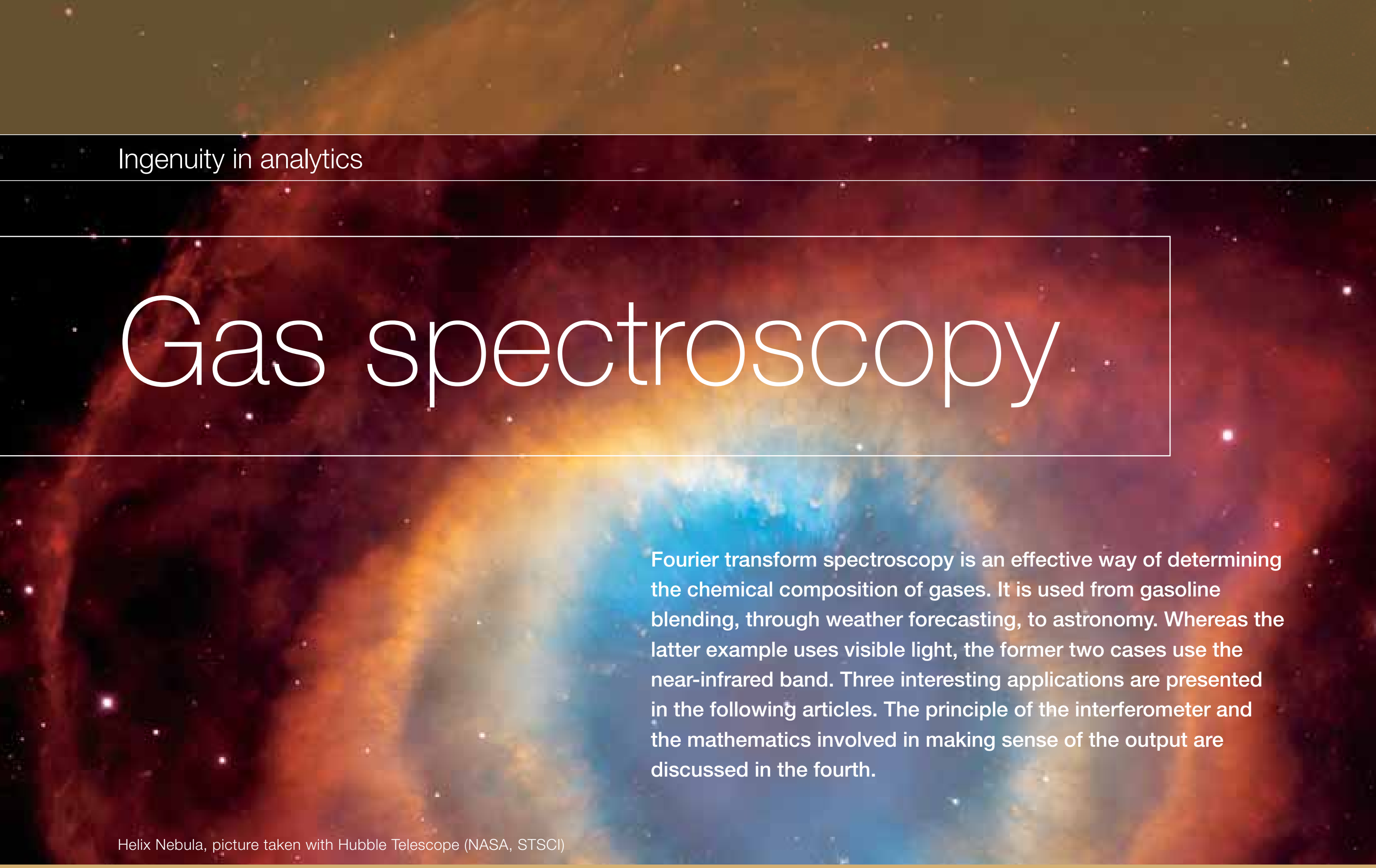
Gas spectroscopy

Fourier transform spectroscopy is an effective way of determining the chemical composition of gases. It is used from gasoline blending, through weather forecasting, to astronomy. Whereas the latter example uses visible light, the former two cases use the near-infrared band. Three interesting applications are presented in the following articles. The principle of the interferometer and the mathematics involved in making sense of the output are discussed in the fourth.



