Journal of Chromatography, 186 (1979) 145–158

CHROM. 12,062

COMPARISON BETWEEN CONVENTIONAL AND CROSS-CORRELATION GAS CHROMATOGRAPHY FOR EVOLVED GAS ANALYSIS

M. KALJURAND and E. KÜLLIK
Institute of Chemistry, Tallinn 200026 (U.S.S.R.)

SUMMARY

In polymer chemistry, it is often of interest to know what are the gases evolved during the degradation of polymers. Cross-correlation chromatography (CCC) permits on-line measurements of an arbitrary number of points on the evaluation rate curve for any evolved gas component, but the rapid changes in the composition of gases generate noise in the chromatograms calculated, which might exceed the detector signal. It is shown that by using a suitable computation algorithm it is possible to suppress the correlation noise in the calculated chromatograms. Computer-simulated patterns are presented to show the usefulness of CCC in evolved gas analysis and its advantages over conventional gas chromatography in this field.

INTRODUCTION

The use of computers in analytical chemistry has increased markedly in the last decade. Laboratory-scale digital computers are acquiring a major role in the design of laboratory instruments and several new computer-based analytical techniques have been developed. A typical example is Fourier transform spectroscopy, in which each resolution element is measured simultaneously, *i.e.*, the information or a signal channel is multiplexed, and a computer calculates the desired spectrum. In chromatography, this kind of experiment has been known since the first report of Izawa *et al.*[1] of the technique of cross-correlation chromatography (CCC). Although several examples of the application of the techniques are known[2–4], CCC has never been used extensively. Unless applications can be found that cannot conveniently be carried out by standard chromatographic methods, CCC will not be used substantially. Another reason for the limited use of CCC is, in our opinion, the fact that although the theory of the method is well established, its mathematical relationships are not simple to understand and deter workers who might otherwise be potential users.

The first part of this paper is therefore devoted to a simplified presentation of the theory. The cross-correlation theory usually formulated via a convolution integral[5] is here formulated via a circulant matrix. This approach seems to be more natural because computations in CCC are performed on a digital computer and con-

tinuous functions must be replaced with the sequence of numbers. Only an elementary knowledge of matrix algebra is assumed by the reader.

The second part of the paper deals with the accuracy of CCC. The baseline instability of the correlated chromatogram was discovered in previous experiments on CCC[6–8]. This phenomenon was explained as an effect of changes in sample concentration[7–8] during the experiment. Because these changes are frequently of interest (*e.g.*, in evolved gas analysis), the question arises of whether it is possible to detect accurately the changes in sample concentration in the presence of correlation noise. The problem of correlation noise is discussed here in a stricter form. It is shown that under some conditions "ghost" peaks may appear on the de-correlated chromatogram. We observed the "ghost" peaks during our first CCC experiments. It is interesting that "ghost" peaks were also observed in Hadamard transform spectroscopy[9], the mathematical basis of which is similar to that of CCC. The other distortions of the detector signal that are dealt with here are linear baseline drift in the original (not de-correlated) chromatogram and the effect of high-frequency noise. For each of these distortions we obtain an equation that determines the standard deviation of the noise on the de-correlated chromatogram.

The third part of the paper discusses a possible new application of CCC in evolved gas analysis. It is shown that CCC should be particularly valuable in this field and it has substantial advantages over conventional chromatography for analysing light gaseous products evolved during the thermal degradation of high-molecular-weight materials. Our first results[10] in this area were promising.

THEORETICAL

Experimental set-up in CCC

In contrast to the conventional technique in which a single amount of a sample is injected and the detector response recorded, in CCC a sample is injected sequentially during the experiment or is introduced continuously to the chromatograph. The injection sequence follows the pattern of a complicated (random) signal and the detector response is cross-correlated with the input signal to estimate the chromatogram. The injection component of the conventional chromatograph must be replaced with a multi-port valve (electric or pneumatic) that is controlled by a random signal generator. Necessary conditions are digital recording of the detector signal and the use of a digital computer to perform the computations.

Usually a pseudo-random binary sequence[5] (PRBS) generator is used in CCC. In principle other forms of input sequences could be used[4,11] but they are difficult to realize experimentally or the computation time increases markedly.

Relationship between input and output

Let us consider n injections of the sample with each injection performed after a time interval Δt. We shall denote the amount of sample at a moment of time i by X_i. Thus we obtain the following input sequence, repeated, say l times.

$$\underbrace{X_1,\ldots,X_n}_{1},\ \underbrace{X_1,\ldots,X_n}_{2},\ \underbrace{X_1,\ldots,X_n}_{3},\ \ldots,\ \underbrace{X_1,\ldots,X_n}_{l}$$

Let X_i be unity if a sample is introduced into the chromatograph and zero if the injection is a "blank".

