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Analysis of Wet Samples by Direct Thermal Desorption GC

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Thermal Desorption, Tenax TA™, Sample drying, Herbs, Peppers

ABSTRACT
The analysis of volatiles in solids is a common analytical problem. Examples include volatile aroma compounds in foods (coffee, tea, herbs), residual fragrances from soaps and fabric softeners on textiles, and volatiles in polymer resins, films and plastic products. When high sensitivity analysis is needed, many of these sample types can be analyzed by direct thermal desorption with cryotrapping before the GC column.

A wide variety of sample types can contain significant levels of water. This poses significant challenges when doing direct thermal desorption and cryotrapping for analysis of volatiles, since water can accumulate and freeze in an inlet or at the head of a column. Introduction of significant levels of water into the GC column can degrade chromatographic performance and shorten column lifetime.

There are several strategies that are useful to reduce the introduction of water into a GC when doing thermal desorption. These range from offline thermal extraction with trapping of volatiles on adsorbent beds to incorporating

drying steps into the thermal desorption process itself. Estimating the amount of water that can be eliminated with each of these approaches is a challenge.

Volatiles in solid samples containing up to 90% water were analyzed by direct thermal desorption incorporating different drying strategies. Offline thermal extraction utilizing Tenax TA™ adsorbent was the most effective approach for eliminating large amounts of water while effectively retaining low boiling analytes. Small amounts of water (tens of milligrams) can be eliminated from samples by using Tenax TA™ packed inlet liners cooled to 20-40°C. General guidelines for choosing appropriate steps for eliminating different levels of water are summarized.

Introduction

Direct analysis of wet samples has often been limited to Static Headspace GC or SPME, both of which tolerate water reasonably well. Both of these approaches are usually much less sensitive than thermal desorption, however, sometimes by factors of 100 or more.

There are strategies available to trap volatile components while eliminating water, the most common of which uses Tenax TA™ adsorbent. Tenax TA™, an adsorbent based on 2,6-diphenylene oxide polymer has long been used for air sampling in humid environments and purge & trap applications since it has a very low affinity for water. Tenax adsorbent can also be used to facilitate Thermal Desorption of wet samples.

Offline Sampling. One approach to managing water in wet samples is offline thermal extraction of a sample, trapping the volatiles on adsorbent tubes packed with Tenax TA™. Under appropriate conditions, enough water can be eliminated from the adsorbent tube to allow Thermal Desorption of the trapped volatiles with cryofocusing in a cold inlet. There is a need to define drying conditions that eliminate water interference in the subsequent GC analysis.

Online Sampling. A second and more easily automated approach is to attempt to dry the sample at low temperature prior to thermal extraction of the analytes of interest. This is possible for semivolatile analytes that will not be lost during the drying step. It is necessary to define starting conditions that provide adequate sample drying, and determine which volatiles can be lost during the drying step. A third automated strategy uses Tenax TA™ adsorbent in the GC inlet liner to trap volatiles from wet samples while allowing water vapor to pass out the split vent.

This paper will define the conditions necessary to eliminate water from wet samples using the above three strategies. Examples illustrating the high sensitivity analysis of volatiles in wet samples by Thermal Desorption are shown.

Experimental

Instrumentation. All analyses were performed on a GC (6890, Agilent Technologies) with Flame Ionization Detection. The GC was equipped with a Thermal Desorption unit with autosampling capacity (TDS 2 & TDS A, Gerstel) and a PTV inlet (CIS 4, Gerstel). Offline extraction of wet samples onto Tenax TA™ adsorbent tubes was done using a heated Thermal Extractor unit (TE, Gerstel).

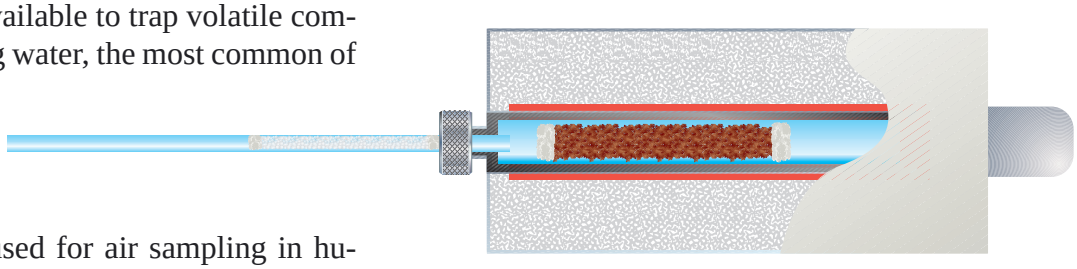

Figure 1. Gerstel TE offline thermal extractor.