Helix Nebula, picture taken with Hubble Telescope (NASA, STSCI)

Counting photons

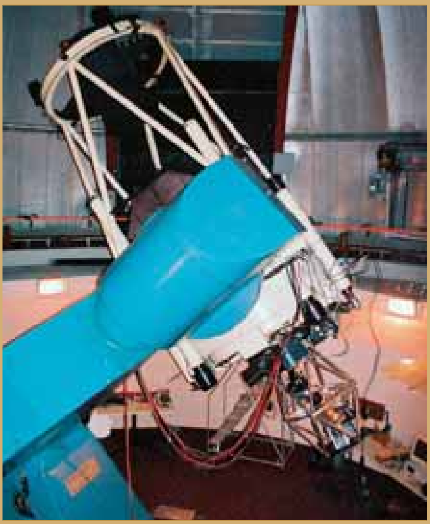
Fourier Transform Spectroscopy (FTS) was developed for astronomical telescopes in the 60ies, but found a far broader market in chemical monitoring in industrial processes. Refined and enhanced the technology is again equipping high-tech telescopes with measurement precision that almost counts individual photons. Today these telescopes are revealing the secrets of matter in the furthest reaches of the universe.

In late 2000 Laval University and ABB launched a joint effort to design an operational ground instrument for the 1.6 meter telescope of the Mégantic observatory in Canada 1. The instrument was first tested on the telescope in February 2004. In terms of the number of pixels (1.7 M) and the field of view (12 arc minutes), this IFTS (imaging FTS) is by far the largest ever used on a ground telescope and the only one to operate in the visible band. ABB is the integrator of the complete instrument, which includes an innovative step-scan FTS module, two CCD (charge-coupled device) cameras, two output optics lens assemblies and a collimating lens set. The instrument's overall dimensions are 133 × 80 × 80 cm and its weight is approximately 110 kg.

The design goal of this instrument is to maximize throughput and transmission to help astronomers collect as many photons as possible. The instrument operates in the 350–950 nm band to match the sensitivity of the two 1340 × 1300 pixel CCD cameras at the interferometer output ports. As the interference occurs at visible wavelengths, a mechanical control is required in the nanometre range. A piezo-based frictionless translation stage has been designed to control the angle and position of the moving three-inch mirror of the interferometer. A sophisticated laser-based metrology system optically reads the position and angle of the mirror 8000 times per second. A dedicated computer determines corrections to apply to the piezo translators in order to stabilize the fringe images and maximize the contrast recorded on the CCDs.

The dual output port design (2 CCDs) is achieved using flat mirrors and by inserting the science beam off-axis. This is the first implementation of this kind described in literature. The arrangement reduces the number of reflections encountered by the science beam. The beam splitter has a sophisticated multilayer dielectric coating that strongly modulates light in the specified waveband without contributing undesired absorption. The seven lenses used for collimating and re-imaging enable the fulfilment of the light-collimation requirement, and also the sub arc-second panchromatic point spread function at the image plane. About a million independent

