

FTIR TALK LETTER

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When making a measurement using the ATR technique, how deeply does the infrared light penetrate in the region of sample and prism contact?

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How to Read Power Spectra

No.2

~Checking Power Spectra~

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The shape of a power spectrum differs according to the window material and optics system in the accessories used for measurements and according to the type of detector used. The measurement environment also has a major influence due to superimposition of noise components from water vapor and carbon dioxide gas, for example. Therefore, the features of the power spectrum must be thoroughly investigated before starting the measurements. Now we will measure the power spectra of various accessories.

(1) Single-reflection Attenuated Total Reflection

Attenuated Total Reflection (ATR) measurements are conducted by placing the sample in close contact with the surface of a prism made of highly refractive material that transmits infrared light.

This method permits measurements using chemical pretreatment of the sample, without mechanical machining. Consequently, the number of accessories using this method is increasing as FTIR sensitivity increases.

Fig. 1 and Fig. 2 show the power spectra obtained from a single-reflection attenuated total reflection instrument (product name: MIRacle) with a ZnSe (zinc selenide) prism and Ge (germanium) prism mounted, respectively.

Both ZnSe (zinc selenide) and Ge (germanium) absorb IR at lower wave numbers, such that spectral data cannot be obtained below about 600 cm^{-1} .

As the ATR method measures the spectrum of IR light from the prism penetrating the sample, close contact between the sample and prism is extremely important. However, as germanium is relatively soft, with a Knoop hardness number of 24, its surface becomes scratched with use. The scratches cause poor contact with the sample and may result in the prism breaking due to the increased clamping force applied.

The diamond ATR accessory has diamond on the sample-contact surface, which allows the sample to be pressed strongly against the prism surface. This accessory allows the measurement of hard samples that are difficult to measure using conventional ATR.

Fig. 3 shows the power spectrum obtained from a single-reflection attenuated total reflection instrument (product name: DuraSampIR-II) with a ZnSe support element mounted below a diamond prism.

A moderate absorption between 2700 and 1500 cm^{-1} is observed in Fig. 3. This is the absorption of diamond, which can shift the baseline in this region during measurements of high-refractive-index samples.

