C103-E080

Access to your success
SHIMADZU

FTIR TALK LETTER

vol.12

September 2009

FTIR Market Amidst Rapidly Growing Economy In India --- 2

Using Infrared Detectors Pyroelectric Detectors --- 5

Foreign Matter Analysis by FTIR
Handling Spectra of Foreign Matter --- 8

Question --- 11
I attached an ATR objective mirror to my infrared microscope to analyze foreign matter using the infrared microscope ATR method, but sometimes I can't get a spectrum. Is there some special way to get round this?

FTIR Market Amidst Rapidly Growing Economy In India

Ms.Joyce (left) in charge of FTIR and Takako author Tokura (right)

Customer Support Centre, Shimadzu (Asia Pacific) Pte. Ltd. Takako Tokura

Introduction

Shimadzu (Asia Pacific) Pte. Ltd. in Singapore, it markets FTIRs and other Shimadzu analytical, scientific and testing instruments in 13 countries from the Philippines to the east to Pakistan to the west. Many countries in South Asia and S.E. Asia are hot and humid. Typically, the relative humidity exceeds 90% most mornings and remains at about 80% throughout the day. This climate presents a severe environment for analytical instruments over the entire year.

You may be aware that the beam splitter component of an FTIR interferometer is made of potassium bromide (KBr). This material is extremely hygroscopic. When potassium bromide absorbs moisture, it becomes cloudy. This causes its infrared throughput to decrease. If optimal data quality to be procured, long-term protection of the beam splitter is critical.

Shimadzu FTIRs offer not only high performance and ease of operation, but both the IRPrestige-21 and IRAffinity-1 models are equipped with a dehumidifier as standard. to It offers stability that greatly pleases our customers.

How do other companies that do not employ dehumidifier deal with this issue? Well, some take extreme precautions by covering the instrument with an acrylic case, putting silica gel in the case, and keeping the instrument switch on 24 hours a day!

India is experiencing rapid economic growth. It is expected its investment in analytical instruments, including FTIR, will follow the growth. In this issue, I will introduce the FTIR market and its applications in India.

Indian FTIR Market

Since Shimadzu entered an distributorship agreement with Toshvin Analytical in India in 1970, Toshvin Analytical has handled all sales, installation, repair and maintenance services of spectrophotometers (FTIR, UV-VIS spectrophotometers, atomic absorption spectrophotometers), thermal analyzers, gas chromatographs, and gas chromatograph - mass spectrometers. The Toshvin Analytical headquarters is located in India's largest city, Mumbai, and it has branches in 12 other major cities. Approximately 100 sales and service staff are employed in these offices. In recent years, application support and method development have become as very important in India as other countries. Consequently, we established an analysis support system in India by opening Shimadzu customer support centres fully equipped with analytical instruments in Mumbai in April 2006 and in Delhi in February 2008. Contributions by Toshvin Analytical and the customer support centres more than doubled our sales of FTIR instruments over the past five years. This growth significantly exceeds Indian economic growth. The scale of the FTIR market in India in 2008 was approximately 350 instruments. General-purpose and mid-class instruments represent the largest share of the FTIR market requirements and we have captured about 40% share of the Indian market. The Shimadzu brand has become firmly established for FTIR instruments. Fig. 1 shows the market sectors for Shimadzu FTIRs last year. Pharmaceutical-related industries represent the largest market sector, followed by universities and education, chemicals, and research institutes. With over 50% of the market, the pharmaceutical-related industries represent an extremely important FTIR market.

