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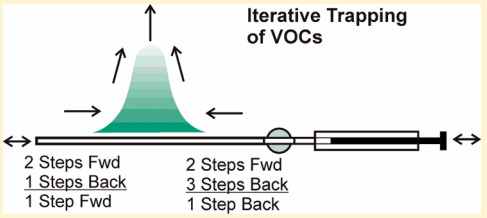
Iterative Trapping of Gaseous Volatile Organic Compounds in a Capillary Column

Abhijit Ghosh,[†] Stacy K. Seeley,[‡] and John V. Seeley*,[†]

[†]Department of Chemistry, Oakland University, Rochester, Michigan 48309, United States

[‡]Department of Chemistry & Biochemistry, Kettering University, Flint, Michigan 48504, United States

ABSTRACT: The iterative trapping method has been developed for concentrating gaseous volatile organic compounds (VOCs) prior to gas chromatographic analysis. VOCs are trapped in a 50 cm × 0.53 mm metal capillary column coated with a 7 μm thick film of polydimethylsiloxane (PDMS). Iterative trapping does not employ the two-step thermal desorption approach used by most VOC concentrating techniques. Instead, a four-step cycle involving synchronized changes in flow direction and temperature is repeated throughout the sampling process. This iterative process causes VOCs to accumulate within the capillary well past the level where a standard two-step method reaches its saturation limit. Iterative trapping is capable of sampling and desorbing C_5 through C_{11} *n*-alkanes with uniform efficiency. This new technique, in its current form, is most appropriate for focusing VOCs from gas volumes on the order of 10 mL. Iterative trapping increases the focusing power of a weak sorbent like PDMS and allows narrow chromatographic peaks to be generated without the use of high desorption temperatures or a secondary focusing stage.



Volatile organic compounds (VOCs) in gaseous samples are often concentrated prior to analysis with gas chromatography (GC). Most concentrating techniques employ a two-step, trap-and-desorb process commonly called thermal desorption. In conventional thermal desorption, the sample is first introduced to a sorbing material that retains VOCs but does not retain permanent gases (e.g., N_2, O_2, CO_2, etc.). The trapped VOCs are then desorbed by passing carrier gas over the trapping material while simultaneously applying heat. The increased temperature causes the VOCs to be released into a small volume of carrier that is then directed to the head of a GC column or sent to an additional focusing stage.

It is advantageous for the trapping/desorption efficiency of the concentrating technique to be similar for each VOC of interest. Uniform trapping is only obtained with conventional thermal desorption when each analyte is far from saturating the sorbent.[1] Uniform trapping is particularly challenging when the VOCs have a wide range of volatilities, because sorbents have much lower capacities for high volatility analytes.[2,3] Different measures can be taken to improve the likelihood of uniform trapping including minimizing the sampled volume, lowering the sampling temperature, increasing sorbent quantity, and switching to a higher capacity sorbent. All of these approaches have drawbacks: decreasing the sample volume decreases the sensitivity of the analysis because lower quantities of analytes are trapped. Decreasing the sampling temperature increases the sorbent capacity but refrigeration is required and an interference from water vapor condensation becomes more likely. Increasing the sorbent quantity increases capacity but also increases the volume of carrier gas required to desorb the analytes, and thus broadens the VOC pulse transferred to the GC. Finally, increasing sorbent strength increases capacity but also requires greater volumes of carrier gas and/or a higher desorption temperature. High temperatures increase the risk of chemical transformations of analytes and the sorbent material.[4] Furthermore, most strong binding sorbents are solids that rely upon the surface adsorption of VOCs. Such materials can exhibit competitive binding, leading to the displacement of volatile analytes during sampling.[5]

Thermal desorption sampling coupled with gas chromatography has now become a well-established method for characterizing gaseous mixtures.[6] Typically, a liter of gas is passed through a tube holding hundreds of milligrams of sorbent. At the end of the sampling period, the trapped VOCs are desorbed at a high temperature (around 300 °C) with a relatively high flow (~50 mL/min) of carrier gas to a refrigerated secondary trap for further focusing prior to injection into the GC column. The dual-stage desorption strategy often produces detection limits well below 1 ppbv.[6] Unfortunately, the cost of purchasing and operating a thermal desorption unit often equals or exceeds that of a gas chromatograph. In addition, many analyses require far less than 1 L of gas to be sampled.

Numerous alternative concentrating techniques have been introduced over the past 25 years. These techniques still employ a two-step, trap-and-desorb process, but much smaller quantities of sorbent are used and the size of the supporting material is minimized. This allows the VOCs to be released as a narrow pulse without requiring a secondary focusing stage. Solid phase microextraction (SPME) is the most widely adopted microscale strategy.[5,7,8] SPME is much simpler to

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implement than conventional thermal desorption, but the small quantity of sorbent reduces the gas volume that can be sampled before saturation occurs.[1] In many cases, VOCs with higher volatilities are trapped far less efficiently than those with lower volatilities. Several modifications to SPME have been introduced in the past 15 years and have been the subject of recent reviews.[8−12] These microscale techniques attempt to address one or more of the shortcomings of SPME while retaining the two-step, trap-and-desorb approach. The most common microscale techniques include Solid Phase Dynamic Extraction,[13] Needle Trap,[14,15] In-Tube SPME or In-Needle Capillary Adsorption Trap,[16] In-Tube Extraction,[17] and Single Drop Microextraction.[18,19]

