

A spectrum of applications

Process Analysis using FT-NIR Spectroscopy

Paul Chabot, Mike Simpson, Fabiano De Melas

Keeping processes under tight control is paramount to achieving quality and throughput improvement and cost reduction. A plant's ability to increase efficiency can easily determine whether it operates at a profit or at a loss. In the past, optimization decisions required laboratory analysis of samples removed at different process stages. To achieve a more responsive control, analysis has shifted to on-line measurement. Analyzers are connected directly to the process through sampling systems, probes or non-invasive sampling interfaces. The prerequisite for such analyzers is high reliability, robustness, simplicity of use and ease of maintenance.

Fourier Transform Infrared Spectroscopy (FTIR) is a widely used analytical technique for the on-line monitoring of processes¹⁾. It offers a fast, accurate and highly repeatable approach to the monitoring of both chemical and physical properties of a process stream. ABB is a global leader in FTIR technology and has dedicated more than 30 years to the development of FTIR analyzers. ABB's FTIR solutions are engineered to meet the tough requirements of process applications for a broad variety of manufacturing industries. They form a unique family of analytical instruments perfectly designed for on-line, real-time monitoring.

FT-NIR (near-infrared FTIR) focuses on the band between approximately 750 and 1400 nm.

The following articles present applications of process FTIR spectroscopy for the monitoring and control of two different types of processes. The first example focuses on an application for the analysis of a gasoline blending process for the Hydrocarbon Processing Industry (HPI), while the second application describes the use of FTIR spectroscopy for the non-invasive analysis of a semiconductor manufacturing process.

Footnote

¹⁾ See also "Principle of the interferometer" on page 53.

On-line analysis of a gasoline blending process

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 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 process FT-NIR in high-value final product optimization applications, including gasoline product blending. The advantages 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. Typical FT-NIR calibration model performance on gasoline data for a refinery with a good reference laboratory are shown in [Table 1](#).

Provided good statistical practices are followed, process FT-NIR will yield an analytical accuracy exactly as good as the ASTM laboratory reference data used to develop the calibration models. 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, which can easily and successfully be prepared for analysis by simple sample-conditioning filtered fast-

Table 1 Typical Process FT-NIR Performance Data

Typical FT-NIR analyzer calibration performance for final product gasoline for a refinery with a good reference laboratory:		
	Accuracy (SECV) at 1σ	Precision (r) at 1σ
RON	0.28	0.01
MON	0.32	0.01
% Aromatics	0.8	0.02
% Olefins	1.2	0.03
% Benzene	0.1	0.005
% Oxygenates	0.2	0.01
RVP (kPA)	0.82	0.16
D10 (°C)	1.8	0.1
D50 (°C)	2.1	0.1
D90 (°C)	3.2	0.1
E170	1.6	0.08
E365	0.8	0.011

Table 2 Typical value of octane giveaway

Cost of octane giveaway, \$M per year 0.1 PON (Pump Octane) per 200,000 bbl/day CDU capacity		
Item	Factor	Value
A	Octane giveaway	0.1 PON
B	Multiplier for APC 99% confidence level	2.58
C	Refinery margin, \$/octane-gallon	0.015
D	CDU to FPB conversion ratio	0.562
E	Average throughput (CDU) bbl/day	200,000
F	Average throughput (CDU) gals/day	8,400,000
	Lost profit, octane giveaway/day	\$18,270
	Lost profit, octane giveaway/year	\$6,668,550

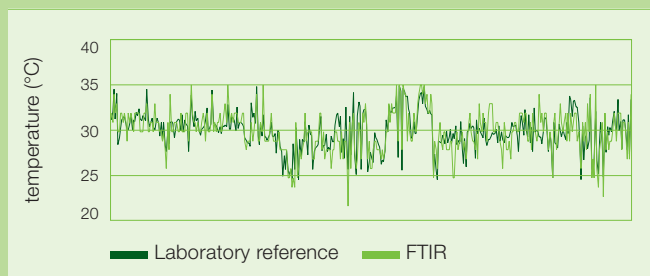
CDU = Crude Distillation Unit

Process Analytics

1 Process FTIR 8 hour repeatability (RON; research octane number)



3 Laboratory versus Process-FTIR trendline



loops, the inherently ultra-low-noise optical technology of FT-NIR can yield exceptional analytical repeatability when compared with conventional physical analyzers.

The outstanding repeatability **1** 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 classical analyses return. 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 **2**, means that a reduction in property giveaway can be achieved.

