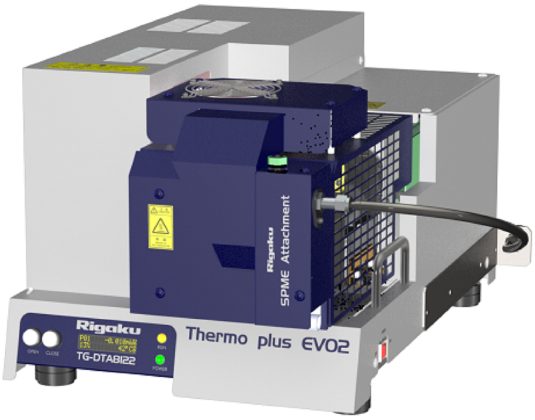
TG-SPME Attachment

—A simple approach to evolved gas analysis with solid phase microextraction—



Abstract

The thermogravimetry (TG)-solid state microextraction (SPME) attachment realizes a simple approach to evolved gas analysis. This attachment allows the insertion of the SPME fiber on the gas pathway of the simultaneous thermal analyzer (STA). The evolved gases are extracted with the SPME fiber. Subsequently, the extracted gases are injected into the gas chromatography (GC)/mass spectrometry (MS) injection port, undergo separation in the GC column, and are detected by MS for qualitative analysis. Some applications of the TG-SPME method include pyrolysis and combustion of polystyrene, thermal oxidation of edible oils, and pyrolysis of tea waste, which are introduced in this paper.

1. Introduction

Simultaneous Thermal Analysis (STA), a powerful technique that combines Thermogravimetry (TG) and Differential Thermal Analysis (DTA), enables measurements of mass changes and exothermic/endothermic reactions as a function of temperature or time. This method plays a crucial role in understanding reactions like pyrolysis and combustion. The logical next step is to explore the substances produced during these reactions. Several manufacturers have developed hyphenated techniques such as TG-Mass Spectrometry (MS) and TG-Fourier Transform Infrared Spectroscopy (FTIR). These techniques allow for both qualitative and quantitative analysis of gases evolved during the reaction. Rigaku, a leading provider of thermal analysis instruments, has significantly expanded its portfolio.

While TG-MS and TG-FTIR are effective for analyzing evolved gases, these techniques involve complex setups. They require the integration of STA with MS or FTIR instruments via transfer lines, which can pose challenges regarding the installation environment and associated costs. Additionally, they may not identify complex gases evolved during the pyrolysis of polymers and biomaterials due to their limited separation capabilities, unlike chromatography. We have proposed the TG-Solid Phase Microextraction (SPME) method to address these limitations. This simplified method enhances evolved gas analysis and is now available as the TG-SPME attachment for Rigaku's STA.

2. TG-SPME

2.1. SPME

SPME is a solvent-free extraction method developed by J. Pawliszyn *et al.* at the University of Waterloo[(1)]. This method allows for the simple and rapid extraction and concentration of samples for subsequent analysis using Gas Chromatography/Mass Spectrometry (GC/MS). The SPME device comprises a needle that encases a fiber, depicted in Fig. 1(a). The fiber is coated with an adsorption or absorption phase for extraction purposes. Typically, the needle is inserted into a septum-capped vial. The fiber extracts and concentrates the volatile compounds present in the vial. The selection of SPME phases is based on the molecular weight and polarity of the target analytes. TG-SPME is primarily utilized for low-molecular-weight gases produced during pyrolysis and combustion, with PDMS (100 μm) or Carboxen®/PDMS phases being the typical choices.

2.2. Procedure of TG-SPME

The TG-SPME attachment must be pre-installed on the Rigaku STA instrument's exhaust port to implement TG-SPME. The attachment introduces a septum-equipped insertion port into the exhaust gas pathway, allowing for the insertion of the SPME fiber. It does not interfere with standard STA measurements. Figure 1(b) illustrates the TG-SPME procedure. We analyze the sample under typical STA measurement conditions. The SPME device is inserted upon observing mass loss. The evolved gases are extracted with the SPME fiber. Subsequently, the extracted gases are injected into the GC/MS injection port, undergo separation in the GC column, and are detected by MS for qualitative analysis. Since STA and GC/MS function independently in the TG-SPME procedure, they can be installed far from each other.

