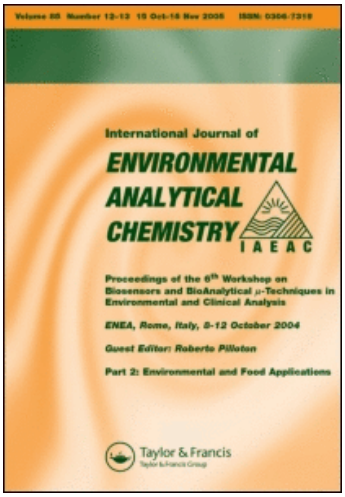

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Monitoring of Environmental Tobacco Smoke Nicotine with a Sorbent Bed-Capillary Gas Chromatograph System

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A sorbent bed-capillary gas chromatographic analytical method well suited to monitor environmental tobacco smoke nicotine in an environmental chamber or in indoor environments has been developed. The sampled air passes directly through a glass tube filled with Tenax after which the tube becomes an insert for a packed column injector port where the sample is heat-desorbed to a cold trap and transferred to a capillary GC column. Nicotine is quantitated by the use of an external standard. The results show that this method can meet the need of monitoring nicotine in an environmental tobacco smoke chamber and can be easily applied to do routine environment monitoring. The method was used to monitor the concentration of gas phase nicotine in environmental tobacco smoke in a 30 m^3 Teflon chamber. The concentration of nicotine was found to be constant with time with ordinary fluorescent room lighting. However, when a UV-light bank was turned on to simulate photochemical conditions, the concentration of nicotine decayed after a short initiation period.

KEY WORDS: Capillary gas chromatograph, nicotine, environmental chamber, environmental tobacco smoke.

INTRODUCTION

Possible health effects associated with involuntary exposure to environmental tobacco smoke have resulted in increased emphasis on the development of techniques for the monitoring of tobacco smoke in the environment.[1–3] The rates of deposition loss of particles and various gas phase components of environmental tobacco smoke in indoor environments may be very different.[1,2,4,5] For example, nicotine is present mainly in the gas phase in environmental tobacco smoke, and gas phase nicotine is removed to surfaces at a faster rate than particles of environmental tobacco smoke or other gas phase nitrogen bases.[2,4,5] Accurate determination of the dynamics of environmental tobacco smoke requires techniques for determining the concentrations of both gas and particulate phase components continuously or at short time intervals. Monitoring of gas phase components in environmental tobacco smoke with an atmospheric pressure chemical ionization tandem mass spectrometer system coupled to a test chamber has been reported by Thome *et al.*[4] The system can accommodate many permeation tubes at once, and has the capability of creating a calibration matrix similar to the expected sampling matrix. However, the system cannot be adapted for routine monitoring.

A simple method to monitor nicotine in environmental tobacco smoke on a semi-continuous basis using a Tenax sorbent trap and subsequent direct analysis by capillary GC is reported in this paper. Capillary GC has previously been used to determine many organic compounds in tobacco smoke.[6,7] Tobacco smoke has been sampled either by condensing whole smoke, followed by distillation of volatile compounds to the GC column;[8–10] or by trapping the tobacco smoke on an adsorbent, followed by heat desorption and transfer to a capillary GC column.[11,12]

There are several kinds of materials which can be used to trap tobacco smoke, including Porapak P, Carbon Molecular Sieve, Tenax,[13] and XAD.[14–16] Of all the materials studied, Tenax proved to be superior as a general adsorbent.[13]

The advantage of collecting nicotine on an adsorbent such as Tenax is that it can be desorbed after sample collection for direct analysis by GC. It is desirable to concentrate the collected sample in a cold trap prior to injection into a GC system to prevent peak

broadening resulting from thermal desorption. The principal difficulty with the use of freeze-out techniques is the presence of water in the collected tobacco smoke.[15] If water in the smoke is adsorbed by the adsorbent, the water released upon thermal desorption will condense in the cooled part of the GC column, thereby blocking the column and resulting in an inefficient transfer of compounds of interest. Therefore, the use of an adsorbent with little or no affinity for water, but capable of efficiently trapping the volatile organic compounds of interest, is highly desirable. Tenax, a porous polymer, meets these requirements. In addition, Tenax has excellent temperature stability to 380 °C, and is easily handled.

