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DETERMINATION OF THE INERTIAL PROPERTIES OF CHROMATOGRAPHIC DETECTORS

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SUMMARY

A method is described for the determination of detector time constants based on the estimation of true distribution of detectable component concentrations in a carrier gas by a flame ionization detector, the time constant of which is essentially zero, and by a detector with a known time constant, *e.g.*, a flame temperature detector.

INTRODUCTION

A chromatographic detector can be treated as a converter of the physicochemical properties of gaseous mixtures into electric or pneumatic signals. The dynamics of many differential detectors can be described by an equation of the form

$$T\cdot\frac{dU(t)}{dt} + U(t) = KX(t) \tag{1}$$

where

$X(t)$ = volume concentration of the materials to be analyzed at the input of the detector;
$U(t)$ = output signal of the detector;
T = time constant of the detector;
K = transmission factor, which defines the detector sensitivity.

T determines the inertial properties of the detector and is dependent on the effective volume of the detector and the physicochemical processes that occur within it. This value makes it possible to establish whether a particular detector can be used at a given rate of elution of a component from the chromatographic column.

So far there have been a few papers on the determination of the inertial properties of some detection systems[1,2], as well as on the control of the distortion of the curve describing the distribution of the material concentration in the carrier gas stream which is caused by the inertness of the system[3].

The main disadvantage of the known methods for the determination of the time constants of detectors is the necessity to create a stepwise concentration change. It is virtually impossible to effect such a change because of diffusion and mixing effects. Therefore, the recovery characteristic of the detector produced under these conditions is approximate and the time constant resulting from it is not true. Also, it should be emphasized that for rapid-response detectors, which are stream sensitive, stepwise concentration changes cause a displacement of the detector baseline, which also distorts the recording of the recovery characteristic. Hence, such methods can be recommended only for a limited number of detectors with high time constant.

The time constant for the sensitive elements of katharometers can be determined via discontinuous variation of the bridge current[4].

Two methods for the determination of the time constant of any detector, independent of its principle of operation and construction, are described in this paper.

CONCEPT OF METHODS FOR THE DETERMINATION OF THE TIME CONSTANTS OF CHROMATOGRAPHIC DETECTORS

The importance of the methods is as follows. If into the detector inlet, the dynamic properties of which are described by the differential eqn. 1, a binary gaseous mixture (carrier gas with any component) is introduced with a known distribution law of the component volume concentration in the carrier gas, $X(t)$, then, by recording the detector signal, one can determine the time constant of the detector from the solution of eqn. 1. In this case, the true nature of the material concentration distribution at the detector inlet, $X(t)$, according to the first technique developed, is defined by the detector, the time constant of which is zero. In this case, a flame ionization detector (FID) can be used. According to the second technique developed, the material concentration distribution at the inlet of the detector under study is measured by a detector with a known time constant, the flame temperature type being the most suitable.

THEORETICAL BASIS OF THE DETERMINATION OF THE TIME CONSTANTS OF CHROMATOGRAPHIC DETECTORS

At present, mainly automatic compensation recorders are used for recording detector signals in chromatographic analysis, the differential equations of which can be expressed as

$$T_r \cdot \frac{\mathrm{d}U_r(t)}{\mathrm{d}t} + U_r(t) = K_r Z(t) \tag{2}$$

where

T_r = time constant of compensation recorder;
K_r = gain factor of compensation recorder;
$Z(t)$, $U_r(t)$ = input and output signals of the compensation recorder, respectively.

The detection system, consisting of a detector and a compensation recorder, can be described by the following differential equation:

$$TT_r \cdot \frac{\mathrm{d}^2U(t)}{\mathrm{d}t^2} + (T + T_r)\frac{\mathrm{d}U(t)}{\mathrm{d}t} + U(t) = KK_rX(t) = K_sX(t) \tag{3}$$

T_r and K_r are generally known from the performance characteristics of the device. K can be defined from its static characteristic.

