



## DEVELOPMENT OF HIGH-TEMPERATURE PULSED SLIT NOZZLE AND ITS APPLICATION TO SUPERSONIC JET ABSORPTION SPECTROMETRY

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**Summary**—A high-temperature pulsed slit nozzle, consisting of a circular pulsed nozzle and an interface to convert a circular flow into a slit flow has been constructed. The absorption spectrum is measured by scanning the wavelength of the monochromator equipped with a xenon arc lamp and by detecting the transmitted light through a jet with a photomultiplier. A rotationally cooled spectrum is clearly observed for aniline only when a long slit nozzle is employed. The absorptivity increases proportionally to the slit length at least up to 6 cm. The time for recording a spectrum is 3.5 min, which is reduced to several seconds by transmitting a white light through a jet and by measuring the spectrum with an optical multichannel analyzer. The detection limit is estimated to a partial vapor pressure of 0.4 torr for aniline. The present system can be conveniently used in routine analysis, because of a wide spectral coverage of the lamp source.

### INTRODUCTION

A molecule is cooled immediately to several kelvin by jet expansion into a vacuum. Consequently, a greatly simplified optical spectrum can be obtained, allowing selective spectrometric analysis.<sup>1-4</sup> In current works, fluorometry or multiphoton ionization spectrometry are employed, and a tunable laser is essential in such applications. High sensitivity and selectivity are provided, due to a strong radiation and a narrow linewidth of the laser. However, the tunable range of the dye laser frequently used for this purpose is limited to 20–30 nm for a single dye solution. Then, the solution must be changed to scan the laser wavelength in the entire visible region, which should be further extended to the ultraviolet by using a nonlinear optical effect such as second harmonic generation. This procedure is tedious and time consuming, and is not suitable for practical applications. An optical parametric oscillator may cover the entire ultraviolet–visible–infrared regions by using fundamental, frequency-doubled, and frequency-differenced outputs, and such an instrument has started to be commercialized. However, the instrument is very complicated and expensive, and so a simpler and

less-expensive spectrometric system consisting of a conventional lamp source is sought.

A nonlaser source has already been used in supersonic jet spectrometry. Excitation and fluorescence spectra of aromatic compounds are measured using a xenon arc lamp.<sup>5-8</sup> The fluorescence intensity is proportional to the intensity of the light source, and the sensitivity is limited when a conventional light source is used instead of a laser. Spectral resolution is also limited owing to the small radiation flux of the lamp source. On the other hand, the sensitivity is rather insensitive to the intensity of the light source in absorption spectrometry. The spectral resolution can be improved by using a large monochromator with a narrow slit, though the base line drift induced by a shot noise may gradually increase with decreasing the number of photons detected. An ultraviolet absorption spectrum has been measured using a short arc xenon flash lamp in supersonic jet spectroscopy.<sup>9</sup> Recently, absorption spectroscopy is demonstrated even in a vacuum ultraviolet region using a deuterium arc discharge lamp.<sup>10</sup>

The sensitivity is proportional to the sample path length in absorption spectrometry. Thus a slit nozzle is essential for sensitive detection. Most analytical samples have a low vapor pressure at room temperature. Moreover, a pulsed valve is desired to decrease the pumping

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capacity of the vacuum system. Therefore, a high-temperature pulsed slit nozzle is strongly recommended for wide application. Such a nozzle has already been developed and used in absorption spectroscopy, but it is driven mechanically<sup>12</sup> and is thus sometimes difficult to synchronize with other electronics.

In this study, we have developed a high-temperature pulsed slit nozzle driven electronically for application to supersonic jet absorption spectrometry. An interface is attached to the top of a circular orifice to convert a circular flow into a slit flow to extend the sample path length. A supersonic jet spectrum is measured for aniline based on absorption spectrometry by scanning the wavelength of a monochromator equipped with a photomultiplier. Furthermore, an optical multichannel analyzer is used for reduction of time recording a spectrum. The advantage and the application field of the present analytical instrument are also discussed.

#### EXPERIMENTAL

A block diagram of the experimental apparatus developed is shown in Fig. 1. A carrier gas of argon was passed through a liquid sample, which was typically maintained at 50°C to obtain sufficient vapor pressure. The sample was introduced by a stainless steel tube into a pulsed nozzle whose repetition rate and duration were adjusted to 10 Hz and 2 msec, respectively. The temperatures of the nozzle and the stainless steel tube were maintained at 80°C. The sample gas was expanded into a vacuum chamber evacuated by a 6-in. pumping system consisting of a cold trap, a diffusion pump, a mechanical booster pump, and a rotary pump.<sup>5</sup>

The high-temperature pulsed nozzle consisted of two parts. One part was an injection valve

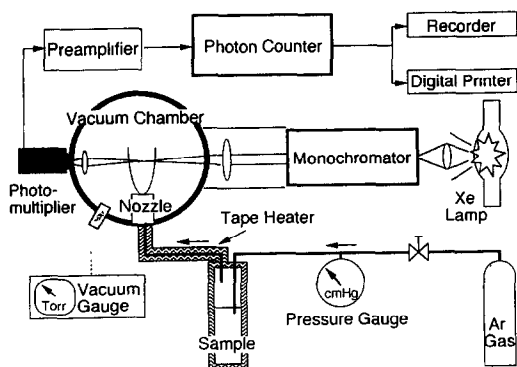


Fig. 1. Schematic diagram of experimental apparatus equipped with photomultiplier.

