Technical know-how in thermal analysis measurement

—Evolved gas analysis by thermogravimetry-differential thermal analysis-mass spectrometry (TG-DTA-MS) technique—

Kazuko Motomura* and Lani Llego Celiz*

1. Introduction

The thermogravimetry-differential thermal analysis (TG-DTA) is a simultaneous measurement technique where the material's mass changes as well as energy changes are measured during heating and the macro-information on the physico-chemical changes of the material can be concluded from the obtained data. However, in order to fully understand the reactions that have occurred, it has to depend on the information obtained from other measurement techniques. Such as in TG-DTA where a mass loss is associated with an endothermic reaction, then we can conclude that reactions such as dehydration, evaporation, sublimation, degradation or reduction have occurred. Although we can conclude the kind of reactions that have occurred if the information on the material's structural formula, degradation temperature or water adsorption percentages are present, but on the contrary, it is difficult to draw conclusions if the material is unknown. In this case, combining TG-DTA with other measurement techniques is helpful in understanding the structural changes in the material and if the volatilized chemical species are known, then the chemical reaction process that can be derived will be a useful information. The combination of TG-DTA and evolved gas analysis is one of the complex measurements. Evolved gas analysis (EGA) is defined as a measurement technique where the gases which evolved from the sample upon heating are qualitatively and quantitatively measured as a function of temperature. It is often combined with other thermal analysis techniques rather than used as a stand-alone module.

Examples of EGA detection analyzers are mass spectrometer (MS), thermal conductivity detector (TCD), flame ionization detector (FID) and infrared spectrometer (IR). Among these, the MS is characterized as highly sensitive and can perform measurements rapidly. During the recent years, the TG-DTA-MS is a combination of MS and TG-DTA where it can also be used as a standard module.

2. Modular Structure

The evolved gases from the sample in the TG-DTA are introduced to the MS chamber via a transfer line called "interface."

* Thermal Application Laboratory, Thermal Analysis Division, Rigaku Corporation.

2.1. Interface

The evolved gases from the sample room of the TG-DTA at atmospheric pressure will be injected towards the MS chamber under high vacuum pressure via the interface. The interface is a structure where it essentially creates a difference in pressure between the TG-DTA and the MS chamber requiring various innovative devices. The interface is classified into two types, the capillary type and the skimmer type. Although both interface types have advantages, the TG-DTA-MS equipped with capillary-type interface will be described first. In the later part, the TG-DTA-MS equipped with skimmer-type interface will also be introduced in the future.

The capillary type interface is composed of a capillary tube (narrow tube) which connects the TG-DTA and the MS as shown in Fig. 1. In order to prevent the transformation and condensation of evolved gases within the capillary, inactivation of the internal walls and temperature retention are necessary. However, it is undesirable to increase the temperature of the interface without any reason from the risk factors such as analyst safety, transformation of evolved gases or secondary reaction. The interface temperature is set at 250°C and the upper limit temperature is set at 300°C. Because of this, measuring high boiling point compounds exceeding the interface's retention temperature causes condensation of gases within the interface, complicating the measurement and then it will no longer be within the measurement objective. Even with this problem, the capillary-type interface has been commonly developed and because of its simplicity in maintenance, it is used as a standard module.

2.2. Mass Spectrometer (MS)

There are different kinds of mass spectrometers and most mass spectrometers used for simultaneous measurements with thermal analysis technique adopt the Quadrupole MS (QMS). The QMS is compact in size, affordable, easy to operate and it is considered as a typical standard in analysis module and also widely adopted in gas chromatography-MS (GC-MS). In the TG-DTA-MS, the evolved gases from the interface are injected towards the mass chamber prior to ionization in the ionization room of the QMS, then the gas ions pass through between the quadrupoles, detected by the secondary electron multiplier and outputted as an ion

