Application Note

Instrument: Pegasus® BT

Essential Oil Characterization with GC-MS and Retention Index Determinations

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Key Words: Essential Oil Analysis, Retention Index, GC, MS, TOFMS

Introduction

Essential oils are extracts from plant materials that capture the plant's scent and flavors and have many uses. Gas Chromatography (GC) and Mass Spectrometry (MS) are excellent tools for the analysis of these, as the volatile and semi-volatile analytes that comprise essential oils are readily separated, identified, and quantified, resulting in detailed information on the individual chemical components. This type of detailed chemical information on an essential oil can be helpful for characterization, authentication, process optimization, and for a variety of quality control objectives. GC-MS, when using the Pegasus® BT, achieves the separation of individual chemicals through chromatography and also from deconvolution of the full m/z range data in instances of chromatographic coelution. The ability to add mathematical separation for chromatographic coelutions provides more information in less time as many chromatographic coelutions can be unraveled. Tentative identifications are determined with GC-MS from both spectral information and chromatographic retention order information. The acquired full m/z range TOFMS data can be matched with NIST library databases for spectral verification. The retention times of observed peaks can be linked to retention index with the use of a known alkane standard allowing for retention index matching with the NIST library databases for added confidence. We analyze and characterize a mint essential oil in this work, demonstrating the benefits of full m/z range data, deconvolution, and retention index determinations.

