Analysis of Thermal Decomposition Behavior of Coals Using High Temperature Infrared Spectrophotometer System

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Abstract

Thermal decomposition behaviors of coals were measured by high temperature infrared (IR) spectrophotometer system. It is important to know the thermal decomposition process of coals in order to understand their chemical properties during coking reaction. The coal samples were heated from 50℃ up to 600℃ in an N_2 ambience, and IR spectra were measured in transmission mode every 10℃. The changes of IR spectra as sample heating were well obtained. Especially, high temperature region over 400℃, a peak intensity based on aliphatic C-H bond was decreased. While a peak intensity based on aromatic C-H bond was stable below 600℃. At least, two type's hydroxyl groups were obtained in coal samples. One type is dehydrate below 400℃, another type is stable in high temperature region over 400℃. Additionally, dehydrate behavior of kaolin which is mineral matter in coal was well obtained. Dehydrate temperature of kaolin is used for good monitor of sample temperature. The high temperature IR system can measure of functional groups during high temperature region, and useful for analysis of thermal decomposition behavior of coals.

1. Introduction

Coking coal for steelmaking begins to soften and melt at around 400℃, shows maximum fluidity at about 450℃ and re-solidifies at about 480℃. Since this behavior of coking coal is considered to have much to do with the strength and other qualities of coke, it has been analyzed using various methods, such as thermal analysis[1], dynamic viscosity/elasticity analysis[2] and nuclear magnetic resonance (NMR) analysis[3,4]. Infrared spectroscopy (IR), which is very effective for analyzing the functional groups of organic compounds, is also used in the structural analysis of coal[5,6]. As means of measuring IR spectra at high temperatures, combinations of the thermal analysis method[7] with a diffusion reflection method[8] or suchlike are known. However, at these high temperatures above 400℃, IR spectra have seldom been observed in transmission mode[9]. Therefore, a study was conducted on a high temperature infrared spectrophotometer system that uses a Fourier transformation infrared spectrophotometer equipped with an infrared microscope (IR micro-spectrophotometer) and a high temperature stage to permit direct measurement of the infrared absorption spectra of specially prepared samples at high temperatures[10].

This paper describes the high temperature infrared spectrophotometer system, the methods of coal sample preparation and measurement and the change in functional groups of coal samples when the samples were heated from 50℃ up to 600℃.

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2. Experimentation

2.1 Samples

As samples, two types of coal were used, one having a relatively high carbon concentration and a relatively low oxygen concentration and the other having a relatively low carbon concentration and a relatively high oxygen concentration. They were crushed into particles no larger than 100 μ m and subjected to measurements. The chemical compositions and fluidities of the samples are shown in **Table 1**.

2.2 Experimental apparatus and measuring conditions

The experimental apparatus and measuring conditions used are as follows.

(1) Fourier transformation infrared spectrophotometer: JASCO Herschel FT-IR 610 (resolution: 4 cm^{-1}, scans: 20 times, measuring interval: 60 s)

(2) Infrared microscope: JASCO Irtron IRT-30 (detector: MCT, measuring field of vision: 150 μ m $\times$ 150 μ m)

(3) Sample heating unit: Japan High Tech's LK-600 FTIR (heating temperature: 50 to 600℃, heat-up rate: 10℃/min)

The configuration of the experimental apparatus is shown in **Fig. 1**, and the sample heating unit construction is shown in **Fig. 2**. The measuring field of vision of the IR microscope is as wide as 150 μ m $\times$ 150 μ m. This wide field of vision, which is closer to that of a beam

Table 1 Elemental composition and fluidity property of sample coals

Coal	Ultimate analysis (dry base, mass%)				
samples	C	H	N	O	S
Coal A	79.0	4.11	0.76	4.11	0.40
Coal B	73.4	4.44	1.81	10.25	0.85

Coal	Ash	H/C	Fluidity		
samples	(mass%)	(−)	ST (℃)	MFT (℃)	RT (℃)
Coal A	11.5	0.62	450	484	505
Coal B	9.1	0.72	394	434	460

ST: softening temp., MFT: maximum fluidity temp.,

RT: resolidification temp.

