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ELECTRONIC SIGNAL DIFFERENTIATION AS AN AID TO QUANTITATION IN GAS CHROMATOGRAPHY

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SUMMARY

The use of electronic signal differentiation in gas chromatography is described. Simple theory is presented to show how narrow peaks are enhanced and broad peaks suppressed. A description of an inexpensive, simple, low-noise circuit is given, and its use in quantitative gas chromatography explained. Quantification of a trace component eluting on the tail of a large solvent peak is shown using comparison of the zero-, first- and second-order derivatives of the signal.

INTRODUCTION

The use of electronic signal differentiation in quantitative analysis is not new[1,2]. Its main application has probably been in the following spectroscopic techniques: ultraviolet–visible[3], fluorescence[4], infrared[5], nuclear magnetic resonance[6], Mossbauer[7] and mass-spectra[8]. More recently, it has been used in liquid chromatography[9–11]. This paper now presents the use of electronic signal differentiation in gas chromatography (GC).

There are two main problems encountered in GC: the measurement of trace components in a large component matrix, which can be solved by heart cutting[12]; and measurement of peaks not fully resolved from other peaks, which can be solved by multi-phase chromatography[13]. Electronic signal differentiation can solve both problems within the limits of present circuitry.

It is only in recent years that such a technique has become feasible due to the advent of small, low-noise components. In this paper it is shown that a small circuit constructed with readily available components can be used to produce sensitive, linear, derivative chromatograms of the first- and second-order without any modification to the chromatograph. For the differentiation technique to be useful, the resolution must be better than that of the zero-order chromatogram and a quantitative measurement of the component must be given. It must be emphasised

that if a peak is not detected on the zero-order chromatogram, then neither will it be detected on the derivative chromatograms. To investigate the technique, small amounts of *n*-heptane in *n*-hexane were analysed. These chemicals were used because their eluted peaks are almost Gaussian in shape and the *n*-heptane peak eluted on the tail of the large *n*-hexane peak.

THEORETICAL BASIS

The output signal of GC is usually a voltage *versus* time trace. For the purpose of the following theory, the GC output is modelled as a set of Gaussian functions. It is appreciated that in practice pure Gaussian responses are rarely met, however it is a basis from which to work in order to design a suitable system. The technique does work with non-Gaussian peaks and also provides a method for assessing the degree of symmetry of peaks. A Gaussian peak would be perfectly symmetrical about its central axis and its first derivative would have a ratio of the height of the maximum to the depth of the minimum equal to one. If the ratio is less than one the zero-order chromatogram would show a leading peak: if the ratio is greater than one the zero-order chromatogram would show a tailing peak.

The Gaussian function may be written as

$$G(t) = Ve^{-(t-t_p)^2/2\sigma_T^2} \tag{1}$$

where t_p is the time at maximum amplitude, σ_T is the standard deviation from t_p, V is the maximum amplitude and t is time from the start of the chromatogram. The function is shown plotted in Fig. 1.

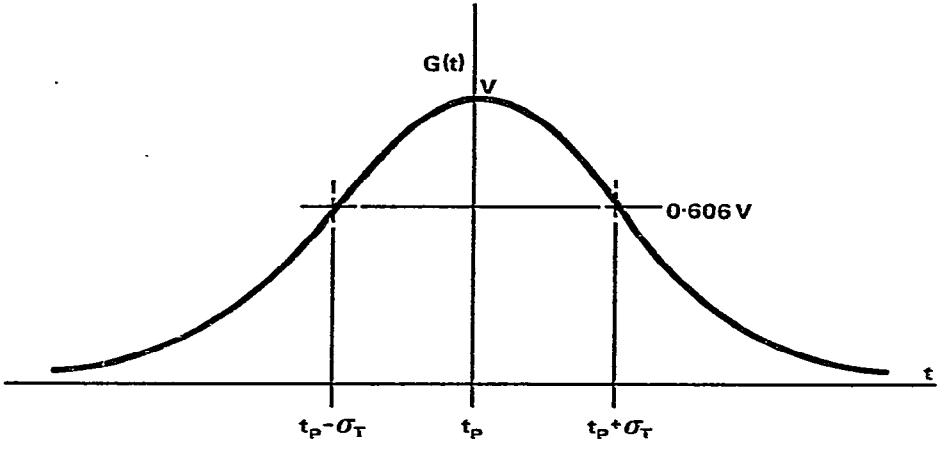


Fig. 1. Gaussian function.