Measuring the detector voltage at m points of time (after every Δt), we obtain the output sequence

$$Y_1, Y_2, \ldots, Y_i, \ldots, Y_n, \ldots, Y_{2n}, \ldots, Y_m$$

This sequence of numbers is fed to the computer for calculations. Because every injection X_i makes a contribution to generating the output voltage Y_j, we can write the following set of equations:

$$\begin{array}{lllllll}
Y_1 & = X_1H_1(1) & & & & & \\
Y_2 & = X_1H_2(1) & + X_2H_1(2) & & & & \\
Y_3 & = X_1H_3(1) & + X_2H_2(2) & + X_3H_1(3) & & & \\
\hline
Y_n & = X_1H_n(1) & + X_2H_{n-1}(2) & + X_3H_{n-2}(3) & + \ldots + X_{n-1}H_2(n-1) & + X_nH_1(n) & \\
Y_{n+1} & = X_1H_1(n+1) & + X_2H_n(2) & + X_3H_{n-1}(3) & + \ldots + X_{n-1}H_3(n-1) & + X_nH_2(n) & \\
\hline
Y_{m-1} & = & & & + X_{n-1}H_n(ln-1) & + X_nH_{n-1}(ln) & \\
Y_m & = & & & & + X_nH_n(ln) &
\end{array} \tag{1}$$

Here $H_j(i)$ is the jth element of the chromatogram corresponding to input X_i.

The desired result of computation is a set of chromatograms describing the changes in sample composition during the experiment (*e.g.*, the chromatograms may describe the changes in the composition of the evolved gases during the heating of high-molecular-weight material).

Eqn. 1 is simpler in matrix notation. Recalling the definition of the matrix product, we obtain

$$\hat{Y} = \hat{X}\hat{H} \tag{1a}$$

where $\hat{X}$ is known as a circulant matrix[12]. A circulant matrix is one for which each row may be obtained from the preceding row by shifting the elements one position to the right (left), and the element at the end (beginning) of a row is moved to the beginning (end) of the next row:

$$\hat{X} = \begin{bmatrix} X_1X_nX_{n-1} & \ldots X_2 \\ X_2X_1X_n & \ldots X_3 \\ \hline X_nX_{n-1}X_{n-2} & \ldots X_1 \end{bmatrix}$$

$$\hat{H} = \begin{bmatrix}
H_1(1) & H_1(2) & H_1(3) & \ldots H_1(n) & \ldots\ldots H_1(ln) & 0 & \ldots 0 \\
0 & H_2(1) & H_2(2) & \ldots H_2(n-1) & \ldots\ldots H_2(ln-1) & H_2(ln) & \ldots 0 \\
0 & 0 & H_3(1) & \ldots H_3(n-2) & \ldots\ldots H_3(ln-2) & H_3(ln-1) & \ldots 0 \\
\hline
0 & 0 & 0 & \ldots H_n(1) & \ldots\ldots H_n(ln-n+1) & H_n(ln-n+2) & \ldots H_n(ln)
\end{bmatrix}$$

The problem with the output matrix $\hat{Y}$ is more complicated because only the entries that fall along main diagonals of the $\hat{Y}$ (spaced at intervals n) are

measurable and the non-diagonal entries must be properly estimated. Hence the measurable elements in $\hat{Y}$ are in the following positions in the matrix:

$$\hat{Y} = \left[\begin{array}{cccccc} Y_1 & \ldots\ldots & Y_{n+1} & \ldots\ldots & Y_{ln+1} & \ldots\ldots\ 0 \\ 0 & Y_2 & \ldots\ldots & Y_{n+2} & \ldots\ldots & Y_{ln+2}\ \ldots\ 0 \\ \hline 0 & 0 \ldots & Y_n & \ldots\ldots & Y_{2n} & \ldots\ldots\ 0 \end{array}\right] \tag{2}$$

It has been shown that an element in row i could be estimated by polynomal interpolation[13]. The polynomal passes through a set of entries Y_i, Y_{i+n}, Y_{i+2n} ,... according to the degree of the polynomial. A proof of this is given in the appendix. Although the degree of the polynomial depends on the values of Y_i, only low orders (up to second) are acceptable. Strictly, up to now only the zeroth degree of polynomials has been used in CCC and this is equiavlent to the assumption that no changes take place in the sample composition during the CCC experiment.

Hence, using linear interpolation for entries in row i between Y_i and Y_{i+n}, we get

$$Y_{i,l} = (Y_{i+n} - Y_i)\frac{l-i}{n} + Y_i \quad i < l < i+n \tag{3}$$

Sometimes it is difficult to introduce a sample into the chromatograph at the same frequency that the detector output is measured. Let us assume that there is a difference in time $k\Delta t$ between every injection. It is easy to show that by using suitable permutations of rows and columns $\hat{X}$, it converts into a block diagonal form. On the diagonals of k, non-zero blocks of the order of n/k are situated. Non-diagonal blocks are zero matrices.