Method I

According to the first method developed, a flame ionization detector was selected as a detector with a known time constant. The distinctive feature of the FID, compared with other types of detectors, consists in its low time constant, of the order 10^{-3} sec (ref. 5). Such a low value enables the FID to be considered as an essentially inertialess detector relative to other detectors. For such a detector, eqn. 1 will take the form

$$U(t) = K\,X(t) \tag{4}$$

while a system comprising an FID with transmission factor K_d and a compensation recorder will be described by an equation of the type

$$T_{0r}\cdot\frac{\mathrm{d}U_{0s}(t)}{\mathrm{d}t} + U_{0s}(t) = K_d K_r X(t) = K_{0s} X(t) \tag{5}$$

where

T_{0r} = system time constant, determined by the recorder time constant;
K_{0s} = system transmission factor;
$X(t)$, $U_{0s}(t)$ = input signal of the system and the response of the system to the signal, respectively.

A schematic diagram of the arrangement for the measurement of the time constant of a chromatographic detector using an FID and a compensation recorder is shown in Fig. 1a.

When analyzing the same amount of material at constant and identical carrier gas flow-rates through two detection devices, we obtain the records of the response of these detection devices to the same input signal. In order to provide a uniform distribution of material concentration in the carrier gas stream at the inlets of the

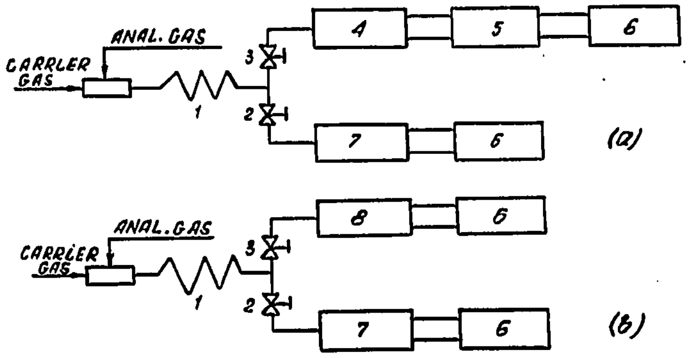

Fig. 1. Schematic diagrams of the arrangements for the determination of the time constants of chromatographic detectors by (a) Method I and (b) Method II. 1 = Column; 2, 3 = valves; 4 = flame ionization detector; 5 = electrometric amplifier; 6 = compensation recorder; 7 = detector under study; 8 = detector with known dynamic properties.

detectors, it is necessary that the line lengths and the total hydraulic resistances of the lines and detectors are identical.

When the above requirements are satisfied, the response of the system consisting of an FID and an automatic compensation recorder to the input signal, $X(t)$, can be found from eqn. 5. However, the response of the detector system under study to a similar input signal, $X(t)$, has been determined from the equation

$$T_r T \cdot \frac{\mathrm{d}^2 U_s(t)}{\mathrm{d}t^2} + (T_r + T)\frac{\mathrm{d}U_s(t)}{\mathrm{d}t} + U_s(t) = K_s X(t) \tag{6}$$

where

K_s = system transmission factor of the detector under study;
$X(t)$, $U_s(t)$ = input signal of the system and the system response to the output signal, respectively.

By determining from eqn. 5 the true value of the concentration at the inlet of the detector under study, $X(t_i)$, in an instant of time i when K_c, T and $U_c(t_i)$ are known, it is possible by solution of eqn. 6 to estimate the time constant T of the detector under study.

The solution of eqns. 5 and 6 will be expressed as a function of $X(t)$. In its turn, the form of this function depends on the method of insertion of the material into the carrier gas stream.

According to the method proposed for the determination of time constants, in order to establish the variation of the component concentration in the carrier gas with time, $X(t)$, an amount of the compounds to be analyzed is inserted into the carrier gas, which was washed out on passing through a neutral column, and the concentration distribution pattern at the detector inlet has the same form as the normal distribution (see Fig. 2), *e.g.*

$$X(t) = X(t)^{\mathrm{max.}} \cdot \mathrm{e}^{-[X(t)^{\mathrm{max.}} \cdot \sqrt{\pi}]^2 \cdot [t - t_M]^2} \tag{7}$$

where

$X(t)^{\mathrm{max.}}$ = maximum concentration of the compound in the peak;
t_M = yield time of the peak maximum.

