C103-E082

Access to your success
SHIMADZU

FTIR TALK LETTER

vol.14

July 2010

Integrating Sphere --- 2

The ABCs of Measurement Methods:
KBr Pellet Method --- 4

Question --- 7
The KBr window pane on our liquid cell has turned a cloudy white color.
Is there any problem continuing to use it the way it is?

Integrating Sphere

Spectroscopy Business Unit, Analytical & Measuring Instruments Div. Katsumi Harada

An integrating sphere is an optical component used to collect diffused light, average non-uniform light, and for other purposes. This article describes how integrating spheres are used.

(1) How an Integrating Sphere Works

Fig. 1 shows the typical construction of an integrating sphere. The interior walls of an integrating sphere are coated with a substance that has high optical diffuse reflectivity so that light is reflected in a diffuse and uniform manner. Since the light reflects off the integrating sphere walls many times before reaching the detector, the surface must have high reflectance. Therefore, the following kinds of materials are typically used on the interior walls of integrating spheres.

(1) Barium sulfate powder
(2) Sintered alumina ceramics
(3) Fluoropolymer
(4) Gold

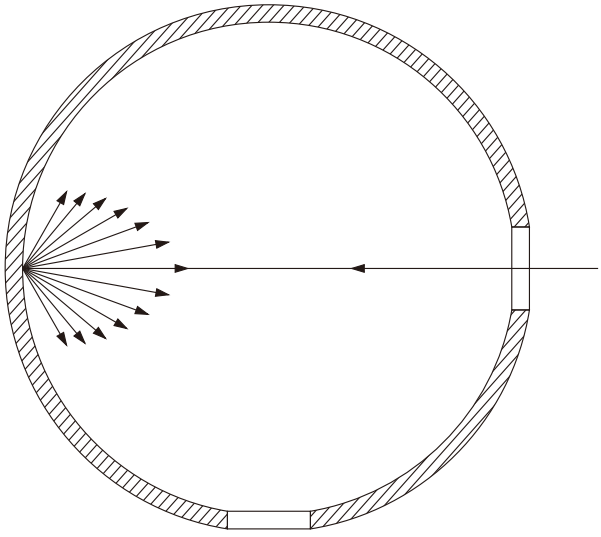

Fig. 1 Structure of Integrating Sphere

Since materials containing water or that are made of polymers have high light absorption in the infrared region, they are not suited for use on the interior walls of integrating spheres. Therefore, gold is typically used. Normally, aluminum or another metal plated with gold is used, where the substrate is sand blasted, or otherwise treated, such as with chemicals, to make its surface rough and more diffusive before gold plating. Shimadzu IntegratIR A near-infrared integrating sphere uses gold- plated interior walls.

(2) Integrating Sphere Efficiency

As illustrated in Fig. 2, the diffused light inside the integrating sphere reflects off the interior walls many times before reaching the detector. Consequently, if the integrating sphere is used as a condenser, only a few hundredths of the incident light would reach the detector. If the material used on the inner walls of the integrating sphere has low reflectance, the light intensity attenuates each time the light is reflected. Therefore, increasing the efficiency of an integrating sphere requires using inner wall material that has nearly 100 % reflectance for the wavelength range being used.

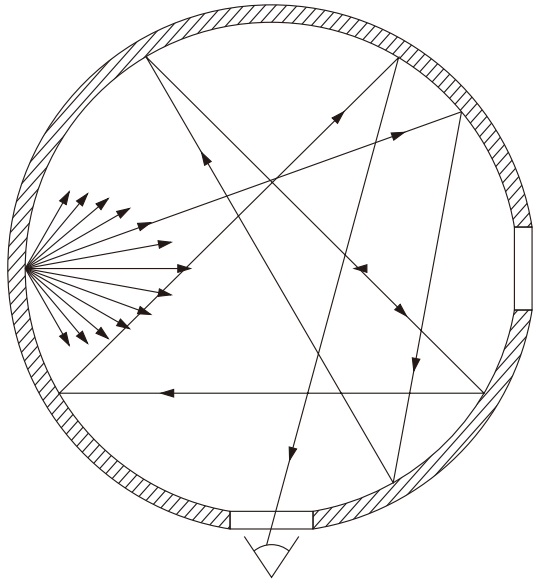

Fig. 2 Integrating Sphere Efficiency

In addition, to ensure it changes non-uniform light to uniform light, the integrating sphere opening must be sufficiently small, relative to the total surface area. Even materials with high diffusivity do not provide a uniformly diffusive surface (Lambertian surface), resulting in non-uniformity in the reflected light, depending on the direction. If non-uniform light reflects only one time within the integrating sphere before exiting via the opening, as shown in Fig. 3, that non-uniformity may not be eliminated. Therefore, the larger the opening to the integrating sphere, the higher the proportion of light with a low reflection count will escape from the opening.