Solution of equation 1

If the actual length of the chromatogram is longer than $n\Delta t$, the end part of the chromatogram starting at point $n+1$ overlaps with the start of the chromatogram. This statement results directly from eqn. 1.

It is well known that $\hat{H}$ should always be found from eqn. 1a if the inverse matrix $\hat{X}^{-1}$ exists, but common methods for the solution of eqn. 1 are too lengthy for more than 50–60 points even for a high-speed digital computer. Using Fourier transformation, eqn. 1a can easily be inverted[4] but if a special form of sampling regime is used, the resolution of eqn. 1a is greatly simplified. Several workers have therefore used a technique in which the sampling regime is determined by the PRBS. The PRBS has two elements, $+1$ and -1.

Many interesting and useful properties of the PRBS are described in the literature. The possible number of members in the PRBS is 2^p-1, where p is any integer and the pattern of $+1$ and -1 is a sequence such as to give an autocorrelation function resembling that of the white noise. This means that if we form an $n \times n$ circulant matrix, $\hat{U}$, where the first row is a PRBS, the following equations hold:

$$\begin{aligned} \hat{U}\hat{U}^T &= (n+1)\hat{I} - \hat{T} \\ \hat{U}\hat{T} &= \hat{T}\hat{U} = \hat{U}^T T = \hat{T}\hat{U}^T = \hat{T} \\ \hat{T}^2 &= n\hat{T} \end{aligned} \tag{4}$$

where $\hat{T}$ is a matrix full of $+1-s$, $\hat{I}$ is a unity matrix and the superscript ^{T} indicates transpose. The generation of PRBSs is not trivial and for more details about PRBS we refer to Annino and Grushka[5]. Some examples of PRBS are as follows:

$n = 3$ PRBS $= \{1, 1, -1\}$
$n = 7$ PRBS $= \{1, 1, 1, -1, 1, -1, -1\}$

Choosing $n = 2^p - 1$ in eqn. 1, we can perform injections X_i according to the PRBS, *e.g.*, if the corresponding ith member of the PRBS is 1, we inject a sample ($X_i = 1$), and when it is -1, we do not inject the sample ($X_i = 0$). Thus, using the PRBS as an injection rule, we can rewrite eqn. 1a as follows:

$$\hat{Y} = \tfrac{1}{2}(\hat{U} + \hat{T})\hat{H} \tag{5}$$

Using eqn. 4 we can obtain $\hat{H}$:

$$\hat{H} = \frac{2}{(n+1)} \cdot \hat{U}^T\hat{Y} \tag{6}$$

It should be pointed out that entries of the digital chromatograms $H_j(i)$ fall on diagonals of $\hat{H}$, but not on the columns of $\hat{H}$. A similar equation was first given by Laurgeau and Espiau[14], although in practical computation it is more convenient to calculate $\hat{H}$ by Hadamard transform[15,16]. While eqn. 6 requires n^2 additions and subtractions, the Hadamard transform is a "fast" transform with $n \log_2 n$ additions and subtractions and so the result should be obtained more quickly. For the real number of points in CCC, *e.g.*, 1024, the ratio $n^2/n\log_2 n$ is more than two orders of magnitude.

CORRELATION NOISE

As was pointed out in the introduction, several kinds of distortions of the chromatogram appear in CCC. According to Annino and Bullock[7], we should call them the correlation noise because this noise is not a real physical noise but is generated during the computation process as a result of non-ideality of the output sequence $\hat{Y}$ or the input sequence $\hat{X}$.

Non-reproducibility of injections

If there is a variation in the amounts of samples injected into the chromatograph during the cross-correlation experiment, the corresponding elements of the input sequence will differ from unity. Let the difference between the mean value of the amounts of the samples injected and the ith injection be E_i ($E_i < 1$). For example, when $n = 7$, we obtain the following input sequence: $1 + E_1$, $1 + E_2$, $1 + E_3$, 0, $1 + E_2$, 0, 0. For this case we may assume that all the chromatograms $H(i)$, $i = 1$, 2, ..., are identical and fall on the columns of $\hat{H}$. Now, for a particular chromatogram $\hat{H}(i)$, eqn. 5 is replaced by

$$\hat{Y} = \left(\frac{\hat{U} + \hat{T}}{2} + \hat{E}\right)\hat{H} \tag{7}$$

Here $\hat{E}$ is a circulant matrix with the element E_l. According to the above theory, we obtain the resolution of eqn. 7 as follows:

$$\frac{2}{(n+1)} \cdot \hat{U}^T\hat{Y} = \hat{H} + \frac{2}{n+1} \cdot \hat{U}^T\hat{E}\hat{H} \tag{8}$$

