ORGANIC AND INORGANIC GASES   **3800**
by Extractive FTIR Spectrometry

FORMULA: Table 1   MW: Table 1   CAS: Table 1   RTECS: Table 1

METHOD: 3800, Issue 2	EVALUATION: FULL	Issue 1: 15 March 2003 Issue 2: 13 January 2016

OSHA: Table 1
NIOSH: Table 1

PROPERTIES: Table 1

SYNONYMS: See example compounds in Table 1

SAMPLING	MEASUREMENT
SAMPLER: PORTABLE DIRECT-READING INSTRUMENT (with filter, if required)	**TECHNIQUE:** EXTRACTIVE FOURIER TRANSFORM INFRARED (FTIR) SPECTROMETRY
FLOW RATE: ~0.1 L/min to ~20 L/min (system-dependent)	**ANALYTE:** See Table 1 (additional compounds may be identified/quantified according to data quality objectives and QA/QC requirements)
VOL-MIN: Instrument dependent **-MAX:** None	
PRESSURE: Extracted gases between 96.6 kPa and 103 kPa (725 mmHg and 795 mmHg) absolute	**ANALYTICAL FREQUENCIES:** See Table 2 for example compounds
	CALIBRATION: Calibration gas standards
TEMPERATURE: Extracted gases between 10 °C and 30 °C	**IDENTIFICATION:** Infrared spectra interpretation and computerized reference library searches
BLANKS: Nitrogen gas, or zero air	
ACCURACY	**RANGE:** See Table 2 (dependent on compound and absorption path length)
RANGE STUDIED: See APPENDIX E	
BIAS: See APPENDIX E	**ESTIMATED LOD:** See Table 2 for example values at 10 m absorption path length
OVERALL PRECISION ($\hat{S}_{rT}$): See APPENDIX E	**PRECISION ($\bar{S}_r$):** See APPENDIX E
ACCURACY: See APPENDIX E	

APPLICABILITY: The usefulness of FTIR techniques has been demonstrated in ambient air and combustion gas mixtures [1,2]. With the participation of an experienced analyst (see APPENDIX A), the method can be used for the characterization of workspace air containing mixtures of volatile organic and inorganic compounds. See Table 1 for examples.

INTERFERENCES: Overlap of infrared absorption features may affect the quantification of each compound. By appropriate use of multivariable least squares analyses, the analyst may be able to obtain accurate compound concentrations for overlapping compounds.

OTHER METHODS: This method is based on portions of EPA method 320 and its addendum [3], which describe the determination of gaseous compound concentrations by extractive FTIR spectrometry. Several compatible ASTM standards describing infrared techniques and terminology are also available [4,5,6,7].

REAGENTS:

1. Nitrogen gas or zero air, high purity or better.
2. Calibration transfer standard (CTS) gas, 2% accuracy or better. The proper concentration depends on both the compound used and the system absorption path length. For ethylene in nitrogen, a standard concentration leading to a concentration-path length product (CPP) of 100 ppm · m to 400 ppm · m is recommended. (For example, a standard of 10 ppm to 40 ppm ethylene in nitrogen is recommended for a 10 m absorption cell).
3. Liquid nitrogen* for cooling the infrared detector, if required.

   *See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. FTIR spectrometer system (source, interferometer, sample absorption cell, and detector) configured for absorption. A minimum instrumental linewidth (MIL) of 2 cm^{-1} or lower is recommended.
   NOTE: A lower or higher MIL may be required or suitable for specific gas matrices. Choose internal absorption cell materials to minimize surface/analyte interactions.
2. Computer system with hardware, software, and required reference spectra for acquisition, storage, and analysis of sample spectra. (A data backup system is recommended.)
3. Sampling pump, 0.1 to 10 L/min, with appropriate particulate filters.
4. Non-reactive gas regulators and sample tubing.
5. Rotameters or other devices, 5% precision or better, for measuring flow rates of sample and calibration gases.
6. Temperature measurement and/or control equipment for all sampling system elements and IR absorption cell.
   NOTE: Temperature control equipment required if ambient temperature <10 °C or >30 °C.
7. Pressure gauge for measuring absolute gas pressure in absorption cell, 5% accuracy at 101.3 kPa (1 atm, 760 mmHg) absolute pressure.
8. For system tests (but not for normal operation): Vacuum pump and gauge capable of 13.3 kPa (100 mmHg) absolute pressure; mid-infrared attenuating filters (50% and 25%); impinger.

SPECIAL PRECAUTIONS: This method requires the use of compressed gases and/or cryogenic liquids and/or toxic chemicals. These materials are dangerous and should be handled only by experienced personnel and according to relevant safety standards. This method does not address all of the safety concerns associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations.

NOTE: Please refer to the appendices for explanations of the terminology used in this document (APPENDIX A) and several FTIR system tests, which must be completed before any testing is performed (APPENDIX B). Appendices C, D, and E provide (respectively) a general description of FTIR spectrometry, considerations for preparing reference libraries, and examples of calculations required for performance of this method.

PRETEST PROCEDURES:

The following procedures (steps 1 and 2) may be performed only by an experienced "analyst" (see APPENDIX A).

1. Verify that the FTIR system has been tested for wavenumber reproducibility, MIL, absorption path length, system response time, residual squared area (RSA), and detector linearity as described in APPENDIX B. If the system is new and/or has been recently assembled and/or has been recently serviced, perform and document results of the tests described in APPENDIX B before proceeding.
2. Prepare a test plan. The plan must include the following:
   a. The proposed system configuration, including the absorption path length and integration time for sample spectra.
   b. The data quality objectives, analytical regions, and expected LOD values for each analyte. See Table 2 and APPENDIX E for example values and calculations.
   c. The names of all "operators" and "analysts" to be involved in the test. Analysts must be experienced in all aspects of the test procedures listed below and may perform any or all of the test procedures. Operators must be experienced in the performance of steps 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, and 13 listed below and may perform *only* those portions of the test procedures.
   d. Verification that the system configuration, existing RSA values, and related LOD values are consistent with the test's data quality objectives. (See APPENDIX E.)

The following procedures (steps 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, and 13) may be performed by an experienced operator or analyst.

3. Activate the FTIR system according to the manufacturer's instructions. Allow sufficient time for the infrared source, the infrared detector, and (if required) the temperature control systems to stabilize.
4. Verify that the computer system is programmed to store interferograms; if the available data storage capacity is insufficient for storage of all interferograms, store single-beam spectra instead. Verify adequacy and performance of the (recommended) data backup system.
5. Bypassing the sampling system, flow nitrogen or zero air directly into the infrared absorption cell until a stable infrared response and moisture levels are reached. Record a background spectrum using an integration time equal to or greater than that planned for subsequent sample spectra.
6. Use the entire FTIR system (including all sampling components) to record an absorbance spectrum of a sample stream of nitrogen or zero air. Use the integration time planned for subsequent sample spectra. Verify that the sample flow rate meets or exceeds that specified in the system response time documentation. Examine the resulting "system zero" (SZ) spectrum and verify the absence of contaminants in the sampling system and infrared absorption cell. If contaminants are detected, clean or replace the appropriate sampling system components and/or infrared absorption cell and record a new SZ spectrum. If contaminants cannot be eliminated, the test results and LOD values may require revision/correction during the quality control procedures (see steps 14, 15, 16, and 17).

CALIBRATION:

7. Using the entire sampling system, acquire two or more pretest CTS spectra and use them to calculate the system absorption path length L_S (see APPENDIX B, section B1). Use the integration time planned for subsequent sample spectra. Verify that L_S is within 5% of the value quoted in the test plan. Verify that the sample temperature and pressure are within 10 °C to 30 °C and 96.6 kPa to 103 kPa (725 mmHg to 795 mmHg), respectively.
8. When possible, perform the following system checks before sampling. If necessary, they may be delayed until performance of the (post-testing) quality control procedures (see steps 14, 15, 16, and 17). If performed after sampling, the results of these procedures may require revision of the test results and LODs.

    a. LOD check. Using one of the SZ spectra, calculate the RSA values (see APPENDIX B, section B2) and LOD values (see Appendix E, section E1) in the analytical regions pertaining to the test analytes. Verify that the system path length (see APPENDIX B, section B1), current RSA values, and current LODs are consistent with the test's data quality objectives (see Appendix E, section E1).

    b. Wavenumber reproducibility check. Record a preliminary workspace air sample spectrum and perform the calculations described in Appendix B, section B4.

SAMPLING:

9. Using the integration time specified in the test plan, obtain samples and record infrared spectra of the desired workplace gases using the entire sampling system. The sampling location may be changed as desired. For tests of duration greater than 2 h, or if the FTIR system is moved during sampling, monitor the system's single-beam response level. If changes greater than 5% in non-absorbing regions of the single-beam spectrum occur, suspend sampling and record a new background spectrum (see step 5). Sample spectra must be acquired at each sampling location for a time period no less than the system response time (see the system test documentation).

10. Repeat step 6; acquire at least one posttest SZ spectrum of nitrogen or zero air; confirm the absence of sampling system contaminates.

11. Record at least one posttest CTS spectrum (see step 7); confirm that the system configuration and the system absorption path length (to within 5%) match those of the test plan.

12. (Optional.) Acquire a posttest background spectrum (see step 5).

SAMPLE ANALYSIS:

13. Using the analytical regions specified in the test plan, employ an appropriate mathematical analysis (see APPENDIX E) to determine preliminary analyte concentrations and their 3σ uncertainties from the sample spectra, reference spectra, absorption path length, and gas pressure.

    NOTE: Reference spectra for all analytes must meet or exceed the QA/QC requirements of APPENDIX D. The reference library must include at least one wavenumber standard spectrum and at least one CTS spectrum. The sample absorption due to any analyte may not exceed the maximum CPP represented in the reference library for that compound.

QUALITY CONTROL:

The following procedures (steps 14, 15, 16, 17, and 18) may be performed only by an experienced analyst.

14. Using one of the SZ spectra, calculate the RSA and LOD values (see APPENDIX E) in the analytical regions pertaining to the test analytes. Verify that the system path length, current RSA values, and current LODs are consistent with the test's data quality objectives. Using a suitable workspace air spectrum, perform the wavenumber reproducibility and resolution tests described in APPENDIX B, sections B3 and B4. If either the wavenumber reproducibility or resolution results fail to meet the specifications, corrective actions are necessary (see step 17).

15. Perform qualitative and/or quantitative analyses of the pretest and posttest SZ spectra and confirm the absence of sampling system contaminants. If contaminants are found that possess significant absorbance in any analytical region, corrective actions may be necessary (see step 17). Perform qualitative and/or quantitative analyses of the pretest and posttest CTS spectra and confirm that the system absorption path length is within 5% of the value quoted in the test plan.

16. Verify that the reference spectra and results meet the data quality objectives of the test plan (see APPENDIX D). If they do not, corrective actions may be necessary (see step 17). Examine the results of the quantitative sample analysis (step 13) and verify some subset of them (including those with relatively high and relatively low concentrations) manually to ensure proper operation of analytical

program. (Techniques for generating spectra representing the analytes at the concentration indicated by the analysis — "scaled spectra," as defined in APPENDIX A — are described in APPENDIX E. The analyst should generate such spectra and compare them, either visually or mathematically, to the indicated sample spectra.)

17. Corrective actions: If the results of steps 14, 15, and 16 indicate that the data quality objectives of the test plan have not been achieved, the analyst may perform one or more of the following actions:
    - Averaging of sequential sample spectra to reduce the RSA.
    - Inclusion of contaminant reference spectra in the mathematical analysis.
    - Development of more accurate analyte or interferant reference spectra.
    - Inclusion of reference spectra for additional compounds in the mathematical analysis.
    - Exclusion from the mathematical analysis of analyte and/or interferant compounds that are clearly absent in the samples.
    - Deresolution or wavenumber adjustment of the reference spectral library to match that of the sample spectra (or vice versa).
    - Revision of the original data quality objectives (those included in the test plan) to levels supported by the test data.
    NOTE: After performing any such corrective actions, the analyst must repeat steps 13, 14, 15, and 16 and reevaluate the LOD value for each analyte compound.

REPORTING:

18. Reporting requirements include the analyte and interferant concentrations, the concentration uncertainties, the FTIR spectrometer configuration, the sampling locations and conditions, the source(s) of the reference spectra, the CTS spectral analysis results, the results of QA/QC procedures, and certificates of analysis for all standard gases. Any variations of the test procedures and original data quality objectives from those included in the test plan should also be documented and reported. (Several of the terms used here are defined in APPENDIX A and described in the following appendices. In particular, see Table D1 for a description of the FTIR spectrometer configuration parameters.)

EVALUATION OF METHOD:

Field evaluations of extractive FTIR methods have been performed for many compounds (see, for example, references 1 and 2) according to EPA method 301 [8].

REFERENCES:

[1] EPA [1993]. Fourier transform infared (FTIR) method validation at a coal fired boiler [www3.epa.gov/ttnemc01/ftir/reports/r03.html].
[2] Reagen WK, Wright BD, Krueger DJ, Plummer GM [1999]. Fourier transform infrared method validation at a carbon bed solvent recovery unit for four gaseous hydrocarbons. Environ Sci Technol *33*(10):1752–1759.
[3] EPA [2014]. Method 320 — Measurement of vapor phase organic and inorganic emissions by extractive FTIR spectroscopy [www3.epa.gov/ttn/emc/methods/method320.html].
[4] ASTM [2012]. D6348-12e1: Standard test method for determination of gaseous compounds by extractive direct interface fourier transform infrared (FTIR) spectroscopy. West Conshohocken, PA: ASTM International [www.astm.org].
[5] ASTM [2015]. D1356-15b: Standard terminology relating to sampling and analysis of atmospheres. West Conshohocken, PA: ASTM International [www.astm.org].
[6] ASTM [2006]. E168-06: Standard practices for general techniques of infrared quantitative analysis (withdrawn 2015). West Conshohocken, PA: ASTM International [www.astm.org].

[7] ASTM [2013]. E1252-98(2013)e1: Standard practice for general techniques for obtaining infrared spectra for qualitative analysis. West Conshohocken, PA: ASTM International [www.astm.org].

[8] EPA [2014]. Method 301 — Field validation of pollutant measurement methods from various waste media [www3.epa.gov/ttn/emc/methods/method301.html].

[9] EPA [1993]. EPA reference absorbance spectra; EPA reference spectra interferograms [www3.epa.gov/ttn/emc/ftir/data.html].

[10] NIST [2016]. Quantitative infrared database [webbook.nist.gov/chemistry/quant-ir/].

[11] EPA [2016]. Software tools and viewers [www3.epa.gov/ttn/emc/ftir/tools.html].

[12] Griffiths PR, De Haseth JA [1986]. Fourier transform infrared spectrometry. New York: Wiley.

[13] Hamilton WC [1964]. Method of least squares and theory of linear hypotheses. In: Statistics in physical science; estimation, hypothesis testing, and least squares. New York: Ronald Press Co., pp. 124–145.

[14] Plummer GM, Reagen WK [1996]. An examination of a least squares fit FTIR spectral analysis method. Unpublished paper (No. 96-WA65.03) presented at the 89th Annual Meeting of the Air and Waste Management Association, Nashville, TN, June 23–28.

[15] EPA [2012]. EPA traceability protocol for assay and certification of gaseous calibration standards. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, EPA/600/R-12/531 [cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryId=245292].

METHOD WRITTEN BY:

Grant M. Plummer, Ph.D. (Rho Squared), William K. Reagen, Ph.D. (3M), and Perry W. Logan (3M).

Table 1. Representative volatile compounds and chemical data

Name	Synonyms*	Formula	MW[†]	CAS No.	RTECS No.	BP (°C)[†]	VP at 20 °C (kPa)[†]	Exposure Limits (OELs)*	
								NIOSH	OSHA
Acetone	Dimethyl ketone, Ketone propane, 2-Propanone	$(CH_3)_2CO$	58.1	67-64-1	AL3150000	56	24	TWA 250 ppm (590 mg/m³)	TWA 1000 ppm (2400 mg/m³)
Ammonia	Anhydrous ammonia, Aqua ammonia, Aqueous ammonia	NH_3	17.0	7664-41-7	BO0875000	−33	1.01×10^3 (26 °C)	TWA 25 ppm (18 mg/m³) ST 35 ppm (27 mg/m³)	TWA 50 ppm (35 mg/m³)
Benzene	Benzol, Phenyl hydride	C_6H_6	78.1	71-43-2	CY1400000	80	10	Ca TWA 0.1 ppm ST 1 ppm	[1910.1028] TWA 1 ppm ST 5 ppm
2-Butanone	Ethyl methyl ketone, MEK, Methyl acetone, Methyl ethyl ketone	$CH_3COCH_2CH_3$	72.1	78-93-3	EL6475000	80	10.5	TWA 200 ppm (590 mg/m³) ST 300 ppm (885 mg/m³)	TWA 200 ppm (590 mg/m³)
Carbon disulfide	Carbon bisulfide	CS_2	76.1	75-15-0	FF6650000	46	48 (25 °C)	TWA 1 ppm (3 mg/m³) ST 10 ppm (30 mg/m³) [skin]	TWA 20 ppm C 30 ppm 100 ppm (30 min maximum peak)
Ethylene oxide	Dimethylene oxide; 1,2-Epoxyethane; Oxirane	C_2H_4O	44.1	75-21-8	KX2450000	11	146	Ca TWA <0.1 ppm (0.18 mg/m³) C 5 ppm (9 mg/m³) [10 min per day]	[1910.1047] TWA 1 ppm 5 ppm [15 min excursion]
Formaldehyde	Methanal, Methyl aldehyde, Methylene oxide	H_2CO	30.0	50-00-0	LP8925000	−19.5[§]	519[‡] (3890 mmHg, 25 °C)	Ca TWA 0.016 ppm C 0.1 ppm [15 min]	[1910.1048] TWA 0.75 ppm ST 2 ppm
n-Hexane	Hexane, Hexyl hydride, normal-Hexane	$CH_3(CH_2)_4CH_3$	86.2	110-54-3	MN9275000	69	17	TWA 50 ppm (180 mg/m³)	TWA 500 ppm (1800 mg/m³)
Hydrogen fluoride	Anhydrous hydrogen fluoride; Aqueous hydrogen fluoride (i.e., Hydrofluoric acid); HF-A	HF	20.0	7664-39-3	MW7875000	20	122 (25 °C)	TWA 3 ppm (2.5 mg/m³) C 6 ppm (5 mg/m³) [15 min]	TWA 3 ppm

See footnotes at end of table.

