

# Infrared Emission Spectroscopy and Its Application to Analyze Non-smooth Metallic Materials Surface

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## Abstract

*I tried to apply the Infrared emission spectroscopy to identify the organic substances on the non-smooth or non-flat metallic surface. The organic substances like oils, fats and coating materials play an important role to enhance the lubricant property just like a processing property of steel and to protect it from corrosion. An organic substance on the flat metallic materials like a steel plate can be analyzed by the spectroscopic analysis that uses reflection method. But, the organic substances on non-flat materials like a fiber, wire rod, ball and powder must be removed and then preceded to various analyses. On the other hand, this infrared emission spectroscopy method can practice contactless analysis of the organic substances getting infrared spectral information just by heating up the target samples and references without any pre-treatment. And this emission is isotropic; therefore it can easily detect the organic substances of the non-flat surface of the metallic surface with limited influence of the surface shape of a material. This method is very simple and easy to expand in application.*

## 1. Introduction

Infrared spectroscopy (IR) is an analytical technique that uses the spectral information characteristics of individual substances. In terms of analytical chemistry, the wave number (wavelength) range used in IR is between 4,000 and 400  $\text{cm}^{-1}$  (2.5 and 25  $\mu\text{m}$ ). The lower-wave-number (longer-wavelength) range is called the far-infrared region, and the higher-wave-number (shorter-wavelength) region is called the near-infrared region. Since the wave-number region for IR coincides with the region of molecular vibration energy, IR is widely used for the structural analysis and qualitative and quantitative analysis of various substances, mainly organic compounds.

Apparatus for IR can largely be divided into two types. One is the dispersive IR spectrophotometer that uses a diffraction grating, etc. for wavelength dispersion of an infrared ray for measurement.

The other is the Fourier transform infrared spectrophotometer (FT-IR) that modulates an infrared light by an interferometer, measures the interference waveform, and subjects it to a Fourier transform to obtain a spectrum. Today, for the reasons given below, FT-IR is applied so widely that it has become synonymous with IR spectrometry. The reasons for this are as follows: (1) Since FT-IR requires no slits, infrared rays can be used efficiently; (2) since a laser beam is used to sample synchronous data, the wave number accuracy is high; and (3) since the time required to measure a single spectrum is no longer than one minute, there is room to improve the signal-to-noise (S/N) ratio through repetitive measurement (i.e., integration of measurement results).

As IR measurement methods, there are the transmission, reflection, and special methods. Infrared emission spectroscopy is classified as a special method.

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The transmission (absorption) method is one in which an infrared ray is irradiated onto a sample to measure the light transmitted through the sample and the transmittance spectrum is then obtained from the quotient of the spectrum before irradiation divided by the spectrum after irradiation. This method is applied to gases, liquids, thin films, powders, etc. On the other hand, to measure a substance on the surface of a highly reflective material, the reflection (absorption) method is used. In the reflection method, both the light reflected directly from the base material and the light reflected through the substance (sample) on the base material surface are measured, and the reflectance spectrum is obtained from the quotient of the former reflected light divided by the latter. In the reflection method, too, the light that passes through the sample and is reflected from the base material surface is measured. Therefore, the information obtained from the sample is absorption spectrum information.

Infrared emission spectroscopy is a method in which a sample is energized by heating and so on, and the infrared light emitted from the sample is measured to obtain a spectrum. This method of measurement is entirely different from the transmission and reflection methods. Emission is a transition opposite in direction to absorption. A highly absorptive substance shows a high degree of emittance, and the number of waves in an emission band (peak) is the same as for an absorption peak.<sup>1)</sup> In the case of emission, however, the probability of there being an excited state is low and hence, the emission intensity is feeble. The spread of highly sensitive FT-IR has made it possible to measure even these weak emissions.<sup>2, 3)</sup>

Infrared emission spectroscopy utilizes the contrast between the sample and the base material and is very useful in measuring an organic thin film of low emission intensity on the surface of a metallic material. This method is applicable to rough metallic surfaces, powders, spherical objects, wires, and so on because (1) the infrared emission is isotropic and is hardly affected by the surface profile of the base material, and (2) it permits nondestructive, noncontact measurement of the sample and so on. In fact, however, there are only a few reports on the practical application of the method.

In the present study, it was found possible to put infrared emission spectroscopy to practical use by increasing the contrast between the sample and the metallic base material. The study results are described below.

