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## Quantitative analysis by TG-MS for reactions with evolved gases

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**TITLE:**

Quantitative Analysis by Thermogravimetry-mass Spectrum Analysis for Reactions with Evolved Gases

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**KEYWORDS:**

Equivalent characteristic spectrum analysis (ECSA), quantitative analysis, evolved gas analysis, calibration, mass spectrometer (MS), mass flow rate

**SHORT ABSTRACT:**

Precise determination of the evolved gases' flow rate is key to study the details of reactions. We provide a novel quantitative analysis method of equivalent characteristic spectrum analysis for thermogravimetry-mass spectrum analysis by establishing the calibration system of the characteristic spectrum and relative sensitivity, for obtaining the flow rate.

**LONG ABSTRACT:**

During energy conversion, material production, and metallurgy processes, reactions often have the features of unsteadiness, multistep, and multi-intermediates. Thermogravimetry-mass spectrum (TG-MS) is seen as a powerful tool to study reaction features. However, reaction details and reaction mechanics have not been effectively obtained directly from the ion current of TG-MS. Here, we provide a method of an equivalent characteristic spectrum analysis (ECSA) for analyzing the mass spectrum and giving the mass flow rate of reaction gases as precise as possible. The ECSA can effectively separate overlapping ion peaks and then eliminate the mass discrimination and temperature-dependent effect. Two example experiments are presented: (1) the decomposition of  $\text{CaCO}_3$  with evolved gas of  $\text{CO}_2$  and the decomposition of hydromagnesite with evolved gas of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , to evaluate the ECSA on single-component system measurement and (2) the thermal pyrolysis of Zhundong coal with evolved gases of inorganic gases  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{CO}_2$ , and organic gases  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_6\text{H}_{14}$ , etc., to evaluate the ECSA on multi-component system measurement. Based on the successful calibration of the characteristic spectrum and relative sensitivity of specific gas and the ECSA on mass spectrum, we demonstrate

that the ECSA accurately gives the mass flow rates of each evolved gas, including organic or inorganic gases, for not only single but multi-component reactions, which cannot be implemented by the traditional measurements.

## INTRODUCTION:

Understanding in depth the real features of a reaction process is one critical issue for the development of advanced materials and the establishment of a new energy conversion system or metallurgy production process<sup>1</sup>. Almost all reactions are carried out under unsteady conditions, and because their parameters, including the concentration and flow rate of reactants and products, always change with the temperature or pressure, it is difficult to clearly characterize the reaction feature by only one parameter, for instance through the Arrhenius Equation. In fact, the concentration implies only the relationship between the component and the mixture. Real reaction behavior might not be affected, even though the concentration of a component in one complicated reaction is adjusted to a great extent since the other components might have a stronger influence on it. On the contrary, the flow rate of each component, as an absolute quantity, can give persuasive information to understand the characteristics of the reactions, especially very complicated ones.

At present, the TG-MS coupling system equipped with the electron ionization (EI) technique has been used as a prevalent tool for analyzing the features of reactions with evolved gases<sup>2-4</sup>. However, first, it should be noted that the ion current (IC) obtained from an MS system makes it difficult to directly reflect the flow rate or concentration of the evolved gas. The massive IC overlap, fragment, severe mass discrimination, and diffusion effect of gases in the furnace of a thermogravimeter can greatly hamper the quantitative analysis for TG-MS<sup>5</sup>. Second, EI is the most common and readily available strong ionization technique. An MS system equipped with EI easily results in fragments and does not often directly reflect some organic gases with a larger molecular weight. Therefore, MS systems with different soft ionization techniques (*e.g.*, photoionization [PI]) are required simultaneously to be hyphenated to a thermobalance and applied to evolved gas analysis<sup>6</sup>. Third, the intensity of the IC at some mass-to-charge ratios ( $m/z$ ) cannot be used to determine the dynamic characteristic of any reaction gas, because it is often affected by the other ICs for a complex reaction with multicomponent evolved gases. For example, the drop in the IC curve of a specific gas does not necessarily indicate a decrease in its flow rate or concentration; instead, maybe it is affected by the other gases in the complex system. Thus, it is important to take into account all gases' ICs, certainly with a carrier gas and inert gas.

In fact, quantitative analysis based on mass spectrum greatly depends on the determination of the calibration factor and relative sensitivity of the TG-MS system. Maciejewski and Baiker<sup>7</sup> investigated in a thermal analyzer-mass spectrometer (TA-MS) system, in which the TA is connected by a heated capillary to a quadrupole MS, the effect of experimental parameters, including the concentration of gases species, temperature, flow rate, and properties of the carrier gas, on the sensitivity of the mass spectrometric analysis. The evolved gases were calibrated by the decomposition of the solids *via* a well-known, stoichiometric reaction and injecting a certain amount of gas into the carrier gas stream with a constant rate. The experimental results show that there is a negative linear correlation of the MS signal intensity of evolved gas to that of the

carrier gas flow rate, and the evolved gas MS intensity is not influenced by the temperature and the amount of analyzed gas. Further, based on the calibration method, Maciejewski *et al.*<sup>8</sup> invented the pulse thermal analysis (PTA) method, which provides an opportunity to determine the flow rate by simultaneously monitoring the changes of the mass, enthalpy, and gas composition resulted from the reaction course. However, it is still hard to give persuasive information about the complicated reaction (*e.g.*, coal combustion/gasification) by using the traditional TG-MS analysis or PTA methods.

In order to overcome the difficulties and disadvantages of the traditional measuring and analysis method for the TG-MS system, we developed the quantitative analysis method of ECSA<sup>9</sup>. The fundamental principle of ECSA is based on the TG-MS coupling mechanism. The ECSA can take into account all gases' ICs, including the reaction gases', carrier gases', and inert gases'. After building the calibration factor and relative sensitivity of some gas, the real mass or molar flow rate of each component can be determined by the calculation of the IC matrix (*i.e.*, the mass spectrum of TG-MS). Compared with the other methods, ECSA for the TG-MS system can effectively separate the overlapping spectrum and eliminate the mass discrimination and the temperature-dependent effect of TG. The data produced by ECSA have proved to be reliable via a comparison between the mass flow rate of evolved gas and mass loss data by differential thermogravimetry (DTG). In this study, we used an advanced TG-DTA-EI/PI-MS instrument<sup>10</sup> to carry out the experiments (**Figure 1**). This instrument consists of a cylindrical quadrupole MS and a horizontal thermogravimetry-differential thermal analyzer (TG-DTA) equipped with both EI and PI mode, and with a skimmer interface. ECSA for the TG-MS system determines the physics parameters of all evolved gases by utilizing the actual TG-MS coupling mechanism (*i.e.*, an equal relative pressure) to implement the quantitative analysis. The overall analysis process includes a calibration, the test itself, and data analysis (**Figure 2**). We present two example experiments: (1) the decomposition of CaCO<sub>3</sub> with only evolved gas of CO<sub>2</sub> and the decomposition of hydromagnesite with evolved gas of CO<sub>2</sub> and H<sub>2</sub>O, to evaluate the ECSA on a single-component system measurement and (2) the thermal pyrolysis of brown coal with evolved gases of inorganic gases CO, H<sub>2</sub>, and CO<sub>2</sub>, and organic gases CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>6</sub>H<sub>14</sub>, *etc.*, to evaluate the ECSA on a multi-component system measurement. ECSA based on the TG-MS system is a comprehensive solution method for quantitatively determining the amount of evolved gas in thermal reactions.

## **PROTOCOL:**

### **1. Calibration of ECSA for the TG-MS System**

#### **1.1. Calibration of the characteristic spectrum**

1.1.1. Prepare the evolved gases of CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, He, *etc.* to be calibrated, modulating the gas pressure at 0.15 MPa.

1.1.2. Connect the gas cylinder to the TG-MS system by stainless steel tube and purge the individual gas into the TG-MS system with a flow rate of 100 mL/min.



1.1.3. Monitor the mass spectrum of the individual gas. Carefully watch and compare the characteristic peak of gases to be calibrated and the possible impurity gases in the mass spectrum by TG-MS to confirm the species and purity of the gases.

Note: The above-mentioned gases can be bought directly in gas cylinders or decomposed from some testing samples (except He). He is used as carrier gas in both the calibration and the test.

CAUTION: For some substances which are harmful to the TG or MS, the carrier gas must be used.