(Continued)

Table 1 (Continued). Representative volatile compounds and chemical data

Name	Synonyms*	Formula	MW[†]	CAS No.	RTECS No.	BP (°C)[†]	VP at 20 °C (kPa)[†]	NIOSH	OSHA
Methanol	Carbinol, Columbian spirits, Methanol, Pyroligneous spirit, Wood alcohol, Wood naphtha, Wood spirit	CH_3OH	32.0	67-56-1	PC1400000	65	12.3	TWA 200 ppm (260 mg/m^3) ST 250 ppm (325 mg/m^3) [skin]	TWA 200 ppm (260 mg/m^3)
Methylene chloride	Dichloromethane, Methylene dichloride	CH_2Cl_2	84.9	75-09-2	PA8050000	40	47.4	Ca	TWA 25 ppm ST 125 ppm
Nitrous oxide	Dinitrogen monoxide, Hyponitrous acid anhydride, Laughing gas	N_2O	44.0	10024-97-2	QX1350000	−88.5	5.06 × 10^3	TWA 25 ppm (46 mg/m^3) (TWA over the time exposed) [Note: REL for exposure to waste anesthetic gas.]	
Styrene	Ethenyl benzene, Phenylethylene, Styrene monomer, Styrol, Vinyl benzene	$C_6H_5CH{=}CH_2$	104.1[‡]	100-42-5	WL3675000	145	0.67	TWA 50 ppm (215 mg/m^3) ST 100 ppm (425 mg/m^3)	TWA 100 ppm C 200 ppm 600 ppm (5 min maximum peak in any 3 h)
Sulfur dioxide	Sulfurous acid anhydride, Sulfurous oxide, Sulfur oxide	SO_2	64.1	7446-09-5	WS4550000	−10	330	TWA 2 ppm (5 mg/m^3) ST 5 ppm (13 mg/m^3)	TWA 5 ppm (13 mg/m^3)
Tetrafluoroethylene	Tetrafluoroethene; Perfluoroethylene; Perfluoroethene; TFE[‡]	$F_2C{=}CF_2$	100.0[‡]	116-14-3	KX4000000	−75.9[§]	3.27 ×10^{3}[‡] (24500 mmHg, 25 °C)		
Tetrahydrofuran	Diethylene oxide; 1,4-Epoxybutane; Tetramethylene oxide; THF	C_4H_8O	72.1	109-99-9	LU5950000	66	19.3	TWA 200 ppm (590 mg/m^3) ST 250 ppm (735 mg/m^3)	TWA 200 ppm (590 mg/m^3)

See footnotes at end of table.

Table 1 (Continued). Representative volatile compounds and chemical data

Name	Synonyms*	Formula	MW[†]	CAS No.	RTECS No.	BP (°C)[†]	VP at 20 °C (kPa)[†]	Exposure Limits (OELs)*	
								NIOSH	OSHA
Toluene	Methyl benzene, Methyl benzol, Phenyl methane, Toluol	$C_6H_5CH_3$	92.1	108-88-3	XS5250000	111	3.8 (25 °C)	TWA 100 ppm (375 mg/m³) ST 150 ppm (560 mg/m³)	TWA 200 ppm C 300 ppm 500 ppm (10 min maximum peak)
Trichloroethylene	Ethylene trichloride, TCE, Trichloroethene, Trilene	$ClCH=CCl_2$	131.4	79-01-6	KX4550000	87	7.8	Ca	TWA 100 ppm C 200 ppm 300 ppm (5 min maximum peak in any 2 h)
Vinylidene fluoride	Difluoro-1,1-ethylene; 1,1-Difluoroethene; 1,1-Difluoroethylene; Halocarbon 1132A; VDF; Vinylidene difluoride	$F_2C=CH_2$	64.0	75-38-7	KW0560000	−83	3.57 ×10³* (35.2 atm)	TWA 1 ppm C 5 ppm [use 1910.1017]	
m-Xylene	1,3-Dimethylbenzene; meta-Xylene; *m*-Xylol	$C_6H_4(CH_3)_2$	106.2	108-38-3	ZE2275000	139	0.8	TWA 100 ppm (435 mg/m³) ST 150 ppm (655 mg/m³)	TWA 100 ppm (435 mg/m³)
o-Xylene	1,2-Dimethylbenzene; ortho-Xylene; *o*-Xylol	$C_6H_4(CH_3)_2$	106.2	95-47-6	ZE2450000	144	0.7	TWA 100 ppm (435 mg/m³) ST 150 ppm (655 mg/m³)	TWA 100 ppm (435 mg/m³
p-Xylene	1,4-Dimethylbenzene; para-Xylene; *p*-Xylol	$C_6H_4(CH_3)_2$	106.2	106-42-3	ZE2625000	138.4	0.9	TWA 100 ppm (435 mg/m³) ST 150 ppm (655 mg/m³)	TWA 100 ppm (435 mg/m³)

*Source: NIOSH Pocket Guide to Chemical Hazards [www.cdc.gov/niosh/npg/]. Date accessed: February 2016.

[†]Source: International Chemical Safety Cards (ICSC) [www.cdc.gov/niosh/ipcs/]. Date accessed: February 2016.

[‡]Source: PubChem [pubchem.ncbi.nlm.nih.gov/]. Date accessed: February 2016.

[§]Source: Haynes WM, Lide DR, Bruno TJ [2013]. CRC handbook of chemistry and physics: a ready-reference book of chemical and physical data. 94th ed. Boca Raton, FL: CRC Press.

Table 2. Representative infrared data for the compounds of Table 1

Compound	Analytical Region (cm⁻¹)	Reference Spectrum Filename*	LOD at 10 m† (ppm)	Maximum concentration at 10 m‡ (ppm)	Maximum RSA§ (cm⁻¹)	Reference Spectrum Source
Acetone	1163 to 1265	192mav01.spc	0.95	148	0.0211	EPA**
Ammonia	998 to 1131	nh3mav01.spc	0.77	470	0.0363	3M††
Benzene	3000 to 3150	015mav01.spc	0.32	149	0.036	EPA**
2-Butanone	1127 to 1235	mekmav01.spc	0.27	463	0.0233	3M††
Carbon disulfide	2109 to 2200	028mav01.spc	0.13	151	0.0123	EPA**
Ethylene oxide	3059 to 3070	084mav01.spc	0.11	138	0.0025	EPA**
Formaldehyde	2727 to 2844	087bb.spt	0.4	1125	0.0267	EPA** ‡‡
n-Hexane	2778 to 3051	095mav01.spc	0.1	150	0.0639	EPA**
Hydrogen fluoride	4034 to 4206	21hfrav	0.93	15.8	0.15	3M††
Methanol	941 to 1100	104mav01.spc	0.28	151	0.0447	EPA**
Methylene chloride	701 to 789	117mav01.spc	0.31	150	0.062	EPA**
Nitrous oxide	1226 to 1333	n2omav01.spc	0.36	904	0.0301	3M††
Styrene	738 to 944	147mav01.spc	1.84	150	0.0363	EPA**
Sulfur dioxide	1290 to 1410	so2.spc	0.35	~200§§	0.1394	NIST§§
Tetrafluoroethylene	1080 to 1215	tfemav05.spc	0.17	25.7	0.093	3M††
Tetrahydrofuran	2750 to 3085	thf405.spc	0.18	41	0.0782	3M††
Toluene	701 to 768	tolmav01.spc	1.16	463	0.0499	EPA**
Trichloroethylene	762 to 966	tcemav01.spc	0.43	464	0.1071	3M††
Vinylidene fluoride	1080 to 1215	dfemav05.spc	0.21	25.7	0.093	3M††
m-Xylene	782 to 805	172mav01.spc	1.36	146	0.0377	EPA**
o-Xylene	709 to 781	171mav01.spc	0.65	150	0.0444	EPA**
p-Xylene	749 to 840	173mav01.spc	1.17	151	0.0561	EPA**

*Used in LOD calculations; averaged spectra from the quoted libraries; data available from the authors.

†Approximate LOD for a 10 m absorption path length. Typical values of the RSA, quoted analytical regions, and quoted reference spectral data were used to calculate the LOD as described in Equation E1. Note: The LOD may vary from laboratory to laboratory, analyst to analyst, instrument to instrument, and day to day. Therefore, any determination of this value should be performed under the same conditions used for sample analysis and reported only with those analyses. It is stressed that the values below are only conservative estimates of the expected performance of this method.

‡The maximum ppm · m value available for the compound in the quoted reference spectrum source.

§Maximum RSA in the specified analytical regions consistent with the quoted LOD values. See APPENDIX E, section E1.

**See reference 9. Average absorbance and accepted standard concentration values for the low-concentration pairs of spectra were used. Interferograms were truncated to 0.5 cm⁻¹ resolution and triangular apodization was employed.

††Data available from the authors.

‡‡From EPA reference spectra recorded at 100 °C [9].

§§NIST quantitative infrared database [10]. The quoted maximum concentration for sulfur dioxide is based on linearity studies of 0.5 cm⁻¹ resolution spectra with triangular apodization. Nonlinear absorbance leads to errors of less than 10% at 1000 ppm · m.

APPENDIX A. TERMINOLOGY

absorbance — in terms of the incident intensity I_0 and transmitted intensity I, the absorbance A is given by $A = -\log(I / I_0)$. From a pair of FTIR single-beam spectra B (the background spectrum) and S (the sample spectrum), the sample absorbance for each wavenumber value (with index i) in the spectra is approximated by $A_i = -\log(I_{Si} / I_{Bi})$.

absorbance linearity — a characteristic of (ideal) absorbance spectrum; for such a spectrum, the measured absorbance is described by Beer's law (Equation C1).

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 cell — a structure that contains a fluid sample, but allows light to pass through a sample at known temperature, pressure, and absorption path length.

absorption path length — 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.

absorptivity — a measure of the fraction of the incident infrared radiation that is absorbed by a particular compound per molecule and per absorption path length; see Equation C1.

analyst — a person familiar with and experienced in performance of all aspects of this FTIR-based method. Analysts may perform any portion(s) of the method and must perform certain portions of the method (see also "operator").

analyte — a compound whose concentrations in a sample is of interest and is to be accurately quantified (see also "interferant").

analytical region — a contiguous wavenumber region (equivalently, a contiguous set of absorbance spectrum data points) used in the quantitative analysis for one or more analytes.
   NOTE: The quantitative result for a single analyte may be based on data from more than one analytical region.

aperture — an optical device that physically restricts the diameter of the optical beam.

apodization — modification of the interferogram through its multiplication by a weighing function whose magnitude varies with the position of the interferometer's moving element.

background spectrum — the single-beam spectrum obtained with all system components and without sample present (or in the presence of a non-absorbing gas replacing the sample).

baseline — any line (or smooth function of wavenumber) 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 compound in a homogeneous sample to its concentration. See Equation C1, which also describes the more general case of gas mixtures.

calibration transfer standard (CTS) gas — a gas standard of a compound used to measure the sample absorption path length; see step 7, step 11, APPENDIX B (section B1), and APPENDIX D (section D5).

cm^{-1} — see "wavenumber."

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

concentration — the quantity of a compound contained in a unit quantity of sample. The unit "ppm" (number, or mole, basis) is recommended and is equivalent to the volume basis for ideal gases.

concentration-path length product (CPP) — the mathematical product of concentration of the species and the absorption path length. For reference spectra, this is a known quantity; for sample spectra, it is the quantity directly determined from Beer's law. The unit "parts per million · meters" (ppm · m) is recommended.

data quality objectives — parameters pertaining to a certain application of this method, including the estimated LOD values for each compound.

deresolve — to form spectra of lower resolution (higher full-width-at-half-maximum) from spectra of higher resolution (lower full-width-at-half-maximum); see reference 11 for a deresolution program.

detector linearity — a characteristic of an (ideal) IR detector; for such a detector, the measured detector output voltage, when plotted against the total IR in a broadband IR signal incident on the detector, would form a straight line.

double-beam spectrum — a transmittance 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.

extractive — the type of spectroscopy that includes extracting and transporting a sample stream from gases at a certain location to an absorption cell and isolating the sample in the absorption cell for analysis. Other types of spectroscopy in which the sample is not isolated in an absorption cell include "remote", "open path", and "local open path" techniques.

FFT (fast Fourier transform) — a discrete (digital) approximation to an FT (Fourier transform; see below) involving the factoring of the original data into sparse matrices containing mostly zeros.

filter — (1) A device, made of inert materials, that physically removes solid and liquid phase particles from a gas stream. (2) An optical device that transmits some fraction of the radiation incident on it; "neutral density" and "mesh" filters transmit an approximately constant fraction of the incident radiation at all wavelengths over a specified wavelength range.

frequency, v — the number of cycles per unit time; for light, $v = c / \lambda$, where c is the speed of light and λ is the light's wavelength. Unlike the speed and wavelength, which are medium-dependent, the frequency of light is independent of the medium through which the light travels. The term "frequency" is often used to denote the wavenumber (w, cm^{-1}) in FTIR spectroscopy because (in a given medium) the wavenumber is proportional to the frequency. (See APPENDIX C, section C4, and "wavenumber" in this appendix.)

FT (Fourier transform) — the mathematical process for converting an analytical (non-discrete) amplitude-time function to an amplitude-frequency function, or vice versa.

FTIR (Fourier transform infrared) spectrometer — an analytical system that employs a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption path length, 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 infrared power vs. infrared frequency. See Figures C1 and C2.

FTIR spectrometry — use of an FTIR system to perform quantitative measurements.

FTIR system — the combination of an FTIR spectrometer and a sample interface.

FTIR system configuration — the set of parameters required to reproduce, as closely as possible, results from a particular FTIR system at a later time. This set includes (at least) the nominal MIL, the absorption path length, the apodization function, the gas temperature, the gas pressure, the zero filling factor, the measured wavenumbers of specific water absorption bands, the sources of the reference library spectra, the integration time, the detector type and serial number, the detector gain (including hardware and software settings).

FTIR system response time — the minimum time required for the output of an FTIR system to accurately reflect a sudden change in the sample gas composition; see APPENDIX B, section B5.

full-width-at-half-maximum (FWHM) — for a single, symmetric absorption band, the full width of the band in wavenumbers (cm^{-1}) between its 50% relative maximum absorption levels.

impinger — a sample collection device, constructed of inert materials, that passes a gas stream through a liquid phase.

infrared detector — a device that (ideally) produces a voltage proportional to the total infrared power incident on it. Examples are 1) the mercury-cadmium-telluride (MCT) detector, which requires cooling (and is often cooled to liquid nitrogen temperature) and 2) the deuterated triglycine sulfate (DTGS) detector, often operated at ambient temperature.

infrared source — a device that emits a pattern, stable in intensity and wavelength profile, of infrared radiation over a wide range of infrared wavelengths. High temperature filaments or ceramic elements, in conjunction with appropriate focusing optics, are often employed.

integration time — the total time over which the interferometric results of single scans are averaged to produce an interferogram (and its subsequent single- and double-beam spectra). Most software packages allow selection of the number of scans rather than the integration time. The integration time is approximately equal to (but is always less than) the time interval over which the selected number of scans is actually executed.

interferant — a compound whose presence in a sample spectrum must be taken into account to accurately determine one or more analyte concentrations, but whose concentration need not be accurately determined.

interferogram — record of the IR detector's response to the modulated component of the interference signal measured as a function of retardation.

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.

least squares fitting (LSF) algorithm — a calculation whereby one or more compound concentrations are estimated from a sample spectrum by minimizing the squared error in Beer's law within a defined analytical region (see Equations C1, C2, C3, C4, C5, and C6).

limit of detection (LOD, ppm) — for a defined FTIR system configuration and sample matrix, an estimate of the lowest detectable concentration of a specific analyte based on the FTIR system's RSA and the analyte's integrated absorbance for a selected analytical region.

line — see "absorption band."

linewidth — see "full-width-at-half-maximum" and "minimum instrumental linewidth."

metering valve — a gas valve allowing reproducible adjustments of a gas stream flow rate on the order of 2% of the valves full flow rate.

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

minimum instrumental linewidth (MIL) — for a given FTIR spectrometer and FTIR system configuration, the minimum measured FWHM for any absorption band. In wavenumbers, the MIL is often estimated as the reciprocal of the retardation expressed in cm. The MIL depends on the choice of apodization function and is often larger than the MIL estimated from the retardation.

multi-pass cell — an absorption cell that uses mirrors to pass the infrared radiation through the gas sample more than once; this leads to an absorption path length larger than the physical length of the cell (see also "White cell").

operator — a person familiar with and experienced in performance of only some aspects of this FTIR-based method. Operators may perform many portions of this method, but specific portions of the method must be performed by an "analyst."

peak — see "absorption band."

qualitative analysis — examination of sample spectra to determine the presence or absence of particular compounds in a sample.

quantitative analysis — estimation of the actual concentrations of a specific set of compounds using a specific set of analytical regions.

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

residual squared area (RSA) — a measure of the noise (random and systematic) and/or spectral artifacts for an absorbance spectrum in some analytical region; see APPENDIX B, section B2 for a mathematical definition. The RSA can be used to estimate the LOD for a given compound measured with a given FTIR system configuration.

retardation — optical path difference between two beams in an interferometer; also known as "optical path difference" or "optical retardation." In the case of a standard Michelson interferometer, the retardation is simply twice the distance moved by a mirror in the interferometer during a scan.

rotameter — a device indicating the volumetric flow rate of a gas by the vertical displacement of an object suspended by the gas stream.

sample interface — that part of the FTIR system that comes in contact with the sample and/or calibration gases. It includes the sample probe, sample filter, sample line, sample pump, gas valves, internal surfaces of the absorption cell, pressure gauge, sample rotameter, the vent lines, and the calibration components (gas cylinders, regulators, and rotameters).

sampling location — the point in space at which sample gases enter the sample interface.

scaling — application of a multiplicative factor to the absorbance values in a spectrum.

