O·I·Analytical

Application Note 27970207

Benzene in Consumer Beverages and Other Products At Single-Digit Parts-per-Billion (ppb) Levels by Purge-and-Trap (P&T)

Keywords
Benzene
Beverages
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VOC

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Introduction

In November 2005, the United States Food and Drug Administration (FDA) received reports that benzene, a human carcinogen, was present at low concentrations in some consumer beverages that contained both benzoate salts and ascorbic acid. A resulting FDA survey of approximately 100 products found that most of the beverages sampled contained either no detectable (ND) benzene or benzene levels that were well below the U.S. Environmental Protection Agency (EPA) water quality standard of 5 ppb. However, several of the beverages tested in the FDA survey contained benzene at levels above 5 ppb. It should be noted that there is no quality standard for benzene in consumer beverages, only in drinking water.

Beverage manufacturers are currently reformulating products containing greater than 5 ppb benzene, but the low-level detection of this human carcinogen in consumer beverages emphasizes the need for a robust procedure for the routine testing of these and other consumer products.

This application note describes a reliable, automated method for the analysis of benzene and other volatile organic compounds (VOCs) in consumer products at single digit and sub-ppb concentrations using a closed-system P&T technique. For this project, benzene was measured in carbonated and non-carbonated beverages, a variety of common table-ready foods, and other consumer products using the method presented. Naturally occurring VOCs, as well as volatile contaminant residues from various sources such as processing and packaging, flavor additives, and breakdown products, can be determined by this method.

Experimental

The equipment used for this project included the OI Analytical Eclipse 4660 Purge-and-Trap (P&T) Sample Concentrator (see Figure 1) and the Model 4552 Water/Soil Autosampler (see Figure 2). VOC extraction, concentration, and introduction to the GC/MS were performed using the autosampler "Soil" mode, which is more sensitive than static or dynamic headspace methods, minimizes the potential for foaming and carryover often associated with carbonated beverages and other consumer products, and does not require cryogenic focusing. Compound speciation was by gas chromatography; mass spectrometry was used for detection, identification, and quantitation by Internal Standard (IS).

Figure 1. OI Analytical Eclipse 4660 P&T Sample Concentrator

Figure 2. OI Analytical Model 4552 Water/Soil Autosampler

Closed System Purge-and-Trap

Samples were purged in a sample vial using the "Soil" mode on the Model 4552 Autosampler. Using this technique, an appropriate aliquot of the test sample is placed in a 40-mL VOA vial that contains a magnetic stir bar. The vial is sealed with a cap and a Teflon®-lined, low-bleed silicon septum and placed into the autosampler tray; the "Soil" mode is selected using the autosampler keypad. The inside of the autosampler and the "Soil" mode sampling station are shown in Figure 3.

Figure 3. Model 4552 Water/Soil Autosampler Interior

The "Soil" mode sampling station is visible within the autosampler.

The vial is raised onto the soil probe where organic-free reagent water and internal standards are added automatically. The sample is heated to 40 °C and stirred inside the sealed VOA vial using the magnetic stir bar to maximize purge efficiency. The volatized compounds are purged from the sample, swept through the top of the double sleeve needle to an inert, heated transfer line, and carried onto the cool analytical trap in the P&T sample concentrator. The trap is then rapidly heated, and the analytes are desorbed under reversed flow of carrier gas onto the GC column. Sample purging in the "Soil" mode is illustrated in Figure 4.