## 1.2. Calibration of the relative sensitivity

1.2.1. Purge the reference gas He with a flow rate of 300 mL/min into the TG-MS system for 20 min to clean the system.

1.2.2. Purge synchronously one type of calibrated gas, such as CO<sub>2</sub> or H<sub>2</sub>O, and the reference gas He into the TG-MS system with a flow rate of 100 mL/min.

1.2.3. Calculate the relative sensitivity of each gas according to the known flow rate and the mass spectrum (Equation 1).

$$\alpha_{r,k} = \frac{q_r}{q_k} \times \frac{l_k^+}{l_r^+} \quad (1)$$

Here,

$\alpha_{r,k}$  = relative sensitivity of the  $k$  gas to the reference gas

$q_r$  = the given flow rate of the reference gas

$q_k$  = the given flow rate of the  $k$  gas

$l_k^+$  = the determined ion current for the  $k$  gas by MS, and

$l_r^+$  = the determined ion current for reference gas.

Note: The volumetric flow rates of the calibrated and reference gas must be known in advance.

## 2. Testing Process of ECSA for the TG-MS System

### 2.1. Preparation of the samples used for the test

#### 2.1.1. Preparation of the samples of CaCO<sub>3</sub> and hydromagnesite

2.1.1.1. Collect 10-g samples of CaCO<sub>3</sub> with an average diameter of 15  $\mu$ m.

2.1.1.2. Collect 10 g of a white block of hydromagnesite, break it into pieces of < 3 mm in size, and grind the pieces with a machine-stirred mill to approximately 10  $\mu$ m.

2.1.1.3. Dry all the samples for 24 h in the oven at a temperature of 105 °C.

Note: The above steps can be implemented in parallel.

### **2.1.2. Preparation of the samples of Zhundong coals**

2.1.2.1. Collect 20 g of Zhundong coal from the coalfield located at the Mori Kazak Autonomous County, Xinjiang province in China.

2.1.2.2. To eliminate any external moisture, dry the coal in the oven at a temperature of 105 °C for 24 h.

2.1.2.3. Break and ground the coal in a mill to obtain a particle size range of 180 - 355 µm.

### **2.2. Test of the thermal reactions**

2.2.1. Purge the TG-MS system with the carrier gas He for 2 h to expel the air and moisture. Meanwhile, preheat the instrument to around 500 °C and, then, cool it down to room temperature.

Note: The He gas was used as carrier gas for all the tests.

2.2.2. Monitor the atmosphere by using MS in the first 20 min, carefully watching and comparing the characteristic peak of CO<sub>2</sub>, He, and the impurity gases of O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O in the mass spectrum, to guarantee the lowest content of air and moisture, not affecting the experimental measurements.

2.2.3. Weigh a sample of 10 mg by using the precision electronic balance and put the sample into an Al<sub>2</sub>O<sub>3</sub> crucible.

2.2.4. Put the Al<sub>2</sub>O<sub>3</sub> crucible with the sample into the TG and close the furnace.

2.2.5. Set the operating parameters. (1) For the CaCO<sub>3</sub> test, start the temperature at 20 °C and heat to 550 °C with a heating rate of 10 K/min; then, for the modulating temperature program, heat to 800 °C with alternating heating rates of 10 K/min and 20 K/min. (2) For the hydromagnesite and coal test, start the temperature at 20 °C and use a heating rate of 10 K/min, a hold time of 15 min, a stopping temperature of 1,000 °C, and a gas flow rate of 20 mL/min; keep an m/z range of 2 - 200 for mode EI and 10 - 410 for mode PI.

Note: Mode PI was used to identify the organic gases, mainly used for the test of Zhundong coal pyrolysis in this study.

### **3. Qualitative and Quantitative Analysis**

3.1. Get the 3-D mass spectrum data recorded by the computer connected with the TG-MS

instrument.

3.2. Calculate the actual parameters, including the mass flow rate and the concentration of each evolved gas, by using the ECSA method, based on the determined calibrated characteristic peak (step 2.1) and the relative sensitivity (step 2.2).

3.3. Analyze the thermal reaction according to the actual parameters<sup>9</sup>.

#### REPRESENTATIVE RESULTS:

The thermal decomposition of  $\text{CaCO}_3$  is a relatively simple reaction, which was used to demonstrate the applicability of the ECSA method. After calibrating the characteristic peak and relative sensitivity of  $\text{CO}_2$  to carrier gas He, the actual mass flow rate of  $\text{CO}_2$  evolved by the thermal decomposition of  $\text{CaCO}_3$  was calculated by the ECSA method and was compared with the actual mass loss (**Figure 3**). It is shown that there is a good agreement between the mass flow rate of  $\text{CO}_2$  calculated by ECSA and the mass loss data by DTG during the entire measurement process. The relative error of mass flow rate of evolved gas to that of DTG is significantly lower, as shown by the blue and yellow lines in **Figure 4**. Also, the thermal decomposition process of hydromagnesite was analyzed by ECSA and the calibration data of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (**Figure 4**). The carrier gas flow rate was chosen as 100 mL/min and the heating rate was set at 5, 10, 15, and 20 K/min. The calculated results were also in good agreement with the experimental TG/DTG data.

To further demonstrate the qualitative analysis of organic gases and the ability of ECSA to quantitatively determine the flow rate of a complicated reaction system, pyrolysis of Zhundong coal was carried out<sup>10</sup>. Combining both the PI and EI measuring modes, 16 types of volatile gases, including  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$  (ethene),  $\text{C}_3\text{H}_6$  (propene),  $\text{C}_4\text{H}_8$  (butylene),  $\text{C}_5\text{H}_{10}$  (pentene),  $\text{C}_6\text{H}_{10}$  (hexadiene),  $\text{C}_7\text{H}_8$  (toluene),  $\text{C}_6\text{H}_6\text{O}$  (phenol),  $\text{C}_8\text{H}_{10}$  (ethylbenzene),  $\text{C}_7\text{H}_8\text{O}$  (anisole),  $\text{C}_9\text{H}_{12}$  (propyl benzene), and  $\text{C}_{10}\text{H}_{14}$  (butylbenzene), were clearly identified (**Figure 5**). After a detailed determination of mass spectrum and sensitivity of each gas to the carrier gas, the mass flow rate of each gas can be calculated. Straightforwardly, the ion current from the mass spectrum can be used to compare based on the same operating parameters (**Figure 6**).

#### FIGURE LEGENDS:

**Figure 1: Schematic diagram of the TG-DTA-EI/PI-MS system equipped with the EI and PI devices and skimmer-type interface.** This TG-DTA-EI/PI-MS system mainly consists of a cylindrical quadrupole MS and a horizontal thermogravimetry-differential thermal analyzer (TG-DTA) equipped both the EI and PI devices. The MS and TG-DTA are connected by the skimmer interface. This figure has been modified from Li *et al.*<sup>10</sup>.

**Figure 2: Process diagram of ECSA for testing the thermal reactions.** The overall analysis process can be divided into three parts that are calibration, test, and data analysis. The calibration part first provides the information of the characteristic spectrum and relative sensitivity of each gas in the reaction; this information is used for the subsequent calculation of the physics parameters, such as the flow rate, following the test.

**Figure 3: Comparison of the mass flow rate of evolved gas with the mass loss of DTG for the thermal decomposition of  $\text{CaCO}_3$ .** A comparison in mass loss between ECSA calculation results and measurement results from DTG was used to validate the reliability of the ECSA method. It is shown that there is a good agreement between the calculation by the ECSA and the measurements by DTG, and the relative error of mass flow rate of  $\text{CO}_2$  to that of DTG is significantly lower.

**Figure 4: Thermal decomposition process of hydromagnesite.** These panels show (a) a 3-D mass spectrum graph plotted against temperature and  $m/z$ , (b) mass flow rates of  $\text{CO}_2$  calculated by ECSA at a heating rate of 5, 10, 15, and 20 K/min, (c) mass flow rates of  $\text{H}_2\text{O}$  calculated by ECSA at a heating rate of 5, 10, 15, and 20 K/min, and (d) a comparison between ECSA-based flow rates and experimental TG/DTG data. Here, the carrier gas flow rate was chosen as 100 mL/min.

