Application Note Booklet

FT/IR SPECTROMETER

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CONTENTS

Introduction of new DLATGS detector for IRT-5000/7000

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

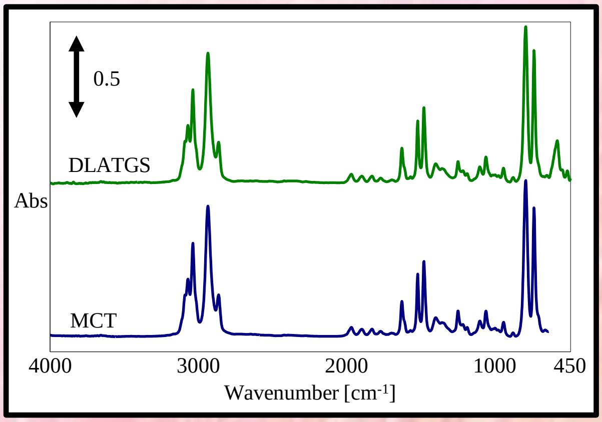


Fig. 1 Spectrum of a polystyrene film using the new DLATGS and an MCT detector

<Measurement 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-band MCT 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.

Measurement of polystyrene

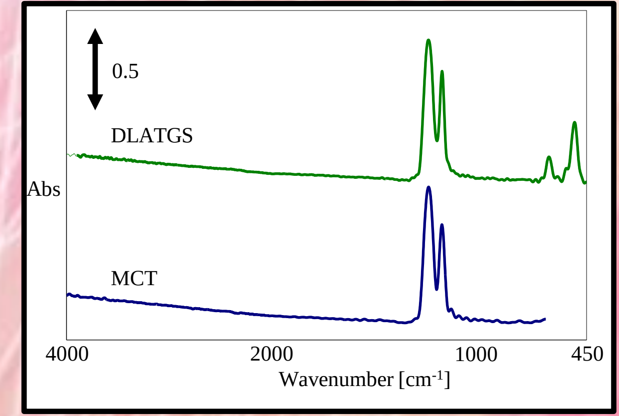


Fig. 2 Spectrum of a Teflon sheet with using the new DLATGS and an MCT detector

<Measurement parameter>
Aperture size: new DLATGS 50 x 50 µm
MCT 10 x 10 µm
Accumulation: new DLATGS: 100 times
MCT: 50 times
Measurement method: transmission

Fig. 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.

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>

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

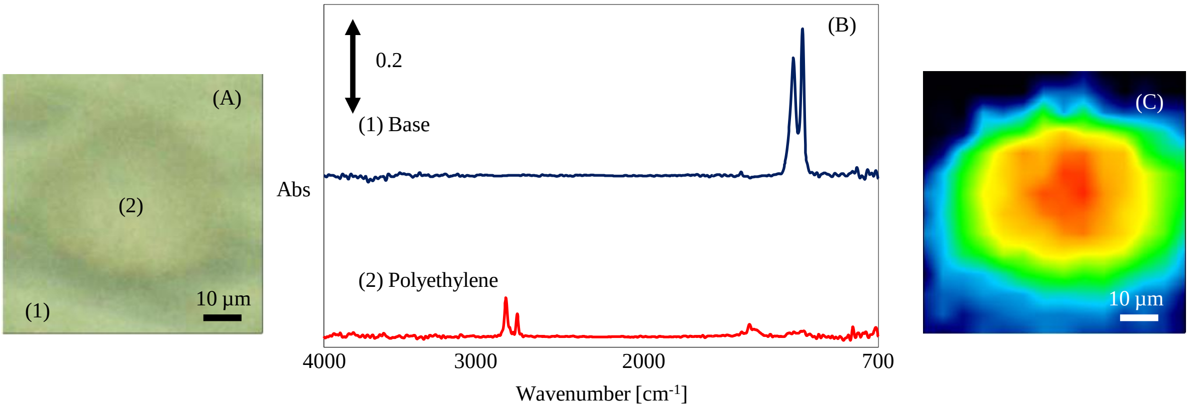


Fig. 3 Smart mapping measurement with use of new DLATGS

Fig. 3 (A) is the visible image while Fig. 3 (B) contains the spectra of 2 single point measurements, which provide recognizable spectra even in a 20 x 20 μm measurement region.

Fig. 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 Fig. 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.

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-5200 (Fig. 1).

Fig. 1 FT/IR-4600 + IRT-5200

<Measurement 1: Mapping by manual stage >

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

[Measurement conditions]

Mode:	Transmittance
Detector:	Mid-MCT
Resolution:	4 cm^{-1}
Accumulation:	1
Cassegrain:	16x,
Aperture:	50 x 50 µm,
Measurement points:	9 x 9
Sampling area:	400 x 400 µm

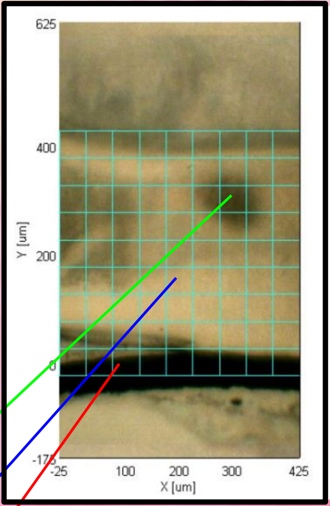
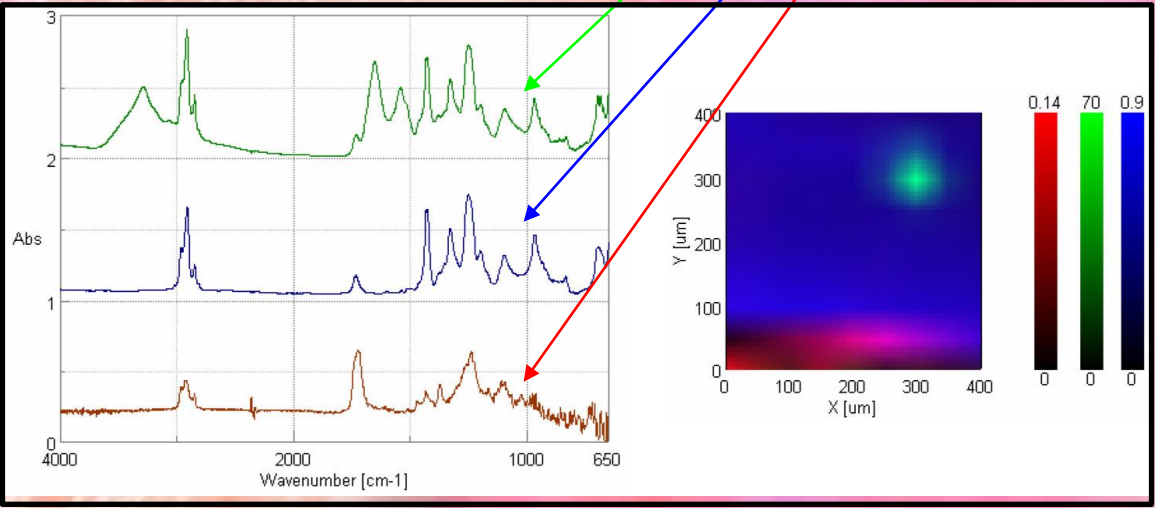


Fig. 2 Observation image (Yellow-green grid shows measurement points.)



By analyzing the spectra in Fig. 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 (Fig. 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 Fig. 5 was measured by using ZnSe as ATR prism.

<Measurement conditions>

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

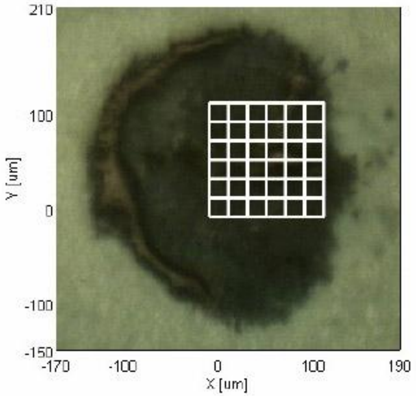


Fig. 5 Sample observation image (White grid shows measurement points)

As a result of mapping measurement, spectra of different components were obtained, depending on different measurement point (Fig. 6).The sample measured was a mixture of water-based and oil-based marker, and specific peaks for each could be identified as in Fig. 6. Color distribution map using the specific peaks for each component at 1666 cm^{-1} and 1282 cm^{-1} is shown in Fig. 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.

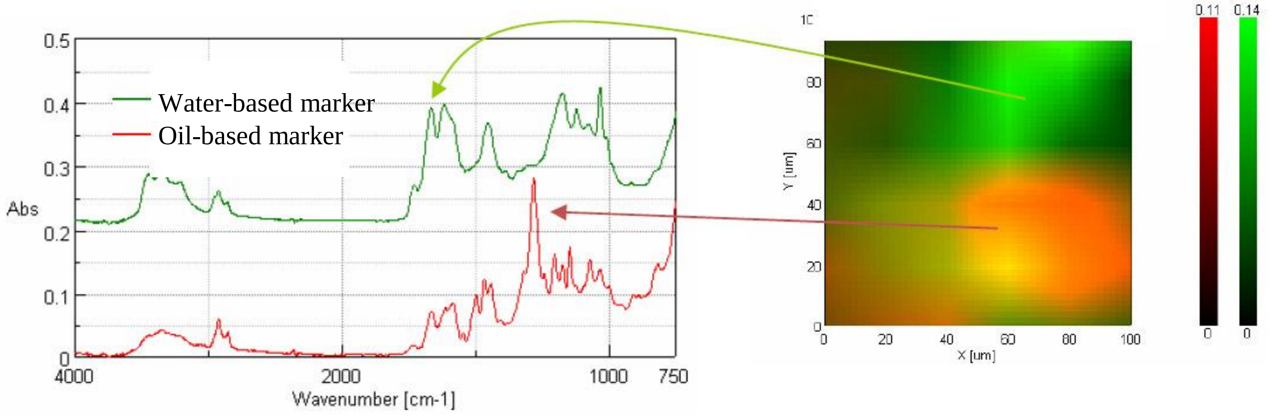


Fig. 6 Measured spectra of impurity

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 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 Micro scope 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.

Fig. 1 Detector replacement by using detachable detector unit

<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: CaF_2
- Detector: InGaAs (Single element)
- Measurement mode: Reflection
- Resolution: 8 cm^{-1}
- Accumulation: 50 times
- Aperture size: 200 x 200 µm
- Measurement points: Surface: 58 x 58 points
  Cross Section: 30 x 40 points

Fig. 2 IR Microscope IRT-7000

Results

Fig. 3 shows NIR spectra obtained by measuring the point in each layer on cross section of tablet. Fig. 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 Fig. 6.

As a conclusion, it can be said NIR Micro Imaging system enables to visualize tablet surface by non-destructive 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.

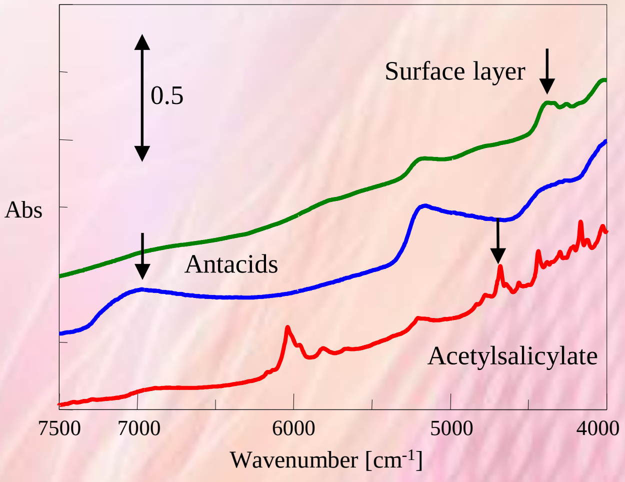


Fig. 3 NIR Spectra of each elements

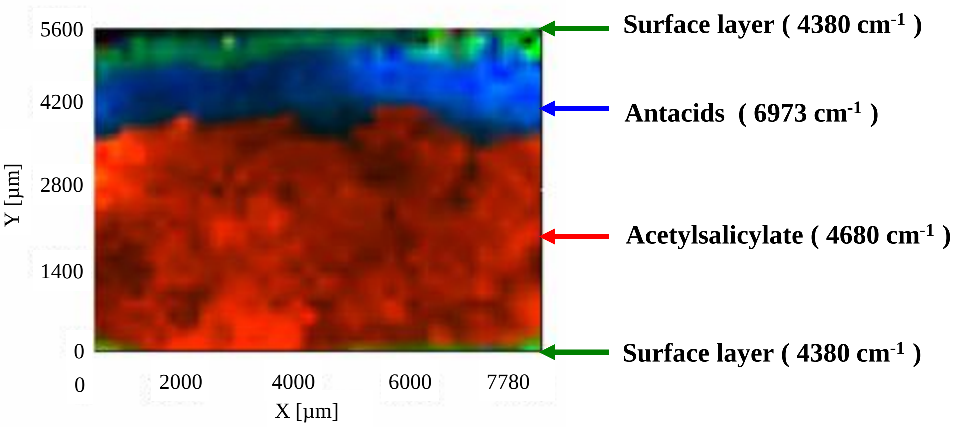


Fig. 4 NIR Imaging of tablet cross section

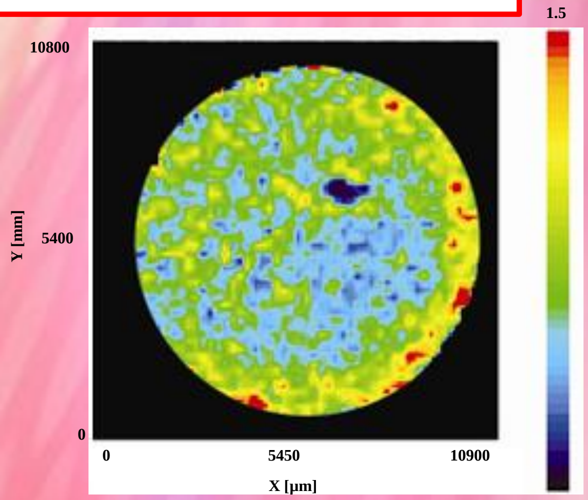


Fig. 5 Picture of general medical tablet (Pain-killer)

Fig. 6 Imaging of surface layer Peak ratio : 4380 cm^{-1}/4680 cm^{-1}

IR microscope is combined with heating stage

Introduction

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 thermophysical properties and crystal structure.

JASCO's IR microscope, IRT-5000 and 7000 combined with the heating system, MHC-5000 (Fig. 1, Chart 1) which we are now introducing enables to have an integrated approach to the geometry change in molecule itself, or the thermopysical 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.

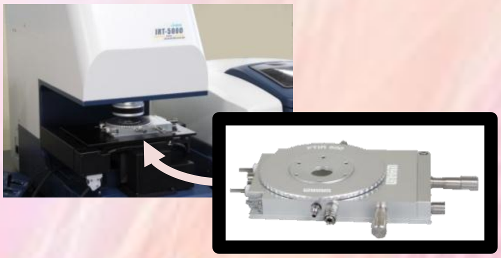


Fig.1 IRT-5200 and heating stage

Chart 1. Temperature control range of heating stage

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

Measurement

Using the system of IRT-5200 with MHC-5000, benzoic acid was heated from 100ºC up to 150ºC with ramping rate of 2ºC per minutes and IR spectra were obtained with 0.5ºC intervals.

Fig. 2 shows 3-Dimensional spectra of benzoic acid with changes in temperature, Fig. 3 shows the change of peak intensity at 930 cm^{-1} against temperature change and Fig. 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 120ºC to 125ºC. Since the melting point of the benzoic acid is 122.4ºC*, 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

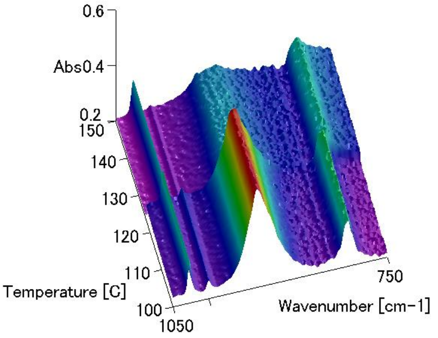


Fig. 2 3D spectrum of benzoic acid

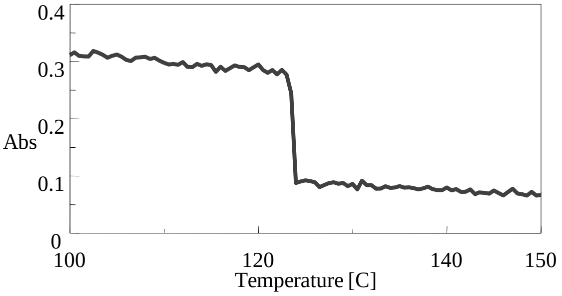
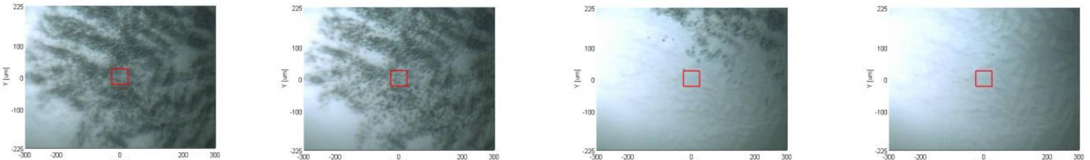


Fig. 3 Change of peak intensity at 930 cm^{-1}



120 ºC

122.5 ºC

124 ºC

125 ºC

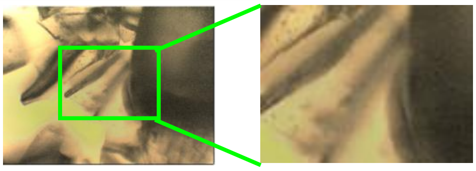
Fig. 4 Observation image of benzoic acid in each temperature(□: measurement area)

Fluorescence Observation, Polarization Observation and Differential Interference Observation methods by IR microscope

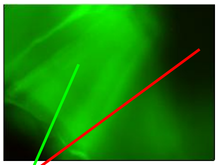
Introduction

JASCO IRT-5200/7200 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



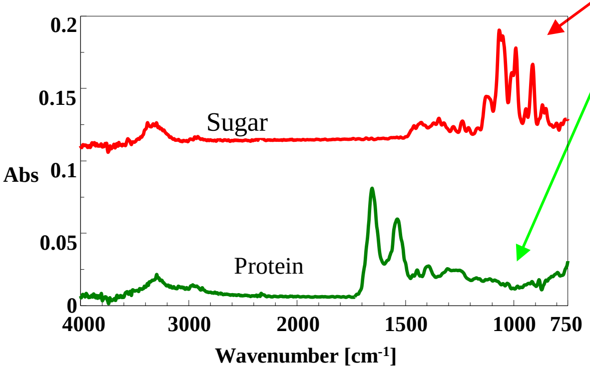
Visible observation view



Fluorescence observation view

Fluorescence observation condition

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



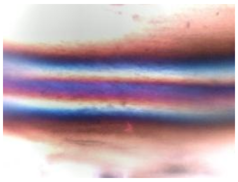
The powder sample that can't be identified by visible observation was observed by using of the fluorescence observation accessory and it's IR spectrum was measured at both green color area which observed as fluorescence and black color area.