A sampling and analysis system for nicotine in environmental tobacco smoke consisting of a Tenax sorbent trap, a thermal desorber to a cold trap and direct injection from the cold trap to a GC has been assembled. The sampling-analysis system has been validated using nicotine spiked Tenax and also by comparison with results obtained by sampling environmental tobacco smoke using an annular diffusion denuder.[2,17] Use of the system for the semi-real time monitoring of gas phase nicotine in environmental tobacco smoke in a Teflon chamber is described.

METHODS

Adsorbent tubes

In order to optimize the design of the adsorbent tube to achieve reproducible results, prevent break-through, and at the same time, provide a convenient method of sampling, transfer and analysis, a few prototype glass adsorbent tubes of varying size (but all of the general design shown in Figure 1) were made. Experiments indicated that the amount of Tenax in the tube was more important than the length of the packing (tubes of various i.d. with the same amount of Tenax) and the Tenax particle size. The final design has the dimensions shown in Figure 1, and holds 3.0 mg of silanized glass wool and 30.0 mg of Tenax TA (20/35 mesh, Alltech Associates, Inc., Dearfield, IL). Silanized glass wool was used to prevent loss of Tenax from the sample tube during sample collection and handling. The Tenax was heat-treated prior to use under nitrogen gas flow at 300 °C for 24 hours to remove impurities. After the heat treatment,

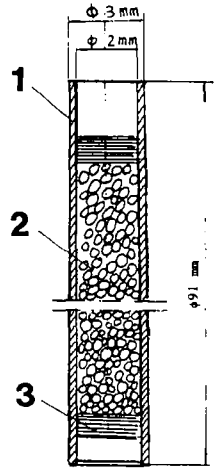

Figure 1 Tenax adsorbent tube. 1, glass tube, 2, Tenax, 3, silanized glass wool.

and after sample collection, the tube was covered with aluminium foil at both ends and stored in a capped vial to prevent contamination.

Sampling system

The sampling system is shown in Figure 2. The Tenax tube was connected to a 9 mm diameter Teflon line from the chamber with a reducing Teflon fitting. The rubber tube after the Tenax trap contained glass wool to prevent pressure surges during system startup. Flow was controlled with a Tylan mass flow controller. In order to collect samples within an exact short time period and to prevent startup errors in the flow control, a three-direction valve was placed in the system with the pump sampling air through a filter with a pressure drop similar to that for the sampling line prior to the start of sample collection. The sampling time could be precisely controlled by turning the valve on or off. When the three-direction valve was turned off, the mass flow controller was connected to the filtered laboratory atmosphere. Because the pressure drop in the chamber and bypass lines are comparable, the controller could keep a stable set flow rate when the three-direction valve was turned on. A typical sampling time was 8 min at a flow rate of 0.100 splm.

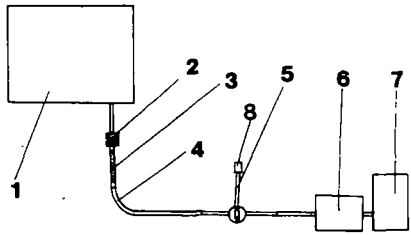

Figure 2 Sampling system. 1, chamber, 2, Teflon fitting, 3, Tenax tube, 4, glass wool in the rubber tube, 5, three-direction valve, 6, mass flow controller, 7, pump, 8, filter.

Freeze-out trap and capillary GC system

The freeze-out trap and capillary GC system is shown in Figure 3. The GC used was an HP 5890 with an NPD detector. To initiate analysis, the Tenax tube was inserted into a packed column injector, the first part of the GC column (20 cm) was cooled with liquid carbon dioxide, and material collected on the Tenax was thermally desorbed onto the top of the GC column in a He carrier gas at a flow rate of 3 mL/min. Thermal desorption was accomplished by heating the packed column injector system to 270 °C.