This article describes the iterative trapping approach for concentrating VOCs. This technique traps VOCs in a 50 cm long segment of a GC capillary column internally coated with polydimethylsiloxane (PDMS). GC capillary columns have been used for concentrating VOCs in a process known as open tubular trapping (OTT) for the past 30 years.[9,20−23] OTT is normally implemented with a conventional two-step, trap-and-desorb approach. Unfortunately, GC columns with liquid stationary phases have limited capacity for volatile compounds. Previous studies have addressed this limitation by using longer column sections,[24] increasing the film thickness,[25,26] or operating several columns in parallel.[27] Iterative trapping attempts to increase trapping capacity without increasing the total quantity of sorbent or resorting to sorbents that strongly bind VOCs. Capacity is increased by replacing the two-step sampling approach with a cyclic process that employs synchronized changes in flow direction and temperature. Numerous iterations of this cyclic process are performed during the collection of a single gas sample.

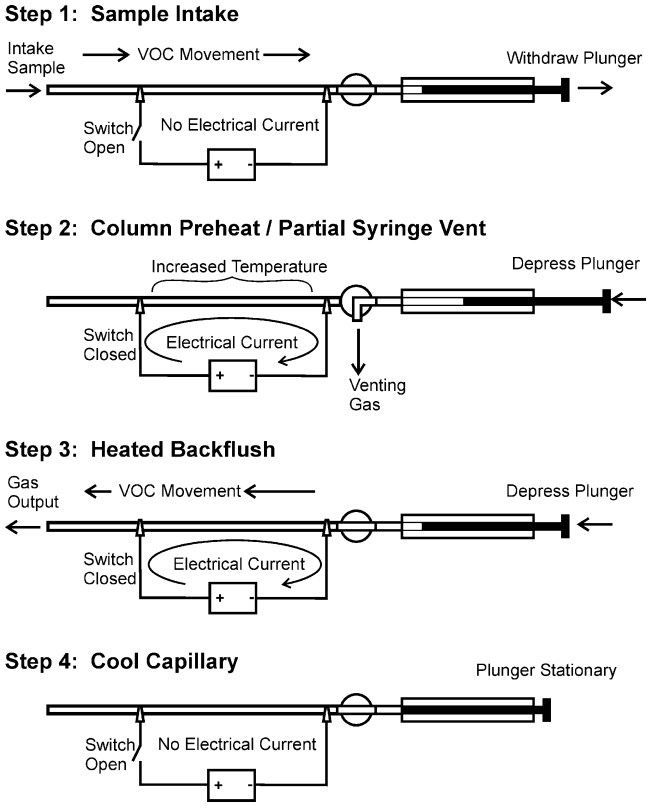

Figure 1. Iterative trapping cycle. Step 1: gas is drawn into the capillary. Step 2: half of the syringe volume is vented. Step 3: second half of syringe volume is backflushed through capillary while heating rear two-thirds. Step 4: pause while capillary returns to ambient temperature.

CONCEPTUAL DESCRIPTION OF ITERATIVE TRAPPING

We have implemented iterative trapping in a variety of configurations, but here we focus on the apparatus depicted schematically in Figure 1. The apparatus employs a metal capillary column that is internally coated with a liquid stationary phase. The capillary is connected to a three-port solenoid valve that is, in turn, connected to a syringe. The open end of the capillary is exposed to a gaseous sample containing VOCs. A DC power supply is used to periodically heat a section of the capillary column near the syringe.

Iterative trapping is generated by repeating a four-step sequence depicted in Figure 1. During the first step, the syringe plunger is withdrawn, causing gaseous sample to enter the capillary column. During the second step, the solenoid valve is actuated and the syringe plunger is depressed until half of the sampled volume is vented out of the system. Electric current is passed through the capillary segment near the syringe. During the third step, the solenoid valve is returned to its original state, electrical heating is maintained, and the syringe plunger is depressed until the remainder of the sampled volume is backflushed through the capillary. During the final step, the plunger is held stationary and the electric current is discontinued. This state is maintained until the capillary returns to ambient temperature. The device then starts a new sampling iteration by proceeding to the first step. The four-step sequence is repeated until the desired amount of gas has been sampled.

The goal of iterative trapping is to create net movement of VOCs away from the ends of the capillary and toward the center. The volume of gas drawn through the capillary during Step 1 is twice as large as the volume of gas expelled through the capillary in Step 3. Thus, in the isothermal side (i.e., the sample side), a VOC molecule will have a net displacement from the entrance of the capillary toward the center in a "two steps forward, one step back" fashion. We are attempting to generate net movement in the reverse direction in the variable temperature side of the capillary (i.e., movement from the syringe end of the capillary toward the center). This is accomplished, at least in principle, by synchronizing the temperature elevation with the backward movement of gas in the capillary. Increased temperature reduces the partitioning of the VOC molecules into the stationary phase and thus increases their mobility. If VOC mobility is increased sufficiently a net "backward" migration away from the syringe end and toward the center of the capillary will occur despite the lower volume of backflushed gas. This will prevent VOC breakthrough. The combination of the net forward movement of VOCs in the isothermal region and net backward movement in the variable temperature region should cause the VOC molecules to accumulate in the interior of the capillary.