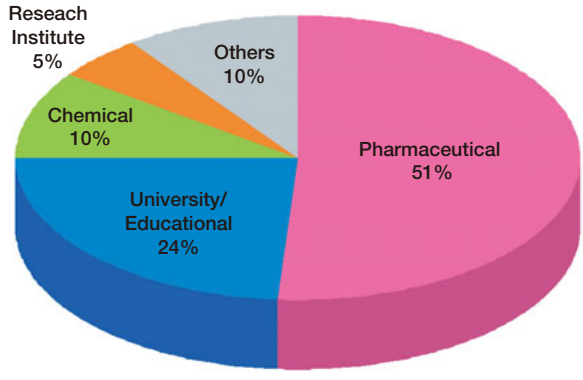


Fig. 1 FTIR Market Sectors in India

Indian Pharmaceutical Industry

Over 20,000 pharmaceutical-related companies exist in India. Most are involved with generic pharmaceuticals but, due to the low product prices, they represent less than one percent of the world market in terms of monetary value. However, these companies are said to have grown at an annual average rate of more than 11% over the past five years.
The export of active pharmaceutical ingredients (API) and pharmaceuticals started in the 1970s and has increased dramatically since 2000. Fig. 2 shows the production values 1) of the Indian pharmaceutical industry since 2004 both for domestic consumption and for export. Domestic consumption was largest until 2005 but has been overtaken by the exports since 2006. The growth of the exports has continued to accelerate. Many companies have been established in India to supply low price drugs to those who cannot afford expensive medications. Since 2005, pharmaceutical patents have become process patents instead of product patents, allowing the Indian pharmaceutical industry to grow by making cheap copies of new US and European drugs. Currently India boasts many influential generic drug companies, making it one of the world's leading drug-manufacturing nations that export pharmaceuticals to Japan and other countries. India boasts the highest number of pharmaceutical factories approved by the U.S. Food and Drug Administration after the United States. These factories produce and supply high-quality pharmaceuticals. The technical level of the technical staff in these factories is high, and India is said to produce more than five times as many university graduates in pharmacy, science, and technology as the United States (with less than four times the population).
Many of the tasks conducted in these pharmaceutical companies are performed according to detailed manuals. One method used for quality control is FTIR. Many FTIR instruments are employed for the analysis of contaminant studies and for the validation testing of APIs and pharmaceuticals manufactured for domestic consumption and export. These FTIRs are mainly used to measure the IR spectrum of the products to check that they contain no impurity and to ensure that they meet the appropriate international standards. As pharmaceutical companies are required to perform testing in accordance with the Pharmacopoeia, many samples have been measured using a basic transmission method, such as the KBr pellet method or liquid film method. However, recognition by the Pharmacopoeia of the diffuse reflectance spectroscopy (DRS) and attenuated total reflection (ATR) methods means that many quicker and easier methods are now available.
In addition, FTIR microscopes measurements are also becoming more commonly used for R&D and quality control.

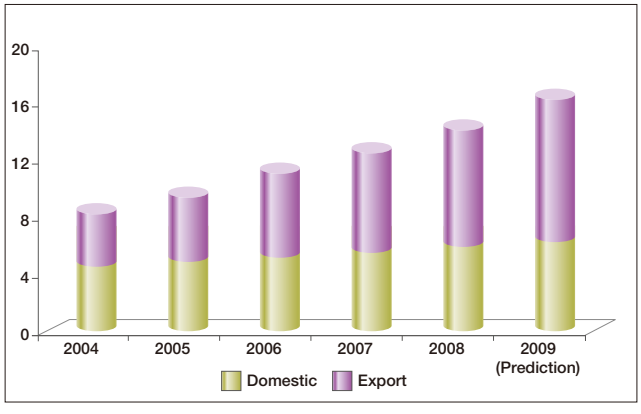


Fig. 2 Market Size of the Indian Pharmaceutical Industry (Units: billion US$)

Indian Infrared Microscope Market

In India, FTIR microscopes methods are used in the pharmaceutical, plastics, automobile, and electronics industries, as well as in universities and other researchorganizations. The packaging industry uses them to analyze multilayer films and contaminants in/on films. The automobile and electronics industries use FTIR microscope for the analysis of trace organic foreign matter for failure analysis. The pharmaceutical industry uses them for drug analyses and increasingly for R&D applications, such as the verification of APIs and polymorphism. Fig. 3 shows the IR spectra of an API measured using the FTIR microscope ATR method. It shows measurements of areas with different form of polymorphism within the same drug (same chemical formula but a different crystalline structure). An FTIR microscope allows measurements of minute areas and can obtain IR spectra of the target without the influence of other components or placebos.

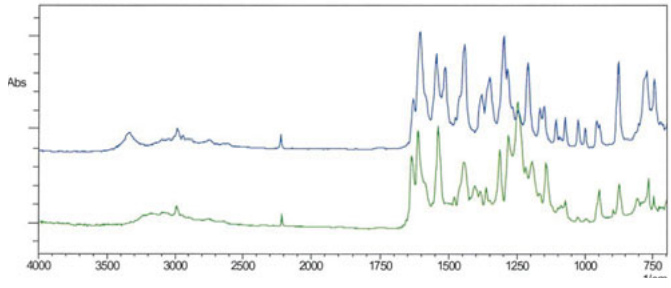


Fig. 3 IR Spectra of Areas of Different Crystal Polymorphism in an API Measured Using the Microscopic FTIR ATR Method (Ge Prism)

Forensic science laboratories are located in each state in indea. They use FTIR microscopes to analyze drugs and counterfeit notes. The author presented a paper on the applications of FTIR microscopes in forensic science at the All India Forensic Science Conference 2009 in Ahmedabad in the state of Gujarat. As FTIR microscopes are not available in some states, the author was asked many questions on forensic investigations and the analysis of criminal evidences. Many presentations were made on each of the three days of the conference. The conference attracted many researchers and scientists involved with forensic science from India and other countries including the USA, Germany, UK, and France who gave keynote lectures and technical presentations. The presentations covered diverse areas, from criminal investigation methods and analysis, methods to investigate dead bodies, and technologies to pursue fugitives. Over 500 people listened to the presentations, indicating the high level of interest in forensic science and criminal investigations that is partly due to the recent terrorists' bombings in a hotels in Mumbai.

All India Forensic Science Conference 2009

India into the Future

The use of FTIR in pharmaceutical-related companies, universities, and government organizations has progressed significantly over the past few years. The demand for sophisticated FTIR has recently increased for research applications in the fields of the life sciences, biotechnology, nanotechnology and PV (Photovoltaics).
Although the Indian pharmaceutical industry has been hit by the recession since last year and many companies have frozen their budgets,. But some companies have established new bioscience buildings and expanded their production facilities. I have visited several pharmaceutical companies lately and they are predicting growth of approximately 7% to 10% this financial year. None of them expected negative growth.In fact, Indians continue to maintain a forward-looking attitude full of optimism. These Indian companies are attracting heightened interest from Japanese companies that are experiencing severe cost cutting book at home. A major Japanese pharmaceutical company caused a stir in 2008 when it took over India's largest pharmaceutical company. India may provide the driving force to change the world economy in the future and will become increasingly. Off course, we, Shimadzu, will continue to be part of India's dynamic growth.

