Identification of Essential Oil Components by EI/MS & Mixed Reagent CI/MS

GC/MS

Varian Application Note

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Introduction

"Fingerprinting" of plant or food extracts can be valuable in quality control of products as well as in identification of adulterated commercial products. Whereas GC/FID can be a good starting point in these typical tasks, at some point qualitative identification of individual peaks is required. GC/MS with electron impact ionization (EI) fulfills some of the requirements for identification, provided that an adequate EI/MS library is available. This is a problem in the case of essential oils because the historical rule has been to maintain propriety over commercial EI/MS spectra. Even if library spectra are available, however, the mass spectra of isomers of flavor components are often almost identical; library searches need to be complemented by retention time information. In addition, the molecular ion is not always observed in EI/MS spectra, so a secondary confirmation of molecular weight would be desirable.

In this application note, the following strategy is presented to improve the qualitative identification of essential oil components:

1) Acquire EI/MS data using the same gas chromatographic conditions employed to prepare a commercially available flavor and fragrance library. This library contains retention time data to improve the quality of the library search process.

2) Acquire CI/MS data using a 50:50 mix of deuterated and undeuterated acetonitrile. These data can confirm molecular weight through the appearance of both M+1 and M+2 pseudomolecular ions.

Experimental

The Saturn 2000 system was used to acquire consecutive runs in EI and CI modes for six different essential oils. Retention times for n-alkanes were also determined to establish Kovat's Index markers. The chemical ionization reagents were a 50:50 mix of acetonitrile and d3-acetonitrile. We will refer to this approach as ***dual CI***. The CI reagents were admitted to the mass spectrometer with a Varian LCI Inlet.

To avoid overloading the GC column and the MS detector, the essential oils were diluted 50:1 in hexane then split 20:1 in the injector. The GC column program was the same used in development of the Adams Flavor and Fragrance Library[1].

Table 1. GC and MS Conditions

Column:	DB5 30m x 0.25 mm ID x 0.25µm film	
GC:	Inject 1 µL, Split 20:1, He flow 1 mL/min, Column 60°C, no hold, ramp to 240°C @ 3°C/min	
MS:	AGC Target:	10,000
	Ion Trap Temperature:	150°C
	Scan Range EI:	40-500u
	Scan Range CI:	90-500u
	Scan Rate:	1.0 sec/scan

Results and Discussion

EI and dual CI chromatograms were acquired for lemon, orange, rosemary, basilic, lavender, and eucalyptus oils. Figure 1 illustrates the

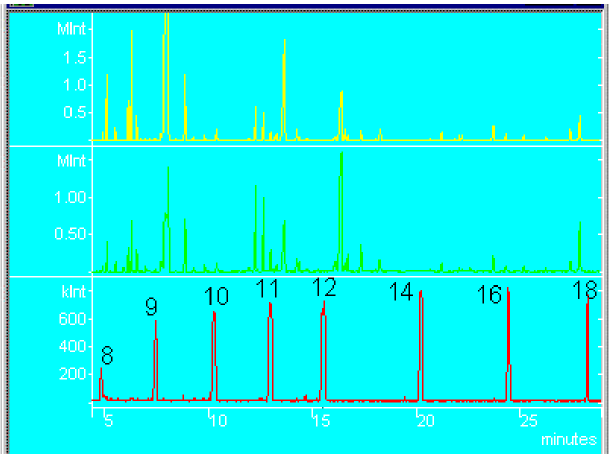

Figure 1. EI (above) and Dual CI (middle) Chromatograms for Rosemary Oil and Dual CI (below) Chromatogram for C8 to C18 n-alkanes

chromatograms for rosemary oil, as well as that for the n-alkanes. The results are typical of the six oils investigated; the acetonitrile CI peak pattern is essentially the same as the EI pattern. Not only does acetonitrile give good CI response for almost all peaks in the chromatogram, but the molecular weight inferred from the EI spectrum or library search is generally confirmed by the appearance of M+1 and M+2 ions in the dual CI chromatogram. Figure 2 shows the EI and CI spectra and Figure 3 shows the EI library search result for menthone (MW 154). Note that the DB5 retention time in the library spectrum matches well with the retention time in the rosemary oil chromatogram. The EI spectrum has a molecular ion at m/z 154 and the dual CI spectrum has strong confirmatory ions at M+1/M+2. The main exceptions to this rule are alcohols, which tend to lose a water molecule after protonation, leading to characteristic M-17 ions.

