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INFORMATION CONTENT OF MULTI-DIMENSIONAL SWITCHING SYSTEMS IN GAS CHROMATOGRAPHY

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SUMMARY

Information content, according to Shannon[24], is used for the optimization and classification of multi-dimensional switching systems (MDSS) in gas chromatography (GC). This criterion transfers the GC specifications into numbers of bits, and allows the appropriate choice of hardware, column efficiencies and polarities and the selection of MDSS modes.

The information content for different column configurations, such as packed–trap–capillary column, are compared with single-column systems. MDSS is found to be a GC system with a higher information content. This is ascribed to the switching possibilities of columns with different polarities.

INTRODUCTION

The task of an analysis is to provide the required amount of interpretable information at the best performance to cost ratio. From this follows the importance of specification of the required amount of information, interpretation of information and the most efficient instrumentation and experiment organization.

Problem specification is a process of selecting a few parameters such as the particular characteristics of an application. These parameters can be specified, for example, as uncertainty of peak identification (index window), duration of analysis and exceeding of the hazard limit. These heterogeneous characteristics (index unit, time, grams, etc.) must be transformed into a common denominator. This is an information content, $I(S)$[1,2], which permits us to penetrate into the essence of chromatography (and, in fact, all analytical methods), namely the obtaining of information[3].

In the process of transformation, the chosen characteristics are qualified in numbers of bits, and this is reflected in the required information content, $I(S)_{req}$, to solve the given problem.

In this context, analytical instrumentation becomes a tool by which the problem specifications can be reached. It means that the experimentally obtained information content, $I(S)_{exp}$, must be larger than the required information content (see Fig. 1). Thus, optimization in gas chromatography (GC) cannot be restricted to column

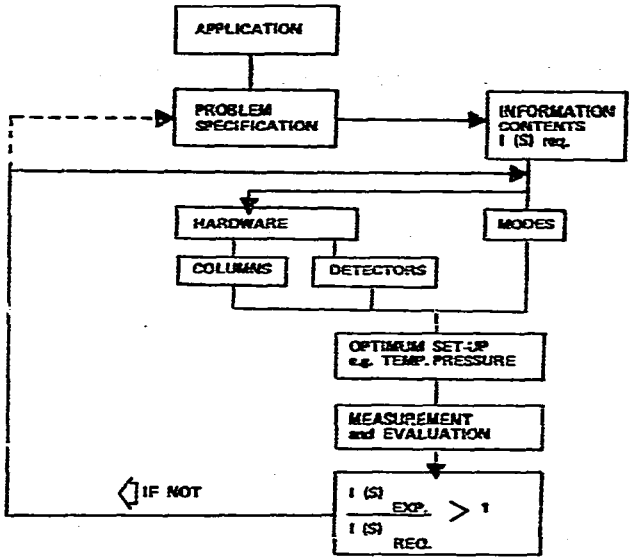


Fig. 1. Schematic diagram of problem-solving path for GC application.

performance optimization only, but should include the choice of stationary phase and detectors, working conditions, experiment organization, etc.

One can speak of a breakthrough in "GC technology" with the introduction of valveless multi-dimensional switching systems (MDSS)[4,5] for multi-dimensional GC (MDGC)[6]. The flexibility of such systems makes system optimization mandatory. The evaluation of the information power of GC systems is one of the possible means of such optimization.

In chromatography, information theory has been used for the selection of preferred liquid phases and their combination in thin-layer chromatography[7] and in gas–liquid chromatography[8–10] evaluating the distribution of retention indices and for hardware optimization of packed-packed MDSS[11].

This paper deals with the characterization of MDSS by means of information content, especially with columns in series.

EXPERIMENTAL

Experiments were carried out on Packard Model 429 gas chromatographs equipped with MDSS units as shown in Table I. Calculations were carried out on a PDP 8 computer.

RESULTS AND DISCUSSION

Multi-dimensional gas chromatography (MDGC) is a GC system (or generally a chromatographic system) in which the capacity ratio, k_i, for a given substance i is changed within the analysis. We can divide MDGC into a non-steady-state configuration with a programmable pressure and/or programmable temperature and a steady-state configuration with columns of different polarities.

TABLE I

HARDWARE CONFIGURATIONS AND AVAILABLE MODES FOR DIFFERENT COLUMN COMBINATIONS

P = packed column; C = capillary column; T = trap; for abbreviations of modes, see text.

	PP	*PC*	*PTC*	*CC*	*CTC*
Mode:					
SFL	×	×	×	×	×
XFR	×			×	×
MON	×	×	×	×	×
BFL	×	×	×	×	×
TRP			×		×
RJN			×		×
Detector:					
FID	××	××	××	××	××
TIDA	××	××	××	××	××
ECD	××	××	××	××	××
TCD	××	×	×		
Sample introduction	××	×	× RJN	×	× RJN
Splitter		After P via 1st detector	After P via 1st detector or after trap	After injection port	After injection port
Glass	××	××	××	××	××
Metal	××	××	××	××	××

An MDSS is a GC system (or generally a chromatographic system) in which the direction of sample flow is changed during the analysis. The "injection port–column–detector" sample flow path is the basic dimension. We can divide MDSS into the so-called injection port splitter and the end column splitter configurations, shown in Figs. 2 and 3.