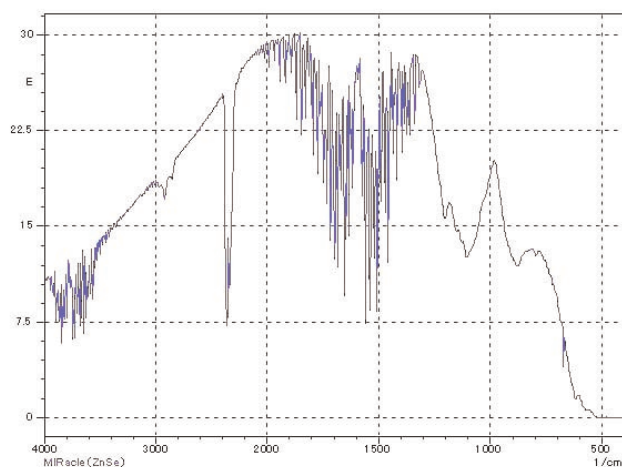


Fig. 1 MIRacle Power Spectrum: ZnSe Prism

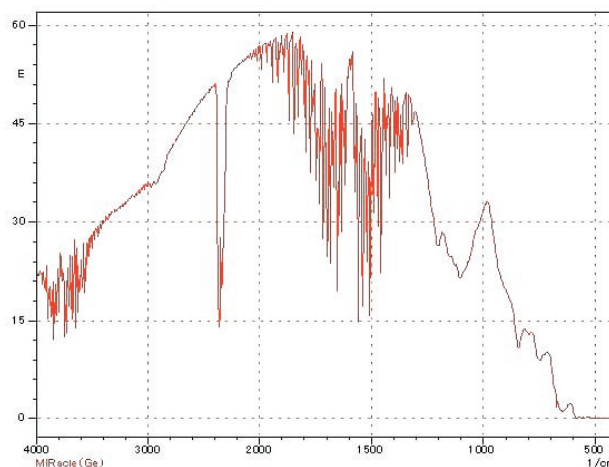


Fig. 2 MIRacle Power Spectrum: Ge Prism

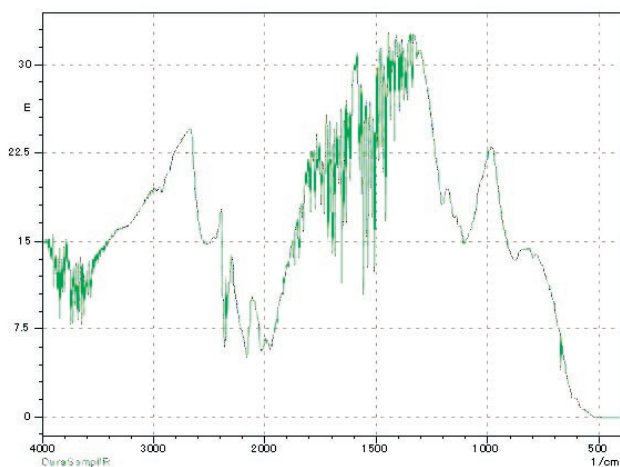


Fig. 3 DuraSampIR-1 Power Spectrum

(2) Gas Cell, Liquid Cell

An IR-transmissive window is essential to seal in a gas or liquid.

Various window types are used for different sample characteristics. However, it is important to check the quantitation peak positions and the transmission range of the window.

(3) IR Microscope

An IR microscope is useful for the measurement of minute samples.

Due to the high sensitivity required, an MCT detector is used to measure minute samples with an IR microscope.

As it can detect extremely low throughput of IR light, the MCT detector is suitable for light intensity attenuated measurements such as IR microscope measurements. However its wavelength-sensitivity characteristics offer no sensitivity below the cutoff frequency (wavelength at which sensitivity becomes zero).

Fig. 4 shows the power spectrum measured with an aperture set at 20 μm square.

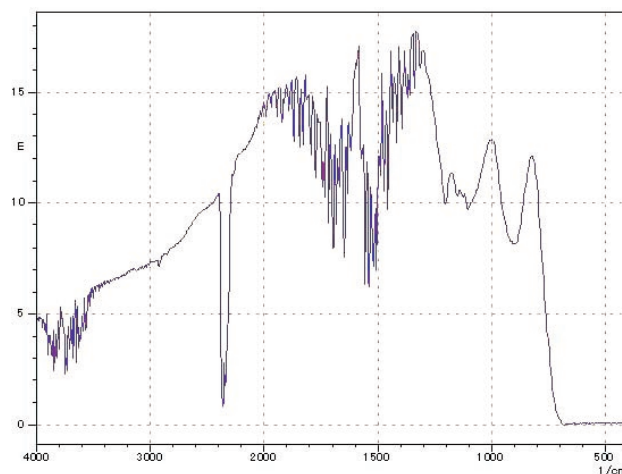


Fig. 4 Power Spectrum using a 20 μm x 20 μm Aperture Set (AIM-8800 IR Microscope)

ATR Precautions

No.2

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ATR Precautions (Part 1) introduced the partial peak shifts due to differences in refractive index of the prism and the spectral changes due to the clamping force between the sample and prism. ATR Precautions (Part 2) describes precautions when using the ATR method for quantitative analysis.

1. Using the Peak Intensity Ratio

The peak intensity (absorbance) of an absorption spectrum is proportional to the peak absorption coefficient, lightpath length, and concentration. The peak absorption coefficient becomes a constant when the target component for quantitation and its peak of interest are determined. In addition, the light path length is constant for the fixed cells often used for the quantitative analysis of a liquid sample by transmittance methods. Consequently, the spectral peak intensity obtained is proportional only to the concentration. This means that a calibration curve can be obtained from the peak intensity obtained by measuring a standard sample of known concentration and the target component concentration. Such methods are known as multipoint calibration-curve methods (including single-point). The calibration curve is normally linear, as the peak intensity is proportional to the concentration.