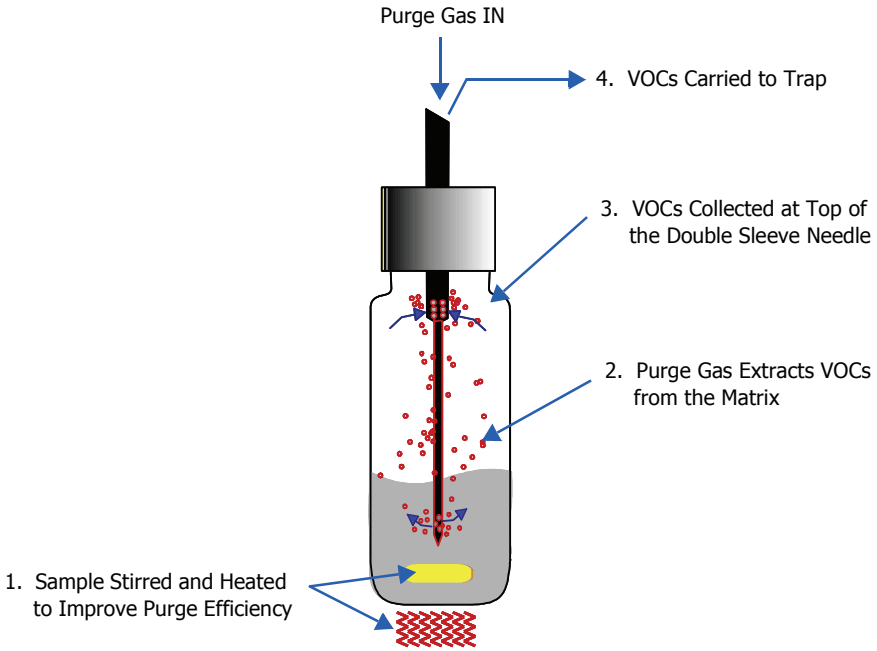

Figure 4. Vial Purging Technique

This illustration represents the purging technique inside the 40-mL VOA vial using the "Soil" mode of the autosampler.

Sample Preparation

Beverages were cooled to 4 °C prior to sampling. A 5-mL gas-tight syringe (refer to Figure 5) was flushed with the sample and then used to transfer 5 mL of beverage from the original container to the 40-mL VOA vial. Care was taken with the carbonated beverages to minimize foaming or dead volume inside the syringe; however, in some cases it was impossible to remove all gas bubbles from the syringe prior to transfer. The non-carbonated beverages did not have any residual air bubbles or dead volume during transfer.

Figure 5. 5-mL Gas-Tight Syringe

The syringe was used to transfer an aliquot of carbonated beverage from its original container to the 40-mL VOA vial. The same syringe was used for non-carbonated beverages, but there was no dead volume or air bubbles.

The table-ready food products were frozen and either chopped or blended, depending on the matrix, then re-frozen. Approximately 5 grams of the frozen sample were weighed into the 40-mL VOA vial. All VOA vials for foods and beverages contained a magnetic stir bar to facilitate agitation of the sample during the purge step. Reagent-free water was used to transfer the IS to the food and beverage samples. Figure 6 shows some of the table-ready foods in VOA vials after purging.

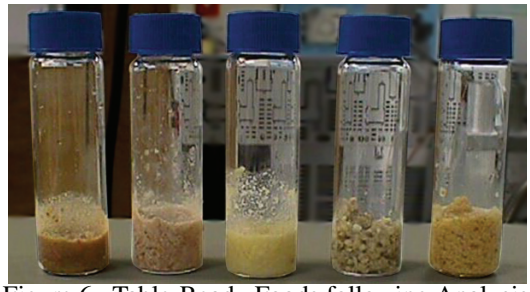

Figure 6. Table-Ready Foods following Analysis

Table-ready foods shown in 40-mL VOA vials after analysis for VOCs by closed-system P&T.

A similar technique was used to determine VOC content in non-food consumer products such as toothpaste and shampoo. A representative aliquot of each sample was placed inside a disposable needle-sparge tube, which was connected to the sparge mount on the front of the P&T concentrator. The samples were heated to 40 °C and sparged through a needle without stirring or the addition of reagent-free water (which can cause foaming). For these matrices, the analytes of interest included primarily flavor and fragrance compounds.

Instrument Operating Conditions

All instrument operating parameters for the beverages are shown in Table 1. The table-ready foods and consumer products were analyzed using the P&T conditions shown in Table 1 using a slightly different column and GC oven program. All samples were analyzed on the mass spectrometer in scan mode.