1: FT-IR, 2: Light source, 3: Interferometer, 4: Sample room, 5: He-Ne laser, 6: FT-IR detector, 7: IR microscope, 8: Cassegrain optical system, 9: Sample stage, 10: Detector for IR microscope
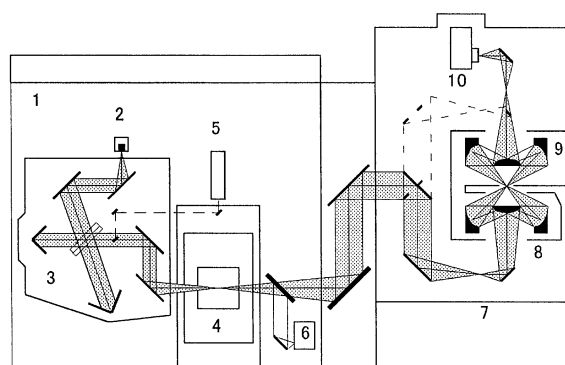
Fig. 1 Schematic diagram of FT-IR microscope

1: Sample stage, 2: BaF$_2$ window, 3: Heat body, 4: Heater, 5: Sample, 6: Purge gas-in, 7: Purge gas-out, 8: Cooling water-in, 9: Cooling water-out, 10: Thermocouple
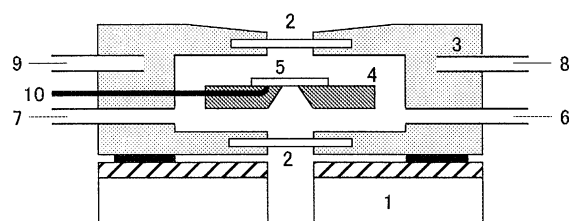
Fig. 2 Outline of the sample heating unit

condenser than a microscope, was adopted so as to secure adequate energy and obtain an IR spectrum of good signal-to-noise ratio (S/N) with a minimal number of scans. At 20 times scan and 4 cm^{-1} resolution, the time required to take in a single IR spectrum was not more than 30 seconds. The measuring interval was 60 seconds. Since the heat-up rate was 10℃/min, it follows that the system measured a spectrum in approximately 10℃ increments.

For the window material of the heating unit, Pier Optics' barium fluoride (BaF$_2$: 22 mm across and 0.5 mm thick) was used. Using the microscopic method, in which infrared rays are condensed, the position of the focal point shifts because the infrared light is refracted by the window material, whereby the infrared energy reaching the detector varies according to the thickness of the window material. Under this method, therefore, the thinner the window material is, the greater the infrared energy that reaches the detector, and the better the S/N ratio of the spectrum obtained. BaF$_2$ hardly deteriorates even in the open air because of its low solubility in water. In addition, it offers excellent mechanical strength. Therefore, this material is sufficient to withstand such intended use even though it is only 0.5 mm thick. As a disadvantage of BaF$_2$, poor transmittance in the low wave number range may be cited. However, as long as an HgCdTe (mercury cadmium tellurium or MCT) detector – a semiconductor detector of optical electromotive force type – is used, this disadvantage of BaF$_2$ is rendered irrelevant since the wave number range in which the MCT detector obtains energy (wave numbers up to about 600 cm^{-1}) almost perfectly coincides with the transmission wave number range of BaF$_2$.

2.3 Sample preparation

There are two representative methods of infrared spectrophotometry of a powder sample: the KBr tablet method that measures the transmission spectrum of the sample mixed with powder of potassium bromide (KBr) and formed into a tablet[11] and the diffuse reflectance method that directly measures the spectrum of a mixture of the sample and KBr or some other diffusing agent which permits infrared rays to pass through[12]. With the KBr tablet method, which permits controlling the amount of powder sample, it is possible to obtain an absorption spectrum with good quantitative characteristics. On the other hand, this method suffers from the fact that when the sample is mixed with KBr powder, the KBr absorbs moisture, causing O-H induced absorption to appear markedly in the spectrum of the mixture. Besides, if some gas is generated when the sample is heated, it is possible for the tablet to become deformed or cracked. With the diffusion & reflection method, the spectrum is influenced by the particle size, surface profile, and diffusion condition, etc. of the sample. Besides, since the sample shows wavelength dependency

during diffusion and reflection, quantitative evaluation of the sample is difficult. Therefore, a new method was devised in which the powder sample is embedded in a KBr crystal sheet and its transmission spectrum is locally measured by an infrared microscope.

