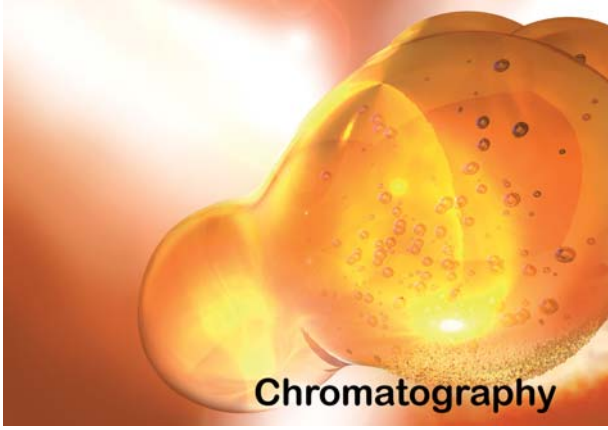
Application Note



Automatic Adjustment of Retention Times (AART) in GCMSsolution 2.5 - An excellent help for complex samples

Whenever a complex GCMS analysis has to be done with a large number of peaks corresponding to samples with dirty matrices the retention times may differ due to aging of the column and/or because the column has to be shortened in order to recover separation performance. Then all the target peaks in the compound table usually have retention times which are no longer correct. GCMSsolution 2.5 offers the possibility to automatically set the new retention times into the compound table of the method and, in addition, all time relevant parameters of the GCMS realtime analysis like SIM (Selected Ion Monitoring) tables are updated. Any compromise on the separation efficiency is avoided as the hardware parameters like the best mean linear velocity is still used. The concept is based on usage of the linear retention index (LRI). The LRI is automatically calculated for the compounds after injection of an n-alkane standard. The corresponding window is indicated in figure 1.

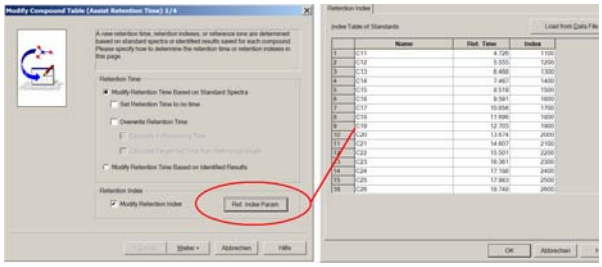


Fig. 1: Retention index calibration based on a n-alkane sample. The retention times are load from the n-alkane data file

Of course, the LRI can also be used as an identification help which is described elsewhere [1]. After loading the n-alkane data file the linear retention indices are calculated for the target compounds. Figure 2 shows a compound table of a pesticide sample with retention times and the LRIs calculated on the basis of the LRI calibration shown in figure 1.

Fig. 2: TIC data and part of the compound table of a pesticide sample

In case the capillary column has to be cut the retention times are shifted. For the pesticide sample this is demonstrated in figure 3. Here the column length was changed from 30 m to 28 m.

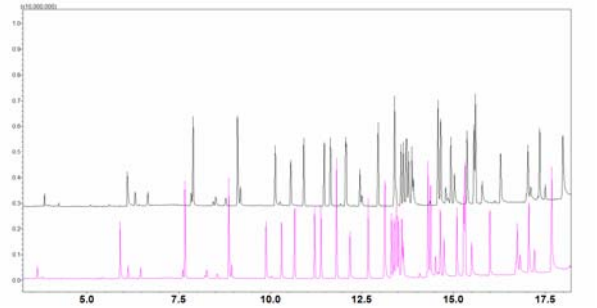


Fig. 3: Two runs of the pesticide sample shown in figure 2. Top: Data corresponding to the 30 m length. Bottom: Data corresponding to 28 m length

To adjust retention times inside the compound table just another injection of the n-alkane sample is done after cutting. Then the retention times of the pesticide compound table is adjusted on the basis of the new rention times of the n-alkanes and the LRI information. The latter is mainly influenced just by the stationary phase material which remains unchanged between the experiments. The main part of the procedure is visualized in figure 4.