The first- and second-order derivatives of the Gaussian function for two values of σ_T are shown in Fig. 2. This shows that differentiation enhances the narrower peak and suppresses the wider peak. This has obvious applications in GC in quantifying a small narrow peak that occurs on the leading or trailing edge of a larger peak.

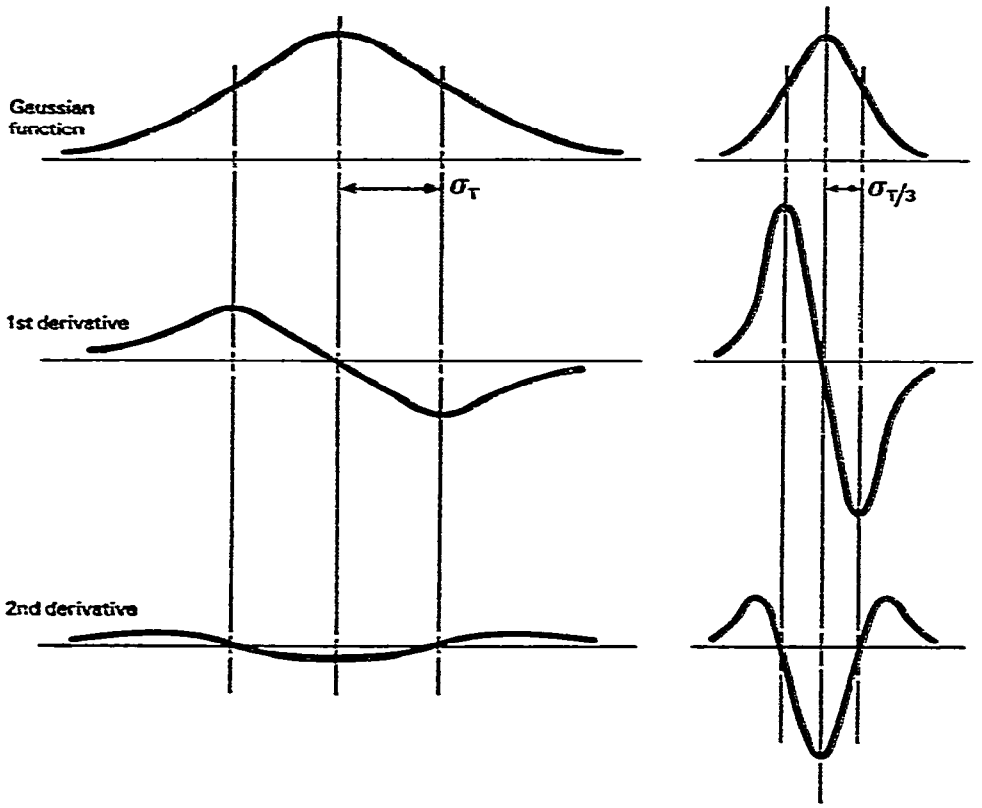


Fig. 2. Two Gaussian functions with their associated first- and second-order derivatives.

By differentiation and substitution of the Gaussian function the peak maximum and minimum of the first differential is 0.606 V/δ_T *i.e.* the magnitude of the first differential peaks is inversely proportional to the width of the Gaussian signal. Similarly for the second differential the maxima have the value 0.44 V/δ_T and the minimum has the value V/δ_T *i.e.* the magnitude of the peask in the second differential are inversely proportional to the square of the width of the Gaussian signal.

