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Technical Report

Development of High-Resolution Vacuum Ultraviolet Single-Photon Ionization Mass Spectrometry

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Abstract

A new mass spectrum method was developed for a fragment-free, high-resolution mass analysis method for aromatic and polyaromatic organic molecules generated from coal by vacuum ultraviolet single-photon ionization high-resolution mass spectrometry. First, we attempted to detect naphthalene, dimethyl-cyclohexanol, and cyclohexane-carboxylic acid, which are model molecules for aromatic and polycyclic aromatic compounds generated from coal. The results showed that high-resolution, fragment-free analysis of naphthalene and dimethyl-cyclohexanol was possible, while cyclohexane-carboxylic acid could not be detected. Thiophene, another sulfur-containing organic molecule generated from coal, was similarly measured. The separation and identification of thiophene and cyclohexane from standard gas and coal dry distillation gas were confirmed. These results indicate that laser ionization multi-turn mass spectrometry, while limited to certain molecules, is effective for measuring gases generated from coal and can be applied to the separation and quantification of various other gases.

1. Introduction

Coal is a fuel that is stably mined worldwide and offers high storage potential, making it an important resource for ensuring a stable energy supply. At the same time, achieving carbon neutrality requires more efficient and advanced utilization of coal. When coal is utilized through combustion or dry distillation, heating generates a wide variety of gaseous organic compounds.

In the iron and steel industry, coal is used as the raw material for coke in blast furnaces, and the coke oven gas (COG) produced during coke manufacturing serves as a vital energy source for multiple processes. To enable more advanced coke production and effective utilization of COG, Nippon Steel Corporation has pursued detailed molecular structure analysis of coal itself,[1] as well as the development of methods for identifying and quantifying molecular species generated during heating.[2, 3] These studies aim to deepen understanding of coal's fundamental molecular structure and the reactions occurring during combustion and dry distillation.

More broadly, in the field of coal combustion, accurate identification and quantification of molecular species generated during combustion reactions are expected to improve combustion efficiency and suppress soot and dust formation by optimizing the theoretical air ratio.[4] As a result, the analysis of complex gas mixtures generated by coal heating represents a critical challenge in both energy and environmental research.

Coal-derived gases consist of numerous organic compounds, and their identification and quantification are essential for process design and combustion calculations. In addition, coal contains oxygen and heteroelements such as sulfur and nitrogen, and considerable attention has been devoted to understanding how these elements are gasified and distributed during thermal processes. For example, during dry distillation, part of the sulfur migrates into the COG as volatile components, while the remainder remains in the coke. Sulfur-containing compounds in COG can deactivate catalysts during tar upgrading processes[5] and may partially dissolve into molten iron during ironmaking, causing operational challenges.[6] Consequently, clarifying the chemical forms of sulfur compounds during coal dry distillation and identifying the factors governing their distribution among gas, tar, and coke are of great importance. Such knowledge is expected to reduce the burden on desulfurization processes and improve their efficiency. Previous studies have evaluated sulfur distribution during coal dry distillation using techniques such as chemiluminescent sulfur detection and gas chromatography.[7]

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Mass spectrometry is a powerful tool for identifying and quantifying organic compounds in gases emitted from coal, particularly trace-level volatile species. However, the complexity of these gas mixtures makes analysis challenging when using conventional electron impact (EI) ionization, as extensive fragmentation occurs and multiple molecular species produce overlapping fragment ions.

To address this limitation, we have been developing a laser-based vacuum ultraviolet single-photon ionization (VUV-SPI) technique.[8] Compared with EI, VUV-SPI is limited to molecules with relatively low ionization energies (below 10.5 eV), such as aromatic and polycyclic aromatic hydrocarbons. Nevertheless, this technique enables fragment-free ionization and the simultaneous measurement of multiple molecules without pretreatment,[9] making it well suited for the analysis of gases emitted from coal.

However, previously developed VUV-SPI mass spectrometers exhibited a mass resolution of only approximately 1 000, rendering some coal-derived molecules difficult to separate and identify. To overcome this limitation, we focused on developing a high-resolution vacuum ultraviolet single-photon ionization mass spectrometry method by incorporating a multi-turn mass spectrometer.[10] This configuration enables high-resolution mass analysis while maintaining fragment-free ionization.

