

Fast Analysis of Citronella Ceylon Oil with GC-TOFMS

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Key Words: GC-TOFMS

1. Introduction

There are two types of citronella oil - ceylon and java - both of which are valued for their lemony aromas. Ceylon is the more common variety and is used as a fragrance in hand soaps, household cleansers, detergents, and aerosols. Characterization of these complex fragrances can require up to several hours by GC-FID for sufficient chromatographic resolution to identify each component. These same analyses can be completed in one-tenth the time with Fast GC techniques and Time-of-Flight Mass Spectrometry (TOFMS) detection.

The LECO Pegasus II GC-TOFMS offers several unique advantages for reducing analysis times.

The Pegasus II provides acquisition rates of up to 500 spectra/second to allow accurate definition of the narrowest GC peaks. Fast GC techniques may now be effectively used to reduce separation times without sacrificing data quality. The unique degree of spectral continuity across a chromatographic peak provided by the Pegasus II has allowed the development of several revolutionary software algorithms. The peak find algorithm effectively locates the position of all peaks in the chromatogram including multiple components in complex coelutions. The deconvolution algorithm effectively resolves the mixed mass spectra of the coelution into accurate individual mass spectra for each analyte, including the accurate distribution of signal from masses shared by several components in the coelution.

Instrument conditions developed previously for a fragrance reference standard (refer to form no. 203-821-062) were used without further optimization to analyze a sample of citronella ceylon oil, resulting in a total acquisition time of just 2.2 minutes. Automated data processing was performed with peak finding and spectral Deconvolution. The resulting mass spectra were searched against both the National Institute of Standards and Technology (NIST) 1998 Mass Spectral Database and the Terpene Essential Oil Library.¹ Analyte identifications are based upon both spectral similarity and DB-5 retention indices.

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

Stored Mass Range: 35 to 400 u

GC: Hewlett Packard® 6890*

Column:

DB-5 4 m x 0.1 mm ID, 0.1 μm 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. 0.1 μL split (150:1) injection.

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

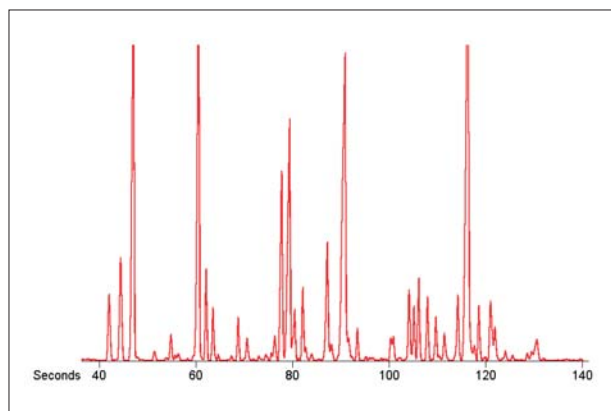


Figure 1. Citronella Ceylon Total Ion Chromatogram (TIC)—85 Analytes in 2.2 Minutes.

3. Results

The effectiveness of the peak find and deconvolution algorithms to accurately locate and identify analytes in complex coelutions resulting from the rapid separation conditions used in this analysis can be evaluated in Figures 2 and 3. In Figure 2, the positions of three components in a coelution between 120.5 and 122.5 seconds are accurately located by the peak find algorithm. The mass spectra for all three analytes are accurately resolved from one another by the deconvolution algorithm. Library search results for these mass spectra versus the NIST and Terpene spectral database are presented in Figure 3. The deconvolution algorithm not only separates out ions unique to the spectra of each analyte but also successfully assigns the appropriate amount of signal to each analyte spectrum for masses that are shared between multiple analytes in the coelution. In the coelution (Figure 3) the signal at 91u and 121u is appropriately proportioned between the three analytes by the deconvolution algorithm.

Table 1. Citronella Ceylon Peak Table With the Similarity and Reverse Similarity Numbers Resulting From Comparison of the Acquired Spectra to the NIST and Terpene Mass Spectral Databases.

