development for the Idaho National Engineering Laboratory (EG&G, Inc.), where he developed sensor techniques for the detection of nitro-organic compounds resulting in 3 issued U.S. patents. In 1993, he began work for 3M and currently holds a position as a Specialist in the 3M Environmental Laboratory. In 1994, he began work with FTIR test methods and has developed and applied extractive FTIR test methods to a wide range of 3M process and environmental needs. He has worked with state regulatory agencies, the US EPA, and regulatory agencies outside the US to validate FTIR test methods at 3M production facilities. He is currently developing FTIR hardware and test methods for applications in materials off-gas measurements and indoor air measurements which have resulted in two patent filings.

Grant Plummer - received degrees in physics from Oberlin College (A.B., 1980) and Duke University (Ph.D., 1985), where he specialized in astrophysics and molecular spectroscopy. He received a Humboldt Foundation Fellowship in 1985 and filled post-doctoral positions at the University of Cologne, the Justus-Liebig University in Giessen, and at the Harvard-Smithsonian Center for Astrophysics. In 1989, he began work in the environmental field at Entropy, Inc. in Raleigh, NC, where he developed emissions test methods under contract to the Environmental Protection Agency. Entropy's FTIR Development Group, which Dr. Plummer organized and oversaw, performed the first extensive field tests of extractive FTIR techniques at many industrial facilities and developed EPA's infrared spectral reference library of hazardous air pollutants. In connection with this work, he authored the "FTIR Protocol" which forms the QA/QC basis for several EPA emissions test methods based on FTIR technology. In 1994, Dr. Plummer started his own consulting firm (Rho Squared) and began working at NC State University, where he teaches physics and performs research with x-ray, infrared, and sub-millimeter wave spectroscopic techniques.

***PROTOCOL FOR EXTRACTIVE FOURIER TRANSFORM INFRARED (FTIR)
MEASUREMENTS OF FLUORINATED COMPOUNDS IN SEMICONDUCTOR
PROCESS TOOL EXHAUST***

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1.0 INTRODUCTION

The intent of this document is to provide procedural and Quality Assurance and Quality Control (QA/QC) bases for gaseous concentration measurements of fluorinated compounds by extractive Fourier transform infrared (FTIR) spectrometry. The compounds of interest are Sulfur Hexafluoride (SF₆), Nitrogen Trifluoride (NF₃), Perfluoroethane (C₂F₆), Perfluoropropane (C₃F₈), Perfluoromethane (CF₄), and Trifluoromethane (CHF₃). They are to be measured in enclosed samples extracted from the effluent of semiconductor plasma tools; the analytes are typically in a mixture of oxygen and nitrogen with low moisture content (less than 0.1% by volume). Typical concentrations of the six analytes are in the 100 to 50,000 part-per-million volume (ppmv) range. Because the tool effluent concentrations can change rapidly, measurements must be made at least twice per minute, and several times per minute if possible. This requirement places special emphasis on the sampling and data acquisition operations for this application.

Substantial field experience in the use FTIR spectroscopy was gained in previous SEMATECH studies and described in reference 1, and has been used in the preparation of this protocol. The nomenclature employed in this document is adopted from reference 2, the U.S. EPA guideline publication "Protocol For The Use Of Extractive Fourier Transform Infrared Spectrometry For The Analyses Of Gaseous Emissions From Stationary Sources." Appendix A (below) lists a number of the salient definitions. The intended audience of the current document is the technical community familiar with plasma tool operation and standard emission testing methodologies. However, because FTIR spectrometry is a relatively new emissions testing technique, it is briefly described in Appendix B. Additional mathematical details of the technique are provided in Appendices C and D. Sections 2.0 and 3.0 outline procedures for the development and application of FTIR spectrometry to the application of interest. Existing documents employed in the development of this protocol are listed in section 4.0.

2.0 METHOD DEVELOPMENT

This section outlines a general procedure for the development and documentation of an extractive, FTIR-based analysis of the effluent from semiconductor plasma tools. This development has been largely accomplished in studies carried out by SEMATECH and 3M Corporation. The procedural outline below therefore serves as a means of summarizing and organizing the techniques employed in those studies within a common terminology and operational approach.

Within this procedural framework, FTIR Method development is seen to consist of two distinct phases, which are 1) a laboratory study phase and 2) a field study phase. In practice, portions of these developmental phases may occur simultaneously, and the results of some later portions of the procedural outline may necessitate adjustment and/or repetition of some activities appearing before them in the outline.

2.1 Laboratory Studies

2.1.1 Proposed Spectroscopic Conditions. Propose a set of spectroscopic conditions under which the field studies and subsequent field applications are to be carried out. These include the minimum instrumental linewidth (MIL), spectrometer wavenumber range, sample gas temperature, sample gas pressure, absorption pathlength, maximum sampling system volume (including the absorption cell), minimum sample flow rate, and maximum allowable time between consecutive infrared analyses of the effluent.

2.1.2 Criteria for Reference Spectral Libraries. On the basis of previous emissions test results and/or process knowledge, estimate the maximum concentrations of the six analytes in the effluent and their minimum concentrations of interest (those concentrations below which the measurement of the compounds is of no importance to the analysis). Values between the maximum expected concentration and the minimum concentration of interest are referred to below as the "expected concentration range." Calculate the expected maximum absorbance level for each compound under the proposed spectroscopic conditions.