## 2. Experimental System

### 2.1 Infrared spectrophotometer

Equipment: JASCO Corporation's Herschel FT/IR-610 FT-IR  
(with an external light admission window)

Detector: MCT (mercury-cadmium-tellurium) detector

Resolution:  $4\text{ cm}^{-1}$

Number of scan times: 200 (All IR emission spectra were measured with 200 scan times.)

The Herschel FT/IR-610 FT-IR was provided with a window to admit infrared emission from outside the equipment. The FT-IR is capable of efficiently diffracting parallel beams let in through the window. Since the infrared emission is weak, an MCT detector, which operates at the temperature of liquid nitrogen ( $-196^\circ\text{C}$ ) and has high sensitivity, was used.

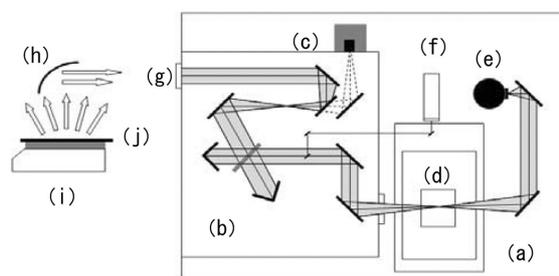
### 2.2 Sample heater

To heat the sample, AS ONE Corporation's Digital Hot Plate HP-1S was used.

### 2.3 System configuration for infrared emission spectroscopy

The system configuration for the experiment is shown in Fig. 1. Photo 1 shows the hot plate and the infrared emission collecting

optics system. The experimental system is extremely simple and easy to operate since all that is necessary for measurement is to heat the material on the hot plate. The infrared emission from the sample on the hot plate is reflected by the collecting mirror and admitted into the FT-IR where it is separated into its spectral components. Infrared emission spectra were obtained as follows. First, the base material placed on the hot plate was heated to the prescribed temperature and the single-beam spectrum of the reference emission was measured. After that, the sample applied to the base material was heated to the same temperature and the single-beam spectrum of the sample emission was measured. Finally, the ratio of sample emission to reference emission was calculated. Thus, the infrared emission spectrum is calculated from the single-beam spectrum ratio between the sample emission and the reference emission. In infrared emission spectroscopy, therefore, it is advantageous to use an FT-IR with a high degree of wave-number accuracy.



(a) FT-IR, (b) Interferometer, (c) Light source, (d) Sample room, (e) MCT Detector, (f) He-Ne Laser, (g) External lighting window, (h) Condensing mirror, (i) Hot plate, (j) Sample

Fig. 1 Schematic diagram of infrared emission spectrophotometer

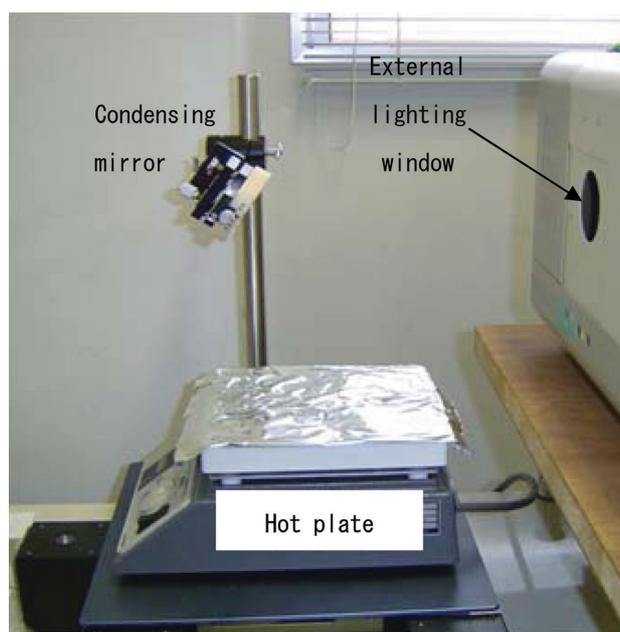


Photo 1 Infrared emission collecting parts

### 3. Measurement of Infrared Emission Spectra and Application of Infrared Emission Spectroscopy to Analyze Rough Metal Surfaces

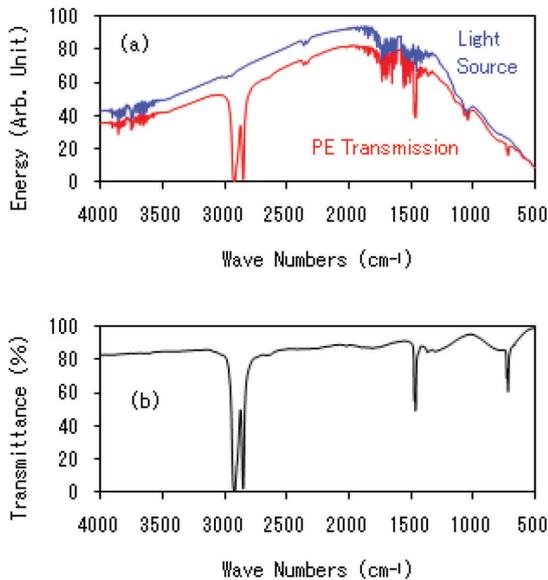
#### 3.1 Measurement of infrared emission spectra