Source: 1) CRIS INFAC & Pharmecil

Using Infrared Detectors —Pyroelectric Detectors—

Spectroscopy Business Unit, Analytical & Measuring Instruments Division Hiroshi Ohta

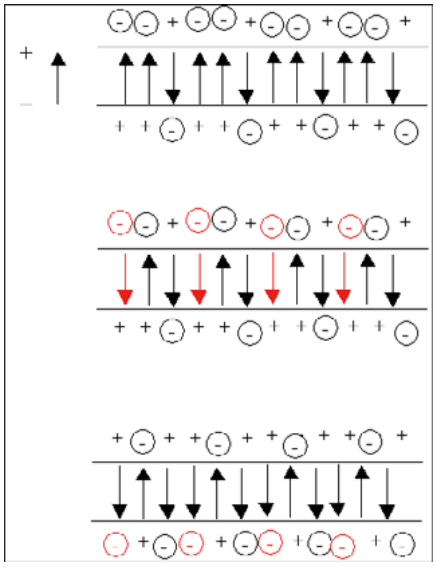
Various infrared detectors can be used with an infrared spectrophotometer to suit the application. The standard type of detector supplied with an instrument is normally a TGS (Tri-Glycine-Sulfate) detector.
Infrared detectors can be categorized into thermal detectors and quantum detectors. TGS detectors are categorized as thermal detectors. A thermal detector converts the infrared energy to heat, which is then converted to electrical signals by the pyroelectric effect or thermoelectromotive force (Seebeck effect). They are used as general-purpose detectors as they feature a wide wavelength range and can be used at room temperature.
However, because thermal detectors have lesst sensitivity and responsivity to detect extremely weak infrared radiation, quantum detectors are used for such applications.
A quantum detector is a semiconductor detector using an element that changes resistance due to the photoconductive effect or photovoltaic effect when infrared radiation is incident on it. It offers excellent sensitivity and responsivity and more than 100 times the detection capacity of a thermal detector. It is used for high-sensitivity measurements, such as infrared microscopy or gas spectrum measurements using a long-light-path gas cell. However, it must be handled with care due to its wavelength characteristics and because it requires cooling by liquid nitrogen.

Infrared sensor	**Quantum type**	**Photodiode, MCT, etc.** Exploits the physical properties of electrons and positive holes formed due to excitation by infrared photons. Sensitivity is generally wavelength-dependent within a limited wavelength range. Rapid response rate. ● Photovoltaic element ····· incident light → photon absorbed at pn junction → electrons and positive holes formed → potential at junction → photovoltaic current (photocurrent) ● Photoconductive element ··· incident light → change in electrical conductivity
	Thermal type	**Pyroelectric sensor, thermopile, thermistor, etc.** Converts light to heat and exploits an induced physical phenomena. In principle, not (or little) dependent on wavelength. Slow response rate. ● Pyroelectric sensor ·····Pyroelectric effect: Exploits the temperature dependence of spontaneous polarization. ● Thermopile, thermocouple···Thermoelectromotive force (Seebeck effect): Electromotive force generated according to the temperature of the junction between different metals. ● Thermistor, bolometer ·····Thermal characteristics of a resistance ● Golay cell ·····Expansion of a sealed gas

Table 1 Types and Characteristics of Infrared Sensors

The TGS detector is a thermal-type detector that exploits the pyroelectric effect. It offers excellent sensitivity and responsivity for a thermal detector. The TGS detector is widely used as a general-purpose detector for Fourier transform infrared spectrophotometers that use frequency modulation by an interferometer.

The pyroelectric effect is the phenomenon that the polarization (surface charge) of a dielectric changes due to variations in temperature. Infrared light shining on a pyroelectric material causes changes in the surface temperature and the resulting charge at the surface generates a voltage. (See Fig. 1.)



Polarization state at temperature T1
Charge appearing at the crystal surface draws a floating electric charge, resulting in an overall neutral state.

State after instantaneous change to temperature T2
Changes occur in the crystal polarization state (red arrows), resulting in an excess or surplus of electrons. (The red electrons in the diagram indicate a surplus.)

When the upper and lower surfaces are shorted in the situation above, the charge moves, resulting in a current flow that reverts the entire system to an overall neutral state.
This current is called the "pyroelectric current."

Fig. 1 Schematic Diagram of the Pyroelectric Effect

A lithium tantalite ($LiTaO^3$) crystal or TGS-series crystal is normally used in the pyroelectric element.
A TGS detector offers higher sensitivity than a $LiTaO^3$ detector but has a lower Curie temperature and is deliquescent, so that a window must be provided to protect it from external humidity. This window is made of a material that transmits infrared, such as potassium bromide (KBr), KRS-5, or cesium iodide (CsI), according to the measured wavelength range. In addition to the basic TGS crystal, other TGS-series crystals have been developed with improved properties that make them easier to handle. For example, if TGS exceeds its Curie temperature, it loses its original properties unless re-polarized. LATGS was developed to prevent this. Replacing the hydrogen in the crystal with deuterium is known to raise the Curie temperature, and DTGS and DLATGS crystals exploit this phenomenon.

