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Gas Cell

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Samples of various states can be analyzed by FTIR by selecting the appropriate accessory attachment. Here we introduce the structures and method for selecting a gas cell used for measurement of gas samples.

1. Lambert-Beer Law

The absorption intensity of a material can be defined according to the Lambert-Beer law. The Lambert-Beer law, expressed by equation (1) of Fig. 1, establishes the relationship among incident light I_0, the light transmitted through the sample I_t, the optical pathlength d, the sample concentration C, and the absorbance A. ε, referred to as absorption coefficient, is a constant that indicates the amount of light that can be absorbed by a substance.

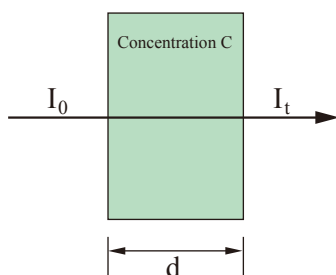$$\log(I_0/I_t)=\log(1/T)=\varepsilon Cd=A \quad (1)$$

Fig. 1   Diagram Illustrating Lambert-Beer Law

Assuming a constant optical pathlength, the concentration can be calculated from the absorbance using a calibration curve. Moreover, if the approximate concentration of the sample is known, the optical pathlength necessary for measuring a sample can be calculated from the ratio of the absorbance to the product of the concentration and the molar absorption coefficient.

The absorption spectra of gas samples can be measured by enclosing them in a container, in the same manner as liquid samples, and irradiating them with infrared light. Since the concentrations of liquid and solid samples are high due to their relatively high densities, measurement is conducted using optical pathlengths shorter than 1 mm. Gas samples, on the other hand, are relatively low in density, and are therefore measured using optical pathlengths from a few centimeters to tens of meters.

2. Types of Gas Cells

There are 2 types of gas cells, those having short optical pathlengths and those with long optical pathlengths.

2.1 Short-Path Gas Cells

Light is transmitted in a straight line from the inlet to the outlet of a short-path gas cell, just as in liquid cells, and is therefore also called a single-path gas cell. Fig. 2 shows cells having a cylindrically-shaped structure within which the sample gas is sealed. Window plates are attached at both ends of the cylinder to allow transmission of infrared light. Although the optical pathlength is actually the length of the gas cell, its maximum length is limited to 15 cm since it is mounted inside the FTIR sample compartment. Shimadzu offers gas cells with optical pathlengths of 5 cm and 10 cm. As infrared light displays little attenuation, it can be measured using a standard FTIR DLATGS detector.

The gas cell is made of glass, and the window plate is selected from among KBr, NaCl, KRS-5, depending on the sample characteristics. The concentration that can be measured depends on the substance, but concentrations from 10 ppm up to several percent can be measured with a 10 cm cell. For example, in the case of methane, a concentration range between 69 ppm to 27,500 ppm can be measured, as indicated in Table 1.
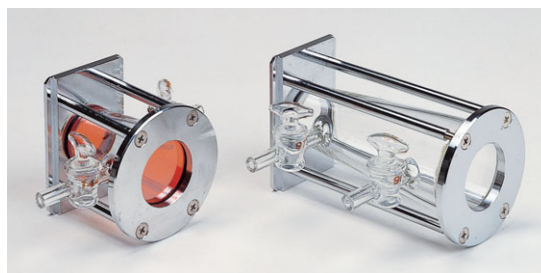

Fig. 2   5 cm Gas Cell (left) and 10 cm Gas Cell (right)