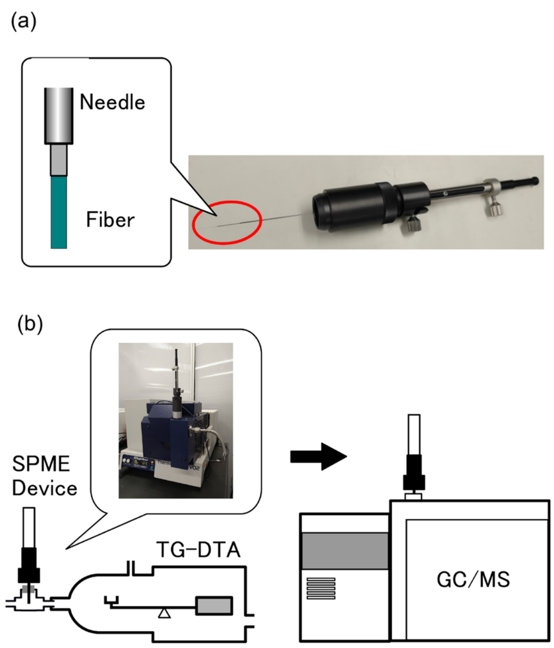


Fig. 1. (a) SPME device and (b) schematic view of TG-SPME.

3. Applications

3.1. Pyrolysis and Combustion of Polystyrene

Evolved gas analysis for the decomposition and combustion of polymers is gaining interest for safety assurance and environmental protection. TG-MS and TG-FTIR are representative measurement techniques for these purposes[(2),(3)]. However, some customers have requested a simpler analysis method. This study demonstrates the TG-SPME analysis of polystyrene heated in inert nitrogen and oxidizing dry air atmospheres.

Figure 2(a) shows the STA results of polystyrene heated in two different atmospheric conditions. In a nitrogen atmosphere, a mass loss accompanied by an endothermic peak was observed around 400°C, suggestive of polystyrene pyrolysis. In contrast, a dry air atmosphere experiment yielded a mass decrease accompanied by an exothermic peak around 250°C, indicating combustion.

Within the temperature range exhibiting the mass loss, evolved gases were extracted with SPME fibers and subsequently analyzed by GC/MS. Figure 2(b) shows the total ion chromatogram. In the nitrogen atmosphere, the monomer and dimer of styrene caused by depolymerization were detected. Similarly, these compounds appeared in the dry air atmosphere, albeit with lower intensities. In addition, presumed oxidation compounds of styrene, such as benzaldehyde and acetophenone, were observed. Consequently, TG-SPME facilitates the qualitative analysis of evolved gases under different atmospheres.

3.2. Thermal Oxidation of Edible Oils

When food products are heated, complex gas evolution occurs, making qualitative analysis challenging using conventional TG-MS. TG-SPME enables the separation of evolved gases through a capillary column in GC/MS. This study focuses on the thermal oxidation of edible oils. Thermal oxidation not only degrades the flavor, color, and nutritional value of edible oils but also has the potential to generate harmful substances. Therefore, it is crucial to comprehend the evolved gases resulting from thermal oxidation.

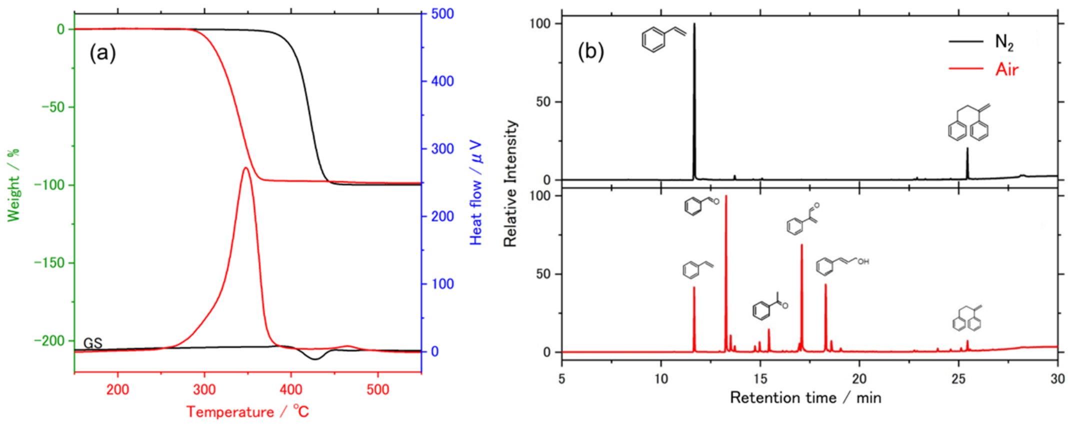


Fig. 2. (a) STA and (b) GC/MS profiles by TG-SPME when polystyrene was heated under N_2 or air atmospheres.

