

FTIR Resolution Requirements For Industrial Gas Analyzers

By RICHARD T. MEYER

A survey of published papers examining FTIR resolution requirements and questioning the need for extremely high resolution

FTIR Spectroscopy is a widely used technique for gas analyses in industrial applications. It is a technique used in the semiconductor industry for measuring the purity of cleaning, etching, and epi-treatment gases used with various process tools, reactors, and abatement devices. Among chemical companies and R&D facilities, FTIR is applied to combustion thermodynamics and stack gas emissions; and it is broadly used for building and plant ambient air monitoring.

There is a belief among some end users and among some FTIR suppliers that high resolution—namely 0.1 or 0.5 cm^{-1} —is absolutely required of an FTIR spectrometer to achieve high accuracy concentration measurements in any of the above applications. However, there are substantial citations in the published literature to discount that supposition on high resolution; those citations indicate that instrument resolutions of 2, 4, 8, or 16 cm^{-1} are more than adequate to provide high quality concentration measurements for most industrial applications.

We cite here excerpts from published papers and a list of other references that confirm this information.

1. "Effect of Resolution on Quantification in Open-Path Fourier Transform Infrared Spectrometry under Conditions of Low Detector Noise: I. Classical Least Squares Regression," B.K. Hart and P.R. Griffiths, *Env. Sci. Technol.*, 34, 1337-1345 (2000).

"For most of the spectra calculated with equidistant backgrounds, there is a small improvement in predictive accuracy as the resolution is degraded from 1 to 8 cm^{-1} , followed by a reduction in accuracy for most compounds as the resolution continues to decrease."

"Only for the cases of methane and ethane computed with equidistant backgrounds are the predictions obtained from 1 cm^{-1} resolution spectra."

"For propane, n-butane, and n-pentane, the accuracy of the CLS predictions improves as the resolution is degraded from 1 to 4 cm^{-1} , remains fairly constant to 16 cm^{-1} resolution, and then starts to become worse as the

resolution is lowered further."

"These data suggest that the resolution required to optimize the measurement strongly depends on whether the analyte is a small molecule with resolvable rotational fine structure or a larger molecule where the spacing of the rotational lines is less than the collision-broadened FWHH of the lines."

"It is clear that the selection of spectral resolution for a measurement is a critical choice."

"An analogous trend is observed for the chlorinated hydrocarbons."

Also see second article "...II. Partial Least Squares Regression," B.K. Hart, R.J. Berry, and P.R. Griffiths, *Env. Sci. Technol.*, 34, 1346-1351 (2000).

2. "Fourier Transform Infrared Spectrometry in Atmospheric and Trace Gas Analysis," David W.T. Griffith and Ian M. Jamie, in *Encyclopedia of Analytical Chemistry*, R.A. Meyers (Ed.), pp. 1979-2007, John Wiley & Sons Ltd., Chichester, 2000.

"...it is clear that the selection of spectral resolution for a measurement is a critical choice. While the spectroscopist would argue for high resolution to resolve all bands, the analytical chemist would argue for the lowest acceptable resolution to maximize S/N and quantitative precision. In practice, a balance must be struck to suit the demands of the individual measurement, and this requires an informed judgment by the operator."

"Several authors have discussed the choice of resolution in long open-path monitoring when using CLS analysis.

...While there is no definitive "best" resolution, there is a general consensus towards 1–2 cm^{-1} as a reasonable compromise between spectral discrimination of overlapping bands and quantitative accuracy. Griffiths and co-workers make the case that lower resolution (8 cm^{-1}) may be practical when using PLS for quantitative analysis."

3. Dr. Henry Buijs, ABB Bomem, Private Communication, 2004.

"When you want to study the molecular structure of different molecules by the disposition of all the spectral lines, you need to be able to see all the spectral lines. Some line groups have very close spacing such as in a Q branch of a rotation-vibration band. At low pressure the Doppler width of lines in the mid-IR for room temperature gas is in the order of 0.004 cm^{-1} ."

"When you are working with gas mixtures for which you don't know beforehand what species might be present, you need to have sufficient resolution to identify species (by eye) that have bands close to other species. A good example is NO or NO₂ in the presence of water vapor. At low concentrations of NO or NO₂ it is very hard to see the spectral lines amongst the usually strong water lines. ... As was shown by [a student] in his studies with Bill Fateley using our DA2, he found that at 0.1 cm^{-1} the spectra were too noisy to be useful. By degrading the resolution you come to a "sweet spot" where you can see a lot of detail with good signal to noise ratio and for long open paths. This sweet spot is around 0.5 cm^{-1} ."

"When you require the quantification of gas mixtures with 'known' components, the resolution requirement is completely different. "The computed quantity of gas does not depend on a visualization of the spectra. It is well known that a multivariate analysis such as PLS works as well on blended overlapping spectral features as on isolated lines: It does not care about resolution. Given this you want to specify a reso-

lution that gives maximum sensitivity of quantification of gas species taking into account signal to noise ratio and interference effects. Based on work by Peter Griffiths, [a company] has decided that this resolution can be as low as 8 cm^{-1} . Because of excessive blending of lines in some cases, I agree with [person] that 4 or 2 cm^{-1} resolution is probably a bit closer to ideal than 8 cm^{-1} because of dealing with excessive overlap in some cases."

"The spec of 0.5 cm^{-1} has been used often to effectively eliminate some competitors. The way to fight it is to provide a turnkey solution complete with calibrations for the gases required and to provide (and insist on) the specifications of analysis sensitivity, selectivity and accuracy."

