

CHROM. 11,307

APPLICATION OF AUTOMATIC CALCULATION OF KOVÁTS' RETENTION INDICES TO ENVIRONMENTAL ANALYSES BY GAS CHROMATOGRAPHY–MASS SPECTROMETRY–CALCULATOR

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(Received April 3rd, 1978)

SUMMARY

Automatic calculation and plots of Kováts' retention indices (RI) from gas chromatographic (GC) analysis of environmental samples is provided by a calculator-controlled GC–mass spectrometric (MS) system. The retention indices framework of carbon numbers is set up using a standard sample containing all the desired *n*-hydrocarbons which are automatically identified in a GC–MS run by the presence of the *m/e* 85.1 $C_6H_{13}^+$ ion and the molecular ion. These standard retention data are used to automatically calculate RI values for samples extracted from airborne particulate matter run under identical GC conditions. *n*-Hydrocarbons present in a sample can be employed as internal standards but an editing subroutine may be necessary to remove ambiguities. Standard deviation of a test of the external standard method is 2.4 RI units, of the internal standard method 1.5 RI units.

INTRODUCTION

The development of gas chromatograph–mass spectrometer–computer systems has provided the chemist with an extremely powerful tool for organic analysis. However, since mass spectrometric (MS) data are not always sufficient to distinguish between closely related compounds, many workers have found it advantageous to supplement MS data with gas chromatographic (GC) retention data. The Kováts' retention index (RI) provides useful, relatively invariant retention data and several complex computer programs have been developed to do such calculations automatically from GC–MS data^{1–5}. Use of such programs has required access to at least a reasonably sophisticated minicomputer, and is based on the use of an internal standard.

An important step in our procedure for rapid analysis of environmental samples extracted from airborne particulate matter is computerized calculation and plotting of RI values for the components⁶. To further improve the procedure it was necessary to develop simplified programs for these calculations and plots which were applicable to a bench-top gas chromatograph–mass spectrometer–calculator system now being employed for the analyses⁷. Simplified programs are necessary because of

the lesser capabilities of a programmable calculator/controller in comparison to larger computer facilities. A block diagram of our calculation procedure is shown in Fig. 1. Data from the analysis of a standard mixture containing *n*-hydrocarbons are combined with data from the analysis of samples extracted from airborne particulate matter to produce the calculated list of RI values for the sample.

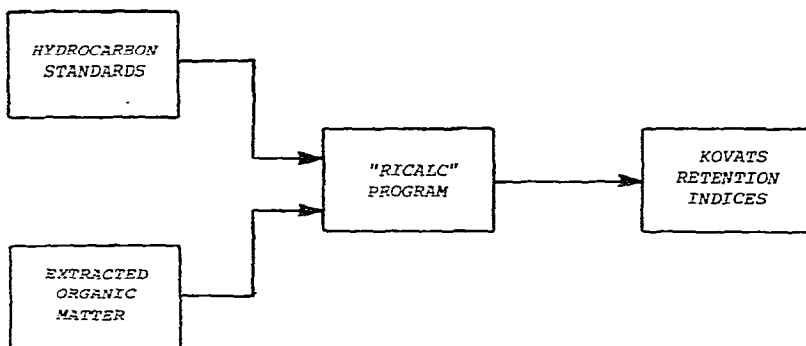


Fig. 1. Block diagram of method for automatic calculation of retention indices.

Only those mass spectra taken at the maxima of GC peaks formed by total ion current are saved in permanent data files. A daily standardization run of a sample containing the *n*-hydrocarbon standards is used to calculate RI values of sample mixtures, rather than an internal standard. Should a given sample contain all the necessary *n*-hydrocarbon standards, the program is capable of picking out these standards from the mixture and using them as internal standards, but the accuracy and lack of ambiguity depend upon the nature of the other compounds present.

n-Hydrocarbons are identified by seeking the presence of a signature $C_6H_{13}^+$ fragment ion at m/e 85.1 followed by assignment of the carbon number according to the observed mass of the molecular ion. The criterion used for molecular ion selection is "significance", the product of the molecular ion mass and its percent relative abundance divided by 100. Use of this value automatically provides more weight to ion peaks of higher mass, and decreases the chance of incorrect assignment as *n*-hydrocarbons those compounds whose spectra contain both a large mass fragment at m/e 85.1 and false "molecular ion" peaks of relatively low mass. Other procedures based on this algorithm are used advantageously to select the ten most significant ions retained for library search procedures⁸.

