Analysis of Perfumes With SPME and High-Speed GC-TOFMS

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

1. Introduction

The quality of indoor air has become a major concern to the entire population as well as the 20 million or more people who have developed allergies from unlabeled allergens in fragrance products.[1] Numerous reports have described the "sick building syndrome" which has been associated with the quality of indoor air in public buildings.[2-4] Building environment related health problems may be due to contamination of indoor air by emissions of volatile organic compounds (VOC's) from a variety of sources including construction materials, fabrics, furnishings, maintenance supplies, adhesives, paints, caulks, paper, cleaning products, foods, and perfumes.[5] Because many of the volatile emissions and by-products from these products are toxic, individuals have become sensitized to them.[6-8] As a result, additional knowledge of the levels of these allergens in the indoor air environment is required in order to determine their human health impact. New methods are required to accurately determine the identity and to accurately quantify the levels of these volatile organics in indoor air. Furthermore, additional studies will be needed to determine the sources of the air contamination.

In this study, several perfumes are analyzed using Solid Phase Micro Extraction (SPME) coupled to a high-speed Gas Chromatograph with a Time-of-Flight Mass Spectrometer (GC-TOFMS). The goal is to determine the identity and range of volatile organic compounds present in the perfume samples and to compare the degree to which these organic compounds are emitted into the atmosphere relative to each other. The main purpose of this work is to develop rapid screening methods to permit the detection and identification of the components from perfumes in indoor air.

2. Experimental Conditions

Three commercially available perfumes were obtained and approximately 1 mL of each sample was placed into a clean 20 mL screw-top vial with a PTFE septum. All three samples were kept at 5°C until sample analysis was performed. The static headspace of each sample was collected with an automated SPME fiber injector. Sample analysis was carried out on a Pegasus® III GC-TOFMS equipped with a CombiPAL autosampler and a low-thermal-mass (LTM) column capable of rapid temperature ramping (up to 1800°C/minute) and rapid cooling (250°C to 30°C in less than 45 seconds). The entire system consisting of the CombiPAL autosampler, LTM column, Agilent 6890 GC and the Pegasus III GC-TOFMS are all controlled by the ChromaTOF® software. Instrument conditions are listed below.

Instrument Conditions (GC-TOFMS)

GC:
Agilent 6890 equipped with a LTM column module (RVM Scientific, Santa Barbara, CA)

Column:
Rtx-5, 2.0 m, 0.18 mm id, 0.2 µm film thickness

Carrier Gas:
He at constant flow of 3.0 mL/minute

Inlet Temp:	250°C
Injection:	SPME
Split Ratio:	50:1
MS:	LECO Pegasus® III GC-TOFMS
Ionization:	EI at 70 eV
Mass Range (u):	40 to 350
Acquisition Rate:	50 spectra/second
Source Temp:	200°C
Transfer Line Temp:	250°C
Solvent Delay:	5.5 seconds

Operating Conditions

Main Oven Program: 250°C isothermal

LTM Program:
30°C isothermal for 0.20 minute, ramped to 250°C at 200°C/minute

SPME Conditions

Fiber:	75 µm Carboxen-PDMS
Equilibration Temp:	30°C
Extraction Time:	2 minutes
Desorption Time:	0.25 minute

3. Results

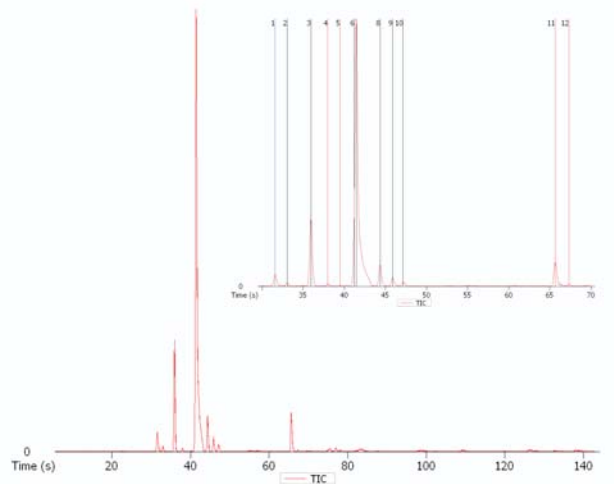

Figure 1. Perfume sample (a). The inset displays identified peaks based upon a S/N of greater than 25. Numbered peaks are listed in Table 1.

