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Practical aspects in the utilization of the Sadtler Standard Gas Chromatography Retention Index Library

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ABSTRACT

Sadtler standard gas chromatographic programmed-temperature retention indices were shown to be reproducible on either Hewlett-Packard standard fused-silica open-tubular (FSOT) columns or laboratory-made **apolar** columns by holding the programmed-temperature gas chromatographic characteristic parameter rt_0/β equal to 0.013 and **0.052°C,** respectively, where r denotes oven heating rate, t_0 the gas hold-up time and β the phase ratio. Nitrogen could be used instead of hydrogen as the carrier gas, and other experimental parameters, such as column length and inner diameter, stationary phase film thickness and initial oven temperature could also be varied to a certain extent. The average linear velocity of the carrier gas, unclearly specified in the Sadtler Standard Gas Chromatography Retention Index Library, was experimentally determined. Special precautions should be taken to ensure that the column used has been well deactivated.

INTRODUCI'ION

Although coupled techniques of GC with mass, FT-IR and atomic emission spectrometry have made tremendous progress in the last decade or so, measurement of GC retention values, especially the retention index, is still widely used as a simple, effective, inexpensive and sensitive means of identification. As nearly 75% of GC analyses have been accomplished under programmed-temperature conditions, pro-grammed-temperature retention indices (PTRI) are more frequently met in practice than isother-mal values and are of particular importance for analysing complex mixtures. In contrast to iso-thermal retention indices, PTRI are susceptible to the variation of more experimental parame-ters and are difficult to reproduce between laboratories. To overcome this difficulty, several chromatographers (Giddings [1], Guiochon [2], Habgood and Harris [3] and Lee and Taylor [4])

proposed correlating PTRI with the isothermal retention index measured at some "equivalent temperature" and others (Grant and Hollis [5], Curvers and co-workers [6,7] and Guan et al. [8]) suggested obtaining PTRI by a calculation meth-od after making isothermal runs at two selected temperatures. A more simple and straightfor-ward way is to compile a PTRI database and numerous chromatographers (Jennings and Shibamoto [9], Sadtler Laboratories [10], Vas-silaros *et al.* [11], Hayes and Pitzer [12], Saxton [13] and White *et al.* [14]) have been involved in such work. The Sadtler Standard Gas Chroma-tography Retention Index Library, published in 1984, is by far the largest. This is the only non-spectroscopic database which Sadtler Re-search Laboratories have ever provided. In com-parison with similar PTRI databases compiled by others, the Sadtler Library paid much more attention to standardizing the instrumentation and the experimental parameters used for PTRI measurement. These include the model of gas **chromatograph,** column geometry (length L and inner diameter D), stationary phase film **thick-**

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ness, d_f, carrier gas used and the temperature programme (initial oven temperature T_0 and oven heating rate r). In order to increase the repeatability and reproducibility of the measurement of PTRI, Sadtler Research Laboratories employed a highly sophisticated gas **chromatograph** and high-quality fused-silica capillary columns commercially available at that time. Weber [15] stressed that in order to reproduce the standard PTRI in the Sadtler Library by other chromatographers, all the experimental conditions should be strictly followed. In recent years, we have investigated how to reproduce PTRI under more flexible experimental conditions and found that rt_0/β is a characteristic parameter for reproducing PTRI in programmed-temperature GC, where r is the oven heating rate, t_0 the gas hold-up time and β the phase ratio [16]. As the average linear velocity of carrier gas was unclearly stated in the Sadtler Library, this characteristic parameter cannot be found from the Library, which makes the use of the PTRI standard data in it very difficult.

The objectives of this work were as follows: (1) to optimize the average linear velocity of carrier gas in order to reproduce the standard Sadtler PTRI; (2) to show that for reproducing standard PTRI on polar Carbowax 20M column a more rigorous test for column performance is needed; (3) to show that the initial oven temperature can be allowed to vary to a small extent without seriously affecting the reproducibility of PTRI; (4) to show that hydrogen is not the only carrier gas that can be used; (5) to show that a less sophisticated gas chromatograph can be applied for reproducing standard PTRI satisfactorily; and (6) to show the laboratory made columns of various geometries and film thickness can also be used, provided that the column used is well deactivated.

EXPERIMENTAL

Instrumentation

Two gas **chromatographs** were used: a Varian Model 3770, an instrument with constant pressure control, similar to the Hewlett-Packard Model **5880A** used for Sadtler standard PTRI measurement, and a Shimadzu **GC-9A,** a constant flow-rate controlled gas chromatograph. Flame ionization detectors were used in both instances. The injector and detector temperatures were both held at **250°C.** Shimadzu **C-R1B** and **C-R2B** data processors were used, respectively. Injections were performed manually. No autosampler was used. The calculation was completed on an IBM PC/XT microcomputer.

