Identification of Essential Oil Components by Gas Chromatography/ Quadrupole Mass Spectroscopy

Robert P. Adams
Allured
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Reviewed by O. David Sparkman
Mass Spectrometry Facility
Department of Chemistry
University of the Pacific
3601 Pacific Avenue
Stockton, CA 95211, USA
E-mail: osparkma@pacific.edu

In the Preface to *Identification of Essential Oil Components by Gas Chromatography/Quadrupole Mass Spectroscopy* [sic], Robert P. Adams, the author, states that he began research on essential oils in 1966. This may account for the reason that he persistently uses the term *mass spectroscopy* rather than *mass spectrometry* (Robert, there are no light bulbs inside those mass spectrometers). Again, as was the case with the second edition, there is no indication that this is a third edition; but, as in the second edition, the author clearly acknowledges this fact in the Preface.

This edition has spectra for 1606 compounds. Adams takes some liberty in saying that this is 400 more than the previous edition, which actually had spectra for 1252 compounds. Because the spectra were acquired on an HP 5970 Mass Selective Detector (spectra in the previous editions were acquired using a Finnigan ITD-800 internal ionization quadrupole ion trap instrument), the display format of the spectra corresponds to that of the Agilent (formerly Hewlett-Packard) ChemStation mass spectral display rather than the Finnigan ITD-800 (now Thermo Electron). The ChemStation has the ordinate of the spectrum labeled in ion abundance rather than percent abundance or relative percent intensity. One of the curiosities of these spectra is that all exhibit exactly the same maximum abundance.

As with the previous edition, each spectrum has a structure showing chirality were appropriate, retention time on a DB-5 column, and Kovat's index. Details are provided about the GC column and the operating conditions of the GC as well as the sample injected into the GC (volume, split ratio, and the internal standard used for retention time). The only important parameter missing from the operation of the mass spectrometer is the rate at which the data are acquired (the number of spectra per second). Another important factor would be the identification of the ChemStation version used. ChemStation has two very different versions of Autotune, and the only way to distinguish between which version was used is by the ChemStation version number. Adams states that data were acquired after using the instrument's "Autotune" to set the operating conditions.

As was criticized in the review of the second edition, this book has some significant shortcomings in the brief text portion. They go beyond the criticism of calling a mass spectral peak an ion. In the discussion of whether or not mass spectra acquired with a quadrupole ion trap (QIT) and a transmission quadrupole are comparable, the author displays what he says are spectra of 3-methyl-4-heptone obtained on both instruments. The spectrum displayed that was reported to have been obtained on the transmission quadrupole is not that of 3-methyl-4-heptone but that of 2-methyl-4-heptone. The telltale peak at *m/z* 58, which is ~30% of the intensity of the peak at *m/z* 57 (the base peak), is the giveaway. This *m/z* 58 peak is obviously missing in the spectrum obtained with the QIT and is also missing from a spectrum for 3-methyl-4-heptone obtained on a transmission quadrupole that appeared in the second edition.

Another area exhibiting a limited understanding of electron ionization mass spectrometry is the comparison of spectra of tricyclene. The author points to the fact that the peak at *m/z* 77 is ~102% of the intensity of the peak at *m/z* 79 in the spectrum obtained with the QIT, whereas the peak at *m/z* 77 is ~98% of the peak at *m/z* 79 in the spectrum obtained with the transmission quadrupole. These relative intensity differences are insignificant, especially when the intensity of the peak at *m/z* 77 relative to the intensity of the base peak is about the same in both spectra (~40%).

More effort could have been put into the proofing of these few pages of text. It is stated that a compound is represented by a chromatographic peak that has a retention-time range of 5.589 to 5.67. Then, in an attempt to show how the recorded retention time is determined using the equation "5.89 min + 0.03 min = 5.62 min" is presented, it is obvious the "5.89" in the equation should have been "5.589", but this should have been caught in the proofing stage.

