Review of Identification of Essential Oil Components by Gas Chromatography/ Mass Spectrometry, 4th Edition

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It is clear that Professor Robert P. Adams carefully read the review of the third edition of this work, *Identification of Essential Oil Components by Gas Chromatography/Quadrupole Mass Spectroscopy* [sic], (Allured, copyright 2001, 2004) that appeared in this journal (*J. Am. Soc. Mass Spectrom.* **2005,** *16*, 1902–1903). The title was changed to use the term *mass spectrometry* rather than mass spectroscopy, information about how the MSD transmission quadrupole mass spectrometer was tuned is included, and the scan rate at which data were collected is also included. Most importantly, the esoteric set of references that appeared in previous editions now includes clear titles for the journal articles. This edition also includes a good description of how the retention times were recorded and how to use retention times in conjunction with a comparison of the mass spectral data. The text editing on this edition is improved over that of the previous edition, although apparently at least part of the Preface was copied from the previous edition. Both editions contain the sentence, "This book is an outgrowth of the previous books (*Identification of Essential Oils by Ion Trap Mass Spectroscopy*, Academic Press, 1989; *Identification of Essential Oil Components by Gas Chromatography/Mass Spectroscopy*, Allured Publishing, 1995), but …" What happened to the third edition published in 2001? Surely, it should have been mentioned along with the first and second editions.

The most significant addition to this edition is an additional spectra of 600 (actual count is 598) compounds to give a total of 2205 spectra, compared with 1607 spectra in the third edition, 1252 spectra in the second edition, and about 700 spectra in the first edition. Like the third edition, the spectra in the fourth edition were acquired on a 5970 mass selective detector. Spectra in the first two editions were acquired using a Finnigan ITD 700 three-dimensional (3D) quadrupole ion trap mass spectrometer that used internal ionization. The whereabouts of these ion trap spectra remains unknown as was the case with the third edition. It would be nice if these spectra were also made available. Also missing from the fourth edition is the text comparison of QIT spectra with those obtained using the transmission quadrupole. Without the inclusion of the QIT spectra, this omission is probably good because it never was well explained in any of the previous three editions.

This edition of the Adam's library includes an arithmetic [retention] index (AI) as described by Van den Dool and Kratz [1] as well as retention time (RT) and Kovats indices (KI). The electronic version includes the RT as the first few characters of the Compound Name. The AI values are in the RI (retention index) field of the library header in the Agilent (referred to in this book and all documentation associated with the electronic version as HP) ChemStation PBM format. When this Agilent format is converted to the format used by the NIST MS Search Program, the contents of this RI field are put in the Comments field of the NIST format as |RI:xxxx|.

Another new (and outstanding) feature of this edition is the inclusion of the source of the compound used to obtain the mass spectrum. In some cases, additional natural sources of the compound are also included. As was the case with three previous editions, in addition to the common name, which along with a prefix of the RT value is used as the compound's main name, there is a chemical name field and a synonyms field in the printed format. Both the chemical name and the synonyms are not available in the electronic format. This is unfortunate. In the printed format, there is a chemical structure showing chirality, where appropriate, for each spectrum. However, an electronic version of the structures database is not provided. Because this edition, like the third edition, does have the Chemical Abstracts Services registry number (CASrn) associated with each spectrum, if the computer having the Adam's library installed also has the NIST Structures Database installed and the compound in the Adam's library is in the NIST Database, a structure will be displayed based on a linking of the NIST structures through the CASrn. However, several compounds in the Adam's library do not have CASrns, or they are not in the NIST Databases; therefore, no structures will be displayed for these compounds. The Preface acknowledges several people who assisted with the drawing of structures. It is too bad that these structures, which must exist in some electronic format, are not provided in electronic format. If the Adam's library is put into the NIST Mass Spectral Search Program format, these structures, retaining their chiral features, can be associated with the spectra. The structures can also be put into a ChemStation structures

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database that allows spectral linking through CASrns; however, the ChemStation structures database does not allow for inclusion of chirality.

An advantage, besides having the availability of structures, of putting the Adam's library into the NIST MS Search Program format is that the NIST05 Database includes a library of Kovats Indices from the literature that are connected to spectra through the CASrn. When a spectrum is displayed from the Adam's library and if there is a corresponding CASrn in the NIST05 database, then the NIST-provided Kovats Index information from the literature will be displayed with the spectrum. This information includes the literature citation (including article's complete title) and the GC conditions (column and temperature program).

