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*chemical methods
in gas chromatography*

V.G. Berezkin

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V.G. Berezkin

*Institute of Petrochemical Synthesis, Academy of Sciences of the U.S.S.R.,
Moscow, U.S.S.R.*



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*The author dedicates this book
to the memory of his parents*

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Introduction

The advances made in science and technology in the second half of the twentieth century are closely associated with the development of analytical methods. 'Science progresses in quantum leaps depending on the advances in methods. Every forward step in the development of methods brings us to a new height from which we observe a broader vista with previously unseen objects' – such was the vivid and accurate assessment of the significance of new methods by Pavlov.

One of the most significant and spectacular achievements in analytical chemistry over the past quarter of a century has been the development and wide practical application of gas chromatography (GC). GC marked dramatic progress in the studying of complex mixtures of organic compounds and inorganic gases.

The application of GC in chemical analysis has substantially advanced many branches of analytical chemistry and brought forth radical changes in the organic analysis of volatile compounds. Many determinations that had been practically impossible or demanded several days of arduous work have become accessible to any investigator in an ordinary laboratory with the aid of GC.

GC was a gigantic leap forward in studies of complex mixtures of organic compounds and inorganic gases. A tremendous improvement has been achieved in such basic characteristics of analytical experiments as sensitivity (detection limit), selectivity (resolving power), accuracy, speed and reliability.

The extensive use of GC in science and industry has given rise to a large volume of literature. Fig. 1 shows diagrammatically the distribution of publications on individual analytical methods in the analysis of organic compounds and gases [1]. It can be seen that in 1975 45% of all publications on the analytical chemistry of organic compounds and gases dealt with chromatographic methods, GC accounting for 26% of the total number of works on chromatography. Table 1 lists analytical methods in decreasing order of their frequency of use by subscribers to *Analytical Chemistry* [2]. The table demonstrates that GC is currently one of the most widely used techniques. Another indication of the wide popularity of GC is the volume of production of gas chromatographs. For example, in the U.S.A. alone one (American) billion dollars worth of chromatographs are produced each year and 47.9% of all research laboratories in that country use GC [3].

The development of GC methods and the extension of areas of their application are continuing even today, with emphasis on combined or, to use Zolotov's definition, hybrid methods [4] incorporating two and more techniques. The promising nature of the combined use of several chemical methods has been pointed out by Ostwald, who wrote that, if separation cannot be achieved directly by physical methods, one has the alternative of providing the right conditions for the isolation of a new phase by appropriately transforming the separated substances and other compounds, the new phase containing a derivative of the sample substance and enabling its mechanical separation [5]. The attractive idea of combining chemical and physical methods was later elaborated by

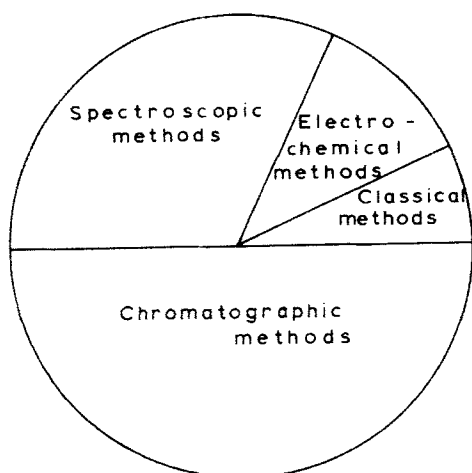


Fig. 1. Distribution of publications on different methods for the analysis of organic compounds and gases (data from 1980). After ref. 1.

TABLE 1

DISTRIBUTION OF USE OF ANALYTICAL METHODS, OBTAINED BY POLLING THE SUBSCRIBERS TO 'ANALYTICAL CHEMISTRY' IN 1978

The total number of those polled, most of whom use several methods, represents 100%. Reprinted with permission from ref. 2.