Columns

The standard columns used, all purchased from Hewlett-Packard, were as follows: (1) HP ultra-performance OV-1, cross-linked **polydi**methylsiloxane, 25 m **x *0.32*** mm I.D., $d_f = 52$ μm, $\beta = 150$; (2) HP ultra-performance SE-54, cross-linked 5% **phenyl–polyphenylmethylsilox**ane, 25 m **x** 0.32 mm I.D., $d_f = 0.52 \mu$m, $\beta = 150$; and (3) two HP high-performance **Carbowax** (CW) **20M,** 25 m $\times$ 0.32 mm I.D., $d_f = 0.32 \mu$m, $\beta = 250$ (columns A and B). Both columns passed the test given by the manufacturer with a test mixture of ethyl undecanoate, nicotine, heptanoic acid and ethyl tridecanoate, giving four symmetrical peaks and excellent column efficiency at 145°C.

Laboratory-made fused-silica open tubular (FSOT) columns were also used. Fused-silica tubing with I.D. 0.22, 0.25 and 0.32 mm was purchased from Yongnian Optical Fibre Factory (Yongnian, Hebei Province, China). Columns of various lengths were coated statically [17] with SE-54 and OV-1 stationary phases purchased from Chrompack (Middelburg, Netherlands). The phase ratio of the column to be coated was estimated from the concentration of the stationary phase in the coating solution and determined experimentally by measuring the capacity factor of benzene on the column prepared and the standard column at an oven temperature of 60°C and then calculated using the equation

$$\beta_x = k_s \beta_s / k_x$$

where β_x and β_s are the phase ratios of the laboratory made and Hewlett-Packard standard columns, respectively, and k_x and k_s are the capacity factors of benzene measured on the two column. The phase ratios of the standard columns were reported to be 150 and those of

the laboratory-prepared columns varied from 60 to 205. The column efficiency was evaluated by determining the peak width at half-height of n-tridecane, the last peak in the chromatogram, in the seven-component Grob test mixture [18] at an oven temperature of 120°C and calculated by the well known equation. Most of the columns tested were carefully deactivated by the method of Woolley et al. [19]. Some were not deactivated in order to make a comparison with those subjected to deactivation. The columns after deactivation were further evaluated with the twelve-component Grob test mixture [20]. Deactivations were proved to be successful with the appearance of all twelve peaks symmetrical in the test chromatograms. The specification and performance of the columns used in this experiment are given in Table I.

Test compounds

Eleven compounds which are separable from each other and from admixed n-alkanes on the above columns were selected from the Sadtler Standard Gas Chromatography Retention Index Library. These compounds are listed in Tables II-VIII. Most test compounds were purchased from Fluka (Buchs, Switzerland). The test com-

pounds were premixed with C_8–C_{23} n-alkanes and dissolved in redistilled n-hexane. The concentration of the solution and the injection splitting ratio were so chosen as to make the amount of each component entering the column inlet less than 10 ng.

Grob test mixture was purchased from Fluka. It consists of twelve components, i.e., 2,3-butanediol, *n*-decane, octanol, n-undecane, nonanal, 2,6-dimethylphenol, 2,6-dimethylaniline, methyl decanoate, methyl undecanoate, methyl dodecanoate, dicyclohexylamine and 2-ethylhexanoic acid, dissolved in hexane and chloroform. Authentic samples of the individual components were also purchased for peak identification.

PTRI calculation

The PTRI were calculated based on Van den Dool's definition [21]:

$$I_{pt} = 100z + 100\left(\frac{T_i - T_z}{T_{z+1} - T_z}\right)$$

where T_i, T_z and T_{z+1} are the retention temperatures of the test component and the *n*-alkanes eluting just before and just after it, respectively.

RESULTS AND DISCUSSION

Optimization of carrier gas velocity

For apolar columns. Carrier gas velocity is an important parameter affecting the reproducibility of the measurement of programmed-temperature retention indices. Golovnya and Uraletz [22] discussed the effect of carrier gas linear velocity on the measurement of the PTRI of n-alkanes and concluded that its effect should not be overlooked. Pell and Gearhart [23] observed that on using different carrier gas velocities in PTGC, elution order inversions might even occur. In the Introduction of the Sadtler Library [10], the compiler(s) wrote as follows: "Hydrogen carrier gas is used and the linear velocity is optimized for each column at 60°C on a routine basis". This statement is not very clear and difficult to follow. First, why is it necessary to optimize the gas velocity for a column having already been stan-

