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APPLICATIONS OF GAS CHROMATOGRAPHY IN PETROLEUM CHEMISTRY*

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SUMMARY

Basic trends in and some prospects for applications of gas chromatography in petroleum chemistry are considered.

INTRODUCTION

The petrochemicals industry is developing rapidly throughout the world. Liquid and gaseous hydrocarbons used in chemical processing are the raw materials for the manufacture of more than half of the chemical products in industrial countries. The use of gas chromatography in petroleum chemistry is one of its most important technical applications and has developed for several reasons. Firstly, the field of application of gas chromatography in petroleum chemistry is potentially very wide, since the primary raw materials and semi-finished and end products in petrochemical processes can, as a rule, be successfully analysed by this method. Secondly, gas chromatography is an excellent method for solving most of the analytical problems in petroleum chemistry, because it is in this field that there is now general agreement between the problems to be solved and the possibilities of the gas chromatographic method. Gas chromatography is characterized by high efficiency, rapid production of results, and sensitivity. It is used with advantage for the automatic control of technological processes and for determining the physico-chemical properties of compounds and mixtures. Thirdly, the application of gas chromatographs in petroleum chemistry is highly economical. This is due mainly to the increased yield of the end product, its better quality, the reduced losses of raw materials and energy and also the decreased expenditures on analytical control methods. According to JANÁK AND VANKO[1], the annual profits of petroleum firms resulting from the use of industrial chromatographs, as far back as 1966, was estimated at 1,000 million dollars, whilst the total cost of their introduction was about 60 million dollars. It is also worth mentioning that the pay-off period of industrial chromatographs is very short, from 30 to 80 days. For this reason, gas chromatography quickly became the principal method of control and analytical investigation in petroleum chemistry, and its field of application is continuously increasing.

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* Plenary lecture.

TABLE I

DYNAMICS OF PUBLICATION OF PAPERS ON GAS CHROMATOGRAPHY (DEVELOPMENT AND APPLICATION)

Journals	Papers on gas chromatography (%)		
	1960	1965	1970
Petroleum chemistry	13[a]	37	62
Chemistry and technology of fuels and oils	5	9	10
Petroleum processing and petroleum chemistry	1.5	6	10

[a] Data for 1961.

Thus, for instance, in one of the most important branches of petroleum chemistry—the production of basic monomers for synthetic rubbers—about 35% of all analytical control techniques involve gas chromatography, 25% colorimetry, and 25% titrimetry[2].

The growing rate of application of gas chromatography in petroleum chemistry is evident from the data on the publication in petrochemical journals of papers dealing with the development of gas chromatography and those in which gas chromatography is used as a method of investigation or control. In Table I are listed the relevant data for 1960, 1965 and 1970. It can be seen that the application of gas chromatography in the petrochemical industry and in scientific research has been growing continuously over the past decade. At present, over 25% of communications containing new information are based on the use of gas chromatography.

In spite of the great number of papers on gas chromatography (at present the total number of papers exceeds 20,000 (ref. 3)), the development of gas chromatographic methods still continues, as a result of both expansion in the field of application of gas chromatography and the development of the theory and new methods and devices.

The purpose of this paper is to single out from the numerous lines of development of gas chromatography those which are, in our opinion, the most promising for solving petrochemical problems.