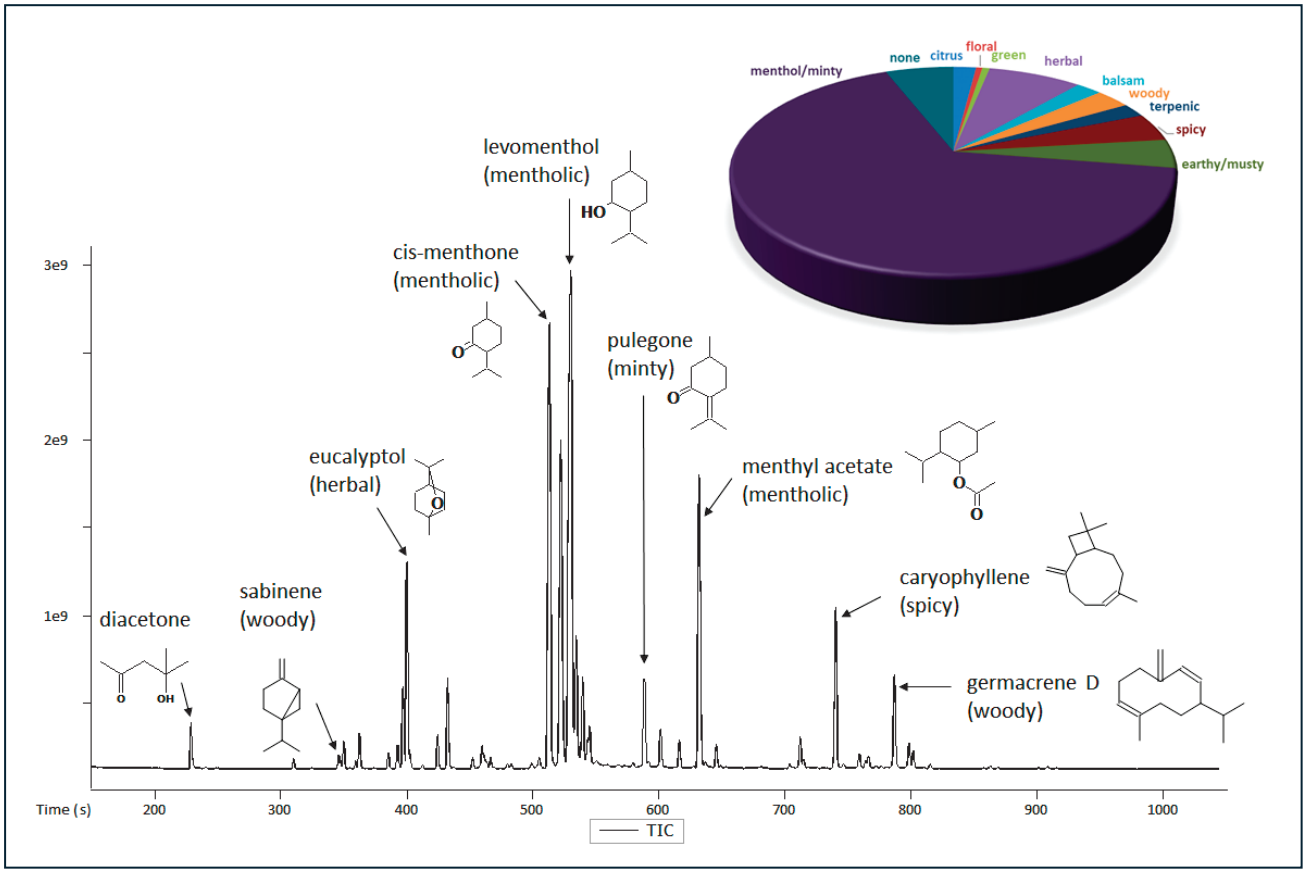

Figure 1. TIC Chromatogram for mint essential oil. Representative analytes of interest are shown along with a summary of the sample's aroma characteristics.

Experimental

A mint essential oil was diluted to 1% in acetone and analyzed with GC-TOFMS, as described in Table 1. Data for an alkane standard (C6 through C24) were also collected with the same methods for Retention Index (RI) determinations.

Table 1. GC-TOFMS (*Pegasus* BT) Conditions

Gas Chromatograph	Agilent 7890 with LECO L-PAL 3 Autosampler
Injection	1 µL, split 100:1
Inlet	250 °C
Carrier Gas	He @ 1.4 mL/min
Column	Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 µm coating (Restek)
Temperature Program	40 °C ramp 10 °C/min to 280 °C
Transfer Line	300 °C
Mass Spectrometer	**LECO *Pegasus* BT**
Ion Source Temperature	250 °C
Mass Range	33-500 m/z
Acquisition Rate	10 spectra/s

Results and Discussion

A representative GC-MS chromatogram for a mint essential oil is shown in Figure 1. LECO's automated data processing software provided information on the detected peaks within the sample. The identifications, aroma properties, and area % quantification information for the 30 most intense analytes in the sample are compiled in Table 2.

Table 2. Identification Information for Top 30 Analytes

	Name	R.T. (s)	Formula	Sim	RI	Lib RI	CAS	Odor Type	Area %
1	diacetone	228.7	$C_6H_{12}O_2$	936	839.8	838	123-42-2		1.102
2	sabinene	346.2	$C_{10}H_{16}$	947	976.5	974	3387-41-5	woody	0.326
3	β-pinene	350.3	$C_{10}H_{16}$	939	981	979	127-91-3	herbal	0.656
4	3-octanol	362.7	$C_8H_{18}O$	944	994.6	994	589-98-0	earthy	0.835
5	α-terpinene	385.7	$C_{10}H_{16}$	902	1019.7	1017	99-86-5	woody	0.38
6	p-cymene	392.9	$C_{10}H_{14}$	925	1027.6	1025	99-87-6	terpenic	0.494