In this report, we describe the development of an analytical instrument that combines a vacuum ultraviolet single-photon ionization source with a multi-turn mass spectrometer for high-resolution, fragment-free analysis of gases generated during coal heating. Using this instrument, various standard gases were analyzed under both EI and VUV ionization conditions to clarify the relationship between ionizable molecules and their fragment ions. Furthermore, we report the identification and quantification of sulfur-containing organic molecules generated during coal pyrolysis and examine their dependence on coal type.

2. Experimental Methods

2.1 Experimental setup

A schematic diagram of the developed apparatus is shown in **Fig. 1**. The system consists of two main components: a vacuum ultraviolet (VUV) laser generation section serving as the ionization source, and an analysis section in which the sample gas is ionized and subjected to high-resolution mass analysis using an ∞-type multi-turn orbit.

In the VUV laser generation section, the third harmonic (ν_{355}, 355 nm) of an Nd:YAG laser is introduced into a xenon-filled gas cell. Within the Xe cell, absorption occurs at a xenon resonance level accessible by the three-photon energy of ν_{355}, resulting in the emission of vacuum ultraviolet radiation (ν_{118}, 118 nm, 10.5 eV) corresponding to this three-photon process. The Xe gas cell incorporates optical components such as lenses, and the generated VUV light is transmitted through an MgF_2 window and focused into the analysis chamber. This optical configuration enables single-photon ionization using only the VUV laser while suppressing the transmission of residual YAG laser light. Consequently, molecules with ionization energies below 10.5 eV can be ionized via a single-photon excitation process.

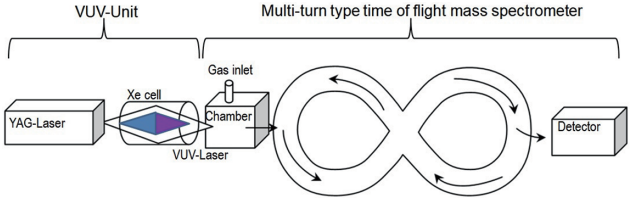

Fig. 1 Diagram of VUV-SPI-high-resolution mass spectrometer

The analysis section employs an ∞-type multi-turn time-of-flight mass spectrometer (inifiTOF-HV, Kanomax Analytical), which has a flight path length of 80 cm per revolution. By utilizing an ∞-shaped ion orbit, the instrument achieves time-of-flight mass spectrometry in a compact, desktop-sized configuration, making it significantly smaller than conventional high-resolution mass spectrometers. This compact design facilitates direct connection to the gas cell and gas inlet system shown in **Fig. 2** and simplifies both the adjustment of the VUV laser focal position and the control of the gas introduction rate.

Ionization is achieved by synchronizing the laser pulse timing with ion extraction from the ionization region into the multi-turn analyzer. Gas molecules introduced into the chamber are ionized by VUV laser irradiation, and the resulting ions circulate within the ∞-shaped orbit to accumulate extended flight time, thereby enabling high-resolution mass analysis. This configuration constitutes a high-resolution vacuum ultraviolet single-photon ionization mass spectrometer.

For comparison, a conventional thermal electron ionization (EI, 70 eV) source is installed within the same vacuum chamber. This allows measurements to be conducted by switching between VUV laser ionization and EI modes as required.

In the multi-turn mass spectrometer, increasing the number of revolutions improves mass resolution but also enhances ion loss within the orbit, resulting in reduced signal intensity. Preliminary evaluations showed that at 30 revolutions, a mass resolution ($m/\Delta m$) of approximately 1×10^4 to 1×10^5 was achieved around $m/z \approx 100$. Under these conditions, peaks with a mass difference of approximately 0.01 could be clearly resolved. Based on these results, subsequent experiments were performed at 30 revolutions under high-resolution conditions and compared with measurements obtained under standard single-pass conditions without multi-turn operation.

2.2 Experimental method and measurement samples

2.2.1 Standard gas analysis

Using the developed high-resolution vacuum ultraviolet single-photon ionization mass spectrometer, polycyclic aromatic hydrocarbons (PAHs) generated during coal heating were analyzed. Fragment-free identification and quantitative measurement were examined for naphthalene ($C_{10}H_8$, 128.062 g mol^{-1}), the most fundamental