IMPROVEMENTS IN GAS CHROMATOGRAPHIC SEPARATIONS

In attempting to characterize the typical analytical problems that can be solved by gas chromatography, it was of interest to draw a comparison between the relative number of published gas chromatographic techniques and the number of components determined. Fig. 1 shows the relevant data for the journals *Neftekhimiya*, the *Journal of Gas Chromatography* and the *Journal of Chromatography* for 1965 and 1970. It is evident from the graphs that the greatest number of papers deal with techniques heaving a number of determined components between 6 and 10, the obvious tendency being towards an increase in the proportion of techniques for the analysis of multi-component mixtures. Thus, at the present time, gas chromatography is mainly used for analysing mixtures containing up to 15–20 components. The complexity of a chromatographic problem, however, depends not only on the number of
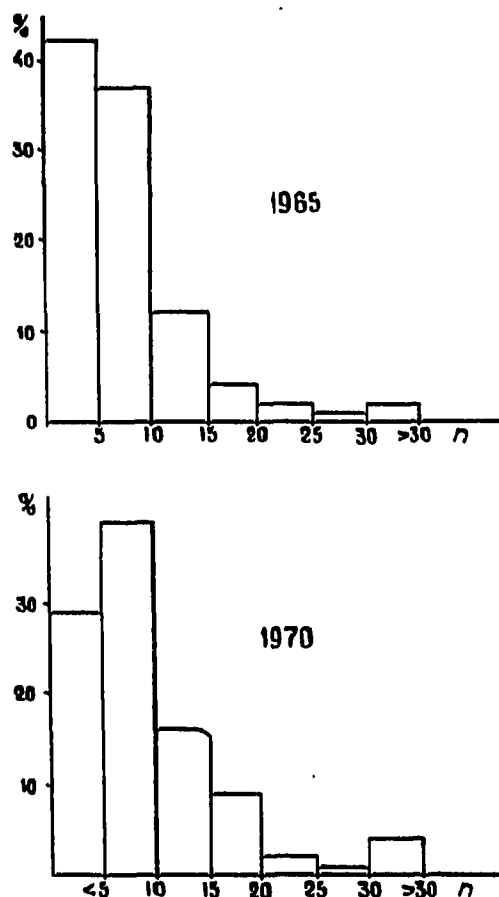
Fig. 1. Distribution of gas chromatographic techniques according to the number of determine components as published in three journals (see text) in 1965 and 1970.

components to be determined, but also on the number of "critical" pairs of compound that possess similar properties and are therefore difficult to separate. The separatio: of each "critical" pair often becomes an independent task.

It is known that separation in gas chromatography is based on the differenc between the partition coefficients of the chromatographed compounds in the gaseou phase and the stationary phase in the column. However, the elution of the chroma tographic bands reduces separation and may, in many cases, lead finally to the forma tion of unseparated zones. Therefore the quantitative characteristic of separatio: — the separation criterion[4], R— is determined both by equilibrium and kineti characteristics[5].