The references to journal articles would be more valuable if they included titles, which is now the requirement for the *Journal of the American Society for Mass Spectrometry*. This is especially true for the M. P. Clay reference that cites an unnamed article that appeared in *Mass Spec Source*, an obscure organ published by Scientific Instrument Services in Ringoes, NJ (http://www.sisweb.com).

As was the case with the second edition, the "Appendices" consist of an alphabetical listing of compounds (mostly common names) with their retention times and Kovat's index on a DB-5 capillary GC column

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(Appendix I), followed by a listing of the compounds arranged in increasing retention-time order (Appendix II). Following the presentation of the bar-graph spectra (Appendix III) is a cross index of common names (Appendix IV). This listing only gives references to other names used in the database with no referenced page numbers or retention times. To find the spectrum of a compound whose synonym appears in this index, the listing name must be found in the alphabetical index to retrieve the retention time, which is necessary to locate the spectrum. This is a little awkward and hopefully will be addressed in subsequent versions.

The bar-graph spectra in the book are nicely presented, three-per-page along with structures of compounds with indications of stereochemistry where appropriate. In addition to the name, DB-5 retention time, and Kovat's index, the compound's Chemical Abstracts Service (CAS) registry number, elemental composition (molecular formula), formula weight (nominal mass), library entry number for the electronic format, and a list of synonyms are provided.

The electronic version of this edition is far better than the previous edition because the header of each spectrum includes a Chemical Abstracts Service registry number (CASrn). This means that if the NIST/EPA/NIH Mass Spectral Database is installed on a ChemStation system or the Adams library is used with the NIST Mass Spectral Search Program, a spectrum will be displayed with each structure. It would have been nice if a structure database in either the MOL or Agilent format had been provided with the distribution of this library. Because these structures appear on the printed spectra in the book, they must exist in some electronic format somewhere. There are a few compounds that do not have a CASrn; therefore, even when the NIST structures are available, these spectra will not have associated structures without an individual structure-library. It should be noted that the database is not available from Allured in the NIST Mass Spectral Search Program format; however, the database can be copied from the ChemStation format to the NIST format using the Lib2NIST Converter utility provided with the NIST MS Search Program or downloadable from http://chemdat.nist.gov. Allured will provide the electronic version in any of 16 different formats, which covers most of the GC/MS system proprietary formats. One of these 16 formats is netCDF, which can be considered a universal format.

Repeating from the review of the second edition [1]: "The collection of compounds of interest to the essential oil chemist that have been amassed for this work is outstanding; however, by the author's own admission, 'Unfortunately, several compounds are not in the [database] because we could not obtain authentic reference compounds.' Just as unfortunately, a list of these compounds is not included in the book." Hopefully, this omission will also be addressed in a future edition.

The quality of all of the spectra appears to be quite good. The spectra appearing in the book have a "library number" for the MSD library and the ITD library. These two numbers generate some questions. The spectrum of phenethyl cinnamate has an MSD LIB#: 1309 and the ITD LIB#: 1611. The questions are (1) "Where are the additional spectra acquired using the QIT since the second edition?" and (2) "Are there spectra of compounds beyond the 1606 spectra in this electronic version of the database?"

There are far more transmission quadrupole mass spectrometers in use in the analysis of terpenes and flavor and fragrance compounds than there are QIT instruments. As emphasized by Adams in the first and second editions, there are some acknowledged differences in spectra of the same compound obtained by electron ionization on the two different types of instruments; therefore, the fact that these spectra were acquired using a transmission quadrupole mass spectrometer and the ready availability of structures through provided CASrns and the fact that there are spectra of ~350 more compounds, even with an increase in price for the book alone of $80 and for the book and electronic version of the database of $230, makes *Identification of Essential Oil Components by Gas Chromatography/Quadrupole Mass Spectroscopy* a welcome addition to any collection of databases, especially for those who are in the flavor and fragrance industry.

References

1. Sparkman, O. D. Identification of Essential Oil Components by Gas Chromatography/Mass Spectroscopy. *J. Am. Soc. Mass Spectrom.* **1997,** *8*, 671, 672.