In general it can be shwon that the magnitude of the *n*th differential peaks is inversely proportional to the *n*th power of the Gaussian signal width. It can thus be appreciated that the degree of small peak enhancement and large peak suppression is proportional to the number of differentiations. A helpful rule to assess the number of differentiations required for signal enhancement can be obtained by considering two peaks of height h_N and h_B at the zero-order (N is a narrow peak, B is a broad peak). If their standard deviations are σ_N and σ_B respectively then the ratio of the heights of the peaks in the *n*th derivative is given by

$$\left(\frac{h_N}{h_B}\right) \cdot \left(\frac{\sigma_B}{\sigma_N}\right)$$

This is effectively shown in the practical example of Fig. 5. Deviations can be

attributed to non-Gaussian peaks, but even so the rule gives some idea of the degree of peak enhancement.

In practice the number of differentiations made is limited by the circuit techniques used to differentiate the signals. This paper describes work done with first and second differentials.

CIRCUIT DESIGN

The basic circuit is shown in Fig. 3 and is used as a single stage to produce one order of differentiation. Two circuits may be cascaded to provide second differentiation. The design criteria is concerned with the relationship between the characteristics of the GC output signal and the resiatsnce–capacitance time constants of the circuit. Fourier transform analysis of the signal, and frequency-response analysis of the circuit, provided this relationship and produced the first design criterion of

$$C_1R_1 = \frac{\sigma_{TS}}{2} \tag{2}$$

where σ_{TS} is the standard deviation of the smallest peak component expected in the GC signal, and C_1 is measured in farads and R_1 in ohms. For minimum noise propagation through the circuit the second design criterion was found to be

$$C_2R_2 \approx 10\, C_1R_1 \tag{3}$$

Finally the ratio R_2/R_1 controls the gain of the circuit and hence the magnitude of the differentiator output.

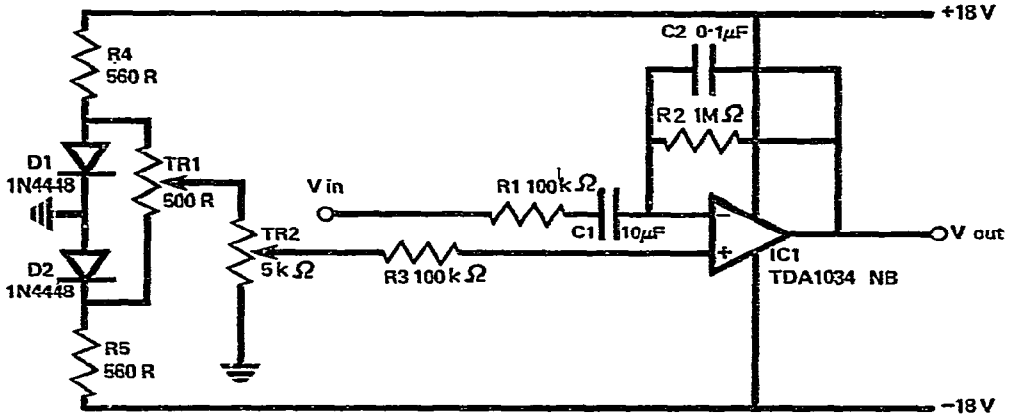


Fig. 3. The circuit to produce one order of differentiation.

The circuit was required to operate at the low signal levels associated with small trace impurities in the solvent and this necessitates the use of a low-noise instrumentation amplifier. The use of such an amplifier gives an order of magnitude decrease in the background noise from the circuits after two stages of differentiation.

Fig. 4 compares the signal from a general purpose amplifier with that from the low-noise instrumentation amplifier. At low signal levels, fine control was required to zero the output offset voltage. Trimpot TR1 provides a crude adjustment and TR2 a fine adjustment. The diodes D1 and D2, and resistors R_4 and R_5 provide the reference voltage supply for the offset adjustment.