Sample Preparation. Fresh Peppers and Herbs. For offline extraction of volatiles, fresh samples (100-500 mg) were weighed into large (14 mm ID x 178 mm) glass extraction tubes. Samples were then extracted under 50 mL/min helium flow in a Thermal Extractor unit (Figure 1), trapping volatiles at ambient temperature on 4 mm ID x 178 mm Tenax TA™ adsorbent tubes. Adsorbent tubes were then thermally desorbed in the TDS A unit, cold trapping the volatiles in the inlet. For online extraction of volatiles, fresh samples (25-50 mg) were weighed directly into glass Thermal Desorption tubes. Samples were extracted under 45 mL/min helium flow, trapping volatiles in the CIS 4 inlet on Tenax TA™ packed liners.

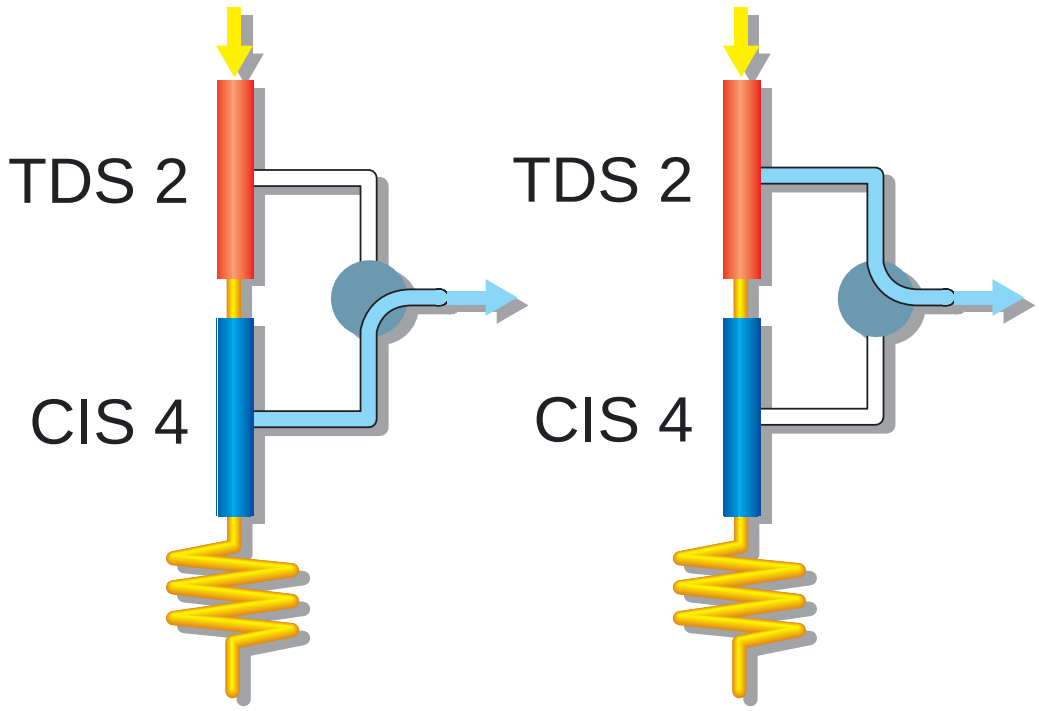

Figure 2. Pneumatics diagram for Gerstel TDS 2/CIS 4 in splitless (left) and solvent venting desorption modes.

Analysis conditions.

Column	30 m HP 5 (Agilent), d_i = 0.25 mm, d_f = 0.25 µm
Pneumatics	He, P_i = 91.7 kPa, constant flow = 1.2 ml/min
Oven	40°C (2 min), 10°C/min, 280°C (4 min)

Analysis conditions offline thermal extraction.

TE 1	50 ml/min (15-30 min), 40° or 60°C
TDS 2	solvent venting / splitless 20°C, 60°C/min, 60°C (20 min), 60°C/min 280°C (3 min)
PTV	0.1 min solvent venting (45-60 ml/min), split see figures -70°C, 12°C/s, 290°C (5 min)

Analysis conditions online thermal extraction.