4. Professor Emeritus William G. Fateley, Kansas State University, Private Communication, April 12, 2005.

"High resolution is not necessary for gas analyses; 8, 16, 32 cm^{-1} is enough."

Prof. Fateley also cited the Thesis of Roseann Hoffman at Kansas State University as supporting evidence.

5. "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Second Edition. Compendium Method TO-16, Long-Path Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases," Center for Environmental Research Information, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, 1999.

"Section 6.2 FT-IR Sensor Requirements"

"6.2.4 The system must be able to operate with a resolution of at least 1 cm^{-1} over the mid-infrared region (700–4200 cm^{-1})."

Summary of Above Five Citations

For analytical measurements of gas concentrations in gas mixtures where most of the compounds are known or expected, an instrument resolution of

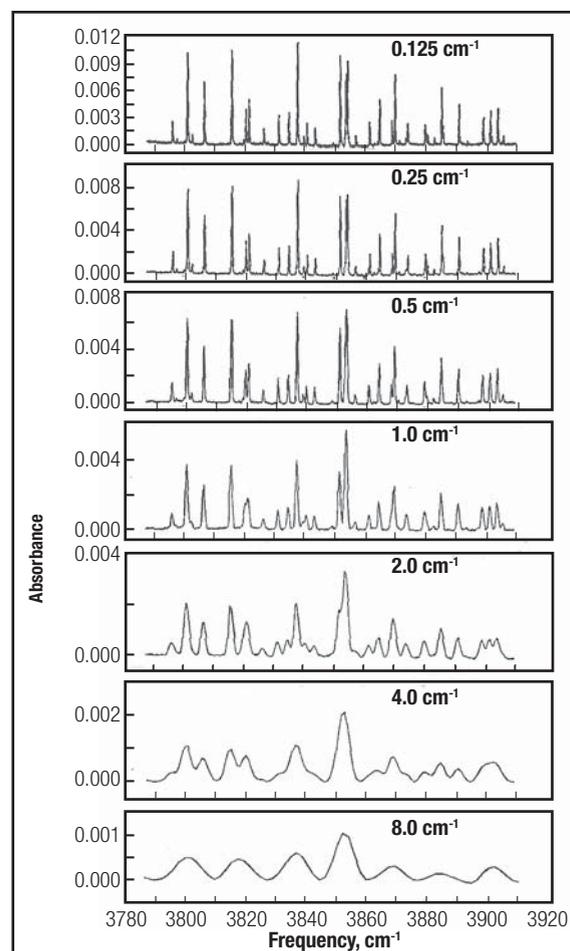


Figure 1. A Series of H₂O absorption spectra at different spectral resolutions." [8]

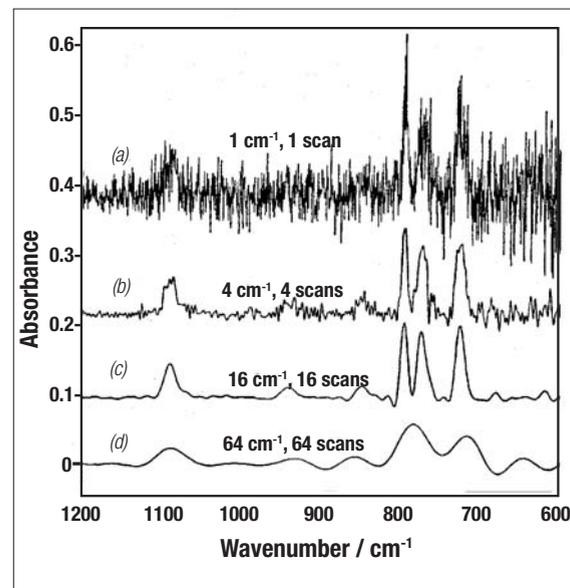


Figure 2. Spectra of a mixture of chlorinated hydrocarbons measured with active data equal acquisition times at resolutions of a) 1 cm^{-1} , b) 4 cm^{-1} , c) 16 cm^{-1} , and d) 64 cm^{-1} . [9]

“The spec of 0.5 cm⁻¹ has been used often to effectively eliminate some competitors.”

1, 2, 4, or 8 cm⁻¹ is fully adequate. Higher resolution of 0.5 cm⁻¹ or better is only required for spectroscopic studies related to molecular structure studies.

Additional Literature Citations

6. “Open-Path Atmospheric Monitoring with a Low-Resolution FT-IR Spectrometer,” P.R. Griffiths, R.L. Richardson, D. Qin, and C. Zhu, Proc. Optical Sensing for Environmental and Process Monitoring, O.A. Simpson, Ed., AWMA, VIP-37 (SPIE Vol. 2365), 274-284 (1995).
7. “FT-IR Measurements of Atmospheric Trace Gases and their Fluxes,” David W.T. Griffith, Handbook of Vibrational Spectroscopy, John M. Chalmers and Peter R. Griffiths (Editors), pp. 1-16, John Wiley & Sons Ltd, Chichester, 2002.

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8. B.R. Stallard, R.K. Rowe, M.J. Garcia, D.M. Haaland, L.H. Espinoza, and T.M. Niemczyk, “Trace Water Vapor Determination in Corrosive Gases by Infrared Spectroscopy,” Sandia Report, SAND93-4026, (December 1993) p. 51.
9. Peter R. Griffiths and James A. de Haseth, *Fourier Transform Infrared Spectrometry*, p. 475, Figure 22.7, John Wiley & Sons, Inc. 2007.