Analysis of Cigarette Smoke by an Online Thermal Desorption System and Multidimensional GC–MS*

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Abstract

Single puffs of cigarette smoke with a wide continuous range of volatility are directly analyzed using a new system. The system consists of a smoking machine, an online thermal desorption system (TDS), and a multidimensional gas chromatograph–mass spectrometer (MDGC–MS) system. The online TDS with the smoking machine collects the single-puff cigarette smoke with glass beads as the cryogenic adsorbent. The MDGC is composed of three capillary columns, Poraplot Q, and DB-WAX for separation and a deactivated capillary column for pressure balance, which enables simultaneous separation of the two different phases. The smoke desorbed from the TDS is divided into vapor and semivolatile phases and analyzed individually with each column by the MDGC. Thus, the system enables the overall analysis of the two phases simultaneously, including acetaldehyde and 1,4-benzenediol. This system also provides more appropriate analysis for compounds crossing the two phases such as toluene and pyridine. For the approach of introducing internal standards, a gas mixture of toluene-d$_8$ and o-xylene-d$_{10}$ is applied and the compounds are detected in the vapor and semivolatile phases, respectively.

Introduction

Cigarette smoke is one of the most difficult samples to analyze by chromatography. It contains at least 4000 compounds, which have a wide variety of volatility including gaseous, volatile, and nonvolatile particle compounds (1).

Generally, the sampling of cigarette smoke was done with a glass-fiber filter (2,3). Cigarettes were smoked through this filter, and then the filter was extracted with solvent. This extract included volatile and nonvolatile particle compounds. When this extract was analyzed by gas chromatography (GC), only the volatile particle compounds were analyzed. The phase including these volatile compounds was called the "semivolatile phase"(4). The gaseous compounds were not collected with this filter and passed through the glass-fiber filter. The phase including these

gaseous compounds was called the"vapor phase". This phase was collected in a gasbag (5), cryogenic trapping (4,6,7), or a trap containing organic solvents (8).

Applying these conventional methods, there were two typical difficulties. One was concerning the sampling method. The use of a glass-fiber filter for sampling brought some problems. Some compounds that crossed the vapor and semivolatile phases were partly collected on the filter and divided into both the two phases. These compounds were underestimated by the analysis of one phase (9). In addition, puff-by-puff analysis was done indirectly in the conventional method. For the puff-by-puff analysis, the amounts of compounds from a single puff were too small for the GC analysis (2) because solvent extraction was required. In this case, certain single puffs from many cigarettes were collected, which distorted the accuracy of individual puff properties. An alternative direct puff-by-puff method with Fourier transform infrared (FTIR) analysis was also tried (10,11), however this method was limited to the analysis of the gaseous compounds.

The other difficulty was concerning the analytical condition. A GC and GC–mass spectrometry (MS) system were used for the analysis of the vapor and semivolatile phase compounds. In the conventional method, the vapor and semivolatile phases were analyzed individually with different analytical capillary columns. However, the single GC could not achieve the overall analysis of the cigarette smoke simultaneously, which contained many compounds with a wide continuous range of volatility (i.e., acetaldehyde and 1,4-benzenediol).

In this study, the online thermal desorption technique was used for sampling the cigarette smoke and direct injection. The cigarette was smoked through the thermal desorption system (TDS). The smoke was collected directly in the system and injected into the analytical apparatus. This smoke included most of the vapor and semivolatile phase compounds. Because the single GC could not analyze this smoke simultaneously as described previously, multidimensional gas chromatography (MDGC)–MS was used for the analytical apparatus. In general, MDGC–MS was used to achieve the two-dimensional separation for the analysis of trace compounds, even in the case of cigarette smoke analysis (6,12). Here, the MDGC was used in a unique manner to achieve the simultaneous analysis of two different phases for the overall analysis of the smoke compounds with a

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317

wide variety of volatility.

Thus, we developed a new system for the direct analysis of mainstream cigarette smoke, which was a combination of TDS, MDGC–MS, and a smoking machine. This system would be a proposal for the solution of the direct analysis of the vapor and semivolatile phases obtained from a single puff of cigarette smoke.

