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APPLICATION OF GAS CHROMATOGRAPHY IN RESEARCH AND CONTROL OF PETROCHEMICAL PROCESSES

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SUMMARY

The problems of the application of industrial chromatographs connected with operating in production cycles, duration of the analysis and dynamic properties of the system for the preparation of the sample are discussed. Equations for obtaining the dynamic properties of the instrument, allowing the performance of the chromatograph as an automatic adjusted system to be estimated, are presented. Systematic data on the economic effects of the application of process gas chromatographs are discussed.

INTRODUCTION

Usually, pipelines in petrochemical plants contain multicomponent mixtures of gases or volatile liquids. Therefore, gas chromatography has proved to be the most effective method of analysis insofar as the application of automatic instrumentation is concerned, namely for transducers in the automatic control and regulation systems in the production process, as well as in the development of new production processes. Such instruments are known as process chromatographs.

A process chromatograph is one used for the analysis of fluid flowing through pipelines at industrial and research installations and operating in an automatic mode. A process chromatograph consists of units that permit the following operations: (a) sampling, including the preparation of samples, (b) gas chromatographic separation of samples into individual constituents, (c) detection of these constituents, (d) processing of the data obtained in the course of analysis, and (e) transmission of data to production control systems¹.

In the mid-1950s, the first automatic process chromatographs were introduced^{2,3} and the number of chromatographs incorporated into pipelines has been steadily growing ever since. For example, in 1960 there were some 500 automatic process chromatographs in operation in the U.S.A., and by 1964 their number had increased to almost 4,000 with 20-25% of the total number being adapted for use in automatic control systems^{2,4}.

In 1967, chromatographs accounted for 25% of all analyzers used in pipelines and their use predominated⁵.

The utilization of chromatographs in pipeline analysis systems permits the process to be substantially improved and increases the efficiency appreciably. In order to optimize the application of process chromatographs, however, a number of problems must be solved, some of which are characteristic of chromatographic analysis as a whole, while others are specific to the use of chromatographs with pipelines.

The wide variety of problems to be solved by process and laboratory chromatographs, the different methods of using the obtained data, possibilities of checking the reliability of these data by repetitive analyses, and the various operating conditions are the main factors that have resulted in the different appearances of laboratory and process chromatographs. A comparison of process and laboratory chromatographs is given in Table I.

The following are the specific requirements imposed on process chromatographs:

- (1) automatic preparation, selection and injection of samples into the chromatograph;
- (2) rapid determination of important components;
- (3) rapidity of analysis (short cycle);
- (4) good reproducibility and stability of the results;
- (5) simplicity and reliability in operation;
- (6) miniaturization of instrumentation;
- (7) explosion- and fire-proof characteristics;
- (8) provision for data storage and long-distance transmission facilities.

Most papers concerned with the application of automatic chromatographs in pipelines also deal with the technological and economic effects attained at particular points in a pipeline^{1,6-10}. These and other papers make it possible to define the main problems for which a solution by means of chromatographs will lead to the attainment of the required economic effects, namely:

- (1) reducing raw material losses;
- (2) increasing the yield of the finished product;
- (3) reducing the idle time of the equipment due to the low quality of raw materials;
- (4) minimizing the consumption of energy;
- (5) improving the quality of the finished product;
- (6) reducing the amount of sub-standard products obtained;
- (7) enhancing safety in operation and minimizing the number of accidents;
- (8) reducing analytical control costs.

The expenses incurred in purchasing, installing and setting into operation a chromatograph can be justified, depending on the point of application, within a few weeks to 8 months. As new and more advanced chromatographs make their appearance, it is possible to achieve the desired economic effects both by installing them at points where older models could not be used because of their incompatibility with the requirements imposed on the analytical control at those points and by using them instead of older models at those points of the pipeline which have already been subjected to analysis. In the latter case, the improvement in the process characteristics is due to the fact that the new chromatograph used instead of an older one possesses better parameters (accuracy, sensitivity, rapid response, etc.), thereby ensuring better control over a production process.

TABLE I
COMPARATIVE CHARACTERISTICS OF PROCESS AND LABORATORY CHROMATOGRAPHS

<i>Characteristic</i>	<i>Process chromatograph</i>	<i>Laboratory chromatograph</i>
Type of analysis	Quantitative analysis of a limited number of key components	Qualitative and quantitative analysis of the entire composition of the tested compound
Purpose of information obtained	For control of production processes	To determine composition of substances and for further calculations
Possibility of checking the data obtained by repetitive analysis	No	Yes
Method of data processing	Automatic	Manual or automatic
Time of data processing	Simultaneously with the analysis	After the analysis or simultaneously with it
Duration of analysis	In accordance with the control system requirements	No limits
Model	Explosion- and fire-proof	Standard
Place of installation	On a process facility, near to the source of the sample	In a laboratory. The chromatograph and source of sample are often separated in space and time
Sampling system	(1) Flow-through sampling system is obligatory (2) Mode of operation—continuous	(1) Usually no sampling system is used (2) Mode of operation—periodic
Sample introduction system	(1) The sample introduction system is constantly connected with the sample preparation system and ensures periodic sampling (2) The sample introduction system must ensure high reproducibility of sample volumes	(1) Usually only one sample is required (2) Usually high reproducibility of sample volumes is not required
Type of columns	(1) Usually use is made of packed columns with highly stable sorbents ensuring results that are reproducible over a long period of time (2) Multi-column arrangements with automatic switch-over of columns are often used	(1) Packed or capillary columns are used; requirements on sorbent stability are less stringent (2) Automatic switch-over is used comparatively less often
Column temperature conditions	Usually isothermal	Isothermal and with temperature programming
Detectors	Differential detectors with highly stable readings; very often a katharometer or a flame ionization detector	Differential and integral detectors of various types

