Evolved gas analysis by simultaneous thermogravimetric differential thermal analysis-Fourier transformation infrared spectroscopy (TG-DTA-FTIR)

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1. Introduction

Simultaneous thermogravimetry-differential thermal analysis/differential scanning calorimetry (TG-DTA/DSC) is the method with which changes in both the mass and energy of a sample upon heating can be measured simultaneously. From the data obtained, macromolecular information with regard to physicochemical change in the sample can be obtained. However, in order to know what specific kind of reaction takes place, information from other analytical methods is indispensable. For example, when the TG-DTA measurement indicates that an endothermic reaction accompanied by a mass loss takes place, this may suggest that one or more of a number of possible reactions occur, such as dehydration, evaporation, sublimation, decomposition, and reduction. In this case, if the structural formula, decomposition temperature, and content ratio of the absorbed moisture of the sample is available, it would be possible to suggest the kind of reactions that might be taking place. However, if the sample is totally unknown, even supposition is difficult. In this case, if information about structural change to the sample and the chemical species volatized were available from other analytical methods combined with the TG-DTA results, this would help understand the reaction processes taking place in the sample.

Evolved gas analysis (EGA), a combination of TG-DTA with analysis of any evolved gases, is one example of the hybrid measurement methods mentioned above. EGA is a technology with which the kind and amount of gas evolved from a sample upon heating are measured as a function of temperature. In many cases, this technology is not used alone, but in combination with other thermal analysis technologies or with multiple technologies associated with them. In the past, we utilized mass spectrometry (MS) —which has characteristics of high sensitivity and rapidity—as a gas detector in EGA; therefore, our instrument development has been focused mainly on TG-DTA-MS. In recent years, an extensive library of Fourier transformation infrared (FTIR) spectroscopy gas data has been developed, making this technique a powerful tool as an EGA detector for TG-DTA. One major benefits of using FTIR as an EGA tool is the fact that molecular fragmentation of the gas during ionization—which would lead to a complicated spectrum pattern—does not occur as it does with MS upon ionization. Also, functional groups of the evolved gas can be directly estimated, making it suitable for the detection of mixed gas compounds evolved upon thermal decomposition[1].

Because TG-FTIR and TG-MS are complementary methods in evolved gas analysis, a significant increase is expected in the utilization of TG-FTIR—in addition to TG-MS—from this point forward for more detailed analysis of gases evolved upon heating.

2. Structure of the Instrument

2.1. Thermogravimetry-differential thermal analysis (TG-DTA)

Rigaku's Thermo plus EVO2 horizontal differential TG-DTA8122 instrument can be expanded to allow for the use of this technique. All gases evolved from the sample in TG-DTA—together with a carrier gas—are transported to the FTIR unit through the transfer line called TGA-IR.

2.2. Fourier transformation infrared spectroscopy (FTIR)

TG-DTA can be connected to Fourier transformation infrared spectrometers in the Thermo Fisher Scientific's Nicolet™ series. The connectable models are Nicolet™ iS10, Nicolet™ iS50, Nicolet™ 380, and Nicolet™ X700, which are all attached directly to the TG-DTA via the gas transfer line (TGA-IR) as described above.

3. System configuration for TG-FTIR

A photograph of the instrument and a schematic of its configuration are shown in Figs. 1 and 2. All gases evolved in the TG-DTA sample unit—together with a

Fig. 1. Photograph of the TG-FTIR system.

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carrier gas—are introduced, without being split, into the gas cell in the FTIR through the TGA-IR attachment (maximum 300°C), which is directly connected to the furnace.

