Qualitative GC-TOFMS Analysis of Nutmeg Extract: Automated Peak Finding and Spectral Deconvolution of Minor Components

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Key Words: GC-TOFMS, Food, Deconvolution

1. Introduction

Nutmeg is one of the old spices, having been cultivated for over a thousand years in the Caribbean. The extract of nutmeg is used as a flavoring in a variety of manufactured foods. The relatively large number of volatile and semivolatile components contained in the mixture complicates analysis of nutmeg oil or extracts. As a result, GC or GCMS analyses of these mixtures can take an hour or more. Previous analytical conditions have focused on complete chromatographic resolution of as many individual analytes as possible. While all mass spectrometers offer multi-channel detection capabilities that may be used to identify coeluting analytes, slow spectral acquisition rates and under developed software algorithms have minimized the impact of MS detectors on faster GC separation times.

The LECO Pegasus® II GC-TOFMS offers several unique advantages for reducing the time of flavor analyses. 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.

2. Experimental Conditions

The potential benefit of these unique features of the Pegasus II in nutmeg extract analysis were evaluated using an extract sample obtained from a local distributor. The analytical conditions used for the two-minute analysis of this mixture are summarized in Table 1. The resulting total ion chromatogram from the separation is shown in Figure 1 with the peak table indicating the analyte, its retention time, and the accuracy of its library search result versus the NIST spectral database summarized in Table 2.

Table 1. GC and MS Conditions for a 2 Minute Analysis of Nutmeg.

Detector:	LECO Corporation Pegasus II Time-of-Flight Mass Spectrometer
Transfer Line:	300°C
Source:	200°C
Acquisition Rate:	30 spectra/sec
Stored Mass Range:	35 to 400u
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 min., then to 280°C at 75°C/min., hold for 1 min.
Injector:	290°C
Carrier Gas:	Helium, 2.0 ml/min. constant flow
Sample:	No preparation required. 0.2 µL split (200:1) injection.

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

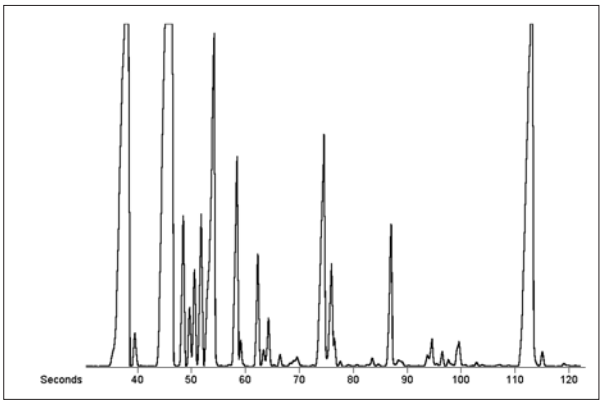

Figure 1. Nutmeg Extract Total Ion Chromatogram (TIC) for 60 Analytes in 2 Minutes.

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 are accurately located by the Peak Find algorithm despite the relatively low concentration of the component eluting in the middle. This component does not even appear in the Total Ion Chromatogram. 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 spectral database are presented in Figure 3.

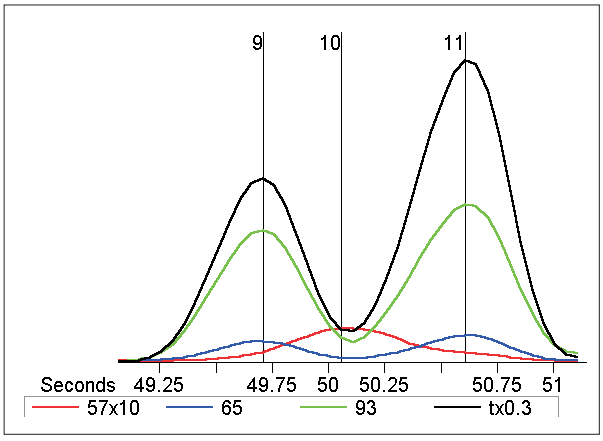

Figure 2. Total Ion Chromatogram (TIC) in Black and Extracted Ion Chromatogram Overlay Showing the Coelution of a Minor Component (Peak 10) With Two More Concentrated Components. The markers indicate peak positions as determined by the Pegasus II GC-TOFMS Peak Find algorithm. Note that the intensity of m/z 57 was magnified by a factor of 10 to be readily observed on the same scale with m/z 65 and m/z 93.