Experimental

Chemicals and samples

Toluene-d_8 and o-xylene-d_{10} were obtained from Nippon Sanso (Tokyo, Japan) and premixed at 5:2 for stock liquid. A gas mixture of toluene-d_8 (74.3 ppm)–o-xylene-d_{10} (28.4 ppm) was prepared

Figure 1. The entire equipment of the system.

Figure 2. Sampling apparatus.

by injecting 100 μL water (13), followed by the 7-μL stock liquid into a vacuumed 6-L canister (Entech Instruments, Simi Valley, CA), and then nitrogen gas was injected to 300 kPa. All of the cigarettes used were the same type that were commercially available on the Japanese market, each was an 8-mg cigarette of tar. The cigarettes were maintained at 22°C for over 48 h before analysis.

Entire equipment of the system

This system was composed of a smoking machine, sampling apparatus, and MDGC–MS (Figure 1).

An RM/1 Plus single-port smoking machine (Borgwaldt, Hamburg, Germany) with software for controlling individual puff conditions was connected to the main valve of the sampling apparatus to obtain a 35-mL puff in 2 s for each puff.

The sampling apparatus (Figures 1 and 2) was based on the online TDS system, TDS-G (Gerstel GmbH, Mülheim, Germany), and placed on top of the MDGC–MS. This apparatus was composed of a TDS unit with a TDS tube, a cooled injection system inlet (CIS) with a liner filled with glass fiber, a main valve, a cigarette holder, and a second valve with a 1.0-mL gas sampling loop. Each device was connected as shown in Figure 1. A ⅛-inch 6-port valve (Valco Instruments, Houston, TX) was used for the main valve. The path inside the valve unit was widened to 1.7 mm. A 178 mm glass tube with a 4-mm i.d. was used for the TDS tube. This TDS tube was filled with 0.95 g of 2-mm glass beads, which made 60 mm length in the tube. For introducing the internal standards, the canister containing the gas mixture was connected to the second valve through a pressure controller and maintained for 82 kPa. A deactivated stainless tube connecting the TDS and main valve was heated to 350°C, the CIS and main valve to 300°C. Stainless tubes connecting the valves and other parts were placed in a valve box and heated to 250°C.