For columns in series, we define the general MDSS modes as follows: solvent flush (SFL), transfer (XFR), monitoring (MON), back-flush (BFL), trapping (TRP) and re-injection (RJN). The order- and time-based combinations of MDSS modes form the MDSS programmes, such as heart-cut, multiple heart-cut and chopping.

The MDSS should fulfil a number of criteria. Firstly, it should increase the separation power of the GC system, using column combinations of either the same polarity (increase of column efficiency), or different polarities (selectivity of separation). Secondly, MDSS should improve the column performance and its lifetime. It should also improve detector performance, especially that of the selective detector, by excluding large amounts of solvent or unwanted compounds and high-boiling substances. The third task of the MDSS modes is to speed up the analysis and, in this way, to increase the performance to cost ratio.

Information content, $I(S)$, according to Shannon and Weaver[24], is defined as

$$I(S) = \sum_{k=1}^{m} p_k \operatorname{ld} p_k \tag{1}$$

where p_k is the probability of finding substance k in a total of m substances and ld is the dual logarithm.

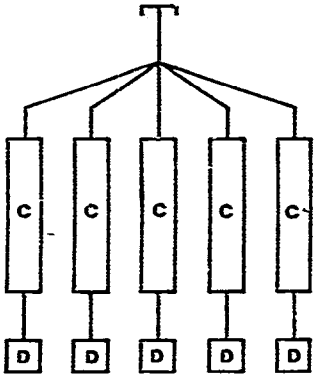


Fig. 2. Injection port splitter MDSS. C = column; D = detector.

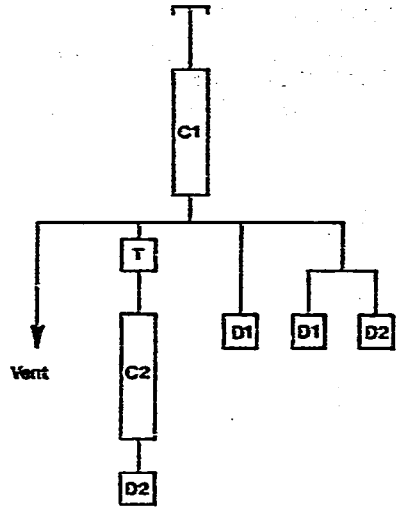


Fig. 3. End column splitter MDSS.

From the point of view of probability, optimization is related to the uncertainty that the eluted peak, k, can be identified in the group of m substances on the basis of retention indices. Thus, if we want to characterize one substance from a group of 100 substances between two neighbouring n-alkanes, we need a system with 100 separated peaks, and expressed in information content $I(S) = \mathrm{ld}\,(100/1) = 6.65$ bits. When the analytical problem is specified, for example the uncertainty of 10 retention index units, then analytical hardware with an information content of $I(S)_{\mathrm{req}} = \mathrm{ld}\,(100/10) = 3.3$ bits, must be used in order to solve the given task.

Generally, for the maximum value of the information content of GC columns (in each of the intervals only one substance will be present) we have

$$I(S) = \mathrm{ld}\left[\frac{1}{4}\left(\frac{A-1}{A}\right) n_{\mathrm{eff}}^{1/2}\right] \tag{2}$$

where A is a measure of column polarity[12,13] (see note below). Thus, using eqn. 2, the chromatographic system (column polarity and efficiency) is transferred to the probability of finding the component in the retention interval $100/[\frac{1}{4}\,(1 - 1/A)\, n_{\mathrm{eff}}^{1/2}]$.

Note

The resolution between two neighbouring n-alkanes having adjusted retention times t'_{R_n} and $t'_{R_{n-1}}$ and corresponding peak widths at half heights w_n and w_{n-1}, respectively, is

$$R = \frac{t'_{R_n} - t'_{R_{n-1}}}{w_n + w_{n-1}} = \frac{r_n - 1}{r_n} \cdot \frac{t'_{R_n}}{w_n + w_{n-1}} \tag{3}$$

where

$$r_n = \frac{t'_{R_n}}{t'_{R_{n-1}}} \tag{4}$$

It is assumed that the value of the relative retention, r_n, is constant. However, as we have shown in previous work[13], r_n changes, especially for small n, while the ratio of the time differences between neighbouring n-alkanes is constant. It holds that

$$\Delta_{n+1} = t'_{R_{n+1}} - t'_{R_n} \tag{5}$$

$$\Delta_n = t'_{R_n} - t'_{R_{n-1}} \tag{6}$$

$$A = \frac{\Delta_{n+1}}{\Delta_n} \tag{7}$$

Then the first term of eqn. 3 can be rewritten as

$$\frac{r_n - 1}{r_n} = \frac{r_{n+1} - 1}{A} \tag{8}$$

Therefore, we can expect that the value of the first term of eqn. 3, which is related to the polarity of the stationary phase, will be practically constant [it will decrease with increasing number of carbon atoms in the n-alkane chain and will be limited to the value of $(A - 1)/A$].

