JASCO Europe

JASCO Applications Book

Macro & Micro FTIR

JASCO Corporation was founded in 1958 to provide the scientific community with optical spectroscopy products.

In the mid-1950's a group of researchers in the Institute of Optics of what is now Tsukuba University needed an Infrared Spectrophotometer for their research.
Since a commercially available instrument was not yet existing at the time, they undertook the challenge to develop their own.

The result was quite a success - a reliable instrument with excellent optical performance. As a second result, other research groups asked them to replicate the instrument for use within their laboratories.

Over the years the JASCO product line has grown to cover instruments used, not only in research but also for routine analysis applications in areas such as quality control, environmental analysis, and process control. The current spectroscopy product line encompasses instrumentation for the following methods:

- ***UV/Visible and NIR***
- ***Microscope Spectrophotomers***
- ***FT-IR, microscope FT-IR and FT-Raman***
- ***Dispersive RAMAN***
- ***Polarimeters***
- ***Spectrofluorometers***
- ***Portable Raman***
- ***Portable FT-IR***
- ***Fully Automated Dissolution Tester***

JASCO is also the world leader in the field of ***Circular Dichroism Spectropolarimeters*** and ***Vibrational Circular Dichroism Spectrometers.***

"serving the Science and Technology World by providing most advanced analytical instrumentation"

With the introduction of HPLC in the mid-1970's JASCO's experience in highly sensitive and accurate optical systems led to the development of a series of chromatographic detection systems. Fixed and variable wavelength UV/Visible and Fluorescence detectors were introduced featuring excellent sensitivity and reliability in compact modules. In order to offer complete HPLC systems JASCO developed a variety of novel solvent delivery systems as well as other accessories such as column ovens, autosamplers, and PC based control and analysis software.

Today JASCO offers a wide variety of ***HPLC modules***, accessories and analysis software. The new ***JASCO LC-4000 Liquid Chromatography*** series is designed to operate at pressures approaching 15,000 psi for either gradient or isocratic separations, providing researchers with a powerful tool when using the new generation of small particle columns. LC-4000 Series includes a versatile series of components offering unique flexibility to build systems for routine and specialized applications. LC-4000 features the widest choice of optical HPLC detector: UV, diode array, fluorescence, chemiluminescence, CD, chiral and refractive index detector.

Finally JASCO's modular ***Supercritical Fluid Chromatography*** and ***Supercritical Fluid Extraction*** platforms provide a low-cost, fast, green technology with reliable and worry-free performance for a wide variety of applications.

JASCO has a strong global presence, supplying customers in ***over 45 different countries***.

***JASCO Europe** is in charge for marketing, sales, service and support for all Jasco products throughout **Europe, Middle East and Africa**.*

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Make the most of your investment with

JASCO Service and Support

JASCO Service and Support agreement plans are designed for those laboratories pursuing superior productivity through the highest level of professional services.
The use of automated instrumentation is the right approach to meet today's laboratories productivity requirements, reducing analysis run times, enhancing sample throughput, and increasing analytical accuracy and precision. In this view, preventive maintenance is very important to maximize laboratory uptime and avoid unexpected expenses.

In addition to the analytical goal, proper installation and maintenance are required to achieve optimal performance. JASCO provides flexible service and support management solutions focused on your laboratory real objectives.

With its service network, JASCO is ready to maintain the perfect reliability of customer's instrumentation and minimize the laboratory down time.

· *Superior productivity*
· *Optimized analytical performance*
· *Lower cost of ownership*
· *Extended instrument life*

If your laboratory has specific Service and Support requirements, JASCO can help you with customized contract agreements. In addition, a full set of Installation Qualification (IQ), Operational Qualification (OQ), and Performance Qualification (PQ) tests are available to verify the system proper installation, operation and performance, respectively.

Get the most from your investment with

JASCO Training Courses

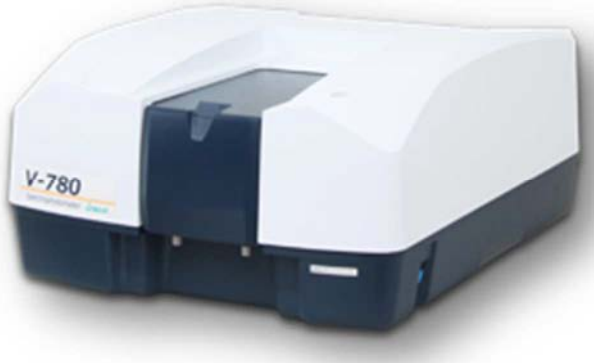
JASCO Training Courses ensure maximum skill development for the best value of your laboratory. Our team of highly-experienced specialists can help your staff to get the most from your instrument reducing your analysis run time and improve performance.

Build your knowledge with JASCO Training Courses:

· *Instrument and Software operation*
· *troubleshooting*
· *Maintenance*
· *Calibration*
· *Applications and Methods developments*
· *Operating Techniques*

V-730 – V-730bio – V-750 – V-760

UV-Vis Spectrophotometers



V-770 – V-780

UV-Vis/NIR Spectrophotometers

With more than fifty years of experience in the design of spectrophotometers, JASCO offers a complete range of UV-Vis/NIR instruments.
The ***V-700 series*** consists of six distinct models designed to meet a wide range of application requirements.

From an innovative optical layout to a simple comprehensive instrument control and data analysis software interface, the ***V-700 series*** does not compromise on accuracy, performance or reliability.

All spectrophotometers are controlled by ***Spectra Manager™ II***, JASCO's powerful cross-platform spectroscopy software package with USB communication.

FT/IR-4600 – FT/IR-4700

FT/IR Spectrometers

FT/IR-6600 – FT/IR-6700 – FT/IR-6800

FT/IR Spectrometers

The ***FT/IR-4000*** and ***FT/IR-6000*** models represent a broad range of instrumentation that redefine infrared spectroscopy as a powerful yet easy to use technique in a compact and reliable line of instruments with the highest signal-to-noise ratio.

All models are controlled by ***Spectra Manager™ II*** , JASCO'S powerful cross-platform spectroscopy software package with USB communication.

All models feature an auto-alignment function which maintains instrument optical alignment after beamsplitter changes or instrument movement.

IRT-5100 – IRT-5200

FT/IR Microscopes

IRT-7100 – IRT-7200

FT/IR Microscopes

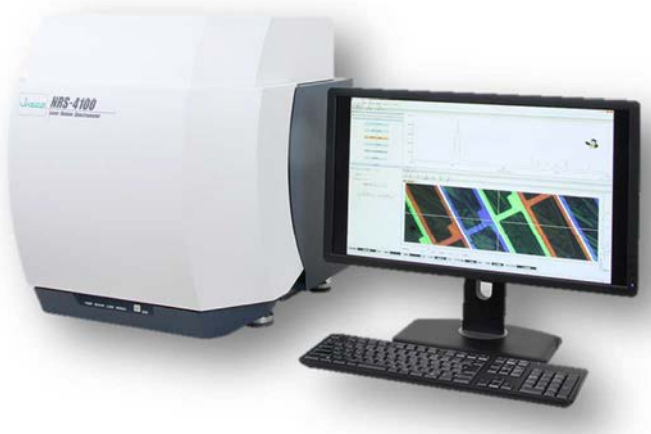
JASCO is proud to release four innovative FT-IR Microscope, the ***IRT-5000*** and ***IRT-7000***, providing several new functions that drastically improve infrared micro-spectroscopy analysis.

Both microscope systems can be easily interfaced with either the FT/IR-4000 or FT/IR-6000 spectrometer, offering the most advanced microscopy and imaging systems available in the market today.

The microscope system automatically scans the specified points or area, rapidly collecting a full spectrum of each point without moving the sample stage.

NRS-4100

Laser Raman Spectrometer



The system offers space-saving, automated switching laser light source and alignment adjustment to assist the analysis, ***NRS-4100*** is easily used to quality control as well as research and development.

The micro-Raman ***NRS-4100*** is equipped with measurement assist function that can be easily setup operation and a user advice function that automatically analyzes the spectrum and obtain a high-quality data even at the first time.

The automatic XYZ stage is equipped with a sample search function. Using a newly developed algorithm (patent pending) the microscope image, sample search function has used to set the measurement position automatically and gives you data from the location that is automatically registered with the click of a button measurement.

NRS-5100 – NRS-5200

Laser Raman Spectrometers

NRS-7100 – NRS-7200

Laser Raman Spectrometers

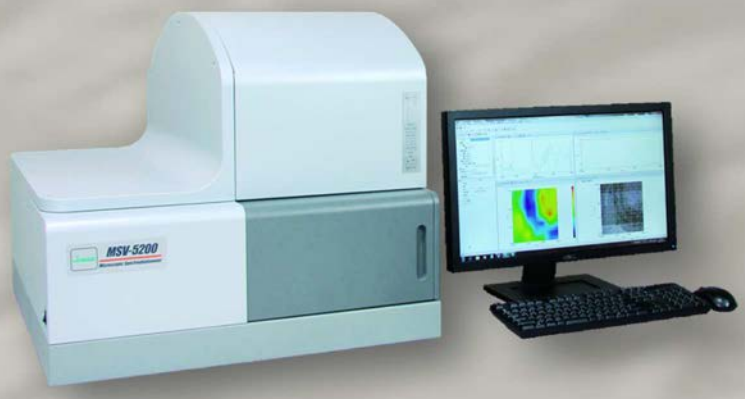
The performance expected on a micro-Raman spectrometer are fully provided with the JASCO ***NRS-5000/7000*** series Raman systems, assuring consistent performance for rapid acquisition of high quality data with automated system control and minimal optical adjustments.

For application expansion, an automated multi-grating turret, 2 internally mounted detectors and a maximum of 8 lasers ranging from the UV through the NIR are capable of integration with the instrument system.

Spectra Manager™ II for the ***NRS-5000/7000*** offers revolutionary features to simplify previously difficult measurement and analysis tasks, while adding various user-support tools such as auto-fluorescence-correction, wavenumber correction, intensity correction, and a novel user-advice function.

MSV-5100 – MSV-5200 – MSV-5300

UV-Vis/NIR Microscopes



The MSV-5000 series is a microscopic spectrophotometer system providing transmittance/reflectance measurements of a microscopic sample area with a wide wavelength range from ultraviolet to near infrared.

MSV-5100 Spectrophotometer is a dedicated UV-Vis microscope with a wavelength range of (200-900 nm).

MSV-5200 Spectrophotometer includes a Peltier-cooled PbS detector and has a wavelength range of (200-2700 nm).

MSV-5300 Spectrophotometer incorporates an InGaAs detector to obtain optimized NIR measurements and has a wavelength range of (200-1600 nm).

J-1100 – J-1500 – J-1700

Circular Dichroism Spectropolarimeters

The latest effort in the JASCO commitment to lead the field of Circular Dichroism.

Unparalleled optical performance and optionally available measurement modes are combined in a manner to make the ***J-1000 Series Spectropolarimeter***, a true "chiro-optical spectroscopy workbench", ***able to work up to 2,500 nm***.

Instrument control and data processing are handled effortlessly by our JASCO's user friendly and innovative cross-platform software, ***Spectra Manager™ II.***

FVS-6000

Vibrational Circular Dichroism

The ***FVS-6000*** not only allows you to easily obtain fingerprint VCD spectra, but also has several unique features such as a measurement range extension option of 4000-750 cm^{-1}.

Since the CD signals in the infrared region are one or more orders of magnitude lower than ECD signals in the UV-Vis region, high sensitivity and stability are required for a VCD spectrometer.

The **FVS-6000** is the VCD spectrometer of choice for highly sensitive VCD measurements.

P-2000

Digital Polarimeter

The ***P-2000*** is designed as a customizable polarimeter with various options for a range of applications and budgetary requirements.

Options such as polarizers, wavelength filters, lamps and photomultiplier detectors provide a wide range of analytical wavelengths from UV-Vis to NIR.

A newly redesigned ***intelligent remote module (iRM)*** with a color LCD touch screen conveniently guides the operator through routines from data acquisition to data processing. The obtained data can be automatically printed to USB printers, or saved to a compact flash memory card for further processing on a PC.

FP-8200 – FP-8300 – FP-8500 – FP-8600

Spectrofluorometers

Designed with the latest technology, the ***FP-8000 Series*** spectrofluorometers incorporate the highest sensitivity, fastest spectral scanning capability and excellent analysis-oriented functionality offering integrated solutions for advanced materials research and biochemical analysis applications.

To meet the most stringent analysis demands, a variety of accessories are available for integration with a range of sophisticated control and analysis applications available in the user-friendly ***Spectra Manager™ II*** software to offer a flexible platform for any fluorescence and phosphorescence application.

RMP-510 – RMP-520 – RMP-530

Portable RAMAN Spectrometers

JASCO's new ***RMP-500*** Series has been developed to meet the needs of Material Science, Manufacturing and Biochemistry by combining the flexibility of a fiber optic probe with a portable Raman Microspectrometer.

The RMP-500 Series consists of three models, ***RMP-510, RMP-520, RMP-530*** ranging from small, portable units suitable for in-situ measurements to research-grade systems that will meet even the most difficult application requirements.

The **RMP-500** Series portable Raman spectrometer systems feature an integrated fiber optic probe with a small X-Y-Z stage, a compact laser, a high-throughput spectrograph and CCD detector.

VIR-100 – VIR-200 – VIR-300

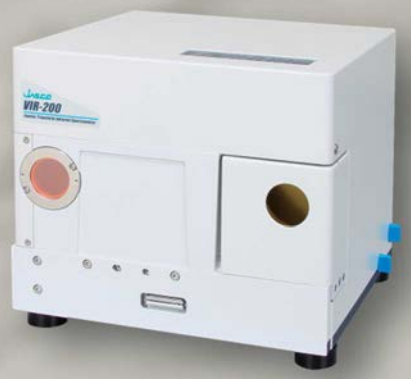
Portable FT-IR Spectrometers

The ***VIR-100/200/300*** series are compact, lightweight, flexible FT-IR systems.

The collimated entrance and exit ports make it an ideal instrument for a wide range of applications.

The standard instrument includes a hermetically sealed interferometer, DLATGS detector, high intensity source, KRS-5 windows and automatic alignment. Options can be added for increased sensitivity, optional spectral ranges including NIR, and battery operation.

For even greater flexibility, external connection optics allows the user to install up to three different attachments in one system, selecting the most appropriate application accessory by simply switching the PC controlled optical configuration.



JASCO is the first manufacturer to develop a powerful, cross-platform software package, "***Spectra Manager***", for controlling a wide range of spectroscopic instrumentation. Spectra Manager program is a comprehensive package for capturing and processing data, eliminating the need to learn multiple software packages and offering the user a shallower learning curve.

Several types of measurement data files (UV-Vis/NIR, FT-IR, Fluorescence, etc.) can be viewed in a single window, and processed using a full range of data manipulation functions.

The latest version, Spectra Manager II, includes four measurement programs, a spectra analysis program, an instrument validation program and the JASCO Canvas program as standard. It is possible to analyze data even during sample measurements.

Spectra Manager CFR provides features to support laboratories in compliance with 21 CFR Part 11.

LC-4000

High Performance Liquid Chromatography

The ***LC-4000*** Series is the latest in a long history of innovative HPLC systems developed by JASCO reaching all the way back to the start of commercial HPLC in the early 1970s.

The concept of the integrated ***LC-4000*** series HPLC provides key separation platforms at 50MPa, 70MPa and 130MPa which correspond to ***conventional HPLC***, the increasingly popular Rapid Analysis ***Fast HPLC*** and sub 2um ***U-HPLC*** respectively.

Each platform is supplied with a dedicated pump and autosampler matched to the operating pressure and share detectors optimized for high-speed 100Hz acquisition and the narrow peak shapes common to both Fast HPLC and U-HPLC.

In the LC-4000 series, SSQD technology (Slow Suction, Quick Delivery) has been re-developed, with a completely new solvent delivery mechanism offering the highest stability in solvent delivery across the entire analytical flow rate range used in the **PU-4100** Fast HPLC and **PU-4200** U-HPLC pump models.

JASCO has the largest range of optical detectors - from **dual wavelenght UV** to **diode array** to unique **chiral detectors**. All the detector are designed to meet U-HPLC requirements, data acquisition rate of 100Hz.

SFC-4000

Supercritical Fluid Chromatography

The JASCO ***SFC/SFE 4000*** integrated Analytical SFC system has been developed for all aspects of analytical SFC; including routine separation, method development and small scale preparation of samples at the mg scale.

With a simple intuitive software and robust engineering, the JASCO SFC system is a powerful tool for analytical separations.

Both HPLC and SFC/SFE systems are coupled with ***ChromNAV 2.0*** data system to offer both HPLC and spectral data handling for most of the detectors even with the dual wavelength UV detector.

A newly added feature of ***ChromNAV 2.0*** is the automatic e-mail notification on your smartphone/tablet, stay always updated on analysis status of your LC-4000. Full GLP compliance and 21 CFR part 11.

Application	Description	Page	Solutions
230GA0193-E	Introduction of the Program for Gas Analysis and the Gas cell		*Environmental*
230-QU-0175	Simultaneous Monitoring Analysis of Multicomponent Gas in the Atmosphere using CLS Automatic Quantitation		*Environmental*
230TR0165-E	Analysis Example by Vacuum Model FT/IR (2) Analysis of Low Concentration Gas using Long Pathlength Cell		*Environmental*
230-TR-0199	Gas Analysis System using Full Vacuum Type FT/IR-6300 (Trace amount of H2O in N2 gas)		*Environmental*
230TR0187-E	Gas Analysis System using Full Vacuum Type FT/IR-6100 (Trace amount of H2O in N2 gas)		*Environmental*
260-TR-0214	Application of long pathlength gas cell for FT/IR		*Environmental*
050-AT-0218	Monitoring of oxidative degradation process for fat and oil using heating single reflection ATR accessory with FT/IR		*Food & Beverage*
080AT0158-E	Analysis of Egg using Thermal ATR		*Food & Beverage*
080-TR-212	Analysis of water content distribution in food by IRT-7000S		*Food & Beverage*
050-AT-0215	Quantitative Analysis of Trans-fats in Food products using an FT/IR-ATR Method		*Food & Beverage*
080AT0189-E	Evaluation of Alcoholic Content of Liquors using ATR Accessory		*Food & Beverage*
080AT0180-E	Two-Dimensional Infrared Correlation Analysis of Maillard Reaction (Non-Enzymatic Browning)		*Food & Beverage*
050-QU-0232	Rapid Quantitative Analysis of Trans-fatty acid of extremely low concentration by Using the Cell for Liquid		*Food & Beverage*
080-IR-205-E	Non-destructive NIR measurement of cherry fruit for evaluation of sugar concentration		*Food & Beverage*
JE-1-FT-16	The simple measurement method of liquid sample in near-IR region		*Food & Beverage*
260-DR-0163	Simple Methods to Measure Powder Samples using FT-IR Spectrometer		*Pharmaceutical*
210-TR-0127	Measurement of Protein in Heavy Water using FT-IR Spectrometer		*Pharmaceutical*
IR-01-03	Secondary Structure Analysis (SSE) Software for Infra Red Interpretation and Modeling of Proteins		*Pharmaceutical*
200DR0188-E	Rapid Identification of an Illegal Drug using NIR (Identification of MDMA Tablet)		*Pharmaceutical*
130-AT-0229	The measurement of filler (particles of facial cleanser) by using Clear-View ATR		*Pharmaceutical*
JI-Ap-FT0507-001	Pharmaceutical tablet characterization using NIR Imaging		*Pharmaceutical*
JI-Ap-FT0507-002	Applications for the IMV-4000 Multi-channel Infrared Microscope		*Pharmaceutical*
JI-Ap-FT0507-004	Secondary Structure Analysis of Proteins using IR Imaging		*Pharmaceutical*
200-MR-0213	NIR Imaging of tablet surface by using IR Microscope		*Pharmaceutical*

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050-QU-0220	Quantitative Analysis of Biodiesel (FAME) in Diesel Fuel by FT/IR		*Petro & Chemicals*
100-AT-0227	Measurement of Oriented Films and Liquid Crystal Molecules by a Polarized ATR Accessory		*Petro & Chemicals*
220-AT-0123	Microscopic ATR Measurement of Thin Polyimide Film on Silicon Substrates		*Petro & Chemicals*
220-AT-0222	Evaluation of a Si Wafer Surface using a 65-degree Incident Angle ATR		*Petro & Chemicals*
220-SO-0211	Multiple components analysis by PCA mapping		*Petro & Chemicals*
220TR0164-E	Analysis Example by Vacuum Model FT/IR (1) Measurement of Silicon Wafer		*Petro & Chemicals*
230TR0165-E	Analysis Example by Vacuum Model FT/IR (2) Analysis of Low Concentration Gas using Long Pathlength Cell		*Petro & Chemicals*
230-QU-0181	Industrial Gas Analysis System - PFC Gas Analysis -		*Petro & Chemicals*
240DR0167-E	Analysis of Catalyst Reactions using Vacuum Thermal Diffuse Reflection Accessory		*Petro & Chemicals*
250-MT-0210	Mapping measurement using IQ Mapping function of IRT-5000		*Petro & Chemicals*
260-MT-0209	Foreign material analysis using both Mixture Analysis function and new library		*Petro & Chemicals*
JINC-TGA-01-01	Thermal Gravimetric-Infrared (TGA-IR) Analysis of Ammonium Acetate		*Petro & Chemicals*
JI-Ap-FT0507-003	Sample Preparation for Infrared Imaging Multilayer Film Measurement Using the SliceMaster		*Petro & Chemicals*
050TR0203-E	Iodine Value Measurement of Fat with FT-NIR System with Peltier Thermostatic Cell Holder		*Petro & Chemicals*
IR-1-04	Infrared Microscopy for the Analysis of Polymer Laminates in a Juice Bottle		*Petro & Chemicals*
IR-03-03	Analysis of Automotive Fluids using with FTIR		*Petro & Chemicals*
140-AT-0221	Terahertz (THz) Measurements of Liquids by a vacuum compatible ATR accessory		*Petro & Chemicals*
030TR0185-E	Simple Analysis of Brominated Flame Retardants with Far-Infrared Spectrometers (RoHS Directive)		*Petro & Chemicals*
030TR0186-E	Simple Method for Quantitative Analysis of Brominated Flame Retardants with Far-Infrared Spectrometers (RoHS Directive)		*Petro & Chemicals*
050-AT-0223	Monitoring of reaction process using the fiber probe		*Petro & Chemicals*
050-QU-0220	Quantitative Analysis of Biodiesel (FAME) in Diesel Fuel by FT/IR		*Petro & Chemicals*
100-AT-0227	Measurement of Oriented Films and Liquid Crystal Molecules by a Polarized ATR Accessory		*Petro & Chemicals*
220-AT-0123	Microscopic ATR Measurement of Thin Polyimide Film on Silicon Substrates		*Petro & Chemicals*
220-AT-0222	Evaluation of a Si Wafer Surface using a 65-degree Incident Angle ATR		*Petro & Chemicals*
220-SO-0211	Multiple components analysis by PCA mapping		*Petro & Chemicals*
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240DR0167-E	Analysis of Catalyst Reactions using Vacuum Thermal Diffuse Reflection Accessory		*Petro & Chemicals*
250-MT-0210	Mapping measurement using IQ Mapping function of IRT-5000		*Petro & Chemicals*
260-MT-0209	Foreign material analysis using both Mixture Analysis function and new library		*Petro & Chemicals*
JINC-TGA-01-01	Thermal Gravimetric-Infrared (TGA-IR) Analysis of Ammonium Acetate		*Petro & Chemicals*
JI-Ap-FT0507-003	Sample Preparation for Infrared Imaging Multilayer Film Measurement Using the SliceMaster		*Petro & Chemicals*
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030TR0186-E	Simple Method for Quantitative Analysis of Brominated Flame Retardants with Far-Infrared Spectrometers (RoHS Directive)		*Petro & Chemicals*
050-AT-0223	Monitoring of reaction process using the fiber probe		*Petro & Chemicals*
080-AT-0235	Application by using of Auto contact ATR for VIR-100/200/300		*Petro & Chemicals*
080-AT-0236	ATR application to granular gum by Auto-contact ATR Accessory for VIR-100/200/300		*Petro & Chemicals*
100-AT-0230	Identification and quantitative determination of plasticizer in A1 size PVC sheet by using of a single bounce ATR for large-sized sample		*Petro & Chemicals*
100-SO-0238	Efficacy of Imaging Data Analysis using “Model Analysis”		*Petro & Chemicals*
190-RF-0217	Measurement of the functional glass by FTIR based on [Testing method on transmittance, reflectance, emissivity and solar heat gain coefficient of flat glasses (JIS R 3106)]		*Petro & Chemicals*
260-AT-0237	Measurement of broadband spectrum using automatic wide-range measurement system		*Petro & Chemicals*
260-MT-0239	Introduction of new DLATGS detector for IRT-5000/7000 infrared microscope		*Petro & Chemicals*
260-PR-0231	Measurement of thin film by Polarization-Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS)		*Petro & Chemicals*

Application	Description	Page	Solutions
260-TR-0153	Variable-angle transmittance measurement attachment with polarizer option		*Petro & Chemicals*
260-TR-0216	Acquisition of molecular orientation information using automated MAIRS measurement unit AM-4000		*Petro & Chemicals*
260-TR-0228	IR/NIR/FT-Raman Measurement using Broadband KBr Beam Splitter		*Petro & Chemicals*
280-SO-0008	Fluorescence Observation, Polarization Observation and Differential Interference		*Petro & Chemicals*
280-TC-0001	IR microscope combined with heating stage		*Petro & Chemicals*
JE-100-FT-16	3 different time course measurement methods of FTIR		*Petro & Chemicals*
JE-101-FT-16	Synchronous and Asynchronous data correlation of FTIR		*Petro & Chemicals*
170-NF-0206	NFIR (Near-Field Infrared spectrometry) analysis of distribution of minerals on cross-section of rock (Part 1)		*Petro & Chemicals*
170-NF-0208	Near Field IR Spectrometer and Microscopic IR Spectrometer		*Petro & Chemicals*
260NF0191-E	Measurement of submicron particle by NFIR (Near Field Infrared Spectroscopy)		*Petro & Chemicals*

Introduction of the Program for Gas Analysis and the Gas cell

Introduction

Recently, Fourier transform infrared spectrometers (FTIR) have been widely used in the field of gas analysis, instead of dedicated gas detector. Gas detector is capable of easy measurement, however, in case of the mixture of multiple gases, sometimes the measurement is very much influenced by other gases. Since the gas detector has to be changed depending on the gas components, it was difficult to analyze the components of multiple gases simultaneously.

FTIR allows the detection of the absorption peaks specific to the vibrational frequency corresponding to the compounds, and almost all gases have the absorption in the specific wavenumber range according to the binding energy. The simultaneous analyses of multicomponent can be done by the creation and registration of each calibration curve for each gas component in each specific wavenumber. And the simultaneous monitoring of multicomponent can be done by utilizing the program of time-course measurement.

By the combination of full vacuum model FTIR and the gas cells, the gas analyses with very low concentration is capable eliminating the influence of water vapor and carbon dioxide in the air. This software program for gas analyses and the gas cells will be explained in this Application Data.

The program overview for simultaneous quantitation of multicomponent

- Simultaneous quantitation up to 20 components
- Capability of interval measurement
- Calibration curve from spectrum quantitation program
- Flexible registration, selection and exchange of calibration curve
- Capability of monitoring by concentration display
- Capability of recalculation after the change of calibration curve

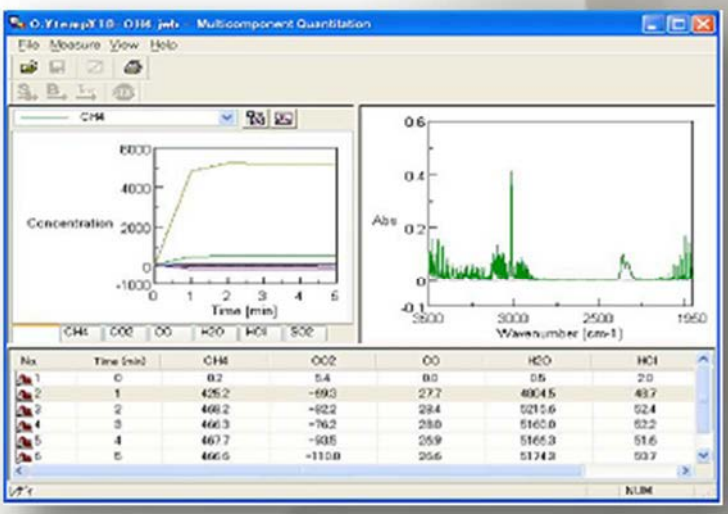


Figure 1 Example of multicomponent measurement using simultaneous quantitation program

Figure 1 shows display example of the result using simultaneous quantitation program for measurement of multicomponent. Time-course monitoring of each component is displayed simultaneously. Picture 1 show the gas cells.

Picture 1 FT/IR-6200 vacuum model and 10 m gas cell

Introduction of the Program for Gas Analysis and the Gas cell

Registration and selection of calibration curve
It is possible to register the calibration curves up to 20, which are created and saved using spectrum quantitation program.

For the desired quantitation analysis, the suitable calibration curve is selected from the registered calibration curves.

Figures 2 and 3 show the registration and selection screen.

Figure 4 shows the spectrum of methane gas and the example of the calibration curve using 8 m gas cell.
The detection limit depends on the type of gas, the state of mixed gas (including content of water vapor and similar gas), measurement conditions (including resolution and accumulation).

Possible quantitation range in terms of cell pathlength is shown as below.

10 cm cell: several% - 100 ppm
3 m cell: several hundreds - 1 ppm
8 m cell: several tens - 0.2 ppm
10 m cell: several tens - 0.2 ppm
20 m cell: several tens - 0.1 ppm

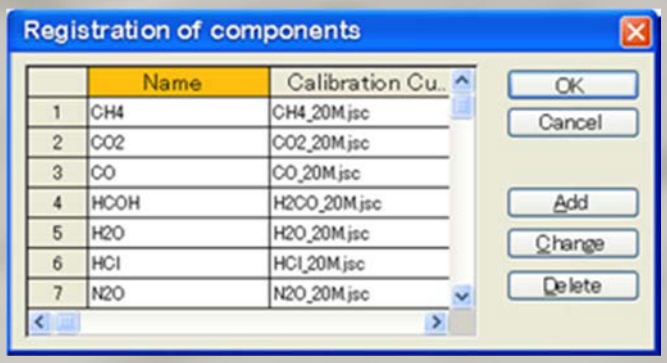


Figure 2 Screen for registration of gas components

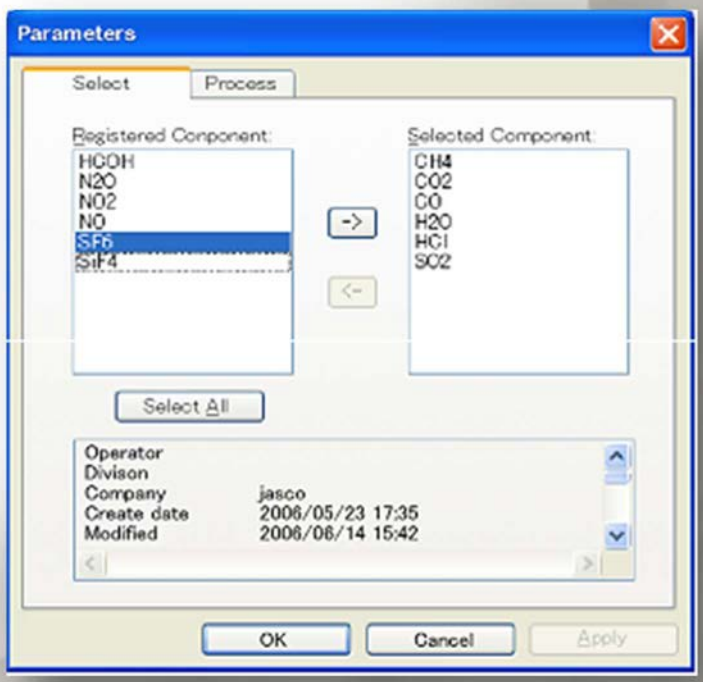


Figure 3 Screen for selection of gas components

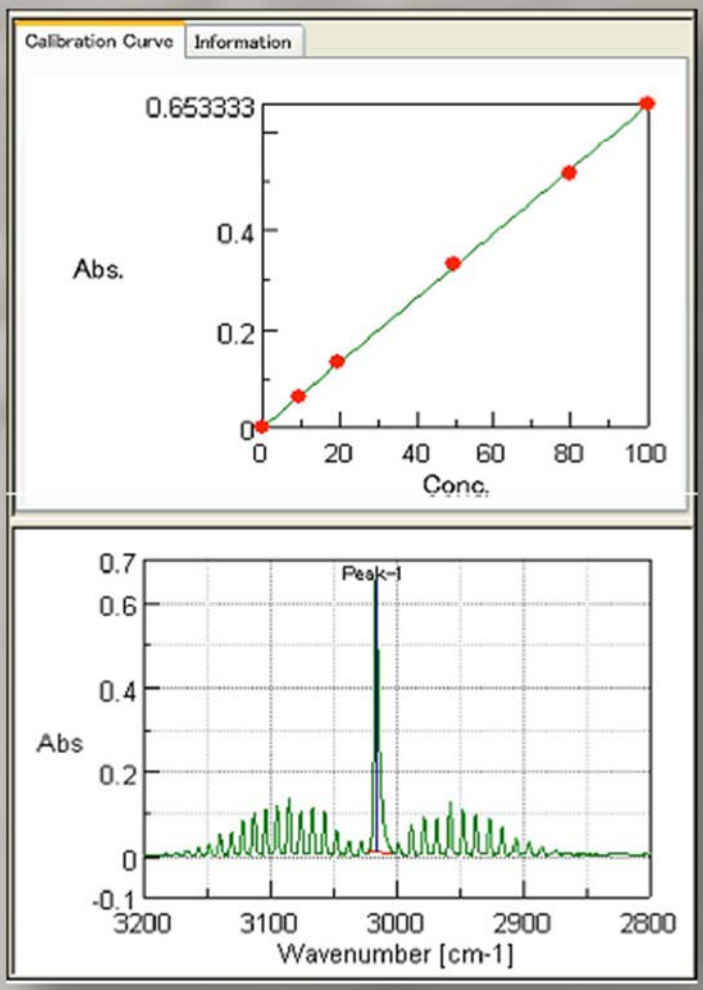


Figure 4 Calibration curve and spectrum

Simultaneous Monitoring Analysis of Multicomponent Gas in the Atmosphere using CLS Automatic Quantitation

Introduction

Quantitation method with one wavenumber is a quantitation using height and area of one peak.
CLS (Classical Least Square) quantitation is one of the multivariate analyses and calculates quantitatively using all spectral data in the varying area depending on concentration.
Therefore, it is an efficient quantitation method in case that it is difficult to find a single peak for quantitation because of overlaid spectra of multicomponent, and simultaneous quantitation of multicomponent is required.
One of the advantages of CLS quantitation is high accuracy by noise averaging from calculation using all spectral data in the specified spectral range. The analyses of pure compound (spectrum) obtained in least squares are easy, and this spectrum is similar to pure spectrum of multicomponent.
Since it is possible to analyze multicomponent simultaneously, utilization as simultaneous monitoring of multicomponent can be done by use of automatic quantitation program.

Measurement

The averaged concentrations of 5 components of gases (CH_4, N_2O, CO, CO_2 and H_2O) in the atmosphere were repetitively monitored using OPEN-PATH FTIR with optical path length 100 m.
Figure 1 shows the quantitative results obtained according to CLS calibration curves model prepared in advance, for specified periods (5 min) for each component, which are shown as time-course curves. The concentration change by time-course is shown.

Conditions

Accumulation: 200
Resolution: 1 cm-1
Apodization: Cosine
Optical path length: 100 m (OPEN-PATH FTIR)
Standard gas cell: 3 m (calibration model)

Figure 1 CLS automatic measurement monitor screen

Figure 2 shows measurement result of each standard gas with concentration 100 ppm by standard gas cell (3m cell). Absorption spectra of gases of CO, CO_2 and N_2O are overlapped.
Regarding detection limit, since the concentration 100 ppm of N_2O gas corresponds to absorbance 0.400, indicating that concentration 1 ppm, to 0.004 ABS, quantitation with concentration less than 1 ppm is considered to be possible.

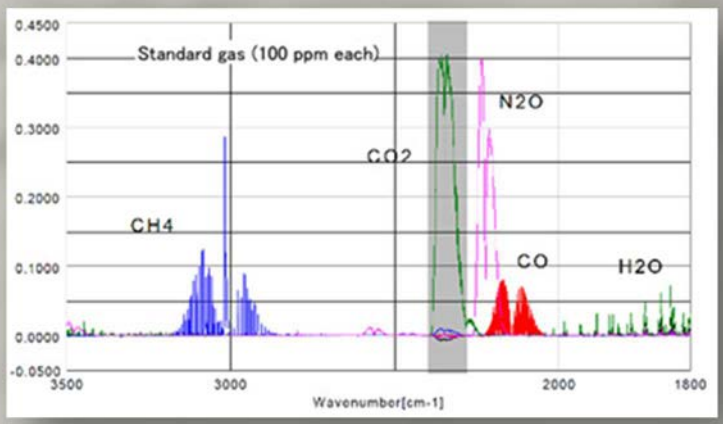


Figure 2 Standard gas (utilizing 3 meters cell)

Simultaneous Monitoring Analysis of Multicomponent Gas in the Atmosphere using CLS Automatic Quantitation

Figure 3 and 4 show the calibration models (CH4 and CO gas) measured by standard gas cell (3 m cell). The curves indicates good linearity in the range of 1-120 ppm. The correlation coefficient is more than 0.98.

The calibration models of CO2, N2O and H2O gas have been also created even if Figure is not shown. The optical path difference is corrected automatically in the measurement utilizing [OPEN-PATH FT-IR].

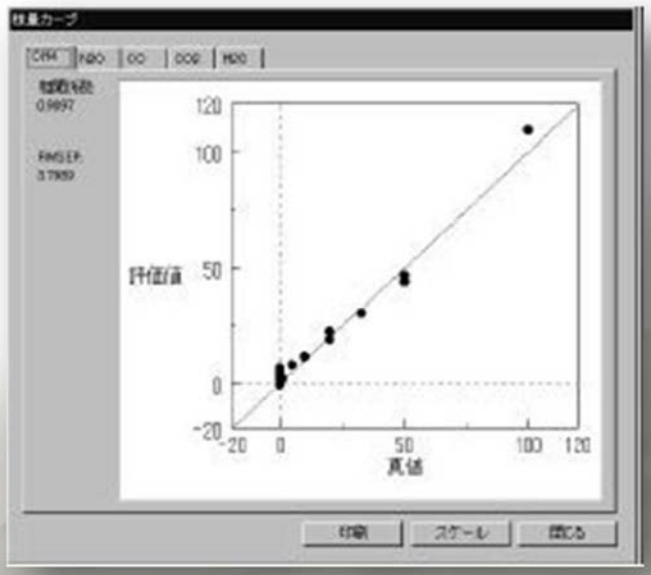


Figure 3 Calibration model: CH4

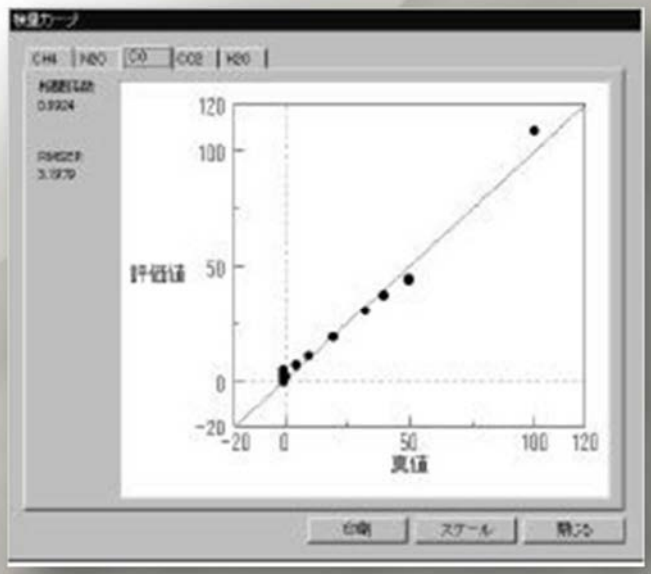


Figure 4 Calibration model: CO

JASCO FT/IR - 6800

Analysis Example by Vacuum Model FT/IR (2)
Analysis of Low Concentration Gas using Long Pathlength Cell

An high S/N measurement is often required for the FT-IR analysis of low concentrations of gas or vapor compounds. In addition, the measurement of certain gas samples can be affected by the atmospheric water vapor and carbon dioxide present in the instrument, even with nitrogen purging. It is especially difficult to analyze NO gas because the absorption band is in the water vapor region, and NO2, CO2 and CO gas, whose absorption bands are near the CO2 absorption.

Using a full-vacuum instrument system, the water vapor and carbon dioxide in the light path can be completely eliminated and the measurement of these gas components can be accomplished even with low concentrations.

Figure 1 illustrates the spectrum of a 2 ppm CO sample by using a 20 m gas cell, demonstrating that the 2 ppm CO gas is measured with a S/N level around 200:1. The noise level with the same measurement conditions is 4 x 10^{-5} ABS as displayed in Figure 2, and with this noise level, the measurement of this gas can be easily accomplished with concentrations as low as 20-50 ppb.

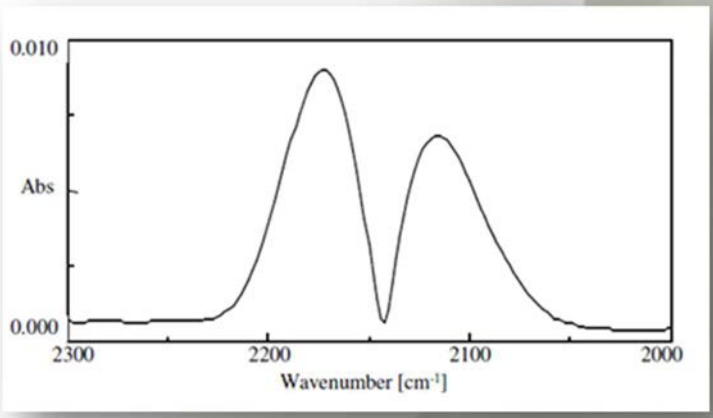


Figure 1 - 2 ppm CO gas

Condition
Resolution: 4 cm^{-1}
Scans: 500
Detector: MCT
Cell: 20 m pathlength gas cell

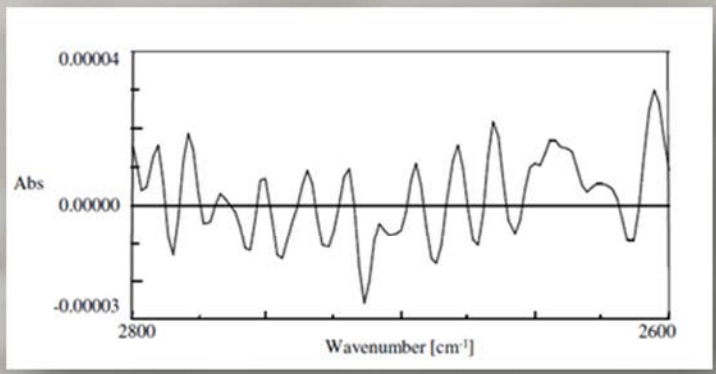


Figure 2 Spectrum S/N using the MCT detector

JASCO FT/IR - 6700FV - Full Vacuum

Gas Analysis System using Full Vacuum Type FT/IR-6300 (Trace amount of H2O in N2 gas)

Introduction

The analysis of low concentration gases using long pathlength gas cells has been reported previously, however, it can be difficult to accurately quantitate gases at low concentrations when the absorption peaks of the target gas overlap with the peaks of atmospheric water vapor or, when the target gas itself is H2O or CO2, which are present in the atmosphere. This is because even with a vacuum FT-IR instrument, it was not possible to evacuate the sample chamber with the long pathlength cell present. The full vacuum gas analysis system introduced in this application note has a special gas cell integrated into the sample chamber, allowing the entire light path to remain under full vacuum with the gas cell in place. This full vacuum model makes it possible to quantitate concentrations of H2O even at the 0.2 ppm level.

Instrument and Measurement

For the measurement, there are separate vacuum lines for evacuation of the FT-IR instrument and the gas cell, with independent evacuation capability for the separate components. Adding a vacuum gauge to the gas cell makes it possible to control extremely low concentrations of the gas samples.

Cell specification

Cell type	:Multi-pass 'White' cell
Pathlength	:10 meters
Cell body	:Stainless steel
Cell inner surface	:Electrochemically polished
Mirror material	:Stainless steel
Mirror surface	:Gold coated
O-ring	:Viton
Window	:CaF2
Heating	:Possible, max. 100°C
Cell capacity	:Approx. 2 L
Gas in/output port	:1/4 inch VCR

Condition

Instrument	: FT/IR-6300
Accumulations	: 100
Resolution	: 2 cm-1
Zero filling	: ON
Apodization	: Cosine
Gain	: Auto (1)
Aperture	: 1.8 mm
Scan speed	: Auto (4 mm/sec.)
Light source	: Standard
Detector	: MCT

Figure 1 Full vacuum type FT-IR gas analysis system (10 meters cell)

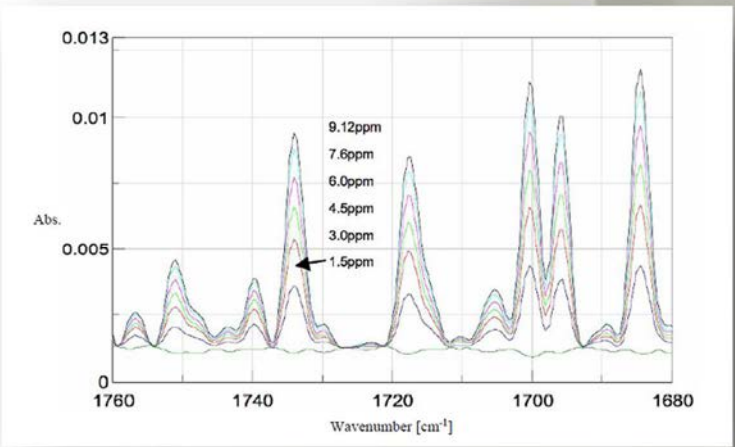


Figure 2 Expanded region for spectra of low concentration H2O

Measurement example

The quantitation of a trace amount of water vapor (H2O) within CO2 in gas cylinder was attempted. Water vapor with a concentration of 15.0 ppm was diluted by monitoring the pressure gauge during dilution of the standard samples with concentrations of 1.5, 3.0, 4.5, 6.0, 7.6 and 9.12 ppm.

Figure 2 shows the IR spectra of water vapor for each concentration. The lowest detection limit calculated from Signal to Noise ratio was around 0.2 - 0.3 ppm.

The calibration curve in Figure 3 was created using the absorption peak at 1734 cm-1. As seen, the precise quantitation of low concentration can be done in this system.

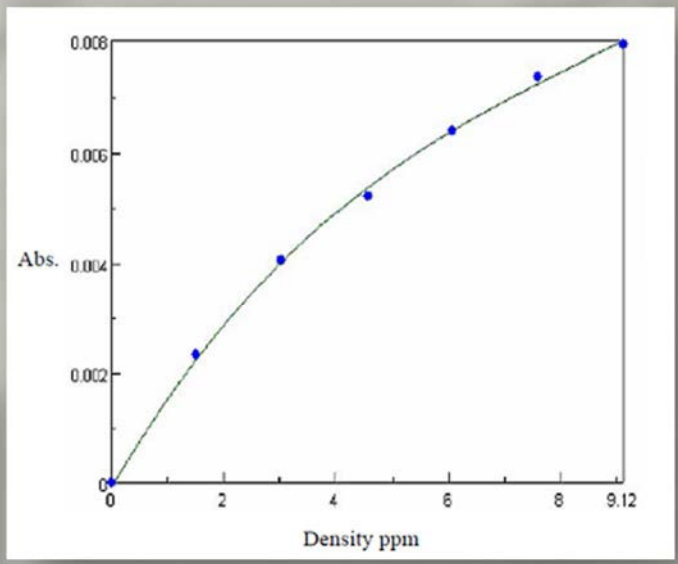


Figure 3 H2O calibration curve

Gas Analysis System using Full Vacuum Type FT/IR-6100 (Trace amount of H2O in N2 gas)

Introduction

The analysis of low concentration gases using long pathlength gas cells has been reported previously, however, it can be difficult to accurately quantitate gases at low concentrations when the absorption peaks of the target gas overlap with the peaks of atmospheric water vapor or, when the target gas itself is H2O or CO2, which are present in the atmosphere. This is because even with a vacuum FT-IR instrument, it was not possible to evacuate the sample chamber with the long pathlength cell present. The full vacuum gas analysis system introduced in this application note has a special gas cell integrated into the sample chamber, allowing the entire light path to remain under full vacuum with the gas cell in place. This full vacuum model makes it possible to quantitate concentrations of H2O even at the 0.1 ppm level.

Instrument and Measurement

For the measurement, there are separate vacuum lines for evacuation of the FT-IR instrument and the gas cell, with independent evacuation capability for the separate components. Adding a vacuum gauge on the gas cell makes it possible to control extremely low concentrations of the gas samples.

Cell specification

Cell type	:Multi-pass 'White' cell
Pathlength	:10 meters
Cell body	:Stainless steel
Mirror material	:Stainless steel
Mirror surface	:Gold coated
O-ring	:Viton
Window	:CaF2
Heating	:Possible, max. 100°C
Cell capacity	:Approx. 2 L
Gas in/output port	:1/4 inch VCR

Condition

Instrument	: FT/IR-6100
Accumulations	: 200
Resolution	: 2 cm-1
Apodization	: Cosine
Gain	: Auto (1)
Aperture	: 1.8 mm
Scan speed	: Auto (4 mm/sec.)
Light source	: Standard
Detector	: MCT

Figure 1 Full vacuum type FT-IR gas analysis system (10 meters cell)

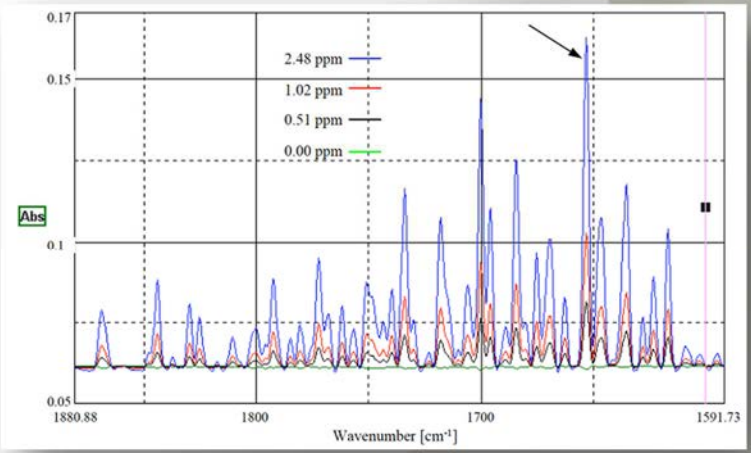


Figure 2 Expanded region for spectra of low concentration H2O

Measurement example

The quantitation of a trace amount of water vapor (H2O) within nitrogen gas was attempted. Water vapor with a concentration of 100 ppm was diluted by monitoring the pressure gauge during dilution of the standard samples with concentrations of 0.0, 0.51, 1.02 and 2.48 ppm. Figure 2 shows the IR spectra of water vapor for each concentration. For the 0 ppm concentration, there was no absorption due to water vapor observed in the spectrum. The calibration curve in Figure 3 was created using the absorption peak at 1653 cm-1.

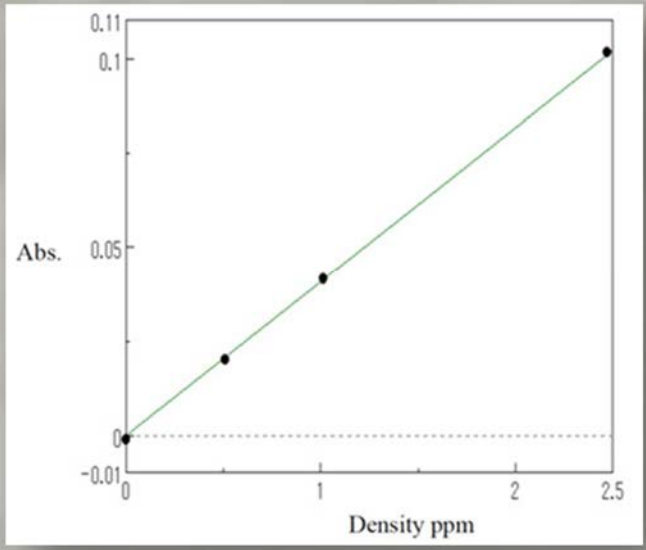


Figure 3 H2O calibration curve

Application of long pathlength gas cell for FT/IR

Introduction

FTIR, non-dispersive infrared analyzer, Gas detector tube system and GC/MS are well known as methods for analyzing gas samples. In addition Gas Analysis using Quantum Cascade Laser is getting popular recently as a new analytical technique. Each of those methods has either merit or demerit actually, however, an analytical method based on FTIR has a remarkable merit such as quick analysis of multiple gas components without any pre-treatment. As examples of FTIR analysis, there are actual applications as 'Monitoring Green House Effect gas', 'Quantitative/Qualitative gas analysis at the fire site' and 'Quantitative analysis of moisture content inside of gas cylinder'. In case of practical measurement of low concentration gas by using FTIR, a long pathlength gas cell needs to be mounted inside of sample compartment of FTIR for measurement. By using a conventional gas cell, measurement throughput was in many cases very low and it was necessary to use MCT detector which needs liquid N2. However, a newly developed JASCO's 12M long pathlength cell with optimized optics allows higher measurement throughput and enables to measure gases with lower concentration than ppm level using TGS detector*1). There are 3 different types of gas cell such as glass type cell, stainless type cell and full vacuum type cell depending on each purpose. Detailed features of each cell are described as below.

Features of cells

LPC-12M-G Glass type cell

- Body material is made of glass for reasonable price.

LPC-12M-S Stainless type cell

- Pressurization up to +0.1 MPa
- Heating up to 70ºC as option
- Heating cell up to 200ºC as option

LPC-12M-FV Full vacuum type cell

- For full vacuum system of FT/IR-6000 series
- High sensitive and precise measurement of water vapor, carbon dioxide gas because of full vacuum condition

*1) Lowest measurement limit depends on each gas component.

Figure 1
Full vacuum FT/IR-6300FV with LPC-12M-FV gas cell

Experimental

Glass type cell : LPC-12M-G

Figure 2 shows measured spectra of CO, SO2, NO2, N2O, CH4. In gas analysis application using FTIR, it is possible to execute simultaneous quantitative analysis of multiple gas samples which have each peak in different wavenumber.

Glass type cell

Stainless type cell

Full vacuum type cell

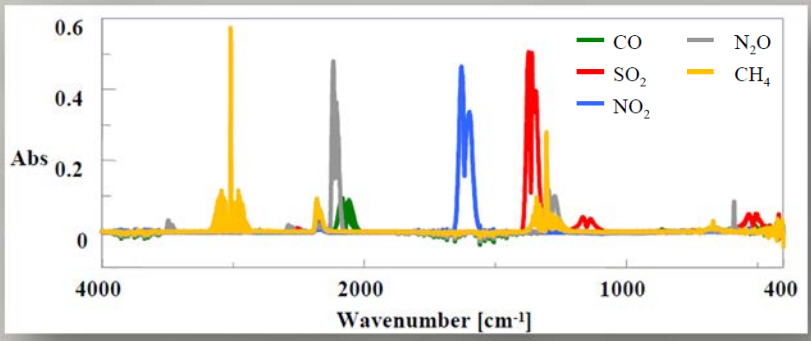


Figure 2 Measured spectra of CO, SO2, NO2, N2O, CH4.

Application of long pathlength gas cell for FT/IR

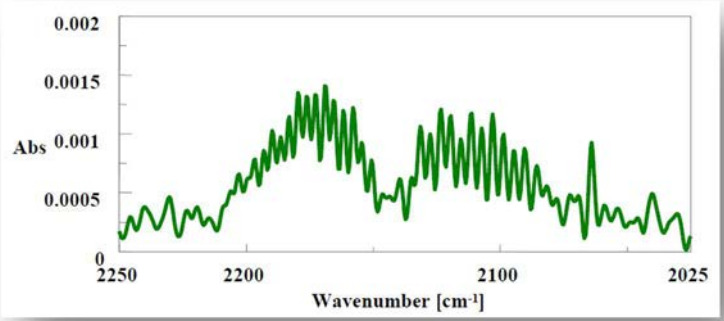


Figure 3 IR spectrum of CO gas (530ppb)

Measurement condition
Resolution : 2 cm-1
Accumulation : 200
Detector : DLATGS
Apodization : cosine

Stainless type cell : LPC-12M-S
Figure 4 shows IR spectrum of CO gas under both atmospheric pressure condition and pressurized condition. Peak intensity in case of pressurized measurement is 2 times larger in proportion to the pressure, which makes it possible to measure low concentration gas in ppm level.

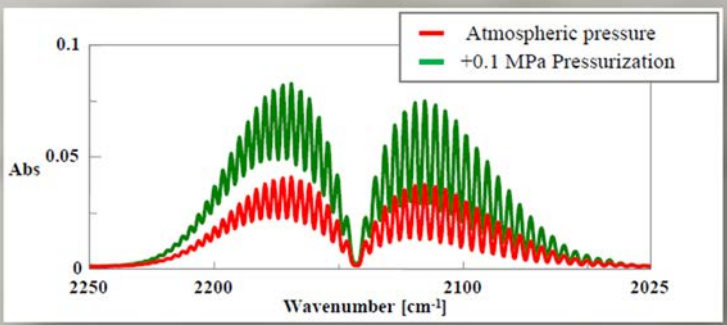


Figure 4 IR spectrum of CO gas

Measurement condition
Resolution : 2 cm-1
Accumulation : 50
Detector : DLATGS
Apodization : cosine

Full vacuum type cell : LPC-12M-FV
It is confirmed that how much water vapor affects the peak intensity through repeated measurement of standard 15 ppm water vapor and its result is shown in Figure 5. Actual measurement procedure in this experiment was to inject standard water vapor gas into gas cell, to measure and to exhaust repeatedly. As a result, peak intensity in 1653 cm-1 obtained was as precise as 0.0316 (Abs) +/- 0.63%, which shows that water vapor in atmosphere didn't affect the measurement and analysis.

