FTIR engine Measurement Examples

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Near infrared spectroscopic analysis using an FTIR engine

Molecules each have unique vibrations, thereby absorbing infrared light of a specific wavelength. Infrared spectroscopic analysis utilizes this characteristic to analyze components contained in substances. In the near infrared region of 1.1 \( \mu \)m to 2.5 \( \mu \)m, many substances have unique absorption spectra, and these are applied to qualitative and quantitative analysis in various fields.

The FTIR engine is a compact Fourier transform infrared spectrometer developed for near infrared spectroscopic analysis. A Michelson optical interferometer and control circuit are built into a palm-sized enclosure. Spectrum and absorbance can be measured by connecting a PC via USB. It can be applied to real-time measurement performed on site without bringing the measurement sample into the analysis room as well as continuous monitoring.

Two types of measurement methods of “transmission measurement” and “reflection measurement” are used for near infrared spectroscopic analysis using the FTIR engine.

### Optical system

The Michelson interferometer is used for the FTIR engine. The FTIR's optical interferometer is composed of a light input section, beam splitter, photodetector, and MEMS chip. Light is separated into two light paths by a dichroic mirror. The MEMS chip has a movable mirror (φ3 mm) that uses MEMS (micro-electro-mechanical systems) technology and a fixed mirror. The photodetector (InGaAs PIN photodiode) acquires light intensity signals that varies depending on the movable mirror position. The optical spectrum is obtained by taking the Fourier transform of this light intensity signal. The built-in semiconductor laser (VCSEL: vertical cavity surface emitting laser) and photodetector (Si photodiode) for monitoring the movable mirror position allow spectrum measurement with high wavelength accuracy.
Near-infrared spectroscopy uses an analytical method that relates band intensity of a spectrum (absorbance) to sample concentration.

Absorbance is defined by the equation $A = \log_{10} \left( \frac{I_1}{I_0} \right)$. And common logarithms of a ratio between incident light level $I_0$ (reference measurement) and transmitted light level $I_1$ (sample measurement) can be taken for analysis.

While transmittance decays exponentially with increasing optical path length, absorbance expressed in logarithmic terms changes proportionally with optical path length.

For example, if transmittance is 0.1 (absorbance = 1) and the thickness of the object is doubled, transmittance will be 0.01, while absorbance will be doubled (absorbance = 2).

### Equation of absorbance

$$A = -\log_{10} \left( \frac{I_1}{I_0} \right) = cIc$$

- $A$: absorbance
- $c$: sample concentration
- $I$: optical path length of quartz cell
- $\varepsilon$: molar absorption coefficient
- $I_0$: incident light level
- $I_1$: transmitted light level

### Absorption spectrum measurement system
Examples of Transmission Measurements (Water, Ethanol)

Water absorption spectrum

The water absorption spectrum has a peak of each 1450 nm (OH groups) and 1930 nm (H₂O groups) band. The absorbance changes according to the optical path length of the quartz cell. Absorbance is measured well up to about 2.0.

Ethanol absorption spectrum

The ethanol absorption spectrum has a peak after 2200 nm. Zero-fill processing is performed before the Fourier transform, and data points are interpolated to display a smooth spectrum.
Comparison of absorbance of alcoholic beverages and estimation of alcohol concentration

Following figure shows the near-infrared absorption spectra of beer, sake, brandy, ethanol, and water. There is absorption by the OH group of water (1450 nm band, 1900 nm band) and by the CH group of alcoholic beverages (2100 to 2500 nm). With transmission measurement results, we were able to obtain characteristic spectra in the absorption bands of water and alcoholic beverages. In addition, with the results of estimating the alcoholic concentration from absorbance in the 2300 nm band, we confirmed that the estimated values and numerical values of components contained in the beverage matched, and that high accuracy measurement is possible.
Concentration Analysis of Liquid Chemicals

Accurate quantitative measurements of various liquid chemical concentrations

Quantitative analysis can be done by measuring samples of liquids with different concentrations. Figures on page 7 and page 8 show the measurement examples of nitric acid aqueous solutions (NO₃⁻) with different concentrations.

