More Than 43,400 High Quality Spectra Added to a Comprehensive Electron Ionization (EI) Mass Spectral Library

Weihua Ji, Lewis Y. Geer, Nirina Rabe Andriamaharavo, Yufang Zheng, Edward P. Erisman, H. Martin Garraffo, James Little, Gary Mallard, Sanford P. Markey, Yuri A. Mirokhin, Quan-Long Pu, Dmitrii V. Tchekhovskoi, Nino G. Todua, Oleg V. Toropov, Kirill V. Tretyakov, William E. Wallace, Stephen E. Stein

Mass Spectrometry Data Center, NIST, Gaithersburg, MD

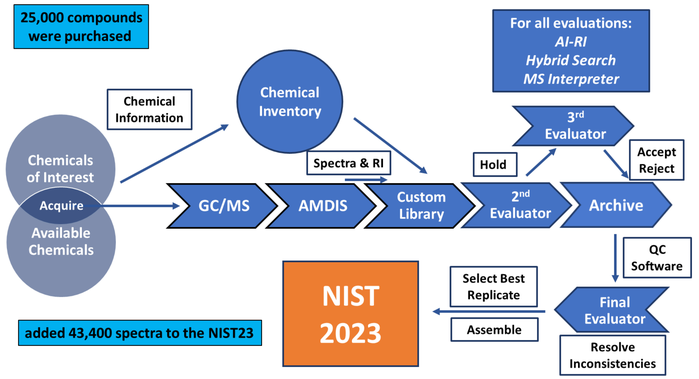
➢ Introduction:

- High quality and comprehensive reference mass spectral libraries provide a fast and reliable means of compound identification.
- The most challenging part of building such a library is the need for expert spectrum evaluation such as confirming molecular ions, examining fragmentation ions, impurities, and contaminants.
- However, because mass spectra of isomers and analogues might be similar and especially because molecular ions are not always present in the spectra, the collection and use of retention indices (RI) become very important. Here, we present how we perform manual inspection and use RI to ensure quality spectra for the library.

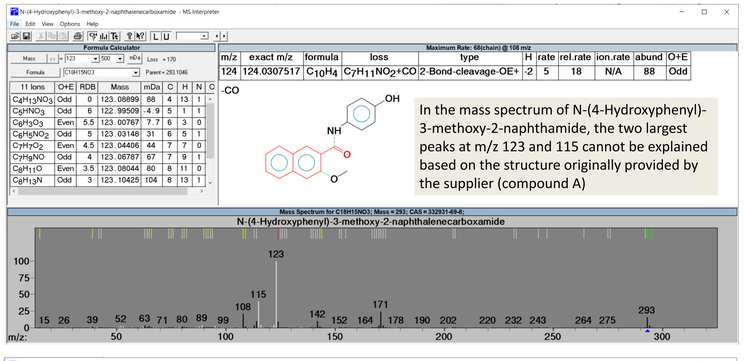
➢ Methods:

- We analyzed authentic compounds using GC/MS, then extracted spectra and their RI values from GC/MS data using the AMDIS program.
- Each spectrum was manually evaluated to ensure that product ions matched with the compound structure. Importantly, each spectrum was compared with spectra of similar compounds in the NIST mass spectral library and 5 other libraries using the hybrid search method. The MS Interpreter program was used to assign peaks with product ions to help examine the spectrum.
- The experimental RI of each spectrum was compared with the artificial intelligence-predicted retention index (AIRI), computed by a deep neural network that takes a molecular structure as input and outputs a predicted RI.
- All software tools used in this study may be freely downloaded from https://chemdata.nist.gov.

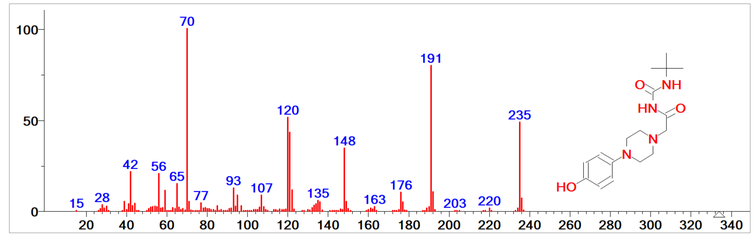
❖ Improved procedure for expanding the EI MS Library



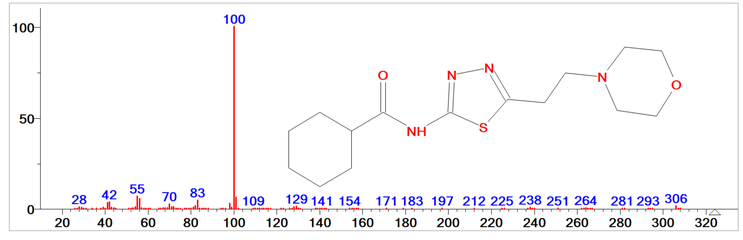
❖ An example of evaluating a spectrum with MS Interpreter.



❖ Retention Index and AIRI can help evaluate spectra.



For example, in the spectrum of N-(tert-Butylcarbamoyl)-2-(4-(4-hydroxyphenyl)piperazin-1-yl)acetamide, the molecular ion is not present. We examined the product ions, and they all matched 2-(4-(4-Hydroxyphenyl)piperazin-1-yl)acetamide, a decomposed product of the original compound. Furthermore, the experimental RI is 2494, which is greatly different from the original compound's AIRI 3009. Therefore, we did not add this spectrum to the library.



In another example, in the spectrum of N-(5-(2-Morpholinoethyl)-1,3,4-thiadiazol-2-yl)cyclohexanecarboxamide, there is no molecular ion peak but the water loss peak was observed. The spectrum confirmed that all other product ions were fragmented from the original compound and the experimental RI is 3031, which is similar to the AIRI 3076. We accepted this spectrum for the library.

➢ Summary:

- Over 45,700 mass spectra were manually inspected. About 5% of the spectra were rejected because of low quality or incorrect peaks in the spectra. More than 43,400 high quality spectra with RI values were added to the NIST23 mass spectral library of 40,200 compounds.

Please visit booth # 713 for more information about NIST Mass Spectral Libraries