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 ongoing SQC (Statistical Quality Control) track-record of performance relative

to laboratory standards is maintained. Useful ASTM guidelines for this practice are covered in ASTM D6122 and ASTM E1655. **3** shows such an example of a laboratory vs. process FTIR comparison for a gasoil blending application.

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.

Better earnings through better analytical accuracy

The calculation in **Table 2** represents the "baseline" giveaway associated with an analytical uncertainty of 0.1 Pump Octane Number (PON).

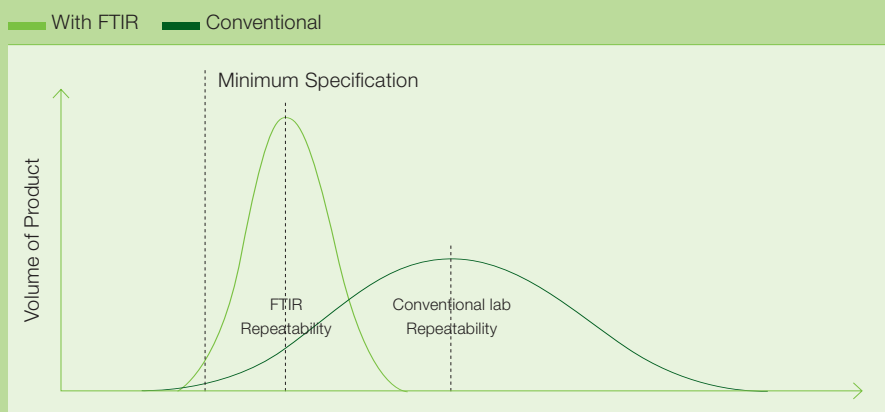
This giveaway can never be reduced to zero, but minimizing it as far as possible makes a decisive contribution to the refinery's overall margin. The numbers of **Table 2** show that a very conservative improvement (an analytical precision of 0.02 to 0.05 PON) in a

real-time and on-line process FTIR analysis of the final product leads to a saving in the range of \$1.5M to \$3.0M per year.

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 terms of multi-stream, multi-property applications as 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. It has been further mitigated through the global development of product databases speeding up calibration development – and the exploitation of novel chemometric modeling procedures has helped to minimize the sensitivity of developed calibrations to changes in blending recipes.

2 Reducing giveaway with precise blending control



Optimization of a Semiconductor Manufacturing Process

Continuous monitoring and control of the wet chemistry used in the semiconductor manufacturing process enhances production yields, decreases risk of failure, and maximizes profitability. Achieving high throughput, competitive quality standards and low production costs in semiconductor manufacturing requires a very precise control strategy. Among the wet processes used, the wafer cleaning procedure is one of the most important. A well-controlled cleaning procedure is essential in removing impurities and ensuring product quality.

ABB's Wet Process Analyzer (WPA) is designed for the continuous on-line monitoring of the concentrations of the chemicals used in a wide range of etching, cleaning and stripping fluids and provides the communications protocols that permit real-time process control.

System configuration

The ABB WPA couples an FT-NIR spectrometer with a Teflon sampling sensor for non-invasive monitoring. The spectrometer includes an optical multiplexer

Table 3 Wet bench module configuration:

1. SPM/QDR
2. BOE/OFR (not used in this RCA process)
3. DHF/OFR
4. SC1/QDR
5. SC2/QDR
6. IPA (not considered)

Where:

SPM is $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{O}_3$ at 120 °C

QDR is Quick Dump Rinse

BOE is $\text{NH}_4\text{F}/\text{HF}$ (not used)

OFR is Overflow Rinse

DHF is diluted hydrofluoric acid, in this case 100:1 for HF: H_2O at 22 °C

SC1³⁾ at 5:1:1 for H_2O : NH_4OH : H_2O_2 at 50 °C

SC2⁴⁾ at 5:1:1 for H_2O : HCl : H_2O_2 at 50 °C

IPA is Isopropyl Alcohol.



and a multi-detector module, allowing sequential monitoring and control of up to eight different sampling points. Through the use of fiber optic cables, each measurement point can be up to 100 meters away from the analyzer. [4](#) shows the system configuration with eight occupied detectors.

Sampling approach

The patented ClippIR⁺ module enables

in-line real-time monitoring. Its installation is fast and simple and does not require an impractical bypass or a cooling unit. Each ClippIR⁺ is clamped onto the external surface of an existing Teflon tube and directs NIR light through the Teflon conduit and then back to the spectrometer. The ClippIR⁺ measurement time is 57 seconds for one sample, regardless of the number of components measured in each stream.