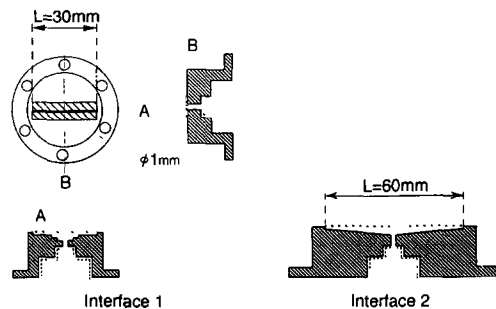


Fig. 2. Structures of interfaces for conversion of circular flow into slit flow.

(Honda, fuel injection valve, orifice diameter 0.8 mm) consisting of an orifice and a plunger driven electronically by an electromagnet, which was rewound with a copper wire coated with alumina for electric insulation. Thus the nozzle can be heated up to 300°C.<sup>13</sup> The other part was an interface to convert a circular flow into a slit flow. The structure of the interface is shown in Fig. 2. This part was attached to the top of the injection valve. Two razor blades were fixed at the top of the interface to convert the rectangular flow formed in the channel into a slit flow. The slit length was changed by replacing the interface. In this study, two interfaces were made and used for spectrometric analysis, the lengths being 3 and 6 cm. The width of the slit was adjustable from 0 to 1 mm. The temperature of the interface was raised up to 300°C by heat conduction from the pulsed nozzle.<sup>14</sup>

A conventional xenon arc lamp for a commercial fluorometer (Hitachi 204, 150 W) was used as a light source. The light collected by a quartz lens (focal length 10 cm, diameter 4 cm) was passed through a 1-m monochromator (Jasco, CT-100) and focused by a quartz lens (focal length 30 cm, diameter 10 cm) to a molecular jet 5 mm away from the nozzle. The transmitted light was collected by a quartz lens (focal length 10 cm, diameter 4 cm) onto the photocathode of a photomultiplier (Hamamatsu, R585). Photoelectron pulses were amplified 100 times and measured by a photon counter (NF Circuit Design Block, PC-545A). The signals ( $I_0$  and  $I$ ) were measured by counting the number of photoelectrons when the pulsed valve was closed and opened. The results were displayed by a printer (Nada Electronic Lab., DP102). The absorbance signal was calculated at every wavelength by a microcomputer (NEC, PC9801NS/T) to construct an absorption spectrum.

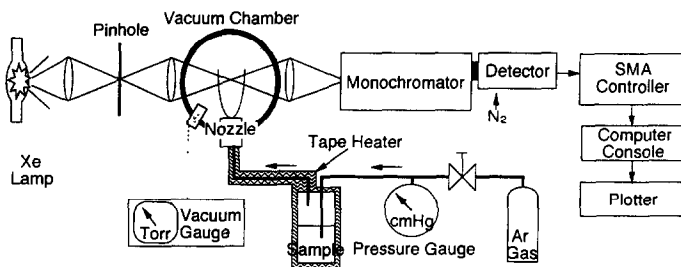


Fig. 3. Schematic diagram of experimental apparatus equipped with optical multichannel analyzer. SMA, spectrometric multichannel analyzer;  $N_2$ , nitrogen purge gas.

An optical multichannel analyzer was used for reduction of the time for recording a spectrum. The block diagram of the apparatus is shown in Fig. 3. A white light from a xenon arc lamp was passed through a pinhole for beam collimation. The transmitted light through a jet was dispersed by the monochromator and measured by a photodiode array equipped with an image intensifier (Princeton Instruments, spectrometric multichannel analyzer, IRY-700). The signal was processed by a controller (Princeton Instruments, ST-100) combined with a microcomputer (Fujitsu, FM16 $\beta$ ). The spectrum was displayed by a plotter (Watanabe, WX4671). A sample of aniline was obtained from Kishida Chemical Co.

## RESULTS AND DISCUSSION

The absorption spectra of aniline measured by scanning the wavelength of the monochromator are shown in Fig. 4. The lowest spectrum was recorded using a circular nozzle with no interface, whilst the medium and upper spectra were recorded using a slit nozzle with interfaces whose lengths were 3 and 6 cm, respectively. The 0-0 transition, corresponding to the optical transition between the pure ground and elec-

tronic excited states,<sup>15</sup> was clearly observed at 293.8 nm, presenting rotational cooling by jet expansion. A hot band was also observed at 294.3 nm, which was probably due to insufficient dilution of aniline with argon; the decrease of the partial vapor pressure of aniline was avoided in order to obtain a sufficient absorbance signal. The peaks were clearly observed only when a slit nozzle was used for sample expansion. The absorbance of the 0-0 transition peak was proportional to the slit length, and then the Lambert-Beer's law was satisfied with respect to the sample path length. This result implies that the sample was uniformly expanded from the entire slit length.