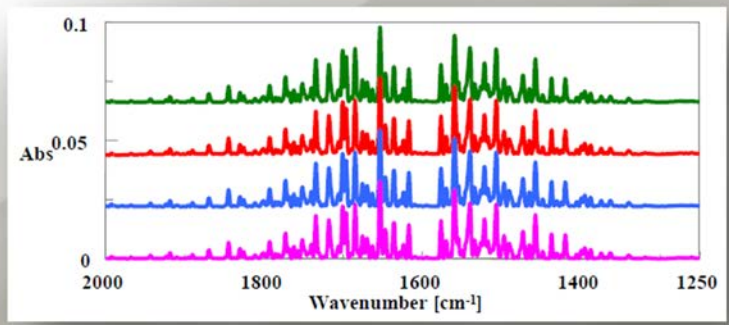


Figure 5 IR spectrum of water vapor

Measurement condition
Resolution : 2 cm-1
Accumulation : 50
Detector : MCT-M
Apodization : cosine
Option*2) : Bandpass filter

*2) Option system with bandpass filter and MCT detector enables high sensitivity measurement, but it is necessary to select the proper bandpass filter depending on the target gas.

Monitoring of oxidative degradation process for fat and oil using heating single reflection ATR accessory with FT/IR

Introduction

Measuring IR spectra under temperature control is an effective method to study denaturation of DNA and protein, and enzymatic kinetic reaction. Oxidative degradation monitoring by IR measurement of unsaturated fatty acid contained in fat and oil is one of the remarkable examples of this application.

There are two different types of unsaturated fatty acid such as Cis-type and Trans-type, and Cistype fatty acid is contained mainly in natural oil and Trans-type, in hydrogenated oil in food. It is well known that Cis-type reacts to form peroxide lipids through oxidative degradation by Radical and isomerizes to Trans-type as shown in Fig. 1. In this report, the commercial vegetable oil sample heated up to 180 °C was measured by using heating single ATR accessory with FTIR and oxidative degradation process was analyzed.

Measurement Method

There are two different types of unsaturated fatty acid such as Cis-type and Trans-type, and Cistype fatty acid has specific absorption peak at 3010 cm-1 and Trans-type, at 966 cm-1 .

It is possible to evaluate oxidative degradation process of unsaturated fatty acid in oil by monitoring IR peaks at 3010 cm-1 and 966 cm-1 , since Cis - Trans transformation will be resulted in the degradation process. Under similar to the actual cooking environment, the sample was heated up to 180 degree C and two absorbance peaks attributed to Cis and Trans fatty acid were measured by interval measurement program, and oxidative degradation process was evaluated by the changes of two peak intensities with time. The same measurement was also implemented under the environment purged by N2 gas.

Measurement condition

Main unit: FT/IR-6100 with Heating Single reflectance ATR
Detector: DLATGS Resolution: 4 cm-1
Accumulation: 64 times Temperature: 180 °C
Apodization function: Cosine
Measurement method: ATR (Crystal: Diamond*)
Sample compartment condition: Air environmental condition or N2 purged condition

*The high temperature type prism was used in this measurement

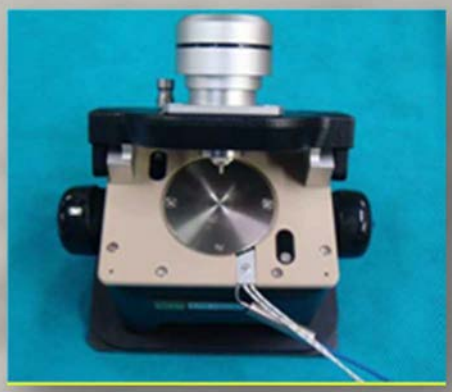


Figure 2
ATR Heating Single Reflection ATR accessory

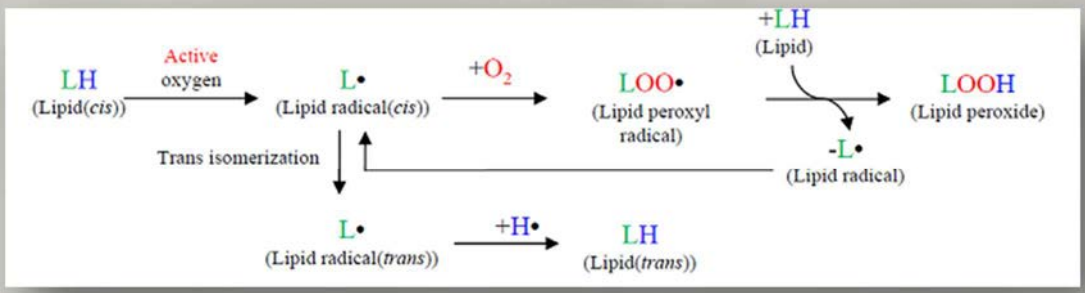


Figure 1 Reaction mechanism of oxidation degradation of the Lipid

Monitoring of oxidative degradation process for fat and oil using heating single reflection ATR accessory with FT/IR

Result and Discussion

Figure 3 shows spectral data of time interval measurement for the oil sample heated up to 180 degree C under air environmental condition. It is seen that peak at 3010 cm-1 attributed to Cis-type is getting smaller with time. On the other hand, peak at 966 cm-1 attributed to Trans-type is getting larger with time. In Figure 4 the spectral data of the same interval measurement but under N2 purged condition are shown, clearly indicating that there is no change of peaks with time. It can be said that Cis-Trans transformation did not occours, proving that oxidative degradation of oil did not happen.

Figure 5 and Figure 6 illustrates that the changes of peak area with time at 3010 cm-1 and at 966 cm-1 are plotted respectively by using the interval analysis program. It is evident that the peak area for Cis-type at 3010 cm-1 is getting smaller with time gradually under air environment, but the peak area for Trans-type at 966 cm-1 is getting larger with time for the initial 30 minutes and then saturated gradually. By comparing the change of peak area for Cis-type and that for Trans-type with time under air environment shown in Figure 5 and Figure 6, it is assumed that after 30 minutes, the reaction to generate lipid peroxide becomes more dominant than the Cis-Transformation as in the reaction process shown in Figure 1. As seen above, it is proved that the FTIR measurement method using a heating single reflection ATR is very effective to monitor and evaluate the reaction process accompanied by thermal changes. It is expected that this method will be expanded to be applied for evaluation of thermodynamic reaction and for measurement under the condition of Radical capture agent added.

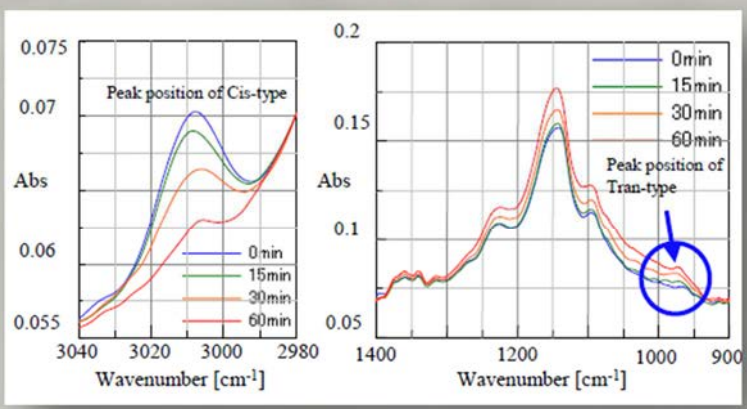


Figure 3 Spectra under air environmental condition

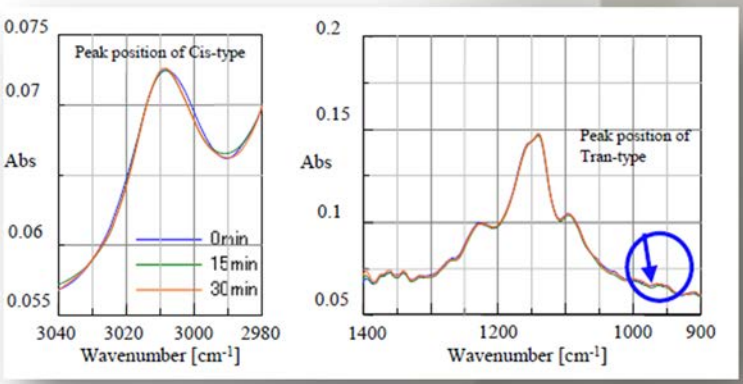


Figure 4 Spectra under N2 purged condition

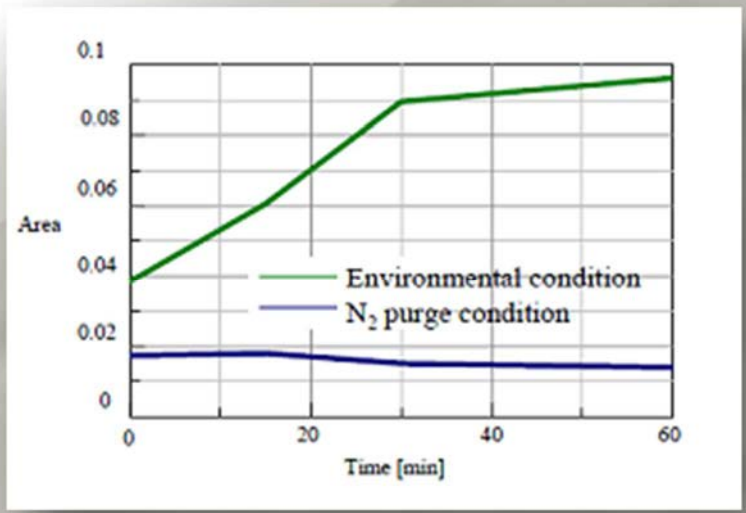


Figure 5 Change of peak area for Cis at 3010 cm-1

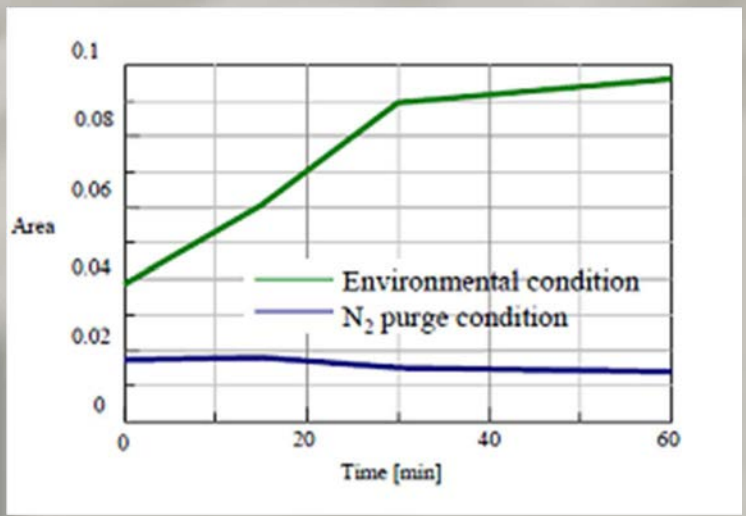


Figure 6 Change of peak area for Trans at 966 cm-1

Analysis of Egg using Thermal ATR

Introduction

Thermal ATR is a real time procedure for analyzing the vibrational structure of molecules using temperatures that range from room temperature to approximately 80°C. Procedures such as Differential Scanning Calorimetery (DSC) are commonly used to analyze solid samples ; however, thermal ATR is more effective than DSC for analyzing liquid samples. Furthermore, although thermal analysis of water content is used in the field of food analysis, monitoring the vibrational structure of samples directly is usually not possible with methods other than ATR. The following is an example of thermal ATR analysis performed on egg, for which water content is approximately 75%.

Albumen (egg white) consists of approximately 88% water and 10% protein, 55% of which is ovalbumin. In contrast, egg yolk consists of 50% water, 30% lipids, and 15% protein. The protein of the yolk consists of 36% high-density lipoprotein, 30% livetin, and 22% low-density lipoprotein. These compositional differences are responsible for the different sol idification characteristics of egg yolk and egg white-yolk begins to solidify at a lower temperature than albumen. Figure 1 shows IR spectra of albumen. The absorption band around 1540 cm-1, assigned to amide II, is decreased by heating. This suggests that denaturation of protein has occurred. Figure 2 shows IR spectra of the yolk, and figure 3 shows the IR spectra of yolk at 30 and 80°C. The carbonyl group (C=O) at the 1740 cm-1. Absorption band reflects the presence of fats and oils. Reduction of the 1540 cm-1 peak assigned to amide II is not apparent.

Instrument: Micro FT/IR + Thermal ATR system
Measurement range: 30 to 80°C
Temperature gradient: 2.5°C/min
Measurement time: 20 min
Measurement interval: 1 min
Accumulations: 50 times
Sample: Albumen, egg yolk

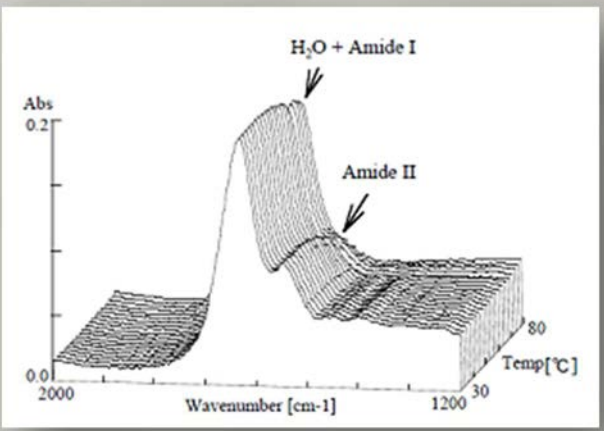


Figure 1 Almond seeds (100 kg/cm2)

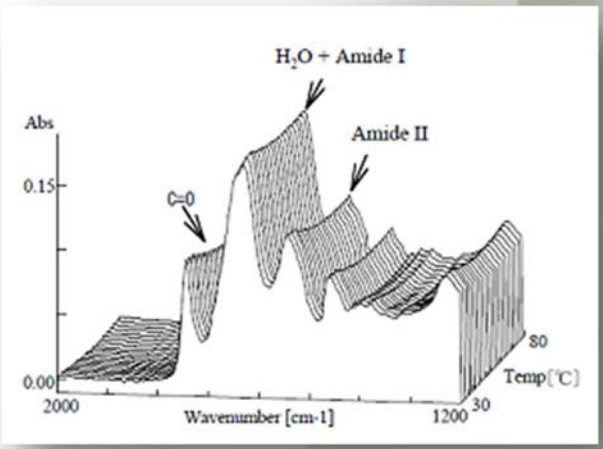


Figure 2 Walnuts (100 kg/cm2)

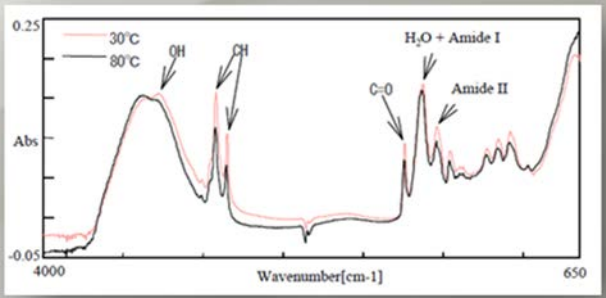


Figure 3 Spectra of egg yolk at 30°C and 80°C by thermal ATR

Figure 4 shows the temperature and absorbance of albumen and yolk at the 1538 cm-1 band (amide II). Absorption is known to decrease at 1538 cm-1 when the denaturation of protein occurs. Figure 4 indicates that for albumen absorption begins to decrease around 50°C and reaches minimum absorbtion just below 70°C. Moreover, for uplk, absorption begins to decrease slowly round 37 °C. Therefore, denaturation of yolk protein begins at approximately 37° C and continues slowly, whereas denaturation albumen protein begins at approximately 60-70°C and proceeds quickly. This explains why eggs cooked slowly at low temperature have a solidified yolk, while eggs cooked quickly at high temperature have a solidified albumen.

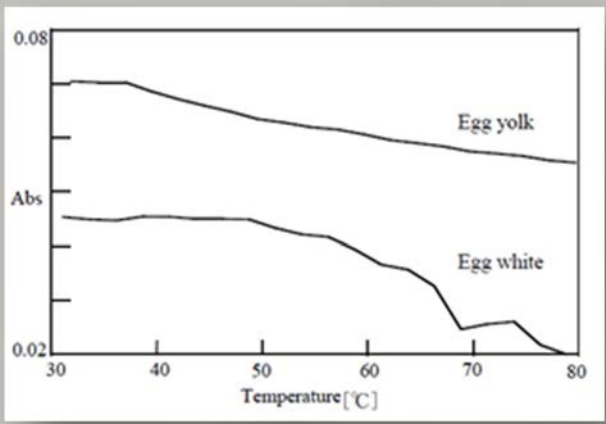


Figure 4 Absorbance with tiem: Albumen and yolk at 30 and 80°C by thermal ATR

Analysis of water content distribution in food by IRT-7000S

Introduction

Even though the detector of IRT-7000S is single-element detector, it enables high speed imaging measurement with 1/10 measurement time due to high speed mapping system as compared with the conventional IR microscope.

Table 1 shows the time required for measurement of 200 x 200 um area by multi-channel detector (16 x 1 linear array detector) and single-element detector (IRT-7000), and Figure 1 shows the image of measurement protocol by each detector. Generally multi-channel detector is used for high speed imaging measurement, and its measurement area size is determined by the magnification of Cassegrain mirror. On the other hand, the measurement area size by single-element detector is determined by the aperture size.

Accordingly, single-element detector is considered to have an advantage because the aperture size is changeable, so that for large area measurement with large aperture size, the measurement time may be shorter than multi-channel detector. Therefore, for the measurement of 200 x 200 um area, the measurement time by single-element detector with 50 x 50 µm aperture size can be shorter than linear array detector with x 32 Cassegrain, even the measurement points are reduced.

One of the significances to measure large area in high speed is the requirement for unstable sample such as food or tissue which may denature in a short time. In this experiment, we would like to show visually the difference of water content distribution in 2 types of noodles cooked by professional and amateur. By using IRT-7000S*1, high speed imaging measurement was done for the samples in a few millimeter block before drying.

Detector	Linear Array (16 x 1)	Single-element (IRT-7000S)	Single-element (IRT-7000S)
Aperture Size	6.25 x 6.25 um	25 x 25 um	50 x 50 um
Measurement Points	32 x 32	8 x 8	4 x 4
Measurement Time *3	Approx. 7 sec	Approx. 7 sec	Approx. 2 sec

Table 1 Comparison of detectors and aperture size in 200 x 200 um area measurement *2

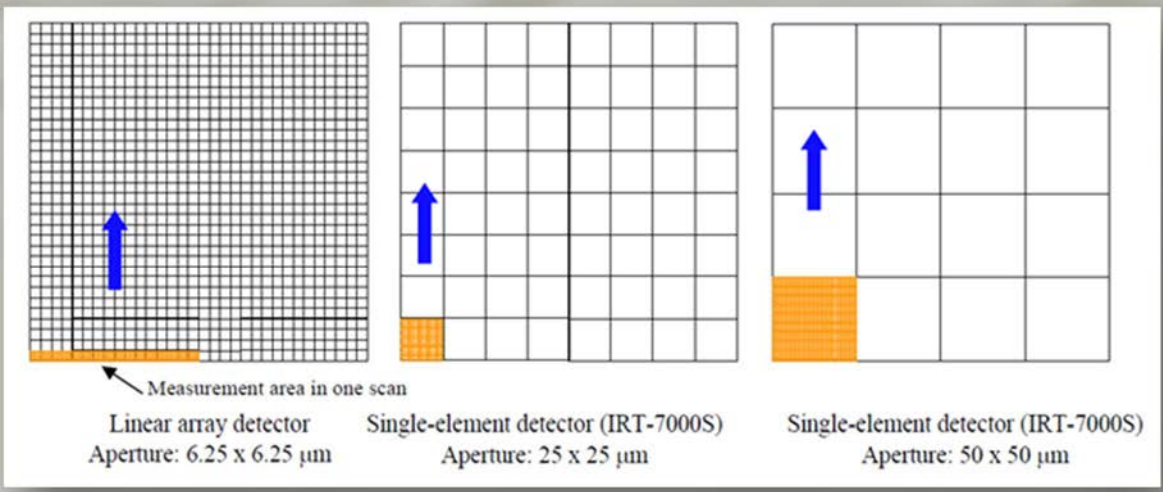


Figure 1 Comparison of measurement area in 200 x 200 µm area

*1: IRT -7000S can be upgraded to IRT-7000
*2 Measurement condition: x 32 Cassegrain, resolution: 16 cm-1, accumulation: 1
*3 Measurement time depends on measurement points

Analysis of water content distribution in food by IRT-7000S

In order to compare water content in noodle cross-section, the sample was prepared quickly and measured with high speed. The noodles cooked by professional and amateur were cut in a few millimeters thickness and sandwiched by CaFs windows in order to avoid drying (Figure 2).

Measurement condition

Instrument: IRT-7000S
Measurement points: 38 x 54 points (2052 points) (professional)
Measurement method: transmittance
Measurement size: 3.7 mm x 5.3 mm (professional), 4.3 mm x 4.6 mm (amateur)
Aperture: 100 x 100 um
Detector: MCT
Measurement time: approx. 5 minutes (professional)
Resolution: 16 cm-1

Results

The water content distribution in both noodle cooked by professional and amateur was compared by calculating the peak area ratio of starch (3872 – 4165 cm-1) and water (1882 – 2321 cm-1) (Figure 3).

Figure 3 shows that water content in the noodle cooked by amateur was rich in the center, while water content in the noodle cooked by professional was distributed in the layer between outer side and core part. In addition, as a results of sensory test, almost all testers of 20 people said that the noodle cooked by professional was more delicious. In this experiment, By high speed mapping of few millimeters sample with 100 um2 measurement spot size, it was confirmed that the taste was related to the water content distribution.

By using single-element detector system with changeable aperture size when combined with high speed mapping, it enables to measure the samples with area as large as few millimeters in a shot time and visualize the sample in molecular level (such as water content distribution in food and medicine).

Using such system will be very useful for the study of food/medicine, if the relationship between the obtained image and food taste or effectiveness of medicine could be determined.

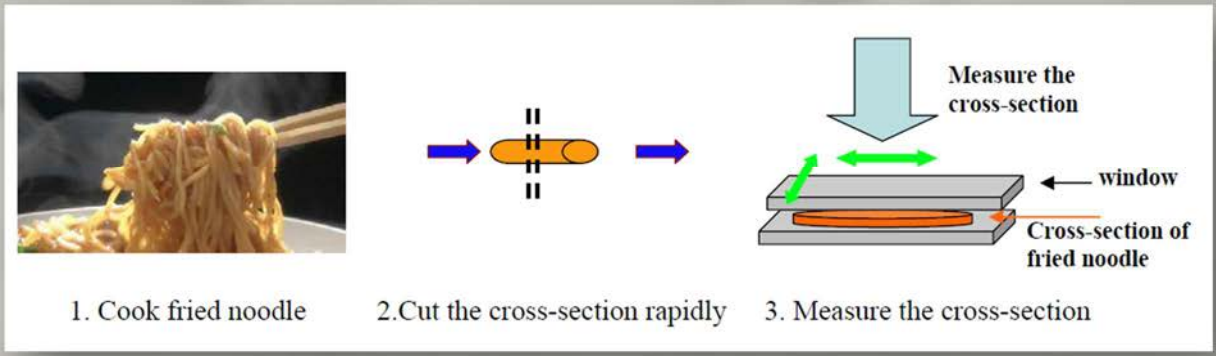


Figure 2 Process of measurement

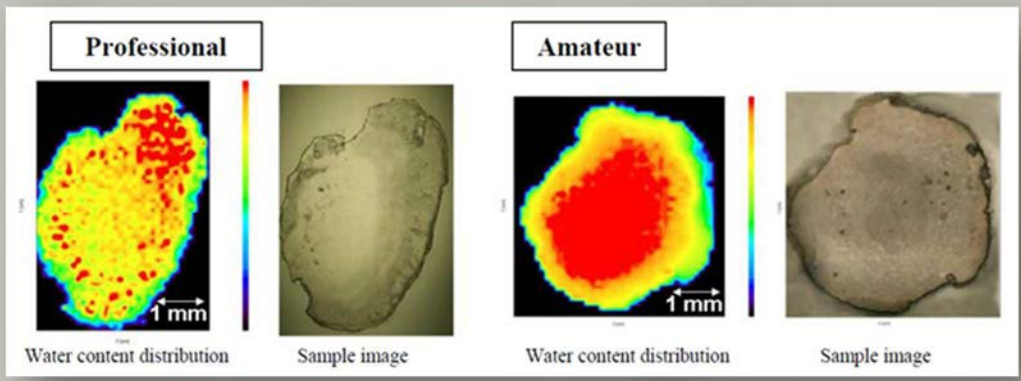


Figure 3 Water content distribution of fried noodle cooked by professional and amateur

Quantitative Analysis of Trans-fats in Food products using an FT/IR-ATR Method

Introduction

Trans-fats can be formed when liquid oils are solidified and used in various food products. The excessive ingestion of trans-fats increases LDL (bad) cholesterol in blood and decreases HDL (good) cholesterol. Consequently, the ingestion of trans-fat products can increase the incidence of ischemic cardiac disease and thus, the trans-fat content in food is of great concern. According to reports by a joint specialists conference of the Food and Agriculture Organization (FAO) and the World Health Organization (WHO) of the United Nations, it is proposed that the intake of trans-fats should be less than 1% of the overall caloric intake. As a result of these findings, many foreign countries are mandating the disclosure of trans-fat content in foods; some of the EU countries control the content in food and some other countries such as U.S., Canada and Korea are obligated to supply the trans-fat content on all food labels. In Japan, the Consumer Affairs Agency recently announced that food producers will be obligated to state the trans-fats content of food products as well.

For these reasons, it is becoming more important to measure the content of trans-fats in food. A quantitative analysis is generally performed according to the official method designated by public institutions, and gas chromatography (GC) or infrared spectroscopy are currently used for the official method for the content measurement of trans-fats. The GC method widely used requires some complicated procedures such as separation extraction of the sample and esterification, and thus requires considerable time and cost. The American Organization of Analytical Chemists (AOAC) formulate method AOAC 2000.10 by using infrared spectroscopy and ATR to evaluate the trans-fat content.

In this application, we demonstrated the quantitative analysis of trans-fats in several kinds of oil with a calibration made according to the official AOAC ATR method.

Experimental

Method AOAC 2000.10 requires a quantitative calibration be developed and the quantitative analysis of the unknown samples performed by measuring the samples with an ATR crystal heated to 65°C to melt the oils completely. The cis- and trans-fats contained in natural fats have their own IR peaks in the range from 1000 cm-1 to 600 cm-1, which is used for the quantitative analysis (Figure 1). In the official method, cist riolein and trans-triel aidin are used as the standard samples. The spectrum of cis-triolein in orange and the spectrum of trans-trielaidin in green are overlaid as displayed in Figure 1. Both spectra have similar absorptions in the mid infrared spectral range except for specific peaks associated wi th the two different forms as displayed from 1000 cm-1 to 600 cm-1.

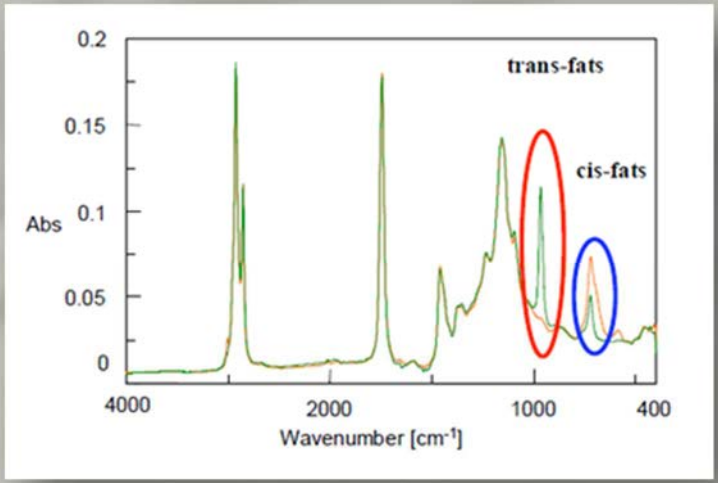


Figure 1 Mid-IR spect ra of cis-fats and t rans-fats (demonstrating the significant peaks in the highlighted areas)

Quantitative Analysis of Trans-fats in Food products using an FT/IR-ATR Method

Measurement Conditions

Instruments: FT/IR-6100 and a thermostatted single reflection ATR accessory
Detector: DLATGS
Resolution: 4 cm-1
Integration time: 64 scans
Temperature: 65 +/- 2°C
Apodization: Triangle
Method: ATR method (Crystal: Diamond)
Standard samples: Triolein and Trielaidin (Combination ratio of trielaidin: 0.5, 1, 5, 10, 20, 30, 40, 50 %)
Measurement samples: Shown in Table 1 (Sample volume: 50µL or less)

Results and Discussion

The trans-fat has a vibrational absorption peak due to the C-H bending mode near 966 cm-1 and the peak area around the peak is used for the quantitation in the official method. The overlaid spectrum for each concentration at 966 cm-1 are shown in Figure 2. Figure 3 is a screen shot of the Quantitative Calibration Program. The calibration curve calculated with the program is displayed in Figure 4 . Table 1 outlines the result of the quantitative analysis of several commercial food oils. In general, margarine contains a trans-fat content of 1 to 10 %, and olive oil and sesame oil contain almost no trans-fat. This shows that the system as outlined is effective for the quantitative analysis of trans-fats. By using the ATR methods, the quantity of transfats in various kinds of oil for food can be determined simply and quickly without complicated procedures.

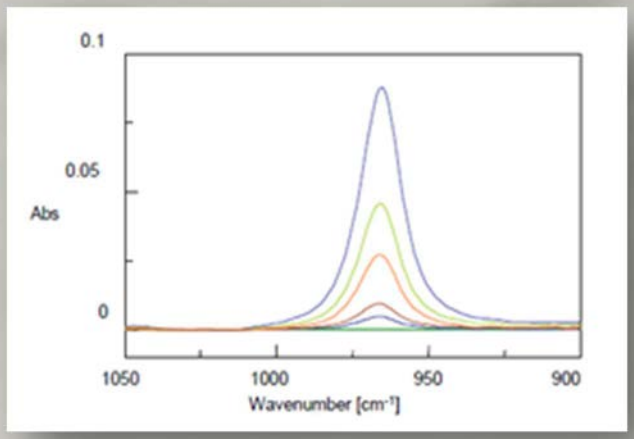


Figure 2 Peaks of trans-fats at 966 cm-1

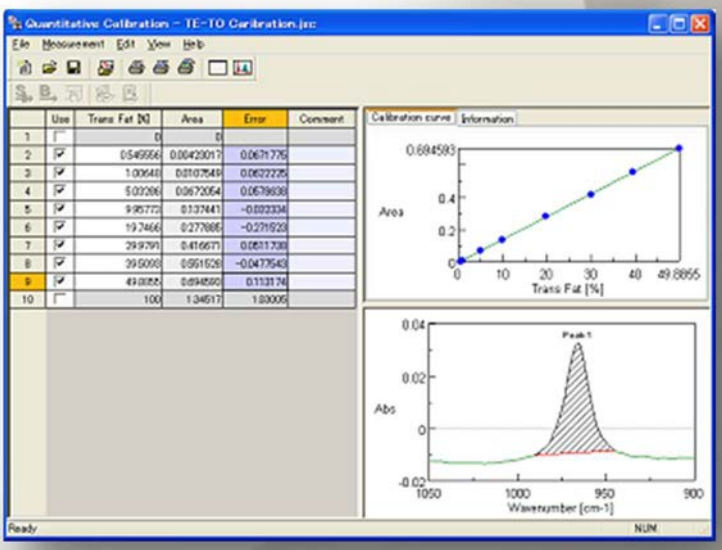


Figure 3 Quantitative Calibration Program

Sample	Content rate of trans-fat [%]
Margarine	3.1
Cooking Oil	1.9
Sesame Oil	0.7
Olive Oil	0.8
Chili Oil	1.2

Table 1 Trans-fat content of food oils

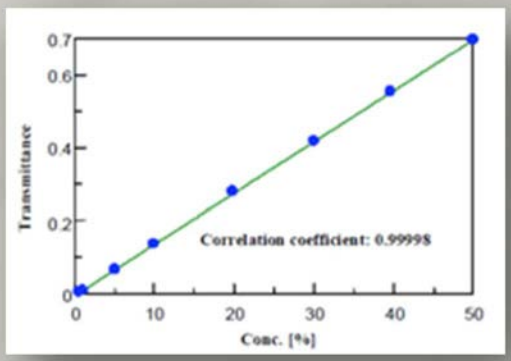


Figure 4 Calibration curve for trans-fat content

Evaluation of Alcoholic Content of Liquors using ATR Accessory

Introduction

The alcohol content of alcoholic drink is an indication of the drinks' ethanol concentration as measured in percent ethanol per 100 mL. This concentration is determined by the manufacturing method and its processes. Alcoholic drinks can be broadly classified into distilled and fermented liquors. Distilled liquors, typical examples of which are whisky, brandy, and shochu, are produced by distilling of fermented liquors, so they generally have a higher alcohol content than the fermented liquors. On the other hand, the alcohol content of fermented liquors such as wine, beer and sake can be varied by the degree of fermentation of sugar by yeast. It also can be varied by material and maturation.

Alcohol content is an extremely important numeric indicator for both manufacturers of liquors and their consumers. It can be easily measured and quantitated by using a Fourier Transform Infrared Spectrometer and an ATR accessory.

This measurement method can be applied to both distilled and fermented liquors.

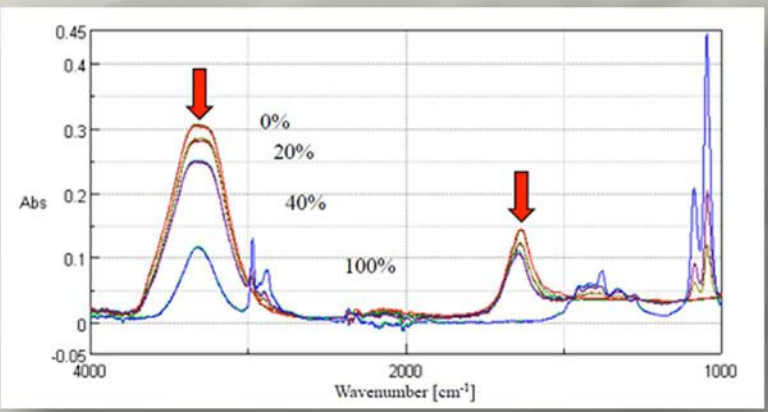


Figure 1 Spectra of Ethanol solution

Calibration curve

Although it would be possible to create a calibration curve from the peak heights of 3400 cm-1 (OH stretching) and 1650 cm-1 (HOH bending), in this application data, a calibration curve was created using a multivariate analysis technique (PCR) in the specified wavenumber range. The calculation range of 3740 to 3014 cm-1 and 1800 to 933 cm-1 were used, while the first derivative data were utilized as spectral data. Fig. 2 shows the calibration model created.

This calibration model indicates an extremely good value of correlation coefficient R=0.999.

Measurement Results

Table 1 shows the results of quantitation of 17 types of off-the-shelf liquors using the calibration model. For reference, the values listed on their labels are also provided. Fig. 3 shows the example of ATR spectra for a number of those liquors.

Liquors	Alcoholic content on labels	PCR calibration model
Beer A	5.0	5.1
Beer B	5.0	5.0
Low-malt beer A	5.5	5.6
Low-malt beer B	5.5	5.3
Fluit liquor	6.0	6.0
Highball	7.0	7.3
Cider	8.0	8.5
Red wine A	14.0	13.4
Red wine B	14.0	12.0
Sake A	15.0	15.8
Sake B	15.0	15.1
Spirits (Sweet potato)	10.0	10.3
Spirits	25.0	25.4
Spirits (Sugarcane)	25.0	22.4
Wisky	39.0	38.5
Brandy	39.0	38.8

Table 1 Results of quantitative measurement

Evaluation of Alcoholic Content of Liquors using ATR Accessory

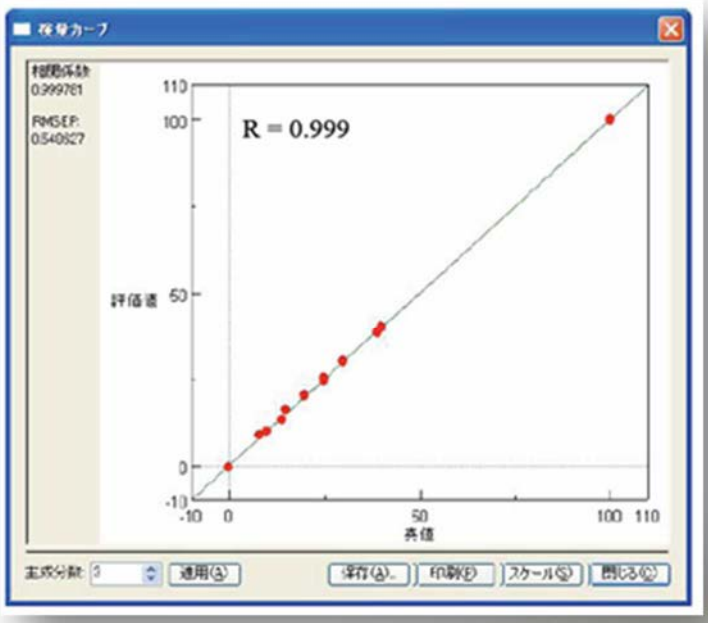


Figure 2 PCR Calibration curve

ATR PRO410-S with diamond prism

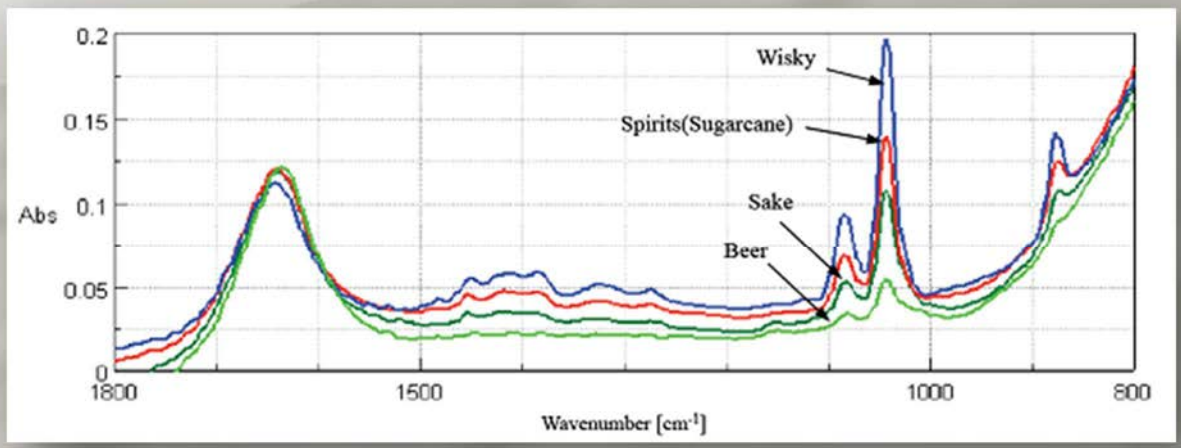


Figure 3 ATR Spectra of Liquors

Two-Dimensional Infrared Correlation Analysis of Maillard Reaction (Non-Enzymatic Browning)

Introduction

Two-dimensional correlation analysis is employed as a method for representing 3D spectra such as time-variance spectra in an easy-to-see manner. In the case of IR 3D spectra, it is possible to analyze the correlation between functional groups by drawing the spectrum on both the x and y-axes and then viewing the band correlation that can be observed on each spectrum. Actually, structural changes in samples brought on by time and temperature are measured as 3D spectra. The obtained time resolved spectrum is Fourier-transformed in the time direction, and then the correlation strength is computed and plotted using the real part and imaginary part. The correlation strength of the real part and the imaginary part is known as synchronous correlation and asynchronous correlation respectively. Analyzing both correlation spectra makes it possible to estimate structural change in substances. And by combining infrared analysis with other forms of spectral analysis, including near-infrared spectroscopy and Raman spectroscopy, it is possible to study peak assignment and the relationship between intramolecular vibration and lattice vibration. This time we employed two-dimensional spectroscopy to analyze the Maillard reaction, which is well known as a non-enzymatic browning reaction in food (see the Application Notes (080AT0179).

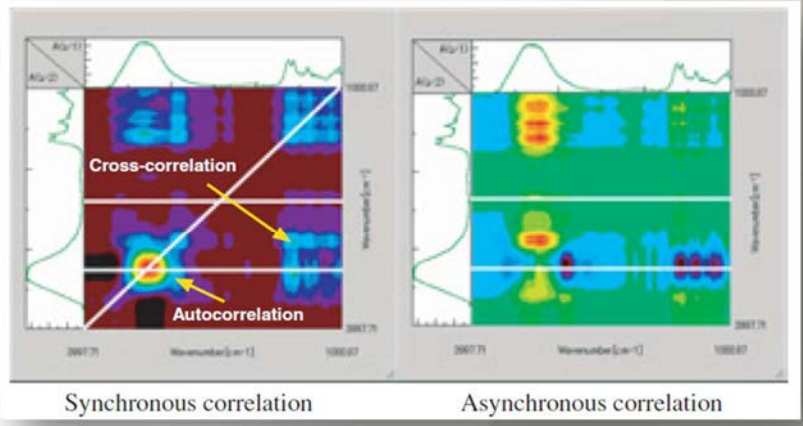


Figure 2 Synchronous and Asynchronous Correlation of Ribose

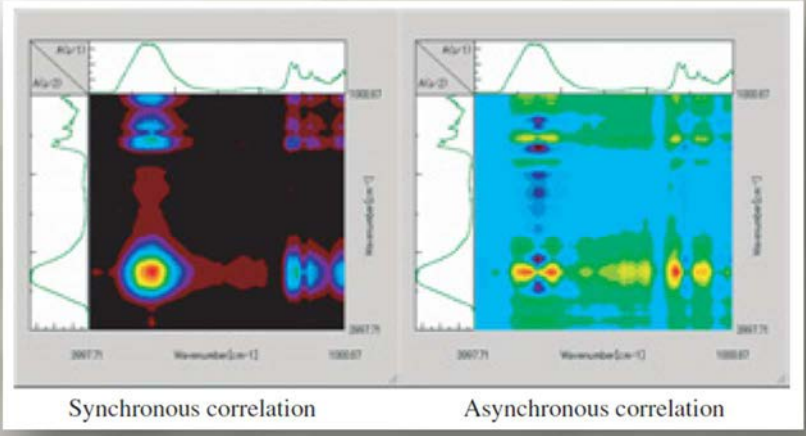


Figure 3 Synchronous and Asynchronous Correlation of Maltose

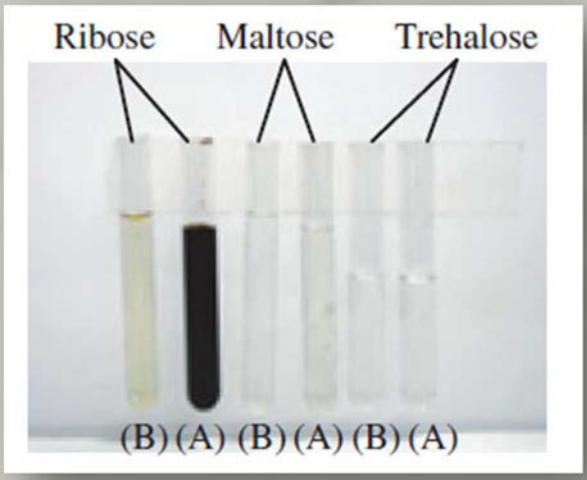


Figure 1 Photo of sample solution before (B) and after (A) reactions

Experimental

Ribose, maltose, and trehalose aqueous solutions (3 mol/L) were each mixed with a β-alanine aqueous solution (3 mol/L), and then each mixture was heated at 80oC for 30 minutes while measuring the IR time-variance spectra (For more information, see the Application Notes (080AT0179). Two-dimensional spectroscopy was then used to analyzethe results.

Two-Dimensional Infrared Correlation Analysis of Maillard Reaction (Non-Enzymatic Browning)

Results and Discussions

Figure 1 is a photo showing the sample solutions of post-reaction. Based on this photo, it was verified that the nonreducing sugar trehalose alone was not experiencing the Maillard reaction. Figures 2 to 4 show the convergent and asynchronous correlation spectra for each type of sugar (warm colors are positive). Synchronous correlation is generally used to evaluate whether peak strength variation is exhibiting the same changes due to perturbation. It is thought that in synchronous correlation, the higher the strength of the autocorrelation peaks (two with same wavenumbers), the greater the change due to perturbation. In addition, cross-correlation peaks (two with the different wavenumbers) take on a positive value when they rise or fall in the same direction due to perturbation and a negative value when they move in opposite directions. Asynchronous correlation has a complementary relationship with synchronous correlation, and it only has cross-correlation peaks. A cross-correlation peak in this case means one that varies at different times, or more precisely, one that takes on a negative value (or positive in the opposite case) when peak strength change on the x axis occurs at an earlier time than on the y axis. In the synchronous correlation for ribose and maltose, a strong autocorrelation near 3500 cm-1 was seen, which is thought to be an OH or NH base, but this was not verified for trehalose. This tells us that OH or NH bases are related to the Maillard reaction. It also indicates that in the synchronous correlation of ribose and maltose, the peaks of the respective sugars rise or fall in the same direction based on the fact that they have positive correlations at 3500 cm-1 and 1560 cm-1. It is also thought that based on the asynchronous correlation of ribose, the changes at 2800 and 1540 cm-1 occur before the OH and NH base changes (which are likely at 3300 cm-1) because the vicinity of 2800 and 1540 cm-1 on the x axis shows a negative correlation to 3300 cm-1 on the y axis. In the asynchronous correlation of maltose, the opposite of what occurs with ribose happens.

Based on the synchronous correlation of trehalose, we can verify that the CH base peak at 2900 cm-1 greatly varies over time. We can also verify that in the asynchronous correlation of trehalose, the CH base peak at 2900 cm-1 varies over time after the OH base and water peak changes occur based on the fact that the peaks at 3300 and 1640 cm-1 on the x axis show a positive value versus the peak at 2900 cm-1 on the y axis. Using two-dimensional spectroscopy in this manner makes it possible to, among other things, analyze reactions in details.

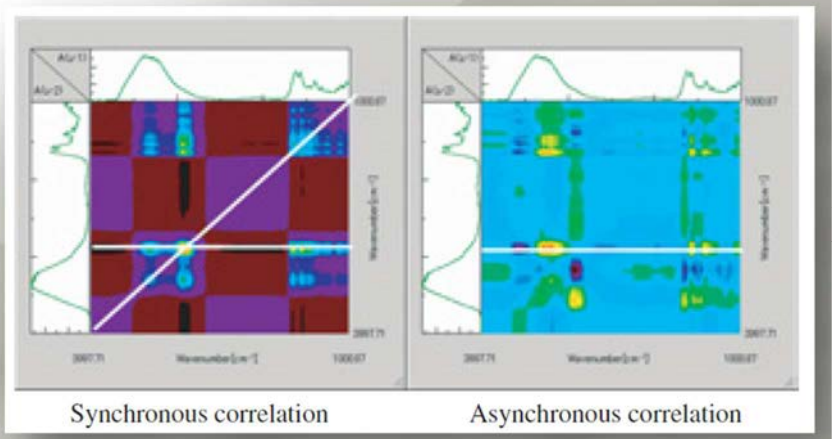


Figure 4 Synchronous and Asynchronous Correlation of Trehalose

Reference:
Noda, Isao and Ozaki Yukihiro, "Spectral Research", 1995: 44

Rapid Quantitative Analysis of Trans-fatty acid of extremely low concentration by using the Cell for Liquid

Introduction

As a method of rapid quantitative analysis of trans-fatty acid in the food, which is becoming a big concern due to the influence to human health, the measurement by FTIR together with thermostatted ATR accessory has been suggested[1,2]. This is specified as an official method by AOAC (American Organization of Analytical Chemists) and AOCS (American Oil Chemists' Society) due to its extremely short analysis time within 1–2 minutes, which is much shorter than the time required by a method using GC (Gas Chromatography) that requires lousy sample preparation as well. However in official method of AOCS, the quantitation limit by ATR method is described as around 1.0%[2], which was also demonstrated in our FT/IR Application data[1] under the same experiment conditions specified by AOCS. Meanwhile, according to "The Guideline for Disclosure of Information on Trans-fatty acid Content" issued by the Consumer Affairs Agency of Japan, it is allowed to show "Zero" in the labeling if the content of trans-fatty acid / 100 g of food (100 ml in case of beverages) is less than 0.3%. In other words, 0.3% is required as the quantitation limit. Furthermore, the similar requirement in other countries is also reported (USA: < 0.5 g / meal, Taiwan: < 0.3 g / 100 g, Korea or South American: < 0.2 g / meal) and accordingly, a rapid and precise method is required for quantitative analysis of trans-fatty acid content in food in less than 1.0%. The method for quantitation of trans-fatty acid described in the Guideline is GC (AOCS Ce1h-05 or AOAC996.06), or other methods which need to have the equivalent performance of this method. The analysis by GC method not only requires the sample preparation before measurement, including the separation after having methylated the fat (being extracted) with BF3 , but also takes more than 1 hour for measurement. This report, describing the quantitative analysis of trans-fatty acid of lower than 1.0% by FTIR transmission method, shows the possibility that the equivalent result by GC method can be obtained in a extremely short time.

Experimental

The peak indicating the absorption at 966 cm-1 by the trans-fatty acid is used for the quantitative analysis (Figure 1). This is also adopted in official method such as ATR method[2]. Calibration curve is created by 5 samples with different content of trielaidin, which are prepared by adding the trielaidin (green color spectrum in Figure 1), being known as an isomer of trans-type of triolein, into the cis-triolein (orange color spectrum in Figure 1) which contains only cis-type.

1) JASCO FT/IR Application data 050-AT-0215 (2010)
2) AOAC Official Method 2000.10, AOCS Official Method Cd 14d-99

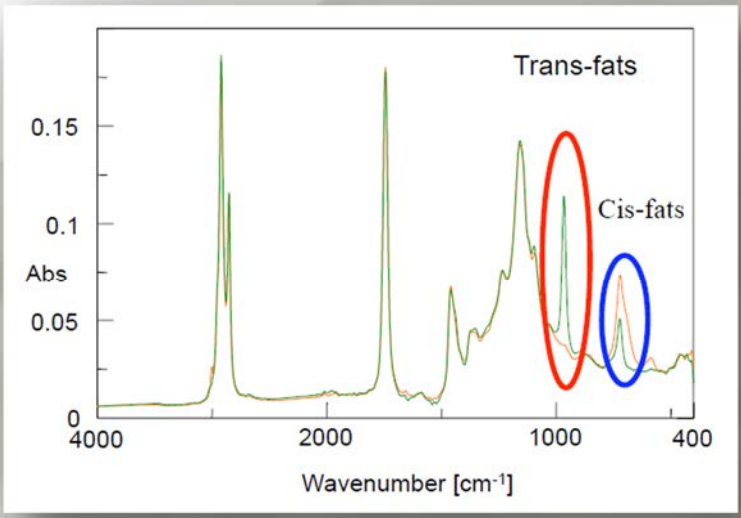


Figure 1 IR spectrum of cis-fats and trans-fats (ATR)

Measurement Conditions

Instrument: FT/IR-4100
Detector: DLATGS
Resolution: 4 cm-1
Accumulation: 64 times
Apodization: Triangle
Temperature: 25°C (ambient temperature)
Mode: Transmission (method of solution)
Cell: Sealed liquid cell *NaCl (thickness: 0.1 mm)
Standard sample: Triolein, Trielaidin (0.05, 0.1, 0.2, 0.5, 1.0%)
Peak calculation: Area within 945 - 990 cm-1
* The sealed liquid cell with KBr can be also used. Please contact local JASCO distributor if the cell needs to be thermostatted.

Rapid Quantitative Analysis of Trans-fatty acid of extremely low concentration by using the Cell for Liquid

Figure 2 Sealed liquid cell

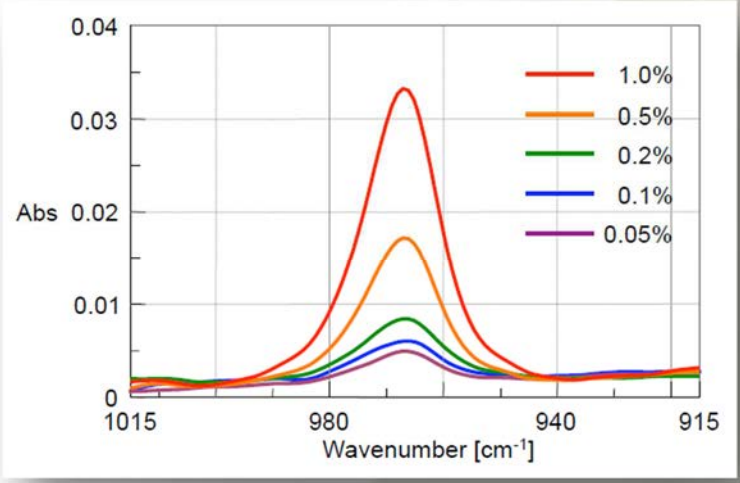


Figure 3 Trans-fats peak at 966 cm-1

Result and Discussion

Transmission spectra of 5 standard samples (with different concentration of trielaidin: 0.05, 0.1, 0.2, 0.5, 1.0%) are displayed in Figure 3. The correlation coefficient of 0.9998 of the calibration curve obtained shows the good linearity of trans-fatty acid concentration to the peak height or area around 966 cm-1 (Figure 4). Since the S/N (Peak-to-Peak) of the peak used for 0.05% quantitative calculation is about 15:1, which is much better than the value of 10:1 being normally accepted as the quantitation limit (Figure 5), this method is considered as the accurate approach to the quantitative analysis of the sample whose concentration is extremely low, such as 0.05%. The above result indicates that the quantitative analysis of 0.05 - 1.0% trans-fatty acid can be performed by the method of FTIR transmission measurement. Although this method has the advantages of no need of sample preparation and fast measurement comparing with the GC method, the cell has to be washed after the measurement each time. From such viewpoint, it is not so convenient as compared with the ATR method. Accordingly, it is considered to be the fast, convenient and accurate method to perform the screening with the ATR method first, and then apply FTIR transmission method only for the sample with concentration of lower than 1.0%.

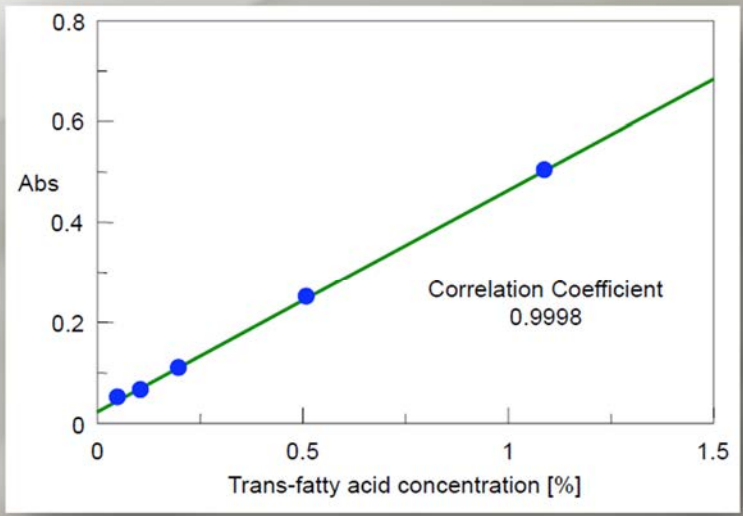


Figure 4 Calibration curve

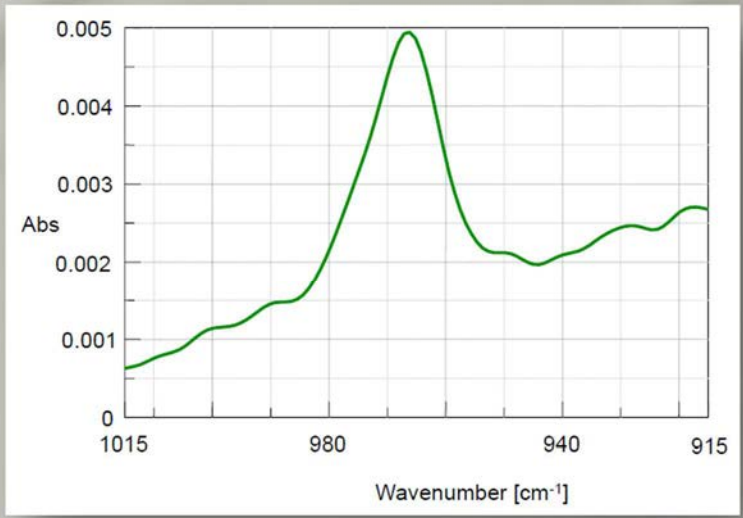


Figure 5 Spectrum of trans-fats of 0.05%

Non-destructive NIR measurement of cherry fruit for evaluation of sugar concentration

Introduction

The NIR technique is widely used for non-destructive measurement of perishable foods and crops for evaluation of freshness, moisture, sugar, protein or fat content, etc. In this application, the correlation between the sugar concentration of cherry fruits (Sato-Nishiki; a Japanese brand) and the NIR spectrum was evaluated. A good correlation between the two parameters was confirmed with the PLS (Partial Least Square) chemometric model as obtained using the NIR spectrum and sugar concentrations examined using a saccharimeter.

Apparatus

The Model VIR-9650 Portable NIR Spectrometer (NIR source; halogen lamp, detector; InGaAs) was used with an accessory, the Model VIR-NRF-N Diffuse Reflectance accessory. The appearance of the instrument and accessory attachment is shown in Figure 1. The sample, a cherry was placed directly on the sample stage of the diffuse reflectance accessory (Figure 2). The NIR source energy is introduced from the bottom of the accessory stage into the sample, the diffusely reflected light from the sample then collimated and introduced into the InGaAs detector. A commercially available saccharimeter (IUCHI SEIEIDO, Japan) was used for the quantitation of sugar concentration.

Figure 1 VIR-9650 and VIR-NRF-N accessory

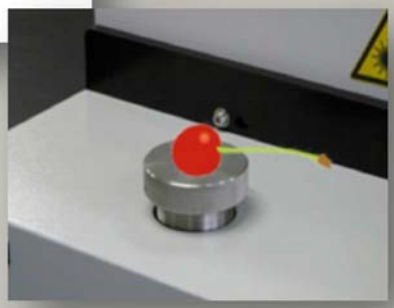


Figure 2 Cherry sample placed on sample stage

Results

The NIR DRIFTS spectra of several different sampling points on a single cherry sample are shown as Figure 3. The spectrum baseline varies as a result of the different color or shape of each sampling point. This variation can be corrected by obtaining the 1st order derivative of the spectra and an optimum selection of the useful calculation range such that a good calibration model is obtained. The highlighted ranges in the figure were selected for the sugar content calculation. The PLS calibration model obtained with the estimated and actual sugar content (saccharimeter) is outlined in Figure 4. A reasonable correlation coefficient (0.9128) was obtained and indicates that the non-destructive NIR measurement can be applied to other products such as perishable foods, crops and pharmaceuticals for quantitation of abstract qualities such as composition, moisture, sugar, protein or fat content, etc.