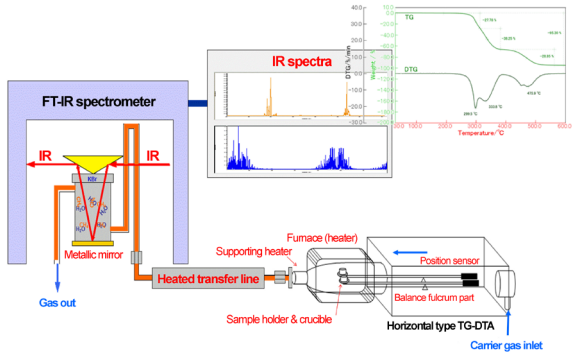

Fig. 2. System configuration diagram of TG-FTIR.

4. Setup of the measurement conditions

4.1. Sample amount, heating rate, and measurement atmosphere

The advantage of TG-FTIR is that the measurement can be made simultaneously under the same conditions relative to the sample amount and the heating rate as with normal TG-DTA analysis. For sufficient signal intensities in both the FTIR spectrum and TG-DTA to be detected, the sample amount should be approximately in the range of about several mg to 10 mg. As the heating rate increases, the sensitivity in the measurement of the evolved gas amount also increases, but the peak resolution of the evolved gas decreases. If high-sensitivity measurement of a small amount of gas from a sample is required, it is preferable to set a faster heating rate; but if a sufficient amount of gas evolution can be expected, it is preferable to set a slower heating rate, thereby enhancing peak resolution. Because the data obtained in FTIR indicates the gas evolution rate from the sample, Gram–Schmidt and the derivative TG (DTG) show similar behavior.

Usually, TG-MS uses He as the carrier gas, while TG-FTIR can use the atmosphere gases used in TG-DTA under the same conditions. Therefore, the measurement can be easily carried out in an oxidative atmosphere or in a humidity controlled atmosphere. In the case of an oxidative atmosphere, dry air or quasi air having an inert gas mixed with 20% of O_2 may be used. In the case of a humidity controlled atmosphere, a humidity generator HUM-1 (manufactured by Rigaku), which can generate any desired humidity concentration, is used. Unlike with TG-MS, where an oxidative atmosphere can accelerate filament deterioration, there are no such concerns about using atmospheric gas in an TG-FTIR measurement.

5. Analysis methods

The main analysis methods of TG-FTIR are described below.

1) Qualitative analysis of evolved gases

The evolved gases are qualitatively analyzed from the TG-DTA curve, the temperature profile, and the spectrum information of the FTIR data (evolved gases) at an arbitrary temperature. In qualitative analysis, compound identification is made using a library search based on the selected FTIR spectrum. First, an arbitrary peak point from Gram–Schmidt (a point of change in the graph of the entire evolved gases) is selected. Next, by using library search software, spectra resembling the target unknown spectrum are retrieved. The similarity between the two spectra is digitized (as a numerical hit rate) and the spectra of candidate compounds are displayed in descending order of this number. An example is illustrated in Fig. 3.

The correct candidate is found among the data listed by the library search program. Assigning the unknown compound only from the numerical hit rate is not reliable. Qualitative analysis is made by judging the congruity to the entire unknown spectrum.

2) Analysis of evolution gas behavior

The area of the measured wavelength region of the characteristic spectrum of each gas shown by the FTIR data (evolved gases) is calculated. The change in the area with time is traced with the passage of temperature (time) so as to analyze the evolution gas behavior (concentration change). An example is illustrated in Fig. 4.

The measured wavelength region of each target spectrum peak is determined and the areas of each are calculated. By following the temperature (time) change of the area value for each component, the evolved gas behavior can be compared with the TG-DTA curve.

