

High-Temperature Pulsed Nozzle for Supersonic Jet Spectrometry and Its Application to Gas Chromatography

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An electrically controlled pulsed nozzle was constructed, which consisted of a stainless steel body and a solenoid coil. The developed nozzle had a minimum pulse width of 1.3 ms, and it could be operated up to 300 °C. By use of this nozzle, a supersonic jet fluorescence spectrum was measured for perylene. The single components in the mixture of anthracene derivatives were selectively excited by a tunable dye laser, and the sharp fluorescence spectra from those compounds were clearly resolved. The nozzle had a dead volume of 0.2 mL, and it was useful as a detector for gas chromatography. The application to a capillary gas chromatograph combined with a multiphoton ionization detector is also presented.

Supersonic jet spectrometry provides a very simple spectrum, and therefore it has great selectivity in analysis of samples (1, 2). This spectrometric technique has already been used for determination of carcinogenic polycyclic aromatic hydrocarbons (PAHs) such as benzo[a]pyrene (3, 4). If a sample molecule with a large molecular weight has a low vapor pressure at a room temperature, then the sample should be heated to maintain a sufficient vapor pressure. In this case a high-temperature nozzle is necessary to expand the sample into a vacuum. A high-temperature continuous-flow nozzle is currently used for this purpose because of its simplicity (4, 5). However, it requires a vacuum system with a large pumping capacity. It is noted that efficient sample cooling is achieved only when the sample gas with sufficient pressure is expanded from a large pinhole. Alternatively, in application of a supersonic jet spectrometric detector to conventional gas chromatography, the flow rate of the expansion gas (~130 mL/min) is larger than the optimum flow rate of the carrier gas (~10 mL/min). In previous studies, the sample is separated under vacuum, and the resolution of the column is degraded (6, 7).

To overcome these problems a high-temperature pulsed nozzle is necessary. It seems to be a key technology of supersonic jet spectrometry especially in the chromatographic determination of less-volatile PAHs. However, commercially available pulsed nozzles are operated below 100 °C (maximum temperature: Quanta Ray, 70 °C; Beam Dynamic, 60 °C; Lasertechniques, 50 °C; General Valve, ?) (8), though Lubman et al. have used a commercial nozzle (Quanta Ray) at 80–150 °C (9). In our previous study we constructed a pulsed nozzle modified from a fuel injection valve for an automobile (7). However, the maximum operating temperature was limited to 150 °C, since it consisted of plastic components and O-ring seals. The sample with a large molecular weight sometimes remained in the nozzle, and the background signal occurring from the sample itself determined the detection limit (7, 10). In the extreme case, the nozzle was completely clogged with sample. In gas chromatography the column is frequently heated to 300 °C, and a high-temperature pulsed nozzle that can be heated to this temperature is required.

A few groups have already constructed high-temperature pulsed nozzles, though their structures have not been clarified in detail. Jortner and co-workers constructed a slit nozzle (0.2 mm wide, 35 mm long, maximum temperature 200 °C), con-

sisting of two concentric cylinders with the inner one rotating (3, 11, 12). They also constructed a circular pulsed nozzle (0.25–0.6 mm i.d., 400–520 °C) used for measurements of PAHs and porphine compounds (13). Chan et al. also used an electrically controlled pulsed nozzle for measurement of fluoranthene (0.25 mm or 0.5 mm i.d., 400 °C) (14). Besides, Zewail et al. recorded the spectra for anthracene and its derivatives by using a pulsed nozzle maintained at 140–160 °C (maximum temperature, 200 °C) (15, 16). However, these high-temperature pulsed nozzles were developed only for spectroscopic purposes, and the samples were placed inside the nozzle. Furthermore, its dead volume is not minimized and it is difficult to apply it to the detector for gas chromatography.

In this study we develop a new type of the high-temperature pulsed nozzle with a small dead volume, which can be operated at least to 300 °C. We apply this nozzle to the detector for gas chromatography for selective determination of aromatic hydrocarbons.