The MDGC–MS (Figures 1 and 3) was composed of two HP5973 GC–MS units (Hewlett-Packard, Palo Alto, CA) with a column-switching unit (Gerstel), which was a combination of three column-switching devices, and connected as described (Figure 3). Two GC–MS units were placed one on top of the other and connected through a cryogenic trap system (CTS), which can cool the inside area with liquid nitrogen and heat with an electronic heater. Columns A, C, and the switching unit were placed in the top oven, and column B was placed in the bottom oven. CIS, two MS units, and the three columns were connected through the column-switching unit as shown in Figure 1. The columns used were: (*a*) a DB-WAX 30 m, 0.25-mm i.d., 0.25-μm film (J&W Scientific, Folsom, CA) (column A); (*b*) Poraplot Q 25 m, with 5 m of deactivated capillary at the outlet, 0.25-mm i.d., df = 8 μm (Chrompak, Varian, Palo
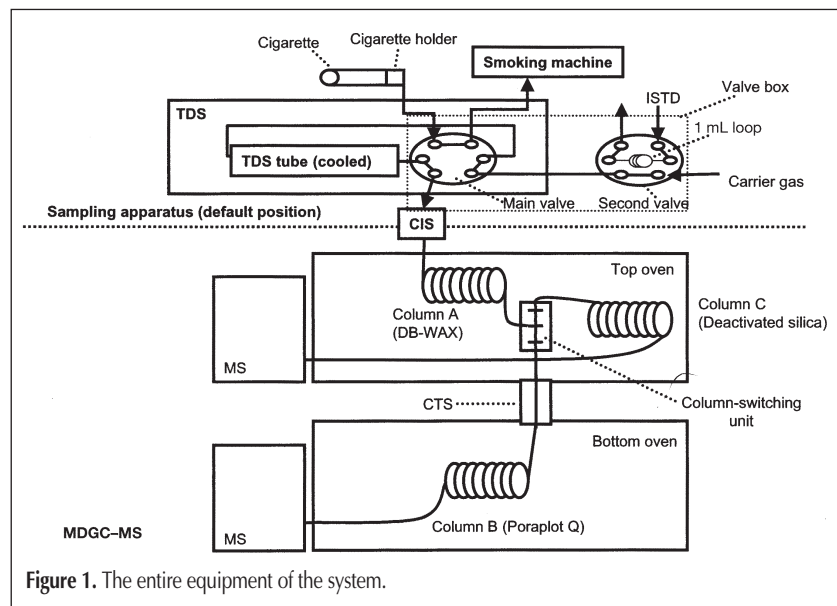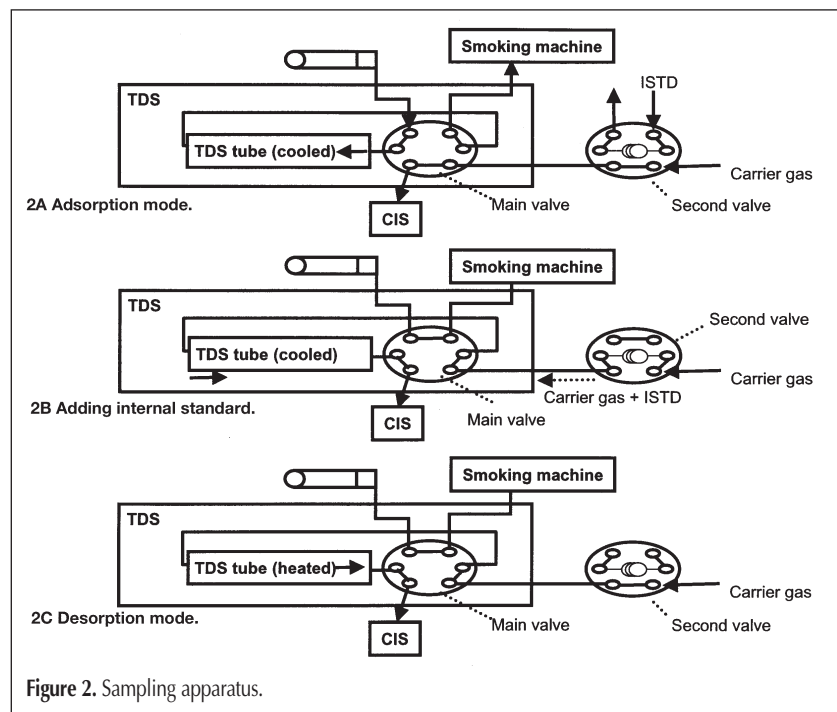
Alto, CA) (column B); and (*c*) deactivated capillary 15 m, 0.25-mm i.d. (GL Sciences, Tokyo, Japan) (column C).

Sampling apparatus

Design

The sampling apparatus was designed to satisfy the following specifications. The cigarette was smoked at a rate of 35 mL/2 s with a bell shape and an interval of 58 s (standard profile). One selected puff of cigarette smoke was collected. The smoke compounds with a wide continuous range of volatility were collected.

For the online collection of the smoke, the path resistance would distort the puff profile, which would distort smoke combustion, and the smoke components would be affected. To keep the standard profile, all paths that the cigarette smoke passed through during smoking were made as wide as possible, which enabled a 35-mL/2-s flow. All of the connecting tubes were heated to avoid smoke condensation. Cryogenic adsorption was appropriate for the collection of the smoke compounds with a wide continuous range of volatility and the small amount of smoke compounds from a single puff. For the adsorbent, 2-mm glass beads were selected in order to collect as many smoke compounds as possible, without irreversible adsorption.

Operation

A cigarette was set in the cigarette holder, lit by an electric lighter, and the smoking machine was started. In this system, the main valve was controlled to select the desorption or adsorption mode. The position of the main valve was set to the default position (Figure 1), and the cigarette was smoked without using the TDS tube. When the target-puff number was smoked, the position of the main valve was changed to the adsorption position (Figure 2A), and the smoke was introduced into the TDS tube. The TDS tube was cooled to –100ºC in advance. After the puff, the positions of the main and second valves were changed, and the internal standard gas was added into the TDS tube (Figure 2B).

After collecting the target puff into TDS tube, the position of the main valve was changed to the desorption position (Figure 2C), the TDS tube was heated from –100ºC to 50ºC (24ºC/min), and then to 270ºC (60ºC/min). The pressure of the carrier gas was 5 kPa, and the TDS was operated in splitless mode. Here, the sample was desorbed and delivered to the CIS by the carrier gas.