With ATR, the "light path length" can be thought of as the product of the light penetration depth and the contact area. The penetration depth value depends on the prism refractive index, angle of incidence, sample refractive index, and position (wave number) of the peak of interest. However, these are constant once the peak of interest and ATR instrument are determined. Consequently, if measurements are conducted with a constant contact area, the peak intensity becomes proportional to the concentration. In practice, calibration curves with excellent linearity can be obtained for liquid samples by dripping the sample over the entire face of the prism during measurement. However, the measurement of solid samples with a constant contact area is difficult, as the contact area between a solid sample and the prism surface is dependent on the clamping force and the hardness and shape of the sample. Such differences in contact area are corrected using the peak intensity ratio, which is the peak intensity of the target component divided by the peak intensity of a main component. Therefore, if the contact area doubles, the peak intensity of the target component doubles but the peak intensity of the main component also doubles, such that the peak intensity ratio remains unchanged. Consequently, it is necessary to create a calibration curve for the peak intensity and concentration when measuring solid samples by ATR.

2. Effects of Contact Status

As described above, the peak intensity ratio can be used to correct for differences in contact area. However, this does not mean that the peak intensity can be ignored completely. Spectra obtained with significantly different contact areas have differences that cannot be corrected by the peak intensity ratio because of poorer calibration curve linearity and poorer result reproducibility.

Such "differences that cannot be corrected by the peak intensity ratio" are differences in the contact status. The contact status can be thought of as the amount of clearance between the prism and sample. The contact status affects the peak intensity ratio.

Fig. 1 shows the spectra for polystyrene measured at three levels of clamping force using a DuraSamplIR single-reflection attenuated total reflection instrument. Changes in the clamping force caused differences in contact area, which are apparent in the large differences in peak intensity across the entire spectrum. Fig 2 shows the normalization results on the peak near 1500 cm^{-1} in the three spectra. An enlarged diagram of the peak near 3000 cm^{-1} appears at the top-left of Fig. 2. If the differences were due to contact area alone, all peak intensities should match after normalization with a single peak intensity. However, they do not match in Fig. 2. In addition, the peak intensities are reversed between the high- and low-wave number ends. The changes in the clamping force result in changes in the contact status, in addition to the contact area, which change the peak intensity ratio as well as the peak intensities in the overall spectrum. The spectrum for a weak clamping force exhibits a relatively small peak intensity at the high-wave number end – similar characteristics to those exhibited in an ATR spectrum measured with poor contact status. As the contact status affects the peak intensity ratio, measurement of the contact status is also required during quantitative analysis, in particular.

