A Presentation by OI Analytical

Analysis of Benzene and Other VOCs in Consumer Beverages and Table-Ready Food by Purge-and-Trap

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ISO 9001:2000 SYSTEM CERTIFICATION SGS

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A World of Solutions

Overview

- This presentation discusses the recent reports of benzene in some consumer beverages and includes the following information:
  - *Introduction*
  - *Project definition*
  - *Analytical method and instrumentation*
  - *Sample preparation*
  - *Results from beverages and table-ready foods*
  - *Results from non-food consumer products*
  - *Conclusion and contact information*

Introduction

- In November 2005, the FDA received reports that benzene, a human carcinogen, was present at low concentrations in some soft drinks containing benzoate salts and ascorbic acid.
- A resulting FDA survey of 100 products found that most of the beverages sampled contained either no detectable (ND) benzene or levels well below the USEPA water quality standard of 5 ppb.
  - *There is no quality standard for benzene in consumer beverages.*
  - *WHO water standard for benzene is 10 ppb.*
- Four of the beverages tested in this survey contained benzene at levels above 5 ppb.

Source: http://www.fda.gov

Introduction (cont.)

- FDA's Total Diet Study (TDS) results from 1995 to 2001 indicated that the levels of benzene may be higher.
  - *Studies are underway to determine why the two sets of test results were different.*
- Benzene has also been found in consumer beverages internationally in the UK, Australia, and New Zealand.
- The 2005 survey test results indicate that benzene levels can be highly variable from lot to lot and may depend on factors such as time at elevated temperatures and exposure to light.
- Manufacturers are currently reformulating products that have been identified as containing greater than 5 ppb benzene.

Source: http://www.fda.gov

Project Definition

- An analytical method is demonstrated for the determination of benzene and other volatile organic compounds (VOCs) in consumer beverages and selected table-ready food products.
- Instrumentation included:
  - *Eclipse 4660 P&T Sample Concentrator*
  - *Model 4552 Water/Soil Autosampler*
- Naturally occurring VOCs, as well as contaminant residues from various sources (processing and packaging, flavor additives, breakdown products, etc.), can be determined by this method.

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Overview of the Analytical Method

- VOC extraction, concentration, and introduction was performed by closed system purge-and-trap (P&T).
  - *More sensitive than headspace methods*
  - *Lower detection limits*
  - *Cryogenic focusing is not necessary*
- Compound speciation by gas chromatography
- Detection and identification by mass spectrometry
  - *Scan or SIM mode*
- Quantitation using Internal Standard (IS)

Sample Introduction Instrumentation

Eclipse 4660 P&T
Sample Concentrator

Model 4552 Water/Soil
Autosampler

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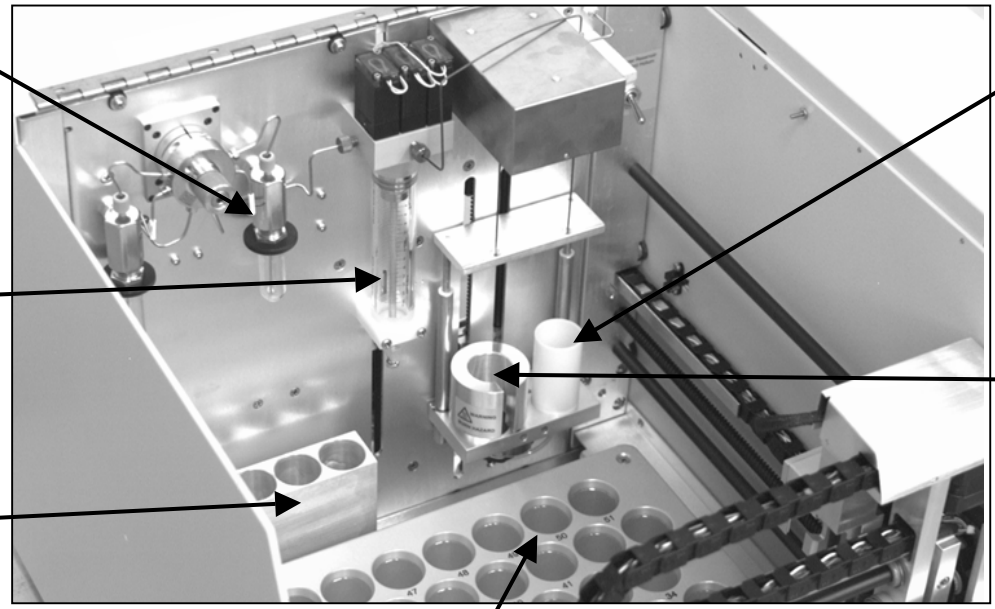
Interior Model 4552 Water/Soil Autosampler



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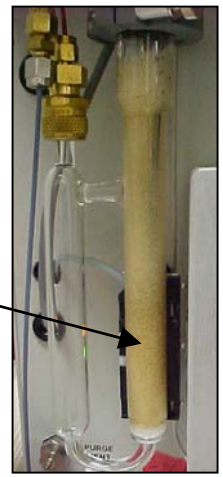
“Water” Mode vs. “Soil” Mode

- For this project, all samples were purged using the “Soil” mode on the Model 4552 Autosampler.
- This technique minimized loss of VOCs in the solid food products and
- Minimized foaming of the beverage samples.
  - *Beverages foamed excessively when purged in the “Water“ mode*



Beverage in the “Soil” sampling station did not foam

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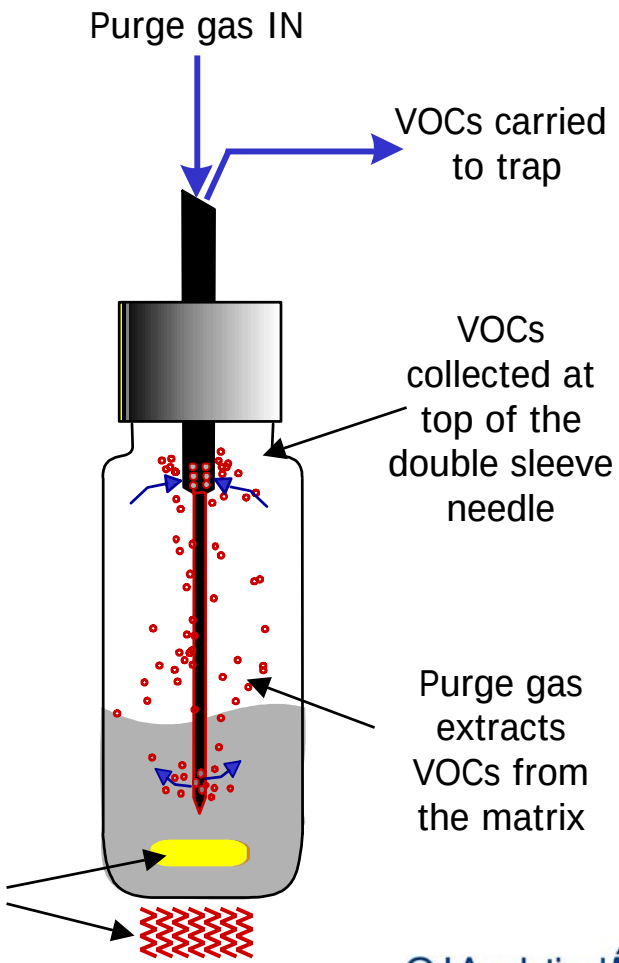
Sample Purging in “Soil” Mode

- Internal standards and water are added to the sample in a sealed 40-mL VOA vial.
- The sample matrix is heated and stirred to improve purge efficiency.
- Purge gas sweeps the VOCs out of the matrix.
- VOCs are then collected at the top of the double sleeve needle and transferred to the trap for concentration.



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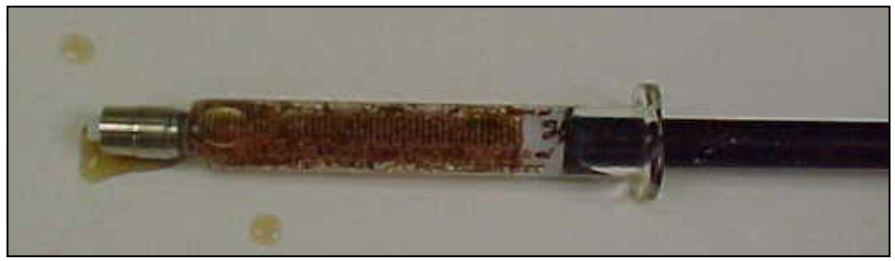
Beverage Sample Preparation

- Samples were cooled to 4°C prior to sampling.
- A syringe was used to transfer 5 mL from the original container to the 40-mL VOA vial.
  - *Magnetic stir bar added to VOA vial*
- The syringe was flushed with sample first.
- Care was taken to minimize foaming during transfer.
- Internal standards were added to vial with 5-mL DI water at the autosampler.