After the sample was delivered from the TDS to CIS, the CIS was heated from –150ºC to 270ºC (12ºC/s), and the pressure of the carrier gas was raised to 100 kPa. The CIS was operated in split mode, and the split ratio was calculated of 36.5:1. Here, the sample was introduced to the MDGC–MS and, at the same time, the analysis of MDGC–MS was started. The sampling apparatus was set back to the default position. The system was conditioned by a blank run once a day, and no unexpected peak was found.

MDGC–MS system

Design

The MDGC–MS system was used for the simultaneous analysis of the smoke compounds with a wide continuous range of volatility. Because no single column could achieve this, a combination of more than two columns that separate different volatile ranges was required.

In general, compounds like acetaldehyde, isoprene, and benzene were detected in vapor phase cigarette smoke (7,14), and a plot column was used for the vapor phase analysis including these compounds (5,15). Compounds like nicotine and 1,4-benzenediol (16) were detected in the semivolatile phase. A wax column was used for these compounds (5,6). Compounds that were found in both phases, such as toluene and pyridine, were analyzed individually by the methods specific for these compounds (8,12,14). Because this system was designed to simulate the chromatograms obtained by the conventional method, the Poraplot Q and DB-WAX columns were selected for the vapor and semivolatile phases separation, respectively.
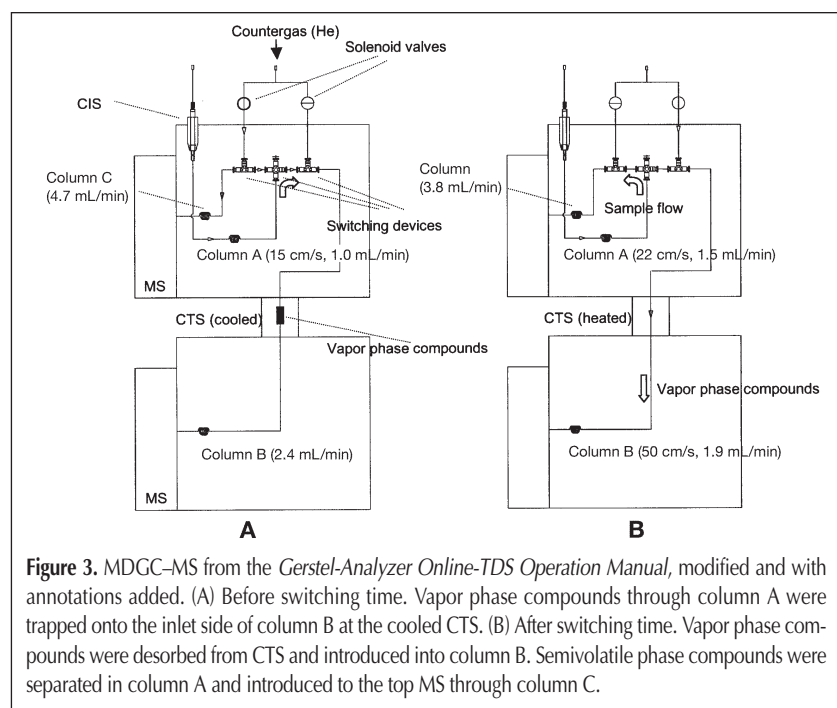

Figure 3. MDGC–MS from the *Gerstel-Analyzer Online-TDS Operation Manual,* modified and with annotations added. (A) Before switching time. Vapor phase compounds through column A were trapped onto the inlet side of column B at the cooled CTS. (B) After switching time. Vapor phase compounds were desorbed from CTS and introduced into column B. Semivolatile phase compounds were separated in column A and introduced to the top MS through column C.

Operation (Figure 3)

The sample delivered from the CIS was first applied to column A. This column separated vapor phase compounds from semivolatile phase compounds. Compounds that eluted from column A earlier than the switching time were introduced to column B through the column-switching unit and analyzed as the vapor phase compounds. Compounds that eluted later than the switching time were introduced to column C and analyzed as the semivolatile phase compounds. These compounds were separated well with column A and introduced into the top MS through column C. Column C was used for pressure balance. The countergas pressure was changed at the same time with the column-switching time, 135 kPa before the switching time and 111 kPa after the switching time. In this condition, the flow rates and carrier gas speeds for column A were 1.0 mL/min (15 cm/s) before the switching time (Figure 3A) and 1.5 mL/min (22 cm/s) after (Figure 3B); 2.4 mL/min before and 1.9 mL/min

(50 cm/s) after for column B; and 4.7 mL/min and 3.8 mL/min for column C. The flow speeds and volumes of the carrier gas were calculated from head pressures, column dimension, and oven temperature with HP flowcalc software (Hewlett-Packard).