A minimum of four reference spectra must be available for each analyte. When the set of spectra is ordered according to absorbance, the absorbance levels of adjacent reference spectra should not differ by more than a factor of six. Optimally, reference spectra for each analyte should be available at absorbance levels which bracket the analyte's expected concentration range; minimally, the spectrum must be available whose absorbance exceeds each analyte's expected maximum concentration.

If reference spectral libraries meeting these criteria do not exist for all the analytes and interferants, or cannot be accurately generated from existing libraries exhibiting lower MIL values than that proposed for the testing, prepare the required spectra according to the procedures below.

2.1.3 Preparation of Reference Spectra. When practical, pairs of reference spectra at the same absorbance level (to within 10%) should be recorded of independently prepared samples. The reference samples should be prepared from neat forms of the analyte or from gas standards of the highest quality commonly available from commercial sources. Either barometric or volumetric methods may be used to dilute the reference samples to the required concentrations, and the equipment used should be periodically calibrated in some independent fashion to ensure suitable accuracy. Dynamic and static reference sample preparation methods are acceptable, but dynamic preparations are more likely than static methods to give consistent results for reactive analytes. Any well-characterized absorption pathlength may be employed in recording reference spectra, but the temperature and pressure of the reference samples should match as closely as possible those of the proposed spectroscopic conditions.

If an MCT or other potentially non-linear detector (that is, a detector whose response versus total infrared power is not a linear function over the range of response employed) is used for recording the reference spectra, the effects of this

type of response on the resulting concentration values should be examined and corrected for. Spectra of a calibration transfer standard (CTS) should also be recorded periodically with the laboratory spectrometer system to verify the absorption pathlength and other aspects of the system performance. All reference spectral data should be recorded in interferometric form and stored digitally.

2.1.4 Sampling System Preparation. Construct a sampling system suitable for delivering the proposed sample flow rate from the effluent source to the infrared absorption cell. For the compounds of interest, the surfaces of the system exposed to the effluent stream should be limited to stainless steel and Teflon™; because of the potential for generation of inorganic automated gases, glass surfaces within the sampling system and absorption cell should be Teflon™ coated. Demonstrate that the system, when sampling from a simulated source at the estimated effluent source pressure, delivers a volume of sample at least four times the maximum sampling system volume in a time shorter than the proposed minimum time between consecutive infrared analyses.

2.1.5 Preliminary Analytical Routines. For the proposed absorption pathlength to be used in actual emissions testing, prepare a simulated spectrum of all the effluent compounds at their expected maximum concentrations plus the field CTS compound at 20% of its full concentration. Prepare a computer program or analytical routine for calculation of the six analyte concentrations plus the CTS compound (and their uncertainties) from a sample spectrum using a subset of the analyte and interferant reference spectra. Apply the program to all reference spectra and to the simulated (maximum expected concentration) spectrum. For each single analyte reference spectrum, ensure that the calculated concentrations and uncertainties of the other five analyte compounds are lower than the minimum concentrations of interest. For each analyte, plot the calculated concentrations versus the known reference spectrum concentrations, and ensure that the degree of linearity of this plot is suitable for the application. For the simulated spectrum, ensure that the calculated concentrations match the known reference and CTS spectrum concentrations to within the calculated uncertainty, and that the uncertainties are suitably low for the application.

2.1.6 Documentation. The laboratory and mathematical techniques used to generate reference spectra and to convert sample spectral information to compound concentrations should be thoroughly documented. The required level of detail for the documentation is that which allows an independent analyst to reproduce the results from the documentation and the stored interferometric data.

2.2 Field Studies

The performance of the proposed spectroscopic system, sampling system, and analytical method should be rigorously examined in a field study. During the field study, all the sampling and analytical procedures envisioned for future field applications should be demonstrated. Additional procedures not to be required during routine field applications, notably thorough dynamic spiking studies of the analyte gases, should be performed during the field study. The field study need be

performed only once if the results are acceptable and if the effluent sources in future field applications prove suitably similar to those chosen for the field study. If significant changes in the effluent sources in future applications are noted and require substantial changes to the analytical equipment and/or procedures, a separate field study should be performed for the new set of effluent source conditions. Ideally, all data taken during the study should be carefully stored and documented, and all spectral information should be permanently stored in interferometric form.

2.2.1 System Installation. The spectroscopic and sampling sub-systems should be assembled and installed according to the manufacturers' recommendations and as used in section B.1.4. For the field study, the length of the sample lines used should exceed the maximum length envisioned for future field applications. The system should be given sufficient time to stabilize before testing begins.

2.2.2 Pre-Test Calibration. Record a suitable background spectrum using pure nitrogen gas. Introduce a sample of the CTS gas directly into the absorption cell at the expected sample pressure and record its absorbance spectrum (the "initial field CTS spectrum"). Compare it to the laboratory CTS spectra to determine the effective absorption pathlength. If possible, record spectra of field calibration gas standards (single component standards of the analyte compounds) and determine their concentrations using the reference spectra and analytical routines developed in sections 2.1.3 and 2.1.5; these spectra may be used instead of the reference spectra in actual concentration and uncertainty calculations.