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Table 2. Nutmeg Extract Peak Table with Similarity and Reverse Similarity Numbers Resulting From Comparison of the Acquired Spectra to the NIST Mass Spectral Database and the Terpene library[1]. The Hit Column indicates the library hit number from the library hit list. RT is the Retention Time.

Peak	Name	R.T.	Similarity	Reverse	Hit
1	Tricyclene	33.81	719	896	1
2	α-Pinene	37.26	927	931	1
3	Camphene	39.56	945	961	1
4	Thuja-2,4(10)-diene*	40.67	749	898	1
5	β-Pinene	46.51	917	919	1
6	Dehydro-1,8-Cineole*	47.56	466	665	1
7	Mesitylene*	47.76	714	894	1
8	β-Myrcene	48.56	889	890	2
9	α-Phellandrene	49.71	886	887	1
10	Decane	50.06	763	870	1
11	3-Carene	50.61	880	893	4
12	α-Terpinene	51.86	914	925	1
13	o-Cymene	53.06	885	885	1
14	Limonene	54.26	870	901	1
15	cis-β-Ocimene*	55.56	802	919	1
16	trans-β-Ocimene*	56.91	819	881	1
17	γ-Terpinene	58.51	918	936	1
18	cis-Sabinenehydrate	59.16	891	893	2
19	Terpinolene	62.36	926	940	1
20	trans-Sabinenehydrate	63.41	897	900	1
21	Linalool	64.36	883	886	1
22	Undecane	64.56	707	779	2
23	endo-Fenchyl alcohol	65.36	819	896	1
24	cis-β-Terpineol	66.46	888	902	1
25	trans-Pinocarveol*	68.41	746	877	1
26	cis-2-Cyclohexen-1-ol, 1-methyl-4-(1-methylethyl)	69.01	852	865	1
27	Isothujol	69.66	792	804	1
28	Borneol	72.61	754	817	1
29	4-Terpineol	74.66	896	914	1
30	p-Cymen-8-ol	75.16	697	843	1
31	α-Terpineol	76.01	907	908	1
32	γ-Terpineol	76.61	824	849	2
33	Dodecane	77.41	855	943	1
34	trans-Piperitol	77.66	870	909	1
35	cis-Limonene oxide	82.56	688	794	2
36	cis-Geraniol	83.56	890	897	1
37	β-Isosafrole	87.01	900	911	2
38	Bicyclo[4.1.0]heptan-3-ol, 4,7,7-trimethyl-, (1α,3α,4β,6α)-	88.36	758	819	1
39	Thymol	88.71	601	718	3
40	Tridecane	88.91	787	856	5
41	p-Pentylanisole	89.21	776	786	1
42	α-Terpinyl acetate*	93.76	814	885	1
43	Eugenol	94.61	863	870	2
44	Ylangene	96.56	874	879	1
45	Geranyl acetate*	97.66	832	908	2
46	Isovanillin	98.36	866	910	1
47	Naphthalene, 2,3-dimethyl-	98.56	690	867	1
48	Longifolene	99.26	865	869	6
49	Methyl eugenol*	99.71	838	906	1
50	Naphthalene, 2,6-dimethyl-	100.36	838	917	1
51	Caryophyllene*	100.86	784	929	2
52	α-Bergamotene	102.86	913	941	1
53	Isoeugenol	103.91	804	905	1
54	β-Farnesene	105.16	653	837	1
55	Germacrene D	107.01	694	905	1
56	α-Zingiberene*	108.91	656	886	1
57	Myristicin	113.26	830	863	1
58	Elemicin*	115.06	815	914	3
59	Methoxyeugenol	119.11	889	910	1
60	Hexadecane	119.46	774	904	1

Matches were found in the Terpene library. All other matches are from the NIST '98 mass spectral database.