The vapor phase compounds separated with the column-switching unit were trapped at the inlet side of column B with the CTS at –150ºC. After all of the compounds were trapped there, the CTS was heated to 240ºC (20ºC/s), and the trapped compounds were desorbed. The desorbed compounds were then separated in column B and introduced into the bottom MS.
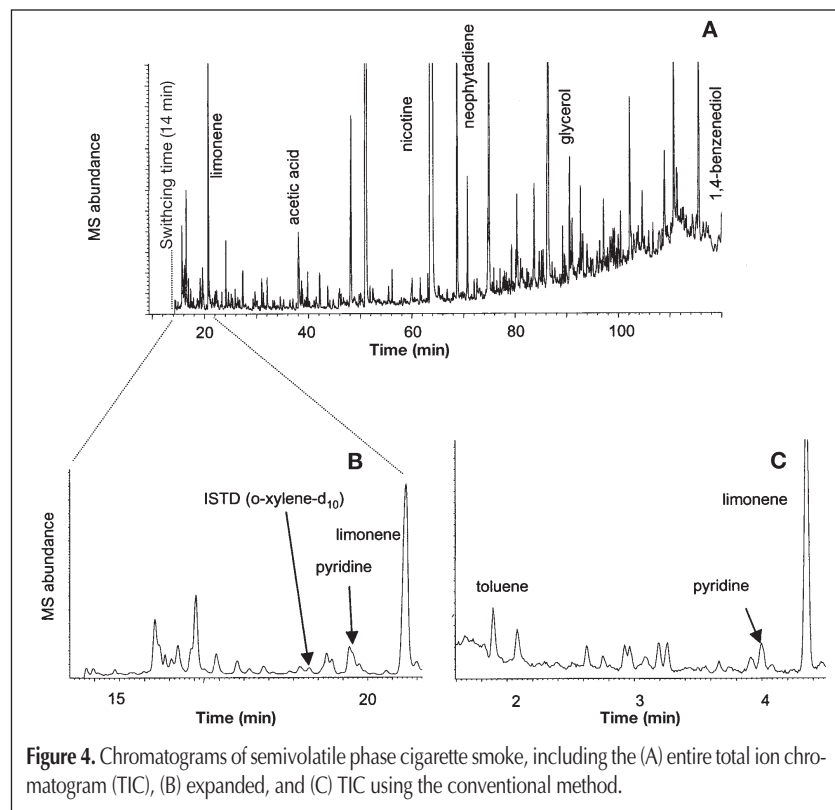

Figure 4. Chromatograms of semivolatile phase cigarette smoke, including the (A) entire total ion chromatogram (TIC), (B) expanded, and (C) TIC using the conventional method.

Figure 5. Chromatograms of vapor-phase cigarette smoke, including the (A) entire TIC, (B) expanded, and (C) flame ionization detection chromatogram (conventional method).

The temperature of both ovens was controlled in the same way: 50ºC was held for 15 min, then raised 2ºC/min to 240ºC, and held for 30 min. The two MS units were operated in scan mode (mass range 33–400), and the temperatures were 150ºC for quadrupole and 230ºC for ion source.

Results and Discussion

Chromatograms of cigarette smoke

The fifth puff of smoke from one cigarette was analyzed with this system. Two individual chromatograms were obtained simultaneously by the analysis. On the whole, this analysis simulated the conventional analysis. The chromatogram of the semivolatile phase in this analysis is shown in Figure 4A. Typical compounds (5) such as limonene, acetic acid, nicotine, neophytadiene, glycerol, and 1,4-benzenediol were detected in the chromatogram of the semivolatile phase. The chromatogram of the vapor phase is shown in Figure 5A. Typical compounds such as acetaldehyde, acetone, isoprene, benzene, 2,5-dimethylfuran, and toluene were detected in the chromatogram of the vapor phase.

