

INFLUENCE OF EXPERIMENTAL CONDITIONS ON PEAK RESOLUTION IN GAS CHROMATOGRAPHY

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(Received November 8th, 1961)

In order to be able to discuss the conditions under which two peaks are resolved, it is clearly necessary first to define an acceptable criterion of minimum resolution, which will often depend on the type of problem under investigation. A convenient measure of resolution is the distance between two maxima expressed in terms of σ , the dispersion of an individual peak. At 2σ separation it is just possible to recognize the two-component character of the peak¹. Hence, for qualitative analysis a resolution of 2σ may be adequate but it will not enable one to estimate the ratio of the peak areas. This only becomes possible when the separation is about 4σ .² For quantitative analysis of traces or for preparative separation in one step an even larger separation is desirable such as a 6σ -resolution³ (*cf.* Fig. 1).

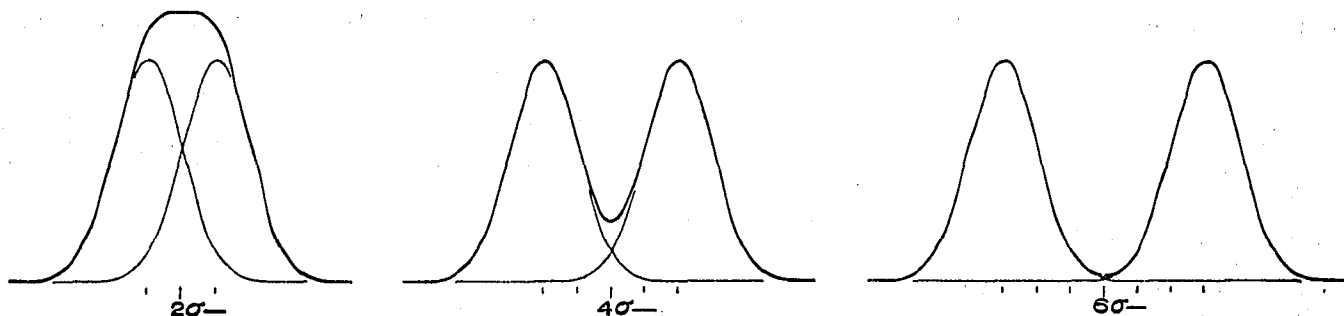


Fig. 1. Resolution of two peaks.

We propose that any of these "minimum resolutions" can be used and that one can speak of a 2σ -, 3σ - and in general of an $N\sigma$ -resolution* of two peaks matching N with the actual problem. In this paper we give a fairly simple method for the estimation of the difference, δI , between the retention indices of two substances which is necessary to achieve an $N\sigma$ -resolution. We discuss therefore the slightly modified form of an equation derived previously^{1**}:

$$\delta I = N\sigma \frac{1}{\sqrt{n}} \left(\frac{\rho + 1}{\rho} \right)$$

* It is possible and equivalent to this definition to measure the resolution in terms of 4σ , see *e.g.* AMBROSE *et al.*⁴.

** See also CHOVIN AND LEBRE⁵. These authors give a relation between the "separation factor S ", of PURNELL² and δI .

where:

δI	=	$I(2) - I(1)$	(—)
N	=	Distance of the maxima of two peaks in σ -units: <i>i.e.</i> the resolution in terms of σ	(—)
σ	=	The half of the peak width at the inflexion point	(cm)
ρ	=	$d'_R(1)/d_R(0)$	(—)
$d'_R(1)$	=	Adjusted retention distance of the substance (1); $d'_R(1) < d_R(2)$	(cm)
$d_R(0)$	=	Uncorrected retention distance of a substance insoluble in the stationary phase	(cm)
Φ	=	$100 RT_c/\beta$	(—)
T_c	=	Temperature of the column	(°K)
β	=	Free enthalpy of vaporisation from the stationary phase given for one CH_2 -group	(cal/mole)

This equation consists of the three main parts:

$$\Phi, 1/\sqrt{n} \text{ and } (\rho + 1)/\rho.$$

The function Φ depends on the separation of two n -paraffins, expressed in terms of β , and on the temperature of the column. A large value of β and low temperatures give good separation. The function β itself increases with lowering of the temperature thus amplifying the total effect of the temperature. The function $1/\sqrt{n}$ shows that the separation increases with the square root of the theoretical plate number of the column.

The function $(\rho + 1)/\rho$ approaches unity as the retention distance becomes larger corresponding to increasing separation efficiency. Summarising, we can con-

TAB

Temperature		Apiezon-L				Emulphor-O				Silicone DC 200*		
°C	°K	Φ	2 Φ	4 Φ	6 Φ	Φ	2 Φ	4 Φ	6 Φ	Φ	2 Φ	4 Φ
40	313	118	236	473	709	129	258	517	775	103	205	410
50	323	122	245	489	734	134	267	535	802	106	213	425
60	333	126	253	506	758	138	276	553	829	110	220	440
70	343	131	261	522	783	143	286	571	857	114	228	455
80	353	135	269	539	808	147	295	589	884	118	235	471
90	363	139	278	555	833	152	304	608	912	122	243	486
100	373	143	286	572	858	157	313	626	939	125	251	502
110	383	147	294	589	883	161	322	645	967	129	259	517
120	393	151	303	605	908	166	332	664	995	133	267	533
130	403	156	311	622	934	171	341	682	1024	137	275	549
140	413	160	320	639	959	175	351	701	1052	141	283	565
150	423	164	328	656	985	180	360	720	1081	145	291	582
160	433	168	337	674	1010	185	370	740	1109	150	299	598
170	443	173	345	691	1036	190	379	759	1138	154	307	615
180	453	177	354	708	1062	195	389	778	1167	158	316	631
190	463	181	363	726	1088	199	399	798	1196	162	324	648
200	473	186	372	743	1115	204	409	817	1226			
210	483	190	380	761	1141	209	418	837	1255			
220	493	195	389	778	1168	214	428	857	1285			
230	503	199	398	796	1194	219	438	877	1315			
240	513	204	407	814	1221	224	448	897	1345			
250	523	208	416	832	1248	229	458	917	1375			

* Calculated from ref. 6.

clude that the separation of two peaks does not depend only on the theoretical plate number of a column but also on the temperature as well as on other specific properties of the stationary liquid.