Table 4 Chemical usage calculations (100% production, no idle time, 96 runs/day)

	H_2SO_4	H_2O_2	HF	NH_4OH	HCl	IPA
Consumption gal/run	0.11	0.34	0.0010	0.030	0.020	0.050
Consumption gal/day	11	33	0.096	2.9	1.9	4.8
Consumption gal/week	74	228	0.67	20	13	34
Consumption gal/year	3800	12000	35	1000	700	1700
Yearly Chemical costs	\$45,068	\$193,560	\$611	\$7,870	\$6,937	\$13,580

Process Analytics

Because of its compact size, it can fit into small chemical cabinets or inside any other part of the wet station. It is also chemically resistant to corrosion and is suitable for highly aggressive environments.

Successful operation

ClippIR⁺ was demonstrated on a wet bench that was equipped with a multiple robot handling system to load cassettes of wafers side-by-side into reduced cassettes, and then move them through a series of chemical baths. The wet bench was a 50-wafer tool. Its module configuration (order of chemical steps, concentrations, temperatures) is summarized in [Table 3](#).

All rinses were based on pre-determined times or dump/fill cycle counts. In such a process, all chemical tanks must be changed periodically. The bath dump rates for the wet bench are 24 hours for SPM (sulfuric acid, peroxide and de-ionized water mix¹), BOE (buffered oxide etch) and DHF (diluted hydrofluoric acid²) and 12 hours for SC1 (standard clean 1³) and SC2 (standard clean 2⁴).

Chemical consumption costs are reduced by at least 20 to 30 percent.

The chemical usage measurements and calculations obtained were performed on the basis of 100 percent production with no idle time. This equates to approximately 96 runs per day. A summary of chemical usage and total annual costs related to the wet bench is presented in [Table 4](#).

The on-line chemical monitoring of each component in a wet station tank improves process control and also extends bath lifetime by buffer-

ing the single tanks with replenishment solutions. These are injected at regular time intervals or when predefined threshold concentration values are exceeded.

This demonstration shows how using a chemical monitoring approach with a

good control strategy can extend the lifetime of chemicals from a few hours up to several days. Chemical consumption costs are reduced by at least 20 to 30 percent (depending on the process recipes).

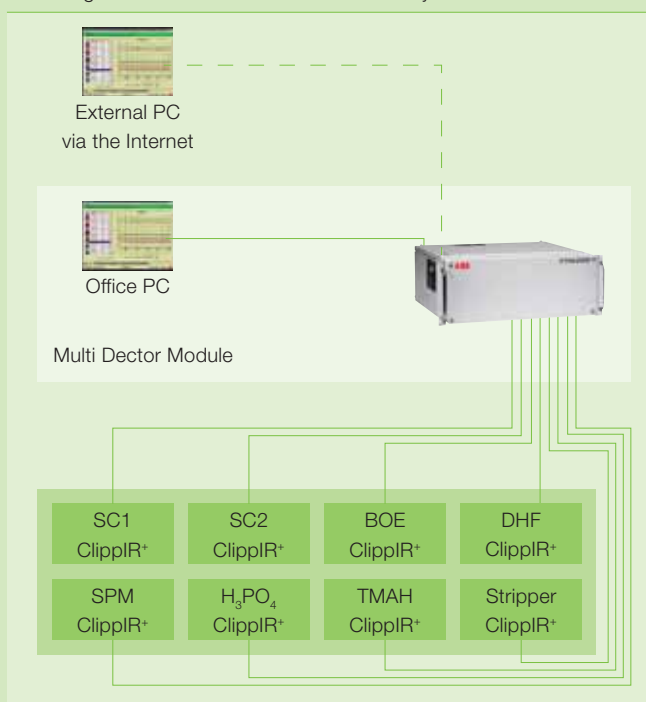
For example, a tight monitoring of HF and NH₄F concentrations in a BOE bath helps production engineers maintain the chemical concentrations within predefined ranges. When predetermined concentration thresholds are reached, the WPA transmits alarm or warning signals to the wet station console. For this to make an effective contribution to process stability and reliability, monitoring repeatability is crucial.

One of the main parameters influencing the WPA performance is the stability of the process temperature.