The second term of the right-hand side of eqn. 8 describes the deviation $\Delta\hat{H}$ from the "pure" signal $\hat{H}$:

$$\Delta\hat{H} = \frac{2}{n+1} \cdot \hat{U}^T\hat{E}\hat{H} \tag{9}$$

As the product of two circulant matrixes is another circulant matrix[17], the conclusion is that eqn. 9 coincides with eqn. 1a, *i.e.*, the matrix equation with a circulant matrix According to the construction of eqn. 1a, we should conclude that $\Delta\hat{H}$ appears as a superposition of chromatograms the shape of which is the same as the $\hat{H}$ but with intensities that are different and determined by several combinations of sums of the E_l. These "ghost" chromatograms are shifted cyclically from the origin. When $\hat{H}$ is a single peak, we can follow the emergence of "ghost" peaks when the points of injections–non-injections are separated by k points. The number of the "ghosts" is n and a distance between two "ghosts" is k points. When $\hat{H}$ is more complicated, baseline instability appears on the chromatogram. This may disturb the result of the analysis when E_l are not small enough in comparison with unity.

The variance of the noise on the chromatogram can easily be computed. As the mean of the $\Delta\hat{H}$ is $\Delta\bar{H}$,

$$\Delta\bar{H} = \frac{1}{n}\sum_{l=1}^{n}\Delta\hat{H}_l = \frac{2}{n(n+1)}\sum_{l,k=1}^{n}(\hat{U}^T\hat{E})_{lk}\hat{H}_k$$

$$= \frac{2}{n(n+1)}\sum_{k=1}^{n}H_k\sum_{l=1}^{n}E_{lk}\sum_{l=1}^{n}U_{ll}^T$$

and because

$$\sum_{l=1}^{n}U_{ll}^T = 1 \quad \text{and} \quad \sum_{l}^{n}E_{lk} = 0$$

it follows that

$$\Delta\bar{H} = 0$$

Now, the variance $s_{\Delta H}^{(E)^2}$ is

$$s_{\Delta H}^{(E)^2} = \frac{1}{n-1}\sum_{l=1}^{n}(\Delta H_l - \Delta\bar{H})^2 = \frac{1}{n-1} \cdot \Delta\hat{H}^T\Delta\hat{H}$$

and from eqn. 9 we obtain

$$s_{\Delta H}^{(E)2} = \frac{1}{(n-1)} \cdot \frac{4}{(n+1)^2} (\hat{H}^T \hat{E}^T \hat{U})(\hat{U}^T \hat{E}^T \hat{H})$$

$$= \frac{1}{(n-1)} \cdot \frac{4}{(n+1)} \cdot \hat{H}^T \hat{E}^T \hat{E} \hat{H} - \frac{1}{(n-1)(n+1)} \cdot \hat{H}^T \hat{E}^T \hat{T} \hat{E} \hat{H}$$

and for large n, assuming that the standard deviation of E_i is s_E

$$\hat{E}^T \hat{E} \approx \frac{n}{2} \cdot s_E^2 \hat{I}$$

and, because $\hat{E}^T \hat{T} \hat{E} = (\Delta E_i)^2 = 0$, we finally obtain for the standard deviation $s_{\Delta H}^{(E)}$

$$s_{\Delta H}^{(E)} = \sqrt{\frac{2\hat{H}^T \hat{H}}{n+1}} \cdot s_E \tag{10}$$

The process of non-reproducibility of the injections was simulated on the computer. Using a random number generator, the areas of the peaks were perturbed and the resulting cross-correlation functions were calculated. The results are presented in Figs. 1 and 2. It is evident from Fig. 2 that the relationship between $s_{\Delta H}^{(E)}$ and s_E is linear according to eqn. 10.

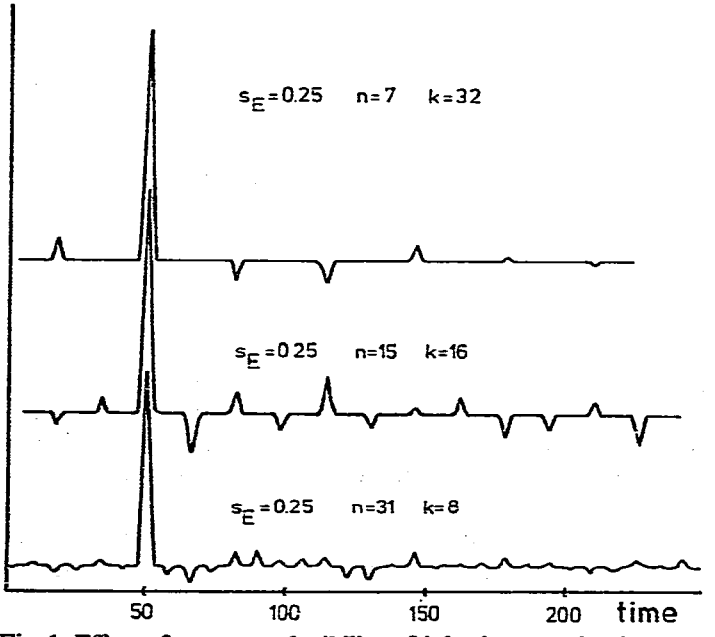


Fig. 1. Effect of non-reproducibility of injections on the de-correlated chromatogram. The "ideal" chromatogram consists of the single gaussian peak at 50 units of time.