The solution of eqns. 5 and 6, when the input signal is of this type, is possible only by numerical integration and also, in order to obtain reasonable accuracy, the function has to be expressed by a series with several terms, and for these reasons the calculations become very complicated.

It is possible to simplify eqns. 5 and 6 by approximation of eqn. 7, which is very convenient for practical calculations. Such an approximation of eqn. 7, ranging from a zero instant of time, is possible because the constant time quantity of the present detector is invariant and can be determined from the response of detectors both on a time interval $t_0 - t_k$ and on the interval $t_0 - t_i$. Therefore, there is no necessity to consider the behaviour of the detector under the influence of disturbances that have the form of a Gaussian curve in the interval from t_0 to t_k. It is sufficient to confine oneself to that time interval (*e.g.*, the interval t_0–t_a) within the limits of which a disturbance that has the form of a Gaussian curve can be approximated by a

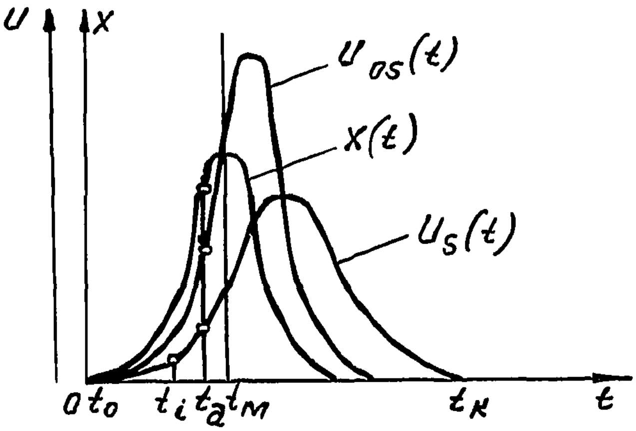

Fig. 2. Types of inlet action and output signals of the detection systems.

simplified function. Thus, the initial sections of the curves $U_{0s}(t)$ and $X(t)$ in the interval from t_0 to t_a (see Fig. 2) can be approximated with sufficient accuracy for practical purposes by quadratic functions, that is, the input function has the form $X(t) = at^2$.

The correctness of such an approximation was checked experimentally on a detection system consisting of an FID and a cathode-ray oscilloscope as a recording system.

Under the above experimental conditions and assuming that the concentration distribution of the compound at the inlets of both detectors has the form $X(t) = at^2$, eqns. 5 and 6 can be written as

$$T_{0r}\cdot\frac{\mathrm{d}U_{0s}(t)}{\mathrm{d}t} + U_{0s}(t) = K_{0s}at^2 \tag{8}$$

$$T_rT\cdot\frac{\mathrm{d}^2U_s(t)}{\mathrm{d}t^2} + (T_r + T)\frac{\mathrm{d}U_s(t)}{\mathrm{d}t} + U_s(t) = K_sat^2 \tag{9}$$

The solution of eqns. 8 and 9 for an instant of time i can be written as

$$U_{0s}(t_i) = K_{0s}a[t_i^2 - 2T_{0r}t_i + 2T_{0r}^2(1 - \mathrm{e}^{-t_i/T_{0r}})] \tag{10}$$

$$U_s(t_i) = K_sa\left\{\frac{[-Tt_i^2 + 2T^2t_i - 2T^3(1 - \mathrm{e}^{-t_i/T})] + [T_rt_i^2 - 2T_r^2t_i + 2T_r^3(1 - \mathrm{e}^{-t_i/T_r})]}{T_r - T}\right\} \tag{11}$$

From eqns. 10 and 11, the equation

$$\frac{U_{0s}(t_i)}{U_s(t_i)} = \frac{K_{0s}}{K_s}\left\{\frac{[t_i^2 - 2T_{0r}t_i + 2T_{0r}^2(1-\mathrm{e}^{-t_i/T_{0r}})][T_r - T]}{[-Tt_r^2 + 2T^2t_i - 2T^3(1-\mathrm{e}^{-t_i/T})] + [T_r^2 t_i - 2_r T t_i + 2T_r^3(1-\mathrm{e}^{-t_i/T_r}])}\right\} \quad (12)$$

is obtained. $U_{0s}(t_i)$ and $U_s(t_i)$ represent the ordinates of the peaks on diagrams for a flame ionization detector and the detector under study at an instant of time i. Eqn. 12 allows one to estimate the time constant of the detector under study by the method of successive approximations, provided that the time constants of the recorder, T_{0r} and T_r, and the system transmission factors, K_{0s} and K_s, are known.