TABLE I

SPECIFICATION OF THE LABORATORY-MADE COLUMNS USED

Column"	*L* (m)	I.D. (mm)	β	n	State
o-1	25	0.32	126	2763	Deactivated
o-2	25	0.22	150	4187	Deactivated
o-3	25	0.32	105	2283	Deactivated
o-4	28	0.22	141	2609	Deactivated
o-5	14	0.22	131	1445	Deactivated
O-6	25	0.22	205	726	Deactivated
o-7"	13	0.25	130	4374	Deactivated
O-8	17	0.22	60	2056	Non-deactivated
S-1	23	0.25	145	3609	Deactivated
s-2	26	0.25	141	3521	Deactivated
s-3	24	0.32	135	2809	Deactivated
s-4	24	0.32	155	1690	Deactivated
s-5	23	0.25	138	—	Non-deactivated, cross-linked

[a] 0 and S denote OV-1 and SE-54 columns, respectively.
[b] The deactivation of column O-7 was unsuccessful.

dardized? Moreover, what solute one should use for carrier gas velocity optimization?

According to the **Golay** equation [24], the dependence of the plate height of OTGC on the carrier gas velocity ii may be expressed as follows:

$$h = B/\bar{u} + C\bar{u}$$

where

$B = 2D_g$ = the coefficient of molecular diffusion term;

C = C, + C_g = the coefficient of mass transfer terms

$$= \frac{r^2}{24D_g} \cdot \frac{1 + 6k + 11k}{(1 + k)^2} \quad \frac{k^3}{+ 6k^2(1 + k)^2} \cdot \frac{r^2}{D_1}$$

$$= \frac{r^2 D_1 \beta^2 (1 + 6k + 11k) + 4D_g kr^2}{24D_1 D_g (1 + k)^2 \beta^2}$$

r = column radius;
k = capacity factor of the test solute;
D_g = diffusion coefficient of solute in gaseous phase;
$D,$ = diffusion coefficient of solute in stationary phase;

K = distribution constant of solute, $K = k\beta$;
β = phase ratio.

The optimum carrier gas velocity can thus be deduced:

$$\bar{u} = {}_0\frac{B}{C}{}^{1/2}$$

$$= \left[\frac{48D_1 D_g^2 (1 + k)^2 \beta^2}{r^2 D_1 \beta^2 (1 + 6k + 11k^2) + 4D_g kr^2} \right]^{1/2}$$

Hence, for a given capillary column, $D_,$, $D_,$ and k being solute dependent, $\bar{u}_{opt}$ becomes test solute dependent, different solutes giving different optimum average gas velocities.

The optimum average linear velocity for reproducing the Sadtler standard PTRI was found experimentally by measuring the PTRI of the test mixture following all the instructions given in the introduction of the Library with the exception of carrier gas velocity. Different carrier gas velocities were tried and the corresponding reproducibilities were compared. The best reproducibility was obtained at 43 cm/s (Table II). From this table it is obvious that the reproducibility of PTRI depended sensitively on the gas velocity applied. The dead time t_0 was

TABLE II

INFLUENCE OF CARRIER GAS VELOCITY ON REPRODUCING PTRI VALUES OF TEST COMPOUND ON THE HP SE-54 COLUMN

Varian 3770, $L = 25$ m, I.D. = 0.32 mm, $d_f = 0.52$ μm, $T_0 = 35°C$, $r = 8°C/min$, $n = 3$.

Compound	I_s [a]	$\bar{u}_1 = 43$ cm/s		$\bar{u}_2 = 35$ cm/s		ii, = 28 cm/s	
		I_{x1}	ΔI_1	I_{x2}	ΔI_2	I_{x3}	ΔI_3
o-Xylene	895.6	895.5	-0.1	896.7	1.1	898.1	2.5
n-Heptanol	970.7	969.6	-1.1	969.2	-1.5	969.1	-1.6
Limonene	1032.4	1032.5	0.1	1033.9	1.5	1035.4	3.0
Isophorone	1127.1	1126.4	-0.7	1128.2	1.1	1130.4	3.3
Camphor	1154.3	1153.5	-0.8	1156.0	1.7	1159.0	4.7
Cuminaldehyde	1250.2	1249.0	-1.2	1251.2	1.0	1253.6	3.4
Anethol	1292.7	1292.6	-0.1	1292.4	1.7	1296.1	3.4
Eugenol	1365.6	1365.3	-0.3	1367.0	1.4	1368.8	3.2
Diphenylether	1414.2	1413.8	-0.4	1417.1	2.9	1420.0	5.8
β-Ionone	1439.9	1438.1	-1.8	1440.4	0.5	1442.4	2.5
Benzyl benzoate	1785.0	1783.8	-1.2	1787.6	2.6	791.8	6.8
Mean absolute difference			0.70		1.70		3.66

[a] I_s is the PTRI in the Sadtler Standard GC RI Library at $r = 8°C/min$.