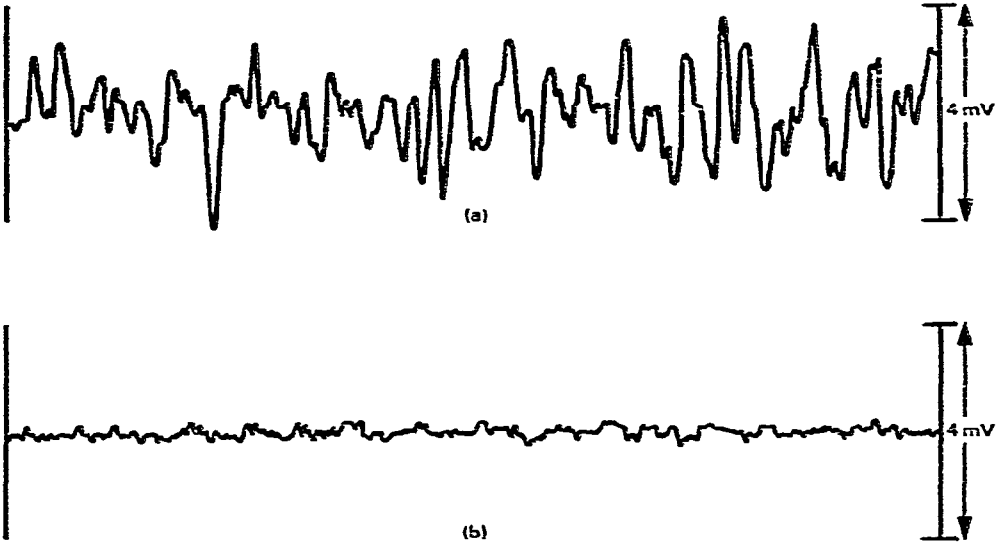


Fig. 4. Noise waveform for (a) general purpose amplifier and (b) low-noise instrumentation amplifier.

Circuits with large time constants tend to be sensitive to leakage in capacitors, these effects were minimised by the use of high quality polycarbonate capacitors. The output impedance of the GC used was 10 kΩ which was low enough not to cause significant interaction with the differentiator circuit input.

EXPERIMENTAL

Materials

All chemicals were analytical reagent grade (Hopkins and Williams, Romford, Great Britain).

Apparatus

A Perkin-Elmer F30 gas chromatograph equipped with a dual flame-ionisation detector was used. The column was 6 ft. × 1/8 in. (O.D.) with 10% OV-101 on 80–100 mesh Chromosorb W AW. The chromatographic conditions were constant throughout at 70°C oven temperature and 30 ml/min flow-rate of nitrogen carrier gas. The injection size was 0.7 μl. Servoscribe 1s recorders (Smith Industries, London, Great Britain) were used to record the chromatograms. The maximum detector sensitivity was chosen so as to feed as large a signal as possible to the differential circuit. The signal was then attenuated, where necessary, at the recorders.

RESULTS AND DISCUSSION

Quantitative experimentation using the technique was preceded by substantiation of the theory. Based on the theoretical work which is illustrated in Fig. 2, chromatograms of a mixture of *n*-heptane and *n*-hexane (1:1 v/v) were produced experimentally (Fig. 5) that confirmed the theory. The ratio of peak heights in Fig. 5 is approximately 1:3:25 for zero-, first- and second-order signal respectively. This illustrates that a narrow peak is enhanced by electronic signal differentiation, and a broad peak suppressed. It may further be appreciated that by taking the fourth-order derivative, suppression of the broad peak would be such as to make the signal a horizontal line with respect to a measurable signal for the narrow peak. The narrow signal peak under these conditions would almost be a single vertical line.