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

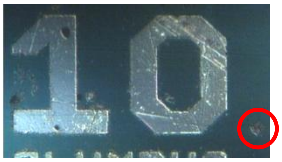


Polarization observation view

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

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.

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

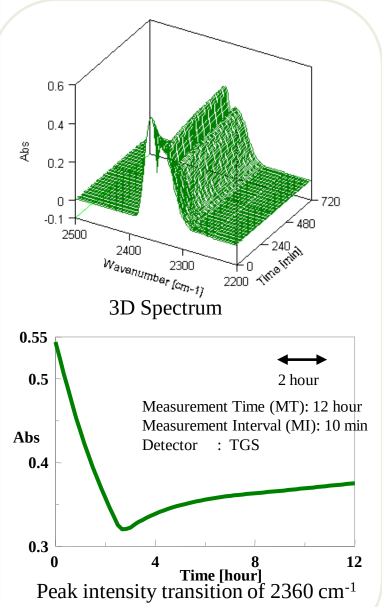
Measurement Ex.: Measured a transition of CO_2 concentration in room air. (Fig. 1) Interval measurement is effective for long-time monitoring of gas analysis. *1 JASCO interval measurement program conducts maximum measurement of 60001 data or 24 days.

Method	Time Res.	Application case
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.

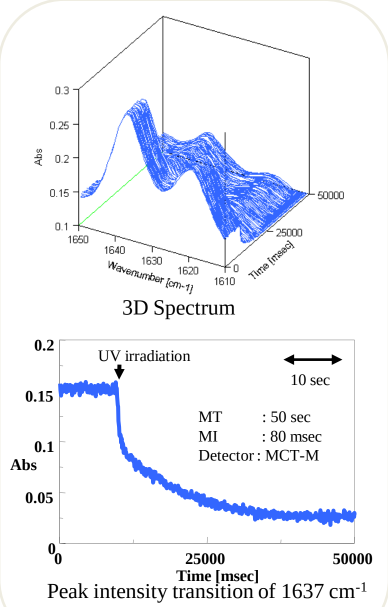
Method	Time Res.	Application case
Step-scan measurement[*2]	**Time Res.:** 5 msec ~ [*3]	**Application case**: relaxation process of liquid crystal orientation

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.



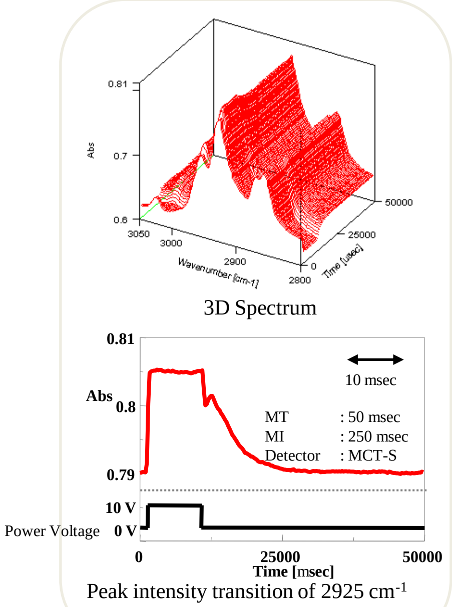
Peak intensity transition of 2360 cm^{-1}

Fig. 1 CO_2 concentration transition
(Interval measurement data)



Peak intensity transition of 1637 cm^{-1}

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



Peak intensity transition of 2925 cm^{-1}

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.

[*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 (Fig. 1 and Table 1) .

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

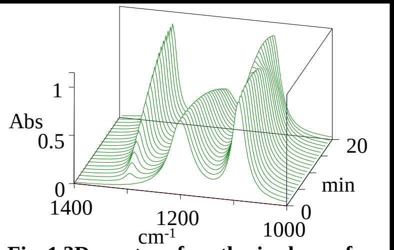


Fig. 1 3D spectra of synthesized waveform

The correlation spectra of synthesized waveform are shown in Fig. 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.

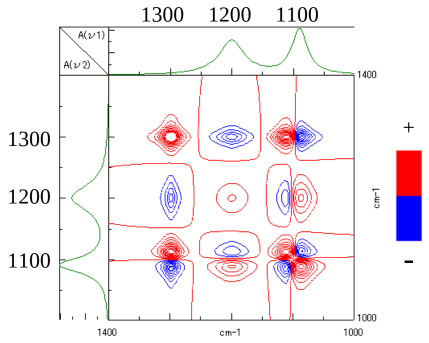


Fig. 2 Synchronous correlation spectra

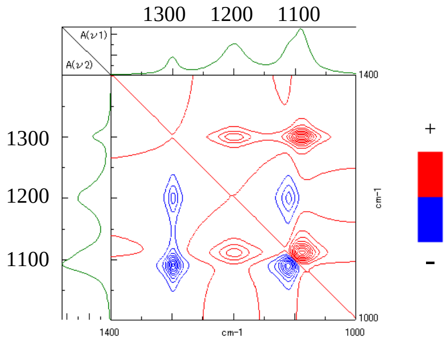


Fig. 3 Asynchronous correlation spectra

Table 2 Estimated peak behavior

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 3 Estimated peak behavior

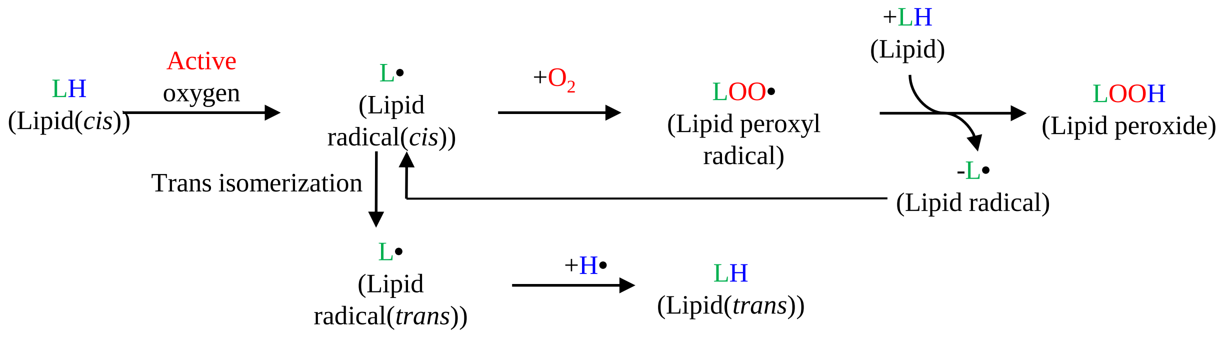
Correlation peak position	Correlation	Peak behavior
1200(X-axis) / 1300(Y-axis) cm^{-1}	Positive	The speed of intensity change at 1300 cm^{-1} is slower than the speed at 1200 cm^{-1}.
1090(X-axis) / 1110(Y-axis) cm^{-1}	Positive	The peak intensity at 1110cm^{-1} increased then, the intensity at 1090cm^{-1}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

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 Cis-type 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 180ºC was measured by using heating single ATR accessory with FTIR and oxidative degradation process was analyzed.



LH (Lipid(*cis*)) → Active oxygen → L• (Lipid radical(*cis*)) → $+O_2$ → LOO• (Lipid peroxyl radical) → +LH (Lipid) → LOOH (Lipid peroxide)

-L• (Lipid radical)

Trans isomerization

L• (Lipid radical(*trans*)) → +H• → LH (Lipid(*trans*))

Fig. 1 Reaction mechanism of oxidation degradation of the Lipid

Measurement Method

There are two different types of unsaturated fatty acid such as Cis-type and Trans-type, and Cis-type 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 180ºC 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 N_2 gas.

Fig. 2 ATR Heating Single Reflection ATR accessory

<Measurement condition>

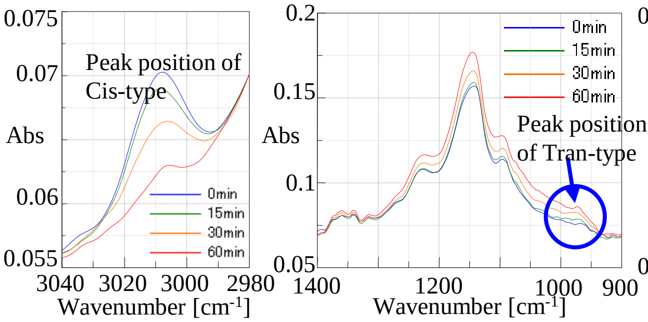
Main unit: FT/IR-6600 with Heating Single reflectance ATR
Detector: DLATGS
Resolution: 4 cm^{-1}
Accumulation: 64 times
Temperature: 180ºC
Apodization function: Cosine
Measurement method: ATR (Crystal: Diamond*)
Sample compartment condition: Air environmental condition or N_2 purged condition

*The high temperature type prism was used in this measurement.

Results and Discussions

Fig. 3 shows spectral data of time interval measurement for the oil sample heated up to 180ºC 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 Fig. 4 the spectral data of the same interval measurement but under N_2 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 occurr, proving that oxidative degradation of oil did not happen.

Fig. 5 and Fig. 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 Fig. 5 and Fig. 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 Fig.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.



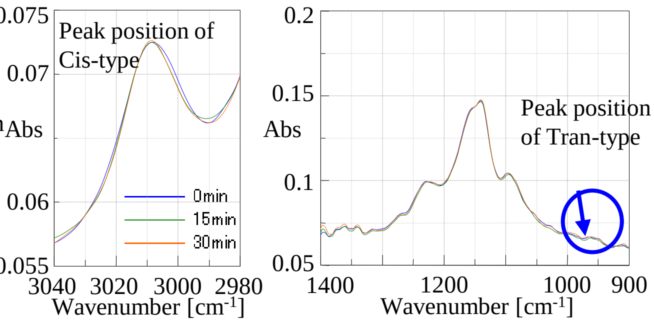
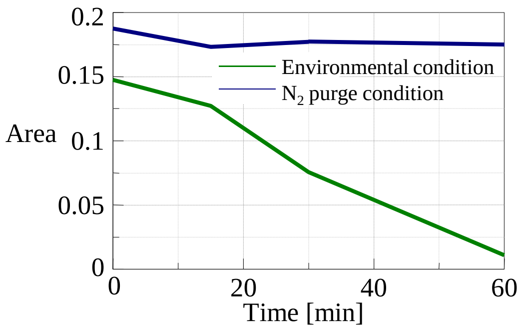


Fig. 3 Spectra under air environmental condition

Fig. 4 Spectra under N_2 purged condition



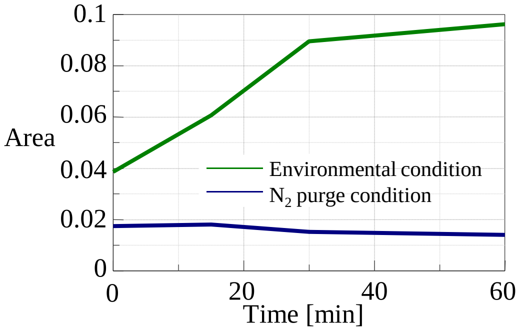


Fig. 5 Change of peak area for Cis at 3010 cm^{-1}

Fig. 6 Change of peak area for Trans at 966 cm^{-1}

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

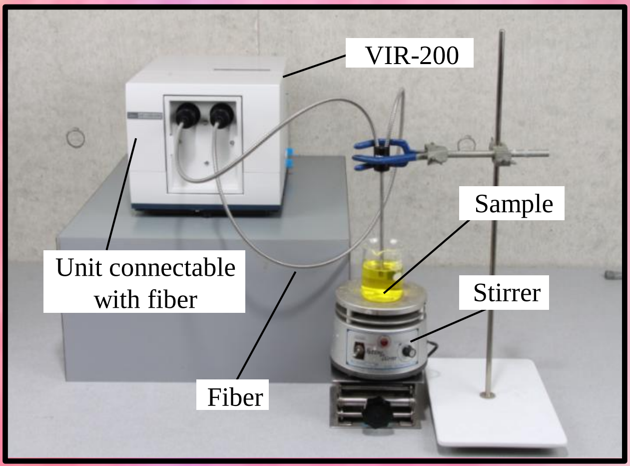


Fig. 1 VIR-200 + Fiber connection unit

Results and Discussions

Fig. 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. 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.

Fig. 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.

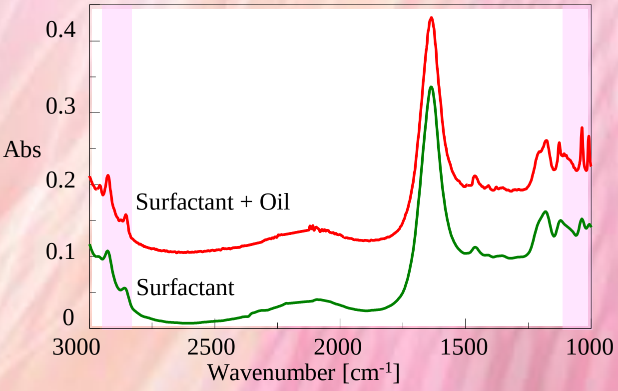


Fig. 3 Spectrum of surfactant after measurement and spectrum of surfactant only

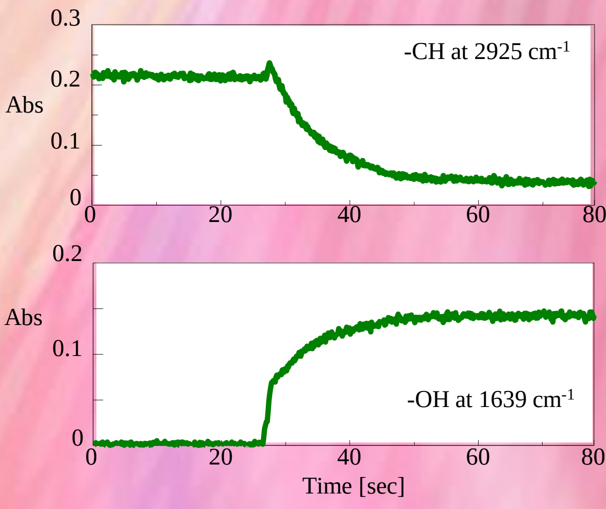


Fig. 4 Time-dependent change of Oil(-CH) & H_2O(-OH) group)

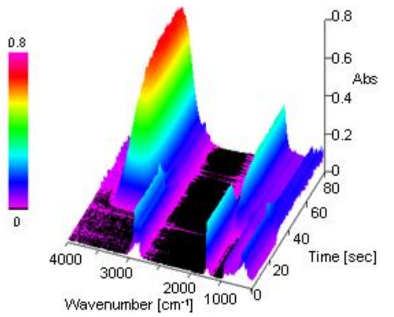


Fig. 2 3D spectrum of reaction process

Conclusion

In this report, the two-steps reaction was monitored by using the fiber probe and rapid scan. In addition, it is expected that VIR-100 series can be utilized in a wide range of field such as the evaluation of lithium-ion 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.

Quantitative Analysis of Biodiesel (FAME) in Diesel Fuel

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 Fig. 1.

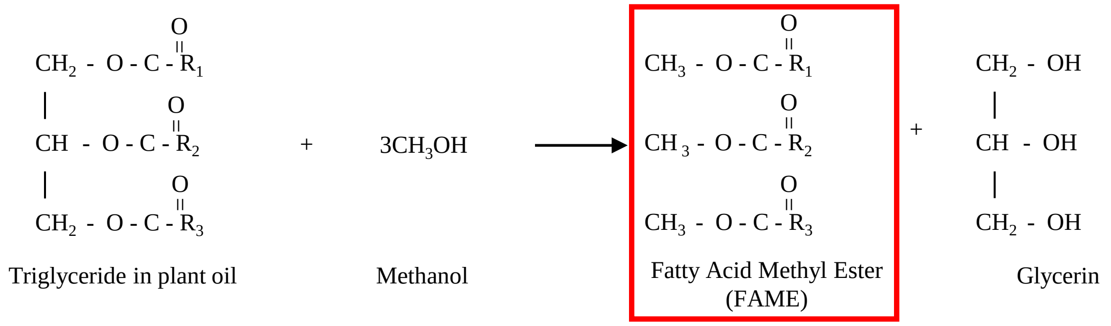


Fig. 1: Reaction pathway from vegetable oil to FAME

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.

Table 1 Standard Test Methods of FAME by FT/IR

Regulation	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-4600 FT/IR Spectrometer	
Resolution	0.7 cm^{-1}	
Other measurement conditions	Accumulation: 32 times Accessory: ATR PRO450-S (ZnSe)	Accumulation: 32 times Accessory: Sealed Liquid cell Window material: CaF_2 Pathlength: 0.5 mm

Quantitative Analysis of FAME for ASTM

Fig. 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 Fig. 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.

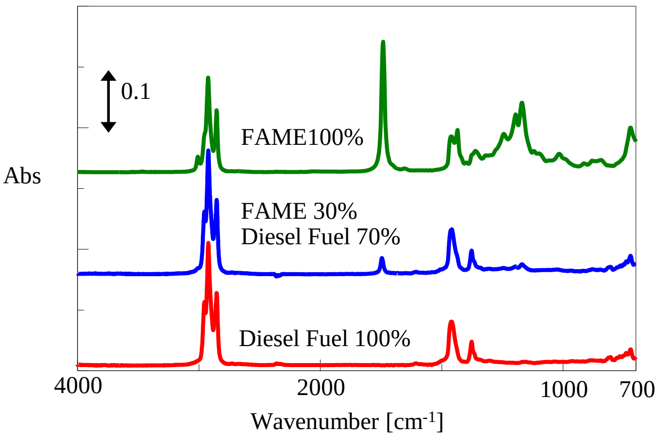


Fig. 2 IR spectra of FAME and diesel oil
(ATR method, resolution: 4 cm^{-1}, accumulations: 32 times)

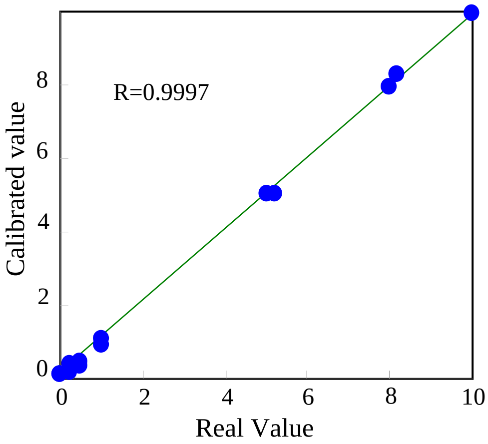


Fig. 3 PLS calibration curve of FAME
Calculation range: 1800-1692, 1327-940 cm^{-1}, No. of Factors: 3

Quantitative Analysis of FAME for EN

Fig. 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.