approximated by measuring the elution time of methane at the initial oven temperature of 35°C. The PTRI values in Table II are the mean values of three measurements. The reproducibility of PTRI can be conveniently expressed by the mean absolute difference (MAD), which is the mean of the absolute differences between measured and standard PTRI values. In this instance, MAD is 0.70 i.u. for the SE-54 column (Table III) and 0.50 i.u. for the OV-1 column (not shown). The maximum absolute difference is 1.8 i.u. for β-ionone. According to Sadtler, it is expected to have a reproducibility within 1 i.u. on non-polar columns. As the instrument we

used was less sophisticated than the HP 5880A and no autosampler or calibration of oven temperature was applied, our results seemed to be satisfactory. The precision or repeatability of PTRI measurements can be expressed by the mean standard deviations of the measurements, MSD, being 0.15 and 0.24 i.u. for the SE-54 and OV-1 columns, respectively. For both SE-54 and OV-1 an average linear velocity of 43 cm/s is used, which is different from the value (35.0 cm/s at 60°C with benzene as test compound on the SE-54 column) calculated from the minimum of the H vs. $\bar{v}$ curve.

For polar columns. Here, the column inert-

TABLE III

INFLUENCE OF CARRIER GAS VELOCITY ON REPRODUCING SADTLER STANDARD PTRI ON HP CW 20M COLUMNS

Varian 3770, L = 25, I.D. = 0.32 mm, d_f = 0.32 μm, = 250, T_0 = 60°C, r = 8°C/min, n = 3.

Column	Compound	I_s [a]	$\bar{u}_1$ = 33 cm/s		$\bar{u}_2$ = 37 cm/s		$\bar{u}_3$ = 40 cm/s		$\bar{u}_4$ = 44 cm/s	
			I_{x1}	ΔI_1	I_{x2}	ΔI_2	I_{x3}	ΔI_3	I_{x4}	ΔI_4
A	*o*-Xylene	1186.5	1189.0	2.5	1180.5	-6.0	1188.1	1.6	1210.0	13.5
	Limonene	1204.3	1206.0	1.7	1207.5	3.2	1204.8	0.5	1204.5	0.2
	n-Heptanol	1444.3	1460.6	16.3	1460.0	15.7	1462.7	18.4	1460.2	15.9
	Camphor	1507.5	1517.5	10.0	1514.1	6.6	1516.8	9.4	1511.7	4.2
	Isophorone	1576.8	1607.8	31.0	1595.8	19.0	1591.5	14.7	1600.0	23.2
	Cuminaldehyde	1767.4	1771.3	3.9	1767.2	-0.2	1772.1	4.7	1762.7	-4.7
	Anethol	1814.5	1810.5	-4.5	1807.4	-7.1	1811.3	-3.2	1802.5	-12.0
	β-Ionone	1835.6	1854.5	18.9	1850.4	14.8	1855.4	19.9	1846.1	10.5
	Diphenyl ether	2000.0	1984.8	-15.2	1980.8	-19.2	1984.0	-16.0	1975.8	-24.2
	Eugenol	2145.3	2167.8	22.5	2164.5	15.2	2167.6	22.3	2162.2	16.9
	MAD [b]			15.5		10.1		9.64		10.3

			$\bar{u}_1$ = 37 cm/s		$\bar{u}_2$ = 40 cm/s		$\bar{u}_3$ = 43 cm/s		$\bar{u}_4$ = 46 cm/s		$\bar{u}_5$ = 4 cm/s	
			I_{x1}	ΔI_1	I_{x2}	ΔI_2	I_{x3}	ΔI_3	I_{x4}	ΔI_4	I_{x5}	ΔI_5
B	o-Xylene	1186.5	1190.3	3.8	1189.3	2.8	1189.2	2.7	1188.9	2.4	1185.1	-1.3
	limonene	1204.3	1205.5	1.2	1204.9	0.6	1204.5	0.2	1204.5	0.2	1201.4	-2.9
	n-Heptanol	1444.3	1446.4	2.1	1446.6	2.3	1446.7	2.4	1446.6	2.3	1446.7	2.4
	Camphor	1507.5	1512.5	5.0	1510.7	3.2	1509.5	2.0	1508.0	0.5	1507.0	-0.5
	Isophorone	1576.8	1582.6	5.8	1581.6	4.8	1579.7	2.9	1578.5	1.7	1577.4	0.6
	Cuminaldehyde	1767.4	1771.8	4.4	1770.0	2.6	1768.6	1.2	1767.9	0.5	1766.7	-0.7
	Anethol	1814.5	1818.4	3.9	1817.7	3.2	1816.2	1.7	1815.6	1.1	1814.8	0.3
	β-Ionone	1835.6	1848.9	5.3	1840.1	4.5	1838.3	2.7	1837.4	1.8	1836.3	0.7
	Diphenyl ether	2000.0	2003.6	3.6	2800.0	0.0	2000.0	0.0	2ooo.0	0.0	20WJ.0	0.0
	Eugenol	2145.3	2147.6	2.3	2146.4	1.1	2145.6	0.3	2144.9	-0.4	2143.7	-1.6
	MAD [b]			3.46		2.28		1.55		0.97		1.00