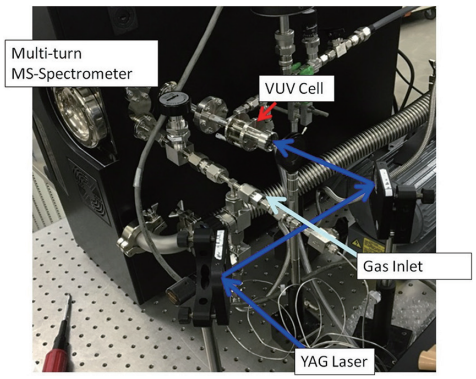

Fig. 2 Overview of the laser and gas introduction section in VUV-SPI-high-resolution mass spectrometer

Table 1 Chemical analysis of the coal

	C (wt%)	H (wt%)	T-S (wt%)
Coal A	81.8	4.9	1.2
Coal B	77.4	4.6	0.6

PAH, together with dimethylcyclohexanol ($C_8H_{16}O$, 128.120 g mol^{-1}), which is presumed to be generated during heating and has a closely related exact mass. In addition, cyclohexanecarboxylic acid ($C_7H_{12}O_2$, 128.083 g mol^{-1}) was included to evaluate the detectability of oxygen-containing compounds with similar exact masses.

Furthermore, standard gases of thiophene (C_4H_4S, 84.0034 g mol^{-1}), a sulfur-containing organic compound generated during coal dry distillation, and cyclohexane (C_6H_{12}, 84.0939 g mol^{-1}), which shares the same nominal mass, were introduced. Fragment-free identification and quantitative measurement of these compounds were similarly investigated.

For standard gas preparation, various reagents were heated to constant temperatures using a quantitative gas generator, and the resulting gases were introduced into the instrument through heated transfer lines connected to the gas inlet.

Regarding measurement conditions, mass spectra in the m/z range of 10–200 were acquired under both electron ionization (EI) and vacuum ultraviolet (VUV) ionization at standard resolution. Fragment ions were identified by comparing the EI and VUV spectra. Subsequently, each standard gas was analyzed under high-resolution conditions to evaluate fragment-free separation and accurate mass identification.

2.2.2 Coal drying gas analysis

Subsequently, cyclohexane and thiophene generated during coal dry distillation were measured using the developed vacuum ultraviolet single-photon ionization (VUV-SPI) multi-turn mass spectrometer. Two types of coal (Coal A and Coal B; **Table 1**) were ground to an average particle size of 75 μm, and 100 mg of each sample was placed on an alumina boat. The boat was positioned inside a quartz tube under a nitrogen flow of 100 mL min^{-1}.

Thermal decomposition was carried out in an electric furnace by heating the samples from room temperature to 800°C at a rate of 5°C min^{-1}. A stainless-steel capillary tube maintained at 200°C was connected to the outlet of the quartz tube, allowing the evolved gases to be transferred to the mass spectrometer without condensation or time delay.

The evolved gases were analyzed under high-resolution conditions. Signal intensities were integrated over temperature ranges of 300–500°C, 500–700°C, and 700–1 000°C, and the relative gas yield ratios of cyclohexane and thiophene were compared between the two coal types.

3. Results and Discussion

3.1 Standard gas analysis using laser ionization multi-turn mass spectrometry

Figure 3 shows the mass spectra acquired over the m/z range of 10–200 when naphthalene was introduced. In the spectrum obtained using electron ionization (EI) (black line, upper panel), a strong peak corresponding to naphthalene was observed at m/z 128, together with numerous peaks below m/z 100. Comparison with the NIST mass spectral database[11] confirmed that these lower-mass peaks originated from fragmentation of naphthalene under EI conditions. In addition, small signals from N_2 and O_2, introduced as trace components with the standard gas, were detected.

In contrast, the spectrum obtained using vacuum ultraviolet (VUV) ionization (red line, lower panel of Fig. 3) exhibited dominant peaks at m/z 128 and 129, with no prominent fragment peaks observed in the lower mass region. The weak peak observed on the low-mass side did not correspond to EI-derived fragment ions and was therefore attributed to sources other than ionization-induced fragmentation. The relatively strong signal at m/z 129 was assigned to isotopic contributions, primarily from naturally occurring ^{13}C and ^{2}H in naphthalene. Similar isotopic peaks were also faintly observed under EI conditions.

Using the same approach, measurements were conducted for dimethylcyclohexanol and cyclohexanecarboxylic acid. Under EI, both compounds exhibited detectable molecular ion peaks accompanied by characteristic fragment ions. Under VUV ionization, however, cyclohexanecarboxylic acid was not detected. This is attributed to its ionization energy slightly exceeding the 10.5 eV photon energy of the VUV laser, preventing efficient molecular ion formation. These results indicate that complementary use of EI is required for simultaneous analysis of compounds with higher ionization energies. Based on this limitation, subsequent high-resolution measurements were performed using only naphthalene and dimethylcyclohexanol.