In Table I the values of the function $N\Phi$ are listed for six stationary phases at different temperatures. In Fig. 2 is shown the graphical representation of the function:

$$\delta I(\infty) = N\Phi \frac{1}{\sqrt{n}}$$

that is, the necessary difference between the retention indices of two substances, δI , whose retention time is very long compared with the zero retention time. In this case $(\rho + 1)/\rho \rightarrow 1$. In Fig. 3 two functions: $(\rho + 1)\rho$ and $[\rho/(\rho + 1)]^2$ are plotted against ρ . To evaluate the difference δI we can now proceed in two equivalent ways:

- (a) (i) Taking the value of $N\Phi$ from Table I;
- (ii) Taking the value of $\delta I(\infty)$ from Fig. 2;
- (iii) Taking the value of $(\rho + 1)/\rho$ from Fig. 3.

We can now calculate δI as follows:

$$\delta I = \delta I(\infty) \frac{\rho + 1}{\rho}$$

- (b) (i) Taking the value of $N\Phi$ from Table I;
- (ii) Calculating the so-called effective plate number with the aid of Fig. 3:

$$n_{\text{eff}} = n \left(\frac{\rho}{\rho + 1} \right)^2$$

<i>Polyethyleneglycol*</i>			<i>Didecyl phthalate*</i>			<i>Di-ethylhexyl sebacate*</i>				
2 Φ	4 Φ	6 Φ	Φ	2 Φ	4 Φ	6 Φ	Φ	2 Φ	4 Φ	6 Φ
191	381	572	99	198	397	595	98	196	392	587
199	398	597	103	206	412	619	102	204	409	613
207	415	622	107	214	429	643	107	213	427	640
216	432	648	111	222	445	667	111	222	445	667
225	449	674	115	231	461	692	116	232	464	695
234	467	701	120	239	478	717	121	241	483	724
243	485	728	124	248	495	743	126	251	502	753
252	504	756	128	256	513	769	131	261	522	783
262	523	785	133	265	530	796	136	271	543	814
271	543	814	137	274	548	823	141	282	564	846
281	563	844	142	283	567	850	146	293	586	879
292	583	875	146	293	585	878	152	304	608	912
302	604	907	151	302	604	906	158	316	631	947
313	626	939	156	312	623	935	164	327	655	982
324	648	972	161	321	643	964	170	340	679	1019
335	671	1006	166	331	663	994	176	352	704	1056

