# "TG-GC" as thermogravimetric and quantitative reactedgas analyses

# Teruki Motohashi<sup>\*</sup>, Yoshiteru Kawahara<sup>\*</sup>, Kenji Arai<sup>\*</sup>, Kenta Suzuki<sup>\*</sup> and Miwa Saito<sup>\*</sup>

# 1. Introduction

Thermogravimetry (TG) is regarded as one of the most powerful techniques to investigate the fundamental characteristics of inorganic compounds. For a certain compound, information on the temperature-vs-mass relationship leads to a deep understanding of thermal behaviors as well as interactions with the surrounding atmosphere. Nevertheless, the interpretation would not be straightforward only with TG, when multiple gas species are involved in the thermal behaviors. Then, TG combined with a gas analyzer will effectively work. The combination of thermobalance and quadrupole mass spectrometer (Q-MS), the so-called "TG-MS," is commercially available, but this technique has the following drawbacks relating to Q-MS: (i) poor quantitative accuracy in the gas amounts, (ii) the complexity caused by fragmentations of gas molecules in the ionization process, (iii) strict limitations of the measuring atmosphere due to the necessity of differential evacuation<sup>(1)</sup>. For detailed studies on inorganic materials, an alternative analytical method that is capable of quantitative gas analyses under various atmospheres is highly desirable to compensate for the drawbacks of TG-MS.

The authors have recently designed and developed a novel system, "TG-GC," which employs gas chromatography (GC) as a gas analyzer instead of Q-MS. As mentioned below, TG-GC has several advantages, making this system a complementary tool to conventional TG-MS. In this article, we will show a basic concept and the capability of TG-GC. Then, some case studies with the use of TG-GC will be reviewed.

#### 2. A Brief Overview of TG-GC

A schematic illustration of the TG-GC system is presented in Fig. 1. This system has a simple structure consisting of TG and GC directly connecting with a gas tube. For our system, TG-DTA 8122 (Rigaku Corporation) and 3000 Micro GC or Micro GC Fusion (INFICON Co., Ltd.) are used. While a carrier gas feeds into the air-tight TG apparatus, the reacted-gas via a sample chamber is analyzed by GC. A part of the flowing gas is pumped out from the backside of TG so as to avoid the reacted gas from being contaminated by a stagnated gas inside the apparatus. Using two mass-flow controllers (=flowmeters) located at the gas-feed and gas-exhaust ports, the gas-feed rate x [mLmin<sup>-1</sup>], the gas-exhaust rate y [mLmin<sup>-1</sup>], and the reacted-gas flow rate x-y [mLmin<sup>-1</sup>] are precisely controlled. This setup enables us to accurately measure the amounts of gas species evolving from the sample.

For our TG-GC, the use of a high-speed GC, the so-called micro GC, is a technical key ingredient. The micro GC has achieved a significant reduction of analysis time owing to its downsized column and detector. In fact, our apparatus completes a single run (measurement+analysis) only within 1–2 minutes. This implies that the micro GC can perform gas analyses



Fig. 1. Schematic illustration of the TG-GC system.

<sup>\*</sup>Department of Materials and Life Chemistry, Kanagawa University.

every 5–10K step when combined with TG running with a heating rate of 5°C min<sup>-1</sup>. It should be noted that if the micro GC was replaced by a conventional GC (10–20 min for data acquisition), the temperature interval would be too large (50–100 K) to relate the gas evolution to the thermal behaviors. Thus, the technological innovation of micro TG has contributed to the implementation of TG-GC. The micro GC can simultaneously detect N<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub> using two parallel columns (zeolite-type and polymertype). In general, gas analyses by GC show high quantitativity, giving rise to a close relationship between the evolved-gas amounts and weight-variation ratios.

