Infrared absorption

Safe and stable measurement of gas concentrations in the ppm range with ACF-NT

Christoph Becker, Bernd Hielscher, Norbert Will

FTIR (Fourier Transform Infrared) technology has the capability to measure more than 100 of the 189 Hazardous Air Pollutants (HAPs) listed in Title III of the Clean Air Act Amendments (USA) of 1990. In fact, when these Amendments were passed, existing measurement methods could only measure 40 of these HAPs.

In 1306 Edward I of England prohibited the burning of sea coal in craftsmen's furnaces because of the foul smelling fumes it produced. Centuries later, for similar reasons, Elizabeth I banned the burning of coal in London when Parliament was in session. In the 1600s, writer and scientist John Evelyn reported that industries were obviously the cause of pollution in London, noting that pollution almost vanished on Sundays. London became famous for its "pea soupers" and "great stinking fogs".

In 1952, more than 4000 people succumbed to respiratory and cardiac diseases during the infamous "London Fog", when a five-day temperature inversion trapped deadly acid aerosols. Air pollution was no longer just an aesthetic concern, but a recognized hazard to health and safety. In 1956 the first Clean Air Act was passed.

While England was slowly coming to grips with the very real risks of industrial pollution, in neighboring France, Jean Baptiste Joseph Fourier was swept up in the tide of events surrounding the French Revolution. One of 12 children from his father's second marriage, Fourier joined Napolean's army as Scientific Advisor. When he returned from the conquering wars, he was appointed Prefect of Grenoble. It was in Grenoble, in 1807, that he completed his most important treatise, "On the Propagation of Heat in Solid Bodies". Like many great works that continue to impact the world today, Fourier's treatise was mired in controversy. No one, at the time, could have guessed at just how critical it would be to monitoring one of mankind's most pervasive problems – pollution.

Fourier Transform Infrared (FTIR) Spectroscopy is a measurement technique. The Fast Fourier Transform (FFT) is a mathematical operation performed on the signal obtained by interferometry Textbox to extract the infrared (IR) spectrum.

FTIR technology has proved mission critical in the environmental field. In 1995, scientists from the United States Geological Survey (USGS) mounted a FTIR spectroscope on a plane to measure gases being discharged from the caldera of one of the most active volcanoes on earth – Kilauea in Hawaii.

In the last few decades, with more and more regulation coming into force, ambient air quality has markedly improved in most Western countries. However, the "Global Burden of Disease" program of the World Health Organization (WHO) estimates that worldwide, 6.4 million lives are lost every year from long-term exposure to Ambient Particulate Matter (APM). Thus, environmental regulations continue to tighten.

Stricter environmental regulations and advanced technologies ensure that the emissions of harmful substances from domestic waste, hazardous waste and sewage sludge incinerators, cement plants and power stations continue to decrease. As the concentrations of harmful substances in waste gases fall, the demands on the measuring technology rise.

In addition to this, demand on the stability of an instrument over its entire operating lifetime increases at the same time as maintenance costs are being minimized. The ABB multi-component measuring system ACF-NT is an example of how innovative technologies enable the safe and stable measurement of gas concentrations in the parts per million (ppm) range.

The imperatives of Automated Measuring Systems (AMS) for continuous emission measurement

Legal provisions for the limitation of emissions have a long tradition in Germany whose standards have been setting the trend in Europe since the '80ies.

Operators of refuse incineration and processes with co-incineration are presently preparing for the implementation of new directives in Europe.

With the introduction of EU Directives 2001/80/EC and 2000/76/EC, emission monitoring is subject to EN 14181, "Stationary source emissions – Quality assurance of automated measuring systems". This was promulgated in September 2004. Compliance with the EN 14181 standard is a legal requirement under both the Large Combustion Plant Directive (LCPD) and the Waste Incineration Directive (WID). All vendor-supplied equipment must be EN 14181-compliant.

The quality assurance levels QAL1/2/3 were introduced to ensure this compliance. Quality level QAL3 obliges the operator to carry out regular checks for precision and drift at the zero and end-point of his analyzer measuring range. These checks are typically carried out during the maintenance interval. Longer intervals between routine maintenance minimize costs .

ACF-NT capabilities for reducing downtime and hence, cost of operation

The range of application of the ACF-NT measuring system, which is based on the FTPA 2000 FTIR spectrometer, includes complex applications for emission monitoring in domestic waste, hazardous waste and sewage sludge incinerators, and in cement plants and power stations with co-combustion. These are pursuant to European Directive 2000/76/EC, and incorporate its quality demands pursuant to EN 14181. The loss-free measurement of the lowest concentrations of water-soluble components is achieved by seamless heating of the system to 180 °C – from the probe element to the analyzer.

