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Short Communication

Application of Hadamard transform to gas chromatography/nonresonant multiphoton ionization/time-of-flight mass spectrometry

The technique of Hadamard transform was successfully coupled with GC/nonresonant multiphoton ionization/TOFMS, for the first time. 1,4-Dichlorobenzene and the fourth harmonic generation (266 nm) of a Nd:YAG laser were employed as a model sample and an ionization laser, respectively. A Hadamard-injector coupled with a capillary-based supersonic jet nozzle (capillary-injector) was also developed in this study. The Hadamard-injector was used to obtain the chromatogram, which was encoded by successive sample introduction based on Hadamard codes, and the capillary-injector was used for injection of GC-elutes into TOFMS. Compared with a conventional single injection method, the S/N ratios were substantially improved after inverse Hadamard transformation of the encoded chromatogram. Under optimized conditions, when Hadamard matrices of 103 and 255 were used, the S/N ratios of the signals for 1,4-dichlorobenzene (concentration level, 4 μg/1 mL ACN) were substantially improved to 4.1- and 6.6-fold, respectively, and those improvements are in good agreement with those obtained by theory (5.1- and 8.0-fold).

Keywords: 1,4-Dichlorobenzene / GC / Hadamard transform / Nonresonant multiphoton ionization / TOFMS
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1 Introduction

Multiphoton ionization (MPI) spectrometry is a well-known technique. It is sensitive and useful when combined with TOFMS, the so-called MPI/TOFMS. This is particularly useful, when a femtosecond laser is used in conjunction with the MPI/TOFMS technique, the ionization efficiency can be improved significantly [1–4]. With such a superior characteristic, the measurements of dioxin precursors and non-chlorinated aromatic compounds have been reported [5–7]. However, the sample injection method used in most GC/MS (or GC/MPI/TOFMS) methods involves a single injection by means of an injection cylinder and the injected volume is typically a 1–10 μL/single injection. Due to such small sample volume, the detection sensitivity is limited, although the use of large volume in a single injection becomes possible and devices to achieve this are commercially available [8–10]. With respect to chromatographic separations, some studies have reported on the use of HT for GC [11]. The advantages of the HT technique using pseudorandom injections in GC have also been proposed but only by means of computer simulation. Trapp reported high-throughput multiplexing GC using the HT method [12]. We recently, developed a novel method for improving the sensitivity of GC/MS, *i.e.* the Hadamard transform (HT)-GC/MS method [13]. In our previous research, a multiple-injection method was used to obtain a Hadamard-encoded chromatogram. The chromatogram was decoded by means of inverse Hadamard transformation, and as a result, the S/N ratios were substantially improved, compared with a conventional single injection method. In fact, the HT technique has been applied in many fields, including TOFMS [14–17], Raman spectrometry [18–20], fluorescence imaging [21–24], ion mobility spectrometry [25, 26] and even NMR [27, 28]. This technique has also been successfully applied to CE separations, where the theoretical background and experimental results were presented to demonstrate the capabilities and analytical advantages of the HT technique [29–33]. In this work, the application of a HT to GC/NR-MPI/TOFMS is described for the first time. 1,4-Dichlorobenzene and the fourth harmonic generation (266 nm) of a Nd:YAG laser were used as a model analyte and an ionization laser, respectively. The performance of a Hadamard-injector (for the introduction of the sample solution), the design of a capillary-injector (for the introduction of a gas sample to TOFMS) and details of the experimental conditions are reported herein.