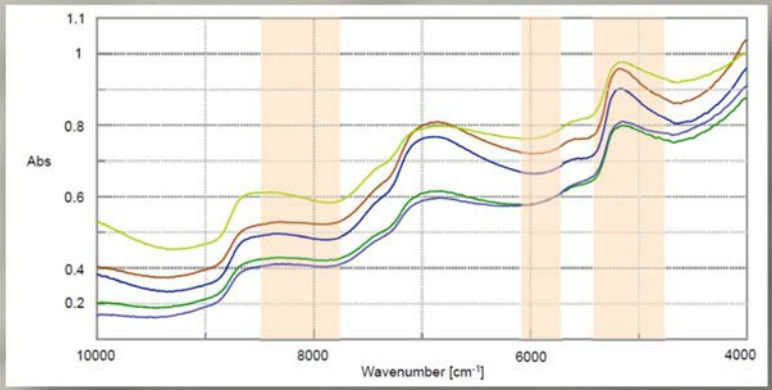


Figure 3 NIR DRIFTS spectra of several different sampling points on a cherry sample

Correlation coefficient: 0.9128
RMSEP: 0.825

Calculation parameters
No. of factors: 7
Pre-processing: 1st derivative
Data thinning: 4
Scaling: off

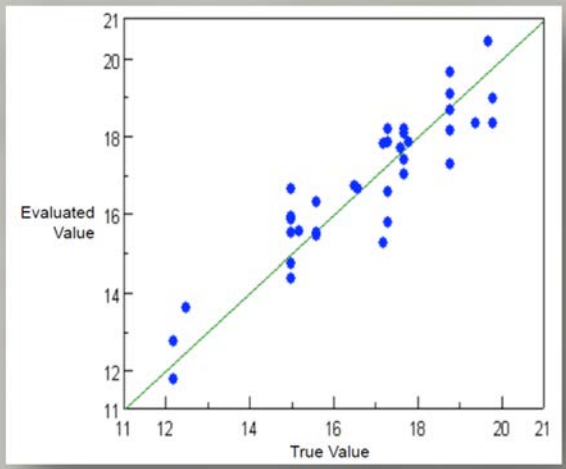


Figure 4 PLS calibration model obtained with NIR spectrum (estimated) and actual sugar content (saccharimeter)

The simple measurement method of liquid sample in near-IR region

Introduction

Since near-IR light is transmissive to glass, it is widely used as the quantitative and qualitative analysis method to measure powder sample in test tube or sample bottle. On the other hand, generally the liquid sample is measured in transmittance method using thin cell with 1-3 mm cell length. The commercial cell is too expensive to use as disposable, and it is difficult to clean the cell due to its thin cell length. In the measurement method by using hematocrit capillary cell, there were some problems that the cell cap cannot be used for strong smell sample such as fragrance, or high viscosity sample cannot be inserted to the cell. In this note, we would like to introduce the simple measurement method by using the test tube with cell cap or easy washable laboratory dish.

Instrument

Portable type near-IR detected instrument VIR-300. Since VIR-series are compact and transportable, and installed easily, they can be widely used depending on the purpose such as manufacture line, outside or acceptance test. In this note, RF-100-VIR is used as optional accessory and test tube holder and laboratory dish are measured (Photos 1, 2 and 3).

Measurement example 1; mini test tube

Photo 2 shows measuring the solution in mini test tube mounted on test tube holder. By setting the flat surface cylindrical stainless spacer in the test tube, cell length can be controlled as solution cell. The light is irradiated from the bottom of the tube, transmit the solution, reflect on the surface of spacer, and then pass back to the bottom. Since the cell length (thickness) can be controlled to optimum length for near-IR, the good spectrum as the same as current transmittance angular cell can be obtained.

Photo 1 Transportable near-IR measurement system

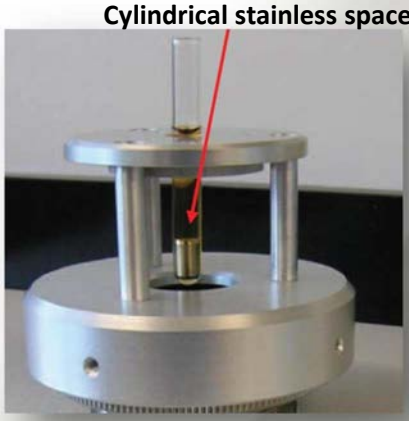


Photo 2 Measurement example of solution using mini test tube

Figure 1 and 2 show the solution spectrum obtained by this method, and good repeatability. Figure 3 show the reference data of the spectrum obtained by using hematocrit capillary cell. It can be confirmed that the saturated absorbance peak in the measurement method using hematocrit capillary cell is obtained without saturating in the test tube method.

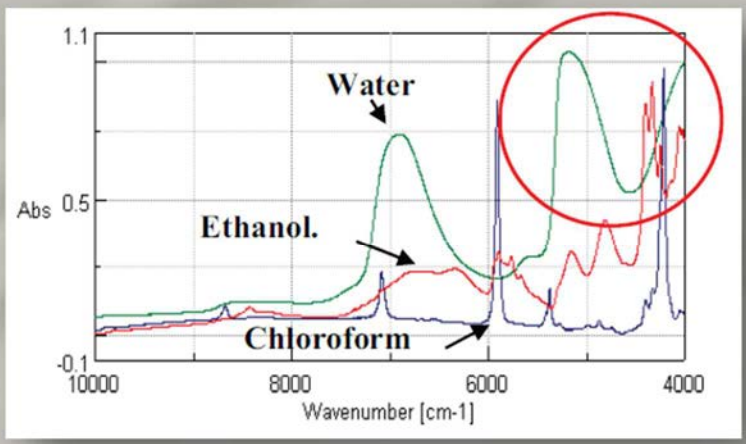
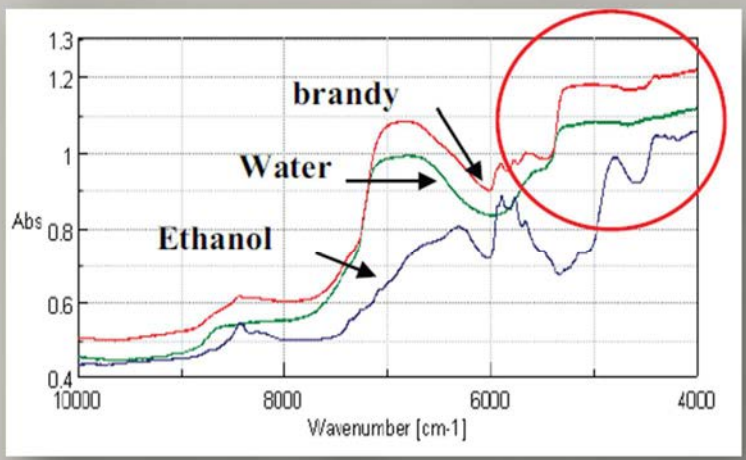


Figure 1-2 Measurement example using test tube



The simple measurement method of liquid sample in near-IR region

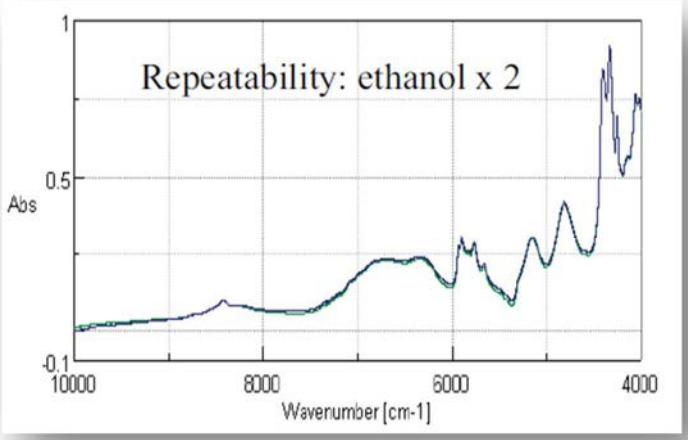


Figure 3 Reference data of the spectrum obtained by using hematocrit capillary cell

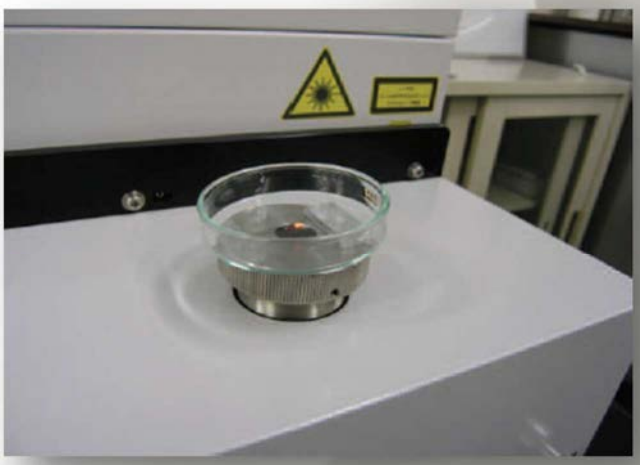


Photo 3 Measurement example of solution sample using laboratory dish

Measurement example 2: Laboratory dish

When the sample has strong flavor and the Amount is enough, it is more suitable to use the easy washable wide mouth case such as Laboratory dish. Photo 3 shows the mounted laboratory dish. Since the incident light is directly reflected on the surface of the flat bottom case such as laboratory dish, sample absorbance spectrum might not be measured. In order to avoid this phenomenon, by tipping the reflectance face on the angle to light axis, the better absorbance spectrum can be obtained. The cell thickness can be controlled by using metal reflectance plate with spacer on the laboratory dish. Figure 4 shows the measurement example of solution sample using laboratory dish. The optimum size of the spacer used with metal reflectance plate is approx. 400 µm. But the thickness of the spacer depends on the sample.

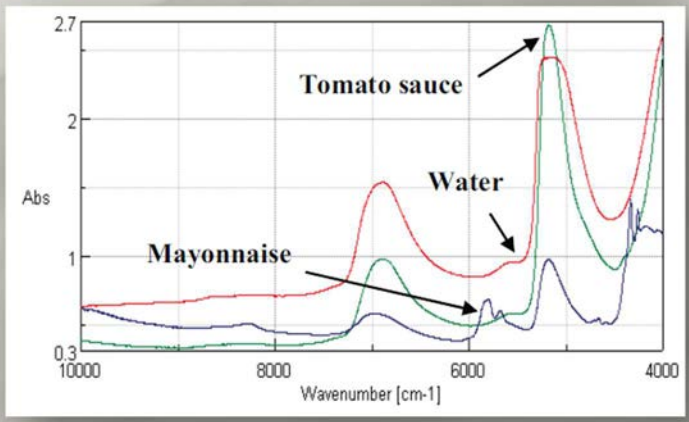


Figure 4 Measurement example using laboratory dish

Simple Methods to Measure Powder Samples using FT-IR Spectrometer

In general for FT/IR, powder samples are measured by using:

1. KBr Pellet method: Sample powder needs dilution with KBr and pressing with KBr pellet die and hydraulic press to make a pellet. Sometimes there may need also repeated pretreatments for the best concentration.
2. Diffuse Reflection method: There is no need of pressing but the dilution with KBr is required as KBr Pellet method. A measurement without dilution may cause the peaks reversed at the strong peaks.
3. Solution method: There may need some apparatus to dilute sample with some solvent, and pipettes to pour sample solution into liquid cell.
4. Microscopic Transmission method: There needs IR Microscope and since it adopts MCT detector, Liquid N2 is required to chill the detector. Hydraulic press may be needed in order to press the powder sample sandwiched between KBr plates.

Such measurements always need some sample pretreatments. Now the new procedure will be introduced, by which the sample can be placed on the sample compartment without dilution enabling to obtain good spectra.

Measurement Method

Existing Diffuse Reflection attachment (DR-81) was used for this measurement with improved optical system and sample cells to delete specular reflection. Sample was rubbed and diffused on the surface of sample cell for measurement. Now Phenacetin, which is generally hard to measure without KBr dilution, was measured.

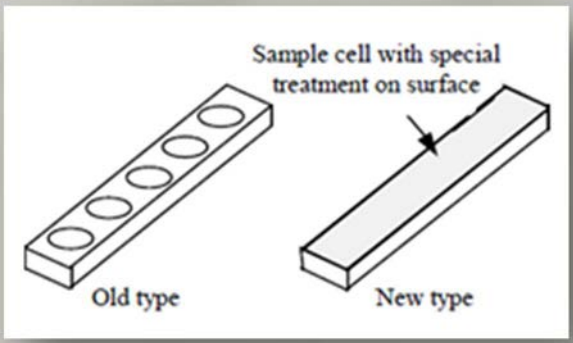


Figure 1 Sample cell for this method

Results

Figure 3 shows zoomed and expanded spectra of Figure 2. Some peaks were found to be reversed or shifted. Figure 4 shows spectra of KBr-diluted sample with existing cell, and of non-diluted sample with improved cell. The spectra show almost no peaks reversed or shifted. As mentioned above, the improved sample cell which has specifically processed surface helps to reduce specular reflection, while existing method is reducing such reflection with KBr-dilution, which proves that it is possible to obtain good quality spectra without KBr-dilution.

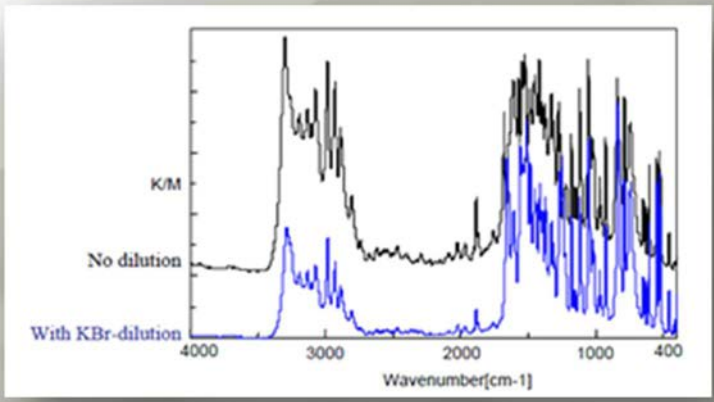


Figure 2 DR-spectra of Phenacetin (in existing sample cell)

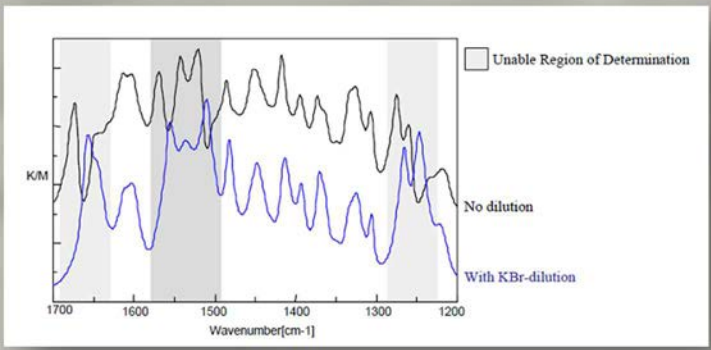


Figure 3 Zoomed and Expanded DR spectra of Phenacetin with existing sample cell

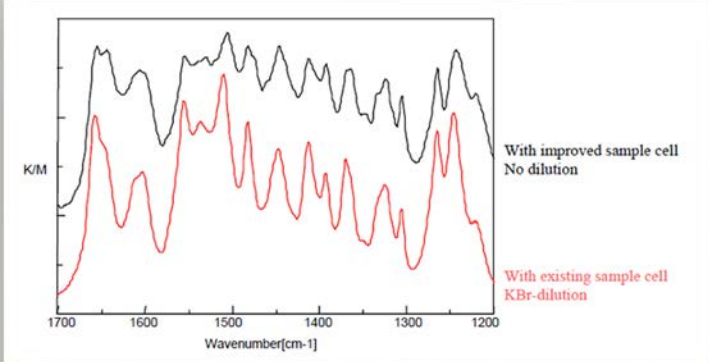


Figure 4 DR spectra of Phenacetin with improved and existing sample cell

Measurement of Protein in Heavy Water using FT-IR Spectrometer

Introduction

Within the past decade, analyzing protein sequences consisting of 30 peptides or fewer has become very common. The number of peptide hormones that have been produced by peptide synthesis has become very large. As a result, the need to evaluate these hormones using analytical instruments has increased rapidly.

This application bulletin demonstrates FT/IR measurement of several types of protein in heavy water. It is well-known that in the IR spectrum of a protein, the characteristic vibration peaks of the principal chain appear in the range of 1700 - 1600 cm-1 (approximately 6 µm) for amide I, and in the 1600 - 1500 cm-1 range (approximately 6.45 µm) for amide II.

If IR measurement of protein is conducted in an aqueous solution, the strong absorption band of normal water occurring at 6 µm prevents meaningful date acquisition. In order to overcome this problem, it is necessary to measure the protein in heavy water. When the protein is immersed in heavy water, the sample can be measured in affixed cell of 50 - 100 µm in width. In this case, a waterproof cell window must be sued (Table 1).
In transmittance mode, CaF2 or BaF2 are typically used; ZnSe, which is typically employed for ATR, can be used as well. These window materials are transparent, offering the advantage of easy detection of air bubbles.

Conditions

Resolution: 2 cm-1
Detector: TGS
Apodization: Cosine
Accumulation: 256

Sample preparation

Solution: Heavy water
Protein concentration: 2% (w/v)
Cell window: CaF2
Cell thickness: 0.1 mm (fixed cell)

When the amount of available sample is small, or when the sample is expensive, we recommend that the demountable cell be used. If the fixed cell is used for such samples, air bubbles trapped in the cell can make the results meaningless, thus wasting the sample. In addition, the instrument should be allowed sufficient time to stabilize after the power is turned on, and the interval between the measuring sample and the blank should be as short as possible.

Measurement data

We measured five protein samples: whale Myoglobin, Lysozyme from the while of the chicken egg, Ribonuclease A from the bovine liver, Cytochrome C from the horse heart, Bovine serum albumin (SIGMA).
Sample measurement was performed using a CaF2 cell measuring 0.1 mm in thickness after 8 mg of each protein was dissolved in 0.4 mL of heavy water and allowed to sit for 24 - 48 hours for deuterium substitution.
The results are shown in Figure 1 - 6. Figure 2 - 6 show the spectra of each protein after subtraction of the deuterium spectrum, and then smoothing.
Figure 1 shows the overlaid spectra of 2 % myoglobin in heavy water, and heavy water alone. Using a cell measuring 0.1 mm in thickness, the usable wavenumber range of the heavy water solvent is 2100 - 1300 cm-1 because the absorbance of the solvent is lower than 1.

Measurement of Protein in Heavy Water using FT-IR Spectrometer

Deuterium substitution causes the band of Amide II, which normally appears around 1550 cm-1, to shift to a much lower wavenumber. Therefore, only the Amide I appearing at 1650 cm-1 absorption band of the principal chain observed.

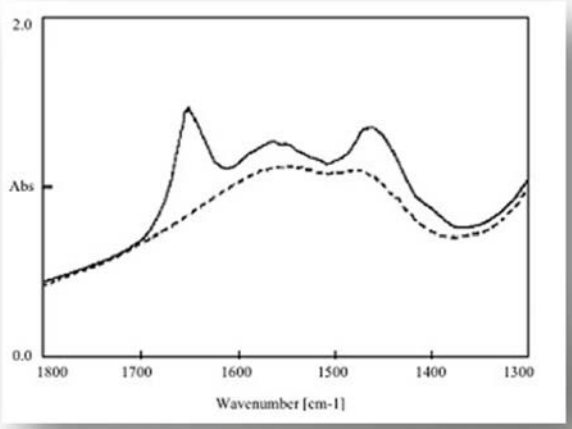


Figure 1 Overlaid spectra of 2% myoglobin in Heavy water, and Heavy water

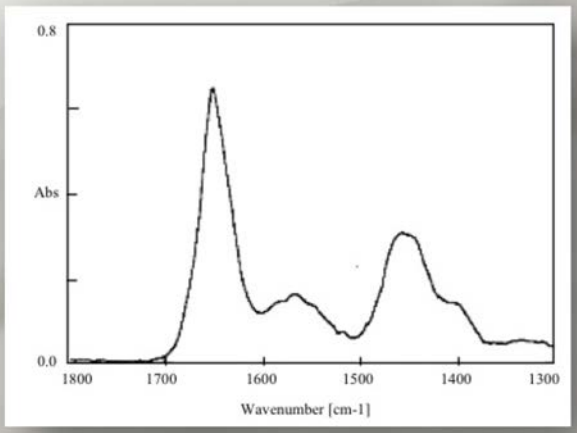


Figure 2 Myoglobin

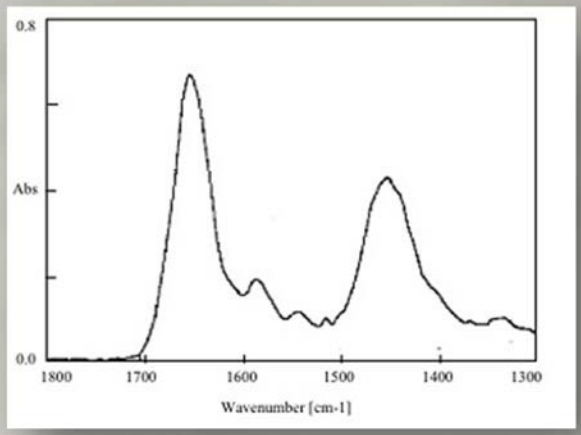


Figure 3 Lysozyme

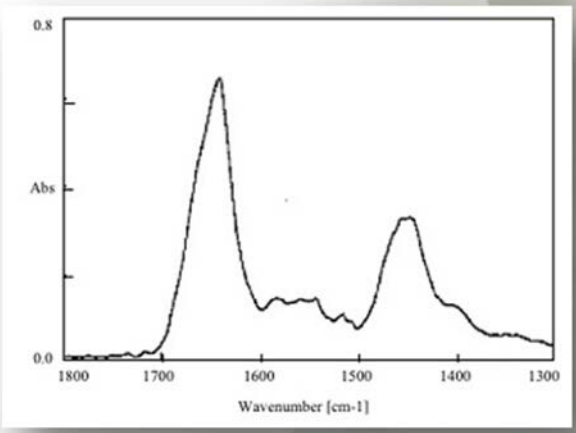


Figure 4 Ribonuclease

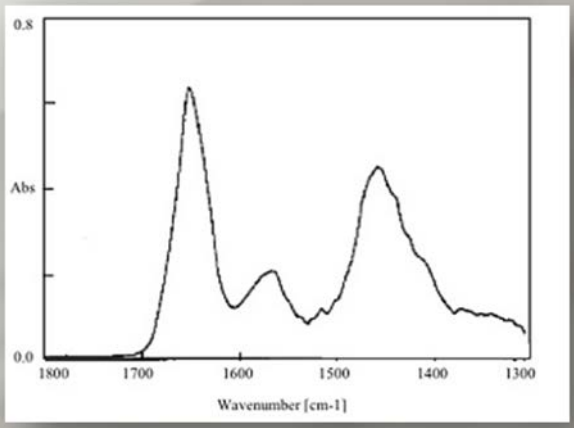


Figure 5 Cytochrome *C*

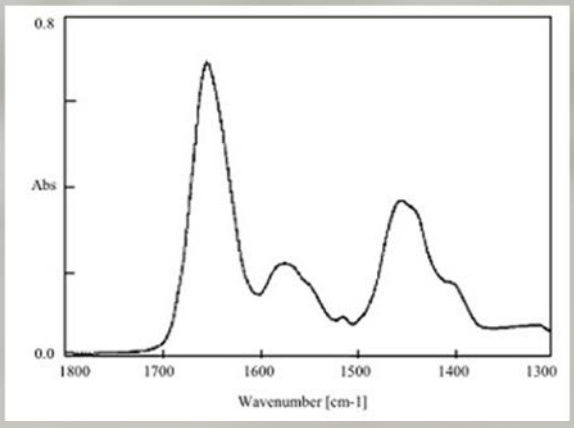


Figure 6 Bovine serum albumin

Secondary Structure Analysis (SSE) Software for Infra Red Interpretation and Modeling of Proteins

As the last strands of the human genome project unravel, the focus now turns to proteomics. There are several instrumental methods to analyze protein chemistry and there is particular interest in the functional activity that can be directly attributed to the physical arrangement of a protein.

Introduction

As opposed to simple chemicals, the 3-dimensional structure of proteins is an inherent part of the protein reactivity and functionality. For instance, muscle fiber is composed primarily of a single type of protein (fibrinogen) with a specific physical structure. In other proteins, rearrangement of the physical configuration can enhance or restrict the protein functionality or reactivity. Thus, the physical arrangement of the protein is as important as the sequence of amino acids. NMR analysis requires very expensive instrumentation. By contrast, FT-IR analysis is readily available in most laboratories, has few constraints on sample type or methodology, is inexpensive and simple to operate. As a result, the study and interpretation of infrared protein spectra has been well documented in the literature[1-5].

Although there are numerous vibrational interactions possible for crystalline proteins, in truth, most of them present infrared spectra much like synthetic polymers (Figure 1). Demonstrating C-H stretching and bending and some skeletal bands, protein spectra are quite simple in comparison to the complexity often presented by individual chemical spectra. Because of the role played by the amide groups as the backbone for the amino acid residues, the amide vibrational data provides the critical information necessary to predict the secondary structure of the protein. But the variations in the amide band structures are subtle and can be difficult to interpret.

The same common backbone, NH2-CHR-COOH, is present in all amino acids with R as one of the possible amino acid residues. The protein 'polypeptide', is a repeating sequence of the amino acid residues. The various functional groups of the amino acids and the sequence defines the protein and specificity. However, the interaction of the various amino acid groups amongst themselves also determines protein functionality with a direct influence on the protein's physical structure.

Proteins are so structurally complex, the 3-dimensional configuration can only be described using four 'structures' (Table 1), defined as primary, secondary, tertiary and quaternary structure. **Primary structure** is simply the amino acid sequence, defined by the DNA template. **Secondary structure** is the physical arrangement of the peptide chains as they fold and bend around the various molecular and steric constraints of the amino acid residues. **Tertiary** and **quaternary structure** define the 3-dimensional arrangement of the peptide chains and are determined by the various 'weak' forces and the interaction of the polypeptide units themselves.

The secondary structure is of intense interest because the configuration determines the reactivity of the protein and can change under certain conditions. There are several methods of analysis used to determine secondary structure (Table 1), but XRD and CD analysis have limited application due to sampling requirements and the JASCO Secondary Structure Estimation (SSE) software uses a spectral modeling procedure for multivariate analysis of infrared protein spectra predicting the secondary structure based on a spectral database of analyzed proteins.

Whether the protein is composed of one type of secondary structure, e.g., α-helix, β-sheet, etc. or multiple structural elements, the SSE software can provide an answer.

Protein Structure	Structure Determined by	Methods of Analysis
Primary	The amino acid sequence (Ala, Gly, Ile, Tyr)	amino acid cleavage, DNA analysis
Secondary	Local, 'steric' structure, shape of peptide chains (α-helix, β-sheet, β-turn, etc.)	XRD, CD, FT-IR, NMR, Computer simulation
Tertiary	Actual 3-dimensional structure (hydrogen bonding, van-der-Waals forces, weak ring interactions, salt bridges, etc.)	XRD, NMR, computer simulation
Quaternary	Interaction between polypeptide units	NMR, computer simulation

Table 1

Secondary Structure Analysis (SSE) Software for Infra Red Interpretation and Modeling of Proteins

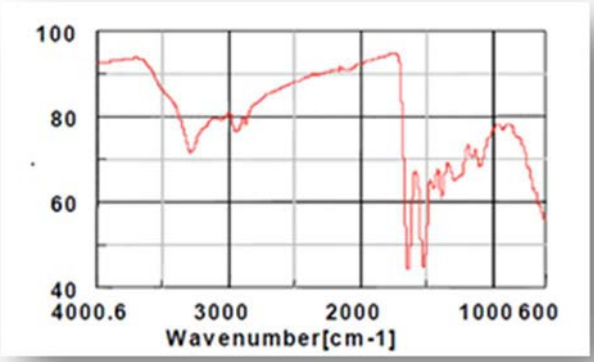


Figure 1 IR of a synthetic polymer material

Predicted Fit	α-helix	β-sheet	β-turn	Other
Hemoglobin	85%	0%	7%	5%
Lysozyme	36%	9%	36%	24%

Table 2 Predicted SSE for Protein Solutions

Experimental Results

All spectra were collected using a Jasco 480 Plus FT-IR equipped with the Spectra Manager software suite and the optional Secondary Structure Estimation (SSE) software program. Protein spectra were collected using 64 scans at 4 cm-1 resolution, coadded and averaged to obtain all single-beam background and sample spectra. Sample spectra were analyzed with the SSE software after data collection. Myoglobin and lysozyme samples were dissolved into buffer solution then analyzed as a thin film between two ZnSe windows in a liquid demountable cell. The fingerprint region of a spectrum of lysozome solution is presented as Figure 2.

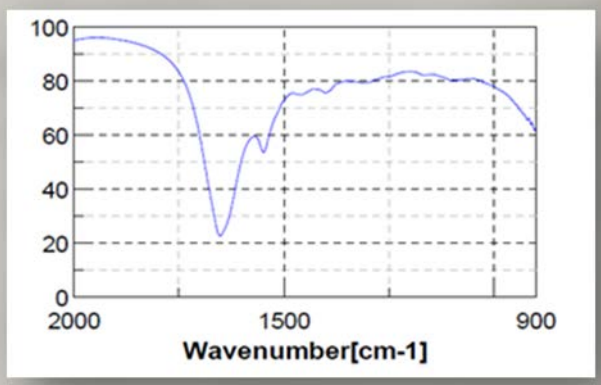


Figure 2 Lysozyme fingerprint region

1. Miyazawa, T. J. Chem. Phys., 32, 1657, 1960.
2. Miyazawa, T., and Blout, E. R., J. Amer. Chem. Soc., 83, 712, 1961.
3. Krimm, S. and Bandekar, J., Advances in Protein Chemistry, 38, 181, 1986.
4. "Spectroscopic Methods for Determining Protein Structure in Solution", H. A. Havel, ed., VCH Weinheim, Germany, 1996.
5. "Infrared Spectroscopy of Biomolecules", H. H. Mantsch and D. Chapman, eds. Wiley-Liss, New York, NY, 1996.

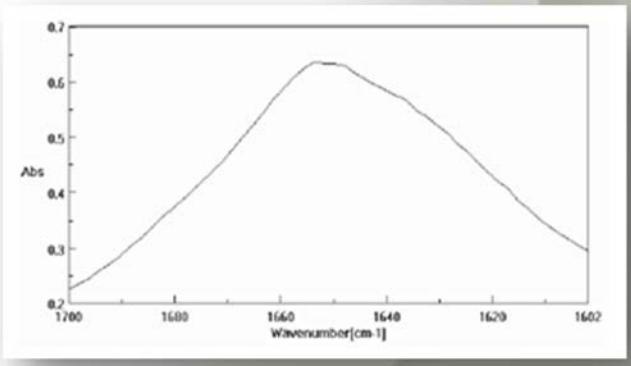


Figure 3 Amide region of lysozyme

Figure 3 is the amide region of the lysozyme solution prior to data pre-treatment while Figure 4 is after the buffer subtraction and water vapor correction. Figure 4 also illustrates the various protein secondary structure models as they are used to fit the lysozyme data (black trace). The SSE prediction results for both protein solutions are presented as Table 2, agreeing with published data3,5. While simple, these examples illustrate the ease with which the analysis is conducted. Simply collect the infrared spectra of the protein solution and the buffer, supply the spectra to the SSE software and the secondary structure prediction is calculated within seconds.

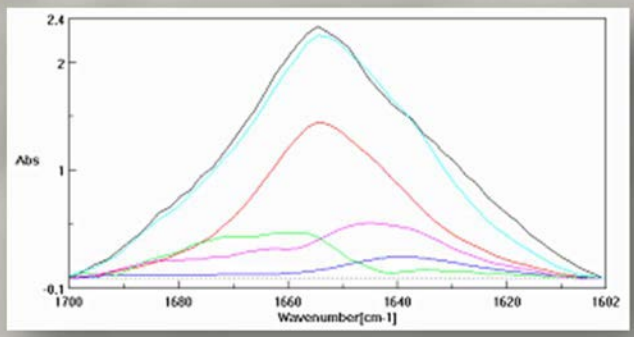


Figure 4 IR spectrum with corrections

In addition, the accuracy of the SSE program increases as corroborated protein spectra are added to your personal database. Supplied with an initial database of over 50 proteins and their substantiated secondary structure, the SSE software package is ready and able to provide answers from the very start of data processing.

Conclusions

The SSE program may not be able to provide a complete confirmation of the various protein structures but it is an extremely powerful tool for the rapid determination of protein secondary structure.

Rapid Identification of an Illegal Drug using NIR (Identification of MDMA Tablet)

Introduction

Near-Infrared (NIR) spectroscopy has unique capabilities as compared to mid-infrared analysis which can often require extensive sample preparation to obtain an identifiable spectrum. As such, NIR can be useful for the non-destructive analysis of a specific sample area or provide an average of a larger sample area, depending upon the required analysis. In recent years, NIR spectroscopy has been widely used for the examination of biological samples and quality control/analysis of food and medical products. The diffuse reflectance technique is ideal for this method due to extremely simple sample handling such that rapid identification of illegal drugs, such as MDMA, can be accomplished by using a search data library created using NIR diffuse reflectance.

Experimental

A diffuse reflection accessory (VIR-NRF-N) is used in combination with a portable Fourier Transform Near-Infrared Spectrometer (VIR-9650) and then by simply placing a tablet, such as MDMA, directly on the sample holder, a measurement can be performed without further sample preparation. An InGaAs detector is used to provide enhanced sensitivity and a rapid scanning capability. Principal Components Analysis (PCA) was performed to simplify positive identification of an MDMA tablet. When the possible grouping of spectral data was confirmed based on the PCA program, a library was established. For establishing the PCA data library, 40 types of tablets were analyzed, namely 25 types of over-the-counter pharmaceuticals, such as gastrointestinal drugs, one type of amphetamine (AP), eight types of MDMA (street name: ecstasy), three types of methamphetamine (MA), and three types of MDA (street name: the love drug). The utility of a simple identification system was examined by the investigation of the algorithm, the calculation parameters and a threshold established from comparison of the search results from randomly selected tablets. Figure 1 shows a photo of the diffuse reflection system installed in the VIR-9650. The tablets were placed on the sample holder directly, as shown in Figure 2. In the case of an extremely small tablet, unable to be placed on the holder, the sample was placed in a test tube like the one shown in Figure 3, and measured.

Figure 1 VIR-9650 and the diffuse reflection accessory

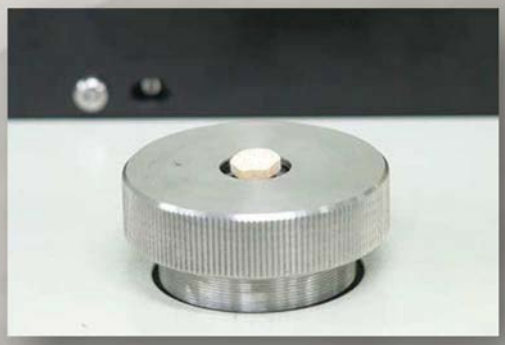


Figure 2 Measurement of a tablet

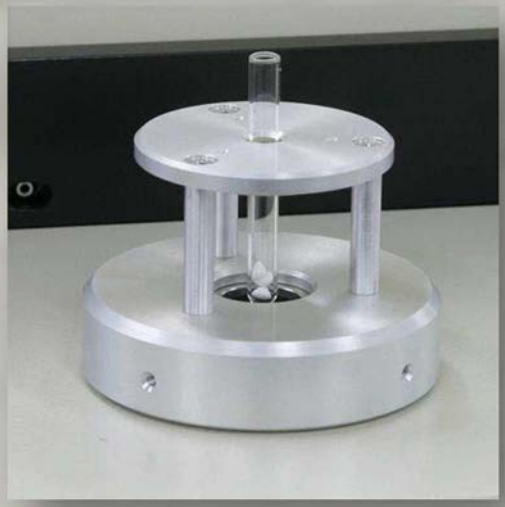


Figure 3 Measurement of crushed and powdered samples

Experimental Results

Figure 4 illustrates the PCA analysis results for an MDMA tablet. Figure 5 includes examples of the Near-Infrared spectra for the 4 classes of illegal drugs. Sample identification can be accomplished by using the region (indicated by the arrow) where the spectral absorptions can provide specific peaks depending on the tablet component.

Rapid Identification of an Illegal Drug using NIR (Identification of MDMA Tablet)

The PCA method, however, provides distinct discrimination between the various drug components due to subtle variations in the NIR spectra. Since NIR spectra do not provide specific discriminatory peaks like mid-IR spectra, the PCA method offers an enhanced discrimination of the various drug components, strengthening the identification of the 'unknown' drug tablet. The NIR diffuse reflection system is ideal as a rapid analysis method because the tablet is simply placed on the accessory platform and the required sample measurement time is only 10 seconds. This method will become more powerful for sample identification as the library data is expanded with additional standard sample data. Figure 6 demonstrates a calibration model illustrating the correlation between tablets containing MDMA and quantitative results of these tablets using GC analysis. With a correlation coefficient of R=0.966, these results demonstrate a sufficient correlation for performing sample quantitation. This would make it possible to analyze the amount of MDMA in illicit tablets by linking the search results of the identification program with the calibration model developed using GC analysis. Figure 7 is an example of the program developed for the identification of the drug formulations using the PCA search method.

Conclusions

We have demonstrated the use of a NIR analysis method utilizing PCA discrimination for the identification of various drug formulations. The NIR system demonstrates a rapid, nondestructive analysis method for various drug tablets that can be extended to provide quantitative analysis of the drug concentration.

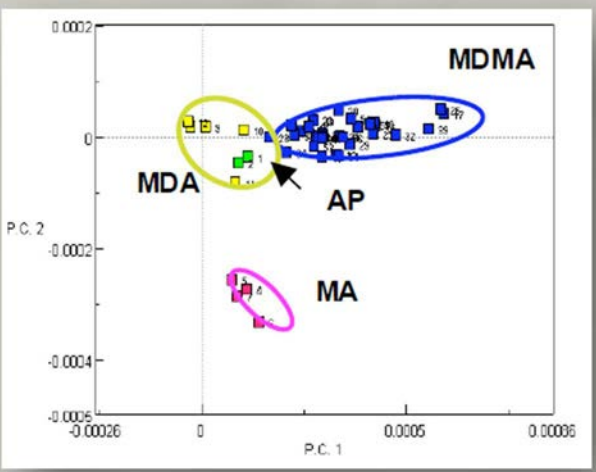


Figure 4 PCA analysis results for street drugs

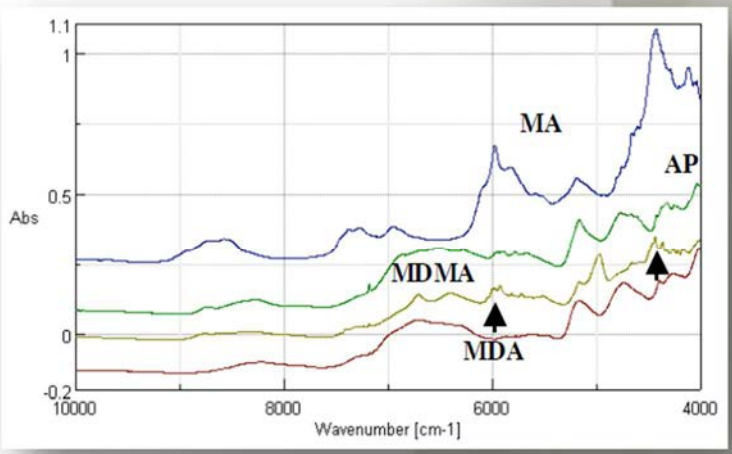


Figure 5 Diffuse reflectance spectra of various street drugs

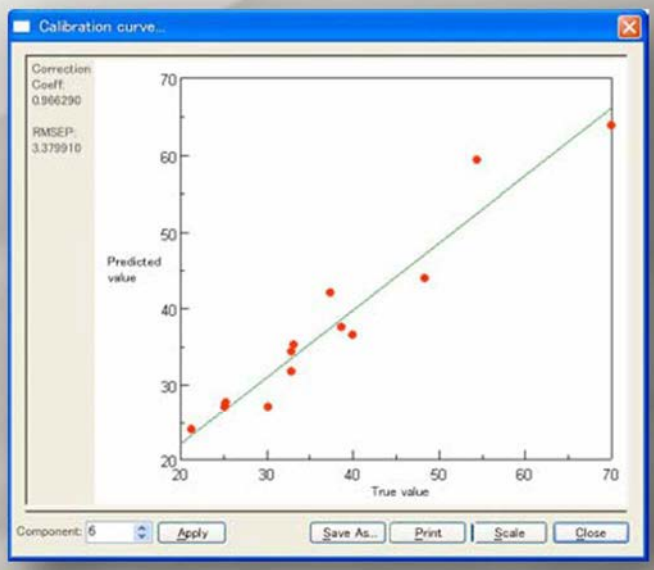


Figure 6: Calibration curve of NIR and GC results for MDMA

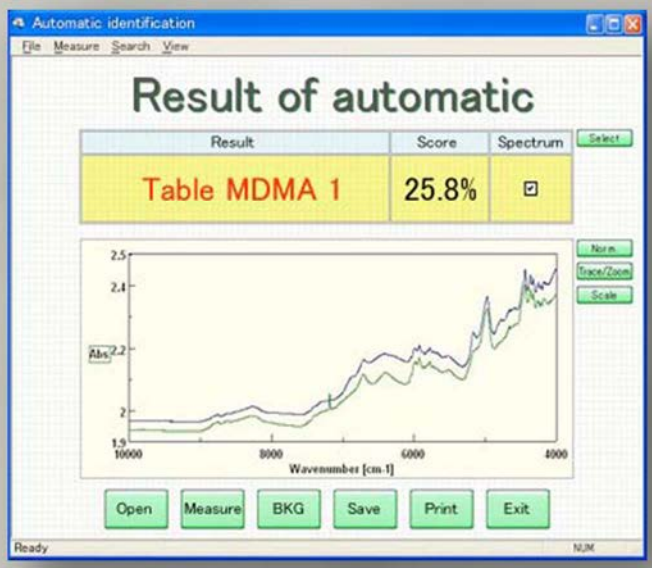


Figure 7 Confirmation test and quantitative analysis result

The measurement of filler (particles of facial cleanser) by using Clear-View ATR

Introduction

IR Microscope has been widely used for the identification of object or for imaging measurement because of the capability of molecular structure analysis of the small object. The microscope ATR method not only makes measurement easy since no sample pre-treatment is necessary, but also is a power tool for the sample or particles as small as less than 5 mm, such as filler, which is in principle difficult to measure by the ordinary transmission / reflection method. However the normal microscope ATR method is not suitable for the measurement in case that sample moves or is crashed when the prism touches sample tightly, since the sample has to be located in the center of the prism while the direct observation of sample is impossible by such method. Microscope IRT-5000 and IRT-7000 are equipped with the standard smart mapping function, which enables the correct measurement even if the sample is not center-located. Furthermore, the Clear-View ATR (series of ATR-5000-S) is developed for observation of the sample even when the prism touches tightly the sample. This report describes the measurement of tiny object (the black particles in the facial cleanser) as a model sample of filler being contained in the fluid sample by using IRT-5000 and Clear-View type ATR (ATR-5000-SS). By this experiment, the molecular structure of the black particles was clearly determined, and hence the functionality of the particles was estimated.

Experimental

The black particle in the liquid of the paste of the facial cleanser being marked by the red square as shown in Fig. 1 was measured as a model sample of filler. The observation image in Figure 2 shows the state when ATR prism is touching the sample tightly. The scattered black particles due to tight contact can be observed through the clear-view ATR. IRT-5000 smart mapping function makes it possible to start the mapping measurement when viewing the sample.

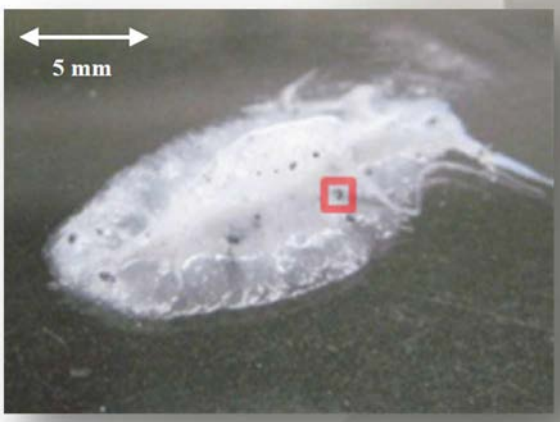


Figure 1 Face cleaner picture

Measurement conditions

Instrument: FT/IR-6100 + IRT-5000
Detector: Narrow-band MCT
Resolution: 8 cm-1
Accumulation: 16 times
Objective: ATR-5000-SS (ZnS Prism)
Measurement spot: 37 x 37 (Smart mapping)
Aperture size: 5 x 5 um
Measurement area: 180 x 180 um

Result and Discussion

Spectra of the paste part and black particles are shown in Figure 3 (Those spectra are processed by ATR correction for the possibility of abnormal dispersion). Judging from the spectra, the main component of both can be identified as Glycerin. The result of further database search for the subtraction of two spectra shows that the cellulose is contained in the black particle (Figure 4). The contour plot of the peak height at 1056 cm-1 ascribed to glycoside bond of cellulose is shown in Figure 5. It is confirmed that the cellulose is evenly distributed to where the black particles are scattered as seen in the observation image. It is assumed that the black particles adsorb the surplus sebum and perspiration, while the liquid of paste washes the dirt and keep the skin moisturized.

The measurement of filler (particles of facial cleanser) by using Clear-View ATR

The combination of IRT-5000 and Clear-view ATR makes it possible to measure the small object in the fluid sample, which was not possible in the past. It is considered as an effective approach to measure the functional filler, and the tiny object in the fluid sample, such as food, liquid crystal etc.

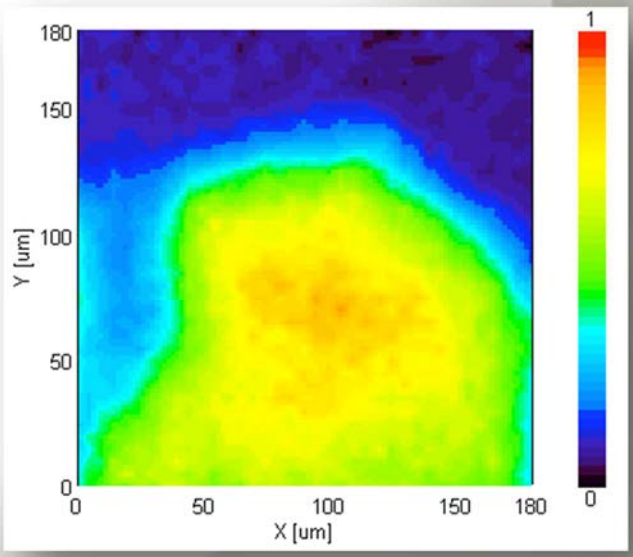


Figure 5 Peak of Cellulose(1056 cm-1)
Contour plot of peak height

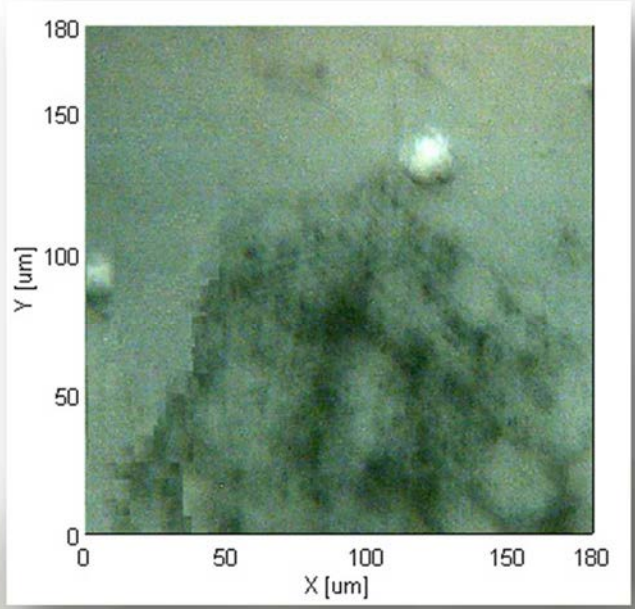


Figure 2 ATR-5000-SS Observation image

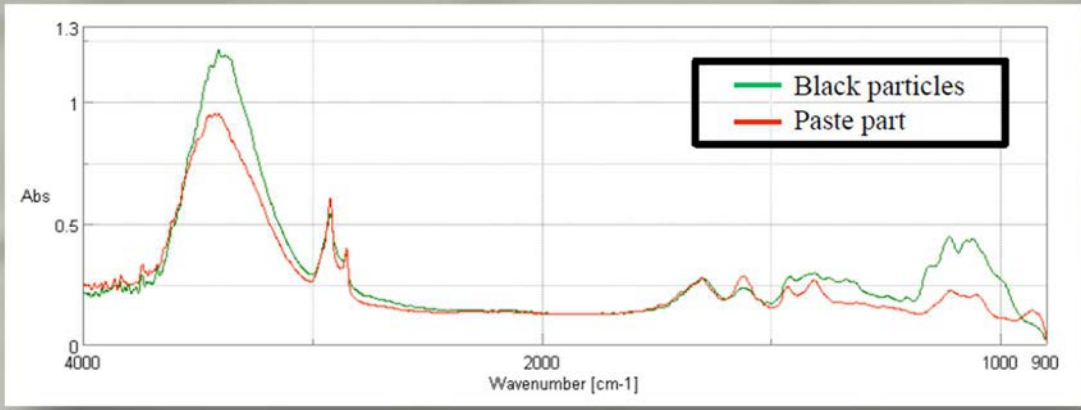


Figure 3 Spectra of the paste part and black particles (After ATR correction)

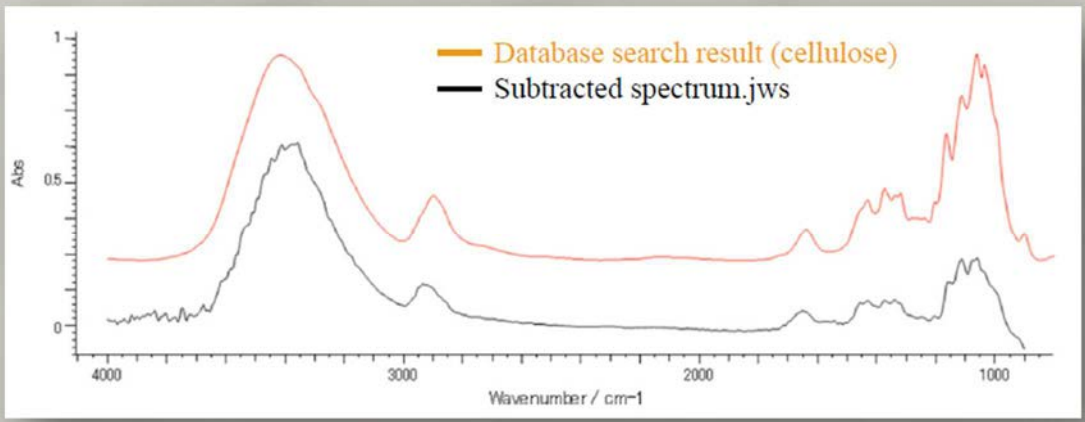
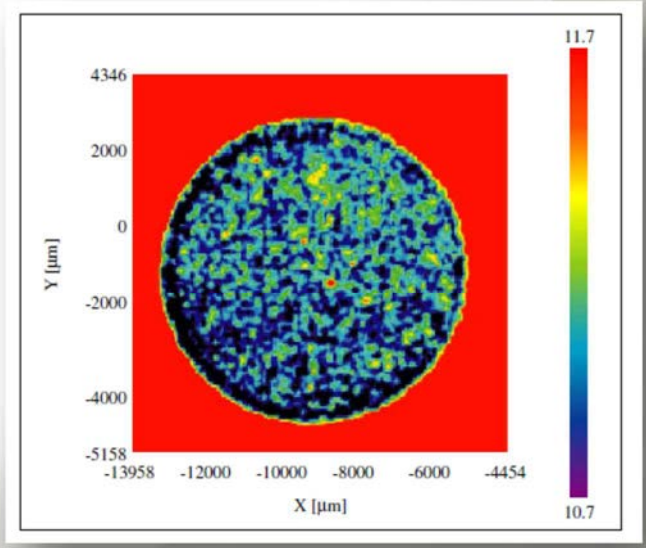


Figure 4 Database search result of the subtracted spectrum of Figure 3

Pharmaceutical tablet characterization using NIR Imaging

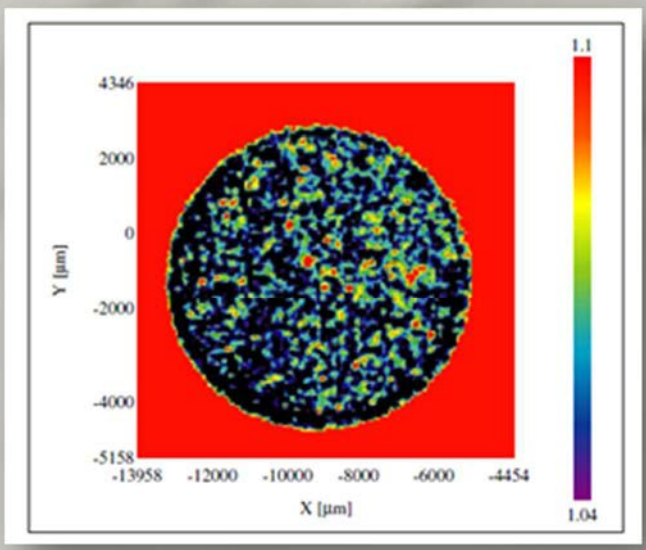
The use of near-infrared (NIR) spectroscopy in the pharmaceutical industry has grown rapidly in the past decade. The IMV-4000 Infrared Multichannel Viewer integrated with a NIR capable FT/IR-4000 or FT/IR-6000 instrument enables NIR Imaging of pharmaceutical tablets, a valuable tool in the estimation of tablet properties, offering measurement data with high specificity and sensitivity. The obtained data can be exported into the Principal Component Analysis (PCA) software for the estimation of tablet characteristics.

Instrument: FTIR-6200 with IMV-4000
CaF2 beam splitter, NIR source, etc
Sample: Antimotion-sickness drug
Measurement mode: Reflectance mode
Measurement area: 10 mm x 10 mm
Measurement points: 100 x 100
Accumulation: 64 scans



PCA mapping

Sample



Peak height (1935 nm)

Applications for the IMV-4000 Multi-channel Infrared Microscope

Over the last two decades, IR microscopy has been widely utilized to identify increasingly smaller samples. Incorporation of a linear array detector and rapid scanning in a FT-IR microscope permits high-speed FT-IR spectroscopic imaging, with applications in semiconductors, polymers, the pharmaceutical industry, biomaterials research and other areas. JASCO's IMV-4000 offers the highest performance in the industry in terms of measurement speed and signal-to-noise ratio.
This report describes the system configuration and several applications of the IMV-4000.

Introduction

Over twenty years have passed since infrared micro-spectrometers (micro-FTIR) were first used in microscopic characterization. As well as measuring the spectra of microscopic sites, such as impurity analysis in manufactured products, early micro-FTIR was used for much the same purposes as normal FTIR. Recently, however, it has increasingly been used for analyzing the two dimensional distribution of samples such as natural products and polymeric materials, resulting in what is termed infrared imaging. Infrared imaging is recognized as a technique that measures the infrared spectrum at each in-plane point and then uses peak heights, peak areas and other criteria to visualize the molecular structure distribution. However, with conventional systems, it takes an extremely long time to complete the image since the method involves moving the sample on the stage with each measurement to obtain data for discrete points (Figure 1).

While the utility of infrared imaging is well known, this problem is probably the reason why the technique has not become more widespread. In the mid 1990's, an infrared microscope was proposed that would perform infrared imaging in a shorter time.
The proposed system featured a focal plane array (FPA) detector capable of nearly instantaneous wide area measurements. However, these detectors with many detector elements arranged on the focal plane (for example, 16 x 16 elements) are extremely expensive (Figure 1). Furthermore, high-speed data processing systems that could perform Fourier transforms on large arrays on interferograms are complicated, so the systems had to be combined with step scanning instruments.
Because of these two cost factors, systems using FPA detectors are extremely expensive and thus have never become widely used. JASCO has developed a multi-channel infrared microscope (IMV-4000) that uses an inexpensive linear array detector, with fewer elements than an FPA detector. The IMV-4000 is an infrared microscope that incorporates a 16 x 1 element linear array MCT detector. By combining the system with a fast-scan FTIR, a high precision auto-stage, a linear array MCT detector and a high-speed parallel data processing circuit, the IMV-4000 imaging system is capable of imaging up to 9,600 points per minute (Figure 1). The system demonstrates that it is possible to perform infrared imaging faster by a figure of two or more than imaging using a conventional single element detector. It has also made it possible to provide a fast infrared imaging system at less than half the price of systems featuring FPA detectors. In the following section, we discuss various measurement examples using the IMV-4000.