A mixed standard gas prepared by heating equal amounts of naphthalene and dimethylcyclohexanol was analyzed under high-resolution conditions, with ions undergoing 30 revolutions in the multi-turn analyzer. The resulting spectra are shown in **Fig. 4**. In the EI spectrum (black line, upper panel), naphthalene and dimethylcy-

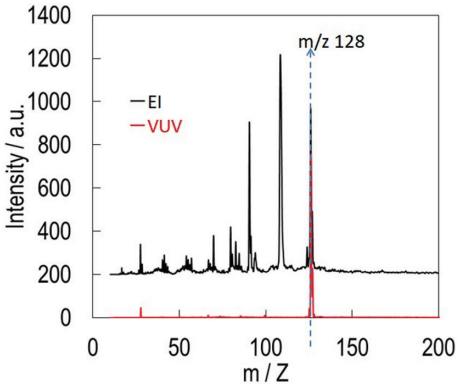

Fig. 3 Mass spectrometry results for naphthalene by ionization source

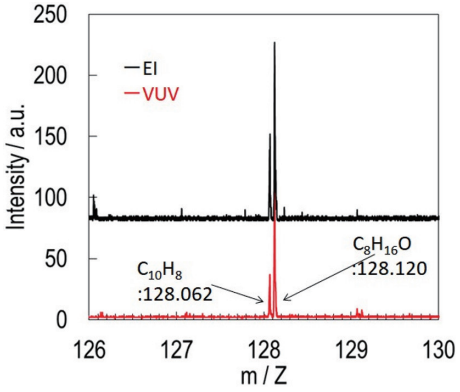

Fig. 4 High-resolution mass spectrometry results for naphthalene and dimethylcyclohexanol by ionization source

clohexanol—both having nominal masses of 128—were successfully separated. However, additional peaks were observed at m/z 126 and 127, indicating fragment ions produced by the loss of one or two hydrogen atoms.

By contrast, the VUV-ionized spectrum (red line, lower panel of Fig. 4) achieved mass resolution comparable to EI while exhibiting almost no fragment peaks in the low-mass region. These results demonstrate that fragment-free, high-resolution mass spectrometry is achievable using VUV ionization even under extended multi-turn conditions.

The concentration of the introduced standard gases was typically on the order of several tens of ppm. Despite the inherently lower ionization efficiency of VUV compared with EI, sufficient signal-to-noise ratios were obtained. This improvement is attributed to fragment-free ionization, which concentrates ion intensity into a single molecular ion peak (m/z 128), thereby enhancing relative signal intensity and S/N.

Subsequently, measurements were performed using cyclohexane and thiophene as introduced components. **Figure 5** shows spectra acquired over the m/z range of 10–100. In the EI spectrum (black line, upper panel), multiple peaks were observed below m/z 70, even though only cyclohexane and thiophene (nominal mass 84) were introduced. Comparison with the NIST database confirmed that these peaks resulted from fragmentation of both compounds under EI conditions, along with contributions from trace N_2 and O_2.

In contrast, the VUV-ionized spectrum (red line, lower panel of Fig. 5) showed strong peaks at m/z 84 and 85, with no distinct fragment peaks in the lower-mass region. As with naphthalene, the peak at m/z 85 was attributed to isotopic contributions, while the weak low-mass signal did not correspond to EI-derived fragment ions.

Figure 6 presents the corresponding high-resolution spectra. Under EI (black line), cyclohexane and thiophene were successfully separated near m/z 84; however, additional peaks were again observed below the molecular ion mass, consistent with hydrogen-loss fragmentation. In contrast, the VUV-based spectrum (red line) achieved equivalent mass resolution without observable fragment peaks in the lower mass range.

These results clearly demonstrate that VUV single-photon ionization substantially suppresses molecular fragmentation compared with conventional EI. By yielding predominantly parent-ion signals, VUV ionization enables high S/N detection and approaches the ideal condition of one peak per component. This characteristic is particularly advantageous for identifying and quantifying individual species in complex gas mixtures generated during coal dry distillation.

