TELEDYNE TEKMAR
A Teledyne Technologies Company

Analysis of Volatile Organic Compounds in Different Beverages

By: Tyler Trent

Abstract

Volatile Organic Compounds (VOCs) have been a major concern of the U.S. Environmental Protection Agency (USEPA) leading strict regulations of VOCs present in drinking water. This study will focus on the amount of VOCs present in commercially available beverages. The analysis will utilize the Atomx, an automated VOCs sample prep system with an in-vial purge, in conjunction with gas chromatography-mass spectrometry (GC/MS). The in-vial purge allowed the difficult matrixes of the beverage samples to be tested utilizing a purge and trap system.

Introduction

Due to their long and short-term adverse health effects, VOCs continue to be strictly regulated by the USEPA. USEPA Method 8260C was used due to the large number of regulated VOCs contained on its approved testing list. VOCs are a group of low molecular weight aliphatic and aromatic compound with low boiling points that could cause harm to the human body if exposed to high levels of certain VOCs.[1] Major sources of VOCs include solvents, chemical intermediates, commercial packaging and drinking water disinfection byproducts.[1]

For this study a market basket survey was performed on commercially available sodas. For each soda, three brands were chosen for analysis. Also each brand contained three subsets: regular, diet and zero calories sodas, analyzed in both cans and plastic bottles.

Commercially available beverages were analyzed for their VOC content utilizing Teledyne Tekmar's Atomx Automated VOC Sample Prep System in conjunction with an Agilent 6890/5973 GCMS. The Atomx integrates a multi-matrix autosampler with a Purge and Trap concentrator. Employing a proprietary adsorbent trap, samples were evaluated using USEPA method 8260C.[2]

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Experimental-Instrument Conditions

GC Parameters	
GC:	Agilent 6890 Series GC System
Column	J&W DB-VRX 30m X 0.25mmID X 1.40µmdf
Oven Program:	35°C for 4 min; 16°C/min to 85°C for 0 min; 30°C /min to 210°C for3 min, 14.29min runtime
Inlet:	220°C
Column Flow	0.9mL/min
Gas:	Helium
Split:	80:1
Pressure:	6.06psi
Inlet:	Split/Split less

MSD Parameters	
MSD:	Hp 5973 Mass Selective Detector
Source:	230°C
Quad:	150°C
Solvent Delay:	0.5 min
Scan Range:	25-300 m/z
Scans:	5.10
Threshold:	400
MS Transfer Line Temp:	230°C

Tables 1 & 2: CG and MSD Parameters

Atomx Soil Parameters			
Variable	Value	Variable	Value
Valve oven Temp	140°C	Purge Time	11.00 min
Transfer Line Temp	140°C	Purge Flow	40mL/min
Sample Mount Temp	90°C	Purge Temp	20°C
Water Heater Temp	90°C	Condensate Purge Temp	20°C
Sample Vial Temp	25°C	Dry Purge Time	2.00 min
Prepurge Time	0.00 min	Dry Purge Flow	100mL/min
Prepurge Flow	0 mL/min	Dry Purge Temp	20°C
Preheat Mix Speed	Medium	Methanol Needle Rinse	Off
Sample Preheat Time	0.00 min	Methanol Needle Rinse Volume	3.0mL
Soil Valve Temp	100°C	Water Needle Rinse Volume	7.0mL
Standby Flow	10mL/min	Sweep Needle Time	0.25 min
Purge Ready Temp	40°C	Desorbs Preheat Time	245°C
Condensate Ready Temp	45°C	GC Start Signal	Start of Desorbs
Presweep Time	0.25 min	Desorbs Time	2.00 min
Water Volume	10mL	Drain Flow	300mL/min
Sweep Water Time	0.25 min	Desorbs Temp	250°C
sweep Water Flow	100mL/min	Bake Time	2.00 min
Sparge Vessel Heater	Off	Bake Flow	400mL/min
Sparge Vessel Temp	20°C	Bake Temp	280°C
Purge Mix Speed	Slow	Condensate Bake Temp	200°C

Table 3: Atomx Soil Parameters

(Parameters highlighted in yellow were not used.)