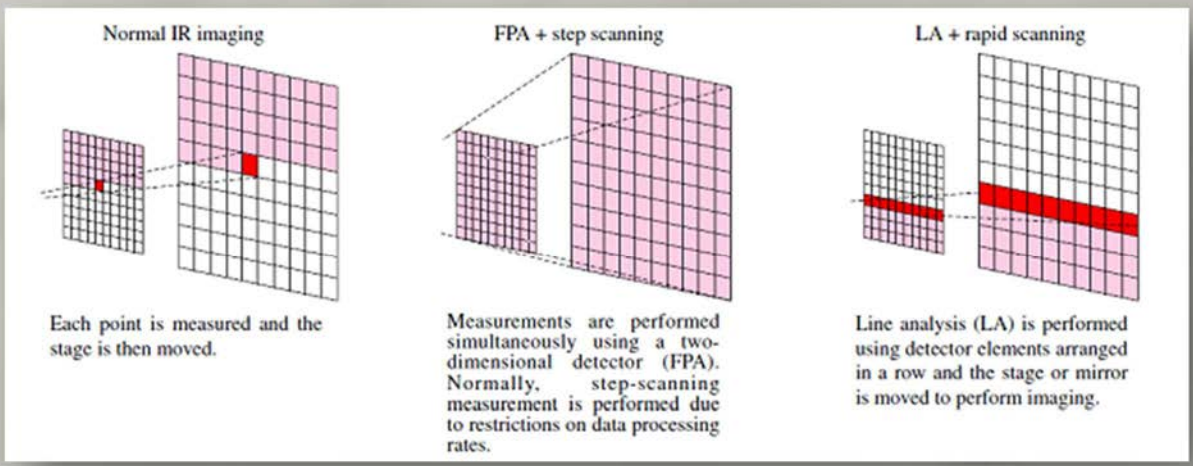


Figure 1 Principles of Multi-Channel Imaging

Applications for the IMV-4000 Multi-channel Infrared Microscope

Measurement Window

Figure 2 shows the computer software window during measurement. Since the IMV-4000 transfers data using a high speed parallel data processor, it can display spectra and peak intensities in real time. The top portion of the window displays the infrared absorption spectra from the individual detector elements and the bottom left portion shows a visible image of the measurement area captured by the CCD camera. The bottom right portion displays a color-coded infrared image of the peak intensity selected prior to the measurement. The sample displayed is a trademark seal for the circuit board of an electronic device. The measurement was done in reflection mode on a 6.2 x 1.75 mm area. Since the spatial resolution was 12.5 x 12.5 mm, 490 x 140 (60,440) points were measured. Spatial resolution is determined by the magnification of the cassegrain objective.

When the 16X objective of the IMV-4000 is used, a spatial resolution of 12.5 x 12.5 mm results while the 32X objective yields a spatial resolution of 6.25 x 6.25 mm. The measurement only required about 7 minutes. Since conventional single point imaging requires at least 5 seconds per point, conventional techniques would have required about 80 hours (including the time for moving the stage) for the same measurement. The IMV-4000 can therefore complete measurements in 1/700 the time of conventional instruments. The color coded image in the bottom-right portion of the window displays the peak intensity of the overtone of the C=O stretch near 3500 cm-1.

Since all data points are being measured as spectra, it is possible to reconstruct a color-coded image at any wave number using the data processing functions after measurement.

Analysis Example Demonstrating the Advantages of Fast Imaging

In this section, an example of a fast imaging experiment is illustrated. To maximize the utility of the imaging system, an imaging analysis program was developed in conjunction with the IMV-4000 imaging system. The imaging analysis program features a variety of computational and data processing functions for infrared spectra, based on the molecular absorption to be visualized, including color-coded images and "birds-eye" views.

The measurement examples discussed below were analyzed using this program. We will also illustrate a program that images molecular structure using a multivariate analysis technique and a tool that was developed for preprocessing samples.

This section discusses the results of measuring patterns on a silicon wafer in order to evaluate whether the visible image and the infrared image of the IMV-4000 match and to demonstrate the speed of the new instrument compared to the conventional technique. Figures 3 and 4 illustrate the measurement examples for patterns and impurities on silicon wafers.

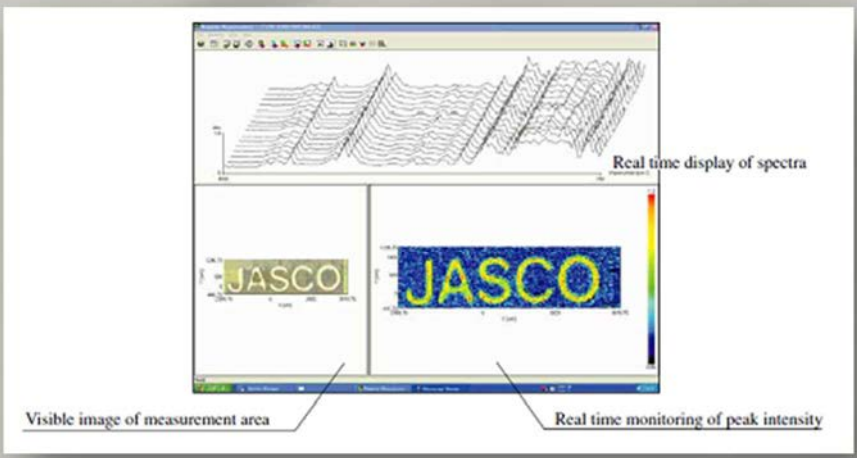


Figure 2 Measurement Window of the IMV-4000

Applications for the IMV-4000 Multi-channel Infrared Microscope

The measurement size of one point was 12.5 x 12.5 mm, since the measured area was 600 x 600 mm and a 16X cassegrain objective was used. Consequently, 48 x 48 (2,304) points were measured. A resolution of 16 cm-1 and 16 coadded scans were used to collect the data. Since visible light cannot penetrate the silicon wafer but infrared light can, the visible light image was captured in reflection mode and infrared imaging was performed in transmission mode.

Using the SiO peak near 1100 cm-1 as a probe, a color-coded image based on the peak intensity was created (Figure 3). The visible image and infrared images closely match. In addition, an impurity appears when a color-coded image is created using the peak near 2900 cm-1, attributed to the stretching vibration of -CH. After extracting and analyzing the spectrum of the impurity area, it was determined that the contaminant was a type of fatty acid. With conventional infrared imaging using a single element, it would have taken several hours to complete the measurement but we obtained data for 2,304 points in approximately four minutes.

Based on the above result, we confirmed that fast infrared imaging is possible. The infrared images and visible images correspond and the analysis of wafer patterns and impurities was facilitated. We measured impurities that could be verified using visible observation but there are also cases where transparent impurities affect product quality. In such cases, it is possible to identify the site of the impurity from an infrared image. When there is an impurity comprising multiple components, conventional techniques measure the heterogenous area and yield a spectrum in which the various components overlap, which may interfere with interpretation.

Infrared imaging enables easy identification of contaminants by spatially resolving them and measuring the contaminant directly.

This technique is expected to be a powerful tool in the analysis of a wide variety of samples.

Figure 3. Pattern Analysis of a Silicon Wafer

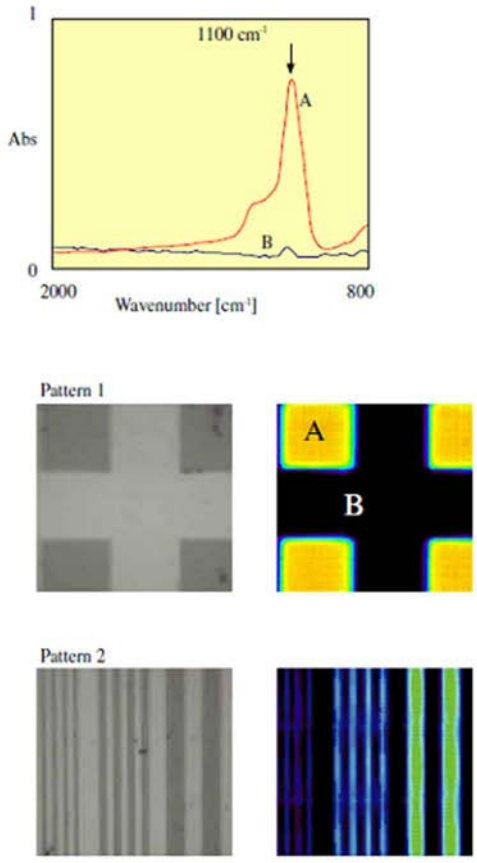
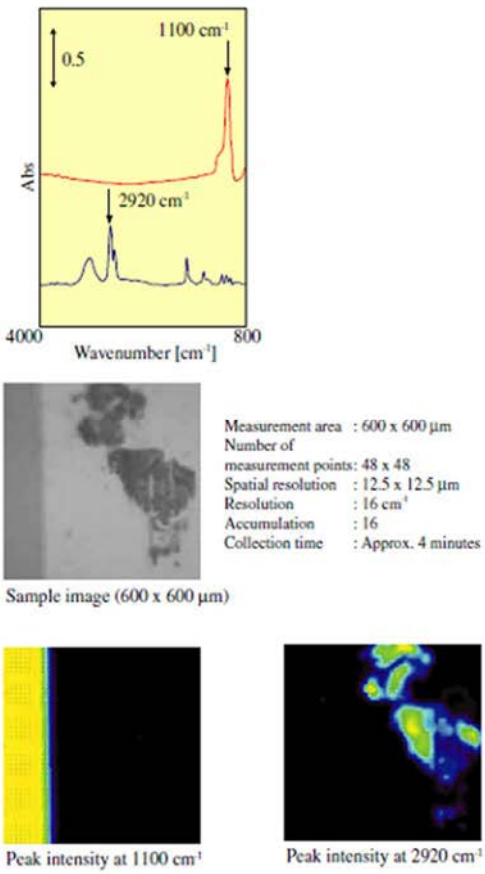


Figure 4. Impurity on a silicon wafer



Secondary Structure Analysis of Proteins using IR Imaging

The IMV-4000 enables infrared imaging by a figure of two or more faster than using a conventional single element detector. A technique that quickly analyzes the results is also desirable. JASCO has proposed an analysis of imaging data with a variety of multivariate analysis techniques to accelerate the processing of infrared imaging data. For example, we have made it possible to easily create a visualization of the distribution map for the various components of multilayer film by analyzing imaging data using principle component analysis (PCA). We have also created a model that performs secondary structure estimation (SSE) on proteins based on IR spectra by principal components regression (PCR) and partial least squares (PLS) regression. In the secondary structure estimation of proteins, crystallizing the protein and performing x-ray structural analysis and measuring aqueous solutions by NMR or CD spectra are all widely used. However, the estimation of the secondary structure of proteins while preserving the tissue structure in multicomponent systems such as biological structures is extremely difficult with those techniques. On the other hand, since IR spectra can be easily measured, even for non-crystalline samples, it is possible to perform analyses in a near italicize *'in vivo'* , this will make the term stand out from the rest of the sentence. state, without having to refine the secondary structure of the proteins included in living tissue. By the use of micro-FTIR, it is possible to perform spatial analysis while preserving the tissue structure. The measurement and analysis of a cancer biopsy sample has been reported for the secondary structure of proteins using imaging data.[1)]

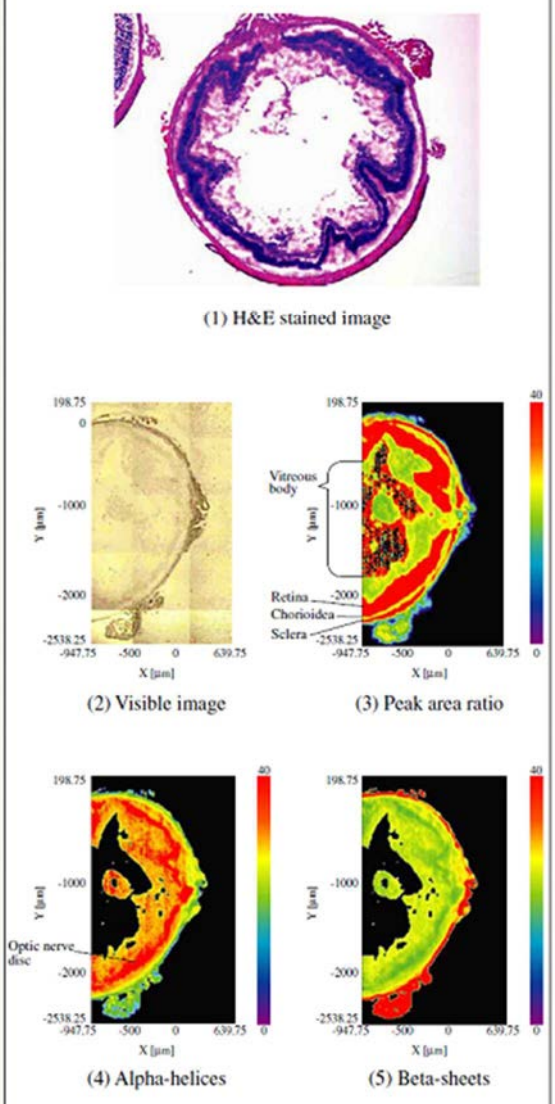
We performed infrared imaging on slices of a mouse eyeball using the IMV-4000. We analyzed the IR spectra of each using primary component regression (PCR) and created an in-plane distribution map of the secondary structure of proteins (Figure 1). The measured area was 2750 x 1600 mm and the measurement size was 12.5 x 12.5 mm since a 16X cassegrain objective was used. 128 x 220 (28,160) points were measured. There were four integrations and the spectral resolution was 8 cm-1. The slice was placed on BaF2 (10mm diameter and 1mm thick) and measured in transmission. Figure 1-(1) shows an H&E (Hematoxylin and eosin) -stained image of the slice and Figure 1-(2) shows a visible image of the measurement area.

Figure 1-(3) shows the ratio of the absorption peak of amide I (near 1640 cm-1) and the peak of the stretching vibration (near 2900 cm-1) of the -CH base. In addition, Figure 1-(4) and (5) shows the distribution maps for the alpha-helix and beta-sheet of the protein. We were able to confirm the correspondence between the H&E stained image and each tissue. In addition, the site corresponding to the two-layer retina and optic nerve disc has an alpha-helix structure and is believed to show proliferation potential. By studying diseased samples, it is hoped to analyze the cause-and-effect relationship between disease and the structure of proteins.

Rererences

(1) Yamada, T., Miyoshi, N., Ogawa, T., Akao, K., Fukuda M., Ogasawara, T., Kitagawa Y., Sano K., Clinical Cancer Research. 8, 2010-2014 (2002)

Figure 1. Measurement Example for a Slice of Mouse Eyeball



NIR Imaging of tablet surface by using IR Microscope

Introduction

Near IR light is widely used for non-destructive analysis as an evaluation method in food and pharmaceutical industry due to it's characteristics such as transmitting the glass container and weaker peak absorbance than Mid-IR light. Recently, this NIR analysis technique is introduced to the Process Analytical Technology which has been proposed by FDA, and it is used for evaluation of uniformity of mixed samples inside of vials, evaluation of water content by in-line measurement, and evaluation of contents in tablet by using of NIR microscope. There are are various analysis methods using NIR spectroscopy such as dispersive type, filter type and AOTF type, while FTIR is considered to be better method due to several advantages such as wave number expandability, high through put and high accuracy of wavenumber.

JASCO IR Microscope system IRT-5000/7000 has a unique feature as option which is detachable detector unit, which makes it possible to extend the measurement range up to NIR in one single FT/IR system. This time, we analyzed the distribution of components on tablet surface by NIR imaging system which consists of FT/IR-6100 and IRT-7000 with NIR expansion.

Figure 2 IR Microscope IRT-7000

Experimental

Imaging of cross section and surface of general medical tablet (pain-killer) was measured by using NIR Microscope system.

Measurement Condition

- Multi channel IR Microscope (NIR version)
- Light source : Halogen
- Beam Splitter : CaF2
- Detector : InGaAs (Single element)
- Measurement mode : Reflection
- Resolution : 8 cm-1
- Accumulation : 50 times
- Aperture size : 200×200 µm
- Measurement points : Surface : 58 x 58 points
- Cross Section : 30 x 40 points

Figure 1 Detector replacement by using detachable detector unit

NIR Imaging of tablet surface by using IR Microscope

Result

Figure 3 shows NIR spectra obtained by measuring the point in each layer on cross section of tablet. Figure 4 is NIR Imaging which describes the color distribution map utilizing the height of each specific peak. As the result, this imaging data (Fig. 4) indicate that this tablet consists of 3 components in 4 different layers.

In addition tablet surface was measured and the color distribution map of surface layer was obtained by utilizing the peak height ratio of Acetylsalicylate. This result clearly shows non uniformity of surface material as shown in Figure 6.

As a conclusion, it can be said NIR Micro Imaging system enables to visualize tablet surface by nondestructive method. Such application is considered to be a very useful tool and solution in the fields of pharmaceutical development and quality control, where there are uncertain factors during the process.

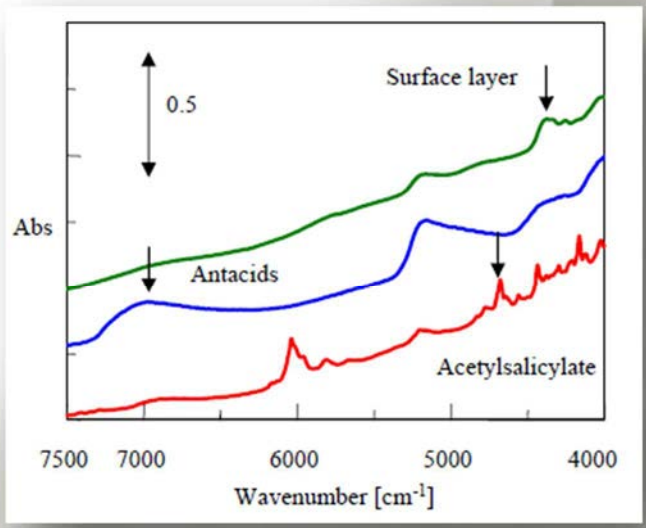


Figure 3 NIR Spectra of each elements

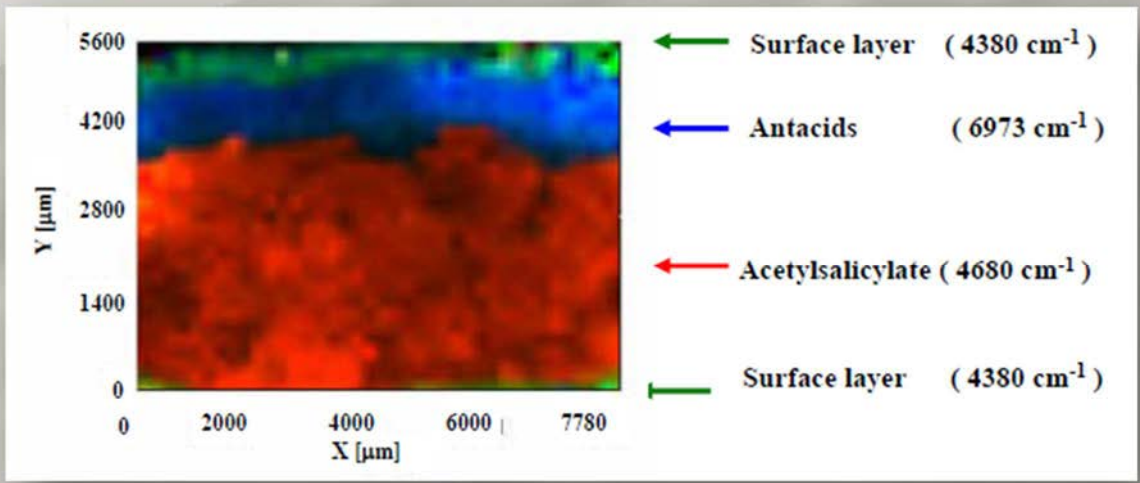


Figure 4 NIR Imaging of tablet cross section

Figure 5 Picture of general medical tablet (Pain-killer)

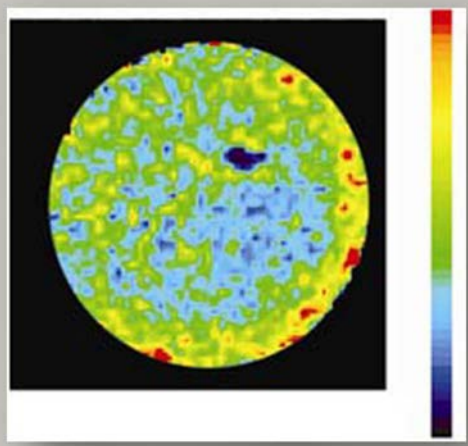


Figure 6 Imaging of surface layer Peak ratio : 4380 cm-1 / 4680 cm-1

Quantitative Analysis of Biodiesel (FAME) in Diesel Fuel by FT/IR

1. Introduction

In recent years, Biodiesel fuel made from vegetable oils or cooking oil waste by a transesterification process has been receiving much attention as an alternative energy to processed fossil fuels. The chemical process of transesterification from vegetable oil to FAME is shown in Figure 1.

The ASTM International and the EN European standards stipulate the determination of fatty acid methyl ester (FAME) in diesel fuel oil and many countries use either neat or blended FAME as biodiesel fuels in accordance with these standards. Since the guidelines differ from country to country for the ratio of FAME blended in diesel oil and other conditions, a simple quantitative analysis method for the determination of FAME in diesel fuel is imperative. The test method of FAME by FT/IR for both the ASTM and the EN standard are shown in Table 1.

The ASTM standard requires the ATR method and the EN test method specifies a transmission method. FAME derived from soybean oil used in European industry was used as a sample and a calibration curve model compliant with each standard method was derived. The measurement results obtained are outlined below.

2. Quantitative Analysis of FAME for ASTM

Figure 2 outlines the infrared spectra of FAME and diesel fuel measured with the ATR method. The PLS calibration curve derived from the standards are shown in Figure 3. The PLS calibration curve was constructed according to the conditions outlined by ASTM using standards that contained the FAME component in the range of 1-10% and using the ATR method. The results demonstrate that PLS and the ATR method is a good combination, which makes reliable results possible without diluting the sample.

	ASTM (D7371-07)	EN14078
Measurement method	ATR method	Transmittance using liquid cell
Wavenumber range	4000-650 cm-1	4000-400 cm-1
Software	PLS Quantitative Program	Quantitative analysis program
Instruments	JASCO FT/IR-4100 FT/IR Spectrometer	
Resolution	4 cm-1	
Other measurement conditions	Accumulation: 32 times Accessory: ATR PRO450-S (ZnSe)	Accumulation: 32 times Accessory: Sealed Liquid cell Window material: CaF2 Pathlength: 0.5 mm

Table 1 Standard Test Methods of FAME by FT/IR

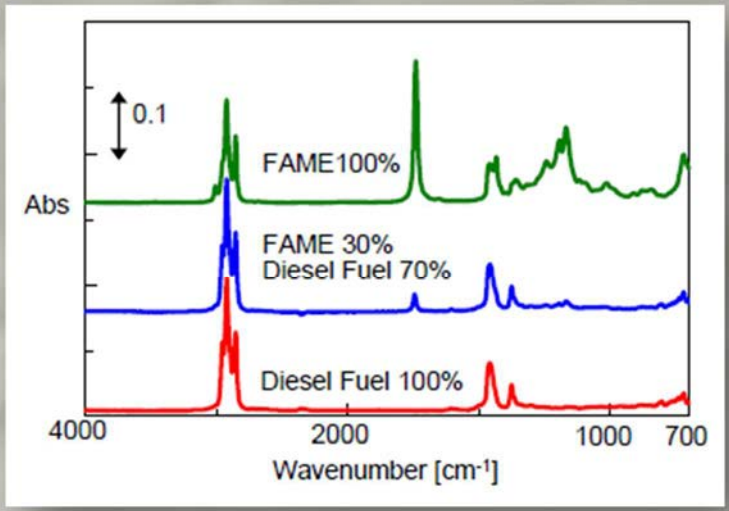


Figure 2 IR spectra of FAME and diesel oil (ATR method, resolution: 4 cm-1, accumulations: 32 times)

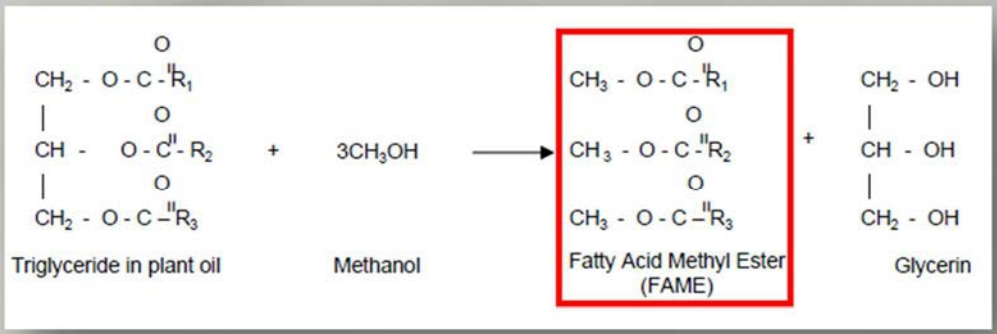


Figure 1 Reaction pathway from vegetable oil to FAME

Quantitative Analysis of Biodiesel (FAME) in Diesel Fuel by FT/IR

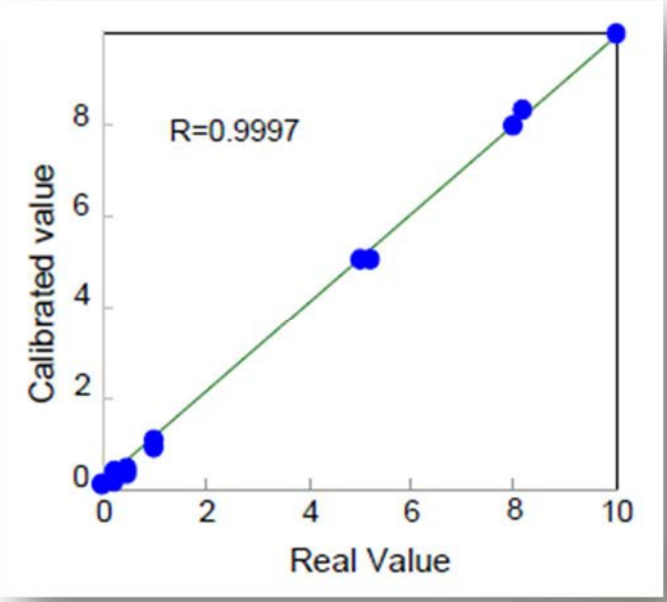


Figure 3 PLS calibration curve of FAME
Calculation range: 1800-1692, 1327-940 cm-1,
No. of Factors: 3

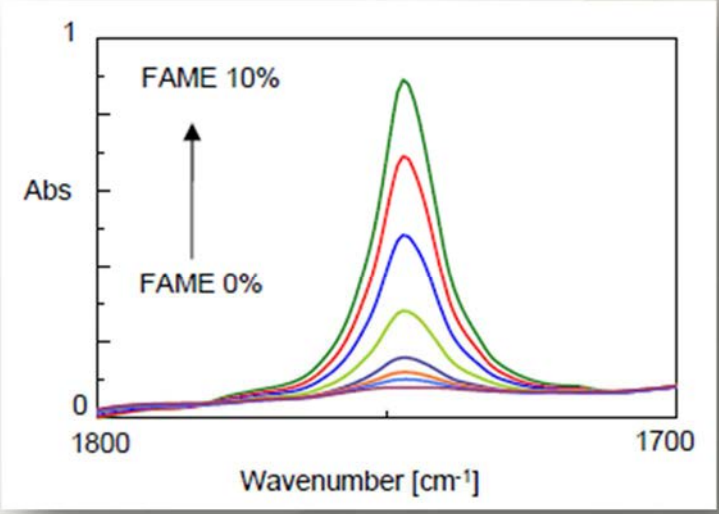


Figure 4 Peaks of FAME
(Transmission, resolution: 4 cm-1,
Accumulation: 32 times)

3. Quantitative Analysis of FAME for EN

Figure 4 shows the overlaid peaks for FAME around the 1750 cm-1 band from the spectra of the standards obtained by the transmittance method. The standard samples were prepared by mixing 0 - 10% FAME with diesel oil and then diluted 10X in cyclohexane. The calibration curve for the FAME concentration was made by measuring the peak at 1750 cm-1 with the standard Quantitative Analysis program as outlined in Figure 5.

The results indicate that a linear calibration model was created for the EN standard although the method for the EN standard requires dilution of the sample in cyclohexane.

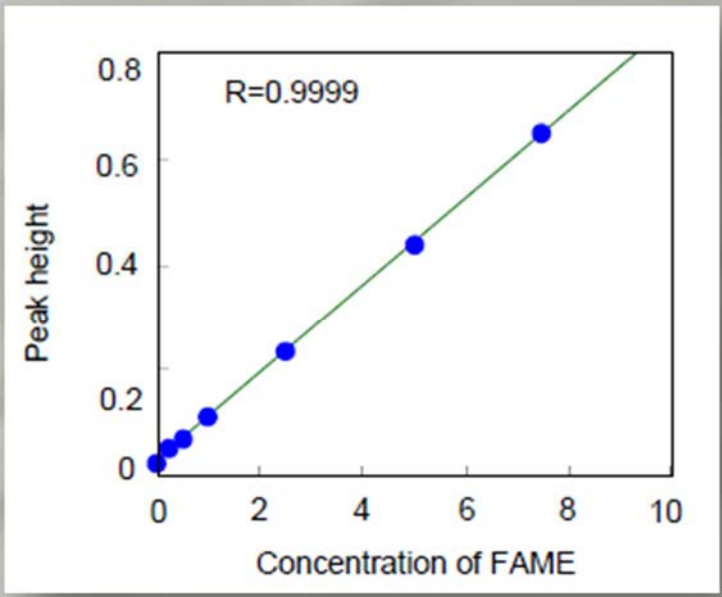


Figure 5 EN calibration curve of FAME

Measurement of Oriented Films and Liquid Crystal Molecules by a Polarized ATR Accessory

1. Introduction

The development of advanced materials, particularly liquid crystals and macromolecules, requires the ability to control and analyze the molecular orientation of these compounds. Molecular orientation is generally analyzed by a method based on birefringence, an X-ray diffraction method that provides information on the solid crystallinity, or infrared spectroscopy, which yields information on molecular vibrational activity. With infrared spectroscopy, orientation is evaluated by measuring the polarization characteristics of the sample with a polarizer placed in the optical path. A polarized ATR accessory has been developed that allows measurements of sample polarization based on the ATR effect and allows analysis of the molecular orientation on sample surfaces in the 1-2 µm range. This technique permits the analysis of molecular orientation on sample surfaces regardless of sample thickness or material. A method for analyzing the molecular orientation of oriented films along a stretched axis within the plane (MD); along a transverse axis within the plane (TD); or along an axis of depth (OP) is described below. When a stretched film is aligned with the axis along which the light beam travels and the film is irradiated by a light beam polarized perpendicular to the sample (s-polarized), information can be obtained on the orientation along the y-axis (perpendicular direction), as shown in the upper left of Figure 2. When a sample is irradiated by horizontally polarized (p-polarized) light, information for the x-axis (stretched direction) and z-axis orientations (axis of depth) can be analyzed, as shown in the upper right of Figure 2. By rotating the sample 90º and irradiating it with a perpendicularly polarized (s-polarized) light beam, information can be obtained for the orientation along the stretched direction, because the sample is positioned as shown in the lower left of Figure 2. Irradiating a sample in this position with a horizontally polarized (p-polarized) light beam yields information for orientation along the transverse axis and axis of depth, as shown in the lower right of Figure 2. This is summarized in Table 1. By calculating the peak intensity for each spectrum obtained, information can be obtained on all molecular orientations, MD, TD, and OP. Changing the direction of the sample and the angle of the polarizer allows three-dimensional analysis of sample orientations.

2. Features of the polarized single-reflection ATR accessory (ATR PRO610P-S, ATR PRO630P-H)

Polarized ATR (Figure 1) provides high polarization purity because the polarizer and analyzer are configured immediately in front of and behind the ATR prism. Removing the polarizer and analyzer makes it possible to use this accessory for standard ATR measurements. The ATR PRO630P-H provides a high-pressure contact option for measurements of samples that require greater crystal contact.

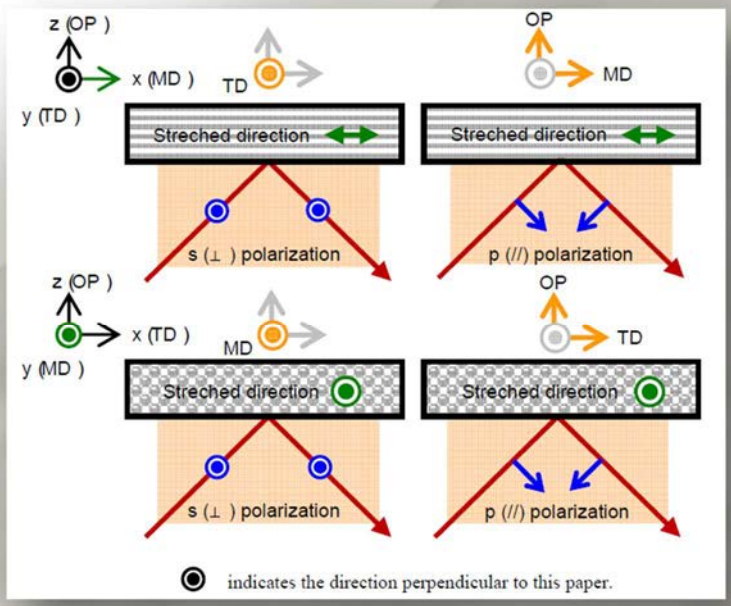


Figure 2 Relationship of the direction of polarizer and stretched axis of the oriented films

Direction of sample	p-polarized	s-polarized
X-axis is stretched axis	MD&OP	TD
Y-axis is stretched axis	TD&OP	MD

Table 1 Obtained information of each direction of samples and polarizer

3. Results and discussions

3.1 Measurement of oriented polypropylene (PP) films

An oriented PP film was measured using four different sample orientations (Figure 2) and the orientation of the surface was evaluated. The result is shown in Figure 3.

Measurement Conditions

System: FT/IR-4100 Resolution: 4 cm-1
Detector: DLATGS Accumulations: 200
Accessory: ATR PRO610P-S (Prism: Ge)

The spectral differences in the region of 1500 to 700 cm-1 indicate that this PP film is composed primarily of isotactic PP and that the sample is oriented.

Measurement of Oriented Films and Liquid Crystal Molecules by a Polarized ATR Accessory

If the sample is rotated 90º, the difference is greater for s-polarization, which does not include information along the axis of depth. To evaluate the state of orientation along the vertical and stretched directions, a sample was irradiated with s-polarized light after rotating the sample and setting the stretched direction to the x direction, and then to the y direction. The degree of orientation was calculated using the peak heights at 809, 841, and 998 cm-1 in the measured spectra. These calculations yielded a figure of 0.95, which closely agrees with measurements obtained by the transmission method. These results suggest that the state of orientation of the measured PP film sample is similar throughout the film and at the surface to a depth of approximately 1 µm to 2 µm.

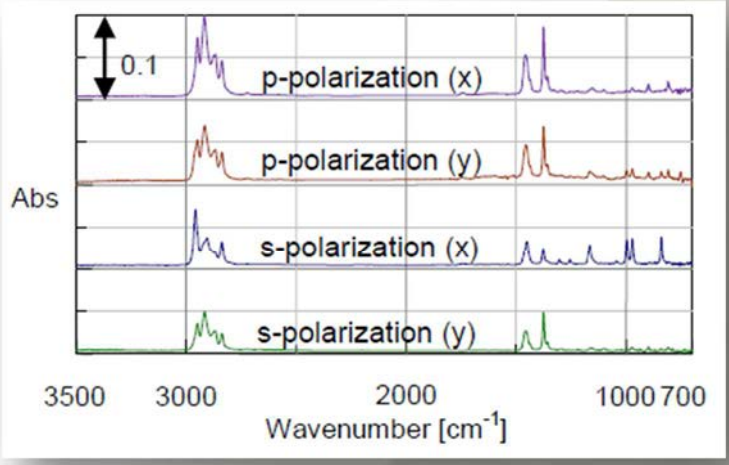


Figure 3 Spectra of a PP film measured by polarized ATR
*Figures in parentheses show the direction of film stretching.

3.2 Measurement of liquid crystal molecules

Normal twisted nematic liquid crystal (TN liquid crystal) molecules were irradiated with p-polarized and s-polarized light beams and the differences were measured. Since liquid crystal molecules are highly fluid, the sample was not rotated for this experiment. The polarizer can be rotated without moving the sample, allowing orientation evaluations of a liquid sample without altering the sample conditions. The measurement results are shown in Figure 5.

Measurement Conditions
System: FT/IR-4100 Resolution: 4 cm-1
Detector: DLATGS Accumulations: 64
Accessory: ATR PRO610P-S (Prism: ZnSe)

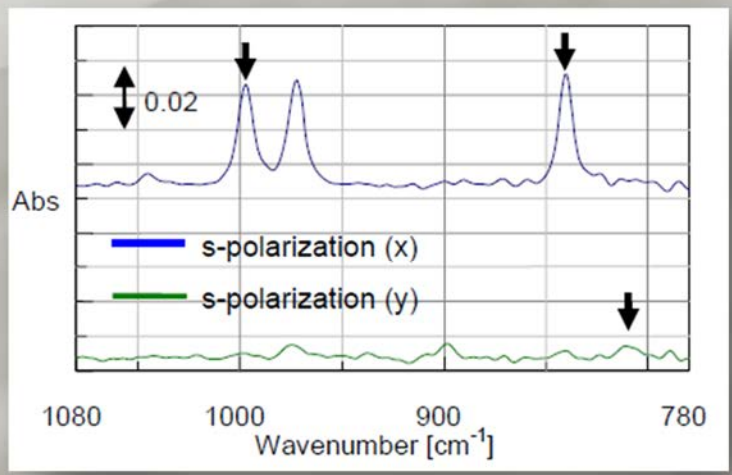


Figure 4 Enlarged peaks used calculation of degree of orientation

A close look at the absorption peak near 2230 cm-1, a peak assigned to the nitrile group at the end of the liquid crystal molecule, shows that the peak is larger when measured with s-polarized light than with p-polarized light. For quantitative processing of the results, the ratio of the absorption of the peak near 2230 cm-1 along the z axis (depth) to absorption in the xy plane was calculated. Due to sample fluidity, the xy plane was assumed to have no orientation. Calculations give a ratio of approximately 0.002 (z direction/xy direction), indicating that the nitrile group is oriented within the xy plane parallel to the prism. This result is consistent with the knowledge that the chains are oriented (inclined) within a plane in TN liquid crystals in the absence of an electric field. Analyzing other absorption peaks that show differences make it possible to achieve a more detailed understanding of the oriented state of such molecules. As described above, polarized ATR spectroscopy is useful for rapidly and non-destructively measuring and evaluating the surface state of oriented molecules, such as film and liquid crystal compounds. The analysis results can also be used to calculate the degree of orientation for each vibrational mode and for quantitative evaluations of orientation along the axis of the molecular depth.

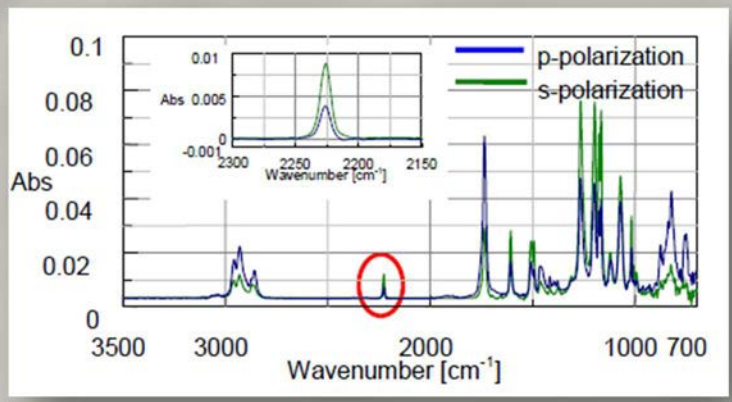


Figure 5 Spectra of a TN crystal measured by polarized ATR

Microscopic ATR Measurement of Thin Polyimide Film on Silicon Substrates

The micro-ATR method, which can measure in situ, is extremely convenient for measuring the processing film on the surface of microelectronic components. The following is as example of measuring a thin polyimide film on a silicon substrate (300 µm thick), which is normally somewhat difficult to do. Fully keeping the sample surface and prism surface in contact without destroying the fragile silicon substrate requires that the packing on which the sample is placed be horizontal. Failing to do so will damage the substrate. In our example, we used Parafilm, which is thin and has elasticity, as our packing material to successfully measure the silicon substrate. The micro-ATR method uses a single reflection, but by fully keeping the prism and sample surface in contact, it is possible to get the excellent spectrum you see in Figure 1.

Measurement conditions
Attachment: Micro FT/IR
Micro ATR + ZnSe prism
Accumulation: 100
Resolution: 8 cm-1
Aperture: 100 µm x 100 µm

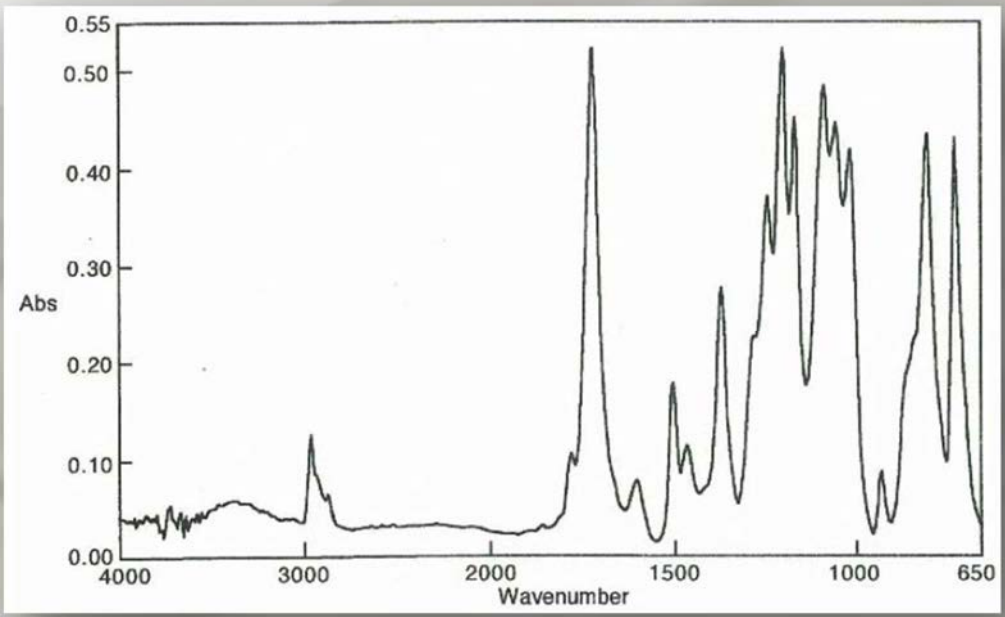


Figure 1 ATR Spectrum of a Polyimide Layer on a Silicon Substrate

Evaluation of a Si Wafer Surface using a 65-degree Incident Angle ATR

1. Introduction

Measuring the surface of a Si semiconductor substrate or other materials is required knowledge of the surface or contamination condition of thermally oxidized films that function as an insulating film for the semiconductor. For the surface analysis, such techniques as XPS (X-ray photoelectron spectroscopy, ESCA) and SIMS (secondary ion mass spectrometry) are popularly employed, and such methods provide elemental information on the sample surfaces. On the other hand, infrared spectroscopy (IR) easily obtains information on the molecular bonding condition, which cannot be analyzed by XPS or SIMS in a non-destructive manner. For the surface analysis using mid-IR, the ATR method is popularly employed. For the 45-degree incident ATR, the most common configuration, measurement of samples of Si wafers with a high refractive index is difficult, since this configuration does not satisfy the total reflection conditions required for ATR measurements. With the single-reflection 65-degree incident ATR recently developed (Figure 1), a Ge crystal with a high refractive index (n = 4.0) is used for the prism, and the incident angle of light to the sample is set at 65 degrees, thereby obtaining information on the topmost surface and providing measurements of samples with a high refractive index, such as Si (refractive index=approx. 3.4) and carbon black filled rubbers whose refractive index can be 2.8 or higher. (See Table 1: JASCO FT/IR application data 280-AT-0003)

Figure 1
Single Reflection 65-degree Incident ATR (ATR PRO650G)

We recently executed measurements of a natural oxide film on Si wafer surfaces using a single reflection 65-degree incident ATR as an application example of the new ATR accessory.

2. Features of Single Reflection 65-degree Incident ATR (ATR PRO650G)

The ATR PRO650G (Figure 1) features a slip clutch pressure clamp to prevent damage to the sample or prism during application of pressure to ensure proper contact of the sample with the ATR crystal. Furthermore, a large sampling surface is available on the top panel, enabling measurements of the center portion of a sample, even as large as a six-inch Si wafer. In addition, since an optional polarizer and analyzer can be added to the light path, analysis of the molecular orientation of the sample surface can also be obtained.

3. Measurement Conditions

System: FT/IR-4100
Measurement Method: ATR method (Reflection: Single)
Resolution: 4 cm-1 Detector: DLATGS
Aperture: 3.5 mm Accumulations: 128 times
Accessory: ATR PRO650G (Prism: Ge)

4. Results and Discussion

Measurement was performed of a Si wafer surface on which a natural oxide film was present. For comparison purposes, the measurement was made using a 45-degree incident ATR and the transmission method. Figure 2 displays the overlaid spectra obtained of the measurement results using the 45-degree and 65-degree incident ATR accessories, and Figure 3 shows the spectra obtained by normalizing the measurement results of the transmission method and comparing to the spectrum of the 65-degree ATR.

Incident Angle	Prism	Lower Measurement Limit at Low Wavenumber Side	n_1	n_2	Penetration Depth (For 1000 cm-1, n_2=1.5)
65°	Ge	- 700 cm-1	4.0	3.6	0.48 µm
45°	Ge	- 700 cm-1	4.0	2.8	0.66 µm

Table 1 Comparison of 65-degree and 45-degree (Standard) ATR Accessories

n_1: Refractive index of prism
n_2: Upper limit of measurable refractive index of sample (Upper limit that satisfies the total reflection conditions)

Evaluation of a Si Wafer Surface using a 65-degree Incident Angle ATR

Figure 2, it can be seen that the spectrum of the 45-degree incident ATR does not satisfy the total refraction condition required for the ATR measurement, and the spectrum presents significant distortion, making it difficult to evaluate the surface condition.

On the other hand, with the 65-degree incident ATR, since the spectrum satisfies the total refraction condition, the spectrum does not present any distortion and the base line remains flat.

From Figure 3, the absorption peak in the vicinity of 1235 cm-1, which can be attributed to the natural oxide film, is noted, and a slight amount of organic contamination of the surface is present based on the peaks from 3000 to 2800 cm-1, which can be attributed to C-H adsorptions.

Also, the results obtained by the transmission method reveal absorptions in the vicinity of 1100 cm-1, which can be attributed to the Si-O in the Si wafer substrate, but the absorption peak at around 1235 cm-1 cannot be positively determined.

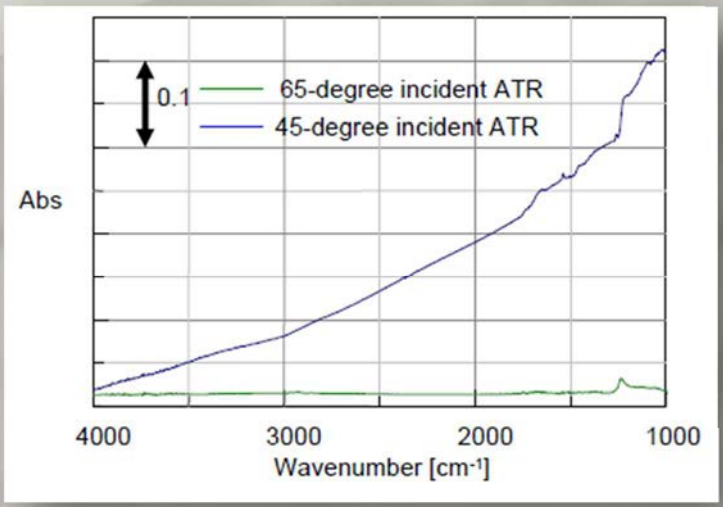


Figure 2 Oxide Film Spectrum on Si Wafer (Offset Indication)

These results demonstrate that using the 65-degree incident ATR enabled acquisition of information on the very surface of samples that could not be determined by using the transmission method.

Using the single refraction 65-degree incident ATR enables evaluation of the surface condition of substrates such as Si wafers with a high refractive index in a nondestructive manner.

In the future, applications for the qualitative and quantitative evaluation of the adhesion condition of organic substances on the Si wafer surface will be evaluated.

The quantitative evaluation of oxide films based on the peak height and area at around 1235 cm-1 and the estimation of SiO and SiO2 percentages in the oxide film will be examined.

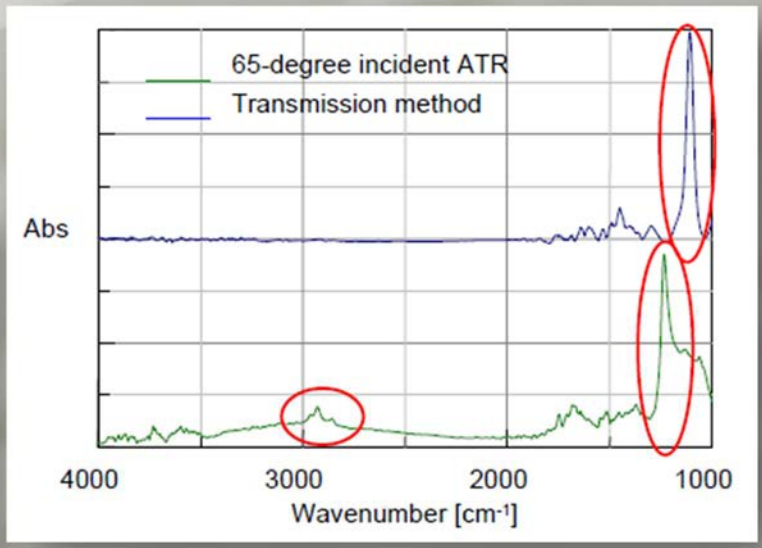


Figure 3 Oxide Film Spectra on Si Wafer (Standardized; Offset Indication)

Multiple components analysis by PCA mapping

Introduction

Mapping measurement with an IR microscope formally had problems such as difficult sampling and long measurement time. Now, the sample can be treated easily for example by using a tool like SliceMaster and the measurement time can be shortened to less than 1/10 by using a multi-element detector as compared with the traditional mapping system. However, although the mapping measurement itself became easier, much more time is needed for data analysis due to tremendous data points. This report shows some examples of analysis by PCA mapping which enables easier analysis of component distribution from mapping data.

Experimental

LCD color monitor shown in Figure 1 was used as a sample with the measurement conditions as follows:

Measurement conditions

Detector: Linear array MCT detector
Resolution: 8 cm-1
Accumulation: 64 times
Method: Transmittance
Cassegrain: 16 ×
Measurement time: approx.7 min
Measurement area: 587.5×187.5 µm (48x16 points)

Results and discussions

An observation image of the measured area on LCD color monitor is shown in Figure 1. Each spectrum obtained at the position of A, B and C in Figure 1 is shown in Figure 2. Since the spectra of A, B and C are similar and it is assumed that especially the discrimination of A and C is difficult. The spectra of the main components obtained by the Principle Component Analysis are shown in Figure 3. The spectrum of glass is seen in common among A, B and C in the first main component. The peaks of red pigment from B are observed in the third main component and some very small peaks of A, B and C which are very difficult to be recognized also can be seen in the fifth main component. It is considered that the third and fifth main components represent the specific peaks for each main component and the identification of the components were attempted by plotting the score value of the third and fifth main components shown in Figure 4.

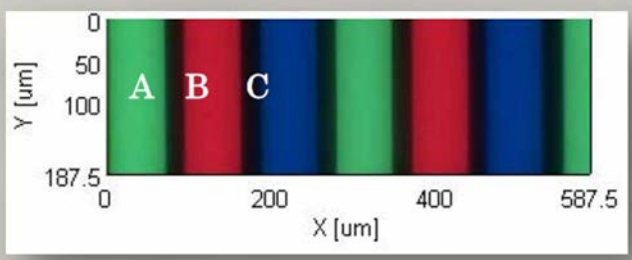


Figure 1 LCD color monitor
(Observation image of the measurement area)

As shown in the area surrounded with dotted line in Figure 4, the plotted score values of the third and fifth main components are eccentrically-located in 3 areas. In PCA mapping, setting color coding of each group from the plot values in the graph in Figure 4 enables to obtain the color distribution diagram shown in Figure 5. In this way, the Principal Component Analysis is considered to be a very useful tool because specific peaks contained in the data can be extracted and compositional distribution is simply figured out by grouping even for the measurement result to be seemingly difficult to identify from the spectra.

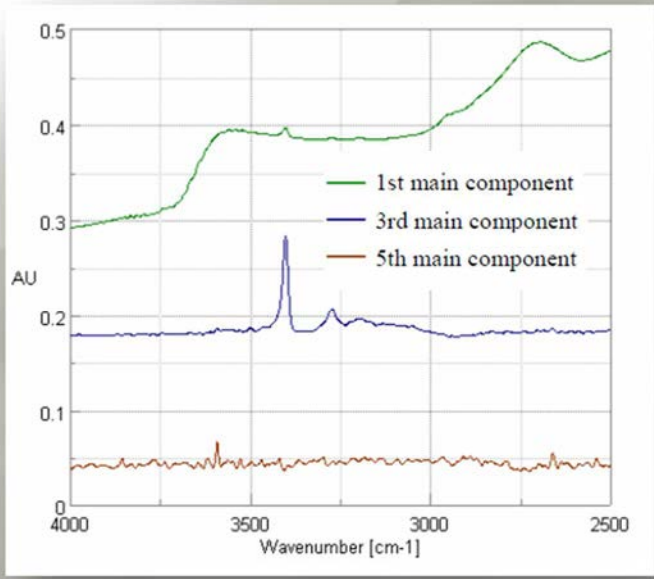


Figure 3 Principal component spectra

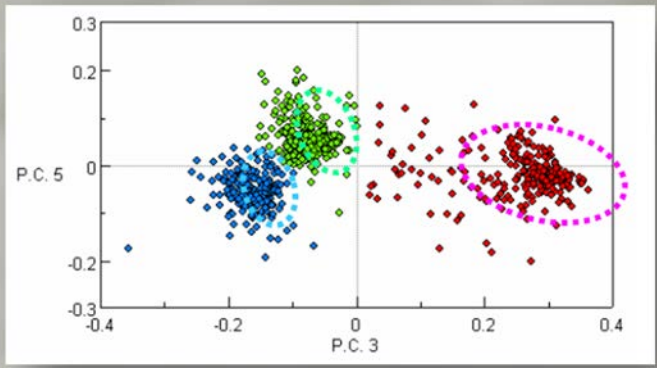


Figure 4 Plot of score values of the third and fifth main components

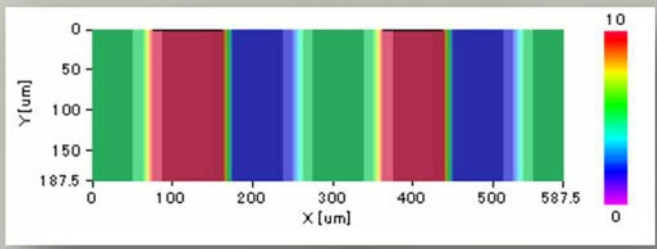


Figure 5 Color distribution diagram of the result by grouping with PCA

Analysis Example by Vacuum Model FT/IR (1)
Measurement of Silicon Wafer

Since the refractive index of silicon wafer is high, the light reflectance on the surface is also high. So there happens the phenomena that if the sample is placed vertical to the incident light, the reflected light from sample surface returns to interferometer, and then such light is reflected by the beam splitter of interferometer and illuminates the sample again. As a result the light pathlength for measurement with a sample is different from the pathlength without a sample, causing the excessive noise due to water vapor for the measurement by transmittance method.

For such reasons, the measurement may need to be implemented by adjusting the angle of the incident light to the sample, however with a vacuum system, the measurement of a sample placed vertical to incident light can be done without any effect by noise due to water vapor.

Condition
Resolution: 4 cm-1
Accumulation: 16 times
Detector: TGS

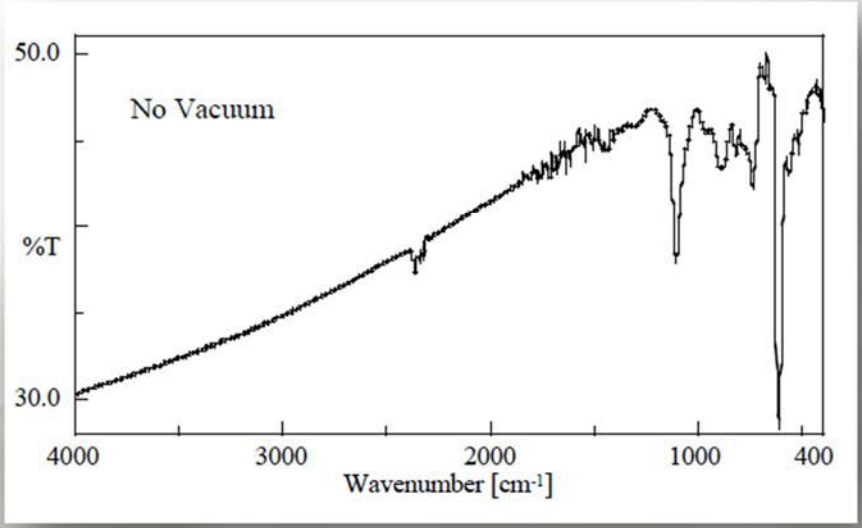


Figure 1 Measurement example of epi-film on the silicon wafer
NO VACUUM conditions

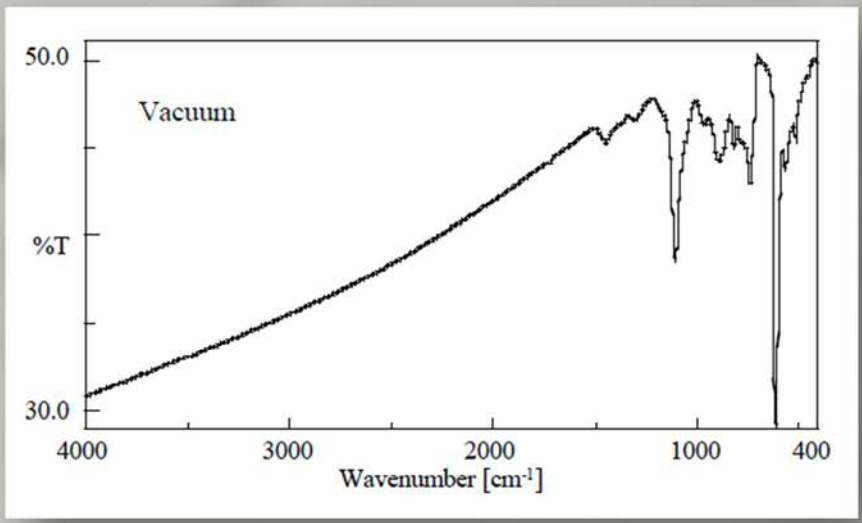


Figure 1 Measurement example of epi-film on the silicon wafer
VACUUM conditions

Analysis Example by Vacuum Model FT/IR (2)
Analysis of Low Concentration Gas using Long Pathlength Cell

An high S/N measurement is often required for the FT-IR analysis of low concentrations of gas or vapor compounds. In addition, the measurement of certain gas samples can be affected by the atmospheric water vapor and carbon dioxide present in the instrument, even with nitrogen purging. It is especially difficult to analyze NO gas because the absorption band is in the water vapor region, and NO2, CO2 and CO gas, whose absorption bands are near the CO2 absorption.