Features of TGS Detectors and Precautions During Use

The features of TGS detectors in comparison with other detectors and the precautions required when using a TGS detector are outlined below.

Feature 1: Good linearity over wide radiation intensity range

The extremely sensitive MCT detector offers high sensitivity for faint infrared radiation. However, when the incident radiation intensity exceeds a certain limit, the output signals become saturated and the linear relationship between the radiation intensity and output signal intensity is lost.
Conversely, a DLATGS detector offers excellent linearity across an extensive radiation intensity range from almost 100% transmittance to less than 1% transmittance, as indicated by a spectrophotometer. It achieves good transmittance and reflectance measured values for normal sample measurements.

Feature 2: Only fluctuations in incident radiation intensity are output as signals.

As a TGS detector exploits the pyroelectric characteristics, signals are output with respect to fluctuations in the infrared radiation intensity incident on the element. The output is not significantly affected by the background radiation, which is not modulated by the interferometer.
Conversely, a quantum detector, such as an MCT detector, generates signals in response to the entire infrared radiation incident on the detector and is therefore significantly affected by changes in the background radiation. Special attention must be paid to saturation of the output signals when measuring a high-temperature sample.

Feature 3: Flat spectral sensitivity characteristics

As a TGS detector maintains constant sensitivity over a wide wavelength range from the mid-infrared to the far infrared, it permits spectral measurements across a wide wavelength range.
Conversely, an MCT detector shifts the spectral sensitivity characteristics to the shorter wavelength side to enhance the sensitivity. Consequently, it is sometimes unable to measure spectra in the fingerprint region or far-infrared region where characteristic peaks of organic compounds occur.

Feature 4: Room-temperature operation

As a TGS detector uses the pyroelectric effect, signals are output only with respect to fluctuations in the infrared radiation intensity, and adequate sensitivity can be obtained when the element operates at room temperature.
Conversely, a quantum detector, such as an MCT detector, generates signals in response to the entire infrared radiation incident on the detector and therefore the temperature of the element itself must be lowered or the output signals will be drowned out by noise. Low cost liquid nitrogen is typically used to chill the element to low temperatures.

Precaution 1: Slow response

As the thermal element in a TGS detector converts the incident infrared light into heat and then converted to electrical signals, the response rate is generally slow and this type of detector is unsuited to high-speed measurements.
Because the modulation frequency increases as the frequency increases in a Fourier transform infrared spectrophotometer using an interferometer, increasing the mirror speed results in a pronounced reduction in sensitivity at higher frequencies.
As the sensitivity is inversely proportional to the mirror speed, the TGS detector is not suited to the analysis of samples with a spectrum that changes in a short time.
Generally, a Fourier transform infrared spectrophotometer

measures a sample spectrum based on up to several dozen calculations. If the sample spectrum changes during this time, accurate transmittance values cannot be obtained and the displayed spectrum will indicate average values of the infrared intensity during the measurements.
On the other hand, a quantum detector such as an MCT detector offers a flat frequency response over a wide frequency band. When measuring an infrared spectrum that fluctuates rapidly, the mirror speed can be increased to reduce the number of calculations and accurately obtain the target spectrum.

Precaution 2: Inadequate sensitivity for measuring faint light

A TGS detector offers excellent linearity across an extensive radiation intensity range but lacks adequate sensitivity with faint light intensities, such as infrared microscope measurements or measuring the infrared spectrum using a long-light-path gas cell. An MCT detector is used for these applications.

Precaution 3: Noise due to sound and vibrations

A TGS detector exploits the pyroelectric effect. As the pyroelectric material is also a piezoelectric material, movement of the element itself due to vibrations or vibrations of the gas around the element due to external sound can produce signals that are superimposed on the original signals as noise.
Consequently, a vibration-proof mechanism is built into the unit and covers keep external sound out of the sample chamber to prevent noise. Care must be taken not to apply vibrations to the instrument or submit it to external sound during measurements.

Terminology

Curie Temperature

The transition temperature at which a ferromagnetic substance becomes paramagnetic or a ferroelectric substance becomes paraelectric. A ferroelectric (piezoelectric) substance loses its spontaneous polarization and piezoelectric characteristics at this temperature (electric dipole moment and spontaneous polarization disappear).

DLATGS Detector

A TGS (Tri-Glycine-Sulfate) element offers extremely high sensitivity for a pyroelectric detector but it suffers several disadvantages. Its Curie temperature is rather low at only 49 °C, making it extremely susceptible to sensitivity fluctuations due to temperature increases or fluctuations, even near room temperature. Once the Curie temperature is exceeded, it must be re-polarized to recover its original properties.
To improve these issues, it is possible to use LATGS that has the glycine in the TGS partially replaced by L-α-alanine, or DLATGS that additionally has the hydrogen in the glycine and alanine replaced by deuterium. These increase the Curie temperature to around 60 °C and eliminate the need for re-polarization. (See Table 2.)