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 relative 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 transmittance and absorbance spectra of a sample.

system zero (SZ) spectrum — the absorbance spectrum of a non-absorbing gas (nitrogen or zero air) acquired using those portions of the sampling interface used to acquire actual sample gases.

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; often presented as %T ($100 \times T$) in spectral representations.

uncertainty — a mathematical quantity determined in an LSF procedure, used to estimate the likely error in the determination of the sample concentration in a procedure; see Equations C1, C2, C3, C4, C5, and C6.

wavelength λ, — the physical distance between successive maxima in the electromagnetic waves that comprise light. The wavelength and speed of light depend on the medium through which the light travels.

wavenumber, w — the reciprocal of the wavelength, also the number of wavelengths of light per unit length, usually expressed in the units cm^{-1}. As is true of both the speed and wavelength of light, the wavenumber is dependent on the medium through which the light travels. (See APPENDIX C, section C4 and "frequency" in this appendix.)

wavenumber adjustment — reassignment of the cm^{-1} values associated with single- and/or double-beam spectra. Adjustments may be made locally by shifting or stretching the wavenumber scale, or globally stretched by changing the laser wavenumber during the FFT.

White cell — alternate name for a multi-pass absorption cell (see "multi-pass" above) indicating its inventor.

zero filling — the addition of zero-valued points to the end of a measured interferogram. In most computer programs, specification of a zero filling "factor" of N results in an interferogram with N times as many points as the original interferogram.

APPENDIX B. SYSTEM TESTS

These procedures must be conducted at least once on new or significantly altered (by replacement of components, dis- and reassembly, etc.) systems. The tests described in sections B2 and B4 must also be repeated during either the pretest preparations or quality assurance procedures. In all cases, activate the FTIR system and allow sufficient time for the infrared source, the infrared detector, and (if required) the temperature control systems to stabilize before proceeding.

B1. Absorption Path Length

Obtain one or more absorbance spectra of a CTS gas (ethylene at 200 ppm · m to 300 ppm · m is recommended) at the gas temperature and pressure of a reference CTS spectrum of the same compound. For each spectrum, calculate the indicated absorption path length as

$$L_S = \frac{L_R P_R A_S}{P_S A_R},$$
(Equation B1)

where: L_S = path length indicated by the sample CTS spectrum (m),
L_R = path length of the reference CTS spectrum (m),
A_S = area of the sample CTS spectrum (cm^{-1}),
A_R = area of the reference CTS spectrum (cm^{-1}),
P_S = pressure of the sample CTS spectrum (kPa), and
P_R = pressure of the reference CTS spectrum (kPa).

When multiple CTS spectra are available, assign to L_S the mean of the single-spectrum L_S results. The reference CTS spectrum path length and concentration used must be based on multiple, high-quality gas standards and physical length measurements (see APPENDIX D, section D5). The analyst must document criteria for the selection of the analytical region and any baseline correction procedures employed.

B2. Residual Squared Area

NOTE: If the following calculations are performed during testing or as part of the QC procedures (steps 14, 15, 16, and 17), perform them using a workspace air spectrum instead of the "water vapor (absorbance) spectrum" described in the two paragraphs below.

Use the integration time selected for field testing in recording the spectra described below. Record a background spectrum of dry nitrogen gas or zero air. Using a suitable impinger, humidify the nitrogen or zero air stream and record a single-beam spectrum at an absolute pressure between 96.6 kPa and 103 kPa (725 mmHg and 795 mmHg). Form the absorbance spectrum of this water vapor sample from the single-beam spectra. Assign the spectrum a unique filename and save it for the calculations described below.

From this water vapor spectrum, subtract a scaled spectrum (see APPENDIX A) formed from the water vapor reference spectrum to be used in subsequent quantitative analyses. The scaling factor may be varied to minimize the absorbance in the resulting difference spectrum in the various analytical regions to be used in the analyses. Subtract a constant offset, a linear function, or a quadratic function from the difference spectrum in each analytical region to form a residual spectrum R for each region. For each residual spectrum R with discrete absorbance value R_i for wavenumber $i = p$ to q, in the wavenumber range w_p to w_q, the RSA, A_{RS}, is defined as:

$$A_{RS} = \frac{w_p - w_q}{q - p + 1} \sqrt{\sum_{i=p}^{i=q} \frac{R_i^2}{q - p}}.$$
(Equation B2)

The RSA has the dimensions (cm^{-1}) and serves as a measure of the integrated absorbance of spectral noise and water subtraction artifacts over the analytical region. The RSA is compared to the total absorbance of a compound in the same region to estimate the LOD for the compound in that region (see APPENDIX D, section D9 and APPENDIX E, section E1).

The calculation described above assumes that water is the only significant infrared absorber in the samples besides the analytes and that only one analyte absorbs in any analytical region. If other analytes or interferants are present, a more conservative RSA may be estimated by adding the absorbance of the additional compounds to the difference spectrum using a set of suitable reference spectra, then subtracting their absorbance using a *different* set of reference spectra.

B3. Minimum Instrumental Linewidth

Evacuate the absorption cell to a pressure below 13.3 kPa (100 mmHg) and record a background spectrum. Obtain a workspace air sample at an absolute pressure of approximately 40 kPa (300 mmHg). Record the absorbance spectrum of this low-pressure sample. Measure at the FWHM linewidth, in cm^{-1}, of at least two isolated water vapor lines (for example, the lines near 1918 cm^{-1} and 2779 cm^{-1}). The MIL is the mean of these FWHM measurements.

B4. Wavenumber Reproducibility

NOTE: If this calculation is performed during testing or as part of the QC procedures (see steps 6 and 10), perform these determinations using a workspace air spectrum instead of the water vapor absorbance spectrum described in section B2.

Using a water vapor spectrum recorded as described in section B2, determine the center wavenumber values w_{S1} and w_{S2} of two isolated water vapor absorption features; the peaks near 1918 cm^{-1} and 2779 cm^{-1} are suggested, though any other pair of isolated lines separated by 500 cm^{-1} or more is suitable. Compare these results to those center wavenumber values w_{R1} and w_{R2} and for the same absorbance features in the water vapor wavenumber standard associated with the reference library to be used in quantitative analyses as follows: Calculate the wavenumber reproducibility, R_W, in cm^{-1} for each of the two absorption bands as

$$R_{Wi} = \left| w_{Ri} - w_{Si} \right|,$$ (Equation B3)

for i = 1, 2.

Compare the maximum of these two values to the MIL for the FTIR system (see section B3). If the wavenumber reproducibility to MIL ratio exceeds 2%, adjustment of the wavenumber scale for the sample spectra may be required.

Mathematical wavenumber adjustments may be made locally by shifting or stretching the wavenumber scale, or globally stretched by changing the laser wavenumber during the FFT. However, large shifts (on the order of 5% or more of the MIL) indicate that the system requires physical adjustments, such as realignment of the laser system responsible for control of the interferometer's moving element. In addition, mathematical wavenumber adjustments require some sort of interpolation procedure in conjunction with the quantitative spectral analysis, and those procedures may result in spectral mismatches whose effects on the accuracy of the analysis are not easily quantified.

The necessity of such wavenumber adjustments depends, in part, on the widths of the absorption peaks of the compounds involved in the spectral analysis. Because many of the absorption bands of water — a nearly ubiquitous interferant in workspace air IR analysis — are very narrow, an accurate analysis usually requires the relatively stringent limits placed above on the wavenumber reproducibility to MIL ratio. However, it is possible to obtain accurate results when this ratio exceeds the recommended limit, especially when only broad absorbance features are actually employed. The analyst may choose to approve analytical results obtained when this ratio exceeds the recommended limit.

B5. System Response Time

Direct nitrogen or zero air through the entire sample interface and record spectra at approximately 30 s intervals. Abruptly replace the nitrogen or zero air gas flow with CTS gas and continue to record spectra. The system response time is the subsequent time required for the FTIR system to generate an absorbance spectrum in which the CTS compound's calculated concentration reaches 95% of the final (stable) concentration value indicated in later spectra.

B6. Detector Linearity

For the chosen optical configuration, attenuate the power incident on the detector by either 1) modifying the aperture setting or 2) placing filters (neutral density or mesh) in the infrared beam path (see Figure C1). At approximately 100%, 50%, and 25% of the system full IR power level, collect pairs of background and CTS spectra. Compare the areas of the CTS bands for the three spectra and verify that they are equal to within 5% of their mean value. If they are not, apply software linearization corrections to the interferometric data according to the manufacturer's instructions. If this option is unavailable, it is necessary to either 1) characterize the system non-linearity and/or apply appropriate concentration corrections or 2) operate the system with attenuation sufficient to ensure linear detector response.

APPENDIX C. GENERAL DESCRIPTION OF FTIR SPECTROMETRY

C1. FTIR Spectrometer Components

Figure C1 illustrates the basic FTIR spectrometer configuration required for gas phase analyses. The infrared radiation emitted by the infrared (IR) source contains energy at all wavelengths between 2.0 µm and 20 µm; this is the portion of the electromagnetic spectrum usually referred to as the "mid-infrared." In the units typically employed in FTIR spectroscopy (wavenumbers, or cm^{-1}), this is the wavenumber range 5000 cm^{-1} to 500 cm^{-1}. The IR radiation passes through an interferometer, where the motion of an optical element, usually a mirror, optically modulates the infrared beam. The modulated IR beam then enters an absorption cell through a window (typically made of potassium bromide or zinc selenide) and interacts with the gases of interest. The physical length over which this interaction takes place is the "absorption path length." In "multi-pass" (or "White") absorption cells, mirrors within the cell direct the IR beam through the sample gas many times; in such cells, the absorption path length can be from 4 to 50 (or more) times the cell's physical length. (A larger absorption path length generally leads to greater sensitivity.) The IR beam then exits the sample cell via a second window and is refocused onto an IR detector. Because this extractive technique requires the transport of gas samples through the FTIR absorption cell, the design and integrity of the sampling system is of great importance. It is also important that the sampling system allow the operator to perform all the necessary calibration and sampling procedures without compromising the speed and flexibility of the analytical system.
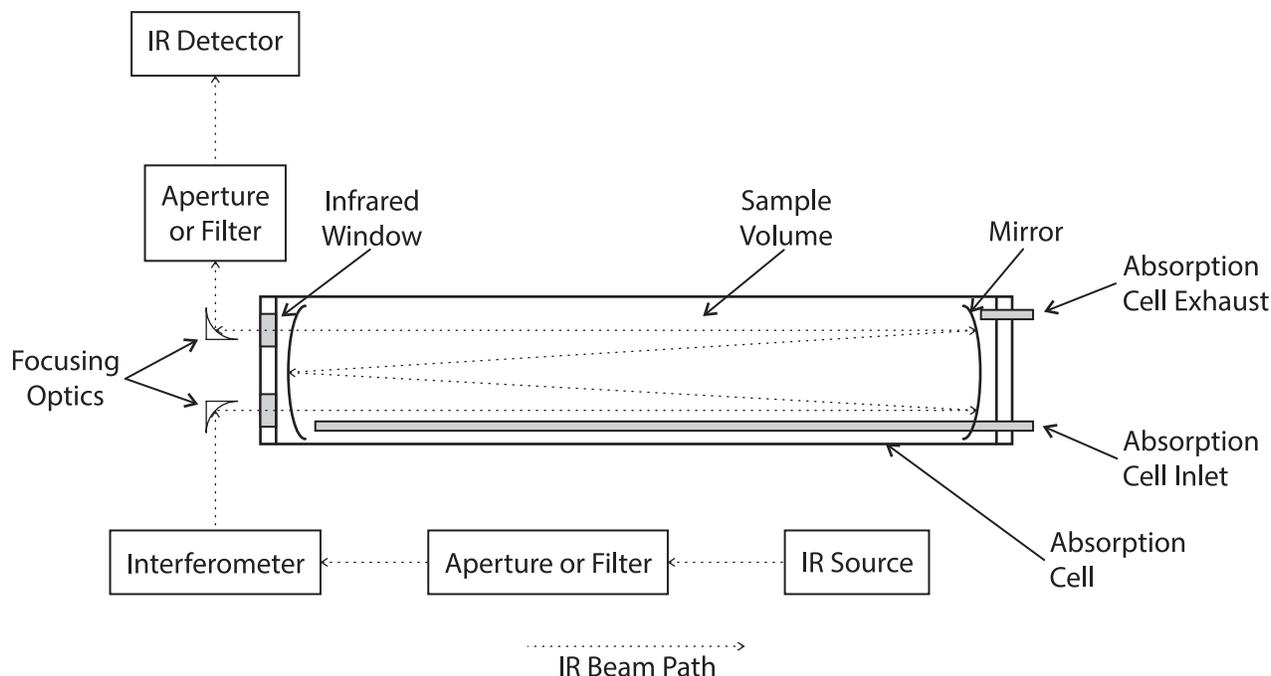

Figure C1. FTIR spectrometer components and beam path.

Figure C2 illustrates a sampling system configuration that meets these requirements, though other configurations are possible. A computer controls the actions of the interferometer and records the voltage output of the IR detector throughout the motion of the interferometer's optical element. Ideally, the detector voltage is proportional to the total power in the IR beam. The computer must accurately record the detector voltage as a function of the position of the moving element in the interferometer, so a secondary, laser-based optical system is usually used to measure the moving element's position very precisely. In most circumstances, the motion of the mirror or other optical element is repeated many times and the resulting individual "scans" are "co-added" (averaged) to reduce the system's RSA.
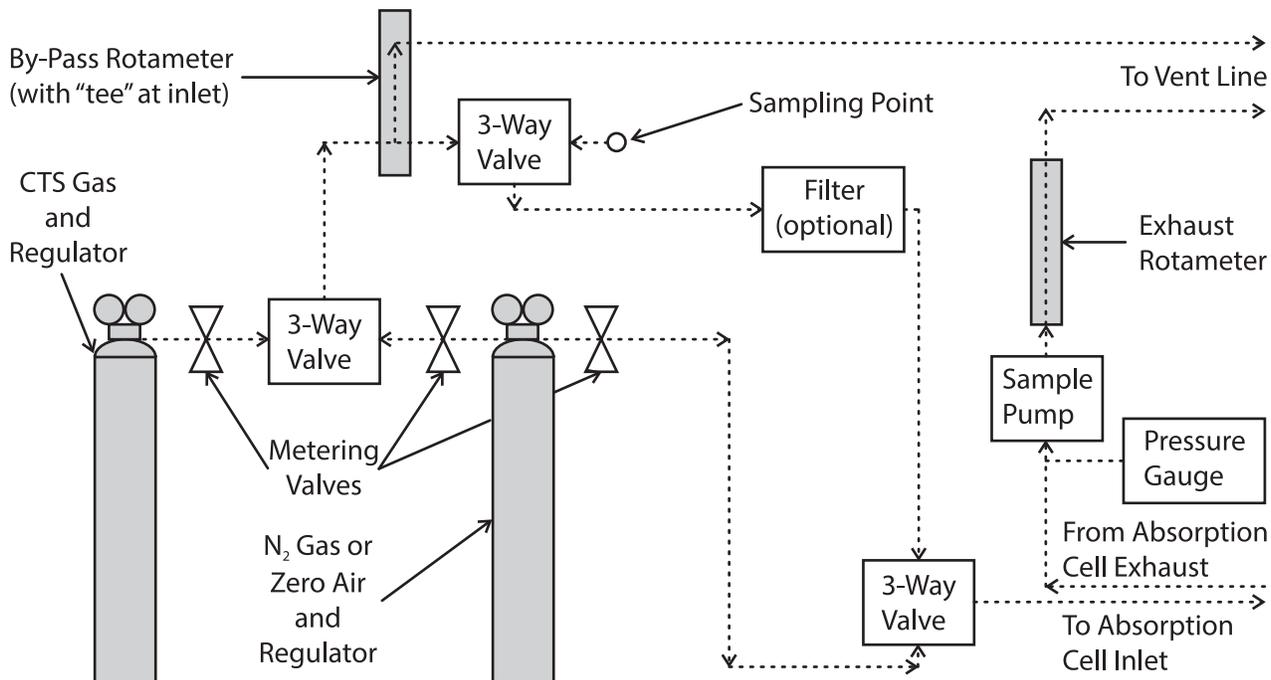
Figure C2. Sampling components and sample paths.

