

A PULSED NOZZLE FOR APPLICATION TO GAS CHROMATOGRAPHY/MULTIPHOTON IONIZATION-MASS SPECTROMETRY

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Abstract

For the present study, a pulsed nozzle for the interface of a gas chromatograph and a time-of-flight mass spectrometer was designed. The nozzle created a supersonic jet gas pulse for a duration lasting several tens of microseconds. This small gas pulse increased the efficiency of sample use by three orders of magnitude, compared with that obtained by a continuous-flow nozzle. Using this modified pulsed nozzle, polychlorinated dibenzofurans were measured in gas chromatography/supersonic jet/multiphoton ionization-mass spectrometry. The full-width, half-maximum values of the signal peaks for 2-monochlorodibenzofuran and 2,8-dichlorodibenzofuran in the mass chromatograms were ca. 3 seconds, which were nearly identical to the values obtained using a flame ionization detector. The results of this study demonstrate that this modified pulsed nozzle can be a successful interface for gas chromatography and the mass spectrometry with no unfavorable effects. Moreover, this technique could be useful in the selective and sensitive measurement of polychlorinated dibenzo-*p*-dioxins/dibenzofurans.

Introduction

Polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) are some of the most serious environmental pollutants. To date, their measurement has been accomplished by gas chromatography/multiphoton ionization-mass spectrometry (GC/MPI-MS).¹ Supersonic jet spectrometry (SSJ) combined with MPI-MS provides further selectivity because of the sharp spectral features. Two types of sample introduction techniques are generally used in MPI-MS. In the first technique, called continuous-flowing, a capillary column is connected to the mass spectrometer and the sample is directly introduced into the ion source as an effusive molecular beam. As an enhancement to this first technique, a capillary-based supersonic molecular beam nozzle was recently developed.² When using this continuous-flowing system, however, the duty cycle, i.e., the efficiency of sample use, was low, including when the system was used in combination with GC, and when the laser had a repetition rate of several tens of Hz which is the norm. The second sample introduction technique was the use of a pulsed nozzle. This technique was advantageous, since the sample was concentrated and ionized by a laser pulse synchronized with the pulsed nozzle, thus allowing a high duty cycle. Unfortunately, the pulsed nozzle had limited performance with GC/SSJ/MPI-MS, because the pulsed nozzle had a high dead volume compared with that of the capillary column, which caused a peak broadening in the mass chromatogram. Several studies report results with the employment of the pulsed nozzle as an interface of both GC and

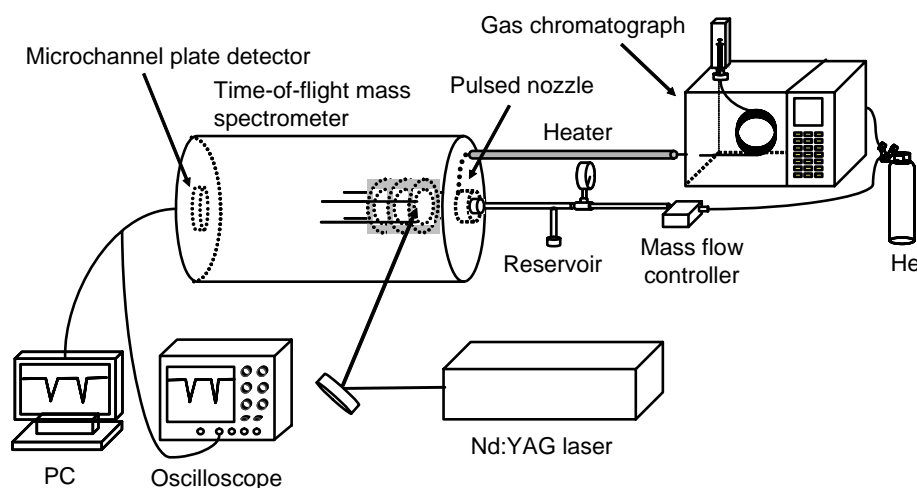


Figure 1. Experimental of GC/SSJ/MPI-MS set up.

MS.³⁻⁵ No pulsed nozzle, however, has been reported for its use as an interface to selectively and sensitively measure PCDD/Fs. In this study, a pulsed nozzle was modified for use as an interface of GC and MS. This nozzle had almost zero dead volume, and generated a short supersonic jet gas pulse. This nozzle was used to measure chlorinated dibenzofurans in GC/SSJ/MPI-MS.