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Table 1. Identified components in perfume sample (a).

Peak #	Name	R.T. (s)	Unique Mass	Similarity	S/N	Area	Area %
1	Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl-, (ñ)-	31.591	93	963	286	117742	3.00
2	Camphene	33.048	93	917	58	25219	0.64
3	á-Pinene	35.964	93	948	1654	595659	15.18
4	á-Myrcene	38.000	93	841	45	22044	0.56
5	Cyclohexene, 4-methylene-1-(1-methylethyl)-	39.498	93	800	30	13016	0.33
6	Benzene, 1-methyl-2-(1-methylethyl)-	41.235	119	891	352	356637	9.09
7	Limonene	41.475	68	890	5013	2312039	58.91
8	à-Phellandrene	44.350	93	818	427	158090	4.03
9	7-Octen-2-ol, 2,6-dimethyl-	45.868	59	849	294	138264	3.52
10	Cyclohexene, 1-methyl-4-(1-methylethylidene)-	47.146	93	847	61	33184	0.85
11	4-tert-Butylcyclohexyl acetate	65.656	82	851	304	136645	3.48
12	4-tert-Butylcyclohexyl acetate	67.333	82	773	36	16476	0.42
	Total					3925015	100.00

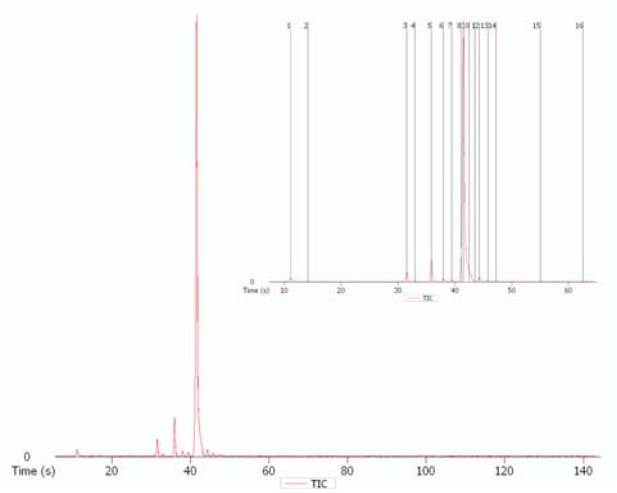

Figure 2. Perfume sample (b). The inset displays identified peaks based upon a S/N of greater than 25. Numbered peaks are listed in Table 2.

Table 2. Identified components in perfume sample (b).

Peak #	Name	R.T. (s)	UniqueMass	Similarity	S/N	Area	Area %
1	Ethane, 1,1-diethoxy-	11.112	45	888	411	413331	3.74
2	1,3,5-Cycloheptatriene	14.147	91	884	53	61274	0.55
3	Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl-, (ñ)-	31.540	93	956	957	376213	3.41
4	Camphene	33.017	93	908	85	37646	0.34
5	á-Pinene	35.913	93	949	2053	732327	6.63
6	4-(4-Methylpent-3-enyl)-3,6-dihydro-1,2-dithiin	37.949	69	849	171	105504	0.96
7	Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl-, (ñ)-	39.447	91	905	128	60227	0.55
8	Benzene, 1-methyl-2-(1-methylethyl)-	41.124	119	949	1682	1150338	10.42
9	D-Limonene	41.524	68	898	17948	7808816	70.70
10	1,5-Decadiyne	42.562	121	752	80	30240	0.27
11	Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl-, (ñ)-	43.500	80	800	16	5232	0.05
12	à-Phellandrene	44.319	93	827	312	113768	1.03
13	7-Octen-2-ol, 2,6-dimethyl-	45.837	59	828	255	100130	0.91
14	Cyclohexene, 1-methyl-4-(1-methylethylidene)-	47.254	93	813	46	30326	0.27
15	1,5-Dimethyl-1-vinyl-4-hexenyl butyrate	55.042	71	783	24	9147	0.08
16	4-Carene, (1S,3R,6R)-(-)-	62.570	93	804	22	10926	0.10
	Total					11045445	100.00