[a] I_s is the Sadtler standard PTRI on the HP CV 20M column at r = 8°C/min.
[b] MAD = mean absolute difference between measured and standard values.

ness became an additional problem. We therefore had to make a reproducibility test by varying the average linear velocity to see whether an optimum average linear velocity for reproducing PTRI could be found. The failure or success of the flow-rate optimization test could provide valuable information on the status of the column.

From Table III (column A), evidently no matter how the average linear velocity varied, the mean absolute difference between the measured and the standard PTRL was always excessively large, usually exceeding 10 i.u., and the individual differences between measured and standard PTRI even exceeded 30 i.u. It was impossible to optimize the linear velocity on the column. When the second HP CW-20M column was tried, the situation was changed [Table III (column B)]. The mean absolute difference never exceeded 3.5 i.u. at any linear velocity tested, and the mean absolute difference showed a progressive decrease with increase in flow-rate from 37 to 46 cm/s. The mean absolute difference at the optimum linear velocity was nearly 1 i.u., with a maximum absolute difference of 2.9

i.u., in accordance with the demand of the Library.

On the first HP CW 20M column (A) a performance test was run with the Grob test mixture [20,25]. On the chromatogram from column A, 2,3-butanediol showed serious tailing with the 2-ethylhexanoic acid peak missing. On the other hand, the same test mixture eluted well with all twelve components giving nearly symmetrical peaks on column B. Evidently there is a close relationship between the inertness of a column and its capability for reproducing PTRI.

Although it is well known that the Grob test is a rigorous test for column evaluation, almost no column manufacturers use it as a routine method for quality control. So far as we know, only a limited number of commercial PEG 20M columns can pass the Grob test [20,26]. The first column that failed to pass the reproducibility test was used immediately after its arrival without being tested with the Grob test mixture. However, it did pass and can still pass the test recommended by the supplier [see column (3) under Experimental] [27]. Hence it is advisable for users who intend to use the polar column for

TABLE IV

INFLUENCE OF INITIAL OVER TEMPERATURE ON REPRODUCIBILITY OF PTRI ON THE HP SE-54 COLUMN

Varian 3770, L = 25 m, I.D. = 0.32 mm, d_f = 0.52 μm, $\bar{u}$ = 43 cm/s, r = 8°C/min, n = 3.

Compound	$I_s{}^a$	$T_0 = 35°C$		$T_0 = 40°C$		$T_0 = 45°C$		$T_0 = 50°C$	
		I_{x1}	ΔI_1	I_{x2}	ΔI_2	I_{x3}	ΔI_3	I_{x4}	ΔI_4
o-Xylene	895.6	895.5	-0.1	896.1	0.5	897.0	1.4	898.0	2.4
n-Heptanol	970.7	969.6	-1.1	969.2	-1.5	969.5	-1.2	968.1	-2.6
Limonene	1032.4	1032.5	0.1	1032.6	0.2	1032.8	0.4	1033.0	0.6
Isophorone	1127.1	1126.4	-0.7	1126.5	-0.6	1126.9	-0.2	1127.4	0.3
Camphor	1154.3	1153.5	-0.8	1153.8	-0.5	1153.8	-0.5	1154.3	0.0
Cuminaldehyde	1250.2	1249.0	-1.2	1249.1	-1.1	1249.3	-0.9	1249.5	-0.7
Anethol	1292.7	1292.6	-0.1	1292.7	0.0	1293.0	0.3	1293.2	0.5
Eugenol	1365.6	1365.3	-0.3	1365.4	-0.2	1365.5	-0.1	1365.2	-0.4
Diphenyl ether	1414.2	1413.8	-0.4	1413.7	-0.5	1413.9	-0.3	1414.0	-0.2
β-Ionone	1439.9	1438.1	-1.8	1437.8	-2.1	1438.3	-1.6	1437.8	-2.1
Benzyl benzoate	1785.0	1783.8	-1.2	1783.9	-1.1	1783.8	1.2	1783.7	-1.3
MAD			0.70		0.75		0.73		1.00

^{a} See footnote to Table II.

reproducing PTRI to run the Grob test and check the quality of the column themselves. It is easy to understand that a column with significant adsorptive activity or excessive acidity or basicity will retain some of the test components with dual mechanisms [ref. 19], and the additional mechanism other than gas-liquid distribution will lead to adverse effects in reproducing PTRI.