**Figure 5: 3-D mass spectrum graph of raw coal with the temperature and  $m/z$  in modes of EI and PI.** (a) The EI mode was mainly used to identify inorganic gases such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , while (b) the PI mode was mainly done to identify organic gases such as  $\text{C}_6\text{H}_6$  and  $\text{C}_7\text{H}_8$ . A joint use of EI and PI provides a comprehensive information for the pyrolysis of coal. This figure has been modified from Li *et al.*<sup>10</sup>.

**Figure 6: Mass ion curves of  $\text{CH}_4$  and  $\text{C}_6\text{H}_6\text{O}$  evolved from the raw coal sample and the pretreated Zhundong coal samples.** One kind of inorganic gas, (a)  $\text{CH}_4$ , and one organic gas, (b)  $\text{C}_6\text{H}_6\text{O}$ , were chosen to be represented in mass ion curves, for interpreting the function of ECSA on a quantitative analysis of the pyrolysis characteristics of different pretreated coals. Here the pretreated method includes the  $\text{H}_2\text{O}$ -washed coal and  $\text{HCl}$ -washed coal. This figure has been modified from Li *et al.*<sup>10</sup>.

## DISCUSSION:

This protocol could be easily modified to accommodate other measurements for studying evolved gases and pyrolysis reactions by a TG-MS system. As we know, the evolved volatile from the pyrolysis of biomass, coal, or other solid/liquid fuel does not always include only the inorganic gases (*e.g.*,  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{CO}_2$ ) but also the organic ones (*e.g.*,  $\text{C}_2\text{H}_4$ ,  $\text{C}_6\text{H}_5\text{OH}$ , and  $\text{C}_7\text{H}_8$ ). Moreover, massive fragments would result from the organic gases, and secondary reactions would occur during pyrolysis<sup>11</sup>. Even though several conventional measurement methods, like the normal TG-MS coupling system, Fourier transform infrared (FTIR) spectrometry<sup>12</sup>, high-performance liquid chromatography (HPLC)<sup>13</sup>, and UV-vis absorption and fluorescence spectroscopies<sup>14</sup>, have been employed for the characterization of the volatile gases and tar, there are still some issues to be solved, including the minimization of the secondary reactions, the mitigation of recondensation of evolved volatile gases during measurement, and the reduction of excessive fragments. ECSA developed based on a TG-DTA-EI/PI-MS system can be used to investigate accurately the pyrolysis characteristics for real-time, *in situ* measurement. Because of the fundamentality, applicability, and generality of the ECSA, the quantitative analysis for massive volatile gases from pyrolysis can be easily implemented<sup>9</sup>.

It should be considered that ECSA based on the TG-MS system is a powerful tool to analyze the thermal reaction processes with evolved gases for not only the simple system but also for the complicated one. A key step to implement the ECSA method is to successfully build the calibration factor and the relative sensitivity of the required gases. It also should be noted that the testing conditions of MS must be the same (or very similar) as those for calibration. Specifically, the reference gas for calibrating the relative sensitivity must be the same as the reference gas for the testing process, and it must never react with the evolved gases. In this study, helium is chosen as the reference gas in order to analyze CO<sub>2</sub> and H<sub>2</sub>O in the measurement. Further, we believe that the ECSA can be used to characterize the elementary reactions if the calibration factor and relative sensitivity of the reactants or products in the elementary reactions are successfully built. On the other hand, since the ECSA separates the mass spectrum of all evolved gases into the spectra of different components, the matrix constructed by the ion current of various evolved gases must be solved before the quantitative results are obtained. The matrix can be expected to be large, should there be a large quantity of evolved gas species. Therefore, matrix solution is also key to the implementation of ECSA.

Finally, ECSA has much more advantages than the traditional TG-MS analysis methods. The key one is that the ECSA can provide the exact quantitative information (*i.e.*, the flow rate, the concentration, and the partial pressure) for all gases. Another advantage is that, since ECSA treats with the IC of mass spectrum from the point of coupling characteristics (*i.e.*, the equal relative pressure between TG and MS), it radically eliminates the mass discrimination of MS and the temperature-dependent effect of TG. And further, the issue of time delay during the measurement of reactions with evolved gases (especially solid particle reactions) can also be effectively resolved by varying the flow rate of the carrier gas and the temperature of TG. However, due to the MS, the ECSA cannot be used to determine reactions without evolved gases, and there is still some difficulty in dealing with the elementary reactions. Since all reactions accompany a change of heat, we are developing a new method to correlate the heat change into the ECSA to provide quantitative information for reactions without evolved gases but with heat change.

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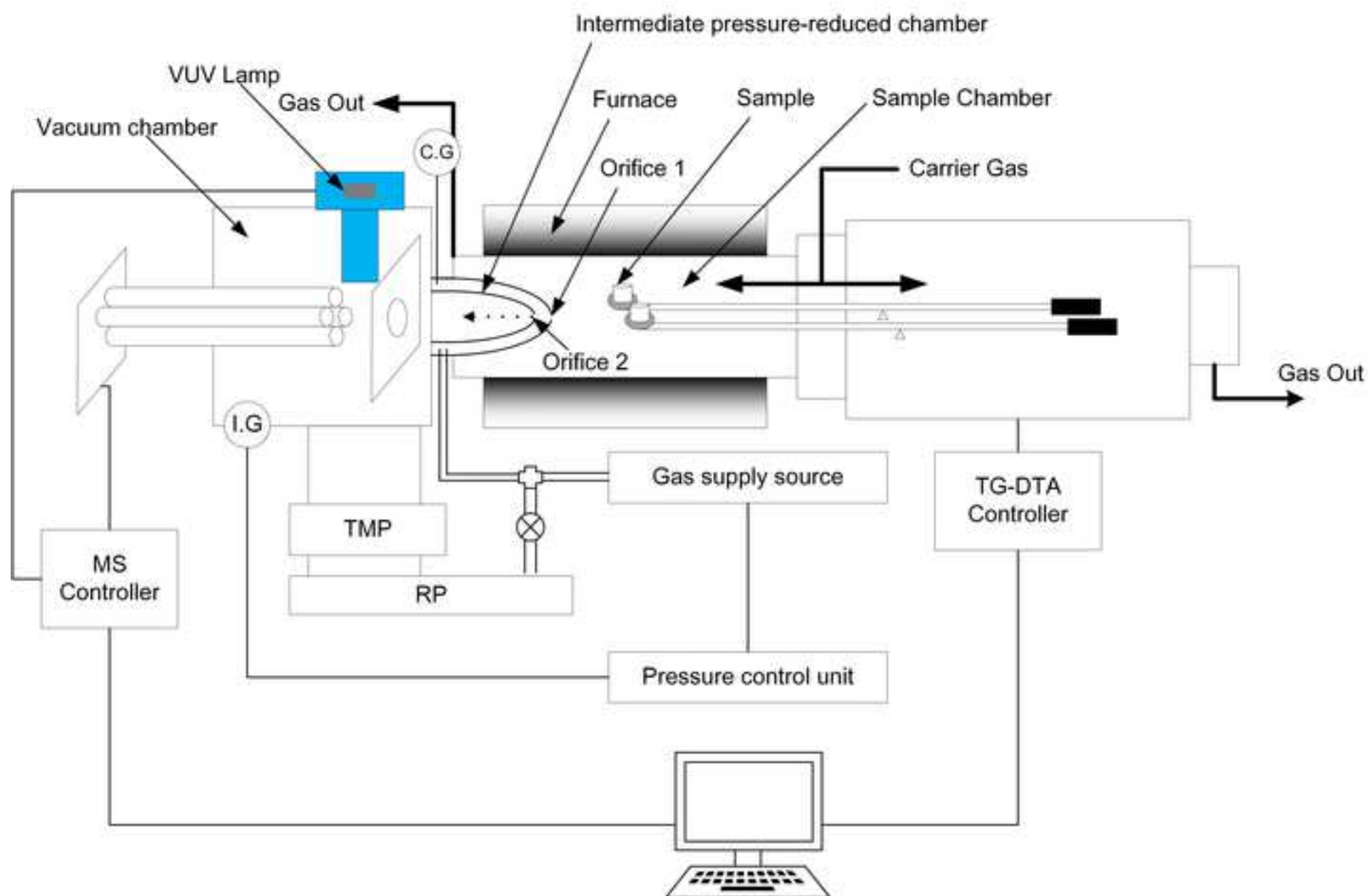
#### **DISCLOSURES:**

The authors have nothing to disclose.