When measuring an infrared absorption spectrum, it is common practice to admit infrared light from the light source into an interferometer for modulation and to detect the light that passes through the sample set in the sample room. The infrared absorption spectrum is expressed as the ratio in intensity between the light from the light source without the sample (reference light) and the light that has passed through the sample (sample light).

Fig. 2 (a) shows the single-beam spectra of light from a light source (reference light) and the light (sample light) that has passed through a sample (polyethylene film: PE 10  $\mu$  m in thickness), and Fig. 2 (b) shows the infrared absorption spectrum of the PE (10  $\mu$  m) calculated from the single-beam spectra (sample light/reference light). Fig. 2 (b) reveals anti-symmetric and symmetric stretching vibrations of  $-CH_2-$  at wave numbers 2,920  $cm^{-1}$  and 2,850  $cm^{-1}$ , respectively, a bending vibration at wave number 1,460  $cm^{-1}$ , and a rocking vibration at wave number 720  $cm^{-1}$ . From this spectrum, it can be seen that the sample is polyethylene.

In infrared emission measurement, no light source is used. Instead, the light emitted from the sample is admitted into an interferometer for modulation and then detected directly. The infrared emission spectrum is obtained from the ratio in intensity between the emission from the base material, which corresponds to the reference light for absorption spectra, and the emission from the sample on the base material surface.

Fig. 3 (a) shows single-beam spectra of aluminum foil (reference light) and PE film (10  $\mu$  m in thickness; sample light) applied to the



(a) Single beam spectra of light source and polyethylene (10  $\mu$  m) film transmission  
 (b) Infrared absorption spectrum of PE (10  $\mu$  m) calculated from single beam spectra

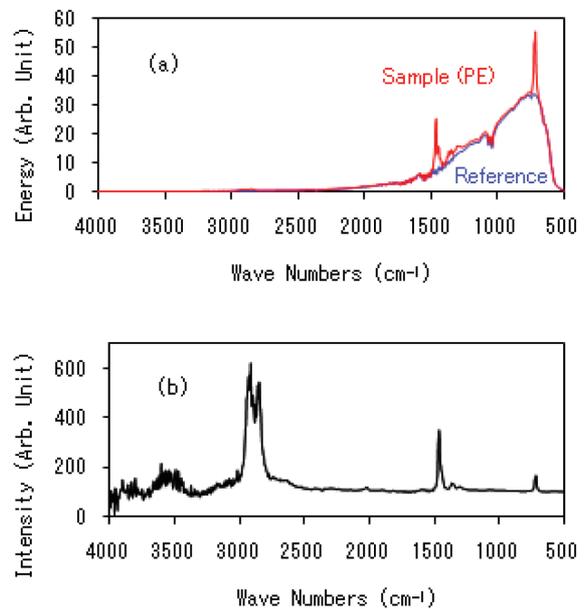
Fig. 2 Single beam spectra of light source and polyethylene (10  $\mu$  m) film transmission and infrared absorption spectrum of PE (10  $\mu$  m)

aluminum foil surface when both were heated to 100°C, and Fig. 3 (b) shows the infrared emission spectrum of the PE film obtained from the single-beam spectra of the aluminum foil and PE film. In the single-beam spectra, the sample light has higher energy than the reference light at wave numbers that coincide with PE molecular vibrations. The infrared emission spectrum of the PE (10  $\mu$  m in thickness) calculated from the sample light/reference light is the same in peak wave numbers as the infrared absorption spectrum of PE shown in Fig. 2 (b), and the intensities are opposite in direction. Thus, the infrared emission spectrum can easily be measured from the contrast between the sample light and the reference light.

#### 3.2 Infrared emission from base materials

For infrared emission spectra, the contrast between the emission from the base material and the emission from the sample is important. Therefore, we studied the infrared emission behavior of six different base materials: (a) Al sheet (1 mm in thickness), (b) SUS 304 sheet (1 mm in thickness), (c) electrogalvanized steel sheet (EG, 0.8 mm in thickness), (d) hot-dip galvanized steel sheet (GI, 0.8 mm in thickness), (e) glass sheet (2 mm in thickness), and (f) polytetrafluoroethylene (PTFE) sheet (1 mm in thickness), at temperatures between 50°C and 200°C.