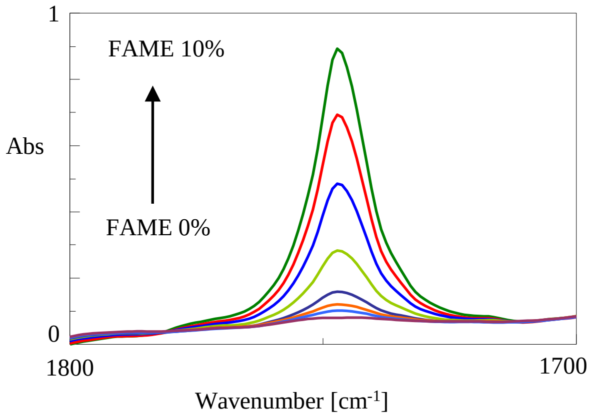


Fig. 4 Peaks of FAME
(Transmission, resolution: 4 cm^{-1}, Accumulation: 32 times)

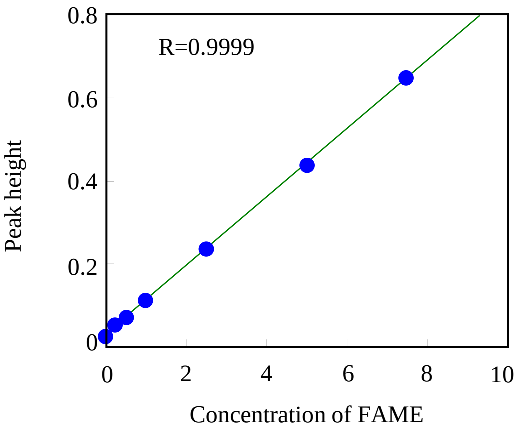


Fig. 5 EN calibration curve of FAME

Rapid Quantitative Analysis of Trans-fatty acid in extremely low concentration by liquid cell

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 BF_3, 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 (Fig. 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 Fig. 1), being known as an isomer of trans-type of triolein, into the cis-triolein (orange color spectrum in Fig. 1) which contains only cis-type.

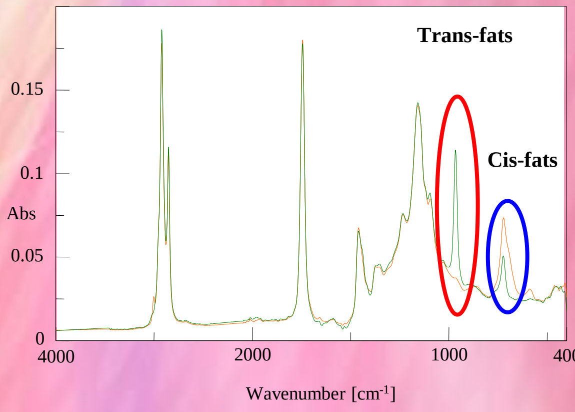


Fig. 1 IR spectrum of cis-fats and trans-fats(ATR)

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

Measurement Conditions

Instrument: FT/IR-4600
Detector: DLATGS Resolution: 4 cm^{-1}
Accumulation: 64 times Apodization: Triangle
Temperature: 25ºC (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.

Fig. 2 Sealed liquid cell

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 Fig.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} (Fig. 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 (Fig. 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%.

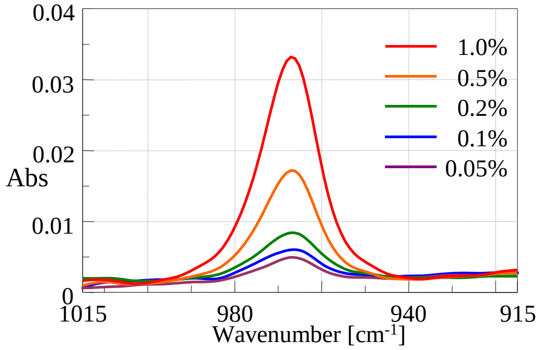


Fig. 3 Trans-fats peak at 966 cm^{-1}

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%.

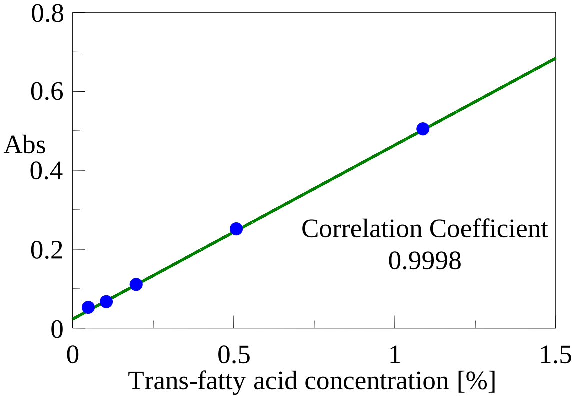


Fig. 4 Calibration curve

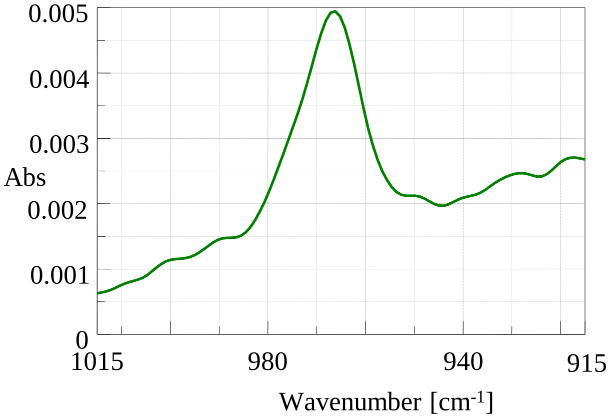


Fig. 5 Spectrum of trans-fats in 0.05%

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).

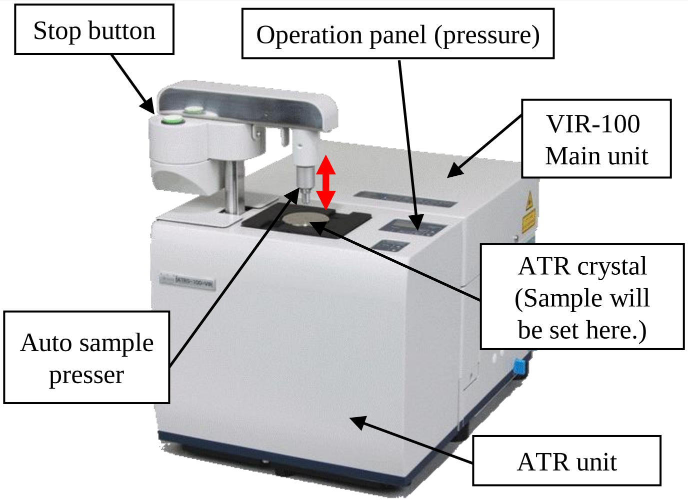


Fig. 1 VIR-100 + Auto contact ATR
(VIR-100 + ATRS-100-VIR + AC-ATR-VIR)

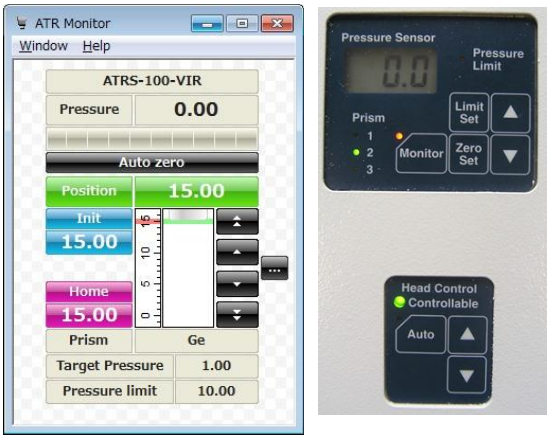

ATRS-100-VIR
Pressure 0.00
Position 15.00
Init 15.00
Home 15.00
Prism Ge
Target Pressure 1.00
Pressure limit 10.00

Fig. 2 Pressure monitor (left)
and operation panel (right)

Measurement

<System configuration>

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

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/cm^2 (Fig. 3), 400 kg/cm^2 (Fig. 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/cm^2 to 400 kg/cm^2 at every 40 kg/cm^2 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/cm^2 and this indicates that the soft capsule was not broken at up to 120 kg/cm^2 so that the starch that is the ingredients of capsule itself was observed.

At the spectrum of 160 kg/cm^2, 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/cm^2 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.

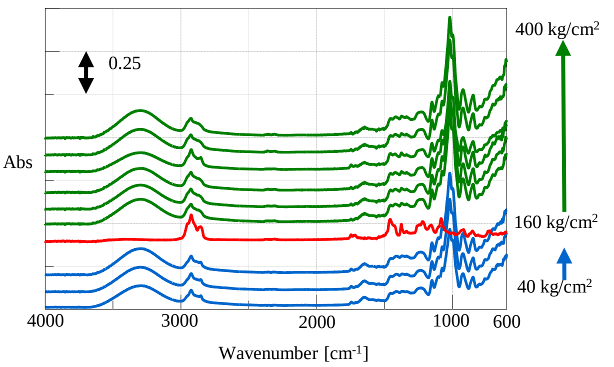


Fig. 3 IR spectra of soft capsule of food supplement

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 (Fig. 4). In addition to the auto contact ATR, "repeat measurement" and "judgment of acceptance" (Fig. 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 pressing the start button. The different polymers from the standard polyethylene were easily detected as shown in Fig. 4 and 5 (spectrum #3 is of polyvinylidene chloride and, the spectrum #5 is of polypropylene.).

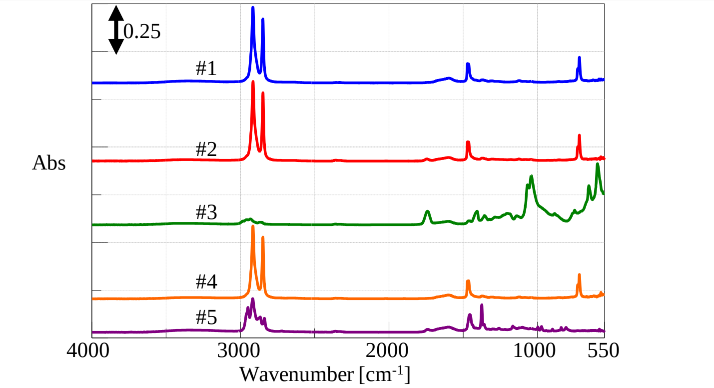
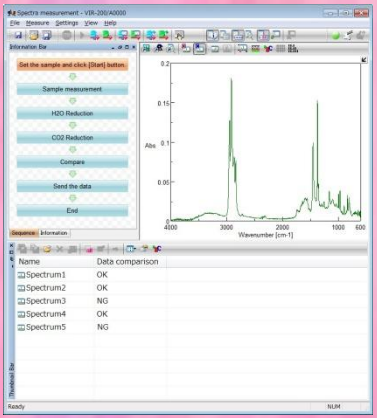


Fig. 4 IR spectra of five polymer samples



Set the sample and click [Start] button

Name	Data comparison
Spectrum1	OK
Spectrum2	OK
Spectrum3	NG
Spectrum4	OK
Spectrum5	NG

Fig. 5 Judgment of acceptance

As we demonstrated, the auto contact ATR offers the highly reproducible IR spectrum. It is also expected to apply this technique to monitoring of production line by a combination with autosampler system.

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 65 Kg that is equivalent to 4.6 Kg per one set of teeth. Therefore, the 4.6 Kg 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.

<System configuration>

P/N: 6999-J011A VIR-100 Versatile FTIR Spectrometer

*Applicable to VIR-200 (P/N; 6999-J012A)

P/N: 6999-J103A ATRS-100-VIR Single reflection ATR attachment

*Applicable to MultiChambIR attachment (P/N: 6999-J101A; MPA-100-VIR)

P/N: 6999-J143A PKS-Z100 ZnSe crystal kit

P/N: 6999-J151A AC-ATR-VIR Auto-Contact ATR for ATRS/ATRH/MPA-100-VIR

Fig. 1 Granular gum place on ATR crystal

<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/cm^2 (Applied pressure on crystal surface)
Equivalent to 4.6 kgf (applied pressure on sample)

Results

Every IR spectrum up to 10 times of presser drive was shown in Fig. 2 and, the IR spectrum at every 10 time drive of 100 time drive was shown in Fig. 3. The peaks derived from esters were appeared at near 1740 cm^{-1} and 1235 cm^{-1}. These results indicate that the gum base included the vinyl acetate. Also the peak derived from xylitol was observed at near 745 cm^{-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 Fig. 4. The intensity increased in the first 5 measurements and, it became stable later. The monitoring of peak intensity at 745 cm^{-1}(xylitol) was indicated in Fig. 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.

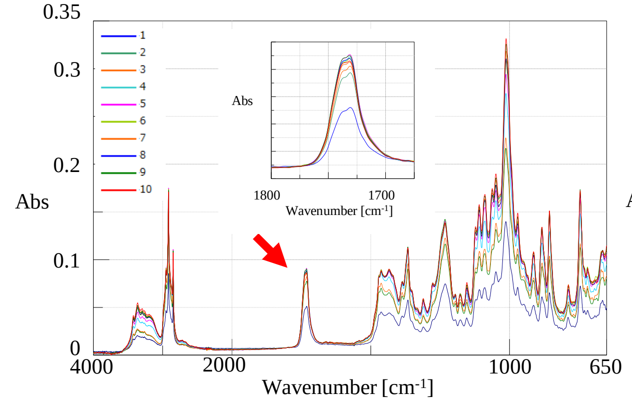


Fig. 2 IR spectra in first 10 trials

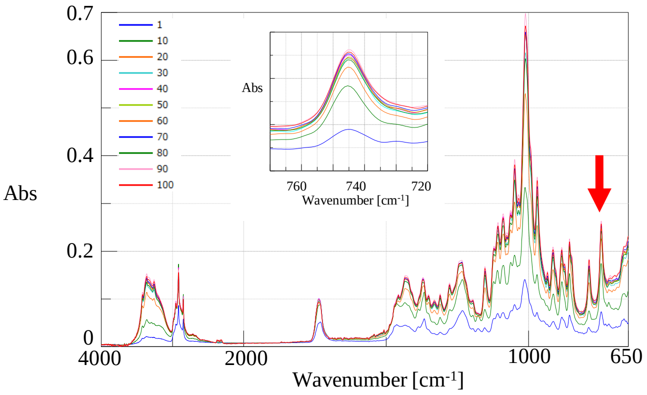
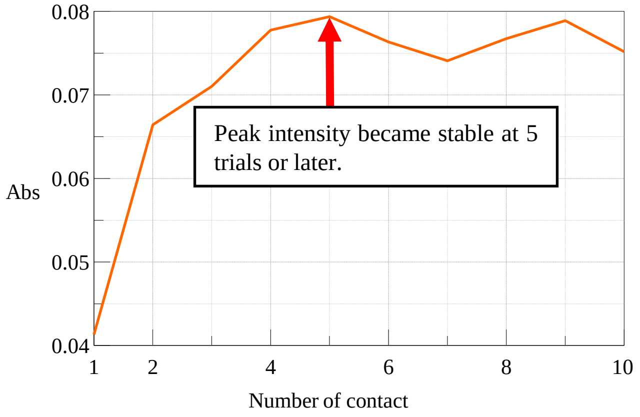
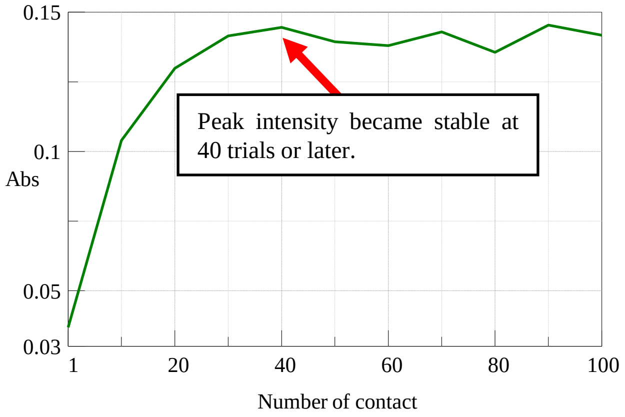


Fig. 3 IR spectra at every 10 trials of 100 trials.



Peak intensity became stable at 5 trials or later.

Fig. 4 Change of peak intensity at 1740 cm^{-1}(vinyl acetate)



Peak intensity became stable at 40 trials or later.

Fig. 5 Change of peak intensity at 745 cm^{-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.

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 µm 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.

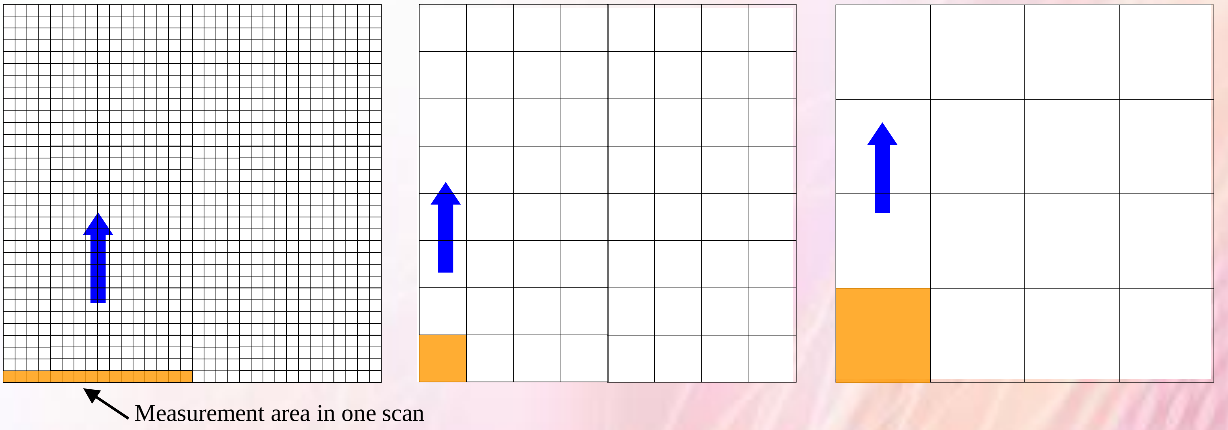
Accordingly, single-element detector is considered to have an advantage because the aperture size is changeable, so that for large area measurement with large aperture size, the measurement time may be shorter than multi-channel detector. Therefore, for the measurement of 200 x 200 µm area, the measurement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

Table 1 Comparison of detectors and aperture size in 200 x 200 µm area measurement[*2]

Detector	**Linear array (16 x 1)**	**Single-element (IRT-7000S)**	**Single-element (IRT-7000S)**
Aperture size	6.25 x 6.25 µm	25 x 25 µm	50 x 50 µm
Measurement points	32 x 32	8 x 8	4 x 4
Measurement time [*3]	Approx. 7 sec.	Approx. 7 sec.	Approx. 2 sec.