Table 1. Instrument Operating Parameters for the Beverages

Parameter	Setting
P&T	Eclipse
Autosampler	4552, soil mode
Trap	#10 (Tenax®, silica gel, carbon molecular sieve)
Sample Temperature	40 °C
Purge Time/Temperature	11 min, trap at 20 °C
Desorb Preheat	ON, 180 °C
Desorb Time/Temperature	0.5 min, trap at 190 °C
Bake Time/Temperature	6 min, trap at 210 °C
Water Management Settings	110 °C during Purge 0 °C during Desorb 240 °C during Bake
Parameter	**Setting**
GC	Agilent 6890N
Inlet	220 °C, split 35:1
Column*	Rtx-624, 30-m x 0.25-mm ID x 1.4-µm film, 0.8 mL/min column flow (He)
Oven*	45 °C (hold 4.3 min) 12 °C/min to 100 °C (no hold) 25 °C/min to 250 °C (hold 5.3 min)
MS	Agilent 5975
Mode	Scan: 35 to 260 amu

* Any standard VOC column can be used for this method. If another type of column is chosen, the column manufacturer's recommended operating conditions should be substituted for the conditions in Table 1.

Results

Beverages

All eight of the tested carbonated and non-carbonated beverages contained benzene at concentrations well below 1 ppb. The benzene concentration was quantified using fluorobenzene as an internal standard and a quantitation ion of m/z 78. Compound identity was confirmed by comparison to a reference spectrum in the NIST library. Figure 7 shows the total ion chromatogram (TIC) for root beer with an expanded view of the benzene peak at 7.26 minutes, Figure 8 shows the Extracted Ion Current Profiles (EICP) for benzene and fluorobenzene, and Figure 9 shows the results of the NIST library search.

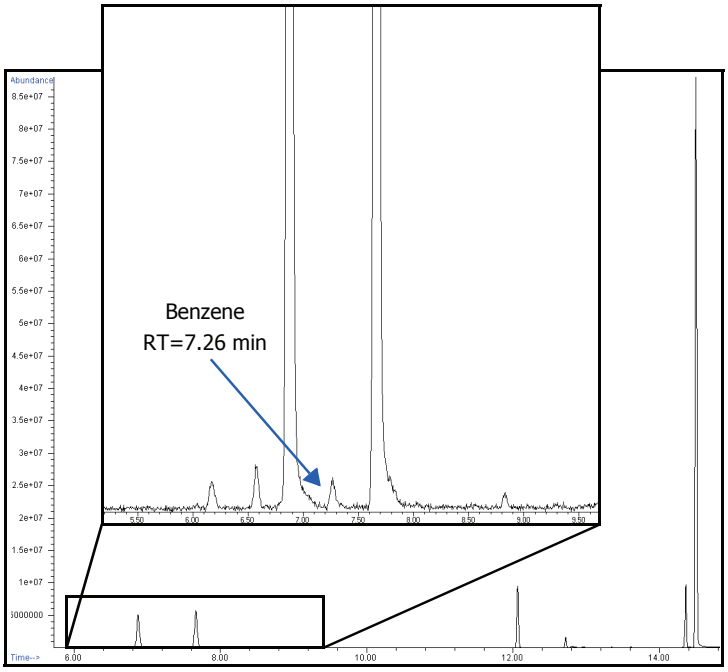

Figure 7. Chromatogram of the Root Beer Sample

The expanded view of the chromatogram shows the benzene peak at RT 7.26 min.

