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REDUCTION OF DETECTOR NOISE IN GAS CHROMATOGRAPHY
BY MEANS OF AN RC FILTER

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SUMMARY

The possibility of reducing detector noise in gas chromatography by electrical means was studied. An RC filter was placed between the detector and recorder and the change in the height of a chromatographic peak depending on the ratio of time constant and standard deviation of the peak was used for noise reduction. An essential decrease in noise was found as a consequence of the fact that the standard deviation of the chromatographic peak is much higher than the standard deviation of the noise if the latter is considered as individual chromatographic peaks. The value of the decrease is in the case of a model experiment using an alkali flame ionisation detector and bromocyclohexane approximately thirtyfold. The value of the decrease obtained with the aid of an RC filter is dependent on the noise character and is especially suitable for the analyses of substances having large retention volumes.

INTRODUCTION

The smallest amount of a substance that can be determined by gas chromatography is characterized by both the character of the substance itself and properties of the detector used. Whatever physico-chemical process is used in a gas chromatographic detector for the determination of a given substance, maximum molar (or weight) response of the detector is determined by the character of the process taking place in the sensing element of the detector. The actual detector response can thus be increased by choosing such construction parameters and operational conditions of the detector that the process taking place in the detector is adopted for the highest possible response, however, it cannot be increased beyond certain limits. As most of the detectors used today are optimal from this viewpoint, an essential increase in sensitivity of these detectors can be hardly reached by increasing their response.

The smallest amount of the substance that is still usable in gas chromatographic analysis is, in addition to detector response, also determined by another property of the detector, *viz.* its noise. By linking these two properties of the detector together into one relation an expression for the minimum detectable amount can be defined. This amount determines the quantity of the substance that can just be dis-

tinguished by the detector. Minimum detectable amount is defined as the quantity of the substance flowing through the detector per unit of time and giving signal twice as high as the noise of the detector. This value is thus also limited by noise. It should be kept in mind that the minimum detectable amount is a value characteristic of the substance for the flow through a given detector and thus remains independent of the chromatographic properties of the column (of changes in retention volume). The height of a chromatographic peak of a particular substance is lowered as a consequence of broadening with increasing retention volume during its passage through a chromatographic column. It is therefore obvious that with increasing retention volume the quantity of substance sampled must be increased in such a way that the height of the chromatographic peak always remains twice that of the noise level.

The noise level of some detectors in gas chromatography exceeds the noise of the transfer channel behind the detector by several orders of magnitude (*e.g.* argon detector¹, alkali flame ionisation detector^{2, 3}, flame photometric detector⁴, coulometric detector⁵, etc.). The suppression of the noise caused by the detector would result in an appropriate decrease in minimum detectable amount. Up to the present time a whole series of experiments have been carried out in order to reduce noise level by means of changes in construction, and has led to substantial suppression in the case of some detectors (argon detector⁶); this suppression is considerably lower^{7, 8} with other detectors and a larger difference between the noise values of the detector and transfer channel has thus remained.

Another possibility of noise reduction is represented by the use of correction elements in the transfer channel of the signal, *i.e.* by electrical means. This means is also common in other disciplines such as radiotechniques⁹, spectroscopy^{10, 11}, etc. The aim of this paper is to show the possible application of an electrical means of noise suppression in gas chromatography.

EXPERIMENTAL

A flame ionisation detector with a jet tip of pressed alkali metal salt built in Chrom 3 gas chromatograph (Laboratorní přístroje n.e. Prague, Czechoslovakia) was used to demonstrate the practicality of an RC filter for noise reduction. A solution of bromocyclohexane in carbon tetrachloride was used as a model compound. The stainless-steel chromatographic column was 68 cm long, 0.6 cm I.D., and filled with 25 % of dodecyl phthalate on Celite. The column temperature was 27°, the carrier gas flow rate was 60 ml/min.

RESULTS AND DISCUSSION

Accidental changes in the output signal of the detector are of two kinds: (1) the changes proceeding essentially more slowly than the useful signal ("drift"), (2) the changes proceeding essentially more rapidly than the useful signal (noise). A block diagram of the signal transmission from the chromatographic column outlet to the recorder is shown in Fig. 1. The useful signal from the column, resulting from the concentration of the substance analysed in the carrier gas leaving the chromatographic column outlet, is after passage through the detector distorted by its noise. This output signal of the detector is subsequently transmitted by means of a transfer channel

(cable, amplifier, correction elements, recorder) to a recording chart. It is generally distorted by the transfer channel in such a way that the output signal (recorder chart) does not have the same form as the detector output signal. It is possible to eliminate rapidly proceeding changes — of the noise — from a slowly proceeding signal by suitable selection of the translation channel.

