

Fast Analysis of an 84-Component Essential Oil Standard

LECO Corporation; Saint Joseph, Michigan USA

Key Words: GC-TOFMS

1. Introduction

Essential oils are complex mixtures of fragrance and flavor compounds originating in plants. They are generally used as odorants, flavorings, and pharmaceutical ingredients in hundreds of consumer products. Minor differences in the composition of these oils can significantly alter product odor or flavor. For this reason, careful analysis of essential oil components is important to ensure that consistent products are manufactured over time.

Gas chromatography (GC) with flame ionization detection (FID) is commonly used to characterize essential oil extracts. However, these analyses are lengthy requiring several hours per essential oil to allow complete chromatographic resolution of the individual components for identification.

These same analyses can be completed in less than five minutes with GC-Time-of-Flight Mass Spectrometry (TOFMS). The mass spectra are used to identify individual components. In addition, the MS information coupled with a fast spectral acquisition (up to 500 spectra/second) allows for unique automated deconvolution of overlapping chromatographic peaks.

General GC and TOFMS conditions were developed for the analysis of a variety of essential oil extracts and reference standards. The conditions were validated using a complex 84-component flavor and fragrance reference standard (provided by Carl Frey of Dragoco Analytical Services). The total acquisition time for the analysis was 3.5 minutes. The data was processed using automated peak finding and deconvolution algorithms and the resulting spectra were searched against both the National Institute of Standards and Technology (NIST) Mass Spectral Database and the Terpene Essential Oil Library¹. The peak table (Table 1) lists peak number, Retention Time (RT), and component name as well as the spectral similarity index and library hit number. The spectra of those compounds not present in either the NIST Database or Terpene Library were compared to spectra provided by Dragoco for identification.

2. Experimental Conditions

Detector:

LECO Corporation Pegasus II Time-of-Flight
Mass Spectrometer

Transfer Line: 300°C

Source: 200°C

Acquisition Rate: 30 spectra/second (35 to 400 u)

GC: Hewlett Packard® 6890*

Column:

DB-5 4 m x 0.1 mm ID, 0.1 m phase film

Oven:

40°C for 0.5 minute, then to 280°C at 75°C/minute,
hold for 1 minute

Injector: 290°C

Carrier Gas: Helium, 2.0 ml/minute constant flow

Sample: No preparation required, 0.2 mL split
(200:1) injection

*HP6890 GC is equipped with fast oven temperature ramp capabilities and a high pressure EPC module.

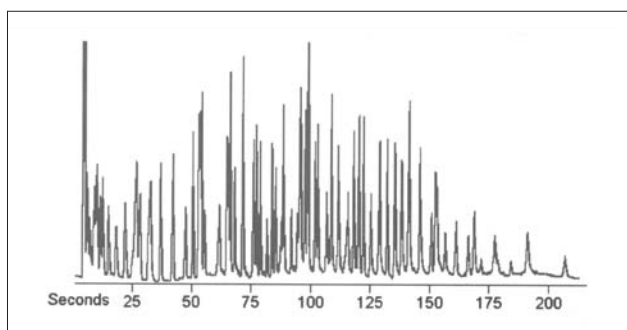


Figure 1. Essential Oil Reference Standard Chromatogram—84 Analytes in 3.5 Minutes.

3. Results

The strength of the Pegasus II GC/MS system can be seen in the significantly reduced analysis time of 3.5 minutes and the quality of the analyte identifications. Essential oil analysis times routinely range from 45 minutes for specific sample conditions up to several hours for general analytical conditions comparable to the work in this document. The automated peak find and deconvolution algorithms successfully located all 84 components with 77% of the analytes properly identified as the first library match and 92% of the analytes identified in the top two library hits. The first library hits for peaks 9, 17, and 48 consist primarily of structural isomers of the correct compound. For peaks 72, 74, and 78 (C16 and C18 ethyl and isopropyl esters), the first library hits are also long chain esters with slightly different carbon counts. Proper identifications were easily made from published retention index information.²

Table 1. 84-Component Essential Oil Standard Peak Table. Compound Name, Retention Time (RT), Library Hit Number, and Spectral Similarity Index for Essential Oil Reference Standard Analysis. Unless otherwise noted, the NIST database was used.