Fig. 4 shows single-beam spectra of the six types of base material. With a rise in temperature, all the base materials show higher infrared emission energy. However, the infrared emission energies of the Al sheet, EG, and GI (metals) are relatively low, whereas those of the glass sheet (oxide) and PTFE sheet (organic substance) are high. The emission energies of the glass sheet and PTFE sheet at 200°C are so high that both materials radiate heat when you draw your hand near towards them. By contrast, none of the metallic materials feels hot.



(a) Emission single beam spectra of Al-foil and PE (10  $\mu$  m) film at 100°C heating  
 (b) Infrared emission spectrum of PE film (Sample / Reference)

Fig. 3 Infrared emission spectrum of PE (10  $\mu$  m) film on Al-foil (100°C)

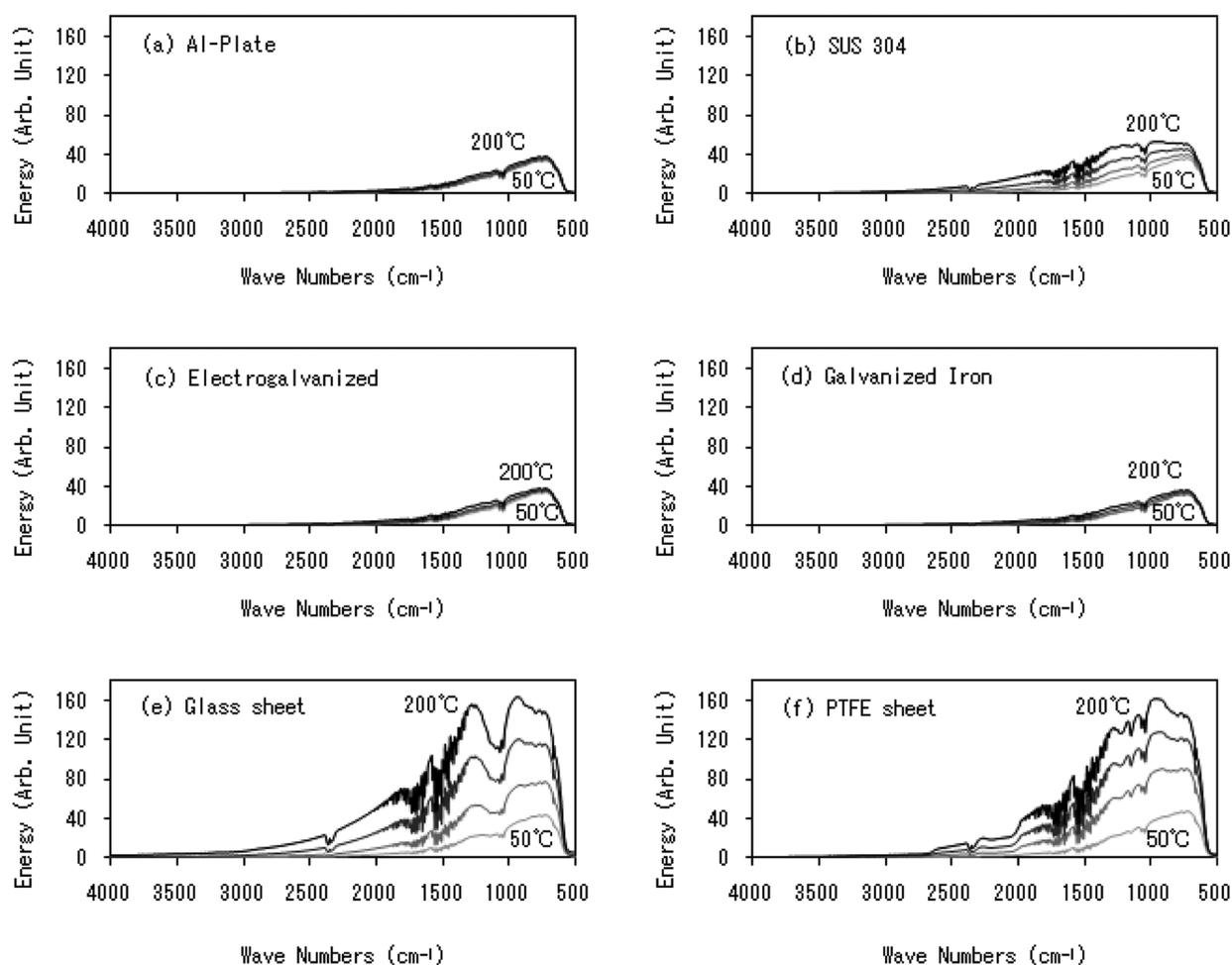


Fig. 4 Emission single beam spectra of various substrate materials

The emission energy of the SUS 304 sheet is lower than that of the oxide and organic substance but somewhat higher than that of the Al sheet and galvanized sheet. The reason for this is probably that emission from the extremely thin passive-state film (oxide film) on the surface of SUS 304 is slightly stronger than that from the metal. It may be said, therefore, that SUS 304 is a “warm” metallic material. Strong emission means intense absorption. A comparison of infrared reflectivity between SUS 304 sheet and Al, EG, and GI sheets shows that SUS 304 has lower reflectivity since it has higher absorptivity.

Fig. 5 shows infrared emission/absorption spectra of PE (10  $\mu$  m in thickness) applied to the surface of each of four base materials: (a) Al sheet, (b) SUS 304 sheet, (c) glass sheet, and (d) PTFE sheet, measured at 100°C. For each of the Al and SUS 304 sheets, an infrared emission spectrum is shown; for each of the glass and PTFE sheets, an infrared absorption spectrum is shown. The peak intensity of the infrared emission spectrum is higher when the base is