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Calibration

A 50ppm working calibration standard was prepared in methanol utilizing six commercially available stock standards from Restek Corporation to provide a list of 94 compounds of USEPA Method 8260C regulated compounds. Standard preparation for the final working solution is outlined in Table 4.

Cat#	Name	Concentration	Amount	Vol.	Final Conc.
30633	8260B MegaMix®	2000µg/mL	250µL	10mL	50 ppm
30489	8260B Acetate Mix	2000µg/mL	250µL	10mL	50 ppm
30465	California Oxygenates Mix	2000 – 10,000µg/mL	250µL	10mL	50 ppm
30042	502.2 Calibration Mix (Gases)	2000µg/mL	250µL	10mL	50 ppm
30265	2-Chloroethyl Vinyl Ether	2000µg/mL	250µL	10mL	50 ppm
30006	VOA Calibration Mix (Ketones)	5000µg/mL	100µL	10mL	50 ppm

Table 5: Stock Standard Solution

Working stock standards were generated from 1-200ppb similar to the 8260C soil analysis method by diluting the stock standard to final volume in a flask using reagent water. A 25ppm internal standard (IS) was prepared in methanol and transferred to one of the three standard addition vessels on the Atomx. Using the standard addition feature, the Atomx transferred the IS in 5µL aliquots providing a constant final concentration of 25ppb.

Agilent Chemstation software was used to process the calibration data. The relative response factors (RRF) of all target analytes were evaluated for average RRF and percent relative standard deviation (%RSD) over the calibrated range. The calibration met the USEPA 8260C performance criteria for the soil analysis method.[2]

Sample Analysis Technique

This study utilizes 8260C soil analysis method to purge the beverage sample in-vial instead of the standard water method sparge vessel. 5mL or 5 grams of sample is placed in a 40mL VOA vial along with a magnetic mixing bar and then is capped and sealed. The Atomx adds 10mL of reagent water, while an inert purge gas is introduced directly into the sample by a patented 3 stage needle. The purge gas exits the vial along with the extracted compounds of interest on to a sorbent tube or “trap”. Once all of the analytes have been deposited onto the trap it is heated and desorbed to the GC/MS system for separation and identification. Illustrations 1 and 2 below show the purge and desorb flow paths respectively.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

