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Quartz tip for supersonic molecular beams in gas chromatography/electron impact mass spectrometry

Hiroshi Kishi[a,*], Ai Tahara[a], Toshihiro Fujii[b]

[a]*Oyama National College of Technology, 771 Nakakuki, Oyama, Tochigi 323-0806, Japan*
[b]*National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-0053, Japan*

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Abstract

A new quartz tip for capillary gas chromatography/electron impact mass spectrometry (EIMS) was developed. The tip was designed to produce a supersonic molecular beam (SMB), permitting transport of samples into the ion source of a mass spectrometer and at the same time cooling its vibrational temperature to a cryogenic level. A fly-through Brink-type electron impact ion source was used. The performance of the tip was demonstrated by using selected organic molecules from two different chemical classes. The mass spectra of these molecules showed enhanced molecular ions as well as ionization and fragmentation patterns characteristic of the compounds studied. Some unique features of SMB-EIMS are discussed. (Int J Mass Spectrom 209 (2001) 133–140) © 2001 Elsevier Science B.V.

Keywords: Quartz tip; Supersonic molecular beam; Vibrational supercooling; Electron impact mass spectrometry; GC/MS

1. Introduction

Amirav and Danon have demonstrated the considerable effect of the vibrational supercooling encountered in supersonic molecular beams (SMBs) on the electron impact mass spectrometry (EIMS) of bromopentane isomers [1]. This effect was also studied in cholesterol [2], straight-chain alkanes, and various isomers of octane [3]. Amirav et al. showed that the parent undissociated molecular ion becomes the dominant peak, even at 70 eV electron energy, and that the conventional complex fragmentation pattern is retained in spite of the large vibrational cooling [1–3].

Although the development of supersonic molecular beam electron impact mass spectrometry coupled with gas chromatography (SMB-EIMS/GC) by Amirav was a major breakthrough in the analysis of some classes of compounds, the sensitivity, selectivity, and versatility of the technique have not been fully exploited. The reason for this is probably due, in part, to the limited number of investigations of SMB-EIMS, which is currently unavailable commercially as a complete instrument.

We describe in the present article a new "quartz tip" for capillary GC/EIMS. The homemade quartz tip is similar to Amirav's design in that a supersonic free jet technique is used to produce a supersonic molecular beam. However, the new quartz tip has the following advantages over the nozzle described by Amirav et. al. The orifice diameter is smaller than that of the ceramic nozzle, and the carrier gas flow rate

* Corresponding author. E-mail: kishi@oyama-ct.ac.jp

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through the nozzle is reduced to at least 1/10–1/20 of them, making the load to the vacuum pumping system smaller. As a consequence, one-stage vacuum pumping system is enough to maintain the working vacuum of the quadrupole mass spectrometer. Therefore, the SMB/EI technique can be available with only a minor modification to the commercial GC/mass spectrometry (GC/MS) system: to attach the new quartz tip to the end of the capillary column. The molecular beam divergence characteristic of the quartz tip has no major difference from the ceramic nozzle. For both quartz tip and ceramic nozzle, the SMB cross-sectional areas are much the same; the area diameters are ~1 mm at a distance of 10 mm from the nozzle top. This means that the new quartz tip does not suffer from the sensitivity reduction compared to the ceramic nozzle.

The purposes of this study are as follows: to design and construct a new quartz tip for capillary GC/EIMS; to construct the GC/SMB/MS interface and show the enhanced molecular weight peak; to describe the optimal operation parameters of the tip for mass spectrometry of organic compounds; to explain its detection mechanism, at least to the extent that the experimental results and the influence of working parameters can be understood; and to demonstrate the utility of this tip design with a variety of samples (fatty acid esters, and alkanes).