By working a KBr crystal available on the market (5 to 8 mm square product of JASCO) along the cleavage plane, a microcrystal sheet can be readily obtained. In the present experiment, crystal sheets each measuring approximately 4 mm × 4 mm × 1 mm were cut out from the KBr crystal and a coal powder sample was pressed into each of the crystal sheets to obtain a sample 7 mm in diameter and about 0.5 mm in thickness. Since the amount of moisture absorbed by the crystal sheet worked on in this way is negligible, it is possible to observe only the O-H absorption ascribable to the sample. In addition, since the gas generated from the sample during heating easily disperses from the crystal sheet, the crystal sheet does not deform during measurement. The sample powder is unevenly dispersed in the crystal sheet. First, only the KBr part free of the sample powder is measured using an infrared microscope in order to obtain a reference. Next, the sample part that shows an appropriate amount of absorption is measured. By so doing, the IR transmission spectrum of the sample can be obtained from the two measurements. The melting point of KBr is 730℃, and the method of sample preparation described above was very effective for the measurement of high temperature samples.

3. Experimental Results and Discussion

3.1 IR Spectra of coal samples

Fig. 3 shows the IR spectra of coals A and B obtained by the ordinary KBr method (at normal temperature). Each of the IR spectra was obtained using 2.0 mg of coal mixed with 300 mg of KBr, the mixture of which was crushed and formed into a tablet 13 mm across. The influence of the absorption of moisture by KBr can be left out of consideration by previously measuring the IR spectrum of a tablet made entirely of KBr and eliminating it from the spectrum of the coal sample. The IR spectra shown in Fig. 3 were obtained by going through this procedure.

The IR spectra of coals reveal O-H stretching in the wave number range 3,600 to 3,200 cm^{-1}, aromatic C-H stretching at around 3,050 cm^{-1}, aliphatic C-H stretching in the range 2,960 to 2,850 cm^{-1}, C = O stretching in the range 1,760 to 1,640 cm^{-1}, C = C stretching at 1,600 and 1,500 cm^{-1}, respectively, etc. They also reveal O-H, (Si, Al)-O,
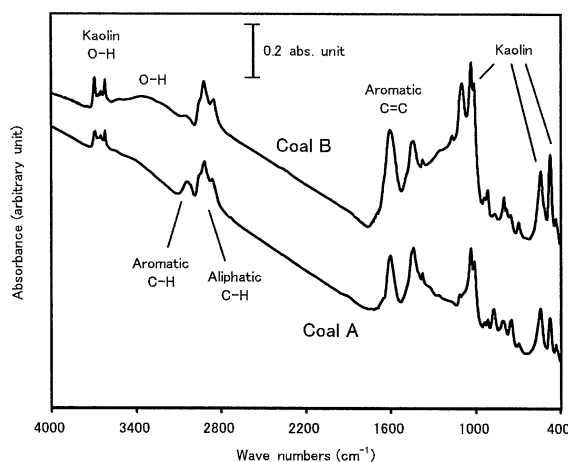
etc. which come from kaolin – a clayey mineral contained in coal. A comparison between coal A and coal B shows that coal A has a higher proportion of aromatic C-H relative to aliphatic C-H. This is considered due to the H/C of coal A shown in Table 1. Coal B shows a marked absorption of O-H, which is considered to have come from hydroxyl groups. This reflects the oxygen content of coal B shown in Table 1.

3.2 High temperature IR spectra and change in C-H peak intensities of coals

Fig. 4 shows the high temperature IR spectra of coal A (Fig. 4 (a)) and coal B (Fig. 4 (b)) when the coals were heated from 50 to 600℃. The IR spectra obtained are of good S/N ratio and show that the functional groups of the coals changed with the rise in temperature[5]. It is said that the increase in inclination of the baseline in the high temperature region is due to the influence of dispersion, which is considered ascribable to a structural change in the carbon skeleton, etc.[13-15].