The second term of eqn. 3, $\frac{t'_{R_n}}{w_n + w_{n-1}}$, expresses the column efficiency.

We can discuss two limiting cases:

(a) the column is very good ($w_n \rightarrow w_{n-1}$); then the second term is

$$\frac{t'_{R_n}}{w_n + w_{n-1}} \approx 0.5\,(n_{eff}/8\ln 2)^{1/2}$$

(b) the column is rather poor ($w_n = 2w_{n-1}$); then the second term is

$$\frac{t'_{R_n}}{w_n + w_{n-1}} \approx 0.67\,(n_{eff}/8\ln 2)^{1/2}$$

A coefficient of 0.6 is found to be acceptable, introducing a maximum inaccuracy of $\pm 10\%$ for the total range of column efficiencies. Thus, eqn. 3 can be rewritten as

$$R \approx \frac{1}{4}\left(\frac{A-1}{A}\right) n_{eff}^{1/2} \tag{9}$$

The polarity of the stationary phase plays a very important role in MDSS techniques. From recent publications on liquid-phase optimization[3,8–10], it appears that the best separation system is formed by the combination of liquid phases with different separation characteristics such as different polarities. Let us assume that to solve the problem a resolution of 100 has to be reached. This means that the system has $I(S) = 6.65$ bits. Calculating the required column efficiency for a medium polarity column with $A = 2$, we find *ca.* 650,000 n_{eff} plates. It is clear that this will not be the way to solve the problem. A combination of columns with different polarities will be a better solution. The distribution of retention indices on the stationary phases is assumed to be normal, with a mean and estimated standard deviation (see Fig. 4). With increasing polarity of the stationary phase, the mean shifts to higher values of the retention indices and the estimated standard deviation of this distribution are higher[9]. When the polarity test mixture according to Rohrschneider[14] and McReynolds[15]

is used for demonstration, then the closest index difference between the substances of this mixture is 1 index unit on squalane, 3 index units on OV-17, 11 index units on Carbowax 20M and 17 index units on BCEF. For a constant pair of compounds (benzene–nitropropane), there is 1 index unit difference on squalane, 123 index units on OV-17, 249 index units on Carbowax 20M and 419 index units on BCEF. It can be seen that with increasing polarity of the stationary phase, we can use a system with a lower separation efficiency (smaller value of n_{eff}) to reach the same information content. Therefore, it is preferable to use column combinations to reach a large value of $I(S)_{exp}$, and thus reach the condition of eqn. 10.

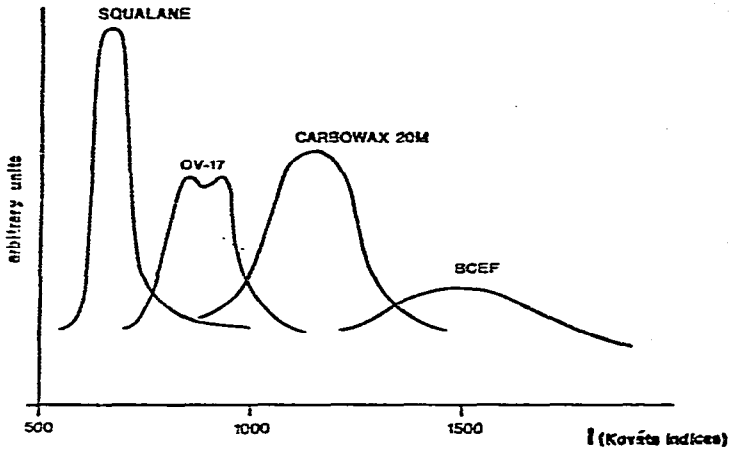


Fig. 4. Retention index distribution on selected stationary phases.

When MDSS techniques are applied in analysis, there is a multiple choice between efficiency and polarity of column systems within one analytical run. Thus, MDSS modes increase the information content of GC instrumentation (see below), and lead to systems with a high redundancy[16] expressed by the inequality

$$I(S)_{exp}/I(S)_{req} \geq 1 \tag{10}$$

MDSS solvent flush mode

This mode brings only an indirect improvement in column efficiency. In a one-column system there is normally an overload of solvent, causing a shift in k' values. Solvent flushing overcomes this problem. With the elimination of the solvent, the read-out quality, by either manual or electronic means, is improved. This phenomenon can be expressed in numbers of bits by the equation

$$I(S)_{SFL} = \mathrm{ld}\left(\frac{s_1}{s_2}\right) \tag{11}$$

where s_1 and s_2 are the estimated standard deviations of the read-out before and after the use of solvent flushing, respectively. When we expect the precision to be twice as good, then $I(S)_{SFL}$ will reach a value of 1 bit. One should take into account

the fact that the passage of a large amount of solvent through the stationary phase in a continuous run erodes the column. The use of solvent flushing therefore increases the lifetime of the column, and thus increases the information effectivity[17,18].