TABLE II

ECONOMIC EFFICIENCY OF PROCESS CHROMATOGRAPHS IN THE ANALYSIS OF DIFFERENT MEDIA¹⁰

<i>Application</i>	<i>Medium analyzed</i>	<i>Capital investment (U.S.\$ × 1000)</i>	<i>Recoupment period (months)</i>
Alkylation	Feedstock, end-products	21.5	10
Alkylation	Reflux of butane and isobutane stripping column	21.5	6
Alkylation	Deisobutanizing agent	15.0	3
Gas trapping	De-ethanizing agent	15.0	1.5
Gas trapping	Propane	10.5	3
Gas trapping	Feedstock, end-products	10.5	12
Production of ammonia	Synthesis gas	8.0	6
Production of oxo-alcohols	Starting olefin, end-product	5.0	1
Production of oxo-alcohols	Hydrogenating agent	20.0	less than 12
Production of naphthalene	Hydrogen purifier	18.0	less than 12
Polymerization	Depropanizing agent, debutanizing agent, head fraction, etc.	21.0	10
Crude oil pressing	Depropanizing agent	21.0	7

Tables II, III and IV give data on the technological and economic efficiency of process chromatographs.

It should be noted, however, that the efficient application of chromatographs in a pipeline is possible only if the point at which analytical control is performed is properly selected from the point of view of technological requirements, and if the data obtained as a result of such an analysis is properly processed. The decision as to which

TABLE III

ECONOMIC EFFICIENCY OF PROCESS CHROMATOGRAPHS IN DIFFERENT APPLICATIONS

<i>Application</i>	<i>Initial costs, (roubles × 1000)</i>	<i>Annual saving, (roubles × 1000)</i>	<i>Recoupment period (months)</i>
Feedstock and contact gas lines in production of isoprene rubber	6.0	10.0	7
Control of impurity content in ethane-ethylene fraction	6.0	4.2	18
Gas composition control in production of divinyl	6.0	39.8	2
Sulphuric acid alkylation plant	6.0	6.1	12
Determination of hydrogen sulphide content in gaseous mixtures	6.0	15.7	5
Divinyl rectification plant	6.0	17.6	4
Butane fraction sampling line	6.0	28.5	2.5
Adsorption column stripping line	6.0	115.0	0.5
Isoamylene-isoprene fraction composition control	6.0	17.3	4
Azeotropic distillation plant	6.0	29.3	2.5

TABLE IV
ECONOMIC EFFICIENCY OF PROCESS CHROMATOGRAPHS IN DIFFERENT APPLICATIONS

<i>Application</i>	<i>Factors contributing to higher efficiency</i>	<i>Initial costs (roubles × 1000)</i>	<i>Annual saving (roubles × 1000)</i>	<i>Recoupment period (months)</i>
Gas fractionating plant. Adjustment of product separation in butane and isobutane columns	(a) Reducing butane losses due to entrainment with propane fraction; (b) reducing butane losses due to entrainment with isobutane fraction	9.0	49.2	2.5
Ethylene-sulphuric acid hydration plant. Maintaining maximum content of ethylene in the adsorber waste gas	Reducing ethylene losses in waste gas	9.0	42.0	3
Production of divinyl. Adjustment of the absorption process	(a) Reduction in the amount of C ₂ and C ₃ hydrocarbons fed for circulation; (b) additional extraction of butane and butylenes from stripped gas	9.0	59.9	2
Production of isopropanol. Control of C ₄ content in propane-propylene fraction used for the production of isopropanol	(a) Reduction in idle time in the isopropanol production plant due to low quality feed stock; (b) reduction in analytical control costs	9.0	25.4	4
Gas fractionating plant. Impurity control in <i>n</i> -butane taken from the butane column still	Raising the quality of <i>n</i> -butane	9.0	34.8	3
Production of butyl rubber. Control of isoprene content in direct charge	(a) Reduction in the yield of sub-standard rubber; (b) reduction in analytical control costs	12.0	35.2	4
Plant for contact decomposition of ethanol into divinyl. Control of content of ethanol contact decomposition gases	Increase in the yield of divinyl	17.0	17.5	12
Production of synthetic fatty acids. Control of content of C ₇ -C ₉ fatty acids	Increase in the yield of C ₇ -C ₉ fatty acids	17.0	35.4	6

point should be used for analytical control should preferably be taken only after extensive control experimental studies have been conducted with the aid of a stationary or portable chromatograph.

When switching over from a laboratory to a process chromatograph, account should also be taken of the specific conditions under which the latter will operate when incorporated into a pipeline. The sorbent should, in this instance, have a high stability, and the duration of the analysis should conform to the requirements imposed on the particular system being controlled¹¹.

Specific problems encountered in the application of process chromatographs are considered below.

EVALUATION OF THE LAG IN OBTAINING INFORMATION BY THE USE OF PROCESS GAS CHROMATOGRAPHS

The information on the volumetric composition of a mixture obtained from the process chromatograph used as a transducer in a controlled system corresponds to the state in which the system was at the moment preceding the analysis. The lag between removing a sample from the process stream and obtaining the required information is determined by the dynamic properties of the chromatograph and depends on the time period during which a sample is delivered to the instrument, prepared and analyzed, and also on the cyclic nature of the operation of the instrument.

Such a lag in obtaining information results in the deviation of pre-set parameters, impairs the quality of control and affects the stability of the system. Oscillatory phenomena take place and the system may become unstable¹². The most essential problem in switching over from laboratory analysis to on-line analysis, from the point of view of the quality of process control, is to minimize the lag in obtaining the information required for control purposes.