7	limonene	397.0	$C_{10}H_{16}$	938	1032.1	1030	138-86-3	citrus	1.978
8	eucalyptol	400.1	$C_{10}H_{18}O$	924	1035.4	1032	470-82-6	herbal	5.836
9	γ-terpinene	424.6	$C_{10}H_{16}$	909	1062.1	1060	99-85-4	terpenic	0.81
10	(Z)-sabinene hydrate	432.6	$C_{10}H_{18}O$	895	1070.7	1070	15537-55-0	balsam	2.248
11	linalool	459.9	$C_{10}H_{18}O$	883	1100.4	1099	78-70-6	floral	0.538
12	cis-menthone	513.4	$C_{10}H_{18}O$	946	1160.4	1164	491-07-6	mentholic	16.828
13	menthofuran	521.7	$C_{10}H_{14}O$	893	1169.6	1165	494-90-6	musty	3.12
14	(±)-menthol	522.4	$C_{10}H_{20}O$	781	1170.4	1169	1490-04-6	mentholic	2.842
15	l-menthone	523.1	$C_{10}H_{18}O$	857	1171.3		14073-97-3	minty	3.258
16	levomenthol	530.6	$C_{10}H_{20}O$	923	1179.7	1175	2216-51-5	mentholic	29.868
17	(-)-terpinen-4-ol	534.8	$C_{10}H_{18}O$	883	1184.3	1185	20126-76-5		3.113
18	neoisomenthol	539.9	$C_{10}H_{20}O$	939	1190	1188	491-02-1	mentholic	2.075
19	(1S,2R,5R)-(+)-isomenthol	543.9	$C_{10}H_{20}O$	886	1194.5		23283-97-8	musty	0.503
20	α-terpineol	545.4	$C_{10}H_{18}O$	911	1196.2	1189	98-55-5	terpenic	0.848
21	pulegone	588.7	$C_{10}H_{16}O$	916	1247.4	1237	89-82-7	minty	2.196
22	p-menth-1-en-3-one	601.4	$C_{10}H_{16}O$	902	1262.4	1253	89-81-6	herbal	0.944
23	neomenthyl acetate	616.4	$C_{12}H_{22}O_2$	909	1280.3	1274	2230-87-7		0.661
24	menthyl acetate	632.1	$C_{12}H_{22}O_2$	937	1298.8	1295	89-48-5	mentholic	9.468
25	isomenthyl acetate	645.8	$C_{12}H_{22}O_2$	935	1315.7	1305	20777-45-1		0.599
26	(-)-β-bourbonene	712.4	$C_{15}H_{24}$	922	1398	1384	5208-59-3	herbal	0.716
27	caryophyllene	740.6	$C_{15}H_{24}$	953	1434.9	1419	87-44-5	spicy	4.379
28	germacrene D	787.0	$C_{15}H_{24}$	922	1496	1481	23986-74-5	woody	2.316
29	β-cyclogermacrane	798.7	$C_{15}H_{24}$	899	1512	1495	24703-35-3	green	0.632
30	β-himachalene	801.9	$C_{15}H_{24}$	928	1516.6	1500	1461-03-6		0.432