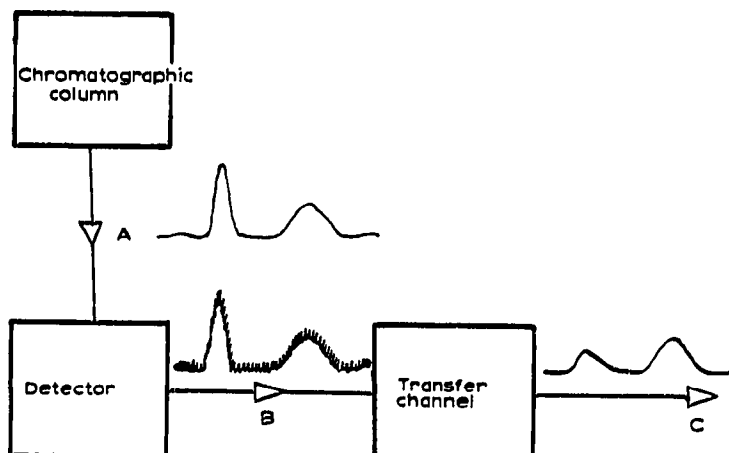


Fig. 1. Block diagram of signal transfer. A = useful signal (input detector signal); B = useful signal distorted by detector noise (output detector signal); C = output signal.

The properties of a detector and translation channel are selected according to usual chromatographic practice in such a way that the distortion which occurs is as small as possible even in case of the most rapid elution of chromatographic peaks (e.g. with capillary columns). The effect of transfer properties of the detector on the

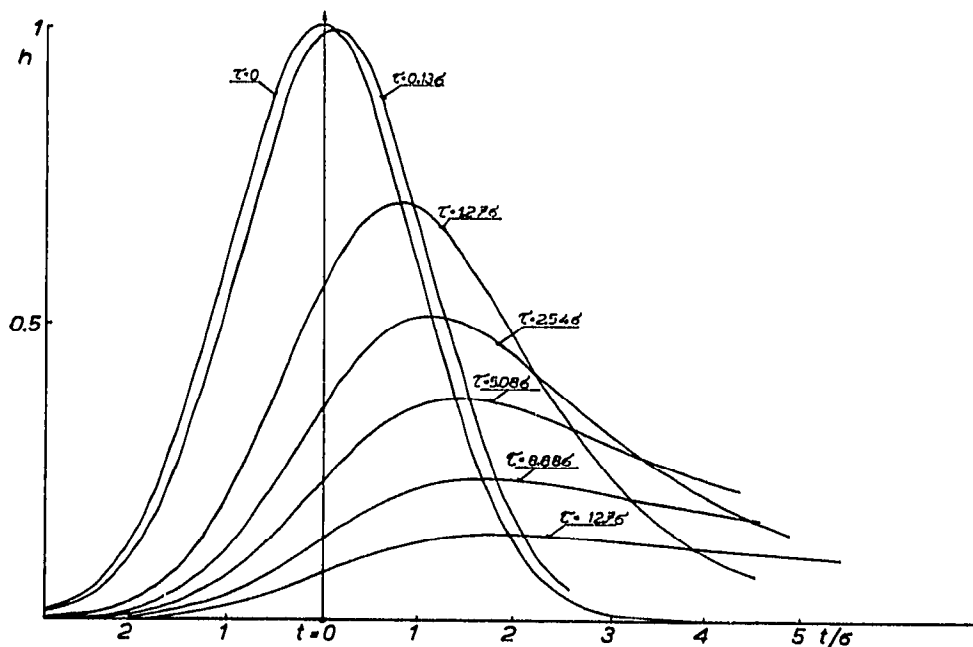


Fig. 2. The effect of the time constant of translation channel on the shape of chromatographic peak having the form of a Gaussian curve. h = relative height of chromatographic peak; σ = standard deviation of chromatographic peak; t = time; τ = time constant.

shape of a chromatographic output signal has been studied earlier, assuming the inlet detector signal has the shape of a Gaussian curve and the detector is an element with transfer function¹²⁻¹⁵ $1/\tau p + 1$ and this effect has been analysed in detail by STERNBERG¹⁶. The element with the transfer function $1/\tau p + 1$ (in Laplace transformations) can, however, be in any position in a signal channel and it need not be realised by the detector itself. On the other hand, this element can be intentionally realised electrically in the signal transfer channel as a noise filter.