1 The Mégantic telescope in Canada uses an imaging Fourier Transform Spectroscope from ABB

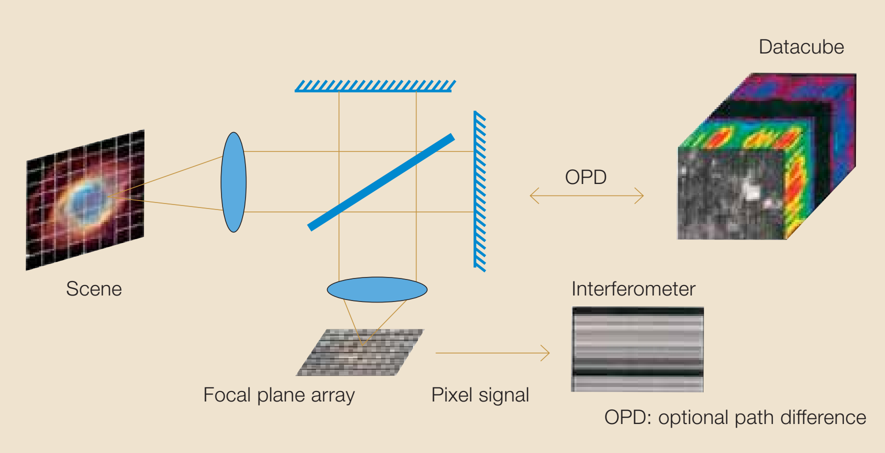


spectra can be collected from distinct scene elements. This is more than what is offered by traditional multi-objects/imaging spectrometers by a factor of about a thousand. The total system transmittance reaches over 60 percent (30 percent per CCD) at 500 nm thanks to the 90 percent quantum efficiency detector used. This is a value that is unmatched by any other spectrometer. The cameras are cooled with liquid nitrogen, enabling a very low readout noise (three electrons) and hence a high sensitivity. This instrument can literally count photons.

About a million independent spectra can be collected from distinct scene elements.

An imaging spectrometer produces cubes of data. This means that not only the two spatial coordinates of a light source are recorded but also the wavelength (or energy) of the photon. In other words, multiple images of the scene are recorded at various wavelengths. This set of images is called a datacube 2.

2 Schematic representation of an imaging FTS forming a datacube



The wealth of data from this IFTS comes at the cost of measurement time. A typical cube acquisition runs from minutes to hours depending upon selected parameters. However, as astronomers are accustomed to sitting and waiting for light to shine into their instruments, this is no impediment.

The instrument is still under commissioning at the Mégantic telescope. It is foreseen that it will be released to the astronomers in 2006 for use on any type of science programs. ABB hopes the interest raised in the community from the scientific papers published using this instrument will bring opportunities to build other units for the current generation of large ground based telescope (>10 m) or future space based facilities.

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Eye on the storm

The chemical composition of the atmosphere is rapidly being modified by gas emissions. High-quality measurements of the concentration and geographical location of these gases are keys to the understanding of the long term effects of these changes on weather patterns and the environment of the Earth.

Each molecule possesses a fingerprint signature in the infrared spectrum. These fingerprints can be visualized with Fourier Transform Infrared Spectroscopy (FTIR). Satellites equipped with ABB analyzers are providing data for a deeper understanding and early warning of environmental risks.

Human activity continues to increase emission of gases into the atmosphere. These are transforming its composition and properties. The resulting environmental effects, such as global warming, ozone layer depletion and air quality problems, have drastic consequences. (See also “Fourier analysis and the Greenhouse Effect” on page 71). Global warming accelerates water evaporation, which in turn increases average global precipitation. Soil moisture is likely to decline in many regions, and intense rainstorms could become more frequent. Air quality and climatic change also have significant economical and social impacts: Extreme weather conditions pose risks to human populations, either directly or, more frequently, to their means of production. To improve our ability to predict these phenomena accurately and to improve the scientists’ atmospheric models, more powerful data capturing tools are required. ABB Analytical Business in Quebec City makes Fourier Transform Spectrometers (FTS) that are carried onboard weather observing satellites.

The thermal infrared radiance emitted by the Earth’s atmosphere contains all the relevant information about the column of air being observed. When dealing with pollution measurement, atmospheric chemistry or the monitoring of ozone, the concentration of molecules is determined by measuring the absorptivity or emissivity of the molecules in the infrared band. For weather applications, the absorption and emission behavior of carbon dioxide at wavelengths around 15 micrometers allows an indirect measurement of the atmosphere’s temperature. Atmospheric windows, ie, parts of the spectrum where the atmosphere is transparent to infrared light, permit the temperature of the Earth's surface to be determined. The portion of the spectrum between five and eight micrometers permits an indirect determination of the water content or moisture in the air. Not only do these measurements provide a total apparent temperature or humidity at the top of the atmosphere but they can also be used to retrieve precise profiles of temperatures and water vapor concentrations. This retrieval process transforms the FTS instrument into a powerful sounder, dedicated to the measurement of valuable atmospheric parameters, which are used to feed weather forecasting models.