2.2.3 Reactivity and Response Time Checks. While sampling ambient air and continuously recording absorbance spectra, suddenly replace the ambient air flow with CTS gas introduced as close as possible to the probe tip. Examine the subsequent spectra to determine whether the flow rate and sample volume allow the system to respond quickly enough to changes in the sampled gas. Substitute the field calibration standards for the CTS gas and repeat the process for each reactive analyte. Examine the subsequent spectra to ensure that the reactivities of the analytes with the exposed surfaces of the sampling system do not limit the time response of the analytical system. Monitor the absorption cell temperature and pressure; verify that the (absolute) pressure remains within 2% of the pressure specified in the proposed system conditions.

2.2.4 Sampling System Integrity Checks. While sampling ambient air, and using a mass flow meter or controller, introduce a known flow rate of CTS gas into the sample stream as close as possible to the probe tip. Measure and monitor the total sample flow rate during this process. Verify from the observed CTS concentration and the two flow rates that the sampling system has no leaks and that the flow rate measurements are accurate. During this process, monitor the absorption cell temperature and pressure; verify that the pressure remains within 2% of the pressure specified in the proposed system conditions.

2.2.5 Analyte Spiking. While sampling actual source effluent, introduce a known flow rate of CTS gas into the sample stream as close as possible to the probe tip. Measure and monitor the total sample flow rate during this process, and adjust the

spike flow rate until it represents between 10% and 20% of the total flow rate. After waiting until at least four absorption cell volumes have been sampled, record four spectra of the spiked effluent, terminate the CTS spike flow, pause again until at least four cell volumes are sampled, and then record four (un-spiked) spectra. Repeat this process until 12 spiked and 12 un-spiked spectra have been obtained. During this process, monitor the absorption cell temperature and pressure; verify that the pressure remains within 2% of the pressure specified in the proposed system conditions. Calculate the expected CTS compound concentrations in the spectra and compare them to the values observed in the spectrum.

Repeat this spiking process with all effluent compounds which are potentially reactive with either the sampling system components or with other effluent compounds.

2.2.6 Post-Test Calibration. At the completion of a sampling run and at the end of the field study, record the spectrum of the CTS gas as described in section 2.2.2. The resulting "final field CTS spectrum" should be compared to the initial field CTS spectrum to verify suitable stability of the spectroscopic system throughout the course of the field study.

2.2.7 Amendment of Analytical Routines. The presence of unanticipated interferant compounds and/or the observation of compounds at concentrations outside their expected concentration ranges may necessitate the repetition of portions of the Appendix B procedures. Such amendments are allowable before final analysis of the data, but must be represented in the documentation required in section 2.1.6.

2.2.8 Documentation. The sampling and spiking techniques used to generate the field study spectra and to convert sample spectral information to concentrations should be thoroughly documented. The required level of detail for the documentation is that which allows an independent analyst to reproduce the results from the documentation and the stored interferometric data.

3.0 METHOD APPLICATION

When the required laboratory and field studies have been completed, and if the results indicate a suitable degree of accuracy, the methods developed may be applied to practical field measurement tasks. During field applications, the procedures demonstrated in the field study (see section 2.0) should be adhered to as closely as possible, with the following exceptions:

- 1) Ideally, the sampling lines employed should be as short as practically possible and not longer than those used in the field study.
- 2) Variations from field study conditions, equipment, and analytical techniques must be noted and included in reports of the field application results.
- 3) Analyte spiking (section 2.2.5) and reactivity checks (section 2.2.3) are required only immediately following the installation of or major repair to the sampling system. Four samples spiked with CTS or a surrogate analyte should be compared to four un-spiked samples recorded under the same conditions.

4) Sampling and other operational data should be recorded and documented as during the field study, but not all the interferometric data need be stored permanently. It is sufficient to store only that amount interferometric data to sufficient reproduce and verify some portion of the reported data; typically, less than 5% of the interferometric data (including interferograms for related background and sample single-beam spectra) are required for this purpose.

4.0 REFERENCES

1. M.D. Tucker et. al., "S68 Final Report: Template Methodology and Lessons Learned for Sampling and Analyzing Tool Effluents," SEMATECH Technology Transfer #95123039A-TR, 1995.
2. "Protocol For The Use Of Extractive Fourier Transform Infrared Spectrometry For The Analyses Of Gaseous Emissions From Stationary Sources" (U.S. EPA Emission Measurement Center; available on-line from the Emission Measurement Technical Information Center Bulletin Board System, telephone 919-541-5742).
3. P. Bernath, Spectra of Atoms and Molecules, Oxford Press, New York, 1995.
4. P. Griffiths and J. de Haseth, Fourier Transform Infrared Spectroscopy, John Wiley and Sons, New York, 1986.
5. D.M. Haaland and R.G. Easterling, "Improved Sensitivity of Infrared Spectroscopy by the Application of Least Squares Methods," Appl. Spectrosc. 34(5):539-548 (1980).
6. D.M. Haaland and R.G. Easterling, "Application of New Least-Squares Methods for the Quantitative Infrared Analysis of Multicomponent Samples," Appl. Spectrosc. 36(6):665-673 (1982).
7. D.M. Haaland, R.G. Easterling and D.A. Vopicka, "Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Samples," Appl. Spectrosc. 39(1):73-84 (1985).
8. W.C. Hamilton, Statistics in Physical Science, Ronald Press Co., New York, 1964, Chapter 4.