2.2 Long-Path Gas Cells

Measurement of gas samples of low concentration in the order of ppm, requires a long optical pathlength cell. The detection limit of methane is on the order of 1 ppm, which is 1/100 of what can be measured in a 10 cm gas cell. To measure methane at this detection limit, a gas cell with a pathlength 100 times greater, one of 10 m, would be required. But a 10 m-long single-path gas cell cannot be mounted in an FTIR. Therefore, a long-path gas cell permitting back-and-forth light travel between two mirrors is used. Since light repeatedly travels back and forth in the cell, this type of long-path gas cell is also referred to as a multipath gas cell.
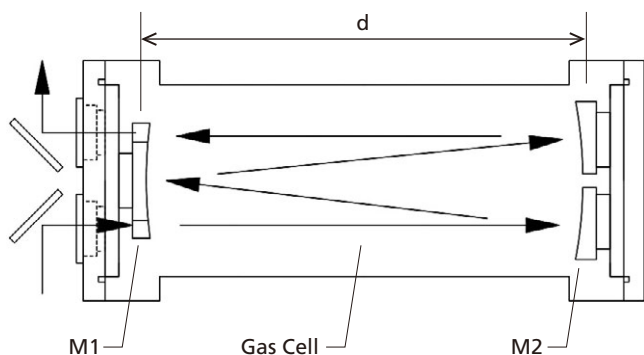
Fig. 3   Diagram of Long-Path Gas Cell

After traveling repeatedly back and forth between mirror M1 and mirror M2, as shown in Fig. 3, the light exits the gas cell toward the detector. One round trip of infrared light is equivalent to twice the distance d between the mirrors. If d is 50 cm, the optical pathlength using 10 round trips becomes 10 m. Long-path gas cells can be of a fixed optical pathlength or a variable optical pathlength. In general, the fixed optical pathlength type of gas cell is convenient since no maintenance is required. Although the variable optical pathlength gas cell is convenient for measurement of gases of varying concentration ranges, a laser must be used for adjustment of the M2 mirror when changing the pathlength.

When light conducts N round trips to travel the optical path, it is reflected (2N - 1) times by the mirrors. With 10 round trips it is reflected 19 times. When using a 95 % reflectivity mirror, infrared light is attenuated up to 38 % ($0.95^{19} = 0.38$) after 19 times reflections. For that reason, a high-sensitivity MCT detector is used instead of the standard FTIR DLATGS detector.

In addition, installation and removal of the tubing can be a time-consuming, burdensome chore due to the large size and weight of these gas cells. Thus, rather than installing it inside the FTIR sample compartment, it is convenient to set up the long-path gas cell along with a gas cell box beside the FTIR unit.

Fig. 4   Gas Cell and Gas Cell Box Positioned Beside the IRPrestige-21

Gas cells are available with a glass body or a metallic body, as shown in Fig. 5. The glass type is inexpensive and more commonly used, but is not applicable for gases that contain hydrogen fluoride, which etches glass. In such cases, a metallic gas cell with a fluorine resin-coated interior surface is used. In addition, both the glass and metallic types are available with heater-wrapped bodies to allow heating of the gas cell. Window plates consisting of KBr, CaF_2, BaF_2, etc. can be used. When used in combination with an MCT detector, BaF_2 window plates are convenient because they are resistant to steam and are applicable to measurement over a wavenumber range comparable to that of an MCT detector.
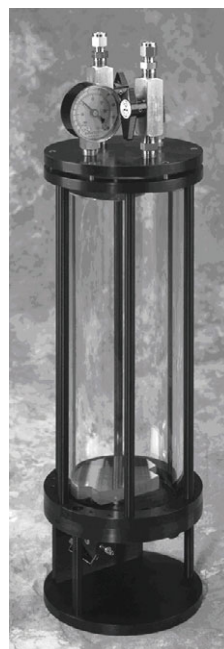
Glass Body Gas Cell   Metallic Body Gas Cell

Fig. 5   Glass Body and Metallic Body Gas Cells

2.3 Heated Gas Cell for TG-FTIR System

Fig. 6 shows a TG-FTIR system used for measurement of the gas generated from the thermal analyzer. A heated gas cell is used in the TG-FTIR system. A temperature of 200 °C or 250 °C is possible using a gas cell pathlength of 10 cm, and gas generated during heating of the sample in the TG passes to the gas cell. Window plates consisting of KBr, NaCl, CaF_2, BaF_2, etc. can be used.

