

Compuestos orgánicos volátiles en productos de consumo.

Aplicación 046

RESUMEN

Los compuestos orgánicos volátiles (VOC) se han determinado en aguas de consumo y productos farmacéuticos. El interés por su determinación ahora se traslada a los alimentos. El sistema de preparación de muestra automatizado Modelo Atomx en conjunción con cromatógrafo de gases y detector de masas (GC/MS) permite la determinación de los compuestos VOC en alimentos. El sistema dispone de dos métodos de extracción; la purga directa desde el vial y la extracción automatizada con metanol.

Introduction

In the wake of the recent tragedy in the Gulf of Mexico, many have serious concerns about contamination from petroleum and the chemicals used to clean up the oil spill in the sea food produced from the Gulf of Mexico. In recent studies, the United States Food and Drug Administration (FDA) analyzed the nation's food supply for many chemical classes, such as residues of pesticides, industrial chemicals, metals, nutrients, and Volatile Organic Compounds (VOCs). In the past, the United States Environmental Protection Agency (USEPA) and FDA have analyzed drinking water for VOCs. Now that more people are concerned about contaminants in their food, the FDA has started to look for VOCs in everyday food. For this study, food samples were analyzed for VOC content. VOCs, by definition, are low molecular weight aliphatic and aromatic compounds with low boiling points¹. VOCs can come from solvents, chemical intermediates, and chlorination of drinking water. Some VOCs are allowed as indirect food additives from components of commercial packing.

In this study, an Atomx, automated sample prep system with an integrated purge and trap concentrator, was used in conjunction with an Agilent 6890/5973 gas chromatograph-mass spectrometer (GC-MS). Employing a proprietary #9 trap, food samples were evaluated using USEPA method 8260C².



Figure 1: Teledyne Tekmar Atomx Automated VOC Sample Prep System and Purge and Trap Concentrator. VOCs in Everyday Food

Experimental-Instrument Conditions

GC Parameters	
GC:	Agilent 6890 Series GC System
Column	J&W DB-VRX 30m X 0.25mmID X 1.40µm _{df}
Oven Program:	35°C for 4 min; 16°C/min to 85°C for 0 min; 30°C /min to 210°C for 3 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:	Agilent 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: GC 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	10 mL/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	10 mL	Drain Flow	300 mL/min
Sweep Water Time	0.25 min	Desorbs Temp	250°C
sweep Water Flow	100 mL/min	Bake Time	2.00 min

Spurge Vessel Heater	Off	Bake Flow	400 mL/min
Spurge Vessel Temp	20°C	Bake Temp	280°C
Purge Mix Speed	Slow	Condensate Bake Temp	200°C

Table 3: Atomx Soil Method Parameters

(Parameters highlighted in yellow were not used.)

Calibration

A 50ppm working stock standard was prepared in methanol utilizing six Restek stock standards providing 94 compounds of USEPA Method 8260C. Standard preparation 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 4: 50ppm Stock Standard Solution

Using the same scheme outlined in USEPA Method 8260C, calibration standards were generated from 2-200ppb by diluting the 50ppm stock standard with distilled water in volumetric flasks. 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 Atoms transferred the IS in 5µL aliquots providing a constant 25ppb concentration.

Agilent Chemstation software was used to process the calibration data. The relative response factors (RRF) of all target analytes were evaluated for average relative response factor (RRF) and %RSD. The calibration met all USEPA 8260C performance criteria².

Sample Preparation

For this study, the sample preparation is straightforward. Foods that required cooking were prepared per package instructions. Foods from fast food restaurants were obtained ready to eat. Once the foods were prepared the samples were chopped and frozen until analysis. Analysis utilized the Atomx soil method with an in-vial purge. 5 mL or 5 grams of sample was placed in a 40mL VOA vial along with a magnetic mixing bar, and then capped and sealed. The Atomx adds 10 mL 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 onto a sorbent 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.