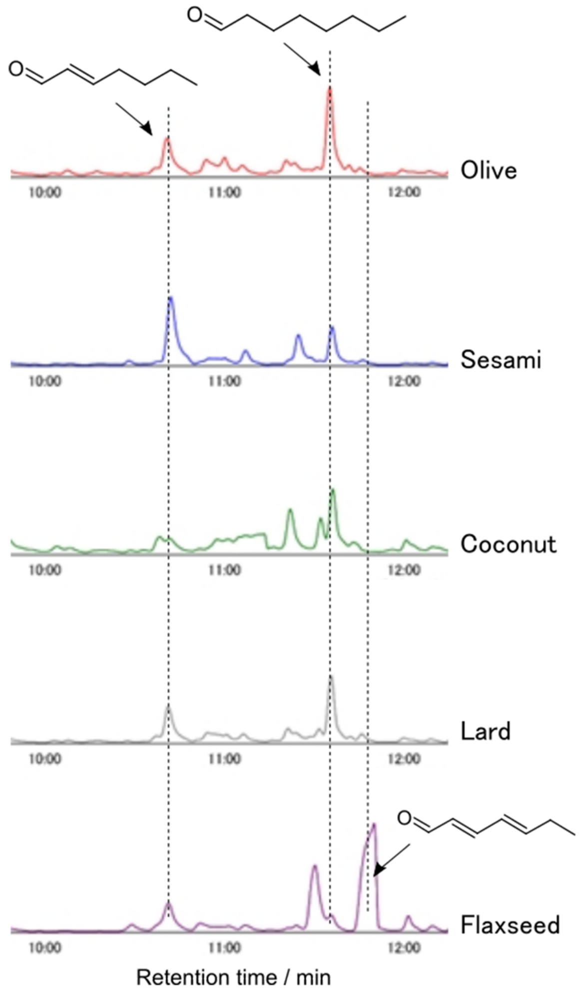


Fig. 3. TG-SPME analysis of evolved gases for thermal oxidation of edible oils. The vertical axis is an arbitrary unit for MS intensity.

When various edible oils were heated in a dry air atmosphere, a mass loss of nearly 5% was observed between room temperature and 300°C. The evolved gases were extracted using SPME and analyzed by GC/MS. The total ion chromatograms of olive oil, sesame oil, coconut oil, lard, and flaxseed oil are shown in Fig. 3. The primary components in the evolved gases were aldehydes produced by the oxidation of alkyl chains in fatty acids. Oxidation proceeds from the radicals formed near the double bonds. Flaxseed oil, which contains a relatively large amount of linolenic acid, generates aldehydes with two double bonds.

3.3. Pyrolysis of Tea Waste

The pyrolysis of carbon-neutral biomass to produce valuable chemicals for fuel, chemical products, and fertilizers has been explored globally. Our study focused on tea waste as a type of food waste biomass. Figure 4(a) shows the results of STA with sample observation when the tea waste was heated in nitrogen and dry air atmospheres. In a nitrogen atmosphere, two distinct mass loss stages were observed, beginning at approximately 200°C and 350°C, respectively.