This article describes our initial efforts to demonstrate iterative trapping. The efficacy of our device for sampling a mixture containing C_4 through C_{11} *n*-alkanes has been determined and compared to that obtained with SPME and OTT.

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EXPERIMENTAL DETAILS

GC analyses were performed with an Agilent 6890N gas chromatograph equipped with a split/splitless inlet and a flame ionization detector (FID). The inlet was fitted with a 0.75 mm id liner (Supelco, 2637501) held at 250 °C. A 2.0 mL min^{-1} flow of ultra high purity (UHP) hydrogen exited the inlet and was directed through a 40 cm × 0.25 mm deactivated fused silica transfer line to the iterative trapping device. A second transfer line with identical dimensions served as the return line from the trapping device back to the gas chromatograph. This transfer line was connected to an SPB-Octyl GC column (Supelco, 30 m × 0.25 mm × 0.25 μm) housed inside the main oven of the gas chromatograph. The column outlet was connected to the FID (260 °C). The following oven temperature program was employed: 40 °C for 2.0 min; ramp to 230 °C at 16 °C min^{-1}; hold for 2.0 min.

A schematic of the iterative trapping device is shown in Figure 2. The apparatus follows the basic setup of the conceptual device shown in Figure 1, with the exception that a rotary valve was added to allow the trapped VOCs to be automatically transferred to the GC after completing a prescribed number of collection iterations. The iterative trapping device was placed on top of the gas chromatograph. The trapping capillary was not shielded from the room environment, but care was taken to ensure that the capillary was not directly in the convective output of any fans. A 6-port, two-position rotary valve with electric actuator (Valco, E60) served as the center point of construction. The side ports of the valve were connected to two 3 cm × 0.53 mm pieces of deactivated fused silica that were both connected via low mass unions (Valco, EU.5L) to a metal capillary column (Restek, MXT-1 50 cm × 0.53 mm × 7 μm) internally coated with polydimethylsiloxane (PDMS). The two upper ports of the valve were connected to a Teflon sampling line and a stainless steel line leading to the solenoid valve/syringe assembly. The 6-port valve temperature was maintained at 100 °C with a cartridge heater. The solenoid valve/syringe assembly was constructed from a 3-port solenoid valve (Parker-General Valve, Part No. 009-0284-900) and a 250 μL gastight syringe (Hamilton, #1725). The syringe plunger was attached to a small stepper motor/leadscrew assembly (Portescap 35DBM10B2U-L) that served as a linear actuator. The MXT-1 capillary was heated by passing direct electric current through specific portions of the capillary. An adjustable DC power supply (BK Precision 9110) was connected to the capillary through an assembly of wires, miniature alligator clips, and relays. The positive terminal of the power supply was directly connected to the syringe-end of the capillary (shown in Figure 2 at the 5 o'clock position on the capillary). The ground terminal of the power supply was connected at a point that was a distance two-thirds of the capillary length from the syringe end (shown in Figure 2 at the 10 o'clock position). This electrical connection was routed through a relay. Heating the back two-thirds of the capillary was achieved by activating this relay and thereby completing the circuit and causing current to pass through the rear two-thirds of the capillary. The ground terminal of the power supply was also connected through a second relay to the capillary at the sample-end (shown in Figure 2 at the 7 o'clock position). Activating this relay caused current to pass through the full length of the capillary thereby heating the entire capillary.

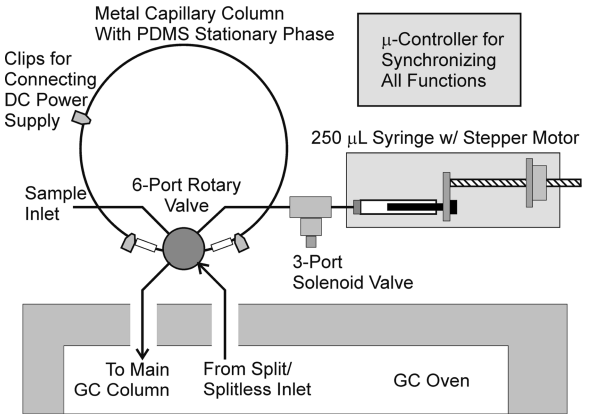

Figure 2. Schematic of the iterative trapping apparatus used for the experimental studies.

Sample collection with iterative trapping was done using a 4-step sequence similar to that shown in Figure 1. During Step 1, the syringe plunger was withdrawn to generate an incoming flow rate of 1.0 mL/min and halted after an intake of 250 μL. The device then transitioned to Step 2 where the solenoid was actuated and the plunger was depressed to vent 125 μL of gas. An electric current of 1.8 A was simultaneously passed through the 33 cm long portion of the capillary nearest to the syringe. In Step 3, the solenoid valve was actuated to reconnect the syringe and the capillary. Heating was maintained until the syringe plunger had returned to its original position, backflushing 125 μL of gas through the capillary. In Step 4, the current was shut off and the capillary was allowed to cool for 8.0 s. The total time for a complete iteration was 38 s. After a predetermined number of iterations, the VOCs were transferred to the GC by actuating the 6-port valve and heating the entire 50 cm length of the sampling capillary with 1.8 A of electric current. Valve actuation, plunger movement, the application of electric current, and communication with the GC were all controlled with an Arduino Uno (www.arduino.cc) microcontroller programmed with software written in-house.