EXPERIMENTAL SECTION

Nozzle. The constructed pulsed nozzle is shown in Figure 1. This nozzle is basically identical with the electric fuel injection valve for an automobile produced by Honda (main injection valve, City Turbo). But, it is completely redesigned and reconstructed for operation at a high temperature. The top needle of the plunger for the commercial parts is ground off to form a uniform jet. The commercial orifice (0.8 mm i.d.), which is made of hardened stainless steel, is machined to a cylindrical shape by a cutting tool with a ceramic tip. The orifice is mounted to the stainless steel body by an 8-mm Swagelock. The plunger is attracted by an electromagnet and is pushed back by a spring. The iron core for the electromagnet is machined from the commercial parts and is driven inside the body. The solenoid coil is made by winding a copper wire insulated by Teflon (Junko-sha, 0.32 mm o.d., 15 m, insulator thickness 50 μ m) which is heat resistive to 325 °C. The end of the nozzle is machined to a 1/4-in. stainless steel tube. The sample is introduced from a 1/16-in. stainless steel tube (0.8 mm i.d.), which is connected by a 1/4-in. to 1/16-in. reducing union. The tube is inserted into the spring to reduce the dead volume of the nozzle. The nozzle is mounted to a 6-in. flange by an 18-mm Swagelock. The nozzle is heated by a tape heater or a nichrome wire insulated by a ceramic tube. The electric current is supplied from an power inlet port (Anelva, 954-7227) mounted on the flange. The temperature of the nozzle is monitored by a thermocouple. The nozzle is heated, and the flange is cooled by circulating the tap water. The 1/16-in. stainless steel tube for sample introduction was also heated by a tape heater. The temperature was monitored by a thermocouple, which was adjusted to the nozzle temperature.

The electronic circuit for driving the nozzle is shown in Figure 2. The TTL input pulses are amplified by the three-stage transistors, and they control the electromagnet in the nozzle. The pulse width of the jet was determined by the pulse width of the TTL signal, and the sample density was adjusted by the output voltage of the driver.

Apparatus. A block diagram of the supersonic jet spectrometer combined with a gas chromatograph system is shown in Figure 3. The sample is introduced from an injection port of the gas chromatograph (Shimadzu, GC-8A). The separation column for conventional chromatography is 25 cm long (stainless steel, 3 mm i.d.), and is packed with silicone SE-30 (Gas Chromatograph Co.). The sample is separated to two streams by a three-way union.

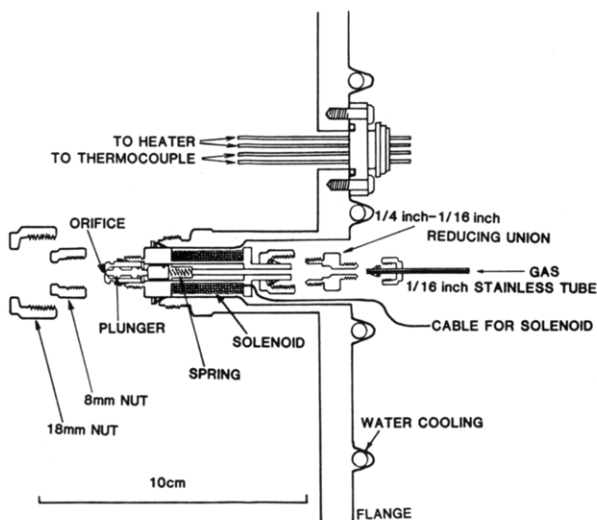


Figure 1. Structure of the high-temperature pulsed nozzle.

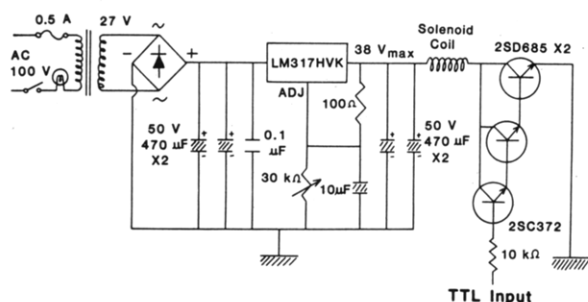


Figure 2. Electronic circuit for driving pulsed nozzle.