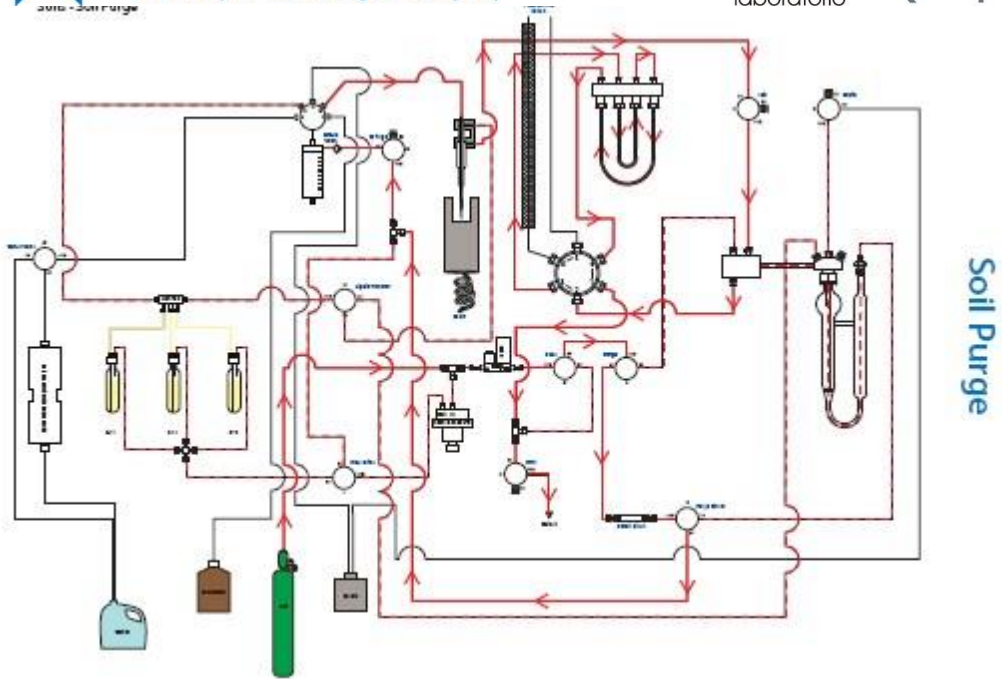


Illustration 1: Purge Flow Diagram

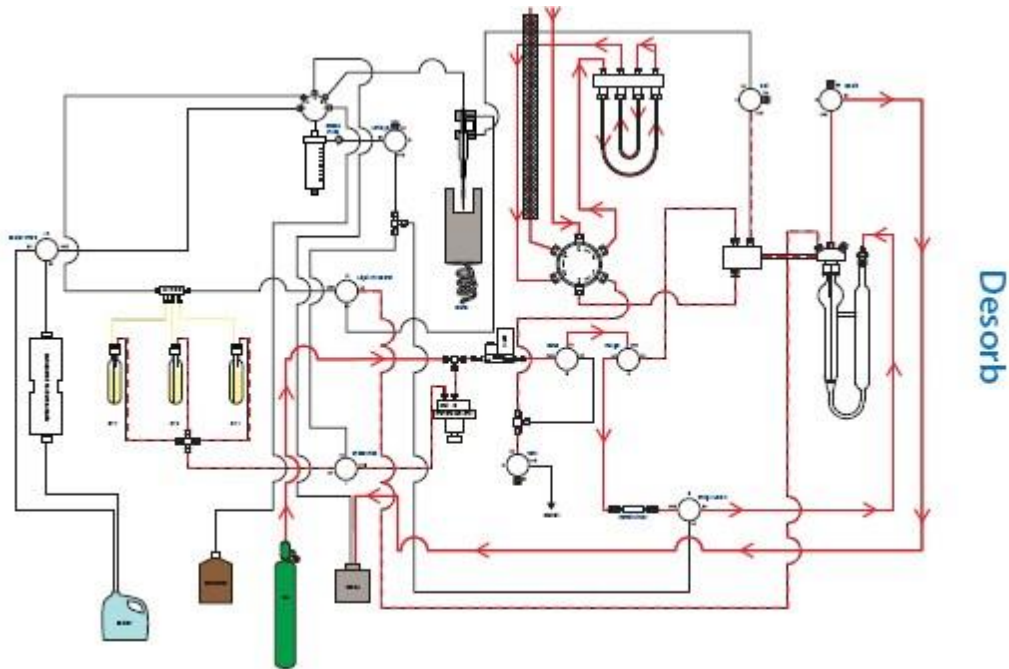


Illustration 2: Desorb Flow Diagram

Experimental Results

The table-ready foods (Table 5.) analyzed for this study have potentially complex matrixes of sugars, fats and acids which may contaminate other systems. The Atomx utilizes an in-vial purge, minimizing the potential sample matrix effects, while also permitting VOCs to be purged from the food and adsorbed on to the trap. In conjunction with the Atomx, a GC/MS will