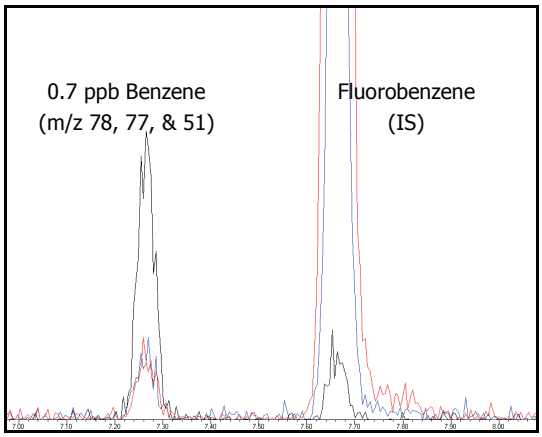

Figure 8. EICP of Benzene and Fluorobenzene (IS)

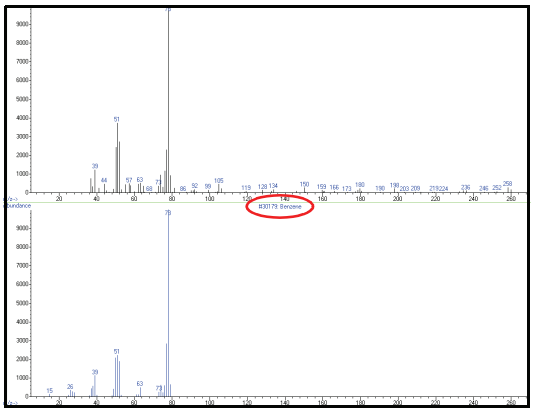

Figure 9. NIST Library Search Results on Peak at RT 7.26 min

Four of the beverages that contained sodium benzoate and either ascorbic acid or citric acid (pineapple soda, citrus-flavored iced tea, root beer, and a colorless carbonated beverage) had concentrations that were slightly elevated when compared to the other 4 beverages, with root beer having the highest concentration at 0.7 ppb. This was similar to findings in the FDA study which showed that these additives were instrumental in the formation of benzene in the final product. None of the beverages contained benzene at concentrations above the USEPA 5-ppb limit for drinking water. Table 2 shows the benzene concentrations and types of additives in the eight beverages tested.

Table 2. Benzene Concentrations and Additives in the Beverages

	Benzene Conc. (ppb)	Ascorbic Acid	Sodium Benzoate	Phosphate Benzoate	Potassium Benzoate	Citrit Acid	Phosphoric Acid
Cola	0.1					X	
Diet Cola	0.1				X		X
Orange Soda	0.1	X		X		X	
Pineapple Soda	0.2	X	X				
Pink Lemonade	0.1		X			X	
Citrus-Flavored Iced Tea	0.2	X	X			X	
Root Beer	0.7	X	X			X	
Colorless Carbonated Beverage	0.2		X			X	

Table-Ready Foods

Benzene was found in most of the table-ready foods at concentrations slightly higher than was found in the beverages and ranged from ND in the butter to 2.8 ppb in the strawberries. As shown in the chromatograms in Figure 10, most of the food samples also contained many additional volatile compounds that are quantifiable by this method. Some of the VOCs in the chromatogram are those found in USEPA VOC methods 524.2 or 8260; however, the majority of volatile compounds that were detected are flavors, fragrances, and other types of volatiles present in the matrix.