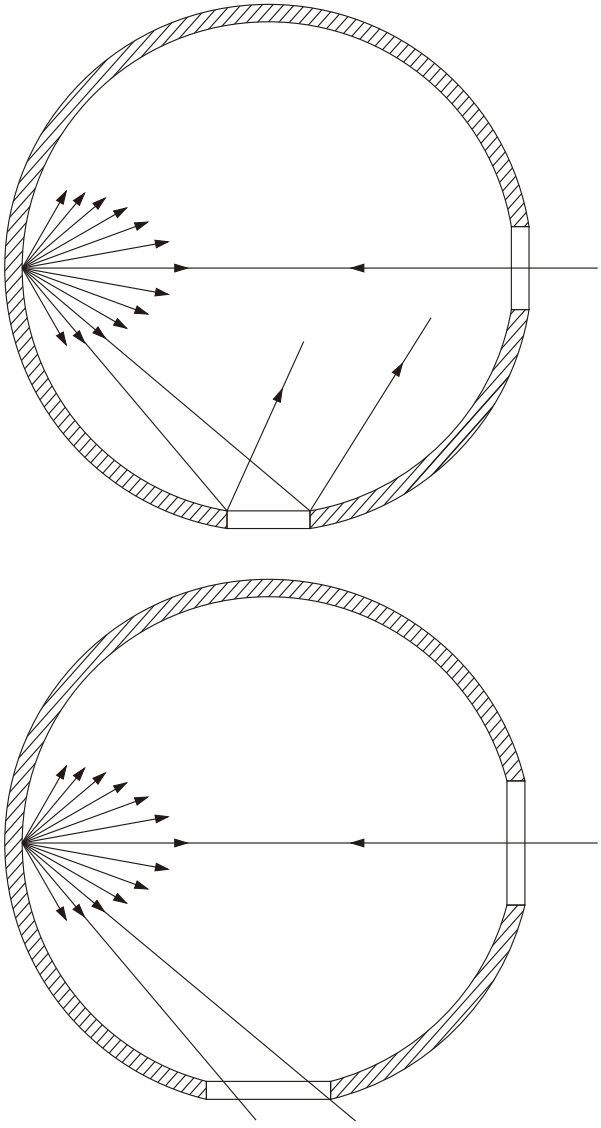

Fig. 3 Integrating Sphere Opening

(3) Integrating Sphere Used as a Light Source

Though integrating spheres are usually used as detectors, some are used as a light source, as shown in Fig. 4. For standard light source and other light sources used to adjust or inspect optical sensors, it might not be possible to obtain accurate measurements, due to the influence of variations in brightness depending on the location. In such situations, the light source is placed inside or outside the integrating sphere and measures are taken to prevent direct light from hitting the detector. Shimadzu offers a black body furnace on an emittance measurement system (available on a special order basis) that is equivalent to such a light source.