A plot of the resulting IR power-vs.-position signal, referred to as an interferogram, is shown in Figure C3. This interferogram is the co-added result of 64 scans with only nitrogen gas (and some low level of water vapor) present in the absorption cell. Nitrogen is one of the few compounds that does not interact with infrared radiation, so this interferogram very closely represents the fundamental FTIR system response in the absence of a sample. Note that the signal is relatively large near the beginning of the interferogram, where the "zero phase difference (ZPD) burst" is located. The ZPD is often used to rapidly obtain an estimate of the IR signal strength during alignment of the optical system.
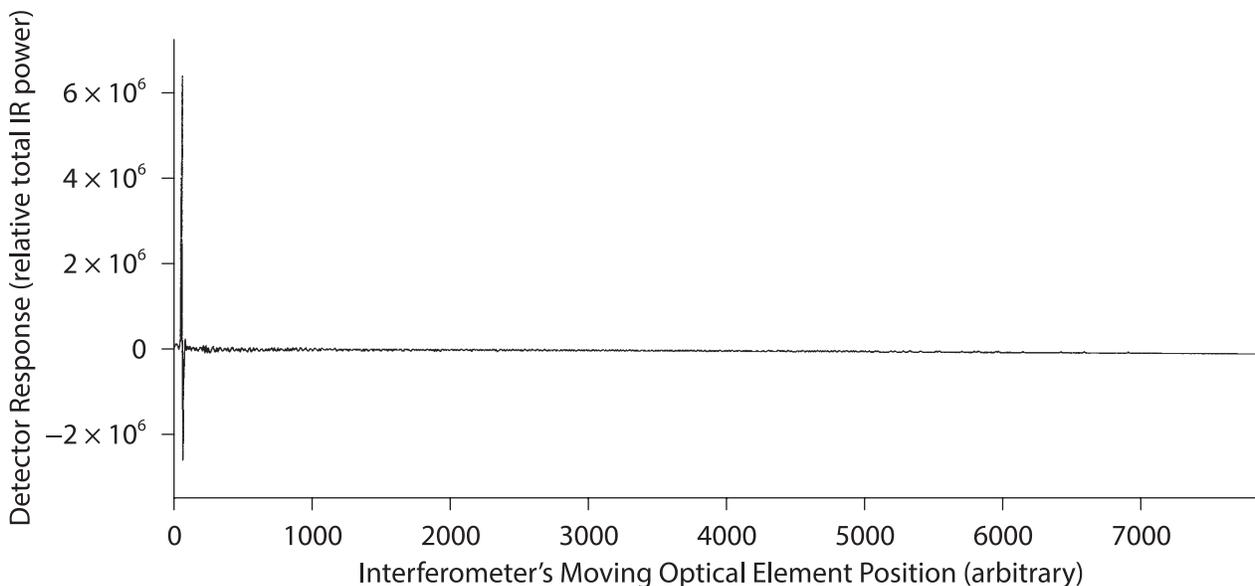

Figure C3. Mid-infrared interferogram.

C2. The FFT

Every data point in the interferogram contains intensity information about every infrared wavelength transmitted from the source to the detector. It is possible to recover the intensity information as a function of wavelength through application of an FFT, from which the FTIR technique's name is derived. This digital transformation of the interferogram can be thought of as the mathematical inverse of the optical modulation applied to the infrared beam as it passes through the interferometer. Its function is similar to that of the human brain and ear, which provide intensity information (loudness) versus wavelength (pitch) for complex signals (sound waves) incident on the eardrum. (Note that, as for an interferogram, each point in a complex sound wave contains intensity information about every pitch contained in the wave. Yet the ear and brain allow a symphony audience to immediately perceive, for instance, that the piccolo is playing very loudly while the tuba is playing very quietly.) Reference 12 (chapter 3) provides a complete mathematical description of the FFT.

C3. Instrument Resolution, Apodization Function, and MIL

Most software packages supplied with FTIR systems provide several options associated with the collection of data and application of the FFT. These typically include - at least - the nominal "instrument resolution" (specified in cm^{-1}) and the "apodization function" (e.g., "boxcar" and "triangular"). These parameters are very important in quantitative spectroscopy and are addressed in turn below.

The instrument resolution is the most fundamental and important instrument parameter. It specifies the nominal minimum FWHM, in cm^{-1}, of any spectral "peak" (or "line") in the final instrument output. Every FTIR instrument has a minimum FWHM determined by the maximum distance traversed by the interferometer's moving element during a single scan. (For the basic Michelson interferometer, the FWHM in cm^{-1} is equal to $(2d)^{-1}$, where d is the distance in cm traversed by a moving mirror during a scan.) Clearly, instruments with low FWHM provide more spectral information than instruments with higher FWHM capability. However, this additional information comes at high costs associated with the design, construction, size, mechanical stability, portability, speed, and RSA of the instruments.

It is important to recognize the two uses of the word "resolution" in the nomenclature used to describe FTIR spectrometers: Instruments of high resolving power, or "*high* resolution," provide spectral features of *low* FWHM; when the nominal resolution is specified in units of cm^{-1}, a *lower* cm^{-1} specification corresponds to *higher* resolving power, or "higher resolution". Most commercially available FTIR spectrometers suitable for field use provide FWHM values greater than or equal to 0.5 cm^{-1}, that is, they are systems whose nominal spectral resolution is specified as a number higher than 0.5 cm^{-1} Most of the instruments capable of higher resolution (lower FWHM) are suitable for use only in very stable laboratory environments.

Standard FTIR operating software always provides options for recording spectra with FWHM values higher than the instrument's actual lower FWHM limit. These options simply move the mirror (or other optical element) through only some fraction of its maximum possible travel. Operating the instrument in this manner results in larger FWHM values ("lower" resolution, and shorter interferograms) than the instrument is mechanically capable of providing. Spectra of lower resolution (higher FWHM) provide less information, but can be generated more quickly and, in most cases, with lower RSA than spectra of higher resolution.

The instrument operator can also choose the apodization function to be used in the generation of FTIR spectra. Apodization is a mathematical alteration of the interferogram that can be performed before application of the FFT. Several standard alteration functions have been devised and each affects the final absorption spectrum of the sample gas in a different way. As with the selection of instrument resolution, each choice has its advantages and drawbacks. The simplest choice, known as the "boxcar apodization" function, results in the lowest FWHM but also in relatively low signal to noise (S/N) ratio. (Spectra generated with the boxcar function are often referred to as "unapodized" spectra.) Other choices (triangular, Norton-Beer, and several other apodization functions) provide higher S/N ratio

at the cost of higher FWHM values and other trade-offs in quantitative spectroscopy. Reference 12 provides a more thorough description of the characteristics of various apodization functions.

For a given instrument configuration — which includes the nominal spectral resolution and the choice of apodization function — every FTIR system is capable of generating absorption bands with an MIL. Unlike the actual spectral resolution (which has several accepted physical definitions — see reference 12, chapter 1, section IV) and nominal spectral resolution parameters, the MIL is a parameter that is readily measured to the accuracy required for practical applications of FTIR spectrometry. It can be measured using the water absorption bands present in low-pressure workspace air samples (see APPENDIX B, section B3).

C4. Single-Beam Spectra

The mathematical result of the FFT (applied to an apodized IR interferogram) is a called a single-beam spectrum. Single-beam spectra represent the infrared power transmitted through the FTIR spectrometer as a function of the infrared "wavenumber" w, which is usually expressed in the units of reciprocal centimeters (cm^{-1}). The wavenumber is actually a measure of the frequency, rather than the wavelength, of the infrared radiation. In a vacuum, the wavelength and frequency are related through the equation $v = c / \lambda$, where λ is the wavelength (cm), v is the frequency (s^{-1}, or Hz), and c (cm/s) is the speed of light, equal to $2.99792954 \times 10^{10}$ in a vacuum. In these units, the wavenumber in cm^{-1} is given by the equation $w = 1 / \lambda = v / c$. Figure C4 presents the single-beam spectra for two samples consisting mainly of nitrogen gas (≥99%) but with different concentrations (≤1%) of water vapor. The vertical scales of the two spectra are nearly identical, but they have been offset for clarity. The detected infrared power in certain wavenumber regions is clearly lower in the high moisture sample, indicating both the qualitative nature and strength of water's absorption of infrared radiation.
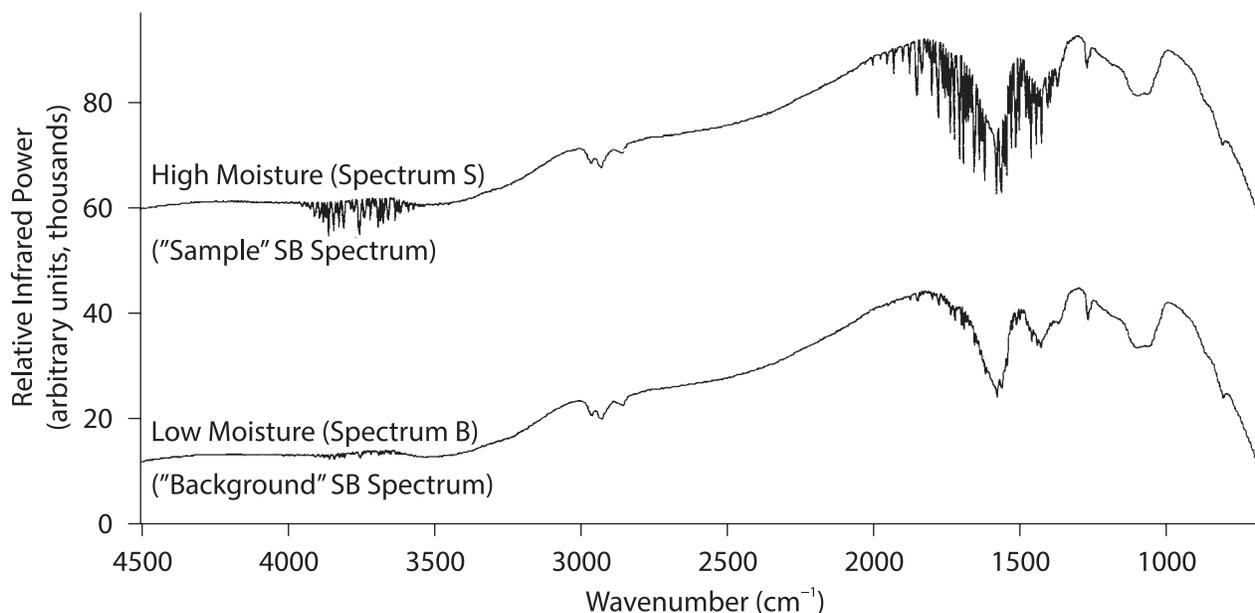

Figure C4. Single-beam spectra of nitrogen at different moisture levels.

C5. Double-Beam Spectra — Transmittance and Absorbance

Combinations of pairs of single-beam, such as the pair of spectra S and B shown in Figure C4, are referred to as double-beam spectra; they provide the quantitative basis for FTIR spectroscopy. One type of double-beam spectrum is the transmittance. The percent transmittance of a sample gas possessing the single-beam spectrum S — with respect to the background single-beam spectrum B — is defined as $T = 100 \times I_S / I_B$ (%), where I_S and I_B are the respective transmitted intensities; a transmittance value is

defined for each wavenumber value of the two spectra. If the background spectrum B closely represents the response of the FTIR system to a transparent sample, then the percent transmittance closely approximates the percentage of the infrared radiation transmitted by the sample (represented by the spectrum S). Because water is the only absorbing compound present in the single-beam spectrum B, the spectrum transmittance (shown in Figure C5) closely approximates the percent transmittance spectrum of water.
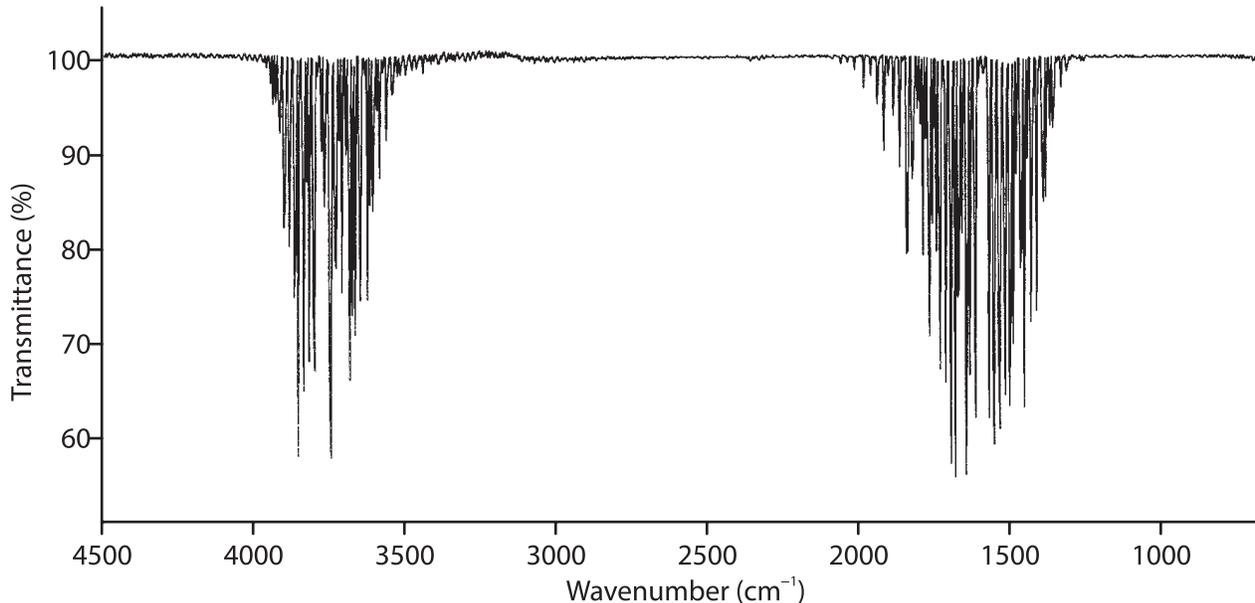

Figure C5. Double-beam transmittance spectrum of water.

The same pair of spectra define the (double-beam) absorbance A of the sample through the equation $A = -\log(I_S / I_B)$. The absorbance spectrum of water, as approximated by the two single-beam spectra S and B, is shown in Figure C6. The absorbance is the desired quantity because it appears in the general linear absorption model known as Beer's law (see below).
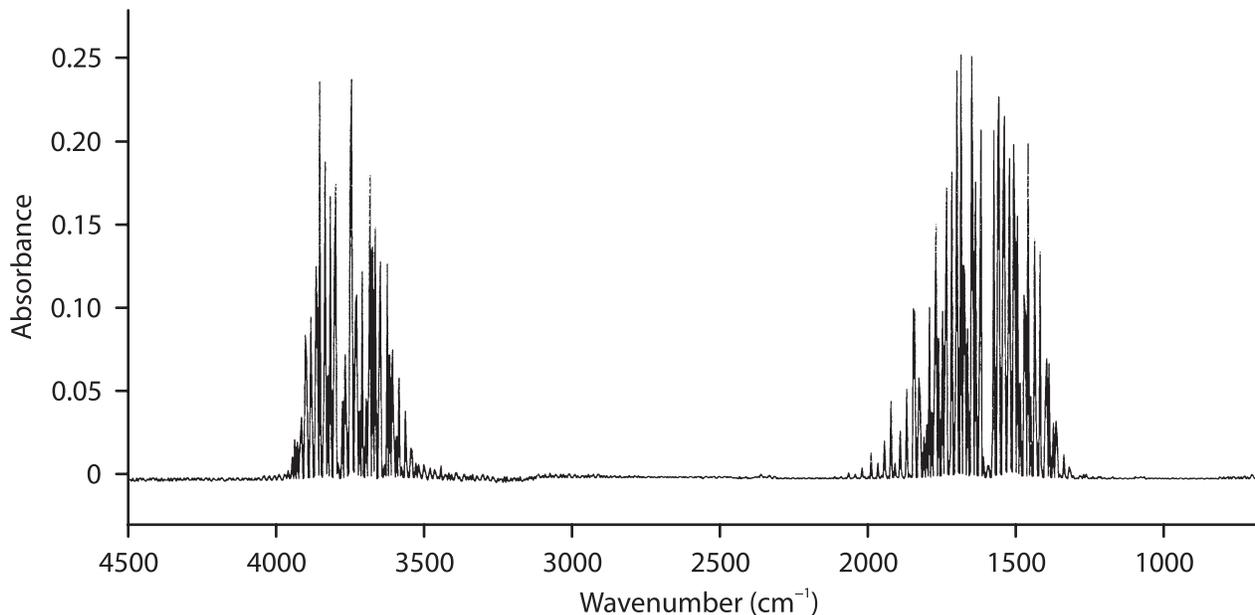

Figure C6. Double-beam absorbance spectrum of water.

C6. Beer's Law

The absorbance spectrum of a sample gas is determined from single-beam spectra of an infrared-transparent gas (the background spectrum) and the sample gas (see section C5). The fundamental relationship connecting the absorbance spectrum of a sample gas to the concentrations of the compounds comprising the sample is referred to as Beer's law. This relationship can be written as

$$A_i = \sum_{j=1}^{j=M} L_S a_{ij} C_j,$$
(Equation C1)

where: i = an index labeling the frequencies of the observed absorbance values in the sample's absorbance spectrum,
A_i = the observed absorbance of a sample at the ith wavenumber,
L_S = the sample absorption path length (m),
j = an index labeling the absorbing compounds comprising the sample,
a_{ij} = the absorptivity of the jth compound at the ith wavenumber (ppm/m),
C_j = the volumetric concentration of the jth compound (ppm), and
M = the number of absorbing compounds in the sample.

The procedures described in this method are all related to the parameters that comprise Beer's law. The following list describes these procedures and relationships in a general context:

1. Record a reference absorbance spectrum for each interesting compound of a nitrogen-diluted sample of the pure compound, at a known concentration and path length, then divide the absorbance at each point in that spectrum by the CPP. This process yields the absorptivity spectrum (a_{ij}), or reference spectrum, for each compound.
2. Measure the absorbance A_i for the mixture of compounds (see steps 5 and 9 above).
3. Determine the path length L_S for the current measurement of A_i (see steps 5 and 7 above).
4. Select the analytical region — that is a set of frequencies, corresponding to the possible values of the index i — that are to be used to determine the concentration of each compound, and then mathematically invert Equation C1 to determine the desired concentrations C_j. (APPENDIX E addresses the topic of spectral analysis in detail.)

NOTE: The true absorptivity for a single gaseous compound is a characteristic only of the compound's structure. However, details of the FTIR system performance and operation affect the observed absorptivity and its accuracy. Similarly, FTIR measurements provide only an approximation of the true absorbance spectrum of a mixture of gaseous compounds, though it is, under many circumstances, a sufficiently accurate approximation. It is the responsibility of the analyst to verify and ensure that the reference and sample spectra provide a sufficiently accurate quantitative analysis according to Beer's law. The following sections of this appendix describe the mathematics of such an analysis. APPENDIX D addresses the topics of developing and using reference spectral libraries. APPENDIX E provides an illustrative example of the design and evaluation of the quantitative analytical process.