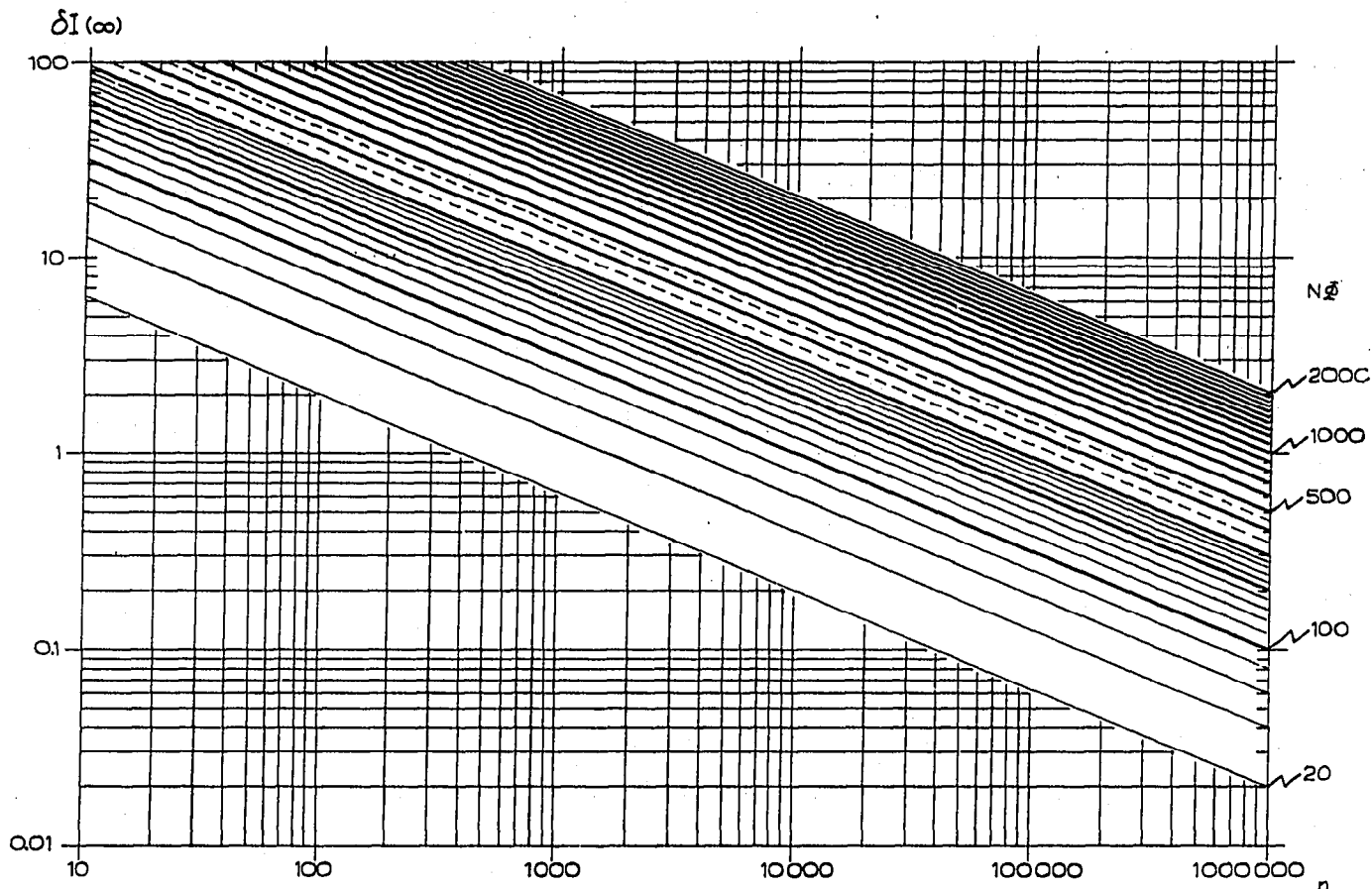


Fig. 2. Graphical representation of the function $\delta I(\infty) = N\Phi \frac{1}{\sqrt{n}}$.

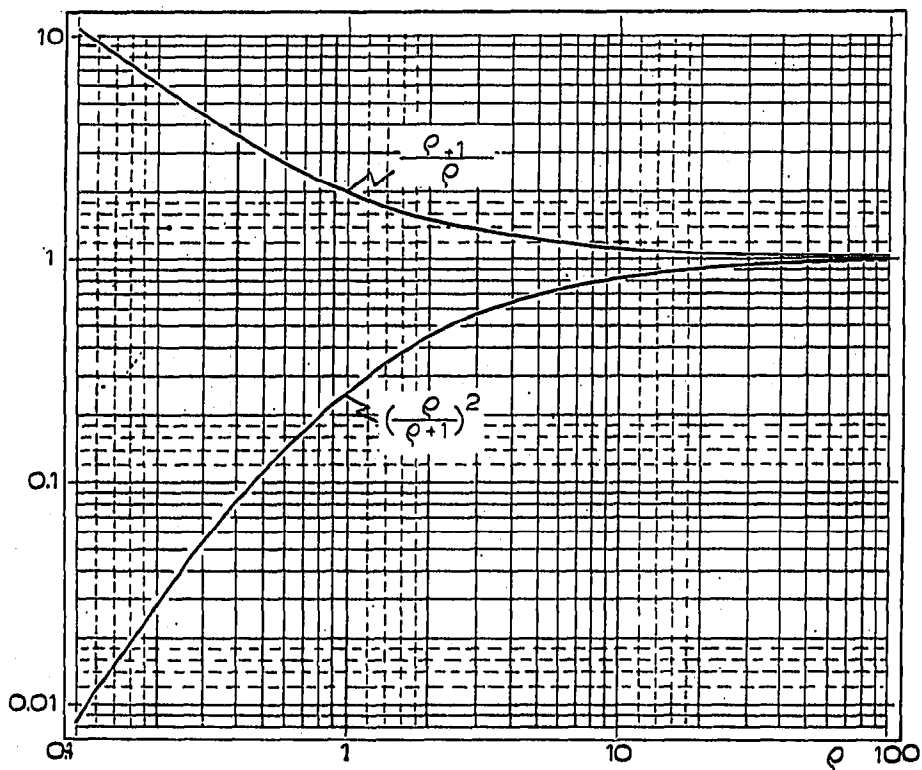


Fig. 3. Plots of the functions $(\rho + 1)/\rho$ and $[\rho/(\rho + 1)]^2$ versus ρ .