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



Linear array detector
Aperture: 6.25 x 6.25 µm

Single-element detector (IRT-7000S)
Aperture: 25 x 25 µm

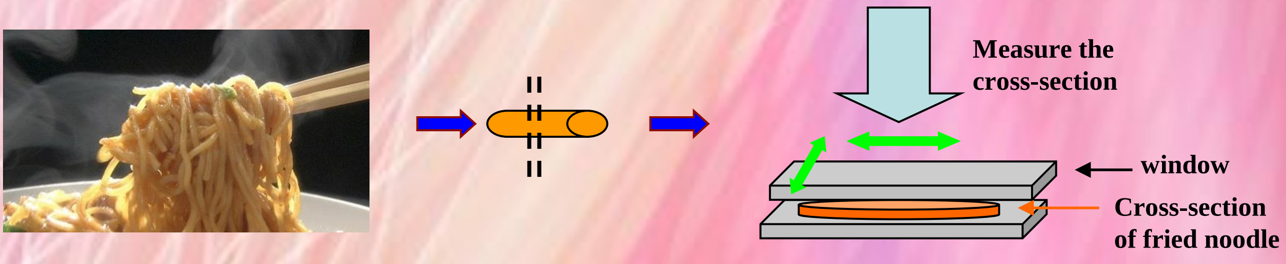
Single-element detector (IRT-7000S)
Aperture: 50 x 50 µm

Fig. 1 Comparison of measurement area in 200 x 200 µm area

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 × 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 µm
Detector: MCT
Measurement time: Approx. 5 minutes (professional)
Resolution: 16 cm^{-1}



1. Cook fried noodle

2.Cut the cross-section rapidly

3. Measure the cross-section

Fig. 2 Process of measurement

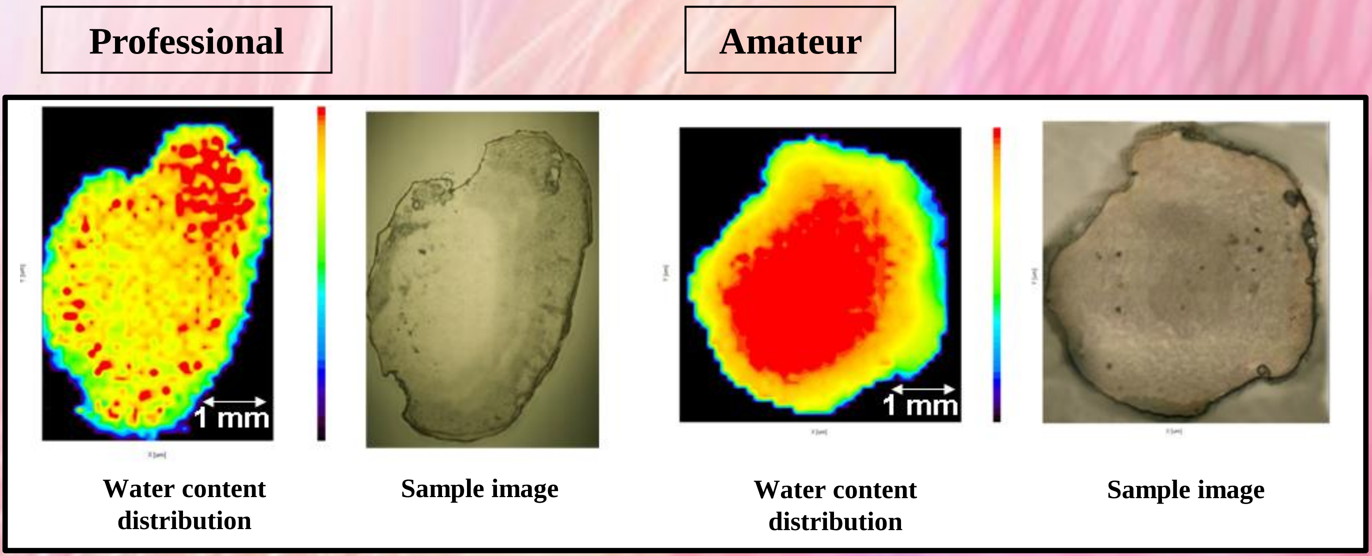
Results

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).

Fig. 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 μm^2 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 milimeters 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.



Professional

Amateur

Water content distribution

Sample image

Water content distribution

Sample image

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

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

Introduction

Fig. 1 Polarized ATR

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 Fig. 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 Fig. 2. By rotating the sample 90° 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 Fig. 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 Fig. 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.

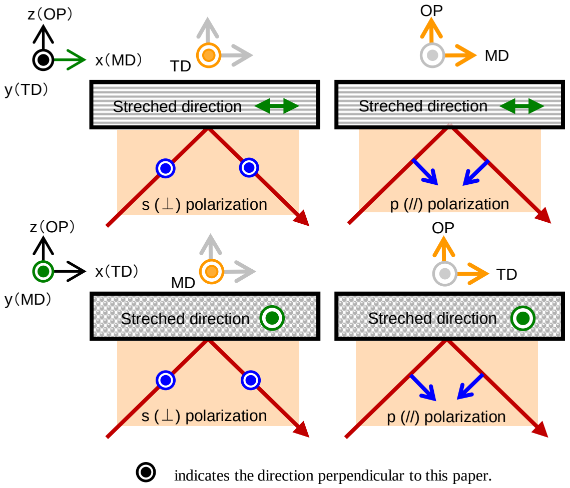


Fig. 2 Relationship of the direction of polarizer and stretched axis of the oriented films

Table 1 Obtained information of each direction of samples and polarizer

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

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

Polarized ATR (Fig. 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.

Results and discussions

Measurement of oriented polypropylene (PP) films

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

<Measurement Conditions>

System:	FT/IR-4600	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. 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 calculated1 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.

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 Fig. 5.

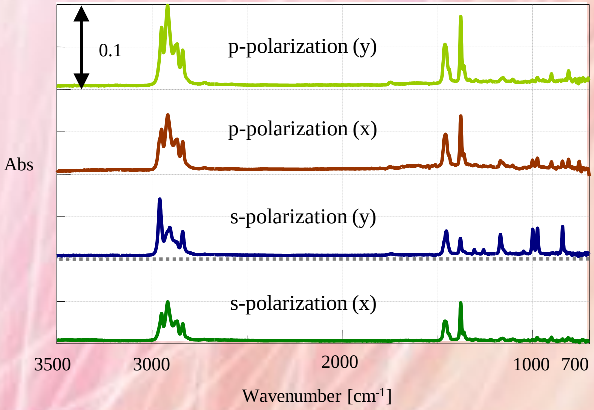


Fig. 3 Spectra of a PP film measured by polarized ATR

*Figures in parentheses show the direction of film stretching.

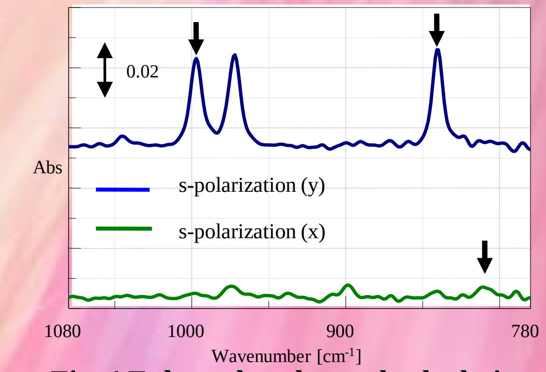


Fig. 4 Enlarged peaks used calculation of degree of orientation

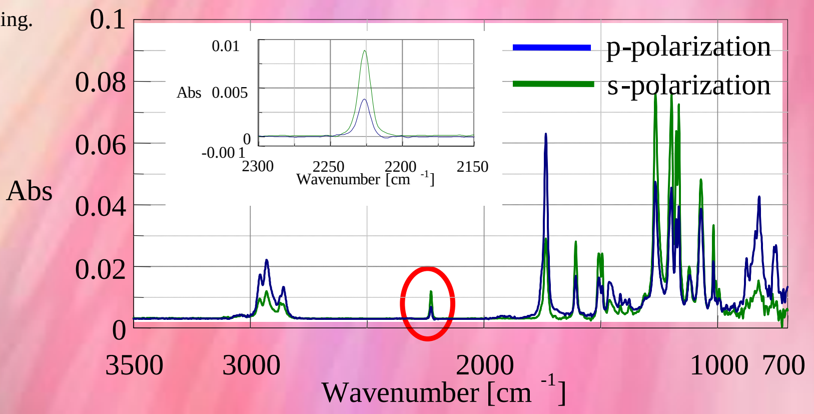


Fig. 5 Spectra of a TN crystal measured by polarized ATR

<Measurement Conditions>

System: FT/IR-4600 Resolution: 4 cm^{-1}
Detector: DLATGS Accumulations: 64
Accessory: ATR PRO610P-S (Prism: ZnSe)

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.

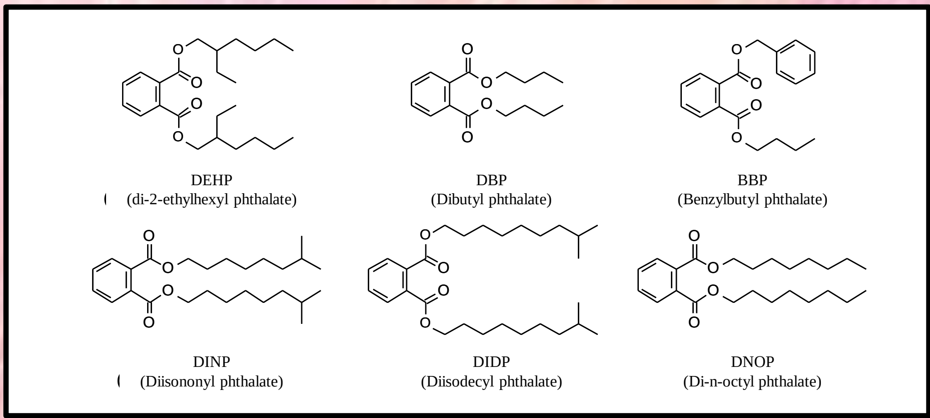
As described above, polarized ATR spectroscopy is useful for rapidly and non-destructively measuring and evaluating the surface state of oriented molecules, such as film and liquid crystal compounds. The analysis results can also be used to calculate the degree of orientation for each vibrational mode and for quantitative evaluations of orientation along the axis of the molecular depth.

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; Fig. 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 four esters will be regulated from July 22th in 2019.



DEHP
(di-2-ethylhexyl phthalate)

DBP
(Dibutyl phthalate)

BBP
(Benzylbutyl phthalate)

DINP
(Diisononyl phthalate)

DIDP
(Diisodecyl phthalate)

DNOP
(Di-n-octyl phthalate)

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 (Fig. 2).

Fig. 2 Single reflection ATR for large-sized sample (FT/IR-4600 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 Fig. 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 (Fig. 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.

Measurement

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

Measurement conditions

Instrument:	FT/IR-4600
Method:	ATR (ATR PRO510T-S, ZnSe crystal)
Detector:	DLATGS
Resolution:	4 cm^{-1}
Accumulation:	64

Fig. 3 A1 size sheet on ATR PRO510T-S

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 (Fig. 4), such peaks of phthalate esters plasticizer can also be observed.

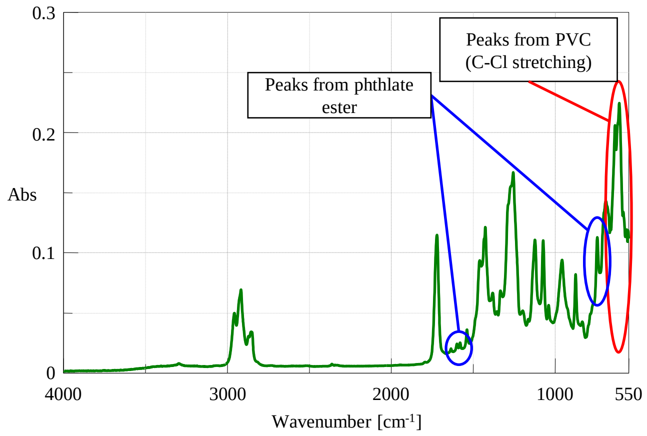


Fig. 4 IR Spectrum of PVC sheet

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} (Fig. 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 bounace ATR for large-sized sample can be applied to the non-destructive and quick measurement of surface of extra large sample or molded sample.

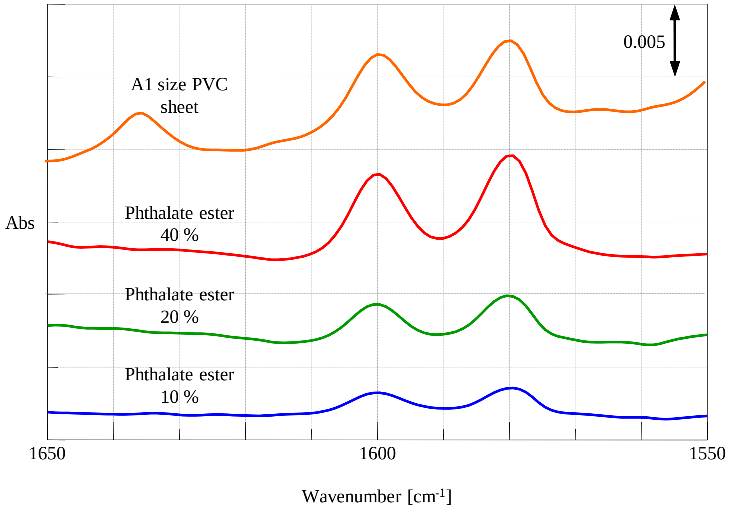


Fig. 5 IR spectra of known DEHP content PVC

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 Fig. 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.

Measurement conditions

Instrument: FT/IR-6600+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 µm
Measurement area: 180 x 180 µm

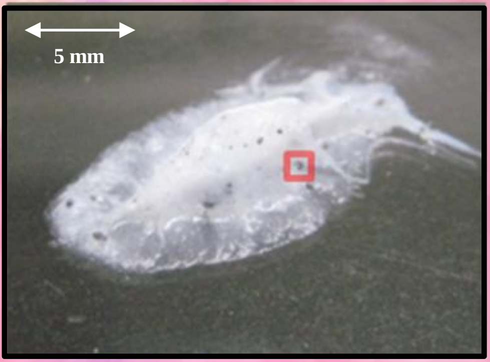
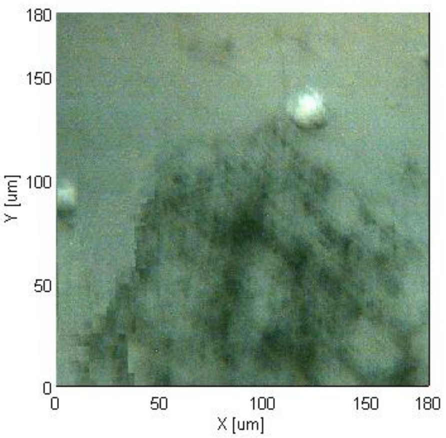


Fig. 1. Face cleaner photo

Result and Discussion

Spectra of the paste part and black particles are shown in Fig. 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 (Fig. 4). The contour plot of the peak height at 1056 cm^{-1} ascribed to glycoside bond of cellulose is shown in Fig. 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 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.



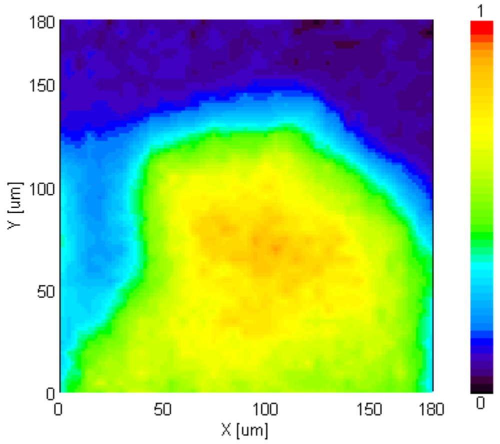


Fig. 2 ATR-5000-SS Observation image

Fig. 5 Peak of Cellulose(1056 cm^{-1}) Contour plot of peak height

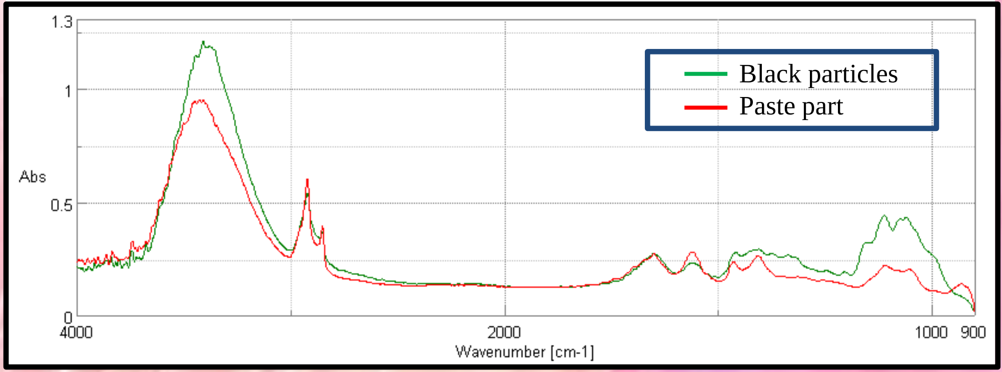


Fig. 3 Spectra of the paste part and black particles (After ATR correction)

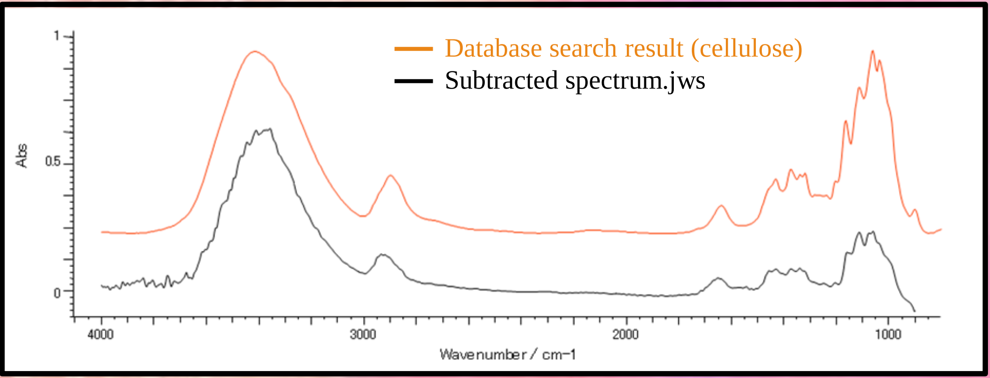


Fig. 4 Database search result of the subtracted spectrum of Fig. 3

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, Fig. 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 Fig. 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.