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Abbreviations: HT, Hadamard transform; **MPI,** multiphoton ionization; **PSV,** pulsed supersonic valve

2 Materials and methods

2.1 Reagents

All chemicals were of analytical grade and were purchased from commercial sources. 1,4-Dichlorobenzene was purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2 Apparatus

Figure 1 shows a schematic diagram of the HT-GC/NR-MPI/TOFMS system used in this study. A commercially available GC (5890Hewlett-Packard, Avondale, PA, USA) equipped with a separation capillary column (HP-5MS, Agilent Technologies; 30 m × 0.25 μm id) was used. Helium was used as carrier gas. Temperatures of inlet, column oven and transfer line were maintained at 250, 150 and 200°C, respectively. The linear type TOFMS was a modified Wiley-McLaren design. The flight distance was 1.3 m; two turbo pumps were used for flight tube and ionization region to maintain a vacuum below 10^{-5} Torr during the experiments. The applied voltages of repeller/acceleration grids and deflection/focus plates were set at +1550/+1400 V and +45/+700 V, respectively. Mass resolution of this system was determined to be ~650. The ionization source (266 nm radiation, <20 mJ at 10 Hz) was generated from a Nd:YAG laser (Spectra Physics GCR-170, Mountain View, CA, USA). Ions were produced by nonresonant process in a field-free region and then directly migrated toward the detector, where a 25 mm triple microchannel plate was used for ion detection. Similar to a SIM method, the signal of a molecular ion was selected and accumulated by a boxcar (Stanford Research System, SR-250), where gate width was set at 0.2 μs. The averaged signal was transferred to an analog/digital device (PCI 6221 device, National Instruments) and then recorded by a personal computer. The encoded HT-GC chromatograms were decoded using the LabVIEW 8.6 program. The ion signals were observed by using a LeCroy 9350A digital oscilloscope (500 MHz), which was connected to a personal computer. A total ion current chromatogram also can be recorded by means of a home-built LabVIEW 8.6 program.

3 Results and discussion

3.1 Hadamard-injector

The Hadamard-injector, as shown in Fig. 2, was made by modifying a regular pulse nozzle. Instead of a pinhole, which is used in general pulse nozzles, a piece of a capillary was used for the introduction of the pressurized sample solution (id, 50 μm; 8 cm in length). The body of the Hadamard-injector was made of brass; the plunger had a diameter of 9.5 mm and a length of 34 mm. A 24 V electromagnetic coil and the spring were removed from a solenoid valve (SMC model VX2110: 0–1.5 MPa, Japan), respectively, and used directly. A septa-BTO (Item No. 298735) was inserted into a brass holder, which was used to firmly attach the capillary and prevent gas or liquid leaks, and was sealed with a brass stopper. The Hadamard-injector can be heated and directly inserted into the GC inlet; the injection volume of the sample solution can be adjusted by changing the background pressure (nitrogen gas), the id of the capillary, the capillary length and the injection time to

