# Technical Report

UDC 547 . 52 : 543 . 51

# Development of VUV-SPI-TOFMS Instrument for the Detection of Polycyclic Aromatic Hydrocarbons

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# Abstract

To develop the automotive exhaust catalyst and optimize the pyrolysis process, the correlation between the time of emission and emitted molecules must be observed directly. The problem with conventional analytic methods is that pretreatment is required, making direct observation impossible. The VUV-SPI-TOFMS method is a possible solution to this problem. Using this method, several types of molecules can be measured. Moreover, with the development of real-time analytical techniques, the high-sensitivity measurement of 1-nitronaphthalene, which is one of the environmentally hazardous substances present in gas emitted from cars, has been successful, and simultaneous measurement of several types of molecules present in pyrolysis gas has also been enabled.

# 1. Introduction

Understanding the emission behavior of polycyclic aromatic hydrocarbons (PAHs), which are environmentally hazardous substances, would make it possible to develop the next-generation catalyst or engine or to optimize driving mode, in the case of automobiles. In the case of coal carbonization, molecules that are monitored under operating conditions as a guideline generally have relatively small molecular weight. Since coal contains a large quantity of aromatic hydrocarbon molecules as its main components, the emission behavior of these aromatic hydrocarbons may possibly offer important insights into the effective application of coal.

The important point in monitoring real exhaust gas is to clarify a causal relationship between operating environments and emitted molecules, since emitted molecules and concentration considerably change depending on the atmosphere and emission environment. It is also necessary to accurately measure a broad range of molecules, since it is unknown what types of molecules are in exhaust gas. GC-MS is a commonly used method for measuring gas. Although it allows high-sensitivity measurement, <sup>1–4)</sup> the GC-MS method is not suitable for real-time measurement because it requires condensation or other pretreatment. The FT-IR method, a gas measurement technique with superior real-time performance, allows the measurement of molecules with relatively small mass numbers such as carbon monoxide and methane, but does not easily allow simultaneous

measurement of various aromatic hydrocarbons.

An analytical instrument required to solve these issues would be capable of (1) high-sensitivity ppb level measurement, (2) real-time detection on the time scale of seconds, and (3) simultaneous measurement of multiple molecules including aromatics. In addition to the above capabilities, measurement of nitropolycyclic aromatic hydrocarbons (NPAHs) is required in the case of gas emitted from cars.<sup>5-8</sup> NPAHs are difficult to detect with high sensitivity using other measurement techniques and are highly carcinogenic.

In this study, with the goals of satisfying the analytical needs described in (1) to (3) above as well as being able to quantitatively measure 1-nitronaphthalene (hereinafter referred to as 1 NN), which is a typical molecule of NPAHs, without molecular fragmentation, we developed a vacuum ultraviolet single-photon ionization (VUV-SPI) technique, which allows soft ionization without involving an intermediate state to cause molecular fragmentation. In addition, using the developed equipment, we evaluated the quantitative property of 1 NN, and measured pyrolysis gas to determine whether other multiple aromatic hydrocarbons can be measured simultaneously and in real time.

#### 2. Experiment

The measurement principles, equipment and conditions for this experiment are summarized below.

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# NIPPON STEEL & SUMITOMO METAL TECHNICAL REPORT No. 118 MARCH 2018

#### 2.1 Measurement principles

In this experiment, in addition to measuring 1 NN and aromatic hydrocarbons in pyrolysis gas by the VUV-SPI method, we also measured 1 NN by the non-resonant multiphoton ionization method for comparison purposes. A brief description of each ionization method is given below. **Figure 1** illustrates each ionization principle.

(a) Vacuum ultraviolet single-photon ionization (VUV-SPI)

Figure 1-a shows the ionization principle. Single-photon ionization is an ionization technique to detect multiple molecules all at once with a single photon. Each molecule has its own unique ionization potential and is ionized upon receiving energy higher than the potential. In other words, when photon energy (vuv) exceeds the ionization potential (IP0) of a molecule, the molecule can be ionized by a single photon. The IP0 of 1 NN, one of the subjects of this study, is 8.59 eV. Therefore, 1 NN can be detected using a laser with ionization energy equal to or higher than this.

If incident ionization energy is equal to or higher than the ionization potential of a molecule, multiple molecules can be detected all at once. In multi-step ionization, a transition from an intermediate state to dissociation potential may take place, potentially causing molecular fragmentation. However, this method enables fragment-free detection.

In order to apply this ionization method, having the aforementioned characteristics, to regular organic molecules, it requires a laser in the vacuum ultraviolet region, which can only exist in a vacuum and thus is difficult to handle.