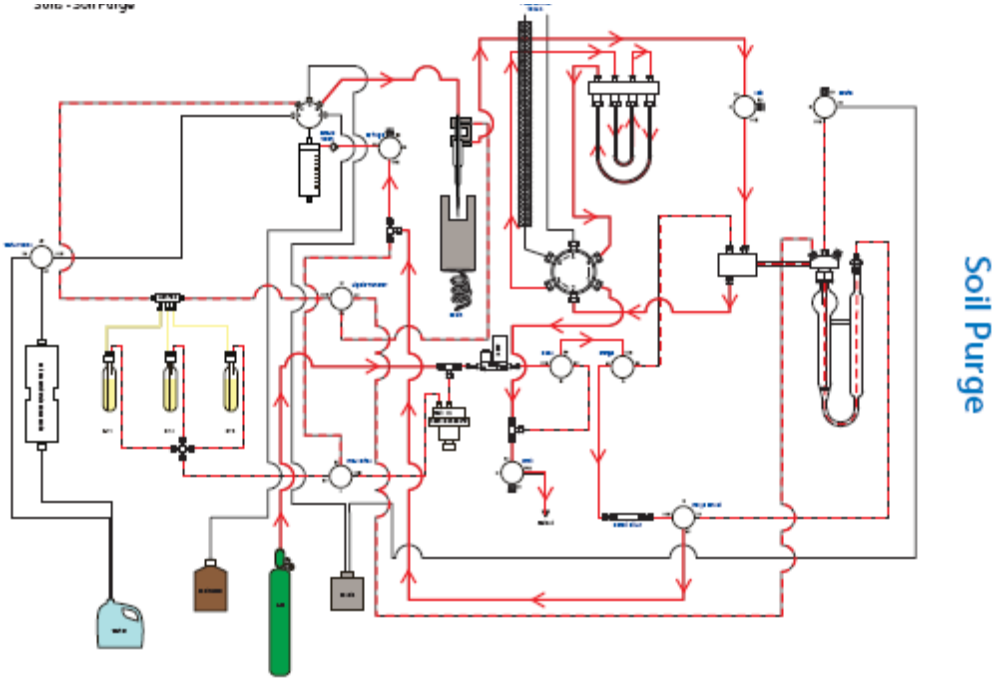

Illustration1: Purge

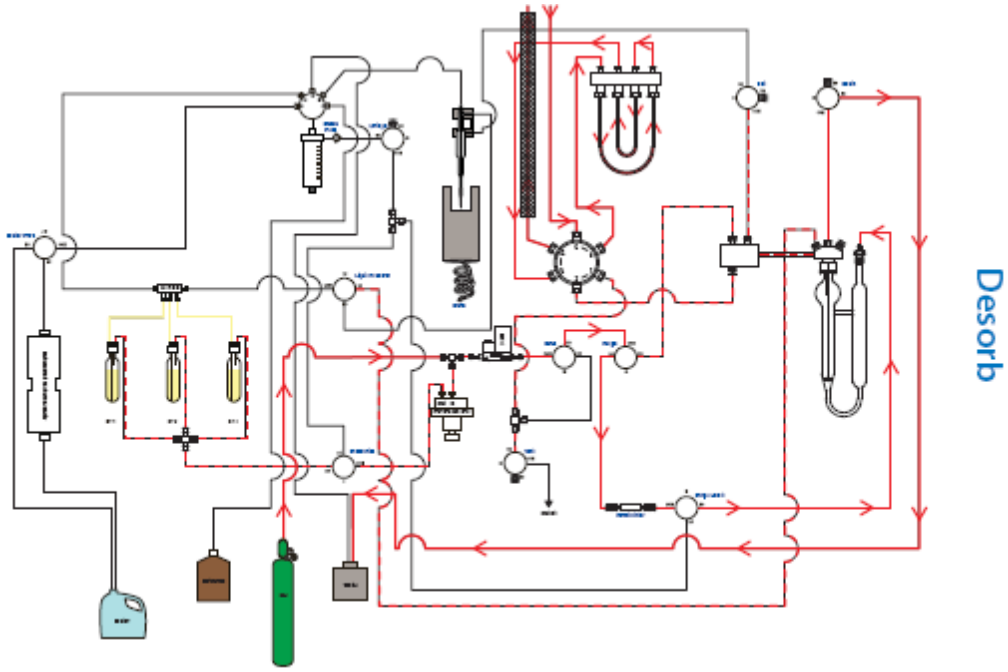

Illustration 2: Desorb

Results and Chromatograms

The beverages analyzed have a complex matrix of sugars and acids which may contaminate the system. Some of the beverages are also carbonated and may de-carbonate during sample transfer creating potentially different sample volumes when transferred from the vial to the purge vessel. Since the Atomx utilizes soil methods, the in-vial purge is critical to minimizing these potential sample matrix effects.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

The in-vial purge will permit for both the flavoring agents and the VOCs to be purged from the beverage sample on to the trap. In conjunction with the Atomx, a GC/MS will allow for the compounds to be adequately separated and indentified.

There are two main regions identified in the Total Ion Chromatogram (TIC) shown in Figure 1. The first region occurs in the two to ten minute range, where the VOCs are most likely to be present. The second region, from ten to thirteen minutes is the flavoring agents that elute from the beverage samples.

