Design and application of Hadamard-injectors coupled with gas and supercritical fluid sample collection systems in Hadamard transform-gas chromatography/mass spectrometry

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ABSTRACT

A novel Hadamard transform-gas chromatography/mass spectrometry (HT-GC/MS) system equipped with on-line sample collection systems is described. A Hadamard-injector was successfully designed and then coupled with an on-line adsorption/desorption system for detecting volatile organic compounds (VOCs) and a supercritical fluid extraction (SFE) system, respectively, by HT-GC/MS. Six VOCs and three pesticides were used as model compounds. In the former case, an activated-charcoal trap was used to trap VOCs from the indoor air. After 10 L of indoor air had passed through the trap, the condensed components were heated and simultaneously injected into the GC column through the Hadamard-injector, based on Hadamard codes. In a second experiment, a sample of rice was spiked with three types of pesticides and the sample then extracted using a commercially available supercritical fluid extractor. After extraction, the extracted components were transferred to a holding tank and simultaneously injected into the GC column also using the Hadamard-injector. The findings show that, in both cases, the combination of on-line sample collection methods and the use of the Hadamard transform resulted in improved sensitivity and detection. Compared to the single injection used in most GC/MS systems, the signal-to-noise (S/N) ratios were substantially improved after inverse Hadamard transformation of the encoded chromatogram.

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1. Introduction

The Hadamard transform (HT) technique has been applied in a variety of fields, including time-of-flight mass spectrometry [1–4], Raman spectrometry [5–7], fluorescence imaging [8–11], ion mobility spectrometry [12,13], and NMR [14,15]. In addition, the application of the cross correlation technique to chromatographic separation was first proposed by Izawa et al. [16]. In the 1970s, the HT and cross correlation techniques were applied to gas chromatography [17–21]. In our previous studies, this technique was successfully applied to capillary electrophoretic separations, where the theoretical background and experimental results were presented to demonstrate the capabilities and analytical advantages of the HT technique [22–26]. Conversely, Trapp reported on high-throughput multiplexing GC using the HT method [27]. More recently [28], we reported on applications of the Hadamard transform to GC/MS (gas chromatography/mass spectrometry) and LC/MS (liquid chromatography/mass spectrometry),

in which the signal-to-noise (S/N) ratios were improved compared to the theoretically predicted values. However, little information is available concerning the use of a combination of on-line sample collection and the Hadamard transform in chromatographic separations, although substantial improvements in sensitivity would be expected.

In this work, a novel Hadamard-injector coupled with on-line sample collection systems was successfully prepared, for the first time. The developed system permits a pressurized gas or pressurized liquid to be injected into a separation column according to a pseudorandom binary sequence (PRBS), i.e. a Hadamard code. The Hadamard-injector, the design of which is quite simple, permits precise sample introduction and results in clearly modulated chromatograms at the command of the PRBS. Six volatile organic compounds (VOCs) and three types of pesticides (diazinon, parathion-methyl and chlorpyrifos, commonly used in treating rice) were used as model samples, respectively. The design of the Hadamard-injector equipped with an on-line sample collection system (VOCs adsorption/desorption system or supercritical fluid extraction system), details of the experimental conditions for the determination of VOCs from indoor air and pesticides from a sample of spiked rice are reported herein.

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2. Experimental

2.1. Reagents

All VOC chemicals were of analytical grade and were purchased from commercial sources. Activated-charcoal was obtained from Shimakyu Ltd. (Japan). Diazinon, parathion-methyl and chlorpyrifos were purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.2. Apparatus