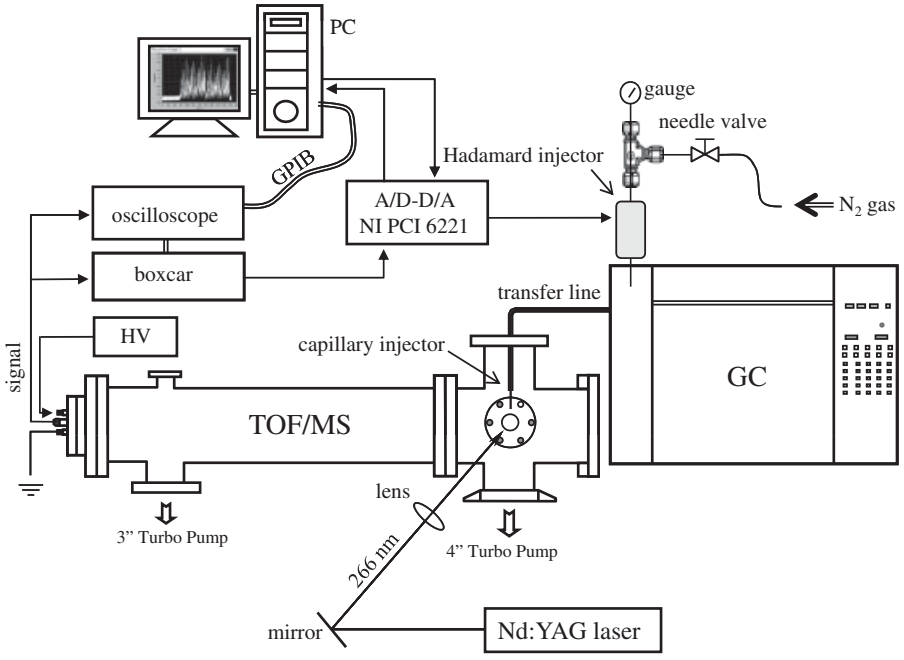

Figure 1. A schematic diagram of the HT-GC/MPI/TOFMS used in this study.

achieve a micro-controlled injection. During the sample injection process, a personal computer was used to rapidly turn the Hadamard-injector on and off through the PCI 6221 device, according to a series of Hadamard codes, leading to the introduction of the pressurized sample solution through the capillary into the GC column. The injection volume of the pressurized sample solution can be adjusted by changing the background pressure (nitrogen gas), the id of the capillary, capillary length and injection time. The RSD values of intra-day and inter-day were determined to be 0.56–1.06 and 0.92–1.67%, respectively, indicating that the procedure is stable and reproducible.

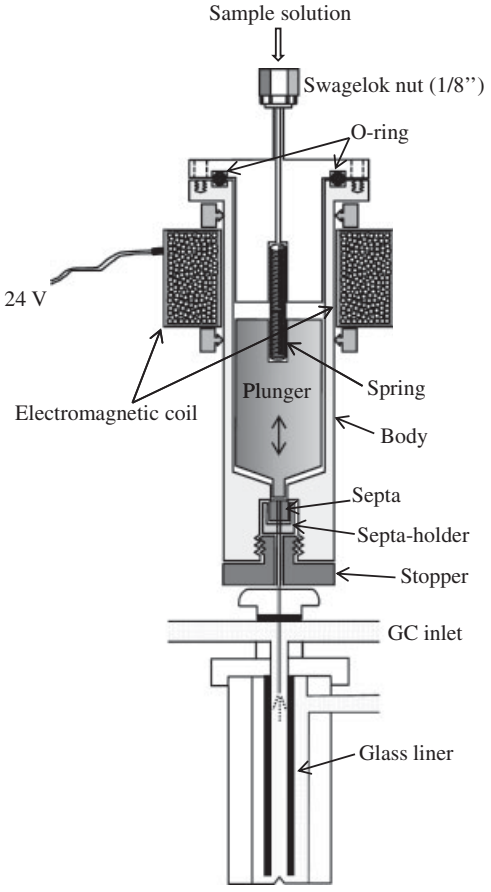

Figure 2. A schematic drawing of the Hadamard-injector used in this study.

3.2 Capillary-injector

The use of a commercially available pulsed supersonic valve (PSV) is convenient in MPI/TOFMS experiments. However, when a PSV is utilized as the interface of the GC and TOFMS, the dead volume of the PSV is too large to create a link between the GC and TOFMS. Capillary-based supersonic jet nozzles (abbreviated as a capillary-injector in this article) have been developed, with typical diameters of 50–200 μm [34–36]. In this approach, the gas sample can be injected in a continuous mode into a vacuum without using a complicated mechanical valve. Recently, we found that the use of the capillary-injector was useful for on-line concentration where an analyte is adsorbed on the tip of the capillary and subsequently desorbed by laser ablation, resulting in the production of a supersonic jet [37]. The capillary-injector was made by the following procedure; a piece of a capillary (id = 250 μm; 50 cm in length) was sealed using a high temperature flame (> 1200°C), and the sealed part was then polished until the diameter of the outlet reached approximately 50 μm. The capillary-injector was directly inserted into the electrode region of TOFMS, where the ionization laser was focused ~1 mm downstream of the capillary-injector. Using the capillary-injector, a supersonic beam was ejected into the TOF vacuum chamber the vacuum of which was maintained below 10^{-5} Torr during the GC-TOFMS experiments. Figure 3 shows photographs of the tip of the capillary-injector at different stages of manufacture; in (A), a capillary is closed because of melting the tip, and in (B), the tip is polished to make the capillary-injector. The nozzle is opened (ϕ~50 μm) by abrasion with fine sandpaper (No. 2000). A continuous supersonic jet expansion of high quality was generated