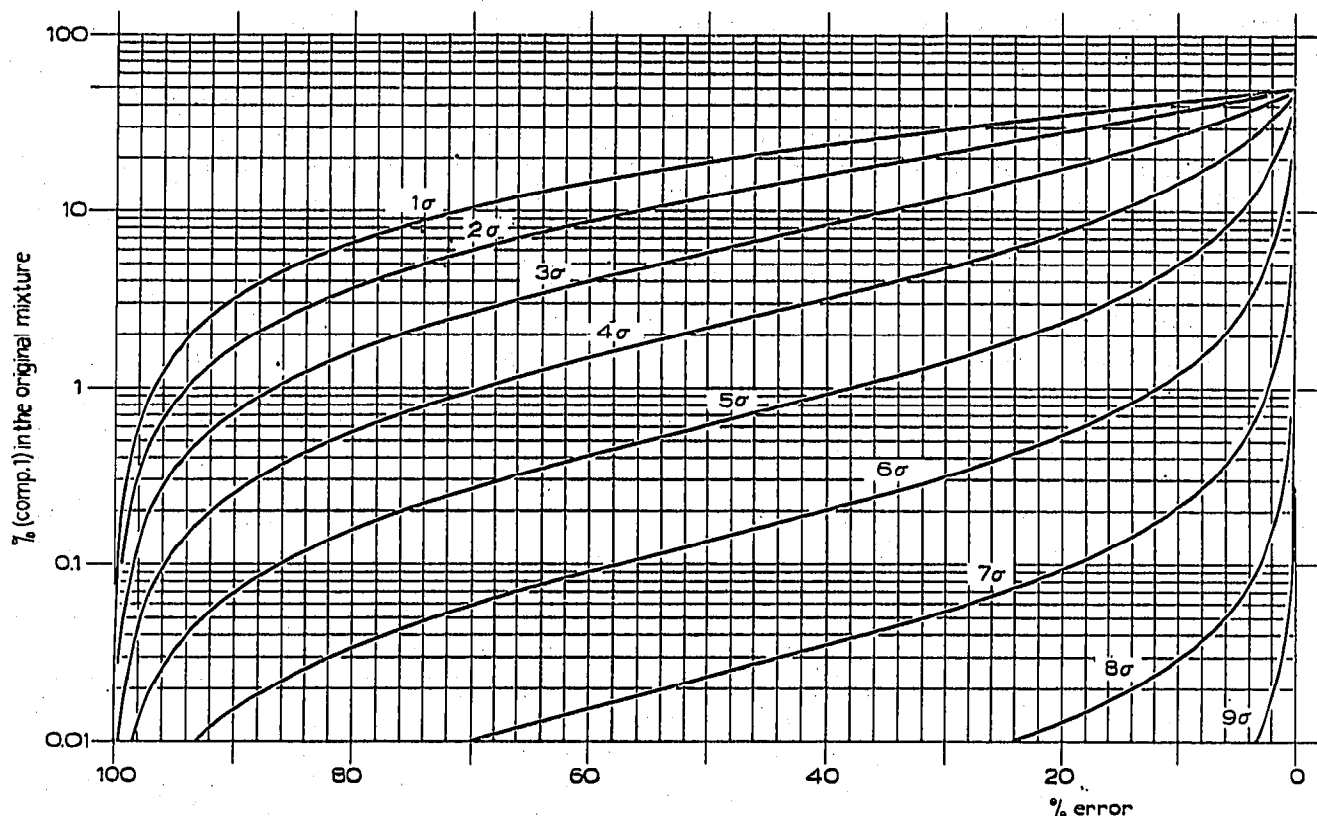


Fig. 4. Percentage error *versus* original percentage of a minor component.

(iii) Taking the value of δI in Fig. 2 using n_{eff} instead of n . In this case the diagram gives δI instead of $\delta I(\infty)$.

A further question is how to choose N for a given quantitative analytical problem. In Fig. 4 the percentage error is plotted against the original percentage of a minor component. We can see that for the quantitative determination of a trace component of 0.1 %, approximately 7σ -resolution is required if we do not want to make a larger error than 20 %. The diagram, of course, does not take account of errors caused by asymmetrical peaks or tailing effects.

The last question is the choice of N for the preparative separation of two substances*. Fig. 5 shows the percentage of substance (2) in the prepared substance (1) as a function of the original percentage of (1) in the binary mixture. The cut was chosen to be exactly midway between the two maxima of the pure components.

Examples

(i) A packed column ($i.\phi:0.6$ cm; $l:240$ cm) with emulphor-O as stationary phase (celite:emulphor-O = 65:35; ϕ of celite 120–150 μ) gives about 1200 theoretical plates. A normal retention distance is such that ρ is about 15. The evaluation of δI for a resolution of 4σ at 190° proceeds as follows:

Method a. In Table I we find for 4Φ the value: 798. Using this value for $N\Phi$ and 1200 for n we find in Fig. 2 $\delta I(\infty)$ to be 23 index units. The value of $(\rho + 1)/\rho$ is

* The formula of GLUECKAUF⁷ is derived with the assumption that the percentage impurity is very small.

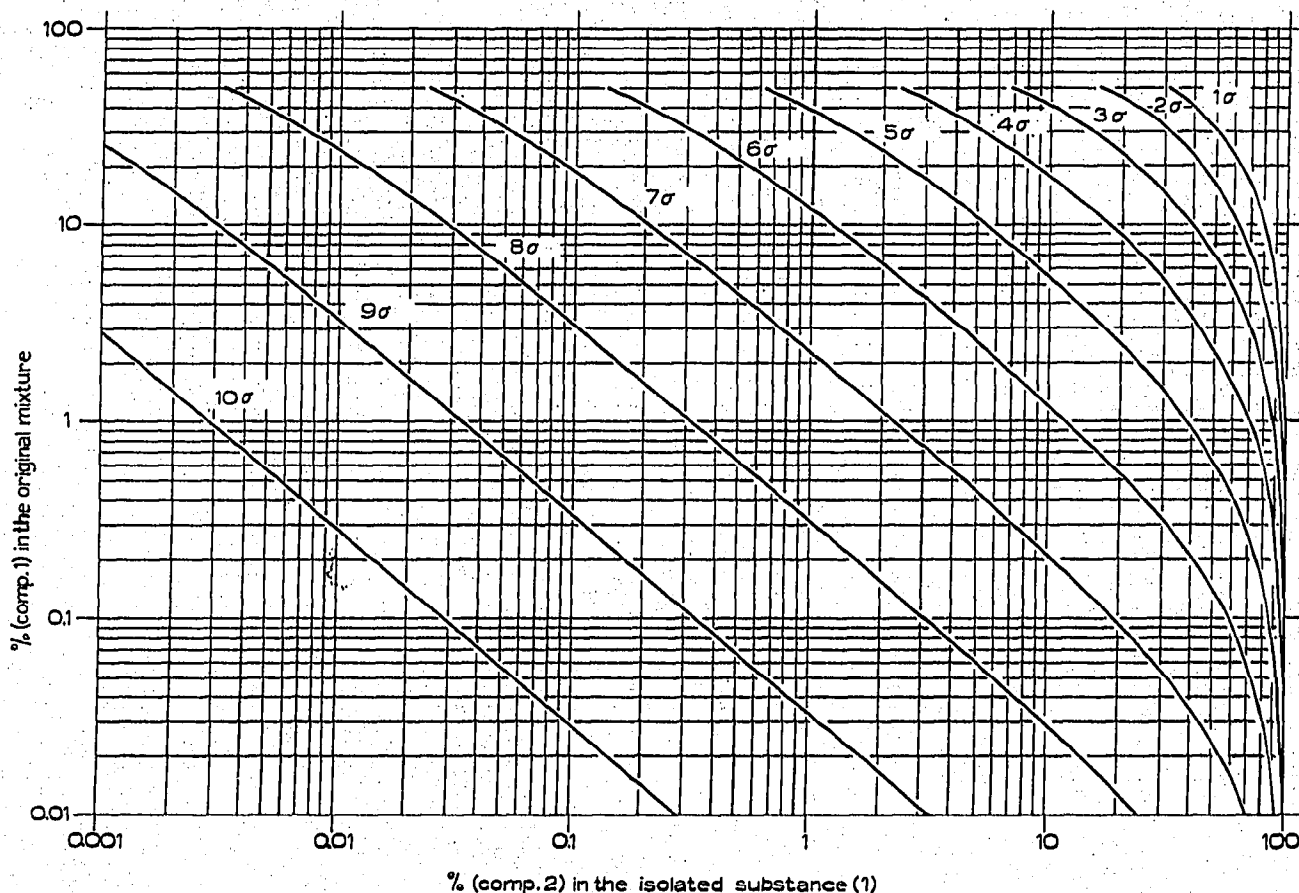


Fig. 5. Percentage of substance (2) in the prepared substance (1) as a function of the original percentage of (1) in the binary mixture.