There is a little confusion regarding the numeric values listed for the formula weights, "...(or molecular weights) in AMU [sic]." The formula weight (FW) is usually based on atomic masses (average masses–weighted average masses) of the elements that comprise the compound. In the case of dichloroethane, the FW is listed as 98 Da in the text version, which is the nominal mass. The FW of dichloroethane would be 2(12.00) + 4(1.0078) + 2(35.453), which would equal 99 Da to the nearest integer. In the ChemStation electronic format, this compound is listed as having a "Mol. Weight" of 97.968, which is very close to the compound's monoisotopic mass. When library entries are created using the ChemStation Library Editor, the "Mol. Weight" is automatically calculated to the nearest millidalton. This could account for the "Mol. Weight" in the electronic version being close to the monoisotopic mass for 1,8-Cineole (C10H18O), 154.128 Da (listed) versus 154.136 Da (calculated) but not in very good agreement. This difference of 18 mDa is significant. On the other hand, eicosane (C20H42) in the electronic version of the Adam's library had the same exact monoisotopic mass as the reported "Mol. Weight" to the nearest millidalton. Eicosane contains only atoms of carbon and hydrogen, whereas 1,8-cineole contains carbon, hydrogen, and oxygen atoms. Possibly the monoisotopic mass tables for the various elements in the ChemStation have slight errors, which could explain these observations of apparent errors in the reported mass. With respect to nominal mass, these variations will not be a problem.

Problems with figure presentations and calling mass spectral peaks "ions" have been completely eliminated in this version because there is no longer any real discussion of spectra or differences in spectra between QITs and transmission quadrupoles. The book is arranged with an eight-page text section divided into seven parts and, like the previous edition, four appendices. *Appendix I* is an alphabetical listing of compounds by their common (primary) name with their retention time and arithmetic retention index on a DB-5 column in segregated columns following the names. *Appendix II* is a listing of compounds sorted in order of increasing retention times and arithmetic retention index. *Appendix III* consists of the mass spectra presented in bar-graph format along with all the header information described above. The spectra are presented in increasing retention-time order. Spectra are positioned three per page, whereas there were four per page in the third edition. This type of display and the 37% increase in the number of compounds is what accounts for the near doubling of the number of pages over the previous version. The spectra are presented in a normalized format (maximum value on the *y*-axis is 100). All spectra were acquired at a scan rate of 1 spectrum s^{-1} over a range of *m/z* 41 to *m/z* 415. No information was provided as to acquisition threshold. *Appendix IV* is a cross reference of compound names (other synonyms referenced to the primary name). Also new in this edition is the fact that Appendix IV now includes retention times, so that it is much easier to get to a spectrum from one of these synonyms. This was a critical point in the review of the previous editions.

Allured will provide the electronic version in any of 13 different formats, which covers many of the GC/MS manufacturer's proprietary formats. One of these 13 formats is netCDF, which can be considered a universal format; and as stated above, the ChemStation proprietary format can be converted to the NIST MS Search Program format (using the NIST Lib2NIST program).

Compatibility with MS Data Systems as Listed in the Book

In addition to this printed book, a computer searchable library is available for use on the following systems:

1. Palisade Bench Top/PBM, (PBM2205.SPC)
2. Finnegan [sic] GCQ/ (GCQM2205.LBR)*
3. Varian Saturn (VARS2205.LBR)*
4. Finnegan [sic] Ion Trap (ITD2205.LIB and ITD2205.INX)*
5. Finnegan [sic] INCOS (FINC2205.LS and FINC2205.LX)*
6. Fisons/VG JCAMP (FISV2205.JDX)*
7. Fisons/VG Mass Lab (FIML.2205.IDB, .IDI, .PDB, and .PDI)
8. HP JCAMP, Unix (HPJC2205.HPJ)*
9. HP Chemstation [sic] [Dir \ HPCH2205.L, plus 7 files: ROOT; HEADER; HEADER.IND; CAS.IND; CONDENSE; CONDENSE.IND; FULL.D]
10. net CDF (NETC2205.CDF)
11. PE Turbomass (PETU2205.IDB, .IDI, .PDB, and .PDI)*
12. Shimadzu QP5000 (6 files: SHIM2205.NAM, .FOM, .LIB, .SPC, .COM, .FLG)
13. MassFinder (MF32205.mfl)
14. Finnegan [sic] Triple Quad can automatically convert the .LS, .LX (no. 5. above) formatted library*
15. Finnegan [sic] ICIS can read Finnegan [sic] Ion Trap (.LIB, .INX, no. 4. above) formatted library* (Web site states that the Finnigan ICIS uses a .LBR format that *Xcalibur* can import)

16. Teknivent Vector 2 can read PBM (no. 1. above) formatted library*

*No longer supported by the instrument manufacturer.

It is interesting to note that Finnigan is misspelled in the book (on page 5 in the list of compatible instruments) but spelled correctly on page 1 and on the Allured Web site. This is another one of those overlooked copy-editing problems that appear to be growing with all publishers. Another one of those copy-editing issues is that the book states the data were acquired using an HP 5970 MSD in one place, and an HP 5970b in another place, the Web site states that the data were acquired using an HP 5971. Which was it?