TDS 2	splitless -20°C, 60°C/min, 60°C (10-30 min)
PTV	1 min solvent venting (45 ml/min), split ratio 1:10 5-60°C, 12°C/s, 275°C (3 min)

Results and Discussion

Model Drying Studies. Dried cotton terrycloth towel samples (50 mg) were placed into glass Thermal Desorption tubes (4 mm ID x 178 mm) and spiked with 10 mg or 25 mg water. Wet samples were then dried under helium flow at 30°C in the TDSA to simulate drying a sample prior to thermal extraction. Table I summarizes the percent water removed under different time and flow conditions.

Drying Time (min)	10 mg water 50 (ml/min)	25 mg water 50 / 100 (ml/min)
5	68%	33% / 60%
10	98%	45% / 97%
20	108%	78% / N.D.
40	105%	100% / N.D.

Table I. Percent water removed from terrycloth towel @30°C.

The same terrycloth towel samples were spiked with 25 mg water + 10 µl of a low boiling C_5-C_{18} hydrocarbon mix in methanol (5080-8768, Agilent). Wet samples were then dried at 30°C under 40 mL/min helium flow in the TDSA solvent venting mode (Figure 2) prior to desorption at 150°C for 10 minutes. Hydrocarbons were trapped onto a Tenax TA™ packed inlet liner at 5°C.