The transferred material was then analyzed by GC. The GC conditions were: detector temperature was 250 °C; desorption time was 6.5 min with the cooling tube held at −20 °C; after the desorption step, the cooling tube was heated to 35 °C; the capillary column was then held at 35 °C for 1 min and programmed to 200 °C at 20 °C/min; the fused silica capillary column (12 m × 200 μm i.d., 0.25 μm d_f, SB-methyl-100) was obtained from Lee Scientific (Salt Lake City, UT); carrier gas was He at 3 mL/min.

Quantitative analysis

Nicotine was quantitated by the use of an external nicotine standard prepared by dissolving pure nicotine (Eastman Kodak Company, Rochester, NY) in benzene (Reagent, Fisher Scientific, Fair Lawn, NJ). Aliquots of the standard nicotine solution were injected into the Tenax tube, dried with nitrogen, and then analyzed by GC as described above.

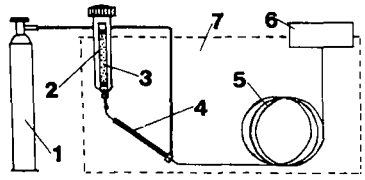

Figure 3 Freeze-out trap and capillary GC system. 1, liquid carbon dioxide tank, 2, packed column injector, 3, Tenax tube, 4, cooling tube, 5, capillary column, 6, detector, 7, GC oven.

Diffusion denuder sampling

An annular diffusion denuder sampling technique was also used to monitor nicotine in environmental tobacco smoke in a Teflon chamber[2,17] to compare with the results obtained with the Tenax sampling system. The denuder separates nicotine into gas and particulate phase components. The flow rate through the denuder was 20 slpm. Details of the sampling and analysis methods for the denuder system have been previously published.[2,17]

Sample collection

The environmental test chamber used for monitoring environmental tobacco smoke has been described.[2,17] Four cigarettes (1R1 Research Cigarettes, University of Kentucky) were smoked in the 30 m^3 Teflon chamber using a standard cycle. The mainstream portion of the smoke was vented outside the chamber. Tenax adsorbed samples were collected as a function of time over approximately a two hour period after combustion of the cigarettes. Samples were also collected over a two hour period after the environmental tobacco smoke had been exposed to UV light (385 nm). Diffusion denuder samples were collected for 1- to 2-hour sampling periods during the time the short-time Tenax samples were obtained in experiments both with and without exposure of the environmental tobacco smoke to UV radiation.

RESULTS AND DISCUSSION

A typical chromatogram of organic nitrogen compounds collected by two sequential Tenax tubes soon after combustion in the environ-

mental chamber is shown in Figure 4. The efficiency of the Tenax tube for collection of nicotine was determined by the analysis of nicotine collected on the two Tenax tubes arranged in series (Figure 4). The top profile in Figure 4(A) represents the nitrogen components collected by the front tube with the nicotine peak identified. The bottom profile (B) shows the nitrogen containing compounds which broke through the front tube and were collected on the back-up tube.

If the amount of nicotine collected by the two traps is G_1 and G_2 for the first and second adsorbent traps, respectively, then the efficiency of each section for collection of the total amount of nicotine entering the trap is,

$$\text{Efficiency} = E = \frac{G_1 - G_2}{G_1}, \tag{1}$$

and the total amount of nicotine entering the front trap is given by eq. (2).

$$\text{Total} = \frac{G_1}{E}. \tag{2}$$

The efficiency of a single Tenax trap for collection of nicotine was $88 \pm 3\%$. The efficiency was independent of the total nicotine up to the highest amount collected (9 nmol).

The calibration curve obtained by spiking different amounts of nicotine onto Tenax tubes is given in Figure 5. Peak area was linearly related to the nmol of nicotine. The equation derived from the least square linear regression fit of the data ($r^2 = 0.996$) was

$$\text{Nicotine (nmol)} = 0.02 \pm 0.22\text{(nmol)}$$

$$+ (3.38 \pm 0.08) \times 10^{-6}\text{(nmol/Area)} \times \text{Peak Area} \tag{3}$$

The quantitative results obtained from the Tenax-GC sampling and analysis system agreed with those obtained by the diffusion denuder sampling method. The comparison between the two techniques is given in Table 1.