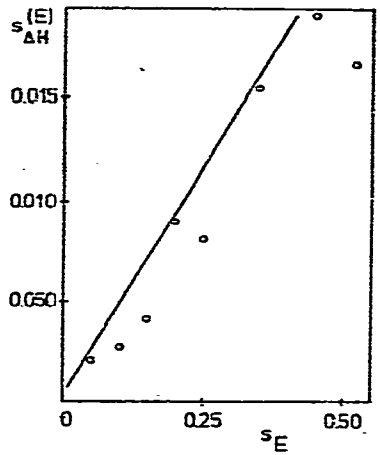


Fig. 2. Dependence of the standard deviation, $s_{\Delta H}^{(E)}$, of the noise on the de-correlated chromatogram on the mean square error of the injected samples, $n = 127$, $k = 2$. Solid line, theoretical value.

Detector noise

In discussing the detector electronics noise, we can present eqn. 5 as follows:

$$\hat{H} = \frac{2}{(n+1)} \cdot \hat{U}^T(\hat{Y} + \hat{R})$$

where $\hat{R}$ is a vector the elements of which are random numbers R_i. A deviation from the "pure" signal $\Delta\hat{H}$ appears as follows:

$$\Delta\hat{H} = \frac{2}{(n+1)} \cdot \hat{U}^T\hat{R} \tag{11}$$

Assuming that the mean of the R_is is zero, and the standard deviation is s_R, we obtain the result that the mean of $\Delta\hat{H}$ is also zero and the standard deviation of $\Delta\hat{H}$ is

$$s_{\Delta H}^{(R)} = \sqrt{\frac{\Delta\hat{H}\Delta\hat{H}}{n-1}} = \frac{2}{\sqrt{n}} \cdot s_R \tag{12}$$

Eqn. 12 is well known in multiplex spectroscopy and in ensemble averaging experiments. The validity of eqn. 12 in CCC was shown in numerical simulation experiments[15] and attenuation of the noise was also obtained in real experiments[2,3]. Recently, Lub *et al.*[18] reduced the detection limit by a factor of 100 in correlation high-performance liquid chromatography.

When $\hat{R}$ is a single spike of detector voltage (a frequent phenomenon when measuring at extreme sensitivity on the detector signal), it should be regarded as follows:

$$R = (0, 0, \ldots, r, \ldots, 0)$$

where r is the spike hight. The noise is determined by eqn. 11 and it is easy to calculate the standard deviation for this case:

$$s_{\Delta H}^{(R)} = \frac{2}{n} \cdot r \tag{12a}$$

When r is large, considerable distortion of the signal appears on the calculated chromatogram.

Linear drift of the detector baseline

A vector of the linear drift of the detector baseline can be expressed as follows:

$$L_k = Sk \qquad k = 1, 2, 3, \ldots, n$$

where S is the slope. Now, from eqn. 11

$$\Delta\hat{H} = \frac{2S}{(n+1)} \cdot \hat{U}^T L$$

An analytical expression is available for the variance of $\Delta\hat{H}$:

$$\begin{aligned} s_{\Delta H}^{(L)2} &= \frac{1}{(n-1)} [\Delta\hat{H}^T \Delta\hat{H} - n(\Delta\bar{H})^2] \\ &= \frac{1}{n-1} \left[\frac{4S^2}{(n+1)^2} \cdot L^T U U^T L - \frac{4S^2 n}{n^2(n+1)^2} \left(\sum_{k,i=1}^{n} U_{ik}^T L_k\right)^2\right] \\ &= \frac{1}{(n-1)} \frac{4S^2}{(n+1)^2} \left[\frac{(n+1)(2n+1)n(n+1)}{6} - \frac{n^2(n+1)^2}{4} \right. \\ &\quad \left. - \frac{n}{n^2} \cdot \frac{(n+1)^2 n^2}{4}\right] \end{aligned}$$

Neglecting small terms we finally obtain for the standard deviation

$$s_{\Delta H}^{(L)} = S\sqrt{\frac{n}{3}} \tag{13}$$

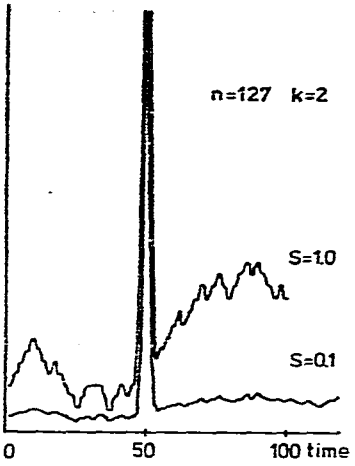
Eqn. 13 was tested by numerical computer simulation and the results are presented in Figs. 3 and 4.