3.2 Analysis of coal drying gases and high-resolution analysis of thiophenes and cyclohexanes

Next, direct-introduction analysis was performed for gases generated during actual coal dry distillation. **Figure 7** shows an example of gas analysis for Coal A under standard dry-distillation conditions over the m/z range of 20–200. In the spectrum obtained using electron ionization (EI) as the ionization source (upper panel), a large number of peaks were observed, particularly below m/z 50. These peaks are considered to include fragment ions originating from larger molecules, which makes individual molecular identification difficult. Nevertheless, light gas components such as water (H_2O, m/z 18), carbon monoxide (CO, m/z 28), and carbon dioxide (CO_2, m/z 44) were readily identified. Because CO and CO_2 are difficult to ionize by VUV, the combined use of EI remains necessary

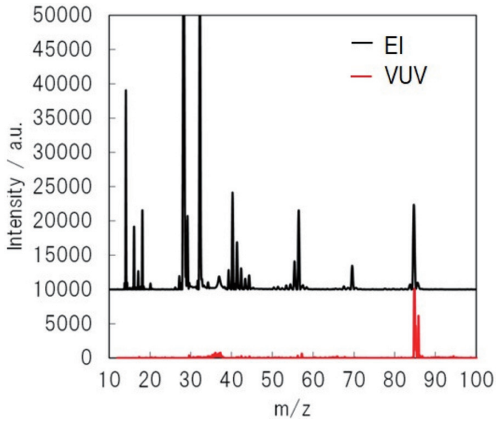

Fig. 5 Mass spectrometry results for cyclohexane and thiophene by ionization source

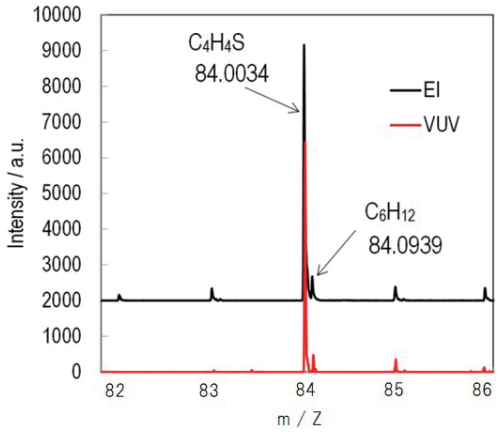

Fig. 6 High-resolution mass spectrometry results for cyclohexane and thiophene by ionization source

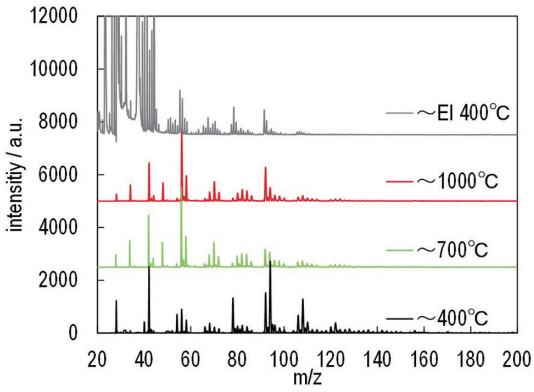

Fig. 7 Example of mass spectrometry results by ionization source for gases generated at different coal dry distillation temperatures

for comprehensive analysis of pyrolysis gases.

When vacuum ultraviolet (VUV) ionization was applied from the second stage onward, aromatic hydrocarbons such as benzene (C_6H_6, m/z 78) and toluene (C_7H_8, m/z 92) were clearly detected at temperatures exceeding 500°C, with maximum intensities observed around 600°C. In addition, oxygen-containing aromatics including phenol (C_6H_5OH, m/z 94) and cresol (C_7H_8O, m/z 108), as well as polycyclic aromatic hydrocarbons such as naphthalene ($C_{10}H_8$, m/z