Sample Name	Properties
TGS	Curie temperature (Tc) 49 °C Temperature fluctuations affect sensitivity, even near room temperature. Polarization easily disrupted. Re-polarization required after the Curie temperature is exceeded.
DTGS	Replacing TGS hydrogen with deuterium increases Curie temperature (Tc) to approx. 60 °C. Temperature fluctuations have little effect on sensitivity near room temperature. Re-polarization required after the Curie temperature is exceeded.
LATGS	TGS is doped with L-α-alanine to create internal bias field. No re-polarization required after the Curie temperature is exceeded. Curie temperature (Tc) 49 °C Temperature fluctuations affect sensitivity, even near room temperature.
DLATGS	Replacing TGS hydrogen with deuterium increases Curie temperature (Tc) to approx. 60 °C. Doping with L-α-alanine creates internal bias field. Temperature fluctuations have little effect on sensitivity near room temperature. No re-polarization required after the Curie temperature is exceeded.
$LiTaO_3$	Curie temperature (Tc) 660 °C Slightly higher dielectric constant than TGS results in slightly larger tanδ (that causes noise), resulting in inferior properties to TGS when used in a detector element.
PZT	Curie temperature (Tc) 200 °C Higher dielectric constant and tanδ than TGS results in inferior properties to TGS detectors.

Table 2 Pyroelectric Materials and Their Properties

References

1. Shimadzu Review Vol. 51 (3.4) Development of a DLATGS Pyroelectric-Type Infrared Detector Module. J. Kita, H. Kishihara, J. Kobayashi (Central Research Laboratory); pp 205 – 210 (1995.2)
2. DLATGS Detector In-House Material, Shimadzu Corporation

Foreign Matter Analysis by FTIR

Handling Spectra of Foreign Matter

Kyoto Applications Development Center, Analytical Applications Department, Analytical & Measuring Instruments Division
Tsuyoshi Tsuchibuchi

FTIR is convenient and effective for the analysis of foreign matter and other defect analysis and is widely used in many fields of application. FTIR encompasses many measurement methods and accessories, including infrared microscopy and single-reflection ATR. The selection of the appropriate measurement method and accessory for the aim and target of the analysis is extremely important to obtain a satisfactory spectrum. Therefore, FTIR TALK LETTER previously introduced information on accessories for infrared microscopy (Vol. 3 and 4) and measurement techniques (Vol. 5 and 6).
However, details about the information contained in the measured spectra and how to use it have not yet been presented. This article, "Foreign Matter Analysis by FTIR —Handling Spectra of Foreign Matter—", introduces the basics of reading the analysis results for foreign matter.

1. The Effects of Sampling

In many cases, foreign matter analysis by FTIR is conducted on discovered foreign matter after performing sampling. If only the foreign matter can be extracted during sampling, the subsequent analysis yields information (spectra) on the foreign matter only. However, if other substances are sampled together with the foreign matter, the other substances will have an effect on the analysis results. For example, when foreign matter is extracted from a powder or liquid, powder or liquid can adhere to the surface of the foreign matter or seep inside it, and any effects they cause must be identified.
The upper spectrum in Fig. 1 is the result of analyzing fibrous foreign matter discovered in food by single-reflection ATR (diamond prism). These results indicate that the major component of the fibrous foreign matter is cellulose based, but peaks unrelated to cellulose are apparent, such as near 1740 cm^{-1} .
The middle spectrum in Fig. 1 is the analysis results on the food in which the foreign matter was discovered, using the same analysis method. These measured results are the spectrum of a fatty acid ester (fat or oil), and this spectrum partially matches the spectrum for the foreign matter above.
The lower spectrum in Fig. 1 is the differential spectrum of the two above (fibrous foreign matter - fat/oil). Eliminating the fat or oil reveals the spectrum of cellulose.
As in this case, the analysis of sampled foreign matter can be affected by where it was discovered. In addition, as sampling can be conducted using adhesive tape, a paper or other filter, or by drying, it is possible for the adhesive or some of the filter to adhere to the foreign matter. These effects must be identified and eliminated before proceeding to the subsequent qualitative or analysis stage.

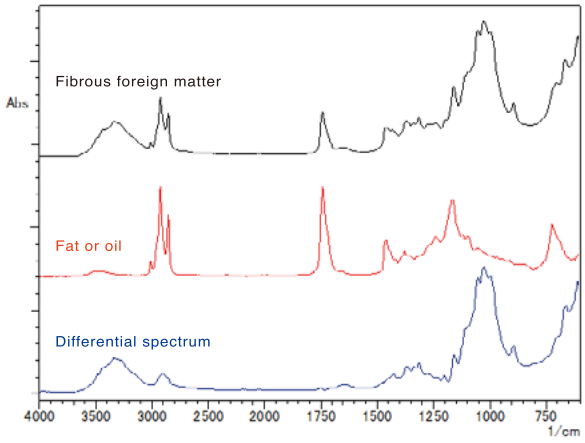


Fig. 1 Measurement Results on Fibrous Foreign Matter in Food

Upper spectrum: Fibrous foreign matter;
Middle spectrum: Fat or oil;
Lower spectrum: Differential spectrum