Al sheet than when the base is SUS 304 sheet. Namely, the spectrum is determined by the contrast in emission between the base material and the sample. Thus, when a metallic base material having low emission intensity is used, the spectrum of the organic substance applied to the surface becomes an emission spectrum, whereas when an oxide or organic substance having high emission intensity is used as the base material, the spectrum obtained becomes an absorption spec-

trum. Besides, even with the same metallic base material, the spectral intensity of emission spectra varies according to the slightest difference in emission intensity. Thus, as long as due attention is paid to the characteristics of the base material, infrared emission spectroscopy may be said to be one of the most effective techniques for analyzing the surfaces of metallic materials.

### 3.3 Influence of temperature on the infrared emission spectrum

Since an infrared emission spectrum is measured with the sample heated, we studied the influence of temperature on it. Fig. 6 shows the infrared emission spectra of polyvinylidene chloride (PVDC) film applied to an Al sheet, obtained at 50°C, 60°C, 80°C, and 100°C. When an Al sheet is used as the base material, an emission spectrum of the fingerprint region can be obtained even at 50°C. This emission spectrum provides information sufficient for a qualitative analysis of a sample. With a rise in temperature, the peak intensity of the emission spectrum increases and the S/N ratio on the higher-wavenumber side improves. Taking into account the heat resistance of the organic substance (PVDC), the practical measurement temperature is considered to be about 100°C at most.

### 3.4 Influence of sample thickness on the infrared emission spectrum

In order to study the possibility of applying infrared emission spectroscopy for the quantitative analysis of samples, we measured the infrared emission spectra from samples of different thicknesses.