Measurement samples

Measured using 6 samples each of 3 types (18 total) of nitric acid aqueous solutions with different concentrations:

1. High concentration (NO₃⁻: 0%, 2%, 4%, 6%, 8%, 10%)
2. Medium concentration (NO₃⁻: 0%, 0.2%, 0.4%, 0.6%, 0.8%, 1%)
3. Low concentration (NO₃⁻: 0%, 0.02%, 0.04%, 0.06%, 0.08%, 0.1%)

Absorption spectra of nitric acid in aqueous solution (High concentration)

(Ta=25 °C, halogen light source, optical path length of cell=0.1 mm)

Measurement by: Hamamatsu Central Research Laboratory
Following figures show regression coefficient and calibration curb of different concentration of nitric acid aqueous solution (NO$_3^-$).

In the high and medium concentration measurement samples, there is a large absorption change in the 2000 nm band (OH group of water), and there is a small change in the 2200 nm band (OH group and NH group of nitrogen). While for low concentration measurement samples, there are little change of absorption peaks at particular wavelength. A calibration curve is formed by using the data from the entire wavelength range.

When the concentration is lower, quantification accuracy will also be lower, but the level is high enough to do concentration measurement.

Measurement by: Hamamatsu Central Research Laboratory
Diffuse Reflection Measurements
Principle of Diffuse Reflection Method

While a portion of light irradiated onto a sample is regular reflected by surface of particles, the rest penetrates into the sample. The light is repeatedly diffused through refractive transmission, light scattering, surface reflection inside the sample, and some light emitted out from the sample's surface is measured. The diffuse reflection spectrum is similar to the absorption spectrum because the light is repeatedly transmitted through the interior of the sample during the light diffusion process. In diffuse reflection measurement, common logarithms of a ratio between incident light level $I_0$ (reference measurement) and transmitted light level $I_1$ (sample measurement) can be taken for analysis, which is common to the transmission measurement.

\[ \frac{K}{S} = \frac{(1-R)^2}{2R} = \cosh \left( \log_{10} \frac{I_1}{I_0} \right) - 1 = \log_{10} \left( \frac{I_1}{I_0} \right) \]

**Equation of absorbance**

- $K/S$: Kubelka-Munk
- $S$: scattering coefficient
- $K$: absorption coefficient
- $R$: Reflectance = $I_1 / I_0$
- $I_1$: transmitted light level
- $I_0$: incident light level

**Reflected light spectrum measurement system**

A halogen light source is connected to a 6:1 reflection probe, and light is incident on the FTIR engine. A reference plate is installed at the tip of the reflection light probe, and the diffuse reflection light is measured by the FTIR engine.

**Recommended structure of diffuse reflection light source**

Diffuse reflection signals are generally very weak. Multiple lamps are placed in close proximity to the sample, and diffuse reflected light is taken into the NIR spectrometer via an optical fiber to improve the light detection efficiency.
Moisture Content Measurements

Measures absorption at 1450 nm and 1930 nm

We prepared a dry cloth and a wet cloth soaked in water, then compared their absorption spectra with the FTIR engine. The wet cloth has a stronger absorption spectrum than the dry cloth in the 1450 nm band (OH group) and 1930 nm band (H₂O group), which are the water absorption bands.

Comparison of absorbance spectra of wet cloth and dry cloth samples

![Graph showing absorbance spectra](image-url)

SNV: Standard Normal Variate
Identification of Powder Samples

Comparison of absorbance of sugar

Sugars such as monosaccharides (glucose and fructose) and disaccharides (sucrose) can be found in food, defining its nutritional and flavor content. The near infrared spectroscopy is applied for composition measurement of saccharide content in fruits. The FTIR engine is capable of accurately measuring the most minute peak patterns, resulting in spectra that are similar to those produced using a benchtop spectrometer.

Comparison of absorbance spectra of powder sugar samples

<table>
<thead>
<tr>
<th></th>
<th>Glucose</th>
<th>Fructose</th>
<th>Sucrose</th>
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<td>Wavelength (µm)</td>
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<td><img src="image" alt="Absorbance spectrum (Fructose)" /></td>
<td><img src="image" alt="Absorbance spectrum (Sucrose)" /></td>
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</tbody>
</table>

Measurement by: Hamamatsu Central Research Laboratory
Identification of Additives in Various Plastics

Classification of brominated flame retardants

Various types of plastics are used in consumer electronics. For the measurement of white polypropylene (PP), differences in spectra in a region from 2000 to 2500 nm make separation of brominated flame retardants used in their plastics possible.