MDSS transfer mode

The mixture to be analysed is separated on the first and the second columns, with only one output (second detector). When the first column has an efficiency n_{eff_1} and a polarity A_1, the second column an efficiency n_{eff_2} and a polarity A_2, and the system has the index shift ΔI due to the different column polarities, the information content can be expressed by the equation

$$I(S)_{XFR} = \mathrm{ld}\,\frac{1}{4}\left\{n_{eff_1}\left(\frac{A_1 - 1}{A_1}\right)^2 + n_{eff_2}\left[\left(\frac{A_2 - 1}{A_2}\right)^2 + \left(\frac{\Delta I}{100}\right)^2\right]\right\}^{1/2} \tag{12}$$

Eqn. 12 demonstrates the influence of the index shift on the total information content. As demonstrated in Table II, the dominant factor in MDGC is related to increases in ΔI. When the polarities of columns 1 and 2 are the same, $A_1 = A_2$ and thus $\Delta I = 0$, and eqn. 12 becomes

$$I(S)_{XFR} = \mathrm{ld}\,\frac{1}{4}\left[\left(\frac{A - 1}{A}\right)^2 (n_{eff_1} + n_{eff_2})\right]^{1/2} \tag{13}$$

This demonstrates directly the small improvement in information content for columns of the same polarity with respect to the combination of columns of different polarities (Table III).

MDSS monitoring mode

The mixture to be analysed is separated on the first and the second columns. This system can be presented as a parallel column system with independent outputs, related to the first column and to the sum of the first and the second columns. With a first and a second column, having efficiencies n_{eff_1} and n_{eff_2} and polarities A_1 and A_2, respectively, the information content of this system is

$$I(S)_{MON} = \mathrm{ld}\,\frac{1}{4}\left[\left(\frac{A_1 - 1}{A_1}\right) n_{eff_1}^{1/2} + I(S)_{XFR}\right] \tag{14}$$

When there is no first detector, the information from the first output is zero and $I(S)_{MON} = I(S)_{XFR}$.

It can be seen that the monitoring mode significantly improves the information content of the MDSS system.

MDSS back-flush mode

After the separation of the required part of the sample, the remainder is "washed out" of the column by changing the direction of the carrier gas flow. This leads to a shortening of the analysis time, reconditioning of the column and also elimination of ghost peaks. Back-flushing does not change the column efficiency,

TABLE II

INFLUENCE OF COLUMN POLARITY ON INFORMATION CONTENT OF THE SYSTEM

Column efficiencies: $n_{eff_1} = 1000$, $n_{eff_2} = 5000$.

Column polarity		*Retention index shift*		
A_1	A_2	*100*	*200*	*300*
1.5	2.0	4.32	5.19	5.75
1.5	2.5	4.38	5.21	5.76
2.0	2.5	4.39	5.22	5.76
2.0	1.5	4.25	5.17	5.74
2.5	1.5	4.27	5.18	5.74

TABLE III

INFLUENCE OF COLUMN EFFICIENCY ON THE INFORMATION CONTENT OF THE SYSTEM

A = columns with the same polarity ($A = 2$); B = columns with different polarities, polar ($A = 1.5$) or apolar ($A = 2.5$); index shift $\Delta I = 200$.

Column efficiency, n_{eff} (plates)		*I (S)*		
Pre-column	*Analytical column*	*A*	*B*	*C**
1000	1000	2.48	4.06	4.96
1000	3000	2.98	4.84	5.28
1000	5000	3.28	5.21	5.50
1000	20,000	4.18	6.21	6.29
1000	60,000	4.98	7.00	7.03
1000	100,000	5.31	7.37	7.39

* Pre-column efficiency, $n_{eff} = 100{,}000$.

and therefore it does not contribute to the information content. However, because more analyses can be performed, it brings an improvement in the information effectivity.

MDSS trapping mode

This MDSS mode should be discussed from the point of view of qualitative and quantitative analysis. Qualitative analysis is related to peak identification: only a small uncertainty is allowed. This leads to a narrow index window and a high column efficiency, calling for a narrow starting peak width. Under this condition, the partly separated compounds are once again put together, and the separation process starts from the beginning. The trap thus neglects the information from the first column. An important question at this point is whether, in the absence of a trap, identification would be possible on the second column using retention indices.

When columns of the same polarity are used, the elution order is not changed and there is no need for trapping. When columns of different polarities are used, however, the only alternative to trapping is the heart-cutting programme.

The quantitative aspect of the analysis is related to the sensitivity of the detectors. If, in trace analysis, the amount of sample is very low, the trap can be used in the enrichment mode. Under these conditions, the total amount of part of a mixture can be trapped and quantitatively transferred to the second column.

MDSS re-injection mode

Trapped compounds are rapidly flushed from the trap and introduced on to the second column. The duration of re-injection contributes to the extra-column effects, and thus influences the column efficiency. Under the proper conditions the re-injection is comparable to standard injection methods. The information content of this mode is drawn from the second column only:

$$I(S)_{RIN} = \mathrm{ld}\,\frac{1}{4}\left[\left(\frac{A_2 - 1}{A_2}\right) n_{eff_2}^{1/2}\right] \tag{15}$$

Thus, in general, an increase in instrumentation costs and prolongation of the time of analysis with a simultaneous decrease of the information content lead to the decrease in information effectivity. However, when a broad cut is required, and heart-cutting cannot be used, a trap is necessary.