Two gas chromatograph/mass spectrometers (GC 5890/6890 equipped with 5972/5973 mass selective detectors; Hewlett-Packard, Avondale, PA, USA) were used in this study. Two types of Hadamard-injectors, one equipped with a VOCs adsorption/desorption system and another comprised of a supercritical fluid extraction system, were prepared in our laboratory: one of the systems was used for pressurized gas injection and the other for pressurized liquid injection. The Hadamard-injectors were controlled via a personal computer through a PCI 6221 device (National Instruments, USA), according to a series of Hadamard codes. A stainless activated-charcoal trap (YUJAY Technology Co., Ltd., Hsinchu, Taiwan) was used for the adsorption/desorption of VOCs; a commercial supercritical fluid extractor (CO_2 pump, PU-1580-CO_2/HPLC pump, PU-2080; JASCO, Japan) was used to the extract the spiked pesticides. The HT-GC chromatograms were calculated using the LabView 8.6 program, as described previously [28].

3. Results and discussion

3.1. Hadamard-injector

Fig. 1 shows a drawing of the Hadamard-injector, which was designed and built by modifying a standard pulse nozzle [29]. As shown in Fig. 1, in place of the orifice used in a typical pulse nozzle, a piece of a capillary was used to introduce pressurized gas (I.D., 25 μm; 6 cm in length) or a liquid sample (I.D., 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
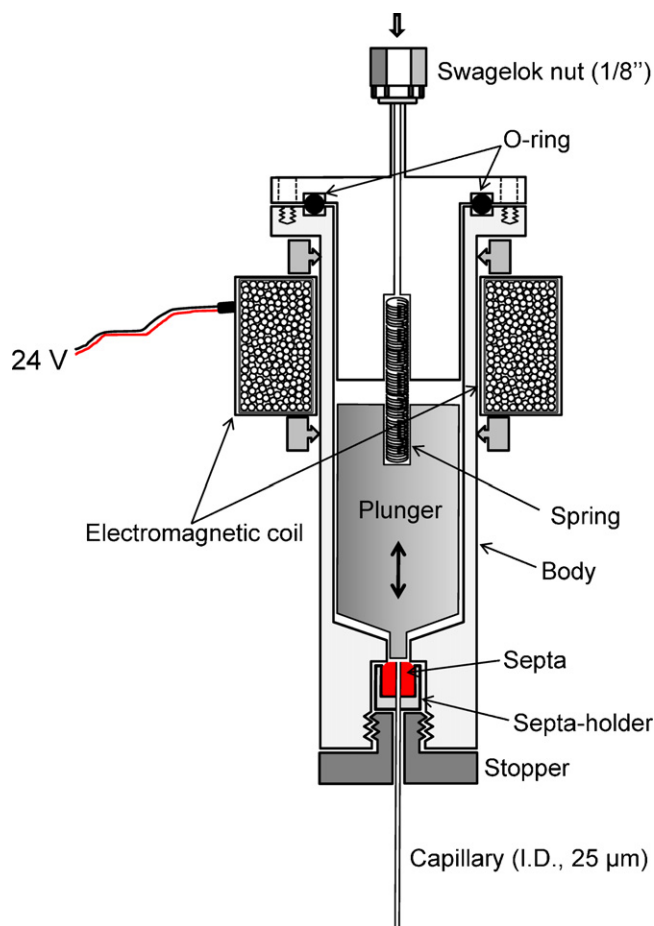

Fig. 1. A drawing of the Hadamard-injector used in this study.