allow for the compounds to be separated and quantified. Figures 2-5 show the total ion chromatograms (TIC) for some of the table-ready foods that were tested in this application.

Orange (raw)	French Fries
Red Apple (raw)	Hard Boiled Egg
Bananas (Baby Food)	Bologna
Peaches (Baby Food)	Salami
Green Beans (Baby Food)	Mozzarella Cheese
Chicken Nuggets	Pouched Tuna
Cheese Burger	Pouched Salmon

Table 5: Foods Analyzed for VOCs

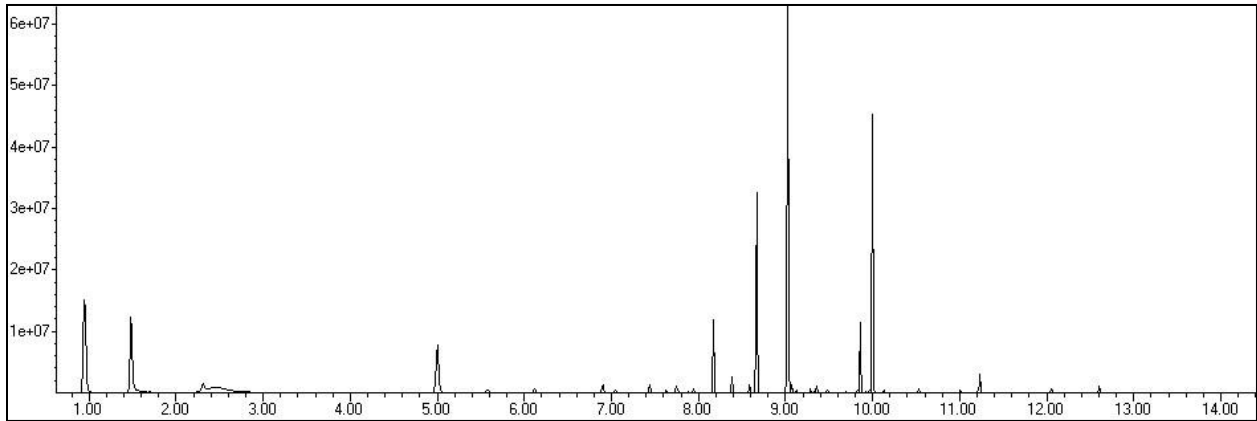


Figure 2: Total Ion Chromatogram (TIC) of VOCs present in an Apple sample.

