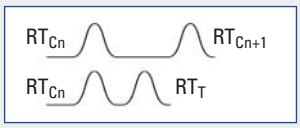
Sniff, sniff, take a whiff

Accurate determination of flavours and fragrances



RT : Retention Time
RT_{Cn} : RT for n-alkane with n-carbons
RT_{Cn+1} : RT for n-alkane with n+1-carbons
RT_T : RT for target compound

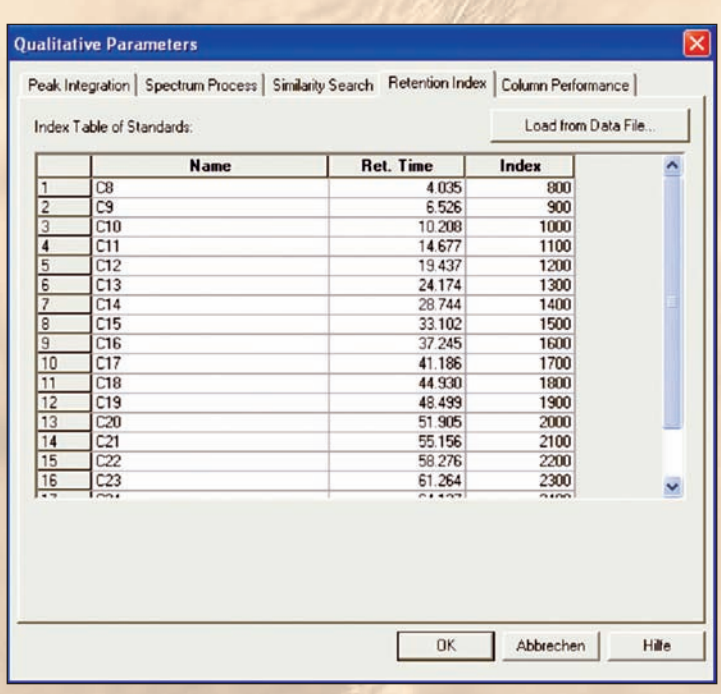
- **The retention time is calculated using n-alkanes as reference standards**
- **$LRI = 100 \times n + 100 \times (RT_T - RT_{Cn}) / (RT_{Cn+1} - RT_{Cn})$ (Temperature Program Condition)**

Figure 1: Calculation algorithm for Linear Retention Index (LRI)

In the flavour and fragrance industries as well as in basic research of essential oils, analysis of the materials of interest is quite complex even when using modern equipment. A common problem occurs when dealing with groups of compounds having similar structures (e.g. sesquiterpenes in essential oils) due to similarity of fragments generated by the ionization process, thus leading to acquisition of nearly identical spectra for different compounds. In this case, commercial libraries are not always capable of giving the correct peak assignment. Also, multiple entries of a compound inside one library have often been observed, making identification rather difficult.

Linear Retention Index (LRI)

In order to eliminate false positive or false negative identification, the concept of linear retention index (LRI) can be used. This concept is based on numbers derived from the retention times of alkanes observed when applying a linear temperature ramp (Figure 1). The basic theory is described in the literature [1]. LRI values depend only on the type of stationary phase used (e.g. polymethylsiloxanes, wax etc.) but are independent of the column dimensions. As mentioned before, the retention index relationship is linear if temperature program conditions are used.



	Name	Ret. Time	Index
1	C8	4.035	800
2	C9	6.526	900
3	C10	10.208	1000
4	C11	14.677	1100
5	C12	19.437	1200
6	C13	24.174	1300
7	C14	28.744	1400
8	C15	33.102	1500
9	C16	37.245	1600
10	C17	41.186	1700
11	C18	44.930	1800
12	C19	48.499	1900
13	C20	51.905	2000
14	C21	55.156	2100
15	C22	58.276	2200
16	C23	61.264	2300

Figure 2: n-alkanes used for the calculation of LRIs in an unknown sample

Automatic calculation of LRI values for unknown compounds

In the GCMSsolution software, the Linear Retention Index is calculated automatically. First, a standard sample of n-alkanes is measured. This data file is then linked to the data file to be analyzed (Figure 2) and the Linear Retention Indices of all unknown compounds are calculated automatically.

FFNSC library

Professor Luigi Mondello, University of Messina in Italy, has been working in this field for years [1-3], acquiring much experience on the complexity of the subject. Over this time, he and his research group developed a database known as the Flavour & Fragrance Natural & Synthetic Compounds Library (FFNSC 1.2) for electron impact (EI) analysis. At present, this library contains approx. 1200 mass spectra with retention indices, all of which have been measured with a Shimadzu GCMS-QP2010 quadrupole.