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 injection volume of the pressurized gas or liquid can be adjusted by changing the background pressure (nitrogen gas), the inner diameter of the capillary, the capillary length and the injection time to achieve a micro-controlled injection. Fig. 2 shows the relationship between the injected volume and injection
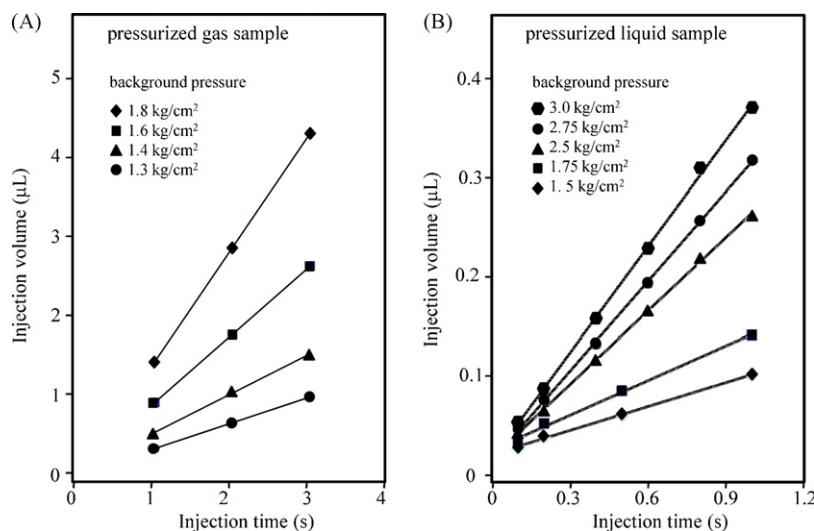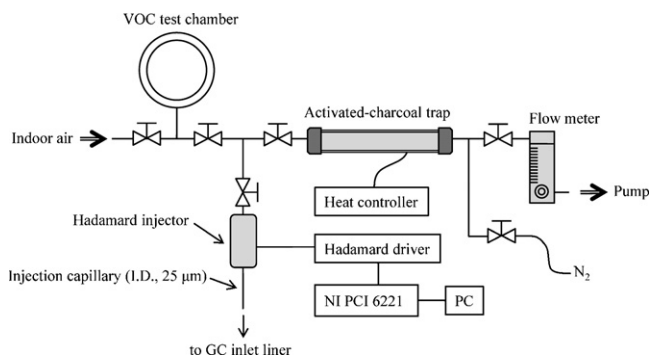

Fig. 2. Relationships between injected volume and injection time based on various background pressures (A, pressurized gas: 1.3–1.8 kg/cm²; B, pressurized liquid: 1.5–3 kg/cm², respectively).

Fig. 3. A schematic diagram of the on-line VOCs adsorption/desorption-HT-GC/MS system.

Fig. 4. A schematic diagram of the on-line SFE/HT-GC/MS system.