The equations obtained by PURNELL[5] allow the estimation only of the boundar; values for the number of theoretical plates of the column, N, and for the selectivit; of the sorbent, d, necessary for obtaining the desired separation R at certain fixec values of the parameter $f = k/(\beta + k)$ (k is the partition constant and β is the ratio o the volumes of the gas phase and the stationary phase in the column). Fig. 2 depict this dependence for certain typical conditions. It follows from the dependence presented in Fig. 2 that the necessary degree of separation can be obtained either b; the use of highly efficient columns or by choosing selective sorbents. The use of botl these methods of solving a problem of separation is justified and necessary. A mor
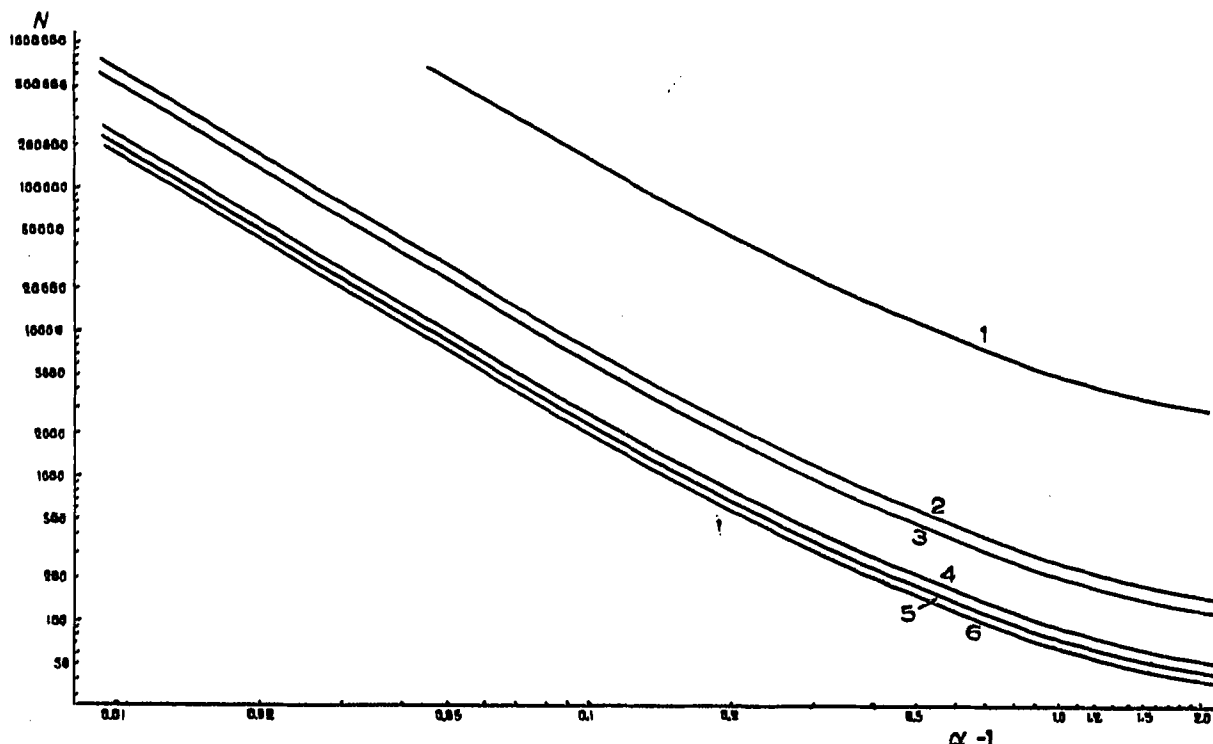
Fig. 2. Dependence of the number of theoretical plates necessary to attain separation of two compounds, with $R = 1.0$, on $\alpha - 1$ (α is the relative detection time for the chromatographed compounds) for certain typical conditions: (1) $\beta = 400$, $k = 50$; (2) $\beta = 50$, $k = 50$; (3) $\beta = 400$, $k = 500$; (4) $\beta = 10$, $k = 50$; (5) $\beta = 50$, $k = 500$; (6) $\beta = 10$, $k = 500$ (β is ratio of volume of gas phase in column to volume of stationary liquid phase, k is partition coefficient).

elegant solution, however, is to choose a selective sorbent for separation, since in the range of sorbent selectivities close to 1.00 even a small improvement in selectivity makes it possible to reduce drastically the number of theoretical plates required for separation and to pass from the application of capillary columns to simpler and more reliable packed columns. Thus, for example, the separation of *meta-* and *para*-xylene could formerly be achieved only on weakly selective liquid stationary phases on columns with an efficiency of several tens of thousands of theoretical plates[6,7]. The application of new types of selective sorbents—liquid crystals[8] and bentones (organic derivatives of montmorillonite clays)[9,10]—enabled this separation to be carried out on columns with an efficiency about 100 times lower. Therefore it is expedient to continue research to develop the scientific basis for choosing selective sorbents for gas chromatography. We believe that investigations in the field of complexing phases are most promising.

In practice, separation is achieved by the use of both packed and capillary columns, but the former find the widest application. Thus, in 1970 the *Journal of Chromatography* contained only 9% of papers based on the use of capillary columns. This is attributed to the better reproducibility of the properties of the packed columns (especially with the use of polar liquid phases), their higher stability in service, and the possibility of using a cheaper detector, although the efficiency of packed columns is about 0.1–0.01 that of capillary columns. The further development of gas chromatographic columns will probably involve improvement of columns of both types rather than supplanting one type of column by the other, because the application of a particular type of column depends on the analytical problem to be solved.