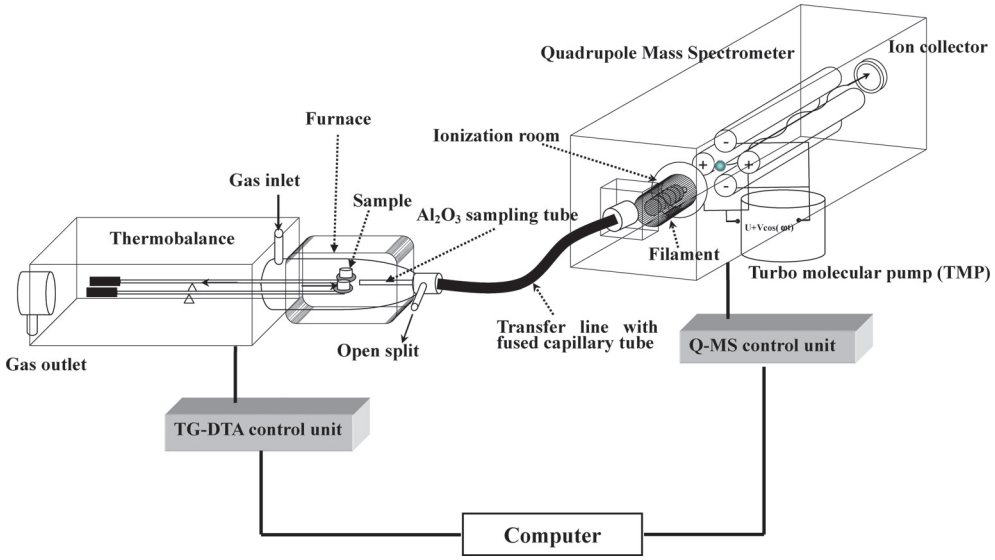

Fig. 1. Schematic diagram capillary-type TG-DTA-MS.

current value.

3. Measurement condition settings

3.1. Sample amount

Since the MS is a highly sensitive detector, caution is necessary because it is easily influenced by contaminants. If large amount of gases have evolved from the sample, it may contaminate the furnace of the TG-DTA and the capillary interface, posing a risk on affecting the next measurement. In case of contamination, it is necessary to perform blank (empty pan) measurement up to the maximum temperature, baking of the MS and changing of the capillary tube.

Setting the sample amount is important to avoid maintenance trouble. Especially when measuring an unknown sample, it is desirable to start the measurement using a small amount (1mg) of sample. Also when measuring unknown samples, performing preliminary measurements with a stand-alone TG-DTA will provide an estimation of the amount of evolved gases from the unknown sample which allows adjustment for ideal sample amount and preventing the contamination of the MS.

3.2. Heating rate

When a mass loss is observed on the TG curve of the TG-DTA, then gas components have volatilized from the sample.

At this time, the gases evolving instantly within a short period of time has a good measurement sensitivity than gases evolving slowly at a wide temperature range even if the same amount of gases have evolved because the MS detects the amount of evolved gases per unit time. However, a higher heating rate leads to a better sensitivity in the measurement of the amount of evolved gases but leads to poor peak resolution. In case where minute amount of gases evolve from the sample, increasing the heating rate will enhance the sensitivity of the measurement, expecting some amount of gases while a slow heating rate will increase the peak resolution.

Since the MS data obtained from the evolved gases in the sample shows the gas evolution rate, the TIC (total ion current) of the MS and the derivative TG (DTG) curve have a similar relationship.

3.3. Measurement atmosphere

Generally, the carrier gas used in QMS is helium (He). Therefore, it is necessary that the measurement atmosphere of the TG-DTA-MS is also helium. Moreover, it is also possible to measure under oxidative atmosphere as well as water vapor atmosphere. When an oxidative atmosphere is required, a 20% O_2 mixed in 80% He is used and when a water vapor atmosphere is required, a humidity generator called HUM-1 (Rigaku) that can control an arbitrary water vapor concentration is used.

But, when performing measurements under artificial atmosphere, increasing a significant amount of O_2 in the MS will hasten the degradation of the filament. As a result, it is necessary to base it on the increased number of maintenance and component replacement frequency around the ion source compared with the use of He atmosphere.

4. Measurement of Calcium Oxalate Monohydrate

Used as a standard material in the TG-DTA, a 2 mg calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) was measured using TG-DTA-MS under helium gas flow (300ml/min) at a heating rate of 20°C/min and the measurement results are shown in Figs. 2 and 3.