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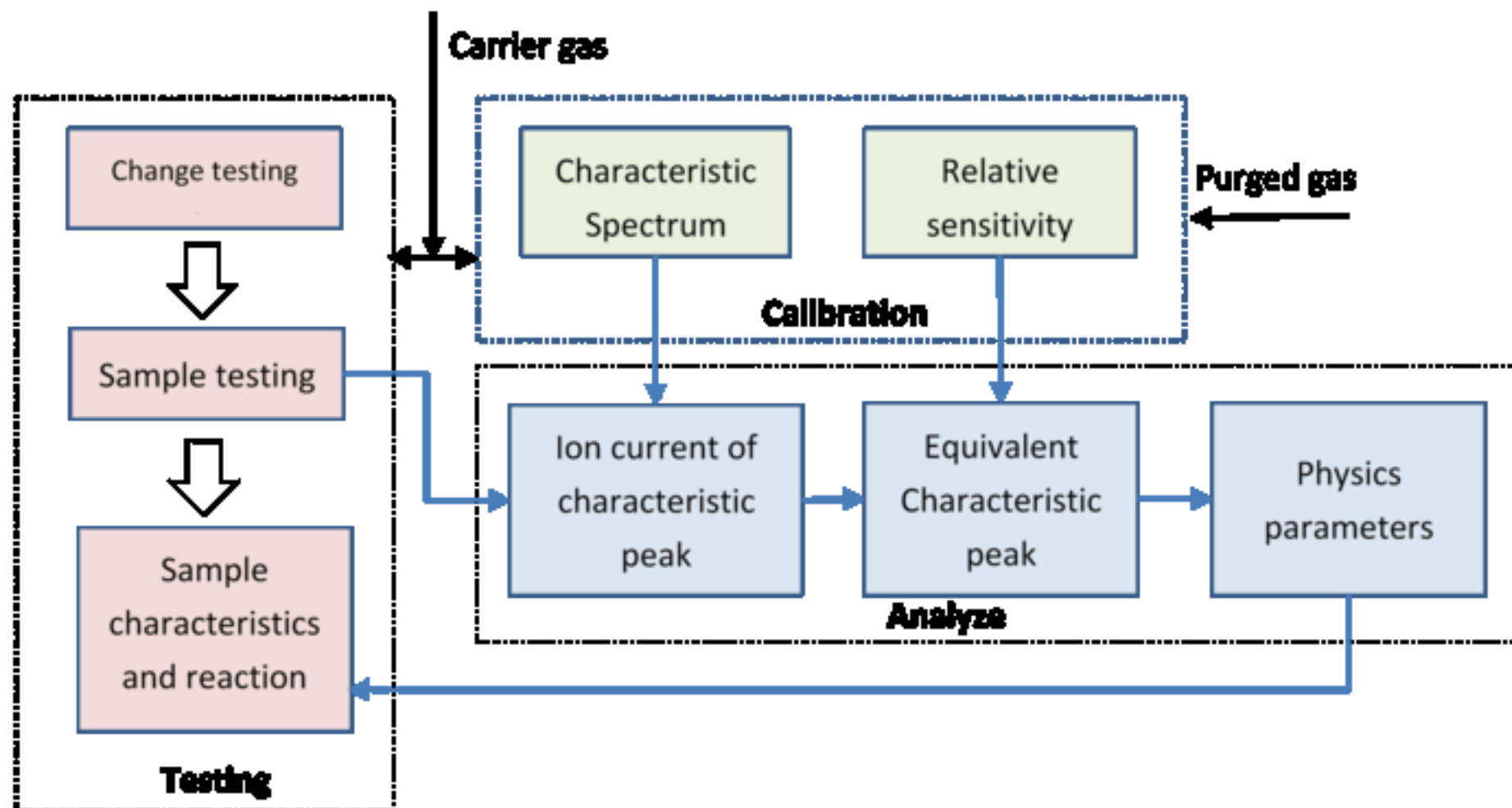