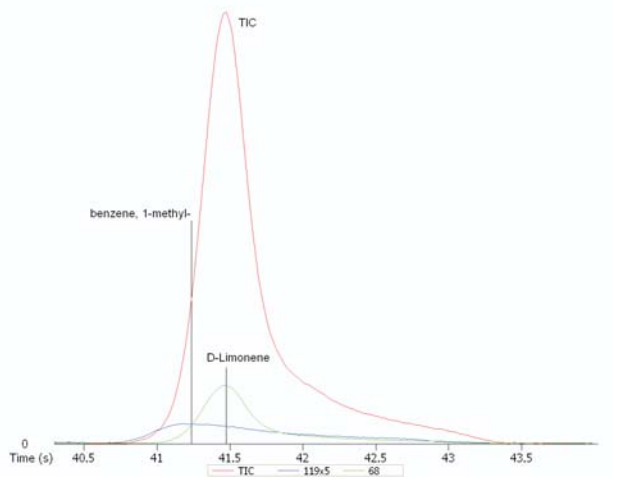

Figure 2.2. Deconvoluted chromatogram of peak #8 (benzene, 1-methyl-) and peak #9 (D-Limonene) for sample (b). The TIC is shown along with unique masses 119 and 68. Acquiring full mass range spectra at high acquisition rates allows for component identification even during coelution.

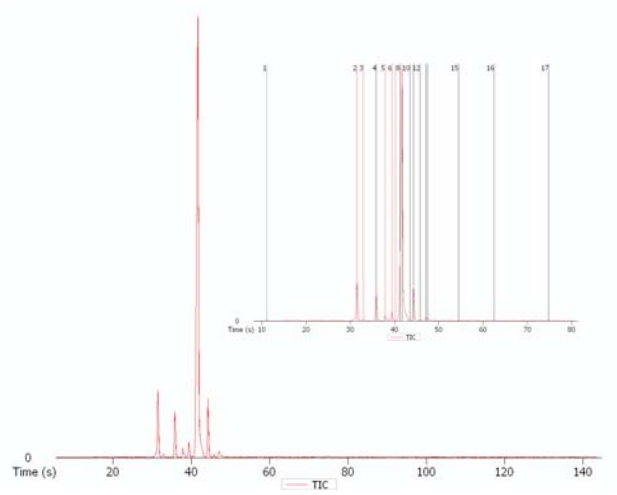

Figure 3. Perfume sample (c). The inset displays identified peaks based upon a S/N of greater than 25. Numbered peaks are listed in Table 3.

Table 3. Identified components in perfume sample (c).

Peak #	Name	R.T. (s)	UniqueMass	Similarity	S/N	Area	Area %
1	Ethane, 1,1-diethoxy-	11.132	45	832	103	121837	0.39
2	Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl-, (ñ)-	31.520	93	962	7745	3276255	10.38
3	Camphene	32.937	93	946	242	110199	0.35
4	á-Pinene	35.853	93	949	5101	2016561	6.39
5	á-Myrcene	37.869	91	870	263	125743	0.40
6	Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl-, (ñ)-	39.407	91	917	985	436521	1.38
7	Cyclohexene, 1-methyl-4-(1-methylethylidene)-	40.206	121	855	97	50821	0.16
8	Benzene, 1-methyl-2-(1-methylethyl)-	41.204	134	805	597	511742	1.62
9	D-Limonene	41.683	68	910	42895	22062732	69.92
10	1,3,6-Octatriene, 3,7-dimethyl-, (E)-	43.460	80	837	36	9073	0.03
11	4-Carene, (1S,3R,6R)-(-)-	44.279	93	852	5895	2235169	7.08
12	7-Octen-2-ol, 2,6-dimethyl-	45.757	59	838	440	163635	0.52
13	Cyclohexene, 1-methyl-4-(1-methylethylidene)-	47.095	93	947	436	279516	0.89
14	o-Isopropenyltoluene	47.414	132	935	79	74605	0.24
15	2H-Oxireno[3,4]cyclopenta[1,2-c]furan-2-one,	54.443	75	714	32	12980	0.04
16	1,3,7-Octatriene, 3,7-dimethyl-	62.470	93	849	40	20529	0.07
17	Naphthalene, 1,2,3,4,4a,7-hexahydro-1,6-dim	74.810	119	866	94	46259	0.15
	Total					31554177	100.00

Processing Data against a Reference Chromatogram (Compare Feature)