Syringe used for sample transfer

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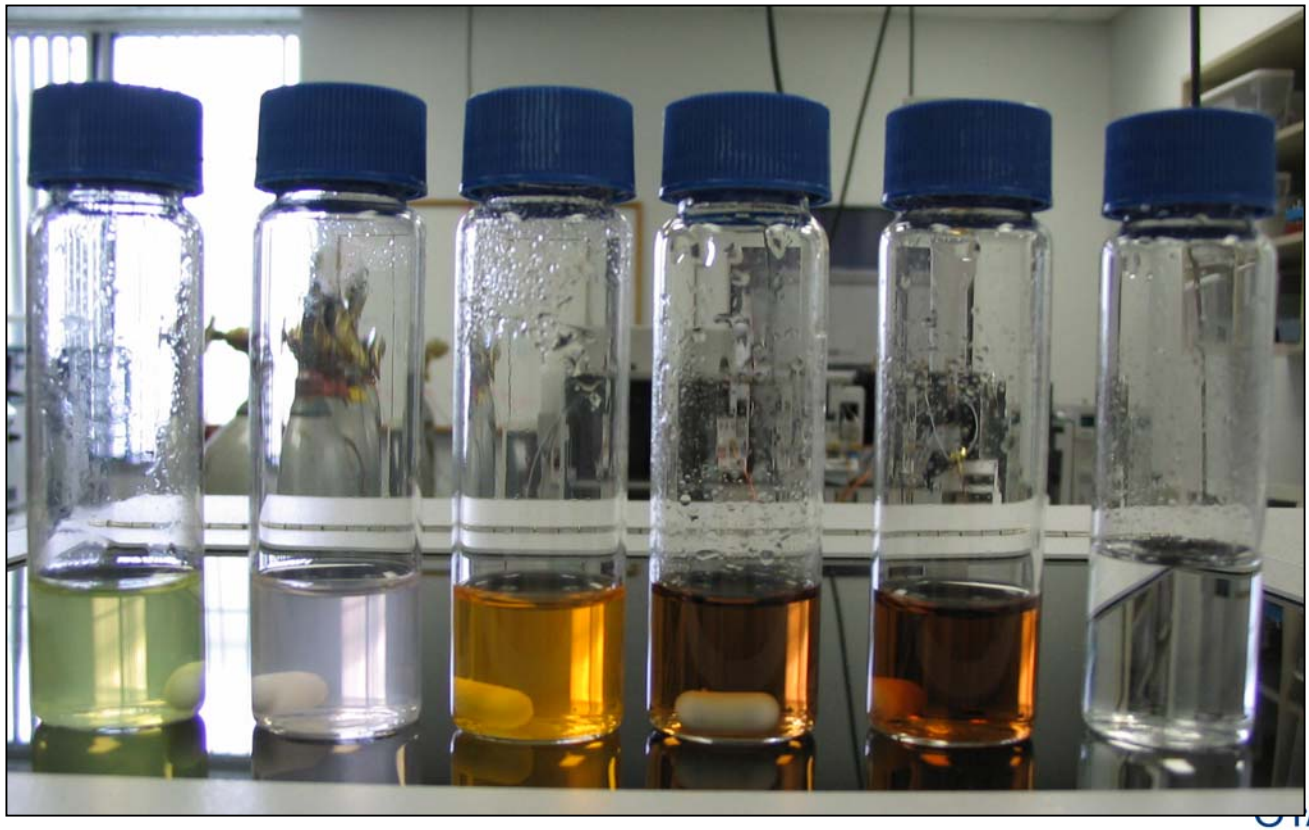
Beverage Sample Preparation (cont.)

Pineapple Drink | Pink Lemonade | Orange Soda | Cola | Diet Cola | Colorless Carbonated Drink



Instrument Conditions - Beverages

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 SIM; m/z 78, 77, and 51

*Any standard VOC column can be used

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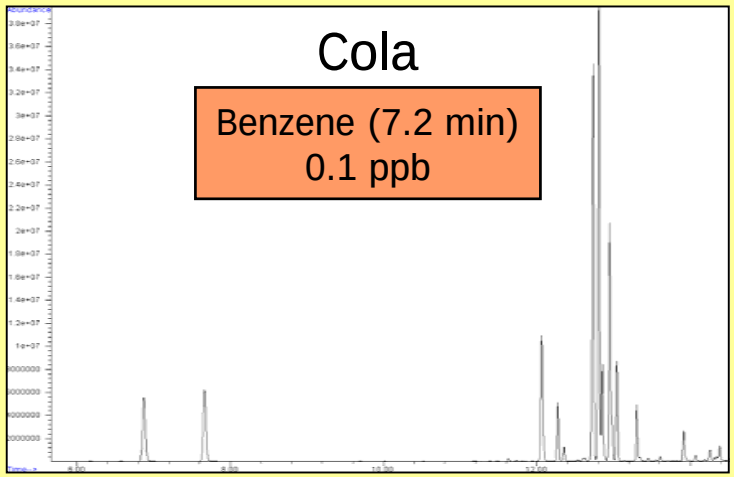
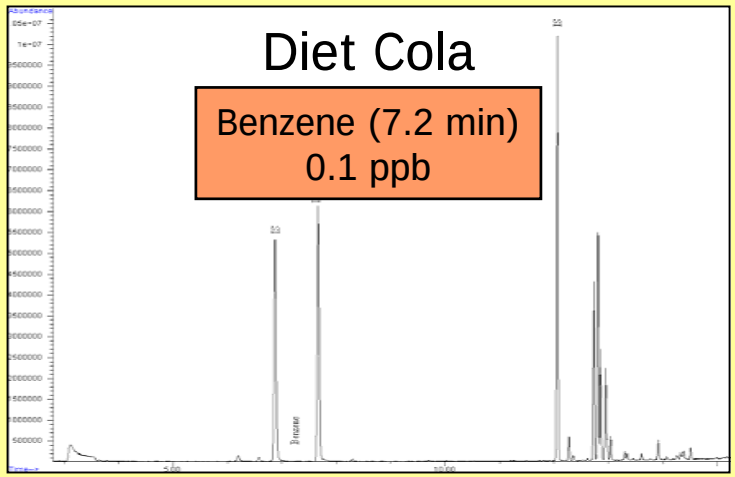
VOCs in Consumer Beverages (cont.)



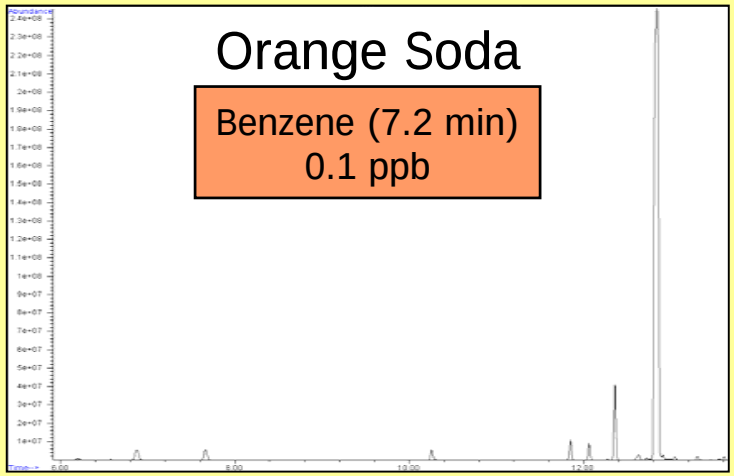
Cola

Benzene (7.2 min)
0.1 ppb



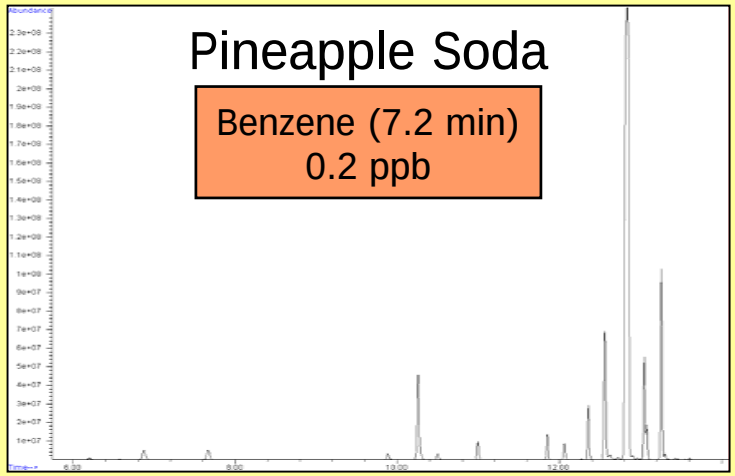
Diet Cola

Benzene (7.2 min)
0.1 ppb



Orange Soda

Benzene (7.2 min)
0.1 ppb



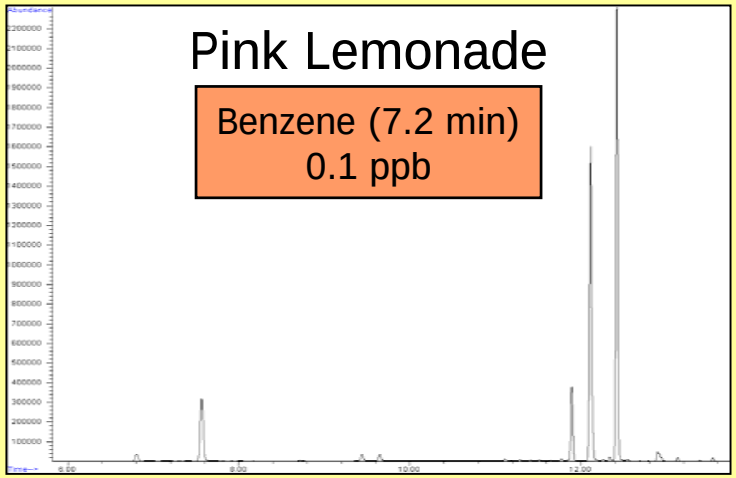
Pineapple Soda

Benzene (7.2 min)
0.2 ppb

VOCs in Consumer Beverages (cont.)