The repeatability of WPA is excellent: typical analytical performances are shown in [5](#) – repeatability on NH₄F and HF in a BOE bath can exceed 0.1 percent. On the HF monitoring, the target concentration is considered at 5 percent (by weight) and the WPA can follow the concentration with an absolute repeatability of +/-0.03 percent (by weight). For ammonium fluoride, the target concentration is approximately 35.5 percent (by weight) and the achieved repeatability is 0.07 percent.

One of the main parameters influencing the WPA performance is the stability of the process temperature. For instance a DHF process controlled with a temperature tolerance of 5 °C (+/- 5 °C) can be typically monitored with repeatability on HF observa-

4 Configuration of the ABB Wet Process Analyzer



tion of 0.08 percent. With highly performing in-line heaters (tolerance of around 0.5 °C or less), the repeatability at 1 sigma on HF can reach up to 80 ppm.

6 shows continuous production monitoring of SC1 and SC2 processes: production cycles and chemical bath changes are monitored with the WPA. In the SC1 process **6a** trends of H₂O₂ and NH₄OH are shown. The SC2 process **6b** monitoring reports trends of HCl and H₂O₂.

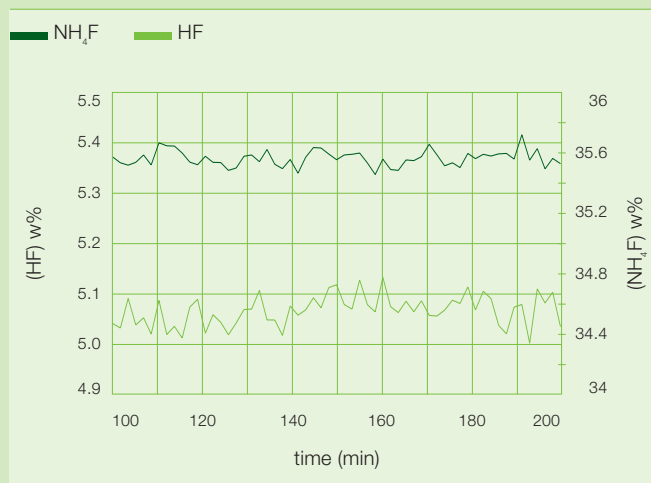
The WPA is of a great value for the optimization of process quality. It helps keep chemical concentrations within predefined limits.

In this SC1 process, the concentration of ammonium hydroxide decreases over constant time periods, while hydrogen peroxide remains constant over time. The WPA helps identify the component in the SC1 solution that is the limiting factor in terms of concentration, defining the threshold concentration values (ie, lower limit on NH₄OH concentration) and finally triggering a complete bath change based on predefined concentration limits. In the example discussed here, SC1 baths are changed when the concentration of NH₄OH drops below 0.37 percent. As an additional precaution, a time limit can be also defined for bath changes.

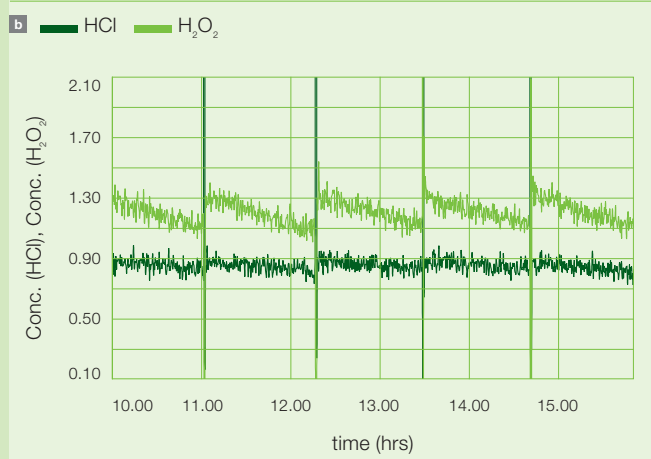
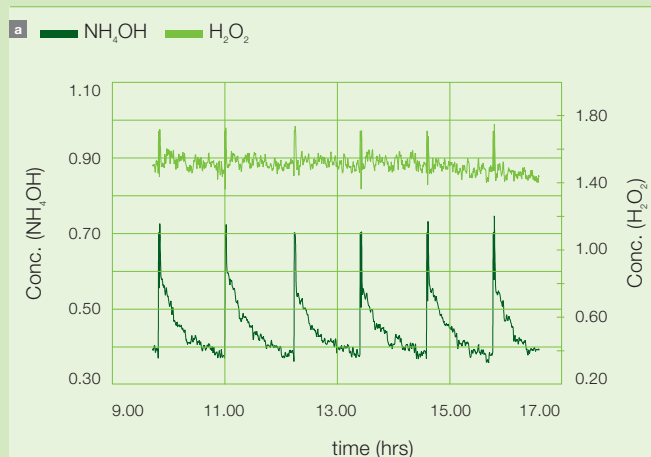
WPA delivering added value