2. Experimental

2.1. Apparatus: the newly developed system

The apparatus used in this study was a newly developed system, modifying our previous supersonic molecular beam apparatus [5,6]. Figure 1 is a schematic drawing of the SMB-EIMS apparatus. The fused-silica quartz tip was inserted into a connector and extended 0.2 mm beyond the orifice of the connector. The tip was easily installed and its position easily optimized. The gas manifold consisted of a tee connection that was used to pass a make-up flow of He. The hydrogen-seeded uncollimated beam axially entered the electron impact ionizer (radially to the quadrupole mass spectrometer) and left it without striking its walls. Standard fittings, unions, and tee pieces were used for connecting the quartz tips. The quadrupole mass spectrometer used as a detecter is AQA-200 (ANELVA, Tokyo) equipped with a microchannel plate (MCP) as an ion multiplier, maximum gain of which is around 10^4.

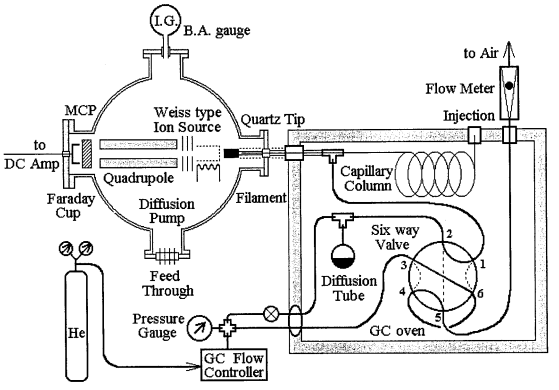

Fig. 1. Schematic diagram of GC/MS with supersonic quartz tip. The supersonic molecular beam (SMB) is produced at the capillary quartz tip, which was placed 3 mm from the entrance grid of the ion source. An *X–Y* manipulator (not shown) is used to control the position of the quartz tip. The make-up gas is fed through a tee union and a 1/8 in. stainless steel tube. The apparatus has two modes of sample introduction, interchangeable by a six-way valve: diffusion tube mode and GC capillary column mode.

2.2. Quartz tip

The capillary GC/MS quartz tip configuration was optimized according to the preceding discussion. The physical dimensions of the tip must be such that the tip can be inserted into the mass spectrometer ion source.

The quartz tip was fused directly onto the end of the capillary column. The end of the column was first installed in the chromatograph by attaching it to the splitter tee. A separate short piece of capillary column was drawn in a flame from a miniature gas torch (Kinoshita, Tokyo, Japan) to produce a tapered 20 μm i.d. tube. The fabrication process was similar to that used for making a restrictor for supercritical fluid chromatography [6], except for the dimension of the opening. A small, high-temperature flame was pref-

erable, we used LPG-gas/O_2 mixture at approximately 3:1. The tubing was heated in the flame until the fused silica gradually closed to make a hemisphere-holding conical closure. To ensure a straight end, a rotary drill was used to rotate the tube slowly at around 20 rpm. This closed tip end was then gently grinded with a grinder until a conical closure was reached.

The volumetric flow rate of escaping gas through the opening was measured and selected for the desired flow rate. The Q-tip was selected so that the expected vacuum pressure with one-stage pumping system be below the working pressure of a quadruple mass spectrometer (QMS) (1×10^{-4} Torr). Estimated flow rate should be below 1/20 of that for the two-stage pumping system. Orifice diameter was not measured. The tip was inserted into the ion source and positioned so that the top of the tip was even with the ion source edge. The utility of this tip design was demonstrated with a variety of samples (fatty acid esters, and alkanes) and its performance evaluated.

In order to avoid clogging of the quartz tip with the sample molecules, tip top was kept heated to around 200 °C during the experiment.

2.3. Ion source

One of the major instrumental problems associated with the present study was detecting the neutral beam in a sensitivity way. To address this problem, the SMB was directed through a fly-through Brink-type EI ion source [7], where the beam was ionized. The ions were then extracted into the QMS for detection.