2. Checking Reproducibility

Multiple analyses are performed when repeated samplings are conducted for multiple foreign matter items or when the foreign matter sample is large enough to change the measurement position. Even if differences exist in the peak intensities or baseline in the measured results, the substances are considered to be the same (or uniform) if the shapes of the spectra match. It is possible to proceed directly to the subsequent qualitative or analysis stage.
However, differences in the shapes of the measured spectra indicate possible errors in the sample collection or other measurement operations, different samples, or non-uniform contaminants. The former case can be remedied by repeating the sampling and other operations. If multiple repetitions lead to identical results, the cause is likely to be one of the latter factors.
If the measured results differ according to the measurement position, the foreign matter is deemed to be non-uniform or not a single item. If the foreign matter comprises individual, separate substances, the measured spectra are also

completely separate. In this case, it is possible to proceed directly to the subsequent qualitative or analysis stage. However, a non-uniform mixture of multiple components results in similar spectra with different peak intensities. In this case, the differential spectrum is used to obtain more detailed information. Fig. 2 shows the spectrum for foreign matter rolled onto a diamond cell and measured using transmission infrared microscopy. It shows differences in peak intensity ratios near 2900 cm^{-1} and 1650 cm^{-1} due to the measurement position. However, as the number and peak positions do not differ significantly, this sample is thought to be a non-uniform mixture of two components. Fig. 3 shows the differential spectra for the two spectra in Fig. 2 (measurement position A - measurement position B and measurement position B - measurement position A). They represent protein (A - B) and polyisoprene (B - A), respectively, suggesting that the sample is a non-uniform mixture of these two components.

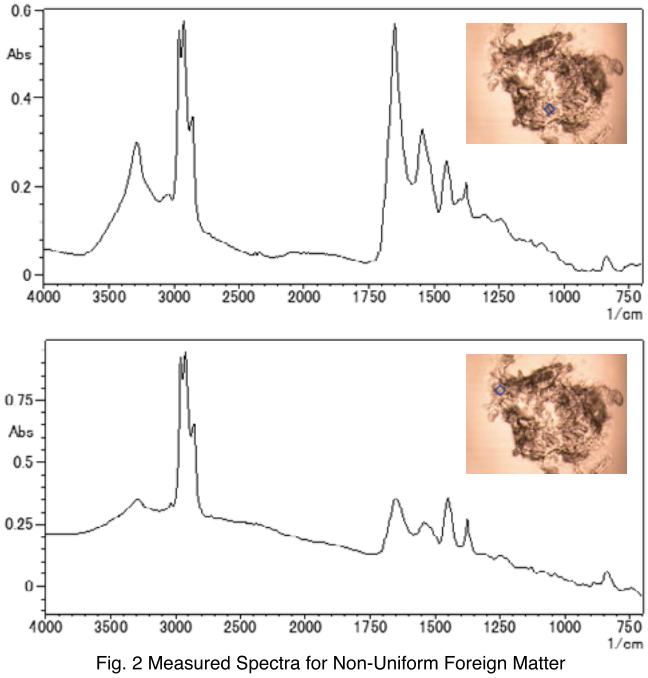


Fig. 2 Measured Spectra for Non-Uniform Foreign Matter

Upper: Measurement position A; Lower: Measurement position B;
Blue frames in photos show positions (20×20 μm)

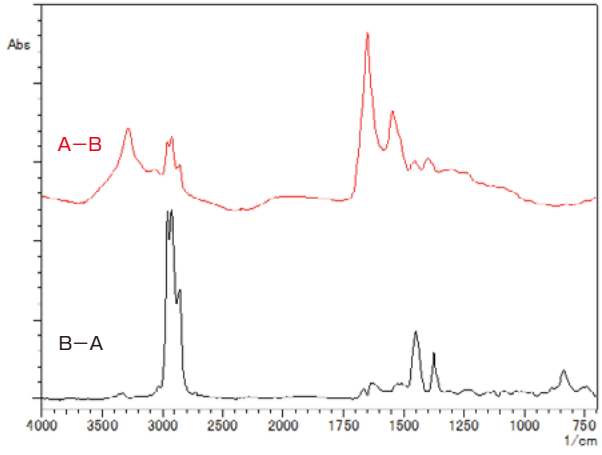


Fig. 3 Difference Spectra

Upper: Measurement position A - Measurement position B (protein);
Lower: Measurement position B - Measurement position A (polyisoprene)

3. Comparison with a Normal Area or a New Part

During defect analysis it is common to compare the defective area with a normal area or a new part to determine the cause of the defect. In particular, if the defect does not result from ingress of a completely different substance such as foreign matter but is due to deterioration or other change in part of the product, comparison with a normal area clarifies the differences before and after the change and indicates what kind of change occurred.
Fig. 4 shows the results of single-reflection ATR analysis (diamond prism) on both a normal area and the discolored area, after a discolored area was discovered on a resin component. Both measured spectra are the spectra for acrylonitrile butadiene styrene (ABS) resin. However, a comparison of the two reveals that the peaks in the spectrum for the discolored area near 1720 cm^{-1} and 3400 cm^{-1} are more intense than for the normal area, while the peak near 968 cm^{-1} is much weaker.
The peaks near 1720 cm^{-1} and 3400 cm^{-1} are thought to be C = O stretching vibrations and O - H stretching vibrations, respectively, and neither of these peaks exists in ABS resin. The peak near 968 cm^{-1} is thought to result from the = C - H out-of-plane vibrations of the trans-vinylene group in the butadiene of the ABS resin. These results suggest that the discoloration resulted from oxidative degradation that broke the C = C double bonds of the trans-vinylene group, forming a C = O group and O - H group.