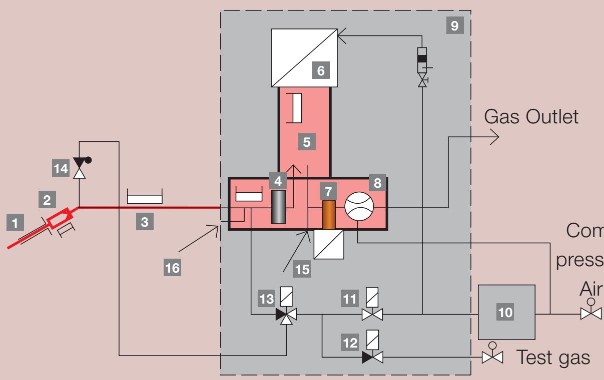
Seeing inside air with infrared interferometry

All molecules in the air – including pollutants – leave a "fingerprint" in the infrared by absorbing certain frequencies. The resulting infrared spectrum not only permits the molecules to be identified, but also permits their concentrations and temperatures to be evaluated. Fourier Transform Infrared (FTIR) Spectroscopy is a measurement technique that extracts this spectrum from incoming infrared light.

FTIR combines the Fast Fourier Transform (FFT) with the Michelson interferometer. The physicist, Albert A. Michelson, performed several experiments to measure the speed of light. He developed an interferometer in 1881, with which together with E.W. Morley in 1887, he showed that the speed of light is independent of the movement of the reference system (The Michelson-Morley experiment is often quoted in conjunction with Einstein's Special Relativity Theory). It is a development of this device that is used in FTIR today[1)]. The FFT is a mathematical operation performed on the signal obtained by the interferometer (the interferogram) to extract the infrared (IR) spectrum[2)].

1 Flow diagram of the working of the ACF-NT

1 Probe tube
2 Heated filter
3 Heated sampling line
4 Stainless steel filter
5 Heated meas. cell
6 FTIR spectrometer
7 ZrO_2 Sensor (option)
8 Aspirator pump
9 Spectrometer purge
10 Compressed air cleaner
11 Zero gas solenoid
12 Test gas solenoid
13 Switch test gas local or probe. Emergency purge
14 Check valve
15 FID port
16 Hg° port



Footnotes

1) For an explanation of the interferometer, see textbox "Principle of the interferometer" on page 53

2) For more background on Fourier Transform spectroscopy see the textbox "From waves to data: a quick guide to Fourier Transform spectroscopy" on page 60.

A low-maintenance electronically controlled air injector system conveys the sample gas from the chimney stack to the analyzers at constant pressure. In order to avoid pressure dependencies, which could arise if an uncontrolled feed pump were used 1, no moving parts are employed.

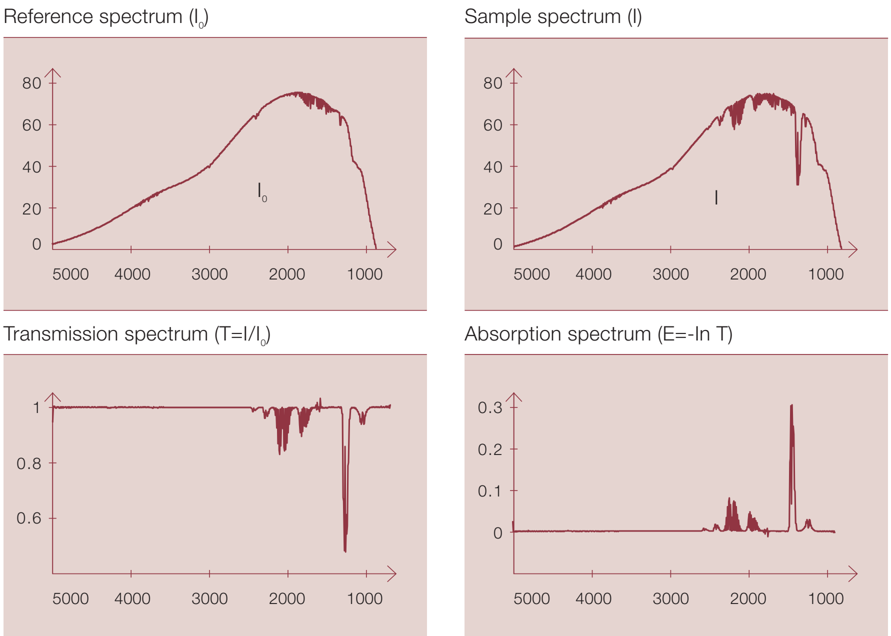
The spectrometer measures gaseous pollutants such as HCl, CO, NO and SO_2 as well as NH_3, H_2O, CO_2, HF, N_2O and NO_2. Measurements at very high moisture content are possible using a chemometric model optimized for refuse incineration processes. For measurements of O_2 a zirconia sensor and organic C_{tot} with a Flame Ionised Detector (FID) are optionally integrated in the system and are supplied with sample gas from the same sampling system.