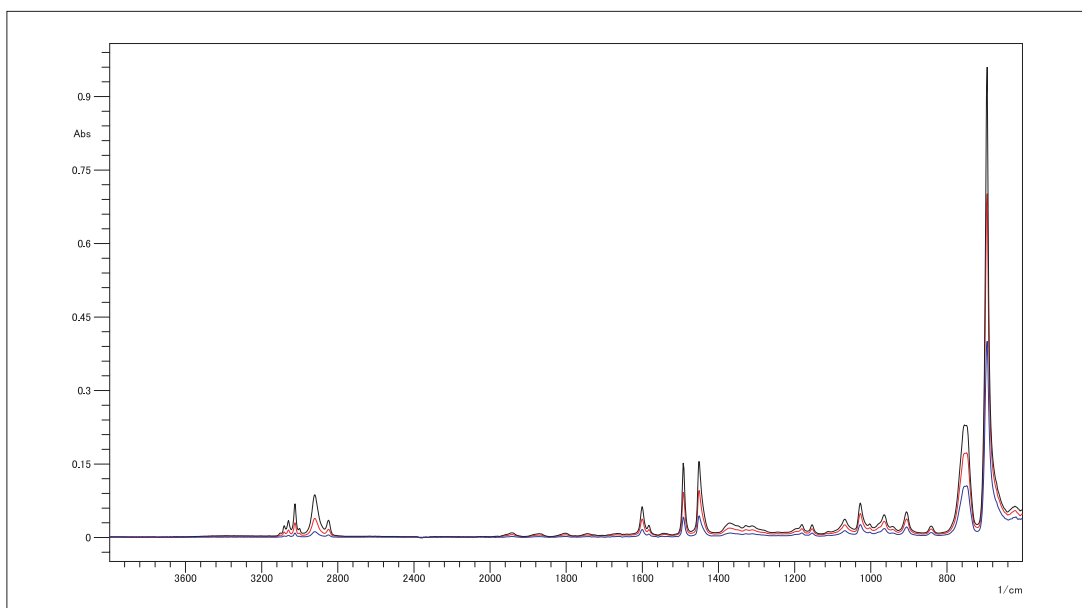


Fig. 1 ATR Spectra of Polystyrene

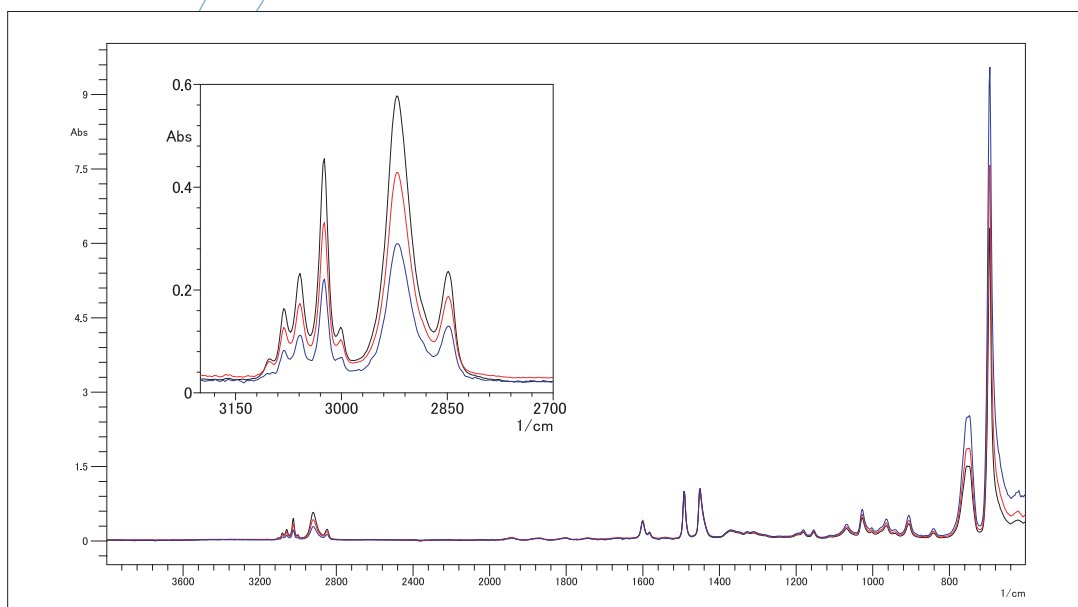


Fig. 2 Peak Normalization Near 1500 cm^{-1}

3. Reproducibility of Peak Intensity Ratio

So, how should we match the contact status? Also, what degree of reproducibility can be achieved? Analysis results on Ethylene vinyl acetate copolymer with an ATR probe optical fiber system are introduced below as an example. Sample measurements were conducted five times each with the clamping force adjusted to achieve a peak intensity near 2920 cm^{-1} of approximately 0.7 ABS and 0.3 ABS in monitor

measurement. Fig. 3 shows these ten spectra. The peaks near 2920 cm^{-1} and 2850 cm^{-1} are mainly C-H stretching vibrations of ethylene, while the peaks near 1735 cm^{-1} and 1235 cm^{-1} are vinyl acetate C=O and C-O vibrations, respectively. Consequently, the peak intensity ratio of the former and latter peaks changes due to the abundance ratio of vinyl acetate. The abundance ratio was constant for these measurements, as the same sample was measured multiple times.

The reproducibility was checked using the peak height ratio between the peaks near 1735 cm⁻¹ and 1235 cm⁻¹ and the peak near 2920 cm⁻¹. The results are shown in Table 1. Table 1 indicates that the Cv% value calculated individually for similar levels of peak intensity are significantly improved compared to the Cv% value calculated using all spectra.

Consequently, differences in contact status can be reduced and the reproducibility enhanced by matching the peak intensities during measurements. The improvement in reproducibility for peaks with high peak intensity is thought to be due to the lower effects of noise.