APPENDIX A. Definitions of Symbols and Terms

A, absorbance - the logarithm to the base 10 of the reciprocal of the transmittance (T).

absorption band - a contiguous wavenumber region of a spectrum (equivalently, a contiguous set of absorbance spectrum data points) in which the absorbance passes through a maximum or a series of maxima.

absorption pathlength - in a spectrophotometer, the distance, measured in the direction of propagation of the beam of radiant energy, between the surface of the specimen on which the radiant energy is incident and the surface of the specimen from which it is emergent.

apodization - modification of the instrument line shape function (ILS) by multiplying the interferogram by a weighing function whose magnitude varies with retardation.

background spectrum - the single beam spectrum obtained with all system components without sample present.

baseline - any line drawn on an absorption spectrum to establish a reference point that represents a function of the radiant power incident on a sample at a given wavelength.

Beer's law - the direct proportionality of the absorbance of a sample to the concentrations of its constituent compounds (see Equation B.1-3).

calibration transfer standard (CTS) gas - a gas standard of a compound used to achieve and/or demonstrate suitable quantitative agreement between sample spectra and the reference spectral library.

compound - a substance possessing a distinct, unique molecular structure.

concentration (c) - the quantity of a compound contained in a unit quantity of sample. The unit "ppmv" (part-per-million volume) is employed in this document, and is equivalent under the assumption of ideal gases to the same quantity expressed on a number, or molar, basis.

double beam spectrum - a transmission or absorbance spectrum derived by dividing the sample single beam spectrum by the background spectrum.

Note: The term "double-beam" is used elsewhere to denote a spectrum in which the sample and background interferograms are collected simultaneously along physically distinct absorption paths. Here, the term denotes a spectrum in which the sample and background interferograms are collected at different times along the same absorption path.

fast Fourier transform (FFT) - a method of speeding up the computation of a discrete FT by factoring the data into sparse matrices containing mostly zeros.

Fourier transform (FT) - the mathematical process for converting an amplitude-time spectrum to an amplitude-frequency spectrum, or vice versa.

Fourier transform infrared (FTIR) spectrometer - an analytical system that employs a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption pathlength, an infrared detector, optical elements that transfer infrared radiation between components, and a computer system. The time-domain detector response (interferogram) is processed by a Fourier transform to yield a representation of the detector response vs. infrared frequency.

Note: When FTIR spectrometers are interfaced with other instruments, a slash should be used to denote the interface; e.g., GC/FTIR; HPLC/FTIR, and the use of FTIR should be explicit; i.e., FTIR not IR.

frequency, ν - the number of cycles per unit time.

infrared - the portion of the electromagnetic spectrum containing wavelengths from approximately 0.78 to 800 microns.

interferogram, $I(\sigma)$ - record of the modulated component of the interference signal measured as a function of retardation by the detector.

interferometer - device that divides a beam of radiant energy into two or more paths, generates an optical path difference between the beams, and recombines them in order to produce repetitive interference maxima and minima as the optical retardation is varied.

linewidth - the full width at half maximum of an absorption band in units of wavenumbers (cm^{-1}).

MIL, minimum instrumental linewidth - the minimum linewidth (observed in absorbance spectra) exhibited by the FTIR, in wavenumbers.

Note: The MIL of a system may be determined by observing an absorption band known (through higher resolution examinations) to be narrower than indicated by the system. The MIL is fundamentally limited by the retardation of the interferometer, but is also affected by other operational parameters (e.g., the choice of apodization function).

mid-infrared - the region of the electromagnetic spectrum from approximately 400 to 5000 cm^{-1} .

reference spectra - absorption spectra of gases with known chemical compositions, recorded at a known absorption pathlength, which are used in the quantitative analysis of gas samples.

retardation, σ - optical path difference between two beams in an interferometer; also known as "optical path difference" or "optical retardation."

scan - digital representation of the detector output obtained during one complete motion of the interferometer's moving assembly or assemblies.

single beam spectrum - Fourier-transformed interferogram, representing the detector response vs. wavenumber.

Note: The term "single-beam" is used elsewhere to denote any spectrum in which the sample and background interferograms are recorded on the same physical absorption path; such usage differentiates such spectra from those generated using interferograms recorded along two physically distinct absorption paths (see "double-beam spectrum" above). Here, the term applies (for example) to the two spectra used directly in the calculation of transmission and absorbance spectra of a sample.

TR - absolute temperature of gases used in recording reference spectra.

TS - absolute temperature of sample gas as sample spectra are recorded.

transmittance, T - the ratio of radiant power transmitted by the sample to the radiant power incident on the sample. Estimated in FTIR spectroscopy by forming the ratio of the single-beam sample and background spectra.

wavenumber, $\bar{\nu}$ - the number of waves per unit length.

Note: The usual unit of wavenumber is the reciprocal centimeter, cm^{-1} . The wavenumber is the reciprocal of the wavelength, λ , when λ is expressed in centimeters.

