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COMPOUND CHROMATOGRAPHY

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SUMMARY

Compound chromatography is a method for analysing mixtures of organic and inorganic substances, in which the separation is carried out on a liquid chromatographic (LC) column, while the separation is performed with the aid of a gas chromatographic (GC) column. The sample is fed from the LC column to the gas chromatograph automatically at a pre-set frequency and the eluent is separated from the component of interest on the GC column with subsequent detection using a thermalconductivity or flame-ionization detector. The advantages and limitations of the proposed method are discussed. The advantages include its versatility and the possibility of applying advances in gas chromatography, particularly in detection, to liquid chromatography; on the other hand, the method is limited to the analysis of volatile compounds. Compound chromatography has been used in the determination of fatty acids in vegetable oils, fats and products of their processing.

INTRODUCTION

Over the past 10–20 years, several combined methods have been introduced in chromatography[1,2]. One combination of practical interest is that of liquid (LC) and gas chromatography (GC), which, unfortunately, has received less attention than it deserves. This combined technique can be implemented through a continuous or a discontinuous (step-by-step) procedure. The latter implies that the two chromatographic methods are used independently of each other, LC being employed as a micropreparative technique prior to subsequent GC[3,4].

Quantitative analysis by thin-layer chromatography (TLC) in combination with GC can be accomplished by re-extraction of separated zones from the sorbent layer in TLC and subsequent quantitative analysis of the separated fractions by GC. The rationale of combining liquid TLC with GC is that LC permits the separation of compounds that cannot be separated by GC. For example, Daisey and Leyko[5] have proposed a combined chromatographic technique for analysing polyaromatic and acyclic hydrocarbons, based on their separation by TLC with 20% acetylated cellulose as sorbent with subsequent analysis of the separated fractions by GLC with Dexyl 300 as stationary phase. TLC permits a clear separation of isomers that are almost impossible to separate by GC, such as benzo(*a*)pyrene and benzo(*e*)pyrene, and benzo(*k*)fluoranthene and benzo(*b*)fluoranthene.

Another example of combining LC with GC is as follows. A fraction of gasoline produced by high-temperature catalytic cracking of petroleum, boiling at up to 100°, was subjected to preparative separation by LC[4]. The same technique has been used to separate paraffin–naphthene hydrocarbons from olefinic hydrocarbons, the resulting fractions then being analysed by GLC on a packed column with 7,8-benzoquinoline as the stationary phase. About 70 components were detected and identified as a result of the analysis. GLC on a copper capillary column with squalane has revealed more than 90 individual paraffin–naphthene and olefinic hydrocarbon components. This problem could not be solved by GC alone.

Bearing in mind, firstly, that column LC can be applied to the separation of volatile compounds that are impossible to separate by GC, secondly, that no suitable versatile and highly sensitive detector has yet been developed for LC that is comparable to those used in GC, and thirdly, in some instances the separation has to be improved by a two-dimensional separation with the successive application of LC and GC, it seems very appropriate to combine column LC with GC. This combination was first proposed about 15 years ago and has been termed "compound chromatography". The literature on compound chromatography was reviewed about 5 years ago by Berezkin *et al.*[5].

Compound chromatography is essentially a combination of column LC and column GC techniques, integrated into a single procedure for qualitative and quantitative analysis of separated mixtures, the separation first being carried out on an LC column, a GC column then being used to separate the eluent from the components and/or with an additional separation of the compounds being analyzed (see Fig. 1).

A particularly promising combination of LC and GC is that in which a modified gas chromatograph is used as a detector in LC. In this instance, the GC column is intended only for the separation of the highly volatile solvent from the compound of interest, the boiling point of which exceeds that of the solvent by more than 100°, which is why the column can be short. In some applications, this method can also be