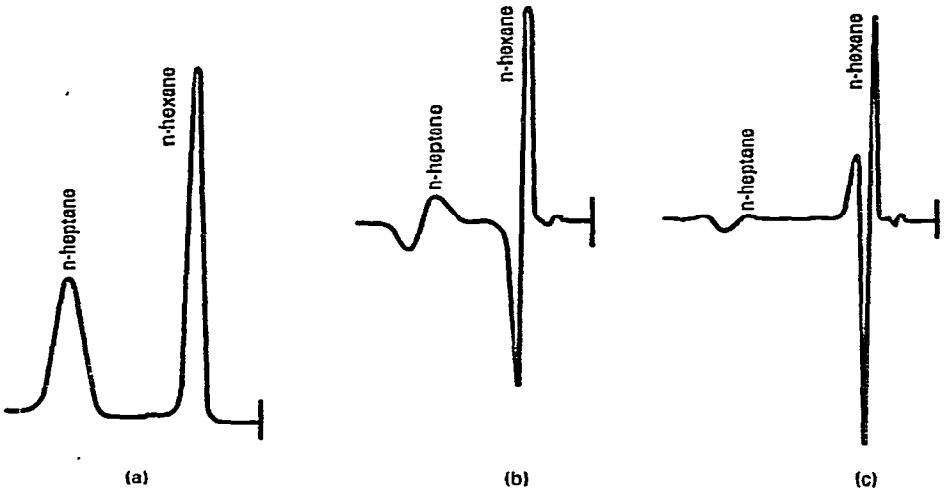


Fig. 5. (a) Zero-, (b) first- and (c) second-order derivative chromatograms, showing enhancement of a narrow peak and suppression of a broad peak.

Fig. 6a, b and c show zero-, first- and second-order chromatograms produced by mixtures of 0.1, 0.5 and 1.0% (v/v) *n*-heptane in *n*-hexane. The zero-order chromatograms show that quantification is difficult at the 1.0 and 0.5% level, and almost impossible at the 0.1% level, since the *n*-heptane signal is almost completely obliterated by the *n*-hexane signal. The first- and second-order chromatograms, however, produce a measurable *n*-heptane signal. In addition, all the signals show excellent linearity of response, thus allowing a poorly resolved peak (Fig. 6a) to be accurately quantified. Amplification of the zero-order chromatogram signal only exacerbates the problem by further distorting the signal. By differentiating first, the signals are separated and can be amplified allowing very accurate measurements to be made.

Table I shows the amplitude (in mV) of the response for zero-, first- and second-order chromatograms over a wide concentration range. All have been normalised to the same amplification although to get accurate measurements at the