The effect of the time constant τ of the translation element on the shape of output signal is demonstrated in Fig. 2. The curves in Fig. 2, representing the shape of the chromatographic peak having the shape of a Gaussian curve after the passage through an element with a transfer function $1/\tau p + 1$, were calculated by means of AP 4 analogue computer, Tesla n.e. Pardubice, Czechoslovakia. If a chromatographic peak with a constant standard deviation σ is considered, the decrease in the height of the chromatographic peak, the change in its shape, and the shift of its maximum towards higher values of retention volumes occurs with increasing value of the time constant τ of the transfer element. For constant τ the height and the shape of the output signal will then be dependent on σ of input signal in such a way that the changes in these values will be higher, the lower σ of the input signal is (Fig. 3). The changes in the height of output signals depending on the σ of the input signal and on the time constant of the filter are demonstrated in Fig. 3. This dependence was plotted from

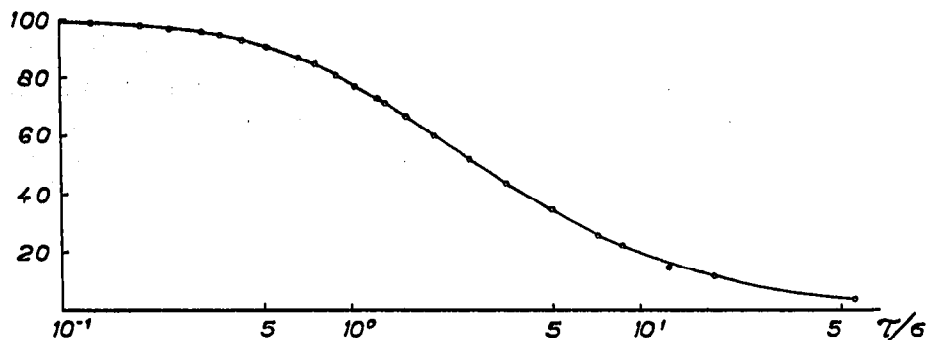


Fig. 3. The effect of ratio τ/σ on the relative height of chromatographic peak. h = relative height of chromatographic peak.

STERNBERG's data¹⁶ for the effect of the detector on the changes of a chromatographic peak and from the data obtained by the authors of this paper with the aid of analogue computer. It then holds generally that for any τ and σ of the input signal the higher the ratio τ/σ , the higher will be the changes in output signal also (chromatographic peaks). If the detector noise is assumed to be represented by the chromatographic peaks, the average σ_N of these noise peaks is very small. Regarding the dependence of peak height on the ratio of the time constant of transfer element and σ of the peak (Fig. 3), the height of this noise after passage through such a transfer element as is placed behind the detector as a noise filter, will essentially be decreased. If, at the same time a substance is studied, the record of which is a chromatographic peak having σ_S large enough in comparison with τ , this curve passes through the filter without any substantial change (compare Figs. 2 and 3). Noise level can obviously be reduced by placing a filter with a suitable time constant in the translation channel behind the detector without simultaneous substantial changes in the chromatographic

peaks having large σ_s , however it results in simultaneous changes in the chromatographic peaks having small σ_s .

The noise of the alkali flame ionisation detector recorded in the course of 1 min is demonstrated in Fig. 4a. Supposing that the noise is in shape of Gaussian curves, σ_N for the noise of this detector is approximately 0.28 sec. The chromatogram of bromocyclohexane, the σ_s of which is equal to 78 sec, is shown in Fig. 4b. 1% was chosen as an acceptable decrease in the height of the chromatographic curve. Neither substantial distortion of the curve nor substantial shift of the peak maximum occur with this height decrease. It follows from the plot in Fig. 3 that the filter time constant of 8.5 sec must be selected for the given case. Thus for bromocyclohexane $\tau/\sigma_s = 8.5/78 = 0.109$ and for the noise τ/σ_N is $8.5/0.28 = 30.5$. It also follows from the same plot that for this value of τ the height of noise will be reduced by 93%, which means that the noise would be reduced approximately 15 times under these conditions. An actual chromatogram of bromocyclohexane obtained with the use of the filter with the given time constant is shown in Fig. 4c. The height of the chro-