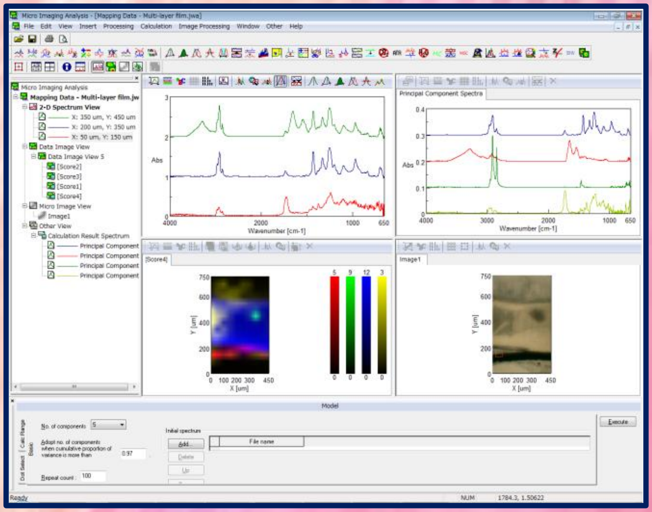
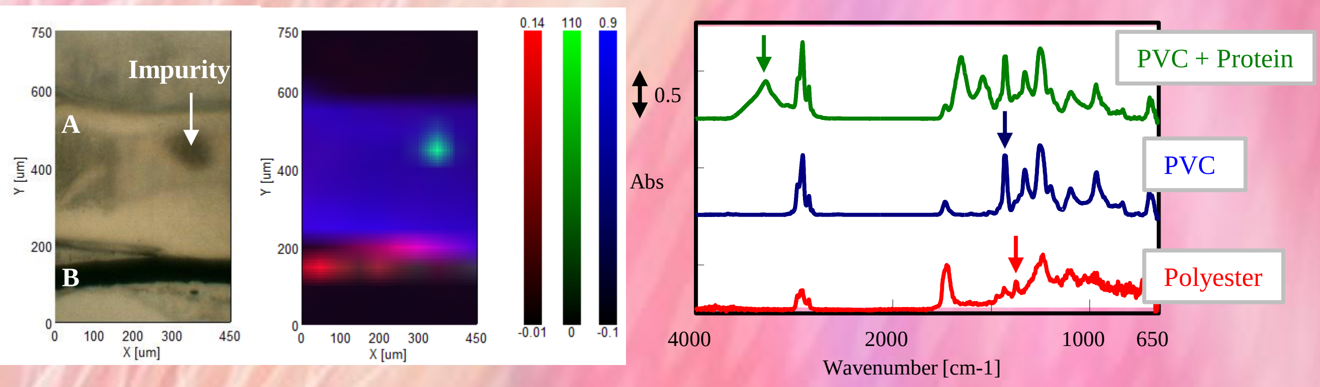


Fig. 2 Micro Imaging Analysis Program



Observation image

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

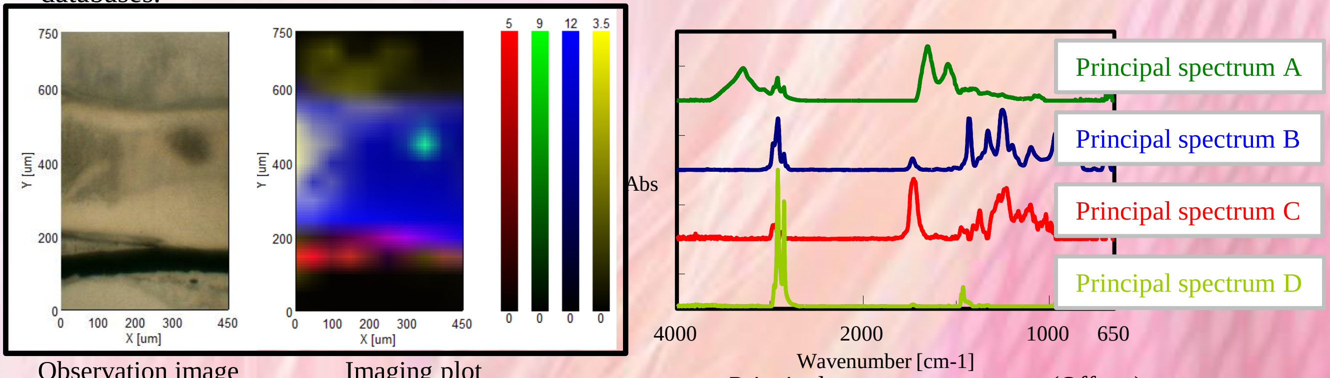
Measured spectra (Off-set)
(Imaging plot was made based on
the key peaks indicated by arrows)

Fig. 1 Imaging analysis result of multilayer film with key peaks

“Model Analysis” Results

Fig. 3 shows the imaging analysis result of a multilayer film using “Model Analysis”. Comparing the data in Fig. 1 with the data in Fig. 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. Fig. 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)

Fig. 3 Imaging analysis result of multilayer film with “Model analysis”

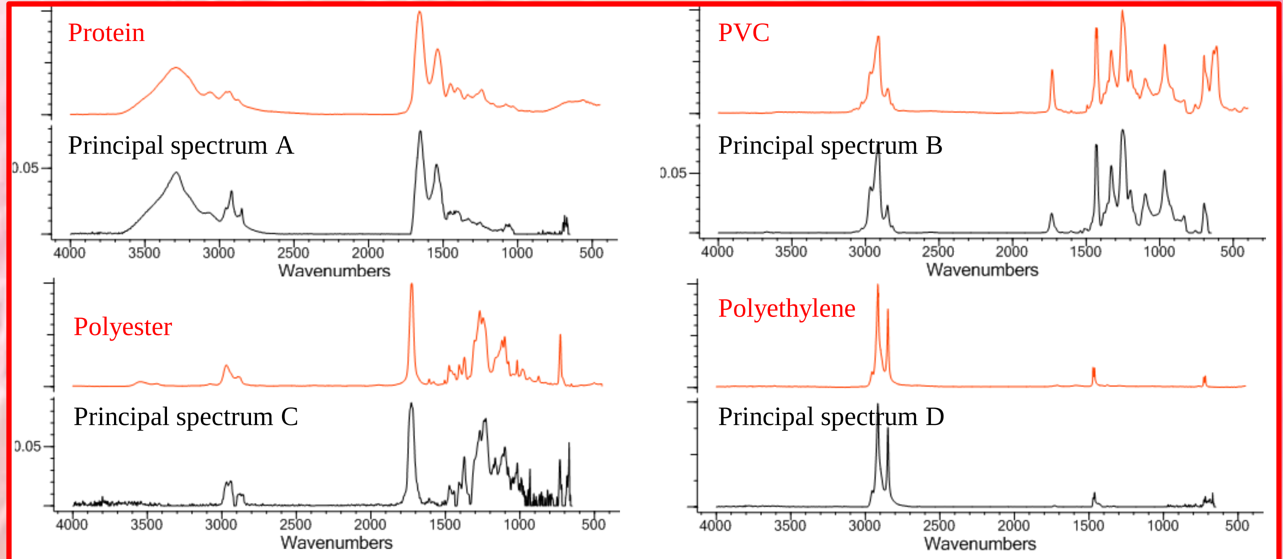


Fig. 4 Database search result of principal components spectra

System configuration

P/N: 7084-J002A	FT/IR-4600 FT/IR Spectrometer
P/N: 7081-J051A	IRT-5200-16 Infrared Microscope
	Micro Imaging Analysis Program (Standard for IRT-5200/7100/7200)

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

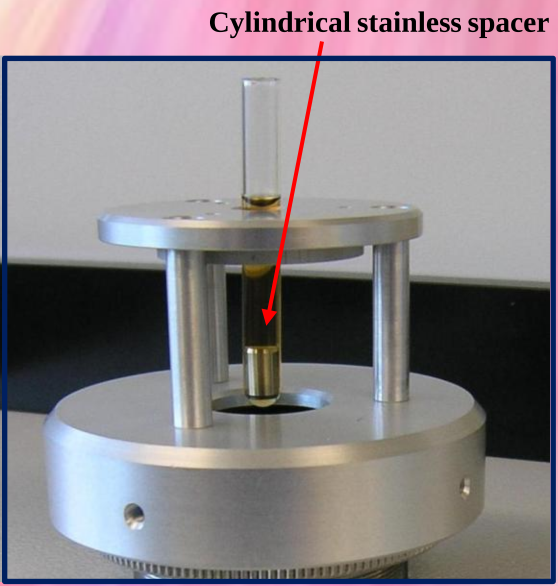


Photo 2 Measurement example of solution using mini test tube

Fig. 1 and 2 show the solution spectrum obtained by this method, and good repeatability. Fig. 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.

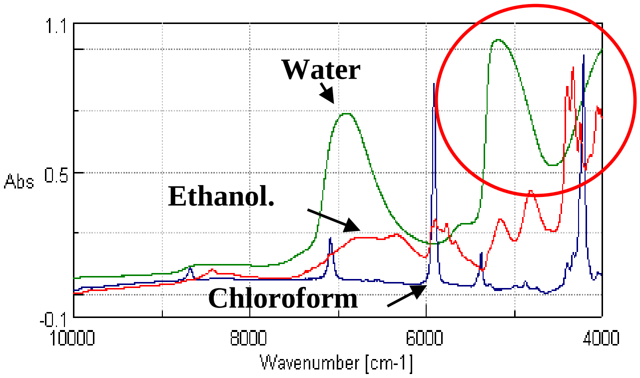
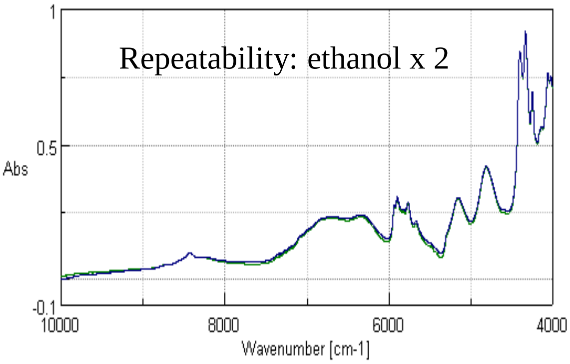


Fig. 1 Measurement example using test tube



< 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.

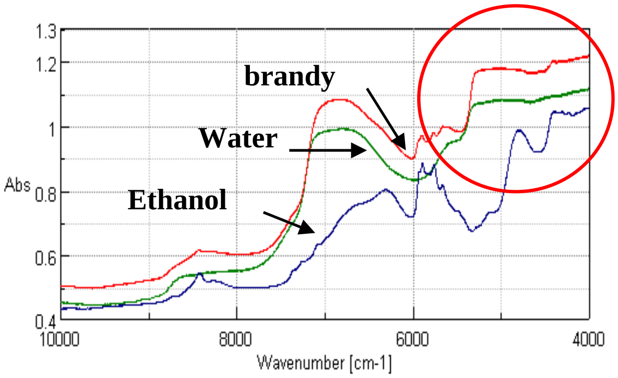


Fig. 2 Reproducibility using Ethanol

The cell thickness can be controlled by using metal reflectance plate with spacer on the laboratory dish. Fig. 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

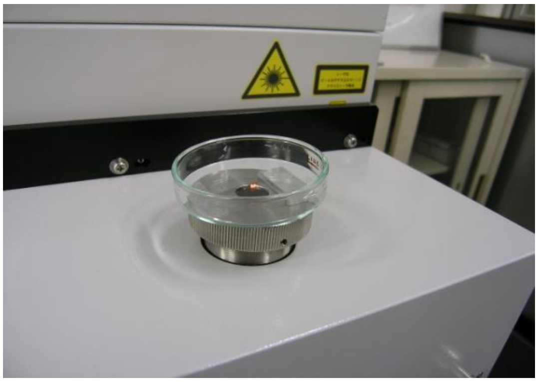


Photo 3 Measurement example of solution sample using laboratory dish

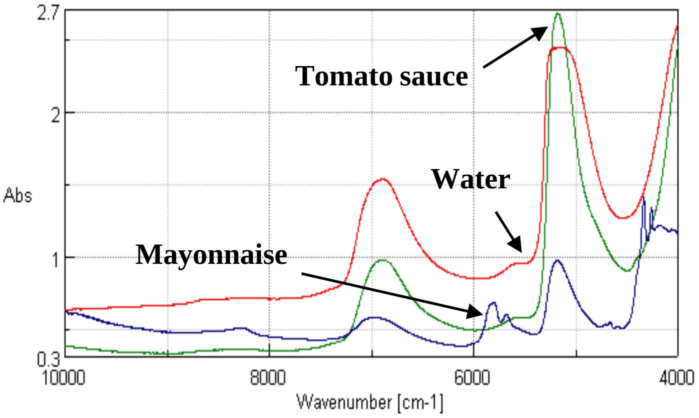


Fig. 4 Measurement example using laboratory dish

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

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.

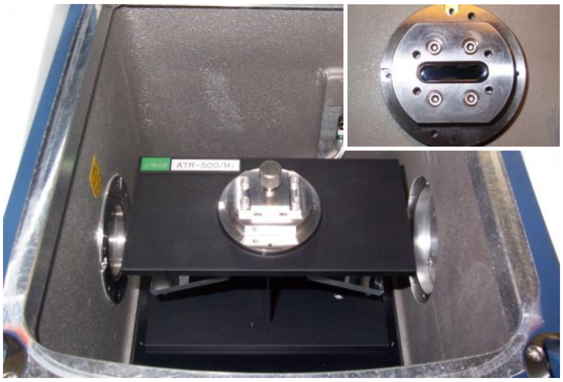


Fig. 1 ATR-500/Mi＋ATR crystal plate (Upper right: Prism and liquid cell)

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 μm 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 μm 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-6800FV, and a liquid triple-reflection ATR crystal plate. The results of these measurements are outlined below.

Measurement Conditions

System:	FT/IR-6800FV	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		

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 Fig. 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 Fig. 2. Another peak was observed near 180 cm^{-1} (yellow border in Fig. 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.

Table 1 Measurement Conditions for Mid-IR and Far-IR region

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.

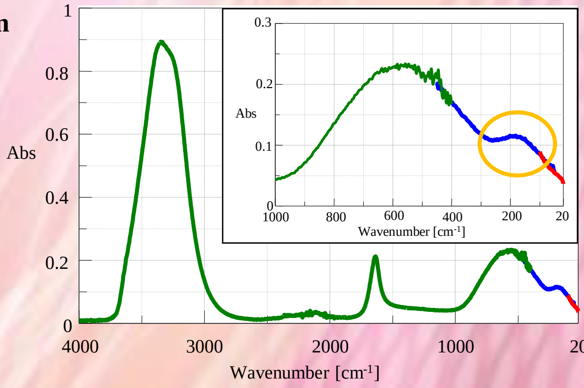


Fig. 2 ATR spectra of pure water (Upper right: Enlargement below 1000 cm^{-1})

The stack graph (Fig. 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 peaksignificantly toward the low frequency side, as compared to the Sodium solution (Na^+). In an aqueous solution containing Calcium (Ca^{2+}), 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.

Table 2 Peak Shift of Each Sample

Sample (Valence)	Ion radius [nm]	Conc. [mol/L]	Peak top [cm^{-1}]	Peak shift [cm^{-1}]
H_2O	-	-	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

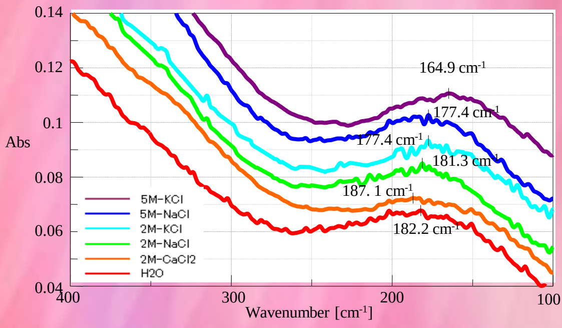


Fig. 3 ATR spectra of Each Sample

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

Simple Identification of Illegal Drug using NIR
-Identification of MDMA Tablet-

Introduction

Since light in the Near-Infrared region has the characteristic of penetrating into the substance, it is useful in the non-destructive analysis of certain area or an overall volume in average. In recent years, utilizing this characteristic, NIR spectroscopy has been widely used in the observation of biological samples and quality control/analysis of food and medical products. A sample holder for NIR diffuse reflection system is so designed for the extremely easy sample handling. In addition simple identification of illegal drugs, such as MDMA can be done by combining the system of search data library created by NIR diffuse reflection system.

Experimental

A diffuse reflection measurement accessory (VIR-NRF-N) is placed in a portable Fourier Transform Near-Infrared Spectrometer (VIR-300) and then by simply placing a tablet, such as MDMA directly on the sample holder, the measurement can be done. An InGaAs detector is used. Firstly, grouping was performed by means of Principal Components Analysis (PCA) in order to identify the MDMA tablet. Since as the result, the possible grouping was confirmed, the library was tried to be established. For establishing the data library, 40 types of tablets were used, 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 optimal value of simple identification system was examined by the investigation of algorism, calculation parameters and threshold from comparison of search results of tablets selected in random. Fig. 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 Fig. 2. In case of extremely small tablet unable to be placed on the holder, the sample was placed in a test tube like the one shown in Fig. 3, and measured.