However, there were differences in the chromatograms between this and the conventional analysis. For example, toluene was found only in the vapor phase with this system (Figures 4B and 5B), however it was found in both the vapor and semivolatile phases by the conventional method (Figures 4C and 5C). Similarly, pyridine was found only in the semivolatile phase with this system, but was found in both phases by the conventional method. The amounts of compounds that were delivered to both the vapor and semivolatile phases would be underestimated by the conventional method. These differences occurred because of the difference of the sampling method and the use of a glass-fiber filter to divide the vapor and semivolatile phases. Theoretically, these phenomena did not occur in this system because the phase separation was performed by the MDGC–MS system, which achieved complete separation of the two phases.

In addition, this system analyzed the single-puff cigarette smoke directly. In the conventional method, the tar was collected from as many as 90 cigarettes (Figure 4C) or 54 cigarettes (Figure 5C) for puff-by-puff analysis in order to save the smoke concentration, which would bring low accuracy. More accuracy would be expected by the direct analysis of one-puff cigarette smoke analysis.

Characterization of sampling apparatus

This sampling system adsorbed the smoke compounds at –100ºC and desorbed at 270ºC. Most of
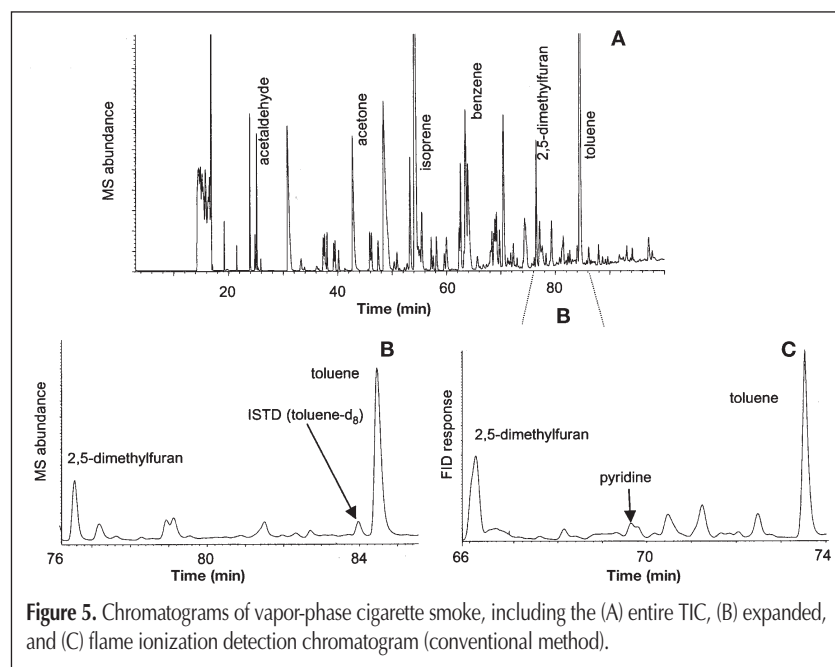
the vapor and semivolatile phase compounds (i.e., acetaldehyde and 1,4-benzenediol) were qualitatively adsorbed and desorbed under these conditions. For example, relative peak areas of 1,4-benzenediol based on nicotine were quite similar to those when using the conventional method, and the tar did not come out through the cooled TDS tube during adsorption. However, the permanent gases (i.e., ethylene) (11) could not be adsorbed by the adsorbent, and low volatile hydrocarbons (i.e., hentriacontane) were not desorbed well and showed low abundance, even though hentriacontane could be analyzed by GC (5). These compounds should be analyzed by other methods that are specified for these compounds.

Analytical conditions for MDGC–MS

In this system, MDGC was used in a different manner compared with the usual heart-cutting two-dimensional GC systems (6). At first, DB-WAX columns were used for column C, as well as column A; in a general manner, to the two-dimensional GC systems. This combination intended that column A would work for preseparation and column C for detailed semivolatile phase separation (15). But this did not work because of severe tailing of all the semivolatile peaks, possibly by excessive separation of the two columns. However, column A must have a feature of a precolumn that separates the vapor and semivolatile phases first, instead of the use of the glass-fiber filter. For this reason, a DB-WAX column, which also works for detail semivolatile separation, was selected for column A, and a deactivated capillary column was selected for column C.