The ionization cage was 25 mm high and 5 mm in diameter and has no source heater. The ionizer was surrounded by a mesh metal cylinder kept at a negative bias potentioal that served as an electron reflector and total pressure measurement. A thoriated tungsten filament was placed between this electrode and a grid operating at a positive potential so that electrons were accelerated through it. This ionizer was capable of detecting a molecular beam with high efficiency. This efficiency appeared to be directly related to the geometry of the cylinder and the resulting electron current.

2.4. MS, GC/MS, and separation conditions

GC/MS was performed with a Shimadzu QP 5050A GC/MS instrument. A fused-silica capillary column (FFS ULBON HR-1; Sinwakako Japan; 0.45 mm o.d., 0.32 mm i.d., and 25 m long) was used. Make-up gas (helium) was introduced through the tee union and the stainless steel tubing (1/8 in. o.d.).

2.5. Samples and Reagents

All sample compounds were guaranteed grade, purchased from Kanto Chemical Inc. (Tokyo, Japan) and used without further purification. Samples were introduced into the system by the diffusion tube method [8,9] when a constant introduction rate was necessary for examining optimum operational conditions. Care must be taken, because this method suffers from the discriminative vaporization for high vapor pressure impurities, even at their trace level concentration. We introduced the sample molecules at a rate of $\sim 1 \times 10^{-8}$ g/s.

3. Results and discussion

The GC/SMB/MS interface was constructed to maintain the performance of the open tubular column and to efficiently produce molecular ions with low fragmentation. Methyl decanoate, a fatty acid ester, was employed as a test sample to optimize and characterize the system.

3.1. Vacuum pressure

The selected quartz tip has a He-carrier gas flow rate of 6.0 mL/min (0.076 Torr L/s) at room temperature. Using a 1200 L/s diffusion pump, the tip is expected to be small enough to maintain the vacuum pressure around 6×10^{-5} Torr without differential pumping. The vacuum pressure was measured with a QMS ion source and with another ionization gauge, attached to the nozzle pumping chamber (B.A.-gauge; type MIG721, ANELVA, Tokyo; not corrected for the exact indication of pressure). With the 6.0 mL/min

quartz tip, the vacuum pressure measured with QMS was 1.0×10^{-4} Torr, whereas B.A.-gauge showed 1.1×10^{-5} Torr. The one order of magnitude higher indication with QMS source may be due to the direct and axial introduction of SMB and the short distance between the Q-tip and the source. Under this conditions the QMS worked well, however, too much introduction of organic molecules caused the lowering of the resolution of QMS and had some effect on MCP performance.

3.2. Response characteristics

Many factors influence sensitivity; however, only a few can potentially contribute to a significant gain in sensitivity. Of these, the SMB conditions associated with the backpressure (flow rate) and the electron energies are by far the most important.

3.3. SMB area profiles

SMB area profiles of the jet flux that goes to the ion source were examined. The profiles were obtained by exposing the jet flux to UV light-sensitive TLC plates in the vacuum. The spots observed under the UV light were photographed. Several nozzle tip to TLC plate distances were examined for the quartz tip and a ceramic nozzle. Although the spot diameter increased gradually with increase in the distance, the diameter did not exceed 1 mm even at 10 mm of the distance. Concerning the beam molecule divergence, no major difference between the homemade quartz tip and the 100 μm ϕ laser-drilled ceramic nozzle was found (Fig. 2). The results suggest that maximum sensitivity and signal stability for ionization is obtained when the quartz tip is approximately 3 mm from the tip top. This configuration corresponds to the maximum current, for which the ion signal is very reproducible, varying less than 5% for many months of operation.

3.4. Distance

The distance from the tip to the ion source influenced the fraction of gas flux entering the ion source. When the distance was short, there was an apparent increase in the signal response. A very short tip-to-ion source distance, however, caused large increases in the noise level as well as the background current. The noise appeared to be generated by the tip assembly, which emitted alkali metal ions, especially when it was heated. However, repositioning the tip could markedly reduce the background current.