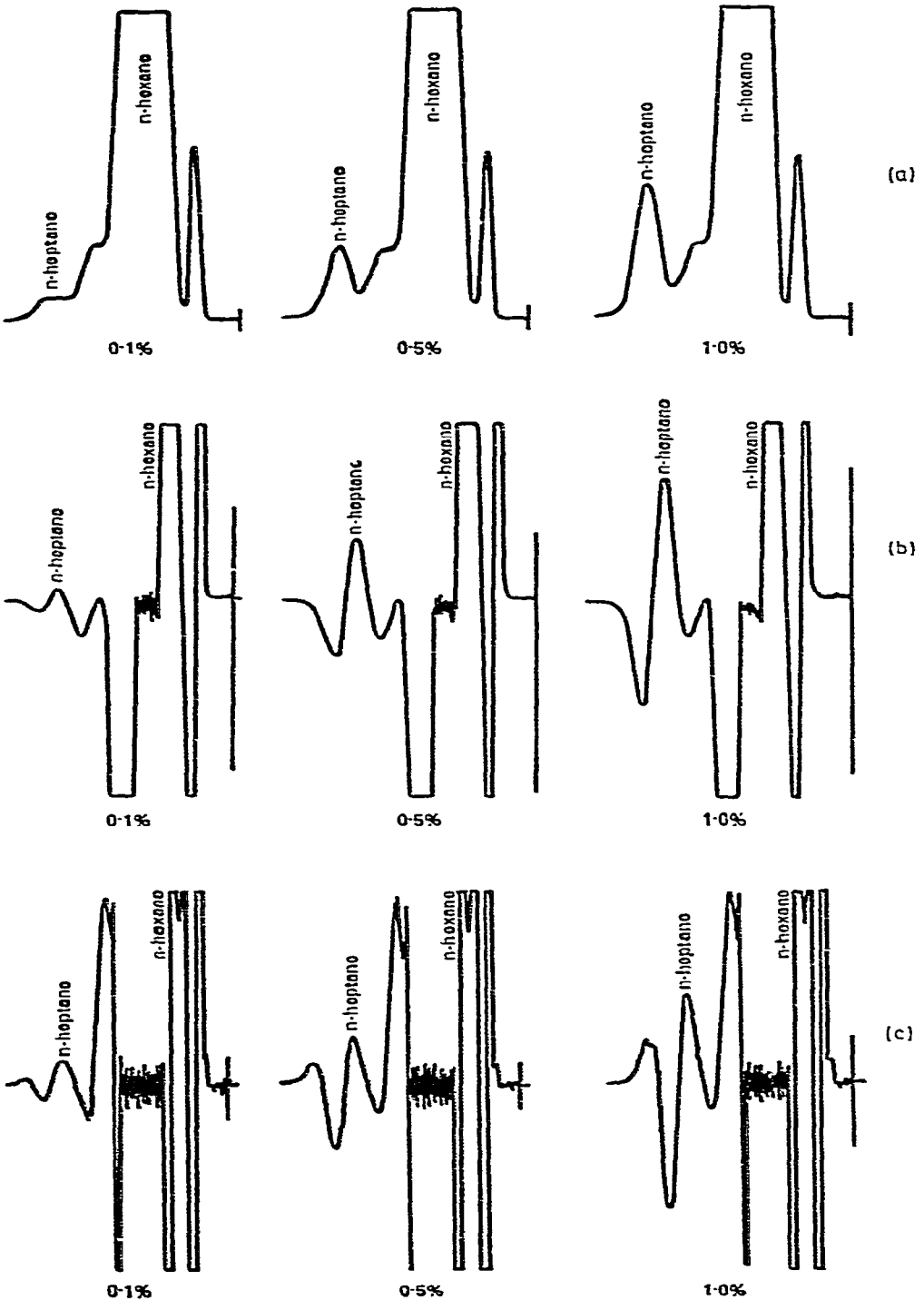


Fig. 6. (a) Zero-, (b) first- and (c) second-order chromatograms of varying *n*-heptane concentration.

TABLE I

AMPLITUDE OF RESPONSE FOR ZERO-, FIRST- AND SECOND-ORDER CHROMATOGRAMS

n-Heptane concentration (%, v/v)	*Zero-order*	*First-order*	*Second-order*
1.0	281 (14.3)	63.3 (0.7)	9.7 (0.1)
0.5	135 (4.5)	31.7 (0.4)	4.8 (0.1)
0.1	—	5.9 (0.6)	0.9 (0.1)
0.05	—	2.9 (0.4)	—
0.01	—	0.6 (0.5)	—

lower concentrations the amplification was steadily increased to give a measurable signal.

Higher concentrations were not considered as these present less of a problem for zero-order chromatography. For lower concentrations, measurement of the *n*-heptane peak becomes impossible on the zero-order chromatograms, since the signal cannot be amplified further without being obliterated by the solvent peak.

The bracketed figures in Table I are the standard deviation for five injections showing that the first and second-order chromatograms produce more accurate data than the zero-order chromatograms as the concentration decreases. In fact worthwhile measurements for the zero-order chromatograms cease at about the 0.1% level.

From Table I it can also be seen that the first- and second-order chromatograms are capable of lower detection limits. The limit of detection being about 0.01% for the first derivative and about 0.1% for the second derivative. For the first derivative this is about an order of magnitude lower than that for the zero-order chromatogram.

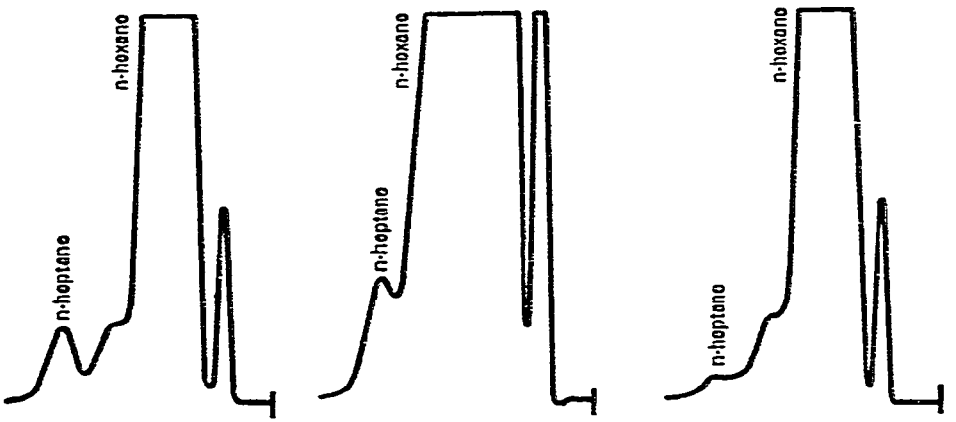
The noise shown particularly in the first- and second-order chromatograms (Fig. 6b and c) is caused by saturation of the gas chromatograph detector amplifier. It is greater for the second-order since this gives greater amplification.