The adverse effect of this information lag on the quality of control and the considerable deviations that arise from it can be illustrated by the following example.

Let us assume that the composition of a product at the outlet of a controlled system is maintained constant by means of an automatic control system in which a chromatograph is used as a transducer. If we assume that the slow response and lag that take place throughout the system are non-existent in the example under consideration, the range of regulating the composition of the product will depend on the dead zone of the chromatograph and a control signal will be sent at an instant t_1 (Fig. 1).

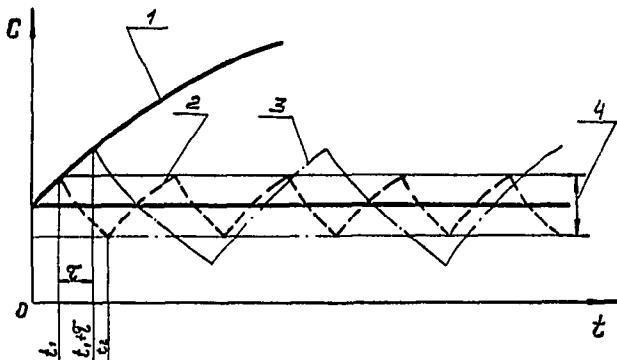


Fig. 1. Variation in the quality of a product at the outlet of a pipeline as a function of the information lag in the control system. 1, Variation in quality in the case of deviations in the control system; 2, variation in quality in the case of absence of an information lag in the control system; 3, variation in quality in the case of an information lag in the control system; 4, chromatograph dead zone.

For a lag τ in obtaining information, the control signal will be sent at a time $t_1 + \tau$ and, as a result, the deviation of the composition from a pre-set level becomes more pronounced, thus affecting the production process.

The lag in obtaining information also affects the stability of a closed control system and may give rise to oscillatory processes and loss of stability.

A decrease in the stability limits of a system resulting from an increasing lag in obtaining information can be best seen if use is made of the Nyquist criterion for evaluating stability, in accordance with which a closed system is considered to be stable if the frequency transfer locus of the open system does not cover the point that has coordinates $(-1, j0)$.

Assume that a system has, without taking the lag into account, a frequency transfer function $W(j\omega)$, which is a complex number:

$$W(j\omega) = A_o(\omega)e^{j\psi(\omega)} \quad (1)$$

where $A_o(\omega)$ is the frequency transfer function modulus and $\psi(\omega)$ is the frequency transfer function phase (argument). The locus of the transfer function is shown in Fig.

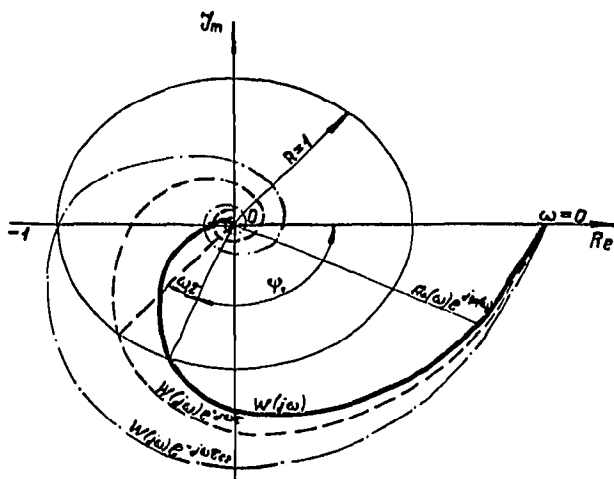


Fig. 2. Effect of information lag on the position of the frequency transfer locus of the control system.

2. It does not cover the point $(-1, j0)$ and therefore the system is stable. When a lag takes place, the frequency transfer function of the system is written as follows:

$$W(j\omega)e^{-j\omega\tau} = A_o(\omega)e^{j(\psi - \omega\tau)} \quad (2)$$

where τ is the time of lag.

It can be seen from eqn. 2 that the presence of the lag factor does not affect the modulus but rotates the whole locus of the frequency transfer function, bringing it closer to the critical point $(-1, j0)$, thus reducing the system phase stability limits.

With given conditions, one can determine the lag at which the system will be on the boundary of stability. Having drawn a circumference with a unit radius, let us determine the point of the frequency transfer locus with a modulus equal to unity. Let the frequency corresponding to this point be ω_1 , and the respective phase be ψ_1 . The system is on the boundary of stability when the point with a modulus equal to unity has coordinates $(-1, j0)$, due to the rotation of the locus in the case of a lag, which

corresponds to a phase equal to $-\pi$. Hence, the conditions of boundary stability can be written as follows¹³:

$$\begin{aligned}\psi_1 - \omega_1 \tau_{cr} &= -\pi \\ \tau_{cr} &= \frac{\pi + \psi_1}{\omega_1}\end{aligned}\quad (3)$$

where τ_{cr} is the critical lag at which the system is on the boundary of stability.

The permissible lag in obtaining information is determined in each particular instance by the properties of the system being controlled, the control system and the desired characteristics of the production process. Oglesby and Hobbs¹⁴, for example, described the effect of the duration of the analysis cycle of a chromatograph used as a transducer in the control system of a rectification column on the quality of control. Studies of a control system with analysis cycles of different durations, conducted with the aid of an analogue computer, indicated that the periodicity of sampling influences the quality of control. In the event of a load disturbance, it will take almost twice as long to maintain the composition of a medium at a pre-set level with the aid of an analyzer that has a 4-min analysis cycle as with the aid of an analyzer that has a 1-min cycle. The quality of control is considerably impaired when the duration of an analysis cycle exceeds 4 min.