The principal drawback of packed columns—their rather low efficiency—can be eliminated either by the use of columns of small diameter or by the use of circulation schemes. Thus, CHIZHKOV AND USUROV[11], using a circulation chromatograph with two packed columns (300 × 0.4 cm) filled with 3% silicone SE-30 on Chromosorb W (60–80 mesh), separated isomeric cyclothienones with a relative detection time $\alpha = 1.012$ in 4 h and with a total separation efficiency of 106,000 theoretical plates. The drawbacks of the capillary columns include the necessity for working with very small quantities of analysed substances, the high gaseous: stationary phase ratio and the low reproducibility of the method (this can be eliminated by developing columns with a porous layer[12-14] and the application of large-diameter columns[15]).

DEVELOPMENT OF COMBINED METHODS

In the last decade, new combined methods of analysis have been devised in gas chromatography which are based on the simultaneous use of chromatographic and non-chromatographic (chemical and physical) methods.

The information which the investigator obtains by using combined methods is more extensive and comprehensive, since it is determined both by the chromatographic and other physico-chemical properties of the analysed compounds. This increases the analytical possibilities of the combined methods as compared with the individual ones.

The use of combined methods allows considerable progress to be made in solving problems on identification and in the quantitative determination of compounds in chromatographically unseparated zones, i.e., in solving the basic problems of the qualitative and quantitative analyses of complex mixtures. Combined methods based on gas chromatography and physical methods (mass spectroscopy, polarography, potentiometry, infrared spectroscopy, ultraviolet spectroscopy, flame photometry, liquid chromatography, etc.) are used in gas chromatography for the selective detection of separated compounds; chemical methods are used in all stages of chromatographic analysis, including the preliminary preparation of the sample. Particular aspects of the combined methods are considered elsewhere[16,17].

For the further development of reaction chromatography, simple and reliable selective detectors for combined chromatographic methods appear to be promising, especially for the separation of complex mixtures.

INCREASING THE RATE OF CHROMATOGRAPHIC ANALYSIS

Speeding up chromatographic analysis is an important problem, because it makes possible an increase in the productivity of chromatographs (which reduces the cost of analysis) and the use of gas-chromatographic methods for control and study of fast processes in industry and in scientific research. The duration of analysis depends largely on the time spent on the preparation of the sample, the carrying out of the chromatographic separation and the processing of primary experimental data in order to obtain the final result for the qualitative and quantitative composition of a mixture.

Formerly the two last stages were the limiting ones. However, with the devel-

opment of special digital integrating systems and the use of electronic computers for the rapid processing of primary chromatographic data, the duration of the last stage was drastically reduced. Thus, for instance, a chromatogram of a 100-component mixture is processed with the use of a digital electronic integrator within 3.5 min instead of 2.5 h with manual processing, *i.e.* 43 times as fast[17].

At present, the limiting factor in increasing the rate of analysis is therefore the duration of the chromatographic separation. Although methods for the analysis of 5- to 15-component mixtures within several seconds have been described in the literature in the past, in chromatographic practice such rapid analyses are applied only on a limited scale.