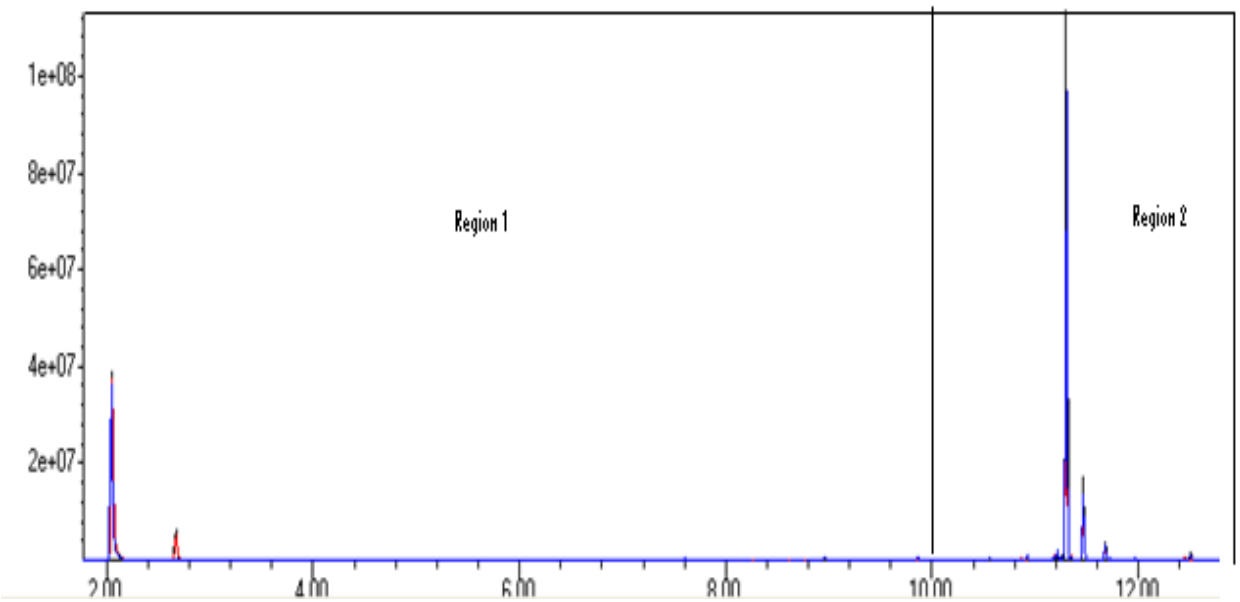

Figure 1: Comparison of the Total Ion Chromatogram (TIC) from regular (Blank), diet (Red), 0 Calorie (Blue) sodas highlighting the VOC and flavor range in a can. The VOC range is from 2.5-10 minutes while the flavoring range is from 10-12 minutes.