for $\rho = 15$ about 1.1 (Fig. 3) so that:

$$\delta I = 1.1 \cdot 23 = 25$$

Method b. With the aid of Fig. 3 the effective plate number is found to be:

$$n_{\text{eff}} = 0.88 \cdot 1200 = 1056$$

Using the values 798 for 4Φ and 1056 for n_{eff} , we find from Fig. 2 δI to be 25.

(ii) A capillary column (i.ø: 0.2 cm; l : 10,000 cm) with apiezon-L as stationary phase gives a plate number of about 50,000. The zero retention time under normal conditions is about 15 min. A monoterpene hydrocarbon appears after about 22 min so that $\rho \approx 0.5$. We now wish to find δI which is necessary for a 6σ -resolution.

Method a. 6Φ from Table I: 934. For 50,000 plates $\delta I(\infty)$ is 5. The value of $(\rho + 1)/\rho$ is 3, so that:

$$\delta I = 3 \cdot 5 = 15$$

Method b. We find for the function $[\rho/(\rho + 1)]^2$ from Fig. 3 (with $\rho = 0.5$) the value 0.11, so that:

$$n_{\text{eff}} = 0.11 \cdot 50,000 = 5500$$

With the aid of n_{eff} we find in Fig. 2: $\delta I = 15$.

The necessary δI is much lower if the substance has a longer retention time. For instance we find for a substance which appears after 45 min on the same column ($\rho = 2$), δI to be 6.

(iii) In Fig. 6 the chromatogram of the mixture: *p*-cymene/ β -pinene is shown. Under the experimental conditions indicated the plate number was about 930 and the value of ρ about 13.0. The value of Φ is 181 (Apiezon-L, 190°) thus the necessary resolution for a 1 σ -resolution is $\delta I(\infty) \approx 6$ IU and $\delta I = 6.5$ at $\rho = 13$. The retention index of *p*-cymene is 1071, of β -pinene 1043; the difference between them being 28 IU. The calculated resolution is therefore $28/6.5 = 4.3\sigma$. For the measured resolution we obtain 3.8σ .

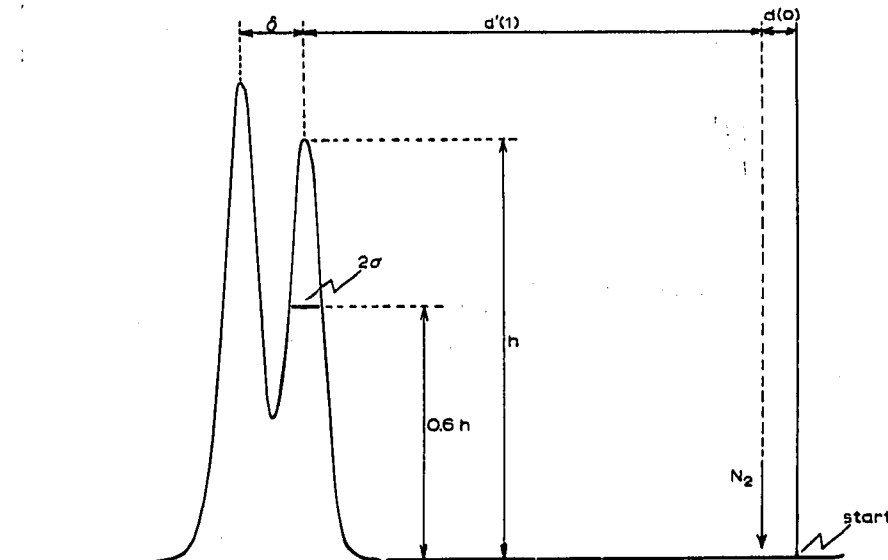


Fig. 6. Chromatogram of a mixture of *p*-cymene and β -pinene. 1 = β -pinene; 2 = *p*-cymene; $T_c = 190.1^\circ\text{C}$; $T_f = 25^\circ\text{C}$; $M = 1000\ \mu\text{g}$; $\dot{v}_c = 51.5\ \text{ml/min}$; column = pyrex glass; length = 240 cm; $\phi = 0.6$ cm. Celite-C: Apiezon-L = 65:35; $n = 930$. Detector: katharometer/tungsten filament. $\rho = d'(1)/d(0) = 13.0$; $N = \delta/\sigma = 3.8$.

(iv) Fig. 7 shows the chromatogram of the binary mixture of *p*-cymene and limonene. This mixture has been chromatographed in a stainless steel tube with apiezon-L as stationary phase. Under the experimental conditions indicated the plate number obtained was 35,000. For the difference 12 IU between the indices of the two components at 130° we calculate with $\rho = 0.7$ and $\Phi = 156$ a theoretical resolution of 5.7 ($n_{\text{eff}} = 5950$). The measured value of 5.0 is in good agreement with the calculated value.

(v) The same mixture as in example iv is separated by 41 IU [$I_{190}^P(\text{limonene}) = 1180$; $I_{190}^P(\text{p-cymene}) = 1221$] on the stationary phase emulphor-O (Fig. 8). The calculated separation is 6.8σ ($\rho = 6.9$; $\Phi = 199$) against the measured 6.7σ .