Library search using Linear Retention Index Filter

For the identification of unknown compounds additional to the comparison of the mass spectra, the Linear Retention Indices in the new FFNSC Ver. 1.2 are compared with the Linear Retention Indices calculated for the compounds to be analyzed (Figure 3).

with FFNSC library

Automatic update of Retention Times

At the same time, the retention times in the list of compounds to be quantitated (targets) are also updated using the AART (Automatic Adjustment of Retention Times) function button which utilizes the LRI values. The AART function is particularly useful if a column was changed or part of the column was cut due to contamination. With one measurement of n-alkanes the retention times in the ID table of all target compounds are updated. The method parameters (pressure, temperature) are not changed, ensuring that the chromatographic performance is still effective.

Summary

In GC-MS, identification of unknown compounds is usually performed by comparison of the measured mass spectra with mass spectra obtained from a commercially available MS library. However, there are drawbacks to this identification method. In many cases, very similar mass spectra for isomeric compounds e.g. terpenes can be found.

Linear Retention Indices are useful for the identification of unknown compounds in a sample, especially isomers. Although the concept of Retention Indices is well known, it has never been calculated automatically before now in a GC-MS software and used in combination with MS library search.

In the new GCMSsolution software, the LRI values are calculated automatically from a measurement of n-alkanes using the same column. The LRI can be used as filter criterion in MS library search to enhance the accuracy of identification of compounds with very similar mass spectra, e.g. isomers.

The new FFNSC library contains the mass spectra and the LRI values of almost 1200 compounds. All data were acquired from pure standard compounds using the GCMS-QP2010.

The LRI values are also used to update retention times automatically if a column was changed or cut (AART), as the LRI values depend only on the type of column stationary phase and are independent of column dimensions.

References

[1] Luigi Mondello, Paola Dugo, Annamaria Basile, Giovanni Dugo, Keith D. Bartle. Interactive Use of Linear Retention Indices on Polar and Apolar Columns with a MS-Library for Reliable Identification of Complex Mixtures. J. Microcol. Sep. 7(6), 581-591 (1995). ISSN 1040-7685 (November 1995, John Wiley & Sons Inc., New York, USA).

[2] Robert Shellie, Luigi Mondello, Philip Marriott, Giovanni Dugo. Characterisation of lavender essential oils by using gas chromatography-mass spectrometry with correlation of linear retention indices and comparison with comprehensive two-dimensional gas chromatography. J. Chromatogr. A, 970, 225-234 (2002). ISSN 0021-9673 (September 2002, Elsevier, B.V., Amsterdam, The Netherlands).

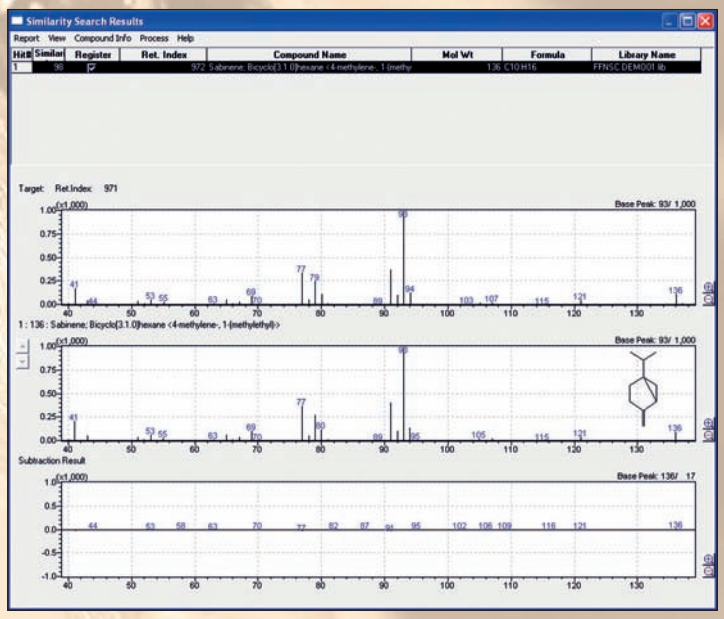
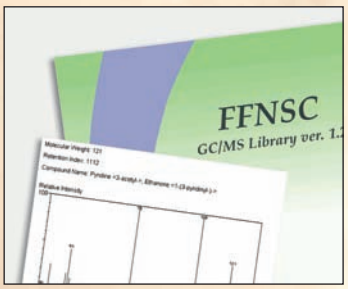


Figure 3: Library search result for Sabinene from FFNSC library using LRI in addition to the mass spectrum



[3] Robert Shellie, Giovanni Zappia, Luigi Mondello, Giovanni Dugo, and Philip Marriot. Interactive use of Linear Retention Indices, on Polar and Apolar Columns, with a MS Library for Reliable Characterisation of Australian Tea Tree and other melaleuca Sp. Oils. J. Essent. Oil Res., 15, 305-312 (2003). ISSN 1041-2905 (July 2004, Allured Publishing Corporation, Carol Strema, IL, USA).