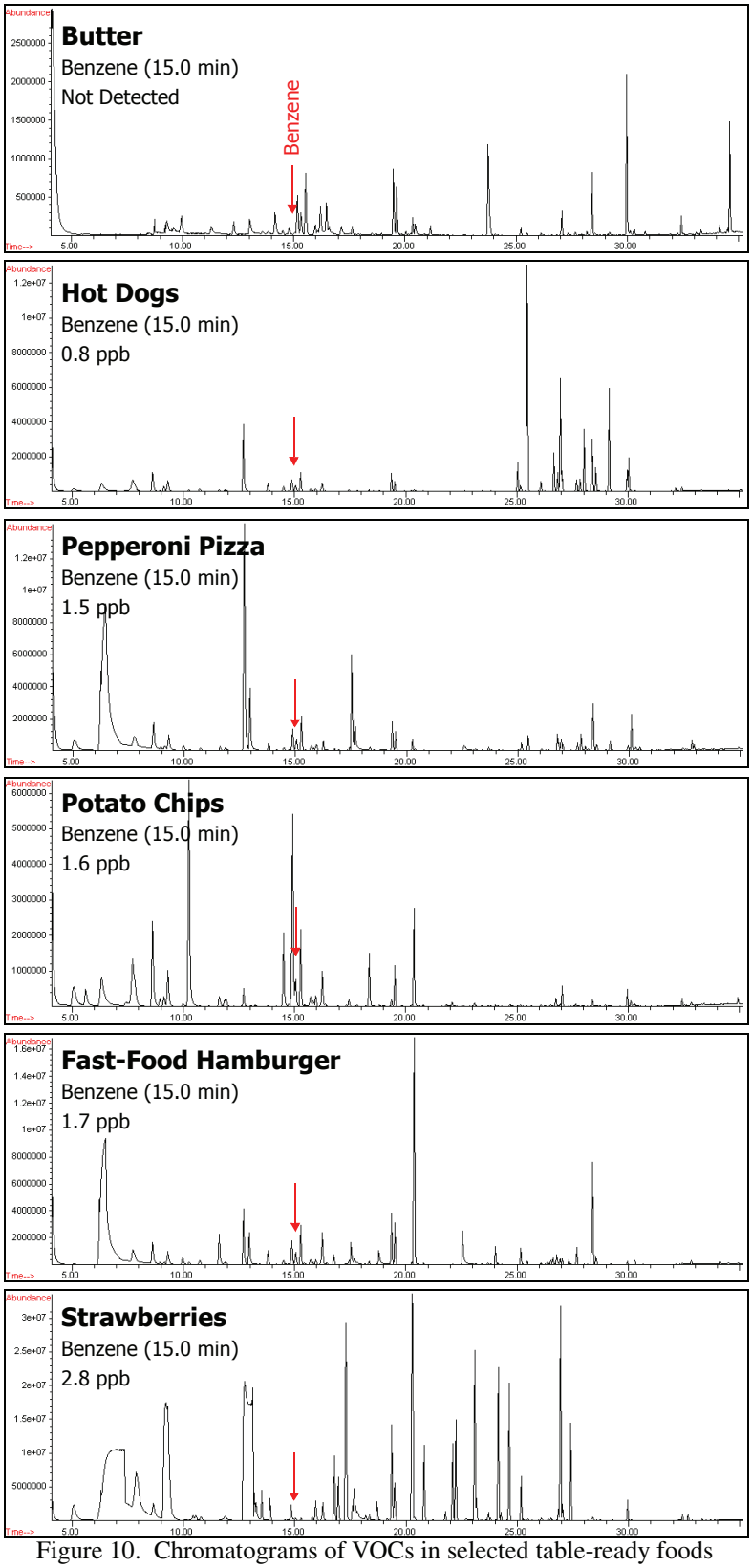

Figure 10. Chromatograms of VOCs in selected table-ready foods

The table-ready foods were analyzed using the Eclipse P&T Sample Concentrator. Benzene concentrations ranged from ND in the butter to 2.8 ppb in the strawberries.

Toothpaste and Shampoo

As expected, the VOCs detected in the non-food consumer products were primarily flavor and fragrance compounds. Identification of the individual peaks in the toothpaste and shampoo samples was performed by comparison to NIST library spectra (see Figures 11 and 12). No standards were available for quantitation of the flavor and fragrance compounds, but they generally fell within the normal range of detection for VOCs by P&T using MS scan mode: roughly between 0.1 and 200 ppb.