**Figure 2** is a schematic diagram of a vacuum ultraviolet laser generation.<sup>9)</sup> The third harmonic ( $v_{355}$ : 355 nm) of the YAG laser is introduced to the cell filled with Xe gas. Absorption takes place with the energy potential of the 3 photons of  $v_{355}$  at the resonant level of Xe, causing vacuum ultraviolet light ( $v_{118}$ : 118 nm, 10.5 eV) to oscillate as the energy of these 3 photons. That is, a molecule with ionization energy (IE) smaller than 10.5 eV can be ionized by a single photon using the developed vacuum ultraviolet laser light source.

On the other hand, the IE of nitrogen and oxygen, whose concentration in the atmosphere is relatively high, as well as argon, carbon dioxide, etc. is significantly larger than 10.5 eV, and therefore they cannot be ionized by a single photon. When measuring a trace amount of an environment load molecule, there is characteristically little negative impact of atmospheric matrix gas on a detector and other units. Here, not all  $v_{355}$  are converted in vacuum ultraviolet light generation. A majority is emitted as  $v_{355}$  in the same direction as  $v_{118}$ . Since ultraviolet light is extremely intense compared to vacuum ultraviolet light, molecules in the sample, for which ultraviolet light is introduced to the equipment, may possibly undergo multiphoton ionization, resulting in molecular dissociation. Therefore, by utilizing a difference in the refractive index of the lens due to wavelength differences, only ultraviolet light is separated and vacuum ultraviolet light is introduced.

#### (b) Non-resonant multiphoton ionization (NRMPI)

Figure 1-b shows the ionization principle. Non-resonant two-photon ionization is a technique based on the principle that ionization detection is possible, without consideration of intermediate levels unique to molecules, as long as the ionization potential is exceeded by two photons. Thus, this method allows the use of ultraviolet light or visible light, which in general is relatively easy to handle. In addition, this method has very few wavelength requirements, since it can be used if wavelength exceeds the ionization potential. Howev-



single-photon ionization ionization

Fig. 1 Ionization principle



Fig. 2 Vacuum ultraviolet generation scheme

er, sensitivity is relatively low because no resonance effects are used, and thus laser intensity must be set higher. As a result, two or more photons may be absorbed for ionization, and excess energy may cause molecular fragmentation.

#### 2.2 Equipment and measuring conditions

2.2.1 Laser ionization mass spectrometer

Figure 3 is a schematic diagram of the developed laser ionization mass spectrometer. This instrument is roughly divided into a sample introduction part, mass spectrometer part (ionization chamber, mass spectrometer, and detection system), and laser system.

We heated and vaporized sample gas, mixed it with carrier gas, and continuously introduced it into the ionization chamber through a 1/8 inch stainless steel pipe and a pin hole. Before introducing the gas into the ionization chamber, we heated the pipe route to prevent vapor deposition to the pipe due to cooling. While suppressing vapor deposition, we continuously injected the gas into the ionization chamber.

In this experiment, we ionized and measured 1 NN using two different types of wavelengths described above. In both methods, we introduced laser-ionized molecules from a cylindrical extraction electrode into the time-of-flight mass spectrometer. Using a



Fig. 3 Schematic diagram of laser ionization apparatus



Fig. 4 Schematic diagram of vacuum ultraviolet generation system

multi-channel plate at the ion detection part of the mass spectrometer, we amplified detected current signals with a preamplifier and converted them to voltage. Using a digital oscilloscope, we added up signal intensity at every second, and recorded it on a personal computer. For the relationship between laser oscillation and time of flight, we used a signal oscillated at the same timing as laser emission timing as a trigger. The vacuum degree of the equipment was adjusted to  $1.0 \times 10^{-1}$  Pa during sample introduction. 2.2.2 Single-photon ionization optical system

As illustrated in **Fig. 4**, by introducing the third harmonic  $(v_{355})$ : 355 nm) of the Nd: YAG laser (Big Sky Laser Series Ultra 100 of Quantel) into a cell filled with Xe gas, vacuum ultraviolet light was generated. In this optical path, a magnesium fluoride lens was placed at such an optimal angle that only vacuum ultraviolet light would be introduced to the equipment. We separated ultraviolet light in the aperture at a later stage. We used this lens to maintain the difference in vacuum degree between the Xe gas-filled cell and the mass spectrometer. In this way, by having only one optical system in the optical path after vacuum ultraviolet light is generated, light intensity loss by the optical system can be minimized. Using this lens, we also adjusted the focus distance so that vacuum ultraviolet light would focus on the area of free molecular flow. The intensity of ultraviolet laser was set to 30 mJ/pulse, and the oscillation frequency to 20 Hz. A mass spectrometer that utilizes this optical system is the vacuum ultraviolet single-photon ionization mass spectrometer (VUV-SPI-TOFMS).