Thus, the rapid response of a chromatograph, determining the lag in obtaining information, is one of the most critical characteristics of a process chromatograph, and in most instances it is precisely this factor that is taken into account when a decision is being made as to the suitability of a particular instrument for use at a particular point on a pipeline. This has been emphasized in a number of papers on the application of process chromatographs^{15,16}.

LAG IN OBTAINING INFORMATION FROM A CHROMATOGRAPH WITHOUT TAKING INTO ACCOUNT THE LAG DUE TO THE PREPARATION OF SAMPLES

This lag is determined by the duration of analysis, cycling of the operation of the chromatograph and, when the results of the analysis are calculated manually, the time required to carry out such calculations. Here the duration of analysis is the time period from the introduction of a sample to the moment when the required information is obtained, and a cycle is the time period between two consecutive sample injections. Both the duration of the analysis and that of the cycle depend largely on the method of calculating the results of the analysis that is used. For example, if the calculation of the concentration of a component of a mixture is performed relative to the peak height of the principal component, the duration of analysis is equal to the retention time of the principal component, while the duration of a cycle may be substantially reduced by back-flushing or partial flushing. However, if the calculation of this concentration is effected by internal normalization, the duration of analysis is equal to the emergence time of all the components of the mixture, as such a calculation is based on data concerning the peak areas of each component.

Depending on the purpose for which the information is intended, the following methods of calculation of the results of analysis obtained by means of automatic process chromatographs can be used: absolute calibration, *i.e.*, determination of the

concentration of principal components by the heights or areas of their peaks, and internal normalization; both methods permit the use of electronic computers.

The method of absolute calibration consists, together with the analysis of a process mixture, in the analysis of a calibrating sample containing principal components of known concentration. Calibration (check analysis) is usually performed with strict periodicity, normally at 10-day intervals. Therefore, the calculation of the concentration can be performed immediately after the emergence of the principal component. As such a calculation is performed automatically and rapidly compared with the duration of analysis, in most instances the time of calculation can be disregarded. Then the time during which information is obtained (duration of analysis) can be taken, when calculations are performed relative to peak heights, as being equal to the retention time of the principal component and, when calculations are performed relative to peak areas, to the lifetime of an entire peak of the principal component. In some instances, when the accuracy of the results is especially important or when it becomes difficult to maintain certain parameters constant over a long period of time, calibration is performed after each analysis of the process mixture and the principle peak of the calibrating mixture is compared with that of the process mixture. In such a case, one operating cycle of the instrument includes both the analysis of the process mixture and the immediately following analysis of the calibrating sample. The calculation of the concentration of the principal component in this instance is performed only after the occurrence of a corresponding peak in the calibrating mixture.

When the concentration is calculated by internal normalization, the time period during which the required information is obtained, without taking into consideration the time of calculation, is equal to the lifetime of all the peaks in the mixture.

Thus, at the instant when the concentration of the components of the analyzed mixture is being determined, the information emanating from the chromatograph is characterized by a certain lag with respect to the composition of the mixture at the control point, this lag being equal to:

$$\tau_{\min.} = t_k \quad (4)$$

where $\tau_{\min.}$ is the lag associated with the information emanating from the chromatograph at the instant when the analysis is completed, and t_k is the flow time of the information.

The information obtained in the course of the analysis is stored and used for process control purposes until new information is obtained from the next analysis cycle. By that time, the lag in obtaining the information has reached its maximum and becomes equal to:

$$\tau_{\max.} = t_k + T_c \quad (5)$$

where $\tau_{\max.}$ is the lag associated with the information at the moment of its being updated and T_c is the duration of an analysis cycle.

The mean information lag time can therefore be obtained from the above expressions:

$$\tau_{\text{mean}} = \frac{\tau_{\min.} + \tau_{\max.}}{2} = t_k + \frac{T_c}{2} \quad (6)$$

Fig. 3 shows the lag associated with the information obtained from a chromatograph without taking into account the lag due to the sampling system, in accordance with eqns. 4 and 5 for the case of calculating the concentration relative to the peak height of a principal component.

It is precisely the mean value of lag that characterizes the dynamic properties

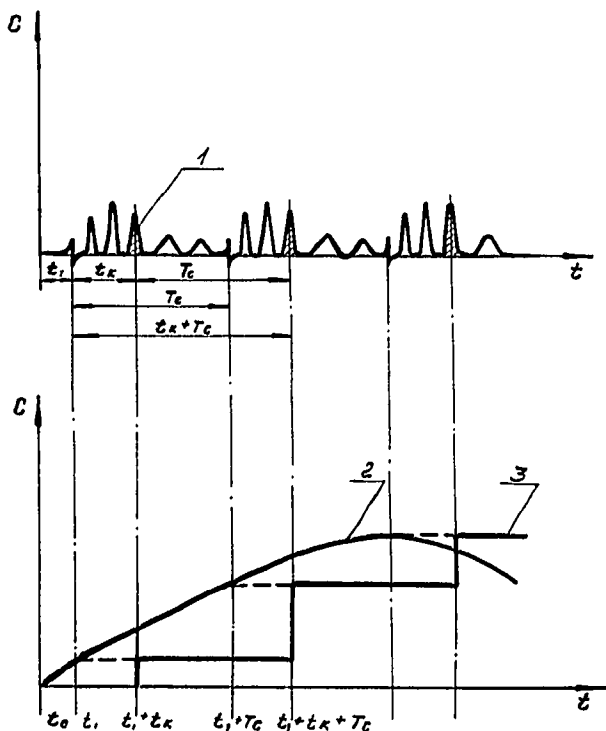


Fig. 3. Effect of information lag on information error. 1, Reference component; 2, concentration of reference component in the analyzed mixture at the sampling point; 3, chromatograph signal.

of a chromatograph serving as a component of an automatic control system, and it is this value that allows a decision to be taken as to whether a particular chromatograph can be incorporated into a particular pipeline.