EXPERIMENTAL

GC-MS analyses were performed on a Hewlett-Packard 5992 calculator-controlled bench-top gas chromatograph-mass spectrometer with Hewlett-Packard 9885M Flexible Disk Drive (Hewlett-Packard, Palo Alto, Calif., U.S.A.). The GC column was 1.8 m \times 2 mm I.D. glass packed with a highly deactivated support, referred to here as Aue Packing (AP)^{9,10}. Unless otherwise specified, GC analysis conditions used were: solvent elution time, 0.40-0.60 min; helium flow-rate, 30 ml/min; injection temperature, 235°; initial temperature, 100° for 4 min; programming rate, 4°/min; final temperature, 240° for 15 min. MS scan conditions were: electron multi-

plier, 2000 V; mass scan range, 40–500 a.m.u.; samples per 0.1 a.m.u., 2. These scan conditions yielded a mass spectrum approximately every 1.8 sec. All mass spectra were background stripped. A membrane separator was employed.

The solution of hydrocarbon standards dissolved in cyclohexane employed contained *n*-hydrocarbons from *n*-C₁₂H₂₆ to *n*-C₂₆H₅₄ inclusive, as well as *n*-C₂₈H₅₈, *n*-C₃₀H₆₂, *n*-C₃₂H₆₆, and *n*-C₃₆H₇₄. This solution was run at the beginning of each day that an analysis was to be performed. RI values for each sample analyzed were then calculated using data from the previously run standard. Under temperature-programmed conditions eqn. 1 is used to calculate RI values¹¹:

$$\text{Index} = 100 C_n + 100 (C_{n+1} - C_n) \frac{(T_n - S_n)}{(S_{n+1} - S_n)} \quad (1)$$

where C_n and C_{n+1} are the carbon numbers of the standards which bracket the unknown peak in retention time, T_n is the retention time of the unknown, and S_n , S_{n+1} are retention times of the standards which bracket the retention time of the unknown. Eqn. 1, applicable for temperature-programmed analyses, will also linearly extrapolate RI values for peaks whose retention times are outside the range covered by the hydrocarbon standards.

Program description

Software was written in a high-level language called HPL, which is similar in structure to BASIC. Two different versions of the program have been written: one (TAPERICALC) to access mass spectra stored on cartridge tapes, and the other (DISKRICALC) to access mass spectra stored on flexible disk. Both programs are essentially identical in operation and are designed for a high degree of user interaction. Keyboard entry of sample and standard data is possible in addition to automatic entry from mass spectral files. These programs are logical developments of earlier FORTRAN versions used in our laboratory which relied exclusively on manual punched-card entry¹².

Automatic identification of *n*-hydrocarbon standards is performed as part of a general subroutine to access sample data. A simplified flow chart of the sequence followed is shown in Fig. 2. A mass spectral file with its associated sample identification number, retention time, and total abundance stored on the flexible disk or cartridge tape is read into the calculator memory. The mass spectrum is checked for the presence of a C₆H₁₃⁺ peak at *m/e* 85.1; if this peak is found at a relative abundance greater than a threshold set by the operator (usually 20%), and if the base peak abundance exceeds 50 counts, the mass spectrum is deemed to be that of a prospective *n*-hydrocarbon standard. A search is then begun for its molecular ion, starting at the high-mass end of the spectrum. The highest-mass ion found whose mass corresponds to the formula C_{*n*}H_{2*n*+2}, and whose significance value is greater than a threshold set by the operator (usually 10), is assigned as the molecular ion of the hydrocarbon, and the carbon number is allotted accordingly. At this point, the mass spectrum may be plotted if desired. If no ions satisfy the test criteria, the mass spectrum is deemed not to be that of a *n*-hydrocarbon, and the spectrum number is saved for later printout. The next mass spectrum is then accessed and the loop repeated. If both the current mass spectrum and the preceding standard have been assigned the same carbon