time based on various background pressures (A, pressurized gas: 1.3–1.8 kg/cm^2; B, pressurized liquid: 1.5–3 kg/cm^2, respectively). Herein, the injected volume was determined by means of a gas drainage method (Fig. 2A) and by weighing the collected liquid (Fig. 2B), respectively. As can be seen in Fig. 2A (for pressurized gas), when the injection time is adjusted in the range of 1–3 s, the injection volume can be controlled in the range of 0.3–4.2 μL; in Fig. 2B (pressurized liquid), when the injection time is adjusted in the range in the range of 0.1–1 s, the injection volume can be controlled in the range of 0.04–0.3 μL. It should be noted that both show very good linear relationships, indicating that the engineering of micro-valve controllers has progressed substantially. The RSD (related standard deviation) values for within-day and between-day were
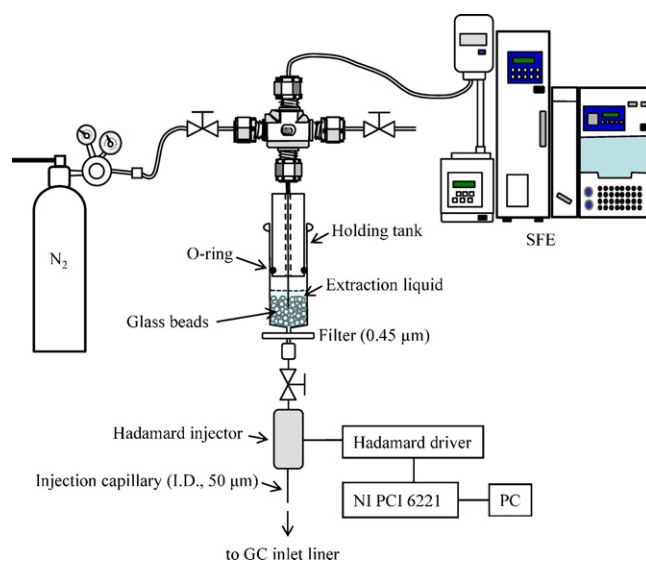
determined to be 0.24–0.38 and 0.27%, respectively, indicating the stability and reproducibility of the procedure. Furthermore, the sample injection time, volume and split-ratio were investigated