As demonstrated by eqns. 2 and 12–15, the information content of MDSS is determined by the polarity and the efficiency of the columns. From the column efficiency point of view, there are five configurations:

(a) packed-packed column MDSS;
(b) packed-capillary column MDSS;
(c) packed–trap–capillary column MDSS;
(d) capillary–capillary column MDSS;
(e) capillary–trap–capillary column MDSS.

These combinations of columns with different column efficiencies (n_{eff} from 1000 to 100,000 plates) are generally discussed from the viewpoint of the column polarity: (i) columns with the same stationary phase polarity; (ii) columns with different stationary phase polarities.

It follows from eqn. 13 that the information content of columns with the same polarity is rather low. To increase the information content by 2 bits, the step from packed column to capillary column must be made. We can say that this combination will be used mainly to protect the analytical column, increase the lifetime of the capillary column, improve the detector performance and speed up the analysis.

A combination of columns with different polarities dramatically improves the separation efficiency of the system: a shift of 2 bits can be realized (see eqn. 12). We can say that this combination should preferably be used for complicated analyses. The above-mentioned advantages of columns with the same polarity, such as protection of the analytical column, increased lifetime of the capillary column, improved detector performance and speeding up of the analysis, are also realized here.

Packed–packed column (PP) MDSS

This column combination is characterized schematically in Fig. 5. Either glass or metallic columns can be used with different detectors. The possibilities and available switching modes are summarized in Table I.

Columns with the same and/or different stationary phase polarities can be employed. Using columns with different polarities, short first columns (pre-columns) and/or narrow cuts should be used if identification is required. On the other hand, this column configuration has a great impact on all applications where separation by means of selectivity can be used in spite of the column efficiency. As shown above,

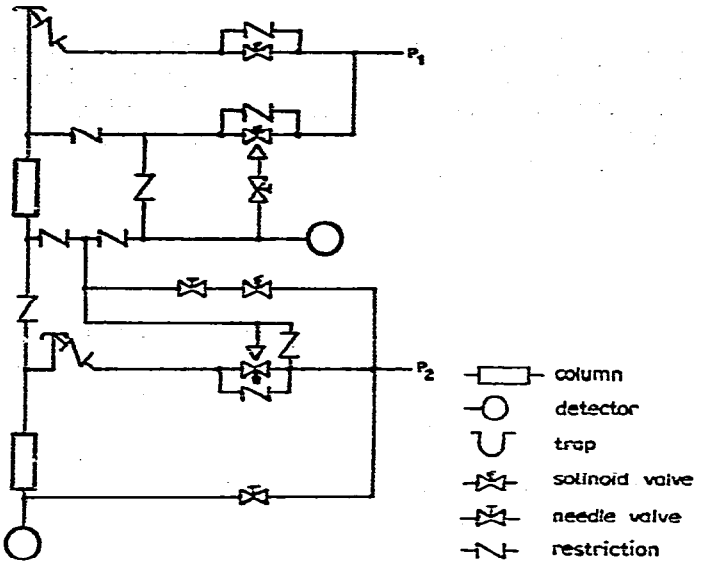


Fig. 5. Flow schematics of packed-packed column MDSS configuration.

the information content of two packed columns with different polarities, having 5000 plates, can exceed the information content of a capillary column with 100,000 plates (5.77 bits compared with 5.31 bits).

To separate the mixture specified in Table IV on a single column system for all compounds, high-efficiency columns should be used. For the separation of benzene and *n*-butanol on OV-17, the required information content is $I(S)_{req} = \text{ld}\,(100/2) = 5.6$ bits, which corresponds to a column with 150,000 plates. For the separation of *n*-decane and pentanone on Carbowax 20M, the required information content is $I(S)_{req} = \text{ld}\,(100/3) = 5.1$ bits. Using MDSS for separation, the pairs benzene–*n*-butanol and *n*-nonane–pyridine can easily be separated on Carbowax 20M and *n*-decane–pantanone on OV-17. Under these conditions, the closest peaks differ by 15 retention units, and the required information content is $I(S)_{req} = \text{ld}\,(100/15) = 2.7$ bits. Two short packed columns were used (OV-17 with 3600 plates for C_{10} and $A = 2.05$ and Carbowax 20M with 2700 plates for C_{10} and $A = 1.76$). Use of the