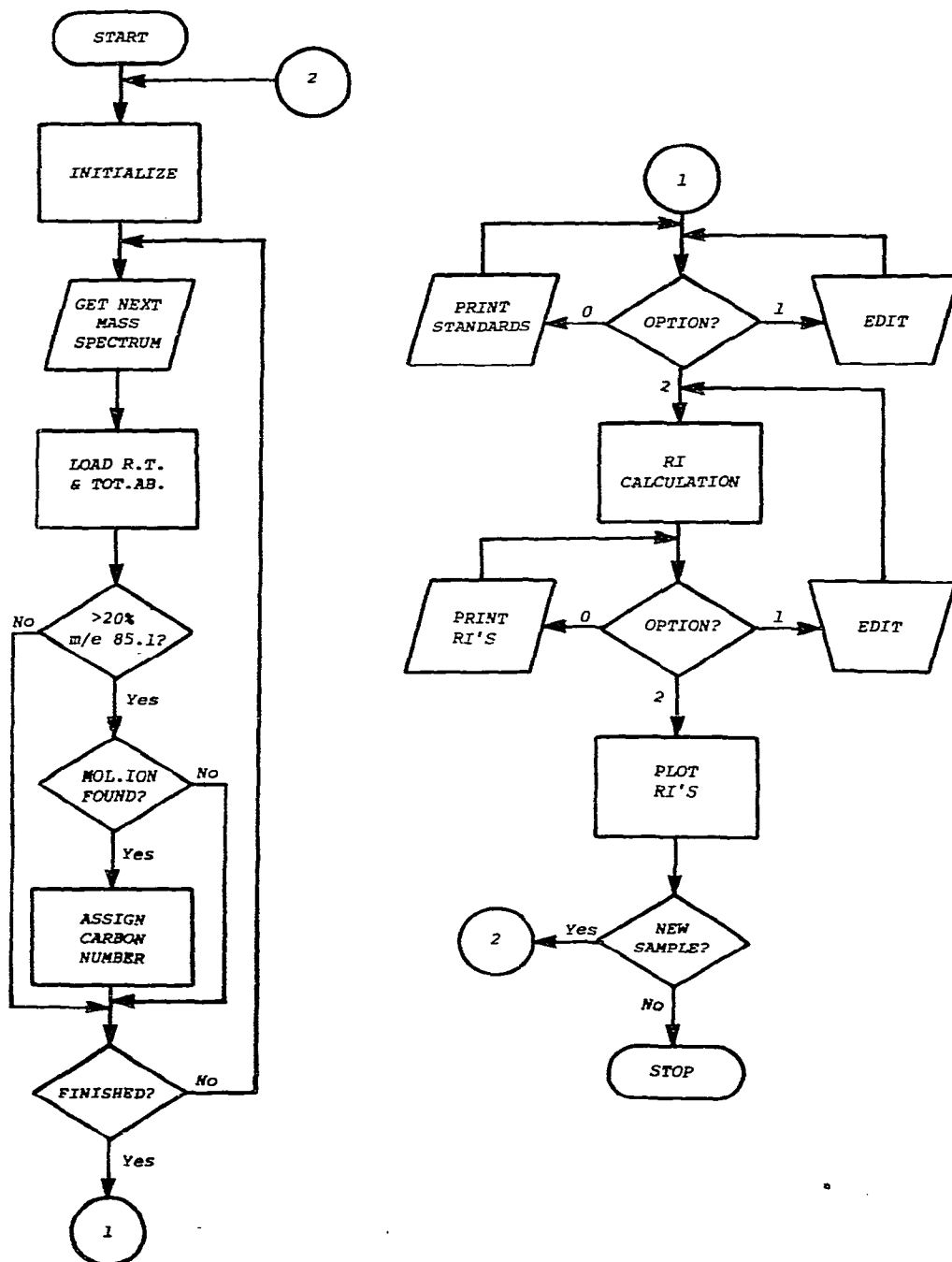


Fig. 2. Program flow chart.

number, the conflict is resolved by designating as the standard the mass spectrum having the greater ratio of abundance at m/e 85.1 to total abundance.

When all mass spectra have been accessed, a message is printed giving the file numbers of mass spectra that satisfied the criterion for a $C_6H_{13}^+$ ion, but failed the criterion for molecular ion identification. A spectrum number list is also printed of those mass spectra that satisfied criteria for both relative abundance at m/e 85.1 and molecular ion significance, but were superceded by mass spectra having a greater ratio of abundance at m/e 85.1 to total abundance. If any carbon numbers appear in decreasing sequence out of retention order, a warning message will be printed. The operator may now obtain a printout list of the file numbers of the mass spectra of the hydrocarbon standards identified. The plot shown in Fig. 3 indicates that the n -hydrocarbon can be properly identified even when present in an unresolved GC peak containing a significant amount of another compound. At this point the retention times and carbon numbers of standards which did not have a molecular ion within the mass scan range used may also be inserted manually via the edit subroutine using the standard n -hydrocarbon run for guidance.