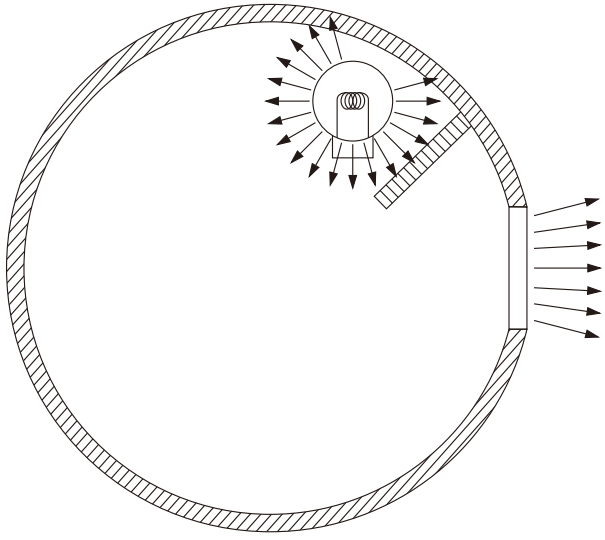

Fig. 4 Integrating Sphere Used as a Light Source

(4) Measuring Diffuse Reflection in the Infrared Region

Diffuse reflection in the infrared region contains more specular reflection components than ultraviolet light or visible light. Therefore, sometimes it can be measured without using an integrating sphere. For samples with relatively high specular reflection and low diffuse reflection levels, the proportion of diffuse reflected light can be increased by placing a concave mirror sufficiently close to where the measured light is irradiated, as shown in Fig. 5. This method is recommended if measurement sensitivity is inadequate using an integrating sphere. Shimadzu DRS-8000A diffuse reflectance attachment is designed for this purpose.

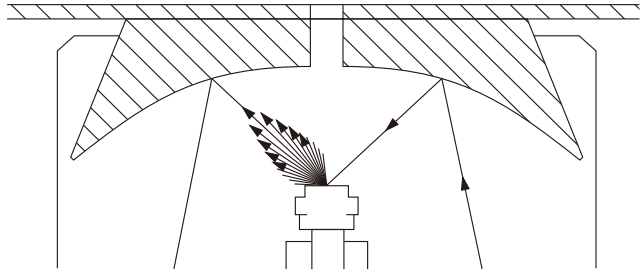

Fig. 5 Measuring Diffuse Reflectance

The ABCs of Measurement Methods: KBr Pellet Method

Tokyo Applications Development Center, Analytical Applications Dept., Analytical & Measuring Instruments Div.
Hirokazu Abo

A variety of measurement methods are used with Fourier transform infrared spectrometers (FTIR). One of the more popular methods is the potassium bromide (KBr) pellet method, the most fundamental measurement method. It can be used for a wide variety of samples and analytical objectives, but there are several characteristics and key points to keep in mind. This article explains how to prepare samples for the KBr pellet method and describes an actual measurement example.

1. Pellet Methods

There are several light transmission measurement methods that involve shining light on a sample and detecting the light that passes through the sample.
For example, the liquid membrane method is used for measuring liquid samples using the transmission method. The KBr pellet method is mainly used to measure solid samples. Pellet methods utilize the pellet's property of becoming clear to infrared light when pressure is applied, due to the plasticity of its alkali halides. The type of alkali halide most commonly used in pellets is potassium bromide (KBr), though potassium chloride (KCl) and cesium iodide (CsI) are used as well.
The Japanese Pharmacopoeia 15th Edition describes the pellet method as follows. "Powder 1 to 2 mg of a solid sample in an agate mortar, triturate rapidly with 0.10 to 0.20 g of potassium bromide or potassium chloride for infrared spectrophotometry with precautions against moisture absorption, and compress the mixture with a press in a suitable die (disk-forming container) to make the sample disk."
Creating the pellets requires preparing about 100 times more potassium bromide than the amount of measurement sample.

2. Handling Substances Such as Potassium Bromide

Potassium bromide and other substances used in preparing pellets are deliquescent materials, so they tend to absorb moisture from the atmosphere. However, since water causes absorption in the mid-infrared region, it is important to store potassium bromide used for KBr pellets with a desiccator or other means to prevent absorption of moisture.
It is better to store potassium bromide in crystalline form, as shown in Fig. 1, rather than in powdered form. This is because crystalline potassium bromide has a smaller surface area for its mass than powder, so it will absorb less moisture per unit mass.

Fig. 1 Crystalline Potassium Bromide

3. Forming KBr Pellets

Form pellets using the following procedure.
Note: Use equipment (agate mortar and pellet form) that has been cleaned with alcohol and dried.
(1) Grind the measurement sample in an agate mortar.
(2) Grind the KBr in the agate mortar. Do this as quickly as possible, because the KBr tends to absorb moisture from the atmosphere.
(3) Add 0.5 to 1 mg of sample for every 100 mg of KBr, as shown in Fig. 2, then grind the sample and KBr powder together in the mortar until they are thoroughly mixed. Just as with the KBr powder, work quickly.
(This amount should be sufficient to form several 4 mm diameter KBr pellets. Make adjustments according to the pellet size.)
(4) Prepare pellets.
(5) Separately, prepare pellets that contain only KBr for measuring background levels. Using the KBr-only pellets to measure background absorption enables making corrections for infrared scattering losses and the effects of moisture absorbed by the KBr.