The efficacy of iterative trapping was tested by sampling a commercially prepared mixture containing 1.0 ppmv of C_4 through C_{11} *n*-alkanes in nitrogen. For the purposes of comparison, several preliminary runs were performed by directly injecting the *n*-alkane mixture into the GC without preconcentration. This was done with an additional 6-port valve fitted with a 125 μL loop held at 225 °C. The loop contents were flushed with a 20 mL/min carrier stream and directed into the split/splitless inlet (10:1 split ratio). Several runs were also performed with SPME sampling. The SPME fiber (Supelco, Part Num 57300-U) had a 10 mm × 100 μm fused silica core and was coated with a 100 μm thick film of PDMS. This fiber was exposed to a flow of the *n*-alkane mixture. At the end of the sampling period the SPME fiber was injected through the split/splitless inlet operated in splitless mode.

Studies were performed to determine the relationship between the electric current and the capillary temperature. A 3.0 m section of the MXT-1 capillary was placed in a gas chromatograph with air as the carrier gas. The retention factor of *n*-hexane was determined first with oven temperatures ranging from 40 to 120 °C. The oven door was then opened, the oven fan was turned off, and the retention factor of *n*-hexane was determined again, but this time with heating supplied by DC currents ranging from 0.0 to 1.90 A. Similar peak shapes and widths were observed with oven heating and

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Table 1. *n*-Alkane Peak Areas Obtained With a Variety of Sampling Techniques

conventional	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
direct	0.447	0.541	0.64	0.932	0.909	1.04	1.18	1.25
OTT	4.38	16.3	54.3	202	518	1520	4420	12 400
SPME	[a]nd	[a]nd	4.39	19	51.9	161	474	1330
iter. trapping without heat	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
20 cycs	5.65	19.4	57.3	155	150	168	186	200
40 cycs	5.62	20.0	57.4	219	299	332	363	383
80 cycs	5.67	19.3	57.9	215	538	667	733	776
160 cycs	5.64	19.3	55.8	212	541	1340	1470	1560
iter. trapping with heat	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
20 cycs	6.09	93.1	108	151	146	163	180	191
40 cycs	5.75	184	216	305	295	329	360	376
80 cycs	5.79	363	434	614	594	663	727	758
160 cycs	5.87	714	873	1230	1190	1330	1470	1540

[a]nd = not detected.

electric heating. A mathematical function was used to map electric current to capillary temperature via the hexane retention factors. This study determined that 1.80 A produced a steady state temperature of 110 °C. The experiment was repeated with a 48 cm long section of MXT-1 capillary and an identical relationship between the *n*-hexane retention factor and the capillary current was observed indicating that any temperature decreases near the ends of the heated region have an insignificant effect on the net retention of *n*-hexane.

RESULTS AND DISCUSSION

Direct Injection of the *n*-Alkane Mixture. Our test sample was a commercial gas mixture containing eight *n*-alkanes ranging in size from butane to undecane with each nominally present at a concentration of 1.0 ppmv. We first characterized the *n*-alkane mixture by performing direct injections of the gas into the GC. The peak areas are shown in Table 1.

In the absence of sampling artifacts, the peak areas obtained with direct sampling, A_D, are proportional to the product of the FID response factor, R, and the concentration of each alkane in the gas mixture, $[C]$:

$$A_D \propto R[C] \tag{1}$$

Previous studies have shown that FID response factors for *n*-alkanes are proportional to n, the number of carbon atoms.[28] Thus, if each alkane is present at exactly 1 ppmv, then the observed peak areas should be proportional to n. The peak areas of the direct injection analyses generally increased with n, but there were deviations from linearity. For example, the heptane peak area was slightly greater than that of octane. Thus, the heptane concentration is estimated to be approximately 10% greater than the octane concentration. A 10% variation is within the manufacturer's specified precision for the individual *n*-alkane concentrations.

Saturative Sampling With OTT and SPME. We then sampled the *n*-alkane mixture with OTT and SPME to determine the maximum enrichment that could be generated by a conventional two-step approach with PDMS as a sorbent. In the case of OTT, component breakthrough occurs when the front edge of the concentrated zone reaches the downstream end of the trapping capillary. After full breakthrough, the quantity of a trapped VOC no longer increases because the amount entering the capillary is balanced by the amount leaving the capillary.