Fig. 7 shows three zero-order chromatograms and Fig. 8 the corresponding first derivative chromatograms. Fig. 7a shows the *n*-heptane peak at the 0.5% level, Fig. 7b shows 0.1% *n*-heptane amplified five-fold, and Fig. 7c shows the *n*-heptane peak at the 0.1% level with the same amplification as Fig. 7a. The difficulty of measuring the small peak at the 0.1% level using the zero-order signal is shown, since amplifying the signal changes the general shape of the chromatogram. Ideally the 0.1% *n*-heptane peak amplified five-fold should be equivalent to the 0.5% *n*-heptane peak without amplification; this is obviously not the case.

Considering those parts of the chromatograms that correspond to *n*-heptane, it can be seen from the first-order chromatograms that the 0.5% level signal is equivalent to the 0.1% level signal amplified five-fold; furthermore the 0.5% level signal is five times larger than the 0.1% level signal, when both have the same amplification. This example clearly illustrates the possible use of derivate signal chromatography in quantitative analysis.

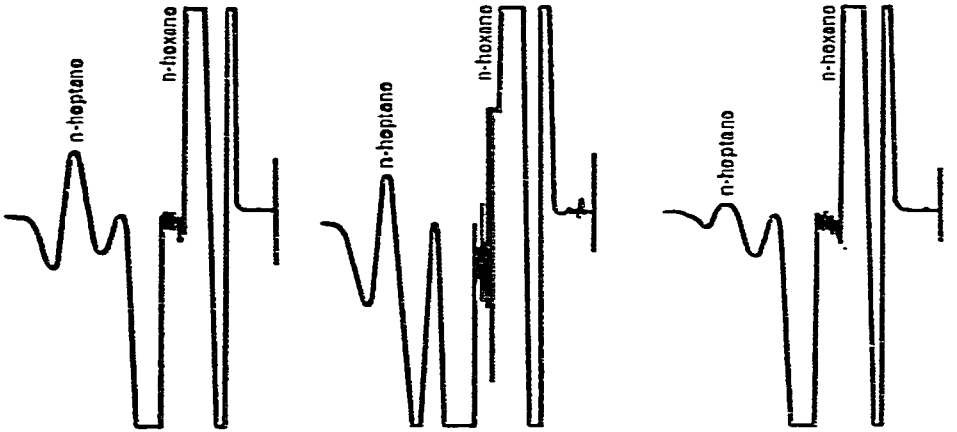
It may be noted that an impurity is eluting on the tail of the *n*-hexane peak before the *n*-heptane peak; the derivative chromatogram produces a constant size signal which could also be quantified in a similar manner to the *n*-heptane.

The selection of the best parameter for measurement has not presented any



(a) 0·5% (unity amplification) (b) 0·1% (5 x amplification) (c) 0·1% (unity amplification)

Fig. 7. Zero-order chromatograms of varying *n*-heptane concentration in *n*-hexane.



(a) 0·5% (unity amplification) (b) 0·1% (5 x amplification) (c) 0·1% (unity amplification)

Fig. 8. First-order chromatograms of varying *n*-heptane concentration in *n*-hexane.

problems. For the first- and second-order derivative, the vertical height between the maximum and minimum of the signal was measured.

The use of higher-order derivatives is now being considered, together with quantification at much lower levels.

CONCLUSIONS

The use of first- and second-order electronic signal derivatives in gas chromatography can give improved quality in the quantification of poorly resolved peaks. These derivatives can be obtained by the use of a simple circuit, and without any modification to the chromatograph or recorder system. At present, first-order derivative signals appear to be sufficient for the quantification of gas chromatographic peaks.

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