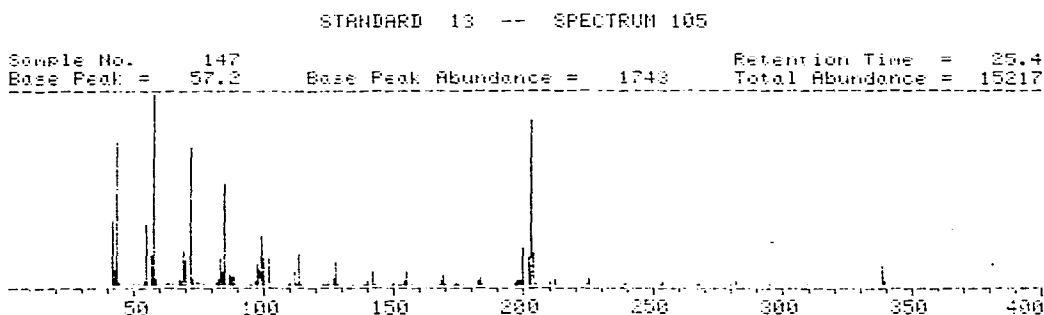


Fig. 3. Plot of reference spectrum identified as n - $C_{24}H_{50}$ from an unresolved GC peak which also contains pyrene.

When the hydrocarbon standards have been satisfactorily identified, retention indices are calculated first for the components of the standard mixture using eqn. 1. This calculation produces a list of retention indices for the standard mixture itself, in which the n -hydrocarbons are assigned values of 1200, 1300, etc., and any other components are assigned values from eqn. 1 using the hydrocarbons as an internal standard. This equation, although it does not calculate RI values for compounds other than hydrocarbons directly comparable to those obtained under isothermal conditions, does provide reproducible values applicable to temperature-programmed GC conditions¹³. The calculated data may then be printed, and saved as a check on day-to-day column performance. A bar-graph plot of total abundance versus retention index may also be provided. This completes the standardization procedure.

With n -hydrocarbon standardization data now in memory, automatic calculation of RI values for sample runs may now proceed. The same subroutine as de-

scribed above is used to automatically load the retention times and total abundances of sample mass spectra, but sections relating to standard identification are not executed. RI values are then calculated as described above, using data from the previously-loaded standard.

A complete listing of both DISKRICALC and TAPERICALC programs is available from the authors.

RESULTS AND DISCUSSION

An example of the use of DISKRICALC to perform an analysis is given in Fig. 4. Fig. 4a shows the bar-graph output of maximum ion current *versus* RI value