Fig. 1 VIR-300 & Diffusive reflection accessory

Fig. 2 Measurement of tablet

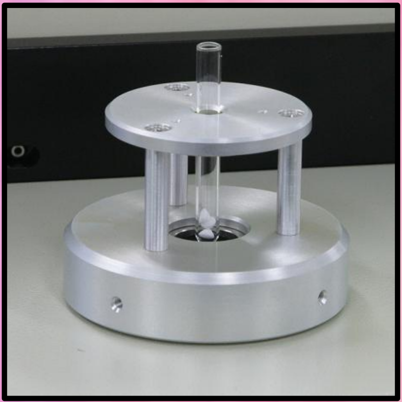


Fig. 3 Measurement of crushed sample & powder sample

<Measurement example>

Fig. 4 shows the PCA analysis results for tablet such as MDMA. Fig. 5 shows their Near-Infrared spectra. Simple identification is possible by using the region (indicated by the arrow) where the spectra shape varies depending on the type of each tablet. The NIR diffuse reflection system is a simple method by only placing the tablet on holder, and the main unit is simply the expanded system of conventional FT-IR, so that the single measurement time required is only 10 seconds. It will be more powerful as a simple identification system by enhancing the library and further increasing the number of standard samples.

Fig. 6 shows a calibration model that indicates the correlation between tablets containing MDMA and the quantitative results by their GC. With a correlation coefficient of R=0.966, it shows a sufficient value for performing simple identification. It is also possible to analyze the amount of MDMA in the tablets by linking the search results of the identification program with the calibration model.

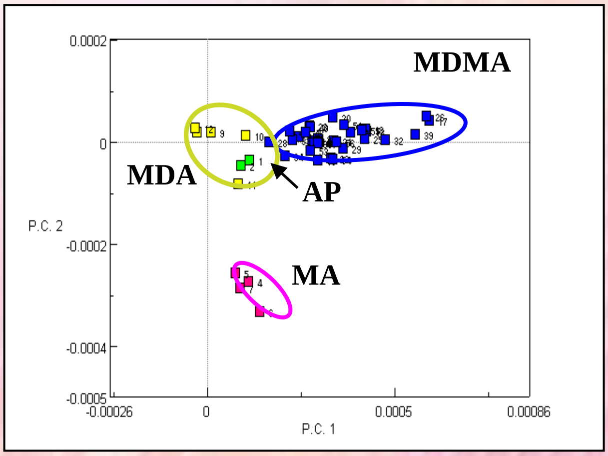


Fig. 4 PCA analysis results for tablet

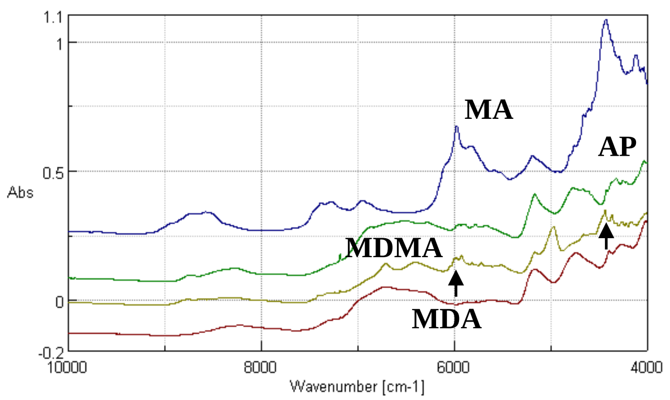
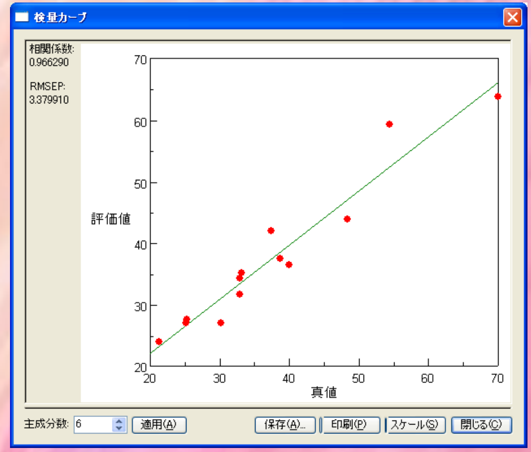


Fig. 5 Diffuse reflectance spectra of tablet


検量カーブ

相関係数: 0.966290

RMSEP: 3.379910

主成分数: 6

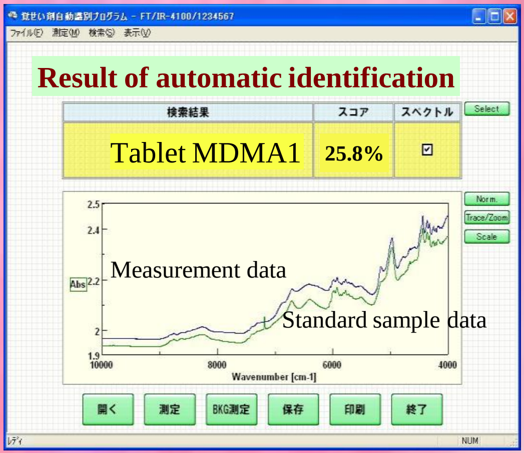
Fig. 6 Calibration curve of MDMA


臭素系難燃剤確認試験 – FT/IR-4100/1234567

Illegal drug identification

試料室にサンプルをセットし
測定ボタンを押してください。

Fig. 7 Illegal drug identification program


覚せい剤自動識別プログラム – FT/IR-4100/1234567

Result of automatic identification

検索結果	スコア	スペクトル
Tablet MDMA1	25.8%	☑

Fig. 8 Confirmation test and quantitation results

Measurement of Protein in Heavy Water (D_2O) by FT-IR

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 (D_2O). 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, CaF_2 or BaF_2 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.

Condition

Resolution: 2 cm^{-1}
Detector: TGS
Apodization: Cosine

Sample preparation

Solution: Heavy water (D_2O)
Protein concentration: 2% (w/v)
Cell window: CaF_2
Cell thickness: 0.1 mm (fixed cell)

Table 1

Material	Chemical formula	Limited to Low wavenumber (cm^{-1})	Note
Potassiume fluoride	CaF_2	1100	For trancemittance
Bariume fluoride	BaF_2	750	For trancemittance
Zinc selenide	ZnSe	625	Trancemittance / ATR
Arsenic selenide	As_2Se_3	650	Specify of poison
Germanium	Ge	830	For ATR

Note:

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 CaF_2 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 Fig. 1 - 6. Fig. 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. 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.

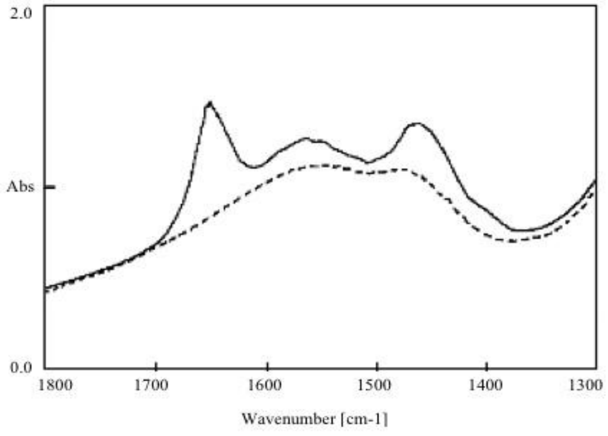


Fig. 1 Overlaid spectra of 2% myoglobin in Heavy water, and Heavy water

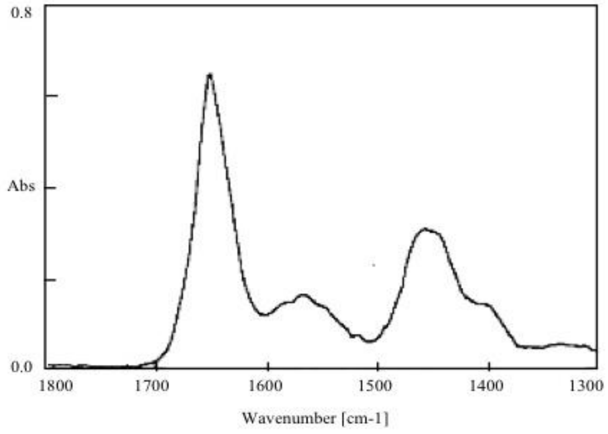


Fig. 2 Myoglobin

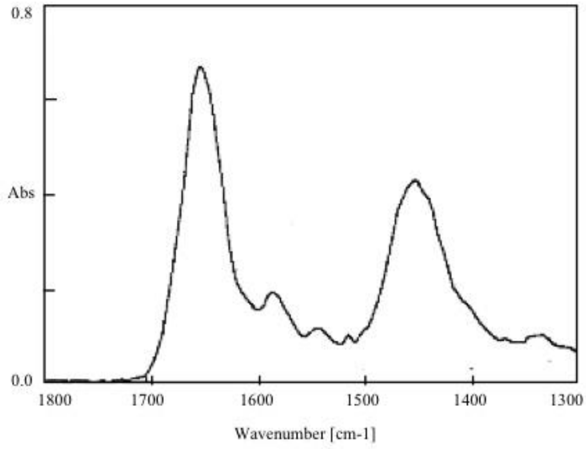


Fig. 3 Lysozyme

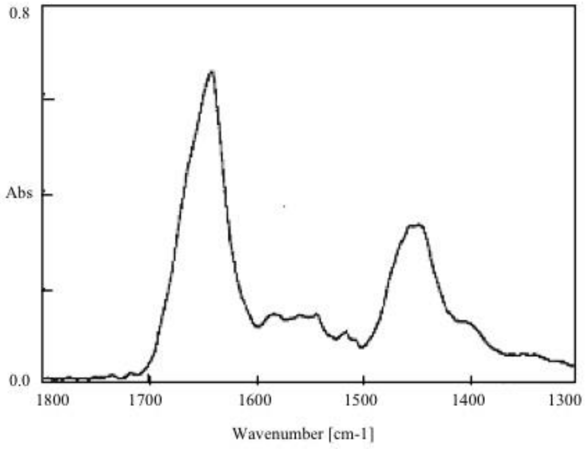


Fig. 4 Ribonuclease

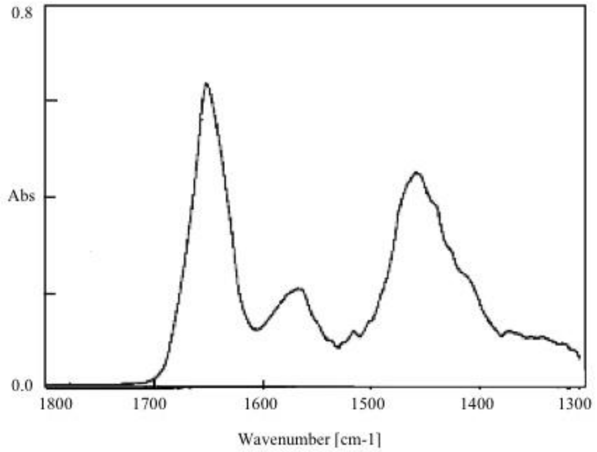


Fig. 5 Cytochrome C

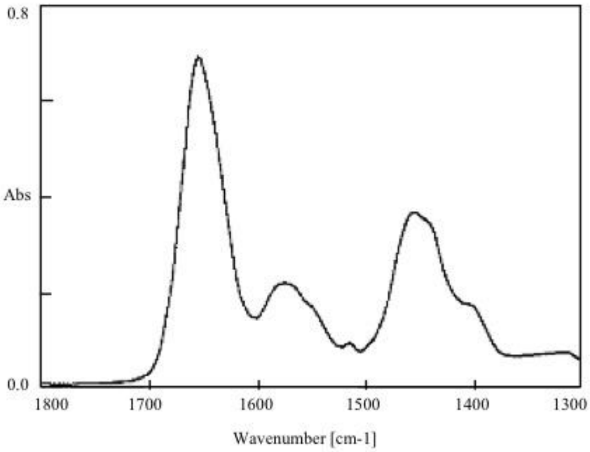


Fig. 6 Bovine serum albumin

Evaluation of Si Wafer Surface Condition using of 65º incident ATR PRO650G

Introduction

Measuring/analyzing the semiconductor surface of an Si substrate or the like is mandatory for knowing the condition or the contamination condition of thermally oxidized film that functions as insulating film. For the surface analysis, such measures as XPS (X-ray photoelectron spectroscopy, ESCA) and SIMS (secondary ion mass spectrometry) are popularly employed, and such measures give 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 nondestructive manner. For the surface analysis in IR, the ATR method is popularly employed. For the 45-degree incident ATR, which is used in general, measurement of samples of Si wafers or the like with a high refractive index was difficult, since it does not satisfy the total reflection conditions required for ATR measurement. With the single reflection 65º incident ATR we developed recently (Fig. 1), Ge 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 measuring samples with a high refractive index, such as Si (refractive index = approx. 3.4) and rubber containing carbon whose refractive index is 2.8 or higher. (See Table 1 JASCO FT/IR application data 280-AT-0003)

Fig. 1 Single Reflection 65º Incident ATR (ATR PRO650G)

Table 1 Comparison of 65-degree Incident ATR and 45º Incident (Existing Type) 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)
65º	Ge	- 700 cm^{-1}	4.0	3.6	0.48 µm
45º	Ge	- 700 cm^{-1}	4.0	2.8	0.66 µm

n_1 : Refractive index of prism

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

Features of Single Reflection 65º Incident ATR (ATR PRO650G)

The ATR PRO650G (Fig. 1) features a slip clutch to prevent damage to the sample or prism as standard equipment for a design that does not allow application of pressures exceeding a certain level during the process of bonding the sample and the prism. Furthermore, a wide space is secured around the top panel, thereby enabling measurement of the center part of the sample even for a six-inch Si wafer. In addition, since a polarizer and an analyzer can be introduced to the light path as an option, analysis of the molecular orientation condition of the sample surface can also be executed.

Measurement Conditions

System:	FT/IR-4600	Measurement Method:	ATR method (Reflection: Single)
Resolution:	4 cm^{-1}	Detector:	DLATGS
Aperture:	3.5 mm	Integration:	128 times
Accessory:	ATR PRO650G (Prism: Ge)		

Results and Discussion

As a sample, measurement was made of the Si wafer surface on which a natural oxide film was generated. For comparison purposes, the measurement was made using a 45º incident ATR and the transmission method. Fig. 2 shows the spectra obtained by overwriting the measurement results of the 45º incident ATR on it, and Fig. 3 shows the spectra obtained by standardizing and overwriting the measurement results of the transmission method. From Fig. 2, it can be seen that the spectrum of the 45º incident ATR does not satisfy the total reflection 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 65º incident ATR, since the spectrum satisfies the total reflection condition, the spectrum does not present any distortion and the base line remains flat. From Fig. 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 substances adhere to the surface starting from the peak at 3000 to 2800 cm^{-1}, which can be attributed to C-H adsorption. On the other hand, the results measured by the transmission method reveal adsorption in the vicinity of 1100 cm^{-1}, which can be attributed to the Si-O in the Si wafer substrate, but the adsorption peak at around 1235 cm^{-1}, or the peak that can be attributed to C-H adsorption, cannot be determined. More specifically, this reveals that using the 65º incident ATR enabled acquisition of information on the top surface of samples that could not be determined by the transmission method.

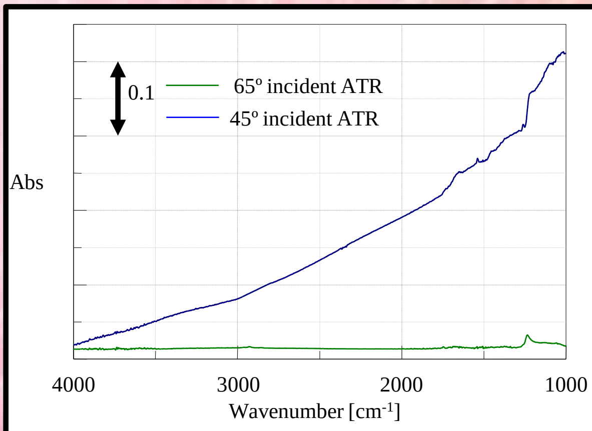


Fig. 2 Oxide Film Spectrum on Si Wafer (Offset Indication)

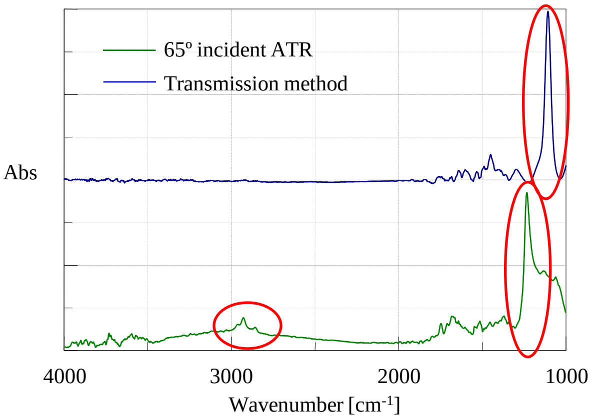


Fig. 3 Oxide Film Spectra on Si Wafer (Standardized; Offset Indication)

As stated above, using the single refraction 65º incident ATR enables evaluation of the surface condition of substrates such as Si wafers with a high refractive index in a nondestructive manner. As further development, applications for the qualitative/quantitative evaluation of the adhesion condition of organic substances on the Si wafer surface and the quantitative evaluation of oxide films by evaluating the peak height and area at around 1235 cm^{-1}, estimation of SiO and SiO_2 percentages in the oxide film utilizing the fact that the adsorption peak position is different between SiO (around 1100 cm^{-1}) and SiO_2 (around 1235 cm^{-1}) can be expected.

Gas Analysis System using Full Vacuum Type FT/IR
(Trace amount of H_2O in N_2 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 H_2O or CO_2, 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 H_2O 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:	CaF_2
Heating:	Possible, max. 100°C
Cell capacity:	Approx. 2 L
Gas in/output port:	1/4 inch VCR

Fig. 1 Full vacuum type FT-IR gas analysis system (10 meter cell)

Measurement example

The quantitation of a trace amount of water vapor (H_2O) within CO_2 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. Fig. 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 Fig. 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.