Method II

According to this technique, the determination of the time constant of a detector is accomplished by the detector the time constant of which is known and has a defined quantity.

It is suggested that a flame temperature detector (FTD) should be used for this purpose as its time constant can be easily defined by a classical method by means of the instant areous change of the thermocouple position in the flame volume.

A schematic diagram of the arrangement for the measurement of the time constant of a chromatographic detector using a flame temperature detector and automatic compensation recorders is shown in Fig. 1b.

The equations describing the dynamic properties of detection systems can be expressed as follows:

(*i*) for a detection system with known dynamic properties:

$$T_{0r}T_0\cdot\frac{\mathrm{d}^2U_{0s}(t)}{\mathrm{d}t^2} + (T_{0r} + T_0)\frac{\mathrm{d}U_{0s}(t)}{\mathrm{d}t} + U_{0s}(t) = K_{0s}X(t) \quad (13)$$

(*ii*) for the system of the detector under investigation:

$$T_rT\cdot\frac{\mathrm{d}^2U_s(t)}{\mathrm{d}t^2} + (T_r + T)\frac{\mathrm{d}U_s(t)}{\mathrm{d}t} + U_s(t) = K_sX(t) \quad (14)$$

As, when using the accepted method of analysis, the material concentration distribution in the carrier gas stream at the inlets of both detection systems has the form of a Gaussian curve, then, approximating the initial section of the curve by the function at^2, we can write the solution of eqns. 13 and 14 in the form

$$U_{0s}(t) = K_{0s}a\left\{\frac{[-T_0t^2 + 2T_0^2t - 2T_0^3(1-\mathrm{e}^{-t/T_0})] + [T_{0r}t^2 - 2T_{0r}^2t + 2T_{0r}^3(1-\mathrm{e}^{-t/T_{0r}})]}{T_{0r} - T_0}\right\} \quad (15)$$

$$U_s(t) = K_sa\left\{\frac{[-Tt^2 + 2T^2t - 2T^3(1-\mathrm{e}^{-t/T})] + [T_rt^2 - 2T_r^2t + 2T_r^3(1-\mathrm{e}^{-t/T_r})]}{T_r - T}\right\} \quad (16)$$

Eqns. 15 and 16 are true for those instants of time in the limits of which the input function $X(t)$ is approximated by at^2.

Selecting the instant of time $t = t_l$ in the limits of the approximation interval and using the ratio of eqns. 15 and 16, the equation

$$\frac{U_{0s}(t_l)}{U_s(t_l)} = \frac{K_{0s}}{K_s} \times$$

$$\frac{\{[-T_0 t_l^2 + 2T_0^2 t_l - 2T_0^3(1 - \mathrm{e}^{-t_l/T_0})] + [T_{0r} t_l^2 - 2T_{0r}^2 t_l + 2T_{0r}^3(1 - \mathrm{e}^{-t_l/T_{0r}})]\}(T_r - T)}{\{[-T t_l^2 + 2T^2 t_l - 2T^3(1 - \mathrm{e}^{-t_l/T})] + [T_r t_l^2 - 2T_r^2 t_l + 2T_r^3(1 - \mathrm{e}^{-t_l/T_r})]\}(T_{0r} - T_0)} \tag{17}$$

is obtained.

From eqn. 17, by using the method of successive approximation, the time constant of the detector under study is determined, if T_{0r}, T_r, K_{0s}, K_s, $U_{0s}(t_l)$ and $U_s(t_l)$ are known. The last parameter represents the ordinates of the peaks on diagrams for the detector under study and the detector with a known time constant.

RESULTS AND DISCUSSION

An experimental check of Method I was carried out on the flame temperature detector. For this purpose, a cell was designed consisting of a flame temperature detector and an FID (Fig. 3).