Fig. 6   TG-FTIR System

3. Sample Concentration Ranges Measurable by a Gas Cell

The range of sample concentrations that can be measured by a 1 m pathlength gas cell is shown in Table 1 Superscript Note). Since intensity is proportional to the optical pathlength according to the Lambert-Beer law, the sample concentrations that can be measured will be 10-fold those listed when using a 10 cm gas cell, and 1/10 those listed when using a 10 m gas cell.

Table 1 Quantitation Upper and Lower Limits for Typical Gases (with 1 m gas cell)

Gas Substance	Concentration (ppm)	
	Lower Limit	Upper Limit
1,3 Butadiene	5.2	2,080
2-Methyl Pentane	3.5	1,410
Acetaldehyde	10.0	4,060
Acetone	9.4	3,760
Acetylene	0.6	230
Benzene	0.9	340
CCl_2F_2	0.9	347
CCl_3CF_3	2.9	1,175
CCl_3F	0.9	360
CCl_4	0.9	357
$CClF_2CClF_2$	2.3	920
CF_4	0.1	36
CH_3COOCH_3	5.3	2,130
CH_3COOH	4.2	1,670
$CHCl_3$	1.8	739
$CHClF_2$	1.8	705
CO	9.4	3,750
CO_2	1.9	770
Cyclohexane	1.3	500
Diethyl Ether	4.9	1,940
Ethane	7.8	3,100
Ethanol	19.0	7,500
Ethylene	4.2	1,680
H_2O	24.0	9,720
HF	2.0	800
HCl	7.8	3,120
HBr	40.0	16,100
HCN	1.4	578
HCHO	4.3	1,710
HCOOH	3.8	1,500
HNO_2	0.9	363
HNO_3	3.6	1,450
HS	1420.0	570,000
Isoprene	5.4	2,180
Methane	6.9	2,750
Methanol	5.4	2,160
NH_3	2.7	1,090
n-Hexane	5.0	2,010
NO	18.0	7,040
NO_2	2.5	1,000
N_2O	2.7	1,090
n-Pentane	6.6	2,640
Ozone	10.0	4,070
Phosphine	39.0	15,800
Propane	4.0	1,611
SF_6	0.2	70
SO_2	5.2	2,060
Styrene	7.6	3,020
Toluene	6.7	2,680
o-Xylen	4.4	1,740
m-Xylen	7.5	3,006
p-Xylene	7.7	3,100

Note) These values should be used only as a guideline because the upper and lower limits will vary with such measurement conditions as integration frequency, etc.

4. Gas Cell Selection and Considerations

Select a gas cell based on the following considerations.

Concentration of Measurement Target Gas
Select the optical pathlength based on the gas concentration. Select a short-path gas cell for a sufficiently high concentration, and a long-path gas cell for low concentrations.

Types of Gases in the Sample Matrix
Depending on the types of gases present, overlapping of absorption peaks may occur, preventing analysis. If the matrix includes corrosive gases, select a glass gas cell or a corrosion-resistant metallic gas cell. Since a glass gas cell cannot be used with a gas mixture containing hydrogen fluoride, such gas mixtures will require the selection of a metallic gas cell with a fluorinated resin coating.
For gases that contain water vapor, select KRS-5 (5 cm / 10 cm gas cell) or BaF_2 window plates.

Detector and Installation Method
When using a short-path gas cell, it should be installed in the FTIR sample compartment, and a standard DLATGS detector can be used.
A long-path gas cell can either be mounted in the FTIR sample compartment with installation of the optional FTIR MCT detector, or it can be mounted in the MCT detector-equipped gas cell box positioned beside the FTIR.

Heating Option
Water vapor and hydrogen halides can be adsorbed to the interior walls of tubing and the gas cell body, preventing the output of correct concentrations as well as the complete replacement of gases. This adsorption can be prevented by heating the tubing and gas cell body.