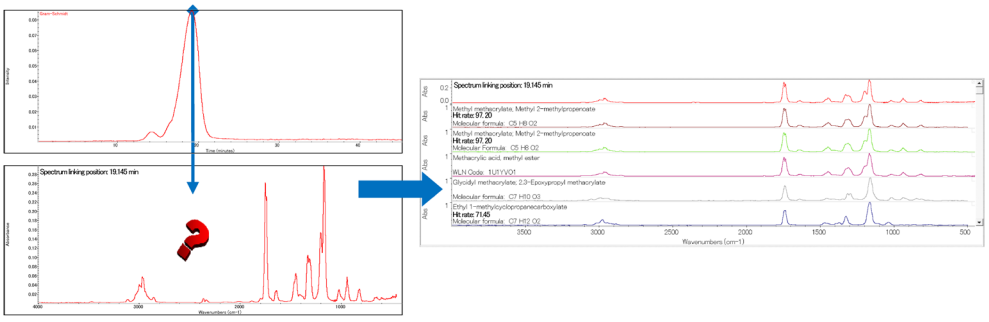

Fig. 3. Example of qualitative analysis of the evolved gas in TG-FTIR.

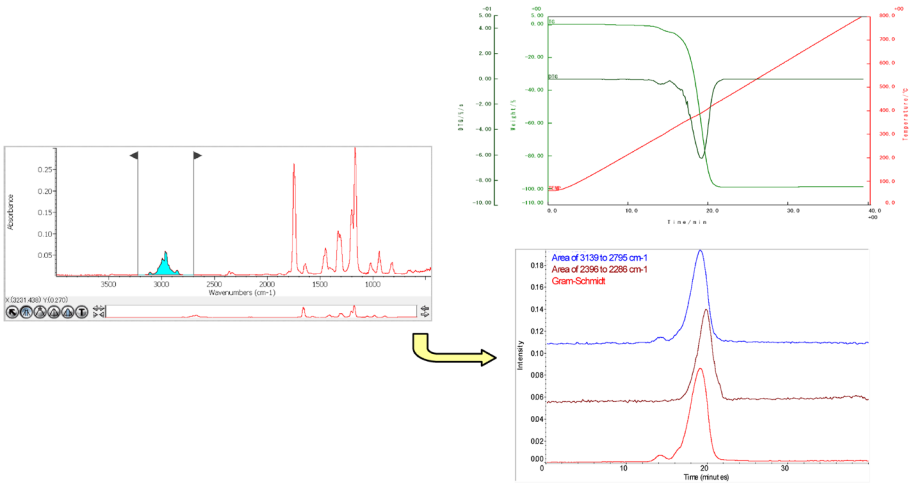

Fig. 4. Analysis example of evolution behavior of the evolved gas by TG-FTIR.

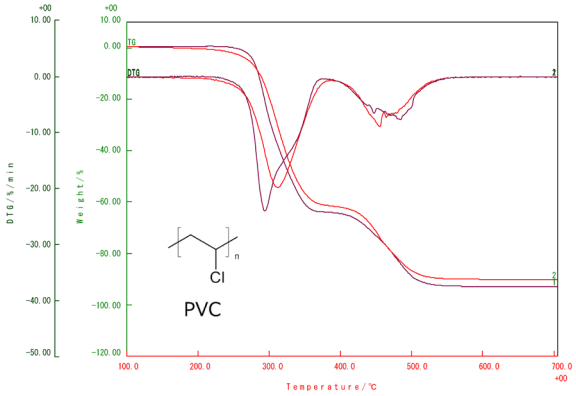

Fig. 5. Comparison of TG (DTG) curves of two different PVCs.

6. Application examples

6.1. Thermal decomposition of PVC (polyvinyl chloride)

With regard to two different commercially available PVCs, TG measurement was carried out for 10 mg of each sample under Ar gas flow (250 mL/min) at a heating rate of 20°C/min. Results are shown in Fig. 5. A difference is observed in the mass loss behavior between the two PVCs, although the difference is very small.

The mass loss takes place in roughly two stages. In the decomposition at each stage, the evolved gases are analyzed with TG-FTIR. These results are shown in Fig. 6.