Figure 3

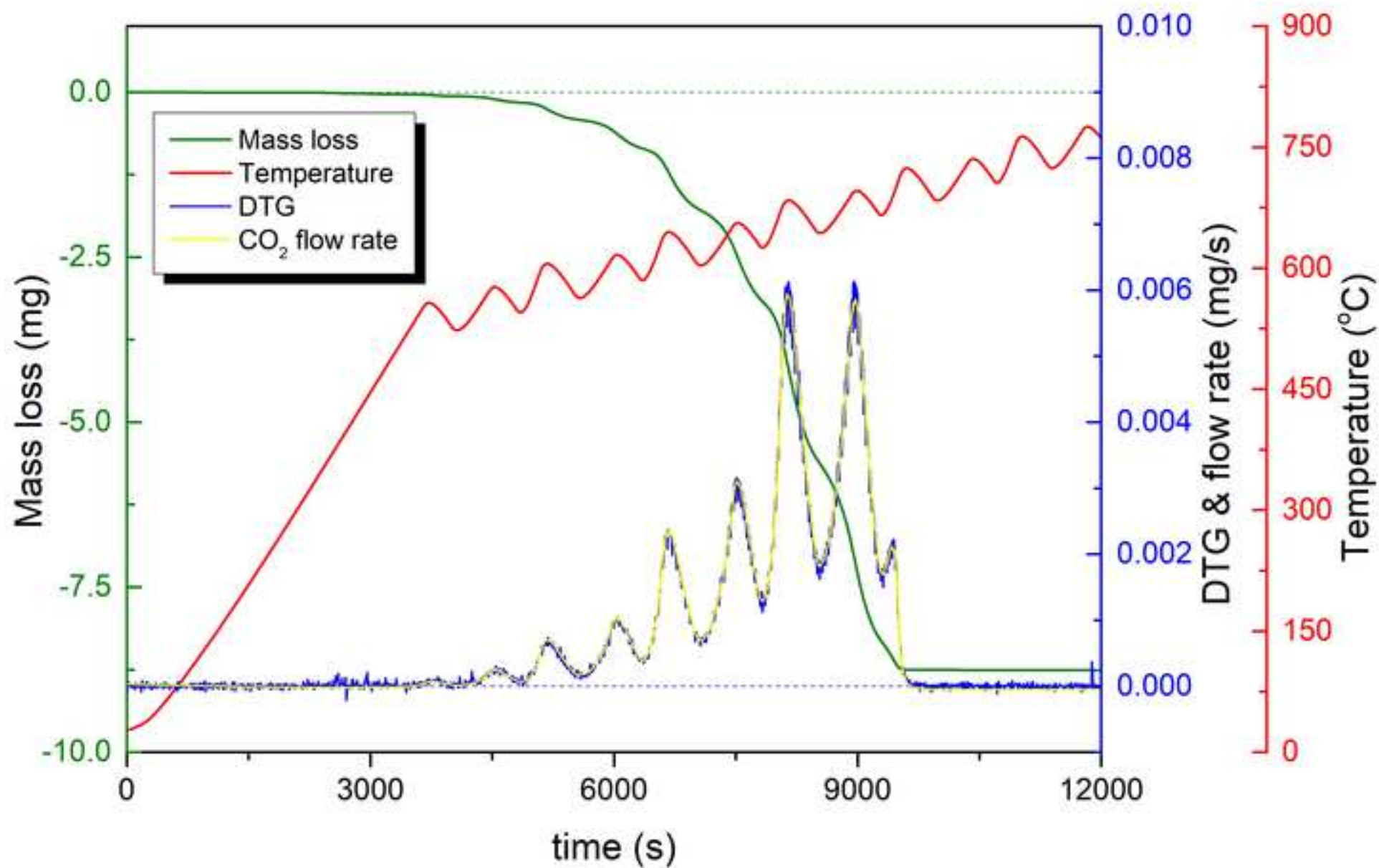
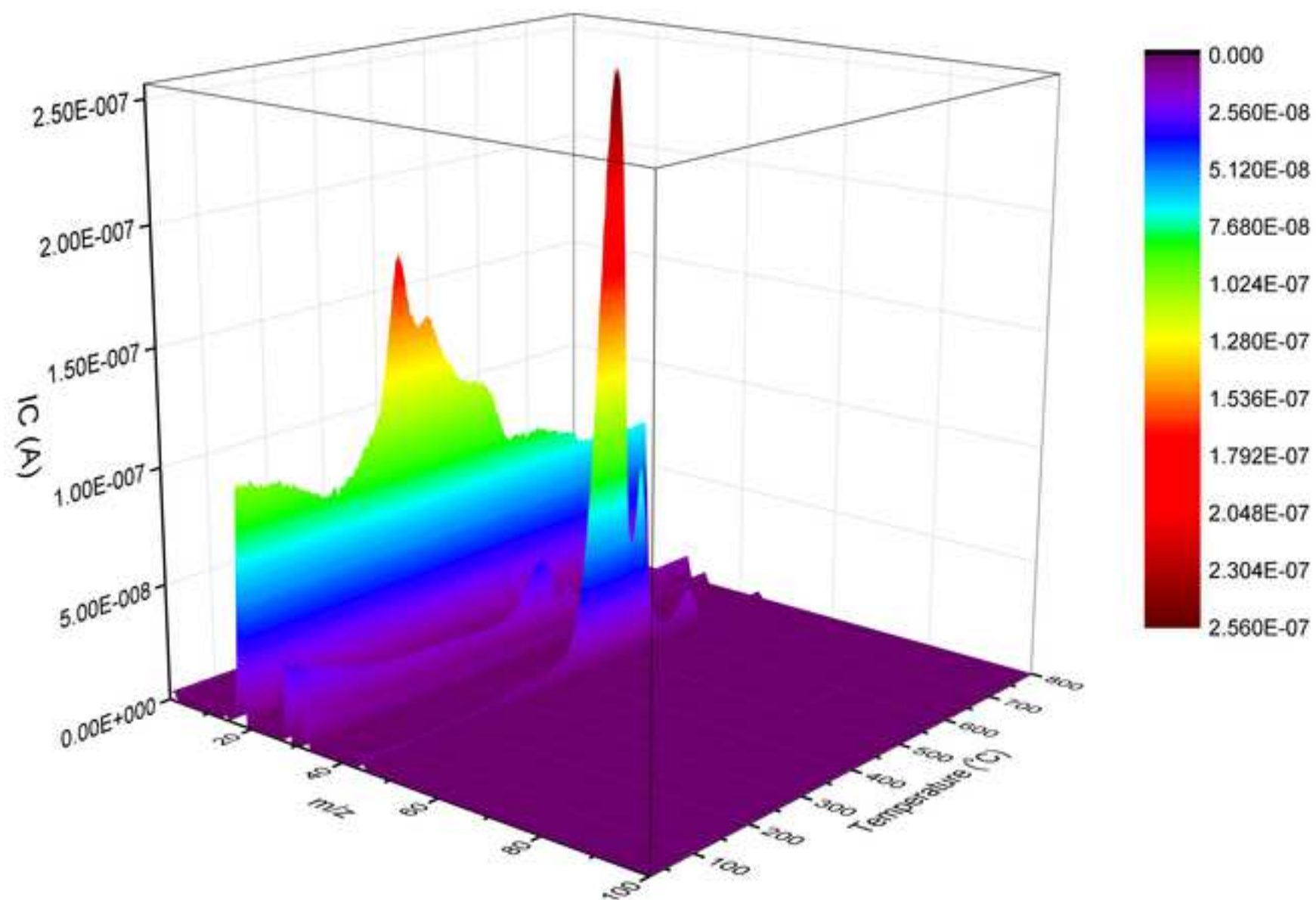