Measurement Method ABCs: Diffuse Reflectance Method

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Along with the widespread use of the single-reflection ATR method, measurement of samples in the solid, powder and liquid states has become quite easy. However, when measuring hard solid objects with coarse surfaces, and powders, it can be difficult to obtain a good infrared spectrum due to insufficient contact of the sample with the ATR prism. For these samples, the diffuse reflectance method is applicable.
Here we introduce and describe the features, measurement principle and application examples of the diffuse reflectance method.

1. Introduction

One method of measuring infrared spectra of powder and solid samples by FTIR is the KBr (potassium bromide) pellet method. The KBr pellet method involves mixing the sample with KBr powder, pressing it into pellet form and then measuring the infrared transmittance spectrum. For a detailed description, refer to FTIR Talk Vol. 14.
On the other hand, the diffuse reflectance method is, as indicated by its name, a method by which an infrared spectrum is obtained by measuring the diffuse light that is reflected from the surface of the sample. According to the 15th Edition of the Japanese Pharmacopoeia, the KBr pellet method, the ATR method, and the diffuse reflectance method are all specified as applicable for measurement of solid samples. The diffuse reflectance method requires little time for pretreatment since pellet formation is unnecessary; therefore, it is often used as a confirmation test method.
In addition, while the ATR method permits extremely easy measurement of solids, powders and liquids, close contact between the surface of the sample and the ATR prism is critical for obtaining a good infrared spectrum. Since it is difficult to achieve such close contact with solid samples having a rough surface, as well as with powders, it may be difficult to obtain sufficient peak intensity.
Also, cautioun is necessary when forcing a close contact between a hard crystalline sample and the ATR prism to avoid damaging the ATR prism.
With the diffuse reflectance these concerns do not exist. Furthermore, this method features better capability than the transmittance method in providing information regarding substances that are attached or adhering to the sample surface.

2. What Is the Diffuse Reflectance Method?

When light is irradiated onto a powder sample, as shown in Fig. 1, specular reflected light from the sample surface is produced. In addition, diffuse reflected light (scattered light) emerges from the sample surface after first being transmitted into the interior of the sample particles and repeatedly reflected among the particles. Because of this scattering of light, the method of generating an infrared spectrum of a powder using diffuse reflected light is referred to as the diffuse reflectance method.
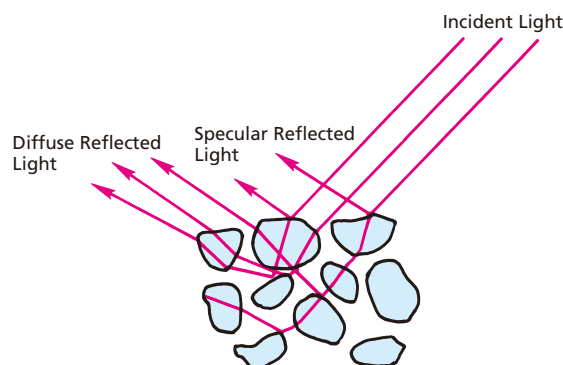

Fig. 1   Diagram of Light Dispersion with Powder Sample

Diffuse reflected light, which has been repeatedly transmitted within the powder sample, gives a spectrum similar to an ordinary transmission spectrum. However, light in a wavenumber range where absorption is weak may be repeatedly reflected inside the sample particles and emerge in such a way that it is not collected for detection. Because of this, bands in diffuse reflected spectra may appear weaker than the corresponding transmittance-acquired bands and not be proportional to concentration. This, therefore, led to the manipulation of diffuse reflectance spectra by the Kubelka-Munk function (K-M function) to make the spectra more comparable to transmittance spectra and suitable for quantitative analysis.

$$f(R\infty) = \frac{(1-R\infty)^2}{2R\infty} = \frac{K}{S}$$

Here, $f(R\infty)$ is the K-M function, $R\infty$ is the absolute reflectance, K is the molecular absorption coefficient, and S is the scattering coefficient. However, due to the difficulty in measuring the absolute reflectance $R\infty$ of the sample, in actual measurement, it is obtained by measuring the relative reflectance $r\infty$ of a standard powder, such as KBr or KCl (potassium chloride), with a molecular absorption coefficient K near 0 in the measurement region.