APPENDIX B. Description Of Extractive FTIR Spectrometry

B.1 Molecular Rotation-Vibration Absorption and Beer's Law

The energy of a molecule associated with its vibrational and rotational motions is quantized, that is, may take on only particular, discrete values. The allowed values are determined by the molecular structure, the atomic masses, and certain other internal molecular interactions. A molecule can (but need not) absorb light when the energy of an incident photon closely matches the energy spacing between two of its allowed energy levels. For most molecular structures, the allowed vibrational/rotational energy level spacings correspond to the energies of photons in the mid-infrared range, so most molecules exhibit some degree of absorption in that spectral range. The probability of an absorption occurring in a bulk sample containing a large number of similar molecules is dependent on several factors besides the incident infrared photon energy, including (but not limited to) the number of absorbing molecules, the total gas pressure, the gas temperature, and the distance the photon is allowed to travel through the sample.

The energy of a photon is proportional to its frequency; mathematically, the energy is given by $E = h\nu$, where h is Planck's constant and ν is the frequency of the photon; ν is related to the speed of light c and the photon wavelength λ through the relation $c = \lambda\nu$. It is customary in infrared spectroscopy to describe radiation by its wavenumber $\bar{\nu}$, defined by the relation $\bar{\nu} = 1/\lambda$; when λ is expressed in centimeters, the units of $\bar{\nu}$ are cm^{-1} . These units, which are proportional to the frequency and to the energy of the photon, are used almost exclusively in the remainder of this document. The spectral range of interest, namely the mid-infrared region, is usually taken to lie between 400 and 5000 cm^{-1} .

FTIR spectrometers rapidly provide accurate estimates to the total energy in an infrared beam at hundreds to tens of thousands of particular wavenumber values across the mid-infrared region. These estimates are arranged in wavenumber order to form a "single beam spectrum" of the infrared power versus wavenumber. In extractive spectroscopy, two such spectra are used to determine molecular concentrations. The first spectrum, recorded using a non-absorbing gas as the sample, is called the "background" spectrum; its value at the i^{th} wavenumber value is referred to here as B_i . The second, or "sample," spectrum is recorded under the same conditions using the sample gas of interest; its value at the i^{th} wavenumber value is referred to here as S_i . It is the direct availability of the quantities B_i , measured under the same conditions as the quantities S_i , which most clearly differentiates extractive FTIR spectroscopy from other types described in the literature (e.g. "remote" or "open path" FTIR spectroscopy).

The "transmittance" spectrum of the sample, representing the fraction of the incident infrared power transmitted by the sample at each wavenumber value, is calculated point-by-point from the sample and background single-beam spectra according to

$$T_i = \frac{S_i}{B_i} \quad (B.1-1)$$

The "absorbance" of the sample at each wavenumber value, A_i , is calculated according to the definition

$$A_i = -\log_{10} T_i \quad (B.1-2)$$

The absorbance of the sample is the quantity of greatest interest in quantitative analyses because it is linearly related to the gaseous concentrations of the absorbing species. The following equation, often referred to as Beer's Law, relates several FTIR experimental parameters to the concentrations in a gaseous mixture of compounds:

$$A_i = \sum_{j=1}^M a_{ij} L C_j \quad (B.1-3)$$

where

i = an index labeling the wavenumber values represented in an FTIR spectrum

j = an index labeling the absorbing compounds in the mixture.

M = the number of absorbing compounds in the mixture.

a_{ij} = the absorptivity of the j^{th} compound at the i^{th} wavenumber value.

L = the absorption pathlength (length of interaction of radiation and sample).

C_j = the volumetric concentration of the j^{th} compound in the mixture.

Instrumentation and techniques for determining the quantities in Equation B.1-3 are found in the following three sections. A modern and more complete description of the molecular physics related to qualitative and quantitative molecular spectroscopy is found in reference 3.

B.2 Spectroscopic Instrumentation

Modern FTIR spectrometers are available from many manufacturers and in many configurations. However, most spectrometers for gas phase analysis consist of the several standard components illustrated in Figure 1. Broad-band, collimated infrared (IR) radiation is produced in a glowbar or other thermal source and directed into an interferometer. The interferometer optically processes the infrared beam, which consists of radiation containing all wavenumbers (wavelengths) across the mid-infrared region, in such a way that the exiting beam is amplitude modulated at an audio frequency which is proportional to the radiation's infrared frequency. The modulated IR beam is directed through one or more enclosed sample volumes; Figure 1 shows a series combination of a multiple-pass (White) sample cell and two

single-pass sample cells. After interacting with the sample, the infrared beam exits the sample region and illuminates a square-law infrared detector.

The interferometer contains at least one moving element; the motion is responsible for the amplitude modulation of the infrared radiation, and a computer records the detector response as a function of the position of the moving element. The resulting plot of the detector response (total infrared power) versus position (more accurately, the optical retardation) is referred to as an "interferogram." Through appropriate mathematical manipulations and a fast Fourier transform (FFT), the same computer (effectively) digitally de-modulates the interferogram, and the resulting single-beam spectrum accurately represents the power in the beam versus wavenumber. Note that, as is characteristic of the Fourier transform, the independent variable in the original function (position, in units of cm) is the inverse of the independent variable in the transformed function (wavenumber, in units of cm^{-1}). As described in section B.1, two single beam spectra (recorded with and without the sample present in the cell) yield the absorbance of the sample in a straightforward calculation.

Many operational parameters are available to the analyst for adjustment and optimization of the spectrometer system, and play important roles in any practical application. Discussions of most of these parameters are beyond the scope of this work, but are available in reference 4 and from many other sources. Of greatest importance to the current application are the choices of integration time, absorption pathlength and spectral resolution; these parameters are discussed in turn below.