Is it permissible to vary the initial oven temperature?

For some less sophisticated gas chromatographs and many laboratories without air conditioning during summer time, it is not convenient to hold the initial oven temperature at 35°C. It is of interest to know whether the initial oven temperature is permitted to increase to a certain extent. On the two apolar columns four different initial oven temperatures were chosen, from 35 to 50°C in 5°C increments. The average linear velocity of carrier gas was maintained at 43 cm/s, which was measured at 35°C without readjustment of the gas flow-rate after changing the initial oven temperature. From Table IV it can be seen that an increase in the initial oven temperature of 10–15°C did not appreciably affect the mean absolute difference between the measured and the standard values on the OV-1 column for the test compounds with PTRI higher than 1000 i.u. This phenomenon can be easily attributed to the initial focusing of the solute at the column inlet. Hence it can be deduced that for compounds with PTRI less than 800 the permissible elevation of the initial oven temperature will be decreased, whereas for compounds with higher PTRI the permissible elevation of the initial oven temperature may be increased. Similar results were obtained on the OV-1 column. The allowable elevation of the initial oven temperature depends on the particular solute tested. For the analysis of flavour and fragrance volatiles in our laboratory the initial oven temperature can usually be varied from 35 to 50°C on these apolar columns. For the polar CW 20M column the standardized initial oven temperature was chosen as 60°C. At this temperature the reproducibility of PTRI is more sensitive to the variation of the initial oven temperature. It is better to maintain the initial oven temperature at 60°C.

Is it allowed to use carrier gases other than hydrogen ?

Hydrogen is undoubtedly the preferred carrier gas to use in open-tubular gas chromatography as it gives the fastest separation with sufficiently high efficiency. However, some chromatographers prefer to use helium whereas others prefer nitrogen. It is also of interest to know whether the Sadtler Standard GC PTRI can meet their needs. Based on previous work [16], the average linear velocity of nitrogen was lowered to 11.6 cm/s, a value near its optimum velocity with a simultaneous decrease in the oven heating rate from 8 to 2°C/min. The PTGC characteristic parameter rt_0/β became 0.048°C, which was close to the characteristic value of 0.052°C necessary for reproducing standard PTRI at $r = 8$°C/min. The experimental results on the SE-54 column with nitrogen as the carrier gas are given in Table V. The mean absolute difference between the measured and the standard values measured at $r = 8$°C/min were 0.90, 0.50 and 0.90 i.u. for the SE-54, OV-1 and CW 20M columns, respectively. The reproducibilities are as good as those obtained with hydrogen as the carrier gas. Moreover, helium can be used instead of nitrogen. The use of nitrogen as the carrier gas can certainly meet the routine requirements of some chromatographers but, as it leads to much longer times for retention index measurements than hydrogen, it is not recommended in practice.

Is it feasible to use a gas chromatograph with constant flow-rate control?

The column inlet of a gas chromatograph may be controlled with either constant pressure or constant flow-rate. Most gas chromatographs today belong to the former category, such as the Hewlett-Packard Model 5880A used for compiling the Sadtler Standard GC RI Library and the Varian Model 3770 used in our experiments. It is worth investigating whether an instrument of the latter type, such as a Shimadzu GC 9A, is suitable for our purposes. The influence of velocity on the reproducibility of PTRI is shown

TABLE V

REPRODUCIBILITY OF SADTLER STANDARD PTRI WITH NITROGEN AS CARRIER GAS ON THE HP SE-54 COLUMN

Varian 3770, $L = 25$ m, I.D. $= 0.32$ mm, $d_f = 0.52$ μm, $T_0 = 35$°C, $\bar{u} = 11.6$ cm/s, $R = 2$°C/min, $n = 3$.

Compound	I_s^a	I_x			S.D.	I_x	A
		1	2	3			
o-Xylene	895.6	895.5	895.6	895.6	0.07	895.6	0.0
n-Heptanol	970.7	969.9	970.0	969.9	0.05	969.9	-0.8
Limonene	1032.4	1032.4	1032.2	1032.3	0.08	1032.3	-0.1
Isophorone	1127.1	1126.6	1126.6	1126.2	0.24	1126.5	-0.7
Camphor	1154.3	1153.3	1153.3	1153.0	0.19	1153.2	-1.1
Cuminaldehyde	1250.2	1248.7	1248.6	1248.5	0.10	1248.6	-1.6
Anethol	1292.7	1292.7	1292.6	1292.3	0.20	1292.5	-0.2
Eugenol	1365.6	1365.0	1365.0	1365.4	0.23	1365.1	-0.5
Diphenyl ether	1414.2	1413.3	1412.7	1413.4	0.42	1413.1	-1.1
β-Ionone	1439.9	1437.7	1437.3	1438.0	0.37	1437.7	-2.2
Benzyl benzoate	1785.0	1783.3	1783.2	1783.6	0.21	1783.4	-1.6
					MSD: 0.20		MAD: 0.90

[a] See footnote to Table II.

in Table VI and cu. 28 cm/s was found to be the best choice. The mean absolute difference reached 1.47 i.u. for the SE-54 column, which is considerably higher than that obtained on the Varian Model 3770. Hence it is recommended that an experiment be run on a constant-pressure controlled gas chromatograph if available.