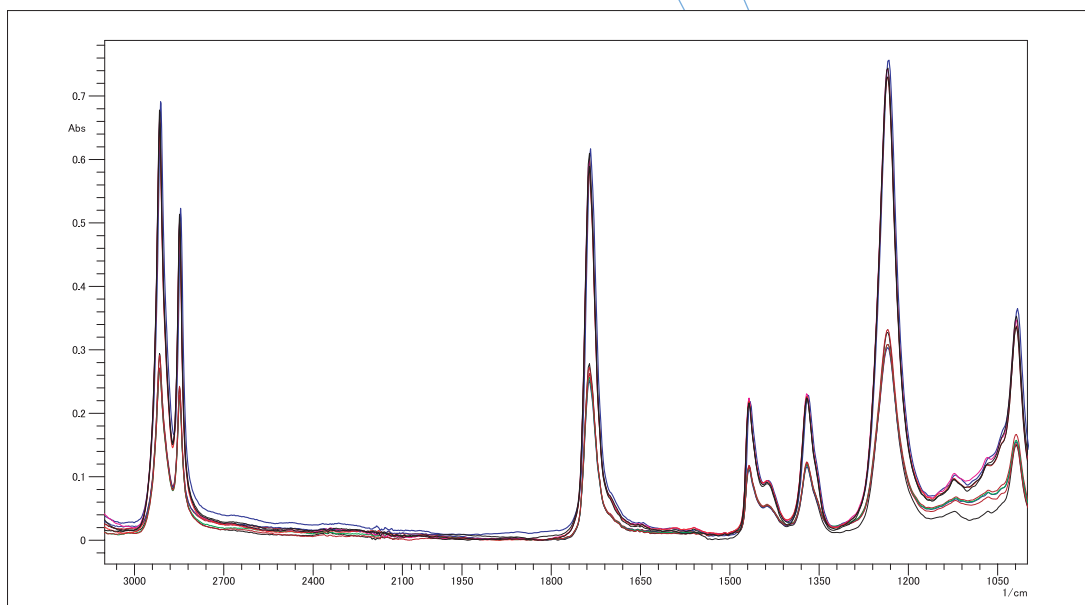


Fig. 3 ATR Spectra of Ethylene Vinyl Acetate Copolymer

Table 1 Calculated Results of Peak Height Ratio

| | Peak Height Ratio (*2920 cm ⁻¹) | |
|--------------------|---|----------------------|
| | 1735cm ⁻¹ | 1235cm ⁻¹ |
| 0.7ABS-1 | 1.045 | 1.225 |
| 0.7ABS-2 | 1.044 | 1.217 |
| 0.7ABS-3 | 1.042 | 1.222 |
| 0.7ABS-4 | 1.045 | 1.231 |
| 0.7ABS-5 | 1.059 | 1.235 |
| 0.3ABS-1 | 1.182 | 1.251 |
| 0.3ABS-2 | 1.164 | 1.251 |
| 0.3ABS-3 | 1.171 | 1.267 |
| 0.3ABS-4 | 1.157 | 1.267 |
| 0.3ABS-5 | 1.151 | 1.274 |
| Mean | 1.106 | 1.244 |
| Standard deviation | 0.063 | 0.021 |
| Cv% | 5.693 | 1.670 |
| 0.7ABS-1 | 1.045 | 1.225 |
| 0.7ABS-2 | 1.044 | 1.217 |
| 0.7ABS-3 | 1.042 | 1.222 |
| 0.7ABS-4 | 1.045 | 1.231 |
| 0.7ABS-5 | 1.059 | 1.235 |
| Mean | 1.047 | 1.226 |
| Standard deviation | 0.007 | 0.007 |
| Cv% | 0.652 | 0.580 |
| 0.3ABS-1 | 1.182 | 1.251 |
| 0.3ABS-2 | 1.164 | 1.251 |
| 0.3ABS-3 | 1.171 | 1.267 |
| 0.3ABS-4 | 1.157 | 1.267 |
| 0.3ABS-5 | 1.151 | 1.274 |
| Mean | 1.165 | 1.262 |
| Standard deviation | 0.012 | 0.011 |
| Cv% | 1.066 | 0.835 |

Corrected in 1800 to 1612 cm⁻¹ for 1735 cm⁻¹,
1300 to 1150 cm⁻¹ for 1235 cm⁻¹,
and 2990 to 2870 cm⁻¹ for 2920 cm⁻¹.