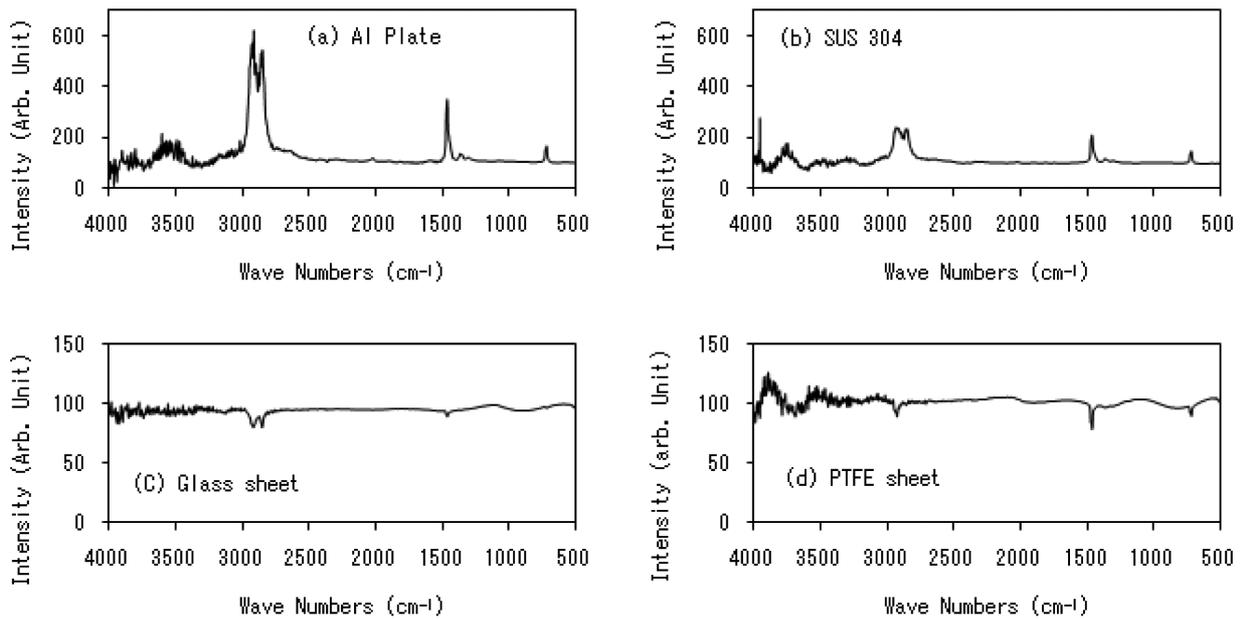


Fig. 5 Infrared emission / absorption spectra of PE on various substrate materials

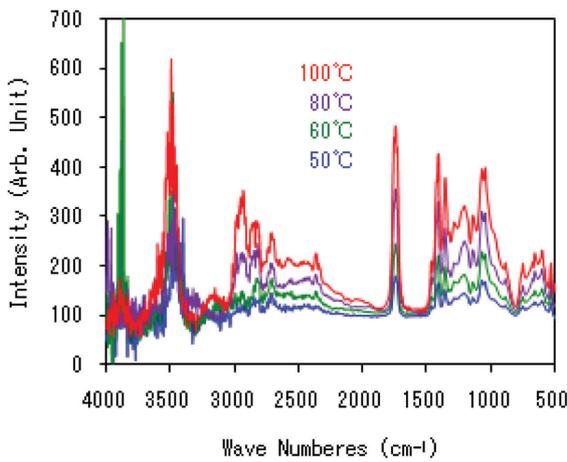


Fig. 6 Temperature influence to infrared emission spectra (polyvinylidene chloride: 20 μm)

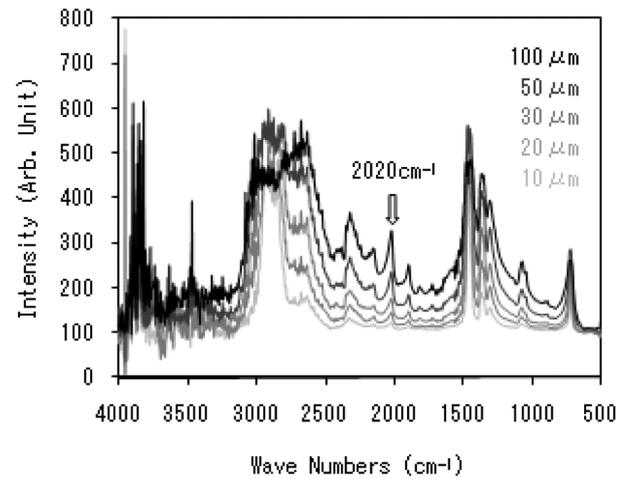


Fig. 7 Influence of sample thickness on infrared emission spectra

Fig. 7 shows the infrared emission spectra of PE samples that differ in thickness. The sample thickness was varied by changing the number of sheets of PE film (10 μm) applied to an Al sheet as a base material. The sample thicknesses were 10, 20, 30, 50, and 100 μm and the measuring temperature was 100°C.

Even when the sample thickness is 20 μm, emissions at wave numbers 2,920, 2,850, 1,460, 1,380, and 720 cm<sup>-1</sup>, which are characteristic absorption peaks of -CH<sub>2</sub>-, show a tendency whereby the peak intensity is saturated and the peak width increases under the influence of self-absorption. Therefore, there is no correlation between peak intensity (area) and sample thickness. On the other hand, when the peak is weaker than the characteristic absorption, like the peak intensity at 2,020 cm<sup>-1</sup> shown in Fig. 7, a linear relationship between the peak intensity and the sample thickness passing through the origin as shown in Fig. 8 can be obtained when the sample thickness is 50 μm or less. If such a calibration curve can be readied beforehand, it is considered possible to apply it in the quantitative analysis