> The thermal infrared radiance emitted by the Earth's atmosphere contains all the relevant information about the column of air being observed.

Atmospheric infrared sounder

These atmospheric infrared sounders can be carried on two types of satellites. The first type is the Low Earth Orbiting (LEO) satellites, whose orbits are at altitudes between 700 and 850 km. The second type is at an altitude of 36,000 km in an orbit that is said to be geosynchronous[1]. These two types of orbits address different needs but also come with different technical challenges and constraints. On a low Earth orbit, the spacecraft takes 100 minutes to circle the planet. To avoid smearing effects (because of the great speed of the satellite relative to the Earth's surface), the measurement time must be very short. This sets high demands on sensitivity. Geosynchronous instruments, on the other hand, always align with the same location on the surface permitting the measurement to take far longer. However, the greater distance between the spacecraft and the Earth's surface means that the amount of light reaching the sensor is small, again affecting sensitivity requirements. Also, geosynchronous sounders cannot provide global measurements of the earth (because they are "locked" at a given latitude).

The sensors currently used for the atmospheric sounding in the thermal infrared area use an array of narrow band filters to provide spectral information. The number of filters that can be carried is limited (often not more than 20). Moreover, due to the nature of the filters and the width of the required spectral coverage, the spectral bands are not contiguous, meaning there are many gaps in the spectrum and hence missing information. An infrared sounder based on a dispersive spectrometer or on a Fourier transform spectrometer (FTS) offers a much more contiguous spectral view. For instance, the CrIS[2] (Cross-Track Infrared Sounder) will provide over 1300 spectral channels of information and will be able to measure temperature profiles with a vertical resolution of one km and to an accuracy approaching one degree Celsius. Due to its on-board spectral reference – a monochromatic laser diode – the instrument spectral response is also very stable over the life of the mission. Furthermore, the FTS technology is very robust and highly reliable – making it ideal for long-term operational missions.

ABB is currently under contract from ITT Industries to build CrIS sounders for the NPOESS (National Polar-orbiting Operational Environmental Satellite System) satellites. ABB is designing and building the interferometer and its metrology system, and the blackbody that will be used for the in-flight radiometric calibration of the instrument. ABB is also involved in

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Footnotes

[1] A satellite in geosynchronous orbit appears stationary to an observer on the Earth's surface.

[2] The Cross-track Infrared Sounder (CrIS) will replace the High-resolution Infrared Radiation Sounder on the next generation of National Polar-orbiting Operational Environmental Satellite System (NPOESS) in the USA. The CrIS will provide improved measurements of temperature and moisture profiles in the atmosphere from an altitude of about 850 km. See "http://www.ipo.noaa.gov/" for more details.

[3] The Canadian SCISAT satellite helps a team of Canadian and international scientists to improve their understanding of the depletion of the ozone layer, with a special emphasis on the changes occurring over Canada and in the Arctic. The ACE-FTS instrument on-board SCISAT measures simultaneously the temperature, trace gases, thin clouds, and aerosols found in the atmosphere from an altitude of 650 km. The satellite was launched by NASA on August 2003 and is successfully operational.

Fourier analysis and the Greenhouse Effect

The Earth receives large amounts of solar radiation (about 1.7 × 10^{17} W outside the atmosphere, or 1366 W per square meter, with a peak wavelength at 500 nanometers). If all this energy were trapped on the Earth, the planet would heat up very quickly. Fortunately, the Earth reflects about 30 percent of this radiation. The remainder is absorbed by the planet (16 percent by the atmosphere, 3 percent by clouds and 51 percent by land and water). It is this radiation that makes life on Earth possible. It drives photosynthesis in plants and powers the water cycle and other natural phenomena. This energy is eventually re-emitted as radiation over a broad frequency range (peaking at about 15 micrometers in the infrared). About 71 percent of the surface radiation is, however, re-absorbed by the atmosphere, slowing down the Earth's natural cooling rate. Without this absorption, the average surface temperature on the Earth would be –17° C instead of +15° C. The observed increase in concentration of greenhouse gases is boosting the ability of the atmosphere to absorb radiation, so further increasing the surface temperature (CO_2 concentration has risen from 313 ppm in 1960 to 375 ppm in 2005 according to Mauna Loa observatory in Hawaii).