Ion current was measured as a function of the position of the tip, using *n*-tetradecane as a test sample. The position of the tip was moved along the center axis of the instrument and normalized to 1 when the tip was 10 mm away from the ion source cage. The ion current was maximal at 3 mm.

In the following experiments, the tip-to-ion source distance was fixed at 3 mm to obtain the optimum signal-to-noise ratio. The position of the tip relative to the ion source had to be carefully adjusted for optimum performance but was easily reproduced once located.

3.5. Backpressure effect

The change of the mass spectral pattern with the hydrogen backpressure was studied, using methyl decanoate as a test sample. The sample molecules expanded in a hydrogen-seeded beam at various backpressures. An increase in hydrogen back pressure to 300 Torr, which enhances vibrational cooling, resulted in an increase in the molecular ion abundance. Above the hydrogen backpressure of 500 Torr, the spectrum was almost totally dominated by undissociated molecular ions.

This confirms that the backpressure is related to the vibrational cooling. However, we did not make special efforts to maximize the performance.

Amirav's group studied many compounds from different chemical classes to illustrate the effects of vibrational cooling in the SMB on EIMS. For example, in the various isomers of bromopentane [1], the relative abundance of the undissociated molecular ion was increased by more than two orders of magnitude in the SMB. In dioctyl phthalate [10], Amirav et al. measured an increase of over four orders of magnitude in the relative abundance of M^+.

