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RESOLUTION OF OVERLAPPING GAS CHROMATOGRAPHIC PEAKS USING FAST FOURIER TRANSFORMATION*

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SUMMARY

A method is presented for the determination of the retention time and the area of overlapping gas chromatographic peaks. Fast Fourier transformation has been used for the resolution of the overlapping peaks, and the results are compared with the actual amounts of the components which are present.

INTRODUCTION

The application of minicomputers to the resolution of overlapping spectral bands requires the use of complicated algorithms. For example, in gas chromatography (GC), least-squares and other methods have been used to process the chromatograms[1–4], and the Fourier transformation has been used in the resolution of spectra[5].

The theoretical aspects of the application of the fast Fourier transformation (FFT) have been presented by Kirmse and Westerberg[6], who separated overlapping chromatographic peaks into the individual components. In order to increase the resolution of GC peaks with the help of FFT, the following procedure is used. A signal obtained from an analytical instrument (spectrometer, gas chromatograph, etc.) is treated by an analog-to-digital converter (ADC) and introduced into the memory of a computer. A fast Fourier transform is then made by the computer. A division by line-shape function and a multiplication by apodizing function are usually carried out simultaneously; this is necessary in order to reduce the truncation effect. It is possible to obtain a better resolution without using the Hamming window[6], but there is interference from side bands in the calculation of the chromatographic peaks (see Fig. 1). After these operations an inverse transform is carried out and the results of the analysis are obtained from the computer.

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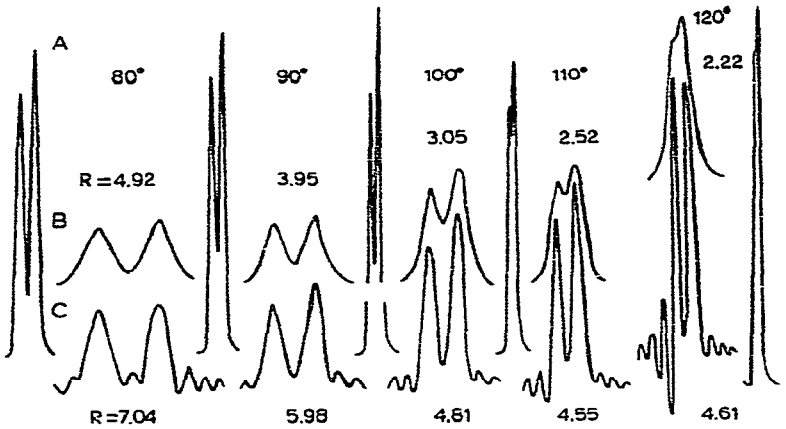

Fig. 1. Resolution of two overlapping peaks by fast Fourier transformation without the use of the Hamming window. A = Recorder output, B = ADC output and C = FFT deconvolution.

EXPERIMENTAL

A mixture of weighed amounts of *n*-, iso- and *sec.*-butanols was separated on a Perkin-Elmer Model 900 gas chromatograph. A signal from a hot-wire detector was converted into digital form by an ADC and then punched on to a tape at a frequency of four points per second. Computations were made with a Videoton-1010B computer (16 K, 32 bit) for which a program was written in Fortran. Different degrees of overlapping of the peaks were obtained by gradually increasing the oven temperature of the gas chromatograph. Measurements were made between 110 and 170°.

When applying FFT for increasing the resolution of peaks, it is necessary to know the half-width of the narrowest peak. Since the half-width of a peak is related approximately linearly to its retention time, the initial values of the half-widths of the overlapping peaks may be determined by constructing a calibration graph from the peaks (two at least) which are completely separated in the chromatogram. In practice, 1-pentanol and 1-hexanol were added to the mixture of alcohols under investigation. The peaks of the compounds which were added (Fig. 2, peaks 4 and 5) did not overlap with the peaks of the components of the mixture. The shape functions of the peaks should also be known when using this method, and the chromatographic peaks were assumed to obey a gaussian distribution.

RESULTS

The ADC output obtained from this experiment is presented in Fig. 3A. Whereas the mixture was almost entirely separated at 110°, it was impossible to separate the individual peaks of the mixture on increasing the temperature to 150°. The separated chromatograms obtained on the basis of the FFT output are presented in Fig. 3B, and the retention times of the overlapping peaks could be determined more precisely. In order to evaluate the accuracy of the FFT separation with reference to the measurements of the retention times, the relative retention times of the separated and overlapping peaks were compared. The results are shown in Fig. 4, in

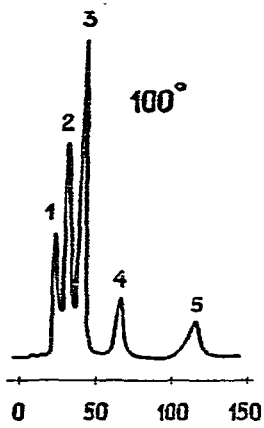

Fig. 2. Gas chromatograms of a mixture of butanols at 100°. Peaks: 1–3 = *sec.*-, iso- and *n*-butanol; 4 = 1-pentanol; and 5 = 1-hexanol.