■ Contents measurement of white polypropylene

The right figure shows absorbance spectra of additives such as DBDE (decabromodiphenyl ether), TBBA (tetrabromobisphenol A) and Talc. From the absorption peak at around 1400 nm, the graph shown in red is possible to infer a talc-specific component. Although TBBA and DBDE have relatively similar spectra, they can be distinguished from each other by the difference in the absorption peak at around 2100 nm.

■ Measurement of concentration level

The right figure shows absorbance spectrum of white polypropylene integrating different concentration additives of TBBA and Sb$_2$O$_3$. The concentration of TBBA additives can be estimated from the difference in absorption intensities at 1700 nm, 2200 nm and 2300 nm.
Analysis of Concrete Degradation

Estimating natural deterioration of concrete blocks

Following shows measurement results of concrete blocks installed outdoors for one and fifty years. Estimating natural deterioration of concrete blocks is possible by measuring progression of hydration and calcium (Ca) dissolution.

It also shows increase of the hydration (OH, H₂O) around 1430 nm to 1930 nm, and CSH around 2210 nm.

Measurement by: Emeritus Professor Satoru Nakashima (Osaka Univ.)
Film Thickness Measurements

Measuring film thickness by spectral interferometry

When white light enters a thin film sample, multiple reflections occur inside the film. These multiple-reflection light waves boost or weaken each other along with their phase difference. The phase difference of each multiple-reflection light is determined by the light wavelength and optical path length (distance that light moves back and forth in the thin film multiplied by the film refractive index).

This phase difference allows the spectrum reflected from or transmitted through the sample to produce a unique spectrum that depends on the film thickness. Spectral interferometry is a technique for measuring film thickness by analyzing that particular spectrum.

Following figure shows the result of film thickness measurement example of 2-layer plastic film and glass plate measured by the FTIR engine.

- Film thickness measurement (2-layer plastic film, glass plate)
Absorbance measurement of medicines

Following shows spectra of five types of medicines including stimulants (Caffeine, Theophylline) and analgesics (Loxoprofen, Paracetamol, Aspirin). Measurement results of Theophylline component using an FTIR engine show peaks in the specific spectrum is assigned and consistent with a published paper 1).

Measurement of Theophylline component and content ratio

Theophylline anhydrate is a phosphodiesterase inhibiting medicine used in therapy for respiratory diseases. In the theophylline spectra, absorption bands near 1,400 nm and 2,260 nm belong to the CH combination tone of the methyl group (CH₃), and the absorption band near 1,670 nm belongs to the overtone of the CH of the methyl group.

![Measurement of Theophylline](image)

The FTIR engine enables process monitoring by quantitative analysis. Following figures show measurement examples of model tablets containing different Theophylline contents (10%, 20%, 30%). The coefficient of determination $R^2$ was 0.9922 showing good quantification of Theophylline content.

### NIR diffuse reflection spectrum of the Theophylline tablets (concentration level)

![NIR diffuse reflection spectrum](image)

### Calibration curve of Theophylline at 1664 nm

![Calibration curve](image)

Measurement by: Hamamatsu Central Research Laboratory
"Zero Fill Processing" Enables Spectrum Detailed Analysis

Zero fill processing is a technique of processing the obtained spectrum data to finer detail. It is a process of adding zeros to each end of an optical interference signal before a Fourier transform is applied. This allows for interpolation between points that are plotted after the Fourier transform. The red graph using the zero fill processing achieves similar data compared with the reference data.

- **Ethanol absorption spectrum**

![Ethanol absorption spectrum graph](image)

- **Reference: Literature data**

Reference:
Yukihiro Ozaki, Near-Infrared Spectroscopy, 2015
In the FTIR engine, the internal temperature heats up 1 hour after the start of operation and then stabilizes. Output variation is suppressed by performing sample measurement and reference measurement alternately.

**Reference Measurement**

Realizing Stability under Continuous Operation

- FTIR internal temperature and output variation during reference measurement

- Connection example of measurement system

  Voltage generator
  Supply voltage: 8.5 V

  Halogen light source
  Optical fiber core diameter: 600 µm
  NA: 0.22

  Cell

  FTIR engine
  Optical fiber core diameter: 600 µm
  NA: 0.22

  USB2.0 cable

  PC
Information described in this material is current as of May 2022.

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