in detail during GC separation experiments. Under optimized conditions, using Hadamard matrices of 255, 511 and 1023 (test sample: ethanol vapor), using the S/N ratios of the signals were substantially
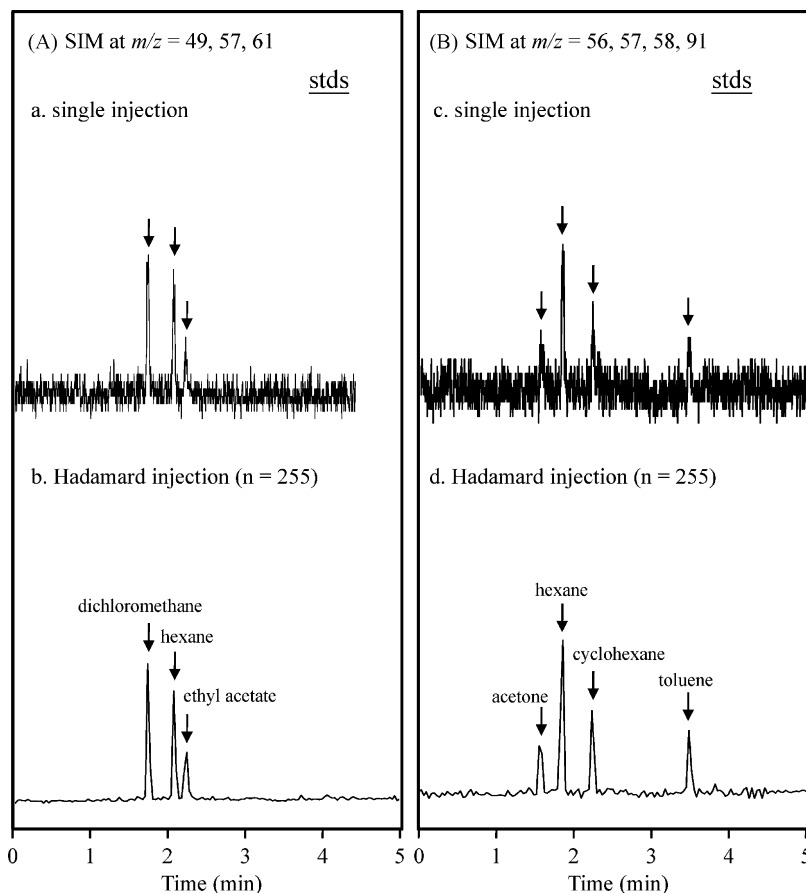
Fig. 5. Typical GC/MS chromatograms of VOC standards based on the SIM mode. Chromatograms a and c, single injection; b and d, Hadamard injection (order of matrix, 255). Head pressure: 8 psi; injector pressure, 1.8 kg/cm^2; split purge, 30 mL/min; oven temperature, 35 °C. Concentration levels: (in frame A) dichloromethane, 0.57 g/m^3; hexane, 0.47 g/m^3; ethyl acetate, 2.56 g/m^3; (in frame B) acetone, 0.57 g/m^3; hexane, 0.47 g/m^3; cyclohexane, 0.56 g/m^3; toluene, 1.24 g/m^3.
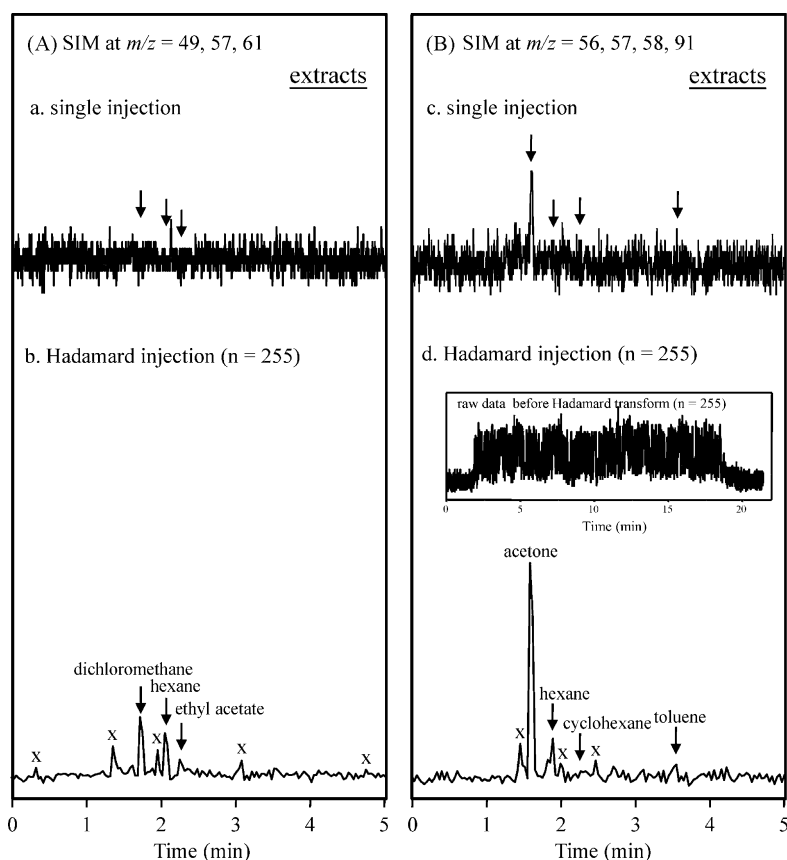
Fig. 6. Typical GC/MS chromatograms of VOCs adsorption/desorption components obtained from a chemistry laboratory, based on the SIM modes. Chromatograms a and c, single injection; b and d, Hadamard injection (order of matrix, 255). Inset, raw data shown before inverse Hadamard transformation. Unknown peaks are indicated by "x".