Note

The derivation of eqns. 10, 12 and 13 is more complicated and formulae are different if there is a difference in time $k\Delta t$ after each injection, *i.e.*, the elements in PRBS are separated by k zeros, but the overall consequences remain.

E.g., if $k = 2$ then

$$s_{\Delta H}^{(E)} = \sqrt{\frac{H^T H}{n+1}} \cdot s_E \quad \text{and} \quad s_{\Delta H}^{(L)} = 2S\sqrt{\frac{n}{3}}$$



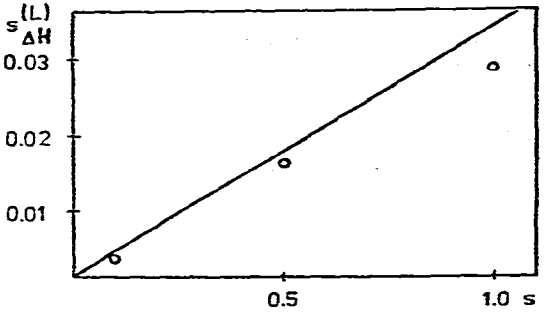


Fig. 3. Effect of baseline drift of the detector signal on the de-correlated chromatogram.

Fig. 4. Dependence of the standard deviation, $s^{(L)}_{\Delta H}$, of the noise on the de-correlated chromatogram on the slope of the baseline drift, $n = 127$, $k = 2$. Solid line, theoretical value.

Changes in sample composition

As was pointed out in the introduction, this case is of most interest in our study. Correlation noise caused by sample concentration changes may be dealt with in two ways. If a chromatogram has one peak, then the changes in the sample concentration should be regarded as a non-ideality of injections, but now E_i is not a random variable in eqn. 7. The results of the digital simulation study and real experiments show that the standard deviation of the correlation noise, $s^{(P)}_{\Delta H}$, depends linearly on the value of the change, *i.e.*

$$s^{(P)}_{\Delta H} = a\Delta P \tag{14}$$

where ΔP is a difference between the maximal and minimal values of the sample concentration during one PRBS and $a \approx 1.4$ for $n = 31$ and a zeroth-order polynomial approximation of non-diagonal elements in $\hat{Y}$ is used. As is concluded from eqn. 14, the value of the correlation noise may be considerable.

Although if the linear approximation for the non-diagonal elements in $\hat{Y}$ is applied, the power of the correlation noise attenuates considerably. The value of the attenuation depends on the function approximated and for the linear change in the sample composition, $s^{(P)}_{\Delta H} = 0$, theoretically.

In general, if there is more than one peak on the chromatogram, the problem should be regarded as an inadequate estimation of $\hat{Y}$. Let ΔY be the error matrix of the estimation of non-diagonal elements. Then

$$\hat{H} = \frac{2}{n+1} \cdot \hat{U}^T(\hat{Y} + \Delta\hat{Y})$$

and

$$\Delta\hat{H} = \frac{2}{n+1} \cdot \hat{U}^T \Delta\hat{Y} \tag{15}$$

The standard deviation of ΔH (along an arbitrary column) is similar to eqn. 12:

$$s_{\Delta H}^{(\Delta Y)} = \frac{2}{\sqrt{n}} \cdot s_{\Delta Y} \tag{16}$$

where $s_{\Delta H}^{(\Delta Y)}$ is the standard deviation of ΔY along the same column. Although eqn. 16 does not give the standard deviation of the noise for a particular chromatogram, it gives a good idea of the expected value of the noise in the chromatograms. From eqns. 15 and 16, it follows that the better the estimation of non-diagonal elements of $\hat{Y}$ the lower is the correlation noise level. In the next section it is shown that if the chromatogram length is about 0.25–0.5 of the half-width of the evolved gas analysis (EGA) curve (approximated by some common function), the linear estimation according to eqn. 3 is good.

COMPARISON BETWEEN CONVENTIONAL CHROMATOGRAPHY AND CCC

Usually EGA curves are used to obtain the kinetic constants of the thermal degradation of polymers according to the common equation for the gas evolution rate known from thermogravimetry:

$$\frac{dx}{dT} = \frac{A}{b} \cdot e^{-\frac{E}{RT}} (1 - x)^n$$

where

$$x = \frac{W_i - W}{W_i - W_f}$$

is a normalized amount of gas evolved at a temperature T, W_i the initial sample weight, W_f the final sample weight, W the instantaneous weight of the sample, b the rate of heating and A, E and n the kinetic constants of the process, *viz.*, frequency factor, energy of the activation and reaction order, respectively. Conventional methods for computing the kinetic constants requires precise measurement and recording of the area under the EGA curve.