The column-switching time determined the compounds that were assigned to be analyzed with either column A or B. Volatile compounds, such as isoprene and benzene, were not separated well with column A and should be analyzed with column B. Compounds such as limonene and nicotine should be analyzed with column A. Compounds such as toluene had to be tested for the column that they should be separated with. The switching time was tested between 8.5 and 14 min. Toluene was separated with column A by the switching time of 8.5 min and column B by 14 min. Toluene showed a better peak shape when analyzed with column B because the compound was refocused with the CTS. The intermediate switching time would divide the compound into both phases. In this analysis, 14 min was selected for the switching time; compounds that eluted from column A before 14 min were introduced into column B (Figure 3A) and compounds after 14 min into column C (Figure 3B).

The carrier gas conditions must be determined to work the column-switching unit properly, as well as appropriate separation. To prevent the crossover of the compounds for both directions, the carrier gas flow at column A could not exceed half of the countergas flow. On the other hand, capillary columns require carrier gas speeds of 20–40 cm/s for appropriate separation. The conditions had to have the advantage that the columns, though not separating the samples before the switching time (column B) and constantly (column C), did not require optimized carrier gas speed. Column C brought the carrier gas up to 4.7 mL/min by the vacuum of the MS. However, the semivolatile compounds were already separated well at column A, and column C did not affect the chromatogram in spite of the high flow speed of the carrier gas up to 99.7 cm/s, which prevented the elution from column A

going to column B. Column B separated the vapor phase compounds well enough at the carrier gas flow 50 cm/s.

All of the parameters used here were suitable both for the separation of the compounds with the columns and for the column-switching unit, and no crossover was found in this condition. However, a shorter capillary column was required for column C to apply this condition, though this unit was originally designed to use the same dimensions as the two outlet columns. The appropriate parameters for the carrier gas were not found when using the columns of the same dimension. In addition, the carrier gas conditions of the countergas pressure had to be changed at the same time the sample direction was changed.

Approach of introducing internal standards

In this system, the individual internal standards for each phase were applied. The internal standards were chosen for these reasons. First, deuterated compounds were useful for the internal standards (6,8) because these compounds are not found in cigarette smoke, even though it contains thousands of compounds. Second, a highly volatile compound such as o-xylene-d_{10} was selected even for the semivolatile phase because the internal standards must be vaporized and applied at once with the gas-sampling loop. Third, one of the internal standards must be detected in vapor phase and the other in semivolatile phase. It depended on the column-switching condition. In this condition, toluene-d_8 was analyzed as the vapor phase compound, and o-xylene-d_{10} was analyzed as the semivolatile phase. To satisfy these conditions, a combination of toluene-d_8 for the vapor phase and o-xylene-d_{10} for the semivolatile phase was selected. Each compound was appropriately detected in the chromatograms (Figures 4B and 5B).

The chromatograms were monitored by the ion peaks. Concerning the internal standards, m/z 98 was selected for toluene-d_8 and m/z 116 for o-xylene-d_{10}; the abundance of the compounds varied within 3% in a day. The specific ion peaks of each compound were selected as targets, and the relative peak areas compared with the internal standards varied 10–20%, the main reason for the variance would be the variance of cigarette smoke combustion. The relative peak areas of semivolatile compounds varied 20–30% by the conventional method.

Applications

Compared with the conventional method, this analysis had two advantages. One was the simultaneous analysis of the smoke compounds. The other was the direct analysis of one-puff cigarette smoke. An example of a study using the advantages of the system was the filtration efficiency study of the cigarette filter (17). Cigarette filters could absorb smoke compounds with a wide continuous range of volatility, including vapor and semivolatile compounds (18). In this case, the effect of additives to the filters, which had continuous effects across both phases, was shown by the direct analysis of cigarette smoke.

Conclusion

This study showed the alternative approach of cigarette smoke analysis by the combination of TDS and MDGC–MS. One-puff

cigarette smoke was directly collected cryogenically using TDS, instead of the glass-fiber filter. The smoke compounds with a wide continuous range of volatility were simultaneously analyzed using MDGC–MS system and consisted of two different analytical columns and a deactivated capillary column. This system provided the direct analysis of cigarette smoke from a single puff of cigarette smoke with a wide continuous range of volatility and was more appropriate for certain compounds crossing the vapor and semivolatile phases, such as toluene and pyridine, than the conventional method. This analysis was suitable for the cigarette filter research.

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