Materials and Methods

Figure 1 shows a schematic diagram of the experimental apparatus used in this study. Either the fourth harmonic emission of a Nd:YAG laser (Continuum, Leopard, 10 Hz, 120 ps, or Minilite, 10 Hz, 4 ns) or the second harmonic emission of an optical parametric oscillator (Spectra Physics, MOPO-730, 10 Hz, 6 ns) was employed as an ionization laser. The samples of *p*-cresol and benzene were placed in a reservoir. On the other hand, the samples of 2-monochlorodibenzofuran and 2,8-dichlorodibenzofuran were diluted with nonane and injected into a gas chromatograph (Agilent Technologies, 6890N). The sample was separated by a capillary column (Agilent Technologies, DB-5) with helium as a carrier gas. The four samples described above were introduced into a time-of-flight mass spectrometer from a modified pulsed nozzle, as described below. The ions induced by the laser pulse were detected by a microchannel plate detector (Hamamatsu, F4655-11). The mass chromatograms were recorded either by a digitizer (National Instruments, NI 5112, 100 MHz) or by a digital oscilloscope (Tectronix Inc., TDS5104, 1 GHz).

The pulsed nozzle (Even-Lavie valve, Type E.L.-7-2004) was used as a sample introduction. In this study, this nozzle was modified to minimize the dead volume. In the original model, the sample flowed into the rear of the nozzle with a carrier gas. In combination with GC, however, the separated samples were diffused inside the nozzle body due to the high dead volume. As a result, the width of the signal peak in the chromatogram was substantially broadened. To solve this problem, the capillary column was connected to the front part of the nozzle, as shown in Figure 2. Furthermore, in GC/SSJ/MPI-MS, back pressure was added in order to prevent the separated samples from diffusing toward the back part of the nozzle. A mass flow controller mitigated the back pressure, as shown in Figure 1, and, consequently, the effect of the dead volume was eliminated. The timing between the ionization laser and the pulsed nozzle was controlled by a delay/pulse generator (Stanford Research Systems, DG 535). In the case of the measurement of PCDFs in GC/SSJ/MPI-MS, the nozzle body and a transfer line (the capillary column connected to the pulsed valve as depicted in Figure 2) were heated to 250 °C and 280 °C, respectively.

Results and Discussion

Figure 3 shows the dependence of the signal intensity on the delay time of the delay/pulse generator for the operation of the pulsed nozzle and the laser for ionization. In this study, *p*-cresol was used as a sample, and was placed in the reservoir. As shown in Figure 2, a peak was observed at the half-maximum (FWHM) value of 25 μ s, when the modified pulsed nozzle was operated at a pulse width of 50 μ s. Moreover, the duration time became short (ca. 15 μ s) when the pulsed nozzle was set at a pulse width of 30 μ s. These results indicate that the sample was spatially localized in a vacuum chamber via the modified nozzle, thus a short gas pulse allowed a high duty cycle. In comparison with the continuous-flowing system, the efficiency of sample use may

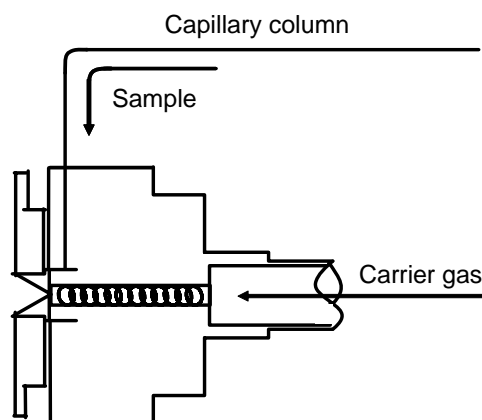


Figure 2. Structure of the developed pulsed nozzle.

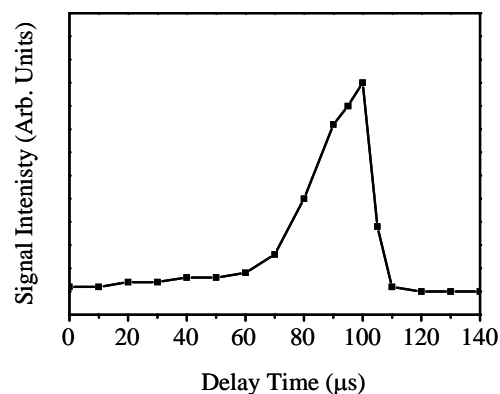


Figure 3. Dependence of the signal intensity on the delay time of the pulsed valve and the laser pulse.

increase $100 \text{ ms}/25 \text{ } \mu\text{s} = 4000$ times by using the pulsed nozzle with a laser emitting at 10 Hz (every 100 ms), as shown by this study.

To confirm the cooling efficiency using the modified pulsed nozzle, the MPI spectrum for benzene was measured. As shown in Figure 4, the line width of the signal peak narrowed, and the rotational temperature was estimated to be less than 10 K, compared to that of the rotational contour of the calculated MPI spectrum for benzene.² These results suggest that the modified nozzle can be employed as a pulsed nozzle for generation of the supersonic jet gas pulse, thus allowing for sufficient cooling. Therefore, optical selectivity can be maintained using the modified nozzle.