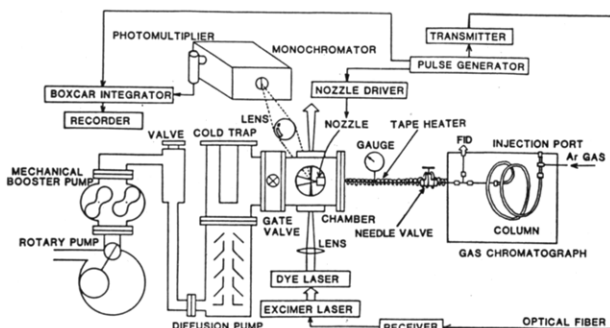


Figure 3. Block diagram of supersonic jet spectrometer combined with gas chromatograph.

The sample is detected by flame ionization and supersonic jet techniques, simultaneously. In the case of capillary chromatography, the fused silica capillary column (Shimadzu, CBP-1-425, 25 m, 0.2 mm i.d., 0.3 mm o.d.) was inserted into the 1/16-in. stainless steel tube for sample introduction, and the argon dilution gas flowed between the stainless steel tube and the capillary column. The eluent and diluent gases were mixed just behind the nozzle.

The vaporized sample diluted with argon is expanded into a 6-in. vacuum chamber from the constructed pulsed nozzle. The stagnation pressure was typically adjusted to 200–300 torr. For fluorescence detection the expanded gas is directly evacuated with a 6-in. diffusion pump (Ulvac, ULK-06, 1400 L/s) equipped with a cold trap, which is followed by a mechanical booster pump (Shimadzu, MB-100, 1500 L/min) and a rotary pump (Shimadzu, DK300, 300 L/min). For ion detection the sample molecule should be multiphoton ionized at a sufficiently low background pressure. Then, a differential pumping system was used. The sample gas was expanded in advance into a 6-in. vacuum chamber evacuated by a 4-in. diffusion pump (Ulvac, ULK-04, 650 L/s) and collimated by a homemade skimmer (1 mm i.d.) placed 7 mm away from the nozzle (7). This vacuum chamber was connected with the main

vacuum system described above.

The molecule in the supersonic jet is excited by an excimer-laser-pumped dye laser (Lambda Physik, EMG 102MSC, FL2002) at 7 mm away from the nozzle. For excitation of aniline derivatives, the dye laser was converted to the first anti-Stokes emission by a homemade Raman shifter. Fluorescence is collected by a quartz lens (focal length 10 cm, diameter 10 cm) and focused onto a slit of the 1-m monochromator (Jasco, CT-100). Fluorescence is detected by a photomultiplier (Hamamatsu Photonics, R212) and is measured by a boxcar integrator (NF Circuit Design Block, BX-530A). The induced ions by multiphoton ionization were detected by a channeltron detector (Murata, Ceratron EMS-6081B), and the signal was measured by the boxcar integrator. Timing of the signals is controlled by a homemade pulse generator through a data-link system (Mitsubishi Rayon, Eskalink, ED0101).

Reagents. The NO_2 was obtained from Takachiho Chemical Co. and perylene from Aldrich Chemical Co. Anthracene, 9-methylanthracene, and 9,10-dimethylanthracene were purchased from Tokyo Kasei Kogyo, Wako Chemicals, and Aldrich Chemical Co., respectively. Aniline and its derivatives were obtained from Tokyo Kasei Kogyo. The laser dye of phenylbiphenyl-1,3,4-oxadiazole (PBD) and *p*-terphenyl (PTP) were obtained from Nakarai Chemical Co. and Dojindo Lab., respectively.