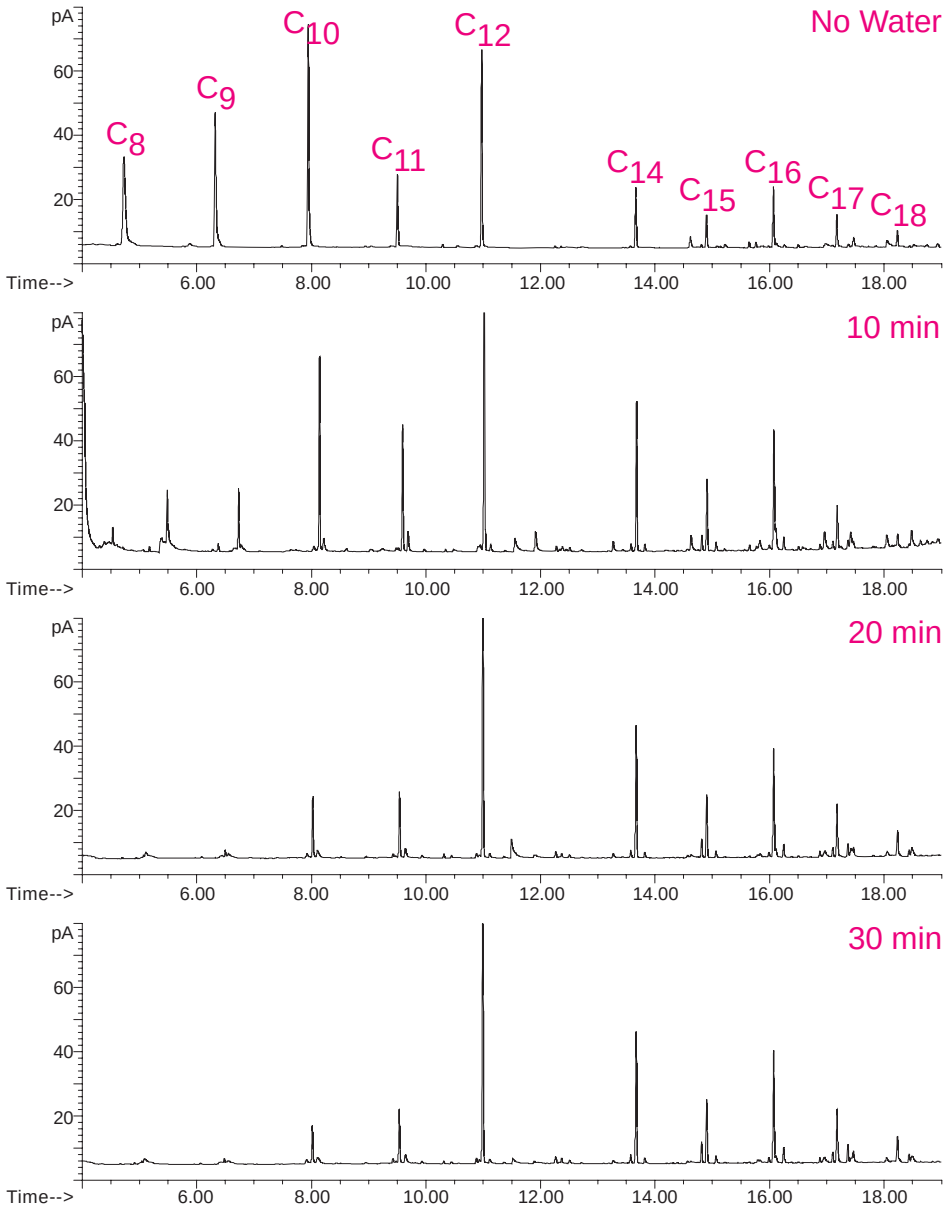

Figure 3. Loss of hydrocarbon mix spiked onto towel at different drying times. Boiling points in parentheses. C_8 (126°C); C_9 (151°C); C_{10} (174°C); C_{11} (196°C); C_{12} (216°C).

Figure 3 shows that drying for 10 minutes results in some loss of C_8-C_{10} hydrocarbons compared to the upper trace with no water present. At 10 minutes drying there is also evidence of the presence of water, which affects the chromatography of the early eluting C_8 and C_9 peaks. Longer drying times result in almost complete loss of C_8 and C_9 hydrocarbons and significant reduction of C_{10}-C_{11}. This is consistent with the general rule for large volume liquid injection solvent venting, which states analytes that boil >100°C higher than the solvent will be retained while lower boiling analytes will be lost at rates related to their boiling point.

Tenax TA™ adsorbent tubes (4 mm ID x 178 mm) were spiked with 25 mg or 50 mg water. Wet tubes were then dried under 50 mL/min helium flow at room temperature (25°C) or 60°C in the TDS A solvent venting mode to simulate drying prior to thermal desorption. Table II summarizes the percent water removed under different time and flow conditions.

Drying Time (min)	25 mg water 25°C / 60°C	50 mg water 25°C / 60°C
5	25% / 97%	11% / 97%
10	71% / N.D.	36% / N.D.
20	95% / N.D.	80% / N.D.
40	N.D. / N.D.	98% / N.D.

Table II. Percent water removed from Tenax™ adsorbent tubes.

It is clear that despite the low affinity of water for Tenax TA™, at low temperatures it is quite possible for adsorbent tubes to retain enough water to adversely affect thermal desorption results. It is therefore necessary to warm the adsorbent to assure elimination of water prior to analysis.

High Water Content Samples

Offline Thermal Extraction. Fresh peppers and basil can contain 50-90% water depending on their age and storage conditions. This precludes direct thermal desorption with direct cold trapping of volatiles in the inlet.

Offline thermal extraction of 250 mg fresh habanero pepper at low temperature (30 min, 40°C) minimized overloading the Tenax TA™ tube with water while trapping volatiles. The Tenax TA™ tube was then heated to 60°C for 20 minutes in the TDS solvent vent mode (45 mL/min) to eliminate residual water before thermal desorption. Volatiles were cold trapped in the inlet at -70°C without freezing the inlet (Figure 4). This procedure resulted in analysis times in excess of 1 hour.

