Determination of Volatile Components in Consumer Products Using Automated SPME and High-Speed GC-TOFMS

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Key Words: GC-TOFMS, SPME, Headspace, Low Thermal Mass (LTM), VOC's

1. Introduction

Increasing use of fragrances in consumer products and the decreasing air exchange rate of workplace buildings has focused attention on the toxicological properties of allergenic fragrance compounds. A growing number of people are claiming that exposure to certain fragrances, including perfumes and scented products, adversely impacts their health. Indoor allergens are biological or chemical substances that trigger the immune system, causing an allergic reaction. Biological sources of allergens include pets, insects, dust mites, plants, bacteria, and mold. Chemical sources are often gases or particles released by items such as building materials, fabrics, glues, paints, solvents, dyes, and perfumes.

More than 5,000 different fragrances are in products that are used on a daily basis. These products include health and beauty aids, household cleaners, laundry aids, paper products, plastics, and even foods. Since fragrance formulas are considered trade secrets, manufacturers only have to print "fragrance" on the label and do not need to identify the chemical makeup.

Allergenic fragrance compounds can enter the body through the nose by inhalation, the mouth by ingestion, or the skin by absorption. Allergens can affect the lungs, nose, skin, eyes, and brain. Studies have shown that shortness of breath or asthma-like symptoms have been caused by allergenic compounds. Most of the fragrance chemicals consist of volatile organic compounds, which are known to be respiratory irritants. Studies have shown that inhaling fragrances can also cause circulatory changes and electrical activity in the brain. These changes can trigger migraine headaches, the inability to concentrate, dizziness, and fatigue. The number one cause of adverse skin reactions to cosmetics and laundry products is allergens in fragrance.

This report describes methodology and instrumentation used to rapidly screen consumer products for known allergens in fragrance. Analytical standards for benzyl alcohol, diethyl phthalate, and linalool are used to generate calibration curves covering a concentration range from low parts-per-billion (ppb) to parts-per-million (ppm).

A Pegasus® III GC-TOFMS equipped with an automated Solid Phase Microextraction (SPME) sample preparation and fiber injector unit is used with a dual-column, Low Thermal Mass (LTM) system for rapid qualitative and quantitative sample analysis. The LTM technology allows the temperature-programming rate of the capillary columns to be ramped relatively fast (up to 1800°C/minute). In addition to fast heating, the LTM columns are mounted outside the GC oven, which allows rapid cooling. The combination of automated SPME sampling, rapid temperature programming, and decreased column cooling time results in High-Speed sample analysis and increased laboratory productivity.

2. Experimental Conditions

Instrument Conditions (GC-TOFMS)

GC:
Agilent 6890 Equipped with LTM column modules connected in series

Column 1:
10 m x 0.18 mm x 1.5 µm, Rtx-TNT

Column 2:
5 m x 0.18 mm x 0.2 µm, Rtx-5

Carrier Gas:
He at constant flow of 1.5 mL/minute

Inlet Temperature:	200°C
Injection:	SPME
Split Ratio:	25:1
MS:	LECO Pegasus TOFMS
Ionization:	EI at 70 eV
Mass Range (u):	35 to 350
Acquisition Rate:	20 spectra/second
Source Temp:	200°C
Transfer Line Temp:	280°C

Operating Conditions

Main Oven Program: 250°C isothermal

LTM Program

LTM column 1:
30°C for 0.5 minute → 400°C/minute → 250°C, hold for 2.0 minutes

LTM column 2:
30°C for 0.5 minute → 60°C/minute → 250°C, hold for 0.5 minutes

Total Program Time: 4.67 minutes

SPME Conditions

Fiber:	75 µm Carboxen – PDMS
Vial Equilibration Temperature:	30°C
Extraction Time:	0.5 minute
Desorption Time:	0.25 minute

Sample Preparation

Neat samples of deodorant, soap, facial cleansing wipe, and men's cologne were transferred into individual 20 mL headspace vials. Samples are listed as D(1), D(2), Face Wash, Soap, C(1), C(2), C(3), and C(4) respectively in Tables 1 and 3. To minimize carryover, a laboratory blank was analyzed after each sample.

3. Results

High-Speed analysis of each sample was performed on the Pegasus III GC-TOFMS according to the developed methodology listed above. This methodology allowed for a qualitative screening of each consumer product. Identified compounds relative to known allergens are listed in Table 1. A chromatogram of a commercial deodorant is shown in Figure 1. Peak deconvolution, as well as mass spectral information is featured in Figure 2 and Figure 3, respectively.