### 3. Development of the TG-GC System: Verification of the Quantitativity

To verify the quantitativity of this technique in terms of gas amounts, TG-GC experiments were carried out for some standard compounds exhibiting simple thermal behaviors. As a representative result, data of the thermal reduction of copper oxide(II) in flowing  $N_2$  (Eq. 1) are shown in Fig. 2.

$$2CuO \rightarrow Cu_2O + 1/2O_2\uparrow$$
(1)

CuO is known to release oxygen gas triggered by thermal reduction of  $Cu^{2+}$  to  $Cu^+$  at elevated temperatures. At 800°C–1000°C, a weight loss, together with oxygen evolution, was observed in TG-GC. The magnitude of weight loss is well correlated with the amount of evolved O<sub>2</sub> gas. The 10.15% weight loss of 41.38 mg CuO corresponds to 4.20 mg, which is in perfect agreement with 4.19 mg estimated from the integrated O<sub>2</sub> amount in GC, demonstrating excellent O<sub>2</sub>-gas quantitativity of our TG-GC system.

The gas-amount quantitativity was also examined for carbon dioxide and water vapor, employing the decarboxylation of calcium carbonate (Eq. 2), and the dehydration of calcium oxalate monohydrate (Eq. 3). The results ensured that both the gas species can be



Fig. 2. TG-GC result of thermal reduction of CuO. (a) TG, (b) GC.

quantitatively analyzed by TG-GC.

$$CaCO_3 \rightarrow CaO + CO_2^{\uparrow} \tag{2}$$

$$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O \uparrow$$
(3)

Note, however, that experimental conditions such as the gas-feed rate  $x \text{ [mLmin}^{-1]}$  and the gas-exhaust rate  $y \text{ [mLmin}^{-1]}$  need to be optimized to attain better quantitativity of water: otherwise, the water amount was found to be underestimated by GC. This is because water molecules are subject to surface adsorption inside the apparatus, eventually being pumped out from the backside port. Such a phenomenon gets more prominent when the reacted gas flow rate  $x-y \text{ [mLmin}^{-1]}$  is relatively small. Based on preliminary experiments, the condition for TG-GC analyses was optimized, as summarized in Table 1.

We next analyzed thermal behaviors of calcium oxalate monohydrate in a wide temperature range to verify the capability of TG-GC for multiple gas species. This compound is known to show, in addition to the dehydration mentioned earlier (Eq. 3), the decarbonylation (Eq. 4) followed by the decarboxylation of the resultant calcium carbonate (Eq. 2) at elevated temperatures.

$$CaC_2O_4 \rightarrow CaCO_3 + CO\uparrow$$
 (4)

As presented in Fig. 3, three distinct steps of weight loss appear in the TG curve, and concurrently, water, carbon monoxide, and carbon dioxide are detected by GC in sequence upon heating. Besides, a slight amount of carbon dioxide is seen in the second step: this is most likely a consequence of oxidation of carbon monoxide by the residual oxygen inside the TG apparatus. Noticeably, the TG and GC data well coincide with each other. In fact, the evolved-gas amounts estimated from the GC data are 100%, 97%, and 98% of those from the TG data for the first, second, and third steps, respectively. This result demonstrates that TG combined GC analyses could be useful to precisely determine the evolved gas amounts even if multiple gas species are involved.

#### 4. Case Study of TG-GC #1: Thermal Behaviors of Cobalt Oxy-Hydroxide

The most notable feature of TG-GC is the superb evolved-gas quantitativity owing to the simultaneous use of TG and GC. This analysis technique may be

Table 1.	Optimized	condition for	or TG-GC	analyses
----------	-----------	---------------	----------	----------

Setting parameter	Value	
Gas-feed rate $(x)$	$160\mathrm{mLmin}^{-1}$	
Gas-exhaust rate $(y)$	$10\mathrm{mLmin}^{-1}$	
Reacted-gas flow rate $(x-y)$	150 mLmin <sup>-1</sup>	
Heating rate	7 K min <sup>-1</sup>	
Data acquision time for GC	1.5 min	



Fig. 3. TG-GC result of  $CaC_2O_4 \cdot H_2O$  upon heating. (a) TG, (b) GC.

best used for "mixed-anion compounds"<sup>(2)</sup>, which have attracted growing attention. Since these compounds contain multiple anions in the crystal lattice and tend to interact with various gas species, correlations of thermogravimetric variations with evolved-gas species are indispensable<sup>(3)</sup>. In the following, a case study of TG-GC will be reviewed: the application to cobalt oxy-hydroxide CoOOH, a member of the mixed-anion family.