The value of the lag in eqn. 6 can be obtained more accurately if account is taken of the amplitude-frequency characteristics of a chromatograph that determine the lag in obtaining information, namely the column and the signal storage unit. The column is responsible for pure lag with t_k , while the signal storage unit introduces a lag equal to $T_c/2$ (refs. 17 and 18).

As the results of a chromatographic analysis correspond to the composition of a process mixture at the instant of sampling, they are certainly different from the actual composition of the mixture at the instant the analysis is completed. The difference between the chromatograph readings and the actual content of the components in the process mixture being analyzed at a given moment can be defined as the error of the information received from the chromatograph. Fig. 3 also shows the effect of lag on

this error. The greater the lag, the less reliable is the information on the composition of the mixture being analyzed.

In accordance with eqn. 6, the lag in obtaining information from a chromatograph can be reduced by decreasing either the information flow time (t_k) or the analysis cycle (T_c). The information flow time can be reduced by using separation columns with a high specific efficiency, which is affected only slightly by the carrier gas flow-rate and enables the mixture to be separated more rapidly. Sometimes the duration of an analysis cycle is also reduced. In some instances, a more rapid information flow can be attained by using highly effective micro-packed columns whose efficiency remains virtually the same no matter how high the carrier gas flow-rate may be.

The duration of an analysis cycle can also be reduced, with given column efficiency and analysis conditions, by employing back-flushing and multi-column arrangements that ensure the removal of less important components, etc. At present, a large number of multi-column systems are known¹⁹ and some of them have been utilized in automatic process chromatographs and applied successfully in pipelines. For example, the Soviet chromatograph XII-499 utilizes systems that include two or three separation columns automatically switched over in the course of analysis²⁰.

From the point of view of minimizing the lag in obtaining information, reducing the information flow time appears to be a more effective measure than reducing the duration of an analysis cycle (see eqn. 6).

Consider the following example. Let an analysis be characterized by the parameters $t_k = 10$ min and $T_c = 20$ min. Then, $\tau_{\text{mean}} = 10 + 20/2 = 20$ min. If, for instance, the use of a multi-column arrangement has made it possible to reduce the duration of an analysis cycle by half, to $T_c' = 10$ min, then $\tau'_{\text{mean}} = 10 + 10/2 = 15$ min, and if the information flow time has been reduced by half, due to the high efficiency of the column, to $t_k'' = 5$ min, then, if the reduction of an analysis cycle duration to $T_c'' = 10$ min is taken into account, $\tau_{\text{mean}} = 5 + 10/2 = 10$ min.

In most instances, the lag in obtaining information can be reduced most effectively by increasing the efficiency of the columns, and, at the same time, employing multi-column arrangements.

EFFECT OF THE SAMPLE PREPARATION SYSTEM ON THE DYNAMIC CHARACTERISTICS OF A CHROMATOGRAPH AND ON THE LAG IN OBTAINING INFORMATION

Regardless of the position of an analytical control point in a pipeline, the following requirements are imposed on the sample preparation system: (a) a sample should be delivered to the chromatograph with a minimum delay; (b) the preparation of a sample, consisting of purifying the sample, adjusting its pressure, etc., should be performed so as to render it adequate, *i.e.*, to ensure the identity of the composition of the controlled medium at the sampling point and at the inlet to the chromatograph.

The preparation of a sample usually consists of the following six operations: adjusting the pressure of the sample, removing mechanical impurities from it, drying it, removing sulphur, resins and other noxious substances, heating or cooling the sample, and evaporating or condensing it. Depending on the requirements imposed on a particular sample preparation system, the sequences of the above operations may vary.

The problem of preparing a high-quality sample can be solved successfully in

most instances and there are many papers dealing with the development and application of sample preparation systems for particular control points. A functional method of designing sample preparation systems has been proposed which enables each of the above operations to be performed by special functional units^{21,22}.

However, when preparing a sample, the composition of the controlled medium may alter, which makes the quality of the sample less reliable and adversely affects the characteristics of the control system.

The composition of a sample may alter for two reasons. The first is that the composition of the controlled medium may alter during the course of preparation of a sample, for example, due to the condensation of heavy components from a gaseous sample or evaporation of light components from a liquid sample, or as a result of chemical transformations of thermolabile components during heating, etc. Such alterations in composition can be described as static because they may occur even when a mixture with a constant composition flows through the sample preparation system. The second reason is that the continuously varying composition of the controlled medium is averaged in the free spaces (volumes) of the system components, with the result that the instantaneous composition of the medium is different at the inlet and outlet of the system. Such alterations occur only when the composition of the controlled medium varies and, therefore, they can be referred to as dynamic. Both dynamic and static alterations cause errors in the results of the chromatographic analysis of a mixture at a given control point. The magnitude of these errors depends on the properties of the system and on the nature of the variations in the composition at the point of sampling.

Static errors have been studied extensively and are at present taken into consideration when designing sample preparation systems and their components. Dynamic errors have not been studied as carefully and are not always taken into account when a chromatographic system is adapted to a different control point, although some papers have described the averaging of mixture compositions due to free spaces in the components of the sample preparation system^{23,24}. Experimental studies on the dynamic characteristics of a standard sample preparation system in a conventional chromatograph²⁵ point to the dependence of its amplitude-frequency characteristic on the volume flow-rate of the medium. However, the results obtained by Biryukov *et al.*²⁵ are too specific and do not allow the properties of individual components of the system to be properly evaluated and cannot be used for designing other sample preparation systems.