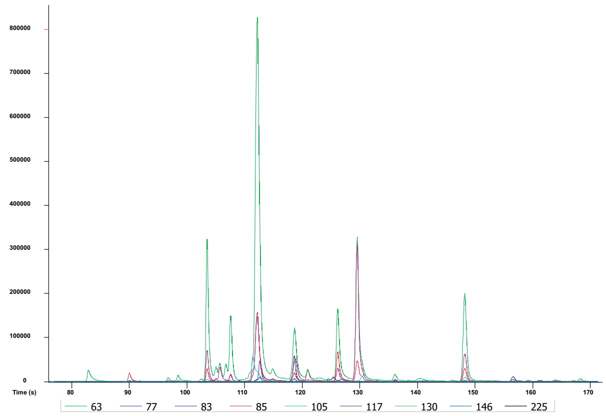


Figure 1. Chromatogram of automated SPME headspace from a commercial deodorant, D(1), analyzed by High-Speed GC-TOFMS. The most abundant unique ions are plotted as a function of time. Over 125 compounds were detected with a signal-to-noise of greater than 100.

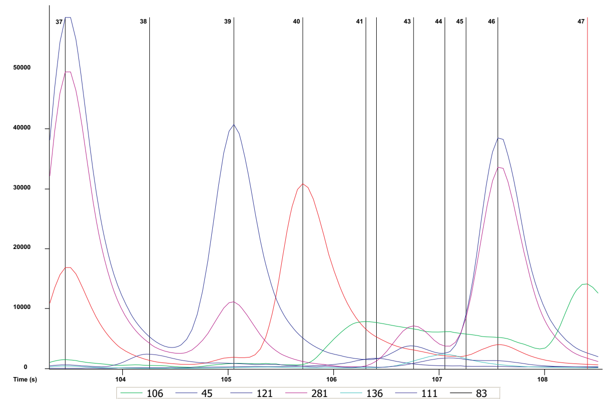


Figure 2. Chromatogram of deodorant-D(1), SPME headspace analysis showing the complexity of the sample between 100 seconds and 110 seconds. Unique ions are plotted for identified compounds as a function of time. The ability to deconvolute overlapping peaks is imperative for High-Speed analysis. ChromaTOF software with spectral deconvolution was able to identify 11 peaks with a signal-to-noise ratio of 100 in this 10-second time window.

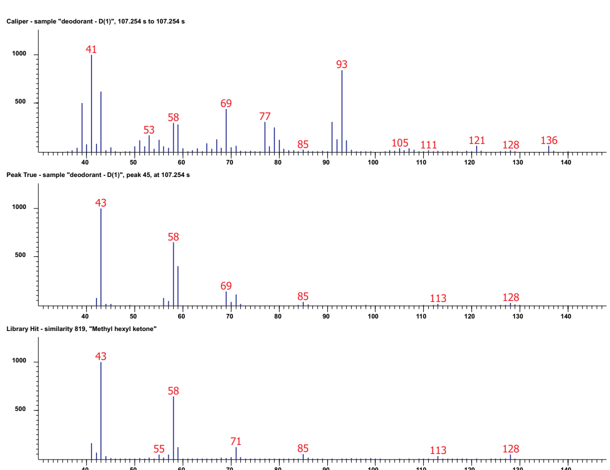


Figure 3. Spectral deconvolution of peak 45 as displayed in Figure 2. Notice the removal of interfering spectra from overlapping compounds 44 and 46 as shown in the 'Caliper' and the 'Peak True', (deconvoluted spectrum). The result of the deconvolution is a spectral similarity match of 819 out of a possible 1000 for methyl hexyl ketone.