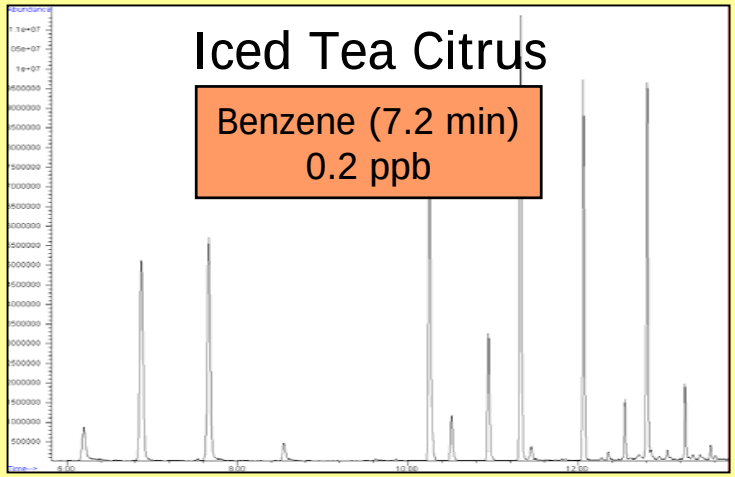
Pink Lemonade

Benzene (7.2 min)
0.1 ppb



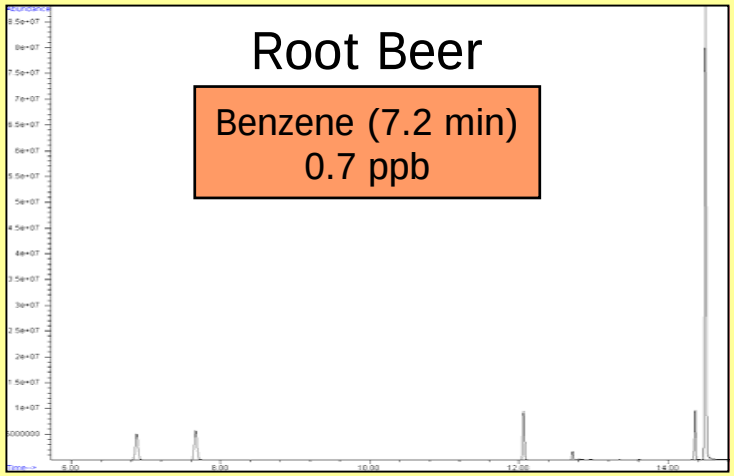
Iced Tea Citrus

Benzene (7.2 min)
0.2 ppb



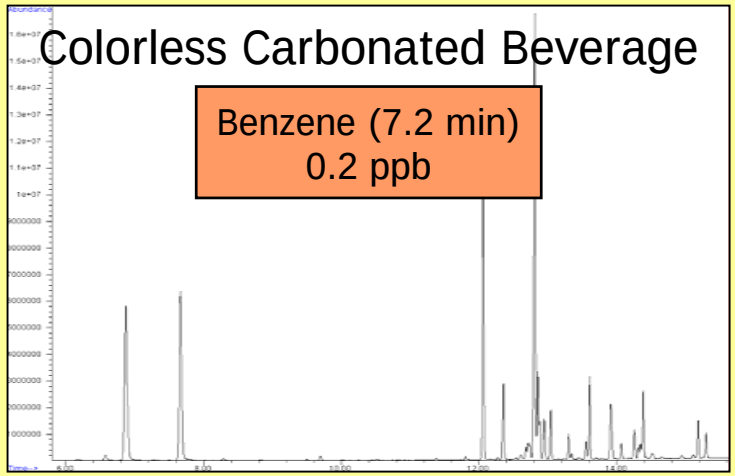
Root Beer

Benzene (7.2 min)
0.7 ppb

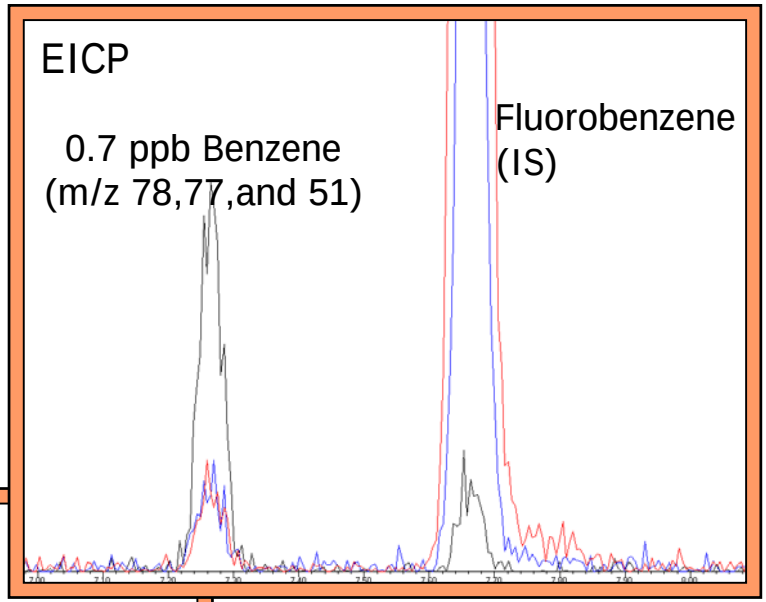


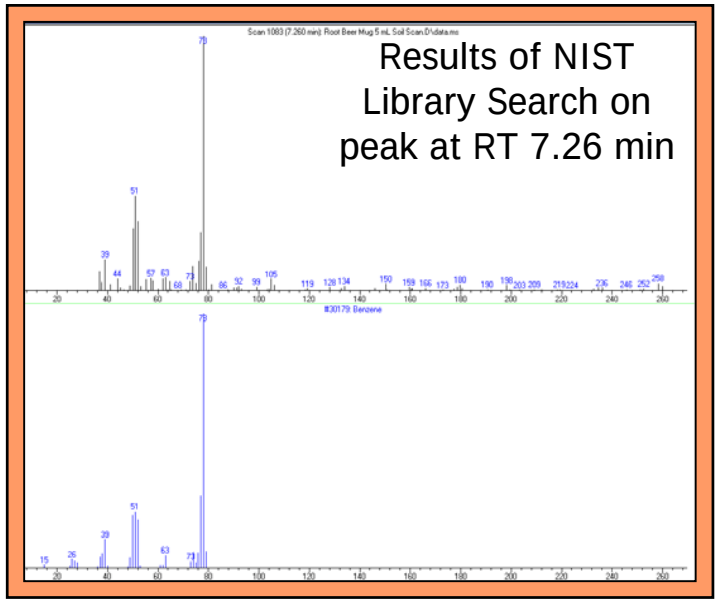
Colorless Carbonated Beverage

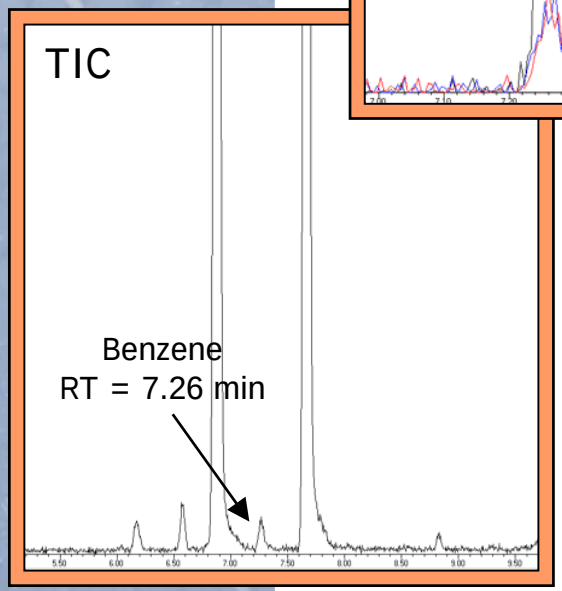
Benzene (7.2 min)
0.2 ppb



Details: Benzene in Root Beer







- Benzene was detected in the root beer sample at a concentration of 0.7 ppb.
- The benzene was quantified using Fluorobenzene as the IS; the benzene quantitation ion was m/z 78.
- Compound identity was confirmed by comparison to a reference spectrum in the NIST Library.

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Beverage Ingredients

	Sodium Benzoate	Citric Acid	Ascorbic Acid	Phosphate Benzoate	Potassium Benzoate	Phosphoric Acid
Pineapple Soda	X		X			
Iced Tea Citrus	X	X	X			
Pink Lemonade	X	X				
Orange Soda #1		X	X	X		
Orange Soda #2	X	X	X			
Colorless Carbonated Beverage #1	X	X				
Colorless Carbonated Beverage #2	X	X				
Cola #1		X				
Cola #2						X
Diet Cola					X	X
Root Beer	X	X	X			

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Summary: Benzene in Beverages

- Benzene was found in most of the consumer beverages at concentrations well below the USEPA 5-ppb limit for benzene in drinking water.
- MS Scan and SIM modes produced equivalent results.
- The model 4552 Water/Soil Autosampler was operated in the “Soil” mode to minimize foaming of the carbonated beverages.
- All beverage samples were analyzed using the Eclipse 4660 P&T Sample Concentrator.