C7. Determining Concentrations with LSF Algorithms

When a sample gas contains only one absorbing compound, Equation C1 simplifies to

$$A_i = L_S a_{ij} C_j.$$
(Equation C2)

This means that in any analytical region where only one gas absorbs, any one (of the usually many) absorbance spectrum values A_i can be used to yield the concentration C_j.

The absorbance area A_S for a single-component spectrum in an analytical region (from $i = p$ to $i = q$) can be written as

$$A_S = \sum_{i=p}^{i=q} A_i = \sum_{i=p}^{i=q} L_S a_{ij} C_j = L_S C_j \sum_{i=p}^{i=q} a_{ij} = L_S C_j A_R,$$
(Equation C3)

where A_R is the area in the reference spectrum for that compound in the same analytical region. (This is the basis of the absorption path length L_S calculation described in step 7 and APPENDIX B, section B1.) Because calculation of the absorbance area involves many points in the sample spectrum, Equation C3 leads to much more accurate results than the single-point calculation represented by Equation C2.

However, when many absorbing compounds are present in a sample, the absorption patterns of the various compounds often overlap. In this case, there is usually not an isolated analytical region for each compound in which only that compound absorbs infrared radiation; no single absorbance point and no simple absorbance area is suitable for determining any of the component concentrations. In this case, the simplest method for determining concentrations is to use an LSF algorithm.

LSF algorithms use the fact that there is some set of estimated concentrations D_j that minimizes the "squared error" in Beer's law for any given analytical region, for any set of compounds. The only requirement on the chosen analytical region is that it must contain a sufficient number of data points; since each FTIR spectrum contains many thousands of absorbance values, this requirement is nearly always fulfilled.

If we use the estimated concentrations D_j (rather that the true concentrations C_j) in Beer's law, they will lead to some estimated error e_i at each value of i (that is, at each point in the analytical region we choose). Equation C1 becomes:

$$A_i = e_i + \sum_{j=1}^{j=M} L_S a_{ij} D_j.$$ (Equation C4)

The estimated squared error E^2 (or "variance") in Beer's law using the estimated concentrations is:

$$E^2 = \sum_{i=1}^{i=N} e_i^2 = \sum_{i=1}^{i=N} \left[\sum_{j=1}^{j=M} L_S a_{ij} D_j - A_i \right]^2,$$ (Equation C5)

where N represents the number of absorbance values in the analytical region. Reference 13 demonstrates that 1) for $N > M$ there is a unique set of estimated concentrations D_j that minimizes the estimated squared error; 2) this set of values is calculable from the known quantities in Equations C1, C2, C3, C4, and C5; and 3) estimates σ_j of the uncertainties in the quantities D_j are also calculable from the same quantities. The value $3\sigma_j$ is generally accepted as a conservative estimate of the statistical uncertainty in the related estimated LSF concentration (see reference 4).

The estimated LSF error at each point in the analytical region,

$$e_i = A_i - \sum_{j=1}^{j=M} L_S a_{ij} D_j,$$ (Equation C6)

is usually stored following the analysis as a "residual spectrum," which can provide an estimate of the LODs for other compounds. In addition, the residual spectrum and the concentration uncertainties can allow the analyst to detect and identify compounds that are actually present in the sample gas but which were not included in the mathematical analysis. APPENDIX E provides an example illustrative of these procedures.

The above description illustrates a simple and easily interpreted LSF analysis. More sophisticated LSF analytical techniques, possibly more accurate for particular types of samples, are described in the literature (see, for example, reference 14 and references therein).

C8. Calibration Transfer and Reference Libraries

Equations C1, C2, C3, C4, C5, and C6 demonstrate the importance of quantities L_S (the absorption path length) and a_{ij} (the absorptivity) in FTIR spectrometry. Accurate determinations of these quantities allow the use of reference libraries for quantitiative analyses without the necessity of compound-specific field calibrations. The system tests described in the procedures and in APPENDIX B are intended to ensure suitability of the system configuration for such calibration transfers, as are the requirements

of obtaining CTS spectra in field. APPENDIX D describes procedures for recording and processing reference library spectra.

C9. Corrections to Deviations from Beer's Law Exhibited by FTIR Spectra

Beer's law is based on fundamental, well-established physical principles. It holds absolutely for gas samples that are at thermal equilibrium and dominated by induced (rather than spontaneous) emission and absorption processes. (See Note below.) However, *this is not to say that the absorbance, as measured by an FTIR spectrometer, follows Beer's law under all conditions*. Deviations from Beer's law in FTIR spectra are often observed; however, they indicate inaccuracies in the FTIR spectra, not "violations" of Beer's law. For example, deviation from Beer's law is commonly exhibited by sets of single-component reference spectra recorded over a range of absorbance levels. At large enough values of the absorbance, the points A_i of stronger absorption bands of such spectra no longer increase linearly with the CPP $L_R \cdot C_j$; this is why Table 2 specifies a maximum ppm · m value for the listed reference spectra. If the assumption of detector linearity does not hold (see APPENDIX B), similar effects are often present in reference and sample spectra; this is the basis for the system test described in APPENDIX B, section B6.

Mathematical correction of the concentration estimates D_j derived from Beer's law can often reduce the error in sample analyses when either type of non-linear effect occurs. Figure C7 provides an example of such a correction. The actual and calculated ppm · m values for a set of reference spectra are plotted against each other, a "piece-wise linear" approximation to the pattern is shown by the solid line, and the dashed line indicates the ideal linear behavior based on the spectrum of lowest absorbance. At any ppm · m value indicated in a Beer's law sample analysis (that is, for any y-axis value up to approximately 900 ppm · m in the example), reasonably accurate values are available from the corresponding x-axis position of the solid line. If the analyst employs such corrections, he or she should also calculate the residual (Equation C6) using the reference spectrum that minimizes the squared error (Equation C5). FTIR analysts and manufacturers have devised other correction procedures to improve the sample analysis accuracy in such circumstances, and these are included in some commercially available software packages.
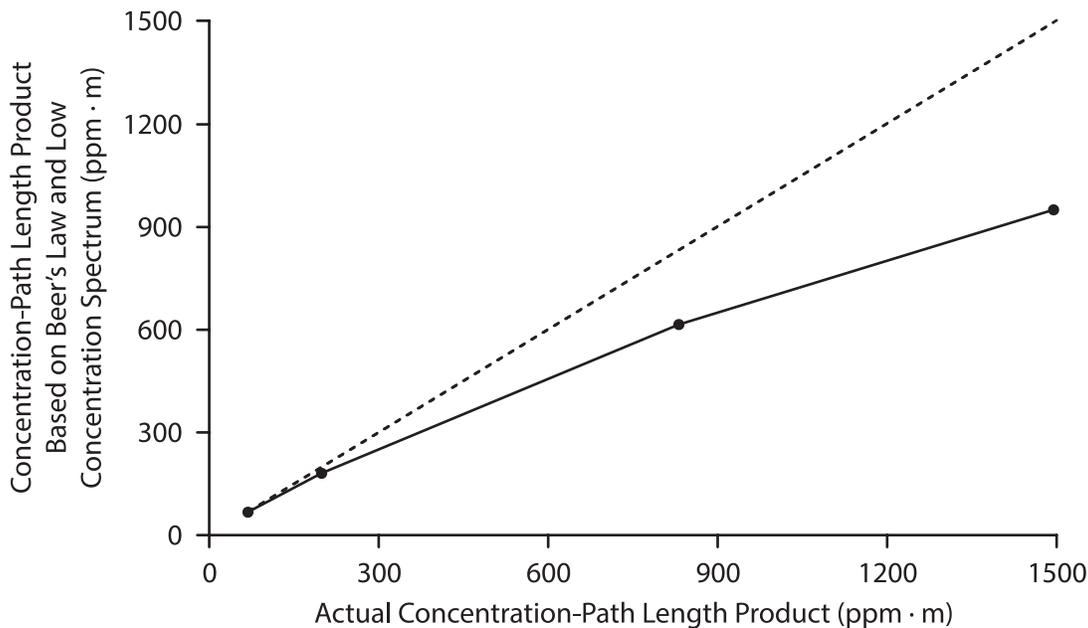

Figure C7. Example absorbance non-linearity for a set of single-component reference spectra.

NOTE: Intense infrared radiation, such as that produced by some lasers, can induce non-equilibrium populations of a molecule's rotation-vibration energy states. However, the thermal infrared sources

used in commercially available FTIR spectrometers are much weaker than such lasers. In gases at atmospheric pressure, the commercially available thermal sources induce transition rates between quantum energy states that are small, compared to those of the competing collisional relaxation processes, and cannot induce non-equilibrium energy state populations. In addition, the induced transition rates related to absorption and emission at mid-infrared frequencies are much larger than the corresponding spontaneous (natural) emission rate. As a result, all *accurate* FTIR measurements at mid-infrared frequencies obey Beer's law to within the uncertainty related *only* to the S/N ratio of the measured spectra.

APPENDIX D. PURPOSES, PREPARATION, AND USE OF REFERENCE SPECTRAL LIBRARIES

D1. Purposes of Reference Spectral Libraries

FTIR analyses rely on the availability of libraries of spectral information on the compounds of interest. For gases, the measured absorbance of a single component is often completely independent of the concentrations of other gases comprising the sample, and single-component reference spectra are usually employed. (For condensed phases, there are often strong interactions between components, and reference spectral libraries of mixtures are usually required.) Reference libraries may be used for quantitative measurements of analyte concentrations, for the mathematical removal of spectral features of interferants in a mixture, or simply for the identification of compounds in a mixture. Clearly, the required level of quantitative accuracy of the library is different for these three tasks; the highest quality is required for analyte concentration determinations, while no quantitative information is required for interferant removal and compound identification.

A useful characteristic of extractive FTIR spectrometry is that it provides accurate field measurements for many compounds, but requires field calibration procedures involving only two compounds. The water vapor available in every ambient air sample serves to calibrate the wavenumber (x) axes of FTIR absorbance spectra; a single CTS gas serves to calibrate their concentration-related (y) axes. When these two field calibrations are combined with an appropriate reference spectral library describing additional compounds, the measurement capability of the technique is practically limited only by the quality and scope of the reference library. If the reference library is carefully prepared and properly employed, this characteristic can lead to greatly lowered field test costs, since the calibration materials need be handled only once and only in the laboratory.

D2. Reference and Field FTIR System Configurations

In the ideal case, the reference library can be prepared on the field instrument, but this is often impractical; the reference library is usually prepared on specific laboratory systems and employed in measurements made with many field systems. Reference libraries recorded on a specific instrument provide accurate quantitative analyses for spectra recorded on other instruments only when the configurations of the various systems are compatible. Table D1 lists compatibility considerations for the reference system configuration parameters.

D3. Wavenumber Standard Spectra

Except in extremely dry conditions, the IR absorption by water vapor in workspace air is detectable at even very short absorption path lengths. The wavenumber positions of water vapor indicated by the reference system allow the analyst to confirm the wavenumber accuracy of sample spectra recorded on a different FTIR system in the field. Reference spectra used for this purpose are referred to here as the wavenumber standard spectra.

Every spectrum in a reference library should be associated with a wavenumber standard spectrum collected under the identical system configuration; even when the reference FTIR system is in a stable environment, it is recommended that a wavenumber standard spectrum be recorded daily with the system.

Before recording reference spectra, the analyst should check the most recent wavenumber standard spectrum against previous wavenumber standard spectra in the library; see APPENDIX B, section B4 for recommended calculations. If the wavenumber reproducibility of the system is poor, the resulting reference spectra may not be suitable for quantitative use on other field systems.

Table D1. Reference and field system configuration parameters

Parameter	Requirements for Reference and Field Systems
Minimum instrumental linewidth	Reference MIL must be less than or equal to field MIL. See APPENDIX B, section B3 for MIL measurement technique.
Gas temperature	Reference temperature within 20 °C of field temperature. Density corrections based on ideal gas law are accurate over only this narrow temperature range and their exact accuracy is compound-dependent.
Gas pressure	Reference pressure within 20% of absolute field pressure. Pressure corrections based on ideal gas law are accurate over at least this range, but their accuracy is compound-dependent. Atmospheric pressure is recommended for all measurements.
Apodization function	Reference and field apodization functions must be the same. A single set of reference interferograms (background and sample) can be used to generate a multiple sets of absorbance spectra using different apodization functions.
Zero filling factor	Reference and field zero filling factors must be the same. A single set of reference interferograms (background and sample) recorded with no zero filling can be used to generate a multiple set of absorbance spectra using different zero filling factors.
Wavenumber accuracy	Characterized by the position of water absorption bands in a wavenumber standard spectrum (see below); if additions to an existing library are being made, care must be taken to match the x-axes of all spectra as closely as possible.
Integration time	Reference integration times (for both background and sample interferograms) should be greater than or equal to expected field integration times. For reference libraries, the longest practical integration time is recommended.
Detector type and serial number	If an MCT or other potentially non-linear detector is employed in the reference system, IR attenuation may be required to ensure linearity; see APPENDIX B, section B6; because each detector may exhibit linearity to a specific degree, the serial number of the detector should be included in any specification of the system configuration.

D4. Obtaining and Preparing Standard Reference Gases

The accuracy of any FTIR quantitative analysis is limited by the accuracy of the concentrations of the gas standards used in preparing the reference library. It is therefore important to use gas standards of the highest available quality. NIST-traceable gravimetric standards are available from many commercial sources and are quoted to 2% accuracy in many circumstances; EPA has also published guidance on the preparation of "EPA Protocol Gases" (see reference 15), though these are available for only a limited number of compounds. Users should obtain documentation from the gas vendors regarding the analytical techniques applied and the stability limits (concentration and time) of the compounds in the cylinders. When possible, an alternative analytical method should be used to verify the quoted cylinder concentrations, especially for compounds that are reactive, corrosive, or have relatively high boiling points.

   If cylinder standards are not available for a compound, the analyst may prepare reference gases based on gravimetric, barometric, or dynamic methods. In any case, the related mass, pressure, and flow measurements should be made with NIST-traceable equipment whenever possible. In general, methods that provide a stream of standard gas (dynamic methods) provide more reliable results than static methods, since the concentrations of static gases are more prone to change when reactions between the standards and the sampling system or absorption cell surface can occur.

D5. Determining the Reference Absorption Path Length

The accuracy of any FTIR quantitative analysis is limited by the accuracy to which the path length of the absorption cell used in preparing the reference library is known. For single-pass absorption cells through which a collimated IR beam is passed, the path length can be physically measured to high accuracy. For multi-pass cells, the nominal path length can be estimated from the base path length and the number of passes. However, because focused beams and curved mirrors are required in multi-pass cells, the path length estimated in this fashion can differ significantly from the actual path length. Because of this, combinations of physical and spectroscopic measurements with multiple CTS gas standards (see below) and single-pass absorption cells should be employed to determine the actual path length of multi-pass absorption cells.

D6. Recording CTS Spectra

The CTS gas is used to characterize the absorption path lengths of the reference and field FTIR systems. Ethylene in nitrogen, at concentrations leading to between 100 ppm · m and 300 ppm · m CPP values for the systems, is recommended; for ethylene, spectra with ppm · m values greater than 300 begin to exhibit non-linear absorbance and must be carefully analyzed (see sections D8 and D9 below). Standards of this gas with 2% accuracy are readily available and both the EPA and NIST libraries contain ethylene spectra that can be used to link those libraries to measurements performed with field instruments. However, almost any other stable compound with appropriate IR absorption characteristics can be used in developing an independent reference library and for accurate field measurements.

In the field, CTS spectra must be recorded both before and after sample spectra are acquired using the same system configuration employed in recording the sample spectra (see steps 7 and 11 above).

When developing reference spectra, the analyst must record CTS spectra at least daily; each reference spectrum should be associated with at least one CTS spectrum. The analyst must use the same system configuration employed in recording the reference spectra, with one exception: The integration time used for the CTS spectra may be less than that used for the reference spectra, if the quality of the resulting CTS spectra is still sufficient for an accurate determination of the absorption path length. It is highly recommended that the analyst store all the interferograms from which the CTS absorbance spectra are generated, including all background interferograms. The interferometric data provide the most direct method of verifying the FFT calculations and/or adding reference absorbance spectra for other apodization function choices.

D7. Recording Reference Spectra

Before recording reference spectra, verify that the requirements specified for system checks, system configuration parameters, gas standards, absorbance path length determinations, and CTS spectra described in the pertinent sections of this appendix and Appendix B have been met. Additional checks of the sample gas pressure and temperature should also be made periodically as the spectra are recorded.

It is highly recommended that the analyst store all the interferograms from which the reference absorbance spectra are generated, including all background interferograms. The interferometric data provide the most direct method of verifying the FFT calculations and/or adding reference absorbance spectra for other apodization function choices.

Beer's law (Equation C1) describes the fundamental linearity of the infrared absorbance versus concentration. However, the resolution (and other) limitations of instruments typically used to generate field FTIR spectra often lead to non-linear behavior for many compounds, even at low absorbance levels. The expected accuracy of FTIR-based measurements results for a particular compound can be

achieved only when 1) the reference absorbance is characterized at a sufficient number of CPP values, up to some maximum value and 2) the sample absorbance associated with any compound represents a value lower than that of the maximum CCP value represented in the reference library for that compound.

For each analyte, the analyst should record two reference spectra at each of two concentration values (that is, at least four spectra) at a single absorption path length; the two concentrations should be separated by no more than a factor of 10, and a maximum factor of 5 is recommended. After recording these spectra, the analyst must 1) permanently record the system parameters and the maximum measured CPP and 2) characterize the linearity of the absorbance across the measured CPP range (see section D8). It may be necessary to record additional reference spectra for the analyte if either the absorbance linearity or maximum CPP value proves unsuitable for later field measurements.

D8. Linearity Checks

The performance of linearity checks on a set of reference spectra is an important aspect of FTIR spectrometry and is best illustrated by a practical example. The following example is based on a series of reference measurements performed on the compound tetrafluoroethylene, hereafter referred to as TFE.