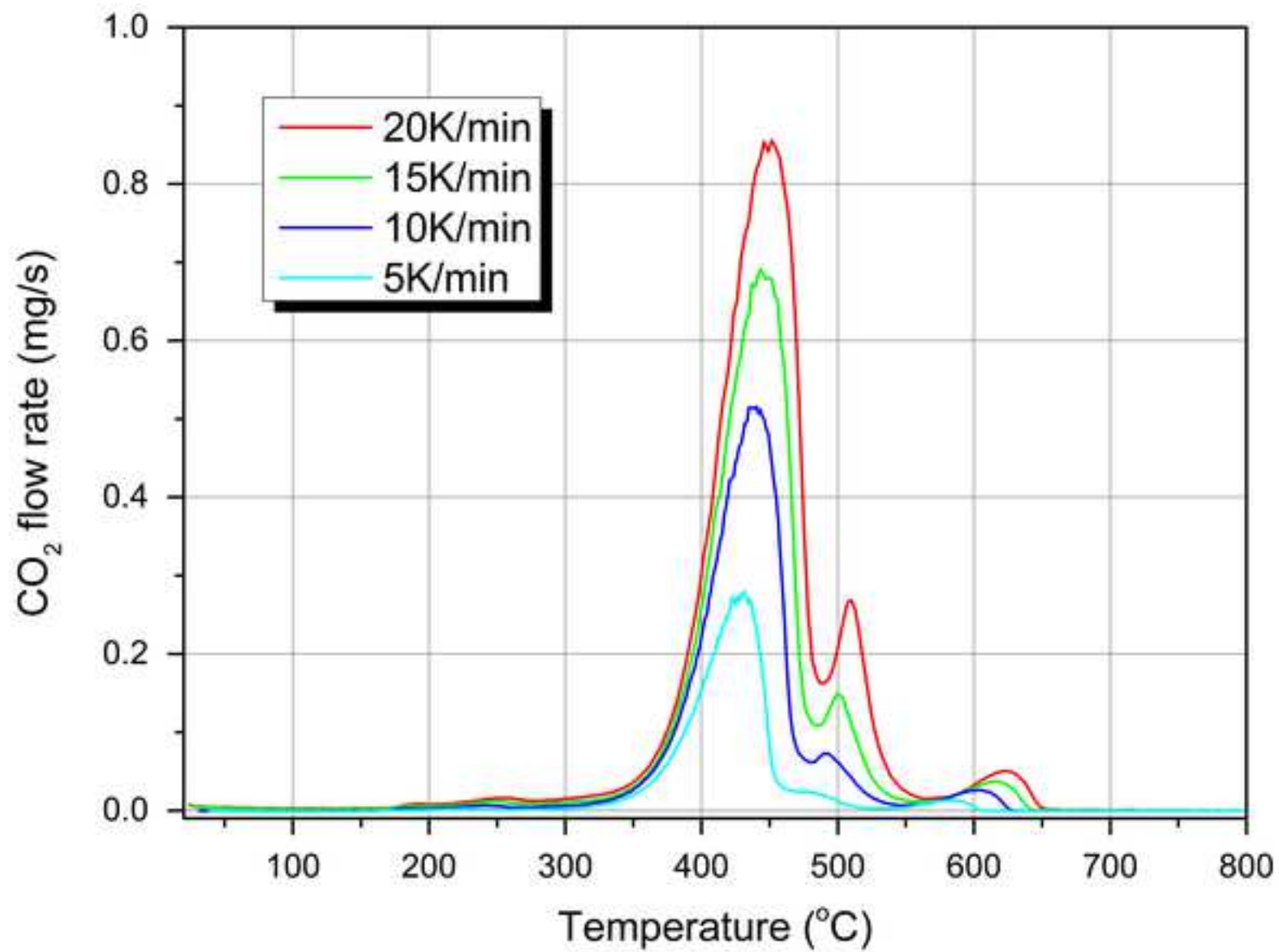
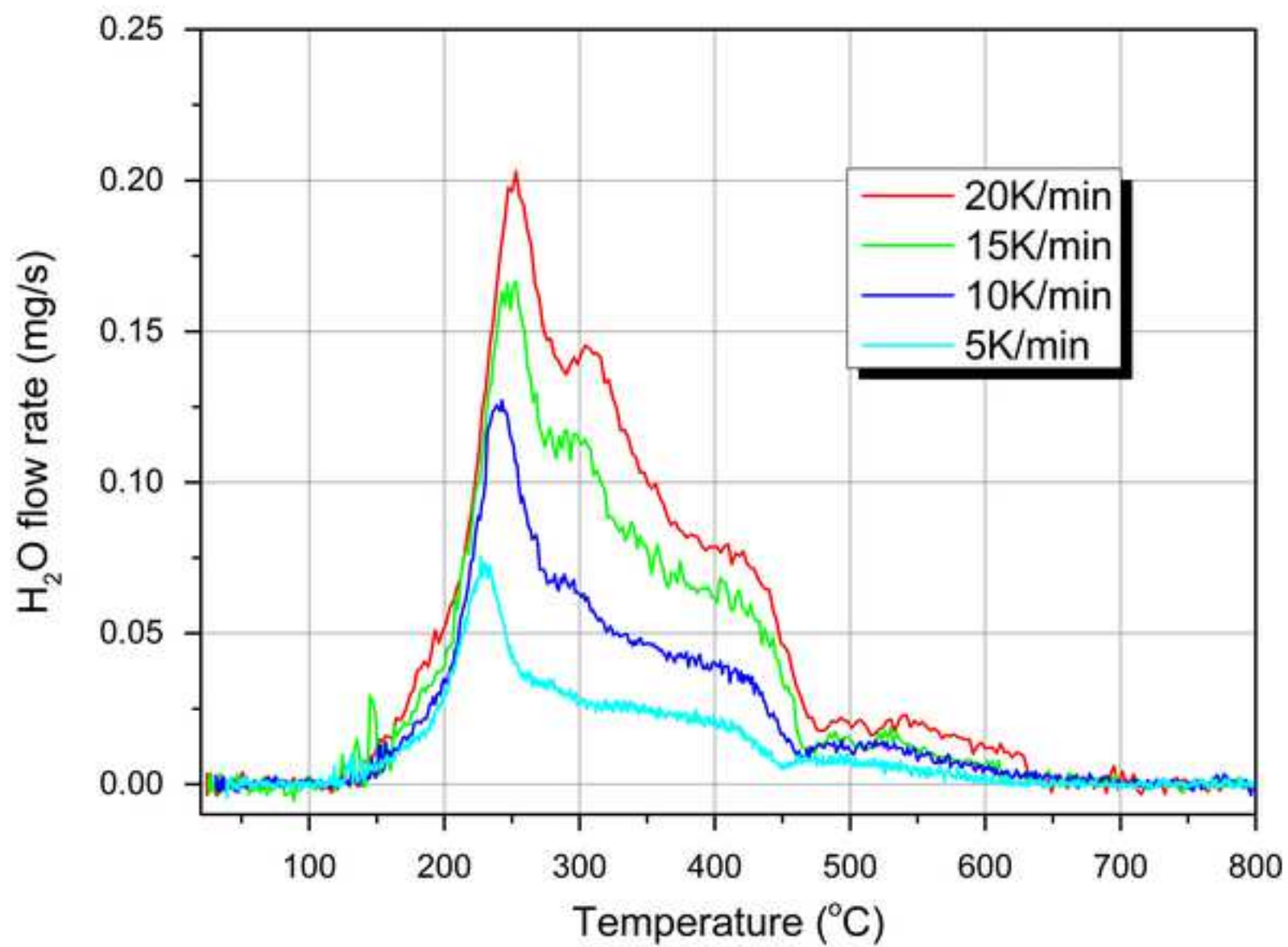