As the reaction scheme of the calcium oxalate monohydrate is commonly known, the 3-stage thermal degradation behavior can be confirmed from the TG-DTA curves. In here, the evolved gas components during the respective thermal degradation can be confirmed from the MS results, practically illustrating the known

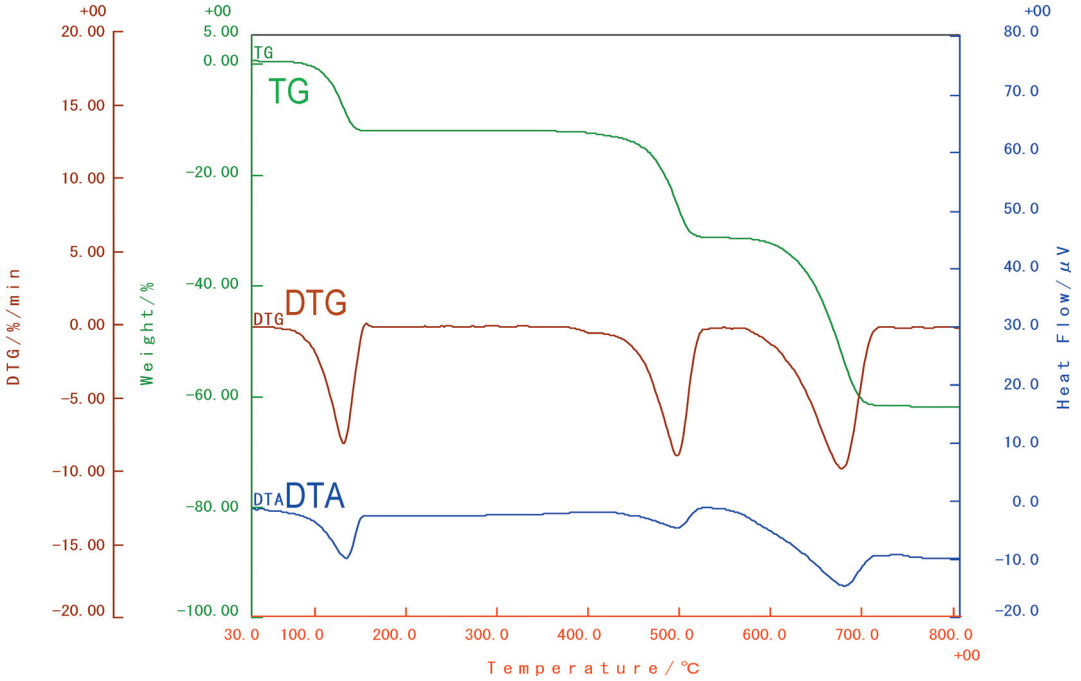

Fig. 2. TG (DTG)–DTA curve.

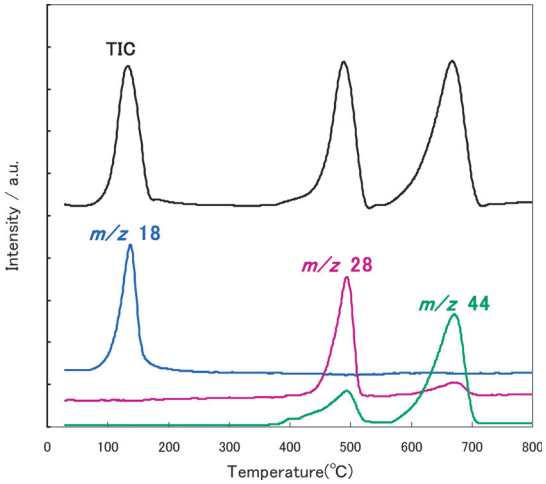

Fig. 3. TIC and ion chromatogram of *m*/*z* 18, 28, 44.