2.2.3 Non-resonant multiphoton ionization laser optical system

In this study, we performed two-photon ionization using the same wavelength of 240 nm, 265 nm, and 275 nm. The laser system

was almost the same as the uv2 oscillation system in resonant multiphoton ionization laser optical systems. For the oscillation of 265 nm and 275 nm wavelengths, we only used laser dye C540 (a product of Exciton).

#### 3. Results and Considerations

# 3.1 Examination of mass spectra of 1 NN using the non-resonant two-photon ionization method and the single-photon ionization method

For the sample to be introduced into the equipment, we used commercially available 1-nitronaphthalene (1 NN) made by Wako Pure Chemical Industries. The sample was heated by a heater under  $N_2$  gas flow atmosphere for gasification.

The results of non-resonant two-photon ionization performed using the same wavelength are shown. Selected wavelengths were: 240 nm, which is about the intermediate of the energy under the single-photon ionization method; 275 nm, a wavelength which is smaller than  $S_1$ -IP<sub>0</sub> energy and larger than the 1 NN ionization potential by two photons; and 265 nm, intermediate energy between the above two wavelengths. **Figure 5** shows the measurement result of the mass spectrum for each wavelength.

In each of the mass spectra in Fig. 5, while precursor ions were detected, we observed fragment ions that had undergone molecular fragmentation, equivalent to naphthalene, indene, etc. having higher intensity than precursor ions. We took into consideration excess energy in measurement, but observed that molecular fragmentation occurred to the same molecule and that the molecular pattern was not consistent. Namely, it became evident that measurement involving an intermediate state would result in the generation of fragment ions. It is possibly because a move to a path of molecular fragmentation occurs when an electronically excited state is reached. In addition, since this molecular distribution changes with laser intensity, it is impossible to estimate the concentration of the existing organic molecular group based on the amount of fragment. In the measurement of exhaust gas that contains multiple molecules as a result of molecular fragmentation like this, mass interference will occur, disallowing quantitative measurement. Thus, use of the NRMPI method is not suitable for quantitative measurement.

Figure 6 shows the mass spectrum of 1 NN measured by the VUV-SPI method. Only the precursor ions of 1 NN at a mass number of 1 NN (173 m/z) were observed, and no fragment ions were observed. When the intensity of UV light used to generate VUV

# NIPPON STEEL & SUMITOMO METAL TECHNICAL REPORT No. 118 MARCH 2018



Fig. 5 Mass spectrum measured by non-resonance two-photon ionization method (Wavelength is 240 nm, 265 nm, and 275 nm.)



Fig. 6 Mass spectrum of 1 NN measured by VUV-SPI-MS method

light was increased, in other words, when the intensity of VUV light was increased, the signal amount increased, but fragment ion did not occur. This has clarified that changes in laser intensity would not cause molecular fragmentation and that the VUV-SPI-TOFMS method is superior in quantitative measurement of 1 NN.

#### 3.2 Simultaneous measurement of multiple molecular species

Next, using the VUV-SPI-TOFMS method, we measured a hazardous air pollutant standard gas mixture (T.E.R.R.A. Series No. TO-14) made by Takachiho Chemical Industrial, which contains 44 types of multiple-molecular volatile organic compounds (VOCs), each in 1 ppm concentration. These gases contain 14 molecular species between m/z=78 and m/z=120, having IE smaller than 10.5 eV that would enable single-photon ionization by the vacuum ultraviolet light used (benzene, toluene, styrene, o-/m-/p-xylene, 1.2.4-/1.2.3-trimethylbenzene, ethylbenzene, 1.1-/cis-1,2-dichloroethylene, 1.1-/1.2-dichloroethane, and cis-1,3-dichloropropene).<sup>10</sup>

Several molecular species of these 14 molecules have multiple species of structural isomers. A combination of elements constituting a molecule can be classified into nine groups. When using VUV-SPI-MS, molecules are ionized all at once, and structural isomers cannot, in principle, be identified. Hence, signals obtained in a mass spectrum are observed as a total sum of the ionization of all species of structural isomers. For instance, in the case of xylene, the overlapping signals of three molecular species o-, m-, and p- are observed as a single spectrum.