For determining the static characteristics of the detectors in the experiments described below, a technique was used in which there was introduced into the carrier gas stream an amount of a binary mixture consisting of a carrier gas and any component, such that in the given length of time, an overall substitution of the binary mixture for the pure carrier gas would have taken place. In addition, a binary mixture of known composition was passing continuously through the detector. The response of the detector to a similar input signal is in the form of a trapezium, the height of which enables one to define the system transmission factor as a ratio of the height of the trapezium, expressed in millivolts, to the volume concentration of the component in the binary mixture, when the input concentration of the material is known. The system transmission factor found, K_s, enables one to determine the transmission factor of the detector as

$$K = \frac{K_s}{K_r} \tag{18}$$

The analyses on the superimposed detector were carried out in the following order. The sample of the material to be analyzed was inserted into the carrier gas and transported by it through the hollow column to the detector. When the sample being analyzed entered the detector, the flame temperature, which was measured with a thermocouple and registered by the recorder, was varied. At the same time, the ionization current was measured, which was amplified by an electrometric amplifier and registered by the compensation recorder.

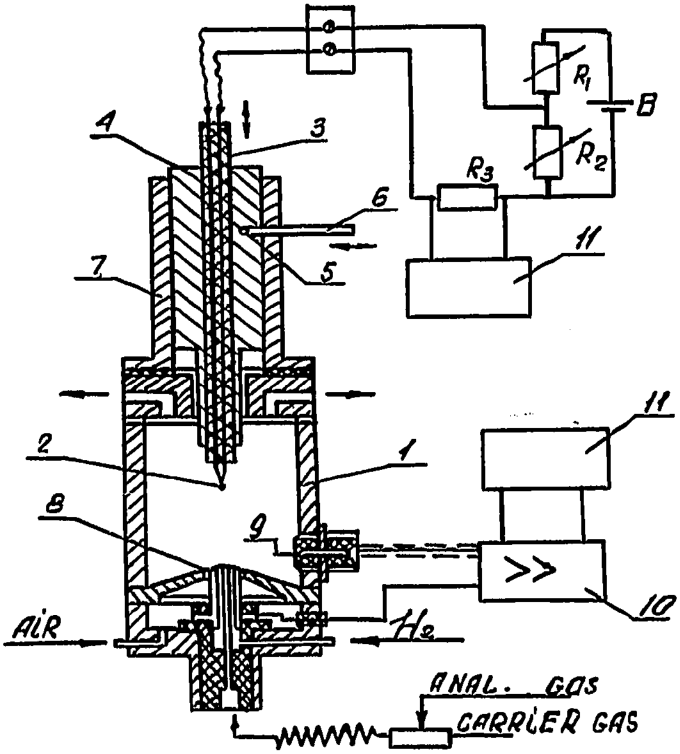

Fig. 3. Diagram of experimental arrangement. 1 = Body; 2 = thermocouple; 3 = china isolator; 4 = cut-off electrode; 5 = hole; 6 = rod; 7 = detection cylinder; 8 = burner; 9 = collecting electrode; 10 = electrometric amplifier; 11 = compensation recorder.

The two chromatographic peaks derived were superimposed on the baseline. As a time reference point, the starting point of the peak yield of the FID was taken. The processing of the superimposed curves for the purpose of estimating time constant of the FTD was accomplished as follows. Points t_1, t_2, t_3, etc., were selected on the time axis so that they fell in a time interval within the limits of which the front of the chromatographic peak of the FID was approximated by a quadratic function. It has been established experimentally that this section is limited by the ordinate, the height of which does not exceed 70–80% of that of the chromatographic peak. The ordinates $U_{0s}(t_i)$ and $U_s(t_i)$ were measured for every point and are given in columns 2 and 3 in Table I. Then, using the technique described above, the transmission factors of the detection systems were estimated (columns 4 and 5 in Table I). The time constants T_{0r} and T_r, determined from the experimental recovery characteristics, were 0.3 sec for the recorder of the FID and 1.2 sec for the recorder of the detector under study.