$$r\infty = \frac{r\infty\,(Sample)}{r\infty\,(Standard\ powder)}$$

$$f(r\infty) = \frac{(1-r\infty)^2}{2r\infty} = \frac{K}{S}$$

The light measured as diffuse reflectance actually includes the specular reflectance light at the sample surface. Obtaining a more accurate diffuse reflectance spectrum requires a reduction in specular reflectance light, which necessitates use of powder consisting of smaller sized particles. By reducing the particle size to the same level of the wavelength, the scattering efficiency is maximized while the ratio of specular reflectance light is reduced. In addition to particle size, the shape and loading state are also important factors. Powder samples are not measured as in a typical measurement, but diluted to an appropriate concentration (about 1 to 10 %) with KBr or KCl standard powder.

3. Diffuse Reflectance Attachment

Fig. 2 is a photograph of the DRS-8000 diffuse reflectance attachment, and Fig. 3 shows its optical system. Infrared light is irradiated onto the sample via mirror M3 in Fig. 3, and the diffuse reflected light collected by mirror M4 is routed to the detector via mirrors M5 and M6. Two types of sample holders (2 mm dia., 4 mm dia., both 1 mm deep) are available for loading of the powder sample; or aluminum disposable sample cups (6 mm dia., 1.5 mm deep) can also be used.

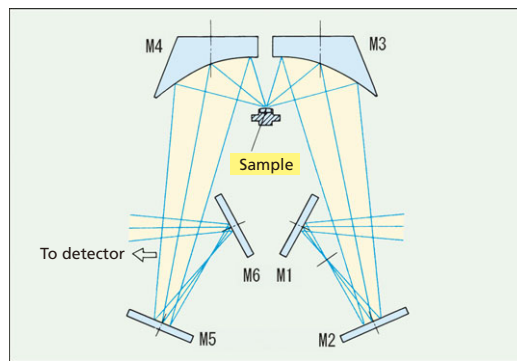Fig. 2   DRS-8000 Diffuse Reflectance Attachment

Fig. 3   Optical System of DRS-8000 Diffuse Reflectance Attachment

4. Diffuse Reflectance Spectrum and Kubelka-Munk Transformation

The effect of Kubelka-Munk transformation (K-B transformation) is explained here using the diffuse reflectance spectrum of caffeine as an example. Fig. 4 shows the diffuse reflectance spectrum, and Fig. 5 shows the spectrum obtained following Kubelka-Munk transformation.
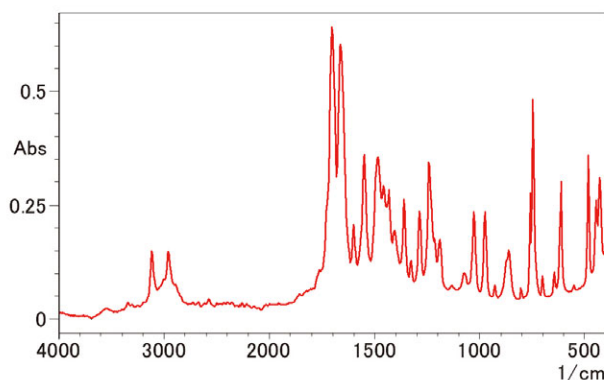

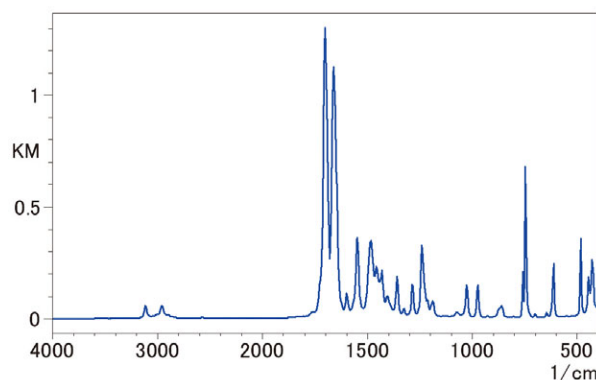Fig. 4   Diffuse Reflectance Spectrum of Caffeine

Fig. 5   Caffeine Diffuse Reflectance Spectrum After K-M Transformation

A weak absorption band is relatively pronounced in the diffuse reflectance spectrum, but following K-M transformation, these absorption intensities are reduced, and the relative intensity between peaks causes the spectrum to resemble a transmittance spectrum. The Y-axis in the K-M-transformed graph shows the K-M function, which should not be confused with the pre-transformation absorbance (A).