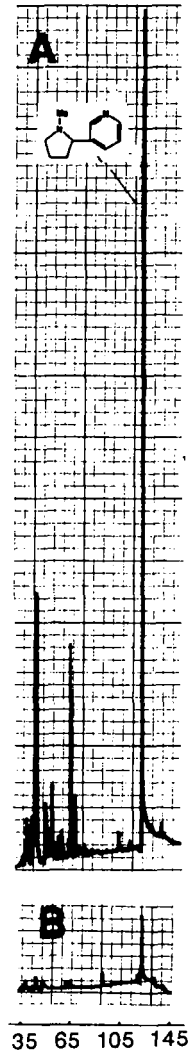

Figure 4 Gas chromatograms of environmental tobacco smoke nitrogen components collected using Tenax tube. (A), front tube, (B), back-up tube.

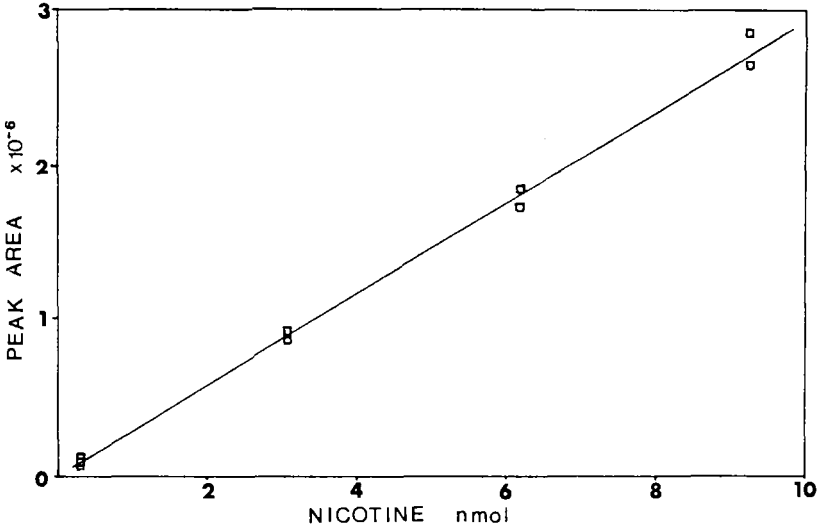

Figure 5 Nicotine calibration curve for the Tenax-GC system. The solid line is the linear regression fit to the data given by eq. (3).

Table 1 Comparison of results obtained by two different sampling techniques

Collection time after burning cigarettes (min)	*Nicotine (nmol/m³)*		
	Tenax tube	*Denuder*	
		gas phase	*Particle phase*
10–18	5600 ± 500		
20–28	6500 ± 500		
34–42	6100 ± 500		
44–52	6400 ± 500		
28–88		5900 ± 400	250 ± 20
Average	6150 ± 400	5900 ± 400	250 ± 20

Nicotine in the smoke from burning four cigarettes in the test chamber was monitored with time over two different conditions: UV-lights on and UV-lights off. With the UV-lights turned off, the concentration of nicotine in the chamber was constant with time

[Figure 6(A)]. But when the UV-lights were turned on, the concentration of nicotine decayed with time. This is illustrated both in Figure 6(B) for samples collected with the Tenax system and in Figure 7 for samples obtained with the diffusion denuders. The denuder samples were collected for one-half hour, beginning every hour after combustion of the cigarettes.