APPENDIX

The difference between the retention indices of two substances resolved by $N\sigma$

The uncorrected retention volume of the component (1) with the shorter retention time is by definition:

$$V_{R(1)}^\circ = V_{R(0)}^\circ + V_{N(1)} \quad (1)$$

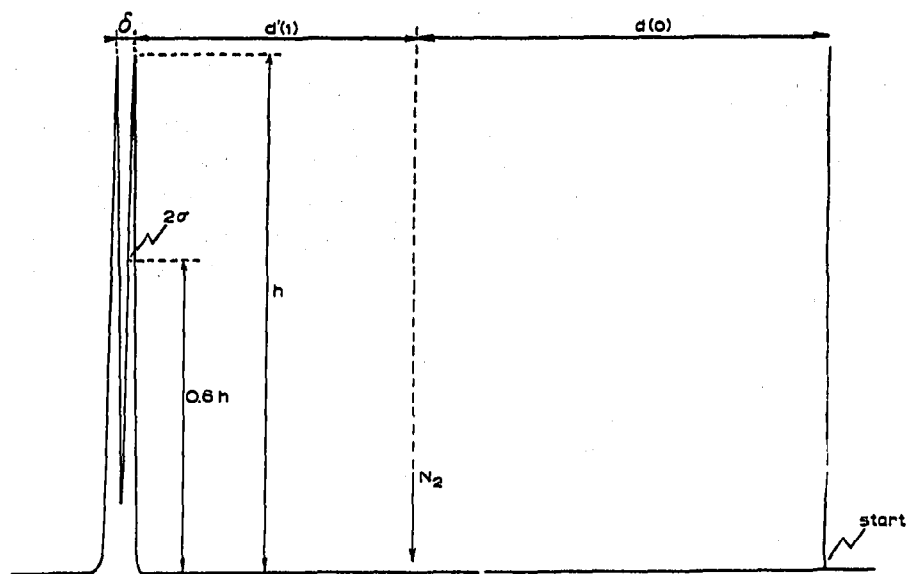


Fig. 7. Chromatogram of a mixture of *p*-cymene and limonene. 1 = *p*-cymene; 2 = limonene; $T_c = 130.7^\circ \text{C}$; $T_f = 25^\circ \text{C}$; $M \approx 100 \mu\text{g}$; $\dot{v}_c = 25 \text{ ml/min}$; column stainless steel tube: length = 10,000 cm; $\phi = 0.2 \text{ cm}$. SP: Apiezon-L, ca. 1 g; $n = 35,000$. Detector: katharometer/tungsten filament. $\rho = d'(1)/d(0) = 0.70$; $N = \delta/\sigma = 5.0$.

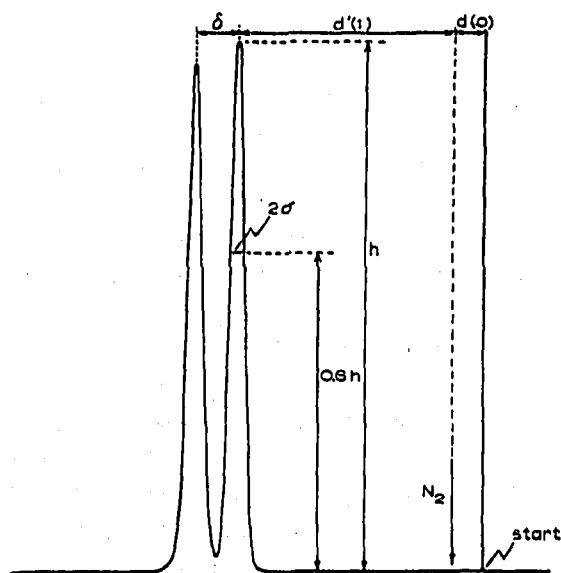


Fig. 8. Chromatogram of a mixture of limonene and *p*-cymene. 1 = limonene; 2 = *p*-cymene; $T_c = 190.2^\circ \text{C}$; $T_f = 25^\circ \text{C}$; $M \approx 700 \mu\text{g}$; $\dot{v}_c = 58.2 \text{ ml/min}$. Column = pyrex glass; length = 240 cm; $\phi = 0.6 \text{ cm}$. Celite-N: Emulphor-O = 65:35; $n = 1440$. Detector: katharometer/tungsten filament. $\rho = d'(1)/d(0) = 6.9$; $N = \delta/\sigma = 6.7$.

Supposing the elution curve is a Poisson distribution curve, we find for the inflexion points which are at $\pm \sigma$:

$$V^{\circ}_{\pm\sigma} = \pm \frac{1}{\sqrt{n}} [V^{\circ}_{R(0)} + V_{N(1)}] \quad (2)$$

For the retention volume of the component (2) which lies $N\sigma$ -units after the maximum of (1) we get:

$$V^{\circ}_{R(2)} = V^{\circ}_{R(1)} + N \cdot V^{\circ}_{+\sigma} = \left[1 + \frac{N}{\sqrt{n}} \right] [V^{\circ}_{R(0)} + V_{N(1)}] \quad (3)$$

For the net retention volume of (2), using the definition equation, we get:

$$V_{N(2)} = V_{N(1)} \left[1 + \frac{N}{\sqrt{n}} \left(\frac{\rho + 1}{\rho} \right) \right] \quad (4)$$

where:

$$\rho = V_{N(1)}/V^{\circ}_{R(0)} = d'_{R(1)}/d_{R(0)} \quad (5)$$

The function ρ is the relative retention of the substance (1) with respect to the gas-holdup; $d_{R(0)}$ is the retention distance of a substance which is insoluble in the stationary phase.