Analytical method	Frequency of use (%)
Gas chromatography	64
Spectroscopy (UV and visible region)	64
Atomic-absorption spectroscopy	64
Spectroscopy (IR)	47
Liquid column chromatography	46
Ion-selective electrodes	35
Ion-exchange chromatography	34
Thin-layer chromatography	33
Computer-aided analysis	22
Electroanalysis and coulometry	22
Emission spectroscopy	22
Flame spectroscopy	22
Gas chromatography-mass spectrometry	21
Fluorimetry	21
Potentiometry	20
Mass spectrometry	20
Nuclear magnetic resonance spectroscopy	16
Molecular sieve chromatography	14
Thermal analysis	13

Siggia [6] and Zolotov [4] in analytical chemistry, and by Ettre and McFadden [7] and Berezkin [8] in GC.

In considering combined methods one should proceed from a classification of analytical methods. The methods adopted in analytical chemistry lend themselves to the following classification into three groups: (1) methods for separating mixtures of elements or compounds, (2) methods for determining the amount or concentration of elements or compounds, and (3) methods for the chemical conversion of elements or compounds. The first two groups have been covered at length by Zolotov [4]. We have extended his classification to include also methods for the chemical conversion of substances or chemical methods [9]. These methods imply controlled chemical transformations involving components of the sample mixture of elements or compounds with a view to obtaining chemical derivatives suitable for the solution of a given analytical task under given conditions.

Analytical GC is essentially a combined, or hybrid, method based on the simultaneous application of two methods: (1) a method for the chromatographic separation of components of the sample mixture in a gaseous flow moving with respect to a stationary phase and (2) a method for the quantitative (and qualitative) determination of the zones of the separated components. The role of the second, or detection, method is no less important than that of the first. As early as 1962 Zhukhovitsky and Turkeltaub wrote that 'the history of advances in gas chromatography is in fact the history of development of the detector' [10]. Initially, analytical GC was regarded as a physical separation technique [10, 11]. However, such a restricted approach, although justified in the early years of GC, inevitably imposed certain limitations on its development and application, namely (1) the range of substances that can be analysed is confined to volatile compounds and compounds thermally stable at the separation temperature, (2) the selectivity of separation, determined only by physical factors, is not always sufficient and (3) the sensitivity (detection limit) of the widely employed thermal conductivity-type detectors and the gas density balance, based entirely on physical principles, is not high. The implementation of chemical methods in GC will help to obviate these limitations. The application of chemical methods has made it possible to broaden the scope of GC (e.g., determination of metals, polymers, anions, ultimate analysis), to develop new effective techniques of identification and group determination of components in complex mixtures of compounds, to improve separation and to enhance the sensitivity and, in some instances, the accuracy of determination of sample compounds. Hence the introduction into GC of a new 'chemical variable' provided the analyst with 'chemical vision' and contributed to advances in analytical chromatographic methods and the solution of practically important problems.

Chemical methods in GC, which can also be termed 'analytical reaction GC', represent a GC technique combining chemical and chromatographic (physical) analytical methods in which chemical transformations can be conducted within and without the chromatographic system. This definition is broader than that proposed earlier [8]; it takes into account the wider experience in and further development of analytical reaction GC, which also includes chemical transformations occurring outside the chromatographic scheme.

Analytical reaction GC combines three basic methods of analytical chemistry:

separation, determination (detection) and chemical transformation methods. Therefore, it may also be called, using Zolotov's terminology [4], a polyhybrid method.

Analytical reaction GC is characterized by specific experimental techniques, a particular, area of application and distinctive design features of the instruments used. It should be emphasized that when chemical methods are used in GC, the efficiency of chromatographic separation, sensitivity and other characteristics of the detector remain virtually the same. However, as a result of chemical reactions, or transformations of the sample mixture, newly formed compounds are subjected to determination or separation, and the separation factors and detection sensitivity can be varied in a controlled manner. It should also be noted that the chemical transformation method is applicable in other fields of analytical chemistry (e.g., spectroscopy, electrochemistry).