TABLE IV

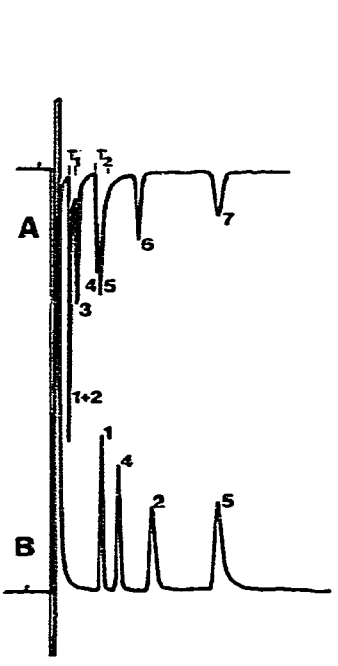
RETENTION INDICES FOR VARIOUS COMPOUNDS ON DIFFERENT STATIONARY PHASES

No.	*Compound*	*OV-17*	*Carbowax 20M*
1	Benzene	785	985
2	*n*-Butanol	787	1157
3	Pentanone	805	1003
4	*n*-Nonane	900	900
5	Pyridine	910	1230
6	*n*-Decane	1000	1000
7	*n*-Undecane	1100	1100

transfer mode results in 4.8 bits and the ratio $I(S)_{exp}/I(S)_{req} = 1.77$. The chromatogram is shown in Fig. 6.

Packed–capillary column (PC) MDSS

If the separation efficiency of packed columns is not sufficient for a particular analysis, capillary columns can be used. The flow diagram is shown in Fig. 7. Columns with the same and/or different polarities of the stationary phase can be used. As demonstrated in Table V, the information content of the system is improved by increasing the column efficiency and the combination of columns with different polarities results in systems with 2 bits more information than columns with the same polarity. It can be seen that the combination of a short pre-column (1000 plates) with a short capillary column (20,000 plates) with a small index shift (100 index units) is comparable to a single capillary column of 100,000 plates.



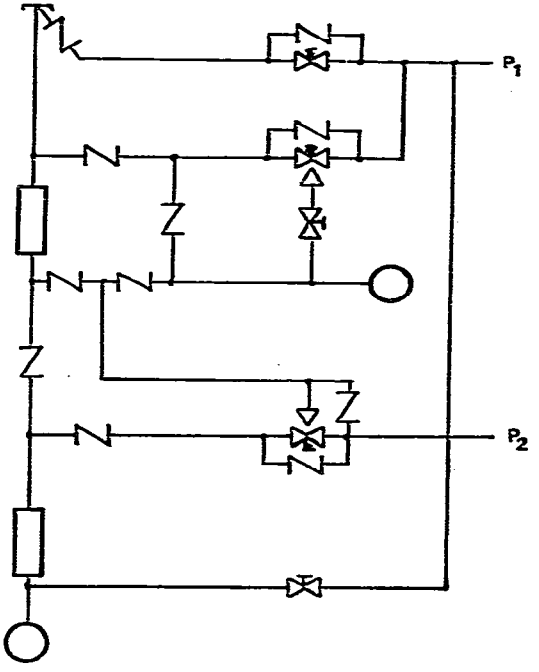


Fig. 6. Example of heart-cut mode. A, OV-17; B, Carbowax 20M. T_1 and T_2 = heart cutting intervals. For peak identification, see Table IV.

Fig. 7. Flow scheme for packed–capillary column MDSS configuration. For symbols, see Fig. 5.

Packed–trap–capillary column (PTV) MDSS

This configuration is characterized by the use of a trap (Fig. 8). As was mentioned under *MDSS trapping mode*, a trap is required for a broad cut. In addition, the trap can be used for enrichment of traces, thus making for better conditions for measurement. Enrichment is carried out with a cold trap and an open vent after the trap. Thus, the components of interest are held quantitatively in the trap and only the excess of carrier gas is vented. In the re-injection mode, the vent behind the trap

TABLE V

INFORMATION CONTENT, $I(S)$ FOR DIFFERENT MDSS COLUMN CONFIGURATIONS

For single column and $\Delta I = 0$, polarity $A = 2$. For columns with $\Delta I \neq 0$, 1st column $A = 1.5$, 2nd column $A = 2.5$. Bold figures: $I(S) > 5.31$ ($= I(S)$ capillary column).

Configuration	n_{eff}		ΔI			$I(S)$ *single column*
	1st column	*2nd column*	*0*	*100*	*300*	
PP	1000	1000	2.48	3.26	4.61	1.98
	5000	5000	3.64	4.42	**5.77**	3.14
PC	1000	20,000	4.18	**5.37**	**6.76**	
	5000	100,000	**5.34**	**6.53**	**7.92**	
PTC	1000	20,000	1.98 or 4.14	1.98 or 4.14	1.98 or 4.14	
	5000	100,000	3.14 or *5.31*	3.14 or *5.31*	3.14 or *5.31*	
CC	20,000	20,000	4.64	**5.42**	**6.77**	4.14
	100,000	100,000	**5.81**	**6.58**	**7.93**	*5.31*
CTC	20,000	20,000	4.14	4.14	4.14	
	100,000	100,000	*5.31*	*5.31*	*5.31*	