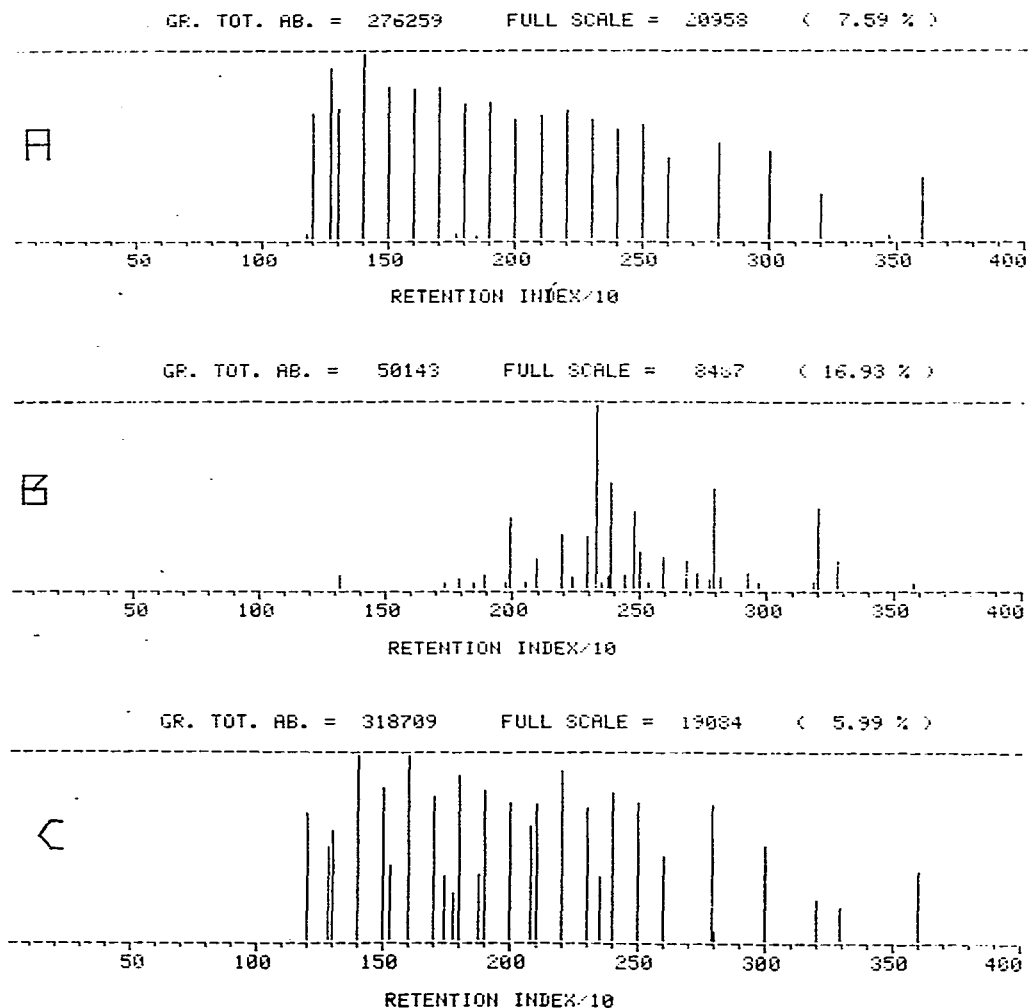


Fig. 4. Plots of maximum total ion current *vs.* retention index for (a) hydrocarbon standards, (b) sample extracted from airborne particulate matter, and (c) test mixture of *n*-hydrocarbons, PAHs, and phthalates.

for a standardization run using the hydrocarbon mixture described previously. These standards have been assigned retention indices of 1200–3600. Fig. 4b shows the results of an analysis of an extracted air particulate sample, showing that this sample contains primarily higher-molecular-weight air pollutants⁷. Fig. 4c shows DISKRICALC output for the analysis of a test mixture described below that contains hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and phthalates,

The printout obtained from the automatic loading of hydrocarbon standards is shown in Fig. 5. Here, since the upper mass scan limit was 500 and the highest-molecular-weight *n*-hydrocarbon (*n*-C₃₆H₇₄) has a molecular weight of 506.6, the retention time for the final entry was entered manually, using the editing subroutines. It is interesting to note that although molecular ion relative abundances vary from 14.2% for *n*-C₁₂H₂₆ to 3.5% for *n*-C₃₂H₆₆, the molecular ion significance values are relatively constant. This constancy aids in setting the threshold for this value.

HC STANDARD 000212STD							
GC COLUMN:		6ft x 2mm	ID	GLASS	AUE PACKING		
DATE:		1978/01/20	SOLVENT PEAK 0.00				
STD. NO.	SPECT. NO.	CARBON NO.	MOL. WT.	R. AB. 85.1	M. ION R. AB.	M. ION SIG.	RETENTION TIME
1	301	12	170.2	36.7	14.2	24	0.88
2	305	13	184.2	40.8	11.8	22	1.38
3	307	14	198.2	44.3	9.3	19	2.32
4	309	15	212.3	48.4	8.8	19	4.12
5	311	16	226.3	49.5	8.2	18	6.02
6	313	17	240.3	50.7	6.3	15	9.62
7	317	18	254.3	52.2	6.8	17	12.26
8	321	19	268.3	52.5	5.9	16	14.76
9	323	20	282.3	54.9	6.1	17	17.12
10	325	21	296.4	54.7	5.6	17	19.38
11	327	22	310.4	54.9	5.3	16	21.50
12	329	23	324.4	55.2	5.2	17	23.56
13	331	24	338.4	58.2	4.8	16	25.50
14	333	25	352.4	56.0	4.4	15	27.38
15	335	26	366.4	53.3	5.0	18	29.12
16	337	28	394.5	54.4	4.0	16	32.62
17	339	30	422.5	52.3	4.1	17	35.88
18	341	32	450.5	51.7	3.5	16	38.82
19	0	36	506.6	0.0	0.0	0	47.88

Fig. 5. Calculator output for identified *n*-hydrocarbons from standardization of Fig. 4a.

We have observed that, although the significance value does not usually vary greatly within a given standardization, it can vary widely from day to day depending upon the tuning of the mass spectrometer. Typical mean values can range from approximately 15 to 50, with the higher numbers being obtained when the autotune⁸ procedure of the mass spectrometer gives a greater high-mass sensitivity. However, much lower significance values, typically around 5 or 6, result from interfering mass spectra such as those obtained from high-temperature bleed of incompletely conditioned GC columns. These interfering mass spectra can have a large mass peak at

m/e 85.1, as well as small mass peaks at m/e 86.1 or 100.1. These latter mass fragments possess the same m/e value as the molecular ions of hexane and heptane, and could result in the incorrect designation of such mass spectra as low-molecular-weight hydrocarbons. The use of significance automatically reduces the probability of interferences of this nature by requiring that low-mass fragments have a greater relative abundance in order to be assigned as the molecular ion of a n -hydrocarbon than do high-mass fragments. A relative abundance of only 2.0% is required at m/e 506.6 to satisfy a threshold significance of 10, but a relative abundance of 11.6% is required at m/e 86.1 for the same significance value.