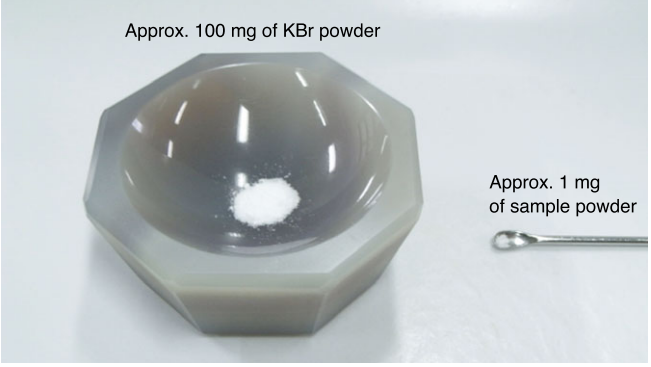

Fig. 2 Approx. 100 mg of KBr Powder and 1 mg of Sample Powder

4. Sample Concentration in KBr Pellets

The concentration of sample in KBr pellets should result in maximum spectral peak intensities equivalent to about 10 % transmittance (about 1 Abs in terms of absorbance). Fig. 3 shows an infrared spectrum for a lactose and KBr pellet, adjusted so that the maximum peak intensity is about 10 % transmittance.
If the maximum peak intensity is too low, the noise will appear higher with respect to peaks.
In contrast, if the concentration is too high, the maximum peak intensity will approach 0 % and saturate the absorption peaks, as shown in Fig. 4. Be careful not to saturate absorption peaks, as this can prevent obtaining an accurate spectrum.
Sample concentration can be adjusted easily by using the absorption level as a reference. This is because absorbance is proportional to sample concentration, according to the Lambert-Beer law. If maximum absorbance is 0.5, then sample concentration should probably be doubled.

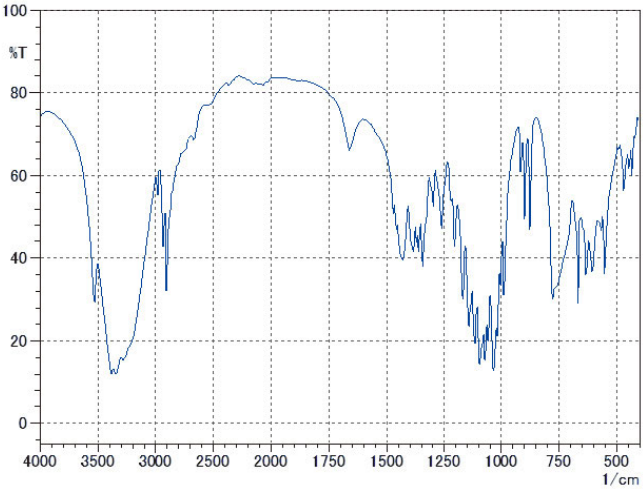

Fig. 3 KBr Pellet with Appropriate Sample Concentration

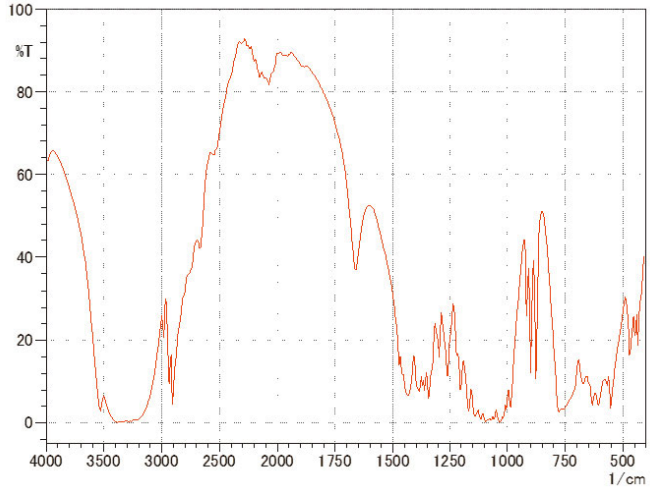

Fig. 4 KBr Pellet Resulting in Saturated Peaks

5. Moisture Effects

Even if KBr pellets are prepared in an identical manner, their moisture content can vary due to environmental variations in the room. If KBr pellets absorb moisture, the water can cause absorption peaks on the infrared spectrum or fluctuations in the baseline due to scattering caused by clouding of KBr pellets. Fig. 5 shows a comparison of results from measuring caffeine and KBr pellets that contain low and high levels of moisture. The baseline for the sample containing high moisture shows fluctuation due to clouding and absorption of water, as well as a change in the shape of the spectrum.