Similar experiments to those described above

TABLE VI

INFLUENCE OF CARRIER GAS VELOCITY ON REPRODUCBILITY OF PTRI VALUES OF TEST COMPOUNDS ON A CONSTANT FLOW-RATE CONTROLLED GAS CHROMATOGRAPH

Shimadzu GC-9A, HP SE-54, $L = 25$ m, I.D. $= 0.32$ mm, $d_f = 0.52$ μm, $T_0 = 35$°C, $R = 8$°C/min, $n = 3$.

Compound	I_s^a	$\bar{u}_1 = 28$ cm/s		$\bar{u}_2 = 30$ cm/s		$\bar{u}_3 = 33$ cm/s		$\bar{u}_4 = 36$ cm/s		$\bar{u}_5 = 43$ cm/s		$\bar{u}_6 = 51$ cm/s	
		I_{x1}	ΔI_1	I_{x2}	ΔI	I_{x3}	ΔI_3	I_{x4}	ΔI_4	I_{x5}	ΔI_5	I_{x6}	ΔI_6
o-Xylene	895.6	897.5	1.9	897.1	1.5	896.7	1.1	896.2	0.6	895.3	0.3	894.6	-1.0
n-Heptanol	970.7	969.4	1.3	969.6	-1.1	969.8	0.9	969.7	-1.0	970.0	-0.7	970.0	-0.7
Limonene	1032.4	1034.3	1.9	1033.8	1.4	1033.3	0.9	1032.8	0.4	1031.0	-0.6	1031.0	-1.4
Isophorone	1127.1	1129.0	1.9	1128.0	0.9	1127.4	0.3	1127.0	-0.1	1125.3	-1.8	1124.1	-3.0
Camphor	1154.3	1156.5	2.2	1155.3	1.0	1154.5	0.2	1153.7	-0.6	1151.4	-2.9	149.8	-4.5
Cuminaldehyde	1250.2	1251.2	1.0	1250.0	0.0	1249.3	-0.9	1248.9	-1.3	1246.8	-3.4	1245.4	-4.8
Anethol	1292.7	1294.1	1.4	1293.5	0.8	1292.8	0.1	1292.4	-0.3	1291.1	-1.6	1290.0	-2.7
Eugenol	1365.6	1366.4	0.8	1365.9	0.3	1365.1	-0.5	1364.8	-0.8	1363.4	-2.2	1362.2	-3.4
Diphenyl ether	1414.2	1415.5	0.8	1438.7	-1.2	1437.7	-2.2	1436.9	-3.0	1435.2	-4.7	1433.7	-6.2
Benzylbenzoate	1785.0	1783.3	-1.7	1782.0	3.0	1780.3	-4.7	1779.6	-5.4	1776.5	-8.5	773.7	-11.3
MAD			1.47		0.73		1.07		1.23		2.69		4.02

[a] See footnote to Table II.

were made to reproduce the Sadtler standard PTRI measured at $r = 2°C/min$, with equally satisfactory results.

It is possible to reproduce Sadder standard PTRZ on laboratory made columns?

Efficient deactivation of the column is of utmost importance for reproducing standard PTRI. Table VII shows that the first six OV-1 columns that passed the stringent Grob test were capable of reproducing the standard PTRI of the eleven test compounds with a mean absolute difference between the measured and the standard values lying between 0.68 and 1.41 i.u. with an average of 0.90 i.u. Similarly, on laboratory made SE-54 columns the average of the mean absolute differences on four columns (S-l-4) is 0.69 i.u. (Table VIII).

In contrast, the results with the non-deactivated columns (O-8 and S-5) and the poorly deactivated column (O-7), which had been washed excessively with solvent, leading to destruction of the deactivated layer, were all unsatisfactory. On column O-7 the influence of poor deactivation on retention index measurement was demonstrated by the exceptionally

large difference for the two polar test solutes, *n*-heptanol and eugenol. As mentioned above, effective deactivation of a column was found to be of utmost importance for reproducing PTRI on a commercially available HP high-performance CW 20M column. The same is necessary for non-polar laboratory made OV-1 and SE-54 columns.