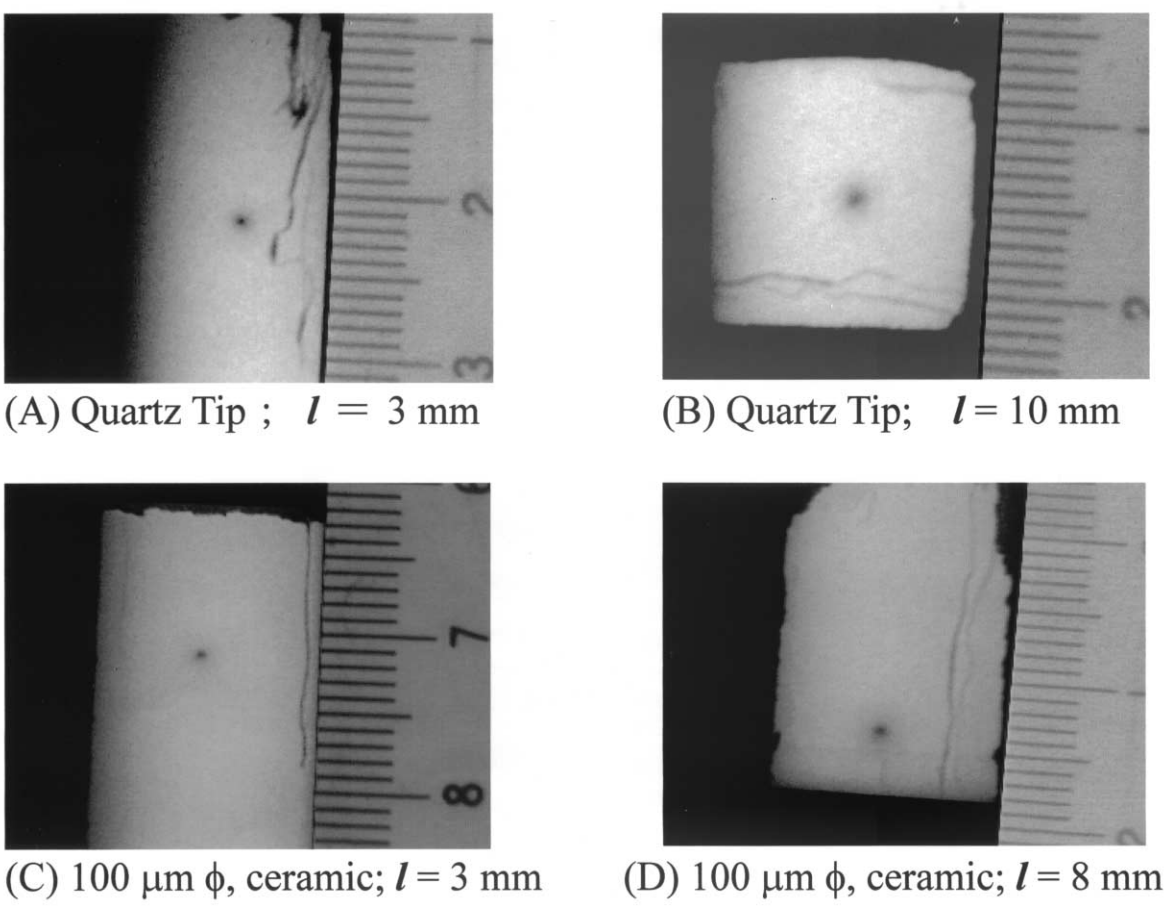

Fig. 2. SMB area profiles of the jet flux. The unit on the scales is mm. A UV light-sensitive TLC plate was placed in front of the nozzle tip, and the trace of *n*-tetradecane, expanding from the tip at a rate of 10^{-8} g/s, was recorded for 30 min. (A,B) Results for quartz tip; (C,D) results for laser-drilled ceramic nozzle (hole diameter, 100 μm). The tip-to-plate distances in mm is indicated by *l*. The hole diameter of the quartz tip was not measured.

3.6. Q-tip spectrum

Fig. 3 shows 70 eV EI mass spectra of *n*-tetradecane; [Fig. 3(A)] acquired with Q-tip nozzle, [Fig. 3(B)] acquired with 100 μm ϕ alumina nozzle, and [Fig. 3(C)] standard NIST spectrum [11]. The standard spectrum shows a relative intensity of 5.0% for M^+, whereas in both of the SMB-EI mass spectra, obtained with Q-tip and alumina nozzle, M^+ are the base peaks, the enhancement of M^+ ion intensity is some 20 times. All of the fragment ion peaks recorded in the standard spectrum are retained in both of the SMB-EI mass spectra at reduced intensity. The fragment ion peaks in Q-tip spectrum are recorded at relatively large intensity compared with alumina nozzle spectrum. The supersonic nozzle performance such as adiabatic super cooling behaves as a function of $P \times d$, where P is the backpressure and d is the nozzle diameter [12]. Therefore, the nozzle hole dimension might be the cause of the difference in the fragment ion intensities, the same back pressure of 800 Torr being used for obtaining both spectra (A) and (B).

The cooling efficiency of Q-tip must be characterized in detail using measurement of the spectrum of, for example, series of normal alkanes as done by Amirav and co-worker [10].