The relation between the absorbance and the concentration of the sample was investigated using the 6-cm slit nozzle. The partial vapor pressure of aniline increased to 290 torr on increasing the reservoir temperature to 150°C. The concentration (partial vapor pressure) was calculated from the data given in a handbook.<sup>16</sup> The relationship observed is shown in Fig. 5. The absorbance increased with increasing concentration of aniline, but was saturated at high concentrations. Thus the Lambert-Beer's law was not satisfied in this case. This was probably due to the fact that the linewidth of the light source (0.2 nm) was much larger than that of the

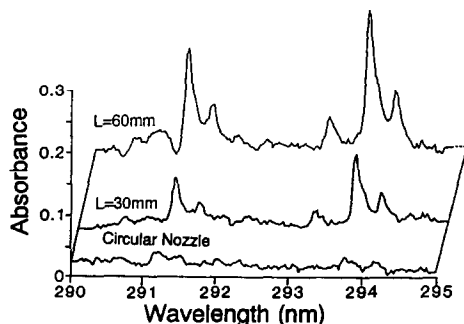


Fig. 4. Supersonic jet absorption spectrum for aniline measured by photomultiplier. The partial vapor pressure of aniline was 4 torr. The stagnation pressure was adjusted to 460 torr. L, slit length.

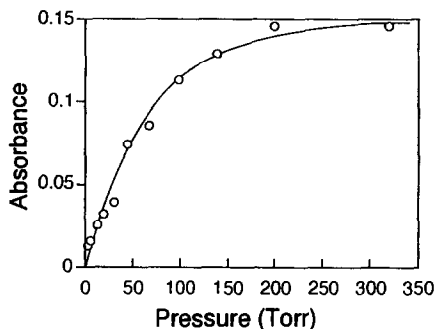


Fig. 5. Relationship between absorbance and partial vapor pressure of aniline. The stagnation pressure was adjusted to 460 torr.

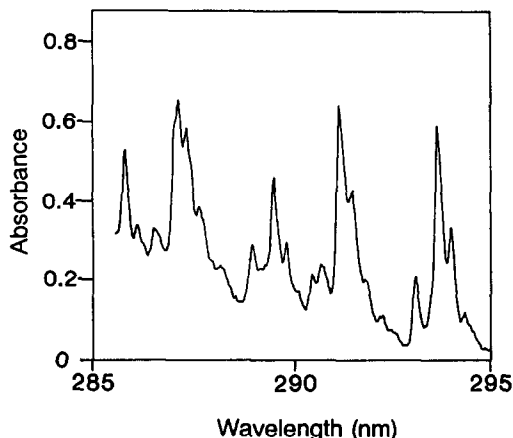


Fig. 6. Supersonic jet absorption spectrum for aniline measured by optical multichannel analyzer. The partial vapor pressure of aniline was 60 torr.

rotational envelope in the spectrum (*ca.* 0.01 nm); the averaged value of the logarithms of the data is not identical with the logarithm of the averaged value in absorbance calculation.<sup>17</sup> Thus the sensitivity might be improved further by using a high-resolution monochromator equipped with a lamp with a larger output power.

Figure 6 shows a supersonic jet spectrum for aniline measured using an optical multichannel analyzer. This spectrum was measured by exposing the photodiode array for only 33 msec. The overall time for recording a spectrum was several seconds; a major part of the time was attributed to data transfer from the controller to the microcomputer. The intensity of the hot band and the spectral width of each vibrational line were slightly increased, probably due to jet expansion of the concentrated sample.

The present method based on absorption spectrometry can be applied even to a nonfluorescent sample. Then, the application field of supersonic jet spectrometry may be greatly extended, *e.g.* to various co-ordination compounds containing heavy metals. The detection limit is estimated to a partial vapor pressure of 0.4 torr for aniline, which is calculated from a baseline drift of  $A_{\text{min}} = 0.02$  in Fig. 4, rather limiting the sensitivity at present. However, the minimum absorbance measured by a commercial absorption spectrometer is of the order of

$A_{\text{min}} = 10^{-4}$  and  $A_{\text{min}} = 10^{-6}$  at research levels. Then, the sensitivity may be improved several orders of magnitude by increasing the averaging time and improving the software for data processing. The use of a conventional lamp instead of a complicated laser makes the analytical system simpler, so that the compact analytical instrument constructed herein may be used advantageously in routine works. Unfortunately, the sensitivity is generally limited in absorption spectrometry, and it may be difficult to use the present instrument in trace analysis. However, the instrument may be conveniently used for measurement of the standard spectrum due to a wide spectral coverage of the lamp source, prior to the application of laser fluorometry or multiphoton ionization spectrometry to trace analysis.

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