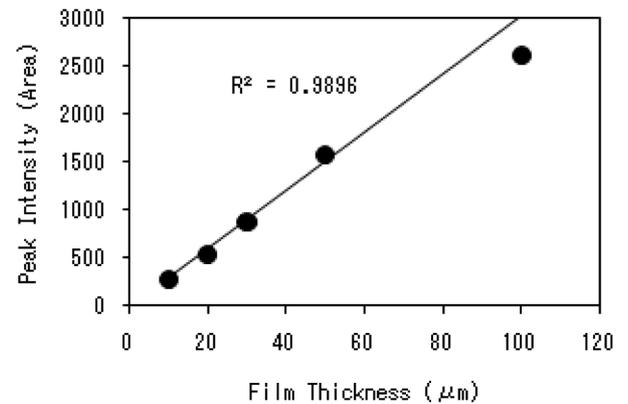


Fig. 8 Relation between sample thickness and infrared emission intensity (2,020 cm<sup>-1</sup>)

of a sample. Since the characteristic absorption peak is intense in both emission and absorption, it is strongly influenced by such self-absorption. However, if the sample thickness is made less than  $10 \mu\text{m}$ , it is considered possible to restrain the peak saturation, etc. and thereby obtain emission spectra that permit quantitative analysis.<sup>1,4,5)</sup> Thus, infrared emission spectroscopy is suited to analyzing extremely thin films of organic matter on the surfaces of metallic materials.

### 3.5 Application of infrared emission spectroscopy to analyze rough metal surfaces

When analyzing the surface of a metal utilizing spectroscopy, it is common practice to apply one of the reflection methods. In infrared spectroscopy, too, the regular reflection method, the reflection-absorption spectroscopy (IR-RAS) method using a large angle of incidence, the attenuated total reflection (ATR) method utilizing the difference in reflective index between the sample and the high-reflective-index medium, and so on are employed for the analysis of metal surfaces. However, these methods are applicable only to metal surfaces that are flat and smooth. Powders, spherical objects, fibers, wire rods, and other materials that diffuse or scatter incident light cannot be measured by the reflection method. The solvent extraction method or some other suitable method is used for their analysis.

Infrared emission spectroscopy is characteristic in that the emission is isotropic and is hardly influenced by the surface profile of the base material. Therefore, as long as a base free of the organic matter to be analyzed is available, it is possible to obtain an infrared emission spectrum from the contrast between the sample and the base material. In this way, infrared emission spectroscopy can be applied to analyze even rough metal surfaces. Here, a couple of examples in which infrared emission spectroscopy was applied in order to analyze the surface of a stainless steel wire and a stainless steel ball, respectively, are introduced.

#### 3.5.1 Analysis of oleic acid on a stainless steel wire surface

There are cases where oleic acid or some other fatty acid is applied as a lubricant or anti-rust oil to the surface of a metallic material during or after working.<sup>6)</sup> **Photo 2** shows the analysis conditions of a stainless steel wire of 0.8 mm in diameter. Samples with and without oleic acid were prepared by cutting the stainless steel wire to about the length of the hot plate. They were placed on the hot plate and heated to  $100^\circ\text{C}$ . Then, single-beam spectra of the reference light and sample light were measured and the emission spectrum was calculated from the ratio between them. With the ceramic top of the hot plate exposed, the emission intensity becomes extremely high. By



Photo 2 Analysis of wire surface by infrared emission spectrometry

covering the ceramic surface with aluminum foil, it is possible to restrain emission from the top. This facilitates measurement of the emission spectrum of the sample.

**Fig. 9** (a) shows the infrared emission spectrum of the stainless steel wire, and **Fig. 9** (b) shows the absorption spectrum of the oleic acid. The peak positions in the emission spectrum and absorption spectrum agree fairly well. From the infrared emission spectrum, it can be seen that it is a fatty acid that has adhered to the stainless steel wire.

#### 3.5.2 Analysis of silicone oil on surface of a stainless steel ball

There are also cases where silicone oil is applied to the surface of

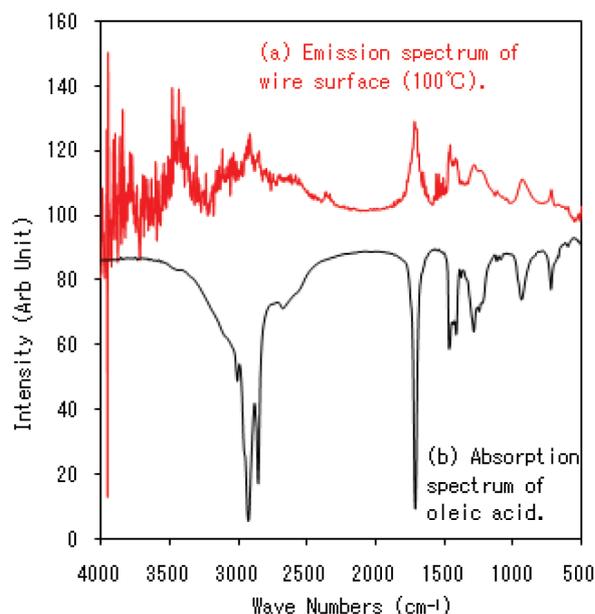


Fig. 9 Infrared emission spectrum of wire surface and absorption spectrum of oleic acid