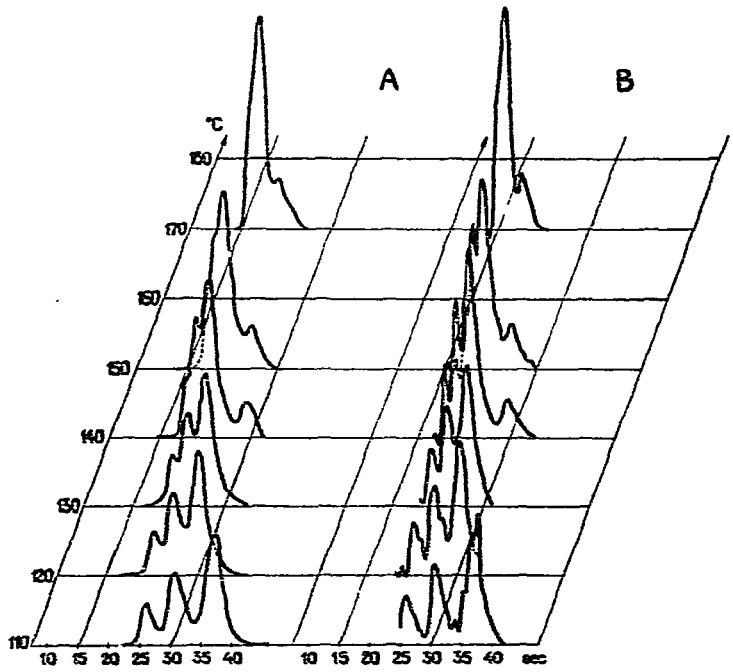

Fig. 3. Resolution of the overlapping peaks of three butanols. A = ADC output; B = FFT deconvolution.

co-ordinates of log α_i and $1/T$, where α_i is the retention time of a peak (i = 1–3) relative to that of peak 4 in Fig. 2. It is evident from the straight lines obtained that in this case by using FFT one can determine the retention times when the oven temperature is 150°, whereas direct measurement is possible only up to 130°. With FFT

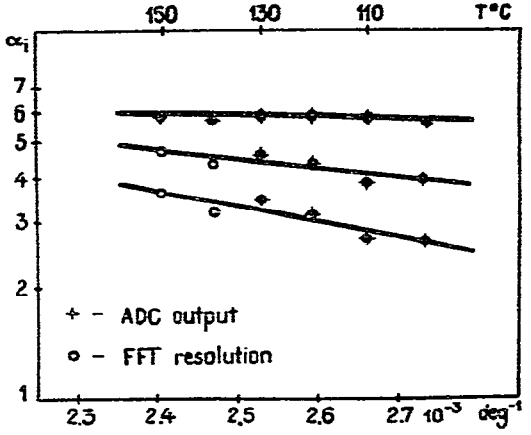

Fig. 4. Graphs of relative retention time against temperature.

it is also possible to determine the retention times with great precision even in a case of wide overlapping of the peaks.

The peak resolution, R, is expressed by

$$R = \frac{t_2 - t_1}{\sigma_2} \tag{1}$$

where t_1 and t_2 are the retention times of two peaks and σ_2 is the variance of the second peak. Hence it is possible to determine the extent of overlapping for which FFT separation is no longer effective. In the present case the value of R was 1.70. If FFT separation is not used, the value of R_2 for which deconvolution for determining the retention time is still possible is 2.7. The precision of the determination of areas of overlapping peaks by FFT is of great interest. A mixture of compounds of precise composition was prepared and the calculated ratio and actual ratio of the components were compared. Peaks which were not separated by FFT were calculated by digital integration. Methods which are available for determining areas are triangular, perpendicular-drop and digital integration, but the best results for FFT were obtained by using the peak amplitude and the retention time. The areas of the overlapping peaks were determined from the peak height and the variance, using the equation

$$S = \sqrt{2\pi} \cdot \sigma \cdot A \tag{2}$$

where A is the peak height, σ is the variance and S is the peak area. The variance, σ, was determined from the equation

$$\sigma = \sigma_1 \sqrt{1 - \left(\frac{\sigma_0}{\sigma_1}\right)^2} \tag{3}$$

where σ_0 is the initial value for FFT deconvolution and σ_1 is determined from the linear relation between the retention time and the variance of the peak. The results are shown in Fig. 5, where the ratios of the areas of the peaks are compared to the actual ratios

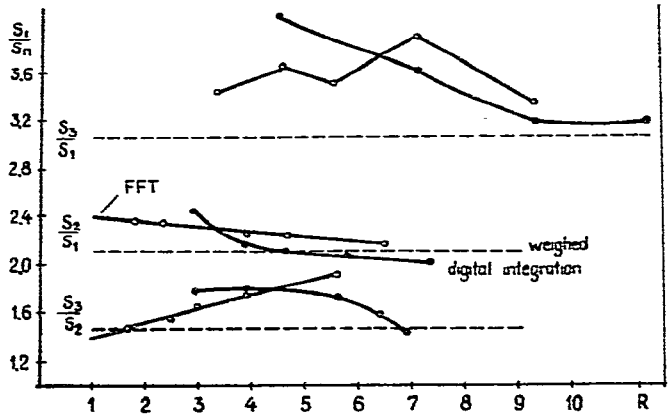

Fig. 5. Graphs of the ratio of the measured areas of overlapping peaks against the peak resolution.

in the cases of different extents of overlapping. It is seen that the results are not precise enough. Whereas the ratios of S_1 and S_2 approximate to the real values, those of S_2 and S_3 are different. This is apparently due to the influence of three overlapping peaks.

CONCLUSIONS

By using FFT in GC the retention times and the location of the individual components of overlapping peaks can be determined with greater precision. This technique may be considered as an alternative to direct separation. The mathematical separation of peaks permits information about the individual components to be obtained more quickly than from direct separation, where columns having different polarity, oven temperature and working conditions should be tested. On the other hand, mathematical data handling distorts the information and it is not quite clear how much information is lost in the processing of overlapping peaks. Thus peak deconvolution by FFT is a quick, but somewhat approximate, method, the application of which is justified only if great accuracy of data handling is not required for widely overlapping peaks.

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