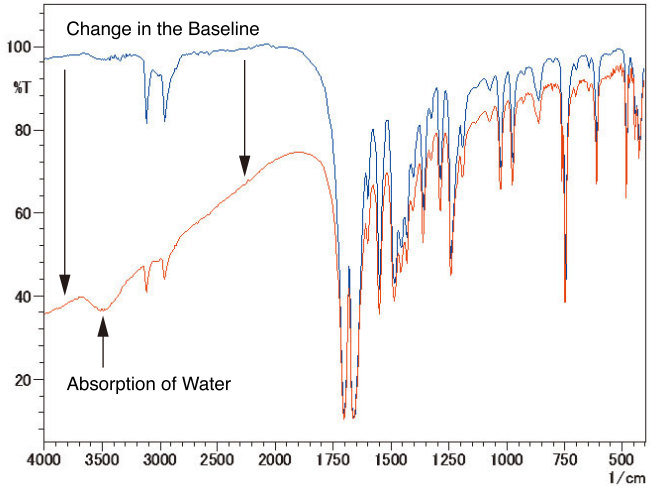

Fig. 5 Pellet with Low Moisture (Blue Line) and
Pellet with High Moisture (Red Line)

Fig. 6 shows the results from measuring L-arginine by the KBr pellet method. The red line shows the results from measuring a pellet immediately after preparation; the blue, green, and black lines are from measuring pellets after drying them with a dryer for 1, 3, and 10 minutes, respectively. The inset is an enlargement of the 1400 to 1800 cm^{-1} range. It shows how in addition to reduced absorption due to the O-H radical near 3500 cm^{-1}, the number of peaks near 1500 to 1750 cm^{-1} has changed from 4 to 3 peaks. In this way, moisture contained in the pellet can affect the shape of the spectrum, depending on the sample.

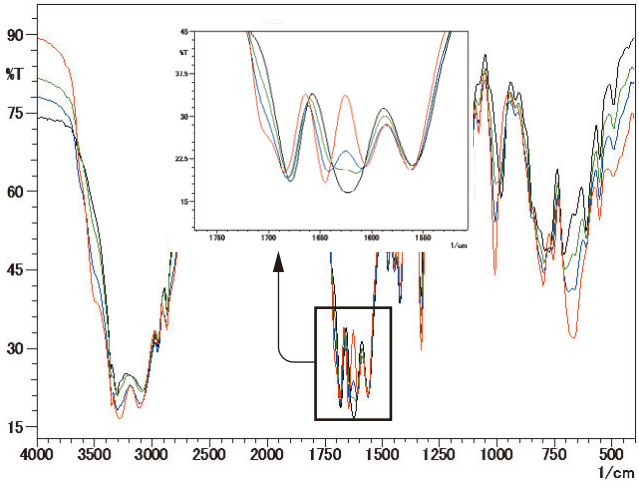

Fig. 6 Change in L-Arginine Spectrum due to Drying Time

6. Measuring Hydrochloride

When measuring hydrochlorides using the KBr pellet method, an ion-exchange reaction can occur between chlorine ions and bromine ions, resulting in different infrared spectra than should be obtained.
Fig. 7 shows results from measuring diphenhydramine hydrochloride using the KBr pellet and KCl pellet methods. These spectra show a clear difference in shape near 3000 cm^{-1}. In addition, there are also other differences in various locations within the low wavenumber region. The infrared spectrum for the KBr pellet method probably varied due to ion-exchange reactions.
For samples where such ion-exchange reactions can occur, the target infrared spectrum can be obtained by using potassium chloride (KCl) as a substitute.
(For more details, refer to Application News A370.)