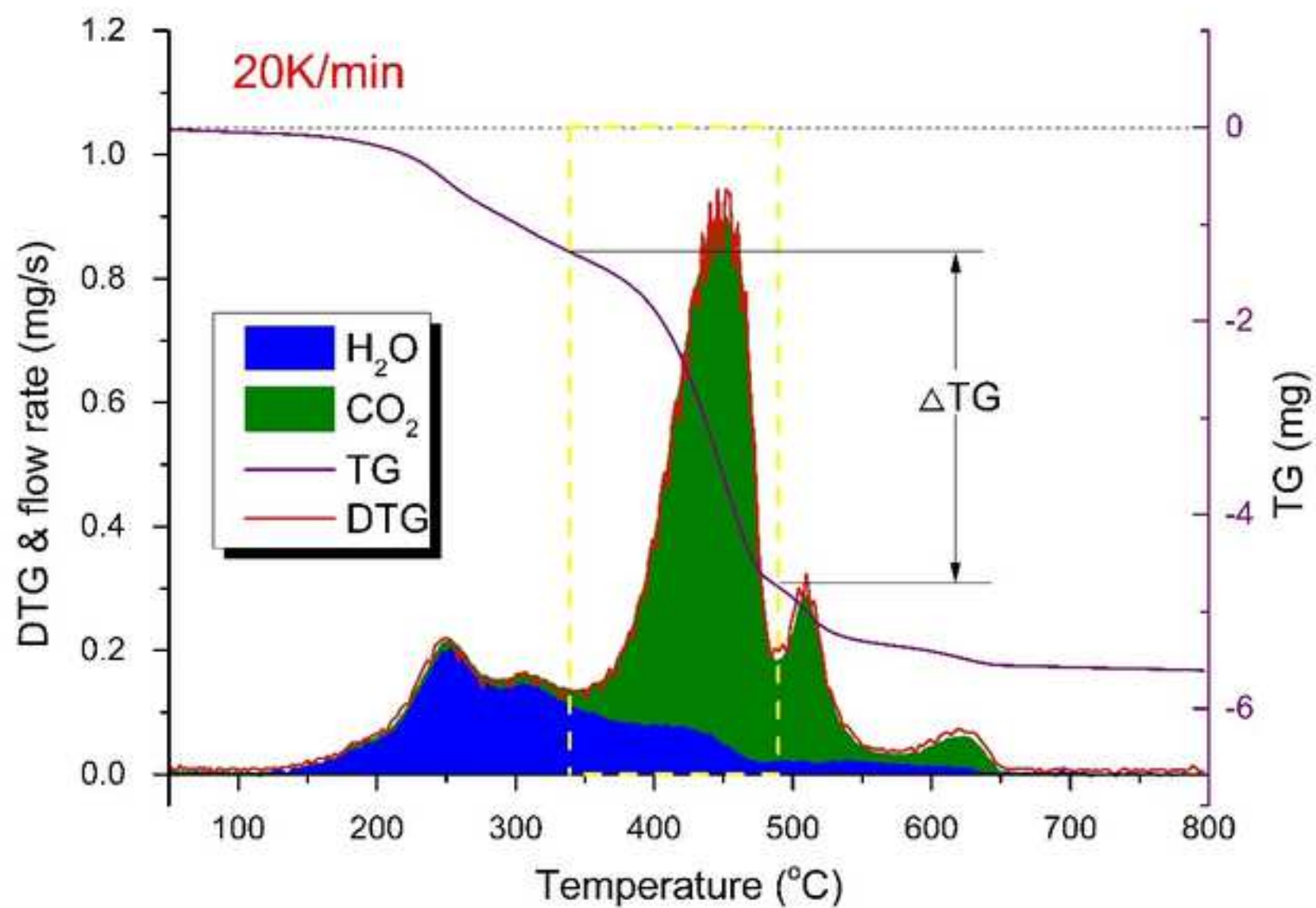
Figure 4a

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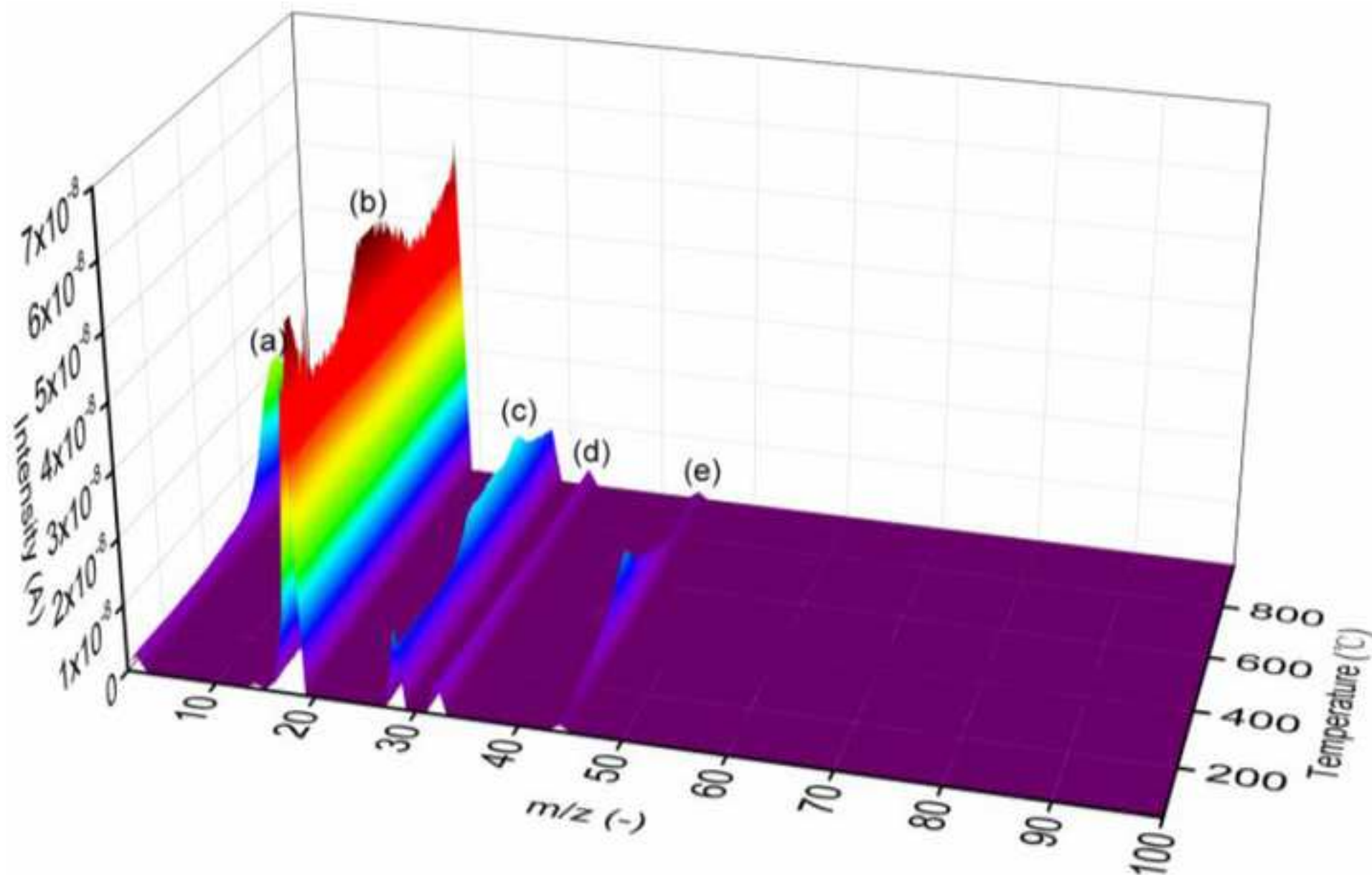




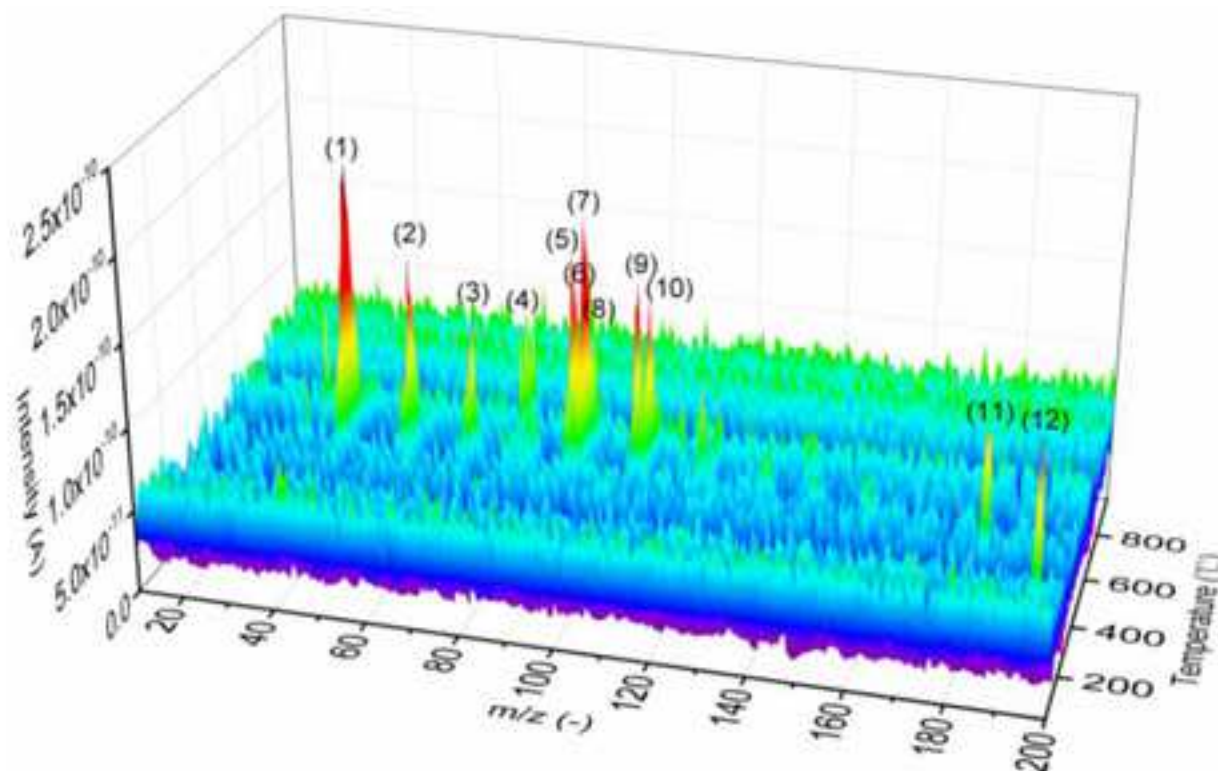








(a)  $\text{H}_2$ ; (b)  $\text{H}_2\text{O}$ ; (c)  $\text{CO}$ ; (d)  $\text{O}_2$ ; (e)  $\text{CO}_2$



(1)  $C_3H_6$ ; (2)  $C_4H_8$ ; (3)  $C_5H_{10}$ ; (4)  $C_6H_{10}$ ; (5)  $C_7H_8$ ; (6)  $C_6H_6O$ ; (7)  $C_8H_{10}$ ; (8)  $C_7H_8O$ ; (9)  $C_9H_{12}$ ; (10)  $C_{10}H_{14}$  (11)  $C_6H_{14}O_6$  or  $C_{10}H_{14}O_3$  or  $C_{11}H_{18}O_2$ ; (12)  $C_{10}H_6Cl_2$  or  $C_8H_5NO_5$