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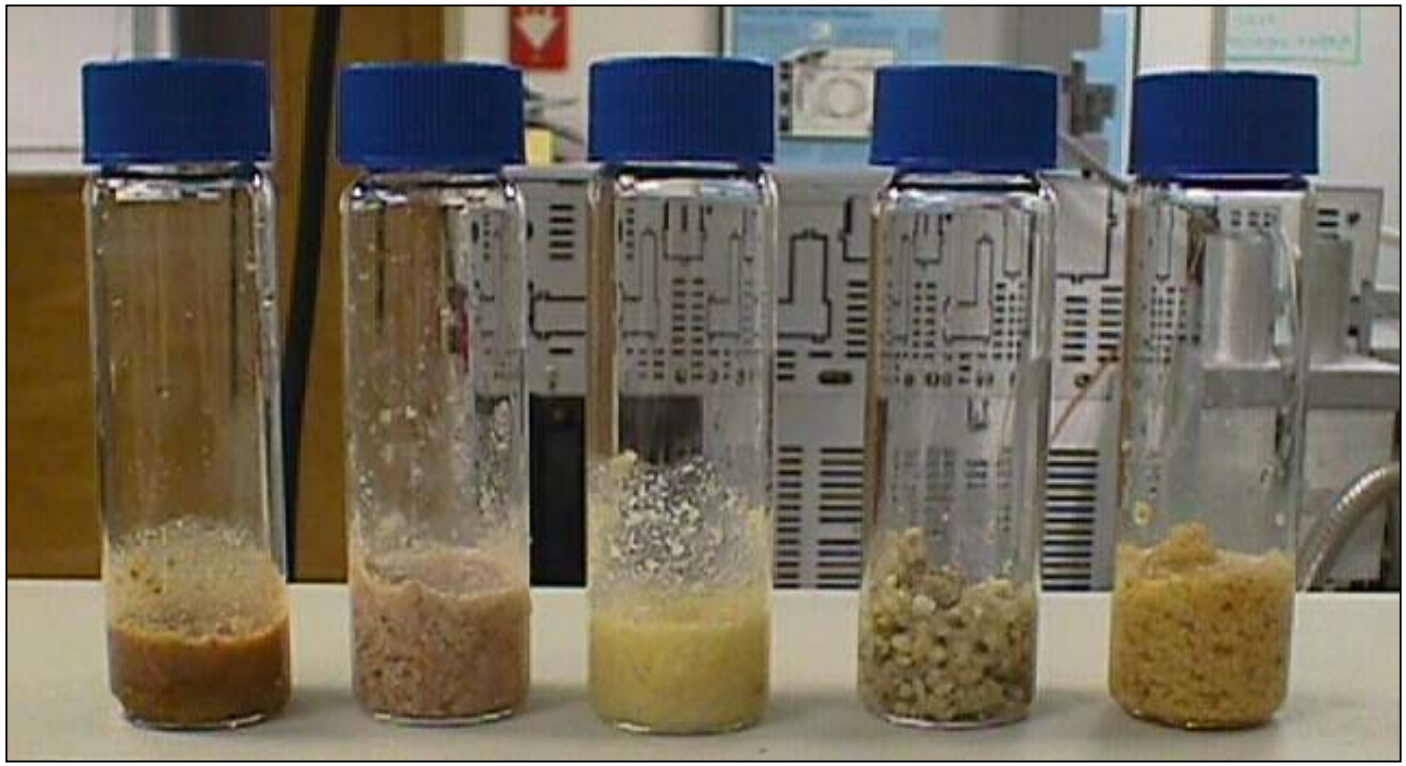
Solid Sample Preparation

- Samples were frozen and either chopped or blended.
- Approximately 5 grams were weighed into 40-mL VOA vial with stir bar.
- The Model 4552 Water/Soil Autosampler was used to add Internal Standards with 5 mL water prior to purging.

Food Samples in VOA Vials

Cereal | Hot Dogs | Potato Chips | Fast Food Burger | Pizza



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Instrument Conditions – Table-Ready Food

GC	Agilent 6890N
Inlet	200°C, split 10:1
Column*	DB-VRX, 60 m x 0.25 mm ID x 1.4 µm film, 1 mL/min column flow (He)
Oven	35°C (hold 6 min) 6°C/min to 175°C (no hold) 10°C/min to 220°C (hold 2 min)
MS	Agilent 5973
Mode	Scan, 35 to 260 amu

*Any standard VOC column can be used, including 30- and 20-m columns

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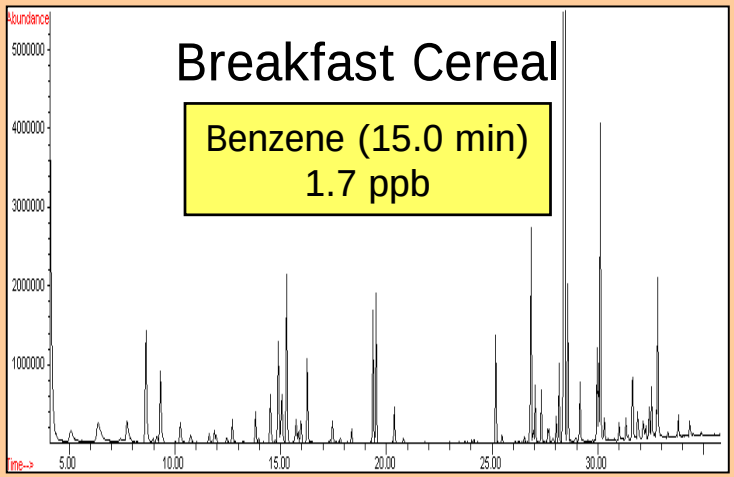
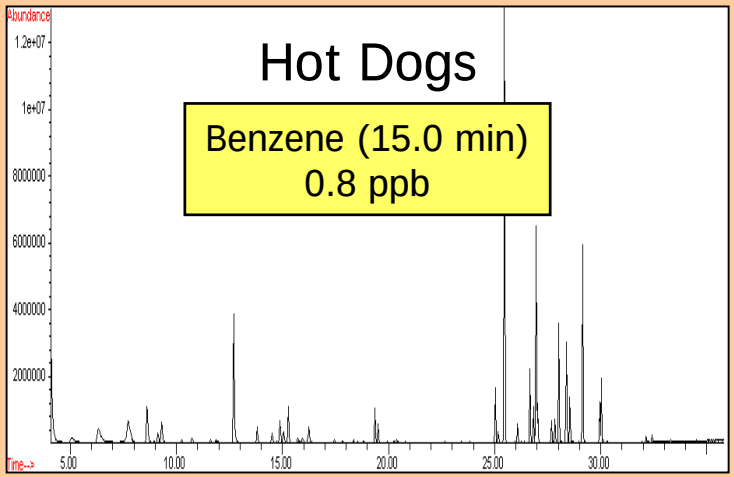
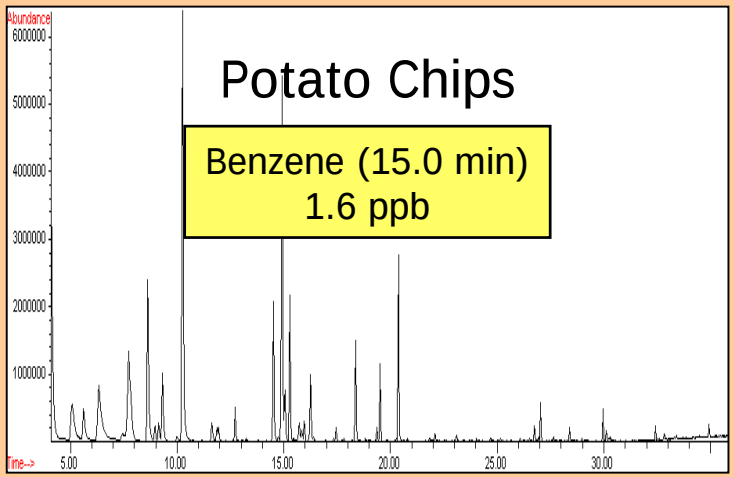
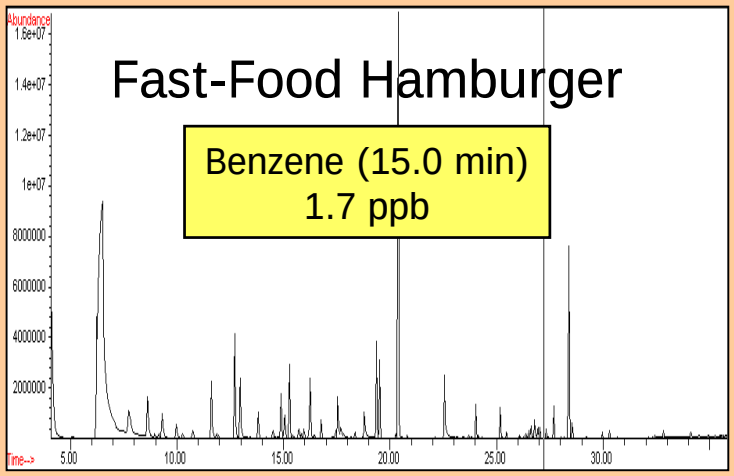
VOCs in Table-Ready Foods