Using a full-vacuum instrument system, the water vapor and carbon dioxide in the light path can be completely eliminated and the measurement of these gas components can be accomplished even with low concentrations.

Figure 1 illustrates the spectrum of a 2 ppm CO sample by using a 20 m gas cell, demonstrating that the 2 ppm CO gas is measured with a S/N level around 200:1. The noise level with the same measurement conditions is 4 x 10^{-5} ABS as displayed in Figure 2, and with this noise level, the measurement of this gas can be easily accomplished with concentrations as low as 20-50 ppb.

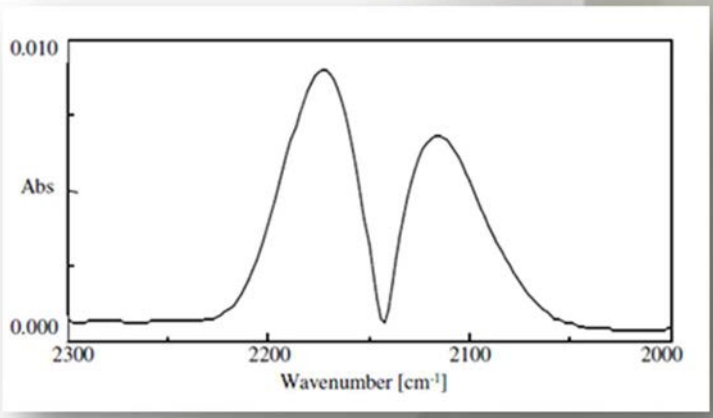


Figure 1 - 2 ppm CO gas

Condition
Resolution: 4 cm^{-1}
Scans: 500
Detector: MCT
Cell: 20 m pathlength gas cell

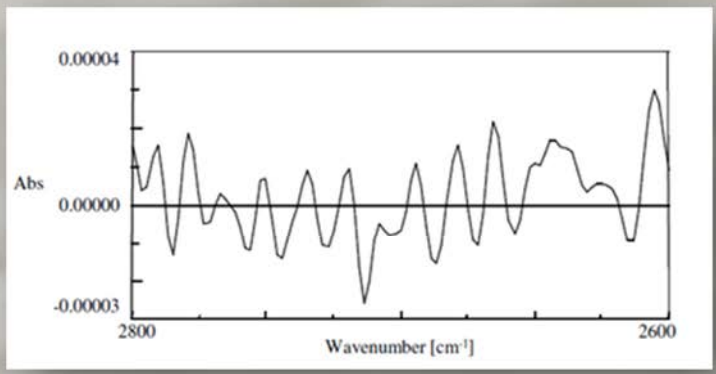


Figure 2 Spectrum S/N using the MCT detector

JASCO FT/IR - 6700FV - Full Vacuum

Industrial Gas Analysis System
- PFC Gas Analysis -

The PFC gases (Perfluorocarbon) such as CF3, C2F6, C4F8 and CHF3 are used as cleaning agents for dry-edging and CVD equipment, a critical process of semiconductor manufacturing. PFC gases are recognized as global warming, or, 'greenhouse' gases and there is an urgent need to control the further emission of these gases, among others.

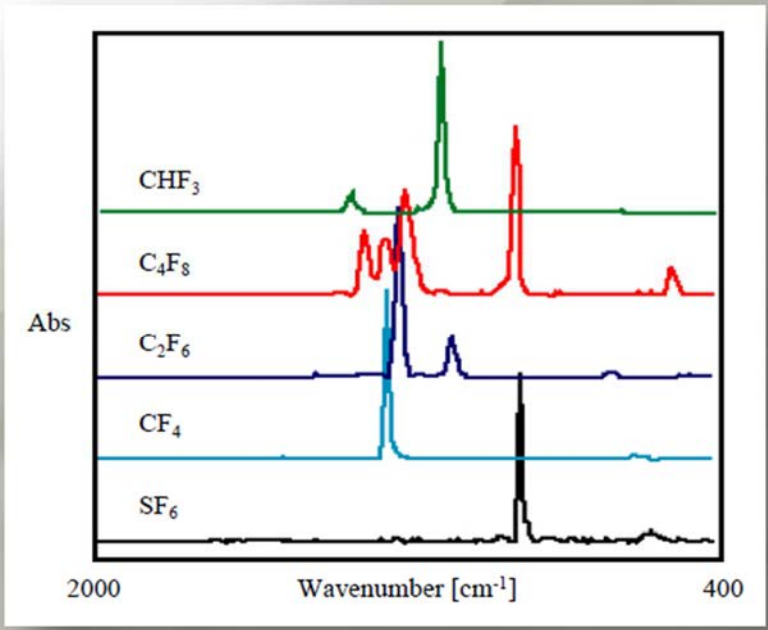
FT-IR (Fourier Transform infrared) spectroscopy is recognized as a powerful tool for the analysis of various gases, including PFCs.

The VIR series FT/IR system developed by JASCO may be small (Footprint: A4 size, Weight: 18 kgs.) but has proven sensitivity for on-line or other monitoring applications, with high ratings by various industrial users.

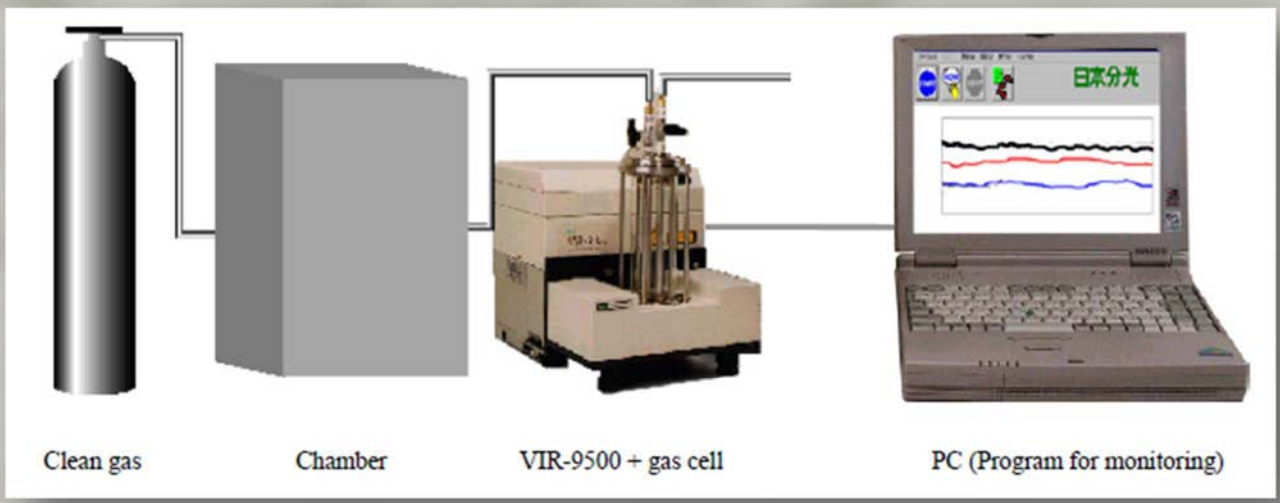
Detection limit of each gas (20 m gas cell)	
CF_4	0.1 ppm
C_2F_6	0.1 ppm
SF_6	0.1 ppm
HF	0.1 ppm
CO	0.2 ppm
NO	0.2 ppm

Utilizing a multi-pass, long-path gas cell to provide maximum throughput and excellent sensitivity, the VIR series can be configured for either flow through or static operation to monitor semiconductor PFC gases.

The various multivariate analysis methods (CLS, PCR, PLS and ellipson) can all be implemented by the VIR series control software for the simultaneous analysis of multi-component samples.



IR spectra of PFC gases



PFC gas analysis system

Analysis of Catalyst Reactions using Vacuum Thermal Diffuse Reflection Accessory

Introduction

Several studies have examined catalytic reactions in an attempt to clarify reaction processes. Spectroscopic methods are essential in determining the mechanism by which organic reactions occur on the surface of solid catalyst. One effective method for analyzing the surface of solid catalyst involves the use of a vacuum thermal diffuse reflection accessory. This reflection accessory enables powdered samples to be measured under heating. The cell of this accessory not only enables gases that limit absorptivity to be purged, but also allows a vacuum to be created so that the adsorption gas can be eliminated. In addition, this accessory supplies a constant volume of gas to the sample surface by connecting the cell to a closed circulating device, and the status of the sample surface can be monitored in real time. Figure 1 shows a photograph of the cell of the vacuum thermal diffuse reflection accessory used in the present experiment and Figure 2 shows a photograph of the closed circulating device. Three types of vacuum thermal diffuse reflection accessories are available, based on the required temperature control range. The temperature specifications are for a vacuum environment; the actual temperature on the sample surface is slightly lower than the temperature specified by the user.

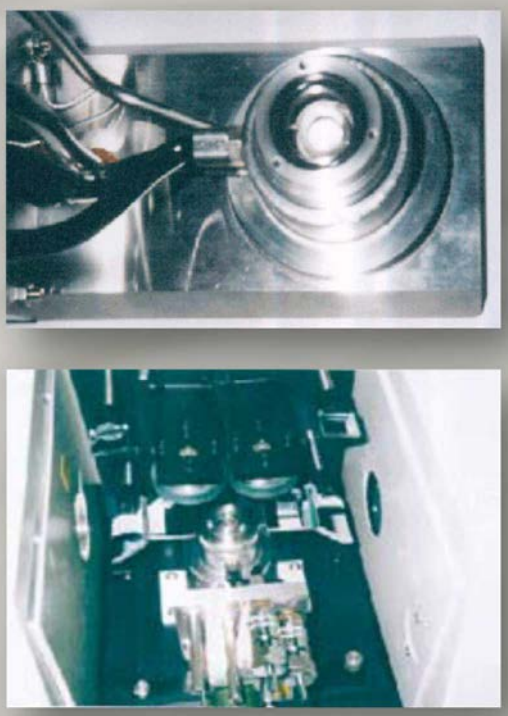


Figure 1 Cell of vacuum thermal reflection accessory

Instrument

FT/IR-620 FT/IR Spectrometer
DR-600A, B, C vacuum thermal reflection accessories
(A : 1000°C B: 800°C, C : 600°C)
Closed circulating device

Experimental

Adsorption of pyridine on the surface of zeolite

1. Place a solid catalyst (zeolite powder) on the cell of the vacuum thermal diffuse reflection accessory.
2. Create and maintain a vacuum in the cell for approximately one hour at 500°C. Then measure baseline (background spectrum) at room temperature.
3. Using the closed circulating device introduce a constant volume of pyridine into the cell.
4. Create and maintain a vacuum in the cell for approximately one hour at 200°C in order to eliminate physical adsorptive activity. Then measure spectrum at room temperature.

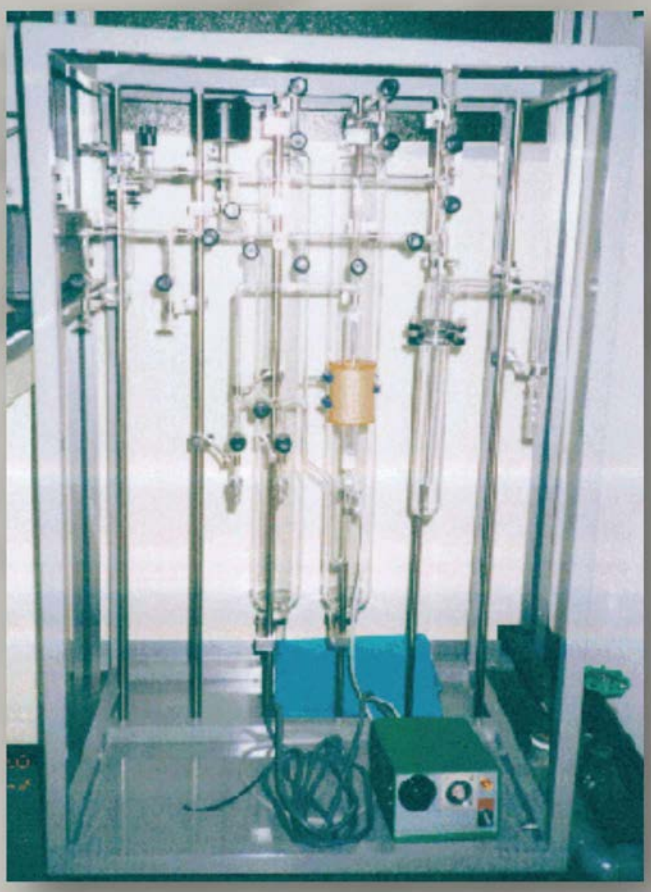


Figure 2 Closed circulating device

Analysis of Catalyst Reactions using Vacuum Thermal Diffuse Reflection Accessory

Conclusion

Acid receptor sites were found on the surface of zeolite. These acid receptor sites function as active site s for the catalyst activity of zeolite. Spectroscopic analysis enables the adsorption of probe molecules at the active sites to be determined. If base molecules, such as pyridine, are adsorbed at an active site, the site can be further classified as B acid (Bronsted acid) receptor sited or L acid (Lewis acid) receptor sites, according to the adsorption. Conversely, an L acid receptor site may be changed into a B acid receptor site by hydration. Figure 3 shows respectively the diffuse reflect ion spectra for the adsorption of pyridine obtained both before and after the application vacuum conditions.

Adsorptive pyridine at a B acid receptor site, where H+ was accepted, is changed into PyB (pyrindium ion), having an absorption peak at 1542 cm-1. However, the amount of adsorptive PyB a t the B acid receptor site is very limited, because zeolite was heated to a high temperature before adsorption. Adsorption PyL at the B acid receptor site shows absorption at 1450 cm-1 and strong peak intensity can be observed immediately after adsorption. Both the 1445 and 1595 cm-1 peaks represent hydrated pyridine (PyH). Figure 4 shows the status of chemical adsorption on the solid surface

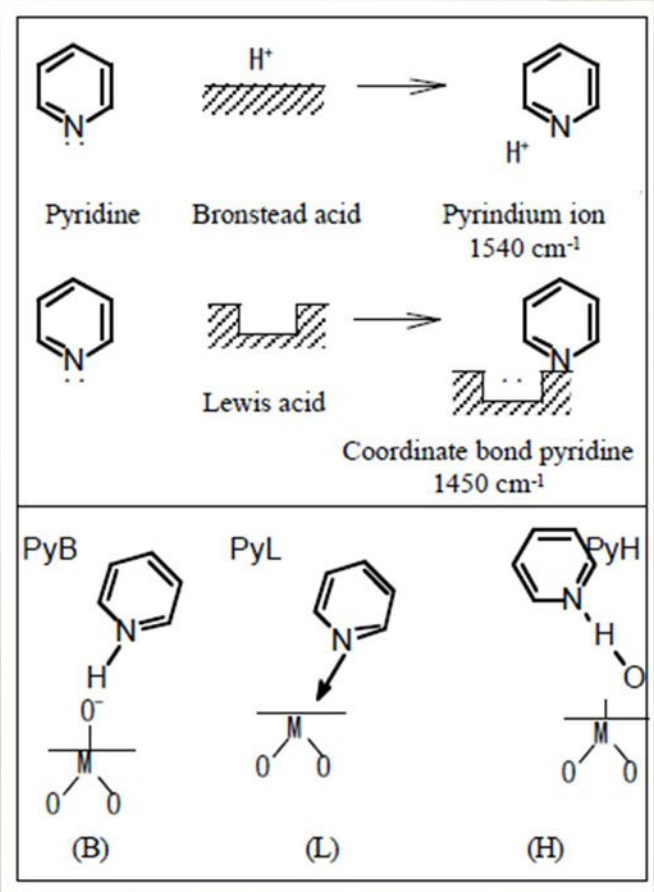


Figure 4 Status of chemical adsorption on the solid surface

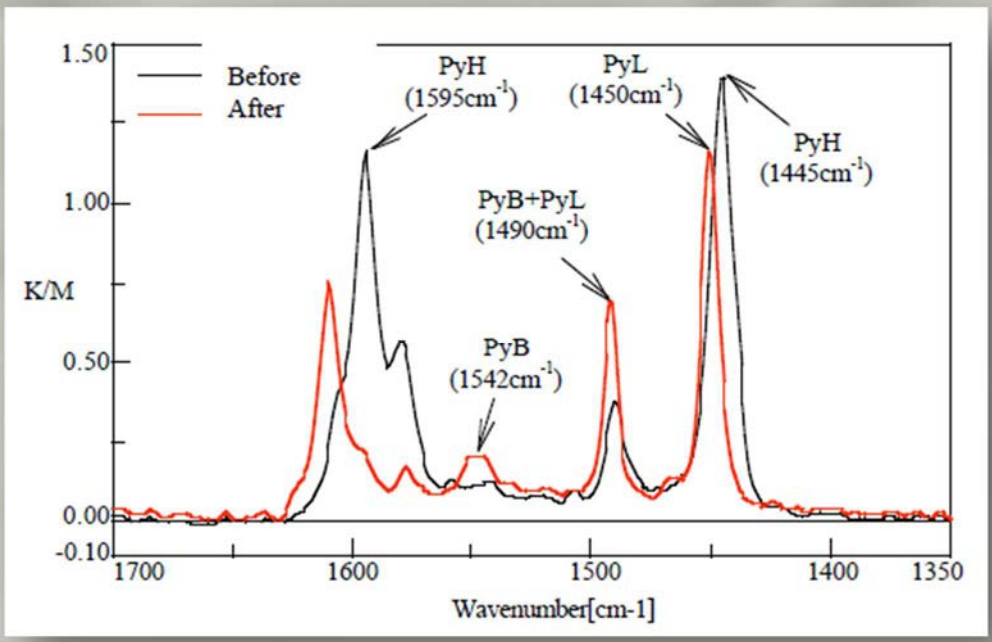


Figure 3 Diffuse reflection spectra obtained, respectively before and after vacuum conditions

Mapping measurement using IQ Mapping function of IRT-5000

Introduction

IR mapping measurement which can visualize molecular structure has been suggested traditionally, however the IR mapping measurement has not been widely utilized because of the several reasons as below.

- Auto stage is required, which will make the instrument too expensive.
- It takes quite a long time for measurement.

Regarding the measurement time, using the system utilizing multi-elements detector enables to shorten the measurement time in more than double digits in comparison with conventional system, and the IR mapping measurement has been gradually used. This time, we are now introducing IQ Mapping which was newly developed in order to solve another problem which is the necessity of auto stage. The IQ Mapping is a technique allowing Mapping measurement with manual stage by scanning IR light, and is applicable to ATR as well as ordinary transmittance/reflectance mapping. We would like to show an example of impurity analysis using IQ Mapping of the IRT-5000.

Figure 1 FT/IR-4100 + IRT-5000

Measurement 1: Mapping by manual stage

Mapping measurement was implemented for multi-layer film (Figure 2)

Measurement conditions

Mode: Transmittance
Detector: Mid-MCT
Resolution: 4 cm-1
Accumulation: 1
Cassegrain: 16×
Aperture：50 × 50 µm,
Measurement points: 9 × 9
Sampling Area: 400 × 400 µm

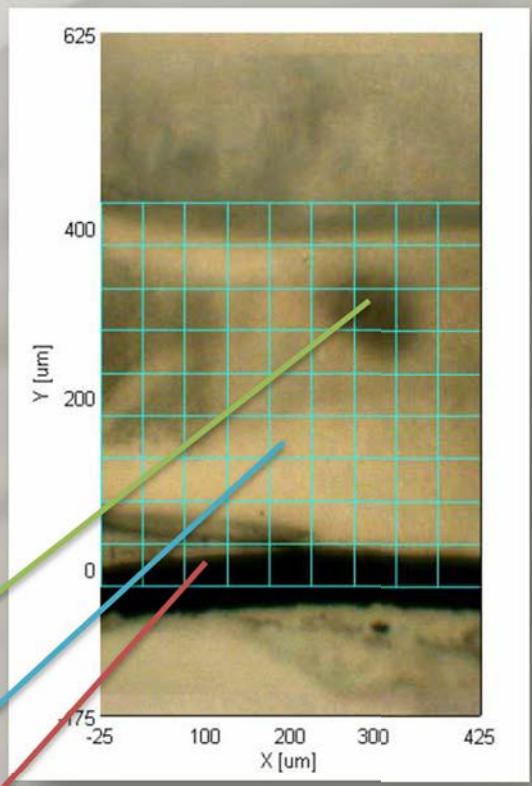
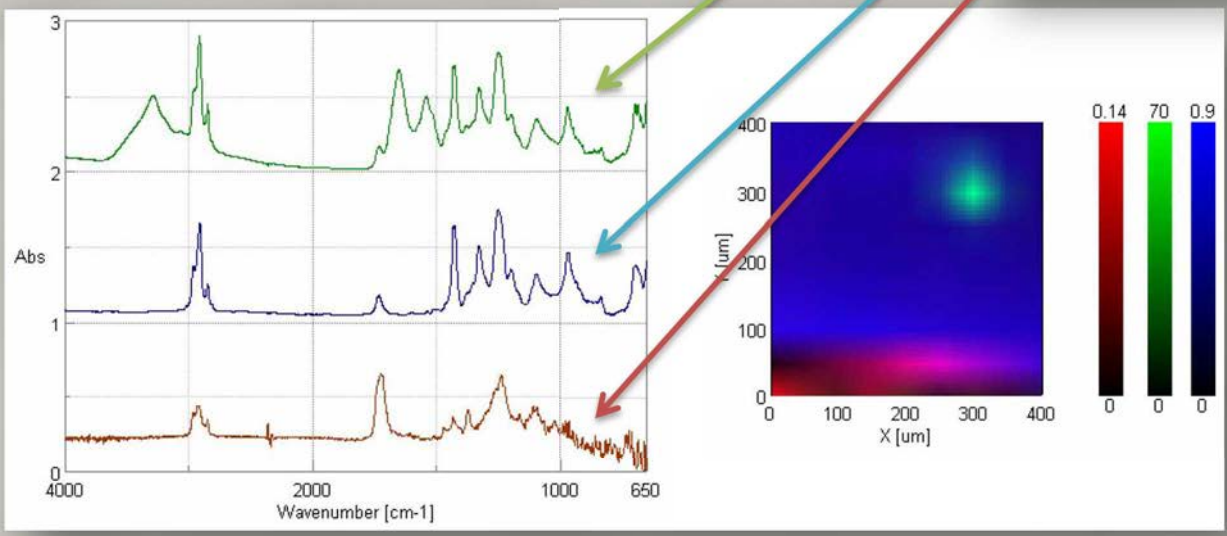


Figure 2 Observation image (Yellow-green grid shows measurement points.)



Mapping measurement using IQ Mapping function of IRT-5000

By analyzing the spectra in Figure 3, it was confirmed that multi-layer film roughly consisted of two components, PVA (red), PVC (blue), and protein(green) was existing in the multi-layer film. By showing color distribution map utilizing specific peaks for each component on the RGB display (Figure 4), components distribution became clear, enabling to detect the impurity which could not be identified by observation image.

Measurement 2: ATR Mapping

Combining IQ Mapping with ATR method enables the measurement without any contamination, as the number of contact between sample and prism is only one. The sample shown in Figure 5 was measured by using ZnSe as ATR prism.

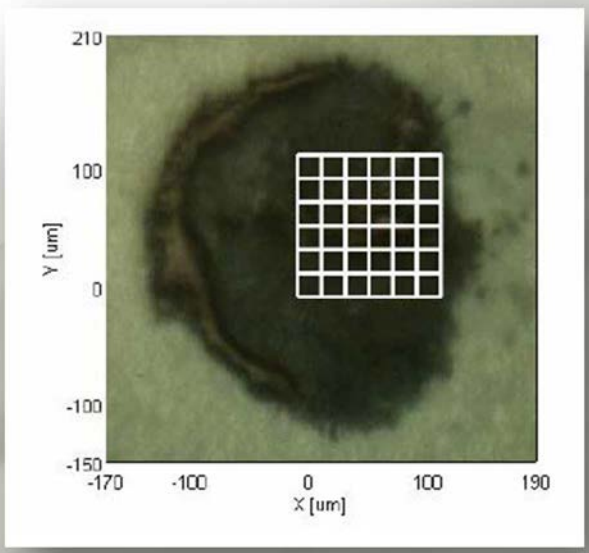


Figure 5 Sample observation image
(White grid shows measurement points)

Measurement conditions

Detector: MCT-N
Resolution: 8 cm-1
Accumulation: 8
Cassegrain: ATR-Z-5000,
Aperture: 20 × 20 µm
Measurement points: 6 × 6
Sampling area: 100 × 100 µm

As a result of mapping measurement, spectra of different components were obtained, depending on different measurement point (Figure 6).The sample measured was a mixture of water-based and oil-based marker, and specific peaks for each could be identified as in Figure 6. Color distribution map using the specific peaks for each component at 1666 cm-1 and 1282 cm-1 is shown in Figure 7. As shown, mapping measurement can detect different components of the sample which appear to be only one component by visible image, assuring accurate qualitative analysis.

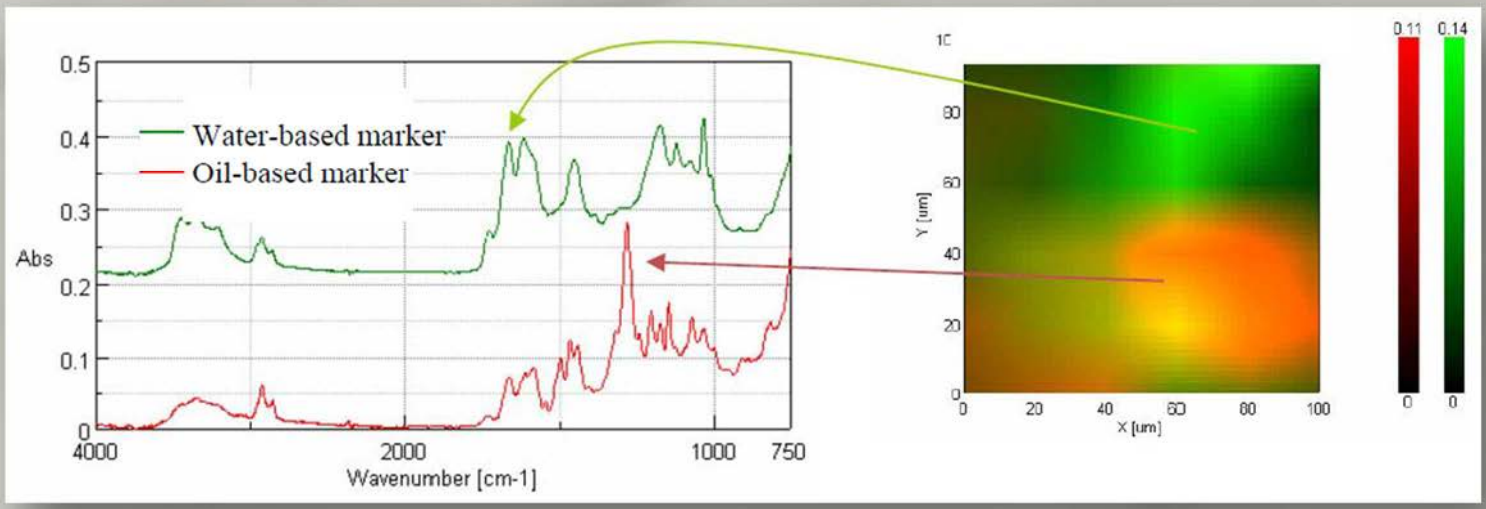


Figure 6 Measured spectra of impurity

Foreign material analysis using both Mixture Analysis function and new library

1. Introduction

A certain level of technique was necessary to identify successfully the IR spectrum of unknown sample which consists of multiple components by using conventional spectrum searching method, because those process was usually very complicated. In order to analyze multi-component sample, first step was to search the spectrum from library, which is the most similar to the spectrum of the main component, then to calculate the difference spectrum by subtracting the searched spectrum from the spectrum of the sample and to analyze other components through re-searching. It is basically possible to analyze 2nd component in the sample if such method is repeated several times, however searching accuracy declines depending on the number of components in sample, and a certain level of technique to analyze spectra properly is necessary. This time, new function named [Mixture Analysis] has been added to our standard search engine [KnowItAll] for easy analysis of the sample with multiple components. [Mixture Analysis] enables to search spectra for multiple components sample (Max. 4 different components) easily without any data processing such as difference spectrum calculation. In addition, JASCO has newly added approx. 400 kinds of Organic, Inorganic, Polymer spectra to our standard library with 10000 spectra. Those 400 spectra have been created through our measurement results for the past 3 years, which include not only foreign material analysis data but also Food Additives, Polymer and Fiber data. Following experiment was done to search foreign material inside of fiber by using [Mixture Analysis] and newly upgraded library with 10400 spectra. As the result, this sample was analyzed to have multiple components.

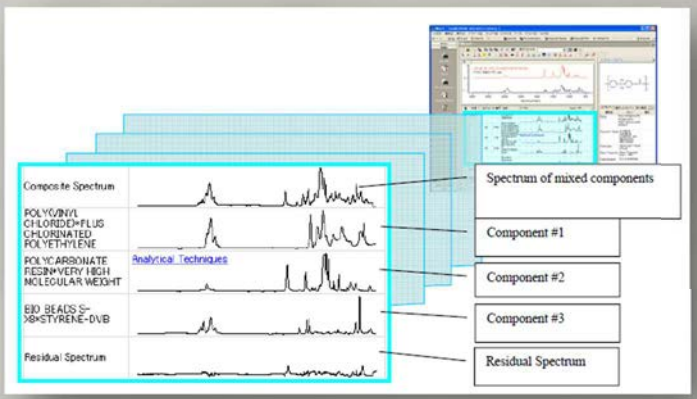


Figure 1 Serch result of unknown sample by using of KnowItAll [Mixture Analysis]

2. Measurement conditions

Instrument Model: IRT-5000
Method: Microscope Transmittance measurement (KBr Plate method)
Resolution: 4 cm-1
Accumulation: 50 times
Aperture size: 100 μm^2

3. Results and discussion

The search results by using [Mixture Analysis] are shown in Fig. 3 for the foreign material contained in the fiber. By these results, unknown sample was identified as calcium carbonate and clay, that is, silicate. For reference, the results by using conventional [SearchIt] are shown in Fig. 4. In this case the spectrum of silicate was searched and then calcium carbonate was identified by calculating the difference spectrum and researching.
As explained in the above, for the analysis of sample with multi-components, [Mixture Analysis] was proved to be a powerful tool and in addition, the foreign material was successfully identified by utilizing the standard library with 10400 spectra.

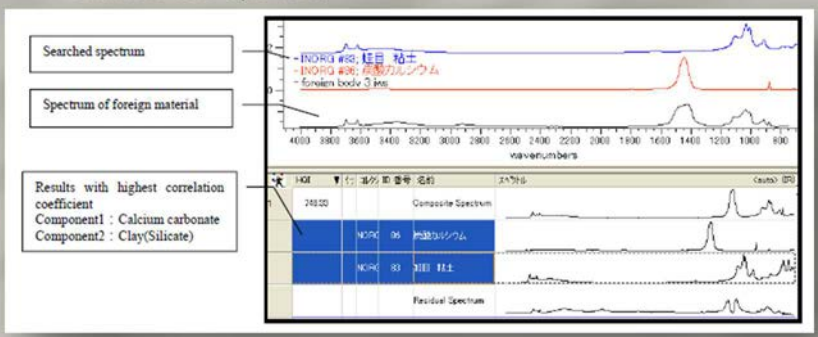


Figure 3 Search of unknown sample by using [Mixture Analysis]

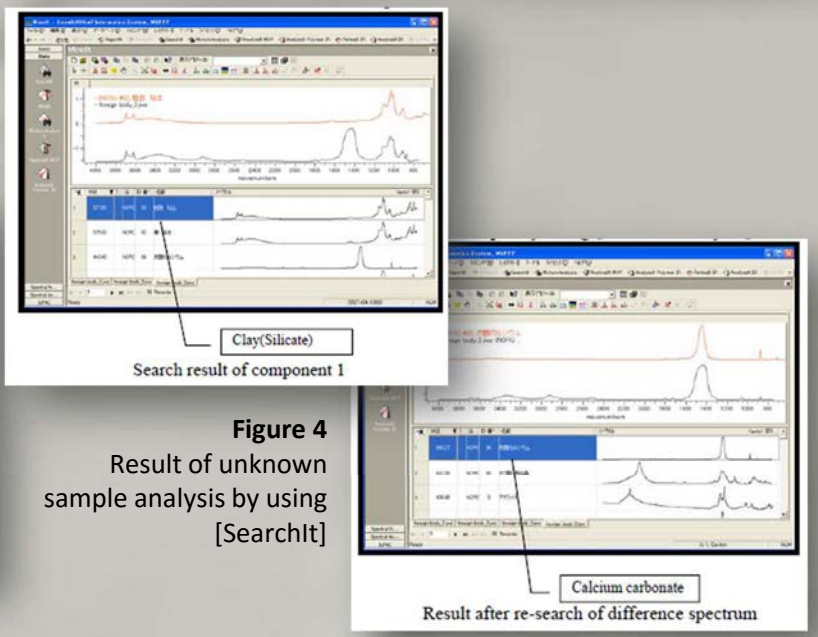


Figure 4 Result of unknown sample analysis by using [SearchIt]

Thermal Gravimetric-Infrared (TGA-IR) Analysis of Ammonium Acetate

Amanda L. Jenkins, Ph.D. and Richard A. Larsen, Ph.D. - Jasco Inc.

The TGA-IR combines the sample analysis tools of a TGA with the identification power of an FT-IR spectrometer to offer real-time monitoring of gases as they evolve from a sample.

The combination of thermal gravimetric analysis and infrared instrumentation allows the measurement of the change in weight of a sample as a function of temperature or time in a controlled atmosphere and the collection of the IR spectra of the evolved gas components. TGA-IR has many applications in today's world. It can be used in polymer research to determine the evolution of residual solvents, monomers, additives, and in the study of flame-retardant materials. In the electronics industry it can be used to study off gassing by components and structural materials. In the study of composites and inorganic materials TGA-IR can be used as confirmation of small molecule loss. The TGA-IR interface is connected to the TGA via a heated transfer line. As gases evolve during the TGA experiment, they pass into the flow cell of the TGA-IR interface where the infrared spectra are collected. The TGA-IR interface is beneficial in determining sample characteristics such as decomposition pathways, thermal stability or sample integrity. Its flexible interface design can be placed in the sample compartment of the FT-IR.

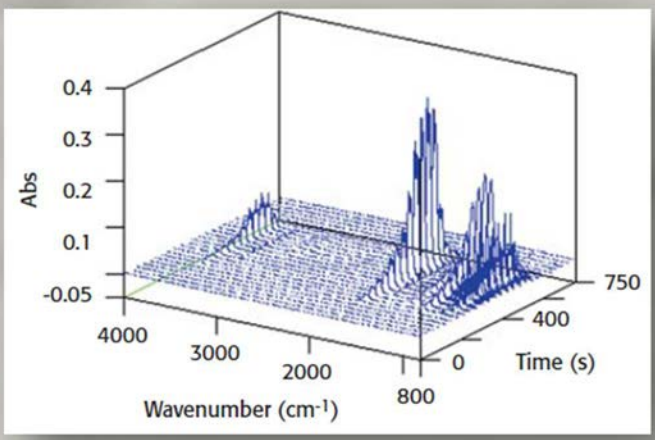


Figure 1 3D FT-IR data of the evolution of gases from the ammonium acetate

Experimental Conditions

The TGA-IR experiment was used to follow the thermal melt of Ammonium Acetate (CH3COONH4). The instrument consisted of a TA Instruments SDTQ-600 TGA unit attached to the Jasco FT/IR-660 instrument with a standard source and the DTGS detector via a heated gas line and 10 cm gas cell (TG-IR interface) from Pike Technologies. A flow rate of 100 ml/min of nitrogen was used to sweep the evolved gases from the TGA furnace to the FT-IR gas cell. The temperature was varied from ~20 °C to 600 °C with a ramp rate of 20 °C/min.

FT-IR scans were collected every 60 seconds, 12 scans at 4 cm-1 resolution used to follow the gases evolved from the thermal melt of the sample. The gases evolved included Ammonia and Acetic Acid. The interval software was used to collect and analyze the data contained in this note.

Results

Figure 1 shows the infrared spectra of the evolution of ammonia and of acetic acid over time. The evolved gas spectra corresponds to the weight loss of the sample in the TGA. Figure 2 shows the weight loss and 1st derivative curves for the sample generated by the TGA instrument.

Acknowledgements

We would like to thank Dr. Michael Baird and Dr. Norman Duffy of Wheeling Jesuit University for allowing us to use this data.

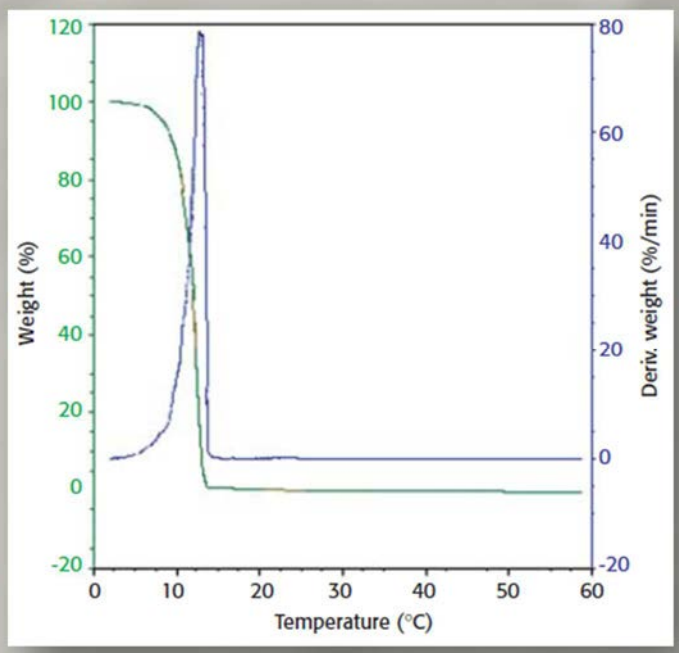


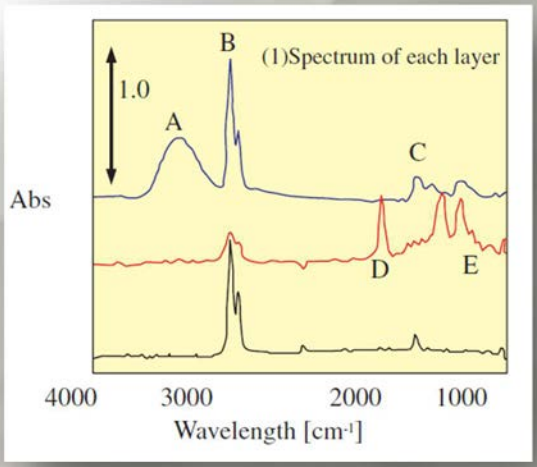
Figure 2 TGA curves
(Top) derivative curve (Bottom) weight loss curve

Sample Preparation for Infrared Imaging
Multilayer Film Measurement Using the SliceMaster

There are various devices that can create cross-sections of multi-layer films for analysis of the molecular structure using infrared spectroscopy. To date, cross sections of multilayer laminates have been created by embedding the sample in epoxy resin and then using a microtome to create the cross-section slices. This technique has various drawbacks, including the time required for the resin to harden (several hours for epoxy resin) as well as resin contaminating the sample. In addition, since the IRT-7000 infrared imaging system can dramatically shorten measurement times compared to conventional imaging measurement systems, the need to reduce the time required for preprocessing samples was required. For the creation of cross sections, the SliceMaster developed by JASCO Engineering Co., Ltd., was used. This accessory can provide thin 'slices' or cross sections of various samples, including multi-layer laminates, without embedding them in resin. In this experiment, we used the vertical SliceMaster (HS-1) (Figure 1) to create a cross-section from a food package that was measured using the transmission method of analysis. The measurement area was 600 × 600 µm with a spatial resolution of 12.5 µm, collecting 16 scans at 8 cm-1 resolution for all spectrum. Based on the spectra collected for each layer, we determined that the laminate was comprised of polyethylene (PE), polyvinyl alcohol (PVA) and poly ethylene terephthalate (PET) (Figure 2 (1)). Figure 2 (2) is the visual image of the sample captured with the integrated CCD video camera in the IRT-7000. Figure 2A is the infrared image based on the peak intensity at 3500 cm-1 attributed to the -OH functional group for the PVA material; Figures 2B and 2C are based on the peak intensity for the C-H stretching absorption at 2920 cm-1 and the C-H bend at 1440 cm-1, respectively, present in all the layers. Figure 2D represents the image based on the C=O peak intensity at 1730 cm-1, present in the PET layer, and Figure 2E is the image for the peak intensity of the 1250 cm-1 absorption. The infrared images obtained for the sample revealed the clear differences among the four-layer structure. Based on these results, information on the adhesive layers between each film layer could not be obtained, but the use of the HK-1 angled SliceMaster and the 32× cassegrain objective, could provide the ability to obtain greater spatial resolution for analysis of the sample.

HK-1 angled slicer

HS-1 vertical slicer



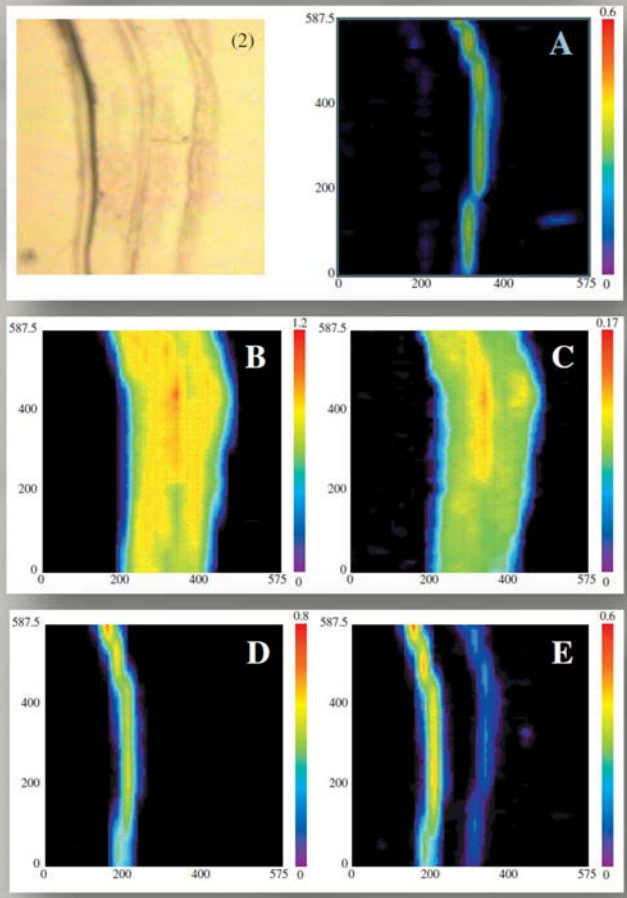


Figure 2 Multi-layer measurements

Iodine Value Measurement of Fat with FT-NIR System with Peltier Thermostatic Cell Holder

Introduction

Iodine value is used as an index for unsaturation degree of fat for evaluating the nature of fatty oil and bio-diesel. Iodine value can be generally obtained by wet method employing redox reaction as described in ASTM, JIS and so on, which, however, has a drawback that the operation is complicated. In order to solve the problem, vibrational spectroscopic method such as IR and Raman spectroscopy for Iodine value estimation has been proposed. (Refer to 050TR0125 FT/IR Application Data.) To further improve the measurement accuracy of Iodine value, an Iodine value measurement system consisting of an air-cooled Peltier thermostated sample cell holder and FT-NIR (Fourier Transform Near Infrared Spectrometers) has been developed. A calibration curve model was generated with PLS method applied to NIR spectra of fatty oil obtained with the system, and Iodine values obtained with a conventional wet method, and it was intended to show the effectiveness of the system by applying the calibration curve model to some actual samples.

Figure 1 FT-NIR system with thermostatted cell holder for Iodine value measurement (customized system)

Experimental

Firstly, 24 kinds of fatty oil having different Iodine value were measured twice and NIR spectra were obtained to make a calibration curve model each time. As a next step, a calibration curve model was generated with PLS method applied to the obtained spectra and the Iodine values obtained with wet method. Finally, the Iodine values of 5 kinds of the actual samples were measured utilizing this calibration curve model.

Experimental Conditions

Instrument: FT/IR-4100
Light source: High-intensity ceramic source
Detector: DLATGS
Accumulations: 16
Resolution: 8 cm-1
Temperature control: EHC-716 Air-cooled Peltier method (customized)
Temperature setting: 60°C
(The samples were solid at room temperature and the temperature was set at higher one than melting point)
Photometric mode: Transmittance
Cell: Quartz cell of 5 mm light pathlength

Results and Discussion

Figure 2 shows NIR spectra of 24 kinds of fatty oil. A calibration curve model was generated with PLS by using the data in the wavenumber range from 4500 to 4800 cm-1 for the calculation. Figure 3 shows the calibration curve model which gives good correlation with the true value (obtained by wet analysis method) and evaluated value (obtained by spectral analysis). The correlation factor is 0.9995. The results of evaluating the quantitation reproducibility (n=30) of 5 kinds of fatty oil with different Iodine values using this model are shown in Table 1. The average value and the standard deviation obtained from the spectra are presented in the table. The values in parentheses are Iodine values obtained by wet analysis method. The error between the results obtained with the two analysis methods is less than 2% and the standard deviation of the reproducibility is less than 0.173, which can be considered as a good result. The over-all results show that the system consisting of FT-NIR spectrometer with high wavenumber accuracy and a Peltier thermostatted cell holder to control the temperature of the sample is very effective for measuring Iodine value because it can provide almost the same quality data in the Iodine value measurement as the one by wet analysis method, in a quicker, easier and nondestructive way.

Iodine Value Measurement of Fat with FT-NIR System with Peltier Thermostatic Cell Holder

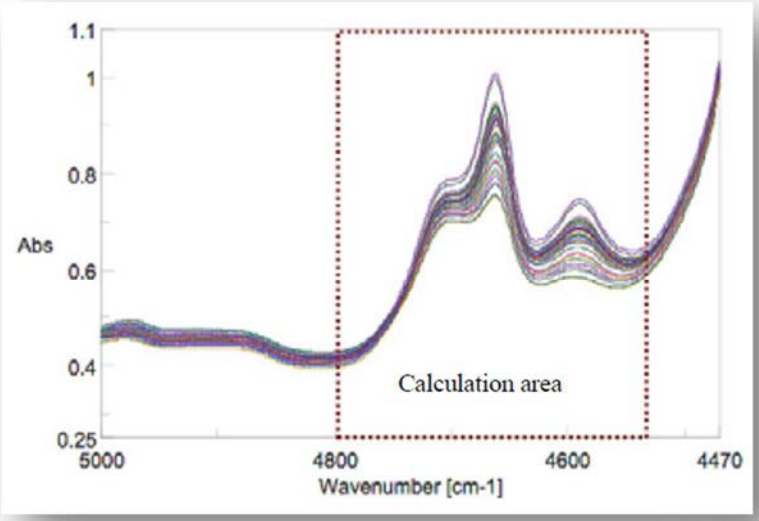


Figure 2 NIR spectra of 24 kinds of fatty oil

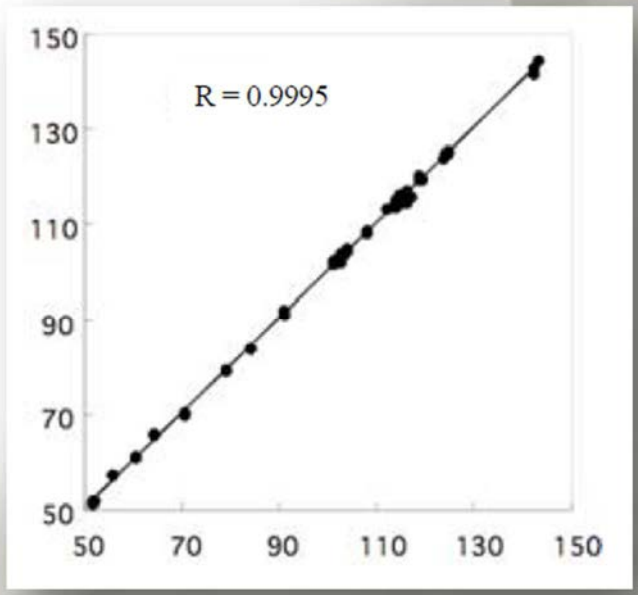


Figure 3 PLS calibration curve model

	A (102.6)	B (115.7)	C (56.3)	D (123.8)	E (116.7)
Average	103.5	115.6	56.4	123.7	119.0
Standard Deviation	0.141	0.173	0.135	0.171	0.161

Table 1 Evaluation result of the actual samples
Values in ( ): Iodine values obtained by wet analysis method
(Standard fatty oil analysis method established by Japan Oil Chemists' Society: Wijs-Cyclohexane method)

Infrared Microscopy for the Analysis of Polymer Laminates in a Juice Bottle

Laminates are combinations of polymers that combine the benefits and properties of the various polymers used in the laminate to create a better material. Polymer laminates have a multitude of uses including packaging for food and other products. Laminates act as moisture and/or oxygen barriers and as such are commonly used to protect foods and chemicals. Analysis of laminates is often required for quality control and to determine laminate adhesion problems

Introduction

Modern polymers are seldom used as pure materials, more often mixtures of different polymers are combined to give the desired physical characteristics. For example, the rigidity of polystyrene is often combined with an elastic polymer to produce stiff yet shock resistant materials. Polymeric laminates are important in the microelectronics, medical, food packaging, and chemical industries.

Since, laminates act as moisture and/or oxygen barriers they are commonly used to protect foods and chemicals. There are many methods that can be used to generate these mixtures but one of the most common is to simply assemble the polymers into layers and create a laminate. The most widely used structural spectroscopic measurement for laminates is Fourier Transform infrared (FTIR).

FTIR spectroscopy is a non-destructive technique that that allows chemical identification of the component materials in the laminate. Infrared spectroscopy provides the ability to study the interactions of the vibrational and rotational energies of atoms or groups of atoms within molecules.

Infrared spectra reflect vibrational motions that produce a change in the permanent dipole moment of the molecule. Infrared spectroscopy is a powerful qualitative and quantitative tool.

There is a large amount of information that can be gained by using infrared spectroscopy for the analysis of polymers. Minor changes to the molecular structure usually result in a spectrum that is clearly distinguishable from the spectrum of the original compound.

Thus, they can be used to identify the presence of a specific chemical compound or mixture of compounds.

Experimental

Several different polymer materials were selected for analysis including a prepared juice bottle and a plastic food container. Laminate samples of controlled thickness were sectioned with a razor blade and the cross section examined using the FT-IR microscope. Microscope apertures ranging from 15 x 15 to as large as 50 x 50 microns were used to define sample areas for analysis.

Figure 1 Juice bottle laminate under the FTIR Microscope, visually, you can identify at least 4 layers in this image.

Analysis was performed using a JASCO FT/IR-620 and IRT-30 FT-IR microscope with a ceramic source, KBr beamsplitter, and MCT detector. The resolution was 4 cm-1, with 64 co-added scans for the single-beam background and sample spectra. The spectral range was from 4000-700 cm-1.

Infrared Microscopy for the Analysis of Polymer Laminates in a Juice Bottle

Initial investigation of the polymer laminate found that the primary components of the laminate were Poly(propylene) (PP) and poly(vinyl alcohol) (PVOH). Further study and careful examination of the laminate polymer immediately adjacent to the PVOH layer revealed a gradient in the ratio of the poly(propylene) (PP) and poly(vinyl alcohol) (PVOH) polymers.

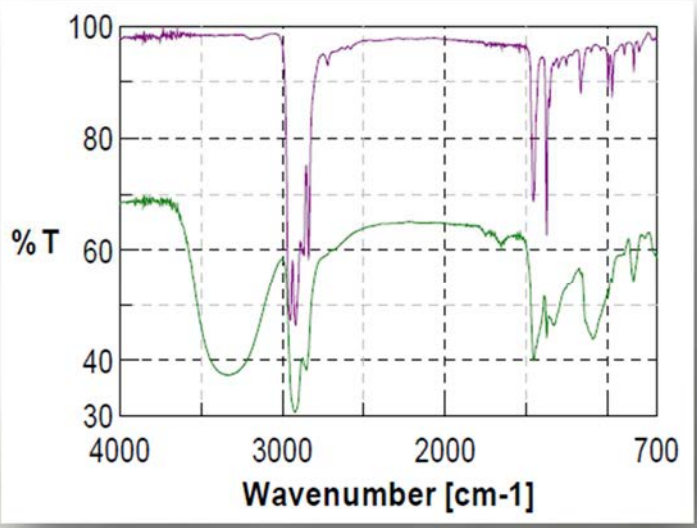


Figure 2 Infrared spectra of laminate polymers. Top: poly(propylene) Bottom: poly(vinyl alcohol)

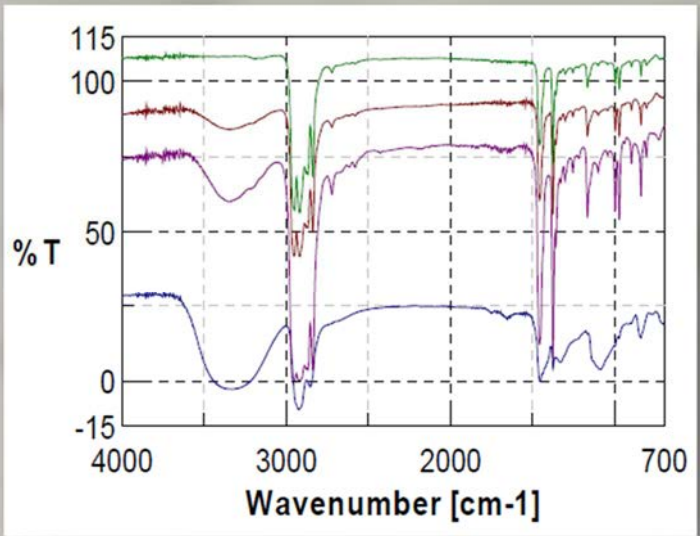


Figure 3 Infrared spectra of the interface. Top: PP, Middle: PP-PVOH blends Bottom: PVOH.

Conclusions

Laminate appears to comprise 6 layers. PP (polypropylene) and a highly hydrolyzed form of the PVOH (polyvinyl alcohol) were identified as the primary components based on the comparison of the infrared spectra to spectral libraries. There appear to be two slightly different PP types; PP1 and PP2 are probably m.wt. variants or PP1 may simply contain a small amount of an additive to provide the change in optical density. Additionally, it was determined that there was a mixing of the polymers at the interfaces. Infrared spectroscopy was not only able to identify the layers but also to give information on the polymer mixing happening at the interface. This valuable information will allow a more accurate determination of the physical properties of the polymer and how it will handle stresses at the interface.

Analysis of Automotive Fluids using with FTIR

Introduction

The liquid sample is one of the most common types of samples submitted for analysis and comprises a vast array of pure compounds and solutions. As an example, several liquids are used in an automobile to sustain critical elements such as lubricating the engine or drive train and to supply mundane functions like washing the windows or generating electrical power. This paper will describe the analysis of several solutions used in automobiles.

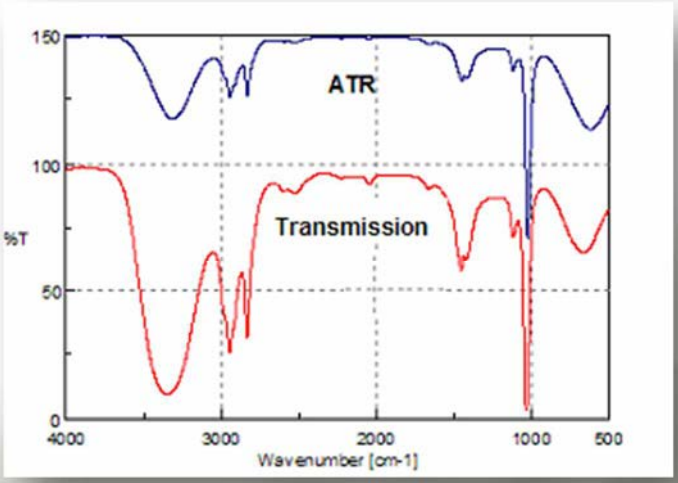


Figure 1 Transmission and ATR spectra of methanol

The traditional infrared analysis method for fluid samples is to collect an infrared transmission spectrum of a thin film of the liquid contained between the windows of an infrared liquid cell. Not all liquids, however, can be analyzed with infrared spectroscopy in this manner. For samples that are aqueous, viscous or chemically reactive, an infrared liquid cell is cumbersome and labor intensive. Frequently, special windows with a reduced spectral range must be used and the cell can be difficult to keep clean to prevent cross contamination.

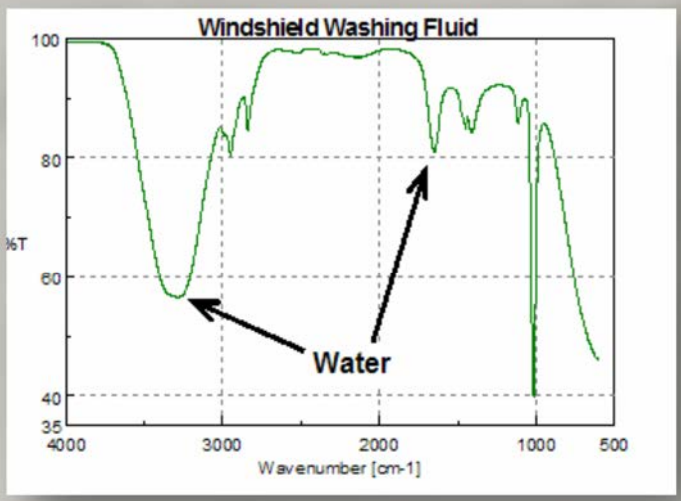


Figure 2 Spectrum of windshield washing solution

Infrared analysis using Attenuated Total Reflectance (ATR) accessories like the diamond single-reflection micro-ATR require no sample preparation and greatly simplify the collection of FT-IR spectra. The liquid sample is placed onto the ATR crystal and the sample spectrum is collected. A volatiles cover supplied with the accessory can be used to cover the sample to prevent evaporation during analysis. The sample is then cleaned from the crystal surface and the accessory is ready to collect additional spectra. ATR analysis methods are less complicated than using liquid cells, are fast and a very small amount of the sample is needed.