The influence of column efficiency on the capability of reproducing standard PTRI was demonstrated to be of only secondary importance. All the columns used in the experiment were prepared by a novice without previous experience in column technology. Among the six OV-1 columns prepared in the experiment, only column 2 was comparable in efficiency to the HP ultra-performance OV-1 column. Columns O-5 and O-6 gave very low efficiencies. Nevertheless, they could reproduce the standard Sadtler PTRI equally well. The reproducibilities of the Sadtler Standard PTRI on our laboratory made columns were slightly poorer than those stated in the Library.

The phase ratio β, film thickness d,, column inner diameter and column length L need not to be standardized. Variations of L from 14 to 28 m,

TABLE VII

REPRODUCIBILITY OF SADTLER STANDARD PTRI ON LABORATORY-MADE OV-1 COLUMNS [DIFFERENCE BETWEEN MEASURED (n = 3) AND SADTLER STANDARD PTRI VALUES]

Compound	I_s	o-1	o-2	o-3	o-4	O-5	O-6	o-7	O-8
o-Xylene	876.7	0.35	-0.35	-0.51	0.07	1.22	0.98	1.38	-0.77
n-Heptanol	953.8	1.56	-0.67	-1.59	-0.81	1.32	-1.17	11.56	6.71
Limonene	1021.4	0.13	-0.42	-0.51	-0.24	-0.71	0.69	-0.24	-1.28
Isophorone	1090.1	-0.61	-0.49	-1.49	-0.11	0.78	0.52	3.24	-1.20
Camphor	1120.5	0.57	-1.21	-1.07	-0.34	0.46	1.03	-0.54	-2.24
Cuminaldehyde	1213.0	0.48	-0.58	-1.31	-0.69	1.70	0.43	3.22	-1.81
Anethol	1261.8	-0.48	-0.52	-1.33	-1.23	1.41	0.43	2.56	-1.86
Eugenol	1329.3	1.44	-0.71	-2.00	-1.60	1.16	0.28	12.54	0.60
Diphenyl ether	1376.3	1.13	-1.83	-2.83	-2.24	-0.58	-0.86	1.26	-3.82
β-Ionone	1408.8	0.59	-1.02	-1.81	-1.10	0.10	-0.53	1.37	-2.14
Benzyl benzoate	1728.4	0.18	-0.67	-1.54	-1.98	0.41	0.89	2.30	-3.54
MAD"	0.68	0.77	1.41	0.95	0.90	0.71	3.65	2.36	
t_0 (min)"	0.95	0.94	0.69	0.95	0.82	1.24	0.83	0.40	
rt_0/β (°C)	0.060	0.050	0.053	0.054	0.050	0.048	0.051	0.053	

[a] MAD-mean absolute difference between the average of measured values and the Sadtler standard values at r = 8°C/min.
[b] u was chosen so as to make rt_0/β approximately equal to 0.052°C.

TABLE VIII

REPRODUCIBILITY OF SADTLER STANDARD PTRI ON LABORATORY-MADE SE-54 COLUMNS [DIFFERENCE BETWEEN MEASURED (**n** = 3) AND SADTLER STANDARD VALUES]

Compound	I_s	S-l	s-2	s-3	s-4	S-5
o-Xylene	895.6	0.15	0.05	0.19	-0.11	0.30
n-Heptanol	970.7	-0.43	-0.24	-0.40	-0.06	4.75
Limonene	1032.4	-0.31	-0.10	-0.31	-0.53	0.75
Isophorone	1127.1	0.59	1.30	1.04	0.16	8.67
Camphor	1154.3	0.50	0.25	0.07	-1.05	5.06
Cuminaldehyde	1250.2	-1.24	-0.38	-0.56	-1.60	1.85
Anethol	1292.7	0.05	0.37	0.37	-0.37	2.12
Eugenol	1365.6	−0.04	-0.02	-0.21	-0.59	3.24
Diphenyl ether	1414.2	-0.97	-0.37	-0.61	-1.84	1.85
β-Ionone	1439.9	-1.45	-1.57	-1.71	-2.12	3.19
Benzyl benzoate	1785.0	-1.45	-0.84	-1.22	-2.90	2.88
MAD"		0.65	0.50	0.61	1.01	3.06
t_0 (ruin)"		0.93	0.96	0.87	0.93	0.87
rt_0/β (°C)		0.051	0.054	0.052	0.048	0.050

ª See footnotes to Table VII.

β from 105 to 205 and inner diameter from 0.22 to 0.32 mm did not significantly affect the reproducibility of the results. Therefore, the Sadtler Standard PTRI Library might be compatible with not only Hewlett-Packard ultra-performance and high-performance columns but also with many other well deactivated commercially available columns.

So far, we have not succeeded in preparing a polar Carbowax 20M fused-silica capillary column with high inertness, so we are still unable to reproduce the standard PTRI on laboratory-made polar columns.

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