Integration time. Under optimal conditions (i.e. when "white" noise in the detector limits the system performance), the signal-to-noise ratio (S/N) in a single beam spectrum is proportional to the square root of the time spent averaging the detector signal during collection of the interferogram, referred to here as the "integration time." In typical systems, the integration time is proportional to the number of "scans" (results of a single motion of the interferometer's moving element) which are co-added to form a complete interferogram. The time required for a single scan depends on details of the detector response speed and the chosen spectral resolution (see below), but is typically between 0.1 and 3.0 seconds. As long as composition of the sample gas changes slowly on the time scale of a single scan, the result of an integration over multiple scans represents a time-average (over the integration time) of the sample composition. Because the generation of absorbance spectra requires two single beam spectra, it is important that the integration time used in collecting both the background and sample interferograms are suitably long; in practice, the background integration is usually carried out over at least twice as many scans as the subsequent sample interferograms, so that the noise in the background spectrum is not dominant.

Absorption pathlength. As stated in Equation B.1-3, the absorbance of a given sample is proportional to the length (the "absorption pathlength") over which the infrared beam is allowed to interact with the sample. If all other spectral properties are held constant, including the S/N, the lowest concentration of a single gaseous component at which its absorbance is detectable in the spectral noise is inversely proportional to the absorption pathlength. For samples containing multiple

analytes over a large range of concentrations, a single absorption pathlength may not allow optimal measurement of all the components. In typical systems, the absorption pathlength cannot be quickly and easily varied; the optical series configuration of absorption cells depicted in Figure 1 represents an approach to the problem of optimizing the absorption pathlength for various sample constituents and/or sample concentrations. Rather than changing the pathlength of a single absorption cell, the operator can choose to direct the sample stream through one of three cells while the others are purged with a non-absorbing gas. This allows relatively rapid adjustment of the absorption pathlength, limited only by the rate at which the sample and purge gases can be replaced in each cell.

Minimum instrumental linewidth. For a given set of operating parameters pertaining to the interferometer and FFT, an FTIR spectrometer exhibits a lower limit to the full width at half-maximum (FWHM) of absorption features present in an absorbance spectrum. This lower limit is referred to here as the "minimum instrumental linewidth," or MIL. Significantly lowering the MIL, or "improving the spectral resolution" of the system, is possible only by increasing the physical length over which a given interferometer's moving element is displaced during a single scan. For a given interferometer, there is always an upper limit to this physical length, and therefore a lower limit to the MIL. Careful consideration must be given to the choice of MIL for a given application, since decreasing the MIL introduces severe costs in both interferometer fragility and S/N achieved per integration time. It is generally accepted that 0.5cm^{-1} is currently the lowest practical MIL value for gas phase spectroscopic field applications. However, if the spectrometer hardware allows both use of a larger MIL and optimization of the effective infrared source size (usually by adjustment of an aperture, or "Jacquinot stop" located somewhere in the beam path), significant improvements in the achievable S/N per integration time can be made.

B.3 Sampling of Effluent Gases

As state above, the direct availability of a background spectrum B_i , measured under the same conditions as the sample single beam spectrum S_i , is an advantage of extractive spectroscopy. However, this advantage comes at the sometimes considerable cost of extracting a truly *representative* sample. Interactions between the components of the gas and the sampling system, as well as interactions of the sample gases themselves, can change the composition of some samples and lead to inaccurate results. The rate at which gas is extracted from the effluent source, relative to the volume of sample required for the analysis, must also be taken into account when the concentrations of the components change over time.

The gas matrix of current interest consists mainly of compounds which are reactive neither with each other nor with the materials used in standard gas extraction systems. However, because of the possibility of reactions between these and other, unanticipated sample constituents or with water vapor, demonstrations of both suitable delivery efficiency and integrity of the sampling system should be performed.

Figure 1 illustrates the standard components of a gas sampling system suitable for the application addressed in this document. It consists of a stainless steel sample probe, Teflon™ sample lines, calibration gas source, and a pump (not shown). The pump attaches to the outlet of the infrared absorption cell (in this case, the cell with 1 cm absorption pathlength), maintains a slight negative pressure ($< 10^{-2}$ H₂O below ambient) throughout the absorption cell, sample lines, and probe, and provides a sample gas flow rate of approximately one liter per minute (lpm). With a suitably calibrated mass flow controller or meter, the operator can introduce known rates of both nitrogen-balance calibration and "spike" gases into the sample stream through the calibration line, which feeds into the probe through a standard "tee" fitting. This allows replacement of any desired fraction of the actual sample flow with known concentrations of analytes or other compounds. Procedures for calibrating and dynamically spiking analytes into the sample stream are discussed in sections 2 and 3 above.

B.4 Data Acquisition and Analysis

Equation B.1-3 (Beer's Law) represents the basis for nearly all quantitative analyses of mid-infrared spectra recorded with a known absorption pathlength. The literature (for example, references 4, 5, and 6) contains substantial discussion and comparison of several types of algorithms used to derive estimates of multi-component gas sample concentrations from a sample spectrum using libraries of reference spectra. These spectral libraries are also referred to in the literature as "training sets." Examples of techniques described in the literature are the "P-matrix," "K-matrix" (or "classical least squares"), "principal component regression," and "partial least squares" algorithms. A simplified classical least squares analysis is described below in Appendix C. Experienced analysts can also employ visual subtraction techniques to obtain accurate concentration data and uncertainties.