Five absorbance spectra for TFE are shown in Figure D1. These spectra were recorded over the entire mid-IR wavenumber range, but only that portion of the spectra showing the most intense TFE absorption bands is included in the figure. Each of the spectra was calculated by mathematically averaging a number of TFE absorbance spectra recorded with the system configuration parameters given in Table D2, and a linear baseline correction was applied to each of these spectra over the range illustrated in Figure D1.
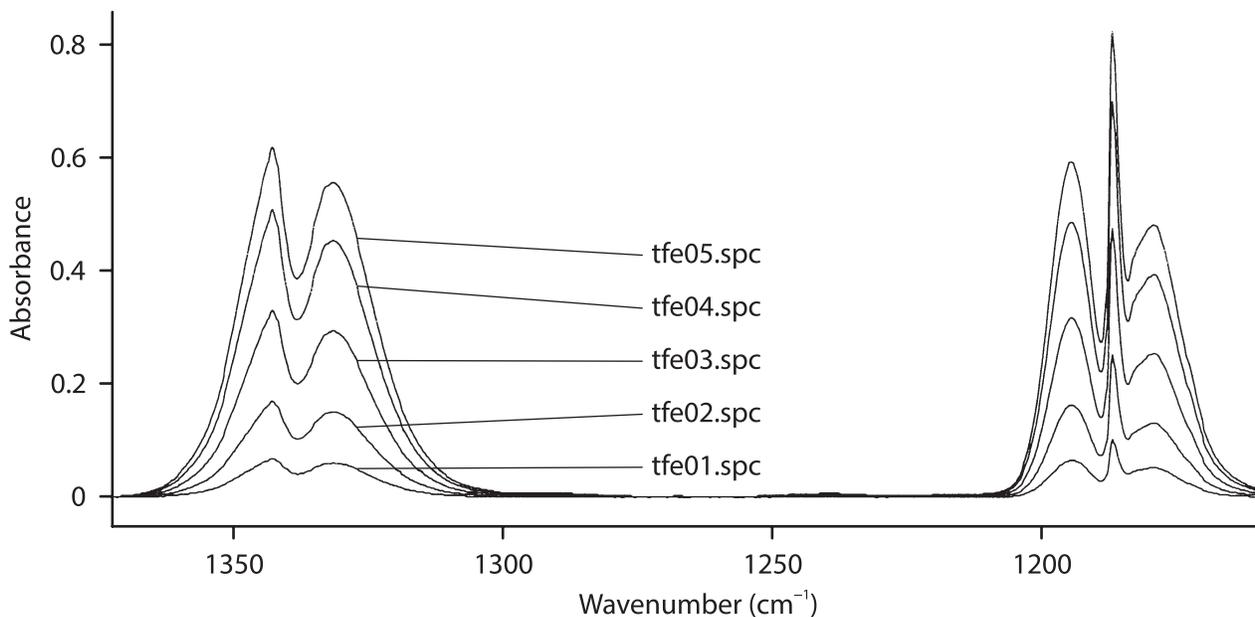

Figure D1. Reference absorbance spectra of TFE (x-axis truncated).

Table D2. System configuration parameters for TFE reference spectra (see Figure D1)

System Configuration Parameters	Values/Notes
MIL (cm^{-1})	0.5
Integration time (s)	1080 (120 s per spectrum × 9 spectra)
Absorption path length (m)	10.23
Gas temperature (°C)	15
Gas pressure (kPa)	101.3 ± 1.3 (760 mmHg ± 10 mmHg)
Apodization function	Triangular
Zero filling factor	Zero
Detector type	MCT
Detector gain (hardware)	Jumpers B, C, and D
Detector gain (software)	1
Reference CTS spectra	j2kety.spc
Wavenumber standard spectrum	j2kety.spc

The reference gas samples were generated by diluting with nitrogen the output of a single standard gas cylinder of TFE. The TFE concentration of the standard cylinder was determined (by the gas vendor) according to NIST-traceable gravimetric measurements and the flow rates of the cylinder gas were measured with a NIST-traceable volumetric device.

One technique to check for the linearity of this set is to form a normalized average of these five spectra and then use it in a linear analysis of the five original spectra. The normalization consists of dividing each spectrum by its CPP; these values, based on the CTS-derived path length of 10.23 m, are given with the actual gas concentrations and new spectral filenames in Table D3. Figure D2 illustrates the normalized spectra, all of which represent spectra of CPP values 1.00 ppm · m. These spectra are nearly equal to one another, as predicted by Beer's law. Only the spectrum tfe01n.spc, based on the original 25.53 ppm spectrum, is easily discernible from the other spectra in the figure.

Table D3. Normalization factors for TFE spectra

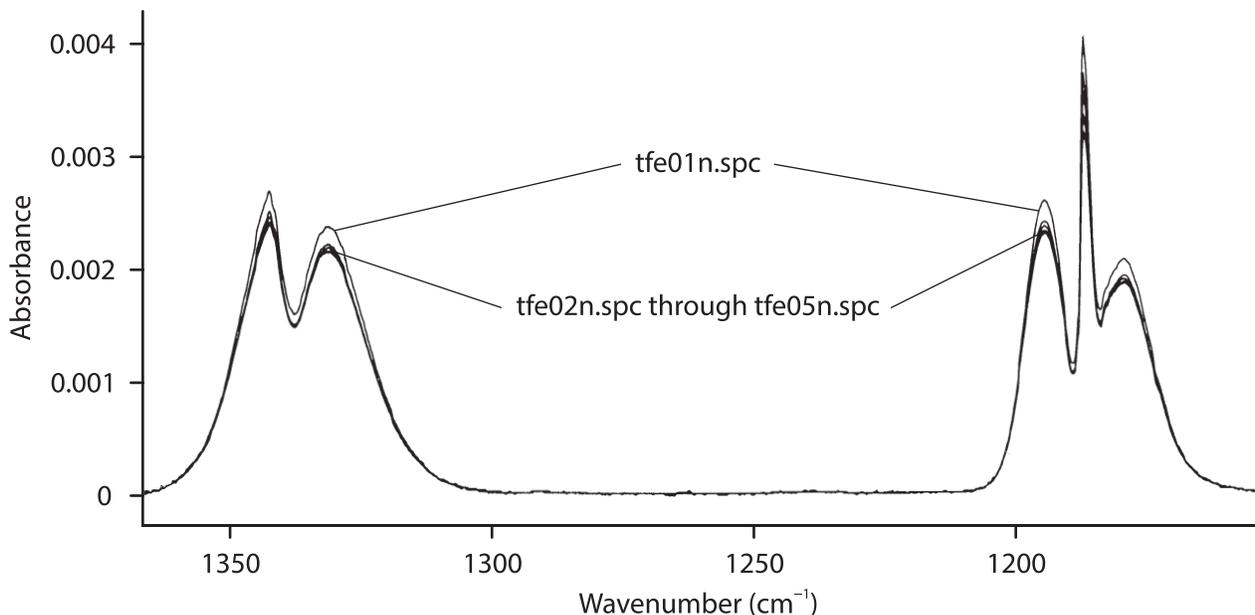| Original Spectrum	Concentration (ppm)	Concentration-Path Length Product (ppm · m)	Normalized Spectrum
tfe01.spc	2.50	25.5	tfe01n.spc
tfe02.spc	6.63	67.8	tfe02n.spc
tfe03.spc	13.3	133	tfe03n.spc
tfe04.spc	20.4	208	tfe04n.spc
tfe05.spc	25.1	257	tfe05n.spc

Figure D2. Normalized reference absorbance spectra for TFE.

Table D4 shows the results of a linear least-squares analysis using the *average* normalized spectrum as a single reference spectrum (with CPP 1.00 ppm · m) over the analytical range 1050 cm^{-1} to 1400 cm^{-1}. The bias in the linear method is clearly evident in the fourth column of the table, which indicates that the analysis yields concentrations that are slightly too high at the lowest concentration and slightly too low at the highest concentration. The average of the last column in the table, which represents the absolute percent difference between the actual and calculated concentrations, the "fractional calibration uncertainty" (FCU; see reference 3), is 3.2%. This value represents the average error over the concentration range for these reference spectra to be expected from the linear analysis up to the maximum CPP value used in the analysis (257 ppm · m). If additional accuracy is required, non-linear analyses or corrections such as those discussed above (Appendix B, section B6) can be employed.

Table D4. Results of linear least squares analysis for TFE reference spectra

TFE Reference Spectrum	Calculated Concentration (ppm)	Actual Concentration (ppm)	Actual – Calculated Concentration (ppm)	Absolute Percent Difference
tfe01.spc	2.69	2.50	0.19	7.7
tfe02.spc	6.64	6.63	0.01	0.2
tfe03.spc	12.8	13.0	−0.2	1.4
tfe04.spc	19.8	20.4	−0.6	2.9
tfe05.spc	24.2	25.1	−0.9	3.7

D9. Calculating the LOD

The estimated LODs are the concentrations — for the given system configuration, reference spectra, and analytical region — at which each compound's absorbance area is equal to the RSA. For a specified system configuration and analytical region, an estimate of the LOD (L_D) for a compound can be made

from the absorbance area of a reference spectrum in that region (A_R, cm^{-1}), the reference spectrum CPP (P_{CP}, ppm · m), the sample absorption path length (L, m), and the RSA values (A_{RS}, cm^{-1}) as

$$L_D = \frac{P_{CP} \times A_{RS}}{L \times A_R}.$$
(Equation D1)

A simple trapezoidal approximation of A_R over the analytical region of interest, including baseline corrections when necessary, is suitable for the LOD estimate. The RSA is formed from the product of the FTIR system's typical root-mean-square noise level in absorbance and the width of the analytical region in cm^{-1} (see APPENDIX B, section B2); the RSA estimate should reflect the error incurred in subtracting known spectral interferences. APPENDIX E, section E1 presents detailed examples of RSA and LOD calculations.

D10. Using Existing Reference Libraries

The analyst may use any of the publicly available reference libraries for quantitative analyses, but it is strongly recommended that quantitative results for analytes be based only on spectra from libraries that meet the requirements discussed in this appendix. If the reference library consists of spectra recorded at a spectral resolution different from that of the field system, the analyst must 1) deresolve the spectra mathematically to that of the field data and 2) ensure that the library data are suitably linear over the desired measurement range *at the spectral resolution of the field system*.

APPENDIX E. EXAMPLE CALCULATIONS

This appendix uses an analysis of TFE and 1,1-difluoroethylene (DFE) in workplace air to illustrate the calculations of RSA and LODs. The topics of designing, applying and verifying, and correcting a spectral analysis are also addressed below.

   The FTIR system configuration assumed for this set of calculations is given below. These parameters are consistent with the LOD values presented in Table 2.

System Configuration Parameters	Values/Notes
MIL:	0.5 cm^{-1}
Absorption path length:	10 m
Apodization function:	Triangular
Gas temperature:	293 K
Gas pressure:	101.3 kPa
Zero filling factor:	None
Wavenumbers of water bands:	1918 cm^{-1} and 2779 cm^{-1}
Reference library sources:	NIST, EPA
Integration time:	70 s (64 scans)
Detector type:	MCT
Detector gain - hardware:	Gain jumpers A, D, and H
Detector gain - software:	1.0

E1. RSA, Analysis Design, and LODs

The analysis is to be carried out in workspace air, so the only potential spectral interferences are due to water and carbon dioxide. Figure E1 illustrates example reference spectra of TFE, DFE, and water. (The water spectrum shown is typical of workspace air samples; carbon dioxide does not absorb in any of the spectrum. As a result, the limited spectral region shown in Figure E2 is actually of the greatest interest for an analysis of DFE and TFE in workspace air.
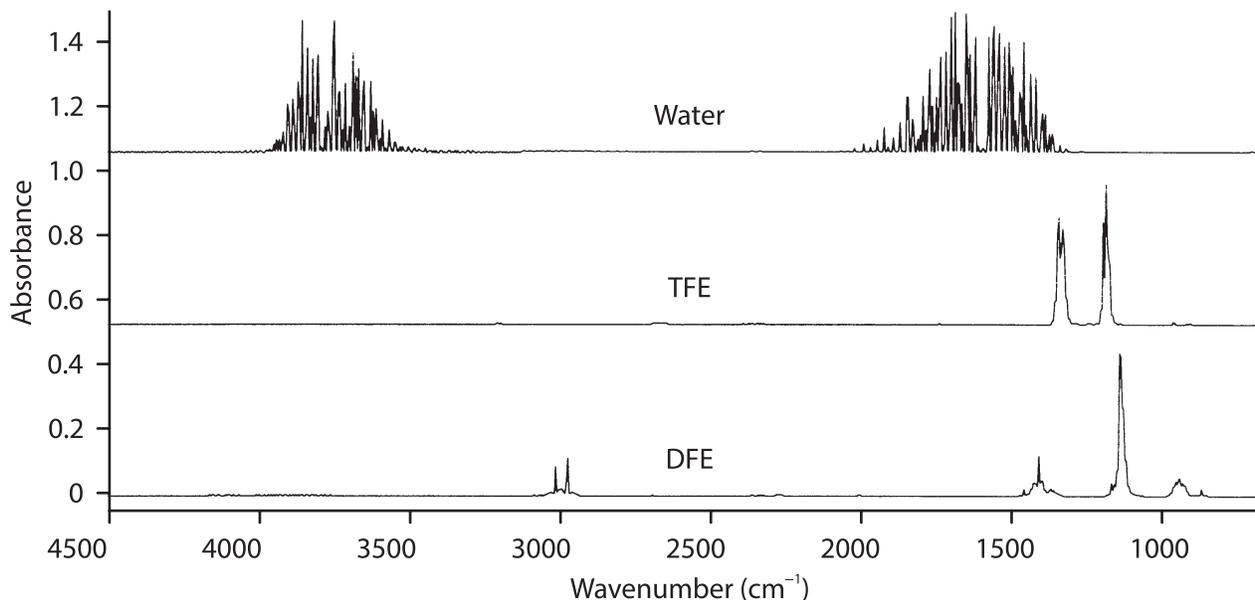

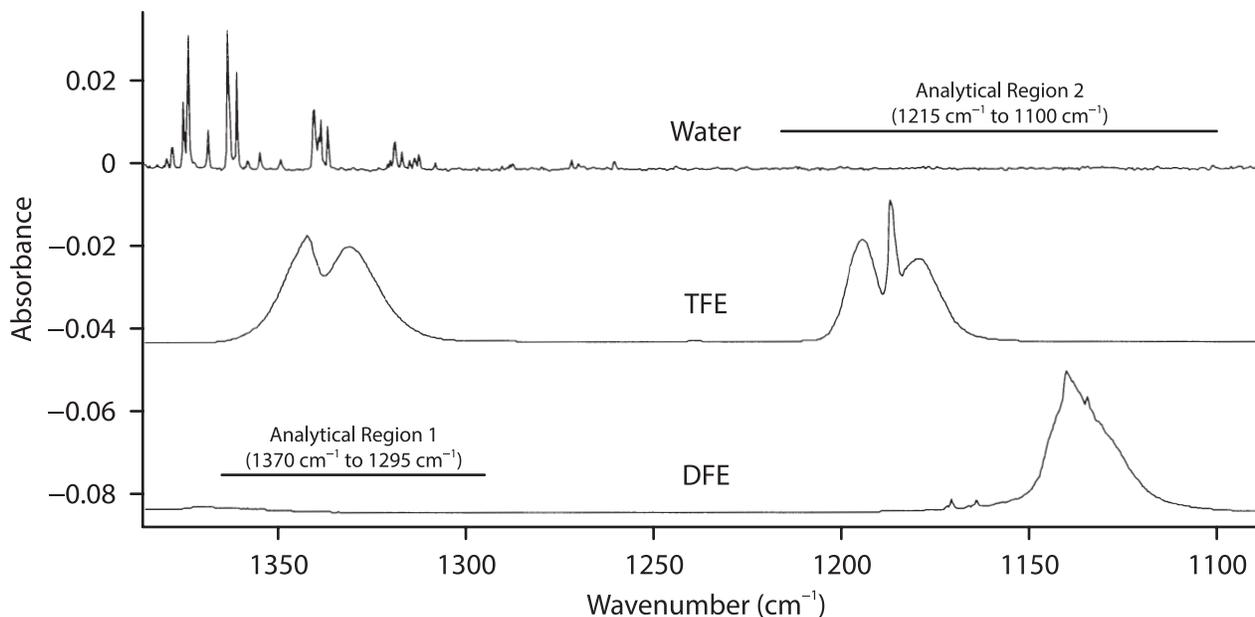**Figure E1. Absorbance reference spectra of TFE, DFE, and water.**

Figure E2. Possible analytical regions.

Shown in greater detail in Figure E2 are the three reference spectra and two possible analytical regions. Analytical region 1, from 1370 cm^{-1} to 1295 cm^{-1}, includes water bands that interfere with the TFE absorbance in the sample spectra. Analytical Region 2 (1215 cm^{-1} to 1100 cm^{-1}) may be the best choice for analyzing samples for both TFE and DFE (though the weaker features near 3000 cm^{-1} remain an option for DFE); it avoids the TFE interference with water, but necessarily includes some spectral overlap between the two analytes. Until the relative TFE, DFE, and water concentrations in the samples are known, it is unclear which of the two regions will provide better concentration estimates for TFE, so calculations for both regions are described below.

Estimation of the LODs for TFE and DFE requires a calculation of the RSA in the actual sample spectra over the selected analytical regions. The RSA represents an estimate, based on the assumed sample matrix and available reference spectra, of the residual absorbance (see Equation C6) that will be used to calculate the concentration uncertainties from the actual sample spectra.