Fig. 3 shows the distribution of techniques published in *Neftekhimiya*, the
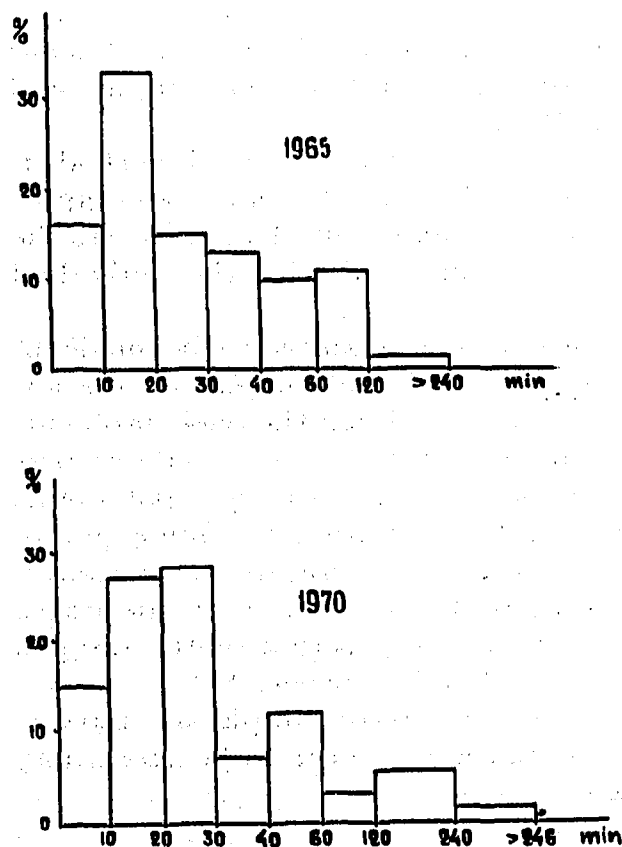

Fig. 3. Distribution of gas chromatographic techniques in respect to duration of analysis as published in three journals (see text) in 1965 and 1970.

Journal of Gas Chromatography and the *Journal of Chromatography* as regards the duration of analysis. It can be seen from the data that only in 15% of techniques was the duration of analysis less than 10 min.

We therefore believe that an important task for mass analyses would be the development of methods that permit the duration of chromatographic analysis to be reduced from several tens of minutes to a few minutes. A second important approach in improving the productivity of laboratory chromatographs is the application of devices with the automatic insertion of previously prepared samples in accordance with a predetermined programme which would operate reliably and continuously.

DEVELOPMENT OF GAS-CHROMATOGRAPHIC METHODS AND DEVICES FOR THE ANALYSIS OF IMPURITIES

Many physical and chemical properties of a substance (such as electrical conductivity, luminescence and radiation stability) greatly depend on the degree of purity of the substance. At the present time, the petrochemical industry is using an ever-increasing scale process which requires the use of extremely pure initial compounds (monomers, solvents, etc.)

Another important problem is the determination of pollutants in the air and in natural waters. For this reason, the analysis of impurities in chemical compounds and the determination of impurities in commercial products are among the chief lines of development of modern analytical chemistry[18]. Gas chromatography is one of the best methods for the analysis of volatile impurities and the analysis of impurities is an important independent branch of gas chromatography[19,20].

Notwithstanding the successes attained in the use of gas chromatography in the analysis of impurities, it is desirable to develop more sensitive methods of determination. In order to solve this problem, it would be expedient to develop new highly sensitive and selective methods of detection and also effective methods for the concentration of impurities. The importance of developing new, highly sensitive systems was recently stressed by MARTIN[21].

EXTENDING THE FIELD OF APPLICATION OF GAS CHROMATOGRAPHY IN PETROLEUM CHEMISTRY

The extensive possibilities of the application of gas chromatography in petroleum chemistry have not been fully realized. To achieve this, it appears expedient to conduct investigations along the following lines: (1) standardization of basic gas chromatographic methods used in the industry for the control of technological processes and the determination of the quality of finished products, and developing new chromatographic techniques to replace the non-chromatographic methods used in the industry; (2) working out industrial methods of separation based on gas chromatography; and (3) developing new methods and devices (attachments) for the automation of typical experimental measurements (determination of kinetic characteristics of liquid-phase and heterophase reactions, study of the properties of the catalyst, determination of the pressure of saturated vapours, etc.).

We would also like to emphasize the necessity of introducing a special course on gas chromatography into the curriculum of chemical educational establishments.

Gas chromatography is thus the basic analytical method in petroleum chemistry and there exist all the necessary conditions for its further development in this branch of industry.

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