To obtain further data, the Japanese Space Agency is developing a satellite mission. Its Greenhouse gases Observing SATellite (GOSAT) uses an interferometer designed and built by ABB. It will certainly provide much more information on the concentrations of the molecules that contribute to the warming effect of the Earth's atmosphere.

The mechanism now known as the Greenhouse Effect is no new discovery. It was first postulated by Joseph Fourier in 1824 and quantified by Svante August Arrhenius in 1896. It is interesting to note, that Fourier was working on the problem of mathematically describing heat conduction and infrared radiation – making it all the more fitting that Fourier's other great discovery, Fourier Analysis, remains an indispensable part of the instrument.

the definition of the level-one data processing algorithms.

To increase reliability, complete redundancy is implemented for the metrology sub-module and for the electronics.

The scanning mechanisms are of a frictionless, flexure-mounted design. These avoid the wearing down of the moving assembly that is so often a problem in space instrumentation.

Delivery of the first flight unit took place in November 2005 and flight models two and three were added in the following months.

Decades of experience

FTIR technology was originally designed to look into Space. After finding its way into a whole range of other applications, the technology has been launched into orbit and is looking back at Earth from Space. ABB's expertise in the design and manufacturing of Fourier Transform Spectrometers, which modulate the IR beam in a wavelength selective way by means of optical interference, (see "Waves to data" on page 73), is based on its experience in the early 1970s with balloon-borne FTS instruments and later on with several additional projects[2),3)]. This elegant and powerful method of obtaining a spectrum will continue to serve atmospheric observation needs for many decades to come.

The CrIS will be able to measure temperature profiles with a vertical resolution of one km and to an accuracy approaching one degree Celsius.

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Spectrum of blending

Product blending is an important technique in the refining industry. It is the final stage in the conversion of crude oil into useful fuels. The blender mixes several streams from various process units to provide fuel that meets government, international or customer specifications. As it represents the final stage in a refinery process, its optimization is vital – the benefits of upstream process optimization are easily negated when poor blending produces either a substandard fuel or – more frequently – sacrifices refining margin through suboptimal use of expensive blend feedstocks. This is the step whose optimization frequently offers the greatest benefits in terms of payback.

A sustained global increase in the demand for light fuel, driven by the emerging economies – especially China and India – has led to the strengthening of refining margins. This development is continuing despite the rising crude oil prices of recent months. The availability of high production margins for final products has re-emphasized the role of on-line process spectroscopy using Fourier Transform Near Infrared techniques, FT-NIR, in high-value final product optimization applications, including gasoline product blending. The benefits offered by process FT-NIR include multi-property, multi-stream analyses, high analysis repeatability (normally significantly better than conventional on-line analyzers), and accuracy meeting ASTM (American Society for Testing and Materials) norms. In addition, process FT-NIR analyzers are able to model not only direct chemical compositional information, but also bulk process stream properties such as octane, aromatics, distillation curves, cetane, cloud point – which are often the properties most required by unit optimizers, or the most constraining in terms of product release. All of these properties can be extracted from a single FT-NIR spectrum.