Processing acquired data with ChromaTOF software gives the analyst a wide variety of analytical options. One unique option available is the Compare feature. The Compare feature allows acquired data to be processed against a reference chromatogram. The references file is created in the References folder located in the main data base panel and then used in the data processing method development. While creating the reference file, the user can adjust tolerances such as retention time deviation, spectral similarity, area percent, and how to display quantitative results. Essentially, the method Peak Finds for an unknown sample and then does a peak-by-peak comparison to the reference. Each found peak is designated as a Match (within retention time, mass spectra and concentration tolerance), an Out of Tolerance (within retention time and mass spectra tolerance, but outside concentration tolerance), a Not Found (a compound in the reference but not in the sample), or an Unknown (a compound in the sample but not in the reference).The compare feature is used to immediately locate similarities between samples as well as being used as a single point calibration relative to the reference sample.

In this work, sample (c) is used as the reference and compared against sample (a) and sample (b). Analytical results are listed below.

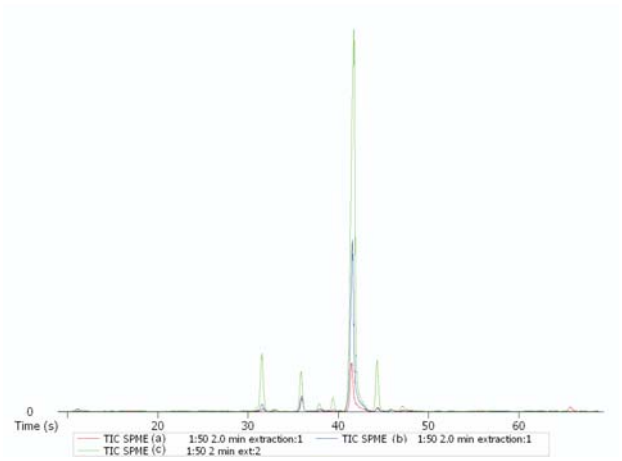

Figure 4. Overlay TIC chromatograms of sample (a), sample (b), and sample (c).

Table 4. Peak table for reference sample (c).

Peak #	Name	R.T. (s)	UniqueMass	S/N	Area	Area %
1	Ethane, 1,1-diethoxy-	11.132	45	103	121837	0.39
2	Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl-, (ñ)-	31.520	93	7745	3276255	10.38
3	Camphene	32.937	93	242	110199	0.35
4	á-Pinene	35.853	93	5101	2016561	6.39
5	á-Myrcene	37.869	91	263	125743	0.40
6	Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl-, (ñ)-	39.407	91	985	436521	1.38
7	Cyclohexene, 1-methyl-4-(1-methylethylidene)-	40.206	121	97	50821	0.16
8	Benzene, 1-methyl-2-(1-methylethyl)-	41.204	134	597	511742	1.62
9	D-Limonene	41.683	68	42895	22062732	69.92
10	1,3,6-Octatriene, 3,7-dimethyl-, (E)-	43.460	80	36	9073	0.03
11	4-Carene, (1S,3R,6R)-(-)-	44.279	93	5895	2235169	7.08
12	7-Octen-2-ol, 2,6-dimethyl-	45.757	59	440	163635	0.52
13	Cyclohexene, 1-methyl-4-(1-methylethylidene)-	47.095	93	436	279516	0.89
14	o-Isopropenyltoluene	47.414	132	79	74605	0.24
15	2H-Oxireno[3,4]cyclopenta[1,2-c]furan-2-one,	54.443	75	32	12980	0.04
16	1,3,7-Octatriene, 3,7-dimethyl-	62.470	93	40	20529	0.07
17	Naphthalene, 1,2,3,4,4a,7-hexahydro-1,6-dimeth	74.810	119	94	46259	0.15
	Total				31554177	100.00

Table 5. Comparison of sample (a) vs. reference chromatogram [sample (c)]. Tolerance level of reference sample was set at 40%.