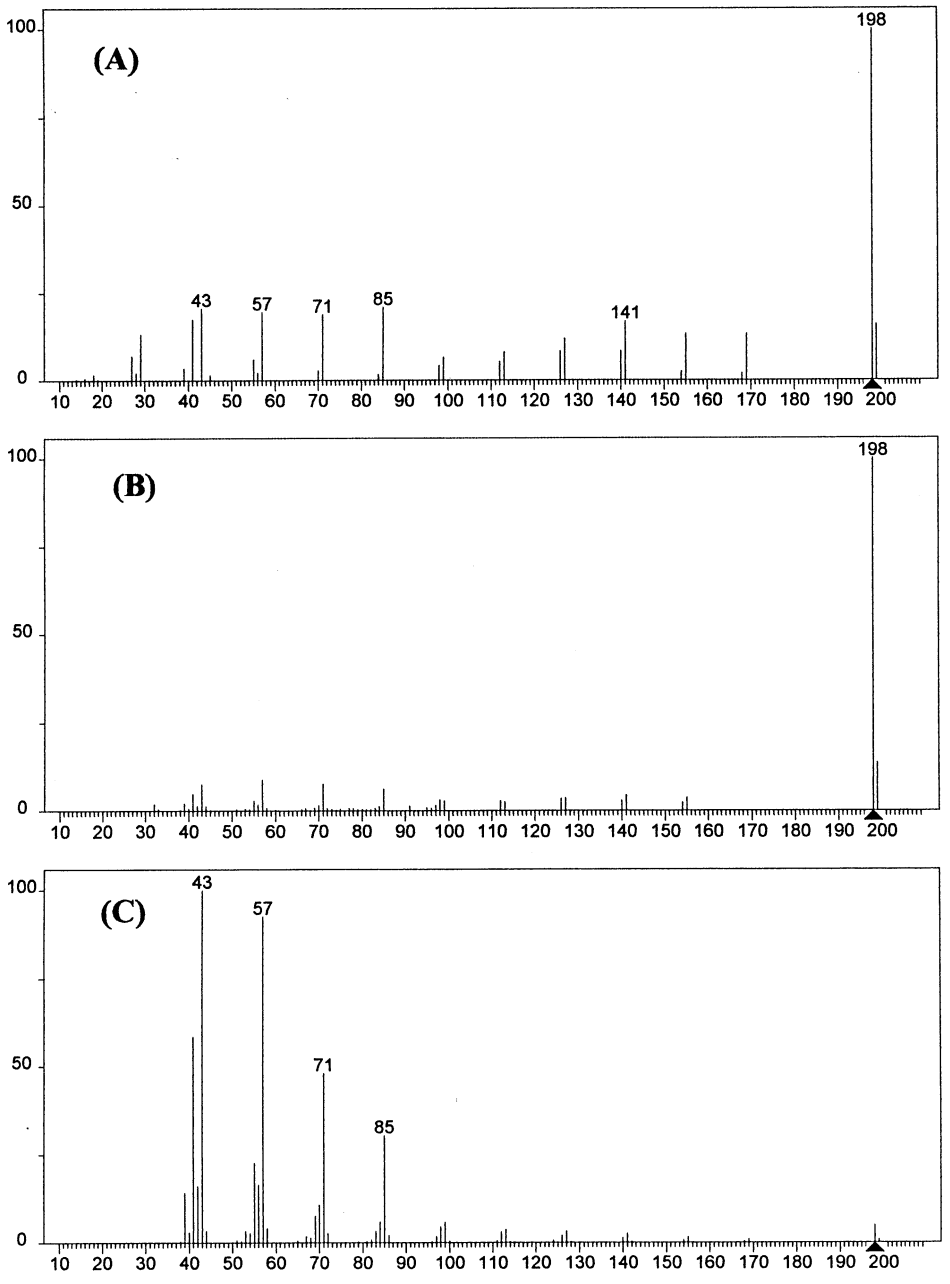

Fig. 3. Comparison of SMB/EI mass spectra between Q-tip and alumina nozzle for vibrationally cold *n*-tetradecane in a hydrogen-seeded supersonic molecular beam. (A) 70 eV SMB/EI spectrum obtained with Q-tip, (B) 70 eV SMB/EI spectrum obtained with 100 μm ϕ alumina nozzle, and (C) standard NIST spectrum. The hydrogen backpressure behind the nozzle was 800 Torr, and the sample introduction rate was 10^{-8} g/s.