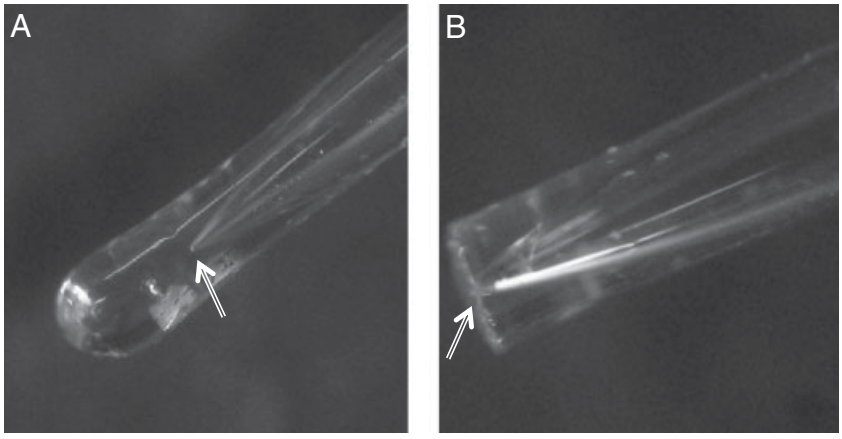

Figure 3. Photographs of the capillary tips at different stages of manufacturing: (A) capillary closed because of the melting procedure; (B) ready, the capillary-injector. The nozzle has been opened (Ø~50 μm) by abrasion with fine sandpaper.