Peak #	Name	Type	R.T. (s)	UniqueMass	Match	S/N	Area	Area %
1	Ethane, 1,1-diethoxy-	Out of Tolerance	11.263	45	837	19	16250	0.46
2	Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethy	Out of Tolerance	31.591	93	979	286	117742	3.35
3	Camphene	Out of Tolerance	33.048	93	956	58	25219	0.72
4	á-Pinene	Out of Tolerance	35.964	93	991	1654	595659	16.94
5	á-Myrcene	Out of Tolerance	37.980	41	963	50	10001	0.28
6	Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethy	Out of Tolerance	39.498	93	888	30	11233	0.32
7	Cyclohexene, 1-methyl-4-(1-methylethy	Out of Tolerance	40.197	121	868	16	7205	0.20
8	Benzene, 1-methyl-2-(1-methylethyl)-	Out of Tolerance	41.235	119	772	352	69774	1.98
9	D-Limonene	Out of Tolerance	41.475	68	965	5013	2312039	65.74
10	4-Carene, (1S,3R,6R)-(-)-	Out of Tolerance	44.350	93	943	427	158090	4.50
11	7-Octen-2-ol, 2,6-dimethyl-	Match	45.868	59	969	294	138264	3.93
12	Cyclohexene, 1-methyl-4-(1-methylethy	Out of Tolerance	47.146	93	948	61	33184	0.94
	o-Isopropenyltoluene/Lauren 2	Not Found			700			
	2H-Oxireno[3,4]cyclopenta[1,2-c]furan-	Not Found			700			
13	1,3,7-Octatriene, 3,7-dimethyl-	Out of Tolerance	62.541	93	888	13	6931	0.20
14	Unknown 1	Unknown	65.656	82		304		
15	Unknown 2	Unknown	67.333	82		36		
	Naphthalene, 1,2,3,4,4a,7-hexahydro-1,6	Not Found			700			
	Total						3516734	100.00

Table 6. Comparison of sample (b) vs. reference chromatogram [sample (c)]. Tolerance level of reference sample was set at 40%.

Peak #	Name	Type	R.T. (s)	UniqueMass	Match	S/N	Area	Area %
1	Ethane, 1,1-diethoxy-	Out of Tolerance	11.112	45	939	411	413331	4.14
2	Unknown 1	Unknown	14.147	91		53		
3	Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethy	Out of Tolerance	31.540	93	988	957	376213	3.77
4	Camphene	Out of Tolerance	33.017	93	947	85	37646	0.38
5	á-Pinene	Out of Tolerance	35.913	93	991	2053	732327	7.34
6	á-Myrcene	Out of Tolerance	37.949	69	986	171	38360	0.38
7	Cyclohexene, 1-methyl-4-(1-methylethy	Out of Tolerance	39.447	91	977	128	60227	0.60
8	Benzene, 1-methyl-2-(1-methylethyl)-	Out of Tolerance	41.124	119	791	1682	229346	2.30
9	D-Limonene	Out of Tolerance	41.524	136	976	2685	7808816	78.29
10	Unknown 2	Unknown	42.322	92		220		
11	Unknown 3	Unknown	43.500	80		16		
12	4-Carene, (1S,3R,6R)-(-)-	Match	44.319	93	791	312	10743	0.11
13	7-Octen-2-ol, 2,6-dimethyl-	Match	45.837	59	973	255	100130	1.00
14	Cyclohexene, 1-methyl-4-(1-methylethy	Out of Tolerance	47.234	79	892	22	30326	0.30
15	o-Isopropenyltoluene	Out of Tolerance	47.314	132	772	11	2077	0.02
	2H-Oxireno[3,4]cyclopenta[1,2-c]furan-2	Not Found			700			
16	Unknown 4	Unknown	55.042	71		24		
17	1,3,7-Octatriene, 3,7-dimethyl-	Out of Tolerance	62.570	93	907	22	10926	0.11
	Naphthalene, 1,2,3,4,4a,7-hexahydro-1,	Not Found			700			
	Total						9974017	100.00

As shown above in tables 5 and 6, the Compare feature allows the analyst to easily and atomically locate similarities between samples without extensive data analysis. The peak table can be set to list peaks of interest, i.e. Match, Out of Tolerance, Not Found, and Unknown.

When the reference [sample (c)] was compared with sample (a) and sample (b) the data from the *Compare* feature identified two components (peaks 12 and 13) that matched with the pre-determined tolerance and many more that had similar retention time and spectral matches but were outside the concentration tolerance.