Figure 6a

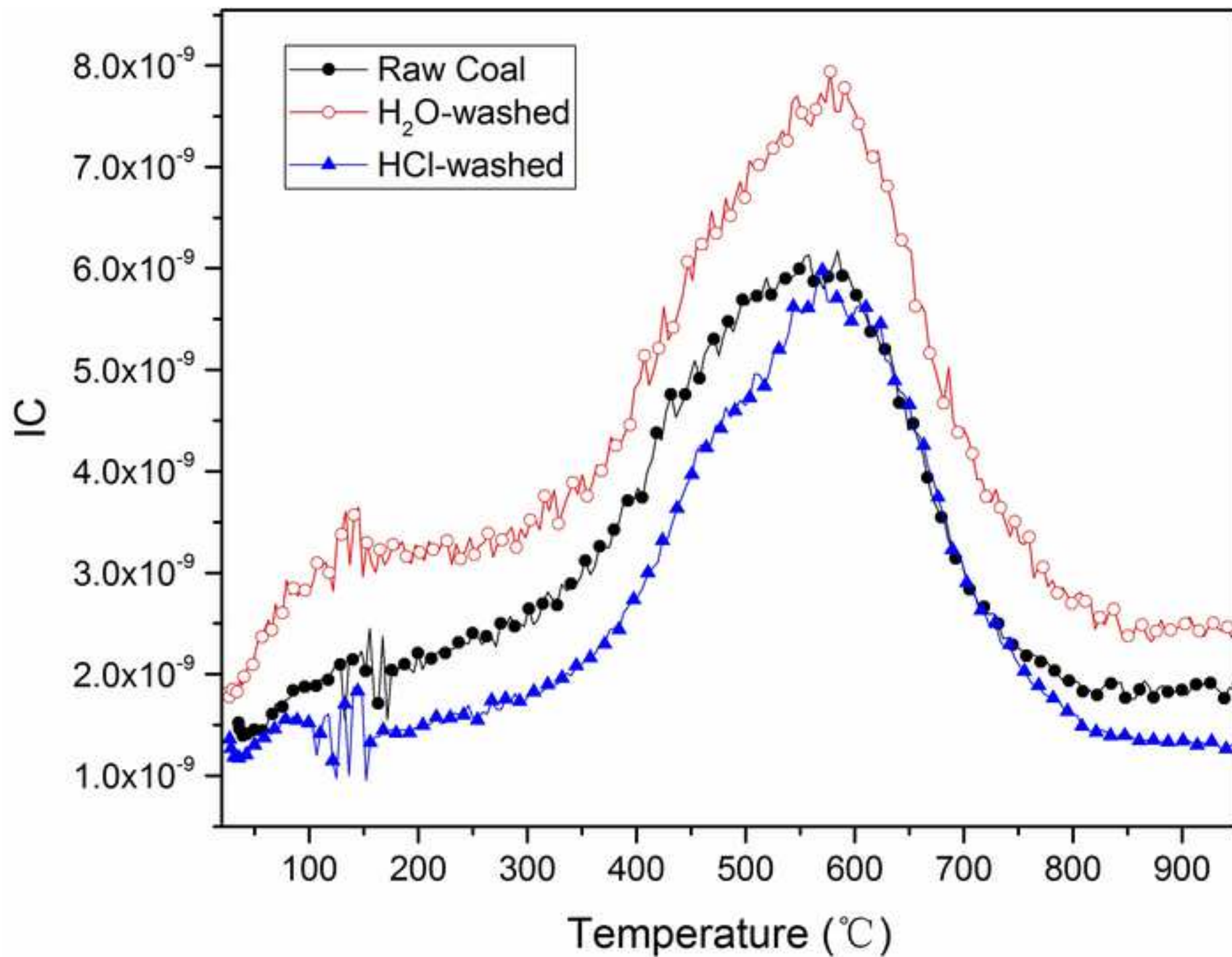
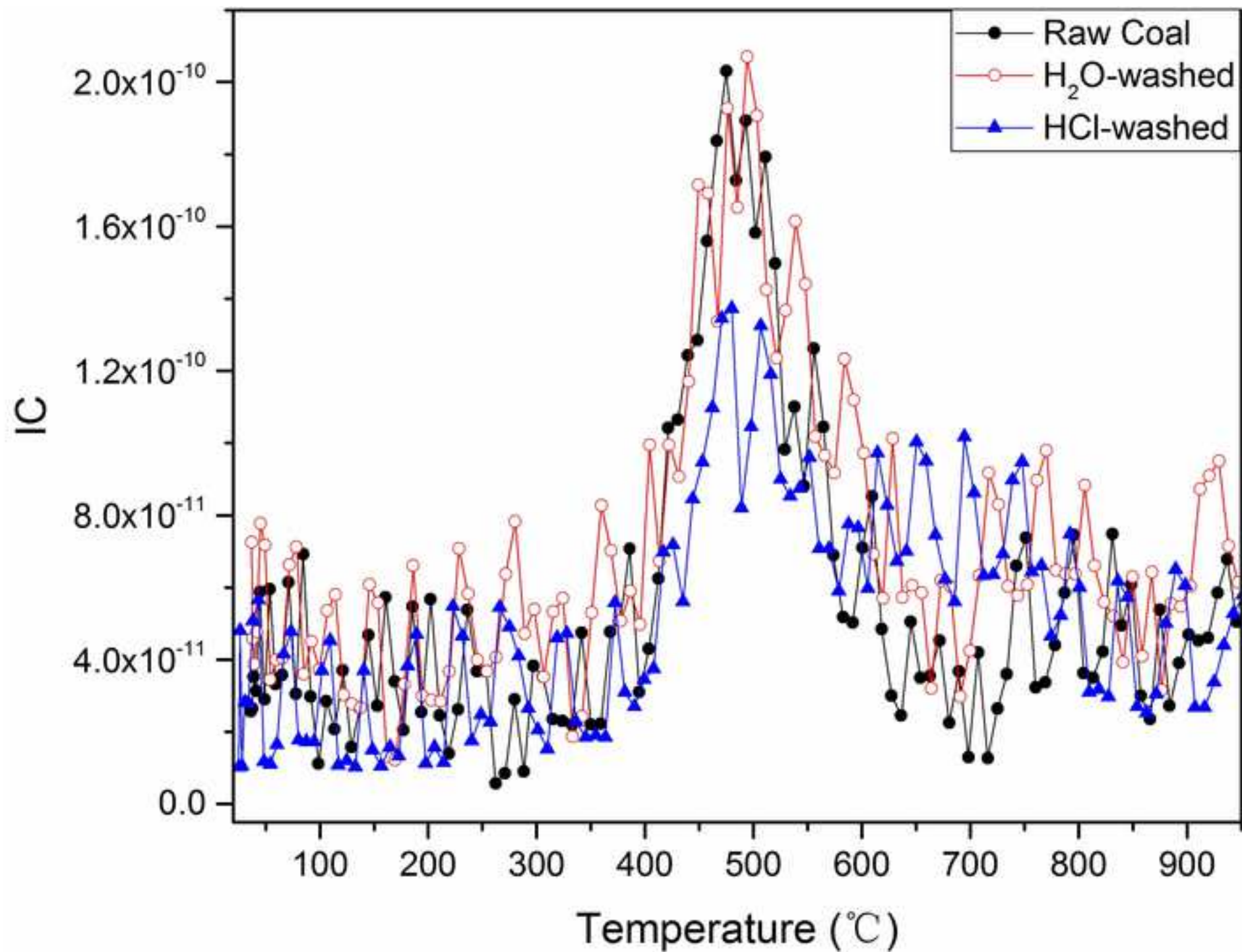
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Figure 6b

[Click here to download Figure Figure 6b - R1.jpg](#)

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
CaCO <sub>3</sub> and Ca(OH) <sub>2</sub>	Sinopharm Chemical Reagent		
hydromagnesite	Bangko Coarea in Tibet		
Zhundong coal			the coal field in the Mori Kazak Autonomous County,Junggar basin, Xinjiang province of Ch
ThermoMass Photo/H	Rigaku Corporation		
The STA449F3 synchronous thermal analyzer and			
QMS403C quadrupole MS analyzer	NETZSCH		

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## Response to Editorial comments for manuscript

### JoVE58233R2

Dear Editor:

Thanks very much for your kind letter dated 14-Jun-2018. We replied your questions and revised the manuscript refer to the comments. Here below is the description on our response and revision.

#### Changes made by the Author(s):

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.
  - ✓ We carefully thoroughly check spelling and grammar errors and revised those.
2. The short abstract is over the 50 word limit.
  - ✓ Now the number of words in short abstract is 50.
3. Step 1.1.1.: How to prepare? Please specify.
  - ✓ The gases are all purchased from company, the purity was checked by TG-MS.
4. 1.1.2: What's the flow rate for each gas?
  - ✓ The flow rate is 100 mL/min, and added the flow rate in 1.1.2.
5. 1.1.3: How to monitor? Please specify.
  - ✓ Monitor the mass spectrum of the individual gas by carefully watching and comparing the characteristic peak of gases to be calibrated and the impurity gases in mass spectrum by TG-MS to make sure the species and purity of gases. We also added the above sentences into the 1.1.3.
6. 1.2.2: What's the flow rate of each gas?
  - ✓ The flow rate is 100 mL/min, and added the flow rate in 1.2.2.
7. 2.1.1.1, 2.1.1.2, 2.1.2.1: How much sample is collected?
  - ✓ The weight of samples has been added in the text.
8. 2.2.1: What carrier gas is used for each sample? Please specify.
  - ✓ Helium (H)e was used as the carrier gas for all the tests, and we have specified this

in the text

9. 2.2.2: How to monitor?

- ✓ Monitor by carefully watching and comparing the characteristic peak of CO<sub>2</sub>, He and the impurity gases of O<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O in mass spectrum. We added the above sentences in the 2.2.2.

10. 3.1: How to get the data?

- ✓ During measurements, the data recorded in-time by the computer which are always connected to the TG-MS instrument. Therefore, we just dumped the data and analyzed by ECSA.

11. For each figure, please provide a title as well as a short description in the figure legend. Please bold the title.

- ✓ The modified legend has been added in the text.

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14. Unfortunately, there are a few sections of the manuscript that show significant overlap with previously published work. Though there may be a limited number of ways to describe a technique, please use original language throughout the manuscript. Please check the iThenticateReport attached to this email.

- ✓ We had modified the overlapping sentences point by point according to the iThenticateReport. However, some words like 'flow rate', 'ECSA', 'mass discrimination' is hard to use another original language to re-express that, so we still reserve those. Thanks again for your consideration.



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