Fig. 7 Mass spectrum of a N<sub>2</sub> based gas mixture containing various VOCs (benzene, toluene, styrene, o.m.p-xylene, 1.2.4. 1.2.3-trimethylbenzene, ethylbenzene, 1.1-. cis-1.2-dichloroethylene, 1.1-. 1.2-dichloroethane, and cis-1,3-dichloropropene, among others) in 1 ppm concentration Spectrum was recorded using a VUV-SPI-TOFMS system.

**Figure 7** shows the measured mass spectrum of the above gas mixture. We were able to attribute all the signals observed to these nine molecular species. This result clearly demonstrates that the VUV-SPI method allows simultaneous measurement of multiple molecular species without causing molecular fragmentation.

If multiple structural isomers exist, the sensitivity coefficient of each molecular species is unknown from this result alone, because the sensitivity of each molecule is different. However, the sensitivity coefficient of the other molecules, which are mixed in the same concentration, is inversely correlated to signal intensity. That is, with respect to benzene, toluene, and styrene, and using benzene as a reference, the sensitivity coefficient of toluene and styrene will be 0.67 and 0.62, respectively. Incidentally, although it is not mentioned in this report, we also prepared a calibration curve separately by varying the concentration of each molecule, which produced a highly linear result. Based on this result, we have learned that there is a first-order correlation between signal intensity and concentration. It is considered that these differences in sensitivity coefficient depend on ionization probability.

#### 3.3 Real-time measurement of pyrolysis gas

Use of the FT-IR method in real-time measurement of pyrolysis gas is being considered. The FT-IR method allows measurement of only those molecular species having relatively small molecular weight such as CO and  $CH_4$ . With the goal of simultaneously measuring multiple molecular species including aromatic molecules, we attempted simultaneous measurement using the FT-IR and VUV-SPI-TOFMS methods.

To generate pyrolysis gas, we charged 30 mg of coal into a tubular furnace and heated it at 10°C/min to 1000°C in an oxygen-free condition. Generated gas was branched out by pipes and introduced to FT-IR and VUV-SPI-TOFMS. The pipes were heated at 100°C during the gas introduction.

Figure 8 shows an example of mass spectrum measured by VUV-SPI-TOFMS. A number of peaks were observed, indicating that it contained many molecular species, a majority of which were aromatics belonging to benzene, toluene, xylene, etc. This clarified that VUV-SPI-TOFMS would enable the measurement of not only standard gas, but also pyrolysis gas, the subject of actual measurement, as well as simultaneous monitoring of multiple molecular species.

We then examined to see whether or not there is any difference in the behavior of emitted molecular species between different coal species having different components. **Table 1** shows chemical analysis results of the main components of four different types of coal. We measured pyrolysis gas using VUV-SPI-MS. Of the detected molecular species, we focused our attention on four of the typical aromatic molecules: thiophene (m/z=84), xylene (m/z=106), phenol (m/z=94), and cresol (m/z=108). **Figure 9** shows time-evolved spectra indicating correlations between pyrolysis temperatures of these four types of emitted molecules and emission concentration.

It was observed that various molecules were generated from the pyrolysis gas that used coal sample C having the lowest concentration of C among the four coals, starting at an early stage of pyrolysis, at a temperature around 300°C. On the other hand, we learned that aromatic molecules would reach the highest concentration at a temperature near 600°C, higher than the temperature at which CO is generated. However, CO was generated from pyrolysis gas that used



Fig. 8 Mass spectrum of the pyrolysis of coal (sample C, pyrolysis temperature 400°C)

Table 1 Chemical compositions of the various coals tested in this study

samples	C(%)	H(%)	N(%)	S(%)	O(%)	Ash(%)	VM (%)
A	75.3	5.63	1.83	0.56	8.54	9.2	37.9
В	73.4	4.04	1.81	0.77	9.33	9.1	32.1
С	71.8	4.84	0.68	0.34	22.2	0.64	50.6
D	90.1	5.4	1.6	1.3	1.5	9.2	27.4

samples A, B, and D at around 750°C, lower than the temperature at which aromatic molecules are generated. This is possibly because of coal ranks. It is considered that pyrolysis and carbonization of coal progress in higher temperature regions, creating a coal of solid structure.

Focusing on oxygen content, coal samples B and C have higher oxygen concentration than the other two coals. In the pyrolysis gas of these coals, we observed signals corresponding to phenol and cresol at the pyrolysis temperatures between 600°C and 800°C. On the contrary, for coal samples A and D, we only observed xylene and hardly any phenol or cresol. We think it is because gas generation of a molecule having an OH group is facilitated in the pyrolysis gas of a coal with high oxygen content. In addition, in the case of coal C, the signal intensity is higher for phenol and cresol than for xylene, indicating that there is a correlation between the oxygen content and the amount of molecules generated in pyrolysis gas having an OH group.