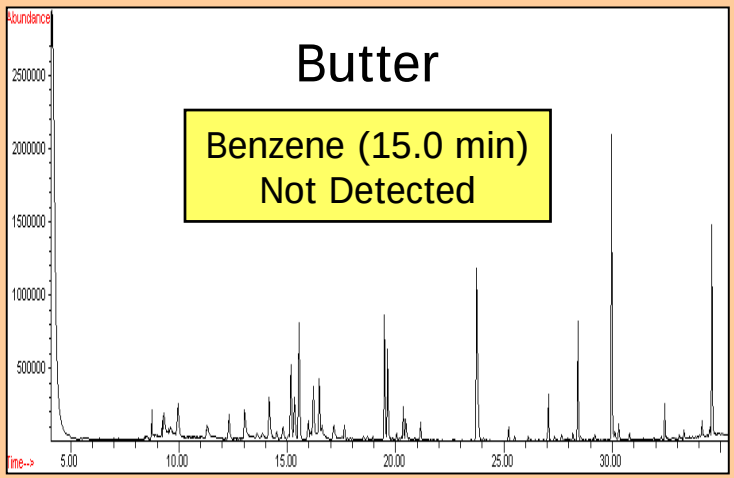






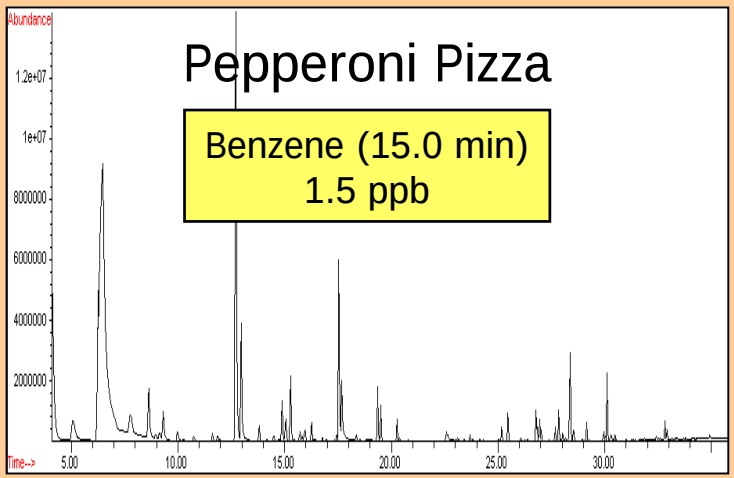


VOCs in Table-Ready Foods (cont.)



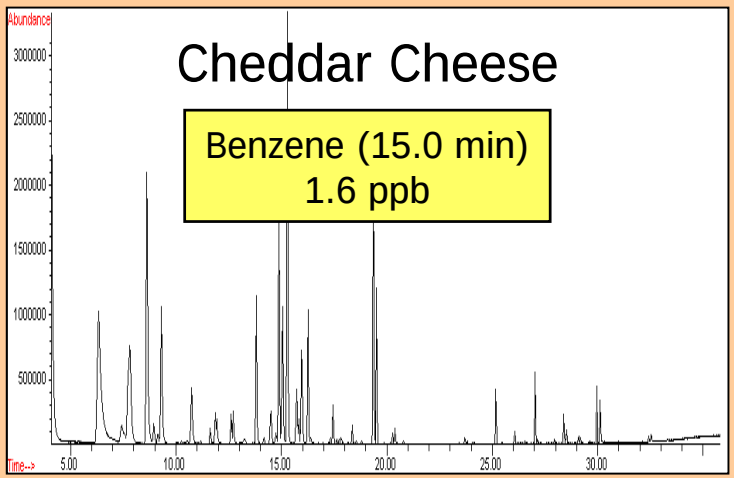
Butter

Benzene (15.0 min)
Not Detected



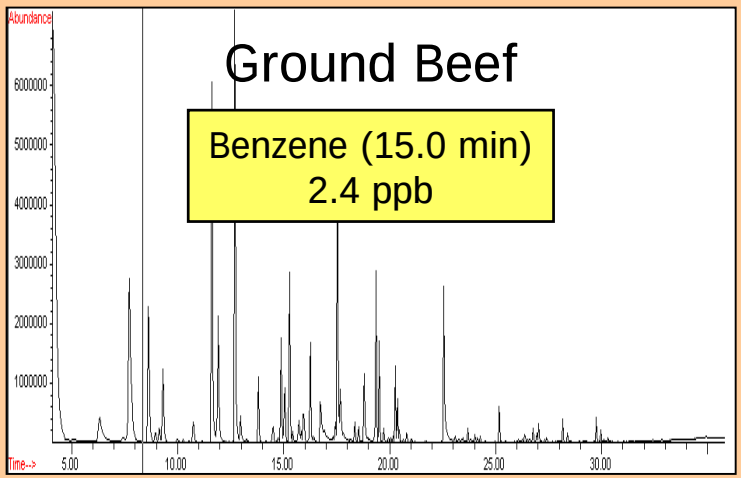
Pepperoni Pizza

Benzene (15.0 min)
1.5 ppb



Cheddar Cheese

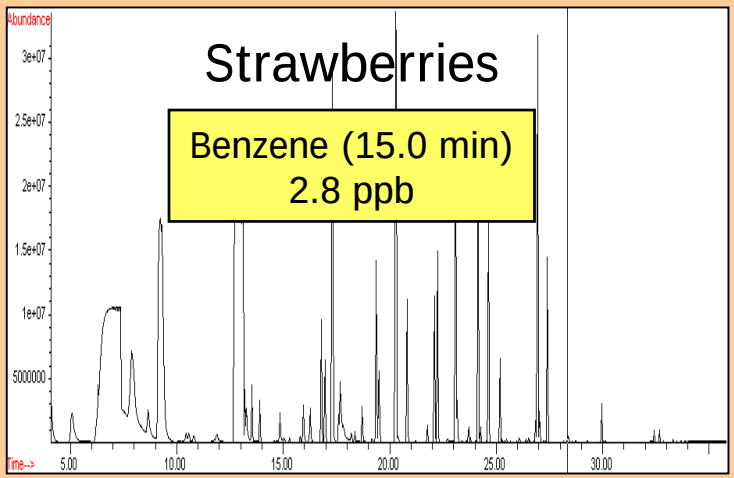
Benzene (15.0 min)
1.6 ppb

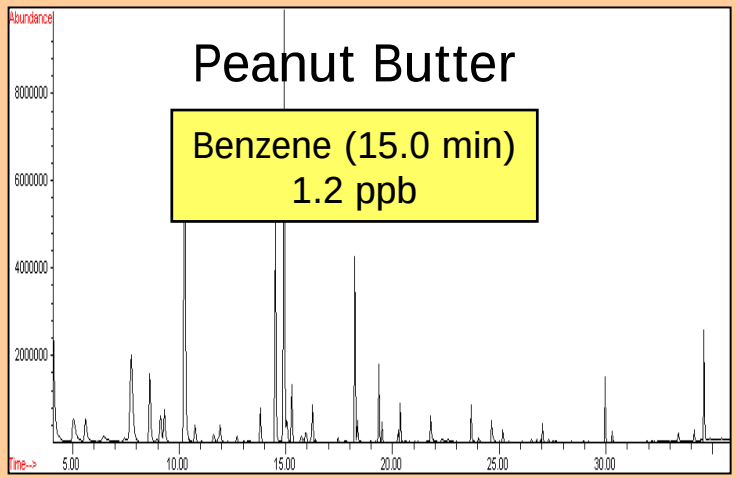


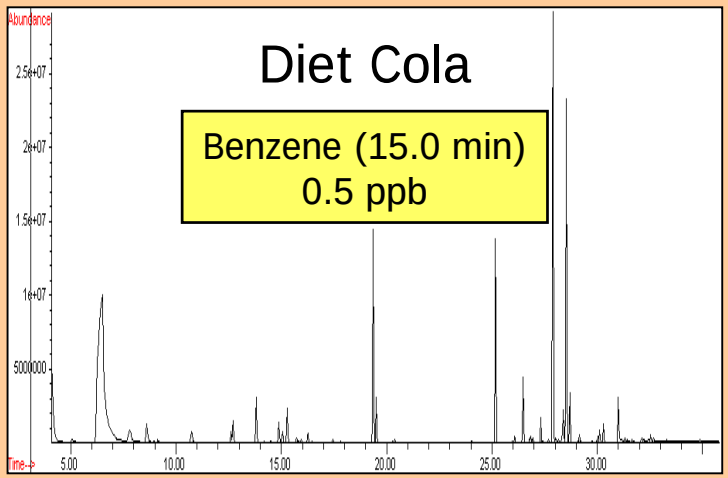
Ground Beef

Benzene (15.0 min)
2.4 ppb

VOCs in Table-Ready Foods (cont.)