The calculated values for the analysis of the sample extracted from airborne particulate matter shown in Fig. 4b are given in Fig. 6. Many of the components of this mixture are different isomers of the various PAHs, and cannot be identified solely on the basis of their mass spectra. In combination with the retention index data shown here, however, it is possible to make a positive assignment of identity. For example, spectrum numbers 372 and 378 give identical mass spectra with a base peak at m/e 202.1. In combination with data from a test mixture such as that described below, it is possible to assign spectrum 372 (RI = 2326) as fluoranthene, and spectrum 378 (RI = 2384) as pyrene.

Since the above algorithm for n -hydrocarbon identification depends primarily

HIVOL 1118758 4uL					
GC COLUMN:		6ft x 2mm	ID GLASS	AUC PAGING	
DATE:		1978/01/20	SOLVENT PEAK: 9.00		
PEAK NO.	SPECTRUM NO.	PET. TIME CORRECTED	TOTAL ABUND.	% GRAND TOT. AB.	RETENTION INDEX
1	348	1.50	694	1.38	1213
2	350	10.38	369	0.74	1729
3	352	12.00	493	0.98	1750
4	354	13.50	332	0.66	1850
5	356	14.50	683	1.36	1890
6	358	15.38	394	0.79	1929
7	360	15.94	3200	6.38	1932
8	362	18.38	387	0.77	2056
9	364	19.26	1461	2.91	2095
10	366	21.38	3503	6.99	2174
11	368	22.06	601	1.20	2227
12	370	23.44	2355	4.70	2274
13	372	24.06	8487	16.93	2326
14	374	24.62	317	0.63	2355
15	376	24.88	575	1.15	2368
16	378	25.18	4842	9.66	2384
17	380	26.32	715	1.43	2444
18	382	26.88	3516	7.01	2473
19	384	27.32	1673	3.34	2497
20	386	28.00	323	0.65	2536
21	388	29.06	1559	3.11	2597
22	390	30.62	1368	2.73	2636
23	392	31.26	776	1.55	2722
24	394	32.18	532	1.06	2775
25	396	32.50	4651	9.28	2793
26	398	32.82	574	1.14	2812
27	400	34.56	793	1.58	2919
28	402	35.32	378	0.75	2966
29	404	38.50	385	0.77	3178
30	406	38.82	3628	7.24	3209
31	408	40.44	1474	2.94	3272
32	410	47.26	369	0.74	3573
GRAND TOTAL ABUNDANCE =			50143	HC STANDARD 000212STD	

Fig. 6. Calculator output of calculated retention indices for the sample shown in Fig. 4b.

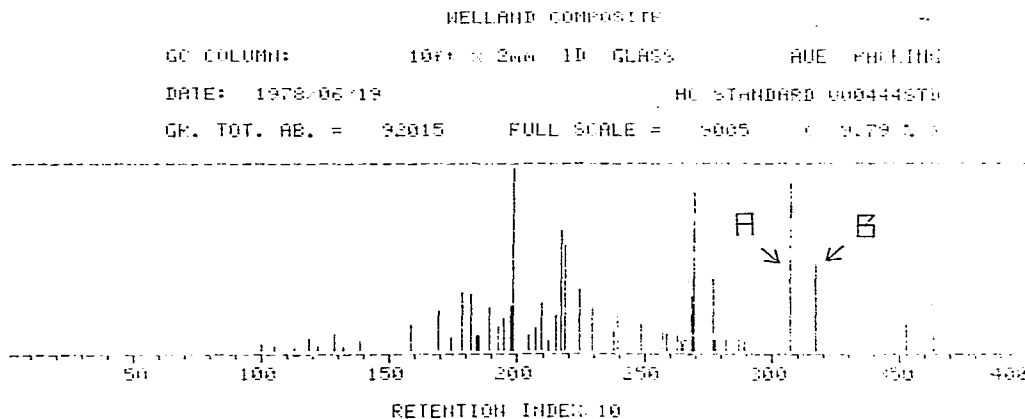


Fig. 7. Plot of maximum ion current vs. retention index for composite of several environmental samples. See text for discussion.

on the presence of an identifiable molecular ion, the above method can readily accommodate changes in the column length or in the temperature program used. In Fig. 7 is shown the DISKRICALC output for a sample made by combining the organic extracts from a series of air particulate samples taken at a site near Welland, Ontario, Canada (see ref. 6). These data were obtained with a 3 m x 2 mm I.D. Aue Packed GC column using an initial temperature of 90° programmed directly to 260° at 4°/min, followed by 10 min isothermal at 260°. The mass scan range was from 50 to 550 a.m.u. Standard data were reentered simply by rerunning the standard mixture under the new analysis conditions. All hydrocarbons in the standard mixture were correctly identified, including *n*-C₃₆H₇₄, whose molecular ion had not been detected under the high mass scan limit of 500 a.m.u. used previously.