4. Conclusion

For quantitative analysis on a solid sample using ATR, we have explained the importance of:

- contact area correction → use peak intensity ratio; and
- matching the contact status → match peak intensities during measurement

The peak intensity ratio reproducibility check for ethylene vinyl acetate copolymer described here used the peak near 2920 cm⁻¹ as the correcting peak to determine the peak height ratio for the peaks near 1735 cm⁻¹ and 1235 cm⁻¹. However, the effects on the peak intensity ratio due to the differences in contact status increase as the distance from the peak position increase. Consequently, choosing a correction peak as near as possible to the target peak reduces the effects due to differences in contact status.

Question

**I want to do some gas analysis.
What types of cell are available?
What are the quantitation ranges
for various gases?**

Answer

Gas cells can be roughly divided into 5 cm and 10 cm cells for high concentrations and long-lightpath cells (from 1 to 100 m) for low concentrations. With both types, the sample gas is introduced into a cylindrical cell and measurements are conducted using a transmittance method. However, in a long-lightpath cell, the IR light is subjected to multiple reflections to increase the lightpath length.

The lightpath length is selected according to the concentration of the target component. Table 1 shows the quantitation upper and lower limits for the measurement of typical gases in a 1 m gas cell. (The actual quantitation upper and lower limits depend on the instrument and

conditions. The values here are the quantitation upper and lower limits calculated to give a largest peak intensity of 5 mABS and 2 ABS for measurements at 0.5 cm⁻¹ resolution.) As the peak intensity is proportional to the lightpath length, the upper and lower limit values for a 10 cm cell are ten times the values in the table. Use the table as a guide for selecting the lightpath length. An MCT detector is required to analyze a low-concentration gas in a long-lightpath cell. Materials used for gas-cell windows include NaCl, KBr, KRS-5, BaF₂, and CaF₂. Select the window material according to the type of sample gas and the measurement range. Table 2 lists the characteristics of each window material. Cells are made of glass or a metal such as aluminum. Some cells are coated internally to withstand corrosive gases such as HF.

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

| Component | Concentration (ppm) | | Component | Concentration (ppm) | |
|-------------------------------------|---------------------|-------------|------------------|---------------------|-------------|
| | Lower limit | Upper limit | | Lower limit | Upper limit |
| 1,3 Butadiene | 5.2 | 2,080 | HBr | 40.0 | 16,100 |
| 2-Methyl Pentane | 3.5 | 1,410 | HCN | 1.4 | 578 |
| Acetaldehyde | 10.0 | 4,060 | HCHO | 4.3 | 1,710 |
| Acetone | 9.4 | 3,760 | HCOOH | 3.8 | 1,500 |
| Acetylene | 0.6 | 230 | HNO ₂ | 0.9 | 363 |
| Benzene | 0.9 | 340 | HNO ₃ | 3.6 | 1,450 |
| CCl ₂ F ₂ | 0.9 | 347 | HS | 1420.0 | 570,000 |
| CCl ₃ CF ₃ | 2.9 | 1,175 | Isoprene | 5.4 | 2,180 |
| CCl ₃ F | 0.9 | 360 | Methane | 6.9 | 2,750 |
| CCl ₄ | 0.9 | 357 | Methanol | 5.4 | 2,160 |
| CClF ₂ CClF ₂ | 2.3 | 920 | NH ₃ | 2.7 | 1,090 |
| CF ₄ | 0.1 | 36 | n-Hexane | 5.0 | 2,010 |
| CH ₃ COOCH ₃ | 5.3 | 2,130 | NO | 18.0 | 7,040 |
| CH ₃ COOH | 4.2 | 1,670 | NO ₂ | 2.5 | 1,000 |
| CHCl ₃ | 1.8 | 739 | N ₂ O | 2.7 | 1,090 |
| CHClF ₂ | 1.8 | 705 | n-Pentane | 6.6 | 2,640 |
| CO | 9.4 | 3,750 | Ozone | 10.0 | 4,070 |
| CO ₂ | 1.9 | 770 | Phosphine | 39.0 | 15,800 |
| Cyclohexane | 1.3 | 500 | Propane | 4.0 | 1,611 |
| Diethyl Ether | 4.9 | 1,940 | SF ₆ | 0.2 | 70 |
| Ethane | 7.8 | 3,100 | SO ₂ | 5.2 | 2,060 |
| Ethanol | 19.0 | 7,500 | Styrene | 7.6 | 3,020 |
| Ethylene | 4.2 | 1,680 | Toluene | 6.7 | 2,680 |
| H ₂ O | 24.0 | 9,720 | o-Xylene | 4.4 | 1,740 |
| HF | 2.0 | 800 | m-Xylene | 7.5 | 3,006 |
| HCl | 7.8 | 3,120 | p-Xylene | 7.7 | 3,100 |