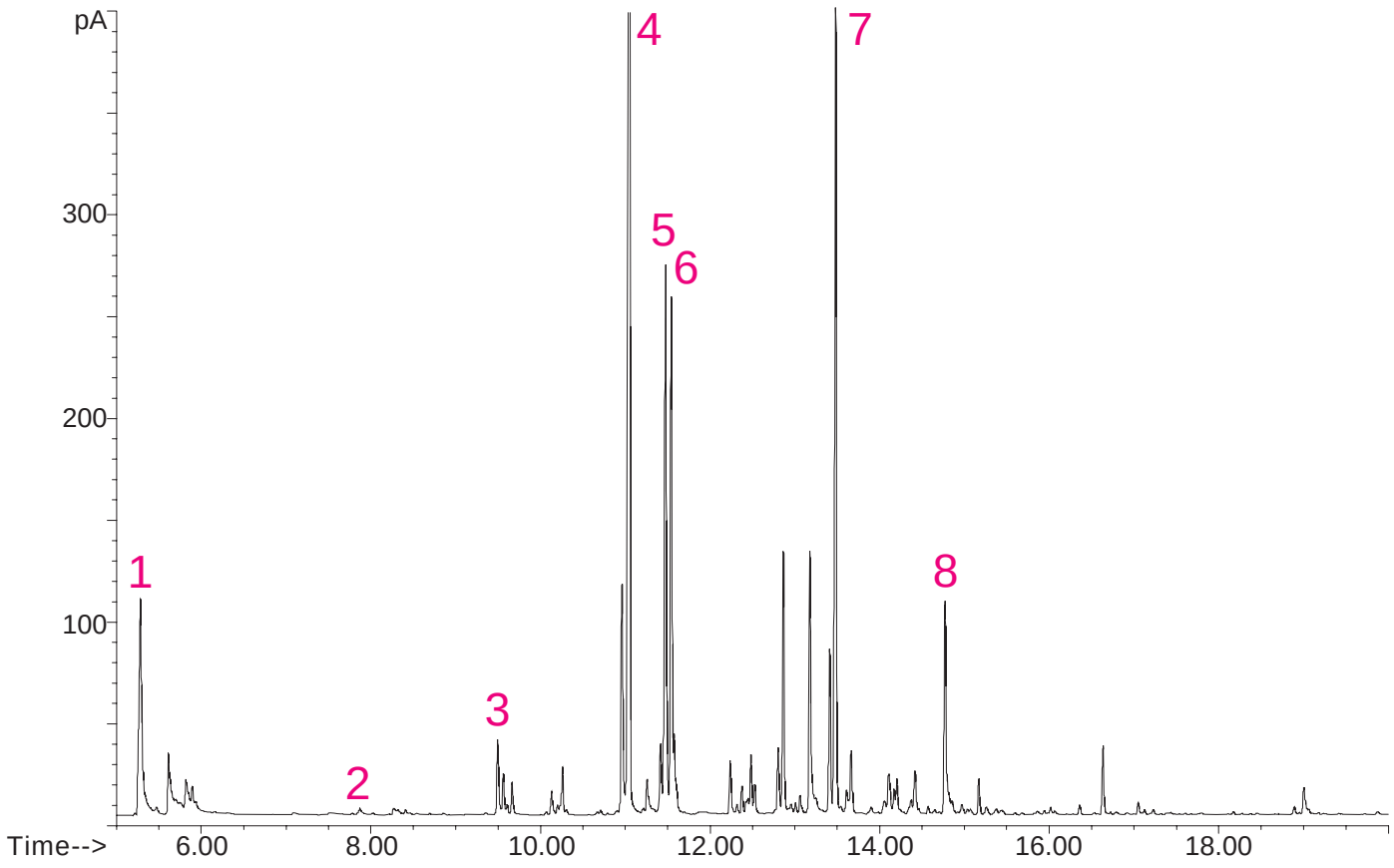

Figure 4. Offline thermal extraction of fresh habanero pepper volatiles, 10:1 split. 4-methyl-1-pentanol (1); benzaldehyde (2); 2-methyl propionic acid ethyl ester (3); hexyl pentanoate isomer (4); cis-3-hexenyl-3-methyl butanoate (5); hexyl pentanoate isomer (6); 2,5-dimethyl-2,4-hexadiene (7); α-gurjunene (8).

To try to speed analysis, 500 mg fresh basil was thermally extracted offline (15 min, 60°C) trapping volatiles on Tenax TA™ adsorbent tubes. The Tenax TA™ tube was then heated to 60°C for 12 minutes in the TDS solvent vent mode to eliminate residual water before thermal desorption. Volatiles were cold trapped in the inlet at -70°C. Although excellent separation was obtained (Figure 5), an increase in inlet pressure during trapping and shifts in early peak retention time indicate some water still remained on the Tenax TA™ adsorbent tube. Analysis time was reduced to 47 minutes.