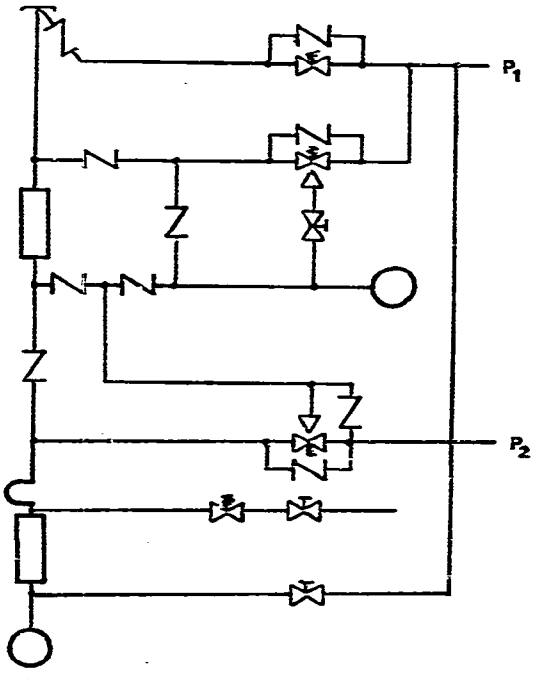


Fig. 8. Flow scheme for packed–trap–capillary column MDSS configuration. For symbols, see Fig. 5.

is closed. The trap is then heated and compounds are flushed out on to the capillary column with the flow required for capillary column operation.

Fig. 9 gives an example of the use of the trap in the enrichment mode to investigate the bleeding of rubber seats in solenoid valves, used in the gas supply system at 50°. In a 10-min trapping period, C_{18}, C_{19} and C_{20} compounds were introduced into the trap as internal standards from the packed column by heart-cutting. After 10 min, the trapped mixture with C_{18}, C_{19} and C_{20} compounds as standards was re-injected on to the capillary column. The resulting chromatogram shows the main part of the rubber bleed in front of C_{18}.

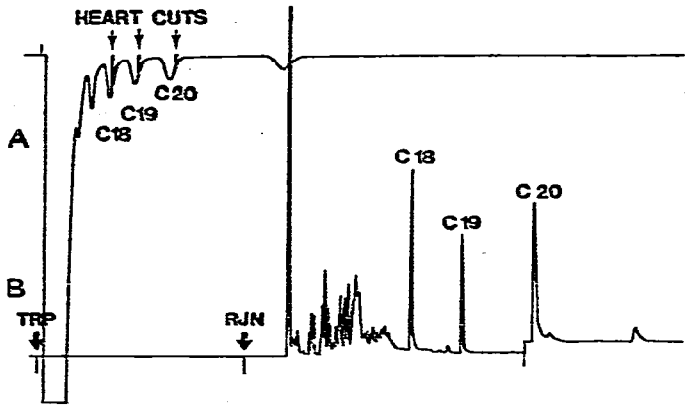


Fig. 9. Chromatogram of rubber bleed analysed with PTC MDSS configuration. A, 1-m 10% SE-30 on Chromosorb WHP (80–100 mesh); B, 25-m 0.25 mm I.D. SE-30. Oven temperature, 220°; two FIDs.

When using a trap in the system, we are decreasing the information content, $I(S)$, because we are neglecting the first column. The information content is equal to that of the second column only. The main performance criteria of the trap are that it should reach very high and very low temperatures in a short time interval, and that it should be chemically inactive.

Heating of the trap during the re-injection mode directly influences the column efficiency by means of the starting peak width. As was shown in previous work[19], the trap realized by a directly heated platinum capillary is the fastest system and is comparable to the standard injection technique. It was found that glass lined tubing is slower in the re-injection mode than a platinum capillary. Owing to the variable thickness of the glass layer, local overheating occurs, which can lead to "multiple injection". This phenomenon does not appear with platinum capillaries. Deterioration of trap performance was found when oxygen entered the carrier gas as an impurity (pressure regulators with a rubber membrane, unclean carrier gas, leakage). This is indicated by tailing of the peaks of polar substances (*n*-butanol, pentanone, pyridine). These changes are reversible when hydrogen is used as the carrier gas.