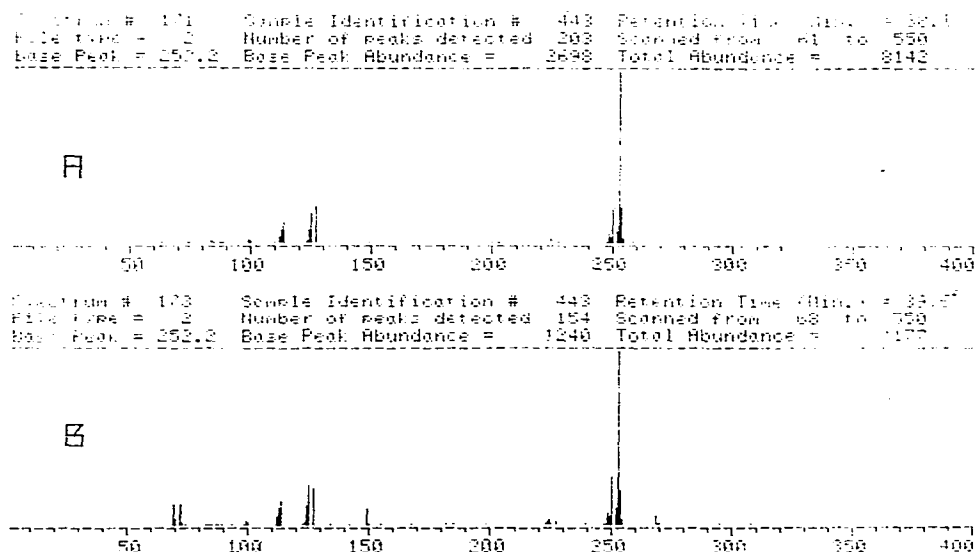


Fig. 8. Mass spectra for GC peaks labelled A and B in Fig. 7. See text for discussion.

Shown in Fig. 8 are the mass spectra for the GC peaks labelled A and B in Fig. 7. These mass spectra are basically identical, and are representative of isomers of benzopyrene (MW 252). Of the two isomers, benzo[*a*]pyrene (BaP) and benzo[*e*]pyrene (BeP), only the asymmetric BaP is a known carcinogen¹⁴. The retention index of the latter compound was determined by automatic RI calculation to be 3159 with the GC column and conditions used. Therefore, identity could be positively assigned to component B in Figs. 7 and 8 as the known carcinogen.

In order to obtain data on the reproducibility of this method, we prepared a test mixture that contains *n*-hydrocarbons, phthalates, and PAH compounds in concentrations of approximately 20 ng/ μ l. These compounds are frequently encountered in the analysis of the organic extract from airborne particulate matter. The short-term

TABLE I

RETENTION INDICES OF 4 DETERMINATIONS OF TEST MIXTURE USING EXTERNAL STANDARDIZATION

<i>Identity</i>	<i>Mean retention time (min)</i>	<i>S.D. (min)</i>	<i>Mean retention index (RI units)</i>	<i>Standard deviation (RI units)</i>
<i>n</i> -C ₁₂ H ₂₆	0.80	0.06	1196	13
Acetophenone	1.16	0.07	1276	16
<i>n</i> -C ₁₃ H ₂₈	1.29	0.03	1304	4
<i>n</i> -C ₁₄ H ₃₀	2.22	0.07	1402	4
<i>n</i> -C ₁₅ H ₃₂	3.92	0.06	1499	2
Biphenyl	4.48	0.06	1520	2
<i>n</i> -C ₁₆ H ₃₄ + acenaphthene*	6.60	0.06	1600	2
<i>n</i> -C ₁₇ H ₃₆	9.34	0.03	1698	1
Fluorene	10.56	0.03	1745	1
Dimethyl phthalate	11.15	0.03	1766	1
<i>n</i> -C ₁₈ H ₃₈	12.02	0.03	1798	1
Diethyl phthalate	13.72	0.05	1866	2
<i>n</i> -C ₁₉ H ₄₀	14.52	0.03	1898	1
<i>n</i> -C ₂₀ H ₄₂	16.91	0.03	1996	2
Diallyl phthalate	18.58	0.03	2072	1
<i>n</i> -C ₂₁ H ₄₄	19.14	0.03	2098	2
<i>n</i> -C ₂₂ H ₄₆	21.32	0.00	2197	0
<i>n</i> -C ₂₃ H ₄₈	23.35	0.03	2296	2
Fluoranthene	24.30	0.03	2343	2
<i>n</i> -C ₂₄ H ₅₀ + pyrene*	25.35	0.03	2396	2
<i>n</i> -C ₂₅ H ₅₂	27.24	0.07	2496	3
<i>n</i> -C ₂₆ H ₅₄	29.06	0.03	2598	2
Diethyl phthalate	32.44	0.05	2790	3
<i>n</i> -C ₂₈ H ₅₈	32.56	0.03	2798	2
<i>n</i> -C ₃₀ H ₆₂	35.94	0.03	2997	2
<i>n</i> -C ₃₂ H ₆₆	39.06	0.07	3198	3
Benzo[<i>a</i>]pyrene	41.26	0.12	3293	5
<i>n</i> -C ₃₆ H ₇₄	48.56	0.06	3596	2
Pooled standard deviation		0.05		4.5
				(all values)
				2.3
				(excluding first two)