In the IR spectrum of coal, attention is paid to the aromatic/aliphatic C-H peak intensity ratio, which is used as a simple indicator. **Fig. 5** shows the temperature dependency of the aliphatic and aromatic C-H peak intensities (absorbance areas) of coals A and B, obtained from the high temperature IR spectra shown in Fig. 4. It can be seen from Fig. 5 that the aliphatic C-H of coal B begins to sharply decrease in intensity at around 400℃, whereas that of coal A begins
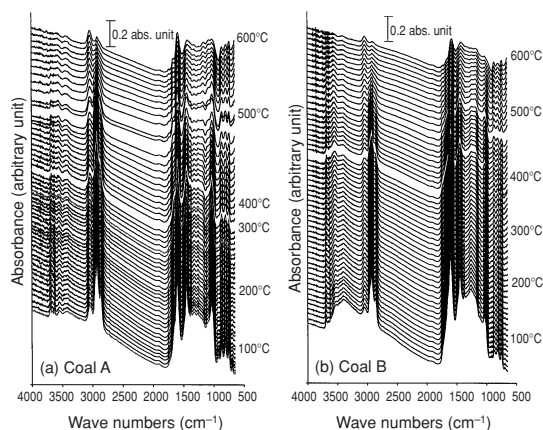
Fig. 4 Changes of IR spectra of the coal accompanying sample heating

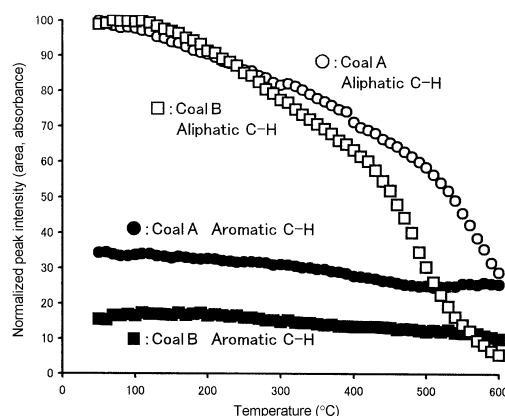**Fig. 3 Original IR spectra of Coal A and B**

Fig. 5 Changes of peak intensities based on C-H stretching. Intensities are normalized by aliphatic C-H peak at 50℃

decreasing in intensity at a higher temperature. In particular, the aliphatic C-H of coal B barely shows any peak at 600℃, whereas that of coal A can clearly be observed even at 600℃, although it continues to decrease. This suggests that the aliphatic constituents (side chains) of coal A are less subject to thermal decomposition than those of coal B.

On the other hand, the aromatic C-H of coal A and coal B, respectively, begins to decrease slightly at a temperature of around 500℃, but it can clearly be observed even at 600℃. This tendency is conspicuously reflected in the aromatic/aliphatic C-H peak intensity ratios shown in **Fig. 6**. This figure shows the temperature dependency of the aromatic/aliphatic C-H peak intensity ratio of coal A and coal B, respectively. As shown in Table 1, H/C of coal A is 0.62 and that of coal B is 0.72. Thus, coal A has a larger proportion of carbon atoms. This indicates that coal A is more 'aromatic' than coal B. Concerning the aromatic/aliphatic C-H peak intensity ratios in the IR spectra at around normal temperature in Fig. 6, coal A shows a higher ratio.

When coal is heated, the aromatic/aliphatic C-H peak intensity ratio shows a tendency to increase as the aliphatic C-H peak intensity decreases. This tendency becomes conspicuous around the temperature at which the coal begins to soften. Since the softening temperature (ST) of coal A is higher than that of coal B, the aromatic/aliphatic C-H peak intensity ratio of coal B is higher than that of coal A at temperatures around 500℃. The strong correlation between the melting behavior of coal and the structure of coal (degree of coalification) has already been recognized. From the results of the present experiment, it can be conjectured that the thermal decomposition of aliphatic side chains in coal has much to do with the melting behavior of coal, including the softening temperature and maximum fluidity temperature.