5. Adjusting the Sample Concentration

To obtain an infrared spectrum of a powder sample using the diffuse reflectance method for confirmation testing, etc., it is necessary to adjust the sample concentration using a dilution agent such as KBr for most of the sample. The target sample concentration at the start of the adjustment process is typically around 5 % by weight, but since the molecular absorption coefficient actually differs depending on the sample, the concentration must be further adjusted while checking the obtained reflectance and absorbance. Generally, sample concentration adjustment is considered to be good if the intensity of the strongest peak in the spectrum is about 10 % using reflectance (or 1 by absorbance). However, with the diffuse reflectance method, peak saturation at 10 % reflectance may occur due to the influence of reflection from the sample surface, making it appropriate to lower the concentration to obtain a slightly higher reflectance. The diffuse reflectance spectra of lactose in Fig. 6, obtained using concentrations of 1, 5, 20 and 100 % by weight, illustrate the effect of concentration adjustment.
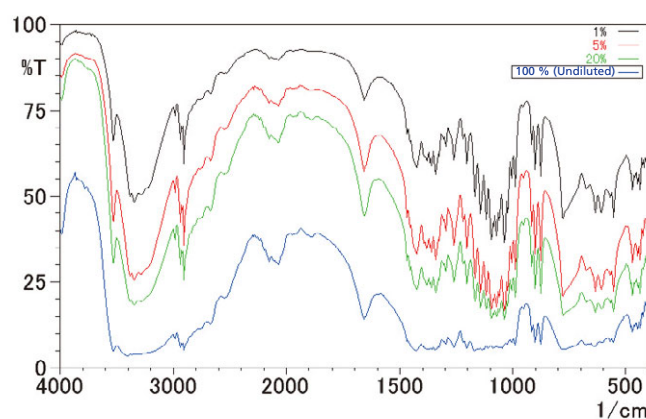

Fig. 6 Lactose Diffuse Reflectance Spectra at Difference Dilution Concentrations

On the other hand, to confirm a peak attributable to a low-concentration substance in a mixture of substances, the concentration of the sample can be increased intentionally to accentuate the target peak.

6. Measurement Example

Introduced here are examples of the measurement of 2 types of commercially available rockwool products. Rockwool, consisting of mineral fibers produced at high temperature, has traditionally been used as a heat insulator and sound absorber material. Rockwool itself is an inorganic compound, but a small amount of bonding resin is often added to commercial rockwool products to improve product form. We conducted single-reflection ATR and diffuse reflectance measurement of the resin bonded rockwool products to investigate the differences between the bonding resin substances.

Fig. 7 and 8 show the infrared spectra obtained using the ATR and diffuse reflectance methods. In both measurements, the samples were measured in their original fibrous state, without pulverizing them. For the diffuse reflectance measurement, the fibers were placed in the sample holder, and the ground surface mirror provided with the instrument was used as the reference.
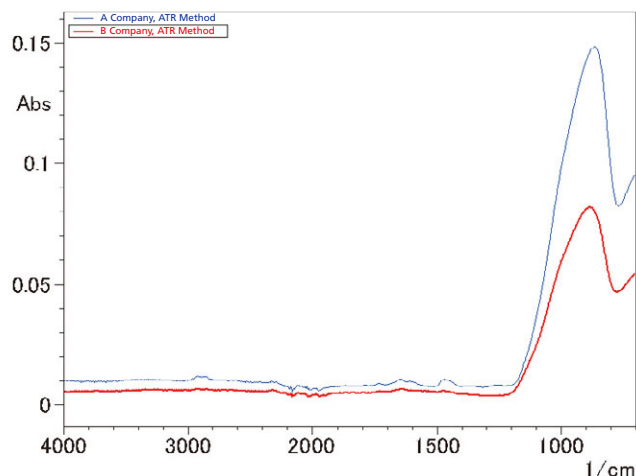