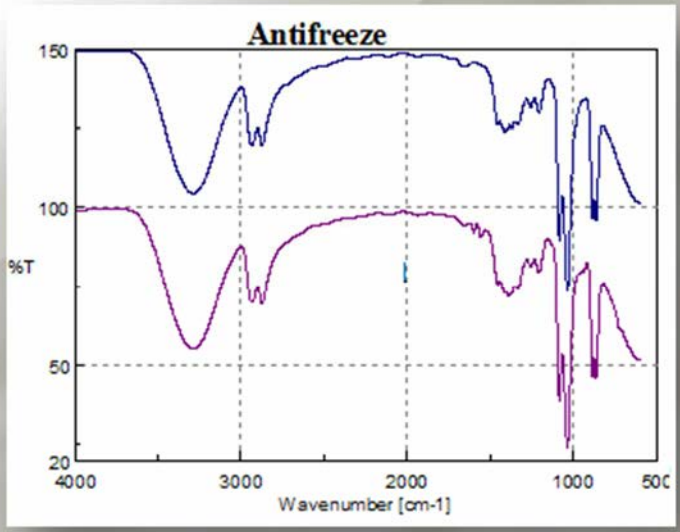


Figure 3 Spectra of two samples of anti-freeze, normal-blue and the extended lifetime-purple.

The resulting data can be searched against a digital database of ATR spectra for positive identification. Despite changes in the relative peak intensity of the absorption bands, due to the internal reflection mechanism of ATR accessories[1], spectra can also be compared to transmission data. As an example, Figure 1 is a plot of the transmission and ATR spectra of methanol.

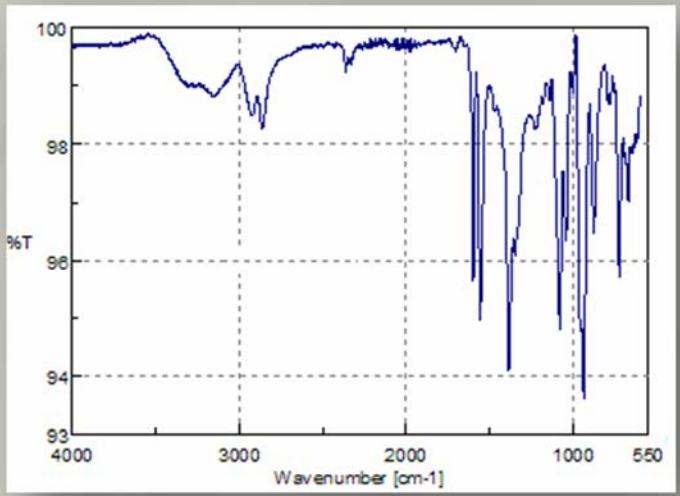


Figure 4 Extended mileage antifreeze minus the normal

Analysis of Automotive Fluids using with FTIR

Experimental Results

Spectra were collected using a Jasco FTIR-460 Fourier transform infrared spectrometer equipped with a Golden Gate™ micro-ATR accessory. Sample volumes of 20 microliters were pipetted onto the ATR surface and the spectra collected. No sample preparation was necessary to obtain the various spectra and the liquid sample is simply wiped from the crystal surface after data collection. If necessary, a solvent that will remove the sample is used to clean the diamond crystal surface.

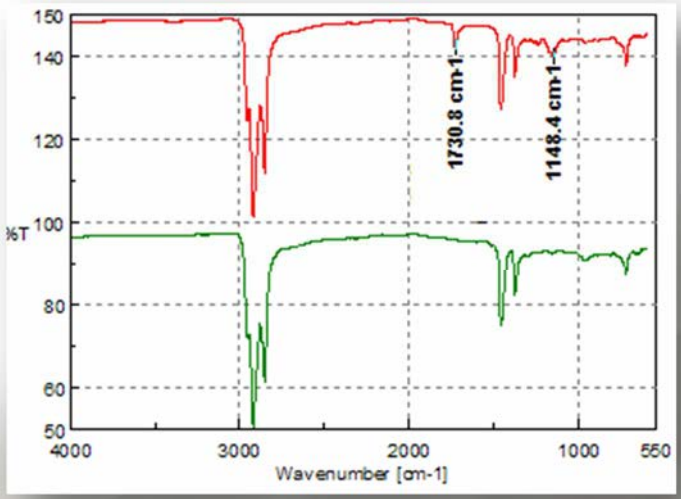


Figure 5 Analysis of 10W30 engine oil (green), power steering fluid and two transmission fluids (red)

FT-IR spectra of 64 scans at 4 cm-1 resolution were coadded and averaged to obtain the single-beam background and sample spectra. Figure 2 is a spectrum of windshield washing solution and it can be readily observed that methanol (Figure 1) is the major component. The water solvent increases the intensity and band broadening for the O-H stretch and bending modes.

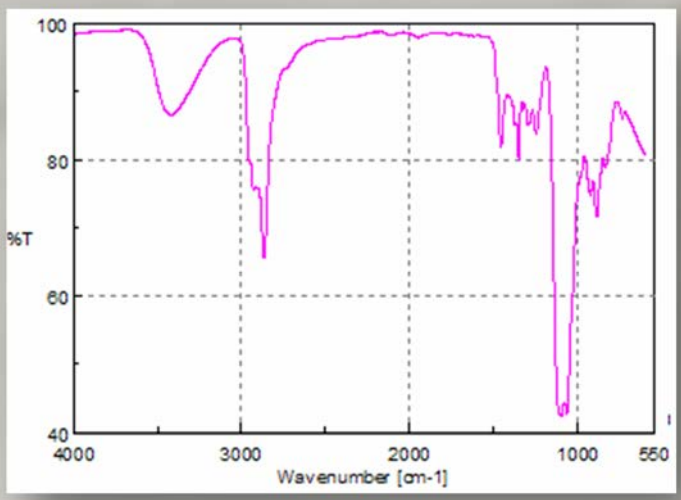


Figure 6 Spectrum of brake fluid

Figure 3 illustrates the spectra of two samples of anti-freeze. While the spectra for the "normal" anti-freeze and the extended lifetime solution appeared identical, a subtraction of the standard ethylene glycol solution from the extended mileage formulation reveals a spectrum of the component(s) that presumably extends the anti-freeze lifetime. Analysis of 10W 30 engine oil, power steering fluid and two automatic transmission fluids (ATF 3 and ATF 4) all yielded spectra representative of long-chain aliphatics as illustrated in Figure 5. The only discernible difference is the additional peaks at 1730 and 1151 cm-1, which highlight a similar additive in the ATF and power steering samples. Figure 6 is a spectrum of brake fluid and was interpreted as a complex alcohol or possibly a diol, providing the requisite lubrication and compression characteristics.

The most challenging sample was battery acid.

Mainly sulfuric acid, battery acid is extremely corrosive and will etch or react with almost every standard infrared window or ATR element. By contrast, the diamond element of the ATR is not damaged during analysis. The spectrum of the acid solution is displayed as Figure 7.

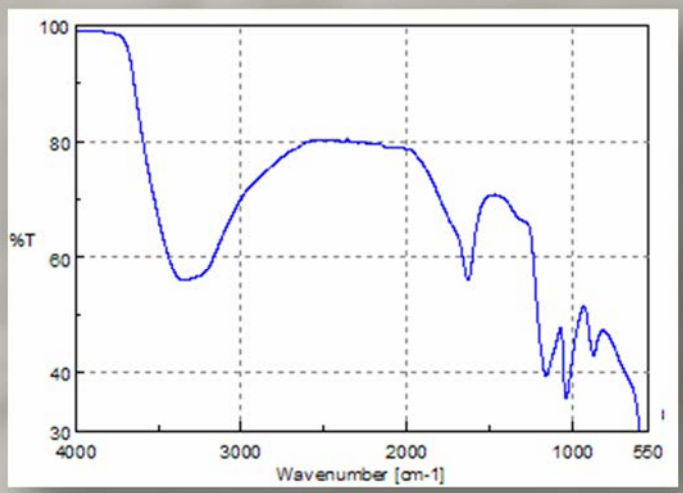


Figure 7 Battery Acid

Conclusions

The Golden Gate™ single reflection micro-ATR is a simple, easy-to-use accessory for the analysis of liquids and solutions. The ATR technique is simple, rapid and very reliable for sample characterization. The analysis method is non-destructive and can be used to collect data from a minimal amount of sample.

Acknowledgements:

Pine Belt Automotive, Lakewood, NJ. and Specac Inc, 500 Technology Court, Smyrna, GA 30082 www.specac.com, for the ATR.

Terahertz (THz) Measurements of Liquids by a vacuum compatible ATR accessory

1. Introduction

Characterized by wavelengths longer than the mid-infrared region, the far-infrared region is also referred to as the terahertz region. In recent years, this region has been used to evaluate crystal polymorphs for pharmaceuticals and semiconductor device materials, as well as for archaeological research applications, including the study of inorganic pigments. Light in the far-infrared region (terahertz waves) corresponds to hydrogen bonding and Van der Waals forces believed to hold the key to an understanding of the functional expressions of and structural changes in biological molecules in liquids, as well as absorption energy in hydrophobic interactions. Calculations, generally theoretical, have been applied for such purposes in the past, but using light in the far-infrared region should allow the acquisition of important experimental information regarding such behavior.

The transmission method is commonly used for measurements in the far-infrared region but is not suitable for measurements of samples with significant absorption in the far-infrared region. For measurements of liquid samples such as biological molecules in an aqueous solution, cell thickness must be reduced to about 10 um or less to avoid the effects of solvent absorption. This makes it difficult to directly measure gel-state materials or biological samples, like protein solutions. ATR measurements utilize infrared light focused into a crystalline prism which penetrates slightly into the sample when the sample and the prism are in intimate contact. The method allows easy measurements of samples with good contact characteristics, such as liquids and gel-state materials, simply by placing the sample on the prism. Although the effects of moisture vapor are more pronounced in the far-infrared region than in the mid-infrared region, maintaining the interferometer and sample chamber in a vacuum during measurements reduces the effects of the water bands, but depressurizing the sample chamber to a vacuum causes liquid samples to vaporize, preventing ATR sample measurements of the sample.

The liquid triple-reflection ATR crystal plate for the THz (far-infrared) region that can be mounted on the ATR-500/Mi, used for these measurements, is configured to allow sealing of the ATR crystal area. This keeps the liquid from vaporizing when the sample chamber is depressurized and enables simple ATR measurements. The Si prism in the ATR accessory can provide a penetration depth of approximately 2 um at 1000 cm-1 and approximately 10 μm at 200 cm-1.

To verify the relationship between hydration and ions in various aqueous electrolyte solutions, Far-IR ATR measurements of pure water and various salt water solutions were performed using the JASCO FT/IR-6300FV, and a liquid triple-reflection ATR accessory. The results of these measurements are outlined below.

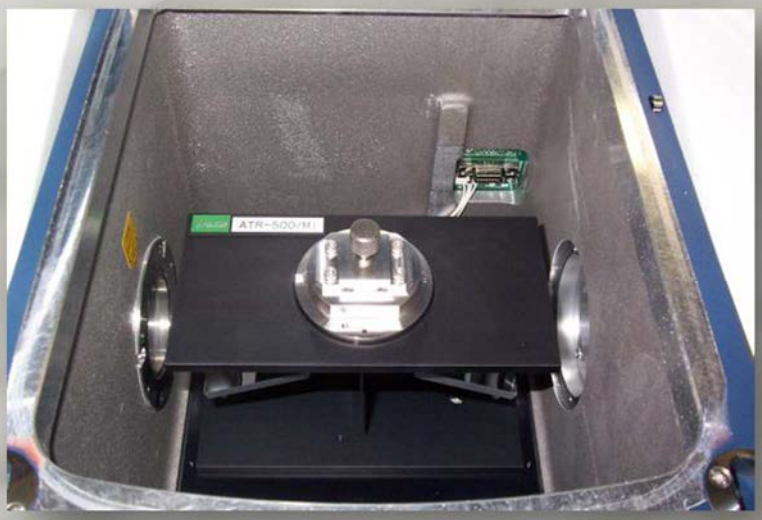


Figure 1 ATR-500/Mi＋ATR crystal plate
(Upper right: Prism and liquid cell)

2. Measurement Conditions

- System: FT/IR-6300FV
- Measurement Method: ATR method (Triple-reflection)
- Resolution: 2 cm-1
- Accumulations: 128
- Accessory: ATR-500/Mi + liquid triple-reflection ATR crystal plate (for Far-IR)
- Sample: pure water, 2 or 5 mol/L- Sodium chloride and Potassium chloride solution, 2 mol/L- Calcium chloride solution

Terahertz (THz) Measurements of Liquids by a vacuum compatible ATR accessory

3. Results and discussions

ATR measurements were performed of pure water in the mid-infrared and far-infrared regions. The results obtained by applying ATR corrections to the measured spectra are shown in Figure 2. The measurement conditions are given in Table 1. As shown in Table 1, the FT/IR-6000 series allows changes in the light source and beam splitter based on measurement frequency, enabling measurements across a broad spectral range. A peak near 600 cm-1 potentially assigned to the absorption resulting from the intermolecular motion of water is shown in Figure 2. Another peak was observed near 180 cm-1 (yellow border in Figure 2), which is assigned to hydrogen bonding. The change in the behavior of the peak near 180 cm-1 resulting from the solute type was also measured.

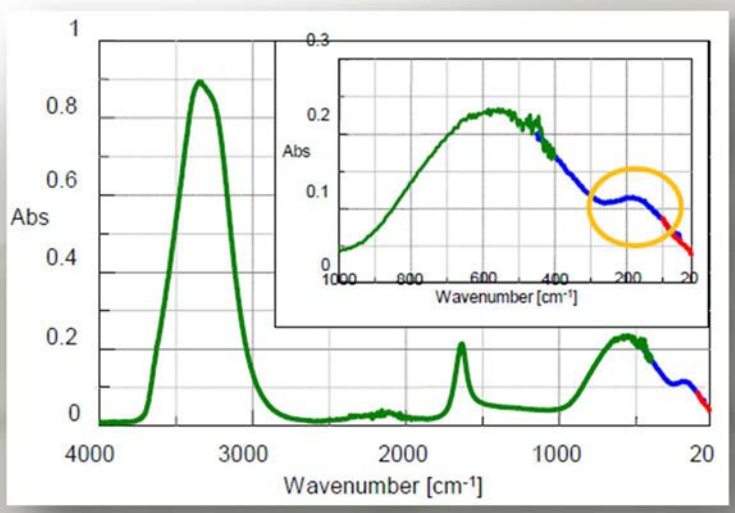


Figure 2 ATR spectra of pure water
(Upper right: Enlargement below 1000 cm-1)

Wavenumber [cm-1]	Beam Splitter	Light Source	Detector
4000 - 400*1 (Green-lined)	Ge/KBr	High-intensity ceramic source	DLATGS (standard)
450 - 100*2 (Blue-lined)	5 µm Mylar	High-intensity ceramic source	Si bolometer (option)
110 - 20 (Red-lined)	25 µm Mylar	water-cooled mercury light source	

*1) The ATR PRO470-H (diamond prism) was used under normal atmospheric conditions.

*2) The S/N ratio is lower in the frequency range of 150 cm-1 and below.

The stack graph (Figure 3) shows the ATR spectra of these aqueous solutions near 180 cm-1. Table 2 and Fig. 3 indicate the positions of the peaks assigned to hydrogen bonding. In all cases, the monovalent cation shifts toward the low frequency side compared to water, indicating a correlation between density and shift width. In the Potassium solution (K+) the large ion radius shifts the peak significantly toward the low frequency side, as compared to the Sodium solution (Na+). In an aqueous solution containing Calcium (Ca2+), a bivalent cation, the peak shifts toward the high frequency side compared to water alone, behavior opposite that of the monovalent cation. This suggests that the ion radius, the electrical charge, and the water solution activity affect the hydrogen bonding energy. As described above, using a liquid ATR accessory for measurements of solutions in a vacuum in the far-infrared region was confirmed to be highly effective in detecting slight changes in the behavior of aqueous solutions. Since significant differences between Na+ and K+ were verified in the measurements, we believe the liquid ATR accessory designed for the Far-IR region should find applications not just in the analysis of hydrogen bonding and intermolecular forces, but also the functions of and structural changes in molecules in solution, but for elucidating phenomena within biological organisms.

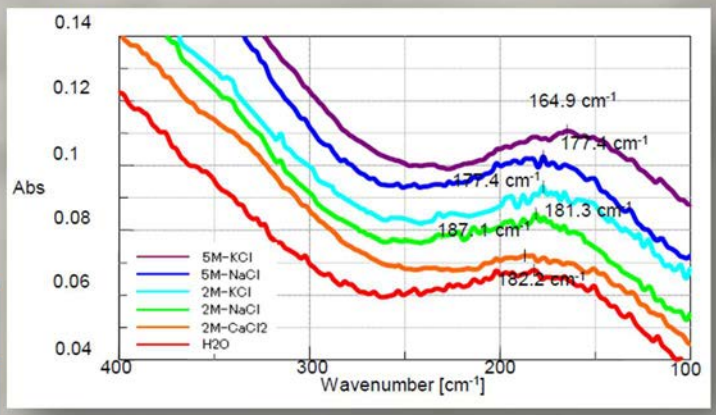


Figure 3 ATR spectra of Each Sample

Sample (Valence)	Ion radius [nm]	Conc. [mol/L]	Peak top [cm-1]	Peak shift [cm-1]
H2O	-	-	182.2	-
CaCl2aq (+2)	0.114	2.0	187.1	+4.9
NaClaq (+1)	0.116	2.0	181.3	-0.9
		5.0	177.4	-4.8
KClaq (+1)	0.152	2.0	177.4	-4.8
		5.0	164.9	-17.3

Table 2 Peak Shift of Each Sample

Reference - Miura, N. et al., Proceedings of 2nd International Symposium on Portable Synchrotron Light Sources and Advanced Applications, 2007, 73-76.

Simple Analysis of Brominated Flame Retardants with Far-Infrared Spectrometers (RoHS Directive)

Introduction

EU Directive for RoHS (The restriction of the use of certain hazardous substances in electrical and electronic equipment) was formally promulgated in 2003. According to the restriction, it was obligated for the electrical and electronic equipments manufacturers to bear the waste disposal cost of the products introduced into Europe. In addition, the use of 6 substances such as mercury, cadmium, lead, hexavalent chromium, PBB (Poly Brominated Biphenyl) and PBDE (Poly Brominated Diphenyl Ethers) stipulated by RoHS was prohibited from the 1st of July, 2006. Along with the restriction, it is now imperative to judge the presence of the restricted substances and to analyze the contents in the products introduced to the market and recalled from the market. This is to report on the PBDE (Poly Brominated Diphenyl Ethers). It is possible simply to identify the presence of PBDE even by the conventional ATR method in the mid-infrared region. However, the identification might be difficult depending on the resin type, the structural isomers and the homologs. Moreover, the absorption by some additives could be sometimes big obstruction. On the other hand, their own peaks of the absorption due to additives and fire retardants sharply appear because there is little absorption of the plastics itself in the far-infrared region. Far Infrared spectroscopy is also quite powerful over the analysis of the isomer. Model FT/IR-6000 series offers the measurement range from the near-infrared to the far-infrared and can be one of the best tools for the analysis of Brominated Flame Retardants with their rich homologs.

Experimental

As the samples, electric and electronic part plastics were broken into pieces of a few millimeters and formed it into a film of 1 mm in thickness, 10 mm in size with a hot press (heated and pressed). The ATR method was used for the measurement in the mid-infrared region and the transmittance method was applied for the far-infrared region. The full vacuum type of model FT/IR-6000 series (for far-infrared) was used for the measurement. Both the measurements in the mid -infrared region and in far-infrared region are possible only by changing the beam splitter and detector. In the far-infrared region, it is possible to perform even the measurement of colour plastics including a large amount of inorganic compounds and also black plastics which are normally difficult with IR spectrometers and Raman spectrometers. The comparison of two methods is shown in Table 1 and the system configuration is shown in Table 2.

Results and Discussions

Figure 1 shows the ATR spectra of the polystyrene containing PBDE.of 0%, 15%, and 30% respectively. When additives such as calcium carbonate, barium carbonate, and silica (SiO2) are little, it is possible to measure without any trouble. However, in case of high concentration of those additives, it influences the accuracy of the quantitative analysis because the peaks of those additives overlap the shoulder of the peak for PBDE.

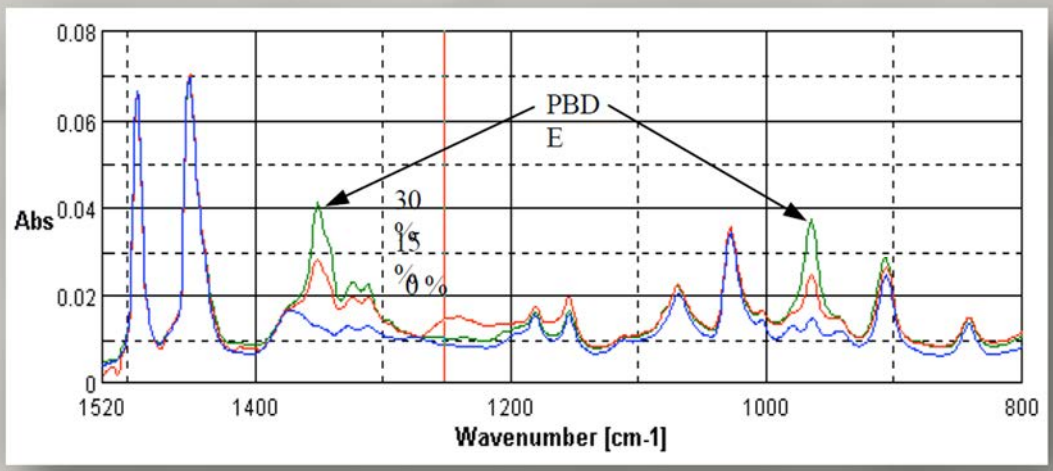


Figure 1 ATR spectra of polystyrene containing PBDE in the middle-infrared range

Simple Analysis of Brominated Flame Retardants with Far-Infrared Spectrometers (RoHS Directive)

	Mid IR (ATR)	Far IR (Transmittance)
Ease of operation	○	×
Obstructing peak	×	○
Identification of homolog	×	○
Non-uniformity samples	×	○
High refractive index samples	×	○
Prices	○	×

Table 1 Comparison of the methods

	Mid IR (ATR)	Far IR (Transmittance)
Measurement range	4000 - 650	650 - 150
Beam splitter	KBr (Ge)	Mayler
Detector	DLTGS(KBr)	DLTGS(PE)
Light source	High sensitivity ceramics	High sensitivity ceramics
Window for sample compartment	KRS-5	PE
Measurement environment	Room air	Vacuum

Table 2 System configuration

Figure 2 shows the spectra of several brominated flame retardants (compounds) in the far-infrared region. Since the peaks are shifted in wavenumber even by the little energy change in FIR, FIR spectroscopy is an appropriate way for the analysis of homologs and structural isomers. Various kinds of PBDE and PBB can be distinguished.

Figure 3 shows the spectra of the polystyrene containing PBDE in the far-infrared region. The peak at 335 cm-1 can be identified as a peak solely due to PBDE. Compared with the spectra obtained in the mid-infrared region, there appears almost no absorption of the polystyrene in this region, proving that there is no influence on the analysis.

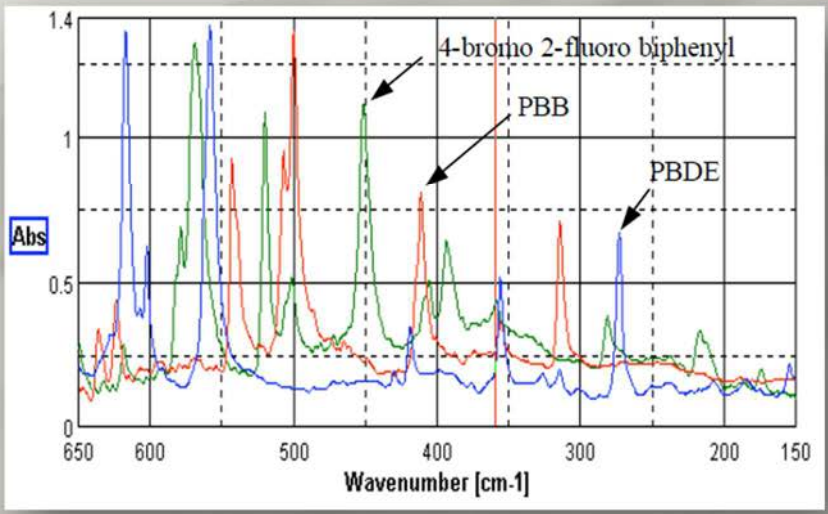


Figure 2 Spectra of several brominated flame retardants (compounds) in the far-infrared region

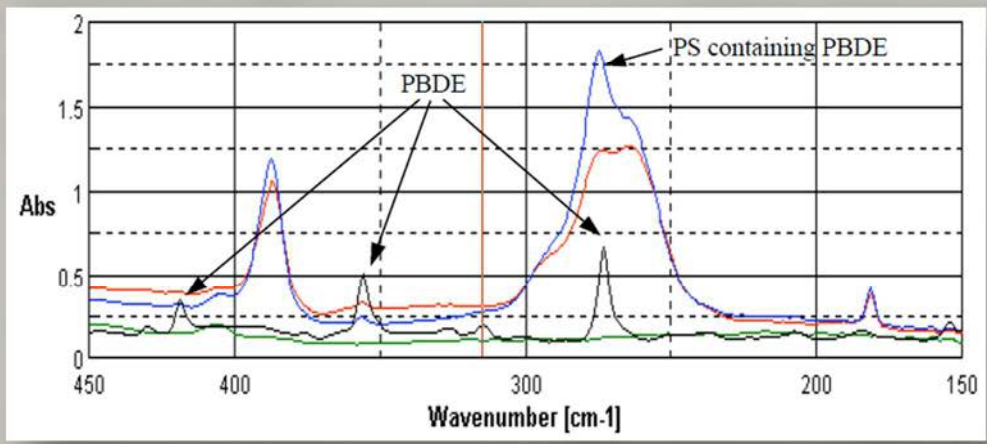


Figure 3 Spectra of the polystyrene containing PBDE in the far-infared region

Simple Method for Quantitative Analysis of Brominated Flame Retardants with Far-Infrared Spectrometers (RoHS Directive)

Introduction

The simple methods for analysis of Brominated Flame Retardants in the mid-infrared region and in far-infrared region were reported in the FTIR application data No.030TR0185-E, and also it was suggested that the quantitative analysis in the mid-infrared region would be possible to some extent. This time, quantitative analysis results by the calibration curve in far-infrared region were compared with the results in the mid-infrared region in order to confirm the usefulness of analysis by FTIR spectroscopy. Based on such calibration curve, PBDE (Decabromodiphenylether) of electric and electronic part plastics were quantitatively analyzed.

Experimental

As the samples, electric and electronic part plastics were broken into pieces of a few millimeters and formed it into a film of 1 mm in thickness, 10 mm in size with a hot press (heated and pressed). The ATR method was used for the measurement in the mid-infrared region and the transmittance method was applied for the far-infrared region. The full vacuum type of model FT/IR-6000 series (for far-infrared) was used for the measurement. Both the measurements in the mid-infrared region and the one in far-infrared region are possible only by changing the beam splitter and detector. In the far-infrared region, it is possible to perform even the measurement of colour plastics including a large amount of inorganic compounds and also black plastics which are normally difficult with IR spectrometers and Raman spectrometers. The calibration curve was generated by utilizing the second derivative of absorption peak, 355 cm-1 of spectra of polystyrene containing PBDE. In this case the correction due to film thickness was implemented.

Results and Discussions

Figure 1 shows the far-infrared spectra of polystyrene (Black) containing 0%, 15% and 30% of Brominated Flame Retardants. There is no absorption peaks of polystyrene in far-infrared region. The peaks of the antimony oxide added to improve the flame resistance are indicated by the red arrow. Since the presence of flame retardants can be confirmed clearly by the absorption peaks, it is very easy to analyze. In addition, it is possible to distinguish whether the sample contains the regulated Br compounds or the nonregulated ones.

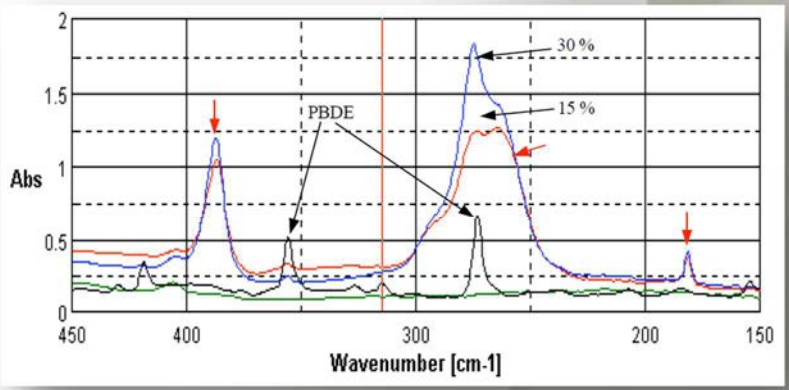


Figure 1 Far-infrared spectra of polystyrene containing PBDE

Figure 2 is an example of the calibration curve in the far-infrared region. It is generated by one-peak method with the thickness correction.

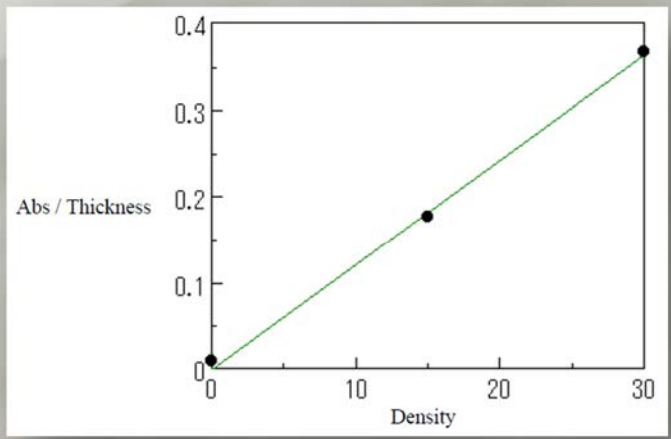


Figure 2 Calibration curve by far-infrared spectra

Figure 3 is another example of spectra of electric and electronic parts made of polystyrene obtained by the same method. Even if A and B look similar as the black plastics containing antimony oxide, B has three peaks due to PBDE, while A shows only one peak at the same three wavenumbers. A can be considered as decomposition product or isomer. C is transparent brown polystyrene and contained neither PBDE nor antimony oxide.

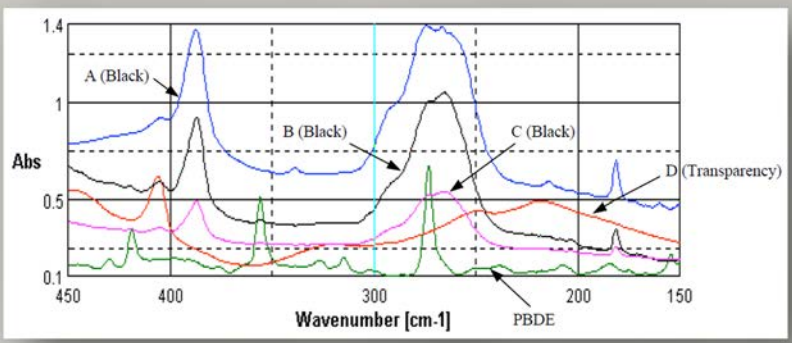


Figure 3 Far-infrared spectra of electric and electronic parts made of polystyrene

Monitoring of reaction process using the fiber probe

Introduction

The reaction mechanism and dynamic parameter of the chemical compounds can be analyzed by monitoring the reaction process using FTIR. Monitoring of reaction process has been widely used for the research in organic synthesis, enzymatic reaction and electrochemistry as well as the on-site measurement such as reactor, and there is a method of putting a fiber probe in the reaction system for such measurement. VIR-100/200/300 series spectrometer mounted with the Fiber connection unit has a capability to control maximum 6 lines of fiber through PC, enabling to monitor multiple reactors by one system.

Moreover, since VIR-200/300 allows the rapid scan measurement of up to 25 msec interval optionally, it is also capable to monitor in real time basis the relatively rapid chemical reaction such as enzymatic reaction. The type of fiber probe can be selected from the one for transmission, reflection and ATR according to the purpose.

In this report, the reaction process between oil applied on the surface of ATR prism and surfactant was measured by the rapid scan measurement using ATR probe.

Experimental

Figure 1 shows the configuration of the system used in this measurement. Since ATR method can analyze the interface between ATR prism and solution, the measurement can be easily implemented by simply putting tip of the ATR prism on the solution without any adjustment of optical pathlength which is usually needed for the transmission method. ATR fiber whose material is chalcogenide (made by Remspec) with ZnSe prism was used. After applying cooking oil to the surface of ATR prism, ATR prism was put on the stirred surfactant in the vial and the reaction process was monitored by rapid scan.

Measurement conditions

- Instrument: VIR-200
- Accessory: Fiber connection unit
- Fiber probe: Chalcogenide (Made by Remspec)
- Measurement method: ATR (ZnSe prism)
- Light source: High-intensity ceramic source
- Beam splitter: KBr/Ge
- Detector: Mid-band MCT
- Resolution: 4 cm-1
- Interferometer drive system: Rapid scan
- Measurement interval: 80 msec
- Max. measurement time: 80 sec

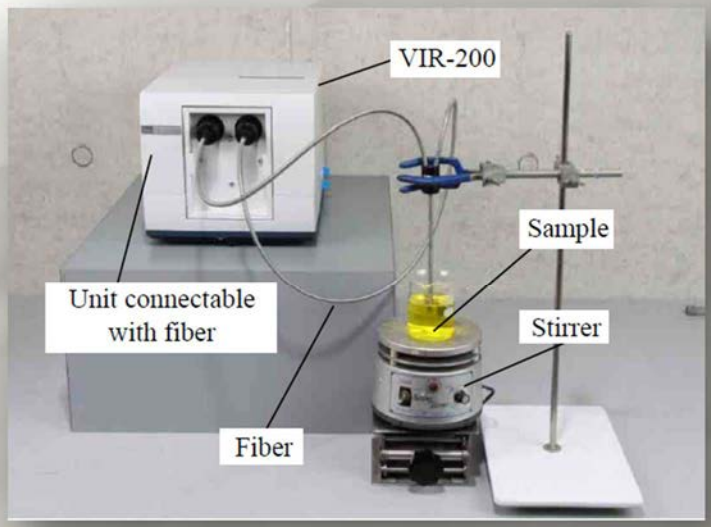


Figure 1 VIR-200 + Fiber connection unit

Results and Discussions

Figure 2 shows the change of spectra with time as 3D spectra. In this measurement, ATR prism was put on surfactant solution after 25 seconds from the start of measurement. As a result, a decrease in intensity of -CH peak (at 2925 cm-1) attributed to oil and an increase in intensity of -OH peak (at 1639 cm-1) attributed to surfactant were observed as time goes by. Also, Figure 3 shows a spectrum (for surfactant and oil) after the reaction between oil and surfactant on the surface of ATR prism and a spectrum (for surfactant only) measured on ATR prism without oil. As shown in the results (pink area) in Figure 3, it was found that the peak shape of spectrum of surfactant only was broader as compared with the spectrum of surfactant + oil.

Monitoring of reaction process using the fiber probe

This is considered to be due to the ordered structure of surfactant forming micell by the interaction of hydrophobic groups between surfactant and oil, and the disordered structure of surfactant in case that oil is not included. Figure 4 shows time-dependent change of the –CH peak and -OH peak. It was found that the intensity of -CH peak slowly decreased gradually after increased rapidly when ATR prism touched the surfactant. On the other hand, the intensity of -OH peak rapidly increased after about 25 seconds from the start of measurement and then slowly increased. This phenomenon indicates that the solubilization (emulsification) and dispersion was occurring in two steps on the surface of ATR prism and it can be said that the high speed reaction process was traced successfully by the rapid scan. It is also expected that the molecule behavior on the solid-liquid interface as well as the monitoring of ordinary chemical reaction can be analyzed by using this system. Accordingly, there is a possibility that this system can be applied to the research of liposome which attracts attention due to DDS as well as the basic study of surfactant and emulsion.

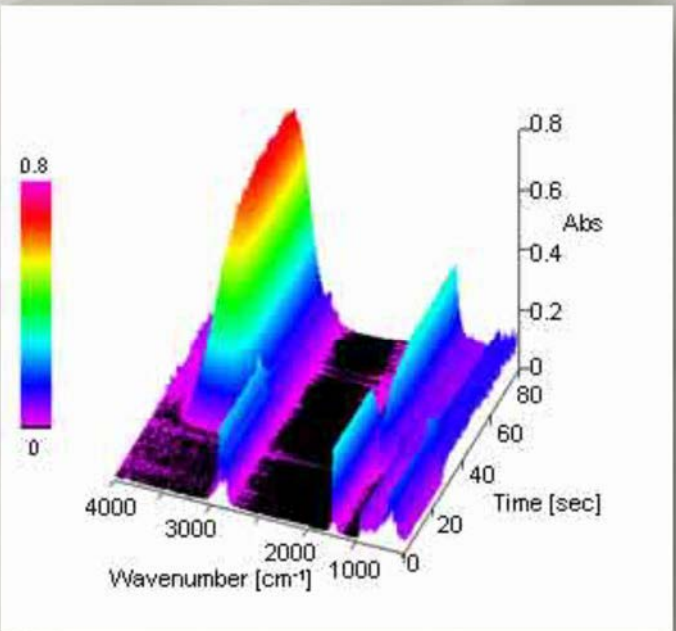


Figure 2 3D spectrum of reaction process

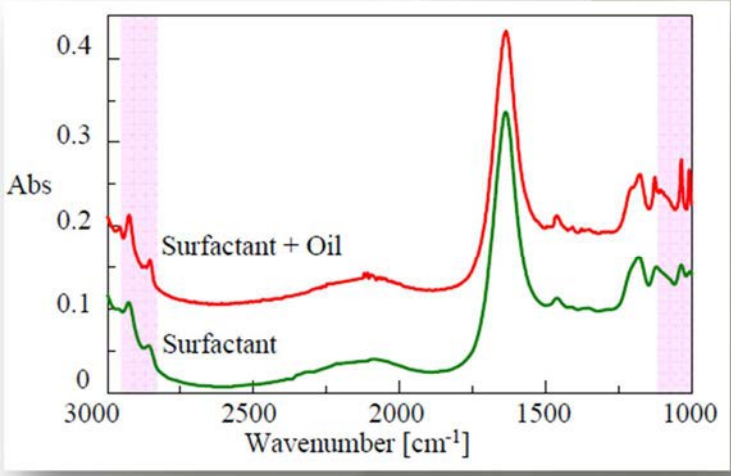


Figure 3 Spectrum of surfactant after measurement and spectrum of surfactant only

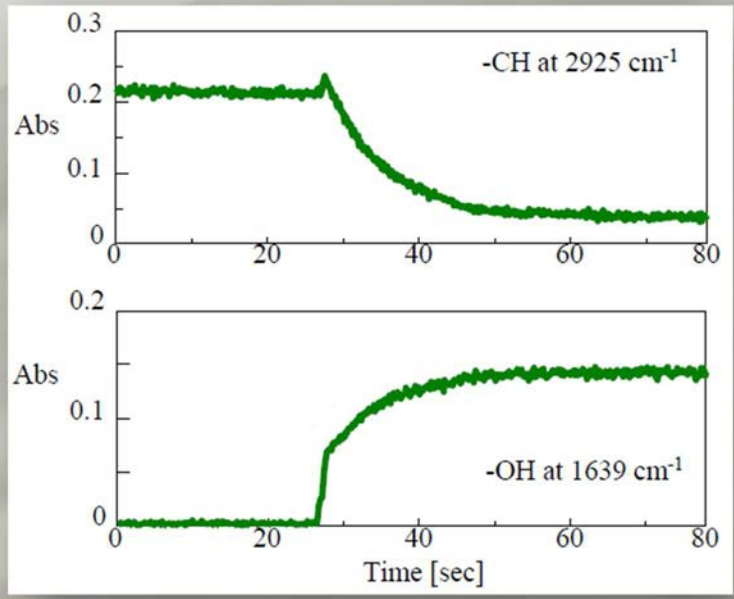


Figure 4 Time-dependent change of Oil(-CH) & H2O(-OH) group

Conclusion

In this report, the two-steps reaction was monitored by sing the fiber probe and rapid scan. In addition, it is expected that VIR series can be utilized in a wide range of field such as the evaluation of lithiumion battery materials that can be measured by the instrument installed in the glove box, the remote measurement in reactor by multi-probes and the measurement in manufacturing line, making full use of the features such as compact size, robustness and free usage of sample compartment.

Application by using of Auto contact ATR for VIR-100/200/300

Introduction

In IR spectrometry, the ATR method has been widely used because of simple measurement procedure which does not require the pretreatment of sample. In most of commercially available ATR accessories, the ATR prism can contact with sample by operating the sample presser manually. In the ordinary sample presser, the pressure limiter mechanism for avoiding the breaking of prism has been implemented. On the other hand, in the auto contact ATR newly developed by JASCO, the auto driving mechanism of sample presser has been adopted for not only avoiding the breaking of prism by the pressure limiter mechanism but also enabling the change of contact pressure stepwise. In addition, the auto contact ATR can offer exactly the same contact pressure at every measurement so that any operator can obtain quickly the IR spectrum highly reproducible. In this application note, the capability to change the contact pressure stepwise was applied to the measurement of food supplement. Also the simulation for applying to acceptance inspection was performed.

About Auto contact ATR (Model AC-ATR-VIR2)

The newly designed auto contact ATR including auto drive of sample presser, enables controlling the contact pressure to be applied to the sample by the built-in pressure sensor. The drive of auto sample presser can be controlled through the operation panel on the accessory or through the PC software. In both cases, you can set the proper contact pressure by observing the preview spectrum of sample. In addition, the sample measurement procedure such as "contact with sample", "measurement" and "release of sample“ can be preprogrammed so that you can complete one sequence of measurement procedure just by pushing the start button. Such automation capability may help the users for reducing their workloads on routine analysis requiring a number of similar samples. The auto contact ATR (AC-ATR-VIR2) can be equipped into either a single reflection ATR (ATRS-100-VIR) or multi chamber IR attachment (MPA-100-VIR).

System configuration

- 6999-J011A VIR-100 Versatile FTIR Spectrometer
  *Applicable to VIR-200 (6999-J012A)
- 6999-J103A ATRS-100-VIR Single reflection ATR attachment *Applicable to MultiChambIR attachment (Model MPA-100-VIR; 6999-J101A)
- 6999-J143A PKS-Z100 ZnSe prism kit
- 6999-J151A AC-ATR-VIR Auto-Contact ATR for ATRS/ATRH/MPA-100-VIR

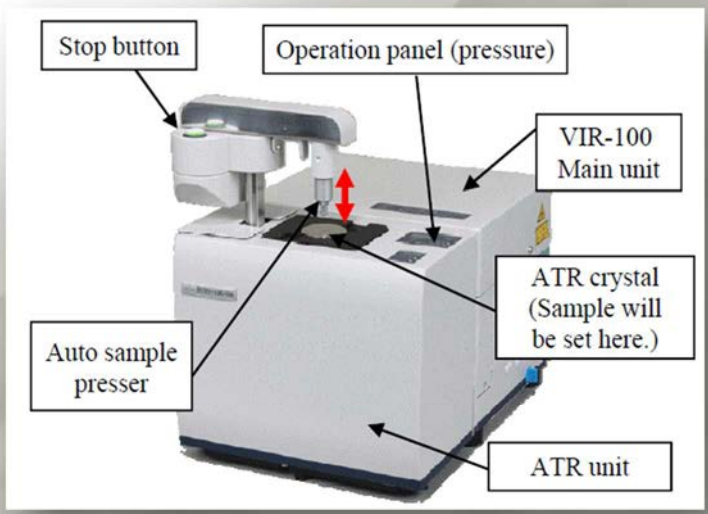


Figure 1 VIR-100 + Auto contact ATR
（VIR-100 + ATRS-100-VIR + AC-ATR-VIR)

Figure 2
Pressure monitor (left) and operation panel (right)

Application by using of Auto contact ATR for VIR-100/200/300

Measurement conditions

- Main Unit: VIR-100
- Resolution: 4 cm-1
- Method: ATR (crystal: ZnSe)
- Detector: DLATGS
- Accumulation: 16 times
- Accessory: ATRS-100-VIR + AC-ATR-VIR
- Contact pressure (based on area of prism): 40 - 400 kg/cm2（Figure 3）, 400 kg/cm2 (Figure 4, 5)

Results

1. Application to brittle sample such as soft capsule of food supplement

Auto contact ATR was applied to the measurement of soft capsule of food supplement. By changing the contact pressure from 40 kg/cm2 to 400 kg/cm2 at every 40 kg/cm2 step, the IR spectrum of each step was obtained (Fig. 3). The IR spectrum of starch was observed in the spectra from 40 to 120 kg/cm2 and this indicates that the soft capsule was not broken at up to 120 kg/cm2 so that the starch that is the ingredients of capsule itself was observed. At the spectrum of 160 kg/cm2, tocopherol peaks appeared. These results suggest that the capsule was broken at this pressure and, the ingredients inside of capsule such as tocopherol was observed accordingly. At 200 kg/cm2 or higher pressure, it is assumed that the ingredients inside of capsule was pushed out of prism surface and therefore, the ingredients of capsule itself such as starch appeared again. By using the auto contact ATR, such an dynamic analysis of soft capsule can be performed at one sequence of measurement pre-programmed.

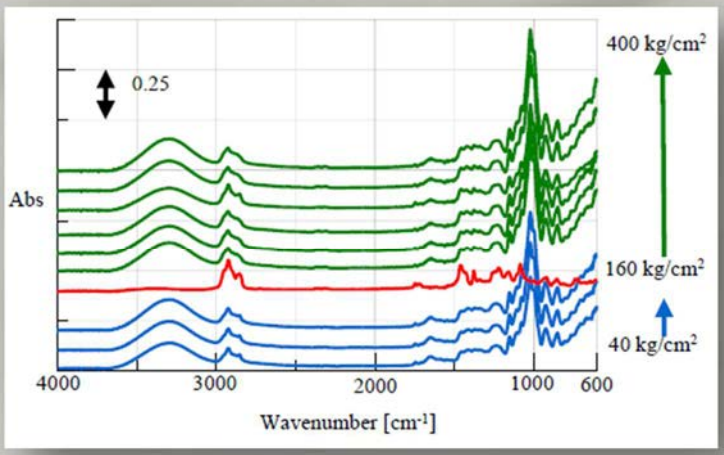


Figure 3 IR spectra of soft capsule of food supplement

2. Simulation for applying to acceptance inspection

In order to simulate the acceptance inspection, the five polymer films having intentionally two different compounds from the other three standard (polyethylene) films were prepared and the IR spectra were obtained (Figure 4). In addition to the auto contact ATR, "repeat measurement" and "judgment of acceptance" (Figure 5) programs that are all standard functions in Spectra Measurement for VIR series, were used so that you can perform repeatedly the measurement routine including the judgment by at one sequence of measurement pre-programmed. Figure 3. pressing the start button. The different polymers from the standard polyethylene were easily detected as shown in Figure 4 and 5 (spectrum #3 is of polyvinylidene chloride and, the spectrum #5 is of polypropylene.).

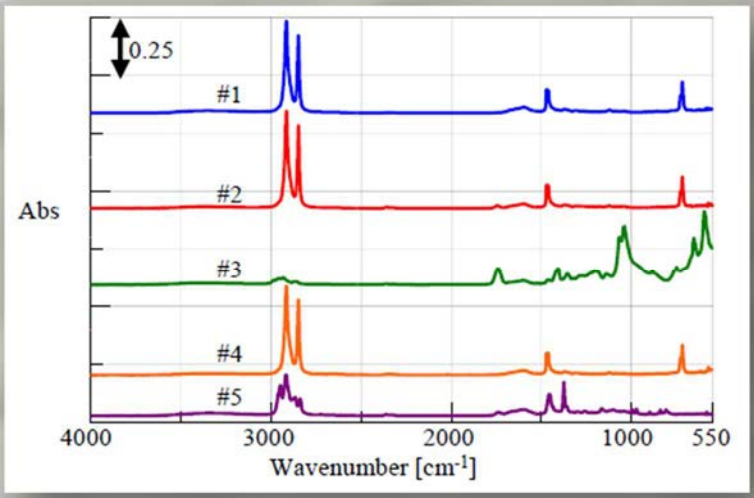


Figure 4 IR spectra of five polymer samples

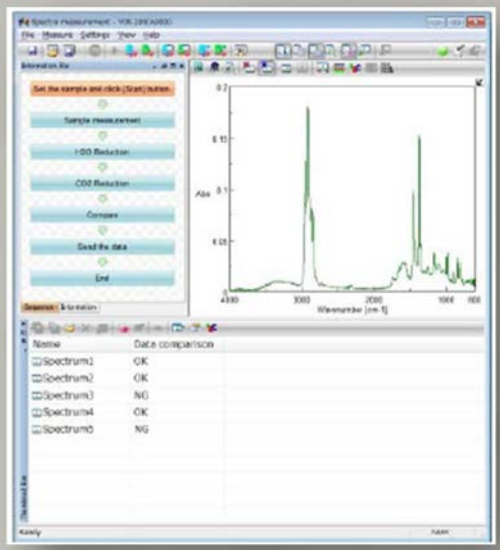


Figure 5 Judgment of acceptance

ATR application to granular gum by Auto-contact ATR Accessory for VIR-100/200/300

Introduction

In IR spectrometry, the ATR method has been applied to obtain the surface information of sample by contacting the sample with crystal. Most of commercially available ATR accessories allow the users to work on the sample contact with crystal only manually, while we, JASCO have developed the auto-contact ATR including auto drive mechanism to contact the sample with ATR crystal. In the auto contact ATR, the contact pressure among crystal and sample can be controlled with good reproducibility. Such capability has been applied to the measurement of brittle sample or we have simulated an acceptance inspection by using this auto contact ATR with "judgment of acceptance" function that is the one of the standard functions in VIR unit (See application note #080-AT-0235). In this application note, the auto contact ATR has been applied to the monitoring of spectral change by changing of number of contact with sample such as granular gum.

Measurement

Several kind of chewing-gum having different shape such as stick or granular and unique mouthfeel or longer duration of taste are commercially available. If such mouthfeel or sensory evaluation can be measured as actual number, it is possible for the measurement system to be applied to the evaluation of food product. In this application note, we have tried to duplicate the chewing behavior of human by using an Auto-contact ATR with a granular gum placed on the ATR crystal. The biting strength of normal adult male is approximately 65Kg that is equivalent to 4.6Kg per one set of teeth. Therefore, the 4.6Kg contact pressure of crystal with sample was applied to the measurement. To duplicate the chewing behavior, the sample presser drove repeatedly 100 times and, the IR spectrum at every pressing obtained. Such a series of measurement can automatically be carried out by using of Auto-contact ATR with repeat measurement function of Spectra Measurement program in VIR system.

Measurement conditions

- Main Unit: VIR-100
- Mode: ATR
- Resolution: 4 cm-1
- Detector: DLATGS
- Accumulation: 16 times
- Number of repeat of sample presser drive: 100 times
- Accessories: ATRS-100-VIR + AC-ATR-VIR (Crystal: ZnSe)
- Contact pressure: 260 kg/cm2 (Applied pressure on crystal surface) Equivalent to 4.6 kgf (applied pressure on sample)

Figure 1 Granular gum place on crystal

Results

Every IR spectrum up to 10 times of presser drive was shown in Figure 2 and, the IR spectrum at every 10 time drive of 100 time drive was shown in Figure 3. The peaks derived from esters were appeared at near 1740cm-1 and 1235cm-1. These results indicate that the gum base included the vinyl acetate. Also the peak derived from xylitol was observed at near 745cm-1. These characteristic peaks were used for monitoring the change of gum base and ingredient. The change of peak intensity at 1740 cm-1 was shown in Figure 4. The intensity increased in the first 5 measurements and, it became stable later. The monitoring of peak intensity at 745cm-1(xylitol) was indicated in Figure 5. The intensity gradually increased up to about 40 measurements, while it became stable later. These results suggest that the gum base can get to fit teeth relatively early chewing and, the taste (xylitol) will be seeped out gradually.

ATR application to granular gum by Auto-contact ATR Accessory for VIR-100/200/300

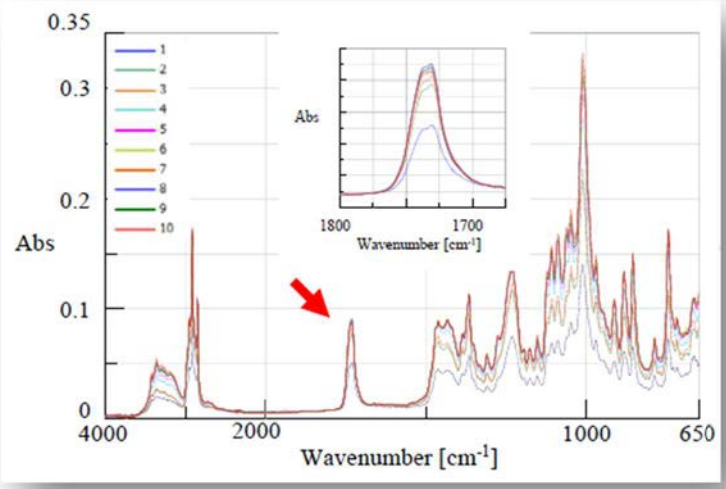


Figure 2 IR spectra in first 10 trials

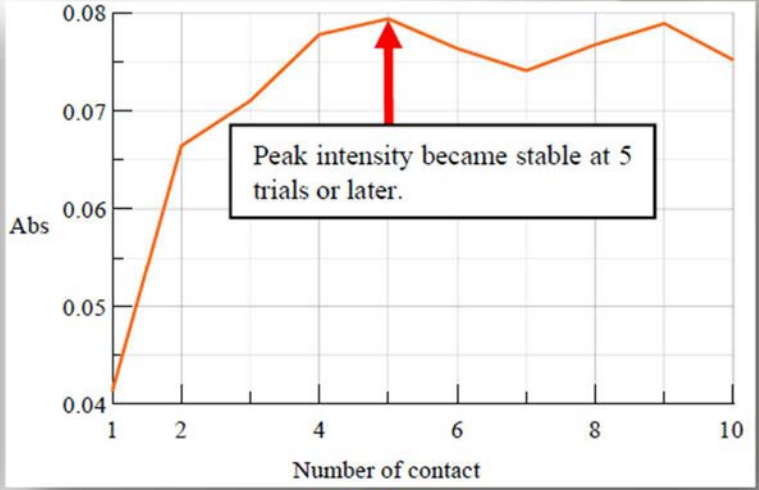


Figure 4 Change of peak intensity at 1740cm-1 (vinyl acetate)

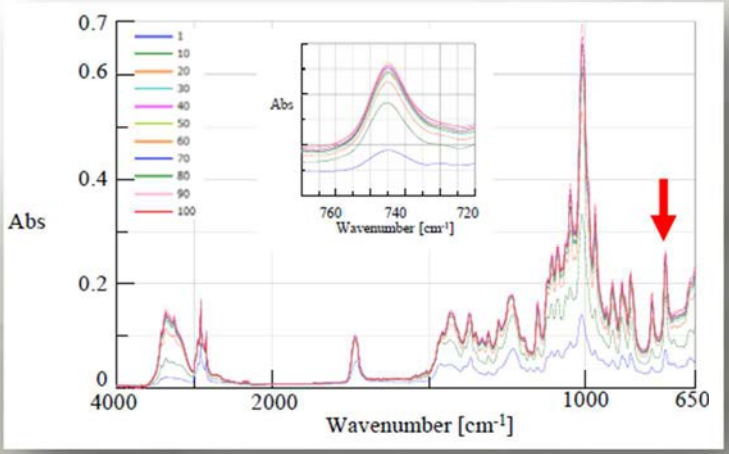


Figure 3 IR spectra at every 10 trials of 100 trials.

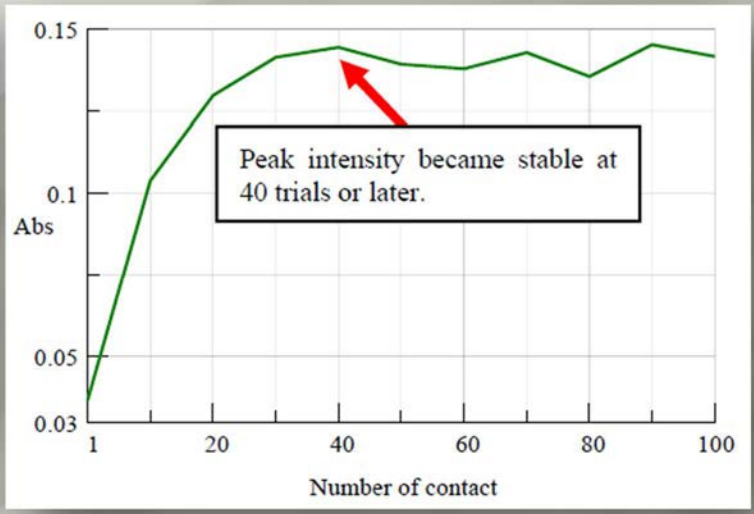


Figure 5 Change of peak intensity at 745cm-1 (xylitol)

As you can see, the Auto-contact ATR can be the effective tool to simulate the dynamic analysis of food samples such as chewing-gum. Further application to this demonstration, the constant temperature ATR measurement at 37ºC with doping of enzyme such as amylase into sample will be considered so that the measurement conditions will be close to the conditions in the mouth.

*A constant temperature or heating ATR is the custom-made option.

Identification and quantitative determination of plasticizer in A1 size PVC sheet by using of a single bounce ATR for large-sized sample

Introduction

Poly-vinyl-chloride (PVC) has been widely used as multi-functional plastic which can be made either hard or soft with flame retardant, waterproof, acid-proof, and alkali-proof feature. For the soft PVC, the ester compound type of plasticizer has been added and in particular the phthalate ester has been widely used as the superior plasticizer. However, it has been pointed out that the use of phthalate ester may cause several risks such as its carcinogenic action or some influence to the reproductive ability. Therefore, EU-Toy-Directive and the US Consumer Product Safety Improvement Act (CPSIA) are regulating the use of six kind of phthalate esters (DEHP, DBP, BBP, DINP, DIDP, DNOP; Figure 1) in toy products. In Japan, Food Sanitation Act is regulating the use of two kind of phthalate esters (DEHP, DINP) in toy products and, since September 2011, such regulation has been applied to the six kind of phthalate esters in the same way as EU-Toy-Directive. Furthermore, the three phthalate esters (DEHP, DBP, BBP) have been selected to be classified as Substances of Very High Concern (SVHC) in REACH regulations. Therefore, to apply RoHS Directive to the three esters is now under consideration.