In the temperature range in which our high temperature infrared spectrophotometer system is applicable (up to 600℃), the absorbance of the aromatic C-H in coal is less subject to change than that of the aliphatic C-H. From the results of coal evaluations using high temperature NMR imaging[4], it is already understood that with the rise in temperature, the highly active mobile component increases to it maximum at about the temperature of maximum fluidity for coal, that it begins to gradually decrease thereafter, and that the half-width
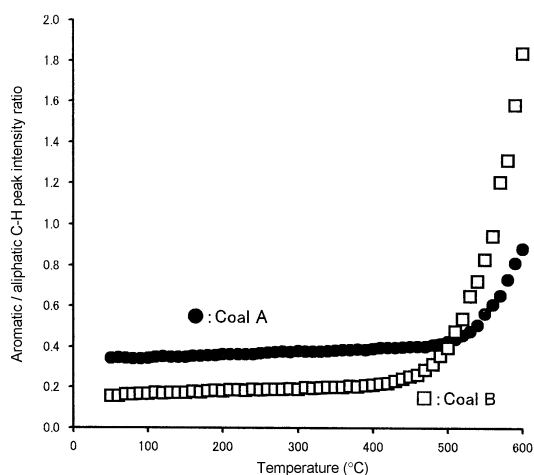
of the mobile component, which is related to the viscosity of coal, is smallest at around the maximum fluidity temperature. In addition, a study of the behavior of gas generation during thermal decomposition of coal[16] has revealed that hydrocarbons, such as methane, occur at temperatures from around the coal softening temperature (400℃) to about 600℃.

Hydrogen begins to be generated at about 500℃ and accounts for the majority of the gas generated at 600℃ at which the amounts of hydrocarbons generated begin to dwindle. The occurrence of hydrogen is considered to be due to the condensation of aromatic skeletons. This agrees well with the results of the present analysis of high temperature IR spectra, that is, the aliphatic C-H begins a marked decrease in peak intensity at a temperature of around 400℃, whereas the aromatic C-H can clearly be observed even at 600℃, although it begins decreasing slightly at around 500℃.

From the present measurements, it was found that the peak intensity of absorption of 1,600 cm^{-1} nearly coincides with the change in aromatic ν C-H peak intensity. Some ascribe the absorption of 1,600 cm^{-1} to aromatic ν C = C, and others ascribe it to ν C = O of carbonyl or carboxyl groups[17]. If the absorption were ascribable to ν C = O, the coal would be subjected to thermal decomposition at relatively low temperatures. It is, therefore, considered that the absorption of 1,600 cm^{-1} is due to aromatic ν C = C.

3.3 Change of hydroxyl groups in coal

In the IR spectrum of coal containing a considerable proportion of oxygen, like coal B shown in Fig. 3, hydroxyl group-based absorption is observed in the range 3,600 to 3,200 cm^{-1}. Concerning the hydroxyl groups of coal, the results of analyses focused on the hydrogen bond from the standpoint of coal structure have been reported[6-9,11] previously. In this paper, study was conducted on the hydroxyl groups with the aim of analyzing the dehydration behavior of coal during carbonization. **Fig. 7** shows the IR spectra of coal B obtained at increments of 100℃, from 100 to 600℃, with attention paid to the hydroxyl groups. The absorbance of O-H for coal shows a tendency to decrease with the rise in temperature. However, as the peaks of about 3,520 and 3,400 cm^{-1} indicate, some hydroxyl groups show considerable absorbance even at high temperatures, such as 400 and 500℃.

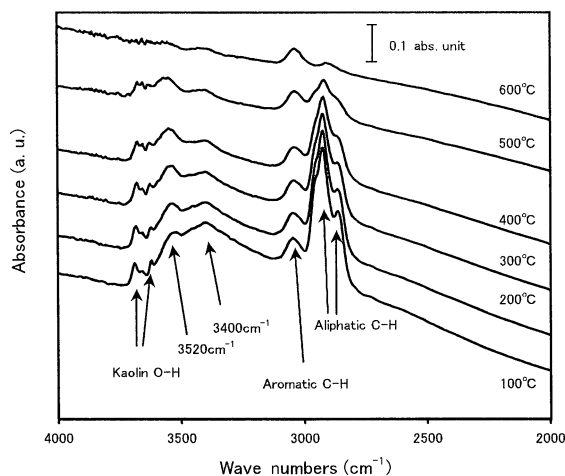Therefore, by using the differential spectra, peak areas of the

Fig. 6　Temperature dependency of a aromatic/aliphatioc C-H peak intensity ratio

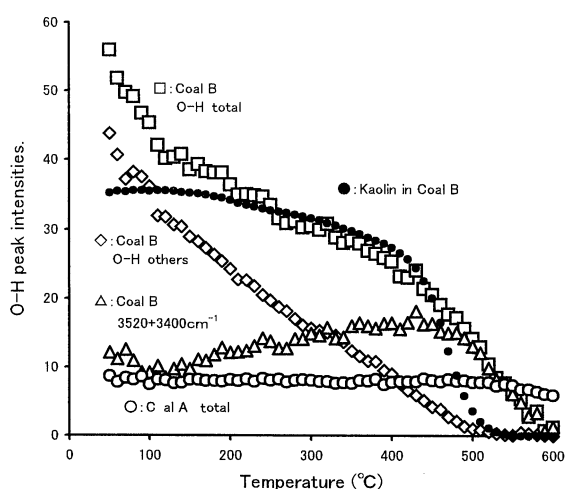Fig. 7　IR spectra of Coal B which paid its attention to OH groups