* Unresolved components.

reproducibility of the method of calculating RI values was tested by making five consecutive injections of 2 μ l each, under the GC conditions specified in the Experimental section. Data from the first injection were used to obtain the retention times of the *n*-hydrocarbons present in the test mixture. The remaining four injections were then treated as sample data. Identification of the components in the test mixture, and results of the RI calculations using this external standardization procedure are summarized in Table I. The pooled standard deviation for all four runs is 2.4 RI units for all components of this mixture except *n*-C₁₂H₂₆ and acetophenone, which elute very quickly under the GC conditions used. These results, while not as precise as the best obtained by Smith *et al.*⁵ using an internal standard, show that quite acceptable reproducibility can be obtained by the much simpler method described here. Differences here in the retention indices of fluoranthene (RI = 2343) and pyrene (RI = 2396) with those reported in Fig. 6 are the result of long-term drift in GC column characteristics in the time period between the different analyses (2 months), and emphasize the importance of frequent monitoring of column performance.

A more detailed comparison of the precision of external vs. internal retention-time standards may be obtained by using the *n*-hydrocarbons present in the samples as internal standards for each of the final four injections, and calculating the RI values for all components of each sample. This internal standard procedure can be used for samples containing many *n*-hydrocarbons. This is usually the case for all samples extracted from airborne particulate matter collected in urban areas⁶. Alternately, the co-injection technique of Sweeley *et al.*³ can be used. These two methods of calculation are compared in Table II. It can be seen that the pooled standard deviation for all compounds except the rapidly-eluting acetophenone has improved only from 2.4 to 1.5 RI units by using an internal standard procedure.

TABLE II
COMPARISON OF INTERNAL AND EXTERNAL STANDARDS

<i>Component</i>	<i>Mean retention index external standard</i>	<i>S.D.</i>	<i>Mean retention index internal standard</i>	<i>S.D.</i>
Acetophenone	1276	16	1272	10
Biphenyl	1520	2	1521	0
Fluorene	1745	1	1747	2
Dimethyl phthalate	1766	1	1768	1
Diethyl phthalate	1866	2	1868	1
Diallyl phthalate	2072	1	2075	0
Fluoranthene	2343	2	2348	1
Diocetyl phthalate	2790	3	2792	2
Benzo[<i>a</i>]pyrene	3293	5	3293	3
Pooled standard deviation		5.8		3.8
		(all values)		(all values)
		2.4		1.5
		(excluding first value)		(excluding first value)

Success in reliably identifying *n*-hydrocarbons with molecular weights as high as 562 (*n*-C₄₀H₈₂) appears to be due to two factors. One is the high mass sensitivity

provided by the hyperbolic rod structure of the mass analyzer. The other is the almost undetectable bleed at 260° of the Aue Packing used which gives well defined, background stripped spectra. The presence of branched hydrocarbons with retention times far different than equivalent *n*-hydrocarbons yet possessing both a large peak at *m/e* 85.1 and an identifiable molecular ion, cannot be automatically accounted for. Nevertheless, these assignments may be removed using the editing subroutine. The most serious limitation of the technique using an external standard run lies in the necessity to maintain the GC analysis conditions closely between standardization and sample runs. It can be seen from Table II that the short-term reproducibility of retention time is of the order of 0.05 min if column conditions are carefully maintained. However, such variables as initial temperature, programming rate, and flow-rate must be sufficiently controlled that retention times do not vary widely. Nevertheless, since precisely-controlled conditions are not difficult to maintain with microprocessor-controlled instrumentation, and since major changes in the GC conditions employed may be accounted for simply by rerunning the standard, this does not appear to be a major drawback.

ACKNOWLEDGEMENT

This research was supported by the Ontario Ministry of the Environment, Air Resources Branch.

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