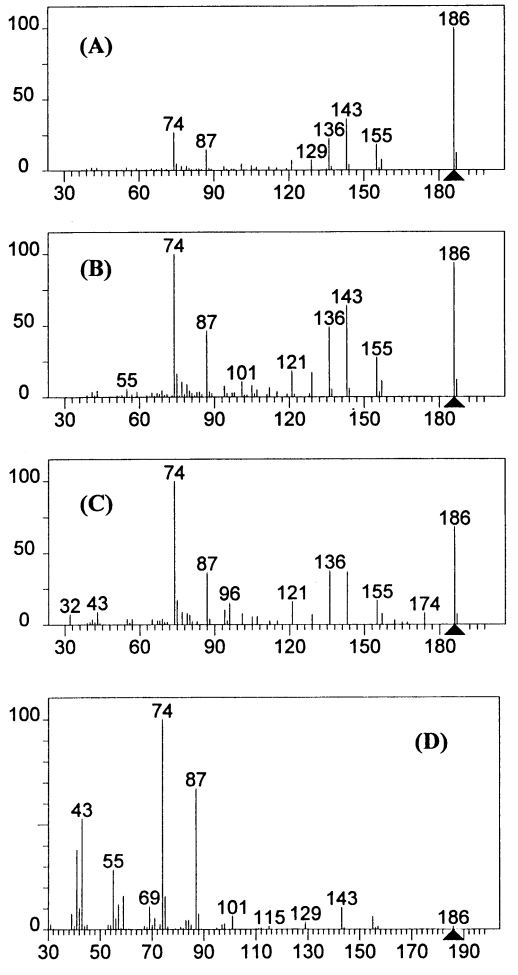

Fig. 4. Electron energy effects on the EI mass spectra of vibrationally cold methyl decanoate in a hydrogen-seeded supersonic molecular beam. The electron energies were (A) 70, (B) 40, and (C) 20 eV. The hydrogen back pressure behind the nozzle was 800 Torr, and the sample introduction rate was 10^{-8} g/s. (D) NIST standard 70 eV mass spectrum.

3.7. Electron energy effect

Amirav's group observed prominent (2–4 times) enhancement of the intensity ratio of (M^+) to (*m/z* 57) for C_{12}–C_{14} alkanes when the electron energy was decreased from 70 to 18 eV [10].

Fig. 4 shows our 70, 40, and 20 eV SMB-EI mass spectra for methyl decanoate obtained with Q-tip nozzle, together with the NIST standard 70 eV mass spectrum for the same compound. The NIST mass spectrum shows a 1.5% relative intensity for M^+; in this case, the M^+ ion intensity is enhanced nearly two orders of magnitude in our experimental spectra. There is almost no decrease of M^+ signal with increasing electron energy. Surprisingly, some enhancement of the relative M^+ intensity is observed at 70 eV, compared with 20 eV. No pronounced simplification of the mass spectral pattern at 20 eV is seen, which was observed by Amirav et al. for the cholesterol molecule [2]. These performance discrepancies in Q-tip and alumina nozzle must be investigated in detail. The peaks of *m/z* 174, 136, and 121 in Fig. 4 (A), (B), and (C) are impurity peaks at trace level concentration, enlarged by the discriminative effect of sample introduction method.

3.8. Open ion source

In an open ion source, the electron emission filament may be placed close to the ion cage and relatively large currents can be used; in our ion source, we routinely used emission currents over 10 mA. For a conventional closed ion source, the emission current is much less than 1 mA. Therefore the increased ionization emission current can compensate for the loss of sensitivity associated with the fast passage and lack of multiple collisions of molecules with electrons in the EI ion source. In monitoring a target molecule through the M^+ peak, which is substantially increased in the SMB, a better overall detection sensitivity is possible. However, we did not carry out a quantitative study of the improvement.

3.9. Nature of carrier gas

Experiments with He or H_2 as a carrier gas showed no significant difference in sensitivity or fragmentation pattern.

3.10. Detection of fatty acid esters by GC/MS with a megabore column

We selected fatty acid esters as a representative class of chemical compounds to illustrate the characteristics of SMB ionization at the GC/SMB/MS inter-