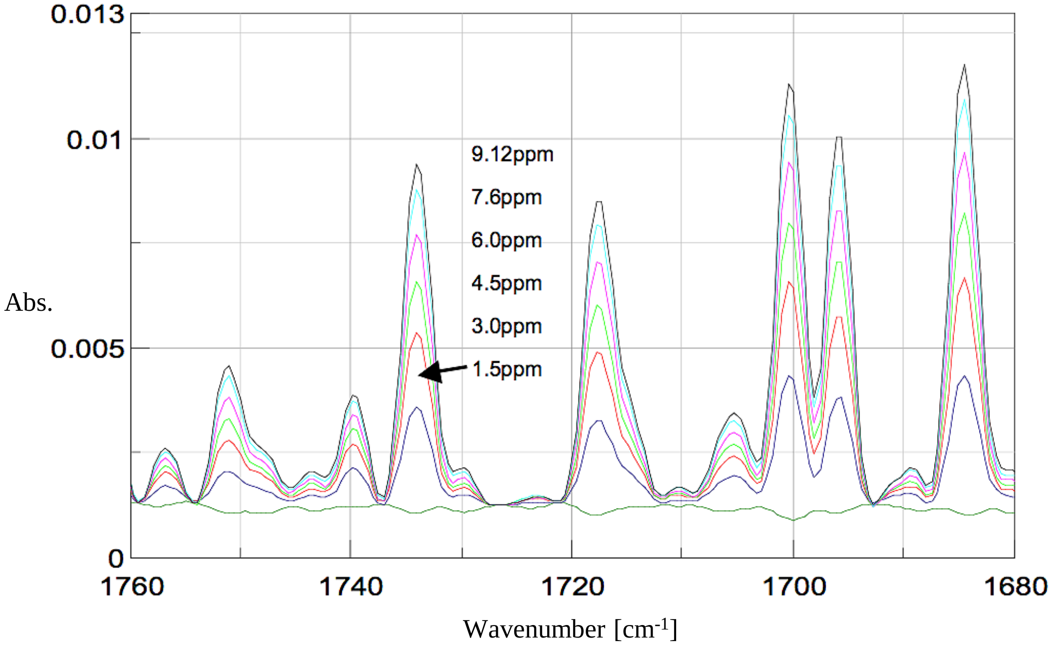


Fig. 2 Expanded region for spectra of low concentration H_2O

<Condition>

Instrument:	FT/IR-6800
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

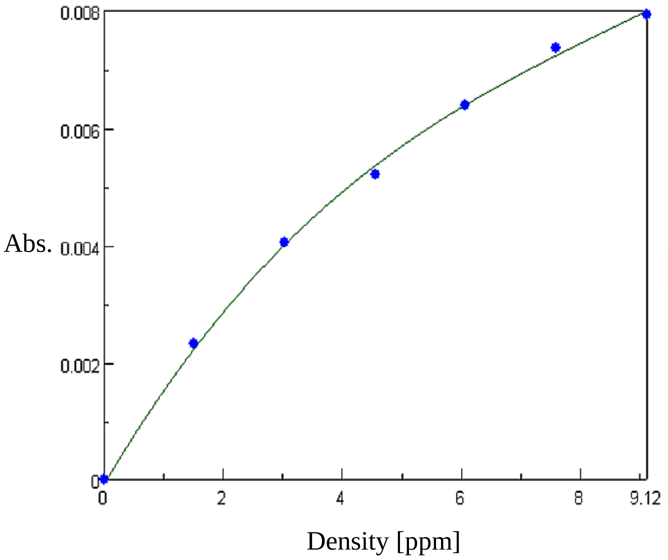


Fig. 3 H_2O calibration curve

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.

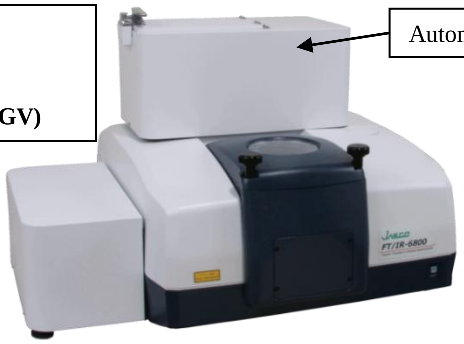
System

Fig. 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 Vis to Far-IR (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.



Automated Window Changer Unit
(EXPT-6000WIN)
or
Automated gate valve unit (EXPT-6000GV)

Automated BS Changer Unit (EXBS-6000)

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

Measurement

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

System configuration

P/N: 7085-J066A	FT/IR-6800FV FT/IR Spectrometer (full vacuum)

* FT/IR-6600FV(P/N: 7085-J062A) or FT/IR-6700FV(P/N: 7085-J064A) is also available

P/N: 7078-J001A	EXBS-6000 Automated BS Changer Unit
P/N: 7078-J003A	EXPT-6000GV Automated Gate Valve Unit

* The combination of Automated Window Changer Unit (EXPT-6000WIN, P/N: 7078-J002A) and PE window (PE-6000WIN, P/N: 6888-J711A) is also available.

P/N: 7078-J004A	EXCU-6000 Controller for EXBS/EXPT-6000
P/N: 6888-J731A	MYLBB-6000BS Beam splitter, broad band, Mylar
P/N: 6888-J712A	PETGS-6000 DLATGS(PE) detector with switching mechanism
P/N: 6909-J142A	ATR PRO ONE Single reflection ATR accessory
P/N: 6909-J342A	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.

Fig. 3 shows the spectra of calcium carbonates that have different crystal structures. As shown in Fig. 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.

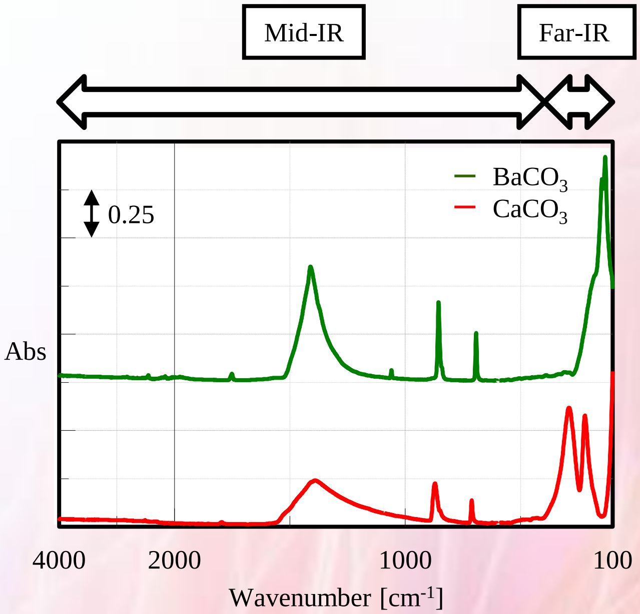


Fig. 2 Spectra of barium carbonate and calcium carbonate (X-axis: 4:1 display, Y-axis: Offset)

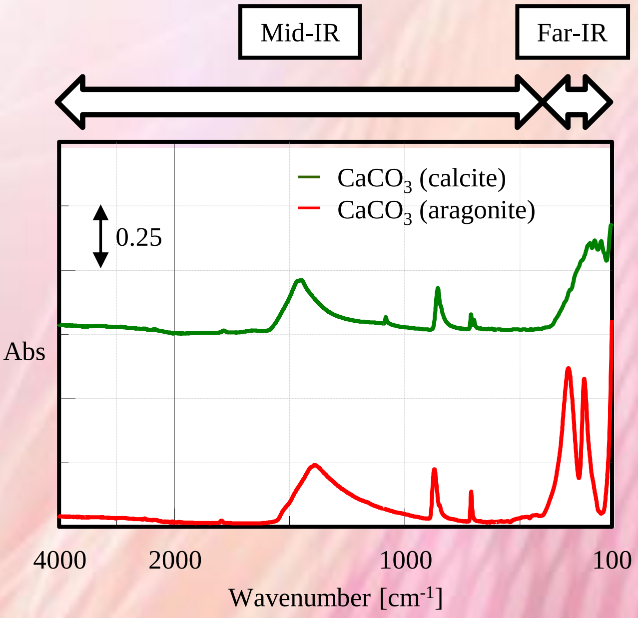


Fig. 3 Spectra of calcium carbonates that have different crystal structures (X-axis: 4:1 display, Y-axis: Offset)

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.

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 Fig. 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 H_2O and CO_2 in atmosphere.

On the other hand, PM-IRRAS is a method of finding intensity difference of s- and p-polarized lights ($DI = I_p – I_s$) 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 ($SI = I_p + I_s$) is used as reference and so there is no need to measure reference substrates. Hence, the effect due to absorption of H_2O and CO_2 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 DI signal using direct lock-in detection by adopting dual modulation spectroscopy of FT/IR interferometer and PEM. Fig. 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.

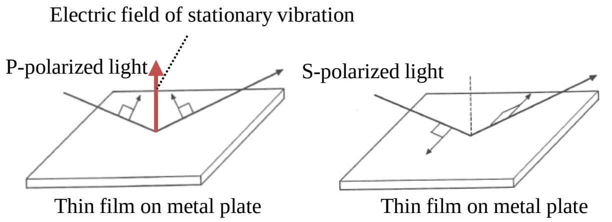


Fig. 1 Diagram of IRRAS method

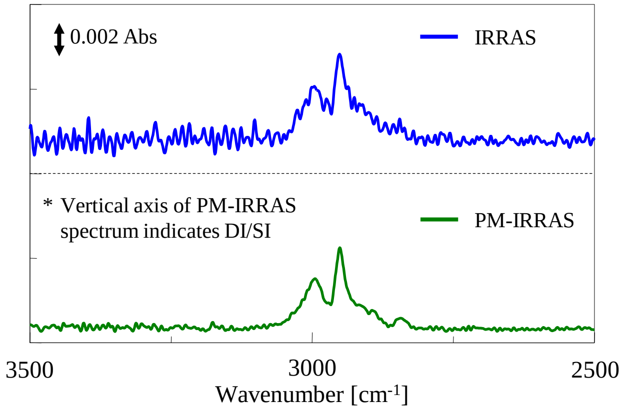


Fig. 2. Comparison between IRRAS spectrum and PM-IRRAS spectrum (normalized, offset plotting)

Instrument

The appearance of PM-IRRAS measurement system and system layout of polarization modulation unit are shown in Fig. 3. The incidence angle of polarized light of this specific system is 85º, while the optimal incidence angle in general is considered as 80 ~ 89º 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 H_2O and CO_2 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.

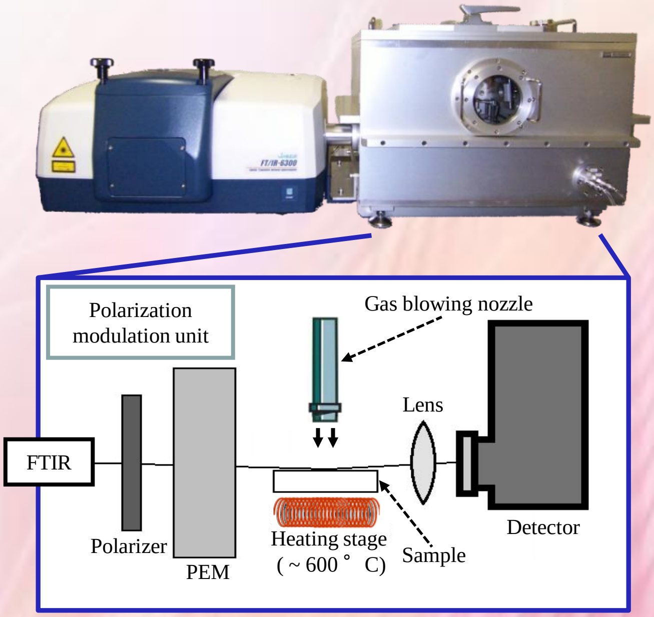
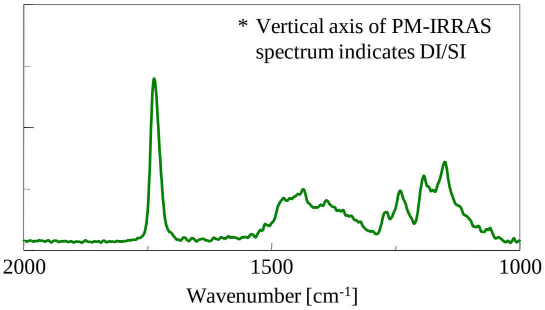


Fig. 3 Appearance of FT/IR-6300FV & Polarization modulation unit (upper)
System layout of polarization modulation unit (lower)

Measurement example

1. PMMA thin film on Al mirror

The measurement result of PMMA thin film on Al mirror is shown in Fig. 4. The obtained spectrum has good S/N without effect of H_2O.



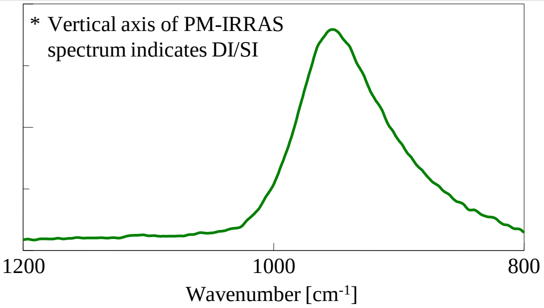
* Vertical axis of PM-IRRAS spectrum indicates DI/SI

Fig. 4 Measured spectrum of PMMA thin film

[Measurement condition]
Instrument: FT/IR-6300FV & polarization modulation unit
Detector: MCT-N detector
Accumulation: 50 times
Resolution: 4 cm^{-1}
PEM center wavenumber: 1700 cm^{-1}

2. PMMA thin film on Al mirror

Measurement result of native oxidation film on Al mirror is shown in Fig. 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.



* Vertical axis of PM-IRRAS spectrum indicates DI/SI

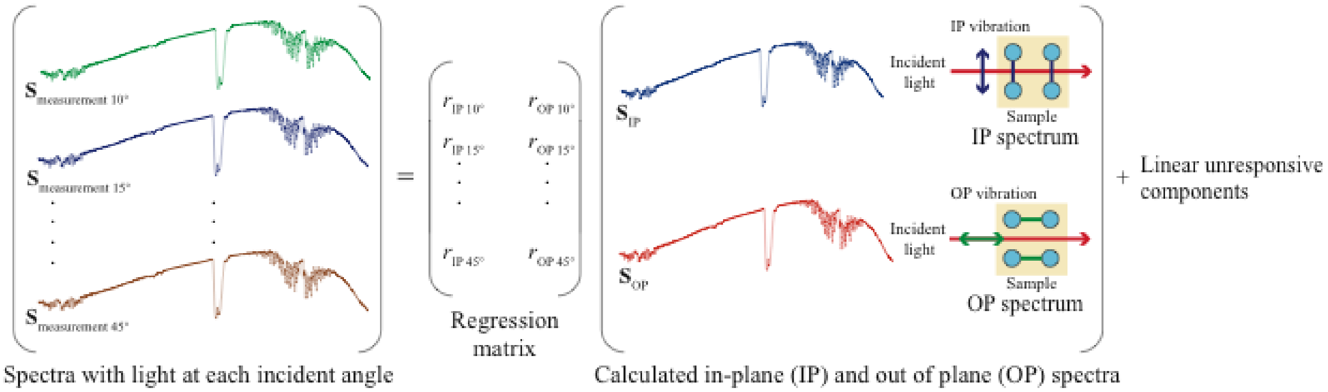
Fig. 5 Measured spectrum of native oxide film on Al mirror

[Measurement condition]
Instrument: FT/IR-6300FV + Polarization modulation unit
Detector: MCT-N detector
Accumulation: 100 times
Resolution: 4 cm^{-1}
PEM center wavenumber: 1000 cm^{-1}

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 Fig. 1, MAIRS measurement enables to acquire simultaneously spectra of vibration of molecules oriented in in-plane direction and out-of plane direction ($\mathbf{s}_{\mathrm{IP}}$, $\mathbf{s}_{\mathrm{OP}}$) 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 ($\mathbf{r}_{\mathrm{IP}}$, $\mathbf{r}_{\mathrm{OP}}$) 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 (Fig. 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.



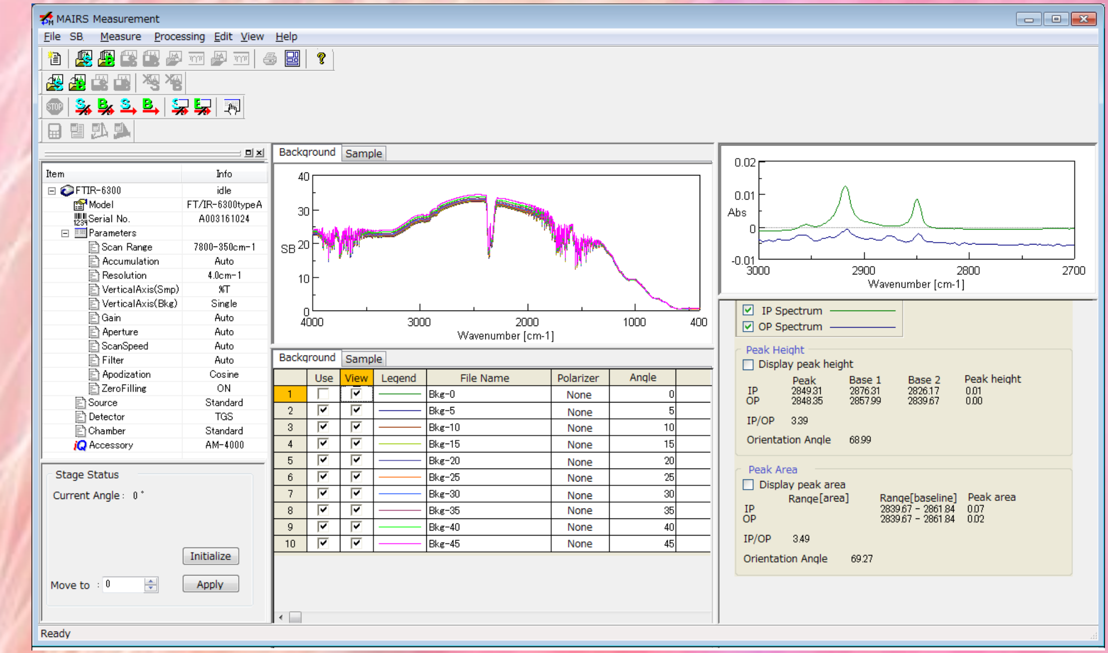
* The same measurement with Y-axis as single beam needs to be implemented for background and sample to calculate the spectra with Y-axis as absorbance.

Fig. 1 Outline of MAIRS measurement

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.