Table 1. Identified Allergens in Consumer Products

Name	Unique Ion	D(1)	D(2)	F.Wash	Soap	C(1)	C(2)	C(3)	C(4)
Benzyl alcohol	108	*	N/D	*	N/D	*	N/D	N/D	*
Limonene	68	*	*	*	N/D	*	*	*	*
Linalool	71	*	*	*	*	*	*	*	*
Eucalyptol	81	*	N/D	*	N/D	*	N/D	*	*
a-phellandrene	93	*	*	*	*	N/D	*	*	*
diethyl phthalate	146	*	*	*	*	*	N/D	*	*
Camphene	93	N/D	*	*	N/D	N/D	N/D	N/D	*
Methyl 2-octynoate	66	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Citronellol	69	N/D	*	N/D	N/D	N/D	N/D	*	*
Nerol	69	N/D	*	*	*	Nerol Acetate	Nerol Acetate	Nerol Acetate	Nerol Acetate
Neral	94	N/D	N/D	N/D	N/D	*	N/D	*	N/D
Cinnamic aldehyde	131	N/D	N/D	N/D	N/D	N/D	N/D	N/D	*
Geraniol	41	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Geranial (Citral)	69	N/D	N/D	N/D	N/D	*	N/D	*	*
p-Anisyl alcohol	138	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Hydroxycitronellal	59	N/D	N/D	N/D	N/D	N/D	N/D	N/D	*
Cinnamic alcohol	92	N/D	N/D	N/D	N/D	N/D	N/D	N/D	*
Eugenol	164	N/D	N/D	N/D	N/D	*	N/D	N/D	*
Coumarin	118	N/D	N/D	N/D	*	N/D	N/D	N/D	*
Isoeugenol	164	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
a-Isomethyl ionone	135	N/D	*	*	N/D	*	*	*	*
Lilial	189	N/D	*	N/D	N/D	*	*	*	*
a-Amylcinnamic aldehyde	129	N/D	N/D	N/D	N/D	N/D	N/D	N/D	*
a-Amylcinnamic alcohol	115	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Farnesol	81	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Hexyl cinnamic aldehyde	129	N/D	*	N/D	N/D	N/D	N/D	N/D	N/D
Benzyl benzoate	105	N/D	N/D	N/D	N/D	N/D	N/D	N/D	*
Benzyl salicylate	91	N/D	N/D	N/D	N/D	*	N/D	N/D	N/D
Benzyl cinnamate	131	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D

**denotes identified compound*
N/D = not detected

Calibration Curves

Analytical standards for linalool, benzyl alcohol, and diethyl phthalate were obtained from Aldrich Chemical Company (Allentown, PA). Aqueous samples were prepared in HPLC grade water and transferred to 20 mL headspace vials. A concentration range of 1 ppb to 1 ppm was covered. The standards were run in replicate under identical chromatographic conditions as the consumer products. Figure 4 shows the calibration curve for linalool. Calibration curves were automatically created with LECO's ChromaTOF® software. Quantitative results were acquired by re-processing the originally acquired data for the consumer products with the analytical curves. ChromaTOF software automatically determines quantitative results based on the addition of the analytical curves into the data processing method. Calibration curve statistics are listed in Table 2. Analytical results for the consumer products are listed in Table 3.

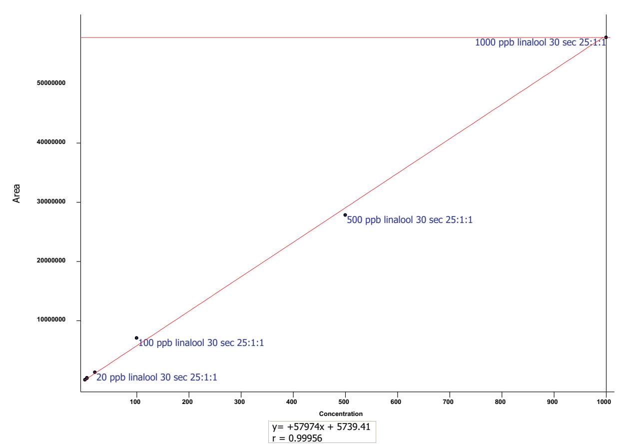
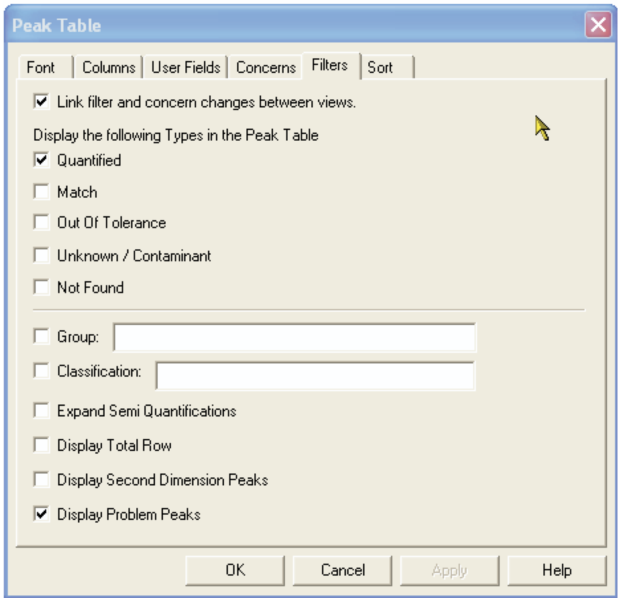


Figure 4. Calibration curve constructed by ChromaTOF software for linalool. A concentration range of 1 ppb to 1 ppm was covered with a regression coefficient of 0.9996.