It is not possible, from the data given in Table 1, to determine if only gas phase nicotine is collected by the Tenax sampling system. This may, however, be determined from the data obtained in the UV radiation experiments. Supporting data on the changes in the concentrations of particle phase nicotine, and other nitrogen containing species and total particulate mass,[18] show that the decrease in

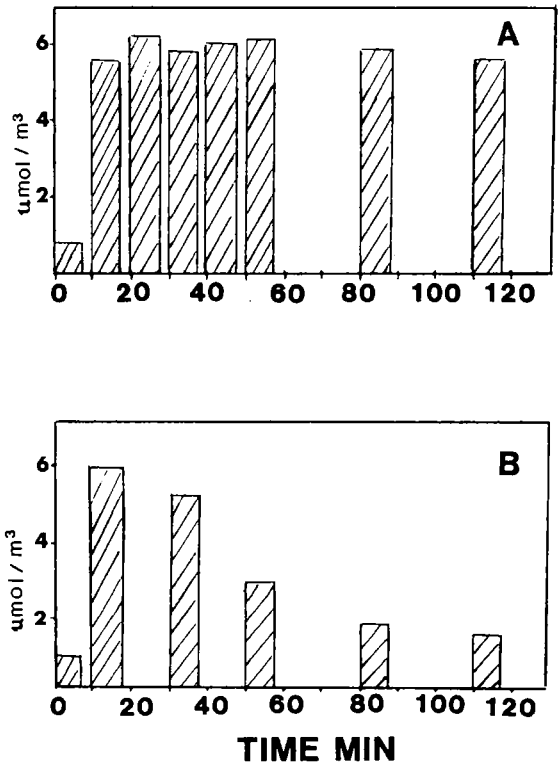

Figure 6 Bar graph of nicotine concentration versus time. Combustion of 4 cigarettes initiated at time 0. (A), UV-lights off, (B), UV-lights on during the entire experiment.

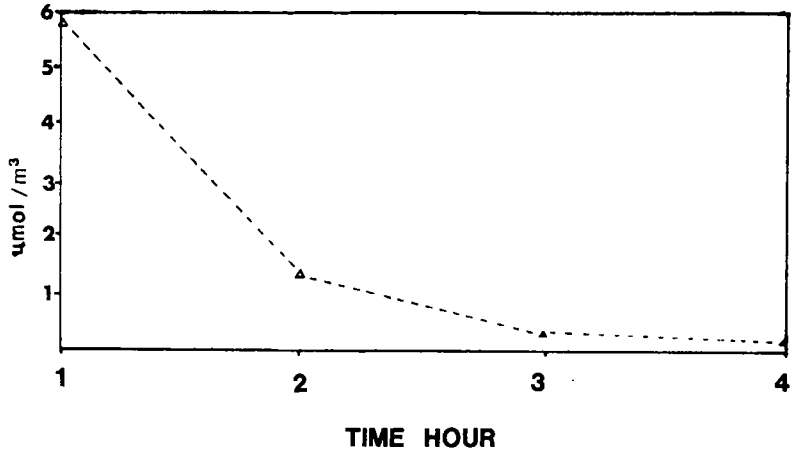

Figure 7 Plot of gas phase nicotine concentration versus time as determined by sampling with diffusion denuders. UV-lights were on during the entire experiment.

the concentration of gas phase nicotine following UV radiation is about 50% due to formation of new compounds from photochemical reactions of nicotine and about 50% due to the formation of particulate phase nicotine. The agreement between the results obtained with the Tenax sampling system in Figure 6(B) and the gas phase nicotine concentrations determined from denuder sampling, Figure 7, suggests that only gas phase nicotine is sampled by the Tenax trap.

The method described here for the sampling and analysis of gas phase nicotine in environmental tobacco smoke is straightforward. The method can be easily applied to routine indoor environmental monitoring. Indoor environmental tobacco smoke may be collected using several Tenax tubes. The tubes can be kept in a refrigerator and then analyzed by GC at a later time.

CONCLUSIONS

A method for the determination of gas phase nicotine in environmental tobacco smoke has been developed and validated. This method meets the needs for monitoring nicotine in tobacco smoke in a chamber, and can be easily applied to do routine environmental monitoring. The method has been used to demonstrate the stability

with time of nicotine in environmental tobacco smoke in a Teflon chamber. The data also show that gas phase nicotine is not stable in environmental tobacco smoke in the presence of UV radiation.

Acknowledgement

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