Analyte identifications were determined by searching the observed mass spectral information against the NIST 2017 MS library database with similarity (Sim) scores listed in Table 2. To add confidence to the identifications, Retention Index values were calculated for all peaks detected. Data for an alkane standard was acquired and used for these determinations. The observed RI value was verified against the Library RI information in the NIST database, as also indicated in Table 2. Retention Index was helpful for sorting out some ambiguous peak identifications, as shown in Figure 2. With preliminary library searching, peaks #23-25 in Table 2 all matched to the same library spectrum, isomenthyl acetate. The observed spectra for each of these three peaks (top spectra in Figure 2) are nearly identical, typically indicating isomers or analytes with very similar chemical structures. In this case, retention index provided additional information related to expected elution order that was helpful for clarifying these isomers, with tentative identifications updated to neomenthyl acetate, menthyl acetate, and isomenthyl acetate.

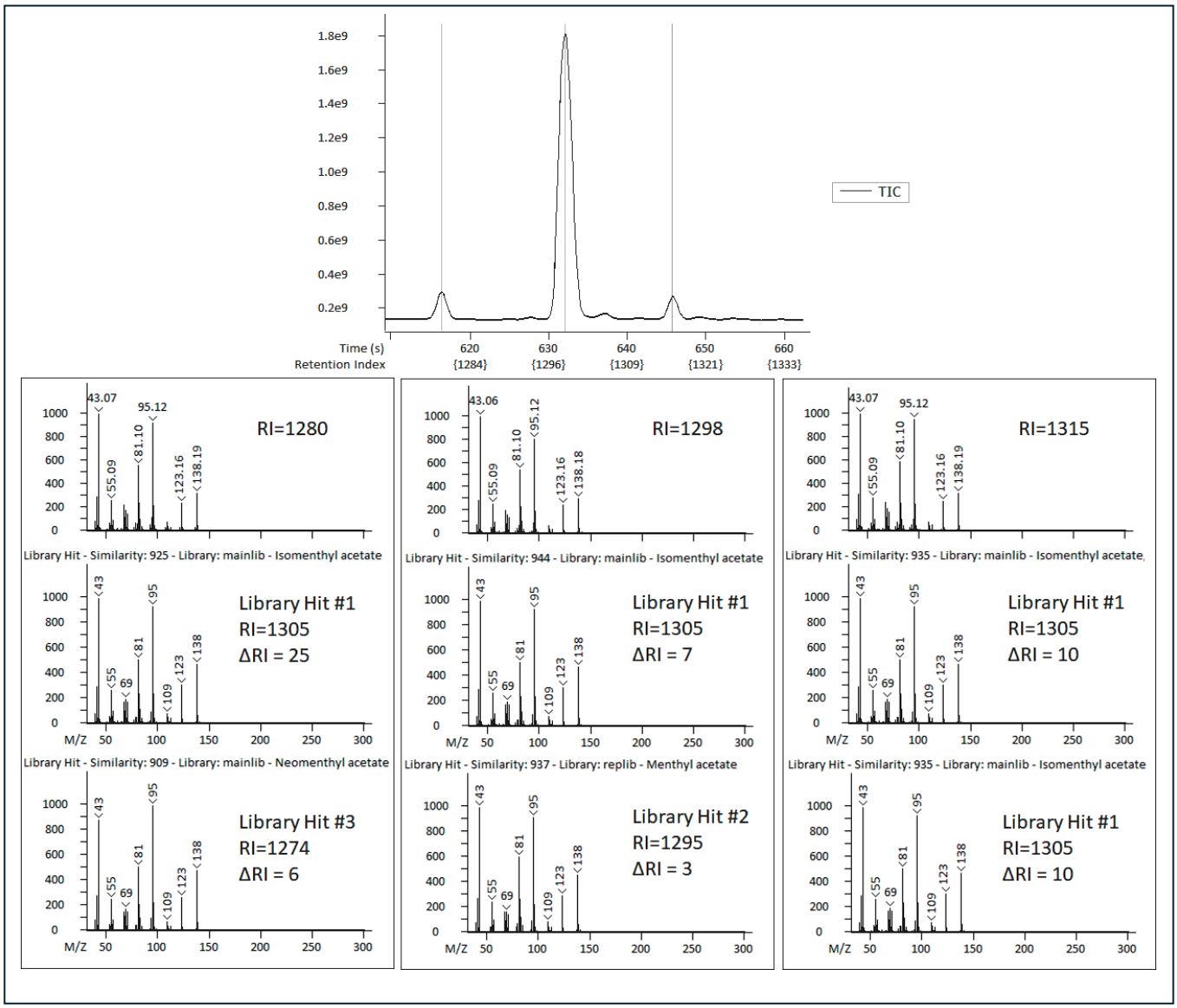

Figure 2. Retention Index can help add confidence to identifications for analytes with very similar spectral information.

The data processing tools in the software also offer the benefit of deconvolution, which is helpful in instances of chromatographic coelution. Some instances of coelution were observed in these data. For example, peaks #13-15 in Table 2 are shown in Figure 3. It appears that there is a single peak in the TIC view, but plotting XICs specific to each analyte clearly shows that three separate analytes are coeluting. Deconvolution provided clean spectral information for each coeluting analyte that led to the identifications (supported by Retention Index) of menthofuran, menthol, and menthone. The raw spectral information at the TIC apex, shown in the upper right corner of Figure 3, is the combination of the coeluting analytes and is what would be available without deconvolution. This spectrum matches to a different analyte, 6-methyl-cyclodec-5-enol, with a similarity score of 727, indicating that the three coeluting analyte would be obscured without deconvolution. Menthofuran, menthol, and menthone have musty, mentholic, and minty odor characteristics and are likely important contributors to the overall aroma profile. These analytes would have been difficult to detect without deconvolution.