In addition to the use of conventional analog and digital interfaces, a modern interface concept offers the possibility of serial transmission of data. This can be effected by Modbus or PROFIBUS, for instance, for a simplified connection to an emission analysis computer or control system. Data can also be transmitted via standard Ethernet – familiar from office technology – and remote maintenance can be carried out via a telephone modem connection, in order to minimize maintenance costs.

The long intervals between maintenance and the resultant low operating costs are a particular advantage of the ACF-NT. Significant costs are incurred for adjustment during the maintenance interval, especially in multi-component measuring systems. The operating costs are estimated to be approximately 70 percent of the life-cycle costs of an analyzer system. In particular, checking water-soluble sample components such as HCl, NH_3 or HF means an increased outlay for the provision of a calibration gas generator for the test equipment. Typically the time taken for complete adjustment of a measuring system with up to 12 sample components is approximately eight hours.

2 Schematic of processing principles of a raw spectrum to an absorption (extinction) spectrum

Lambert-Beer: $I/I_0=e^{-\varepsilon cl}$



The Lambert-Beer Law applies:

$I/I_0 = e^{-\varepsilon cl}$

With

- I Beam intensity, weakened by absorption in the sample cell
- I_0 Beam intensity, unweakened
- ε Extinction coefficient (molecule-specific constant)
- c Concentration of the sample component
- *l* Effective cell length

The signal I, attenuated by the absorption in the sample (spectrum of the sample), is divided by the unweakened signal I_0 (reference spectrum of the zero gas) and thus receives the transmission spectrum. The negative logarithm of the transmission spectrum supplies the extinction or absorption spectrum, which includes the qualitative and quantitative basic information on the composition of the sample. The height and area of the absorption bands (the absolute absorbance) of the individual substances is the dimension of the concentration. Using the Lambert-Beer Law equation, it is easy to see that this absolute absorbance is only dependent on the number of molecules in the measuring cell (ε and *l* are constant)

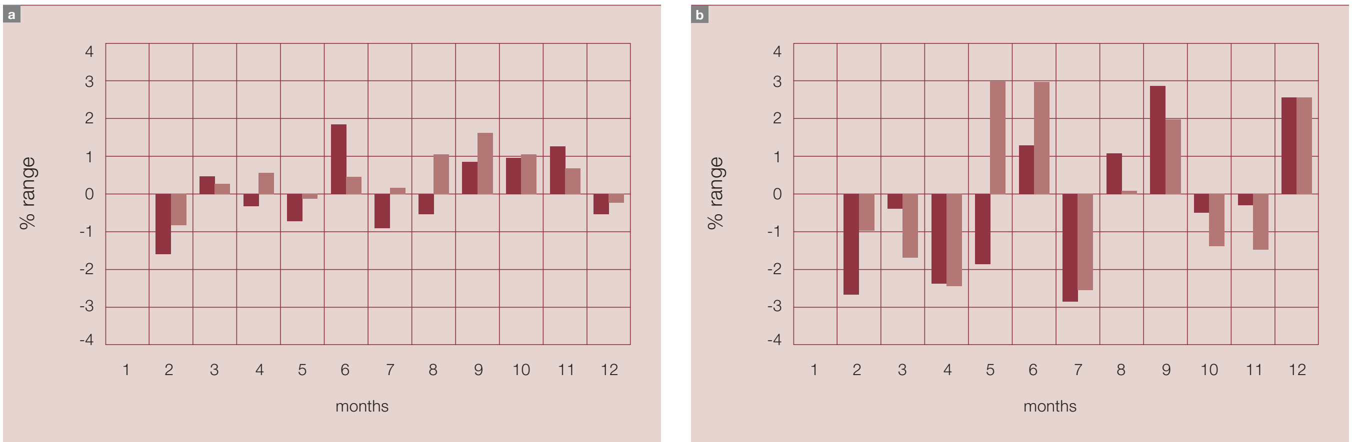
The quotient formation I/I_0 provides a decisive advantage for the stability of the analytical functions of the spectrometer, because the aging processes of modules such as the emitter and detector, as well as any changes in the transmission value of the sample cell (which would manifest themselves as drifting) are automatically compensated for. The basic requirement for this is that a new reference spectrum is a regularly input; this is automatically carried out every 12 hours in the ACF-NT.