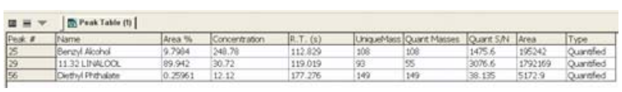
Table 2. Data for Analytical Standards

Name	Quant Mass	R^2 value
Benzyl Alcohol	108	0.9998
Diethyl Phthalate	149	0.9994
Linalool	55	0.9996

Viewing Data After Reprocessing With Calibration Data

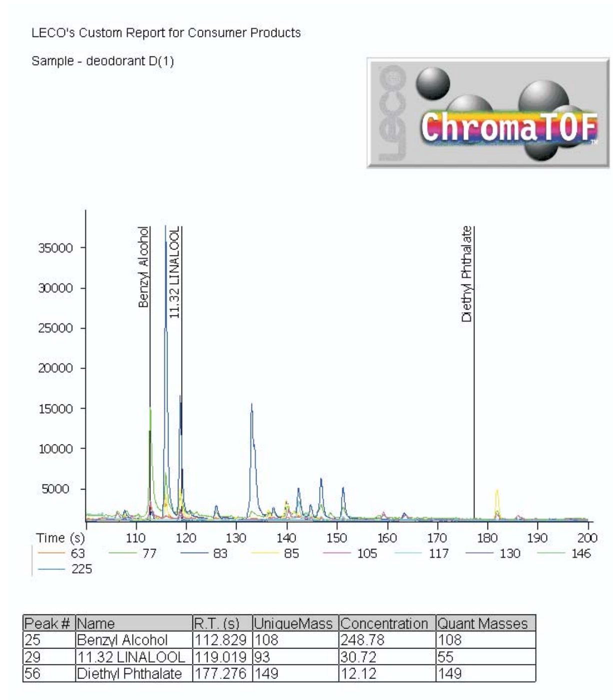


Acquired data can be easily reprocessed with ChromaTOF software for quantitative results. Peak Table results can be filtered to show only quantitative results by selecting the desired filter from the Peak Table properties window (above). The filtered Peak Table results for deodorant-D(1) are shown below.



Peak #	Name	Area %	Concentration	R.T. (s)	UniqueMass	Quant Masses	Quant S/N	Area	Type
25	Benzyl Alcohol	9.7984	248.78	112.829	108	108	1475.6	195242	Quantified
29	11.32 LINALOOL	89.942	30.72	119.019	93	55	3076.6	1792169	Quantified
56	Diethyl Phthalate	0.25961	12.12	177.276	149	149	38.135	5172.9	Quantified

In addition to user-specific Peak Tables, ChromaTOF software can automatically generate custom reports directly from the processed data. In the example below, deodorant – D(1) was processed against the calibration curves for benzyl alcohol, diethyl phthalate, and linalool. The generated report includes the chromatogram with quantified peak labeled and a Peak Table that displays the quantitative data.



Peak #	Name	R.T. (s)	UniqueMass	Concentration	Quant Masses
25	Benzyl Alcohol	112.829	108	248.78	108
29	11.32 LINALOOL	119.019	93	30.72	55
56	Diethyl Phthalate	177.276	149	12.12	149

Table 3. Semi-Quantitative Results for Automated SPME Analysis of Consumer Products with High-Speed GC-TOFMS.

Sample	Benzyl Alcohol	Diethyl Phthalate	Linalool
	Concentration [ppb]		
deodorant - D(1)	248	30	12
deodorant - D(2)	N/D	6	83
Face Wash	86	0.4	15
Soap	N/D	2	3.74
men's cologne - C(1)	24	17.5	5.63
men's cologne - C(2)	N/D	N/D	1.54
men's cologne - C(4)	N/D	11.67	5.18
men's cologne - C(4)	35	0.1	79.38

(N/D) = not detected

Note: Concentration of compounds from neat samples was determined from calibration curves generated from SPME headspace extraction of aqueous standards.

4. Conclusion

The Pegasus III GC-TOFMS equipped with an automated SPME autosampler and LTM column(s) is well-suited for rapid screening of environmental, biological, and food and flavor samples. The work presented here demonstrates the use of LTM technology for rapid screening of allergens in consumer products by automated SPME. Both qualitative and quantitative data was generated. Data processing of the samples, as well as the calibration standards, was easily performed with ChromaTOF software. Final results can be formatted into custom reports or archived to disk for further review. The use of LTM technology allows laboratories to increase daily productivity without sacrificing analytical results.

5. References

Fragrance contact allergy: A Clinical Review. Am. J. Clin. Dermatol. 2003, 4, (11), 789-798.

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