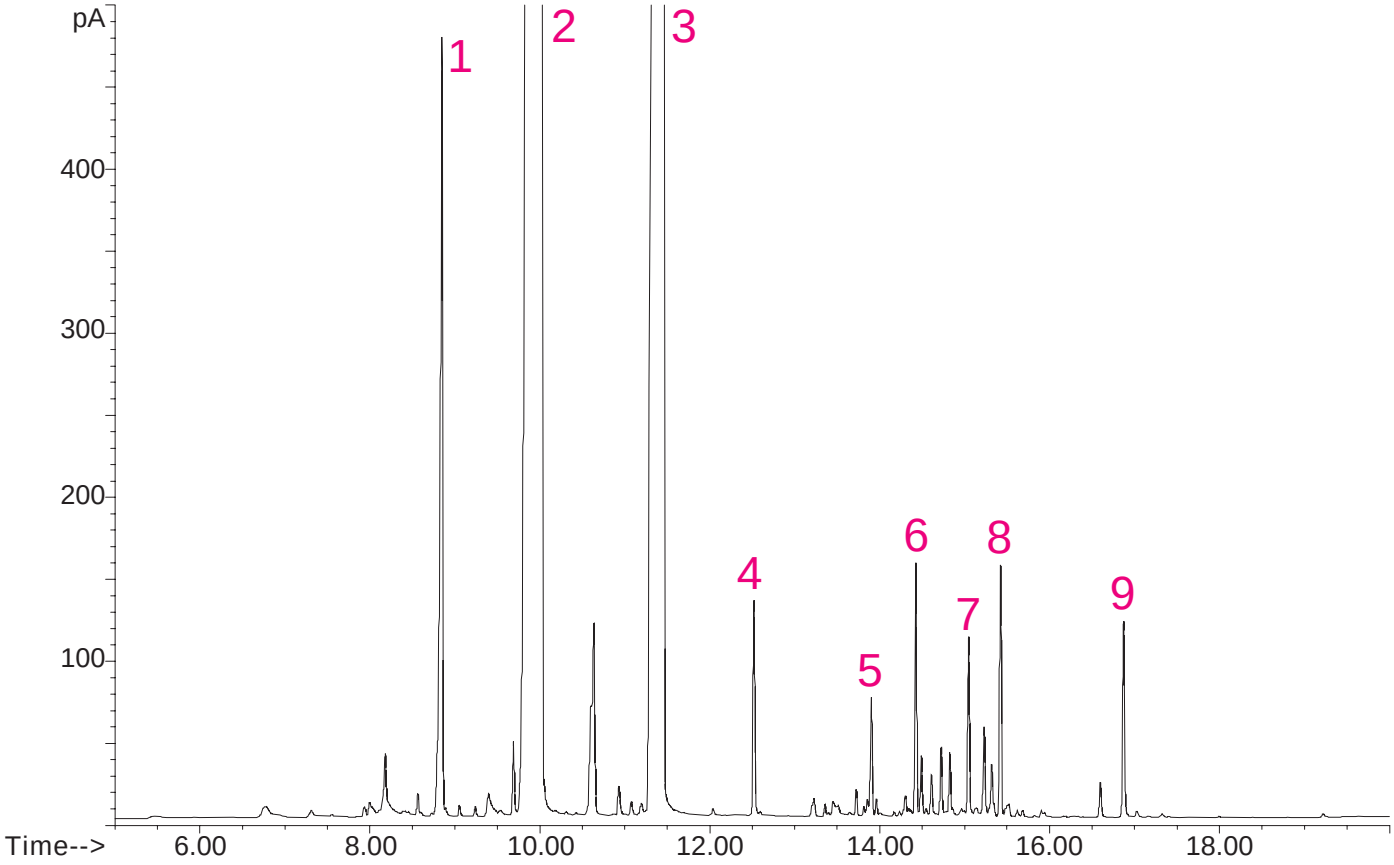

Figure 5. Offline thermal extraction of fresh basil volatiles, 100:1 split. Octene-ol isomer (1); 1,8-cineole (2); a-terpinolene (3); 1-α-terpineol (4); 2-methoxy-4-(2-propenyl)-phenol (5); α-bergamotene (6); β-cubebene (7); δ-cadinene (8); epi-bicyclosesquiphellandrene (9).

Online Thermal Extraction. The CIS 4 inlet liner was replaced with a liner packed with Tenax TA™ adsorbent to allow trapping above 0°C for direct thermal extraction of fresh habanero pepper. Since previous drying studies had shown Tenax TA™ could retain water, inlet temperature was varied to optimize volatile trapping while eliminating water as vapor. 50 mg samples of fresh habanero pepper were thermally extracted for 30 minutes at 60°C using 45 mL/min flow in the TDS splitless mode. The inlet solvent vent mode was used to allow high desorption flow while trapping the volatiles at 5-60°C. To minimize water entering the column during trapping, column flow was reduced by setting the inlet pressure to zero (stopped flow mode).