Peak	Name	R.T.	Hit Number	Similarity	Reverse
1	Tricyclene*	42.03	1	898	898
2	α -Pinene	44.43	8	853	853
3	Camphene	47.03	1	930	930
4	Thuja-2,4(10)-diene*	47.86	1	860	860
5	Cumene	49.26	1	784	801
6	Sabinene	51.43	1	894	894
7	6-Methyl-5-hepten-2-one*	53.86	1	863	863
8	Dehydro-1,8-cineole*	54.09	1	687	734
9	Myrcene*	54.86	1	829	829
10	2-Caren	55.79	2	895	895
11	α -Phellandrene	56.33	2	831	831
12	α -Terpinene	58.29	1	831	839
13	α -Cymene	59.53	2	832	832
14	Limonene	60.56	1	892	892
15	cis- β -Ocimene*	62.13	1	892	892
16	trans- β -Ocimene*	63.53	1	923	923
17	Bergamal*	63.96	1	872	872
18	γ -Terpinene*	64.66	5	770	868
19	cis-Sabinenehydrate	65.66	2	698	733
20	Camphenilone*	67.36	1	846	853
21	Terpinolene	68.76	1	911	911
22	Linalool	70.59	1	857	861
23	cis-Rose oxide*	71.86	1	759	795
24	cis-p-Menth-2-en-1-ol*	73.06	1	830	868
25	α -Campholenal*	73.49	2	851	851
26	trans-Rose oxide*	74.03	3	677	683
27	Allo-Ocimene*	74.46	3	896	896
28	5-Hepten-1-ol, 2, 6-dimethyl-	74.76	1	829	829
29	Camphor	75.66	1	887	907
30	Camphene hydrate*	76.33	1	804	873
31	Isopulegol	76.39	1	806	821
32	Citronellal	77.79	1	876	876
33	β -Pinene oxide*	78.89	1	761	780
34	Borneol*	79.39	2	782	782
35	Terpene-4-ol	80.49	1	762	762
36	Cryptone	81.16	1	788	788
37	p-Cymen-8-ol	81.36	1	726	726
38	α -Terpineol*	82.16	1	881	886
39	Bicyclo[3.1.0]hexan-2-ol, 2-methyl-5-(1-methylethyl)-, (1 α ,2 α ,5 α)-	82.66	1	719	736
40	1,5-Menthadien-7-ol	82.79	1	772	772
41	n-Decanal*	83.93	3	800	880
42	trans-Piperitol	84.09	1	769	781
43	trans-Carveol*	85.49	1	790	826
44	β -Citronellol	87.23	1	858	858
45	Neral	88.09	1	789	789
46	Carvone	88.23	1	694	736
47	Piperitone	89.39	2	815	815
48	Geraniol*	90.86	2	787	797
49	Geranial	91.73	1	766	766
50	Isobornyl acetate*	93.49	2	848	848
51	Geranyl formate	95.23	3	752	752

Peak	Name	R.T.	Hit Number	Similarity	Reverse
52	α -Terpinyl acetate*	100.39	1	851	854
53	Citronellyl acetate*	100.93	2	869	869
54	Neryl acetate	102.06	2	823	823
55	Cyclosativene*	102.33	1	900	905
56	α -Copaene*	103.39	2	672	736
57	Geranyl acetate*	104.16	1	877	877
58	β -Bourbonene*	104.33	1	851	862
59	β -Elemene*	105.19	1	916	921
60	Methyl eugenol*	106.19	1	881	898
61	trans-Caryophyllene*	108.03	1	874	883
62	α -trans-Bergamotene*	109.73	2	877	877
63	cis- β -Farnesene*	110.39	3	795	800
64	α -Humulene*	111.46	1	802	812
65	cis-Methyl isoeugenol*	111.53	2	850	863
66	β -Farnesene	111.83	1	721	721
67	Germacrene D	114.33	1	890	891
68	(Z,E)- α -Farnesene	116.03	1	719	827
69	trans-Methyl isoeugenol*	116.39	2	891	894
70	γ -Cadinene*	117.73	3	838	850
71	δ -Cadinene*	118.66	1	887	892
72	Citronellyl butyrate	118.89	1	852	907
73	α -Cadinene*	119.89	2	744	748
74	α -Calacorene*	120.29	1	847	847
75	Elemol*	121.06	1	898	912
76	Elemicin*	121.39	1	868	927
77	Geranyl n-butyrate	121.99	1	855	859
78	Caryophyllene oxide*	124.16	1	845	876
79	Humulene epoxide II*	126.56	1	731	756
80	10-epi- γ -Eudesmol*	128.69	1	845	869
81	epi- α -Cadinol*	129.56	1	809	826
82	trans-Asarone*	130.19	3	752	769
83	β -Eudesmol*	130.49	1	764	764
84	α -Cadinol*	130.76	2	833	847
85	cis-Nerolidol acetate*	131.99	4	773	815

*Indicates a match found in the Terpene Essential Oil Library. All other identifications are from the NIST database.