The installation CD has 18 self-extracting ZIP files that require a password that is provided as a hard-copy document with the disk (be sure you don't lose this piece of paper!). The Web site lists 19 supported formats, which include those that are in the book plus separate listings for the Finnigan GCQ, ITS-40, and Magnum (all of these instruments are 3D QIT GC-MS that had only internal ionization). The Web site has only one listing for the Finnigan Ion Trap and the ITMS, whereas the installation CD appears to have separate files for these two instruments. The one supported format listed on the Web site that does not appear in the book and there is no apparent installation file is the Waters Millennium system, which is reported to have libraries with the same .SPC extension as used by Teknivent. It is curious that the book states that the numbers listed in brackets use 1 of the 13 other formats, but the installation disk has separate self-extracting files for the 16 above entries, plus files for the Finnigan Magnum and 2 files for the Finnigan ITD and the ITMS. The Web site states that the same library format is used by the Shimadzu QP5000 and QP2010. Be sure this is the case. The Web site does provide all the extensions of all the files that comprise a library for the various support systems, which should be very beneficial in selecting the correct format. When choosing a provided format for this library, be very careful that you will end up with something that is compatible with your system.

Most of the data systems whose formats are supported by Allured are no longer supported by the instrument manufacturer; or, if supported, they have been replaced by newer models. It is good for those still using these older data systems that there is support, but some of the more modern formats should also be included, e.g., the mass spectrometry data system from Varian no longer supports the .LBR format. There are third-party programs such as the MASSTransit from Palisade Corp. (http://www.palisade-ms.com/) and Lib2NIST (http://chemdata.nist.gov – a free download) to convert netCDF or ChemStation libraries to the NIST format that can be used to produce the more modern formats from those currently provided by Allured.

It is surprising that the Adam's library is not provided by Allured in the NIST MS Search Program's format because this is now the proprietary library format for the mass spectrometry data systems from Thermo Fisher, Varian, Perkin Elmer, and JEOL/Shrader regardless of whether or not the NIST Database is also provided. Agilent and Waters provide the NIST MS Search Program any time they provide the NIST Database. The NIST MS Search Program is now recommended over the Agilent PBM version by Agilent in the company's Deconvolution Reporting Software. The NIST format would allow for easy inclusion of the valuable list of synonyms and the source information that is included in the print version but is currently missing from the electronic version. Inclusion of these two items in the electronic version would enhance it even more.

If it already has not, the Adam's mass spectral library of essential oil compounds will become the *de facto* standard in flavor and fragrance research, next to in-house-generated databases. Professor Adams points out that an electronic search can miss some "subtle differences" between the library and sample spectrum. He states, "...it is useful to have the book opened to roughly around the unknown's RT and just look on the pages!" This analog type of comparison can be very valuable, especially when working with a small database (compared with the Wiley or NIST) such as that provided by Professor Adams.

As was the case with the previous three editions, the author states that there are a number of compounds that are interesting to the essential oil chemist that are not included because, "Unfortunately, several compounds are not in the [database] because we could not obtain authentic reference compounds." Again, as was stated in the reviews of the second and third editions, it is too bad that these additional compounds are not at least listed. However, is this book a compilation of compounds of interest to the essential oil chemist or is it a collection of spectra that pertain to essential oil research? I think it is the latter; therefore, the omission of these compounds for which there are no spectra is acceptable and reasonable.

A library may wish to purchase only the book, but a researcher should purchase the book/electronic version package. There has been an increase in price of $125 from the third to the fourth edition for the book and the book/electronic version. The book is now twice the size of the third edition, and there are 600 additional spectra. This $125.00 increase represents a price of $0.20 per new spectrum. The total price of the book/electronic version of 2200 spectra represents a price of less than $0.35 per spectrum, which includes the handsomely hard-bound version of the book. Compared with the price of several other boutique databases that have recently been made available, the Adam's library is a definite bargain. This collection should not fall into the category of being judged by its cover, it should be judged by the

apparent quality of the spectra and coverage of the topic—both of which are more than adequately met. Besides the spectra of the additional compounds, this edition of the Adam's library contains a lot more new information: the AI retention data, sources of the compounds, and retention times with the Cross Index of Names (Appendix IV).

If you are doing research in essential oils components or have to identify unknowns, *Identification of Essential Oil Components by Gas Chromatography/Mass Spectrometry, 4th Edition*, will be a valuable addition to your collection of resources, even if you have the third edition.

Reference

1. Van den Dool, H.; Kratz, P. Dec. A Generalization of the Retention Index System Including Linear Temperature Programming Gas-Liquid Partition Chromatography. *J. Chromatogr.* **1963,** *11,* 463–471.