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.

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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.



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Com	pound Table	Information of Method	File		_
ID4	Name	Ret. Time(Before)	Ret. Time(After)	Ret. Index	-
1	DDVP(Dic	6.103	5.908	1259	
2	Butylate	7.894	7.676	1441	
3	Isoprocarb	9.105	8.872	1555	
4	Ethoproph	10.133	9.891	1651	
5	Bendiocar	10.556	10.310	1691	
6	aipna-BH	10.923	10.675	1726	
/	Deta-BHC	11.478	11.227	1779	
8	Terbutos	11.651	11.399	1/96	
8	Tenuthinin	12.001	11.000	1830	
10	Cella-BHC	12.004	12,100	1039	
11	Tololofoe	12.401	12.190	1075	
12	Mathiacar	12.040	12.002	1923	
13	Diriminhoe.	13,400	13.142	1971	
15	Malathion	13.574	13 315	1990	
16	Diethofen	13.641	13 382	1997	
17	Metolachio	13 721	13.461	2005	
18	(Z)-Dimeth	13 778	13.518	2011	
19	4 4'-Dichlo	13.870	13.610	2021	
20	Isophenph	13.908	13.647	2025	
21	alpha-CVP	14.360	14.097	2074	
22	Isophenph	14.580	14.316	2097	
23	beta-CVP(14.588	14.324	2098	
24	Quinalpho	14.655	14.391	2105	
25	Triadimen	14.663	14.399	2106	
26	Triadimen	14.794	14.529	2121	
27	Quinomet	14.933	14.668	2136	
28	Paclobutra	15.026	14.761	2147	
29	Flutolanil	15.375	15.109	2186	
20	Pretilachlo	15 561	15 294	2207	•
	Com ID 1 2 3 4 4 5 6 7 7 7 7 8 9 9 10 10 10 11 11 12 13 13 13 14 15 16 17 7 7 7 8 9 9 9 10 10 12 2 2 3 2 3 2 4 5 5 6 6 7 7 7 7 7 8 9 9 9 10 10 12 2 3 3 4 4 5 5 6 6 7 7 7 7 8 9 9 9 10 10 11 12 2 3 3 4 4 5 5 7 7 7 8 9 9 10 10 10 10 10 10 10 10 10 10 10 10 10	Congound Table IDF Mame 1 D DVVP(02 2 Bulydal 3 Isoprocati 4 Ethoproph 5 Bendocot 6 alpha BH 7 beta BHC 8 Terbulos 9 Tefutinin 10 detla BHC 11 Ethofenca 12 Todolofe- 13 Methocat 14 Permphos 15 Malathiou 16 Diethofen 17 Metolachto 18 (2-Dometh 10 detla BHC 20 Isopherph 21 alpha CVP 23 beta CVP(24 Quanghlo 25 Tradamen 26 Tradamen 26 Tradamen 27 Quinomet 28 Padobufa 29 Fludial	Compound Table Information of Method. Upf Name Ret. Time(Before) 10 DUV(Dc 6.103 2 Bulyste 7.804 3 Isoprocenty 6.103 2 Bulyste 7.804 3 Isoprocenty 6.103 2 Bulyste 7.804 4 Etoproph 10.355 5 Bendocor 10.556 6 alpha 8H 10.922 7 beta 8HC 11.476 8 Terbufos 11.651 9 Tefutos 11.651 9 Tefutos 11.651 10 deta 8HC 12.024 11 Ethodos 12.454 12 Todolos 12.454 13 Mathicoar 13.389 14 Primphose 13.454 15 Dothofen 13.652 16 Debehofen 13.868 17 Metolacho1 13.721 <td< td=""><td>Computer Table Information of Method File IDF Name Ret. Time(Reforce) Ret. Time(Atter) 1 DVP(De: 6.103 5.908 2. 2 Bulytate 7.294 7.676 3 Isoprocarin 0.105 8.872 4 Ethorpoph 10.133 9.891 5 Bendiocar 10.556 10.310 6 alpha-BH 10.922 10.6755 7 beta-BHC 11.478 11.222 8 Tecturios 11.1651 11.339 9 Telturios 11.6151 11.339 9 Telturios 12.641 12.2061 11.831 11 Ethorfonca 12.451 12.1060 12.2468 12.2064 11.331 11 Ethorfonca 12.451 12.3300 13.131 13.341 13.341 13.345 16 Dethofen 13.461 13.372 13.3461 13.342 13.461 13.342 14.465 14.331 14.3</td><td>Compound Table Information of Method File IDP Name Rel. Time(Storo) Rel. Time(Aftor) Rel. Time(Aftor) 2 Bulylate 7.84 7.676 1.421 3 Isoprocation 9.105 8.872 1555 4 Ethorpoph 10.133 9.691 1651 5 Bandiocation 10.655 10.101 1616 6 apha-BH 10.022 10.675 1726 7 beta-BHC 11.478 11.222 1779 8 Terbufos 11.651 11.309 1786 9 Terbufos 11.651 11.309 1786 10 deta-BHC 12.044 11.313 1839 11 Ethofencin 12.451 12.196 1875 12 Tabulforin 13.342 1972 13.461 1972 13 Methocar 13.358 13.31 1971 14 14972 13.516 1902 15 Addinfon 13.574</td></td<>	Computer Table Information of Method File IDF Name Ret. Time(Reforce) Ret. Time(Atter) 1 DVP(De: 6.103 5.908 2. 2 Bulytate 7.294 7.676 3 Isoprocarin 0.105 8.872 4 Ethorpoph 10.133 9.891 5 Bendiocar 10.556 10.310 6 alpha-BH 10.922 10.6755 7 beta-BHC 11.478 11.222 8 Tecturios 11.1651 11.339 9 Telturios 11.6151 11.339 9 Telturios 12.641 12.2061 11.831 11 Ethorfonca 12.451 12.1060 12.2468 12.2064 11.331 11 Ethorfonca 12.451 12.3300 13.131 13.341 13.341 13.345 16 Dethofen 13.461 13.372 13.3461 13.342 13.461 13.342 14.465 14.331 14.3	Compound Table Information of Method File IDP Name Rel. Time(Storo) Rel. Time(Aftor) Rel. Time(Aftor) 2 Bulylate 7.84 7.676 1.421 3 Isoprocation 9.105 8.872 1555 4 Ethorpoph 10.133 9.691 1651 5 Bandiocation 10.655 10.101 1616 6 apha-BH 10.022 10.675 1726 7 beta-BHC 11.478 11.222 1779 8 Terbufos 11.651 11.309 1786 9 Terbufos 11.651 11.309 1786 10 deta-BHC 12.044 11.313 1839 11 Ethofencin 12.451 12.196 1875 12 Tabulforin 13.342 1972 13.461 1972 13 Methocar 13.358 13.31 1971 14 14972 13.516 1902 15 Addinfon 13.574

	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	Cvfluthrin-1	20.363	20 356	0.007		
48	Cvfluthrin-2	20 446	20.000	0.007		
49	Cvfluthrin-3.4	20.562	20.445	0.003		
50	Halfenprox	20 718	20.303	0.007		
51	Silafluofen	21 095	21.086	0.012		
52	Fenvalerate-1	21 597	21 584	0.003		
53	Fenvalerate-2	21 802	21 788	0.013		
54	Difenoconazole-1	22.054	22 039	0.014		
55	Difenoconazole-2	22 126	22 111	0.015		
56	Imibenconazole	23.516	23 503	0.013		
		20.010	23.303	0.013		

Fig. 4: AART function inside GCMSsolution usin 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. **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