improved by 7.7-, 10.8- and 14.8-fold (data not shown), respectively, in good agreement with theoretical values (8.0-, 11.3- and 16.0-fold).

3.2. On-line sample collection/HT-GC/MS detection systems

Fig. 3 shows a schematic diagram of the on-line VOCs adsorption/desorption-HT-GC/MS system. This system consists of a stainless VOC test chamber, an activated-charcoal trap, a commercial GC/MS and the Hadamard-injector. Herein, the test chamber was used for spiking VOC standards at various concentrations. An activated-charcoal trap was used to collect VOCs from an indoor air sample, where a rotary pump was used to collect the indoor air sample at a flow rate at 100 mL/min. After slowly and continuously passing a 10.0 L air sample through the activated-charcoal trap, the trap and the Hadamard-injector were heated to 120 °C and pressurized by background N_2 gas. In the meantime, a personal computer was used to rapidly turn the Hadamard-injector on and off, according to a series of Hadamard codes, leading to the introduction of the pressurized VOCs sample through the capillary into the GC column. The optimized conditions were a background pressure of 1.8 kg/cm² and an injection time of 2 s. The injection volume was estimated to be ∼370 nL for a single injection.

Fig. 4 shows a schematic diagram of the on-line SFE/HT-GC/MS system. This system consists of a commercial SFE instrument, a commercial GC/MS, a holding tank and the Hadamard-injector. A 2.0 g sample of rice, obtained from a local supermarket, was doped with three different pesticides (diazinon, chlorpyrifos and parathion-methyl, 30 μg each). The extraction liquid was 1.5 mL of acetonitrile. A 0.8 g quantity of glass beads were also placed in the holding tank to suppress bubbling. The CO_2 pressure was set at

20.3 MPa, allowing the pesticides to be extracted at a flow rate at 1 mL/min (oven temperature, 50 °C). After adding 15 mL of supercritical CO_2 fluid, the liquid was slowly passed through the spiked rice sample at a constant rate, the extracts were passed through a filter (0.45 μm) and then directly injected into the GC column by a personal computer, which rapidly turned the Hadamard-injector on and off, quickly, based on the Hadamard codes. The optimized conditions were a background pressure of 3 kg/cm² and an injection time of 0.2 s. The injection volume was estimated to be ∼66 nL for a single injection.

3.3. Application to a pressurized gas sample

Fig. 5 shows typical GC/MS chromatograms for the VOC standards. Because of their molecular weights are different, two types of ion peaks were selected to distinguish between them the compounds by means of SIM (selective ion monitoring) mode (frame A, ion peaks of m/z = 49, 57 and 61; frame B, ion peaks of m/z = 56, 57, 58 and 91, respectively). The concentration levels are shown in the figure caption. The findings show that the S/N ratio was relatively poor in chromatograms a and c, which involved a single injection, whereas under the same experimental conditions, when the Hadamard injection was performed (as shown in chromatograms b and d; matrix order, n = 255), the S/N ratios were dramatically improved. Table 1 summarizes the results and, it can be clearly seen that the S/N ratio is significantly enhanced, as predicted from theoretical observations. In order to evaluate the applicability of the present method to an actual sample, VOC extracts obtained from laboratory indoor air were also collected. Fig. 6 shows typical HT-GC/MS chromatograms obtained for the adsorption/desorption of the constituent components. The GC and MS conditions are the

Table 1
Relationship between the enhancement in S/N ratios and mass conditions for analysis based on on-line VOCs adsorption/desorption and supercritical fluid extraction/HT-GC/MS methods.

Matrix order (255)	Enhancement of S/N ratio	Mass conditions
Theoretical	8.02	
Observed		
Pressurized gas		
Dichloromethane	7.3	SIM mode: m/z = 49, 57, 61
Hexane	7.6	
Ethyl acetate	8.0	
Acetone	6.9	SIM mode: m/z = 56, 57, 58, 91
Cyclohexane	7.4	
Toluene	7.9	
Pressurized liquid		
Diazinon	6.8	SIM mode: m/z = 125, 137, 199
Chlorpyrifos	4.3	
Parathion-methyl	7.6	

The enhancement of the S/N ratio was calculated as the ratio of S/N values obtained in the chromatograms, measured by HT-GC/MS and a single injection method.

same as described above. As can be seen, when a single injection is used (chromatograms a/c) the peaks are difficult or impossible to identify. In contrast, the S/N ratio is substantially improved when the Hadamard injection method is used (chromatograms b/d; matrix order, n = 255). As a result, acetone, dichloromethane, hexane and ethyl acetate were determined to be present in indoor air samples, even at very low concentration levels. The concentrations of these compounds are estimated to be <35, 1, 1 and 6 mg/m^3, respectively. Such levels are legal and safe (permissible minimal

levels: 1780, 174, 176 and 1440 mg/m^3, respectively). If a commercial VOC condenser were to be used, quantitative precision could be improved even further. The inset (above chromatogram d) shows the raw data prior to the inverse Hadamard transformation. The detected peaks are completely consistent with the theoretically predicted values, suggesting that the HT-GC/MS injection device functions very well, even for on-line extracts. The results indicate that the present on-line adsorption/desorption method and the use of a Hadamard-injector, with a simple design, permits precise multiple injections for actual sample determinations.