The reader should note that the RSA and derived LOD are only estimates. If the actual sample matrix differs substantially from that of the sample matrix assumed in the performance of these estimates, the actual concentration uncertainties and LODs may differ substantially from the RSA and LOD values obtained in the calculations described below. For workplace air samples, water is the only interfering compound that is certain to appear in any of the analytical regions considered below. A realistic estimate of the RSA is therefore available by forming the mathematical difference of two water spectra — of substantially different water concentrations — recorded using the same FTIR system configuration. For each analyte, this estimate assumes that only water and that analyte will absorb substantially in the actual sample spectra. Later analyses based on the actual sample matrix could lead to either lower or higher concentration, uncertainty, and LOD estimates; examples of such analyses are detailed below.

Figures E3 and E4 illustrate two absorbance spectra recorded using the system configuration described above. They represent spectra of workspace air at approximately 20% and 40% relative humidity. The upper trace in each figure is slightly offset for clarity.
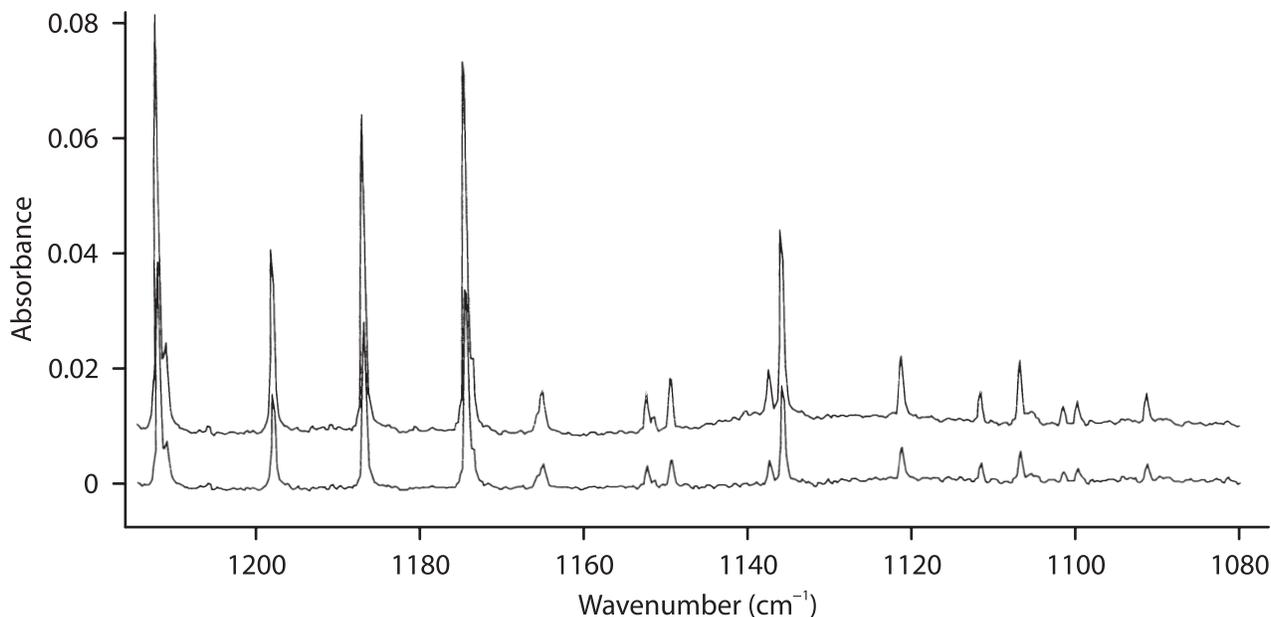
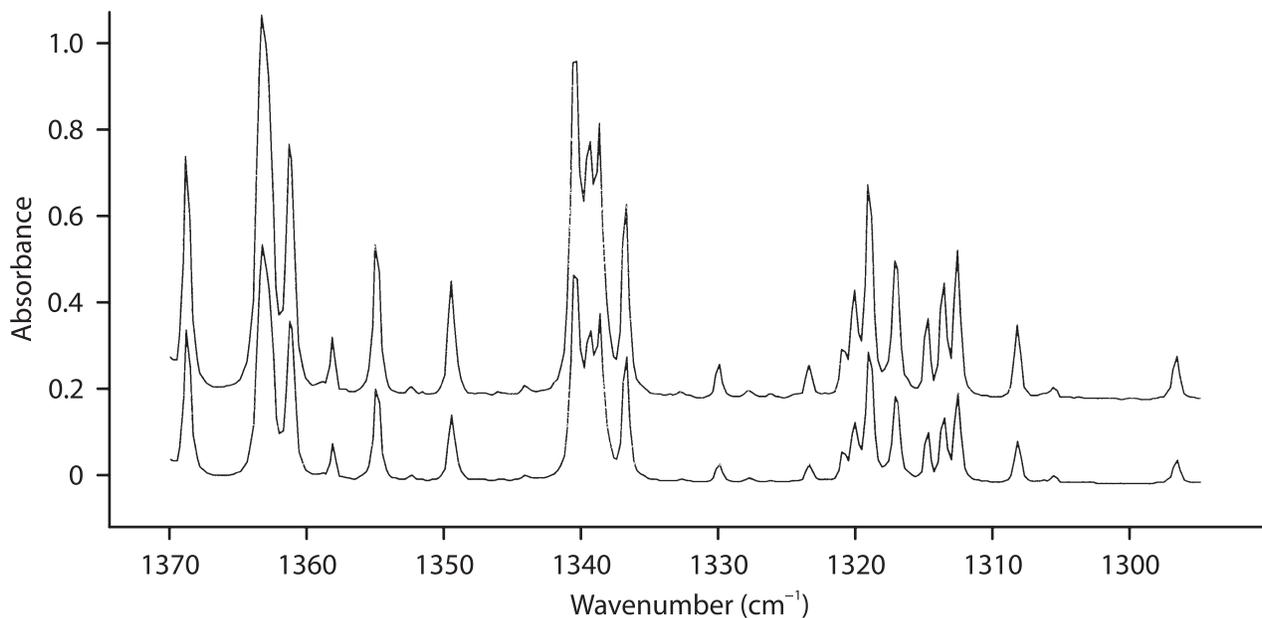**Figure E3. Water spectra 1215 cm^{-1} to 1080 cm^{-1}.**

Figure E4. Water spectra 1370 cm^{-1} to 1295 cm^{-1}.

Figure E5 shows two residual spectra formed by subtracting scaled versions of the lower-absorbance spectrum from the higher-absorbance spectrum. The scaling factors were determined in independent LSF analyses over the two analytical regions. Linear baseline corrections (offset and slope) were also determined during the analyses, so the mean value of each residual spectrum is zero. (These calculations were performed by using the ANOVA data analysis tool in Microsoft Excel 97). The RSA values for the residual spectra are defined in Equation C2 and the related calculations are presented in Table E1. (The calculations also were performed in the program Excel by applying the function STDEV to the regression residuals.)
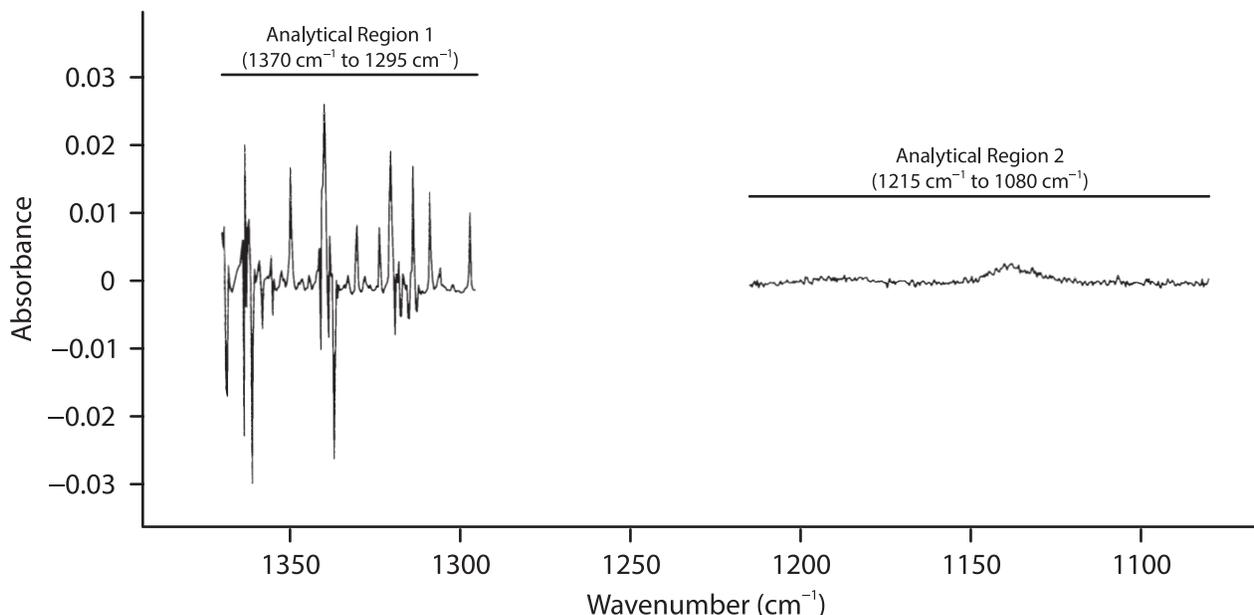
Figure E5. Water residual spectra.

Table E1. Results of RSA analysis from water reference spectra

Analytical Region (cm^{-1})	Calculated Scaling Factor	Scaling Factor Uncertainty (1σ)	Residual RMS Standard Deviation (Absorbance)	RSA; Equation B2 (cm^{-1})
1370 to 1295	1.636	0.003	0.00575	0.431
1215 to 1080	1.870	0.008	0.00069	0.093

An estimate of the LODs (L_D, ppm) for the two compounds — for the specified system configuration — can be made from the absorbance areas of the reference spectra over these analytical ranges (A_R, cm^{-1}), the reference spectra CPPs (P_{CP}, ppm · m), the sample absorption path length L (m), and the RSA values (A_{RS}, cm^{-1}) derived above.

The absorbance areas were determined using a standard trapezoidal approximation without baseline correction. (For these spectra, baseline corrections lead to values that differ from those quoted by less than 3% and have been neglected below.) Figure E6 shows the spectral features of TFE and DFE used to calculate the A_R for the reference spectra tfeav05.spc (CPP = 256.7 ppm · m) and dfeav05.spc (CPP = 197.8 ppm · m).

The estimated LODs are the concentrations — for the given system configuration, reference spectra, and analytical region — at which each compound's absorbance area is equal to the RSA. Mathematically, the LOD estimates are given by

$$L_D = \frac{P_{CP} \times A_{RS}}{L \times A_R}.$$

(Equation E1)

Table E2 lists the pertinent quantities and resulting LODs for DFE and TFE in the two analytical regions considered. The results indicate that the analytical region from 1215 cm^{-1} to 1080 cm^{-1} is likely to provide the most reliable TFE concentrations.
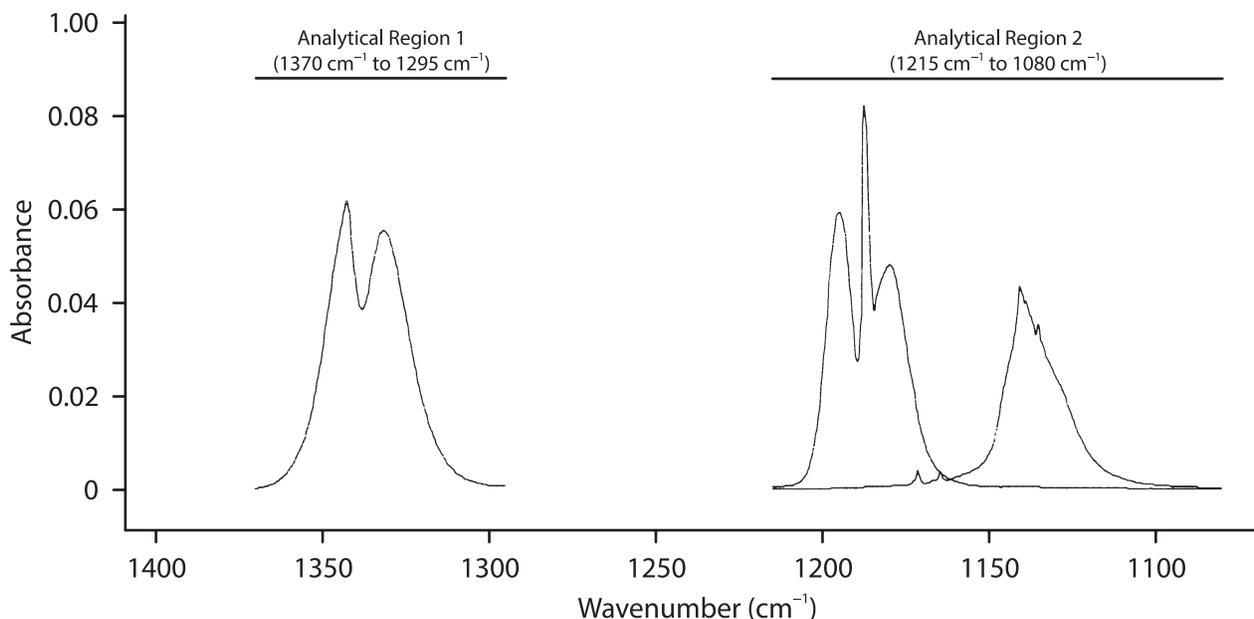
Figure E6. TFE and DFE spectra for absorbance area calculations.

Table E2. LODs for TFE and DFE from RSA analysis of water reference spectra

| Analytical Region (cm^{-1}) | Compound | Reference Spectra | | | System Configuration | | |
		File Name	CPP (ppm · m)	Absorbance Area (cm^{-1})	RSA (cm^{-1})	L (m)	Estimated LOD (ppm)
1370 to 1295	TFE	tfe05.spc	256.7	16.03	0.431	10.0	0.69
1215 to 1080	TFE	tfe05.spc	256.7	13.97	0.093	10.0	0.17
1215 to 1080	DFE	dfe05.spc	197.8	8.72	0.093	10.0	0.21

E2. LSF Determinations of TFE and DFE Concentrations

Presented in this section is a description of an LSF analysis for the two compounds TFE and DFE in ambient air samples. As is always the case before actual measurements are taken, no actual sample data for mixtures of the compounds in the assumed matrix (ambient air) were available as these analyses were performed. Accordingly, the following description is based on synthetic spectra generated from available reference spectra for TFE, DFE, and water.

In order to *not* overestimate the effectiveness of the FTIR technique, the noise levels in the synthetic sample spectra were artificially raised and the reference spectra used are not those most likely to provide an optimal analysis. This is the most prudent course available to an analyst attempting to predict the performance of the FTIR method under essentially unknown conditions and it is the course recommended by the authors to analysts who find themselves in this common situation.

Estimates of the LOD for this sample matrix (see section E1) indicate that the analytical region from 1215 cm^{-1} to 1080 cm^{-1} will likely provide the most reliable TFE and DFE concentrations. The system configuration parameters used in those estimates are assumed to hold in the following description.

E2A. Generation and Analysis of Synthetic Sample Spectra of TFE and DFE

Table E3 describes the mathematical generation of synthetic samples for the following LSF analysis description. Each sample spectrum consists of the sum of scaled reference spectra for TFE (tfe4.spc, CPP = 208.3 ppm · m), DFE (dfeav05.spc, CPP = 197.8 ppm · m) and water (wat02bl.spc). The scaling factors indicated in Table E3 were used to generate synthetic sample spectra at the listed concentrations and the assumed absorption path length of 10.0 m.

Table E3. Parameters used to generate synthetic sample spectra containing TFE, DFE, and water

TFE Scaling Factor	TFE Synthetic Concentration (ppm)	DFE Scaling Factor	DFE Synthetic Concentration (ppm)	Water Scaling Factor	Synthetic Sample Spectrum File Name
0	0	0	0	0.6	S001.spc
0	0	0	0	1.2	S002.spc
1.200	25.0	1.264	25.0	0.6	S551.spc
1.200	25.0	0.253	5.00	0.6	S511.spc
0.240	5.00	1.264	25.0	0.6	S151.spc
1.200	25.0	1.264	25.0	1.2	S552.spc
1.200	25.0	0.253	5.00	1.2	S512.spc
0.240	5.00	1.264	25.0	1.2	S152.spc

A spectrum representing random absorbance noise was added to each synthetic spectrum. The noise spectrum was generated using the function RANDOM within the program GRAMS/32 V4.11 (Galactic, Inc.; see the Array Basic User's Guide, V4.1, page 316); similar functions are also available in other spreadsheet software programs. For the noise spectrum R, with discrete absorbance values R_i for wavenumbers $i = p$ to q, the root mean square (RMS) absorbance noise N_{RMS} (see also Equation B2, which defines the RSA), calculated over the appropriate analytical region(s) according to

$$N_{RMS} = \sqrt{\sum_{i=p}^{i=q} \frac{R_i^2}{q-p}},$$ (Equation E2)

was 0.00034 in the region 1438 cm^{-1} to 1282 cm^{-1}; this is very close to the value obtained from actual absorbance spectra (provided by MIDAC Corporation) recorded with the quoted system configuration in the region 1005 cm^{-1} to 932 cm^{-1}. The synthetic spectra represent four different mixtures of TFE and DFE (including one "mixture" that contains neither compound), each at two different moisture levels.

Table E4 lists the results of a LSF analysis (program 4FTIMD V15, Rho Squared; see reference 14) for TFE, DFE, and water in the analytical region 1215 cm^{-1} to 1080 cm^{-1} using the reference spectral files TFE3.spc (CPP = 133.2 ppm · m), dfeav04.spc (CPP = 133.3 ppm · m), and wat01bl.spc. Note that these are not the same reference spectra that were used in the generation of the synthetic sample spectra and that the results for water are in arbitrary units. The analysis included the determination of two baseline correction parameters along with the compound concentrations.