In this connection, it is advisable to develop an analysis technique for determining the dynamic characteristics of the components of a sample preparation system and to devise a method of calculating, on the basis of these characteristics, the properties of a sample preparation system as a whole.

If it is assumed that the inflowing medium is completely mixed, in the free space of a component of a sample preparation system, with the medium already present, and that the concentration of the medium varies stepwise at the inlet, we may write:

$$V \cdot \frac{dC}{dt} = QC_0 - QC \quad (7)$$

where V is the free space (volume) of the component of the sample preparation system,

C_0 is the new value of the volume concentration at the inlet and C is the volume concentration at the outlet at a given moment.

From eqn. 7, we can determine the value of the outlet concentration as follows:

$$C = C_0 \left(1 - e^{-\frac{t}{T}} \right) \quad (8)$$

where T is the time constant characterizing the rate of variation of the composition in the component of the sample preparation system:

$$T = \frac{V}{Q} \quad (9)$$

It should be noted that the process of averaging in the case under consideration is similar to that in the case when the concentration decreases exponentially, according to Lovelock's method of measuring the linearity of detectors²⁰.

However, the components of the sample preparation system are not provided with any means for mixing the inflowing medium, and complete mixing is therefore not likely to take place in all instances. In the absence of complete mixing, the time constant will most probably decrease compared with that calculated from eqn. 9, and an additional lag will occur at the outlet that may be referred to as a capacitive lag. In fact, when the concentration at the inlet of a component of the sample preparation system varies stepwise, two extreme cases are possible: (1) complete mixing of the medium in the component, and (2) no mixing at all. In the first instance, a variation in the inlet concentration is accomplished by an exponential variation of the outlet concentration in accordance with eqn. 8, and no pure lag takes place. In the second instance, owing to the absence of mixing, the new concentration will reach the outlet after

$$\tau_c = \frac{V}{Q} \quad (10)$$

where τ_c is the capacitive lag.

Evidently, for components of the sample preparation system of different shapes and with different flow-rates, the process will develop under some intermediate conditions rather than under the extreme conditions described above, *i.e.*, incomplete mixing will be accompanied by a certain capacitive lag. It should be noted that capacitive lag was mentioned by Shall²². Stölzel²³ suggested that capacitive lag should be taken into account only provided the length:diameter ratio of a component of the sample preparation system is equal to or greater than 8. Unfortunately, neither of these papers gives any design ratios from which one could calculate the capacitive lag and time constant for particular components of a sample preparation system and their operating conditions.

In an effort to evaluate the time constant and capacitive lag that occur in real components of sample preparation systems, we obtained these values experimentally. Taking into consideration that T and τ_c are affected by the absolute size of a component of a sample preparation system and the flow-rate of the medium through it, experiments were conducted on life-size model systems with a free space (volume) of 90–300 cm³ and a flow-rate of medium of 5–15 l/h. Each model was made in the form of a cylinder with a length:diameter ratio of 2.5–30. The experiment consisted of

determining transient characteristics (functions), *i.e.*, in measuring variations in the outlet concentration with time with stepwise variations in the inlet concentration. The transient function was then used for the calculation of the dynamic characteristics of the component of the sample preparation system.

The model tested was mounted on a test bench and a switching device was connected to its inlet so as to ensure stepwise variations in the inlet concentration by changing over two flows. Connected to the outlet of the model was a chromatographic detector for determining the composition of the medium flowing through the model at its outlet. The signal from the detector, which represented the transient function, was recorded by a recording device. Media with different concentrations were fed into the model from two containers through a flow-rate stabilizing system. The test bench was adapted to run two or more models arranged in series. The mixtures nitrogen-propane (3%) and nitrogen-helium (1%) were fed alternately into the model.

The results of processing the transient characteristics suggest that transient processes for all models are well described by a first-order equation and that the variation in the outlet concentration is in full agreement with eqn. 8; the time constant, with a length:diameter ratio of the model of $\eta = l/d \leq 5$, can be determined by eqn. 9, the capacitive lag being, in this instance, virtually non-existent; when the length:diameter ratio of the model exceeds 5 ($\eta = l/d > 5$), the actual values of the time constant (T_r) become less than those calculated from eqn. 9 for the case of complete mixing

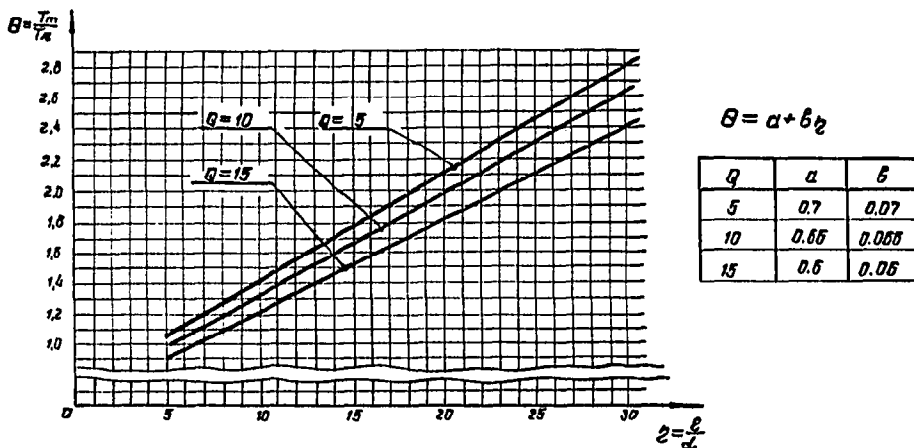


Fig. 4. Dependence of the degree of mixing of a product in the free space of a component of a sample preparation system on the shape of the component.