In most cases, the choice of an appropriate technique for determining sample concentrations is a matter of both trial and error and of convenience. Important features of an acceptable method of spectral analysis include:

- 1) Careful preparation of multiple reference spectra for each compound of interest, and mathematical characterization of the extent to which the quality of the reference spectral data may limit the overall accuracy and uncertainty from sample spectrum analyses.
- 2) Generation of both concentration data and an estimate of the associated error or uncertainty in the determined values for each individual spectrum analyzed and for every concentration quoted.
- 3) Complete documentation of the mathematical processing of the acquired field data, at the level of detail allowing an independent analyst to reproduce quoted concentration results and uncertainties from the interferometric data.

Procedures related to these desired qualities of the spectral analysis routine are presented above in sections 2 and 3.

APPENDIX C. Mathematical Description of Beer's Law

Direct calculation of the probability of absorption for a particular molecular structure is complex, but can be characterized for a bulk sample and radiation at a particular wavenumber $\bar{\nu}$ by the absorption coefficient $\alpha_{\bar{\nu}}$, defined through the relation

$$\alpha_{\bar{\nu}} = -\left(\frac{1}{P_0}\right)\left(\frac{dP(z)}{dz}\right) \quad (C-1)$$

Here, the radiation is traveling in the z-direction, is incident on the sample with power P_0 at $z = 0$, and has power $P(z)$ as a function of location along the z axis. If the sample includes a single molecule with non-zero absorption coefficient $\alpha_{\bar{\nu}}$, integration of Equation B-1 from $z = 0$ to $z = L$ leads to the following expression for the fraction of the incident power left in the incident radiation after the "absorption pathlength" L , defined as the transmittance $T_{\bar{\nu}}$:

$$T_{\bar{\nu}} = \left(\frac{P(z)}{P_0}\right) = e^{-L\alpha_{\bar{\nu}}} \quad (C-2)$$

If two species (1 and 2) in the sample *both* absorb radiation at the wavenumber $\bar{\nu}$, with absorption coefficients α_1 and α_2 , the fraction of power transmitted after distance L , can be seen from Equation C-2 to be

$$T_{\bar{\nu}} = \left(e^{-L\alpha_1}\right)\left(e^{-L\alpha_2}\right) = e^{-L(\alpha_1 + \alpha_2)} \quad (C-3)$$

This relation represents the efficacy of measuring $T_{\bar{\nu}}$ for a sample containing a mixture of compounds, since contributions to the logarithm of $T_{\bar{\nu}}$ from the different compounds are additive.

It can be shown from first principles^{3, 4} that the quantities α_j in gaseous samples are proportional to the average concentrations (per unit volume) of the absorbing species, labeled here by the index j . By defining the "absorbance" at some discrete (i^{th}) wavenumber through $A_i = -\log_{10} T_i$, we can write the following simple relation for the absorbance of a mixture of M compounds with concentrations C_j :

$$A_i = \sum_{j=1}^M a_{ij}LC_j \quad (C-4)$$

Here, the absorption coefficients for the j th compound at the i th wavenumber have been replaced by the "absorptivity" a_{ij} , to which it is proportional. Equation C-4 is often referred to as the "Beer-Lambert Relation", or simply as "Beer's Law." It is rigorously true for gas samples only when all its quantities are perfectly measured at a given sample (equilibrium) pressure, and when the effects of spontaneous emission are small enough to be neglected.

A useful practical strategy, and one often used in conjunction with FTIR spectrometry, is to determine the absorptivities a_{ij} for single components at a large number of wavenumber values under well-characterized experimental conditions. Beer's Law can then be used to determine the concentrations C_j for a gaseous mixture from the absorption pathlength L and the mixture's observed absorbance A_i . As described in section B.2, FTIR spectrometers rapidly estimate several thousand values of A_i (at various wavenumber values), providing a statistically powerful means for determining a large number of gaseous concentrations from a single sample spectrum.

APPENDIX D. Mathematical Description of a Least Squares Analysis

Virtually all quantitative analyses of FTIR absorption spectra are based Beer's Law (Equation B.1-3), or on some physically reasonable adaptation of Beer's Law indicated by the pertinent experimental constraints. For the reader's convenience, this equation and the definitions of its quantities are re-stated here:

$$A_i = \sum_{j=1}^M a_{ij}LC_j, \quad i = 1, 2, \dots, N \quad (D-1)$$

where

M = the number of compounds assumed to absorb in the spectral region analyzed
(with index j);

N = the number of infrared frequencies used in the analysis (with index i);

A_i = the observed sample absorbance at the ith infrared frequency;

C_j = the (unknown) volumetric concentration of the jth component of the mixture;

L = the absorption path length used in recording the sample spectrum;

a_{ij} = the absorptivity of the jth compound at the ith infrared frequency.

Once the absorbance of a sample gas (A_i) and the absorptivities are determined, many mathematical techniques are suitable for an inversion of Equation (D-1). The technique described here is a simple least-squares analysis using a single reference spectrum for each component in the mixture.