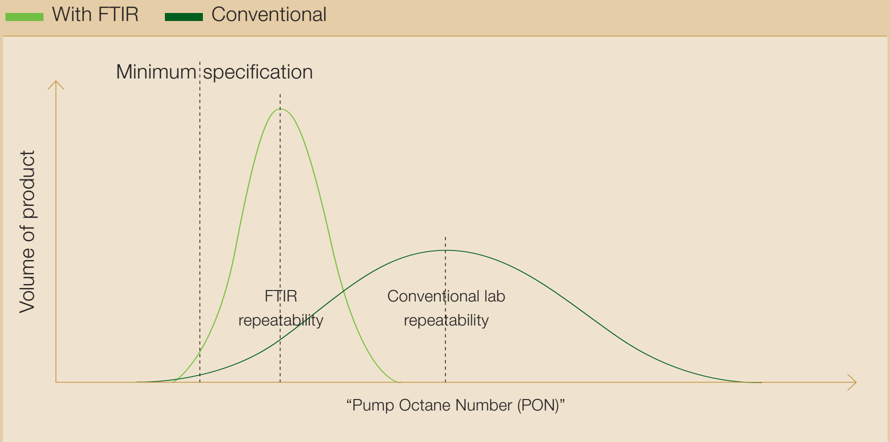
The analytical accuracy of FT-NIR is as good as the ASTM laboratory reference data used to develop the calibration models, provided good statistical practices are followed. It is perhaps not always fully appreciated how much analytical repeatability and analyzer availability can be improved by the use of process FT-NIR as compared to conventional multi-analyzer blend optimization schemes. For light hydrocarbon streams, the inherently ultra-low-noise optical technology of FT-NIR can yield exceptional analytical repeatability.

The outstanding repeatability of ABB's FT-NIR gasoline property measurement is of significant benefit to the blend operator. Changes in blend properties can be tracked precisely during blending. Such changes would otherwise be "lost" in the noisy or infrequent results that are retured by classical analyses. The operator or multi-variable control scheme can make process decisions with the confidence that the observed deviation is real. In addition, the increased repeatability as compared to the traditional laboratory method, means that a reduction in property giveaway can be achieved through tighter control closer to the lower boundary 1.

Giveaway can never be reduced to zero, but minimizing it as far as possible makes a decisive contribution to the refinery's overall margin.

Since the process FTIR analyzers used in refinery process stream analysis and unit optimization are secondary analyzers (depending for their operation on correlation models using laboratory reference data), it is important for validation purposes that an on-going SQC (Statistical Quality Control) track-record of performance relative to laboratory standards is maintained.

1 Reducing giveaway with precise blending control



Better earnings through better analytical accuracy

It is possible to calculate "baseline" giveaway associated with an analytical uncertainty of 0.1 Pump Octane Number (PON). This giveaway can never be reduced to zero, but minimizing it as far as possible makes a decisive contribution to the refinery's overall margin. For every 100,000 bbl/day of plant production a very conservative improvement (an analytical precision of 0.02 to 0.05 PON) in final product leads to a saving in the range of $ 1.5 M to $ 3.0 M per year [1].

Clear arguments for FTIR

FTIR is the technology that currently offers the best trade-off in terms of price, performance, value and risk. As an optically-based technology, it allows for the highest flexibility in multi-stream, multi-property applications. It is compatible with both local, fully extractive sampling and remote, multi-cell extractive fiber-optic based analyzer systems. It offers a multi-property analysis with rapid analysis cycle times, well tuned to the requirements of an APC (Advanced Process Control) optimizer. It is also well established with hundreds of installations globally, providing examples of successful implementation. Historically, the limitation to any spectroscopic measurement for on-line, final blended product control has been the difficulty in developing, and more particularly maintaining, robust stable calibration models. This has been to a large extent mitigated by recent developments, including very well-controlled analyzer-to-analyzer variability, which permits easy maintenance and transportability of developed calibrations. The exploitation of novel chemometric modeling procedures has helped to minimize the sensitivity of developed calibrations to changes in blending recipes.

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Reference

[1] ABB Review Special Report Instrumentation & Analytics, May 2006, pages 54–59

Waves to data

The light transmitted or emitted by a gas contains a wealth of information on its chemical composition in the form of spectral lines. A Fourier transform spectrometer is a device that extracts this spectrum. ABB Review takes a quick tour of two of the basic principles behind the instrument – the interferogram and the Fast Fourier Transform.