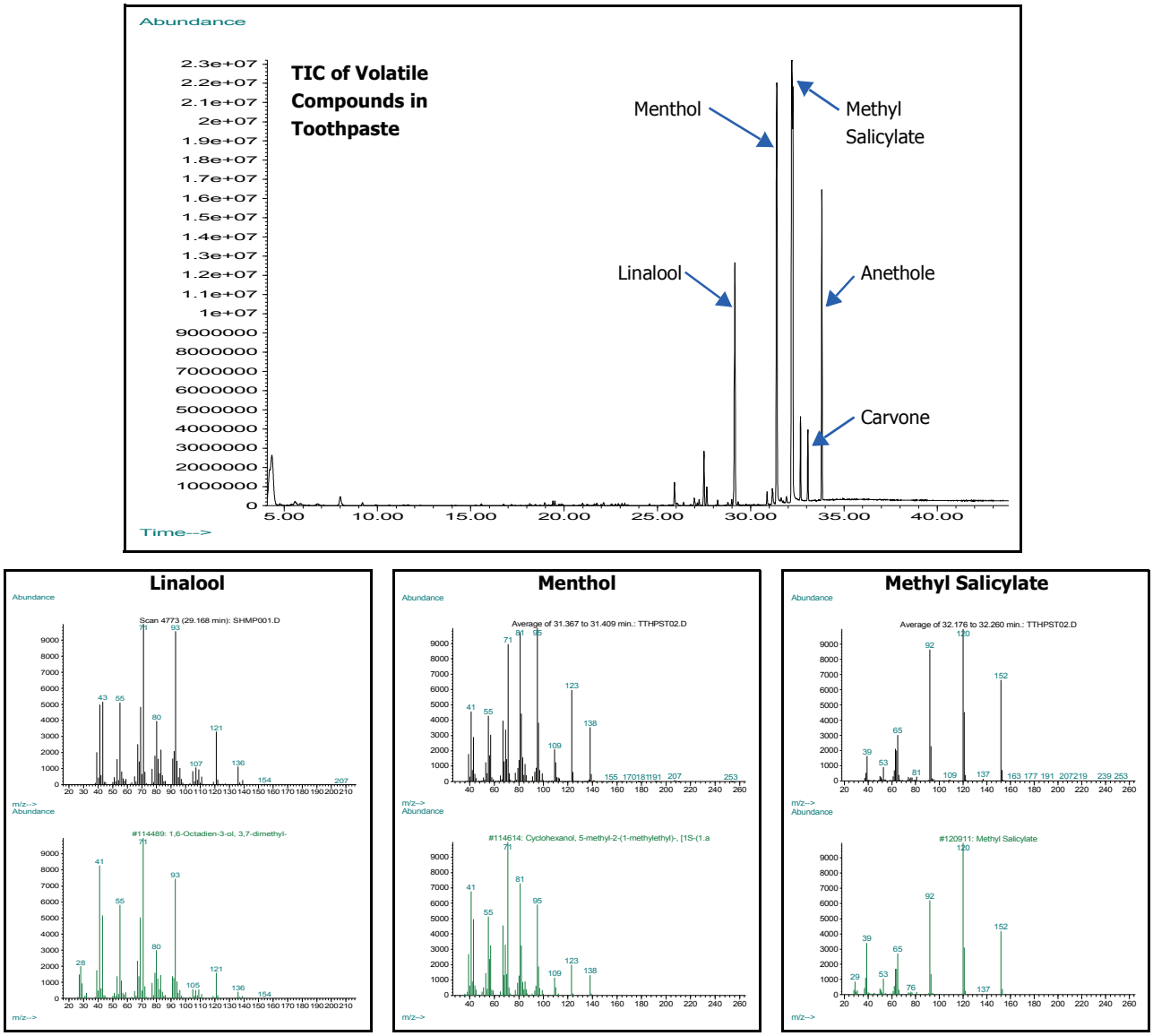

Figure 11. TIC of Volatile Compounds in Toothpaste

Selected flavor/fragrance peaks are identified, and the NIST library search results serve as a comparison.