Putting:

$$zb_z = \log V_{N(P_z + 2)} - \log V_{N(P_z)} \quad (6)$$

we can write the definition-equation of the retention index in a simple form:

$$I(i) = \frac{100}{b_z} [\log V_{N(i)} - \log V_{N(P_z)}] + 100z \quad (7)$$

Thus for the substance (1) we can write:

$$I(1) = \frac{100}{b_z} [\log V_{N(1)} - \log V_{N(P_z)}] + 100z \quad (8)$$

In order to calculate the retention index of the substance (2) we substitute eqn. (4) into eqn. (6):

$$I(2) = \frac{100}{b_z} \left\{ \log \left[1 + \frac{N}{\sqrt{n}} \left(\frac{\rho + 1}{\rho} \right) \right] + \log V_{N(1)} - \log V_{N(P_z)} \right\} + 100z \quad (9)$$

Now we can calculate the difference δI defined as:

$$\delta I = I(2) - I(1) \quad (10)$$

by subtracting eqn. (8) from eqn. (9):

$$\delta I = \frac{100}{b_z} \log \left[1 + \frac{N}{\sqrt{n}} \left(\frac{\rho + 1}{\rho} \right) \right] \quad (11)$$

In practice n is a large number and hence:

$$\frac{N}{\sqrt{n}} \left(\frac{\rho + 1}{\rho} \right) \ll 1 \quad (12)$$

For this case the following equation is a good approximation for eqn. (11):

$$\delta I \approx \frac{100}{b_z} \cdot 0.4343 \frac{N}{\sqrt{n}} \left(\frac{\rho + 1}{\rho} \right) \quad (13)$$

The characterisation of a stationary phase with the aid of the function β

It is well known that the plot of the logarithm of the adjusted retention distance, $\log d'_R(P_z)$, of the normal paraffins (C_zH_{2z+2}) against z is a straight line.

This fact means that:

$$\log d'_R(P_{z+1}) - \log d'_R(P_z) = \log V_N(P_{z+1}) - \log V_N(P_z) = b_z \quad (14)$$

the term b_z thus being independent of z for the higher members of this homologous series. The best (mean) value for b we get from the regression equation:

$$\log d'_R(P_z) = a + b.z. \quad (15)$$

From this slope b we can calculate:

$$\beta = \frac{R \cdot T_c b}{0.4343} \text{ (cal)} \quad (16)$$

The function β is the increment for the free enthalpy of evaporation from the ideal dilute solution. This function varies linearly with the temperature in the temperature range in which a stationary phase is used for gas-chromatographic work. Thus we can express β by the following simple equation:

$$\beta = \beta_{400} + \frac{\partial \beta}{\partial T} (T - 400) \text{ (cal)} \quad (17)$$

that is we take 400° K (ca. 130° C) as standard temperature. The values $\beta_{400^\circ K}$ i.e. $\beta_{130^\circ C}$ and the temperature dependence $10(\partial\beta/\partial T)$ are listed in Table II for 6 stationary phases.

TABLE II

Stationary phase	$\beta_{130^\circ C}$ cal	$10 \frac{\partial \beta}{\partial T}$ cal/10°	Temperature interval °C
Apiezon-L	514.4	-1.25	110-230
Emulphor-O	469.1	-1.33	110-230
Didecyl phthalate ^a	583.8	-4.78	50-150
Di-ethylhexyl sebacate ^a	567.5	-7.50	50-150
Silicone DC-200 ^b	582.9	-2.57	50-150
Polyethylene glycol ^b	589.8	-6.89	50-150

The function β is characteristic for the stationary phase and is independent of column conditions except the temperature.

The difference δI expressed with the aid of β

The combination of eqn. (13) with eqn. (16) gives:

$$\delta I = 198.6 \frac{T_c}{\beta} \frac{N}{\sqrt{n}} \left(\frac{\rho + 1}{\rho} \right) \quad (18)$$

Putting

$$\Phi = 198.6 T_c/\beta \quad (19)$$

and substituting this in eqn. (18) we can write:

$$\delta I = N\Phi \frac{1}{\sqrt{n}} \left(\frac{\rho + 1}{\rho} \right) \quad (20)$$

It is sometimes useful to define a so-called effective number of theoretical plates as follows:

$$n_{\text{eff}} = n \left(\frac{\rho}{\rho + 1} \right)^2 \quad (21)$$

Thus eqn. (20) becomes simpler:

$$\delta I = N\Phi \frac{1}{\sqrt{n_{\text{eff}}}} \quad (22)$$

The function δI is a minimum under given experimental conditions if the retention times of the substances are very long, for in this case:

$$\delta I (\infty) = N\Phi \frac{1}{\sqrt{n}} \quad (23)$$

Substituting eqn. (23) into eqn. (20) we again get a simpler form:

$$\delta I = \delta I (\infty) \cdot \left(\frac{\rho + 1}{\rho} \right) \quad (24)$$

The necessary resolution of two components for analytical work

For the sake of the numerical calculation we replace the Poisson-curve by a Gaussian distribution function. Fig. 9 shows two methods for finding σ by construction. For the peak of substance (1) the intersection of the base line with the tangents gives 4σ . On the peak of the substance (2) the line between the inflexion points gives 2σ . The second method is based on the fact, that the inflexion points are at the height given by:

$$e^{-1/2} \approx 0.6 \quad (25)$$

Let us now suppose that we analyse the mixture by integrating the composite peak up to the point B which lies exactly midway between the two maxima. If we designate the distribution curves by $f(x,1)$ and $f(x,2)$, then we get the two areas:

$$F'(1) = \int_{-\infty}^B f(x,1)dx + \int_{-\infty}^B f(x,2)dx \quad (26a)$$

$$F'(2) = \int_B^{+\infty} f(x,1)dx + \int_B^{+\infty} f(x,2)dx \quad (26b)$$

Thus we calculate the apparent percentages:

$$p'(1) = 100 \frac{F'(1)}{F(1) + F(2)} ; p'(2) = 100 \frac{F'(2)}{F(1) + F(2)} \quad (27 a + b)$$

if we put for the integrals:

$$F(1) = \int_{-\infty}^{+\infty} f(x,1)dx \text{ and } F(2) = \int_{-\infty}^{+\infty} f(x,2)dx \quad (28 a + b)$$