Sampling the gases evolved during the thermal degradation of high polymers into the chromatograph and measuring peak areas is a possible means of obtaining EGA curves. Usually these curves have peak-like features. The problem is to establish how many samples one must take in order to recover an EGA peak exactly.

According to the Nyquist theorem, the number of samples was computed for common peaks[19,20]. The results are given in Table I. The number of samples depends on the standard deviation of the detector noise.

TABLE I

NUMBER OF SAMPLES REQUIRED ON SOME COMMON PEAKS[19,20]

Function	*Equation*	*Standard deviation of noise (in peak maximum units)*		
		0.1%	*1%*	*10%*
Triangular	$y(t) = 1 - \lvert t\rvert, \lvert t\rvert < 1$ $0, \quad \lvert t\rvert > 1$	360	40	6
Exponential	$y(t) = e^{-\lvert t\rvert}$	4500	330	20
Gaussian	$y(t) = e^{-t^2}$	9	7	4

An analytical expression for the EGA curve is not available if the sample temperature is linearrly programmed, but to a rough approximation it is more "exponential" than "gaussian", *i.e.*, it requires a large number of points for an exact recovery.

In order to compare conventional chromatography with CCC in terms of possibility of recovering EGA curves, the process of CCC was simulated on the computer. A chromatogram was considered to have one peak and the height of the peak to change according to the functions listed in Table I. The results of the simulation are presented in Fig. 5. A solid line represents the theoretical function and the points are the results of digital simulation. A linear approximation according to eqn. 3 was suitable. The arrows represent the moments at which a single injection of the sample is possible. The difference between the two following arrows is the actual length of the chromatogram. As can be seen, CCC is able to revocer the theoretical curve exactly except in the region around the peak maximum. Conventional gas chromatography does not guarantee the required number of points on the curve.

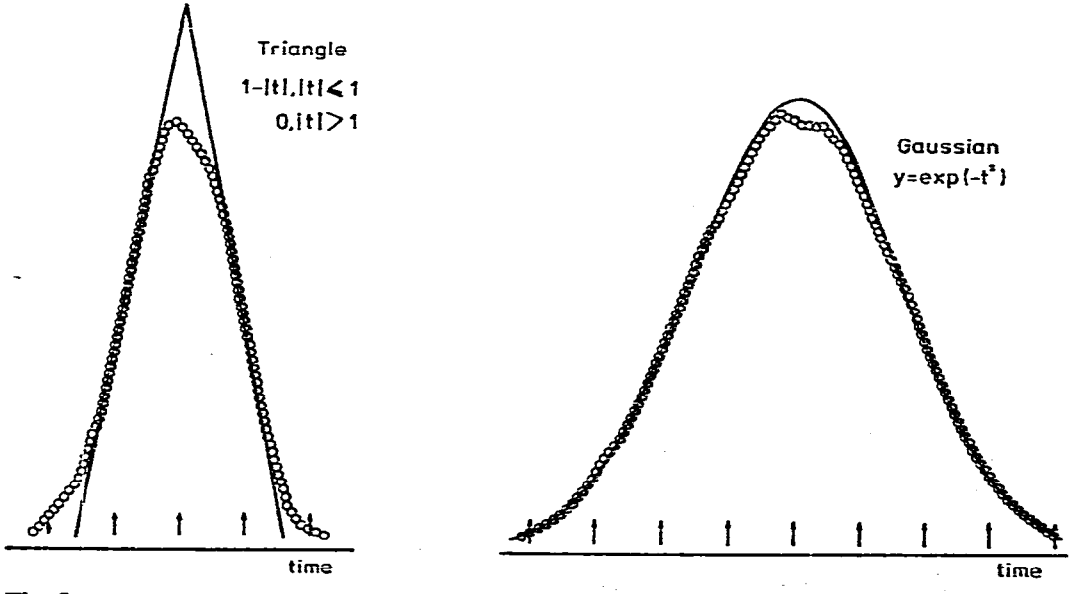


Fig. 5.

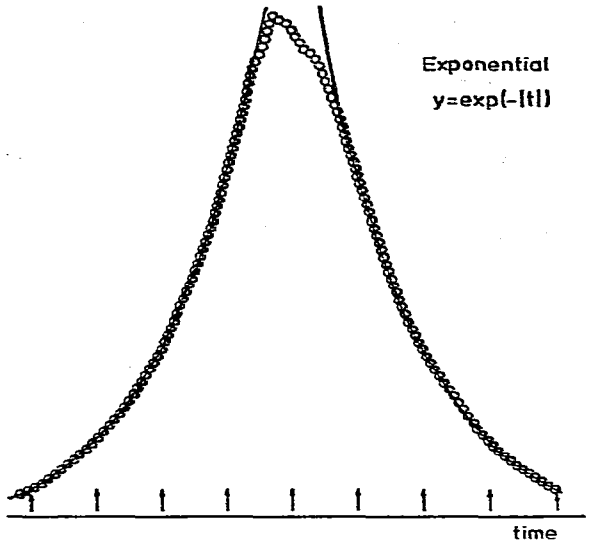


Fig. 5. Regeneration of some idealized evolved gas analysis curves by cross-correlation chromatography. Arrows show the moments when single injection of the sample is possible. ——, True value; O, CCC estimate.

