Gas Monitoring Using Fourier Transform Spectroscopy

Salomaa I K
University of Turku, Department of Applied Physics, Turku, Finland

Introduction

Quantitative and qualitative gas analysis is widely needed in present modern industrialized societies. The reasons for this need range from purely economical interests, to meeting the requirements of environmental and occupational health legislation. Examples of these applications include process effluent monitoring, emission monitoring, workplace safety monitoring, clinical blood gas monitoring, toxic gas monitoring in fires, chemical warfare agent detection and ambient air monitoring. Since the field of different applications is practically unlimited, a wide variety of measurement techniques have been used. Commonly used techiques include gas chromatography, mass spectrometry, ultraviolet spectrometry, chemiluminescence techniques and Fourier transform infrared (FT-IR) spectrometry, the last of which will be the issue of this presentation.

Principles of FT-IR Spectroscopy

Fourier transform infrared spectroscopy is based on the interaction of radiation with material. Infrared radiation, used in FT-IR, consists of electromagnetic waves at the wavelength range of 1 μm–1 mm, or at wavenumber range of 10 000 cm^{-1}–10 cm^{-1}, respectively. The interaction of material with these waves causes energy transitions that are typical for molecular compounds. That is why infrared spectroscopy is used to study molecular composition, especially of gas phase samples.

Generally, in spectroscopy the interaction between matter and radiation takes place via absorption or emission. In infrared spectroscopy, absorption is mostly used. When infrared radiation is penetrating through a gas sample, absorption is dependent on the product $\beta(\nu)cd$, where $\beta(\nu)$ is absorptivity, characteristic for a sample material, $\nu = 1/\lambda$ is wavenumber of the radiation (λ is the wavelength), c is the concentration, and d is the thickness of the sample (1). This is why infrared spectrum is often referred to as a "fingerprint" unique to each molecule. As a result, the presence of most compounds can be established from the infrared spectrum. Furthermore, the absorption is related to the concentration, which makes it possible to perform also quantitative analysis.

A typical FT-IR spectrometer consists of a broad-band radiation source, a sample compartment, a detection system, an electronic and computer unit, and an interferometer as the most important part of the spectrometer. The interferometer is an optical device that can divide a beam of radiation into two paths and then recombine the two beams after a path difference has been introduced. The path difference sets a condition under which interference between the beams can occur. The intensity variations of the beam

emerging from the interferometer are measured as a function of the path difference by the detector (2).

The IR signal, interferogram, yields the entire spectral information of the radiation under examination. The interferogram is finally converted to a spectrum by Fourier transforming it, and the resulted spectrum shows the intensity distribution of the measured radiation as a function of wavenumber.

Due to the method that is used in collecting the spectrum, the FT technique is fast, since the whole spectrum is generated all at once. At the same time Fourier method is extremely accurate because the spectral range is continuously calibrated by the He-Ne laser. The wavenumber accuracy of the spectrum thus depends only on the stability of the laser.

In measuring gaseous samples, many kinds of gas cells are used. In a single pass cell the radiation goes through the sample just once. Since the detection limits, however, are dependent on the absorption path, several kinds of multi pass cells have been developed in order to reach longer absorption paths still remaining the size of the gas cell limited. In certain applications no sample cell is used. Instead, the IR beam from the interferometer is sent through a large volume of the sample under examination and is either detected or reflected back to the spectrometer to be detected there. This open path method is used especially in monitoring air or atmospheric gases with low concentrations. The detection limits with a single pass cell are typically of the order of 1000 ppm, whereas in a multipass cell with the path legth of 10 m they are fwe ppm, and in the open path even ppb-level concentrations are detected.

The measuring sequence of an FT-IR spectrometer begins with determining the background spectrum. This is done by recording the interferogram with an empty gas cell. After Fourier transforming the interferogram the background spectrum, containing the intensity distribution of the radiation source, is obtained. Then the sample cell is filled with the gas to be examined and the same measurement described above is repeated. As a result, a sample spectrum similar to the background is obtained, with the exception that at certain wavenumbers the transmitted intensity has been decreased due to absorption in the sample. Dividing this sample spectrum with the background will result as transmittance spectrum, which may be converted to absorbance scale by taking a logarithm. The absorbance spectrum thus represents the fingerprints of the sample gas, and the heights of the spectrum lines are directly proportional to the gas concentration in the sample cell.

Applications

Fourier transform infrared spectroscopy has a large number of applications in various fields. In the field of science FT-IR spectrometers are one of the most commonly used type of instruments to study the structures of molecules and their behaviour. Infrared spectra are effective to reveal the quantum mechanical phenomena and interactions in molecules. Especially in high resolution molecular spectroscopy the FT-IR spectrometers are used almost solely.

The most important practical application of FT-IR spectrometers is the qualitative and quantitative analysis of unknown gas samples. For a long time this analysis in gas phase was done by merely looking at the spectra with the naked eye and comparing the unknown spectrum to known ones, or commercial search programs based on the correlation between the observed and a library spectrum were used. At present effective mathematical methods for accomplishing the multicomponent analysis of gas mixtures have been developed (3,4). They are primarily based on statistical methods such as partial least squares, principal component regression, inverse least squares, and classical least squares. The basic idea is always to fit the measured unknown spectrum using a set of calibration spectra. Due to the effective computerized algorithms, these methods are fast and capable to perform analysis practically in real-time.

Due to their fastness and efficiency, the FT-IR spectrometers have become common tools in any laboratory doing chemometric measurements. In addition to these traditional applications, numerous new fields of operation have been introduced in recent years. For the needs of industrial process monitoring and environmental quality control many manufacturers have designed FT-IR gas analyzers for continuous on-line analysis. The process monitoring instruments may be permanently installed on the gas line to make continuous automatic measurements of the gas flow. The results can be sent to a remote controller through analog outputs or via digital networks. In the same way these instruments can be used in environmental measurements to monitor e.g. green house gases. The open path method is especially suitable for air monitoring when the concentrations under investigation are very low, and long absorption paths are needed. Additionally, all the time new technologies are making it possible to develop even more flexible FT-IR systems for solving new needs of gas analysis.

References

1. J. K. Kauppinen and M. R. Hollberg. "Spectrometers, Infrared" in Encyclopedia of Applied Physics, Vol.19. New York: VCH Publishers, Inc. (1997).
2. P. R. Griffiths and J. A. de Haseth. Fourier Transform Infrared spectroscopy. New York: Wiley (1986).
3. D. M. Haaland. "Multivariate Calibration Methods Applied to Quantitative FT-IR Analysis" in Ferraro and Krishnan (Eds.), Practical Fourier Transform Infrared Spectroscopy. San Diego: Academic Press Inc. (1990).
4. P. E. Saarinen and I. K. Salomaa. "Analysis of true, imperfect fourier spectra" in S. G. Pandalai (Ed.), Recent Research Developments in Applied Spectroscopy, Vol. 2. Trivandrum, India: Research Signpost (1999).