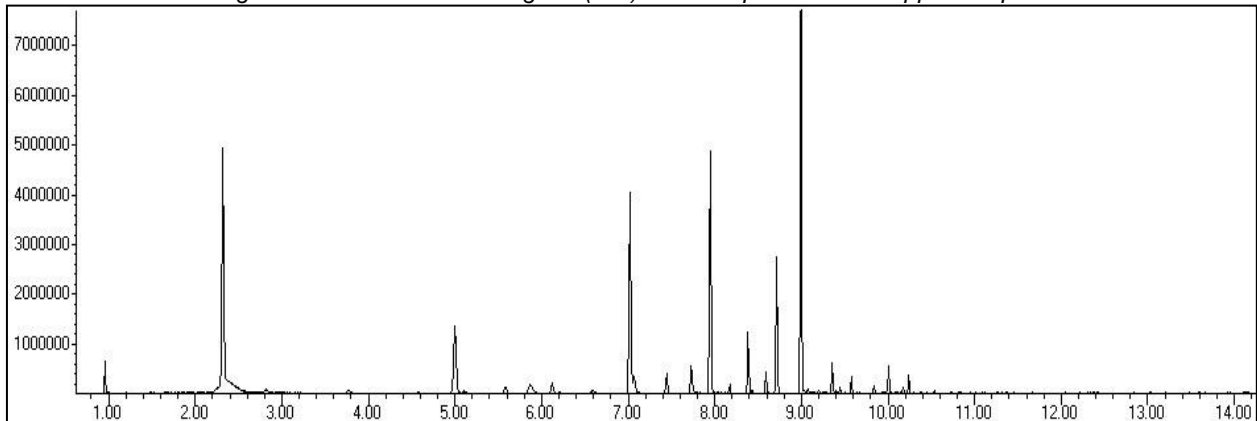


Figure 3: Total Ion Chromatogram (TIC) of VOCs present in a Banana (baby food) sample.

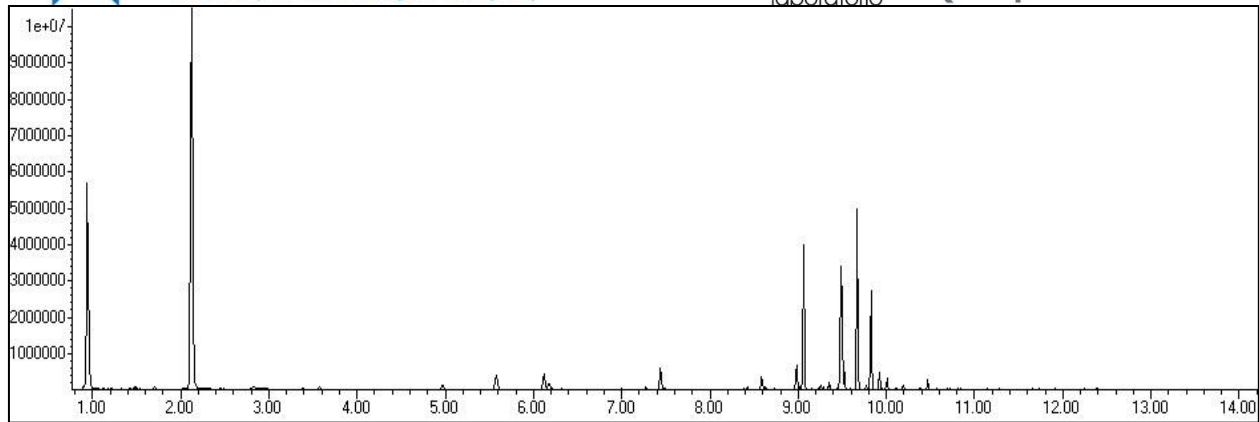


Figure 4: Total Ion Chromatogram (TIC) of VOCs present in Bologna sample.