APPENDIX: COMPUTATION OF NON-DIAGONAL ELEMENTS IN THE OUTPUT MATRIX

First let us define i mod (n) as follows:

$$i \bmod (n) = i - pn$$

where i and n are integers and p is the largest integer, so that $i > pn$. Now, a diagonal element in $\hat{Y}$ is given by

$$Y_{i \bmod(n),i} = \sum_{j=1}^{n} X_{(i-j+1) \bmod(n)} H_j(i - j + 1) \tag{17}$$

This follows directly from eqn. 1. A non-diagonal element $Y_{i \bmod(n),l}$ in the row i between columns i and $i+n$ is given by

$$Y_{i \bmod(n),l} = \sum_{j=1}^{n} X_{(i-j+1) \bmod(n)} H_j(l - j + 1) \tag{18}$$

Let $\tilde{Y}_{i \bmod(n),l}$ be a linear function of l that passes through $Y_{i \bmod(n),i}$ and $Y_{\bmod(n),i+n}$, *i.e.*,

$$\tilde{Y}_{i \bmod(n),l} = [Y_{i \bmod(n),i+n} - Y_{i \bmod(n),i}] \frac{l - i}{n} + Y_{i \bmod(n),i}$$

From eqn. 17, it follows that

$$\tilde{Y}_{l\,\mathrm{mod}(n),l} = \sum_{j=1}^{n} \left\{ [H_j(i+n-j+1) - H_j(i-j+1)] \frac{l-i}{n} + H_j(i-j+1) \right\} X_{(l-j+1)\mathrm{mod}(n)} \tag{19}$$

When $H_j(i)$ is a linear function of i, it follows from eqns. 18 and 19 that

$$\tilde{Y}_{l\ \mathrm{mod}(n),l} = Y_{l\ \mathrm{mod}(n),l}$$

i.e., the approximation is exact. If $H_j(i)$ is a non-linear function of i, a higher order of polynomials should be used for the approximation of non-diagonal elements, otherwise an estimation error $\Delta \hat{Y}$ appears that leads to correlation noise on the calculated chromatograms.

REFERENCES

1 K. Izawa, K. Furuta, T. Fujiwara and N. Suyama, *Ind. Chim. Belge*, 32 (1967) 223.
2 H. C. Smit, *Chromatographia*, 3 (1970) 515.
3 G. C. Moss and K. R. Godfrey, *Instrum. Technol.*, February (1973) 33.
4 J. B. Phillips and M. F. Burke, *J. Chromatogr. Sci.*, 14 (1976) 495.
5 R. Annino and E. Grushka, *J. Chromatogr. Sci.*, 74 (1976) 265.
6 R. Godfrey and M. Devenish, *Meas. Control*, 2 (1969) 228.
7 R. Annino and L. E. Bullock, in S. G. Perry and E. R. Adlard (Editors), *Gas Chromatography 1972*, Applied Science Publishers, London, 1973, p. 1.71
8 R. Annino and L. E. Bullock, *Anal. Chem.*, 45 (1973) 1221.
9 M. N. Tai, M. Harwit and N. J. A. Sloane, *Appl. Opt.*, 14 (1975) 2678.
10 M. Kaljurand and E. Küllik, *J. Chromatogr.*, 171 (1979) 243.
11 C. Laurgeau and F. Barras, *Chromatographia*, 8 (1975) 373.
12 R. Bellman, *Introduction to Matrix Analysis*, McGraw-Hill, New York, Toronto, London, 1960.
13 R. Hoffman, M. M. Gupta and P. N. Nikiforuk, *Proc. Inst. Electr. Eng.*, 119 (1972) 237.
14 C. Laurgeau and B. Espiau, *J. Chim. Phys.*, 71 (1974) 1143.
15 M. Kaljurand and E. Küllik, *Chromatographia*, 11 (1978) 328.
16 R. Kaiser, *J. Magn. Reson.*, 15 (1974) 44.
17 H. F. Tammet, *Vvedenie v Lineinuju Konechnomernuju Teoriju Spektrometrii (Introduction to the Theory of the Linear Finite Spectrometry)*, Valgus, Tallinn, 1975.
18 Tj. Th. Lub, H. C. Smit and H. Poppe, *J. Chromatogr.*, 149 (1978) 721.
19 P. C. Kelly and G. Horlick, *Anal. Chem.*, 45 (1973) 518.
20 Y. Tkatch, *Zh. Fiz. Khim.*, 51 (1977) 1916.