In order to confirm the potential for application to the interface of GC and MS, the modified pulsed nozzle was applied to the measurement of the mass chromatograms for PCDD/Fs. When the capillary column was connected to the rear of the original pulsed nozzle, the FWHM value for the elution peak arising from 2-monochlorodibenzofuran was ca. 20 seconds. This broad feature arose from the high dead volume of the valve body. Figure 5 shows the mass chromatogram for 2-monochlorodibenzofuran using the modified pulsed nozzle, i.e., the separated sample from the GC was introduced into the front part of the nozzle. The FWHM value of the signal peak arising from 2-monochlorodibenzofuran was ca. 3 seconds. This value was nearly identical to that obtained by a flame ionization detector. These results indicate that the effects of dead volume were decreased, and little or no diffusion into the valve occurred. The study also measured the mass chromatograms for chlorinated dibenzofurans using this method. Figure 6 shows the mass chromatogram for 2,8-dichlorodibenzofuran. This compound, as well as tri- and tetrachlorodibenzofuran, can be measured with FWHM to values of within a few seconds. The signal peak of pentachlorodibenzofuran, however, did not appear in GC/SSJ/MPI-MS using this interface. The reason for the absence of this sample was probably due to the insufficient heating of the transfer line for the sample introduction. In all cases, the modified pulsed nozzle was applied for the first time to the interface of GC and MS for the measurement of PCDD/Fs. At present, the detection limit is 7.3 pg for 2-monochlorodibenzofuran using the pulsed nozzle sample introduction technique, as shown in Figure 5. Further improvements may be achieved, however, since the detection limits for pentachlorodibenzofurans were ca. 10 pg using a capillary-based sample introduction technique (a continuous-flowing technique). As well, the duty cycle could increase by a factor of more than 3 orders of magnitude with use of the pulsed nozzle technique.

In this study, the pulsed nozzle was modified for

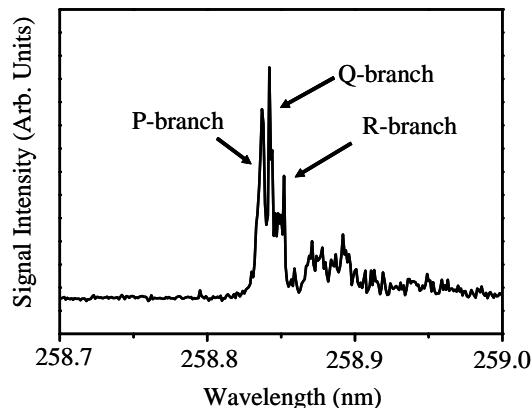


Figure 4. MPI spectrum for benzene.

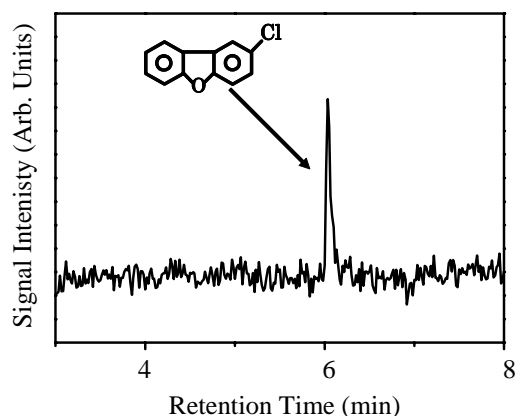


Figure 5. Mass chromatogram for 2-monochlorodibenzofuran. The sample amount is 25 pg.

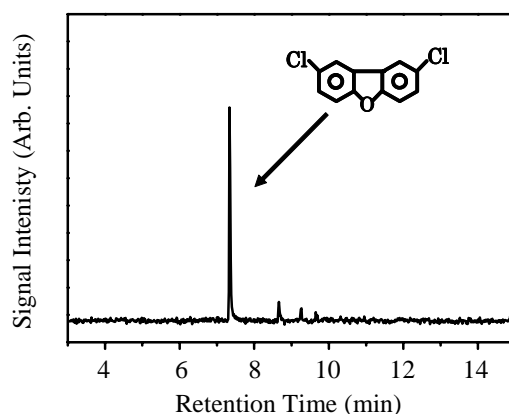


Figure 6. Mass chromatogram for 2,8-dichlorodibenzofuran. The sample amount is 1 ng.

the interface of GC and MS, and this nozzle was applied to the measurement of chlorinated dibenzofurans in GC/SSJ/MPI-MS. This modified pulsed nozzle can be employed for the generation of the supersonic jet gas pulse. It is believed that sensitive analysis can be achieved using a modified pulsed nozzle sample introduction technique, since the efficiency of the sample used was improved by more than 3 orders of magnitude as compared with that obtained by a continuous-flowing sample introduction technique. Further study should be done for the sensitive and selective analysis of PCDD/Fs.

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