The Michelson interferometer was developed in the 1880ies by the physicist Albert Abraham Michelson. In a Michelson interferometer 1, the incoming light 1a is split in two parts by a half-mirror beam-splitter 1b. The reflected part twice travels the distance d_1 to mirror 1c before returning to the beam-splitter. Similarly, the transmitted part twice travels the distance d_2 to mirror 1d. At the output 1e, interference occurs between the two rays. It is from this interference that spectral information is extracted.

Interference

2a shows waves spreading from a point source. In 2b and 2c a second identical source is added and the wave patterns are superimposed. In places, the patterns combine to form waves of up to twice the amplitude (constructive interference). Elsewhere, they cancel out leaving areas of calm (destructive interference). In contrast to these two-dimensional examples, the interference in an inferometer occurs principally along a single axis (shown in red in 2).

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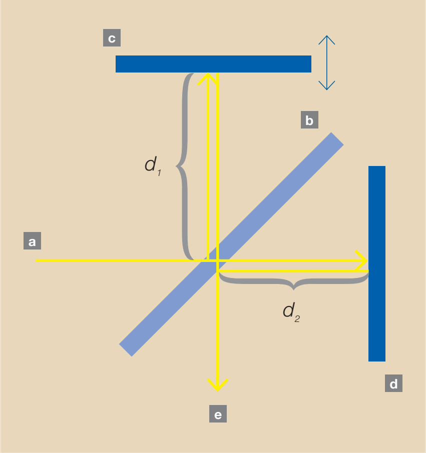
In 2b, the distance between the sources – or difference in path length $2(d_1–d_2)$ – is a multiple of the wavelength. Maximum constructive interference occurs along the axis. In 2c, the distance is shortened by half a wavelength leading to destructive interference. More generally for such a monochromatic input, the strength of the signal at any point on the axis varies sinusoidally as a function of the path difference, and at a wavelength that is identical to the signal wavelength.

$$I(d_1;\lambda) = \frac{I_0}{2}\left\{1+\cos\left\{2\pi\,\frac{2(d_1-d_2)}{\lambda}\right\}\right\}$$

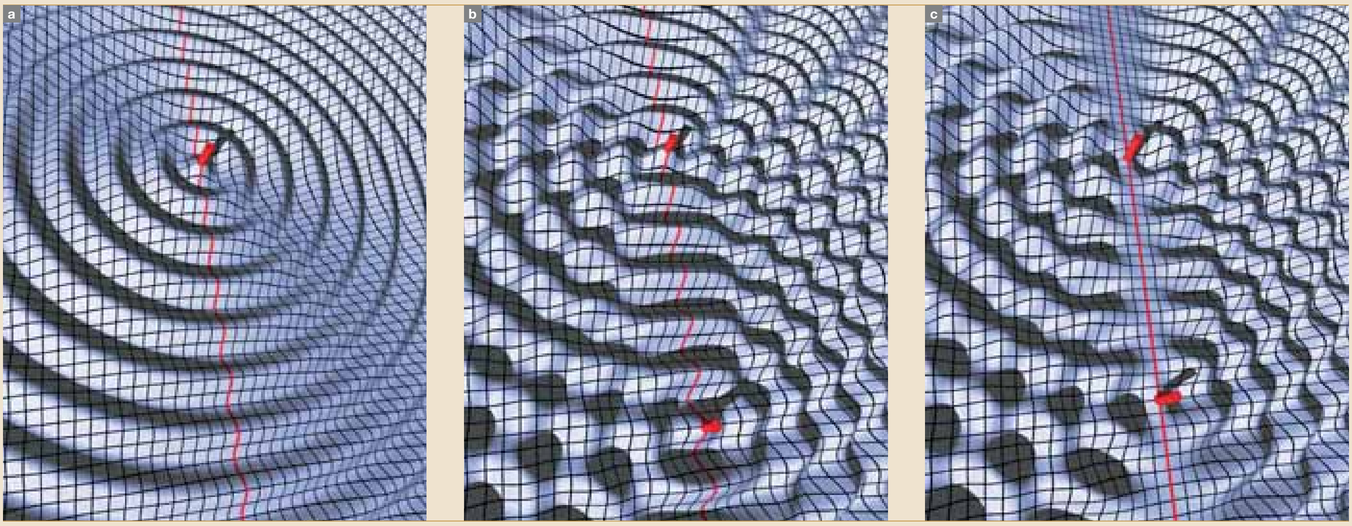
Where I_0 is the amplitude of the incoming ray 1a and λ is its wavelength. Using a detector at the interferometer output 1e and varying d_1, this function (the interferogram) can be plotted and the values of I_0 and λ determined.