In Gram–Schmidt in FTIR, two clear peaks consistent with the derivative TG (DTG) are observed in both PVCs. In this figure, the FTIR spectra at the two peak temperatures are compared. Here, the peak groups in the wavelength range of 2,600 to 3,200 cm^{-1} observed

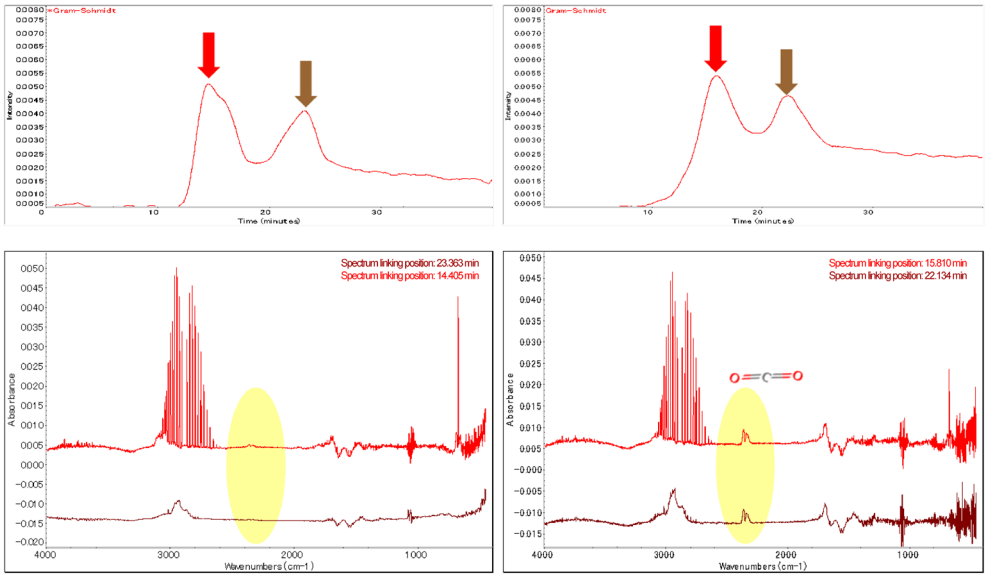

Fig. 6. Comparison of FTIR spectra at peak temperatures in TG-FTIR of two different PVCs.

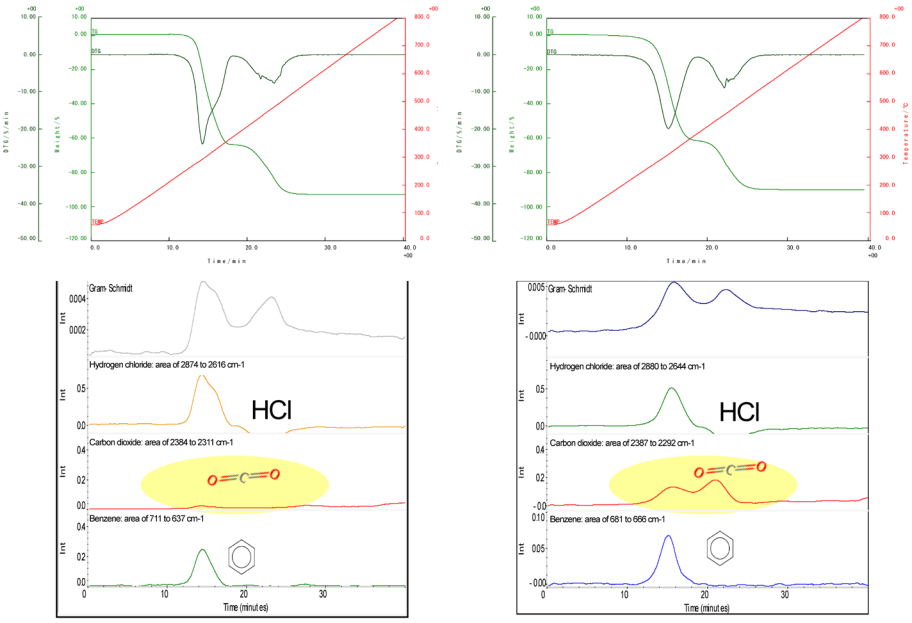

Fig. 7. Comparison of behavior of the evolved gases of two different PVCs.