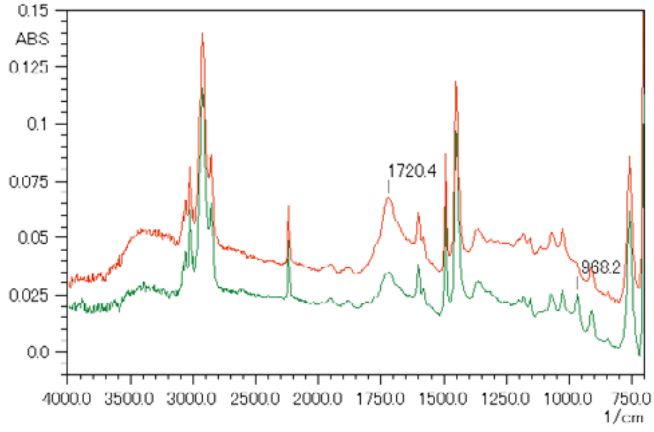


Fig. 4 Measured Spectra for Discolored Area of Resin

Top: Discolored area; Bottom: Normal are

4. Multifaceted Evaluation Using Other Analysis Methods

Infrared spectroscopy using FTIR is an effective method for the identification and qualitative analysis of substances when analyzing foreign matter. However, FTIR alone is often not enough to identify the foreign matter and determine the cause of the defect. Such cases require multifaceted evaluation using information obtained by other analytical methods. Instruments commonly used for foreign matter analysis include the scanning electron microscope/energy dispersive X-ray spectrometer (SEM-EDS; imaging and element information from an electron microscope) and the energy dispersive X-ray fluorescence spectrometer (EDX; easily obtains element information at atmospheric pressure). However, the analysis example presented below uses the confocal laser scanning microscope (CLSM).

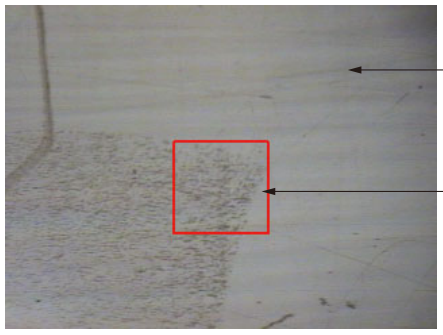


Fig. 5 Infrared Microphotograph of Abnormal Area on a Film Surface
Red frame : 100×100 μm

Fig. 5 shows an infrared microphotograph of an abnormality discovered on the surface of a film. Numerous fine particles appear to be stuck to the surface between the center and bottom-left of the photograph. The infrared microscope ATR method that is effective for the surface analysis of minute areas was used to analyze this abnormality. Fig. 6 shows the measured results for the normal and abnormal areas. The results for both areas reveal the spectrum for polyethylene terephthalate (PET) and no obvious difference is apparent between them. It is therefore considered likely that fine powder from the PET film adhered to the film surface in the abnormal area.

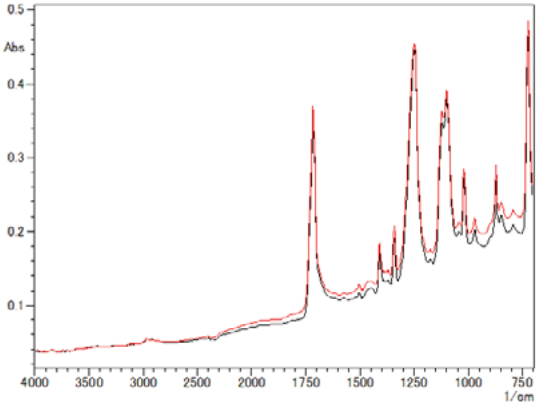


Fig. 6 Measured Results on Film Surface
Black: Normal area; Red: Abnormal area

Subsequently, surface observations and 3D surface shape evaluation of the film surface were performed using a confocal laser scanning microscope (CLSM). A CLSM can take high-resolution images in air of non-conductive samples without the need for special pretreatment. The 3D surface shape evaluation simultaneously acquires information in the height direction. The magnification is from approximately 100× to 15000×.
Fig. 7 shows the CLSM image of the abnormal area of the film. The observed field is 64×48μm. A clear image was obtained that shows the particles and what appear to be scratches. Fig. 8 shows the height profile along the red line at the center of Fig. 7. In addition to the height increases expected where a particle adheres to the film surface (height of the flat film surface plus the height of the protruding particle), the height profile also reveals valley-like depressions in the film surface.
Analysis by the infrared microscope revealed both the normal and abnormal areas to be PET, and the CLSM observations and 3D surface shape evaluation revealed minute irregularities in the abnormal area of the film. This suggests not that PET particles adhered to the surface of the film, rather that the film surface is not smooth but roughened on a minute scale.