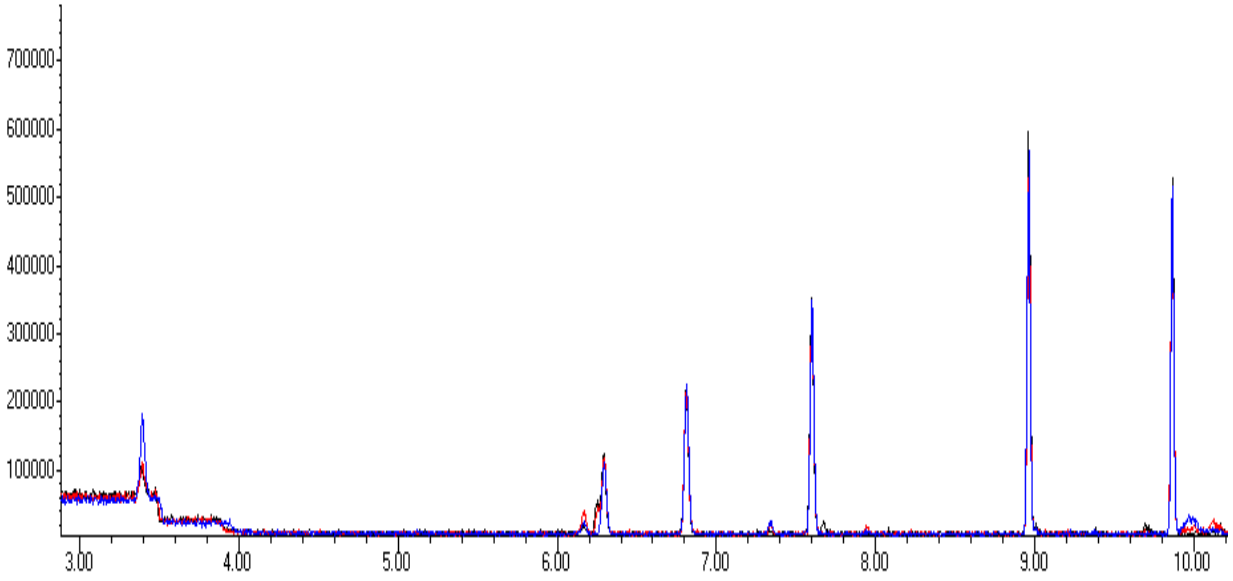

Figure 2: Comparison of the Total Ion Chromatogram Comparison of the Total Ion Chromatogram (TIC) from regular (Blank), diet (Red),0 calorie (Blue) sodas highlighting the VOC range.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

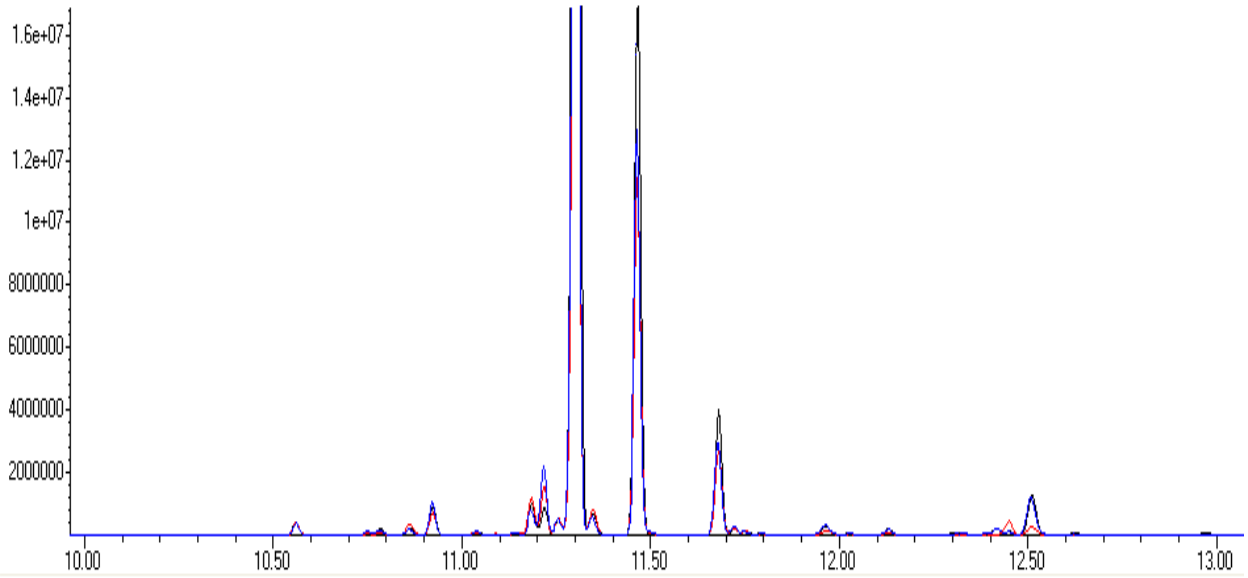

Figure 3: Comparison of the Total Ion Chromatogram (TIC) from regular (Blank), diet (Red), 0 calorie (Blue) sodas highlighting flavor range.

Figures 1-3 clearly demonstrate that the VOCs and flavoring compounds are separated by utilizing the Atomx's in-vial purge in conjunction with the GCMS. The VOCs present in the beverage samples were quantified based on an USEPA method 8260C calibration curve. The flavoring compounds were identified by library search using the Chemstation software.

Figure 2 shows that VOCS present in the beverage sample: acetone, ethyl acetate, chloroform, bromodichloromethane, benzene and styrene. All three brands contained a mixture of these six VOCs. Table 5 shows the differences in VOC content between the different beverages.