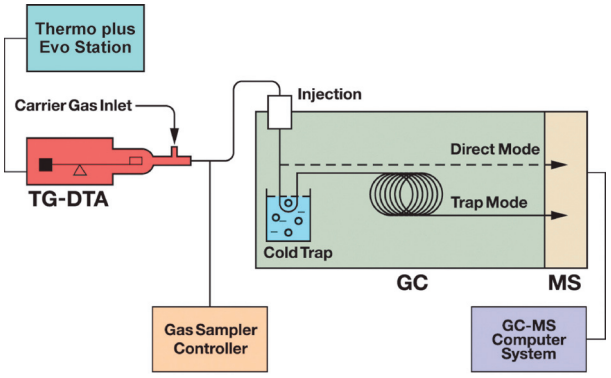

Fig. 4. Schematic diagram of TG-DTA/GC-MS.

reaction process.

At first, the TG-DTA curve showed a mass loss accompanied with an endothermic peak at 100°C and the *m*/*z* 18 (H_2O) was mainly detected in the MS. In this first stage, it is known that dehydration has occurred with the following reaction.

$$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O$$

Then from 400°C, a mass loss accompanied with an endothermic peak and *m*/*z* 28 (CO) was mainly detected. In this second stage, the following thermal degradation reaction has occurred:

$$CaC_2O_4 \rightarrow CaCO_3 + CO$$

Moreover, a mass loss from 600°C associated with an endothermic reaction was seen and *m*/*z* 44 (CO_2) was mainly detected. The third stage which is a degradation process occurs as follows:

$$CaCO_3 \rightarrow CaO + CO_2$$

5. TG-DTA/Gas Chromatography-MS (TG-DTA/GC-MS)

Generally, the ionization method mainly used in the EGA-MS is the electron impact ionization (EI) method. In this EI method, since the fragment ions are generated along with the parent ions and although it can obtain a unique mass spectrum originating from the molecular structure of the measured component, analyzing the mass spectra becomes complicated because each of the mass spectra overlaps with each other when several gas components are evolved simultaneously. Especially in most polymers' thermal degradation, several organic gases evolve simultaneously.

In this case, the TG-DTA/GC-MS is a very useful measurement technique where it aims at qualitatively measuring the complex evolved gases separated by the GC column.

Combining the TG-DTA and the GC-MS uses a special interface system (Rigaku) which can be connected to any GC-MS from any manufacturer. The

schematic diagram is shown in Fig. 4.

5.1. Direct mode and Trap mode

Direct mode is a measurement method where the evolved gases from TG-DTA are directly injected to the MS without passing through a GC column. Similar to the TG-DTA-MS, understanding the evolved gas temperature behavior is possible because the direct mode allows real-time measurement. On the other hand, the trap mode is a measurement method where the evolved gases are cold-trapped, injected and separated in the GC column. Since the evolved gases at an arbitrary temperature are cold trapped using liquid nitrogen and although it no longer allows real time measurement, it is exceedingly useful in qualitative measurement of the simultaneously evolved complex gases. Also, the evolved amount per unit time can be possibly detected even minute amount of gases because condensation effect can be obtained through the collection of gases at a particular temperature region. In addition, the undetected minute gas levels in the direct mode can be possibly detected. However, since the evolved gases are instantly cold-trapped and reheated in the trap mode, thermal hysteresis of the gas components may cause changes which may pose as a risk and a problem. Also, since the detection of minute existence of contaminating components may increase in the gas path of the module through the condensation effect, it is ideal that baking is carefully performed and a blank measurement is measured prior to sample measurement.

5.2. Direct and trap mode measurements of Nylon 6, 6

The Nylon 6, 6 is used to measure the polymer's thermal degradation. The direct-mode measurement result shown in Figs. 5 and 6 was performed by using 1 mg sample measured under helium gas flow (300 ml/min) and heated at 20°C/min. Figure 5 is a multiplot of TG and TIC curves while Fig. 6 is a mass spectrum of the evolved gases at the TIC peak top temperature. A single stage weight loss was found between 400°C to 500°C and the accompanying evolved gases were confirmed. Since the fragment ions of the evolved complex gas components overlap with each other in the mass spectrum of the peak top temperature, identifying gas components becomes complicated. Moreover, trap mode measurement was performed using 0.1 mg sample under helium flow (300 ml/min) heated at 20°C/min and the results are shown in Fig. 7. In this measurement, gases were collected at a temperature range of 400°C to 500°C when the thermal degradation was observed.