Capillary–capillary column (CC) MDSS

In this MDSS configuration two highly efficient columns can be used (see

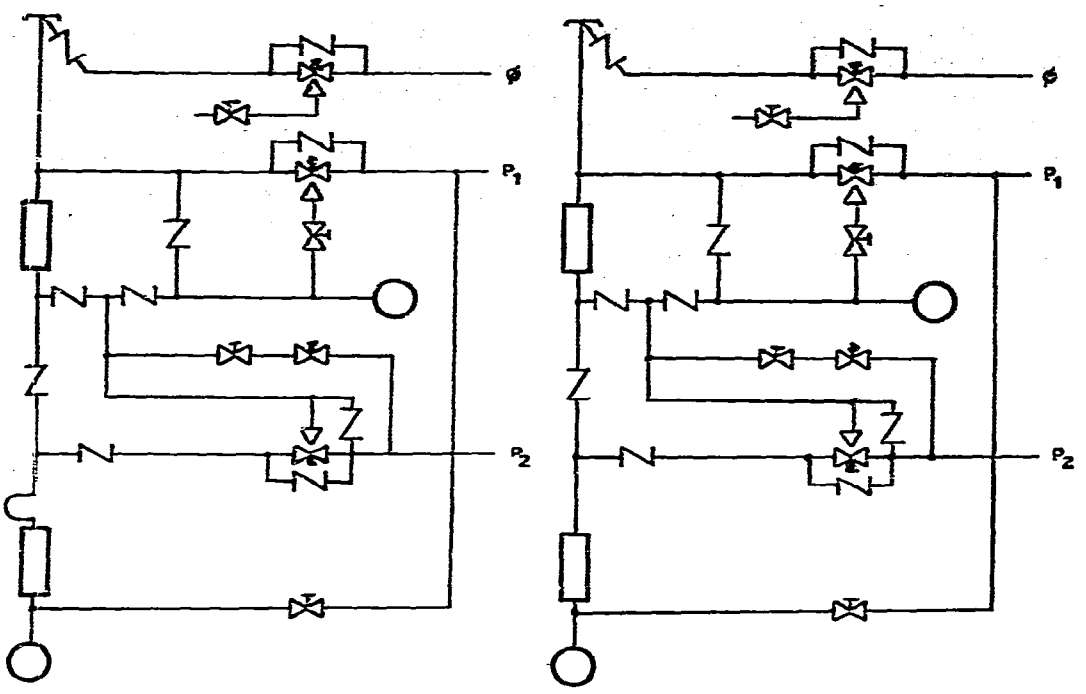


Fig. 10. Flow scheme for capillary–capillary column MDSS configuration. For symbols, see Fig. 5.

Fig. 11. Flow scheme for capillary–trap–capillary column MDSS configuration. For symbols, see Fig. 5.

Fig. 10). As follows from eqn. 13, there is no need to combine two capillary columns of the same polarity. A combination of columns of different polarities is limited to the narrow cut and/or multiple heart-cut programme. However, as shown in Table VI, for constant efficiency of the analytical column there is no improvement in the information content of the system with changing pre-column efficiency. We can say that, except for a pre-separation step, the CC configuration has no advantages over the PC configuration.

TABLE VI

INFLUENCE OF PRE-COLUMN EFFICIENCY ON INFORMATION CONTENT OF THE SYSTEM

Column order is polar ($A = 1.5$), apolar ($A = 2.5$); index shift $\Delta I = 200$.

Column efficiency, n_{eff} (plates)		*I(S)*
Pre-column	*Analytical column*	
1000	100,000	7.37
3000	100,000	7.37
5000	100,000	7.37
20,000	100,000	7.37
60,000	100,000	7.38
100,000	100,000	7.39

Capillary–trap–capillary column (CTC) MDSS

This configuration is shown schematically in Fig. 11. If it is not possible to use heart-cutting programmes, and the broad index interval from the first column should be transferred to the second column, a trap must be used. As already mentioned for the capillary–capillary column configuration, there is no advantage in using columns with the same polarity. Columns with different polarities, when used with a trap, reduce the information content of the transfer mode to the information content of the second column only, so that there is no difference between the PTC and CTC configurations (see Table V).

Using the CTC configuration in the monitoring mode, we can characterize the system as two parallel columns; only in this mode is the increase in the information content obvious. In comparing CTC to PTC we must stress the active role of the first column in CTC operation, and the protective role of the packed column in the PTC configuration. Further, the trap in the enrichment mode can be used in PTC, when no replicate injection in CTC is employed.

CONCLUSIONS

The MDSS, with its wide variety of configurations, requires objective classification. The information content, $I(S)$, was used as a criterion. The resulting number of bits relating to GC systems can be related to the requested information content for the solution of the analytical problem, and thereby the proper choice of hardware, column efficiencies and polarities can be made. It was shown that column polarity change has a large effect on the information content of the system (eqn. 12). It can be said that two packed columns with different polarities of the stationary phase can result in a more powerful separation system than single capillary columns (Table V). However, if the sample is formed from components with the same chemical structure, systems with high column efficiencies are required. If an apolar–polar column combination is used, then separation on an apolar column is dependent on boiling points; the additional separation on the polar column depends on specific interactions. Polar components are retarded during the separation on polar columns, but the separation of apolar compounds is not influenced. Thus, in the transfer mode on a polar column, columns in series are similar to columns with mixed stationary phases[20,21]. In the solvent flush mode, a column with a polarity A_1 is used, and in the re-injection mode the column has a polarity A_2. Identification by means of retention indices can be effected using pure and/or mixed stationary phases.

The first column in MDSS instrumentation should not produce broad peaks. The peak width of compounds eluted from the first column is the starting peak width for separation on the second column in the transfer mode. To make the best use of the second column, the peak width should be as small as possible. Thus, a relatively short column of good quality should be used as the first column.

The trap in the MDSS is the source of extra-column effects, but it is mandatory for the identification of an unknown mixture by means of retention indices. On the other hand, trapping in the enrichment mode and re-injection on to capillary columns offer the chance of analysing only traces in their original pattern on highly efficient columns.

As shown above, the monitoring mode is the most powerful mode of MDSS (see eqn. 14) when expressed in terms of information content.

It may be concluded that, using information content for hardware characterization and optimization, highly efficient systems can be selected that not only produce the required separation but also the required data[22,23].

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