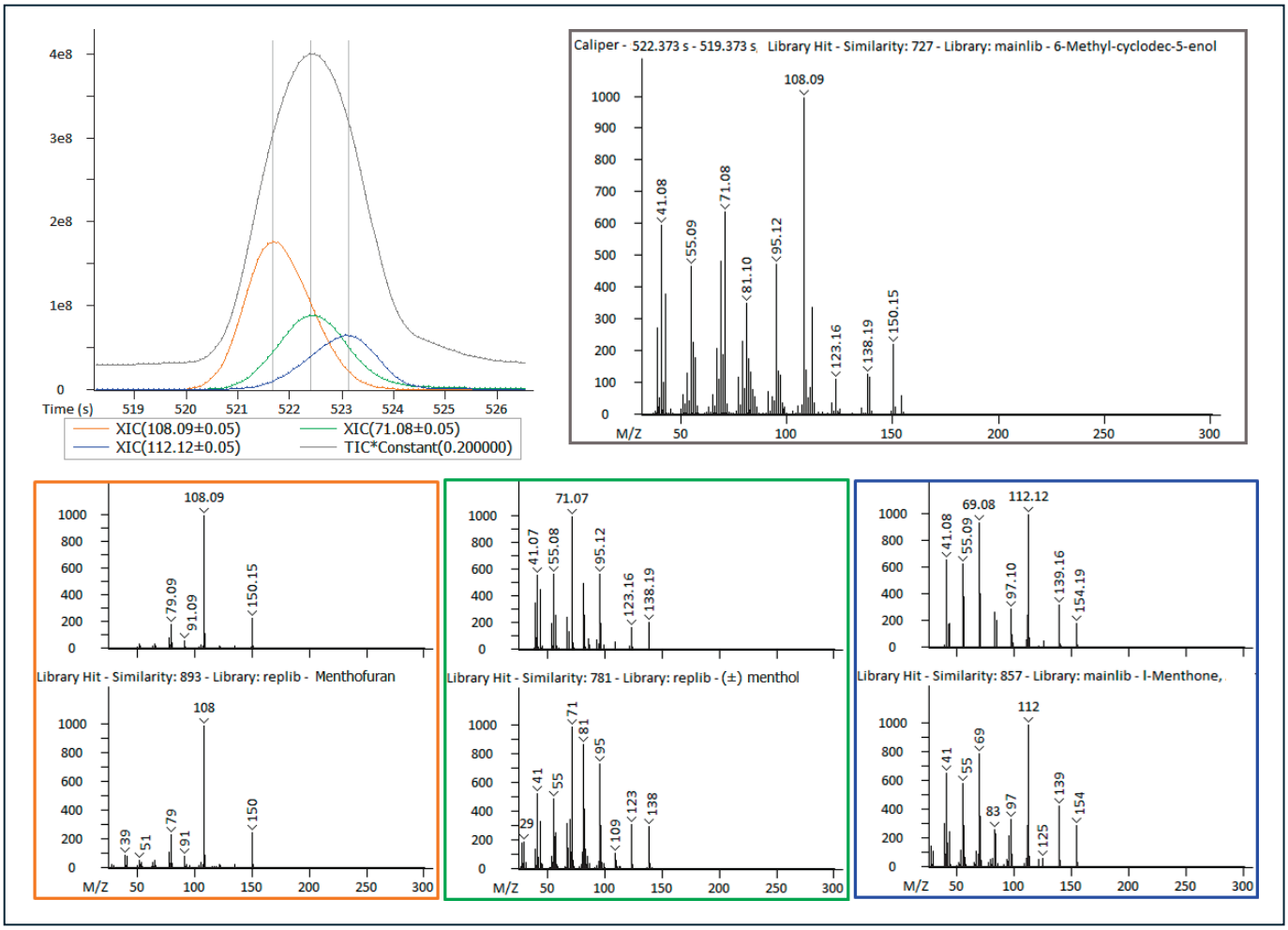

Figure 3. Deconvolution provides information on analytes that chromatographically coelute.

With analyte identifications, the associated aroma properties per analyte were determined with odor types listed in Table 2. The overall sample characterization was then compiled from these aroma properties and the associated peak areas per analyte. To directly connect an analyte peak area to sensory detection, the sensory threshold for that particular analyte as well as the response factor for that analyte on the instrument would be required. In the absence of these values, the peak areas can provide a chemical profile for aroma characterization. The peak areas were determined in the ChromaTOF® brand software by integrating the deconvoluted TIC peaks (the sum of all spectral peaks in the deconvoluted peak true spectrum integrated over the concentration profile for the chromatographic peak), and the Area % per analyte is reported in Table 2. The top 30 analytes included in Table 2 were used to create the pie chart in Figure 1, which compiled peak area % by aroma type. Minty or mentholic is the major aroma descriptor for this essential oil, as expected.

Conclusion

In this work, we have demonstrated the application of GC-MS for the characterization of a mint essential oil. The individual analytes as well as the overall characterization based on aroma types were reported for this sample. Retention Index information was helpful for clarifying ambiguous analyte identifications and deconvolution was crucial for distinguishing chromatographically coeluting analytes. This detailed chemical information on the essential oil provided characterization information. GC-MS is a powerful tool for this type of analysis and helps you learn more about your sample in less time.

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