(T_m); at the same time, a capacitive lag appears; for $\eta = 5-30$, Fig. 4 shows graphs of the relationship $\theta = T_m/T_r$ for flow-rates of 5, 10 and 15 l/h.

The actual time constants are well approximated by the expression

$$T_r = \frac{T_m}{a + b\eta} \quad (11)$$

the values of coefficients a and b being given in Fig. 4.

The results indicate that, in accordance with eqn. 11, the time constant of a

component of a sample preparation system having a length:diameter ratio from 5 to 30 can be calculated from the equation

$$T_r = \frac{V}{Q} \cdot \frac{l}{a + b\eta} \quad (12)$$

The capacitive lag increases with η . The process develops as follows if the gaseous medium passes through part of the volume (ΔV) without mixing:

$$\Delta V = V \left(1 - \frac{T_r}{T_m}\right) \quad (13)$$

the capacitive lag being

$$\tau_c = \frac{\Delta V}{Q} = \frac{V}{Q} \cdot \left(\frac{T_m - T_r}{T_m}\right) = T_m - T_r \quad (14)$$

The experimental values of τ_c are in good agreement with those calculated from eqn. 14. Fig. 5 shows examples of transient curves for two models of the same

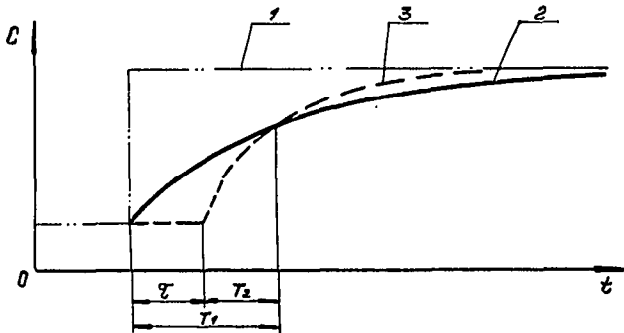


Fig. 5. Transient characteristics of components of a sample preparation system equal in volume but different in size. 1, Variation in concentration at the component outlet; 2, variation in concentration at the outlet of a component with $l/d < 5$; 3, variation in concentration at the outlet of a component with $l/d > 5$.

volume but different in shape. As a result, the transient process in one model occurs without a capacitive lag, while in the other, the capacitive lag is present but the time constant is lower.

Tests carried out on several models interconnected in series by short pipes in a similar manner to components of sample preparation systems have shown that they operate like a single model with the sum of the individual parameters. Therefore, for a sample preparation system, the time constant is

$$T_r = \sum_{i=1}^n T_i \quad (15)$$

where T_i is the time constant of the i th component (model), while the capacitive lag can be written as:

$$\tau_c = \sum_{i=1}^n \tau_{ci} \quad (16)$$

where τ_{ci} is the lag conditioned by the i th component (model).

Now consider the following example. Let the sample preparation system consist of three components with large internal volumes (free spaces). The parameters of these components are as follows:

$$\text{1st component: } l_1 = 300 \text{ mm, } d_1 = 35 \text{ mm, } V_1 = 290 \text{ cm}^3, \eta_1 = \frac{l_1}{d_1} = 8.6.$$

$$\text{2nd component: } l_2 = 150 \text{ mm, } d_2 = 50 \text{ mm, } V_2 = 295 \text{ cm}^3, \eta_2 = \frac{l_2}{d_2} = 3.$$

$$\text{3rd component: } l_3 = 420 \text{ mm, } d_3 = 28 \text{ mm, } V_3 = 260 \text{ cm}^3, \eta_3 = \frac{l_3}{d_3} = 15.$$

If the flow-rate of the gaseous medium through the system is $Q = 10$ l/h, then, as can be seen from Fig. 4, $\theta_1 = 1.22$, $\theta_2 = 1.0$ and $\theta_3 = 1.64$.

From eqn. 9, we calculate that $T_{m1} = \frac{V_1}{Q} = \frac{290}{16.6} = 17.4$ sec, $T_{m2} = \frac{V_2}{Q} = \frac{295}{16.6} = 17.7$ sec and $T_{m3} = \frac{V_3}{Q} = \frac{260}{16.6} = 15.6$ sec; then, in accordance with eqn. 11, the actual constants are $T_{r1} = \frac{T_{m1}}{m2} = 14.3$ sec, $T_{r2} = T_{m2} = 17.7$ sec

and $T_{r3} = \frac{T_m}{3} = 9.5$ sec, and the capacitive lag, in accordance with eqn. 14, is

$$\tau_{c1} = T_{m1} - T_{r1} = 3.1 \text{ sec; } \tau_{c2} = 0; \tau_{c3} = T_{m3} - T_{r3} = 6.1 \text{ sec.}$$

The total time constant of the sample preparation system in accordance with eqn. 15 will be $T_r = T_{r1} + T_{r2} + T_{r3} = 41.5$ sec, while the total capacitive lag will be $\tau_c = \tau_{c1} + \tau_{c3} = 3.1 + 6.1 = 9.2$ sec.

The total lag in a sample preparation system also includes, in addition to the capacitive lag, the delivery lag due to the time required to deliver a sample to the instrument:

$$\tau_p = \frac{\pi d^2}{4} \cdot \frac{l}{Q} \quad (17)$$

where d and l are the diameter and length, respectively, of the connecting pipe.