CoOOH is a layered compound consisting of twodimensional CoO<sub>2</sub> blocks with hydrogen bonding via interlayer protons<sup>(4)</sup>. This compound has been recognized as a highly active catalyst for the oxygen evolution reaction (OER), potentially applicable to electrochemical/photocatalytic water splitting and cathode materials in metal–air secondary batteries<sup>(5)</sup>. A CoOOH sample was synthesized via oxidation and precipitation starting from a cobalt nitrate (II) aqueous solution, and its thermal behaviors were investigated. According to the previous TG-MS study<sup>(6)</sup>, the following two-step reaction occurs upon heating:

 $CoOOH \rightarrow 1/3 Co_3 O_4 + 1/2 H_2 O\uparrow + 1/12 O_2 \uparrow$ (5)

$$\operatorname{Co}_{3}\operatorname{O}_{4} \rightarrow 3\operatorname{CoO} + 1/2\operatorname{O}_{2}\uparrow \tag{6}$$

The result of our TG-GC measurement is presented in Fig. 4. Two steps of weight loss are seen in the TG curve. The GC data indicate that the first step involves desorption of water and oxygen, while oxygen alone is evolved in the second step, basically agreeing with Eqs. 5 and 6. Under the assumption that the cobalt oxy-hydroxide completely reacted and transformed into CoO, the chemical composition based on GC can be written as  $CoO_{0.96(0)}(OH)_{0.98(0)}$ : that is, essentially stoichiometric. Meanwhile, a close look at the GC data highlights a complicated behavior in the low-temperature gas desorption (=first weight loss). In the early stage of weight loss at 200°C–250°C, only water desorption takes place, contrary to the 6/1



Fig. 4. TG-GC result of CoOOH upon heating. (a) TG, (b) GC.

stoichiometric water/oxygen ratio expected from Eq. 5. This result suggests that CoOOH might decompose via unprecedented multiple processes. Detailed studies employing in-situ observations such as high-temperature X-ray diffraction are desirable.

## 5. Case Study of TG-GC #2: A Compositional Study on Aluminum Hydroxide-Bicarbonates

The second case study deals with compositional particles derived analyses on ultrafine from polynuclear ions. A polyaluminum hydroxide ion  $[\varepsilon-Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+} = "Al_{13}"$  is an intriguing chemical species containing plenty of hydroxy groups and aqua ligands that may act as absorption centers or active sites. Recently, Uchida and co-workers successfully fabricated amorphous ultrafine particles of aluminum hydroxide-bicarbonates by mixing an aqueous solution containing Al<sub>13</sub> with an aqueous bicarbonate solution, followed by the addition of a basic solution for controlling pH levels<sup>(7)</sup>. Because of the large specific surface area (> $200 \text{ m}^2 \text{ g}^{-1}$ ), this material may be a potential adsorbent applicable to the removal of toxic dye molecules in wastewaters of the textile industry. As the magnitude of the specific surface area depends on the choice of bicarbonates and bases used for the synthesis, the influences of synthesis conditions on the chemical composition need to be carefully investigated. We thus carried out TG-GC experiments on Al13-derived ultrafine particles to quantitatively analyze water and carbon dioxide incorporated in the samples<sup>(8)</sup>.

The "I-NaOH" sample was obtained with the use of NaHCO<sub>3</sub> and NaOH as bicarbonate and base, respectively. The "I-NH<sub>3</sub>" sample was similarly synthesized using of NH<sub>4</sub>HCO<sub>3</sub> and NH<sub>3</sub>. Shown in Fig. 5 are the TG-GC results of the two samples. For both samples, a gradual weight variation is observed over a wide temperature range such that individual assignments of desorbed gas species are not possible. Meanwhile,



Fig. 5. TG-GC data. (Left) I-NaOH sample, (Right) I-NH<sub>3</sub> sample.

the desorption of water and carbon dioxide is detected by GC. The  $H_2O/CO_2$  contents were determined individually from the total amount of each gas species.