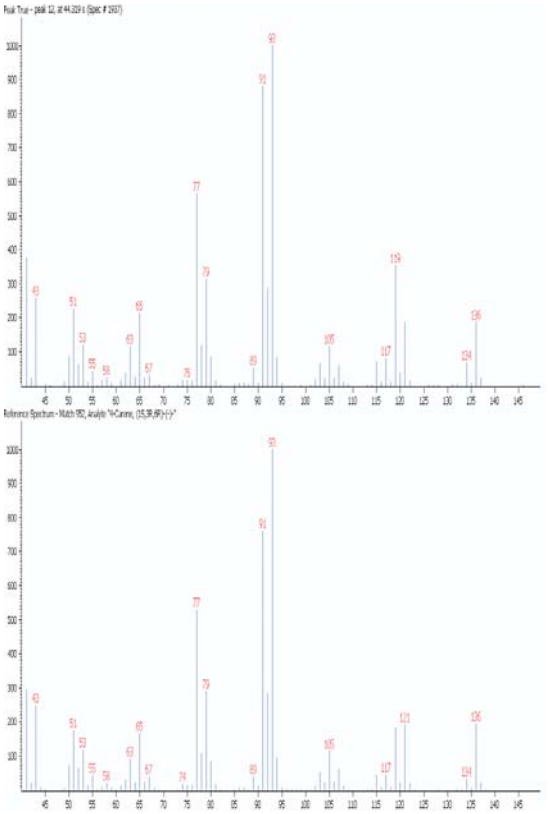

Figure 5. Peak True and the Reference Spectrum from the NIST library match for peak #12 identified as a Match in sample (b).

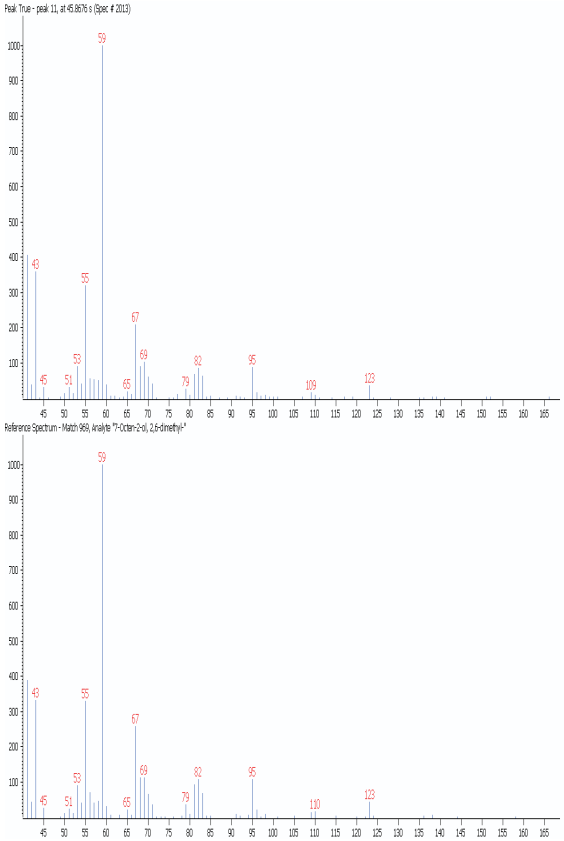

Figure 6. Peak True and the Reference Spectrum from the NIST library match for peak #11 and #13 identified as a Match in sample (a) and sample (b) respectively.

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4. Conclusion

The ability to rapidly identify volatile organic components in air samples is imperative for further research related to sick building syndrome. In this study, the Pegasus III GC-TOFMS was well suited for high-speed analysis. A low thermal mass column and a SPME sampling unit were used to facilitate the rapid analysis. The entire process is automated with the only sample preparation being the loading of the vials into the autosampler tray.

The data collected in this work identified multiple volatile organic components that are produced from commercial fragrances. The volatility of detected components covered a range from 1,1-diethoxyethane (B.P. 102.7°C) to Naphthalene (B.P. 218°C). Note that component identification is based upon the NIST spectral library and does not necessarily represent true peak identification. Analytical standards of the target components would need to be analyzed under similar conditions and used for retention time and spectral reference.

Utilizing the Compare feature of the ChromaTOF software provides an automated qualitative and semi-quantitative comparison between the three perfume samples. This feature gives the analyst a rapid data processing method which provides identification of common components and their respected concentrations relative to the reference sample.

5. References

[1]http://eartheasy.com/article_fragrance_allergens.htm

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