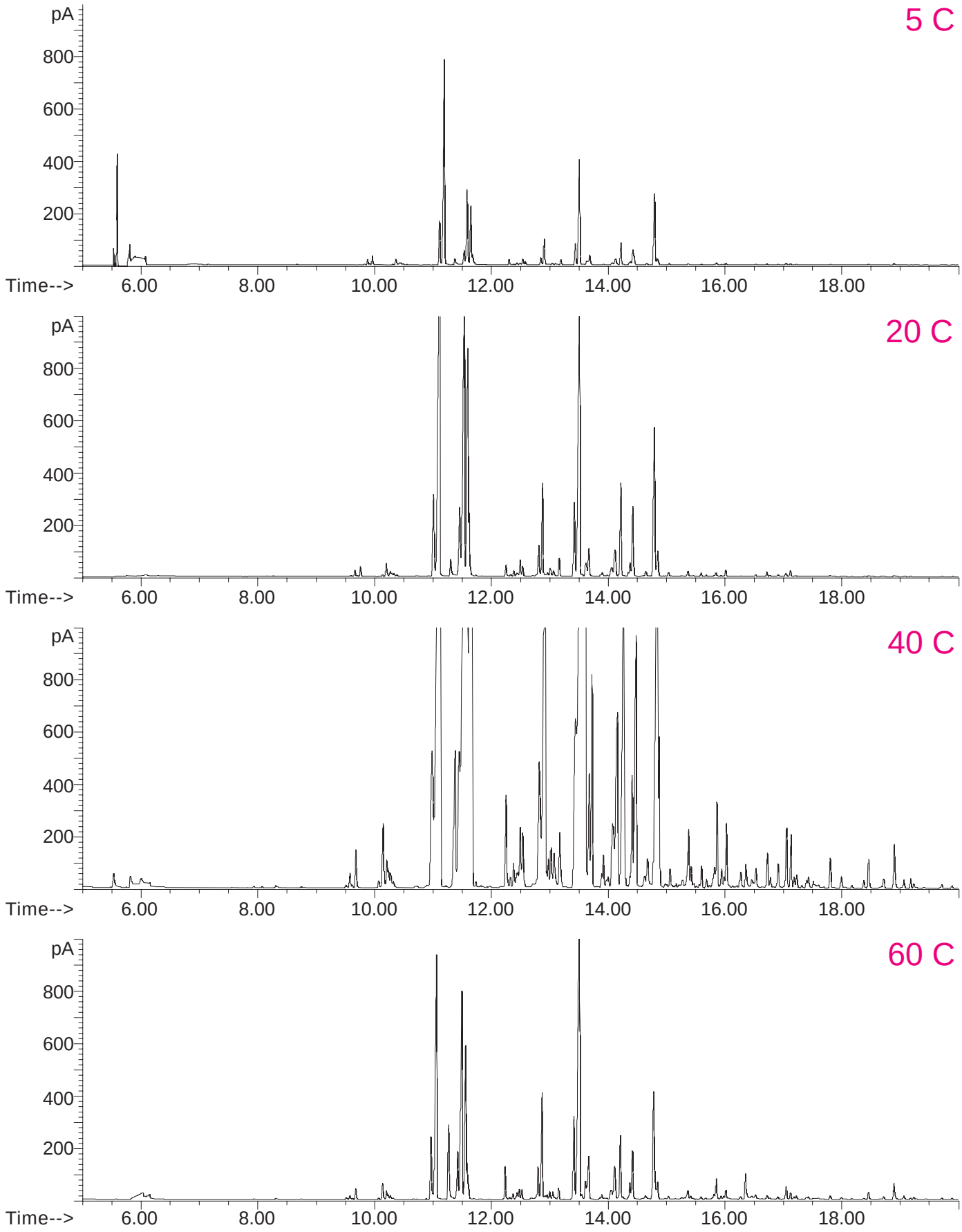

Figure 6. Online direct thermal extraction of fresh habanero pepper volatiles. Inlet liner Tenax TA™, 10:1 split. Inlet temperature listed in figure.

Figure 6 shows maximum trapping efficiency of the Tenax TA™ packed inlet is near 40°C. Increasing the inlet temperature avoids water condensing in the adsorbent, maximizing trapping efficiency. Above 40°C the trapping efficiency of the Tenax TA™ decreases, reducing sensitivity.

The optimized inlet conditions were then used for direct thermal extraction of fresh basil for 10 minutes at 60°C (Figure 7). Excellent separation and peak shape were obtained for the full range of volatiles present. Compared to offline thermal extraction (Figure 2) online direct thermal desorption showed improvement for both early and late eluting compounds. Analysis time was reduced to 30 minutes.