The evolved gas components which are separated by the GC column are detected as peaks. The main peaks observed are cyclopentanone and hexanediamine (Figs. 8 and 9) which are both the backbone polymer structure and the distinguishing characteristics of Nylon-6, 6.

In this way, using the direct and trap mode combination in simultaneously evolving complex organic gases enables good accuracy and allows qualitative analysis. On the other hand, the qualitative analysis of the TG-DTA-MS which is a non-GC function adopting the soft-ionization technique called photoionization (PI) method where fragmentation does not occur enables the real-time selective detection of the

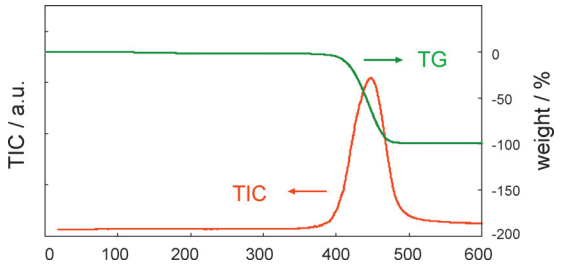

Fig. 5. TG and direct mode TIC curves.

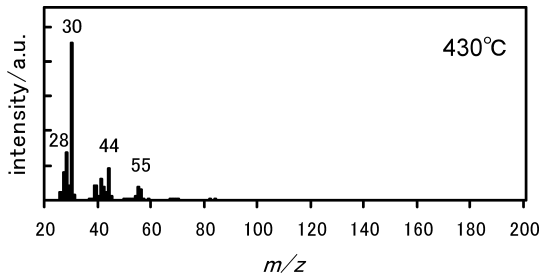

Fig. 6. Mass spectrum at TIC peak top temperature of 430°C.

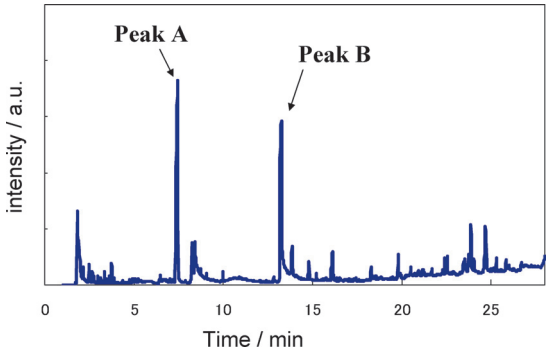

Fig. 7. TIC curve obtained by trap mode.

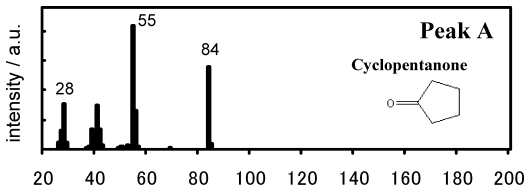

Fig. 8. Mass spectrum of Peak A and identified components.

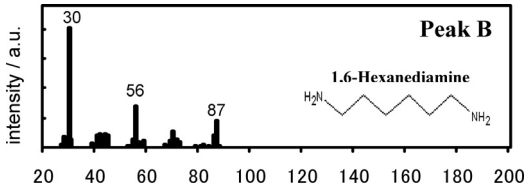

Fig. 9. Mass spectrum of Peak B and identified components.

molecular ions of organic gas components and classification of several gas components. A more detailed explanation of the PI method will be discussed in the future.

6. Conclusion

The TG-DTA-MS and the TG-DTA/GC-MS methods are effective methods for elucidating the reaction process of a material where it cannot be evaluated by a stand-alone TG-DTA.

In addition, the introduced skimmer-type interface adopting the PI method enables an extensively wide measurement which gives rise to obtaining new knowledge with respect to material evaluation.

References

(1) M. Sorai: *Comprehensive Handbook of Calorimetry and Thermal Analysis*, John Wiley and Sons, Ltd., (2004).
(2) T. Arii: *J. Mass Spectrom Soc. Jpn.*, **51** (2003), 235–241.