We altered the iterative trapping apparatus to allow the MXT-1 capillary to be used in OTT mode. The line joining the 6-port valve to the solenoid valve (see Figure 2) was disconnected (i.e., the syringe pump was not used) and the *n*-alkane mixture was passed through the capillary at a flow of 9.1 mL/min. At the end of a specified period of time, the 6-port valve was actuated and the entire length of the MXT-1 capillary was heated using a current of 1.8 A. Three analyses were performed with sampling times of 20, 30, and 40 min. The *n*-alkane peak areas agreed to within 5% indicating that each *n*-alkane had exceeded its breakthrough volume and the concentration within the capillary had reached a steady state. The areas observed for the saturated OTT approach with a 40 min sampling time are listed in Table 1. The peak areas increased exponentially with increasing *n*-alkane size n. In principle, the quantity of a compound trapped in saturated PDMS is given by the partition coefficient K multiplied by the PDMS volume V_P multiplied by the gas phase concentration $[C]$.[29] Thus, the peak areas produced from the desorption of saturated PDMS, A_S, should obey the following equation:

$$A_S = RKV_P[C] \tag{2}$$

The peak areas obtained from direct sampling, A_D, are proportional to $R[C]$ (see eq 1). Thus, eqs 1 and 2 can be combined to yield the following proportionality

$$A_S \propto KV_PA_D \tag{3}$$

which can be rearranged to generate the following relation

$$\ln\left(\frac{A_S}{A_D}\right) = \ln(K) + \ln(V_P) + b \tag{4}$$

where b is a proportionality constant. Millen and Hawkes[2] determined K over a wide range of temperatures. At 25 °C, the partition coefficient is represented by

$$K(25\ ^\circ\mathrm{C}) = 0.822\exp(0.94n) \tag{5}$$

where n is the carbon number of the *n*-alkane. This expression can be substituted into eq 4 to generate

$$\ln\left(\frac{A_S}{A_D}\right) = 0.94n + \ln V_P + b + \ln(0.822) \tag{6}$$

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Thus, eq 6 predicts that plots of $\ln(A_S/A_D)$ as a function of n should be linear with a slope near 0.94. Figure 3 shows such a plot for the saturated OTT data. The points were found to fall on a line with a slope of 0.96. This slope is very close to the value of 0.94 predicted from eq 6.

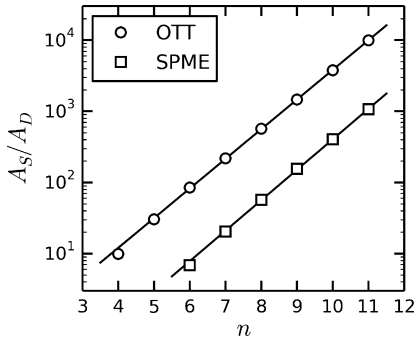

Figure 3. Peak areas observed when the *n*-alkane mix was sampled with a GC capillary column in open tubular trapping (OTT) mode and with SPME. The peak areas have been divided by areas observed from direct injection and are plotted as a function of carbon number *n*.

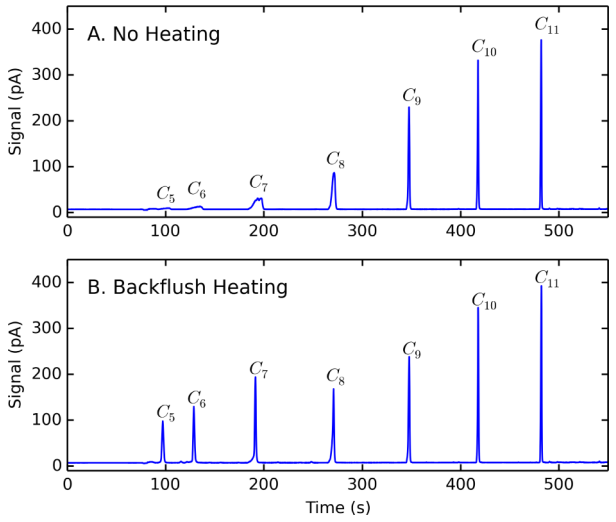

Figure 4. Chromatograms of the *n*-alkane mixture obtained with iterative trapping after 40 cycles when (A) no electrical heating was applied to the capillary during Steps 2 and 3 of the trapping cycle and (B) when electrical heating was applied during Steps 2 and 3.

A SPME fiber coated with PDMS was also used to sample the *n*-alkane gas mixture. The goal was to determine the maximum peak areas that could be produced using SPME with a PDMS fiber. The SPME fiber was placed inline with a 9.1 mL/min flow of the *n*-alkane mixture and exposed for 30, 60, and 90 min. At the end of each sampling period, the SPME fiber was analyzed with the GC-FID system. The peaks showed minimal area increases (<5%) as the sampling time was increased beyond 30 min, and thus we concluded that the PDMS fiber was saturated with each *n*-alkane after 30 min. The peak areas observed for the 90 min sampling period are shown in Table 1. The peaks associated with butane and pentane were too small to be reliably quantified.

The areas of the SPME peaks were analyzed in the same manner as the saturated OTT data (see Figure 3). The slope of the best fit line was 0.99, in good agreement with the predicted value of 0.94. The peak areas produced by OTT with the saturated MXT-1 capillary were approximately a factor of 10 greater than those obtained with SPME. The larger peak intensities produced by OTT is explained by the differences in PDMS volume associated with the two sampling devices. Using the dimensions stated by the manufacturers, the OTT MXT-1 capillary has a calculated V_P of 5.8 μL while the SPME fiber has a V_P of 0.66 μL. The calculated PDMS volume ratio of 8.8 (OTT to SPME) is in good agreement with the experimental area ratio of 10.