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Brand A						
	Regular Soda		Diet Soda		Zero Cal Soda	
Compound	Can	Bottle	Can	Bottle	Can	Bottle
Acetone	30.89	28.55	37.39	19	133.86	17.09
Ethyl Acetate	23.69	57.51	15.22	26.02	>MDL	>MDL
Chloroform	2.11	11.57	5.65	16.41	2.93	15.28
Bromodichloromethane	>MDL	1.94	>MDL	2.38	>MDL	2.6
Benzene	>MDL	>MDL	1.05	>MDL	1.33	>MDL
Brand B						
	Regular Soda		Diet Soda		Zero Cal Soda	
Compound	Can	Bottle	Can	Bottle	Can	Bottle
Acetone	27.21	29.59	19.6	25.82	34.86	86.87
Chloroform	1.67	39.07	21.62	41.2	23.74	47.18
Bromodichloromethane	>MDL	3.98	2.59	3.98	2.64	4.46
Styrene	1.81	>MDL	>MDL	>MDL	>MDL	>MDL
Brand C						
	Regular Soda		Diet Soda		Zero Cal Soda	
Compound	Can	Bottle	Can	Bottle	Can	Bottle
Acetone	21.38	19.61	20.93	23.78	355.46	99.16
Ethyl Acetate	>MDL	15.59	32.91	34.34	>MDL	>MDL
Chloroform	5.51	3.16	4.13	4.19	4	6.82
Benzene	>MDL	>MDL	>MDL	>MDL	1.87	>MDL
Bromodichloromethane	1.4	>MDL	1.096	>MDL	>MDL	1.49
Styrene	1.08	1.5	>MDL	>MDL	>MDL	>MDL

Table 5: Identification of VOCs found during an in vial purge of soda samples.

(All results are listed in ppb)

The USEPA has placed strict limits on the amount of VOCs allowable in drinking and waste water, but not set limits on the amounts allowable in commercially available beverages. Table 6 shows VOC content of both can and bottles for each brand type.

The beverages analyzed contained 2 of the 4 Trihalomethanes (THMs), chloroform and bromodichloromethane. THMs are by products of chlorine disinfection of drinking water. USEPA limits total THMs to 80ppb, with only 70ppb of chloroform allowable. As Table 5 shows the total THMs are below USEPA regulatory limit.[3]

Benzene is another heavily monitored VOC, with a USEPA limit of 5ppb in drinking water. Benzene contamination occurs from sources such as solvents in printing, paints and from water source. Table 5 shows only three samples containing benzene, but is below the 5ppb limit. Styrene was also present in three samples ranging from 1.08 to 1.81ppb, well below the 100ppb USEPA limit.[3]

Two other compounds monitored by the USEAP without regulatory limits are acetone and ethyl acetate. These two compounds were the greatest source of VOC contamination in all the samples. In doing this analysis Table 5 shows that all six compounds were found in compliance with the USEPA regulatory limit in drinking water.[3]

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com

Conclusions

The Atomx proves to be a valuable tool to any laboratory by meeting the strict precision and accuracy requirements of USEPA method 8260C, while retaining the flexibility of a multi-matrix autosampler. This study utilizes an in-vial purge to separate VOCs and flavoring agents. The in-vial purge allows complex matrixes to remain in the vial and be purged instead of sending them through the system keeping the subsystem free and clear of sugars and acids. This promotes rapid analysis to minimize the down time for cleaning and repair. Even though USEPA and USFDA have no regulations on VOCs in soda, all of the beverage samples tested below the drinking water limits set forth by both originations. Given the multiple options integrated into the Atomx Automated VOC Sample Prep System including direct liquid purging, in vial purging and automated methanol extractions. The ability to test or experiment for several types of analyses is available to the user in a single platform.

References

1. Mary Ellen Fleming-Jones and Robert E. Smith Journal of Agriculture and Food Chemistry 2003, 51, 8120-8127
2. USEPA Method 8260C Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Revision 3, August 2006
3. USEPA Drinking Water Contaminants http://water.epa.gov/drink/contaminants/index.cfm

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.teledynetekmar.com