I-NaOH: H<sub>2</sub>O/CO<sub>2</sub>=34.0/5.3 wt%

I-NH<sub>3</sub>: H<sub>2</sub>O/CO<sub>2</sub>=34.6/2.9 wt%

These values are consistent with the chemical formulae deduced from the results of elemental analyses (see below).

$$I-NaOH = [Al_{13}O_4(\mu-OH)_{24}(H_2O)_{6.5}(OH)_{5.5}](HCO_3)_{1.5}$$
$$I-NH_3 = [Al_{13}O_4(\mu-OH)_{24}(H_2O)_6(OH)_6](HCO_3)$$

It is worthwhile to point out that the  $H_2O/CO_2$  desorption behaviors largely differ between **I-NaOH** and **I-NH<sub>3</sub>**, and each of water and carbon dioxide desorbs in two steps, suggesting the coexistence of chemical species of different bonding states. This finding will provide useful information on the molecular adsorbing ability of each sample.

#### 6. Conclusion

In this article, we reviewed "TG-GC," a novel multifunctional system consisting of thermobalance and high-speed gas chromatography for thermogravimetric and reacted-gas analyses, respectively. This system enables us to relate weight variations with multiple gas desorption quantitatively. Our TG-GC has several characteristic features, making this system a complementary tool to conventional TG-MS. For instance, TG-GC is effectively applied to chemical reactions involving the desorption of nitrogen and carbon monoxide. Such chemical reactions often occur in oxy-nitrides, which are the representative members of mixed-anion compounds. Note that TG-MS is unable to distinguish these gas species due to the similarity in their molecular weights (=28). Our research group examined the formation of SrTaO<sub>2</sub>N from a powder mixture of SrCO<sub>3</sub> and Ta<sub>3</sub>N<sub>5</sub>, and successfully detected a simultaneous evolution of nitrogen and carbon monoxide using TG-GC<sup>(9)</sup>.

Table 2. Comparison of TG-GC and TG-MS.

Analytical method	TG-GC	TG-MS
Gas availability	$\bigtriangleup$	O
Detection sensitivity	0	O
Time resolution	$\bigtriangleup$	0
Quantitativity	0	$\bigtriangleup$
Conditional flexibility	0	×
Handleability and cost	0	$\bigtriangleup$

Characteristics of TG-GC and TG-MS are summarized in Table 2. We expect that TG-GC will be utilized as a more common thermoanalytical method because of the affordable price and handleability of micro GC compared to Q-MS. Further research and development are desirable to realize an integrated TG-GC system.

#### Acknowledgment

The authors thank Mr. Satoshi Otake, Mr. Yuki Kamimura (Rigaku Corporation), Mr. Mitch Okuda, and Mr. Yoshinori Misawa (INFICON Co., Ltd.) for their technical advises. Also, Prof. Sayaka Uchida of the University of Tokyo is acknowledged for her help in the analyses of aluminum hydroxide-bicarbonates. The present work was supported in part by JSPS Grant-in-Aid for Scientific Research on Innovative Areas "Mixed anion" (Grant Numbers JP16H6439, JP17H05490, and JP19H04707).

#### References

- G. Hotová and V. Slovák: *Thermochimica Acta*, 632 (2016), 23–28.
- (2) H. Kageyama, K. Hayashi, K. Maeda, J. P. Attfield, Z. Hiroi, J. M. Rondinelli and K. R. Poeppelmeier: *Nat. Commun.*, 9 (2018), 772.
- (3) M. Saito, K. Arai, N. Uekusa, N. Tominaga and T. Motohashi: J. Ceram. Soc. Jpn., 127 (2019), 777–784.
- (4) A. F. Wells: Structural Inorganic Chemistry Fifth Edition, Clarendon Press Oxford, (1984), Chapter 14, 643.

- (5) N.-T. Suen, S.-F. Hung, Q. Quan, N. Zhang, Y.-J. Xu and H. M. Chen: Chem. Soc. Rev., 46 (2017), 337–365.
- (6) C.-W. Tang, C.-B. Wang and S.-H. Chien: *Thermochem. Acta*, 473 (2008) 68–73.
- (7) Y. Kinoshita, R. Osuga, J. N. Kondo, Y. Ogasawara and S. Uchida, *Chem. Lett.*, 47 (2018), 668–670.
- (8) Y. Kinoshita, Y. Shimoyama, Y. Masui, Y. Kawahara, K. Arai, T. Motohashi, Y. Noda and S. Uchida, *Langmuir*, 36 (2020), 6277–6285.
- (9) S.-K. Sun, T. Motohashi, Y. Masubuchi and S. Kikkawa, J. Eur. Ceram. Soc., 34 (2014), 4451–4455.