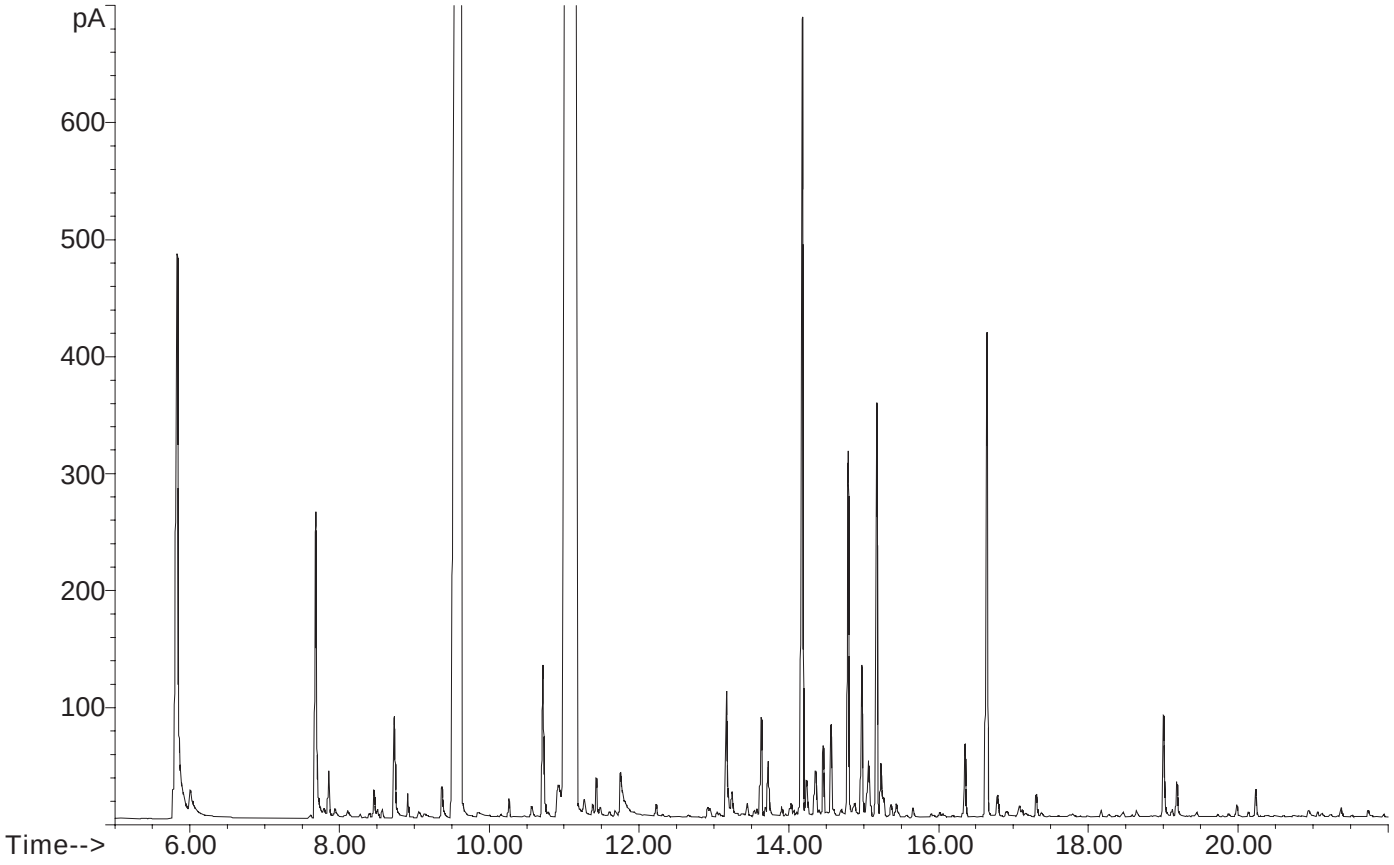

Figure 7. Online direct thermal extraction of fresh basil volatiles. Inlet liner Tenax TA™, 10:1 split, temperature 40°C.

Conclusions

Drying hydrophilic substrates (cotton) under a helium stream at 30°C can effectively remove water from the sample without losing analytes with boiling points above 200°C.

Tenax TA™ adsorbent tubes can be used offline to trap volatiles and eliminate water from wet samples containing hundreds of milligrams of water. This approach may be useful if large, inhomogeneous samples must be analyzed. Drying the adsorbent tube at 60°C for 20 minutes or more may be necessary to avoid interference from water.

Volatiles in wet samples up to 50 mg can be analyzed by direct thermal desorption using Tenax TA™ packed adsorbent liners. Maintaining inlet temperature near 40°C during trapping gives optimal sensitivity.

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