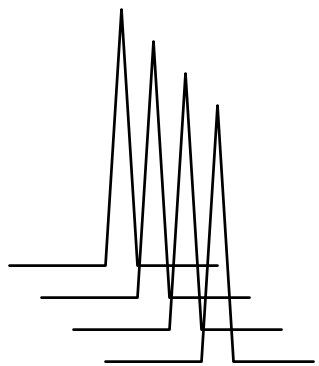


Summary: Benzene in Table-Ready Food

- Benzene was found in most of the table-ready foods at concentrations ranging from ND in the Butter to 2.8 ppb in the Strawberries.
  - *Slightly higher than in the beverages*
  - *There are no specified EPA or FDA standards for benzene in table-ready foods*
- The model 4552 Water/Soil Autosampler was operated in the “Soil” mode.
- All of the samples were analyzed using the Eclipse 4660 P&T Sample Concentrator.

Non-Food Consumer Products

- The same technique can be used to determine VOC content in non-food consumer products.
- Analytes of interest include flavor and fragrance compounds.
- Matrices that can be analyzed using this approach include toothpaste, shampoo, etc.



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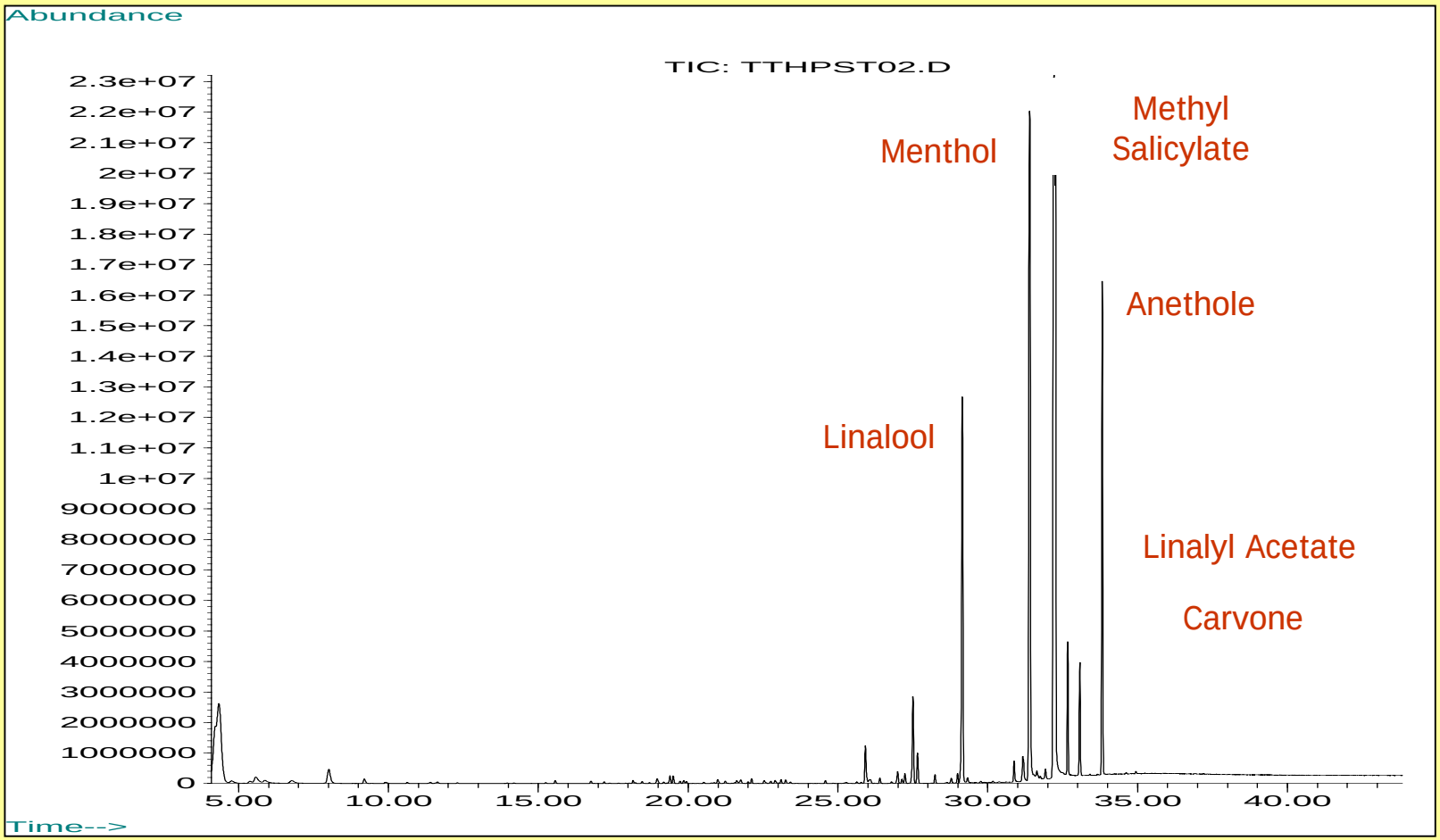
TIC of VOCs in 2.16 g Toothpaste



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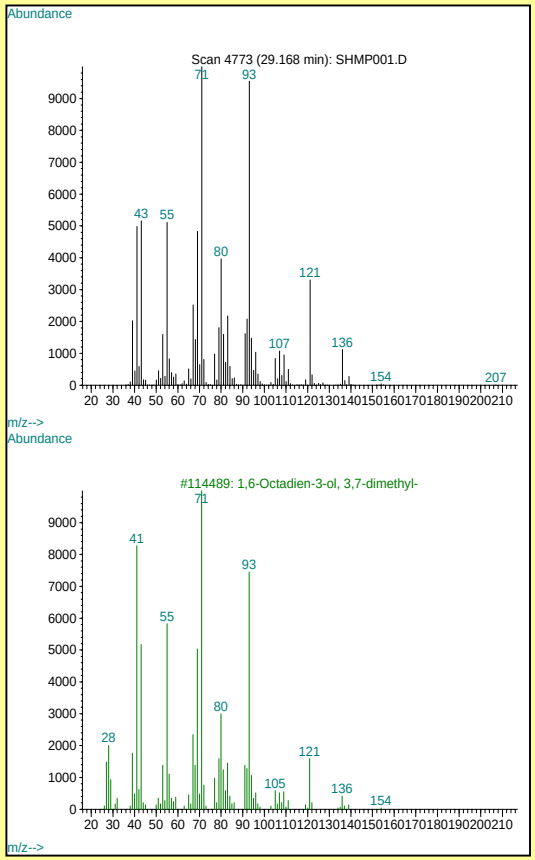
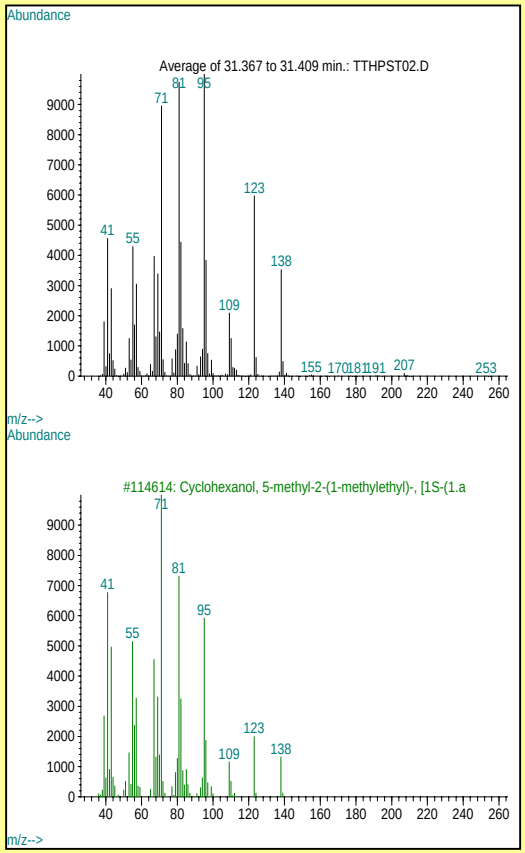
Selected Spectra From Toothpaste