Iterative Trapping Studies. The heated backflush step of the iterative trapping cycle is critical for preventing the breakthrough of VOCs. To demonstrate the importance of this step, we first operated the iterative trapping device without applying electric current during the backflush step. Without heating, the *n*-alkanes should move down the whole length of the capillary in a "two steps forward, one step back fashion", ultimately exiting on the syringe side of the capillary. At that point the capillary will be saturated. We performed analyses with 20, 40, 80, and 160 sampling iterations (i.e., completed cycles). The chromatogram observed for 40 sampling iterations is shown in Figure 4A. The early eluting alkanes such as pentane and hexane produced broad peaks (10 s wide at half-maximum) with low intensities, whereas the late eluting peaks such as decane and undecane were much sharper (1 s wide at half-maximum) and had higher intensities.

The peak areas for the alkanes are listed in Table 1 and plotted in Figure 5A as a function of total sampling iterations. The butane, pentane, and hexane peaks did not display an area increase when increasing from 20 sampling iterations to 40, thus they had broken through the capillary in 20 or less iterations. The heptane peak area leveled off at some point between 20 and 40 iterations, and the octane peak reached a steady state between 40 and 80 iterations. The area plateaus were very close to the areas observed with saturated OTT. The nonane, decane, and undecane peaks had areas that grew linearly for at least 160 iterations. This effect is due to greater retention of these compounds on PDMS, which prevents them from reaching the syringe end of the capillary in 160 iterations.

We then operated the iterative trapping device in the proper manner (i.e., electrical current was used to heat the capillary during the backflush state). Analyses were performed for 20, 40, 80, and 160 sampling iterations. The chromatogram observed for 40 iterations is shown in Figure 4B. The early eluting peaks were much sharper that those produced without backflush heating (1.7 s wide at half-maximum versus 10 s wide) while the late eluting peaks were identical. The heptane and octane peaks both displayed some "fronting", but they were still less than 2 s wide at half-maximum. The peak areas observed for each run are listed in Table 1 and plotted as a function of iteration number in Figure 5B. The butane peak areas did not increase with increasing iteration number, indicating that butane was too volatile to be trapped. In contrast, pentane through undecane all had areas that increased in direct proportion to the iteration number.

If the C_5 through C_{11} alkanes were all sampled with the same efficiency, then the iterative trapping areas A_I should be given by the product of the response factor, half of the intake volume V_I, the gas phase concentration of each alkane, and the number of completed iterations, cycs:

$$A_I = R\frac{V_I}{2}[C](\text{cycs}) \quad (7)$$

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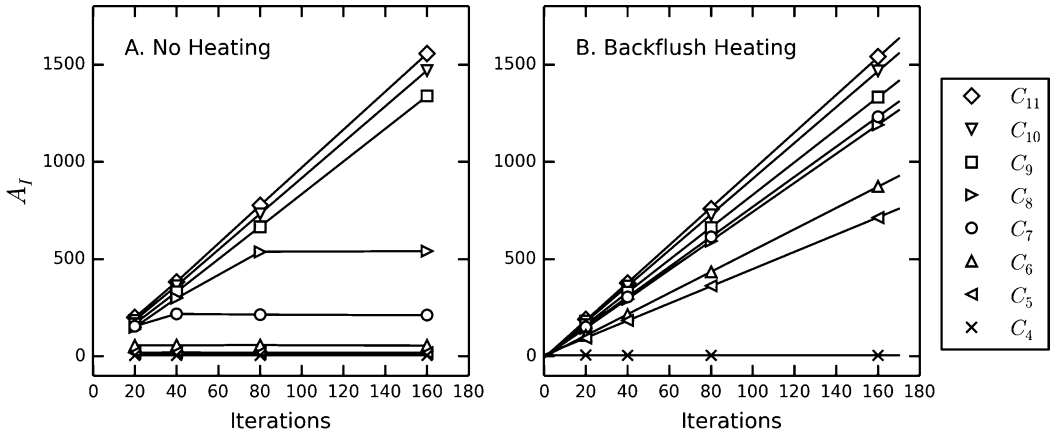

Figure 5. Peak areas obtained with iterative trapping of the *n*-alkane mixture as a function of completed iterations (cycs). (A) Areas obtained without backflush heating. (B) Areas obtained with backflush heating.

The intake volume, V_I, is divided by 2 because half of V_I is expelled during the output stroke. The value of V_I is constant for each compound and the value of $R[C]$ is proportional to the directly sampled areas, A_D (see eq 1); thus, eq 7 can be converted to the following proportionality:

$$A_I \propto A_D(\text{cycs}) \tag{8}$$

This equation can be rearranged to show that the iterative trapping to directly sampled area ratio should be proportional to cycs and all of the *n*-alkanes should essentially fall on the same line:

$$\frac{A_I}{A_D} \propto \text{cycs} \tag{9}$$

The ratio of A_I/A_D calculated from the experimental data is plotted in Figure 6 as a function of iteration number. This plot