A real measured signal usually has a broad range of superimposed frequencies. The resulting interferogram is the sum of the interferograms of its monochromatic components.

1 Principle of the Michelson interferometer



2 Interference of two identical wave patterns: The distance between the sources determines whether constructive **b** or destructive **c** interference occurs along the red axis. The sides of the small squares are equal to a quarter wavelength.



$$I(d_1) = \int I_0(\lambda)\,\frac{1}{2}\left\{1+\cos\left\{2\pi\,\frac{2(d_1-d_2)}{\lambda}\right\}\right\}d\lambda$$

Further processing is required to separate these signals.

From Fourier to Fast Fourier

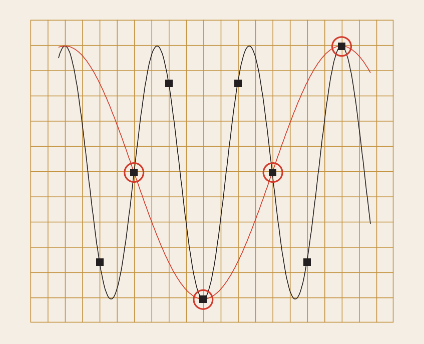
In the early years of the 19th Century, the mathematician Jean Baptiste Joseph Fourier developed a transformation that maps a function to its frequency spectrum:

$$F(k) = \int_{-\infty}^{\infty} f(x)\, e^{-2\pi ikx}dx$$

Where $f(x)$ is the function to be analyzed and $F(k)$ its frequency spectrum.

3 Low sampling rates mean frequencies cannot always be identified unambiguously

— original signal
■ sampling rate = 8
○ sampling rate = 4
— aliased signal for sampling rate 4



Digitally recorded signals usually consist of a finite series of numbers acquired at a regular interval. The corresponding Discrete Fourier Transformation (DFT), derived from the general formula is:

$$F_n = \sum_{k=0}^{N-1} f_k\, e^{-2\pi ink/N}$$

Where f_k is the k-th element of the recorded series, F_n is the n-th element of the corresponding frequency series and N is the number of samples. This algorithm has one major shortcoming: Its complexity rises quadratically with N. Historically, its use was often beyond available computational means. Various, often inadequate, approximations were adopted.

The light transmitted or emitted by a gas contains a wealth of information on its chemical composition in the form of spectral lines.

All this changed in 1965 when Cooley and Tukey published their Fast Fourier Transformation (FFT) algorithm.

How does it work?

One effect of reducing the sampling rate is that information is lost. **3** shows a sinusoidal curve (black) sampled at a rate of eight (black points) and again at four (red circles). At the latter rate, the sampled signal cannot be distinguished from the red curve and consequently its DFT is identical (the red curve is called the *alias* of the black – such aliasing occurs for all frequencies above half the new sampling rate). A separate DFT performed on the omitted points returns an equally ambiguous result, but comparison of the two DFTs restores the lost information. Instead of calculating one eight-point DFT, two four-point DFTs are performed, each of which requires a quarter the computing power of the original. This reduction is repeated recursively. The FFT algorithm is thus most efficient when the number of samples is a power of two.

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For further information on applications of Fourier transform spectroscopy, see *ABB Review Special Report Instruments and Analytics*, June 2006, pages 46–60 and 76–79.