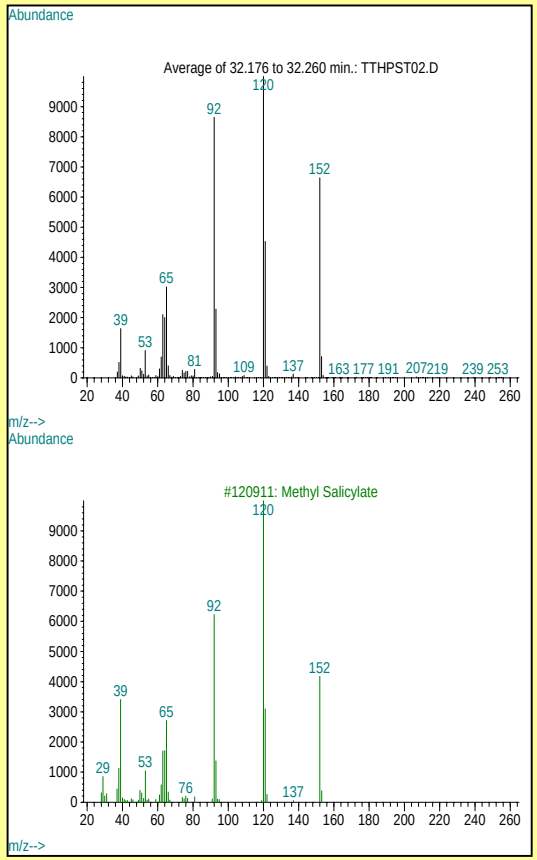
Linalool



Menthol



Methyl Salicylate



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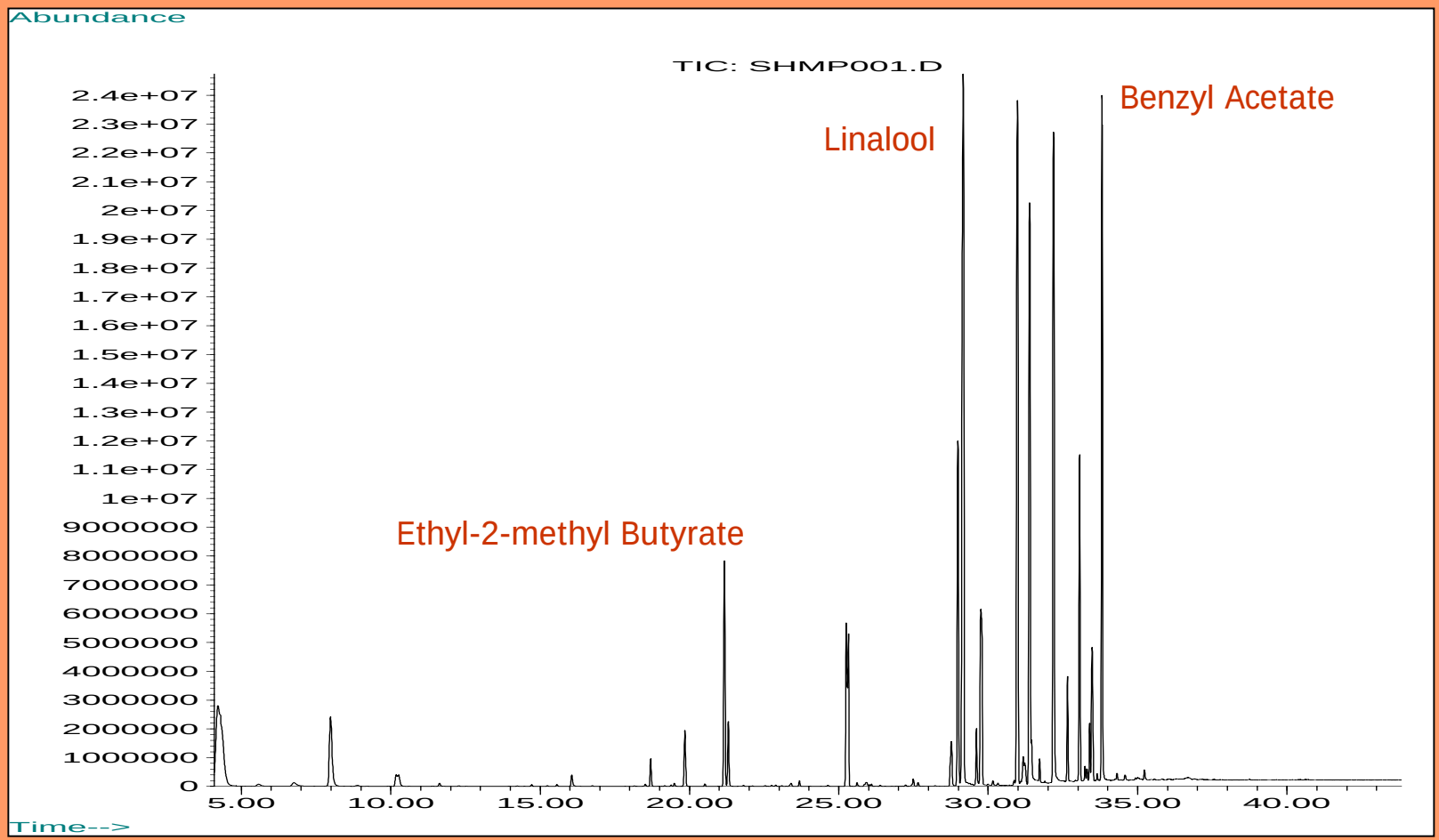
TIC of VOCs in 0.51 g Shampoo



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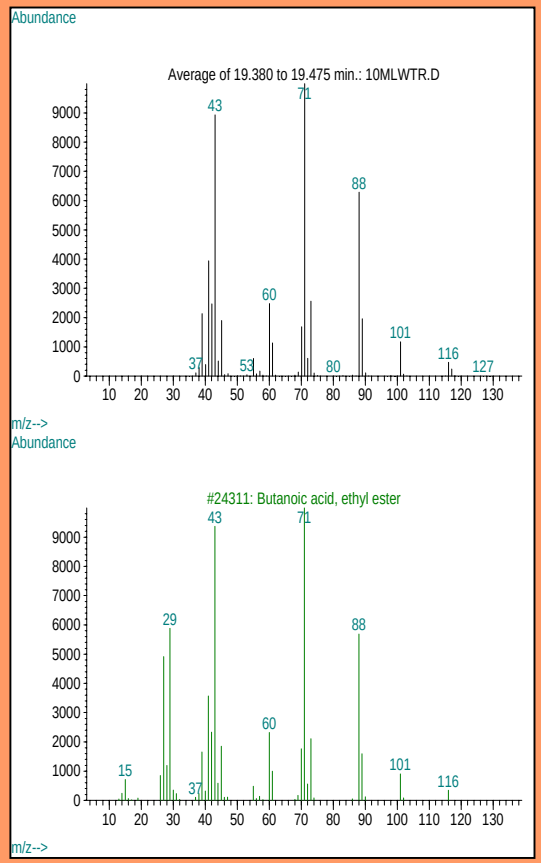
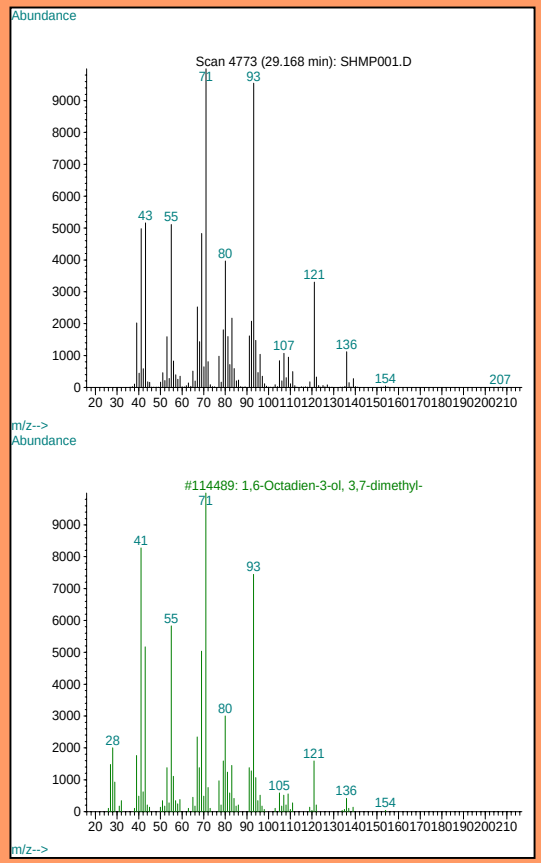
Selected Spectra From Shampoo