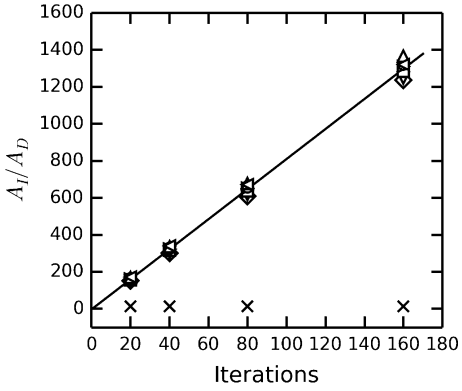

Figure 6. *n*-Alkane peak areas obtained using iterative trapping divided by the direct injection peak areas and plotted as a function of completed iterations. The individual *n*-alkane symbols follow the legend in Figure 5

shows that alkanes with $n \geq 5$ followed the same trend indicating that *n*-alkanes larger than butane are trapped and desorbed with uniform efficiency. The butane peak did not follow the trend due to the inability of the iterative technique to trap butane.

The precision of iterative trapping was characterized by performing eight replicate analyses of the *n*-alkane mixture, 40 iterations each. The relative standard deviations (RSDs) of pentane through undecane peak areas ranged from 0.4 to 1.8% with a mean of 0.9%. These values are similar to those observed for the syringe injection of liquids.[30] Thus, it is concluded that iterative trapping maintains the high precision associated with modern automated GC analyses.

Our iterative trapping studies used 1.8 A to heat the capillary. An additional series of runs was performed with the backflush heating current varied between 1.2 and 2.0 A. Identical chromatograms were observed when the backflush heating currents were ≥1.5 A. However, the pentane peak area was found to decrease significantly at currents below 1.5 A, whereas the remainder of the *n*-alkane peaks were unchanged for currents as low as 1.2 A (i.e., the lowest current studied). We previously found that 1.5 and 1.8 A produced steady state capillary temperatures of 85 and 110 °C, respectively.

Testing for Alkane Leakage. The iterative trapping device expels half of the intake volume during the output stroke. Thus, half of the VOCs that enter the capillary during the intake stroke leave during the following output stroke. However, the VOCs that remain in the capillary after their first complete iteration should remain in the capillary for all subsequent iterations. This is because the VOCs should be drawn further into the capillary with each subsequent iteration in a "two steps forward, one step back" fashion until they reach the boundary between the isothermal and variable-temperature regions of the capillary (i.e., one-third of the capillary length). After reaching that point, they should oscillate across the boundary between these two regions.

This description of VOC movement is speculative, but it is possible to verify that VOCs successfully trapped in an initial iteration remain trapped for subsequent iterations. To this end, we performed the following study: First, the *n*-alkane mixture was sampled for 20 iterations and then analyzed with GC. The resulting chromatogram is shown in Figure 7A. Next, the *n*-alkane mixture was sampled for 20 iterations and then zero air was sampled for 40 additional iterations. The resulting chromatogram is shown in Figure 7B. The areas are listed at the apex of each peak. The peak areas did not decrease when 40 iterations of zero air were added. Based on the consistency of the areas in the two runs, we conclude that an insignificant amount of pentane through undecane escaped during the 40 zero air iterations. This observation supports the notion that compounds successfully trapped in their first iteration remain trapped for all subsequent iterations. It is also interesting to note that peak shape is improved after sampling 40 iterations of zero air. This is especially true for the heptane and octane peaks

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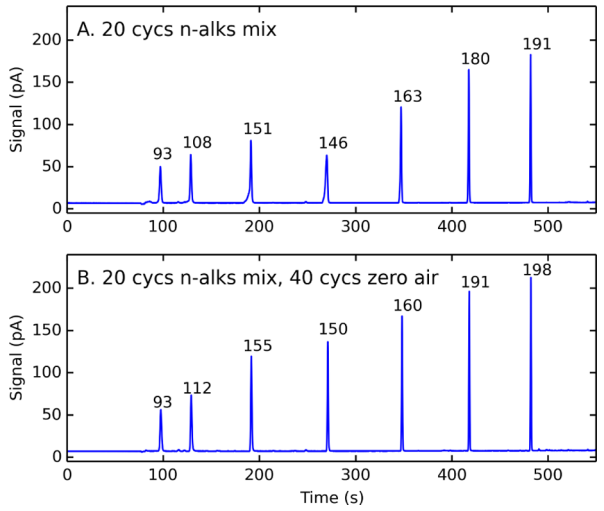

Figure 7. Chromatograms obtained with iterative trapping when (A) the *n*-alkane mixture was sampled for 20 iterations and (B) the *n*-alkane mixture was sampled for 20 iterations followed by sampling zero air for 40 iterations.

(i.e., the peaks at 190 and 270 s). The additional iterations with zero air caused the heptane and octane peaks to lose their "fronted" shape and become more symmetrical.