Table E4. Original LSF results for original synthetic sample spectra containing TFE, DFE, and water

Synthetic Sample Spectrum File Name	TFE*			DFE†			Water‡	
	Synthetic Concentration (ppm)	LSF Result (ppm)	LSF 3σ Uncertainty (%)	Synthetic Concentration (ppm)	LSF Result (ppm)	LSF 3σ Uncertainty (%)	LSF Result (arbitrary)	LSF 3σ Uncertainty (%)
S001.spc	0	0.02	52.5	0	0.07	13.7	1.12	1.23
S002.spc	0	0.03	32.2	0	0.14	8.95	2.24	0.80
S551.spc	25.0	24.41	0.26	25.0	24.30	0.29	0.87	11.8
S511.spc	25.0	24.43	0.25	5.00	4.88	1.43	0.87	11.5
S151.spc	5.00	4.88	0.41	25.0	24.33	0.09	1.07	3.04
S552.spc	25.0	24.43	0.26	25.0	24.35	0.29	1.99	5.20
S512.spc	25.0	24.45	0.26	5.00	4.95	1.43	1.99	5.11
S152.spc	5.00	4.90	0.43	25.0	24.39	0.10	2.19	1.56

*For TFE, excluding samples S001 and S002, the average difference between the synthetic concentration and the LSF result was 2.24%. The average 3σ uncertainty was 0.31%.

†For DFE, excluding samples S001 and S002, the average difference between the synthetic concentration and the LSF result was 2.34%. The average 3σ uncertainty was 0.61%.

‡For water, excluding samples S001 and S002, the average 3σ uncertainty was 6.38%.

The LSF results for the non-zero TFE and DFE spectra are consistently good, being different from the synthetic concentrations less than 3% in every case. The concentration uncertainties listed in Table E4 are the statistically determined 3σ values from the LSF analyses. These percent uncertainty parameters and the visual appearance of the LSF residual spectra are important indicators of the quality of the least squares analysis and are discussed further in the following section.

The TFE and DFE results for the two synthetic spectra that contain no absorption features of TFE and DFE (S001 and S002) are of interest and importance. The LSF concentration results are small. (Their maximum is 0.14 ppm). They are smaller in each case than the LOD estimates of Table E2 and their corresponding 3σ uncertainties from this LSF analysis are smaller still. Unfortunately, no consensus exists on the exact mathematical relationship between the LODs calculated as described in this document and the 3σ concentration uncertainties. This statement is supported by the contents of section A2 in reference 4 — a consensus document — that prescribes three different methods for calculating LODs (or, in the terminology of reference 4, "minimum detectable concentrations"). These three prescriptions include one similar to the LOD method prescribed in this document and one that is based on the concentration uncertainties derived from spectra similar to S001 and S002. In this limited example, two of the three prescriptions included in reference 4 provide very different results and they indicate that the LOD calculation described in this document provides the most conservative estimate — that is, the highest estimate — of the three LOD prescriptions of reference 4.

E2B. Analyses of Synthetic Sample Spectra with an Interfering Compound

Every compound-specific quantitative analytical technique, including FTIR spectrometry, can fail to provide accurate results when interfering compounds appear in a sample. However, the results of a mathematical FTIR spectral analysis designed for a particular set of compounds provides clues to its failure in the presence of interferants. An experienced analyst can often adjust the analysis to accommodate the interferants and provide accurate results.

To illustrate this important aspect of FTIR spectrometry, a synthetic interference was introduced to the spectra described in Table E3. Scaled versions of a reference spectrum (hfpav06.spc, 256.6 ppm · m) of the compound hexafluoropropylene (HFP), representing the compound at two concentrations (5.00 and 10.0 ppm), were added to the original synthetic spectra. The resulting final synthetic sample spectra

are described in Table E5 below. The least squares analysis described above for TFE and DFE only, when applied to these spectra containing spectral features of HFP, gives the results shown in Table E6 below.

Table E5. Parameters used to generate synthetic sample spectra containing TFE, DFE, water, and HFP

Original Synthetic Sample Spectrum File Name	HFP Scaling Factor	HFP Synthetic Concentration (ppm)	Final Synthetic Sample Spectrum File Name
S001.spc	0.195	5.00	S0011.spc
S002.spc	0.390	10.0	S0022.spc
S551.spc	0.195	5.00	S5511.spc
S151.spc	0.195	5.00	S1511.spc
S512.spc	0.195	5.00	S5121.spc
S511.spc	0.390	10.0	S5112.spc
S552.spc	0.390	10.0	S5522.spc
S152.spc	0.390	10.0	S1522.spc

Table E6. Original LSF results for final synthetic sample spectra containing TFE, DFE, water, and HFP

Synthetic Sample Spectrum File Name	TFE*			DFE†			Water‡	
	Synthetic Concentration (ppm)	LSF Result (ppm)	LSF 3σ Uncertainty (%)	Synthetic Concentration (ppm)	LSF Result (ppm)	LSF 3σ Uncertainty (%)	LSF Result (arbitrary)	LSF 3σ Uncertainty (%)
S0011.spc	0	1.00	39.6	0	−1.58	26.5	1.65	0.89
S0022.spc	0	2.01	39.5	0	−3.16	26.4	3.29	1.78
S5511.spc	25.0	25.06	1.51	25.0	22.65	1.89	1.43	43.3
S5112.spc	25.0	25.73	2.90	5.00	1.57	53.8	1.99	61.4
S1511.spc	5.00	5.53	6.64	25.0	22.67	1.84	1.63	37.0
S5522.spc	25.0	25.73	2.90	25.0	21.05	4.01	3.10	39.2
S5121.spc	25.0	25.09	1.52	5.00	3.29	13.1	2.55	24.4
S1522.spc	5.00	6.20	11.87	25.0	21.09	3.96	3.30	36.4

*For TFE, excluding samples S001 and S002, the average 3σ uncertainty was 4.56%.
†For DFE, excluding samples S001 and S002, the average 3σ uncertainty was 13.1%.
‡For water, excluding samples S001 and S002, the average 3σ uncertainty was 40.3%.

The average 3σ uncertainties shown in Table E4 (those of the original LSF analysis *without* HFP interference) and Table E6 (those of the original LSF analysis *with* HFP interference) are clearly quite different. Averaged over the six synthetic spectra containing TFE and DFE in each case, the (absolute) percent concentration uncertainties for TFE, DFE, and water are greater for the spectra with HFP interference. For TFE and DFE, the average percent uncertainties of Table E6 are over ten times greater than those of Table E4. This exercise shows that:
- For sample spectra containing substantial TFE and DFE concentrations, the HFP interference causes large increases in the TFE and DFE relative absolute concentration uncertainties.
- For sample spectra containing low or zero concentrations TFE and DFE, the relative absolute uncertainties are NOT a reliable indicator of the HFP interference. However, for such spectra, the concentration results themselves are often clearly unreliable; note that the DFE concentration

results are negative *and* large compared to the LOD estimate for this compound. (Note also that negative concentration results that are *small* compared to the LOD are statistically valid and do not necessarily indicate a failure of the analysis.)

If the concentration results show anomalies such as those noted above, the residual spectra from the analyses will also exhibit anomalous behavior. This is illustrated in Figure E7, which shows the residual spectra for four analyses. Compared to the residual spectra resulting from analyses of spectra without the HFP interference, those with HFP interference show large absorbance features that cannot be modeled by the three reference spectra employed. The analyst needs to identify the interfering compound before proceeding. This can often be done by visually comparing the suspect residual spectra to reference spectra of a number of likely interferants, as illustrated in Figure E8.
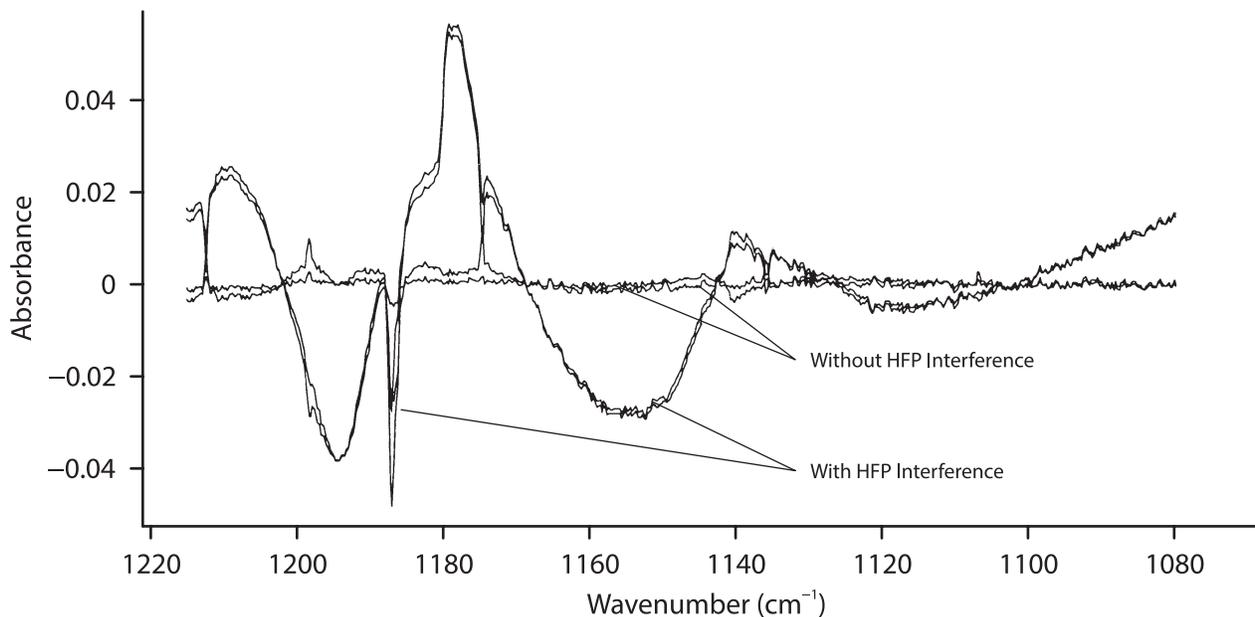

Figure E7. Residual spectra with and without HFP interferance.
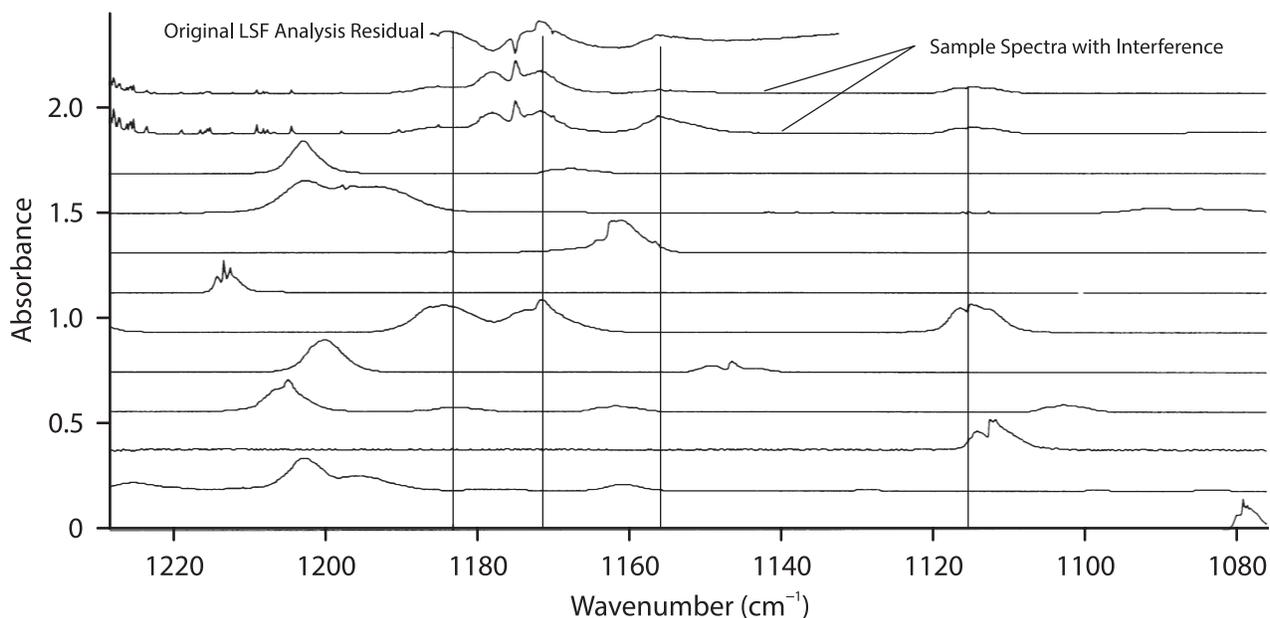

Figure E8. Comparisons of residual, sample, and reference spectra.

Figure E8 shows that the positions of three major relative maxima in the residual spectrum (top trace) correspond well to only one of the nine candidate reference spectra in the lower traces of the figure. (The nine spectra shown are all of light, partially or fully fluorinated hydrocarbons.) An additional absorbance band from this single reference spectrum also corresponds to a large peak in both of the sample spectra (second and third traces from top of the figure).

A closer examination of this reference spectrum — that of HFP, of course — is illustrated in Figure E9. It clearly shows a close relationship between the shape of the residual spectrum and the absorption features of HFP. The relationship is not exact because the sample spectrum has had incorrect amounts of the compounds TFE and DFE subtracted and this distorts the residual spectrum.
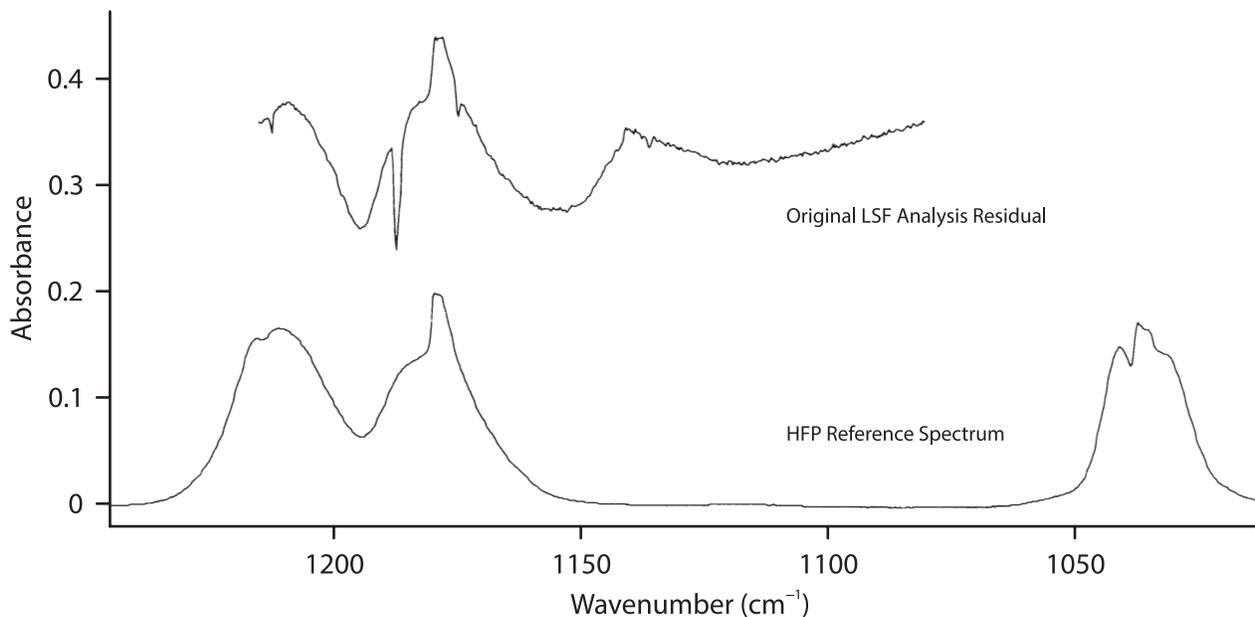

Figure E9. Original LSF residual and HFP reference spectra.

Though this identification is tentative, it can be tested by including HFP in the LSF analysis. Table E7 shows the TFE, DFE, and water concentrations resulting from an analysis identical to those described above except for the addition of HFP as a fourth compound. (As usual, an HFP reference spectrum different from the one used to add the synthetic interference was employed in the analysis.) To facilitate comparisons with the preceding tables, the HFP results have been excluded from Table E7; they were in all cases similar in quality to those obtained for the other compounds.

Table E7. Final LSF results for final synthetic sample spectra containing TFE, DFE, water, and HFP

Synthetic Sample Spectrum File Name	TFE*			DFE[†]			Water[‡]	
	Synthetic Concentration (ppm)	LSF Result (ppm)	LSF 3σ Uncertainty (%)	Synthetic Concentration (ppm)	LSF Result (ppm)	LSF 3σ Uncertainty (%)	LSF Result (arbitrary)	LSF 3σ Uncertainty (%)
S0011.spc	0	1.00	39.6	0	−1.58	26.5	1.65	0.89
S0022.spc	0	2.01	39.5	0	−3.16	26.4	3.29	1.78
S5511.spc	25.0	24.43	0.27	25.0	24.27	0.33	0.87	12.1
S5112.spc	25.0	24.45	0.27	5.00	4.81	1.72	0.88	12.34
S1511.spc	5.00	4.91	0.44	25.0	24.27	0.11	1.08	3.23
S5522.spc	25.0	24.46	0.28	25.0	24.27	0.35	1.99	5.51
S5121.spc	25.0	24.45	0.27	5.00	4.92	1.63	1.99	5.25
S1522.spc	5.00	4.94	0.57	25.0	24.29	0.14	2.20	2.05

*For TFE, excluding samples S0011 and S0022, the average 3σ uncertainty was 0.35%.
[†]For DFE, excluding samples S0011 and S0022, the average 3σ uncertainty was 0.71%.
[‡]For water, excluding samples S0011 and S0022, the average 3σ uncertainty was 6.74%.

The results show that inclusion of HFP in the analysis yields results of the original (high) quality shown in Table E3 for TFE, DFE, and water. The percent relative uncertainties are slightly higher in the final analysis than in the original analysis; this is to be expected because the same amount of spectral information is being used to determine an additional parameter in the final analysis. The quality of the analysis could probably be further improved by extending the analytical region to include the entire HFP absorbance band shown in Figure E9.