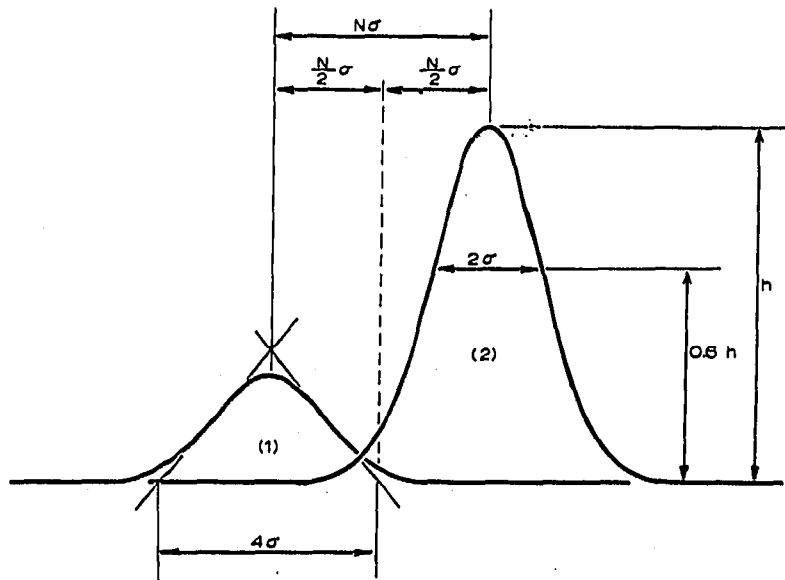


Fig. 9. Methods for finding σ by construction.

TABLE III

Subst. (x) % in the mixture	Perror									
	1 σ	2 σ	3 σ	4 σ	5 σ	6 σ	7 σ	8 σ	9 σ	10 σ
50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20	48.07	32.25	16.70	6.39	1.83	0.40	0.07	0.01	0.00	0.00
10	71.17	55.93	34.83	15.40	4.73	1.07	0.19	0.03	0.00	0.00
5	84.74	74.07	54.60	29.05	10.05	2.37	0.42	0.06	0.01	0.00
2	93.68	88.39	76.23	52.20	22.96	6.09	1.11	0.15	0.02	0.00
1	96.80	93.96	86.75	69.04	37.83	11.68	2.23	0.31	0.04	0.00
0.5	98.39	96.92	92.97	81.83	55.15	21.09	4.40	0.63	0.07	0.01
0.2	99.35	98.75	97.08	91.89	75.56	40.20	10.38	1.55	0.17	0.01
0.1	99.68	99.37	98.52	95.78	86.11	57.40	18.84	3.07	0.34	0.03
0.05	99.84	99.69	99.26	97.85	92.54	72.95	31.73	5.95	0.68	0.06
0.02	99.94	99.87	99.70	99.13	96.88	87.09	53.76	13.67	1.67	0.15
0.01	99.97	99.94	99.85	99.56	98.42	93.10	69.93	24.05	3.29	0.29

The true percentage of the substance (1) is:

$$p(1) = 100 \frac{F(1)}{F(1) + F(2)}$$

Let us take component (1) as the minor component. In this case the apparent percentage is always greater than the true percentage. We can now give the percentage error for the determination of the component (1) as follows:

$$p_{\text{error}} = 100 \left(1 - \frac{F(1)}{F'(1)} \right) \quad (29)$$

A 100% error means that the result for the substance (1) is caused completely by (2); a 0% error on the other hand means that the apparent percentage is equal to the true percentage. In Table III the values of p_{error} are listed for different resolutions and for different amounts (1) in the binary mixture.

The necessary resolution of two components for preparative work

The impurity in the minor component (1) can obviously be calculated for the same separation as defined in Fig. 9:

$$p_{\text{impurity}} = \frac{100}{F'(1)} \int_{-\infty}^B f(x,2) dx \quad (30)$$

This percentage is listed in Table IV for different resolutions and for different percentages of (1) in the binary mixture.

TABLE IV

Dist. (1) in the original mixture (%)	% Impurity (i.e. substance (2)) in the isolated substance (1)									
	1σ	2σ	3σ	4σ	5σ	6σ	7σ	8σ	9σ	10σ
0	30.854	15.866	6.681	2.275	0.6210	0.1350	0.02326	0.023167	0.023398	0.0242867
0.1	64.092	42.998	22.261	8.519	2.438	0.5378	0.09298	0.01267	0.021359	0.021147
0.2	80.064	62.925	39.184	17.322	5.324	1.202	0.2090	0.02850	0.023058	0.0232580
0.5	89.449	78.180	57.631	30.667	10.612	2.504	0.4402	0.06014	0.026455	0.025446
1	95.626	90.235	77.817	53.286	23.441	6.212	1.127	0.1550	0.01665	0.021405
1.5	97.786	94.916	87.635	69.740	38.218	11.803	2.252	0.3126	0.03363	0.022838
2	98.886	97.404	93.441	82.246	55.426	21.197	4.425	0.6263	0.06756	0.025704
3	99.553	98.948	97.277	92.074	75.716	40.281	10.403	1.556	0.1693	0.01430
4	99.776	99.472	98.621	95.877	86.192	57.454	18.861	3.067	0.3383	0.02863
5	99.888	99.735	99.306	97.896	92.588	72.988	31.747	5.954	0.6746	0.05726
6	99.955	99.894	99.721	99.148	96.898	87.109	53.772	13.669	1.6701	0.1431
7	99.978	99.947	99.860	99.572	98.425	93.111	69.939	24.052	3.2857	0.2858

SUMMARY

A method is given for the estimation of the difference between the retention indices of two substances necessary for an $N\sigma$ -resolution of their peaks.

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