Substituting the numerical values of $U_{0s}(t_i)$, $U_s(t_i)$, t_i, T_{0r}, T_r, K_{0s} and K_s into eqn. 12 by the method of successive approximations, the time constant of the detector under study is found. The calculated results for selected instants of time are presented in column 6 in Table I. The time constant T_{av}, calculated as an average value from the values found (see column 7), is adopted as the time constant of the flame temperature detector under study.

TABLE I

RESULTS OF EXPERIMENTAL CHECK USING METHOD I

The results were obtained under the following conditions of analysis: carrier gas consumption (air), 2 l/h; hydrogen consumption, 2.5 l/h; air consumption, 15 l/h; sample analyzed, 0.16 ml of methane; recorder chart speed, 0.6 cm/sec.

t_i (sec)	$U_s(t_i)$ (mV)	$U_{os}(t_i)$ (mV)	K_s (mV/vol. %)	K_{os} (mV/vol. %)	T (sec)	T_{av} (sec)	T^* (sec)
7	0.056	31.2	0.112	20.5	3.22	3.12	3.04
9	0.120	55.2			3.25		
10	0.162	69.1			3.18		
11	0.218	82.2			3.05		
12	0.274	93.0			2.90		

In order to check the correctness of the method developed, the time constant of the FTD, determined by the time constant of its thermocouple, was estimated from the speeding-up curve of the thermocouple, which was taken by the instantaneous change of the thermocouple position in the flame volume. The change of thermocouple position in the flame volume was accomplished by inserting it into the flame.

As the signal of the flame temperature detector involves the temperature change of the thermocouple[6] in the case of a change of fuel component, then the recovery characteristic obtained in this manner can be considered as the response of the detection system to the stepwise change of the volume concentration of the fuel component in the carrier gas. Calculated according to the recovery characteristic the time constant of the detector under study, T^*, is presented in column 8 in Table I.

An experimental check of the correctness of Method II was carried out in two flame temperature detectors, one of them being under study, the other being a model. The results are presented in Table II.

The methods described can be used for the determination of the time constants of any detection device. In this case, it is necessary to select a total hydraulic resistance of the detector tract such that it would be equal to the total hydraulic resistance of the model detector tract (flame ionization or flame temperature detector). For example, the time constant of the thermoconductometric detector of an XL-4 chro-

TABLE II

RESULTS OF EXPERIMENTAL CHECK USING METHOD II

The results were obtained under the following conditions of analysis: carrier gas consumption (air), 2 l/h; hydrogen consumption, 3 l/h; air consumption, 15 l/h; sample analyzed, 0.4 ml of methane; recorder chart speed, 0.6 cm/sec; time constants of recorders, $T_r = T_{0r} = 1$ sec.

t_i (sec)	$U_s(t_i)$ (mV)	$U_{os}(t_i)$ (mV)	K_s (mV/vol. %)	K_{os} (mV/vol. %)	T_0 (sec)	T (sec)	T_{av} (sec)	T^* (sec)
7	0.1020	0.0715				2.46		
9	0.1910	0.1520				2.78		
11	0.3220	0.2680	0.1357	0.1820	6.50	2.90	2.89	3.04
12	0.3750	0.3300				3.10		
13	0.4480	0.4060				3.18		

matograph with a carrier gas consumption (air) of 2 l/h and a detector current of 9 mA, determined by the method described, was 1.18 sec.

REFERENCES

1 L. J. Schmauch, *Anal. Chem.*, 31 (1959) 225.
2 V. N. Lipavskii, *Zavod. Lab.*, 7 (1973) 788.
3 V. G. Zizin, *Tr. Bashkir. Nauch.-Issled. Inst. Pererab. Nefti*, No. 6 (1963) 152.
4 V. N. Lipavskii and V. G. Berezkin, *Zavod. Lab.*, 6 (1972) 657.
5 T. Johns and J. C. Sternberg, *Instrumentation in Gas Chromatography*, Centrex Publishing Company, Eindhoven, 1967, p. 179.
6 N. G. Farzane and L. V. Ilyasov, *Avtomaticheskie detectory gasov*, Izdatel stvo Energiya, Moscow 1973, pp. 68–75.