Fast Analysis and Reporting of a Citrus Reference Standard

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Key Words: GC-TOFMS

1. Introduction

Lemon, lime and orange oils represent the largest segment of U.S. essential oil imports in both volume and value.[1] These oils are primarily used as flavor additives in the manufacture of soft drinks. Detailed analyses of the components in citrus oils are important in ensuring the production of quality beverages with consistent flavors from batch to batch. GC-FID analysis is commonly used to characterize citrus oils, however, this approach can require from 45 minutes to several hours per sample to allow sufficient chromatographic resolution for analyte identification. Alternatively, time-of-flight mass spectrometry (TOFMS) coupled with fast GC techniques can accomplish the same characterizations in less than five minutes. TOFMS detection, with full mass range acquisition rates of up to 500 spectra/second, can readily define narrow gas chromatographic peaks without sacrificing spectral information. These fast acquisition times combined with automated peak finding, deconvolution, library searching, and reporting elements result in greater than a ten-fold increase in productivity over traditional analyses.

A general set of GC and TOFMS conditions were developed and used to analyze a variety of essential oils and reference standards (refer to application note 203-821-062). In this note, the general conditions were applied without further optimization to a 49-component citrus standard prepared from individual citrus components.[2] The total acquisition time for the analysis was 2.5 minutes. Following acquisition, the data was processed with automated processing including peak finding, deconvolution of overlapping chromatographic peaks, library searching, and reporting. Both the National Institute of Standards and Technology (NIST) MS Database and the Terpene Essential Oil Library[3] were used for spectral searching. In addition, because the structure and mass spectra of many flavor components are similar, retention indices (supplied with the Terpene library[4]) were used to confirm the library identifications. The chromatogram for the analysis is shown on the next page. The corresponding peak table (Table 1) includes the Retention Time (RT), the library hit number, and spectral similarity index. The identity of those compounds not present in either the NIST Database or Terpene Library were determined by injection of the neat compound.

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:	Split/splitless at 290°C
Carrier Gas:	Helium, 2.0 ml/minute constant flow
Sample:	No preparation required, 0.2 mL split (200:1) injection

**HP6890GC is equipped with fast oven temperature ramp capabilities and a high pressure EPC module.*

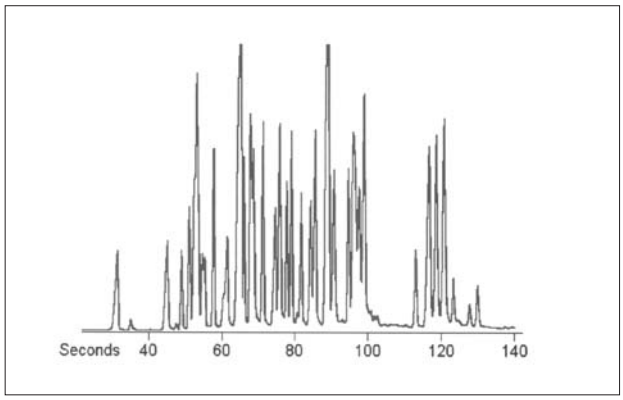

Figure 1. Citrus Reference Standard—49 Analyses in 2.5 Minutes.

Peak Report

Automated data processing and reporting elements decrease the total analysis time of complex essential oil extracts by a factor of 10 or more.

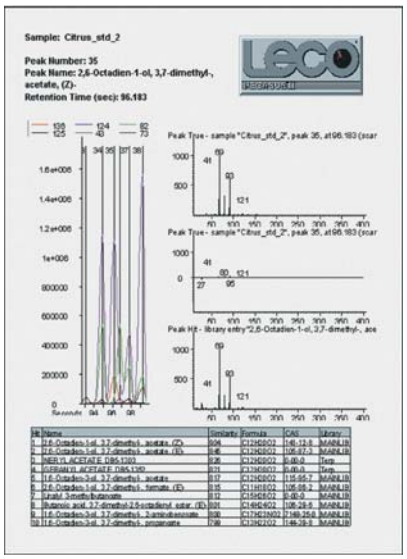

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Table 1. Citrus Reference Standard Peak Table with Standard Peak Identification, Retention Time (RT), Library Hit Number, and Similarity Index.

Peak	Name	RT (sec)	Hit No.	Similarity
1	Hexadienal, 2,4-(E,E)-	31.583	1	905
2	a-Thujene	35.133	3	892
3	Heptanol	45.283	2	900
4	Myrcene	47.633	1	893
5	a-Phellandrene	49.083	1	925
6	a-Terpinene	51.233	1	906
7	p-Cymene	52.633	2	875
8	Limonene	53.383	1	867
9	Dimethyl maleate	53.783	1	896
10	Benzyl Alcohol	54.933	1	888
11	g-Terpinene	57.983	1	916
12	Octanol	61.683	2	866
13	3-(Methylthio)propanoic			
	acid ethyl ester	64.733	1	925
14	6-Nonenal, (Z)-	65.033	1	823
15	Linalool	65.483	1	865
16	Nonanal	65.683	3	757
17	Fenchol	66.283	1	921
18	Octanoic acid, methyl ester	68.033	1	881
19	Hexanoic acid, 3-hydroxy-,			
	ethyl ester	68.883	1	865
20	Citronellal	71.533	1	924
21	Nonanol	74.783	1	910
22	3-Decanone	76.033	1	910
23	a-Terpineol	76.283	1	818
24	Decanal	77.983	1	912
25	Linalyl formate	79.233	2	900
26	Neral	81.933	2	901
27	Decenal, (E)-2-	84.483	2	898
28	Geranial	85.833	1	903
29	2-Undecanone	88.783	1	847
30	Terpeneinyl formate*	89.183	—	—
31	Undec-10-en-1-al	89.433	1	904
32	Decadienal, (E,E)-2,4-	90.983	1	886
33	Citral, Dimethoxy-(E)-	93.133	1	617
34	Citronellyl Acetate	94.883	1	868
35	Neryl Acetate	96.183	1	904
36	10-Undecen-1-ol	96.783	3	884
37	Undecanol	97.833	2	878
38	Octyl butyrate	99.233	1	917
39	Decanoic acid	100.03	1	722
40	Caryophyllene	101.18	2	685
41	cis-Nerolidol	113.23	2	909
42	trans-Nerolidol	116.68	1	922
43	trans-2-Tridecenal	117.03	1	901
44	Decyl butyrate*	118.88	—	—
45	Lauryl acetate	121.08	2	890
46	cis-Amyl Cinnamaldehyde	123.48	3	824
47	trans-Amyl Cinnamaldehyde	124.93	2	827
48	cis-Amyl Cinnamaldehyde,			
	dimethyl acetal*	127.93	—	—
49	trans-Amyl Cinnamaldehyde, dimethyl acetal*	130.13	—	—

**Not present in either the NIST or Terpene databases.*

3. Conclusion

The strength of the Pegasus II GC/MS system can be seen in the significantly reduced analysis time of 2.5 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 49 components with 67% of the analytes properly identified as the first library match and 100% of the analytes identified in the top three library hits.

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

4. References

[1]Value of U.S. Essential Oil Imports on the Rise internet posting.

[2]Individual citrus components were purchased from the Flavor and Fragrance division of the Aldrich Chemical Co.

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

[4]Retention indices are for a DB-5 (5%-phenyl methyl polysiloxane) column.

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