Generally, the GC/MS has been used for the analysis of phthalate esters, however, the measurement time by GC/MS is relatively long and, it requires sample preparation such as isolation and extraction (waste of time and cost). On the other hand, the FTIR enables the completion of analysis in just one minute if the sample contains more than a few percentage of phthalate esters. Particularly, the ATR method enables the non-destructive measurement of surface of sample by just contacting the prism to the sample, without consideration of sample thickness or color. In soft PVC plastic, since usually 10 to 60% of phthalate ester plasticizer is added, the FTIR could be the best suitable method for the 1st screening inspection. In this application, the identification and quantitative determination of phthalate ester plasticizer in A1 size PVC sheet has been carried out by using of a single bounce ATR for large-sized sample (Figure 2).

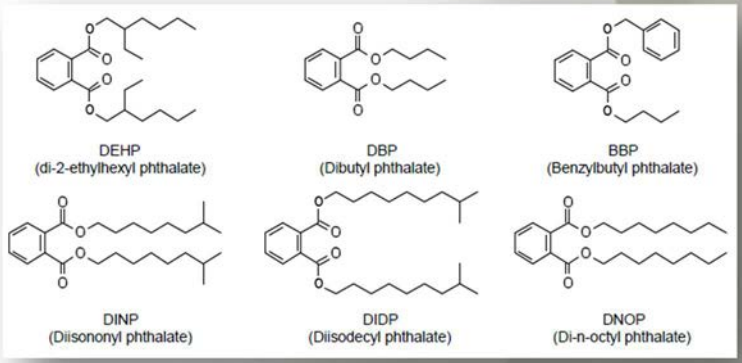


Figure 1 Structure of six kinds of regulated phthalate esters

Figure 2 Single reflection ATR for large-sized sample (FT/IR-4100 with ATR PRO510T-S)

Features of a single bounce ATR for large-sized sample (ATR PRO510T-S/ATR PRO530T-H)

The ATR method offering easy sampling can be applied to the non-destructive measurement. Recently, the request to measure the large-sized product or molded product as it is has been increased day by day. The newly designed Model ATR PRO510T-S/PRO530T-H) is now available and allows the users to let the sample position higher than main unit FTIR (See Figure 2 and 3), allowing the measurement of the very large sample that cannot be accommodated in the standard sample compartment of FTIR main unit. Also, the center of sample can be measured if the sample size is up to 6 inches, and as you can see in the photo (Figure 3.), even the A1 size sheet can be measured as it is. Such capability suggests the possibility for applying this method to the final inspection of all finished products from production line such as of sheet film or of vehicle bumper molded. Similarly to the model of ordinary ATR, the higher contact pressure model (ATR PRO530T-H) is available so that the sample having lumpy or hard surface can be applied to.

Identification and quantitative determination of plasticizer in A1 size PVC sheet by using of a single bounce ATR for large-sized sample

The A1 size PVC sheet (65 x 90 cm; no sample preparation done) was just put onto the sample stage of ATR (Figure 3). The measurement results were shown in Figure 4.

Figure 3 A1 size sheet on ATR PRO510T-S

Measurement conditions

- Instrument: FT/IR-4100
- Method: ATR (ATR PRO510T-S, ZnSe)
- Detector: DLATGS
- Resolution: 4 cm-1
- Accumulation: 64

PVC has the absorption peaks derived from C-Cl stretching vibration in the region from 600 to 700 cm-1, as well as the peaks around 1425 and 1250 cm-1. Such peaks of PVC can be observed clearly in IR spectrum (Fig. 4.). Regarding the peaks of phthalate esters (Fig. 1.), the peaks will appear around 1720, 1280, and 1120 cm-1 as absorption by aromatic esters and, will appear around 1600, 1580, 1465, 1080, and 745 cm-1 as the absorption by aromatic ring in which the ortho position was substituted. In the sample spectrum (Figure 4.), such peaks of phthalate esters plasticizer can also be observed.

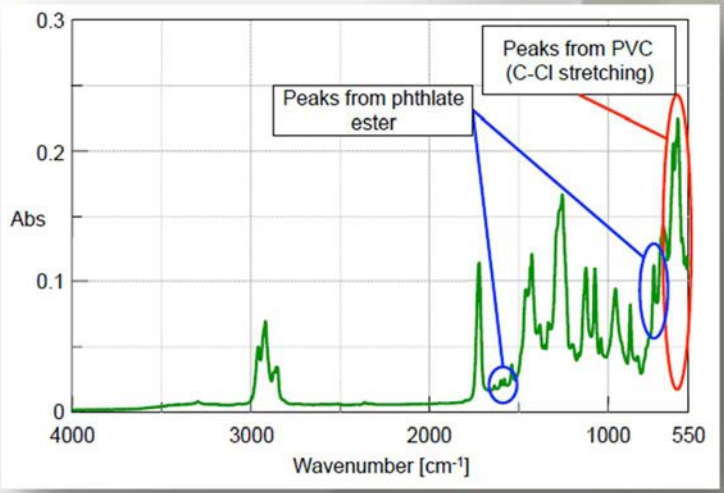


Figure 4 IR Spectrum of PVC sheet

In addition, the quantitative determination of DEHP was tried. Each of 10, 20 and 40% DEHP contained PVC was measured by the same ATR method and then, the calibration curve was generated by the peak height of unique peak at 1600 cm-1 (Figure 5). As a result of quantitative determination, it was confirmed that 37 % of DEHP was contained in A1 PVC. The above results clearly indicate that the ATR can be applied to the quantitative determination as well as to 1st screening inspection of phthalate ester plasticizer contents under the industrial regulations. It is also suggested that our newly designed single bounce ATR for large-sized sample can be applied to the non-destructive and quick measurement of surface of extra large sample or molded sample.

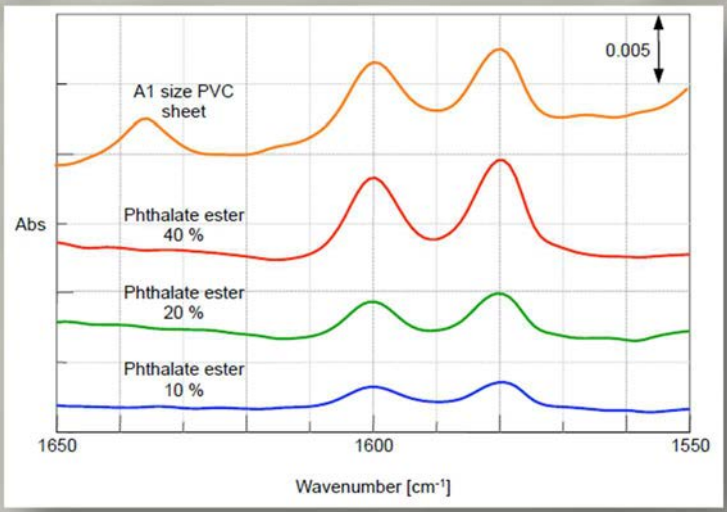


Figure 5 IR spectra of known DEHP content PVC

Efficacy of Imaging Data Analysis using "Model Analysis"

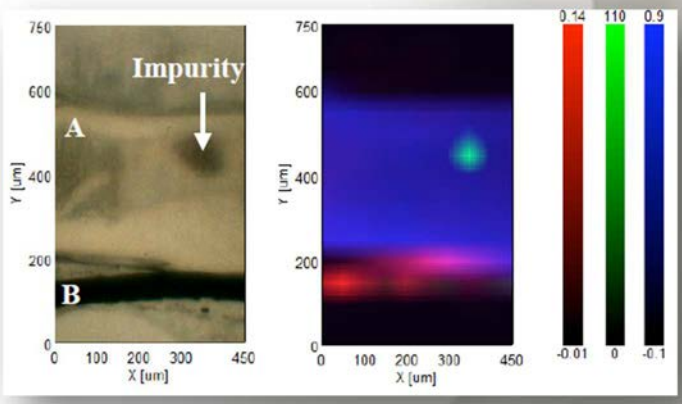
Introduction

Imaging measurement using Micro FT-IR is widely used as a method which can visualize the components distribution. In recent years, the users can chose the most appropriate imaging method in accordance with their purpose because a variety of imaging methods has been available due to the progressive development of the high-speed imaging measurement methods using a multi channel detector and IR microscope. The imaging measurement for handling enormous amount of the data, however, requires significant time and special skill for analysis. For example, Figure 1 shows the imaging analysis result of a multilayer film. It can be seen that the spectrum of each portion is checked and the intensity distribution of the key peaks is shown as the color-coded image. From the spectra, it is seen that three kinds of components were contained in the film, while from the images, it is considered that polyvinyl chloride (PVC) and polyester are found in A layer and B layer of the multilayer film respectively and that protein is contained as an impurity in the PVC layer. As shown in the above, the components distribution can be discerned by analyzing the imaging data. On the other hand, there is a possibility that some components in the sample may be neglected as the number of the data becomes larger.

This report illustrates an example of the imaging data analysis using "Model Analysis" in Micro Imaging Analysis program newly developed for IRT-5200/7100/7200 (shown in Figure 2). The "Model Analysis" is one of the functions to assist the analysis in the Micro Imaging Analysis program such as making an image without checking the spectrum.

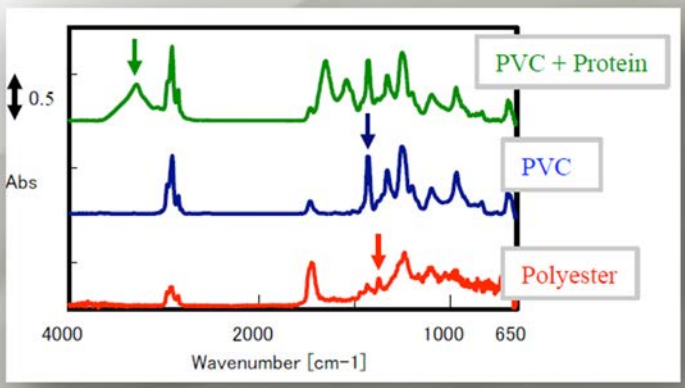
Model Analysis

"Model Analysis" is a function to make a relative concentration distribution by extracting the principal components automatically from the measured spectra. Therefore, the imaging plot can be obtained in a short time without neglecting the components contained in the sample as explained in the above. It is also possible to identify the components by searching the spectrum of principal components in the data base.



Observation image

Imaging plot
(Green: Protein, Blue: PVC, Red: Polyester)



Measured spectra (Off-set) (Imaging plot was made based on the key peaks indicated by arrows)

Figure 1 Imaging analysis result of multilayer film with key peaks

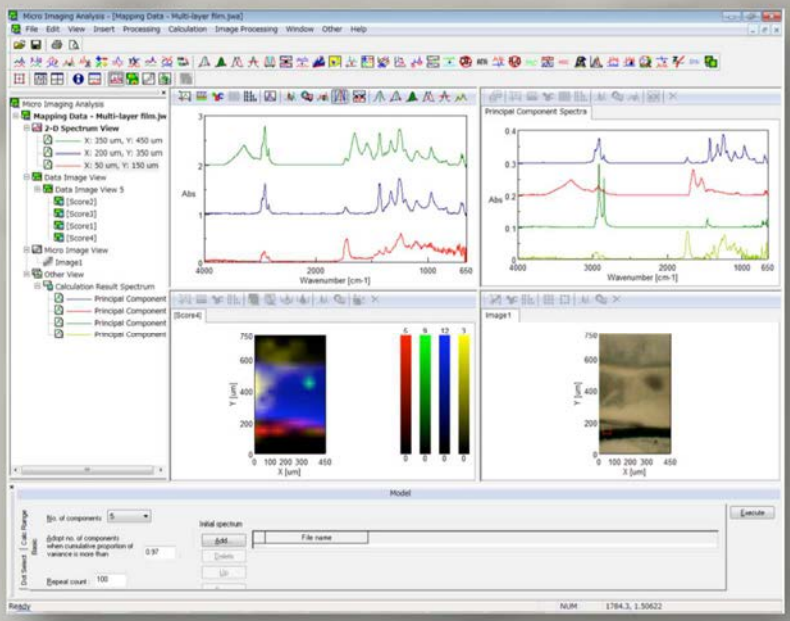
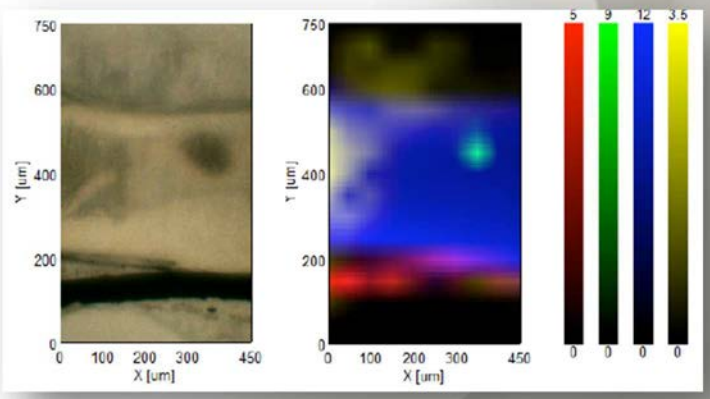


Figure 2 Micro Imaging Analysis Program

Efficacy of Imaging Data Analysis using "Model Analysis"

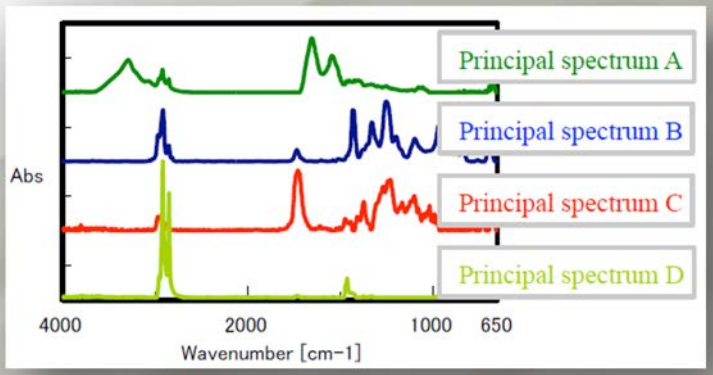
"Model Analysis" Results

Figure 3 shows the imaging analysis result of a multilayer film using "Model Analysis". Comparing the data in Figure 1 with the data in Figure 3, two differences can be observed. One is that the spectrum of the fourth component was contained in the spectrum of primary component. It is indicating that the component possibly neglected by Imaging Analysis using key bands can be accurately analyzed by using "Model Analysis". The other is the difference in the impurity spectra. The pure spectrum of the protein as an impurity can be obtained using "Model Analysis", while the overlapped spectra of protein and PVC in the multilayer were obtained as the measured spectrum by the method using key bands. The spectrum of pure component improves the accuracy for searching databases and facilitates the identification of the components. Figure 4 illustrates the database search result of the principal components. Polyethylene was found to be as a principal component which was neglected by the Imaging analysis using key peaks. As described above, the "Model Analysis" makes it possible to obtain the imaging plot of all contained principal components without checking the spectrum, which improves the accuracy of searching the databases.



Observation image

Imaging plot
(Green: Protein, Blue: PVC,
Red: Polyester, Yellow: Polyethylene)



Principal components spectra (Off-set)

Figure 3 Imaging analysis result of multilayer film with "Model analysis"

System configuration

- FT/IR-4600 FT/IR Spectrometer
- IRT-5200-16 Infrared Microscope with Micro Imaging Analysis Program (Standard for IRT-5200/7100/7200)

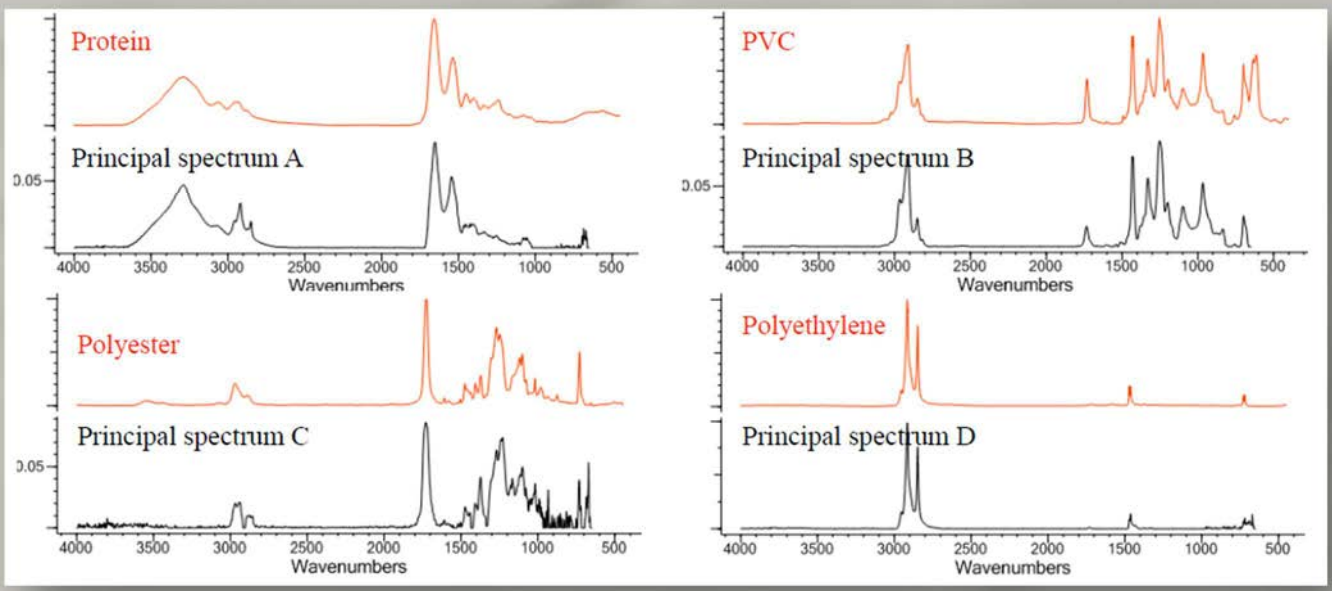
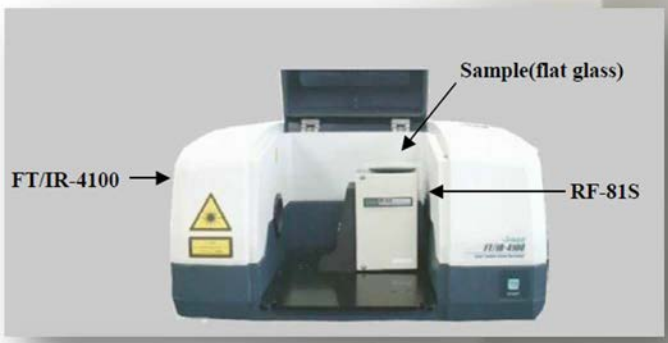


Figure 4 Database search result of principal components spectra

Measurement of the functional glass by FTIR based on [Testing method on transmittance, reflectance, emissivity and solar heat gain coefficient of flat glasses (JIS R 3106)]

Introduction

The method for testing transmittance, reflectance, emissivity and solar heat gain coefficient of flat glasses using a UV-VIS spectrophotometer or an IR spectrometer is prescribed in "JIS R 3106". The energy is released in the form of electromagnetic wave (mainly infrared rays) from the surface of the object depending on the temperature, which is generally called as emission (radiation). As a method of computing normal emissivity, "JIS R 3106" describes a technique to obtain normal emissivity from the reflectance based on spectral reflectance of the flat glass measured by the IR spectrometer. The measurement conditions indicated in "JIS R 3106" for obtaining the normal emissivity of the flat glass using the IR spectrometer, and the specification of JASCO FT/IR-4100 and specular reflection measuring device, RF-81S are shown in Table 1. Adding specular reflection measuring device, RF-81S to standard configuration of FT/ IR-4100 enables the measurement based on "JIS R 3106" and in addition by combining "IR reflectance and the emissivity calculation program" customized to this specification, the emissivity of flat glass can be obtained in an easy and simple manner.



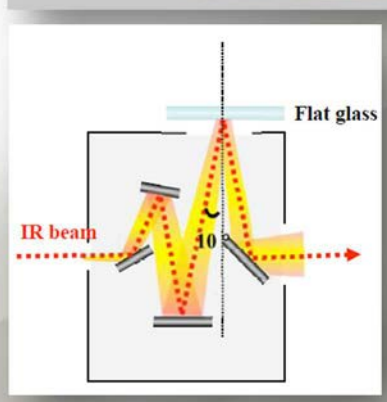


Figure 1 FT/IR-4100+RF-81S and diagram of optical path for RFT-81S

The Low-E glass (Low Emissivity Glass: Low Radiation Glass) which is attracting attention these days is the flat glass coated with the special metallic film on its surface. Since its emissivity is much lower as compared with usual flat glass, it has a superior heat shielding and insulation property and can be called as the material with high energy saving effect. By using FTIR, the quantitative evaluation of emissivity can be done. The spectral reflectance of the Low-E glass coated with the metallic film was measured by FT/IR-4100 this time and the normal emissivity was computed by "IR reflectance and an emissivity calculation program" as reported below.

	JIS R 3106 Requirements	FT/IR-4100	RF-81S*2)
Measuring method	Specular reflection method (Incidence angle: 15 ° or less)		Specular reflection method (Incidence angle: 10 °)
Resolution	4 cm-1 or less	1, 2, 4, 8, 16 cm-1	
Measuring range*1)	5 ~ 50 mm (2000 ~ 200 cm-1) Minimum:5 ~ 25 mm (2000 ~ 400 cm-1)	7800 ~ 350 cm-1 5000 ~ 220 cm-1 (using FIR-4000 kit)	

Table 1 FTIR measurement condition for measuring flat glass in "JIS R 3106" and JASCO FTIR system

*1) FT/IR-6100 series should be selected for the range below "220 cm-1".
*2) Please contact us for the measurement of large-sized flat glass.

Measurement of the functional glass by FTIR based on [Testing method on transmittance, reflectance, emissivity and solar heat gain coefficient of flat glasses (JIS R 3106)]

Measurement conditions

- Instrument: FT/IR-4100
- Detector: DLATGS
- Measuring method: Specular reflection method
- Accessory: RF-81S
- Resolution: 4 cm-1
- Accumulation: 64 Times
- Measuring range: 5 ~ 25 mm (2000 ~ 400 cm-1)

Analysis results

Both sides of the Low-E glass currently used for the residential windows were measured. As a reference the aluminum mirror is used. Normal emissivity was computed from the result of the measured spectral reflectance in accordance with the prescription in "JIS R 3106". By using "IR reflectance and the emissivity calculation program", the reflectance and normal emissivity of each sample can be calculated by simply inputting a spectrum. According to the result of Low-E glass normal emissivity as shown in Figure 2, the normal emissivity of the metal coated side of Low-E glass was determined to be 0.2 or less and it is confirmed that it has a superior property to shield the solar heat as compared with ordinary glasses. Furthermore, overall evaluation of functional glass can be done by combining the program for calculating solar transmittance, reflectance/visible light transmittance and reflectance which is consistent with "JIS R 3106" with an ultraviolet visible spectrophotometer.

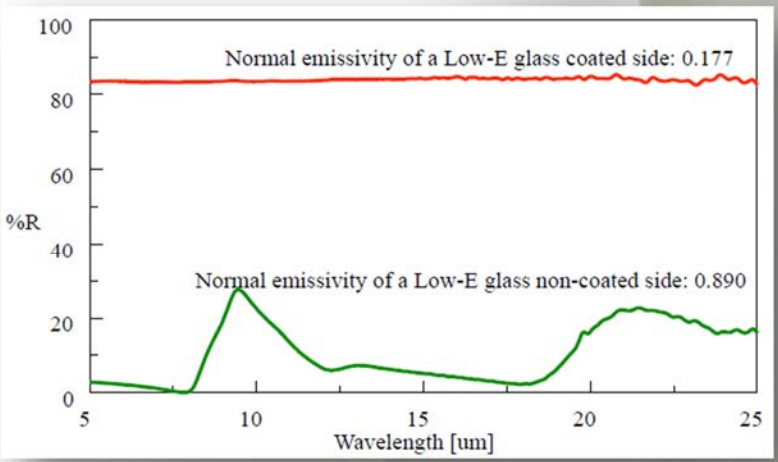


Figure 2 Spectra of Low-E glass

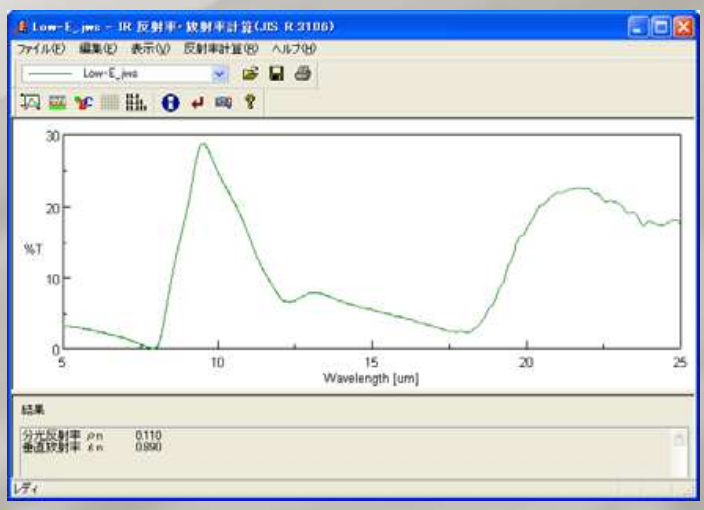


Figure 3 Analysis result by "IR reflectance and emissivity calculation program"

Measurement of broadband spectrum using automatic wide-range measurement system

Introduction

Generally, Mid-IR spectroscopy (4000~400 cm-1) is widely used for qualitative and quantitative analysis of the substance (mainly organic substance), since the information on normal vibration and rotation of molecule can be obtained. Apart from this, Near-IR spectroscopy (15000~4000 cm-1) utilizing overtone and combination tone is used with a focus on the non-destructive quantitative analysis of food, drug and various industrial products, and Far-IR (Terahertz) spectroscopy (400~10 cm-1) using stretching and lattice vibration between heavy atoms is used with a focus on the quantitative analysis of inorganic substance and crystal structure analysis. One spectrum in Mid, Near and Far-IR range can be measured using a single FTIR instrument by changing four elements such as light source, detector, beam splitter (BS) and windows. Namely, one FTIR instrument enables to obtain the information on overtone, combination tone, lattice vibration as well as normal vibration for overall evaluation of a sample. This time JASCO has developed the automatic wide-range measurement system which can be incorporated in FT/IR-6000 series to measure in the range from Near-IR to Far-IR fully automatically. FT/IR-6000 series are originally equipped with the automatic switching system for light source and detector, and automatic wide-range measurement system provides automatic switching for BS and windows. In this report, the details of the system and measurement example using automatic wide-range measurement system are illustrated.

System

Figure 1 shows the external appearance of FT/IR-6800FV and automatic wide-range measurement system, which combines automatic BS switching unit and automatic windows switching unit (or automatic gate value unit). Light source, detector, BS and windows are automatically switched so that the measurement can be carried out in the wavenumber range set in the software. One of the most significant example is a measurement with ATR method in Mid and Far-IR range with automatic wide-range measurement system. For measurement in Far-IR range, full vacuum FTIR system is necessary to prevent absorption by water vapor in the air. In case of transmission method in which diluent materials are different depending on measurement range, the sample needs to be replaced since the different sampling is required depending on the measurement range. On the other hand, in ATR method, the sample doesn't need to be replaced irrespective of the measurement range since the sampling is unnecessary. Therefore, the spectra in Mid and Far-IR can be measured with keeping cohesiveness between sample and prism, which is a very important aspect for the vacuum state of FTIR and ATR method.

* Max. measurable wavenumber range is 25000~10 cm-1
* Wavenumber down to 30 cm-1 can be measured by using ATR PRO ONE equipped with diamond prism of wide-band type.

Figure 1 FT/IR-6800FV + automatic wide-range measurement system and ATR PRO ONE

Measurement of broadband spectrum using automatic wide-range measurement system

Measurement

For identification of carbonate and determination of crystal structure, the spectra in the range of 4000~100 cm-1 were measured.

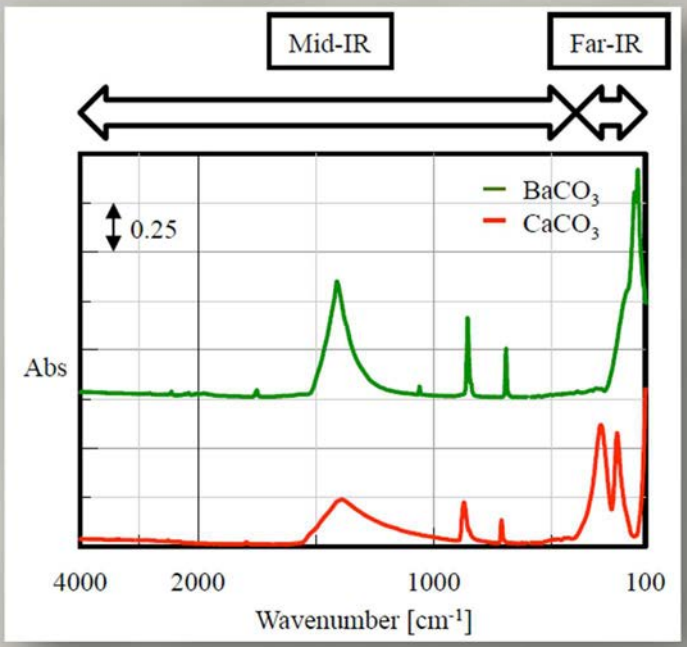
System configuration

- FT/IR-6800FV FT/IR Spectrometer (full vacuum)
- EXBS-6000 Automated BS Changer Unit
- EXPT-6000GV Automated Gate Valve Unit
- EXCU-6000 Controller for EXBS/EXPT-6000
- MYLBB-6000BS Beam splitter, broad band, Mylar
- PETGS-6000 DLATGS(PE) detector with switching mechanism
- ATR PRO ONE Single reflection ATR accessory
- PKS-D1F Diamond crystal kit (Wide-Band Type)

*) Automated Window Changer Unit enables to the wide-range measurement under the conditions of vacuum in interferometer and purge in sample compartment. It is useful for the measurement in which the vacuum cannot be applied in sample compartment for such as the measurement of powder. Automated Gate Valve Unit is mainly used with full vacuum FT/IR Spectrometer.

Measurement conditions

- Instrument: FT/IR-6800FV + Automatic wide-range measurement system.
- Light source: Ceramic light source (Mid-IR, Far-IR range)
- B.S.: Ge/KBr (Mid-IR range), Broad band Mylar (Far-IR range)
- Windows: KRS-5 (Mid-IR range), None (Far-IR range)
- Detector: TGS (Mid-IR range), PE-TGS (Far-IR range)
- Accessories: ATR PRO ONE
- Crystal: Diamond crystal of wide-band type



Results

Fig. 2 shows the spectra of barium carbonate and calcium carbonate. The typical absorption band of carbonate can be confirmed at around 1400 cm-1 in the spectra of Mid-IR range, but it is difficult to discriminate barium carbonate from calcium carbonate. On the other hand, in the spectra of Far-IR range, the absorption peaks are shown at different wavenumber and so the difference can be clearly identified. Carbonate are often contained as a foreign material and now it is recognized that the system used in this report is useful by identification of carbonate as foreign material. Figure 3 shows the spectra of calcium carbonates that have different crystal structures. As shown in Figure 2, the pattern of peaks is also different in Far-IR range, and the difference in crystal structure can be easily identified. As stated above, the information on inorganic compound included in sample and crystal structure as well as the structure of organic substance can be obtained by using the automatic wide-range measurement system and measuring spectra in Far-IR as well as Mid-IR range.

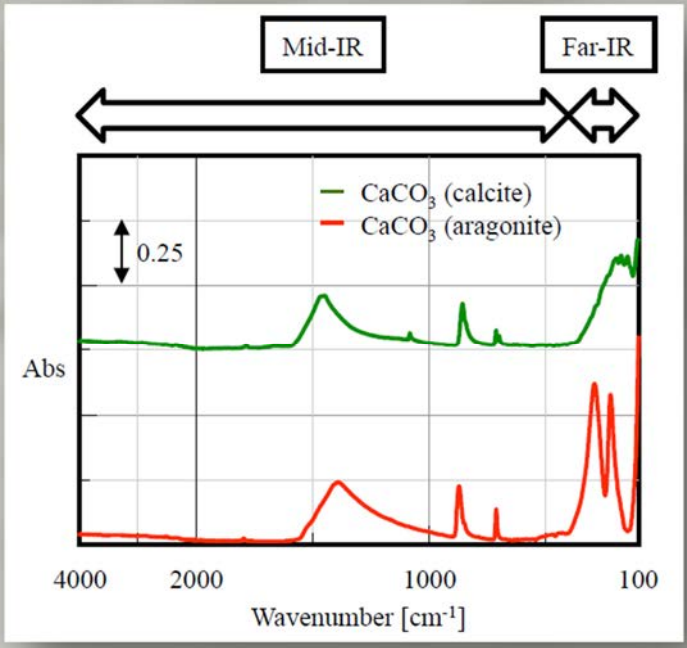


Figure 3 Spectra of calcium carbonates that have different crystal structures
(X-axis: 4:1 display, Y-axis: Offset)

Figure 2 Spectra of barium carbonate and calcium carbonate
(X-axis: 4:1 display, Y-axis: Offset)

Introduction of new DLATGS detector for IRT-5000/7000 infrared microscope

Introduction

Compared to the standard DLATGS (Deuterated L Alanine Triglycine Sulphate) detector mounted on an FTIR for macro measurements, the MCT (Mercury Cadmium Telluride) detector used with an infrared microscope has a much greater sensitivity, which is suited to the measurement of micrometer sized samples common for microscopic measurements. However, the MCT detector has some disadvantages such as the requirement for liquid nitrogen cooling for measurements, a reduced absorbance linearity and a reduced wavenumber range for measurements. JASCO has developed a dedicated DLATGS detector for infrared microscopy, especially focusing on an increased sensitivity.

As a result of many years of work, the new microscope DLATGS detector has been created.

In this application note, microscopic measurements and mapping measurements with the use of the new DLATGS detector are outlined.

Comparison of new DLATGS detector and MCT detector

Measurement of polystyrene – parameters

- Aperture size: 50 x 50 µm
- Accumulation: new DLATGS: 100 times, MCT: 50 times
- Measurement method: transmission

Fig.1 shows the infrared spectra of a polystyrene film using an IRT-5200 using the new DLATGS detector and the

standard mid-bandMCT detector. As demonstrated in Figure 1, the DLATGS detector requires twice the accumulations as compared to the MCT, but the DLATGS does allow the measurement of a 50 x 50 µm region

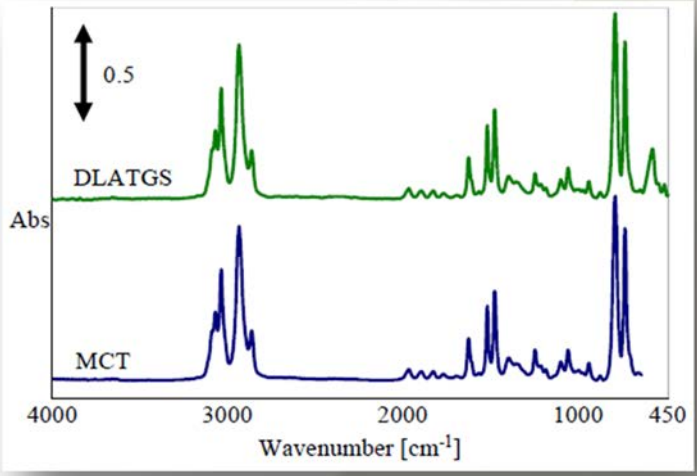


Figure 1 Spectrum of a polystyrene film using the new DLATGS and an MCT detector

Measurement of Teflon – parameters

Aperture size: new DLATGS 50 x 50 µm, MCT 10 x 10 µm

Accumulation: new DLATGS: 100 times, MCT 50 times

Measurement method: transmission

Figure 2 illustrates the infrared spectra of a Teflon sheet using the DLATGS detector and an MCT detector to compare the sensitivity in the low wavenumber region. As shown in Figure 2, the measurement using the new DLATGS detector can detect the absorption peaks of Teflon in the wavenumber range from 650 to 450 cm-1 where narrow and mid-band MCT detectors cannot detect the peaks.

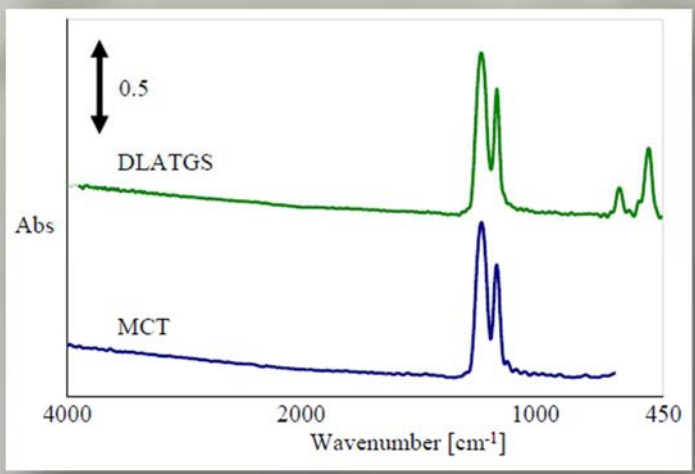


Figure 2 Spectrum of a Teflon sheet with using the new DLATGS and an MCT detector

Introduction of new DLATGS detector for IRT-5000/7000 infrared microscope

Microscopic ATR mapping using the new DLATGS and Smart mapping

The results above demonstrate that the new DLATGS detector is effective for infrared spectra measurements in a 50 x 50 µm region. Now, a mapping measurement of a microscopic region by a micro- ATR cassegrain using the new DLATGS is outlined. The IQ mapping function is installed in the IRT- 5200 as a standard feature, which allows a mapping measurement with the ATR prism in contact with a sample by moving the mirrors within the microscope. In this demonstration, the microscopic ATR mapping of polyethylene particles on a Teflon sheet are accomplished by using the new DLATGS detector.

Measurement parameters - polyethylene particles

- Aperture size: 20 x 20 µm
- Accumulations:
  - single point measurement: 256 times
  - mapping measurement: 50 times
- Measurement points: 14 x 14
- Measurement area: 65 x 65 µm
- Step: 5 x 5 µm
- Detector: new DLATGS
- Measurement method: micro-ATR cassegrain

Figure 3 (A) is the visible image while Figure 3 (B) contains the spectra of 2 single point measurements, which provide recognizable spectra even in a 20 x 20 µm measurement region. Figure 3 (C) displays the infrared image calculated by a Multi-Component Regression analysis based on the spectra within the mapping measurement. The polyethylene particles are shown in warmer colors, consistent with the particle shown in Figure 3 (A). These results indicate that the new DLATGS detector can be applied to an infrared ATR mapping experiment using a 20 x 20 µm aperture.

Conclusion

Single point measurements in the micro region and micro-ATR measurements in a mapping mode can be obtained using a new DLATGS detector designed specifically for the IRT-5000/7000 series of infrared microscope accessories. JASCO now offers a high sensitivity MCT detector mounted as standard and the new DLATGS detector for wide wavenumber range at ambient temperatures to meet various measurement purposes

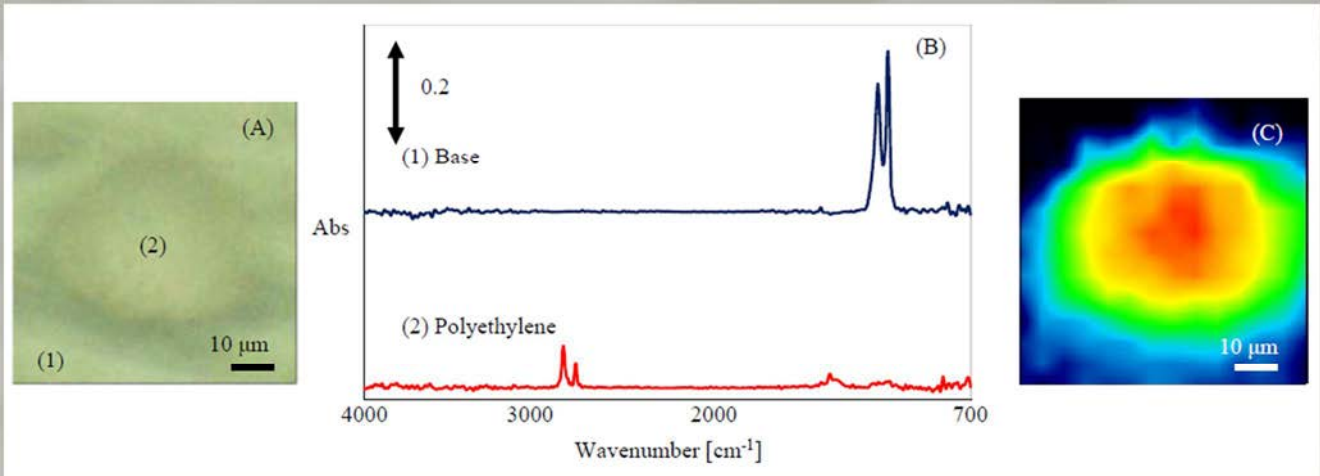


Figure 3 Smart mapping measurement with use of new DLATGS

Measurement of thin film by Polarization-Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS)

Introduction

Several industrial products utilizing the advanced functionalities of thin films such as electric, optical and/or mechanical properties are now getting more and more popular in the market and techniques on generation and evaluation of film are steadily improved in accordance with better quality of products. The Infrared spectroscopy is known as one of the evaluation methods of such thin film providing information on molecular structure and orientation along with optical thickness and electric properties. Especially, Infrared Reflection-Absorption Spectroscopy (IRRAS) method enables to implement molecular structure analysis of a very thin film with a thickness of tens of angstroms on metal substrates. However, there is a growing need for higher sensitivity measurement and also process monitoring of film generation because the recent devices require higher performance and higher functionality. In order to meet such requirement, a monitoring system for film generation in vacuum chamber has been developed by using Polarization-Modulation Infrared Reflection-Absorption Spectroscopy(PM-IRRAS) with greater sensitivity than ordinary IRRAS. This report explains the outline of the system as well as the data for measurement of thin film using PM-IRRAS.

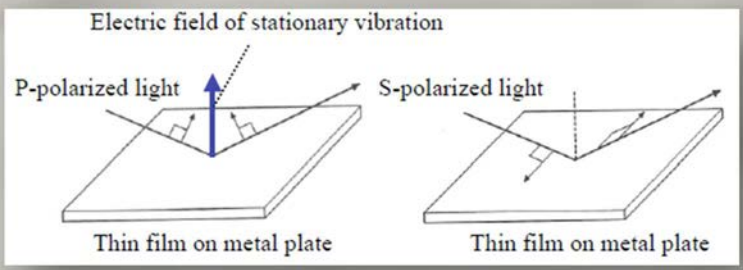


Figure 1 Diagram of IRRAS method

Principle of PM-IRRAS

IRRAS provides IR spectra measurement of thin film on metal substrates with high sensitivity by using p-polarized light parallel to incidence plane. The p-polarized light ingenerates the electric field of stationary vibration which increases sensitivity (See Figure 1). This allows film thickness measurement in Å level. However, absorption peaks obtained by IRRAS are usually very small, which may often require long time accumulation. In addition, both of reference and sample substrates need to be measured. For these reasons, spectrum is significantly affected by absorption of H2O and CO2 in atmosphere. On the other hand, PM-IRRAS is a method of finding intensity difference of s- and p-polarized lights ($\Delta I = Ip - Is$) which is vertical and parallel to incidence plane respectively by using Photoelastic Modulator (PEM). As s-polarized light does not ingenerate the electric field of stationary vibration, absorption is much smaller than that of p-polarized light. In addition, in PM-IRRAS, the sum of s- and p-polarization signal ($\Sigma I = Ip + Is$) is used as reference and so there is no need to measure reference substrates. Hence, the effect due to absorption of H2O and CO2 in atmosphere can be decreased greatly. Since the measurement of reference substrate is not needed, the measurement results can be free from effect of difference between substrates and the measurement time can be shortened. Additionally, this PM-IRRAS measurement system allows higher sensitivity by detecting small ΔI signal using direct lock-in detection by adopting dual modulation spectroscopy of FT/IR interferometer and PEM. Figure 2 shows measurement results of PMAA thin film on Al mirror obtained by IRRAS and PM-IRRAS while other conditions are the same. Spectra obtained using PM-IRRAS is several times better in S/N than IRRAS.

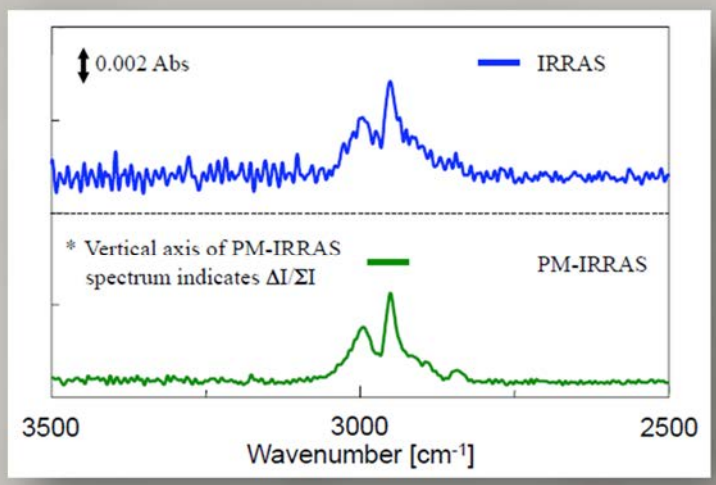


Figure 2 Comparison between IRRAS spectrum and PMIRRAS spectrum (normalized, offset plotting)

Measurement of thin film by Polarization-Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS)

Instrument

The appearance of PM-IRRAS measurement system and system layout of polarization modulation unit are shown in Figure 3. The incidence angle of polarized light of this specific system is 85°, while the optimal incidence angle in general is considered as 80 ~ 89° depending on the kinds of metal and wavenumber of incidence light. In addition, the whole system can be vacuumed. In principle PM-IRRAS can reduce the noise due to H2O and CO2 but vacuum of whole optics can enhance the sensitivity further. Apart from this, the system is capable of blowing gas to sample or heating sample, enabling the system to be used for monitoring of film generation in process or structural changes in such film.

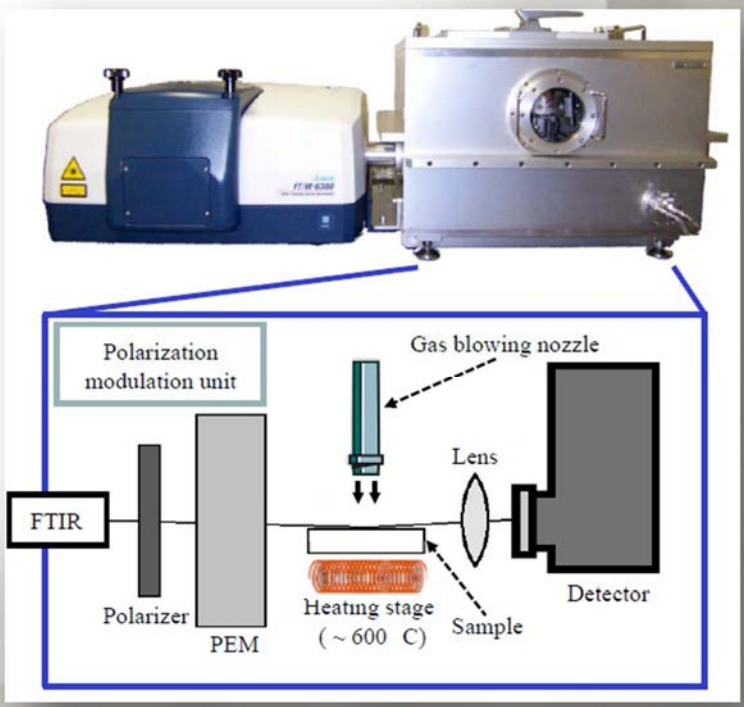


Figure 3 Appearance of FT/IR-6300FV & Polarization modulation unit (upper)
System layout of polarization modulation unit (lower)

PMMA thin film on Al mirror

The measurement result of PMMA thin film on Al mirror is shown in Figure 4. The obtained spectrum has good S/N without effect of H2O.

Measurement condition

- Instrument: FT/IR-6300FV & polarization modulation unit
- Detector: MCT-N
- Accumulation: 50
- Resolution: 4 cm-1
- PEM center wavenumber: 1700 cm-1

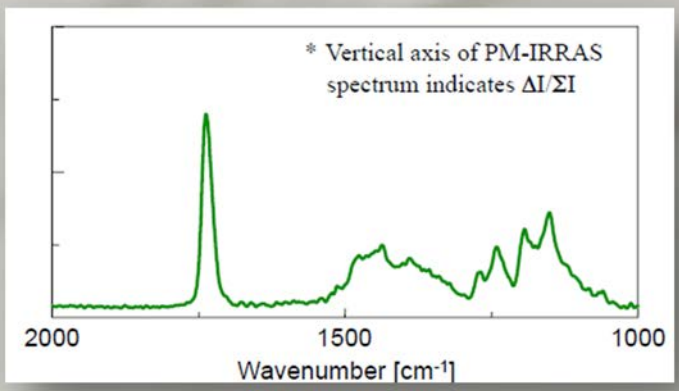


Figure 4 Measured spectrum of PMMA thin film

Native oxidation film on Al mirror

Measurement result of native oxidation film on Al mirror is shown in Figure 5. The thickness of the native oxidation film obtained using ellipsometer (JASCO: M-220) is 46.9 Å and it is confirmed that the measurement of thickness in Å level was implemented in about 1 minute time utilizing PM-IRRAS.

Measurement condition

- Instrument: FT/IR-6300FV + Polarization modulation unit
- Detector: MCT-N
- Accumulation: 100
- Resolution: 4 cm-1
- PEM center wavenumber: 1000 cm-1

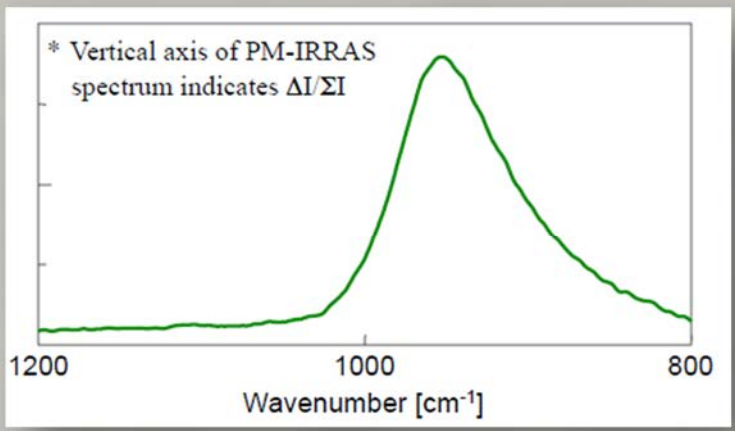


Figure 5 Measured spectrum of native oxide film on Al mirror

Variable-angle transmittance measurement attachment with polarizer option

In semiconductor industry, Infrared spectroscopy is widely used for various routine analysis such as quantitative analysis of impurities like oxygen and carbon, qualitative analysis of insulator film and film thickness analysis of epitaxial film etc. as well as basic researches. Among several analytical methods, the transmission method is the most popular one in those applications, however, Silicon Wafer has high reflectance, which may cause such symptom that the reflected light from surface of Silicon Wafer returns to interferometer, resulting the noise on spectrum due to water vapor since the length of optical path with sample is different from the length without sample. JASCO VAT-500i Variable-angle transmittance measurement attachment can be used for such difficult applications of samples with reflectance. In this attachment by changing the incident angle of light against the sample surface, the reflected light would not go into interferometer. In fact, this design can drastically reduce the level of noise due to water vapor even the incident angle is changed as small as 10 to 20 degree.

Figure 1 shows the transmission spectrum of SiO2 film and Si substrate under 0 degree incident angle condition. The vapor noise cannot be eliminated by spectral subtraction even based on Si substrate as reference.

Figure 2 shows the transmission spectrum of SiO2 film under several different incident angle conditions from 0 to 20 degree.

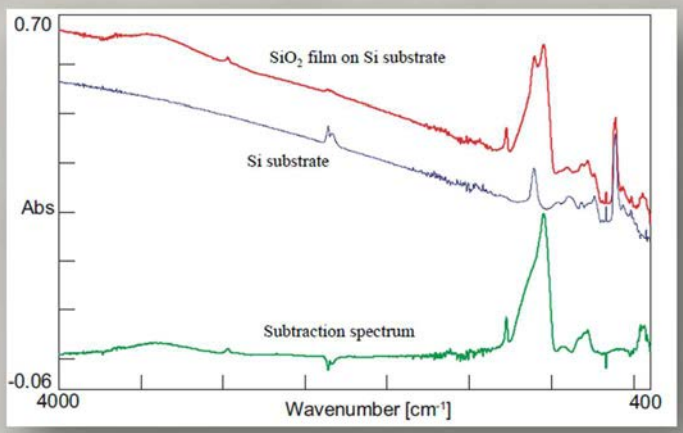


Figure 1 Transmission spectrum of SiO2 film under 0 degree incident angle condition

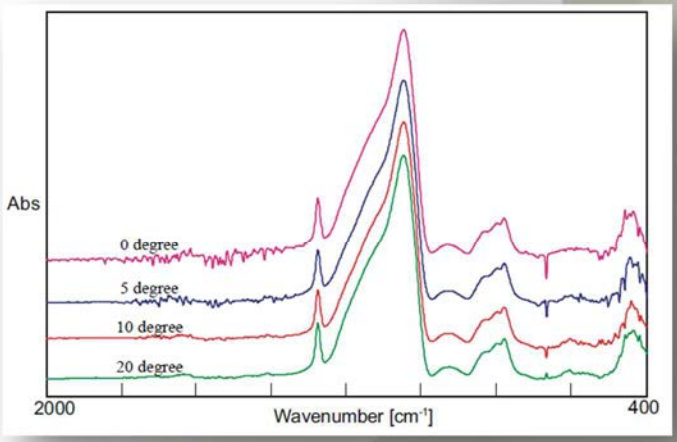


Figure 2 Transmission spectrum of SiO2 film under several different incident angle conditions from 0 to 20 degree

In addition, for this VAT-500, the polarizer can be mounted in optical path if necessary. This capability is effective for other applications such as analysis of polymer film and coating film, and also the measurement of Dichroism of oriented membrane. Fig. 3 shows the spectra showing Dichroism measurement of oriented polypropylene film. Using the rotatable sample holder, the direction of orientation can be confirmed for unknown oriented sample. As a result of measurements with different angles at 0 and 90 degree, it was confirmed that the main axis of this sample was oriented in 0 degree direction. Figure 3 shows the absorbance spectra at 0 and 90 degree position, indicating that this polypropylene is isotactic polypropylene. In addition, the large difference of absorption at 1168cm-1 and 998 cm-1 is affected due to crystallization and isotactic helix structure, which can be utilized as a degree of crystallization.

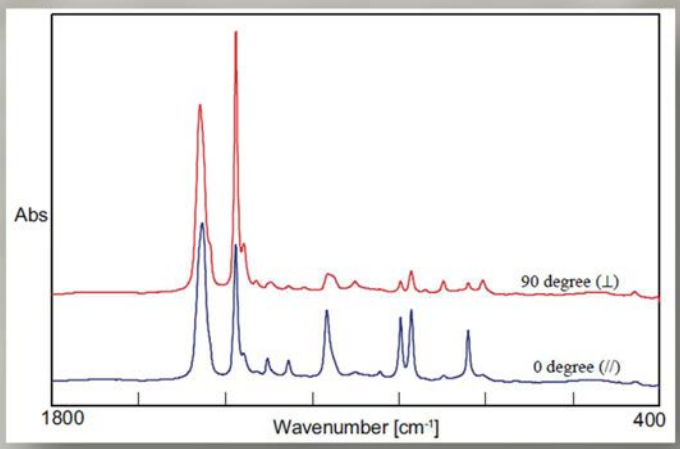


Figure 3 Transmission spectrum of Dichroism measurement of oriented polypropylene film

Acquisition of molecular orientation information using automated MAIRS measurement unit AM-4000

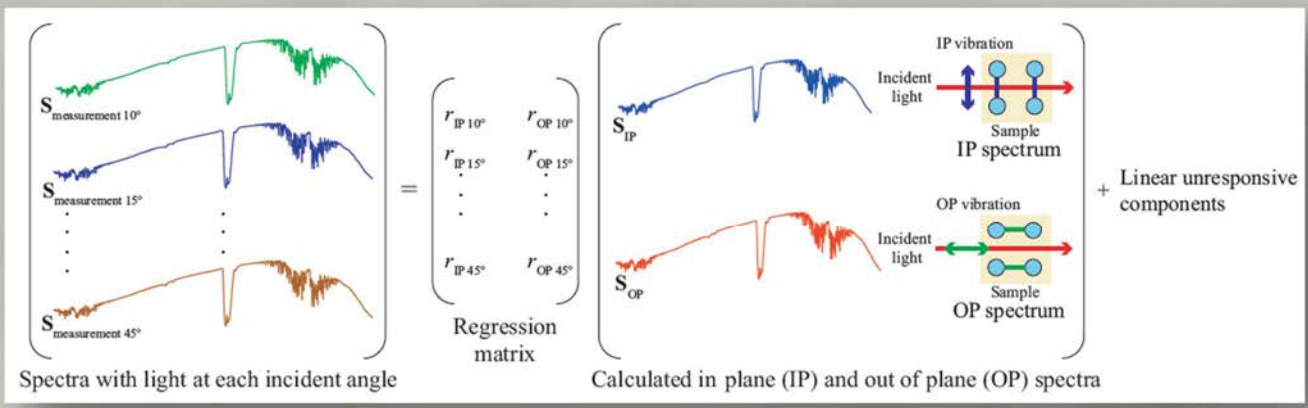
Introduction

MAIRS (Multiple-Angle Incidence Resolution Spectrometry)[1)-4)], which has been invented by Professor Takeshi Hasegawa of Kyoto University, has attracted a lot of attention as a new analysis method for studying molecular orientation of thin film materials used in several fields such as liquid crystals, organic devices and fibers. Conventionally, Transmission and RAS (Reflection Absorption Spectroscopy) measurements in Infrared Spectroscopy have been used in combination for the analysis of molecular orientation, difference of vibration in surface-parallel direction, perpendicular to incident light (in-plane, IP) and vibration in surface-normal direction, parallel to incident light (out-of-plane, OP). However, this method cannot be used for some samples because the metal substrate which is necessary for RAS measurement may affect the molecular structure of thin film. In addition, non-metal substrate is also separately needed for transmission measurement. On the other hand, since MAIRS is a method to analyze molecular orientation only by transmission measurement using incident light with several different angles, the necessary substrate is only non-metal one for transmission measurement. Generally in transmission measurement in which the incident light goes perpendicular to sample plate, the only spectrum due to the molecular vibration in in-plane direction is obtained, while if the transmission measurement is implemented by changing the angle of incident light, the obtained spectrum will be expressed as the summation of the spectrum of in-plane vibration and spectrum of out-of-plane, and linear unresponsive components such as noise.