RESULTS AND DISCUSSION

Performance of Nozzle. For the constructed nozzle the cooling effect was examined by using NO_2 as a sample. The temperature was calculated from the profile of the rotational line structure in the excitation spectrum (17). The estimated temperature was 5 K. The jet temperature was also estimated by using aniline in the case of multiphoton ionization spectrometry. From the rotational envelope of the pure electronic transition ($^1A_1 \rightarrow ^1B_2$, 293.77 nm) in the excitation spectrum the temperature was calculated to be 10 K. These results show that the nozzle has a sufficient performance for sample cooling in the supersonic jet spectrometry.

The maximum temperature for the pulsed nozzle was examined by operating it in a gas chromatograph oven. It was confirmed that the nozzle could be operated at least to 300 °C, though the power of the electromagnet became slightly weak at around 300 °C. The maximum temperature may be limited to 325 °C, at which Teflon used for insulating the solenoid coil decomposes. For operation at higher temperature, other insulating materials such as polyimide might be used. However, the manufacturer informs us that the polyimide film coating is rather poorly bound to copper wire by thermally labile adhesive. Then, it seems to give a poorer performance than Teflon at present.

As an application of this nozzle to supersonic jet spectrometry, we measured the fluorescence spectrum of perylene having five fused aromatic rings. The sample was heated to 175 °C, and the nozzle temperature was maintained at 280 °C. When perylene is excited at 415.3 nm, a jet spectrum was composed of sharp vibrational lines, and the result was identical with the spectrum previously reported using a continuous-flow nozzle (4). The constructed nozzle has a small dead volume (0.2 mL), and the sample can be introduced from the outside. Therefore, it can be applied to a gas chromatograph detector, in which a detector temperature should be frequently raised to 300 °C.

The minimum pulse width of the nozzle was measured by recording the fluorescence intensity by changing the delay time of the TTL signal that drives the excimer laser. The nozzle opened within 0.5 ms and closed in 0.8 ms, the minimum pulse width being 1.3 ms. When the shorter TTL pulse was applied to the nozzle driver, it decreased the electromagnet power and the signal intensity decreased. The observed pulse width is similar to the currently used nozzle modified from the fuel injection valve for an automobile (0.5–1.3 ms) (18, 19). In principle, the jet pulse width is shortened by increasing the current of the electromagnet and increasing the strength of

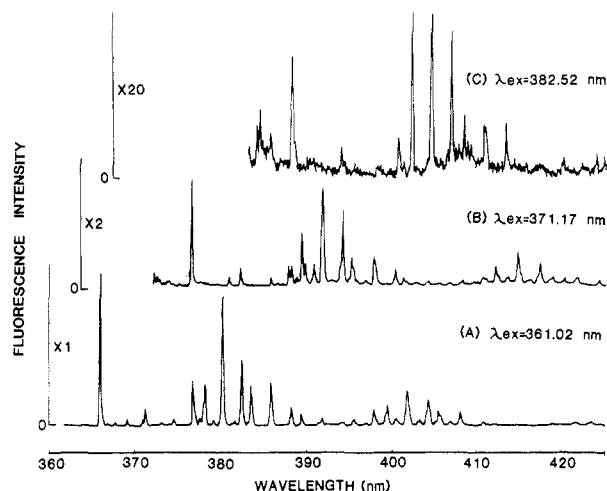


Figure 4. Fluorescence spectra for mixture of anthracene, 9-methylanthracene, and 9,10-dimethylanthracene recorded by exciting at specified wavelengths.

the spring. However, the present pulse width is considered to be sufficient for fluorescence measurements. It is noted that a cold spectrum is observed by using only a rotary pump, though the jet temperature is slightly increased by molecular collisions.

In the application to the multiphoton ionization detector, the chamber pressure should be maintained below 1×10^{-5} torr. By use of a differential pumping system, the pressure in the ionization chamber could be reduced to 5×10^{-6} torr when the pulsed nozzle was operated at 20 Hz. The pressure decreased to 1×10^{-6} torr when the nozzle was closed. The background pressure was measured by replacing the nozzle by a blank flange. The pressure decreased to 10^{-7} torr, depending on the conditions of the vacuum system. Thus the present nozzle may have a sufficient performance for use in multiphoton ionization spectrometry.