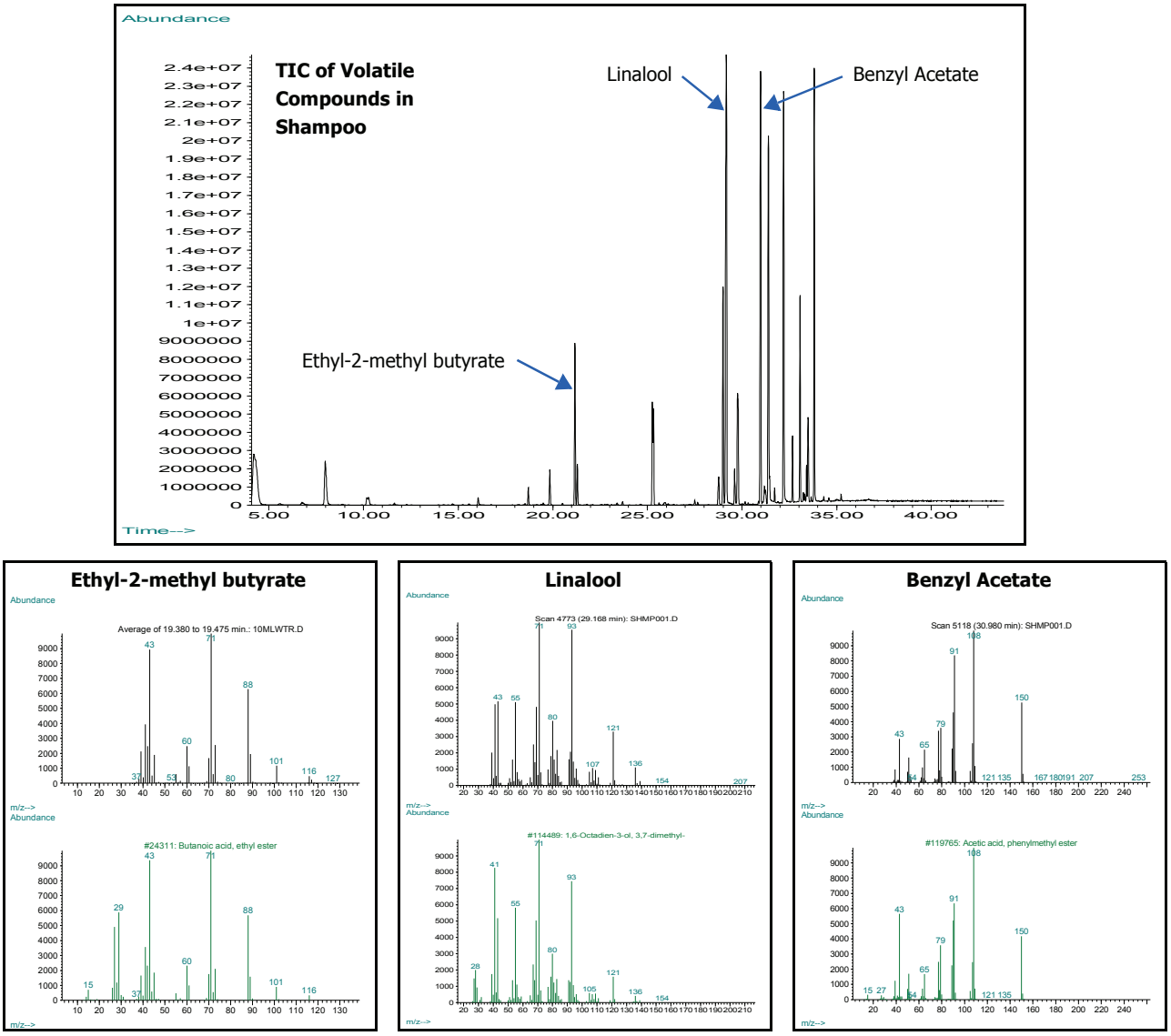

Figure 12. TIC of Volatile Compounds in Shampoo

Selected flavor/fragrance peaks are identified, and the NIST library search results serve as a comparison.

Summary and Conclusions

The OI Analytical Eclipse 4660 P&T Sample Concentrator with the Model 4552 Water/Soil Autosampler can be used to analyze for sub-ppb concentrations of VOCs including benzene, a known human carcinogen, in carbonated and non-carbonated beverages, table-ready foods, and other consumer products. The method presented is robust enough to detect and quantify compounds found in USEPA regulatory methods, as well as a wide variety of volatile flavor and fragrance compounds, additives, breakdown products, or residues from processing and packaging.

References

Complete details of the U.S. Food and Drug Administration study of benzene levels in consumer beverages can be found on the FDA web site at www.fda.gov.

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