As shown in Figure 1, MAIRS measurement enables to acquire simultaneously spectra of vibration of molecules oriented in in-plane direction and out-of-plane direction ($\mathbf{s}_{IP}$, $\mathbf{s}_{OP}$) by extracting components of only in-plane and out-of-plane vibration from single beam spectra (S-measurement) at each incident angle using regression matrix ($\mathbf{r}_{IP}$, $\mathbf{r}_{OP}$) which shows the ratio of in-plane and out-of-plane vibration. In the MAIRS method, in which quite small change of peaks at each incident angle needs to be analyzed, the very high precision measurement is required.

JASCO's Automated MAIRS measurement unit AM-4000 (Figure 2) employs JASCO's original stage for compensation plate as standard and can be mounted on fully vacuumed FTIR (FT/IR-6000FV series), assuring to obtain very high quality spectrum. In this paper, it is reported that the molecular orientation of Langmuir-Blodgett (LB) film was analyzed using Automated MAIRS measurement unit AM-4000.

Figure 2 Automated MAIRS measurement unit AM-4000



* The same measurement with Y-axis as single beam needs to be implemented for background and sample to calculate the spectra with Y-axis as absorbance.

Figure 1 Outline of MAIRS measurement

Acquisition of molecular orientation information using automated MAIRS measurement unit AM-4000

Features of Automated MAIRS measurement unit, AM-4000

AM-4000 employs two symmetric stages electrically driven for rotation. It allows not only the measurement with one stage for sample but also the measurement using both stages by mounting the compensation plate on the other stage (compensation plate stage) so that the light axis shift due to obliquely incident measurement can be corrected. Therefore, AM-4000 is effective for the measurement using detector with small acceptance surface and using small aperture. In addition, the accompanying software can control electrical stage automatically, and IP and OP spectra calculation function and orientation calculation function of each molecular vibration are available as standards.

Measurement

In order to analyze the orientation condition of alkyl chain of LB film consisting of 5 layers of cadmium stearate on both surfaces of Ge (n=4.0) substrate, the measurement was done using automated MAIRS measurement unit AM-4000 with light at several incident angles. As compensation plate, Ge substrate with the same size as sample plate was used. By using compensation plate, the light axis can be corrected to the standard transmission measurement position even with the obliquely incident angle but not perpendicular to the substrate.

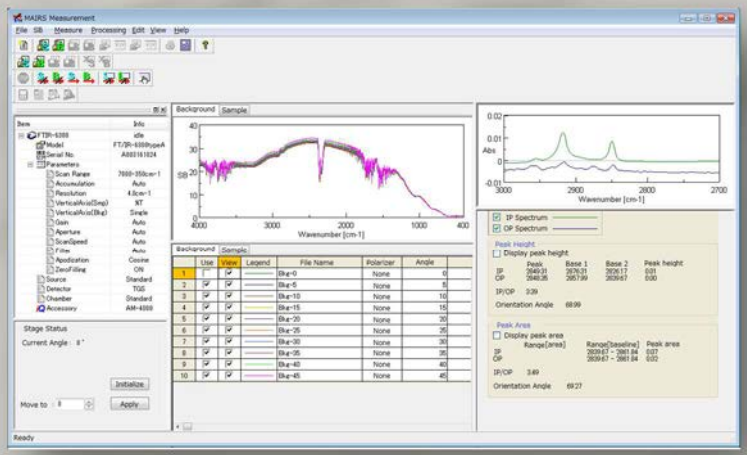


Figure 3 MAIRS measurement program

Measurement conditions

- Instrument: FT/IR-6100
- Measurement method: MAIRS method
- Resolution: 4 cm-1
- Accumulation: 128 x 4
- Detector: MCT-M
- Accessory: AM-4000
- Measurement angle: 10 - 45 degree (7 degree increment)
- Measurement sample: Cadmium stearate film on Ge substrate (5 layers on each surface)

Results and discussions

IP and OP spectra are calculated from the measured spectra at each incident angle in the range of 3000 - 2800 cm-1 in which C-H vibration peaks are observed (Figure 3). The absorption at 2850 cm-1 (C-H symmetric stretch vibration of methylene group) and at 2918 cm-1 (C-H inverse symmetric stretch vibration of methylene group) were seen in IP and OP spectra, but these peak intensities are not the same. The peak of absorption of C-H inverse symmetric stretch vibration of methylene group was seen at 2955 cm-1 in IP spectrum, while it was shifted to 2961 cm-1 in OP spectrum. In addition, the absorption at 2873 cm-1 (symmetric stretch vibration of methyl group) was observed only in OP spectrum. Thus, it can be said that both IP and OP spectra corresponding to transmission and RAS spectra were obtained. As a result, this system is very effective for evaluation of the thin film sample in which the molecules are oriented in in-plane and out-of-plane direction. When AM-4000 is mounted on fully vacuumed FTIR, it enables to obtain high quality spectra without any effect of water vapor and carbon dioxide in shorter time than purged system.

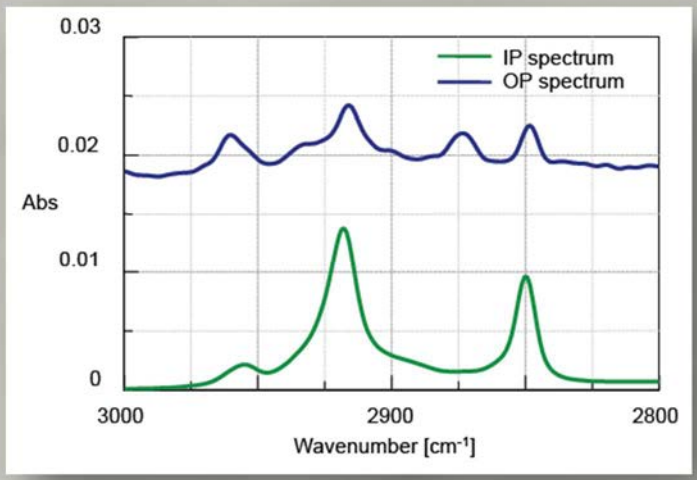


Figure 4 Calculated IP and OP spectra

Reference:

1) Hasegawa, T. J. Phys. Chem. B. 2002, 106, 4112-4115.
2) Hasegawa, T. et al., Anal. Chem. 2002, 74, 6049-6054.
3) Hasegawa, T. Anal. Chem. 2007, 79, 4385-4389.
4) Hasegawa, T. Appl. Spectrosc. Rev. 2008, 43, 181-201.
5) Umemura, J. et al., J. Phys. Chem. 1990, 94, 62-67.

IR/NIR/FT-Raman Measurement using Broadband KBr Beam Splitter

Introduction

IR (Mid-IR), NIR, and Raman spectroscopy are widely used for qualitative and quantitative analysis of polymer, food, medicine, semiconductor material, etc., while if those methods are properly combined, it is possible to obtain more information on basic physical property of the sample. As an example, if IR and NIR spectroscopy are combined, the following information can be obtained.

- Dissociation energy of molecule (**D_e**)
- Absorption index in the IR and NIR region (**α**)
- Optical constant (**n, k**)

These values can provide the important perception for prediction of the chemical reaction or design of various devices. Additionally if IR and Raman spectroscopy are combined, the following information can be obtained.

- Complementary information on molecular vibration
- Information on lattice vibration by measurement in low wavenumber range (specific to Raman spectroscopy)
- Information on molecular vibration when combined with heavy atom

FTIR instrument can measure the IR/Near IR/Far IR spectrum by selecting the proper light source, detector, and B/S, and if the FT-Raman system is used, can obtain the Raman spectrum also. The measurement range covered by general B/S used in FTIR is from 7800 to 375 cm-1, dedicated to IR range, while the newly developed broadband KBr B/S covers the range from 12000 to 375 cm-1, enabling the measurement of IR/NIR/Raman spectrum without replacing the B/S. This application data shows the perception of the basic physical property of the chloroform by measuring the IR/NIR/Raman spectrum using such broadband KBr B/S.

Experimental

The IR and NIR spectrum are measured by the system as shown in Figure 1 under the conditions as shown in Table 1.

Calculation of Dissociation energy (De) and Absorption index (α) of C-H by using IR and NIR spectrum

According to the general interpretation of the IR spectrum, the harmonic oscillator model is employed in which the atoms constituting the molecule are combined by spring (Dotted line by simple quadratic function in Figure 2), however, it is impossible to explain the overtone and combination tone in NIR region by this harmonic oscillator model. Therefore, in order to interpret the NIR spectrum, the Morse function in which the anharmonic oscillation is taken into consideration (Continuous line in Figure 2)[1]. In the Morse function, the energy value is becoming close to Dissociation energy (**D_e**) asymptotically when interatomic distance increases. In this case, the De value of C-H is calculated by using absorption wavenumber of stretching vibration (ν_1, $2\nu_1$, $3\nu_1$) of chloroform and Morse function. The Absorption index (**α**)** is also calculated by absorbance (Abs) at each wavenumber of. The IR/NIR spectrum of chloroform and attribution of each peak are shown in Figure 3.

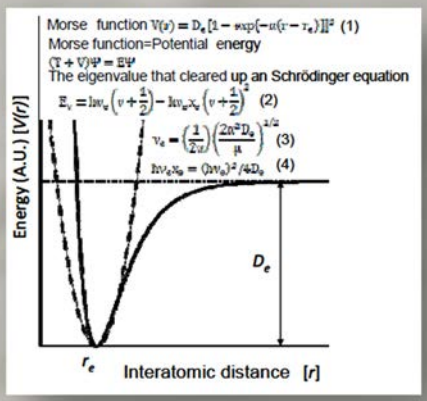


Figure 1 System mounted with broadband KBr B/S (For IR/NIR/FT-Raman)

Table 1 Measuring conditions

Measurement range (cm-1)	Light pathlength of liquid cell	Light source*)	Detector	Beam Splitter
4000~400	0.025 mm	Ceramic	DLATGS	Broadband KBr
6400~4000	1 mm	Halogen		
12000~6400	5 mm			

*) Raman Spectrum: Ex wavelength: 1064 nm, Detector: InGaAs

IR/NIR/FT-Raman Measurement using Broadband KBr Beam Splitter

The dissociation energy (De) of C-H in chloroform Cell path Cell path Cell path is calculated to be 460 +/- 7 kJ/mol from equation 2, equation 4, and value of absorption wavenumber of stretching vibration of C-H (ν_1, $2\nu_1$, $3\nu_1$)[2]. The absorption index α of ν_1, $2\nu_1$, $3\nu_1$ is calculated from measured spectra to be 219, 15.5, and 0.56 respectively as shown in Table 2. From those results, for general organic substances, it is estimated that the sample with high concentration can be quantitated, such as about several 10 times if $2\nu_1$ is used and about several 100 times if $3\nu_1$ is used. Therefore, in NIR range, it is possible to measure the samples in non-destructive method, without dilution which is required for IR measurement.

Figure 4 shows the IR spectrum (Vertical axis: %T) and FT-Raman spectrum (Vertical axis: Int.). The peak intensity ratio in IR spectrum between ν_1 and ν_4 of C-H is about 3.68 from Table 2. Regarding this, since the intensity ratio in Raman spectrum is about 1/4, it is confirmed that the peak intensities of IR and Raman spectrum are complementary. In general, when the change of the dipole moment in the molecular vibration is larger (asymmetric vibration mode), the intensity of peak in IR spectrum appears higher, while the stronger peak in Raman spectrum is detected when the change of the polarizability is larger (symmetric vibration mode). Therefore, the change of the dipole moment for ν_1 of CH is considered to be larger than the one of ν_4 (the change of polarizability is smaller). The vibration of molecule combined with the heavy atom like C-Cl can be considered to be detected in the range less than 400 cm-1 from Raman spectrum. It is important to select IR or FT-Raman depending on the vibration mode even if the structure of molecule is simple like Chloroform.

Summary

This application data shows one of the topics in vibrational spectroscopy taking the Chloroform for example, using broadband KBr B/S. Besides, it can be considered that as well as the general qualitative and quantitative analysis, the broadband KBr B/S can be applied to the 2D correlated spectroscopy based on chemical reaction analysis by time-course measurement using 3 measurement methods. By using broadband KBr B/S which does not require replacement, the measurement mode can be switched without breaking vacuum or interrupting N2 purge. This broadband B/S will expand the potential to wider application fields.

Reference

1) Kenneth W.busch, et,al, Appl.Spectrosc.**54**,1321(2000)
2) Chemical Handbook, the revised third edition

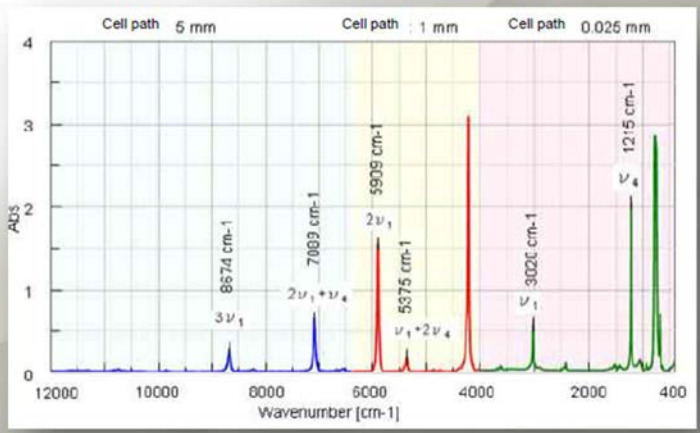


Figure 3 IR/NIR spectrum of Chloroform

Wavenumber [cm-1]	Assignment	Abs	α**)
3020	ν_1 (C-H stretching vibration)	0.55	219
1215	ν_4 (C-H bending vibration)	2.02	806
5375	$\nu_1+2\nu_4$	0.19	1.88
5909	$2\nu_1$	1.55	15.5
7089	$2\nu_1+\nu_4$	0.65	1.30
8674	$3\nu_1$	0.28	0.56

**) α: Absorbance if the light path is 1 cm for this experiment

Table 2 Absorbance index and assignment of Chloroform

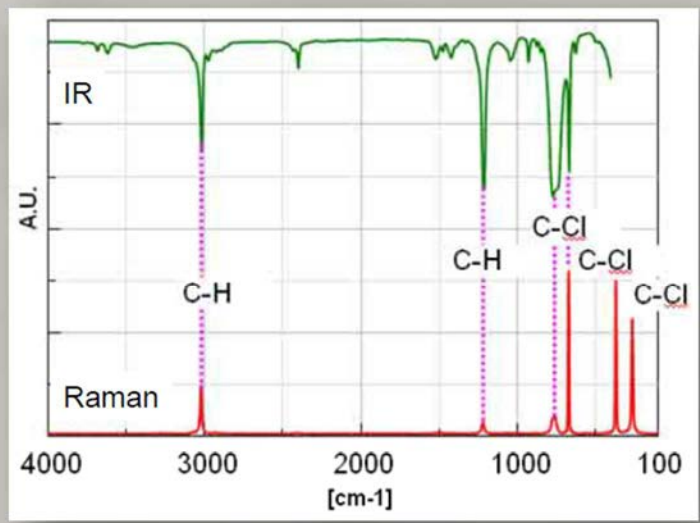


Figure 4 IR and FT-Raman spectrum of Chloroform (Vertical scale: A.U. due to showing %T and Int., Horizontal scale: [cm-1] for wavenumber and Raman shift.)

Fluorescence Observation, Polarization Observation and Differential Interference

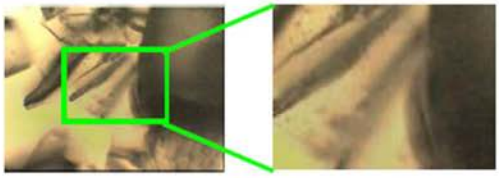
Question. Other observation method with the exception of visible observation by using IR Microscope?

Answer. Fluorescence Observation, Polarization Observation and Differential Interference.

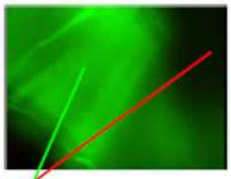
Observation methods are useful optional observation function. These observation methods make possible to observe measurement points more clear than the visible observation.

Jasco IRT-5000/ 7000 Microscope system has the high resolution CMOS camera and 3x optical zoom function as standard, which helps to observe microscopical foreign substance very clearly. Additionally, it is possible to set measurement condition accurately by using those various types of observation accessories since it can identify the fluorescence characteristics or polarization characteristics and the difference of uneven and refractive index visibly even if the sample looks even as visible observation.

Fluorescence observation



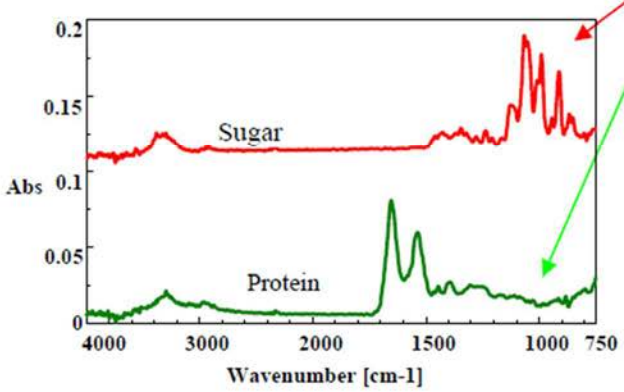
Visible observation view



Fluorescence observation view

Fluorescence observation condition

Ex	330 nm+/-70 nm
Em	450 nm+/-40 nm



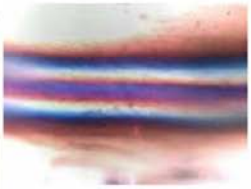
The powder sample that can't be identified by visible observation was observed by using of the fluorescence observation accessory and it's IR spectrum was measured at both green color area which observed as fluorescence and black color area.

As the result of this measurement, IR spectrum of Protein was obtained in this green color area, and also IR spectrum of Sugar was obtained in black color area.

This fluorescence observation method is very useful measurement method for selective measurement the sample which has fluorescence characteristics.

Polarization observation

Visible observation view



Polarization observation view

As the result of polarization observation about stretched vinyl sample, the stretched condition point of the sample was observed very clearly. This polarization observation is useful method for observation about sample has orientation characteristics.

Differential Interference Observation

Visible observation view

Differential Interference observation view

As the result of differential interference observation about board,uneven point and scratch on the sample was observed clearly.
The difference of refractive index and the difference of light path due to shapes of sample surface was observed as contrast between light and darkness.

IR microscope combined with heating stage

Question What can be done if IR microscope is combined with heating stage?
Answer Melting or phase transition of the sample in terms of heating or cooling can be evaluated in molecular level.

Differential Scanning Calorimetry (DSC) or Thermo Gravimetric Analysis (TGA) is generally, used as an evaluation method for thermophysical properties such as melting or phase transition of the sample . In addition, combination with X-Ray Diffraction(XRD) is sometimes used for the multiple evaluation of thermo-physical properties and crystal structure. JASCO's IR microscope, IRT-5000 and 7000 combined with the heating system, MHC-5000 (Figure 1, Chart 1) which we are now introducing enables to have an integrated approach to the geometry change in molecule itself, or the thermo-physical properties and the observation image. It can uniformly heat or cool the measurement area in IR microscope because the measurement area is much smaller than FTIR, assuring high accuracy measurement. You can easily control the temperature and the measurement conditions by interval measurement program of temperature through the PC. Scanning of sample image is available with the sample measurement at the same time.

Figure 1 IRT-5000 and heating stage

Model	MHC-5000	(option)
Temperature range	Room temperature ~ 600 °C	-190 ~ 600 °C

Chart 1 Temperature control range of heating stage

Measurement

Using the system of IRT-5000 with MHC-5000, benzoic acid was heated from 100 ºC up to 150 ºC with ramping rate of 2 ºC per minutes and IR spectra were obtained with 0.5˚C intervals. Figure 2 shows 3-Dimensional spectra of benzoic acid with changes in temperature, Figure 3 shows the change of peak intensity at 930 cm-1 against temperature change and Figure 4 shows observation image the benzoic acid with the change of temperature from 120 to 125˚C. Viewing these figures, the structural changes and the condition of the benzoic acid were confirmed at around 120 ºC to 125 ºC. Since the melting point of the benzoic acid is 122.4 ºC(*), the molecular structure and its condition change due to melting was clearly seen through this system. It can be concluded that this system is applicable for the measurement of structural changes with heating, such as denaturation of proteins or hardening process of thermoset resin.

*Ref.Cyclopedia of chemistry

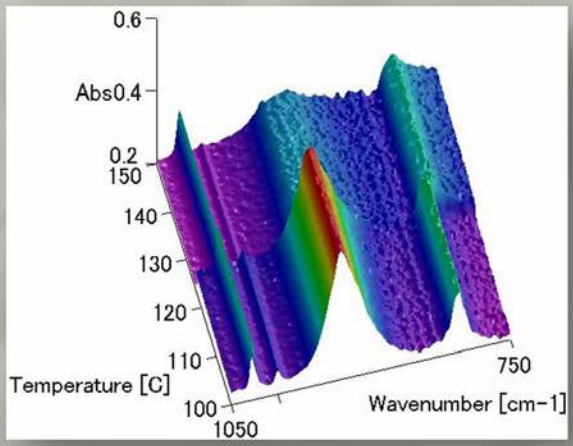


Figure 2 3D spectrum of benzoic acid

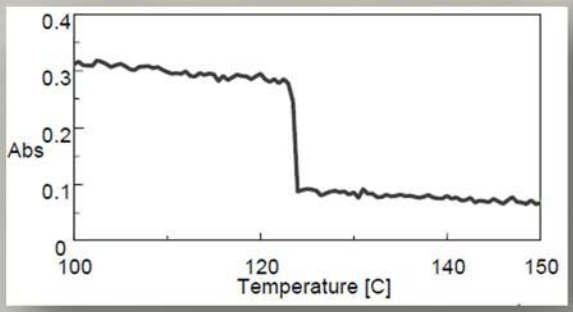


Figure 3 Change of peak intensity at 930 cm-1

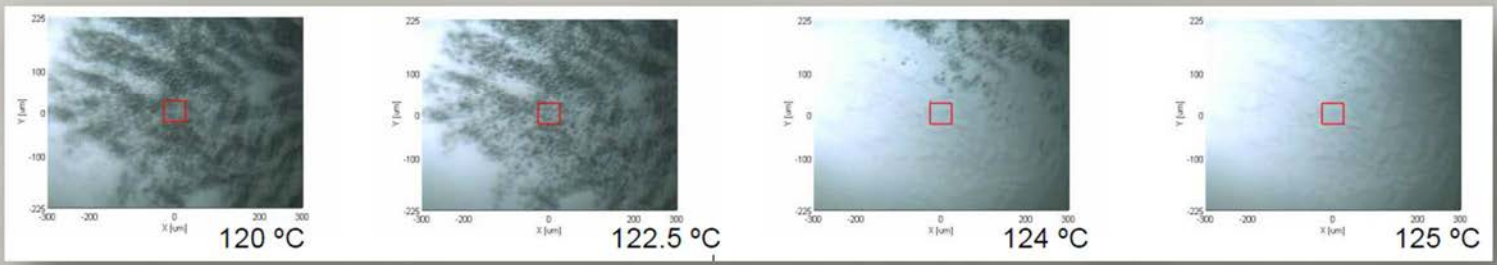


Figure 4 Observation image of benzoic acid in each temperature

3 different time course measurement methods of FTIR

We will show each method's feature and measurement case here. Each method has a different type of scanning method of a moving mirror inside an interferometer. "Interval measurement" is performed with regular scanning and "rapid-scan measurement" is with rapid scanning on time course measurement. On "step-scan measurement," a moving mirror makes a stop at every data-sampling point and perturbation is given at the points.

Interval Measurement*1	**Time Res.**: 1 sec ~	**Application case**: structural transition of a sample, monitoring of gas concentration

Measurement Ex.: Measured a transition of CO_2 concentration in room air. (Fig. 1) Interval measurement is effective for long-time monitoring of gas analysis. *1 JASCO interval measurement program conducts maximum measurement of 60001 data or 24 days.

Rapid-scan measurement	**Time Res.**: 50 msec ~	**Application case**: photo-polymerization reaction, orientation relaxation of polymer film

Measurement Ex.: The cure process of UV cured resin was measured, which represents photo-polymerization reaction. (Fig. 2) Take a look at the peak intensity transition at 1637 cm^{-1} (bottom of Fig. 2), which attributes C=C stretching vibration. It shows the peak intensity rapidly decreased responding to UV irradiation and kept decreasing moderately and tells the initial reaction and reaction process on photo-polymerization was observed very accurately.

Step-scan measurement*2	**Time Res.**: 5 msec ~ *3	**Application case**: relaxation process of liquid crystal orientation

Measurement Ex.: Relaxation process of liquid crystal orientation with electric field response was measured . (Fig. 3) Take a look at the peak intensity transition at 2925 cm^{-1} (bottom of Fig. 3), which attributes C-H stretching vibration. It is observed that its peak intensity fluctuated responding to power voltage turning on and off, and also decreased in two steps, rapidly and then moderately, after power voltage was turned off. It is known that liquid crystal in the area near electrode has faster orientation relaxation than bulk and such difference between them was observed. *2 limited to the materials with repetitive response. *3 10 nsec ~ is optionally available.

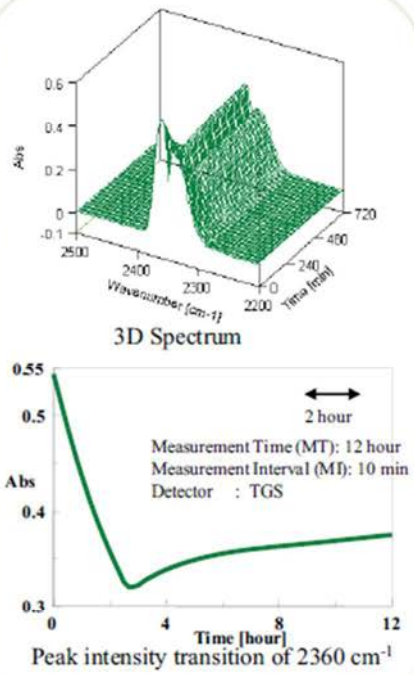


Fig. 1 CO_2 concentration transition (Interval measurement data)

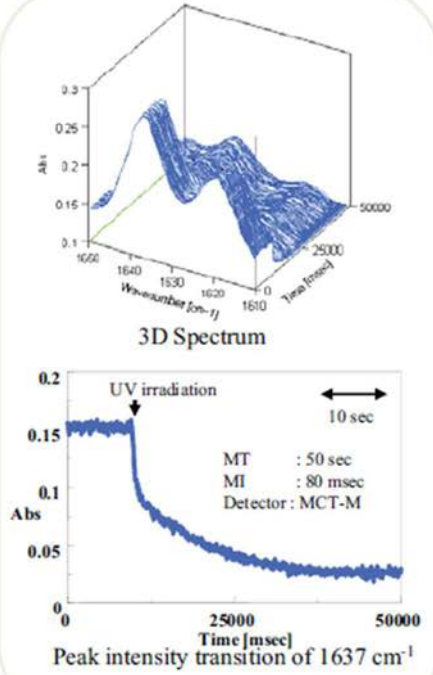


Fig. 2 Cure process of UV cured resin (Rapid-scan measurement data)

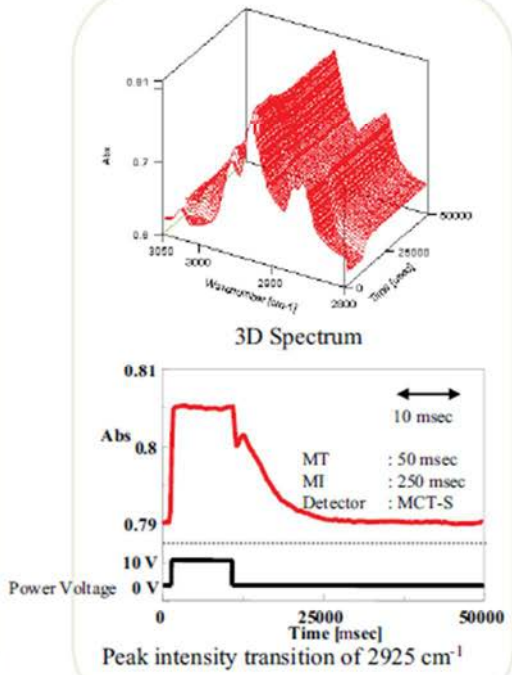


Fig. 3 Relaxation process of liquid crystal orientation (Step-scan measurement data)

Synchronous and Asynchronous data correlation of FTIR

The time-course measurement or the measurement under temperature change is available in the IR spectrometry so that the structure change of sample under the conditions can be observed. In the ordinary analysis mode, it is necessary to check the change of peak intensity or the shift in every peak. Therefore, it is not easy to perform the proper analysis if some peaks are overlapped. On the other hand, the two dimensional correlation program provides the details of even the overlapped peaks or hidden peaks. In the program, the fourier transform of peak behavior at any wavenumber in time-course can be performed resulted in the calculation of real and imaginary parts. The real part is called as synchronous correlation*1 and the imaginary part is called as asynchronous correlation*2. Each of correlation spectra are displayed in two dimensional mode so that you can easily see the details of even the overlapped peaks or hidden peaks.

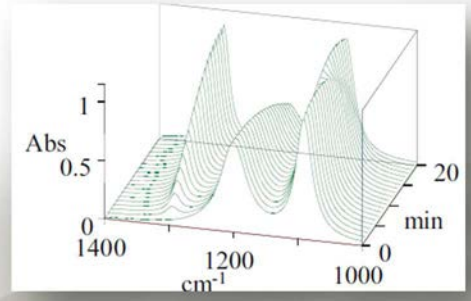


Figure 1
3D spectra of synthesized waveform

Table 1 Conditions of simulation			
Peak position)	**1300cm-1**	**1200 cm-1**	**1100 cm-1 around**
Peak behavior	Increase	Decrease gradually	1090 cm-1: decrease, 1110 cm-1: increase

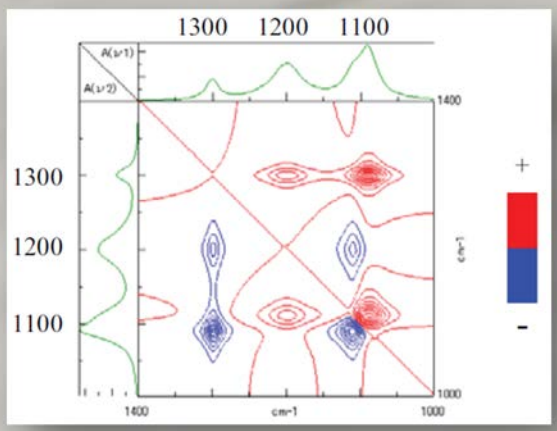


Figure 3 Asynchronous correlation spectra

**1) Synchronous correlation: It indicates how much the behavior of peak intensity change is similar to each other. If the intensity change of peak increases or decreases in same direction, the positive number is displayed. If it is in different direction, the negative number is displayed.*

**2) Asynchronous correlation: It indicates how much the behavior of peak intensity change is different from each other. If the speed of peak intensity change in X axis is slower than the speed of intensity in Y axis, the positive number is displayed. If the speed in X axis is faster than that of Y-axis, the negative number is displayed.*

Test run of two dimensional correlation program

For your better understanding of this program, the synthesized spectra were simulated under the peak intensity change with the following conditions (Figure 1 and Table 1) .

The correlation spectra of synthesized waveform are shown in Figure 2 and 3, while the estimated peak behaviors are displayed in Table 2 and 3 respectively. As you can see, two dimensional correlation program provides you the detailed peak information even under complicated peak pattern.

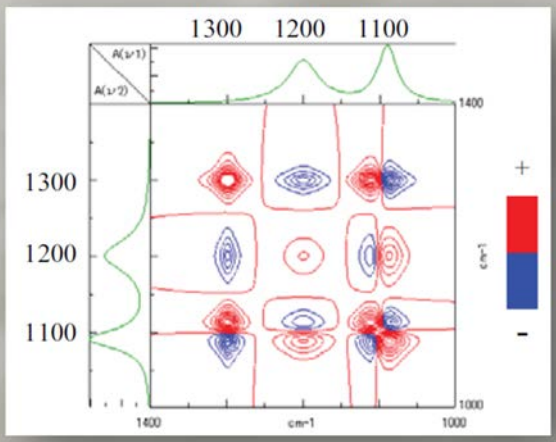


Figure 2 Synchronous correlation spectra

Correlation peak position	Correlation	Peak behavior
1200 / 1300 cm^{-1}	negative	Increase or decrease in opposite direction
1090 / 1110 cm^{-1}	negative	Increase or decrease in opposite direction
1110 / 1300 cm^{-1}	positive	Increase in the same direction
1090 / 1200 cm^{-1}	positive	Decrease in same direction

Table 2 Estimated peak behavior

Correlation peak position	Correlation	Peak behavior
1200(X-axis) / 1300(Y-axis) cm^{-1}	Positive	The speed of intensity change at 1300 cm^{-1} is slower than the speed at 1200 cm^{-1}.
1090(X-axis) / 1110(Y-axis) cm^{-1}	Positive	The peak intensity at 1110cm^{-1} increased then, the intensity at 1090cm^{-1} decreased gradually.

Table 3 Estimated peak behavior

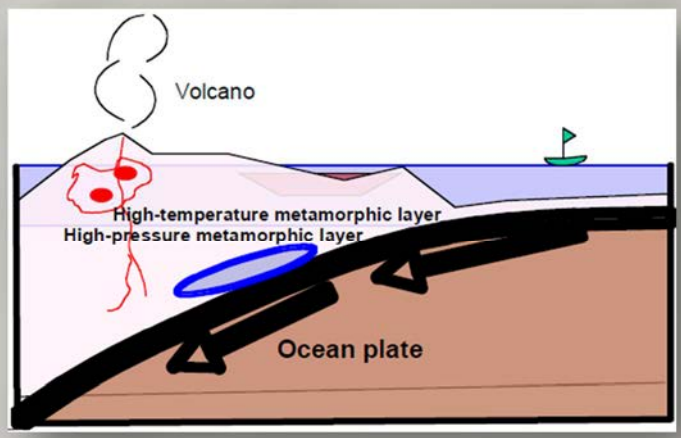
NFIR (Near-Field Infrared spectrometry) analysis of distribution of minerals on cross-section of rock (Part 1)

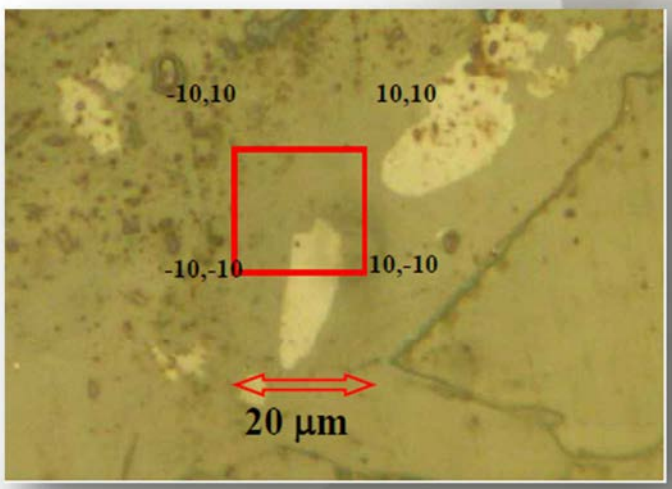
Introduction

The shape of spectrum or spatial resolution of chemical imaging obtained with a scattering type of NFIR (Near-Field Infrared spectrometry) largely depends on the shape of sample surface, optical characteristics of sample or tip diameter of probe, etc. For example, the NF spectrum having strong peak intensity can be obtained if the sample has high refractive index and smooth surface. Also high spatial resolution is achievable if the probe tip diameter is small and the sample surface is smooth. In this application, we obtained the good chemical imaging beyond the diffraction limit of light by performing NFIR measurement of rock with smooth surface in order to obtain the strong peak intensity and high spatial resolution.

Experimental

The sample was a regional metamorphic rock collected in Asemi river (Kouchi Prefecture, Japan). The contents of minerals in the metamorphic rock are different from each other depending on different temperature and pressure when the rock was formed. Such different conditions generated the several types of metamorphic rock such as high-temperature/low-pressure type, low-temperature/ high-pressure type, etc. The high-pressure type of metamorphic rock ordinarily contains minerals such as olivine, white mica, quartz and feldspar. It is very important to check the distribution of these minerals in rock sample so that you can estimate the forming process of ocean plate and the direction of movement. The sampling points on cross-section of rock (smooth surface by polishing, both sides) are shown in the photos.





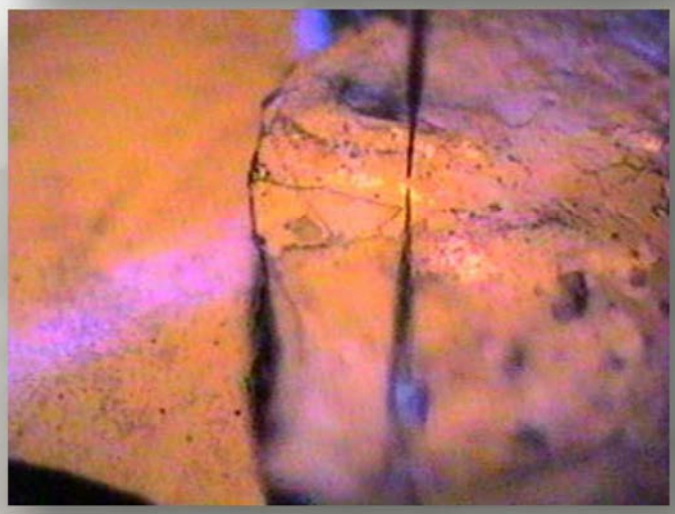


Figure 1 NFIR system

Measurement Conditions

- Apparatus : Model NFIR-200 Near-Field Infrared spectrometer, scattering type
- Probe tip diameter : 1 micron
- Mapping area : 20 x 20 µm
- Measurement interval : 1 µm
- Accumulation : 100 times
- Resolution : 8 cm-1

NFIR (Near-Field Infrared spectrometry) analysis of distribution of minerals on cross-section of rock (Part 1)

Results

The several different shape of reflectance spectra were obtained by mapping of the area shown in the photo. By comparing with standard mineral spectra, it was determined that the obtained spectra were of mica, feldspar and olivine. The standard mineral spectra are shown in Figure 2, while the spectra of actual measured sample are shown in Figure 3. The peaks of three minerals are in good agreement with the standards. The contour maps calculated by utilizing each characteristic peak are shown in Figure 4. The mineral distribution less than 5 micron is clearly seen, indicating that the its spatial resolution calculated from the spectral intensity was less than 2 micron that is well beyond the diffraction limit in the IR range.

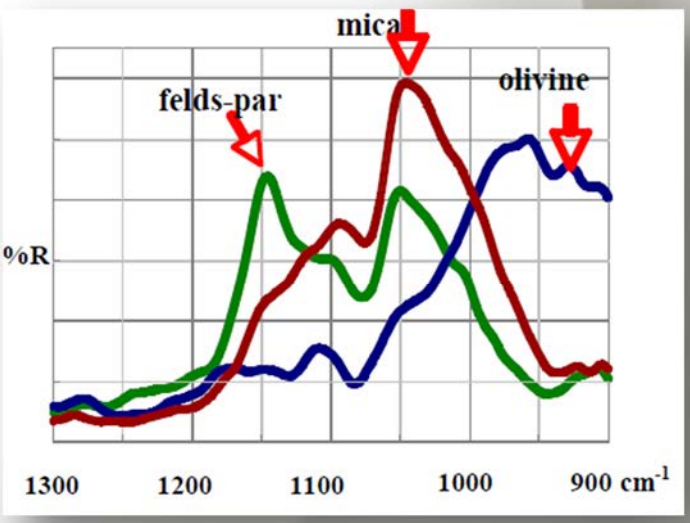


Figure 3 Actual sample

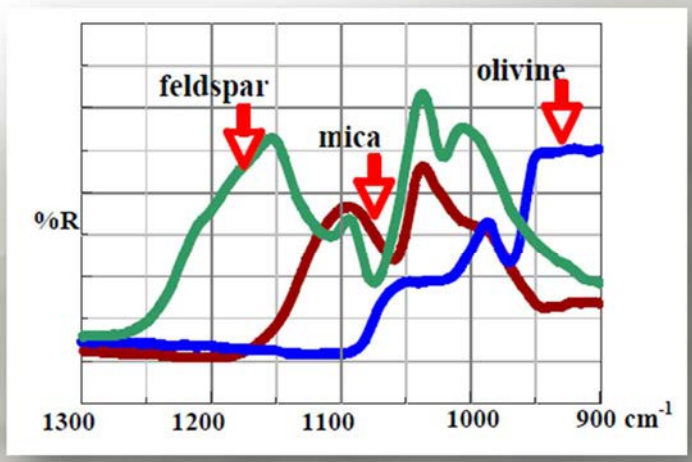


Figure 2 Standard mineral

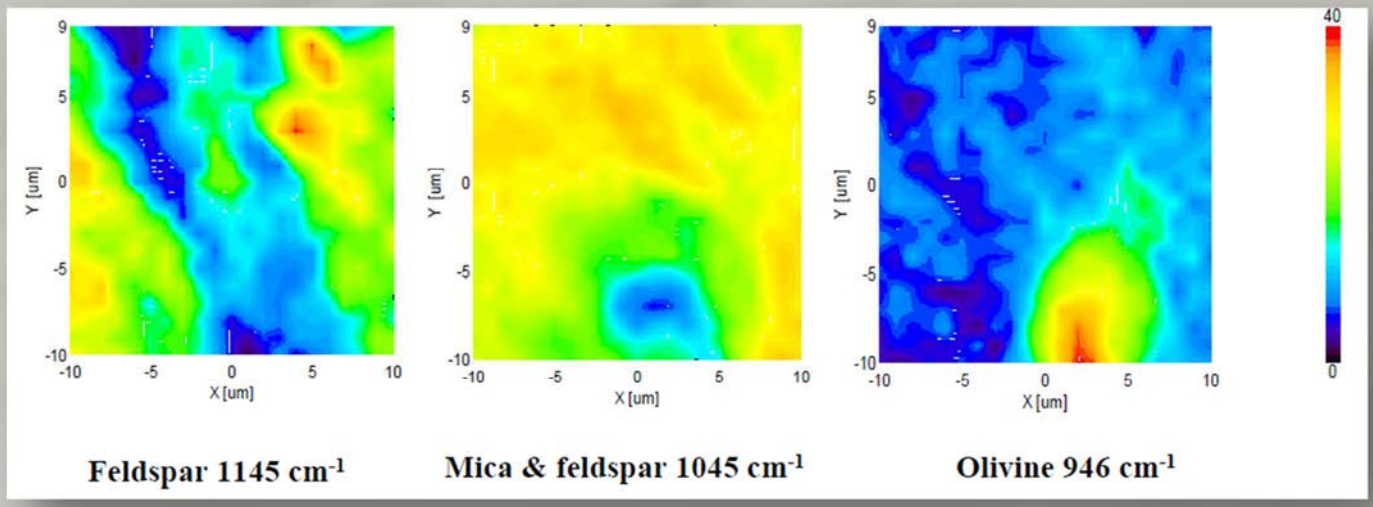


Figure 4 Contour maps by each characteristic peak

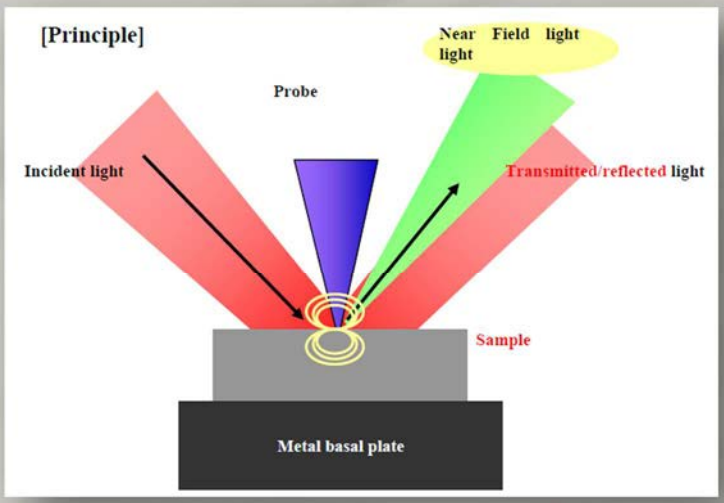
Near Field IR Spectrometer and Microscopic IR Spectrometer

Introduction

The natural materials such as rock consist of mineral substances, and more than 2000 kinds of the mineral substances are said to be existing in the world. Gem is one of the mineral substances, which is considered to be valuable due to its beauty, durability and rarity. Generally, for the analysis of such gem, non-destructive method is the basic approach to be followed. This time we would like to report here below the measurement results of 40 kinds of standard gem substances by using both NFIR and Microscopic IR to obtain spectra of surface reflectance and to show that those two kinds of spectra obtained by NFIR and Microscopic IR are very well consistent.

Experimental

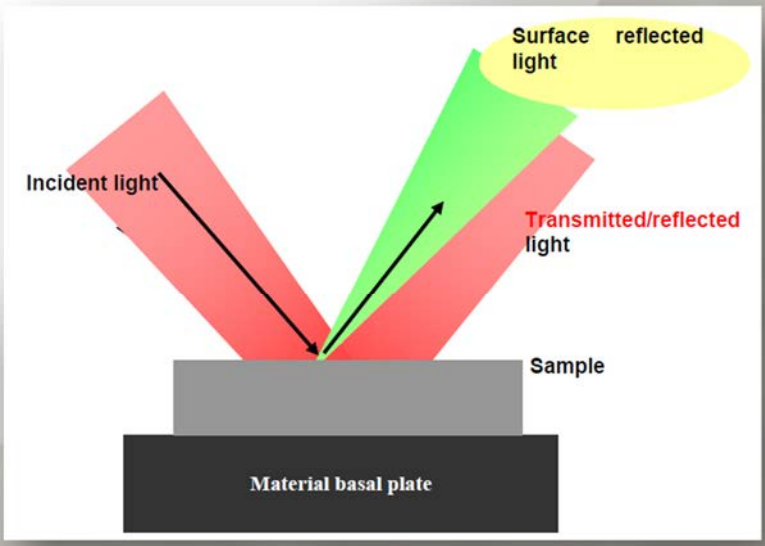
40 kinds of gem substances supplied by Tokyo Science Corporation were used as standard samples. Principle and measurement conditions for each instrument are shown below. NFIR spectrum of the gem surface was obtained by using the probe with its diameter of 1 µm, and the reflectance spectrum by Microscopic IR is obtained by measuring the area of 50x50 mm. The size of the sample gem at this time was about 10 x 10 x 5 mm. The excitation light and incident light were both reflected at the sample surface because the surface was finely polished so that those lights would not penetrate into the sample inside, and so the reflected light was measured.



NFIR-200 Near Field IR Spectrometer

Measurement condition

- Dispersive Near Field measurement system NFIR-200
- Probe diameter : 1 µm
- Resolution : 8 cm-1
- Accumulation : 300 times



IRT-5000 Micro IR spectrometer

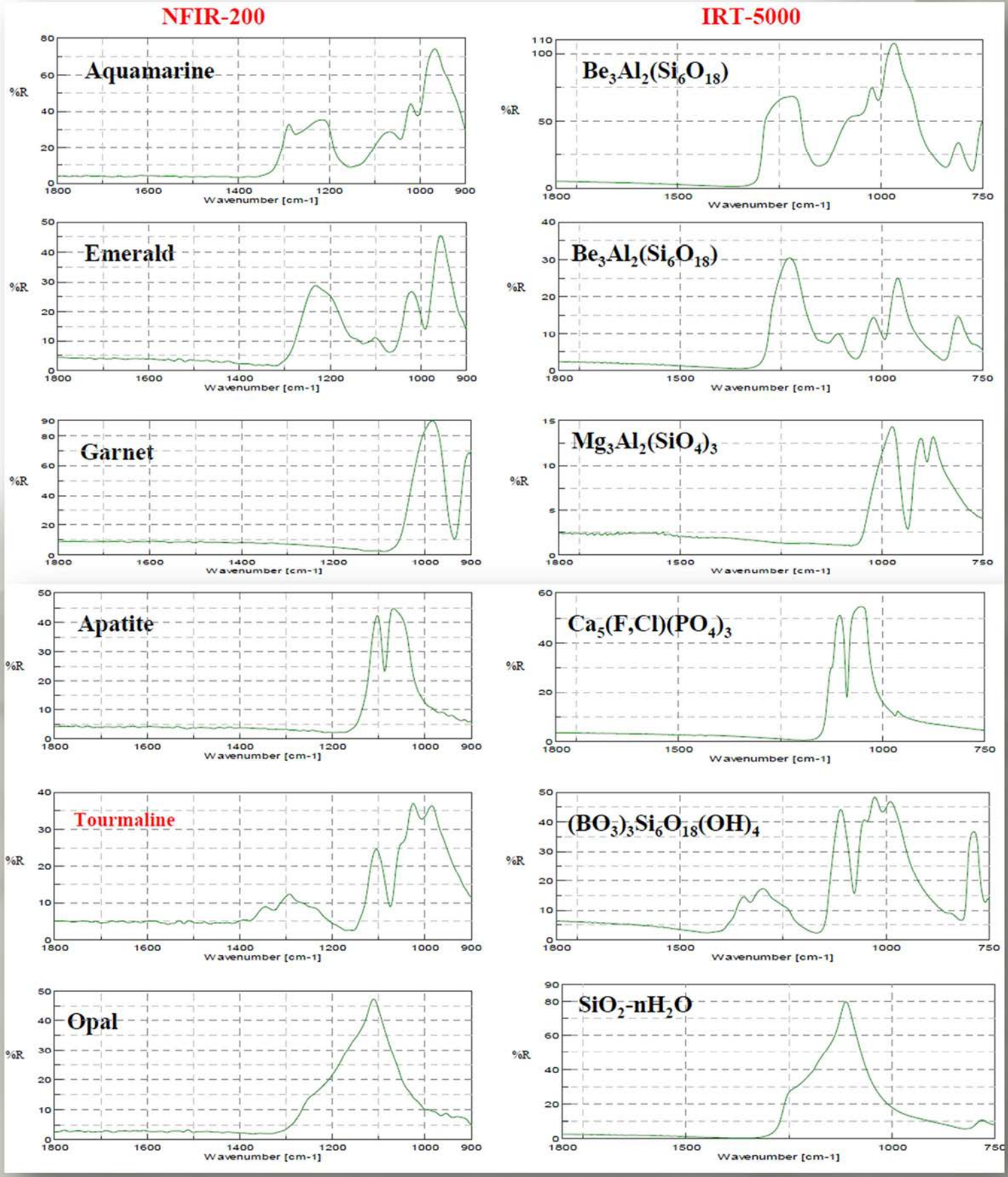
Measurement condition

- Micro IR measurement system IRT-5000 & FTIR-4100
- Measurement area : 50 x 50 µm
- Resolution: 4 cm-1
- Accumulation : 128 times

Measurement result

Measured spectrum of each mineral substance is shown as below; Near field IR spectrum on the left side, and the reflectance spectrum by Microscopic IR on the right side. By comparing the spectra on both sides, it is confirmed that the peak position and the intensity ratio are very well consistent.

Near Field IR Spectrometer and Microscopic IR Spectrometer



Measurement of submicron particle by NFIR (Near Field Infrared Spectroscopy)

Introduction

Research and development of microstructure which is called nanotechnology have been expanding in the field of several devices such as semiconductor and liquid crystal. Moreover in the field of life science, nanoscale studies such as structure and function of biological tissue are now expanding rapidly. Vibrational spectroscopy is an extremely efficient method in order to analyze molecular structure and chemical binding easily for those purpose without destruction, however, since the spatial resolution depends on the wavelength of the light applied, the size of the measurement area has been limited to 1 mm by Raman spectroscopy and 10 mm by conventional transmittance infrared spectroscopy. However, measurement in the area of submicron is now getting capable by Near field infrared spectroscopy system using light scattering probe. Spectrum measurement of submicron particle will be explained in this application data.

Experimental

1. Polystyrene particle (2 mm) on Al mirror Slurry of polystyrene particle (average 2 mm) was dropped on Al mirror and dried. The area where particles were distributed properly was measured.
2. Silica ODS particle (4 mm) on GaAs board Slurry of ODS particle (average 4 mm) was dropped on GaAs board and dried. The area where particles were distributed properly was measured.

Condition

- Instrument: NFIR-200
- Measurement area: 20 x 20 mm
- Accumulation: 128 time
- Resolution: 8 cm-1
- Apotization: Cosine
- Detector: MCT

NFIR-200 Near field IR spectroscopy system

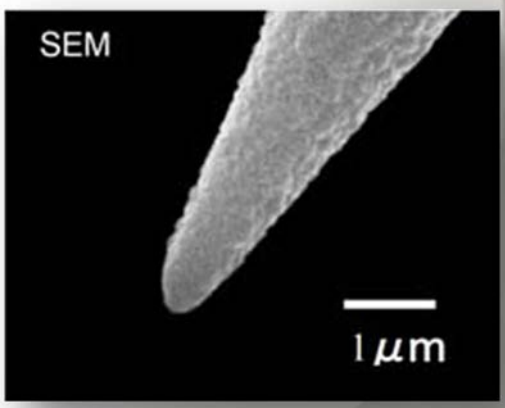


Photo 2 Magnified light scatting probe

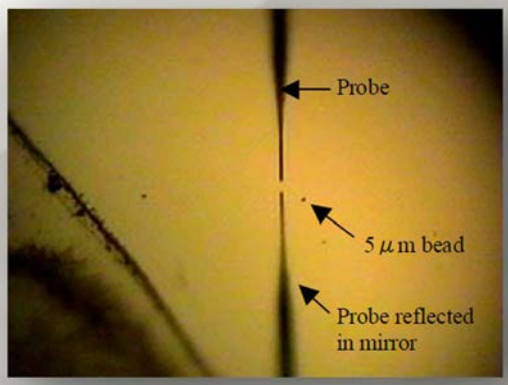


Photo 3 Polystyrene particle on Ao mirror (CCD image)

1) Polystyrene particle on Al mirror (2 mm)

This is the measurement result of one polystyrene particle on Al mirror. As in Photograph 3, the edge of prove was moved to objective position by monitoring CCD image. Measurement area by Near field infrared is up to 20 x 20 mm. Starting position of measurement was determined in the effective area for measurement by moving X-Y stage. Measurement conditions such as accumulation and resolution were determined depending on peak intensity and noise level of spectra. Moreover, by using Near field infrared system, topographic measurement can be done, which is not enabled by conventional and microscope IR. Figure 1 shows result of topographic measurement. Single particle with the size of 2 mm was recognized to be placed clearly on Al mirror. Topographic measurement enables obtaining concavoconvex information in all area of measurement, and elucidating the position where particle is located. Styrene absorption at 3025 cm-1 was confirmed.

Measurement of submicron particle by NFIR (Near Field Infrared Spectroscopy)

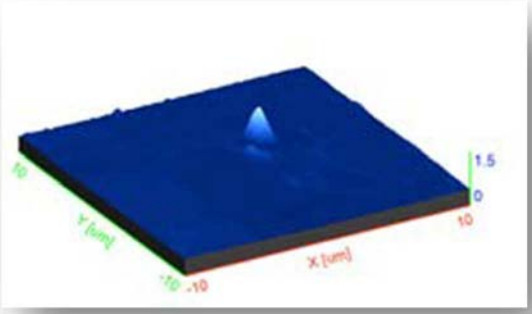


Figure 1 3D display of topographic image

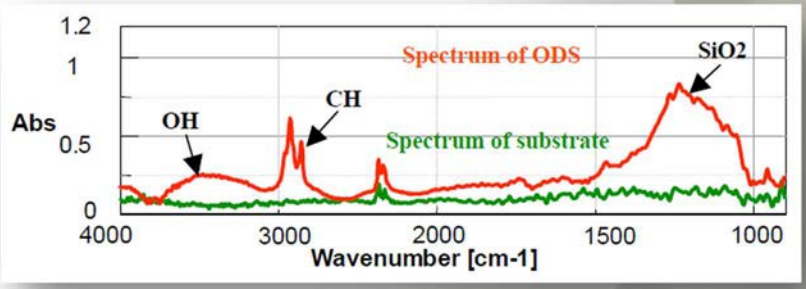


Figure 4 NFIR spectrum of ODS beads

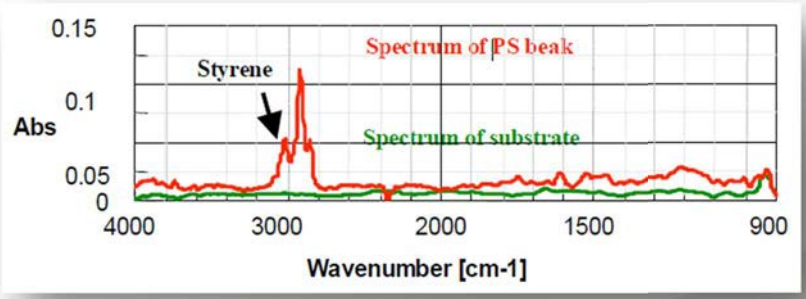


Figure 2 NFIR spectrum of PS beads

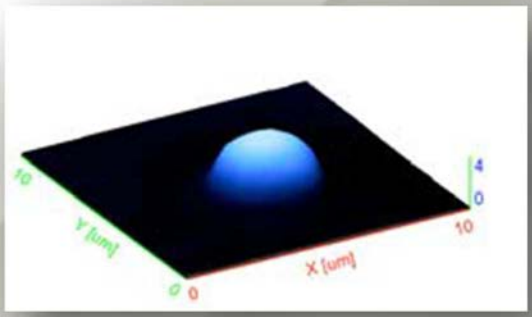


Figure 3 3D display of topographic image

2) Silica ODS particle on GaAs board (4 mm)

Topographic image indicated the size of ODS particle as approximately 4 mm. Near field infrared spectrum of single particle was obtained at the position of particle, and absorption of CH from ODS (Octadecyl silane) and absorption of SiOH from silanol group were identified as in the spectrum. Figure 4 shows microscopic photograph of ODS particle.

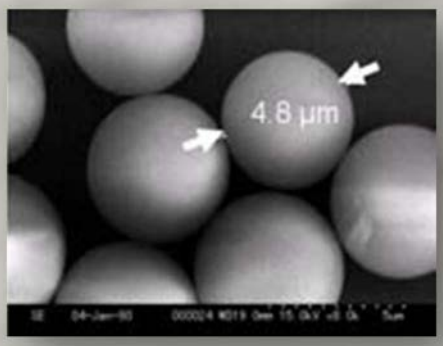


Photo 4 Photograph of ODS by Electron Microscope

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