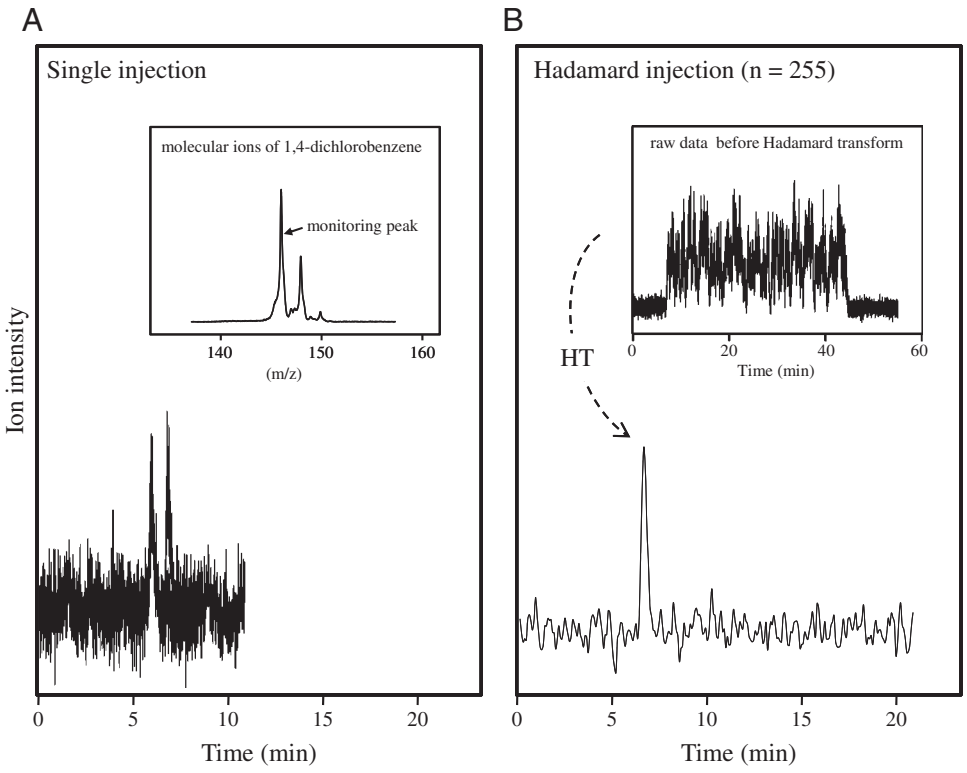

Figure 4. Typical GC/MPI-TOFMS chromatograms (1,4-dichlorobenzene concentration level, 4 μg/1 mL ACN) excited by the 266 nm laser radiation obtained by single injection (frame A) and by multiple-injection (*i.e.* Hadamard injection, frame B), respectively. Inset in frame A, a mass spectrum of 1,4-dichlorobenzene standard. The major molecular ion (m/z = 146, according to flight time = 31.45 μs) was selected as the monitoring peak by the use of a boxcar (gate width, 0.2 μs). Inset in frame B, raw data shown before the inverse Hadamard transformation.

through the capillary-injector at a low carrier gas flow rate (1 mL/min, in this study).

3.3 Application to 1,4-dichlorobenzene

Figure 4 shows GC/MPI-TOFMS chromatograms of 1,4-dichlorobenzene (concentration, 4 μg/mL in ACN). The analyte, 1,4-dichlorobenzene, was excited by the 266 nm laser radiation to obtain the chromatograms. Figure 4A and B was obtained by single injection and by multiple-injection (*i.e.* Hadamard injection), respectively. The inset in frame A shows a mass spectrum of 1,4-dichlorobenzene standard. The major molecular ion (m/z = 146, according to flight time = 31.45 μs) was selected as a peak to be monitored by a boxcar (gate width, 0.2 μs). This procedure functions in the SIM mode, as well as the function used in a commercial GC/MS. As can be seen, the S/N ratio of the peak corresponding to 1,4-dichlorobenzene is poor in the case of a single injection. In contrast to this, when the Hadamard injection method is applied (chromatogram in (B); matrix order, n = 255), the S/N ratio is improved substantially. The inset in frame B shows the raw data before the inverse Hadamard transformation. The signal for 1,4-dichlorobenzene was substantially improved to 6.6-fold, which is in good agreement with theory (8.0-fold). When the matrix order was changed to 103, the S/N ratio was improved to 4.1-fold which is also in good agreement with the theoretical value (5.1-fold, data not shown). Thus, compared with the single injection used in conventional GC/MS systems, the S/N ratios were improved substantially after inverse Hadamard transformation of the encoded chromatogram.

4 Concluding remarks

In this study, the HT technique was successfully applied to GC/NR-MPI/TOFMS. When 1,4-dichlorobenzene and the fourth harmonic generation (266 nm) of a Nd:YAG laser were employed as a model analyte and an ionization laser, respectively, the S/N ratio of the analyte was substantially improved as expected from theory. If a tunable laser is employed for adjusting the wavelength at 279.80 nm (0–0 transition wavelength of 1,4-dichlorobenzene), *i.e.* by the REMPI (resonance enhanced MPI) process, the LOD could be improved even more. Furthermore, if the Hadamard-injector is combined with on-line concentration or extraction methods, such as supercritical fluid extraction method, accelerated solvent extraction, microwave extraction of polycyclic aromatic hydrocarbons or polychlorinated biphenyls. Finally, the methodology described in this study has certain disadvantages. For example, a longer analysis time and no temperature gradient could be applied in the GC separation and the composition of the injected mixture would not increase substantially, *etc.* If these drawbacks could be addressed appropriately, further applications of the methodology can be expected.

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