Peak	Name	RT (sec)	Hit No.	Similarity
1	2,3-Butanedione	5.58	1	848
2	Ethyl Acetate	5.95	1	862
3	1-Propanol, 2-methyl-	6.28	1	850
4	1-Butanol	7.15	1	848
5	2,3-Pentanedione	8.08	1	713
6	Propanoic acid, ethyl ester	8.82	1	881
7	Butanoic acid, methyl ester	9.35	1	872
8	1-Butanol, 3-methyl-	10.28	1	847
9	1-Butanol, 2-methyl-	10.38	7	799
10	Ethyl isobutanoate	11.62	1	869
11	Isobutyl acetate	12.72	1	915
12	Ethyl butanoate	15.15	1	931
13	Furfural	18.42	2	913
14	Ethyl isovalerate	22.18	1	884
15	1-Hexanol	25.65	1	837
16	1-Butanol, 3-methyl-, acetate	26.48	1	887
17	1-Butanol, 2-methyl-, acetate	26.98	4	734
18	Allyl butanoate	28.48	1	880
19	Pentanoic acid, ethyl ester	32.18	1	923
20	Pyrazine, 2,5-dimethyl-	32.98	1	894
21	Hexanoic acid, methyl ester	37.22	1	868
22	Benzaldehyde	42.42	1	925
23	1-Octen-3-ol	47.68	1	907
24	Ethyl hexanoate	50.75	2	853
25	Acetic acid, hexyl ester	53.15	1	948
26	p-Cymene	53.82	2	890
27	Limonene	54.42	1	910
28	Benzyl Alcohol	55.58	1	876
29	1-Octanol	61.88	2	883
31	Linalool	65.52	1	909
32	cis-Rose oxide	66.38	1	868
33	trans-Rose oxide**	68.15	2	796
34	Isoborneol	71.35	1	852
35	Citronellal	71.72	2	760
36	Terpineol	76.22	2	879
37	Octanoic acid, ethyl ester	77.35	1	921
38	Octyl acetate	79.02	1	900
39	Neral	81.85	2	836
40	Linalyl acetate	83.95	1	910
41	Geranial	85.45	1	909
42	Hydroxy citronellal	87.88	1	860
43	Nonanoic acid, ethyl ester	88.65	1	897
44	Cis-Vertenex	91.98	1	896
45	Citronellyl acetate	94.52	1	842
46	g-Nonanolactone	95.82	1	825
47	Trans-Vertenex	96.02	1	926
48	Geranyl acetate	97.92	8	811
49	Decanoic acid, ethyl ester	99.18	1	696
50	a-Ionone	102.02	1	787
51	Florazone*	103.22	—	—
52	1-Dodecanol	107.05	2	913
53	b-Ionone	107.35	1	671
54	Undecanoic acid, ethyl ester	108.98	1	899
55	Eugenyl acetate	111.85	1	915
56	Isoamyl salicylate	112.15	1	884
57	Frambinone	115.42	1	881

Peak	Name	RT (sec)	Hit No.	Similarity
58	Amyl salicylate	115.98	2	880
59	Dodecanoic acid, ethyl ester	118.35	1	891
60	Benzophenone	120.62	1	900
62	g-Dodecalactone	125.55	1	908
63	Veramos	128.58	1	790
64	Celestolide*	129.22	—	—
65	Benzyl Benzoate	132.52	1	917
66	Ethyl tetradecanoate	135.72	2	900
67	Isopropyl Myristate	138.52	1	888
68	Musk xylene	141.48	1	816
69	Tonalid*	141.82	—	—
70	Ambrettolide	146.25	1	889
71	Musk ketone	151.08	1	931
72	Ethyl hexadecanoate	152.65	10	743
73	Ethylene brassylate**	153.35	1	729
75	Phenylethyl cinnamate, cis	156.78	1	895
76	Cinnamyl phenyl acetate*	161.48	—	—
77	Phenylethyl cinnamate, trans	166.55	1	876
78	Ethyl octadecanoate	169.02	7	771
79	Cinnamyl cinnamate, cis	171.88	1	657
80	Methyl abietate, dihydro deriv.	177.75	2	818
81	Methyl dehydroabietate	179.08	1	814
82	Cinnamyl cinnamate, trans	184.48	1	709
83	Cetearyl octanoate*	191.55	—	—
84	Cetearyl decanoate*	207.28	—	—

*Not present in NIST or Terpene databases

**Present in Terpene database only.

4. Conclusion

The general conditions developed in this procedure can be applied to a wide variety of essential oil analyses. The use of consistent analytical conditions also allows for the generation of retention index information to further aid in accurate analyte identifications.

5. References

¹The Terpene Library contains mass spectra of essential oil components compiled by Robert P. Adams, Baylor University Plant Biotechnology Center.

²Robert P. Adams. Identification of Essential Oil Components by Gas Chromatography/Mass Spectroscopy. Allured Publishing Corporation, Carol Stream, IL, 1995.