Fig. 2 Automated MAIRS measurement unit AM-4000



Item	Info
FTIR-6300	idle
Model	FT/IR-6300typeA
Serial No.	A003161024
Parameters	
Scan Range	7800-350cm-1
Accumulation	Auto
Resolution	4.0cm-1
VerticalAxis(Smp)	%T
VerticalAxis(Bkg)	Single
Gain	Auto
Aperture	Auto
ScanSpeed	Auto
Filter	Auto
Apodization	Cosine
ZeroFilling	ON
Source	Standard
Detector	TGS
Chamber	Standard
Accessory	AM-4000

Stage Status

Current Angle : 0 °

Move to : 0

	Use	View	Legend	File Name	Polarizer	Angle
1	☐	☑	—	Bkg-0	None	0
2	☑	☑	—	Bkg-5	None	5
3	☑	☑	—	Bkg-10	None	10
4	☑	☑	—	Bkg-15	None	15
5	☑	☑	—	Bkg-20	None	20
6	☑	☑	—	Bkg-25	None	25
7	☑	☑	—	Bkg-30	None	30
8	☑	☑	—	Bkg-35	None	35
9	☑	☑	—	Bkg-40	None	40
10	☑	☑	—	Bkg-45	None	45

☑ IP Spectrum —
☑ OP Spectrum —

Peak Height

☐ Display peak height

	Peak	Base 1	Base 2	Peak height
IP	2849.31	2876.31	2826.17	0.01
OP	2848.35	2857.99	2839.67	0.00

IP/OP 3.39

Orientation Angle 68.99

Peak Area

☐ Display peak area

	Range[area]	Range[baseline]	Peak area
IP		2839.67 – 2861.84	0.07
OP		2839.67 – 2861.84	0.02

IP/OP 3.49

Orientation Angle 69.27

Fig. 3 MAIRS measurement program

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.

<Measurement conditions>

Instrument:	FT/IR-6600
Measurement method:	MAIRS method
Resolution:	4 cm^{-1}
Accumulation:	128 x 4
Detector:	MCT-M
Accessory:	AM-4000 (Automated MAIRS measurement unit)
Measurement angle:	10 - 45º (7º 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 (Fig. 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.

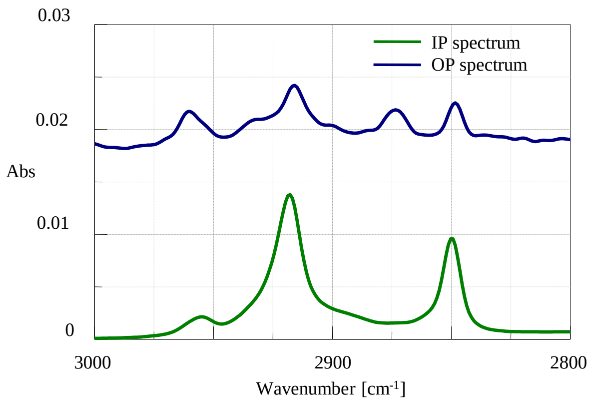


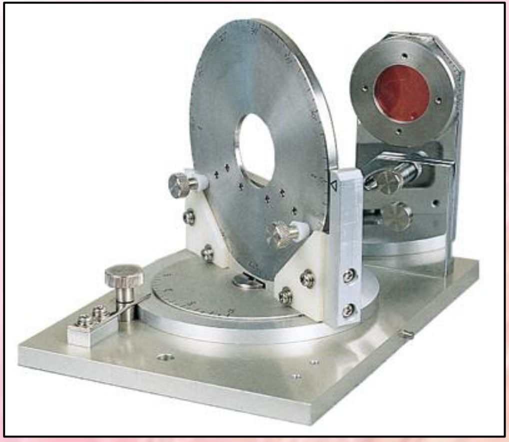
Fig. 4. Calculated IP and OP spectra

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.

Variable-angle transmittance measurement attachment with polarizer option

Introduction

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 20º.



VAT-500i

Specifications

Measurement mode:	Transmission
Sample size:	Maximum: ϕ5 inch Minimum: ϕ34 mm (or 22 x 22 mm) Maximum thickness size: 4 mm
Angle of incidence:	0 to 90º
polarizer:	Wire-grid polarizer, KRS-5

Fig. 1 shows the transmission spectrum of SiO_2 film and Si substrate under 0º incident angle condition. The vapor noise cannot be eliminated by spectral subtraction even based on Si substrate as reference.

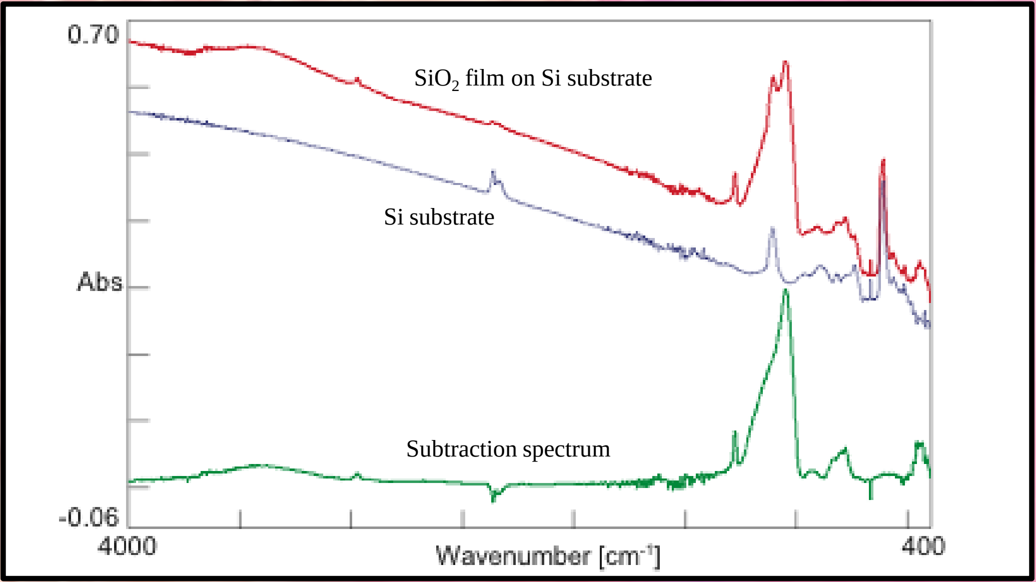


Fig. 1 Transmission spectrum of SiO_2 film under 0º incident angle condition

Fig. 2 shows the transmission spectrum of SiO_2 film under several different incident angle conditions from 0 to 20º.

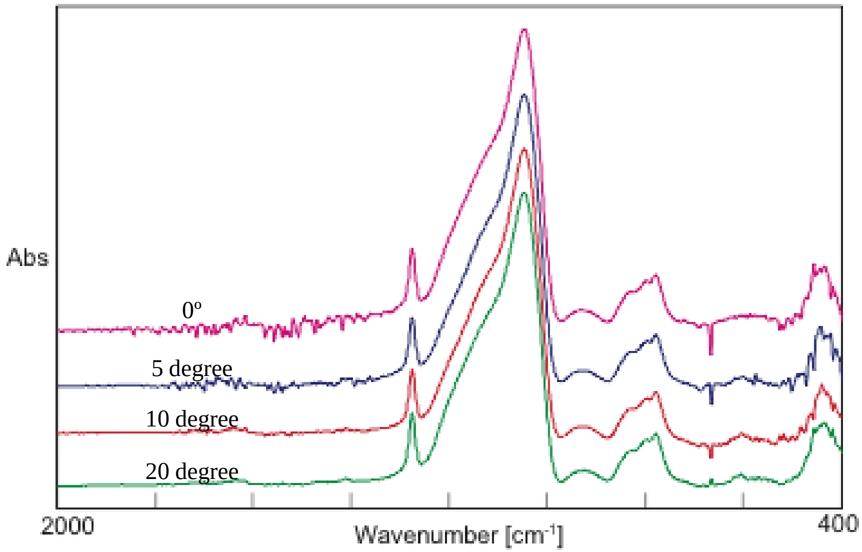


Fig. 2 Transmission spectrum of SiO_2 film under several different incident angle conditions from 0 to 20º

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 90º, it was confirmed that the main axis of this sample was oriented in 0º direction. Fig. 3 shows the absorbance spectra at 0º and 90º position, indicating that this polypropylene is isotactic polypropylene. In addition, the large difference of absorption at 1168 cm^{-1} and 998 cm^{-1} is affected due to crystallization and isotactic helix structure, which can be utilized as a degree of crystallization.

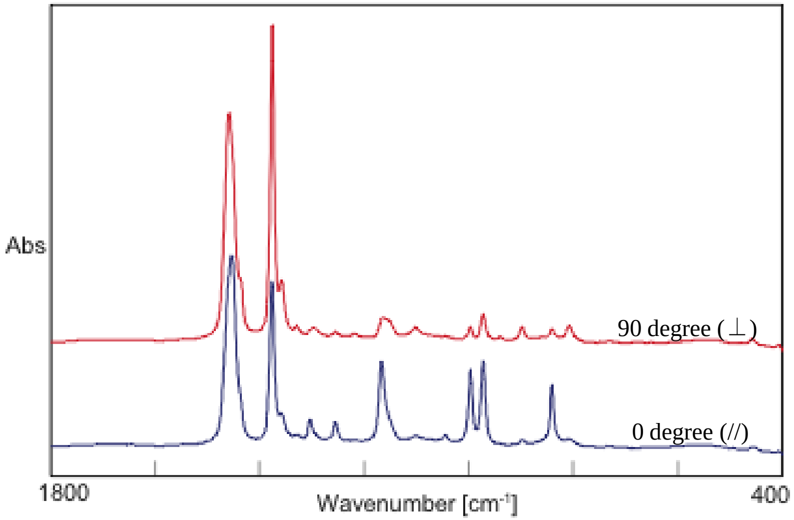


Fig. 3 Transmission spectrum of Dichroism measurement of oriented polypropylene film

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 N_2. 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.


Fig. 1 Full vacuumed FT/IR-6300FV with LPC-12M-FV gas cell

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

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


Glass type cell


Stainless type cell


Full vacuum type cell

Experimental

Glass type cell : LPC-12M-G

Fig. 2 shows measured spectra of CO, SO_2, NO_2, N_2O, CH_4. 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.

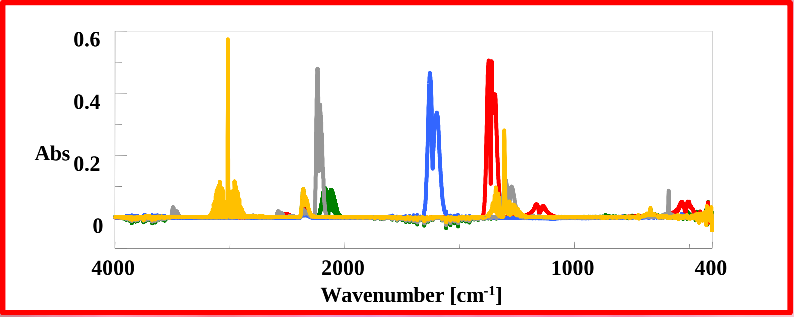


Fig. 3 shows spectrum of 530ppm CO gas with DLATGS detector.

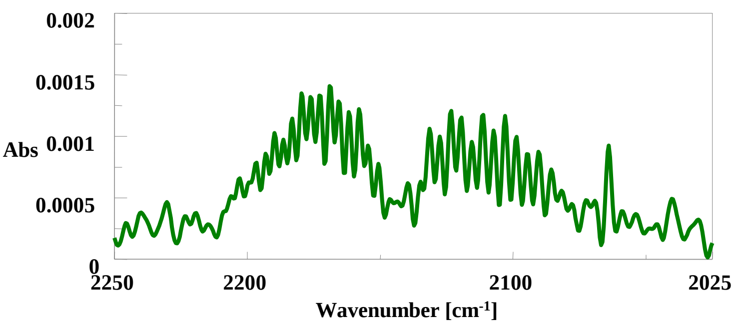


Fig. 3 IR spectrum of CO gas (530 ppb)

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

Stainless type cell : LPC-12M-S

Fig. 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.

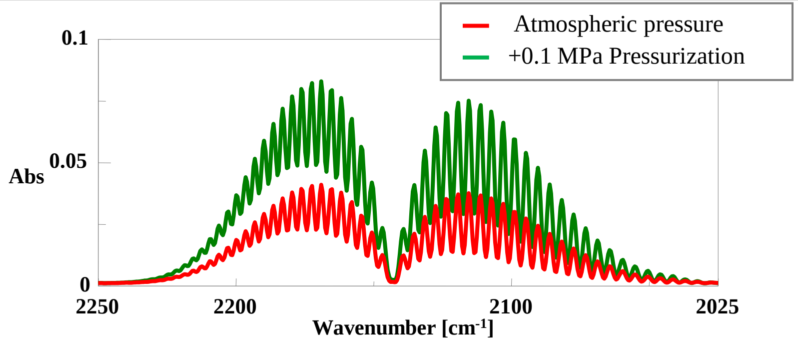


Fig. 4 IR spectrum of CO gas

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 Fig. 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.

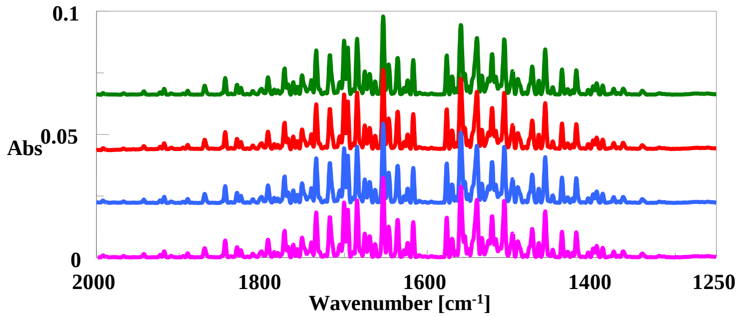


Fig. 5. IR spectrum of water vapor

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.

IR/NIR/FT-Raman Measurement using Broadband KBr Beam Splitter (B/S)

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 (**a**)
- Optical constant (**n, k**)

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

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 Fig. 1 under the conditions as shown in Table 1.

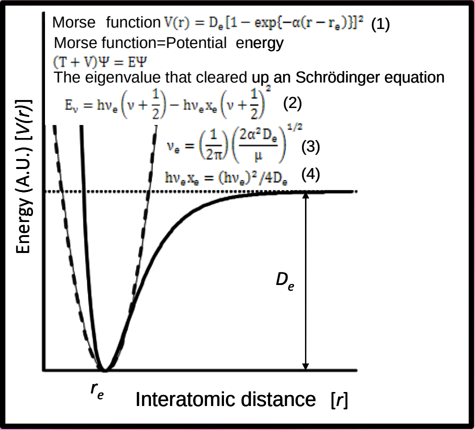
Table 1 Measuring conditions

Measurement range (cm^{-1})	Light pathlength of liquid cell	Light source*)	Detector	B/S
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

Calculation of Dissociation energy (D_e) and Absorption index (a) 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 Fig. 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 Fig. 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 (n_1, $2n_1$, $3n_1$) of chloroform and Morse function. The Absorption index (a)** is also calculated by absorbance (Abs) at each wavenumber of. The IR/NIR spectrum of chloroform and attribution of each peak are shown in Fig. 3.



Morse function $V(r) = D_e[1 - \exp\{-\alpha(r - r_e)\}]^2$ (1)

Morse function=Potential energy

$(T + V)\Psi = E\Psi$

The eigenvalue that cleared up an Schrödinger equation

$E_v = h\nu_e\left(v + \frac{1}{2}\right) - h\nu_e x_e\left(v + \frac{1}{2}\right)^2$ (2)

$\nu_e = \left(\frac{1}{2\pi}\right)\left(\frac{2\alpha^2 D_e}{\mu}\right)^{1/2}$ (3)

$h\nu_e x_e = (h\nu_e)^2/4D_e$ (4)

The dissociation energy (De) of C-H in chloroform is calculated to be 460 +/- 7 kJ/mol from equation 2, equation 4, and value of absorption wavenumber of stretching vibration of C-H (n_1, $2n_1$, $3n_1$)[2)].

The absorption index a of n_1, $2n_1$, $3n_1$ 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 $2n_1$ is used and about several 100 times if $3n_1$ 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 n_1 and n_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 n_1 of C-H is considered to be larger than the one of n_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.

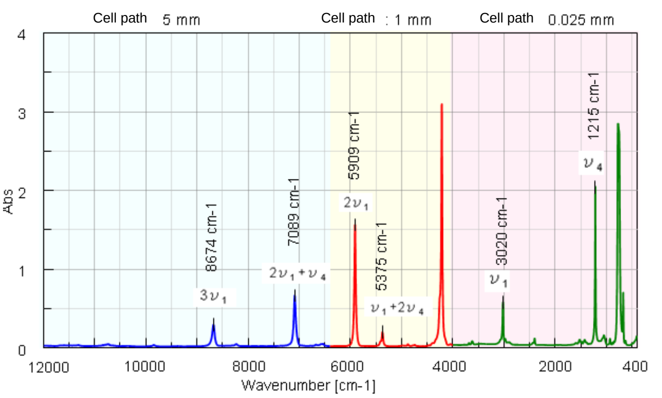


Fig. 3 IR/NIR spectrum of Chloroform

Table 2 Absorbance index and assignment 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

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

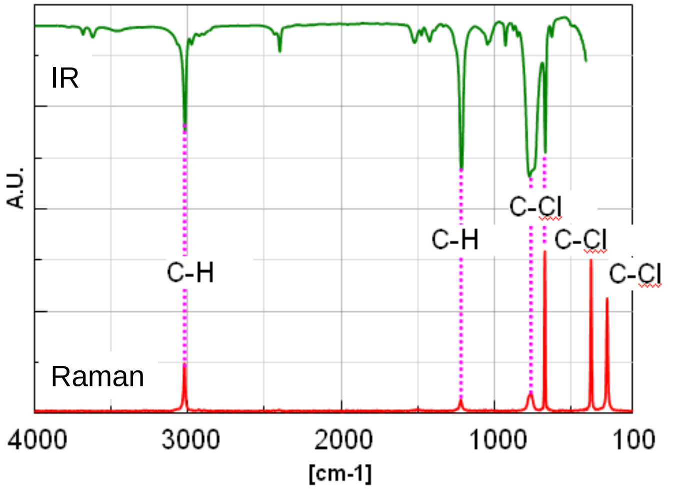


Fig. 4 IR and FT-Raman spectrum of Chloroform

(Vertical scale: A.U. due to showing %T and Int., Horizontal scale: [cm^{-1}] for wavenumber and Raman shift.)

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 N_2 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*