The WPA is a reliable and reproducible analytical instrument. The WPA can be equipped with between one and eight ClippIR's – non-invasive on-line sampling sensors that can easily be inte-

5 Trend line of HF and NH₄F in a BOE (buffered oxide etch)



6 Trend line of **a** NH₄OH and H₂O₂ in a SC1 bath and **b** HCl and H₂O₂ in a SC2 bath.



grated onto existing process lines without introducing contamination risks. The WPA is of a great value for the optimization of process quality. First, it helps keep chemical concentrations within predefined limits, preventing wafers from being processed with out-of-specification solutions while also providing the required confidence on the concentration measurements: both during the mixing or pre-mixing steps or on the recirculation line of process tanks. Moreover, the return of investment of one single WPA equipped with several ClippIR's is enormous because it allows end users to save on the cost of chemicals and reduce chemical waste on multiple chemical baths. Hence the WPA has been shown to deliver added value to wet equipment in terms of increased throughput, reduced costs of ownership and much safer and better controlled wet processes.

Paul Chabot

ABB Bomem Inc.
Quebec, Canada
paul.g.chabot@ca.abb.com

Mike Simpson

ABB Ltd.
Telford – Hortonwood, UK
mike.b.simpson@gb.abb.com

Fabiano De Melas

ABB PS&S S.P.A.
Sesto San Giovanni (MI), Italy
fabiano.de_melas@it.abb.com

Footnotes

- ¹ Also known as "piranha etch", this bath removes organic contaminations.
- ² BOE and DHF are used to remove oxides and reduce metal contamination.
- ³ Uses APM. (ammonium hydroxide, hydrogen peroxide and de-ionized water mixture) to remove particles.
- ⁴ Uses HPM (hydrochloric acid, hydrogen peroxide and de-ionized water mixture) to remove metal contamination.

The interferometer

In an interferometer¹⁾, the incident light ray is split into two branches that traverse different paths before being recombined into a single ray. Due to the difference in path length, the phenomenon of interference occurs.

Interference

1a shows waves spreading from a point source. In **1b** and **1c** 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 examples in which interference occurs in two dimensions, the interference in an interferometer occurs principally along a single axis (shown in red in **1**). In **1b**, the distance between the sources is a multiple of the wavelength and maximum constructive interference occurs along the axis. In **1c**, the distance is shortened by half a wavelength leading to destructive interference. More generally, the strength of the signal at any point on the axis varies sinusoidally as a function of the distance between the sources, and at a wavelength that is identical to the signal wavelength. The signal wavelength can thus be determined by varying this distance while observing the signal strength.

A real measured signal rarely takes the form of a pure sine wave. The signal strength plotted as function of the path difference (interferogram) consists of many superimposed waves of different frequencies. Further processing is required to separate these.

From Fourier to Fast Fourier

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

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

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

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:

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

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.

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. **2** 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

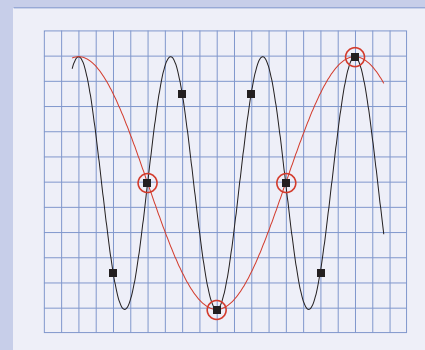
be distinguished from the red curve and consequently its DFT is identical (the red curve is called the alias of the black – such aliasing occurs for all frequencies above half the new sampling rate). A separate DFT performed on the omitted points returns an equally ambiguous result, but comparison of 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 can be repeated recursively. The FFT algorithm is thus most efficient when the number of samples is a power of two.

Footnote

¹⁾ See also the textbox “Principle of the interferometer” on page 53 and “Seeing inside air with FTIR” on page 77.

2 Low sampling rates mean frequencies cannot always be identified unambiguously

- original signal
- sampling rate = 8
- sampling rate = 4
- aliased signal for sampling rate 4



1 Interference of two identical wave patterns: The distance between the sources determines whether constructive **b** or destructive **c** interference occurs along the red axis