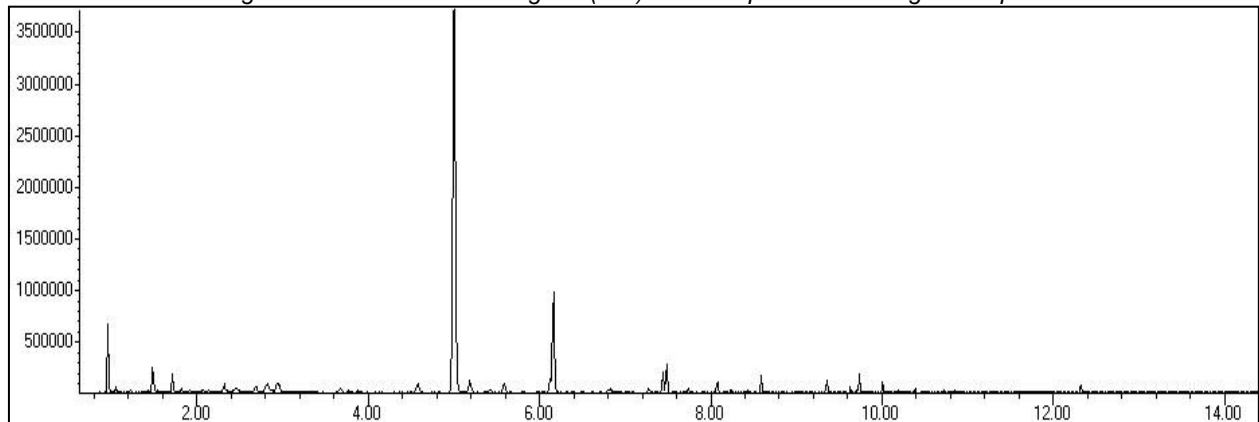


Figure 5: Total Ion Chromatogram (TIC) of VOCs present in Tuna sample.

Figures 2-5 clearly demonstrate capability of the Atomx to trap and separate VOC by utilizing an in-vial purge. The VOCs present in the food samples were quantified based on an USEPA Method 8260C calibration curve due to its wide range of compounds.

VOC content for the foods listed in **Table 5** ranged from 1-3000ppb. Due to the limited calibration range of 2-200ppb, any concentration outside this range is an estimated value. **Table 6** shows ten of the fourteen prospective food products and their VOC concentrations.

Although there is some exposure to VOCs in everyday food, the concentrations are below the maximum contamination limit set forth by the USEPA and the FDA³. Fleming-Jones and Smith state that while having some oral exposure to VOCs from food, they are usually inhaled at higher doses though everyday activity¹.

Salami		Bologna	
Compound	Concentration (ppb)	Compound	Concentration (ppb)
Carbon Disulfide	19.68	Carbon Disulfide	563.43*
Acetone	71.34	Acetone	26.93
2-Butanone (MEK)	48.59	Toluene	0.86*
Toluene	1.59*	p-Isopropyltoluene	10.28
p-Isopropyltoluene	3.76		
Bananas (Baby Food)		Green Beans (Baby Food)	
Compound	Concentration (ppb)	Compound	Concentration (ppb)
Acetone	112.77	Acetone	648.39*
Ethyl Acetate	1069.87*	2-Butanone (MEK)	36.36
n-Butyl Acetate	216.24*	Styrene	3.33
Styrene	2.48		
Cheese Burger		Chicken Nugget	
Compound	Concentration (ppb)	Compound	Concentration (ppb)
Acetone	74.27	Acetone	52.19
Chloroform	1.8	Chloroform	2.24
2-Butanone (MEK)	6.26	2-Butanone (MEK)	7.68
		p-Isopropyltoluene	3.56
Pouch Tuna		Pouch Salmon	
Compound	Concentration (ppb)	Compound	Concentration (ppb)
Carbon Disulfide	2.99	Carbon Disulfide	38.81
Acetone	120.27	Acetone	192.77
Ethyl Acetate	3166.14*	Ethyl Acetate	1483.17*
2-Butanone (MEK)	196.25	2-Butanone (MEK)	107.75
Isopropyl Acetate	5.27	Isopropyl Acetate	4.32
Toluene	24.09	Toluene	14.89
Red Apple		Mozzarella Cheese	
Compound	Concentration (ppb)	Compound	Concentration (ppb)
Ethyl Acetate	1408.95*	Acetone	115.79
n-Propyl Acetate	38.91	Chloroform	3.42
n-butyl Acetate	96.77	2-Butanone (MEK)	75.71
		p-Isopropyltoluene	2.41

Table 6: VOC Contaminates Found in Table Ready Food

* Estimated value, the concentration falls outside the calibration range of 2-200ppb

Conclusions

The Atomx proves to be a valuable tool 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 extract VOCs from table-ready food. The in-vial purge also allows for sampling of complex matrixes without the risk of contamination from the fats, sugars, and acids inherent in the foods. Keeping the system clean promotes rapid analysis, minimizing downtime for cleaning and repair. Even though USEPA and USFDA have no regulations on VOCs in food, all of the food samples tested below the drinking water limits set forth by both originations. The features of the Atomx Sample Prep System, including direct liquid purging, in-vial purging, and automated methanol extractions, give the ability to test several types of analyses on 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>