Table 2 Gas Cell Window Materials and Their Characteristics

| Window material | Measured wave number range | Transmittance (%) | Water-resistant |
|------------------|----------------------------|-------------------|-----------------|
| KBr | 40,000-340 | 90 (5mm) | × |
| NaCl | 50,000-600 | 90 (5mm) | × |
| KRS-5 | 16,600-250 | 70 (2mm) | ○ |
| BaF ₂ | 50,000-770 | 90 (1mm) | ◎ |
| CaF ₂ | 50,000-1,100 | 95 (3.6mm) | ◎ |

Comprehensive Support for WEEE & RoHS Compliance

In accordance with the EU (European Union) Directives on Waste Electrical and Electronic Equipment (WEEE), the Restriction of Hazardous Substances in Electrical and Electronic Equipment (RoHS) will be implemented from 1 July 1 2006 on six specified hazardous substances: cadmium, lead, mercury, hexavalent chromium, polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE).

As a result, major Japanese electrical manufacturers participating in the Japan Electronics and Information Technology Industries Association (JEITA) have listed 15 Level A substances (including the six designated in RoHS) and are urgently implementing measures for them. As a manufacturer of general analytical instruments, Shimadzu helps customers comply with these regulations by providing them with the required analytical and measuring instruments and application techniques.

The X-ray Fluorescence Spectrometer, UV-VIS Spectrophotometer, and Fourier Transform Infrared Spectrophotometer are the recommended analyzers for the screening of toxic metals (cadmium, lead, and mercury), hexavalent chromium, and brominated fire retardants (PBB and PBDE), respectively.

Shimadzu has successfully developed and marketed an optional program for the analysis of brominated fire retardants. This is an interactive program that simplifies the sequence of operations from measurement to evaluation and can be used by anyone.

The Japan Business Council in Europe (JBCE) has adopted the Shimadzu method for the analysis of brominated fire retardants, and is currently promoting it to the European Commission.

Screening Analysis of Toxic Metals (Cd, Pb, Hg)



EDX-700HS
X-ray Fluorescence Spectrometer

Accurate Quantitative Analysis of Toxic Metals (Cd, Pb, Hg)



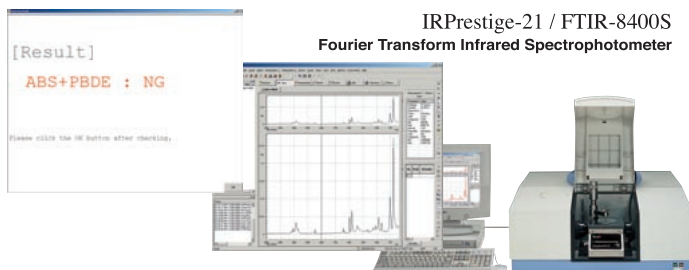
AA-6300
Atomic Absorption/Flame Emission Spectrophotometer

Selective Analysis of Hexavalent Chromium



UVmini-1240
UV-VIS Spectrophotometer

Screening Analysis of Toxic Brominated Fire Retardants



IRPrestige-21 / FTIR-8400S
Fourier Transform Infrared Spectrophotometer

The result above is the evaluation of brominated fire retardants measured in a TV cabinet. It shows that the cabinet is ABS containing the restricted substance PBDE.

Accurate Quantitative Analysis of Toxic Brominated Flame Retardants



GCMS-QP2010
Gas Chromatograph Mass Spectrometer



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