The nozzle could be operated at least to 100 Hz, and the maximum repetition rate was limited by the capacity of the power supply for the nozzle driver. We usually demonstrate our experiment at 20 Hz, and sometimes at 100 Hz in special cases (20). The nozzle temperature increased gradually when it was operated at high repetition rate. Care must be taken when the nozzle is operated at around 300 °C and when a thermally labile sample is measured.

The constructed nozzle is quite reliable, and no damage has been observed in a year. The nozzle is made totally of stainless steel, so that even an oxidative inorganic sample such as NO_2 and a corrosive organic sample such as aniline cause no deterioration in the performance of the nozzle. Unfortunately, sample clogging is not avoided for the molecule with a high boiling point, which sometimes occurs by careless operation of the nozzle. For example, the sample is easily condensed in the nozzle or in the stainless steel tube when the sample reservoir is heated without raising the nozzle temperature. Even in this case, the nozzle can be completely disassembled, so that the nozzle can be easily cleaned and the stainless steel tube can be replaced. This is a great advantage for its practical use. Moreover, the nozzle structure is very simple and does not require great skill for its construction. The diameter of the present orifice is 0.8 mm, but other orifices are also commercially available (0.6 mm or 0.2 mm) and may be chosen depending on the application.

Anthracene Derivatives. Figure 4 shows the fluorescence spectra for the mixture of anthracene, 9-methylanthracene, and 9,10-dimethylanthracene. The sample reservoir was heated to 130 °C, and the nozzle temperature was maintained at 170–200 °C. The spectra were recorded by adjusting the exciting wavelength to 361.02 nm, 371.17 nm, and 382.52 nm,

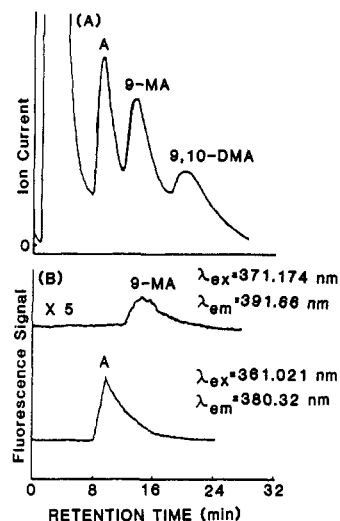


Figure 5. Gas chromatogram for mixture of anthracene, 9-methylanthracene, and 9,10-dimethylanthracene recorded by flame ionization detector (A) and supersonic jet detector (B). The 5- μL sample solution containing 25 nmol of compounds was injected.

which corresponds to the pure electronic transitions (0–0 transition) for anthracene, 9-methylanthracene, and 9,10-dimethylanthracene, respectively. The observed fluorescence spectra of parts A–C were identical with the standard samples of these compounds, and no appreciable difference could be observed. This fact indicates that the single components of mixture are completely selectively excited.

Similar results have already been published for naphthalene and its derivatives using a continuous-flow nozzle by Warren et al. (5) and also for anthracene derivatives using a mechanically rotating planner nozzle by Amirav et al. (3). On the other hand Yamada et al. have demonstrated the determination of anthracene derivatives by nonselective excitation using a xenon lamp source (21, 22). The method using the pulsed nozzle is apparently advantageous to forming a cold dense molecular jet under the limited performance of the vacuum system, and therefore it is useful for sensitive detection. Furthermore, the electrically controlled nozzle is convenient to adjust timing of the laser and other electronics.

Application to Conventional Gas Chromatography. Figure 5 A shows a gas chromatogram for the mixture sample detected by flame ionization. Three components are observed, and their integrated intensities are almost identical. A large peak immediately after sample injection is coming from benzene solvent. Figure 5B is obtained by using a supersonic jet detector. The excitation and emission wavelengths in the lower and upper traces are optimized to detect anthracene and 9-methylanthracene, respectively. In these chromatograms single peaks are observed. These results show that the supersonic jet detector has a distinct advantage over flame ionization detector with respect to selectivity. The peak for anthracene in Figure 5B has a long tail, and it implies that the dead volume for the supersonic jet system is not completely negligible. It is mainly coming from the dead volume of the connection tube (0.5 mL) between the gas chromatograph and the jet nozzle. However, the resolution of the chromatogram measured by the supersonic jet detector is similar to that obtained by a flame ionization detector. Then, the resolution is mainly limited by the separation column. It is noted that the low signal intensity for 9-methylanthracene in comparison with that estimated from Figure 4 is due to degradation of the laser dye. The flame ionization detector is universal; therefore it is useful when several components with different chemical structures are included in the sample. On the other hand a supersonic jet detector is very specific, and therefore it is useful for the sample containing many