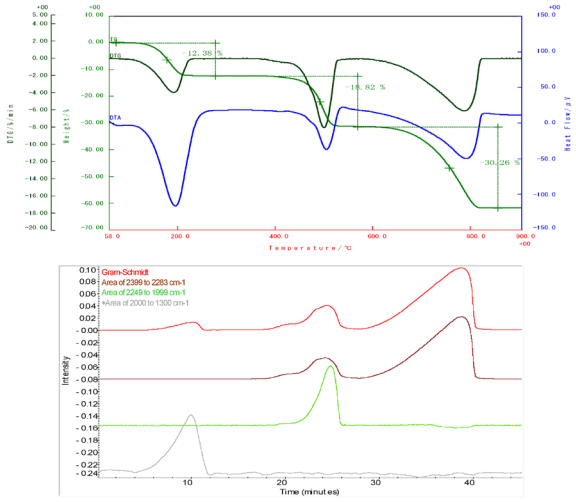

Fig. 8. TG-DTA of calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) in Ar gas.

in the spectrum of the evolved gases in the first stage were assigned to ammonia and benzene, respectively. In a similar manner, the later decomposition stage indicates evolution of hydrocarbon compounds due to thermal decomposition of the polyene.

A point worthy of special attention in the comparison of the spectra is the clear peaks observed near 2,349 cm^{-1} and 667 cm^{-1} in both temperature ranges, suggesting the existence of carbon dioxide, CO_2. A comparison of two PVCs clearly catches the difference between the existence and nonexistence of CO_2. Results of the evolution behavior of major detected gases, including the CO_2 gas, are shown in Fig. 7.

In the pyrolyzated gases of two PVCs, a clear difference can be seen in the CO_2 evolution behavior (evolution amount), so that it is presumed that part of the terminal function group in one PVC is carboxylated.

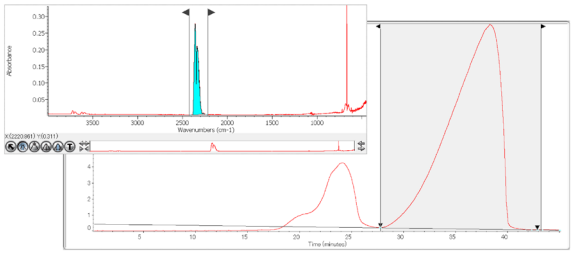

Fig. 9. Preparation of the calibration curve for CO_2-evolution from $CaC_2O_4 \cdot H_2O$.

6.2. Quantitative analysis of evolved gases by TG-FTIR

Using calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$), the standard sample for thermal analysis, the calibration curves of CO_2 and H_2O were prepared so as to evaluate their usability in the quantitative analysis.

Thermal decomposition of $CaC_2O_4 \cdot H_2O$ takes place with the reaction process of the following clear three stages in temperatures ranging from room temperature to 900°C. A typical result of TG-FTIR in Ar gas is shown in Fig. 8.

1. $CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 \cdot + H_2O \uparrow$
2. $CaC_2O_4 \rightarrow CaCO_3 + CO \uparrow$
3. $CaCO_3 \rightarrow CaO + CO_2 \uparrow$

For example, in order to estimate the evolution amount of CO_2, the peak area of the characteristic component absorbance of the IR spectrum of CO_2 was calculated by the procedure illustrated in Fig. 9, as described below.

The initial sample amount of $CaC_2O_4 \cdot H_2O$ was changed to range between 1 and 25 mg, and the mass losses by dehydration and decarbonation versus the component absorbance (measurement atmosphere: Ar gas) were calculated to obtain the calibration curves of the respective gases, as shown in Fig. 10.