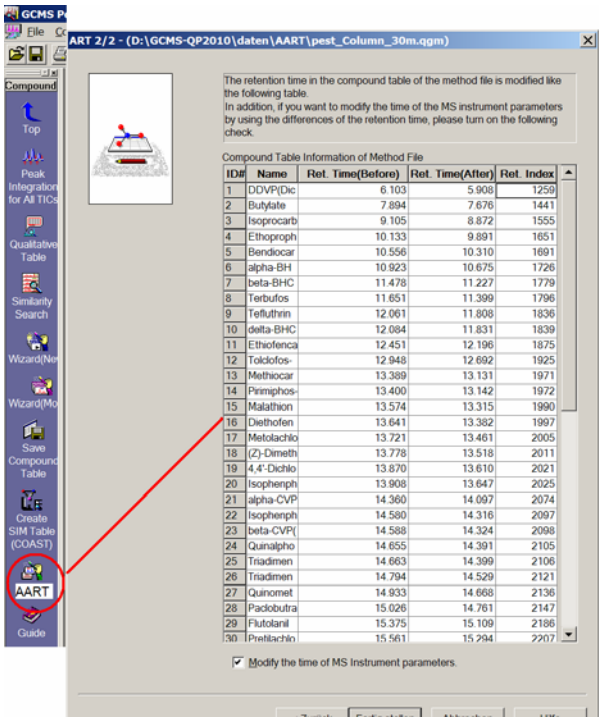


Fig. 4: AART function inside GCMSsolution 2.5 and box with retention times before and after adjustment.

There the retention times of the compounds before and after adjustment is indicated together with the LRI information. After completing this step the whole compound table contains the new retention times for reanalysis of unknowns measured with the column after cutting. The method is very reliable and precise. This is derived from a comparison where the retention times of the pesticides were manually checked and compared with the ones predicted from the automatic method. The result is shown in figure 5 for the 28 m length.

	Column Length	28m		
	Column Length in System Configuration	28m		
	Compound Name	Real	Predicted	Diff(RT)
1	DDVP(Dichlorvos)	6.120	6.103	0.017
2	Butylate	7.927	7.923	0.004
3	Isoprocarb	9.143	9.134	0.009
4	Ethoprophos	10.174	10.162	0.012
5	Bendiocarb	10.599	10.594	0.005
6	alpha-BHC	10.968	10.952	0.016
7	beta-BHC	11.526	11.513	0.013
8	Terbufos	11.700	11.689	0.011
9	Tefluthrin	12.113	12.117	-0.004
10	delta-BHC	12.134	12.121	0.013
11	Ethiofencarb	12.500	12.489	0.011
12	Tolclofos-methyl	13.000	12.988	0.012
13	Methiocarb	13.442	13.432	0.010
14	Pirimiphos-methyl	13.453	13.452	0.001
15	Malathion	13.628	13.627	0.001
47	Cyfluthrin-1	20.363	20.356	0.007
48	Cyfluthrin-2	20.446	20.443	0.003
49	Cyfluthrin-3,4	20.562	20.555	0.007
50	Halfenprox	20.718	20.706	0.012
51	Silafluofen	21.095	21.086	0.009
52	Fenvalerate-1	21.597	21.584	0.013
53	Fenvalerate-2	21.802	21.788	0.014
54	Difenoconazole-1	22.054	22.039	0.015
55	Difenoconazole-2	22.126	22.111	0.015
56	Imibenconazole	23.516	23.503	0.013

Fig.5: Comparison of automatic calculation of retention times set into the compound table using AART and the observed retention times in the data file

As can be seen from Figure 4 the box “Modify the time of MS instrument parameters” is checked. This makes sure that all time related MS parameters like SIM windows or time events for detector gain are automatically updated.

[1] Shimadzu Application Note:
Linear Retention Index Function (LRI) in GCMSsolution 2.4
An excellent help for identification confirmation of target compounds in complex chromatograms