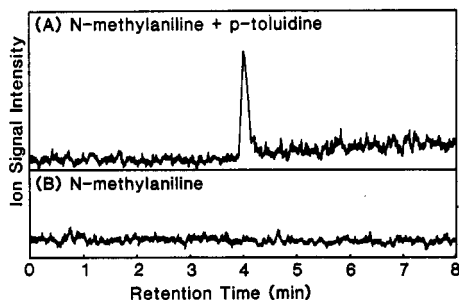


Figure 6. Chromatograms for mixture of *N*-methylaniline and *p*-toluidine (A) and *N*-methylaniline (B). The wavelength is optimized to *p*-toluidine (302.2 nm). The 1- μ L sample (1%) dissolved in cyclohexane was injected to the chromatograph.

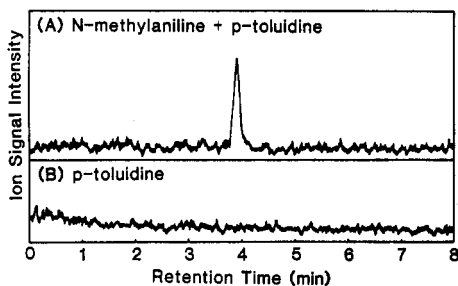


Figure 7. Chromatograms for mixture of *N*-methylaniline and *p*-toluidine (A) and *p*-toluidine (B). The wavelength is optimized to *N*-methylaniline (300.3 nm). Other experimental conditions are identical with those given in Figure 6.

components with similar chemical structures.

Application to Capillary Gas Chromatography. High-performance capillary gas chromatography is advantageously used to improve the separation resolution. In this case a pulsed nozzle with a much smaller dead volume is required. The dead volume of the present nozzle is not sufficiently small when directly applied to the detector for the capillary gas chromatograph. However, if the eluent is mixed with the diluent gas just behind the nozzle to increase the flow rate for use in supersonic jet spectrometry and the effective dead volume can be reduced to 0.2 mL/dilution ratio, then the present nozzle might be used for the detector in capillary gas chromatography.

First, we measured the multiphoton ionization spectrum for aniline, *N*-methylaniline, *m*-toluidine, and *p*-toluidine. The jet spectra were composed of sharp line structures as reported (10, 23, 24). Second, we measured the capillary gas chromatograms for aniline derivatives. Figure 6 shows the results obtained by adjusting the exciting wavelength for *p*-toluidine (302.2 nm). It is apparent that *p*-toluidine is selectively ionized and determined. The chromatograph resolution was mainly limited by the separation column since the chromatograph conditions are not necessarily optimized. Figure 7 was ob-

tained by adjusting the exciting wavelength for *N*-methylaniline (300.3 nm). When the selective ionization of *N*-methylaniline was achieved, the detection limits were 3 μ g for these compounds and were determined by the background noise occurring from the sample itself remaining in the sample introduction line. The present study is performed by using a split injection method, and only several percent of the sample is introduced into the capillary column. An updated cold-on-column technique allows 100% sample introduction, and its use might readily improve the detection limit 1–2 orders of magnitude. We wish to emphasize that time-of-flight mass spectrometry combined with this system provides further information for assignment of the sample species (24).

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Registry No. Anthracene, 120-12-7; 9-methylantracene, 779-02-2; 9,10-dimethylantracene, 781-43-1; *N*-methylaniline, 100-61-8; *p*-toluidine, 106-49-0; perylene, 198-55-0.

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