The following approach to estimating the quantities C_j in Equation (D-1) is similar in most respects to one described in a series of papers written by David Haaland and co-workers.^{5, 6, 7} The following treatment follows the notation of reference 8. We rewrite Beer's law as

$$A_i^S = \alpha + \beta\bar{\nu}_i + \varepsilon_i + \sum_{j=1}^M \gamma_{ij}S_j \quad (D-2)$$

where

- the measurements of the sample absorbances A_i^S are made at absolute temperature T, absorption path length L (meters), and pressure p (atm);
- $\bar{\nu}_i$ is the wavenumber value of the ith absorbance point;

- $\alpha + \beta \bar{v}_i$ represents a linear baseline error in Beer's Law for the selected (contiguous) data points;
- ε_i represents the non-baseline error in Beer's law at v_i ;
- S_j is a "scaling factor" for the j^{th} compound included in the analysis.

We define the quantity γ_{ij} in Equation (D-2) as the "reduced absorptivity" of the j^{th} compound at the frequency v_i . For the purposes of the present calculation, it may be estimated by

$$\gamma_{ij} = \frac{T_j}{L_j p_j C_j^R} A_{ij}^R \quad (\text{D-3})$$

where

A_{ij}^R = the absorbance of a single reference spectrum of the (pure) j^{th} compound, recorded with absorption path length L_j (meters) at absolute temperature T_j and pressure p_j (atm), and concentration C_j^R (ppmv).

If we can use Equation (D-2) to form least squares estimates of α , β , and the scaling factors S_j , denoted by $\bar{\alpha}$, $\bar{\beta}$, and \bar{S}_j , then the desired least squares estimates of the concentrations C_j are given by

$$\bar{C}_j = \frac{T}{L_p} \bar{S}_j \quad (\text{D-4})$$

The least squares estimates $\bar{\alpha}$, $\bar{\beta}$, and \bar{S}_j can be formulated from the linear model of Equation (D-2) as follows.⁸ We form the "design matrix" \mathbf{D} of with $M+2$ columns and N rows; each the first M columns of \mathbf{D} corresponds to the j^{th} compound, and consists of the N values γ_{ij} . The $(M+1)$ th column consists of N entries of any non-zero constant, representing the constant baseline offset term α , the $(M+2)$ th column consists of the N values v_i . If we define similar vectors \mathbf{A} to represent the values A_i , \mathbf{X} to represent the $M+2$ unknown quantities $\{S_1, S_2, S_M, \alpha, \beta\}$, and \mathbf{E} to represent the errors ε_i , the linear model in Equation (D-2) takes the form

$$\mathbf{A} = \mathbf{DX} + \mathbf{E} \quad (\text{D-5})$$

In the over-determined case of interest to us ($N \gg M+2$), we may proceed by assuming the errors ε_i possess a joint distribution with zero means, and a variance-covariance matrix of the form

$$\mathbf{M}_f = \begin{pmatrix} \sigma_1^2 & \sigma_1\sigma_2\rho_{12} & \cdot & \sigma_1\sigma_N\rho_{1N} \\ \sigma_1\sigma_2\rho_{12} & \sigma_2^2 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \sigma_1\sigma_N\rho_{1N} & \cdot & \cdot & \sigma_N^2 \end{pmatrix} \quad (D-6)$$

We assume further that \mathbf{M}_f is known only to within a scaling factor σ^2 , that is,

$$\mathbf{M}_f = \sigma^2 \mathbf{N} \quad (D-7)$$

Denoting the matrix transpose with the superscript "t" and the matrix inverse with superscript "⁻¹", the least squares estimate to the desired quantity \mathbf{X} is given simply by

$$\bar{\mathbf{X}} = (\mathbf{D}^t \mathbf{N}^{-1} \mathbf{D})^{-1} \mathbf{D}^t \mathbf{N}^{-1} \mathbf{A} \quad (D-8)$$

The matrix \mathbf{N}^{-1} is the "weight matrix." In the simplest case where all the observed quantities A_i have equal variances σ^2 , \mathbf{N}^{-1} is the identity matrix \mathbf{I} , and $\mathbf{M}_f = \sigma^2 \mathbf{I}$.

Least squares estimates of several other important quantities are available from $\bar{\mathbf{X}}$, including the errors in the components of $\bar{\mathbf{X}}$ itself, that is, the errors in the scaling factor estimates. We can immediately calculate the residual vector

$$\mathbf{V} = \mathbf{A} - \mathbf{D}\bar{\mathbf{X}}, \quad (D-9)$$

which gives the point-by-point difference between the measured A_i^s and its least squares estimate according to our linear model; from \mathbf{V} , the parameter moment matrix \mathbf{M}_X can be estimated according to

$$\mathbf{M}_X = \left(\frac{\mathbf{V}^t \mathbf{N}^{-1} \mathbf{V}}{N - M - 3} \right) (\mathbf{D}^t \mathbf{N}^{-1} \mathbf{D})^{-1}, \quad (D-10)$$

and the uncertainty Δ_i in the parameter estimate \bar{X}_i is given by

$$\Delta_i = \sqrt{(\mathbf{M}_X)_{ii}} \quad (D-11)$$

The least squares estimates of the concentrations and the uncertainties in these estimates are obtained by combining Equations (D-4), (D-8), and (D-11) for the appropriate elements of the set $\{S_1, S_2, \dots, S_M, \alpha, \beta\}$.