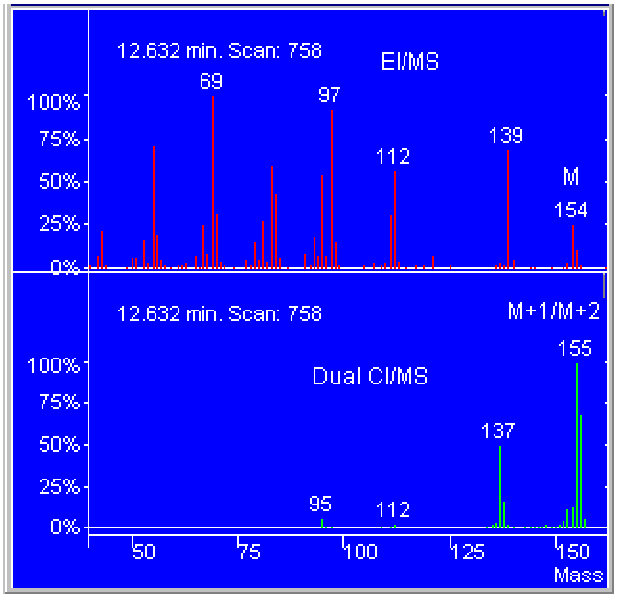

Figure 2. EI and CI Spectra for Menthone

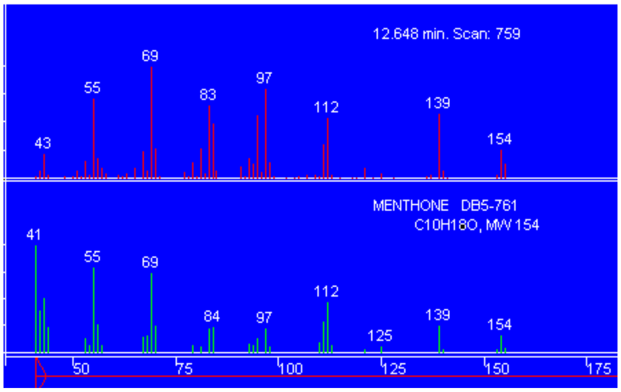

Figure 3. Library Search Identifies Menthone. Retention Time Match Also Good.

Figure 4 shows the library search results for another peak. Borneol is identified as the top hit in the search although there is no molecular ion in the EI spectrum at m/z 154. EI and dual CI spectra of borneol are shown in Figure 5. The EI spectrum has no molecular ion and the dual CI spectrum shows not M+1/M+2, but a single strong ion at M-17 after a loss of water from the protonated molecular ion.

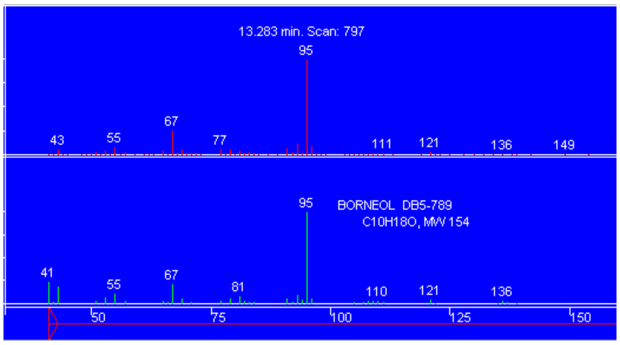

Figure 4. Library Search with Adams Flavor and Fragrance Library Identifies neo-Menthol (MW 154) at the Expected Retention Time

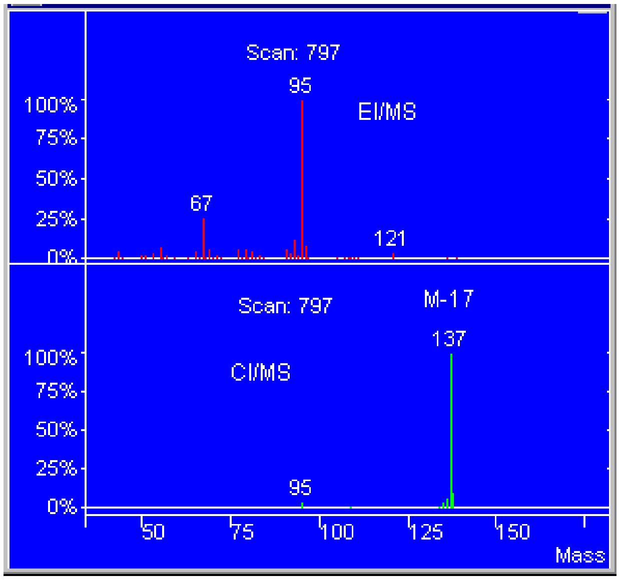

Figure 5. EI & CI Spectra of Borneol

Conclusions

The combined use EI/MS (with Adams Flavor and Fragrance Library search) and dual CI confirmation provides enhanced capability in the identification of essential oil components.

Reference

1.The Adam's Flavor and Fragrance Library on diskette and the companion book "Identification of Essential Oil Components by Gas Chromatography /Mass Spectrometry" are available from Allured Publishing, 362 S. Schmale Rd., Carol Stream, IL, 60188-2787, USA. Telephone (630) 653-2155.