Focusing on the sulfur (S) content, coal sample D has the highest concentration of sulfur. Thiophene is an organic molecule containing S. Since it is contained in tar,<sup>11)</sup> we assumed that it would also be contained in pyrolysis gas. However, the result was that of the four samples, the highest concentration of thiophene was in the pyrolysis gas of sample D. In other words, there is clearly a correlation between S content and thiophene concentration. Further study must be conducted to determine whether this correlation applies to all coals. Furthermore, in order to learn in what form S exists in coal, it is necessary to investigate emission behaviors of S-containing molecules other than thiophene, such as hydrogen sulfide and COS.

The above results have clearly demonstrated that the information on the intensity and temperature range at which these molecules are generated depends on coal structure, indicating that it is possible to deepen the understanding of coal structure by thoroughly investigating pyrolysis gas.



Fig. 9 Real-time monitoring of the various compounds produced during the pyrolysis of different coal samples CO was monitored using FT-IR spectrometry and thiophene, xylene, phenols, and cresol were monitored using VUV-SPI-TOFMS.

# NIPPON STEEL & SUMITOMO METAL TECHNICAL REPORT No. 118 MARCH 2018

#### 4. Conclusion

In order to develop catalysts for gas emitted from cars or optimize pyrolysis gasification processes, it was necessary to directly observe correlations between the state of emission and emitted molecules. To be able to directly observe them, there has been a demand for the development of equipment that will: (1) require no pretreatment, (2) allow observation of molecules without fragmentation of these molecules, (3) allow simultaneous measurement of multiple molecules (including aromatics), (4) allow high time resolution (real-time monitoring), and (5) have high sensitivity. Therefore, with our focus set on vacuum ultraviolet single-photon ionization mass spectrometry that is highly sensitive and capable of soft ionization, we developed technologies for on-site, real-time analysis that allow simultaneous, highly sensitive, and real-time measurement of multiple molecular species. By using the developed equipment, we succeeded in high-sensitivity measurement of 1-nitronaphthalene, an environmentally hazardous substance, whose release from gas emitted from cars is a concern, as well as real-time measurement of multiple molecular species contained in pyrolysis gas.

This equipment is capable of simultaneously measuring multiple molecules at high time resolution, and therefore its applications are expected to be used in areas beyond gas emitted from cars and coke carbonization gas. An example of possible expansion of applications is air monitoring, where the condition of road-side atmospheric environmental impact molecules is investigated. In the future, we would like to contribute to process optimization by evaluating pyrolysis gases, etc. using the developed VUV-SPI-MS, while considering the expansion of its applications.

While SPI is a superior ionization method, it is impossible to identify organic molecules having the same mass weight. In order to solve this problem, quantitative evaluation of trace-amount organic molecules can be achieved by combining the Jet-REMPI technologies we have developed in the past.

#### References

- 1) Kanno, N., Tonokura, K.: Applied Spectroscopy. 61, 896 (2007)
- 2) Suzuki, T., Hayashi, S., Saeki, M., Ishiuchi, S., Fujii, M.: Anal. Sci. 21, 991 (2005)
- 3) Yamakawa, M., Sarai, E., Hayakawa, S.: Annual Report of Mie Prefecture Health and Environment Research Institute. 47, 77 (2002)
- 4) Tong, H.Y., Sweetman, J.A., Karasek, F.W.: J. Chromatogr. 264, 231 (1982)
- 5) Uraki, Y., Suzuki, S.: Journal of Environmental Chemistry. 12 (4), 797 (1998)
- 6) Hayakawa, K., Toriba, A., Kameda, T., Tang, N.: Bunseki Kagaku. 56 (11), 905 (2007)
- 7) Environmental Health and Safety Division, Environmental Health Department, Ministry of the Environment Government of Japan: Report on Development of Chemical Substances Analysis, 1989
- 8) Klasine, L., Kovac. B., Gusten, H.: Pure Appl. Chem. 55, 289 (1983)
- 9) Kasuya, T., Tsukakoshi, M.: Laser Spectroscopy in Vacuum Ultraviolet Region. 1991
- 10) NIST Chemistry WebBook, [Online]. Available: http://webbook. nist. gov/chemistry
- 11) Edited by the Japan Aromatic Industry Association, Inc.: Aromatic and Tar Industrial Handbook, 2000



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