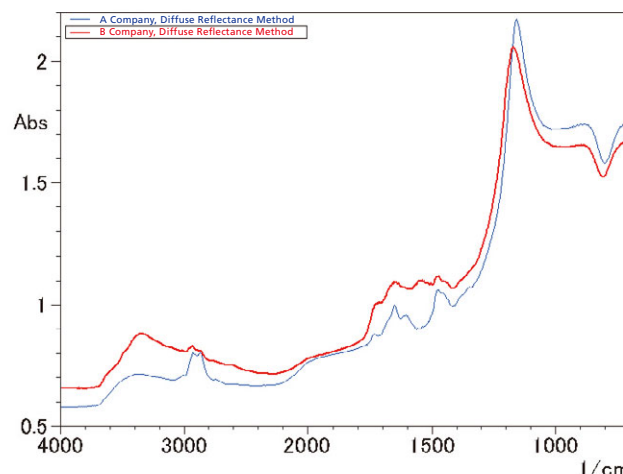Fig. 7 Infrared Spectra of Rockwool Products by ATR Method

Fig. 8 Infrared Spectra of Rockwool Products by Diffuse Reflectance Method

In the infrared spectra obtained by ATR, broad peaks attributable to inorganic compounds can be seen in the region below 1200 cm^{-1}, and faint peaks believed to originate from the bonding resin are seen from 4000 to 1200 cm^{-1}. However, the intensities of these peaks remain at a very small level due to the poor contact between the samples and the ATR prism. On the other hand, in the infrared spectra obtained using the diffuse reflectance method, the peaks from 4000 to 1300 cm^{-1} are relatively pronounced, and the differences between the 2 products are quite apparent.

7. Heated Chamber Diffuse Reflectance Measurement

Use of a diffuse reflectance attachment equipped with a heated chamber permits measurement of the sample chemical changes and molecular state changes during heating of the sample. Measurement is also possible under vacuum or in a controlled atmosphere (replacement gas) environment. Here we introduce an example of measurement of the thermal dehydration process in silica gel using the heated chamber diffuse reflectance attachment.

Fig. 9 shows a surface model of silica gel. The surface of silica gel contains hydroxyl groups covalently bound with silicon (silanol groups). These silanol groups can exist not only independently as free, isolated silanol groups, but bonded to other silanol groups via hydrogen bond, and bound to water through adsorption.
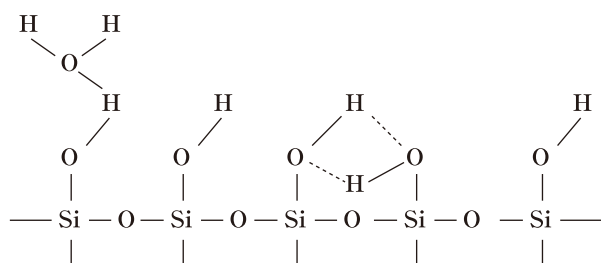
Fig. 9 Silica Gel Surface Model