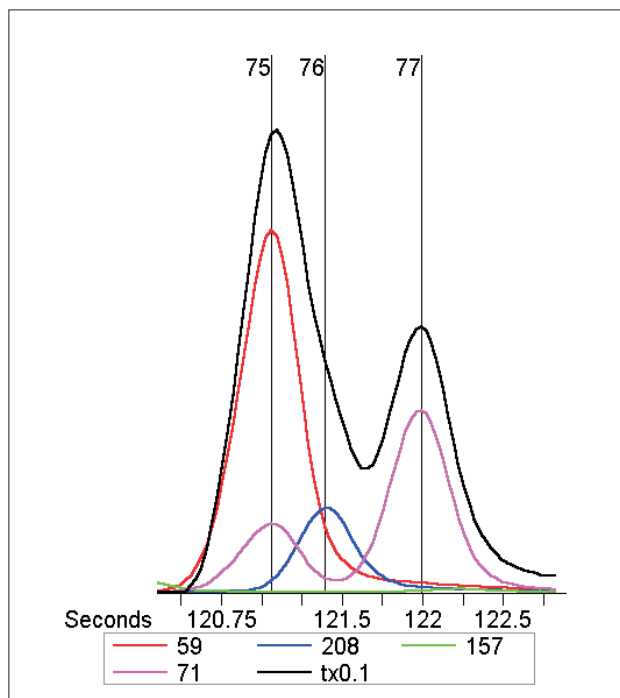


Figure 2. Extracted Ion Profile Chromatogram Showing the Coelution Between 120.5 and 122.5 Seconds. The markers indicate peak positions as determined by the Pegasus II GC-TOFMS peak find algorithm. The Total Ion Chromatogram (TIC) is shown in black.

4. Conclusions

The combination of Fast GC techniques (shorter microbore columns and faster temperature program rates), fast mass spectral acquisition rates, and unique peak find and spectral deconvolution algorithms allow accurate analysis of 85 components in citronella ceylon oil using the Pegasus II GC-TOFMS. The 2.2 minute acquisition time represents at least a 10 fold decrease over more traditional analyses. The unique software features also significantly reduce data processing time resulting in an overall decrease of analysis time of well over one order of magnitude.

5. References

¹The Terpene Library contains mass spectra of essential oil components and DB-5 retention indices compiled by Robert P. Adams, Baylor University Plant Biotechnology Center.

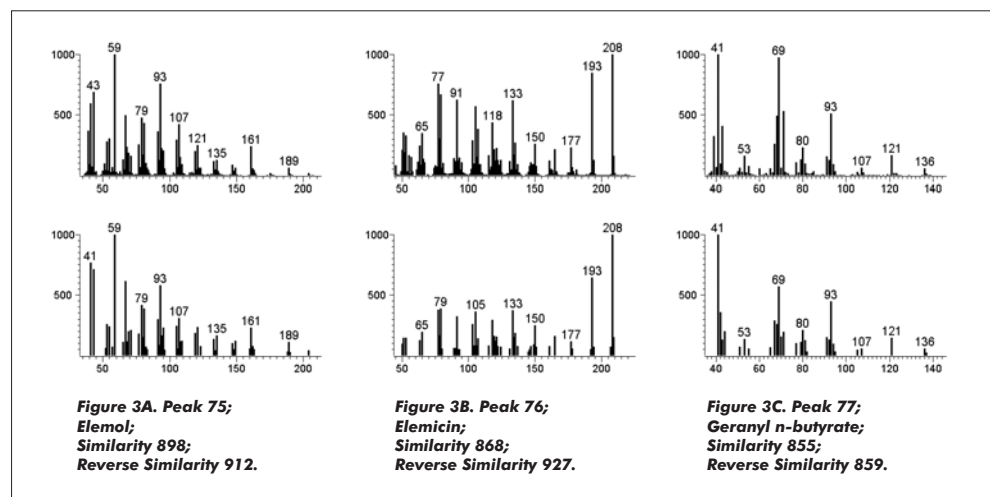


Figure 3. Mass Spectra for Coeluting C11 Benzene Isomers as Determined by the Pegasus II GC/TOFMS Deconvolution Algorithm. Top: Pegasus II spectrum. Bottom: NIST Library spectrum.