The total lag in obtaining information due to the sample preparation system is:

$$\tau_s = \tau_p + \tau_c \quad (18)$$

Thus, one can calculate the time constant and capacitive lag of each component of the sample preparation system and, by summing them, the total time constant and capacitive lag of the entire system. The total lag associated with the information emanating from a chromatograph can be determined as the sum of the lag due to the sample preparation system (eqn. 18) and the lag due to the chromatograph itself (eqn. 6):

$$\tau_g = \tau + \tau_c + \tau_p \quad (19)$$

APPLICATION OF CHROMATOGRAPHS IN MICRO-PILOT PLANTS

The development of novel production processes involves much research and requires that each stage of the development be checked experimentally. The use of micro-pilot plants instead of conventional pilot plants for this purpose makes it possible to cut down substantially the research time and equipment costs, which, in turn, has a considerable economic effect. Therefore, the number of micro-pilot plants in use is steadily increasing. For example, 16 micro-pilot plants were employed as early as 1967 by the American Oil Company²⁷. Comparative analyses of the experimental data obtained in pilot and micro-pilot plants indicate that most experimental work can be performed in micro-pilot plants without affecting the reliability of the data obtained²⁷. The amount of information obtained in a micro-pilot plant is substantially greater, while the time necessary to obtain this information is much less than in conventional pilot plants, which is why automated micro-pilot plants have gained wide acceptance in recent years as effective means for developing individual stages of new production processes. In addition, in many instances, in order to evaluate properly the results obtained, one should know the composition of the substances at the outlet of a micro-reactor. As these substances are multi-component compounds in most instances, chromatographs appear to be the most suitable instruments for analyzing their composition.

The following characteristic features of micro-pilot plants should be taken into account when selecting the most appropriate chromatograph for a particular purpose:

(a) micro-pilot plants are intended primarily for research, and therefore the qualitative and quantitative composition of analyzed media may vary to a considerable extent even during the period of developing one production process;

(b) analyzed substances are usually multi-component compounds that are difficult to separate;

(c) in order to optimize research activity, a number of reactors operating in parallel are incorporated into micro-pilot plants (multi-reactor micro-pilot plants); it is expedient that the composition of the medium at the outlet of all the reactors should be determined by means of a single chromatograph;

(d) micro-pilot plants operate continuously in an automatic mode, *i.e.*, they simulate actual operating conditions;

(e) the flow-rate of the medium is, in terms of volume, low;

(f) micro-pilot plants are compact enough to be used in a laboratory.

Consideration of the above characteristic features of micro-pilot plants makes it possible to define the basic requirements for a chromatograph. It should be an automatic instrument, capable of recording components that belong to different classes of substances, and operating within a wide concentration range. The instrument should be compact and quick-acting with a sufficiently short analysis cycle. The sample preparation systems are much simpler in this case than in chromatographs used on-site, but the samples are small. The analyzer need not be explosion-proof. In addition to recording the analytical results in the form of a standard chromatogram, the apparatus should also be capable of automatically calculating and recording the values of concentrations of principal components.

The above requirements can be most successfully met by a chromatograph unit with high-performance micro-packed columns. By using these columns, one

can have a compact instrument characterized by high efficiency and rapid action. Moreover, such an instrument with micro-columns has the following advantages from the view point of design: (a) small volume, (b) a simpler thermostat and (c) smaller weight.

An automatic chromatograph has been developed to meet the requirements imposed on a micro-pilot plant based on micro-packed columns and possesses the following characteristic features.

The chromatograph is built around a single-column arrangement that ensures complete analysis of a sample with recording of all components. As far as automation is concerned, this chromatograph is similar to process chromatographs and ensures automatic removal of gaseous samples from a pipeline and their injection into the column, correction of the base-line, and switching over of recorder scales to permit recording, within the range of measurement, of components that differ sharply in concentration. A special computer has also been provided for automatically calculating, on the basis of analytical results, the concentrations of three principal components. In order to facilitate calibration and checking of the instrument, provision has been made for manual injection of liquid samples. A universal thermal conductivity cell is used as a detector so as to permit operation with micro-packed columns, namely a micro-katharometer. The chromatograph is modular and the analytical unit can be incorporated into the plant itself, while the electronic unit can be arranged in a separate cabinet.

The above chromatograph has been tested in an automated micro-pilot plant designed at the All-Union Petroleum Refining Research Institute to study the degree of deactivation of catalysts in hydrocatalytic cracking. The reactor of the plant can operate at pressures up to 300 atm and at temperatures up to 700°. Sampling is performed automatically.

The chromatograph was used to analyze the products of hydrocracking of heptane and toluene. Fig. 6 shows a chromatogram of the analysis of the products of

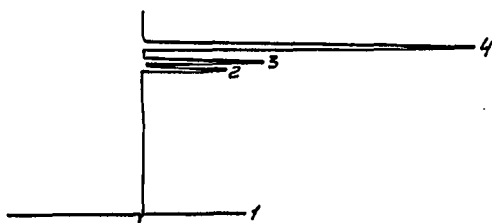


Fig. 6. Chromatogram obtained from the analysis of the products of hydrocracking of heptane. 1 = Sample injection; 2 = 2-methylhexane; 3 = 3-methylhexane; 4 = *n*-heptane.

hydrocracking of heptane. The analysis was performed under the following conditions: column temperature, 135°; carrier gas flow-rate, 2.4 cm³/min; carrier gas, nitrogen; column length, 8 m; column diameter, 1.0 mm; sorbent, Celite 545 (0.11–0.13 mm) and 5% of squalane. The efficiency per metre of column length was 2,100 theoretical plates.

The chromatograph was tested in a micro-pilot plant over a period of 1 year and the positive results obtained were sufficient proof of the efficiency of the method.

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