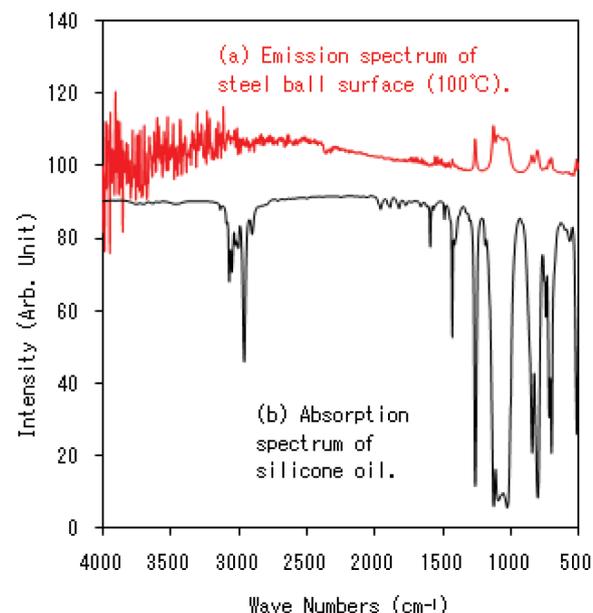


Fig. 10 Infrared emission spectrum of stainless steel ball surface and absorption spectrum of silicone oil

a steel material as a water repellent, film release agent, lubricant, and so on.<sup>6)</sup> Fig. 10 (a) shows an infrared emission spectrum of the surface of an 1/8-inch-diameter stainless steel ball to which silicone oil was applied. From the stainless steel ball surface area and the silicone oil specific gravity, the thickness of the silicone oil film is estimated to be approximately 10  $\mu$  m. As a rule, measurement of the stainless steel ball was conducted in the same way as measurement of the stainless steel wire. Samples with and without silicone oil were placed on the hot plate and heated to 100°C and an emission spectrum was then calculated from the single-beam spectra of the reference light and sample light.

Stainless steel balls roll about easily. By spreading them neatly in a sample dish made of aluminum foil, it is possible to prevent them from rolling about. The infrared emission spectrum of the silicone oil agrees well with the absorption spectrum shown in Fig. 10 (b). Hence, the infrared emission spectrum is sufficient for a qualitative analysis of the silicone oil. If the ball is not made of stainless steel but has a plated steel surface, the contrast in the infrared emission spectrum becomes stronger, making it easier to analyze the sample surface.

#### 4. Conclusion

We attempted to apply infrared emission spectroscopy as a technique to analyze organic matter on irregular and rough surfaces of steel materials easily and accurately and with high sensitivity. As a result, it was found that infrared emission spectroscopy provides an effective way to analyze an extremely thin film of organic matter (10  $\mu$  m or less) on the surface of steel, that by heating a base material and a material with adhered organic matter on a hot plate to about 100°C, it is possible to easily obtain an infrared emission spectrum, and that when the organic film is extremely thin, the emission intensity is proportional to the film thickness. Since its emission is isotrop-

ic, infrared emission spectroscopy can be applied to analyze even rough surfaces of steel materials. Examples of its application to the analysis of fatty acid on the surface of stainless steel wire and silicone oil on the surface of a steel ball are also introduced. The equipment required for measuring infrared emissions is very simple and subject to only a few limitations on the size and shape of samples. Furthermore, infrared emission spectroscopy allows noncontact measurement of samples. Therefore, it will become possible to apply the technique in remote measurement and on-line measurement<sup>7)</sup> with optimization of optics systems and so on.

Infrared emission and infrared absorption complement each other. A good absorber is a good emitter. Emission and absorption also influence the temperatures of materials and the environment. For example, a 200°C metallic material does not raise the ambient temperature by radiation, but an oxide or organic substance heated to 200°C causes the ambient temperature to rise. Infrared emission spectroscopy can also be applied to the analysis of such phenomena. Thus, it has a wide scope of application.

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