Fig. 8 Temperature dependency of various O-H peak intensities

hydroxyl groups which remain absorbent even at high temperatures (peaks of 3,520 and 3,400 cm^{-1}) were calculated and those of the other hydroxyl groups to study the temperature dependency of O-H peak intensities. The study results are shown in **Fig. 8**. The kaolin shown in the figure is a clayey mineral contained in coal. Its ideal chemical composition is expressed as $Al_2Si_2O_5(OH)_4$. Kaolin begins to dehydrate at temperatures of around 400℃ and is completely dehydrated at 600℃. This dehydration behavior can also be observed as a change in peak intensity in the IR spectra and hence, it can be used to monitor the sample temperature.

It is assumed that the peaks of 3,520 and 3,400 cm^{-1} of coal B remain almost the same in intensity at temperatures up to about 500℃. However, since the intensities of the other O-H peaks decrease with the rise in temperature, it is considered that the hydroxyl groups exist in different modes in the coal. The water that is desorbed at relatively low temperatures is adsorbed water, free water, etc. The desorbing temperature may depend more or less on the mechanisms of adsorption, such as the affinity of water to the coal itself or inorganic minerals. In terms of hydroxyl groups that are stable even at high temperatures, the phenolic hydroxyl groups, etc. may be considered. Coal A originally contains few hydroxyl groups. The mode of existence of those hydroxyl groups is close to the 3,520 and 3,400 cm^{-1} peaks of coal B, and some of the hydroxyl groups are observed even at considerably higher temperatures. In analyzing such hydroxyl groups, the method of measurement described in this paper (i.e., using a sample embedded in a KBr sheet) is effective because such measurements are hardly influenced by the absorption of moisture by the KBr.

4. Conclusion

An experimental high temperature infrared spectrophotometer system equipped with an infrared microscope and a high temperature stage were built to study a new method for directly measuring the infrared transmission spectrum of coal while heating the coal up to 600℃. Two types of coals having different properties were meas-

ured using the system. As a result, the following facts were found.
(1) Although the thermal decomposition of aliphatic constituents of coal begins at a temperature around 400℃, the temperature region in which the thermal decomposition is active varies according to the type of coal.
(2) The rate of thermal decomposition of the aliphatic constituents also varies according to the type of coal. The lower the degree of coalification, the higher is the rate of thermal decomposition in the low temperature region.
(3) Although the aromatic constituents of coal begin to decrease slightly at a temperature around 500℃, they can clearly be observed even at 600℃.
(4) In coal containing a considerable proportion of oxygen, ν O-H ascribable to hydroxyl groups can be observed markedly. Such hydroxyl groups exist in several different modes: some of the hydroxyl groups show a decline in peak intensity at relatively low temperatures, whereas others can clearly be observed at 500℃ or higher temperatures.
(5) Since the kaolin contained in coal begins to dehydrate at temperatures of around 400℃ at which many types of coal begin softening, it can be used to monitor the temperature of a coal sample while heating and measuring it.

The microscopic infrared spectrophotometer has become widespread. By providing it with a high temperature stage and using a suitable method of sample preparation, it is possible to measure the IR spectrum of a heated coal sample easily and accurately. Incidentally, when it comes to measuring the IR spectrum of a hot coal sample, there is concern that the IR spectrum might be influenced by the emission of light from the sample. With the microscopic infrared spectrophotometer, however, the IR spectrum is hardly influenced by external disturbance since, as shown in Fig. 1, infrared light that is modified by an interferometer is irradiated onto the sample through the microscope. The narrow field of vision for measurement is also considered one of the reasons why the IR spectrum is hardly influenced by the emission of light from the sample. If the sample can be heated up to 600℃, the system will be applicable to the analysis if inorganic matter as well, as demonstrated by the dehydration of kaolin mentioned earlier.

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