3.4. Application to pressurized liquid sample

Fig. 7 shows typical HT-GC/MS chromatograms of the on-line SFE extracts from the spiked rice sample. In this case, the SIM mode was used (ion peaks at m/z = 125, 137 and 199 were selected for monitoring). Chromatograms a and b show the results obtained for a single injection and a Hadamard injection (matrix order, n = 255), respectively. As can be seen, the S/N ratio is substantially improved. The inset (above chromatogram b) shows the raw data before the inverse Hadamard transformation. The detected peaks are also completely consistent with the theoretical prediction. The results indicate that the on-line SFE/Hadamard-injector described herein also permits precise multiple injections and that it can be used for the determination of actual samples.
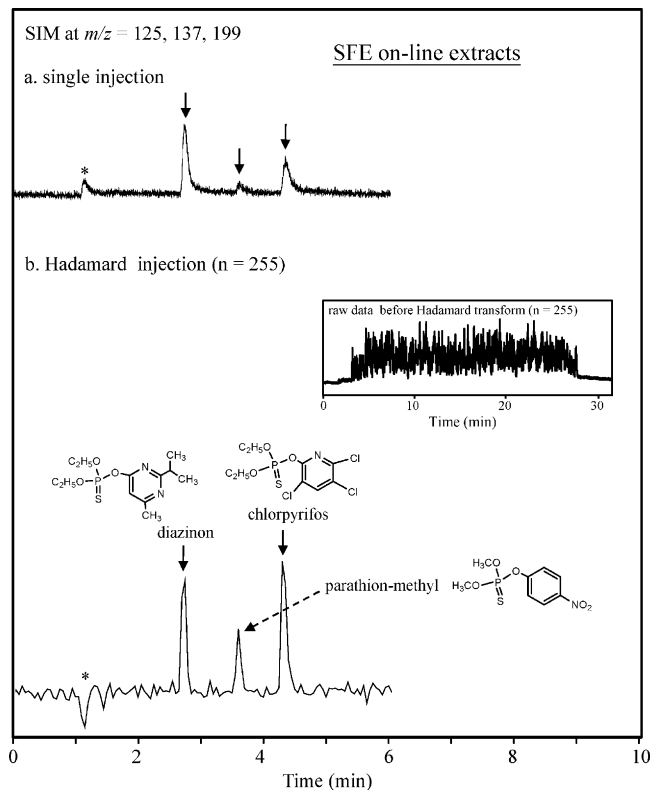
4. Conclusion

In this study, we describe the development of novel Hadamard-injectors coupled with sample collection systems. On-line VOCs adsorption/desorption and SFE systems were successfully interfaced with the Hadamard-injector. The VOC adsorption/desorption and SFE system was used successfully to collect gas and pressurized liquid samples, respectively. The utility of the method was demonstrated using some representative VOCs and pesticides as model compounds. In both cases, the devices permitted continuous and precise sample injections in HT-GC/MS, resulting in a substantial improvement in S/N ratios through the application of the Hadamard transformation. The enhancement factors for the S/N ratios were in good agreement with theoretical values. Furthermore, using the Hadamard-injector, various types of on-line concentration or extraction methods could be combined, such as measurements of VOCs in exhaled human breath, accelerated solvent extraction or microwave extraction, etc. In addition, the present technique has applicability for the monitoring of air and exhaust, and quality control of agricultural products and foods, since samples can be collected and determined at constant intervals. Thus, the present methods have a variety of applications and could potentially be used in practical trace analysis.

Fig. 7. Typical GC/MS chromatograms of SFE extracts based on the SIM mode. Chromatograms a and b show single injection and Hadamard injection (order of matrix, 255), respectively. Diazinon, chlorpyrifos and parathion-methyl (30 μg of each) were spiked to 2.0 g rice. Inset, the raw data shown before inverse Hadamard transformation. The solvent peak is indicated by "*".

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