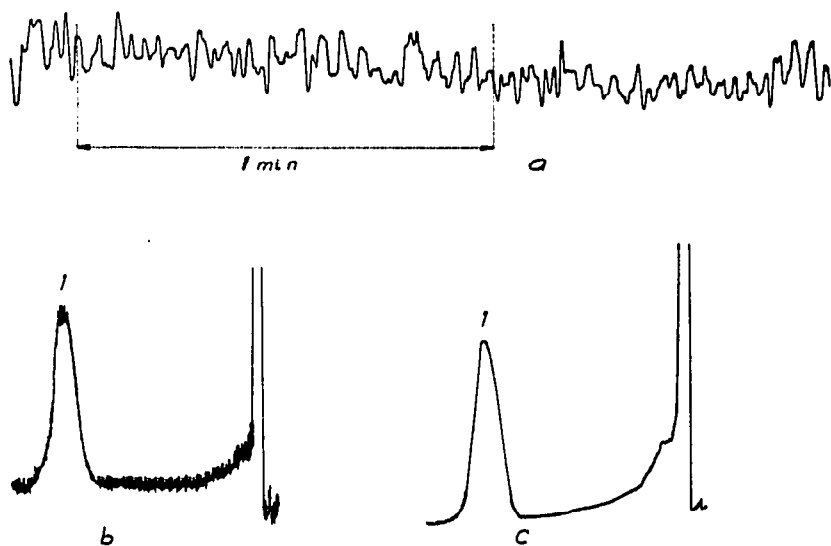


Fig. 4. (a) Noise of alkali flame ionisation detector. (b) Chromatogram without filter: 1 = bromocyclohexane. (c) Chromatogram with filter: 1 = bromocyclohexane.

matographic curve obviously remains practically the same, the distortion is also negligible (σ_s remains the same), as well as the shift of maximum. Noise level is essentially decreased and the reduction is approximately 30 fold. The difference in the noise decrease assumed and the actual one is probably caused by the assumption that the noise is in the form of chromatographic peaks with a Gaussian curve. The actual course of the noise only approaches this assumption; the actual attenuation of the filter is higher. More precise results could be obtained by carrying out harmonic noise analysis and determining attenuation for individual harmonic components. However, the procedure described is quite sufficient for a good estimate of the noise production.

In cases when a higher ratio of τ/σ must be selected, larger changes in curve parameters could appear. These changes can be followed directionally in Fig. 2 (in Fig. 3 height), more detailed results depending on time constant of the detector are

described by STERNBERG¹⁶. As the course of the noise differs for individual detectors, each detector must be considered independently. The higher the frequency of the detector noise, the higher will be the noise reduction.

As the changes in the chromatographic peak are higher, the higher the ratio τ/σ_S is, the use of this method of noise reduction is obviously especially suitable for compounds having large retention volumes, the σ_S of which, in relation to the noise, is fairly large. Hence for these σ_S larger τ can be selected and this can result in a larger decrease in noise level, which is also the larger, the larger is τ/σ_N . By decreasing noise in this way, the minimum detectable amount of the substance can be decreased and that the more, the larger retention volume the substance has. It is thus not necessary to sample higher concentrations of the sample when determining substances with large retention volumes (high σ_S) than in the case of a determination of a substance with a low retention volume (low σ_S).

CONCLUSIONS

The introduction of the element with transfer function $1/\tau p + 1$ into the translation channel of the signal changes the parameters of the chromatographic peak (height, shape, and maximum position) having the shape of a Gaussian curve and the extent of these changes is generally proportional to the ratio of time constant of an element τ and standard deviation of the curve σ . This property can be used for the reduction of detector noise. Intentional placing of such an element with a suitable time constant as a filter between the detector and the recorder results in the height of the noise, the σ_N of which is much smaller (if the noise is considered to be a chromatographic peak) in comparison with σ_S of an analysed substance, being substantially reduced, while the peak height is reduced relatively less. The relative ratio of the values of the changes in the height of chromatographic peak and the noise is dependent on the appropriate ratios τ/σ_S and τ/σ_N . If a change of 1% in the height of the chromatographic curve is allowed, a time constant for the filter of 8.5 sec must be selected for the alkali flame ionisation detector used with bromocyclohexane, the σ_S of which is 78 sec, as the model compound. The reduction is 30 fold under these conditions

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