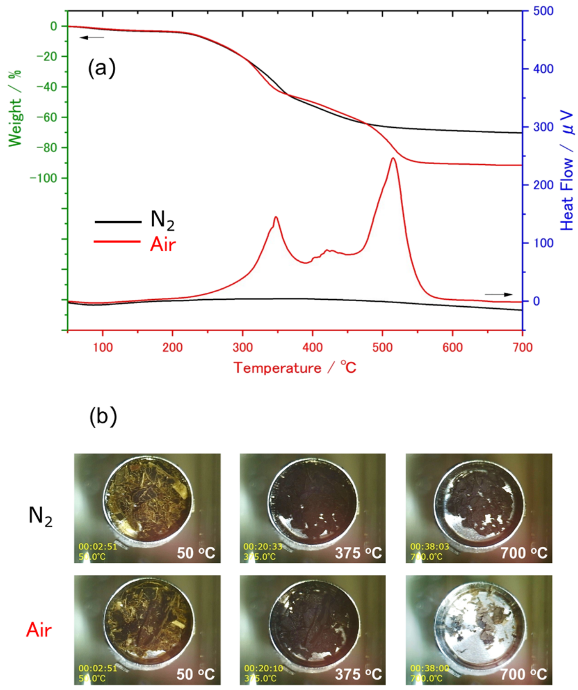


Fig. 4. (a) STA results and (b) Sample pictures of tea waste heated in N_2 or air atmosphere.

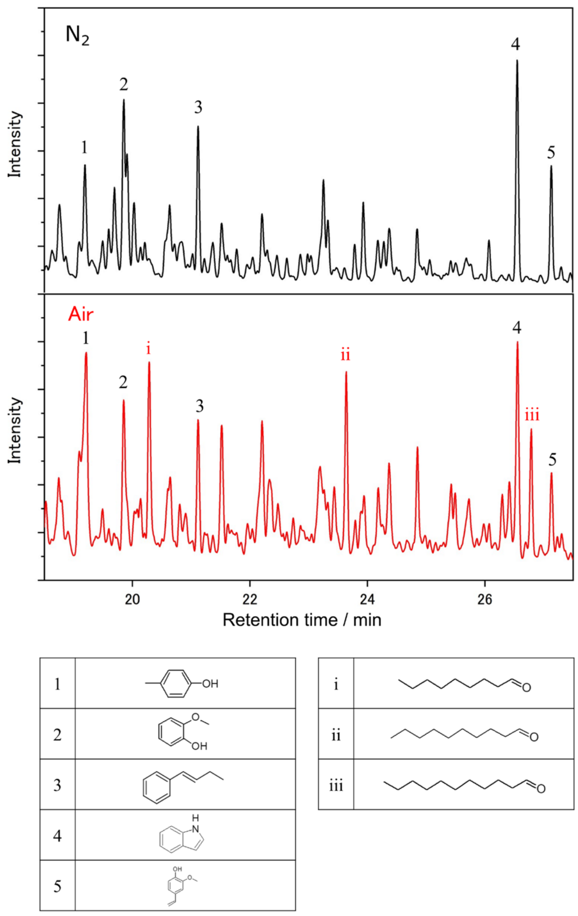


Fig. 5. TG-SPME analysis of evolved gases of tea waste heated in N_2 or air atmosphere.

The sample picture in Fig. 4(b) confirms progressive carbonization and shrinkage with heating. On the other hand, two stages of mass loss with exothermic DTA peaks were observed in an air atmosphere, indicating combustion. The sample picture illustrates initial carbonization during the first mass loss stage, followed by combustion of the carbonized sections, resulting in white ash residues in the second stage.

We excerpted relevant profiles of total ion chromatograms for the evolved gases of tea waste extracted by the SPME fiber at the temperature range of 300–400℃ in Fig. 5. Numerous peaks were detected in both atmospheres, indicating a variety of evolved gases, such as benzene, phenols, and indoles. Various organic gases with relatively large molecular weights are produced in dry air and nitrogen atmospheres. The TG-SPME study revealed the presence of such diverse evolved gases that had not been previously addressed in TG-MS or TG-FTIR studies. Furthermore, we identified aldehydes unique to the dry air atmosphere, which result from the oxidation of alkyl chains in fatty acids.

4. Summary

TG-SPME is a simple approach for identifying evolved gases during STA measurements. It can be applied to various samples, such as polymers, biomass, and foods, where complex gas evolution occurs during heating.

References

(1) J. Pawliszyn: “*Handbook of Solid Phase Microextraction*,” Elsevier (2011).
(2) Y. Hosoi：*Rigaku Journal*, **31** (2015), No. 2, 18–21.
(3) T. Arii：*Rigaku Journal*, **34** (2018), No. 2, 30–34.