FTIR measurement technique with emphasis on optimum signal processing and stability

FTIR spectrometry is a full-spectrum method. This means that absorption processes in a wide spectral range are used for analysis of the substances and not just narrow wavelength ranges, as is the case for interference filter, gas filter correlation or dispersive photometry.

In the Michelson interferometer in the FTIR instrument, each individual wavelength is modulated in extremely small sections, corresponding to the resolution of the instrument by means of interference. The modulated infrared radiation, as a sum of all the modulated (encoded) wavelengths, known as an interferogram, undergoes selective changes in the intensity distribution during interaction with the material, as it passes through the measuring cell filled with gas. The complete IR spectrum is calculated from the interferogram by means of a Fast Fourier Transformation. All the individual selective changes in intensity, based

3 Span deviation for two gases



on emission absorption in the sample, can be qualitatively and quantitatively evaluated as a result.

The processing of a raw spectrum to an absorption (extinction) spectrum is shown in 2.

Theory put to the test

The applied theoretical stability considerations are confirmed by the experience gained from more than 600 systems that have been installed throughout the world since 1993. It has emerged from scheduled tests with test gases in the maintenance interval that the ACF-NT permits adjustment intervals of over a year. All the deviations identified so far can be attributed to incorrect handling in the test, incorrect adjustment, or the use of test gases of incorrect concentrations.

ABB's own experience concerning the stability of the FTIR spectrometer is borne out by two independent long-term studies carried out by the German Technical Inspection Authorities (TÜV) of the Rhineland region. The latter study tested the predecessor of the current ACF-NT for the first time in 1995, and the current ACF-NT system in 2004–5. Two systems were tested in parallel in each of the field tests. The first long-term study ran for six months, the second for 12 months. Both field tests met the respective requirements with regard to stability and availability.

The results of a test on two lines of a refuse incineration plant – which ran for a year, taking the components NH_3 and SO_2 as example – further validate the findings on stability 3. The end-points of all sample components tested by the TÜV (CO, NO, SO_2, HCl, NH_3, H_2O) were validated at monthly intervals. The deviations of all components were always within permissible limits.

The statistical scattering of the data for ammonia 3b clearly shows the problematic nature of this gas (the same as for HCl and HF). As a result of adsorption and desorption processes on the gas-bearing surfaces, a lengthy waiting period is required till equilibrium is reached. This clearly shows that special care is called for in the adjustment and validation of these components.

Field test results for two lines of a refuse incineration plant

The new European Standard EN 14181 defines the maintenance interval as the maximum permissible period within which compliance with the stated values of the process variables is guaranteed, without external maintenance requirement, eg, refilling, calibration or adjustment. According to this definition, a maintenance interval of 12 months results for the current ACF-NT on the basis of the field test of 2004–5, ie ACF-NT is a measuring system with proven stability in field tests of one year. Tests with test gases only have to be carried out once a year.

Remote maintenance with the Analyze[IT] Explorer

The Analyze[IT] Explorer can be used in Ethernet TCP/IP networks to display all available data in a suitable manner and make it available for remote maintenance. The extent of servicing work can, therefore, be reduced, and reliability increased by means of "look-ahead" maintenance. This results in increased system availability through rapid troubleshooting and reduced cost through planned, predictive maintenance.

Operational stress can accelerate deterioration of equipment in a corrosive environment and move both equipment and processes to the brink of failure. Limiting stresses within the operating environment maintains reliability. Hence, predictive maintenance is a crucial feature for leading environmental monitoring instruments for air quality and industrial emissions.

The ACF-NT is a leading environmental monitoring system. It is proven to be safe, stable, industry-compliant and capable of detecting gases in the lowest ppm concentrations.

Christoph Becker
Bernd Hielscher
Norbert Will
ABB Automation GmbH
Frankfurt-Praunheim, Germany
christoph.becker@de.abb.com
bernd.hielscher@de.abb.com
norbert.will@de.abb.com