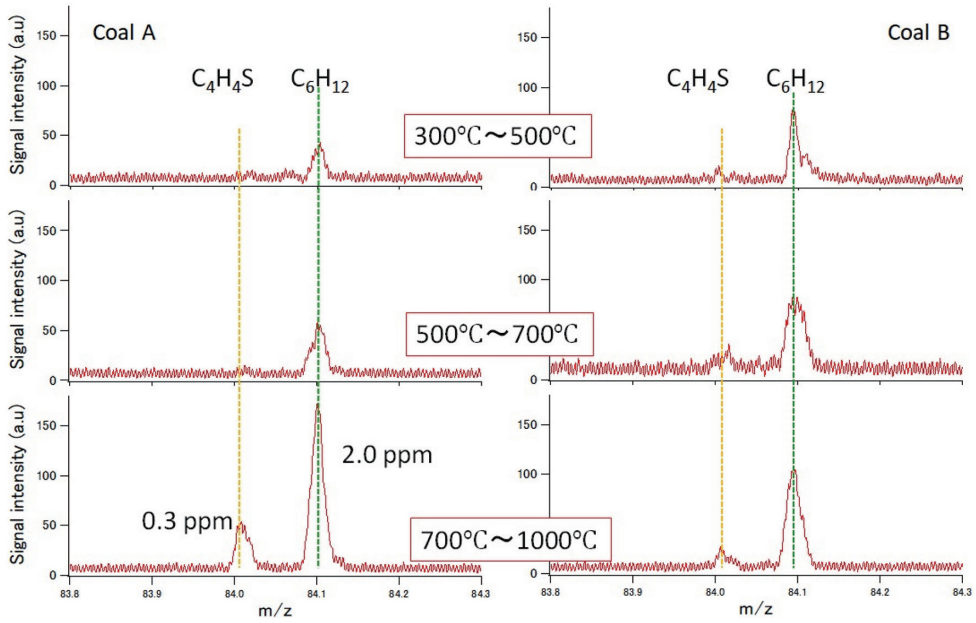

Fig. 8 Analysis results of cyclohexane and thiophenes in various coals by drying temperature

128), were identified. These compounds are difficult to distinguish based on fragment ions in EI spectra and are also challenging to detect using conventional gas analysis techniques such as FT-IR. In contrast, VUV ionization enabled their detection as distinct molecular-ion peaks, demonstrating its effectiveness for real pyrolysis gas analysis.

Subsequently, thiophene and cyclohexane were analyzed and quantified under high-resolution conditions in gases generated during dry distillation of Coal A and Coal B. The results showed that VUV ionization enabled clear separation and identification of these compounds, which was difficult to achieve using EI due to extensive fragmentation.

Figure 8 compares the effects of pyrolysis temperature on the generation behavior of cyclohexane and thiophene. For both coal types, cyclohexane generation was strongly dependent on pyrolysis temperature, with maximum yields observed at higher temperatures rather than during the early stages of pyrolysis. In contrast, thiophene was detected over a broad temperature range and exhibited no clear temperature-dependent trend, particularly for Coal B. Although thiophene concentrations occasionally decreased below 1 ppm depending on the temperature range, reliable detection was still achieved.

4. Conclusion

We developed a high-resolution vacuum ultraviolet single-photon ionization mass spectrometry technique as a fragment-free analytical method for aromatic and polyaromatic organic molecules emitted from coal.

To evaluate the feasibility of this method, model compounds representative of coal-derived organics—naphthalene, dimethylcyclohexanol (an oxygen-containing compound with a similar molecular mass), and cyclohexanecarboxylic acid—were examined. Fragment-free, high-resolution detection of naphthalene and dimethylcyclohexanol was successfully achieved using laser ionization. In contrast, cyclohexanecarboxylic acid could not be detected, indicating that while the method is effective for gas-phase species emitted from coal, it is also essential to identify molecular components that are not amenable to detection.

Subsequently, fragment-free separation and measurement of cyclohexane were investigated. Cyclohexane has a molecular mass close to that of thiophene, a sulfur-containing organic compound generated during coal pyrolysis. The results confirmed that this technique enables high-resolution, fragment-free analysis under standard gas measurement conditions. Separation and identification of thiophene and cyclohexane in coal dry distillation gas were successfully achieved. Furthermore, it was observed that even molecules with closely spaced mass numbers exhibit different generation temperature ranges depending on the coal type.

These findings demonstrate that laser ionization multi-turn mass spectrometry is an effective method for analyzing pyrolysis gases generated from coal and is applicable to the separation and quantification of various other gaseous components. However, species with ionization energies exceeding 10.5 eV cannot be detected using a vacuum ultraviolet laser. To achieve more comprehensive analysis, the introduction of multi-wavelength laser systems or hybrid operation with electron ionization is considered effective, and further development is ongoing.

This technique is positioned as a complementary and enhancing technology to conventional GC-MS and mass spectrometry methods. Its application is anticipated across a wide range of fields, including environmental gas monitoring, combustion science, and materials evaluation. Ultimately, the high-precision gas analysis enabled by this technique is expected to contribute to CO_2 reduction and the realization of carbon neutrality through the effective utilization of coal.

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