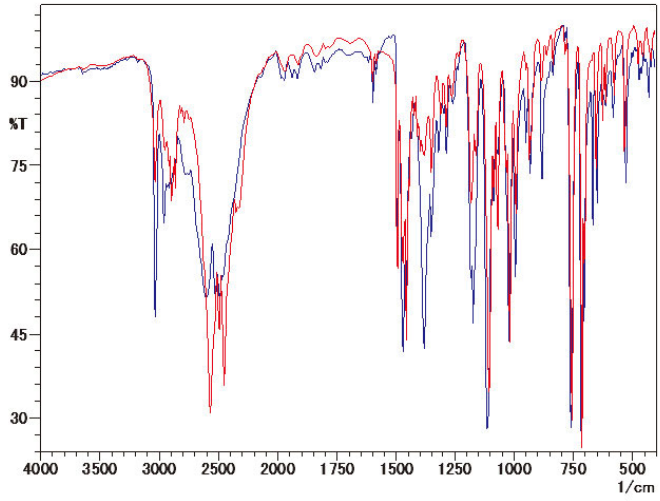

Fig. 7 KBr Pellets (Red Line) and KCl Pellets (Blue Line)

7. Summary

The KBr pellet method is known as a fundamental method for measuring the infrared absorbance of solids. However, KBr is a deliquescent prone to moisture effects and requires special care when used to analyze hydrochlorides, due to ion-exchange reactions and other factors. If such considerations are kept in mind, this method can be used to measure a wide variety of samples.

Q&A

Question

The KBr window pane on our liquid cell has turned a cloudy white color. Is there any problem continuing to use it the way it is?

Answer

KBr and NaCl windows absorb moisture readily, so when they are cleaned with chloroform, for example, they absorb some of the vaporization heat, then cool off. This process causes them to absorb moisture from the air and gradually turns the windows white. Fine surface scratches, or other innumerous bumps, can make it difficult to get the surface of measurement samples completely clean, leaving residue on the window. When such residue dries, it can appear white as well.
Windows with a cloudy surface can scatter light, which lowers the transmittance level. That effect can be large, especially toward the high wavenumber end of the spectrum. Over time, though, the clouding can progress to reduce transmittance across all wavenumber regions. In addition, a substance adhered to the window surface can affect absorption.
These effects can be cancelled out by using the window to measure the background, so they normally do not affect sample measurement results. However, if window clouding becomes too severe or uneven, the effects remain. As the effects of scattering or absorption become greater, the amount of light measured decreases, which can cause correspondingly worse S/N ratios.
Cloudy KBr and NaCl windows can be polished relatively easily. By removing the cloudy portion of the window surface, the window can be restored to almost as good as new. The procedure for polishing the window is indicated below.

1. **Sand off the cloudy portion of the window surface using coarse waterproof sandpaper (about 500 to 1000 grit).**
2. **Remove the rough surface that resulted on the window by using a finer grit waterproof sandpaper (about 1200 to 2000 grit).**
3. **Polish the window on deer skin soaked in methanol until clear.**
4. **Clean the window surface with a cleaning solvent, such as chloroform.**

Perform Steps 1 to 3 on a level table. Place the sandpaper or deer skin on the table and move the window in a circular motion. The waterproof sandpaper and other supplies can be obtained at a typical hardware store. Using the cell polishing equipment sold by Shimadzu is also an option.

Fig. 1 shows photos of a KBr window before and after polishing. Before polishing, the window appears cloudy and white, but polishing results in a clear shiny surface.

Note that KRS-5 windows are toxic and should not be polished.

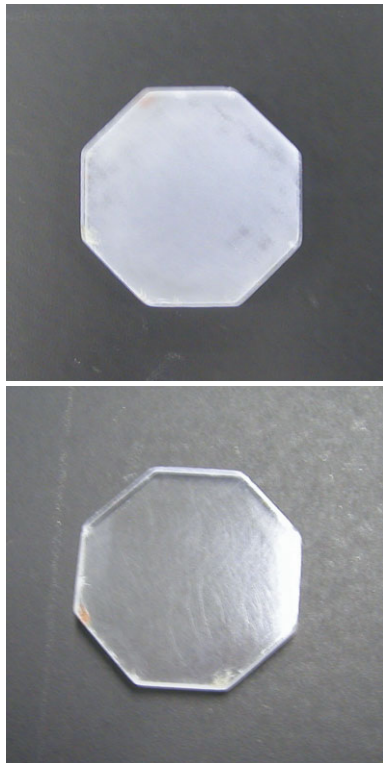

Fig. 1 Photos of KBr Window
Upper: Before Polishing, Lower: After Polishing

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**

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 3295-06008-15ANS