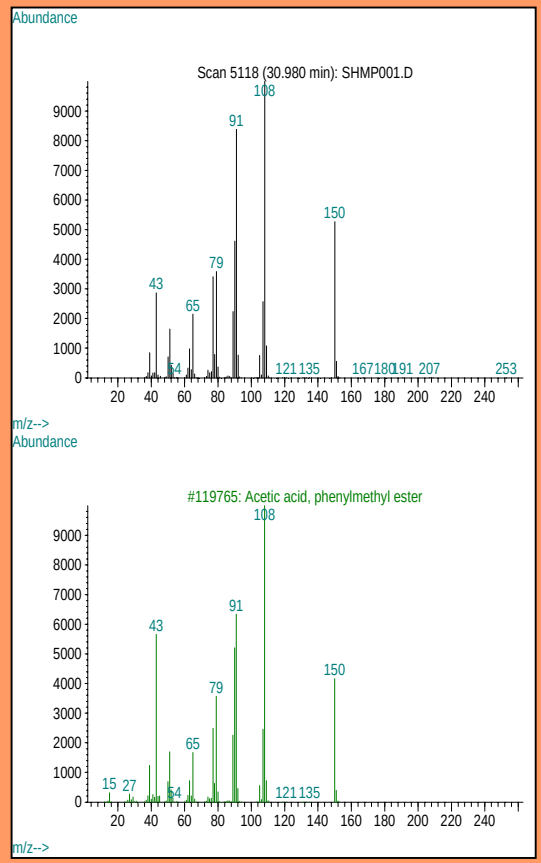
Ethyl-2-Methyl Butyrate



Linalool



Benzyl Acetate



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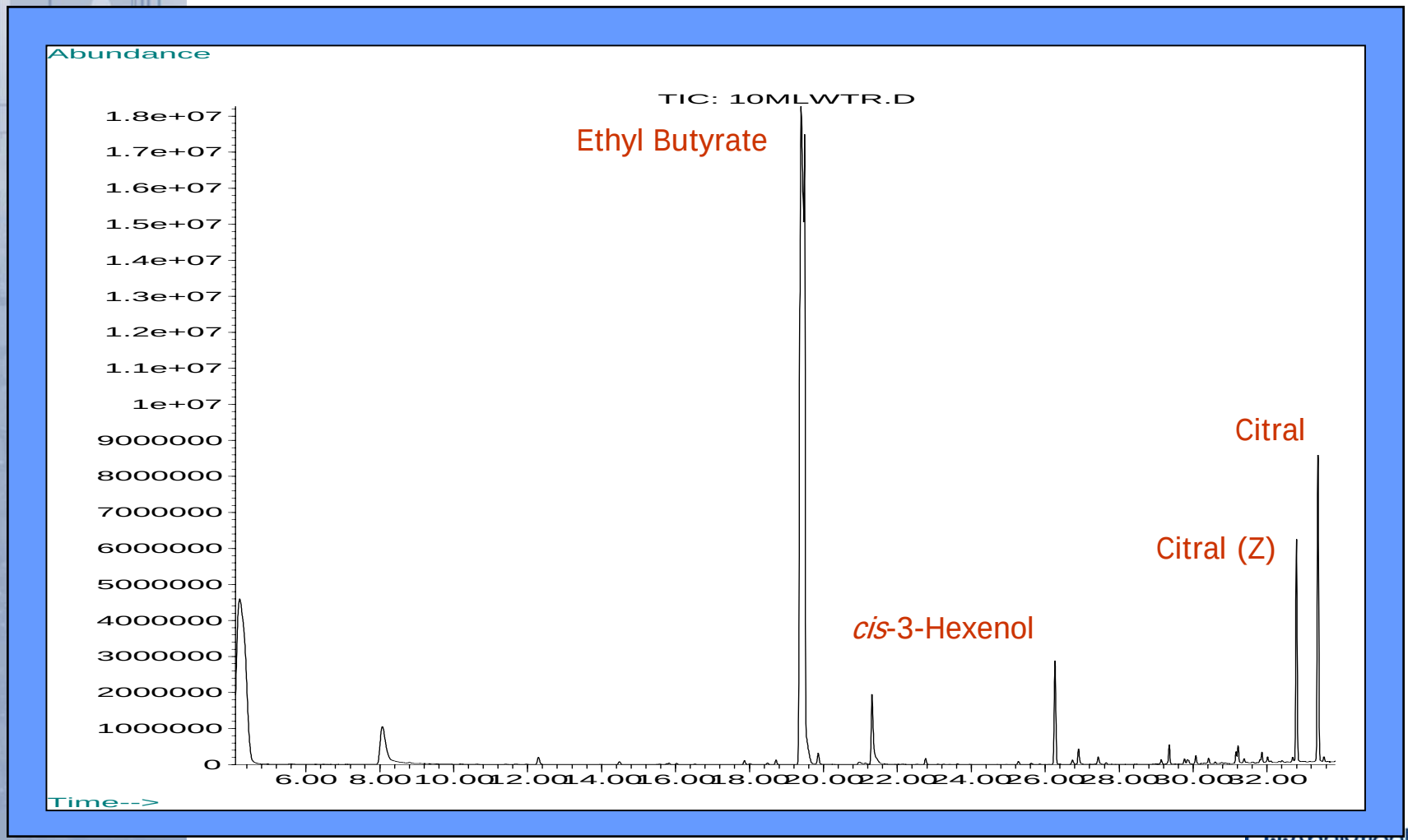
TIC of VOCs in 10 mL Flavored Water



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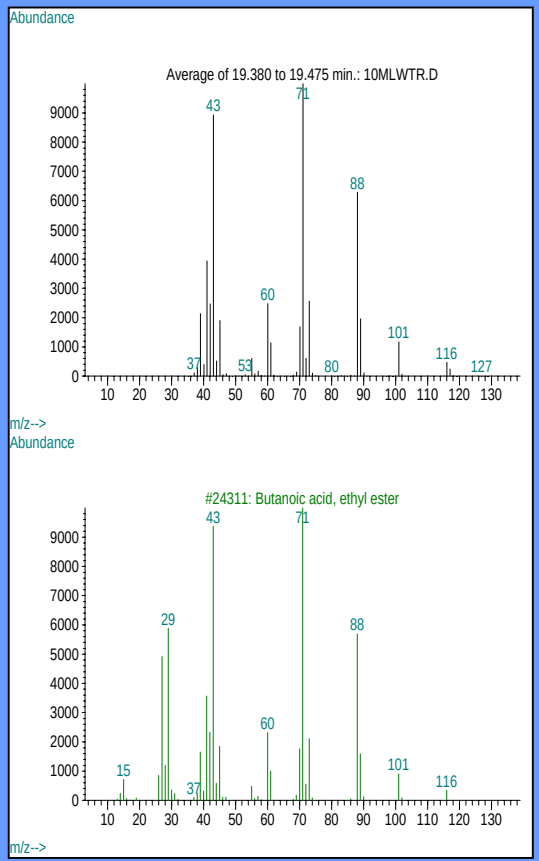
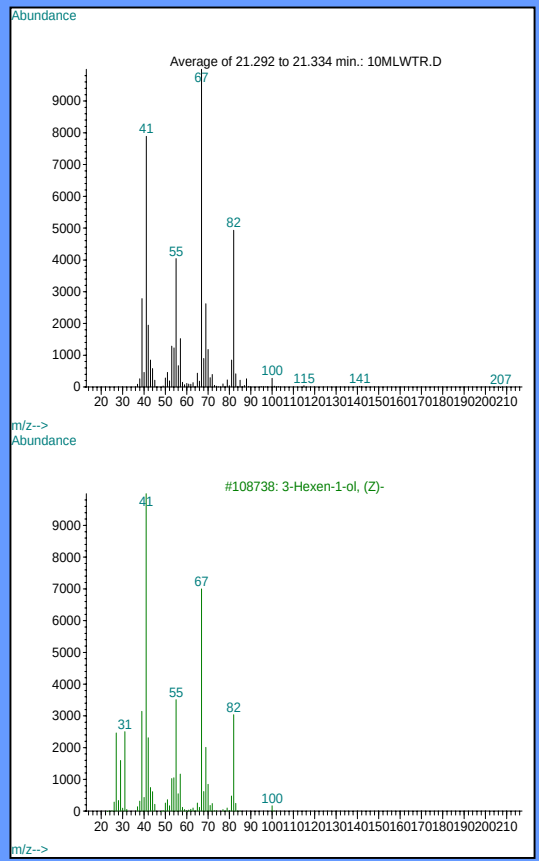
Selected Spectra From Flavored Water

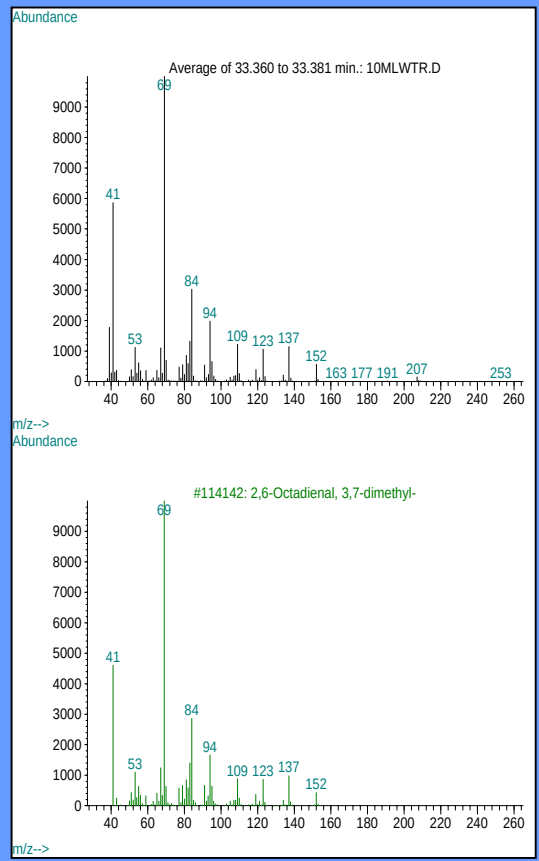
Ethyl butyrate



cis-3-Hexenol



Citral



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Summary: VOCs in Non-Food Products

- The VOCs detected in the non-food consumer products were primarily flavor and fragrance compounds.
  - *Identification by comparison to NIST Library spectra*
- The model 4552 Water/Soil Autosampler was operated in the “Soil” mode.
- All of the samples were analyzed using the Eclipse 4660 P&T Sample Concentrator.

Conclusion

- The Model 4660 Eclipse P&T Sample Concentrator and Model 4552 Water/Soil Autosampler can be used to test for low levels of benzene and other VOCs in beverages, table-ready foods, and non-food consumer products.
- All of the beverage and food samples tested for this project were either ND for benzene or contained benzene at concentrations below the USEPA water quality level of 5 ppb.
- For information on the Eclipse P&T Sample Concentrator and the 4552 Water/Soil Autosampler, contact your OI Account Representative or call 979-690-1711.

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