Comparison to Conventional Sampling. Although iterative trapping involves a relatively simple set of mechanical and electrical components, it is still easier to use OTT or SPME. It is therefore important to compare the concentrating powers of iterative trapping with these conventional strategies. Figure 8 shows the iterative trapping areas divided by the OTT

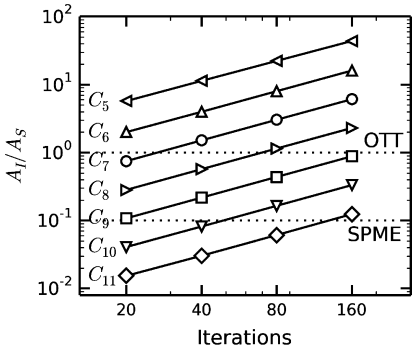

Figure 8. Peak areas obtained with iterative trapping of the *n*-alkane mixture relative to the peak areas obtained with saturated open tubular trapping.

areas (A_I/A_S) plotted as a function of the iteration number. The upper dotted line drawn in Figure 8 depicts an A_I/A_S ratio of 1. This ratio represents the point at which iterative trapping generates the same peak area as saturated OTT sampling. Pentane and hexane are already above the A_I/A_S = 1 line after 20 sampling iterations. This is due to the low partition coefficient for smaller alkanes into PDMS. Thus, volatile compounds like pentane quickly saturate the capillary when OTT is performed, but iterative trapping allows such compounds to continue to accumulate in the capillary. Heptane and octane exceed A_I/A_S = 1 after 40 iterations and 80 iterations, respectively. In contrast, the iterative trapping areas of nonane, decane, and undecane are still below the A_I/A_S = 1 line after 160 iterations. This analysis demonstrates that iterative trapping allows high volatility compounds to be enriched to greater levels than can be produced by conventional sampling. However, iterative trapping does not provide improved enrichment for components that have lower volatilities (like decane and undecane) unless a very large number of iterations are performed.

It is important to determine if our theoretical understanding of the iterative trapping process matches the experimental results. Equation 7 and eq 2 can be combined to generate the following expression that estimates the number of iterations required to reach a specified A_I/A_S ratio:

$$(\text{cycs}) = \frac{2KV_P}{V_I}\left(\frac{A_I}{A_s}\right) \tag{9}$$

The number of iterations required to reach A_I/A_S = 1 can be predicted by inserting the values of V_P and V_I calculated for the experimental configuration (V_P = 5.8 μL, V_I = 250 μL), setting A_I/A_S = 1, and using the expression for K shown in eq 5. The resulting equation is given by

$$(\text{cycs})_{I=S} = 0.038\exp(0.94n) \tag{10}$$

Equation 10 was used to theoretically predict the number of iterations required to reach A_I/A_S = 1. The following values were obtained: pentane = 4.2 cycs; hexane = 11 cycs; heptane = 27 cycs; octane = 70 cycs; nonane = 180 cycs; decane = 460 cycs; undecane = 1180 cycs. Least squares fits of the experimental data in Figure 8 were interpolated/extrapolated to a value A_I/A_S = 1 yielding the following experimental estimates: pentane = 2.2 cycs; hexane = 10 cycs; heptane = 27 cycs; octane = 70 cycs; nonane = 182 cycs; decane = 480 cycs; undecane = 1290 cycs. In general, there is excellent agreement between the theoretical prediction and the experimental results.

As was described previously, the SPME peak areas were approximately a factor of 10 lower than the OTT peak areas. Therefore, the iterative trapping areas are essentially equal to the SPME areas when the A_I/A_S ratios in Figure 8 equal 0.1. This condition is represented by the lower dotted line in Figure 8. The plotted data show that the iterative trapping areas for the C_5 through C_9 *n*-alkanes are all greater than the SPME areas when 20 sampling iterations have been completed. Thus, the combination of the enhanced enrichment of iterative trapping and the small PDMS volume of SPME allows iterative trapping to accumulate far greater amounts of volatile *n*-alkanes than SPME-PDMS. However, we have not compared the iterative trapping technique to SPME fibers impregnated with higher capacity solids such as Carboxen.[31]

CONCLUSIONS

Iterative trapping can trap and desorb C_5 through C_{11} *n*-alkanes with uniform efficiency. This new technique allows a weak sorbent like PDMS to accumulate volatile compounds well past the saturation limit imposed on conventional OTT and SPME methods employing PDMS as a sorbent. Furthermore, the cyclic sampling process produces sharp peaks that can be directly injected into a GC column without requiring a secondary trapping stage. Quantitative studies can be performed by adjusting the number of sampling iterations to achieve adequate sensitivity and then analyzing both gaseous samples and calibration mixtures with the selected settings. Despite the dynamic nature of the concentrating mechanism, replicate analyses have shown that iterative trapping maintains high quantitative precision (i.e., RSDs < 1%). Iterative trapping

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is effective for sampling total gas volumes on the order of 10 mL. Conventional thermal desorption with multilayer sorbent tubes and a secondary focusing stage can sample gas volumes 2 orders of magnitude greater than those practical for iterative trapping. However, many applications do not require sampling liter quantities of gas. Thus, the uniform trapping and low desorption temperatures associated with iterative trapping make it an attractive option. Future publications will describe our successful application of iterative trapping to the GC analysis of siloxanes in biogas and the headspace analysis of alcoholic beverages.

AUTHOR INFORMATION

Corresponding Author

*J. V. Seeley. Phone: (248) 370-2329. Fax: (248) 370-2321. E-mail: seeley@oakland.edu.

Notes

The authors declare no competing financial interest.

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