Fig. 10 shows the infrared spectra measured during heating of silica gel powder from ambient temperature (30 °C) to 800 °C (30 °C, 100 °C, and thereafter at 100 °C intervals). The peak at 3740 cm^{-1} is due to absorption by isolated, free silanol groups, and the broad peak from 3700 to 3000 cm^{-1} is due to water molecules that are hydrogen bound to the silanol groups. As the temperature is increased, the hydrogen-bound water molecules are driven off as seen from the elimination of the broad peak from 3700 to 3000 cm^{-1}.
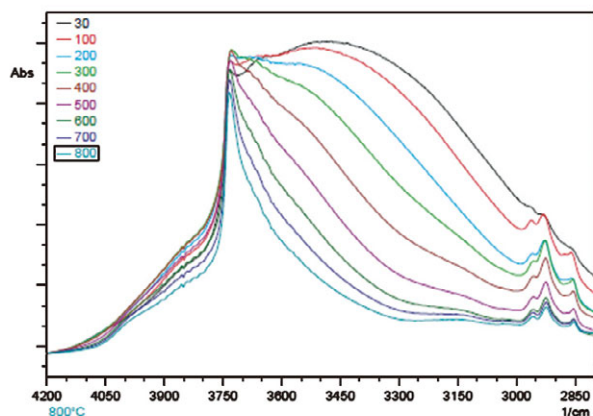
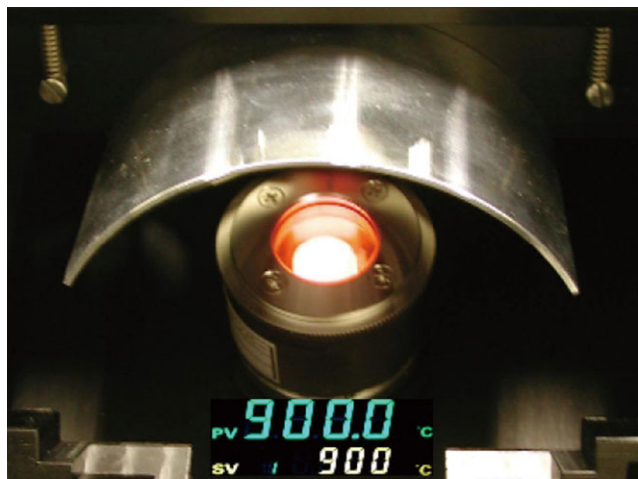Fig. 10 Diffuse Reflectance Infrared Spectra During Heating of Silica Gel

Fig. 11 Sample Heating Chamber
(Heated Vacuum Diffuse Reflectance System by S.T. Japan Inc.)

In addition to the silica gel discussed here, heating-associated measurement of kaolin (aluminum silicate) and ABS resin (acrylonitrile butadiene styrene copolymer) is addressed in Application News A398.

8. Conclusion

The diffuse reflectance method is widely used for various types of measurement in addition to those introduced here. Refer to FTIR Talk Vol. 10 for an in-depth discussion. Because absorption is weak in the infrared region, diffuse reflectance measurement of infrared spectra can be measured without pretreatment procedures such as sample dilution with KBr powder. Furthermore, powder samples can be measured as is by placing them in a glass or plastic cup, and special accessories are available.

Due to insufficient space in this issue,
the Q&A section is omitted.

Sample Compartment-Integrated ATR Measurement Attachment Series for Shimadzu IRAffinity-1 Fourier Transform Infrared Spectrophotometer

Introduced here are accessories that further enhance the effectiveness of the Shimadzu IRAffinity-1 Fourier Transform Infrared Spectrophotometer. Customers that have the IRAffinity-1 can utilize the sample compartment-integrated ATR attachment. For details, please contact your Shimadzu representative.

Three total reflectance measurement attachments are available:

GladiATR 10
Single-Reflection Attenuated Total Reflection Attachment

MIRacle 10
Single-Reflection Attenuated Total Reflection Attachment

HATR 10
Horizontal Type Total Attenuated Reflection Attachment

IRAffinity-1 with MIRacle 10 attached

Integration with the sample compartment greatly facilitates operation and purge performance.
Since the space above the sample compartment can be effectively used, efficient sampling is enabled. Further, complete enclosure of the sample compartment prevents contamination of the interior.

With the MIRacle 10, the sample mounting face is positioned higher than the IRAffinity-1 main unit cover, thereby allowing measurement of samples wider than the sample compartment (area width) without cutting them.

＊These accessories are specific to the IRAffinity-1. Existing accessories must be used for the IRPrestige-21 or the FTIR-8000 Series.

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