The tasks accomplished by analytical reaction GC are varied but basically they fall into four distinct categories:

- (1) Broadening of the scope of application (analysis of polymers, metals, etc.).
- (2) Detailed analytical study of a substance. This task is accomplished by the following GC analyses: ultimate, molecular (component), isotopic functional group, kinetic and others.
- (3) Improvement of analytical determination characteristics: separation, sensitivity, speed, etc.
- (4) Production of standard mixtures for qualitative and quantitative analysis.

Table 2 compares classical 'physical' chromatography with analytical reaction GC. It suggests that the rational application of chemical methods in chromatography permits all of its basic characteristics to be substantially improved.

Chemical reactions are conducted at all of the main stages of the analytical chromatographic experiment, including (1) sample preparation, (2) separation and (3) detection or measurement of the separation result. The employment of chemical transformations as early as the initial stage makes it possible to extend drastically the area of application of the GC method as a whole. As is well known, GC can be applied directly only to

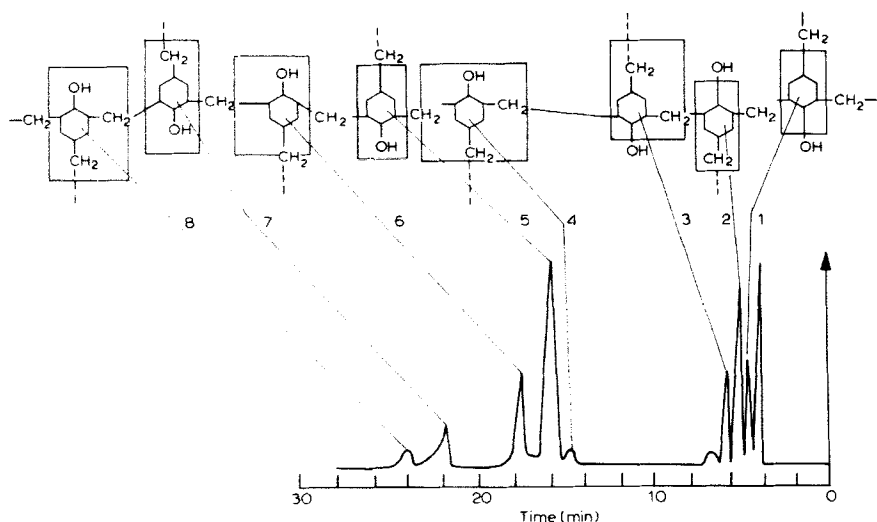


Fig. 2. Correlation between volatile pyrolysis products and structure of starting phenol-formaldehyde resin [11]. Pyrolysis temperature: 900°C. 1-8: identified pyrolysis products.

TABLE 2

COMPARISON OF ANALYTICAL REACTION GAS CHROMATOGRAPHY WITH CLASSICAL CHROMATOGRAPHY

Characteristic	Classical 'physical' chromatography	Analytical reaction gas chromatography (physico-chemical chromatography)
Application area		
General	Stable and volatile compounds	Plus unstable and non-volatile compounds (amino acids, metals, polymers, etc.)
Ultimate analysis	Usually impossible	Possible
Functional analysis	Usually impossible	Possible
Separation	Restricted to physical, predominantly non-selective interactions between the separated substances and the stationary phase	Efficient enough as a result of additional use of (1) sufficiently strong interactions between the analyte and the stationary phase (e.g., use of complexing agents) and (2) chemical reactions whose products are separated more easily than the initial substances
Detection sensitivity	Detection limit is restricted (e.g., in the case of a thermal conductivity detector, 10^{-4} – 10^{-5} mg/ml)	(1) Detection threshold of physico-chemical detectors is very low (e.g., 10^{-8} mg/ml for flame-ionization detector, 10^{-10} mg/ml for electron-capture detector) (2) To ensure high sensitivity undetectable compounds are converted into those detectable by high-sensitivity detectors