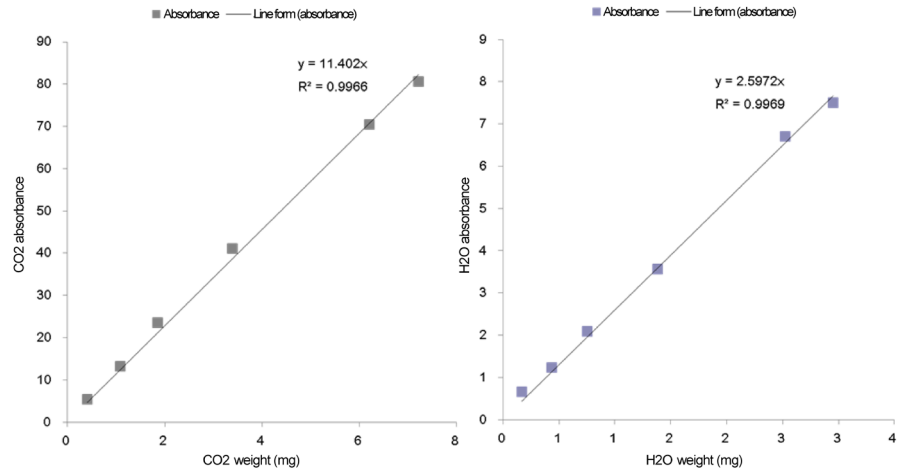

Fig. 10. Calibration curves of evolved gases (H_2O and CO_2) from $CaC_2O_4 \cdot H_2O$.

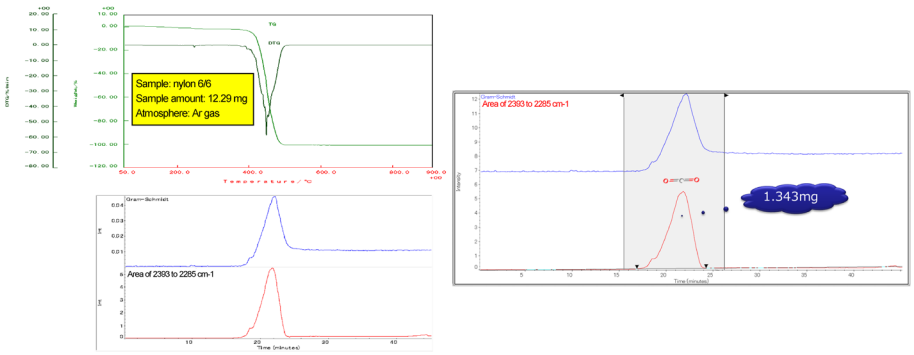

Fig. 11. Quantitative analysis of CO_2 gas evolved during thermal decomposition of nylon 66 in the Ar gas.

Next, on the basis of the calibration curve for CO_2 prepared as described above, the amount of CO_2 gas evolved during thermal decomposition of nylon 66 (sample amount: 12.29 mg) in Ar gas was estimated. The result is shown in Fig. 11. From the result, the amount of CO_2 evolved during decomposition of the resin could be estimated as 1.343 mg (10.9%).

7. Conclusion

Evolved gas analysis (EGA) is a method to analyze the gases evolved from a sample upon heating; and its application is implemented especially in TG-MS and TG-FTIR nowadays. This is because even when multiple thermal analysis technologies are used independently, the conditions of the sample are not always the same due to the dynamic nature of thermal analysis. It is concluded that hyphenated technologies (such as TG-MS, TG-FTIR) are very powerful analysis methods because they not only dramatically increase the information produced, but also comprehensive information can be obtained from the same sample. TG-FTIR can be used for various materials such as organic compounds, polymers, drugs, ceramics, and inorganic materials, etc.

Reference

(1) T. Arii, M. Komatsu and M. Hattori: *8th International and 10th Japan-China Joint Symposium on Calorimetry and Thermal Analysis*, (2017), 65.