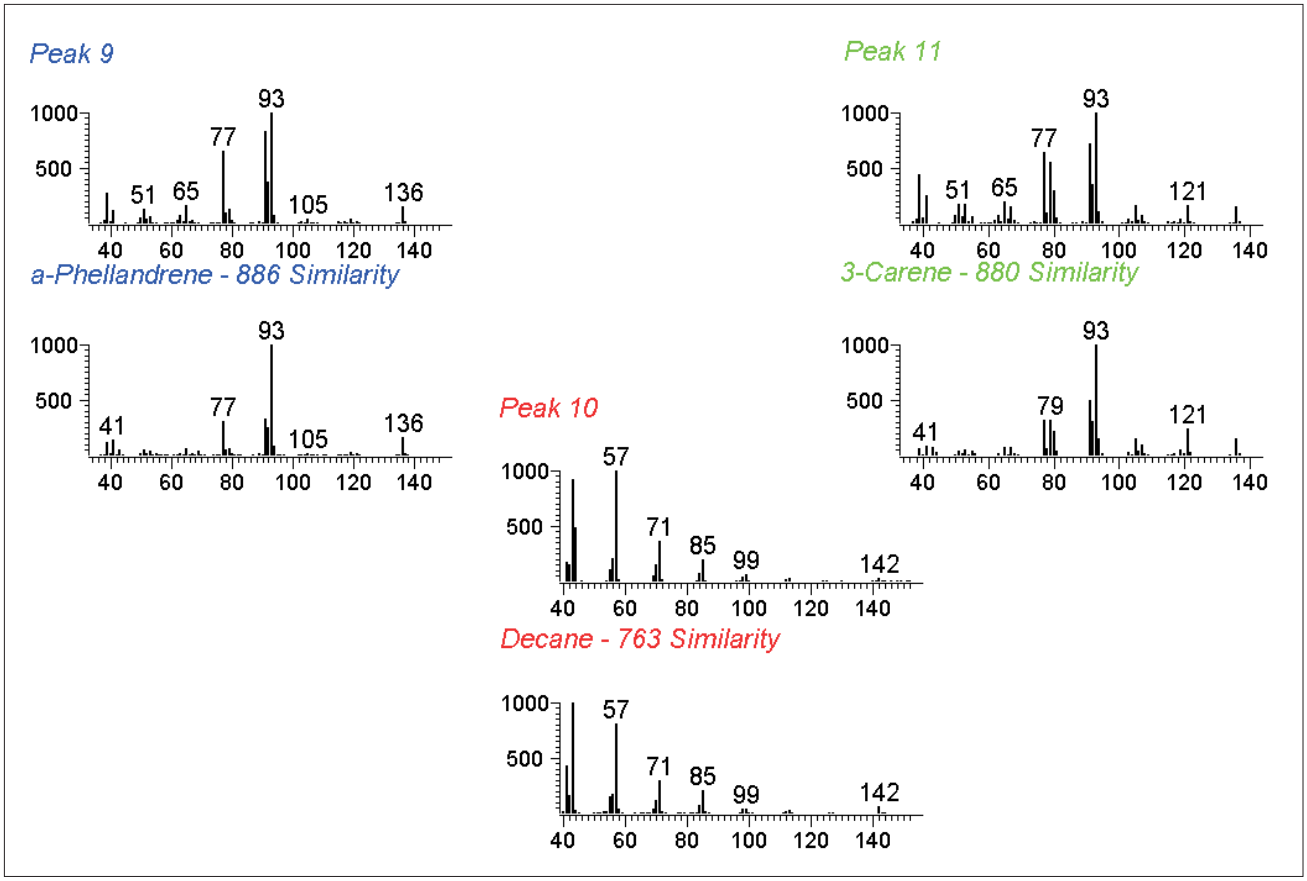

Figure 3. Mass Spectra for Coeluting Components as Determined by the Pegasus II GC-TOFMS Deconvolution algorithm. Top: Pegasus II spectrum. Bottom: NIST Library spectrum.

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 60 nutmeg components in only two minutes using the Pegasus II GC-TOFMS. This represents a 10 fold decrease in data acquisition time. The unique software features also significantly reduce data processing time resulting in an overall decrease of analysis time of well over 1 order of magnitude.

5. Acknowledgements

[1]The Terpene library is compiled by Robert P. Adams, *Identification of Essential Oil Components by Gas Chromatography/Mass Spectroscopy*, Allured Publishing Corporation, Carol Stream, IL. 1995.

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