samples that can be vaporized at the separation temperature without any chemical changes. To apply GC to such objects one must, using appropriate chemical methods, convert them into stable volatile compounds that can be analysed successfully by GC techniques. For example, in polymer pyrolysis, GC may be used for identifying polymers and determining the monomeric composition of copolymers. Fig. 2 illustrates as an example a chromatogram obtained in the pyrolysis of phenol-formaldehyde resin and showing macromolecular fragments corresponding to particular pyrolysis products [11]. Fig. 3 shows chromatograms obtained in the determination of beryllium in some rocks, including rock samples from the moon [12]. The chromatogram in Fig. 4 [13] represents amino acid derivatives. Free amino acids cannot be analysed directly by GC. Fig. 5 shows a chromatogram of halogenated heptanes, obtained by thermal decomposition of tetraheptylammonium salts of iodine, bromine and chlorine in the sample injector of a chromatograph. The halogen derivatives of tetraheptylammonium were produced by extraction of aqueous solutions with a solution of tetraheptylammonium carbonate in toluene–undecanol solution [14].

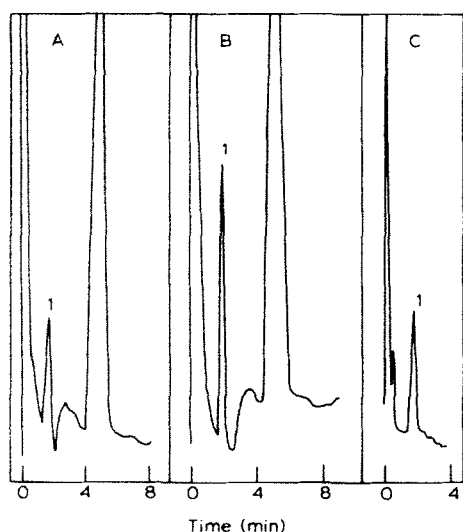


Fig. 3. Chromatogram of beryllium trifluoroacetylacetonates, obtained in analysis of moon rocks. A, Crystalline rock (Apollo II); B, breccia rock (Apollo II); C, standard containing $100 \cdot 10^{-12}$ g of beryllium; peak 1, beryllium trifluoroacetylacetonate. From ref. 12.

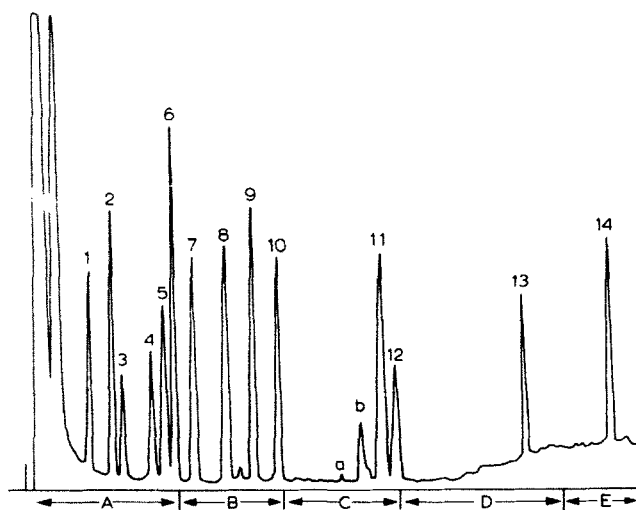


Fig. 4. Chromatogram of separation on a silicone stationary phase of methyl esters of trifluoroacetylated amino acids of hydrolysate of human fingernail. Sorbent: silicone stationary phase. Temperature programme: A, 100°C , isothermal; B, heating from 100°C at $1.5^{\circ}\text{C}/\text{min}$; C, heating from 116.5°C at $4^{\circ}\text{C}/\text{min}$; D, 140°C , isothermal; E, heating from 140°C at $6^{\circ}\text{C}/\text{min}$ to 210°C . Peaks: 1 = alanine; 2 = valine; 3 = glycine; 4 = isoleucine; 5 = threonine; 6 = leucine; 7 = norleucine; 8 = internal standard; 9 = proline; 10 = asparagine; 11 = glutamine; 12 = phenylalanine; 13 = tyrosine; 14 = lysine. From ref. 13.