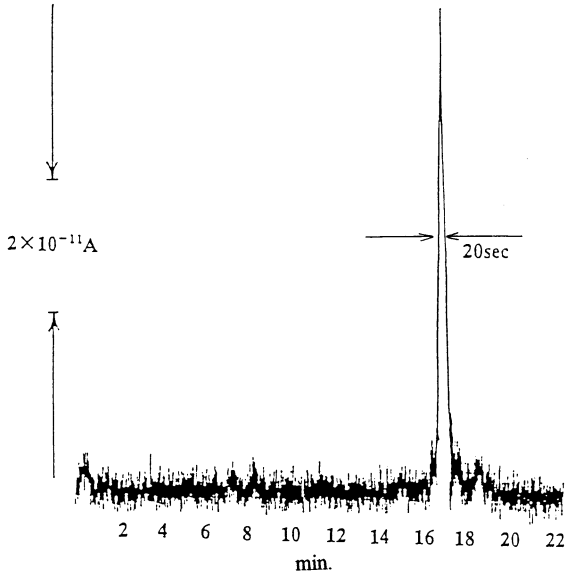

Fig. 5. GC/MS operation of methyl decanoate in hydrogen-seeded supersonic molecular beams. The (single ion monitoring) of *m/z* 74 peak with the electron energy 70 eV, 5 mA of emission, are shown under the hydrogen backpressure of 800 Torr. The sample size is 10 ng.

face. Fig. 5 shows a single ion monitoring of *m/z* 74 with 70 eV, 5 mA ionization. Ten nanograms of methyl decanoate in hexane was measured under the following conditions: carrier gas flow rate, 1 mL/min; sensitivity, 1×10^{-10} A full scale; MCP gain, 10^4. Under these conditions, the sensitivity was 1.2×10^{-1} C/g. This sensitivity is the same order of magnitude compared with that of ceramic nozzle. The noise level amounted to few picoamperes, which may be the result of the axial introduction of the molecular beam. The mass spectra exhibited pronounced molecular ion peaks in addition to typical fragment ions at *m/z* 74, 87, and 143. These results demonstrate that SMB-EIMS is able to detect molecules that do not exhibit a M^+ peak in EI and require CI to be observed. Moreover, in SMB-EIMS the M^+ peaks are considerably enhanced and clearly appear with their exact molecular mass. Fatty acid esters tend to give rise to complex spectra, providing the combined information of conventional EI and CI mass spectra. However, this complexity can be partially controlled by adjusting the electron energy.

4. Concluding remarks

We have demonstrated that the quartz tip is a suitable means for obtaining unique mass spectra, as expected with SMB-EIMS. The tip was fabricated on a portion of a 0.45 mm o.d. fused-silica capillary, which acted as a supersonic nozzle. Quartz tips were reproducible, mechanically stable, and easily applied to conventional capillary column GC/MS.

The GC/MS quartz tip configuration and construction of the EI ion source in a supersonic molecular beam mass spectrometer apparatus were discussed and evaluated in terms of enhancement of the molecular ion peak and overall sensitivity.

Acknowledgment

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References

[1] A. Amirav, A. Danon, Int. J. Mass Spectrom. Ion Processes 97 (1990) 107.
[2] A. Amirav, J. Phys. Chem. 94 (1990) 5200.
[3] A. Amirav, Org. Mass Spectrom. 26 (1991) 1.
[4] E.J. Guthrie, H.E. Schwartz, J. Chromatog. Sci. 24 (1996) 236.
[5] H. Kishi, T. Fujii, J. Phys. Chem. 99 (1995) 11153.
[6] H. Kishi, T. Fujii, J. Mass Spectrom. Soc. Jpn. 43 (1995) 293.
[7] G.O. Brink, Rev. Sci. Instrum. 37 (1966) 857.
[8] A.P. Altshuller, I.R. Cohen, Anal. Chem. 32 (1960) 802.
[9] J.M. McKelvey, H.E. Hoelscher, Anal. Chem. 29 (1957) 123.
[10] S. Dagan, A. Amirav, J. Am. Soc. Mass Spectrom. 6 (1995) 120.
[11] NIST Database 1A: NIST/EPA/NIH MassSpec Win; U.S. Department of Commerce, National Institute of Standards and Technology, Washington, DC, 1996.
[12] E. Kolodney, A. Amirav, Chem. Phys. 82 (1983) 269.