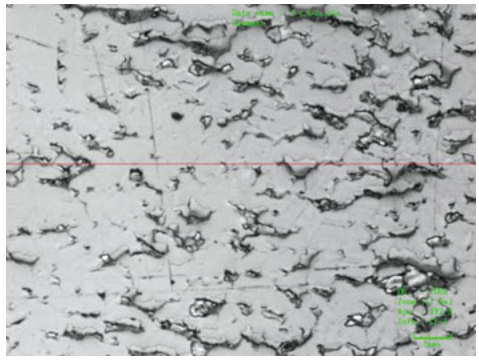


Fig. 7 Confocal Laser Scanning Microscope (CLSM) Image of the Film Surface
Observed field: 64×48μm

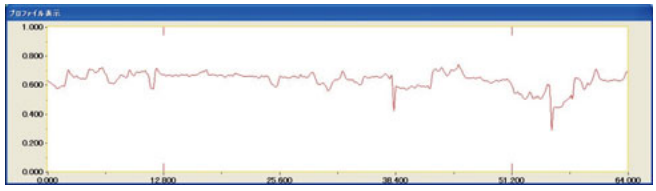


Fig. 8 Height Profile Along Red Line on Fig. 7
(Horizontal/vertical axis units:μm)

Conclusions

The final goal of the analysis of foreign matter and other defect analysis is to clarify and identify the cause of the defect. This necessitates reading the required information from the measured results. The measured results contain a range of information related to the measured target and some of this information may not be required. Alternatively, the measured results may not contain some information that is required. The first step in reading the required information from the measured results is to decide where the required information appears in the spectrum. This article introduced the most basic items for this process.

Question

I attached an ATR objective mirror to my infrared microscope to analyze foreign matter using the infrared microscope ATR method, but sometimes I can't get a spectrum. Is there some special way to get round this?

Answer

Unlike the transmission and specular reflection methods that directly irradiate the sample with infrared light, the attenuated total reflection (ATR) method irradiates the sample with light through a prism that is in contact with the sample. A good spectrum is obtained if the prism is in close contact with the sample. However, poor contact results in not only lower spectral intensity but also deformations of the spectrum shape (peak ratios) or in not spectrum at all if there is no contact.

The ATR method using an infrared microscope is often used for the analysis of foreign matter. With this method, a prism attached to the end of the ATR objective mirror is pushed into close contact with the sample on the sample stage. If the measuring surface on the sample is flat, good contact can be made even with a hard object such as a glass plate. However, care is required in the following cases.

Samples that make poor contact
1. Irregular measuring surface
2. Inclined or bent measuring surface
3. Hard particles on a soft substrate
4. Unstable sample base

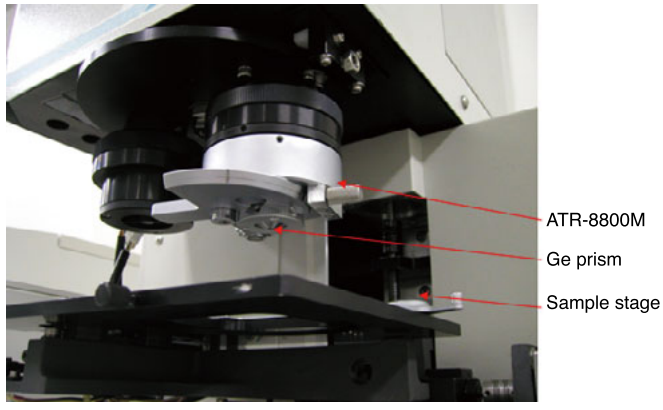
1. If the sample surface is irregular, good contact may be made at the protrusions but not with the indentations. Therefore, the spectral intensity may change each time the measured position changes. In such a situation, it is important to search for a position that yields a satisfactory spectrum.

2. If the measuring surface is inclined or bent, the prism will contact the sample in a different position from the measurement position, making good contact impossible. Mount the sample with the point to be measured at the highest position.

3. Hard particles on a soft substrate such as paper or rubber may be pushed down into the substrate through contact with the prism. Conversely, if the substrate is hard and flat, the sample is compressed to produce good contact and obtain a good spectrum.

4. If the sample has an unstable base, the measuring surface may tilt when the prism presses on the sample. In this situation, it is essential to carefully fix the sample to prevent it from moving.

In addition, contact with a soft sample like cloth may cause the sample to move as the prism makes contact. In a situation like this, the spectrum will change as the prism makes contact with the sample. You are recommended to conduct monitor measurements to check the spectrum while making contact.



ATR-8800M ATR Objective Mirro

Founded in 1875, Shimadzu Corporation, a leader in the development of advanced technologies, has a distinguished history of innovation built on the foundation of contributing to society through science and technology. We maintain a global network of sales, service, technical support and applications centers on six continents, and have established long-term relationships with a host of highly trained distributors located in over 100 countries. For information about Shimadzu, and to contact your local office, please visit our Web site at **www.shimadzu.com**

JQA-0376

SHIMADZU

SHIMADZU CORPORATION. International Marketing Division
3. Kanda-Nishikicho 1-chome, Chiyoda-ku, Tokyo 101-8448, Japan
Phone: 81(3)3219-5641 Fax. 81(3)3219-5710
URL http://www.shimadzu.com

Printed in Japan 3295-08904-15A-NS

The contents of this brochure are subject to change without notice.