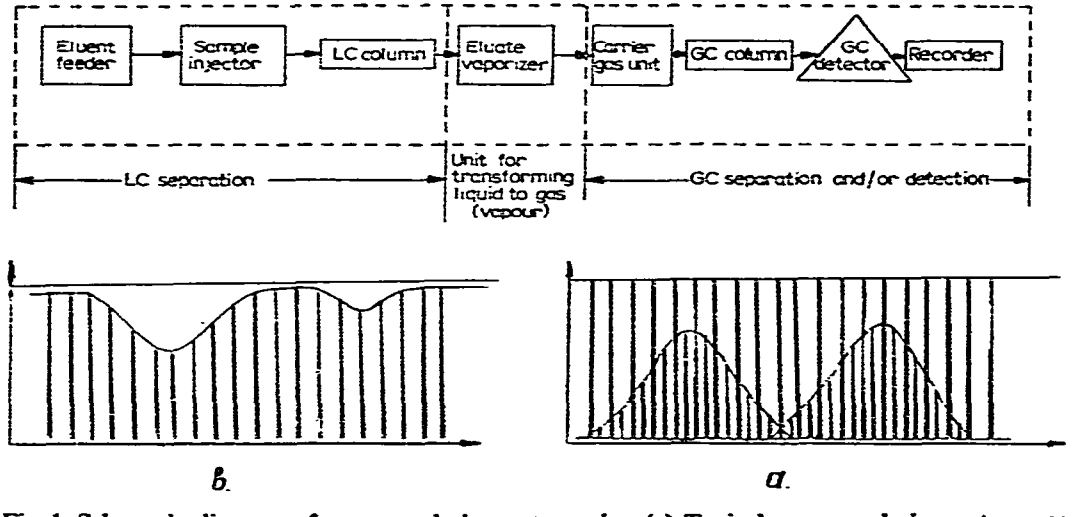

Fig. 1. Schematic diagram of compound chromatography. (a) Typical compound chromatogram; (b) compound chromatogram with vacancy.

used for the analysis of thermolabile compounds, as the solvent can be separated quickly from these compounds on the GC column at a lower temperature. The method is also applicable to compounds that send to decompose, provided that the decomposition process is rapid and the products of decomposition can be separated from the solvent.

The most important advantages of compound chromatography as applied to the analysis of volatile (and thermolabile) components include the following: (1) high sensitivity of determination of components; (2) versatility; (3) possibility of selective detection by using selective GC detectors; (4) easy quantitative evaluation of the content of components of interest; (5) applicable to micro- and preparative LC; (6) simple instrumentation; (7) applicable to gradient liquid chromatography; and (8) possibility of simultaneous determination of volatile and non-volatile compounds.

The common limitation of compound chromatography is its restriction to compounds that can be vaporized without any marked decomposition or that form only volatile products separable from the eluent when heated.

The idea of using a gas chromatograph as a detector in LC chromatography and the first practical model were proposed about 15 years ago[6]. In the GLC column of the gas chromatograph, the highly volatile solvent is separated from one or several (if the compounds are not fully separated in the LC column) high-boiling components of the analysed mixture in each drop of the eluate. Therefore, the column used can be short (30 cm or less). After separation on the column, the composition of each drop is recorded on the chromatogram in the form of one (solvent only) or two (solvent and analysate) peaks. The total content of the components is determined by adding the peak areas or heights corresponding to the components of interest.

A prerequisite for reliable operation of the compound chromatograph is highly reproducible and stable sample injection into the vaporizer of the gas chromatograph. An appropriate technique for injecting the eluate into the gas chromatograph was proposed by Andreev[8]. The injector ensures a high reproducibility of injection (0.5%) and high stability (1.5%).

The idea of using a gas chromatograph as a detector in LC and employing a reliable sample injection method has been embodied in a "compound chromatograph" developed at the Designing Bureau of the Institute of Organic Chemistry, U.S.S.R. Academy of Sciences, integrating an LC column with a sample injection system and a solvent supply unit together with an analytical gas chromatograph into a single chromatographic system. The instrument is intended for the preparative separation and analysis of mixtures of volatile, high-boiling and thermally unstable compounds that exhibit comparable physico-chemical properties by LC techniques, and for the identification of petroleum product mixtures by combined LC and GC methods.

Fig. 2 is a compound chromatogram obtained from the preparative separation of methyl esters of fatty acids.

With a view to expanding the range of applications of compound chromatography, it has been proposed[9,10] to determine volatile and non-volatile compounds simultaneously, as well as inorganic salts, using the so-called vacanto detection principle[11]. When a sample of a volatile compound is detected, the composition of each drop is recorded in the form of two (solvent and analysate) peaks. The peak height of the compound of interest varies with its concentration in the eluate drops. The varying peak height of the compound under investigation is accompanied, on the

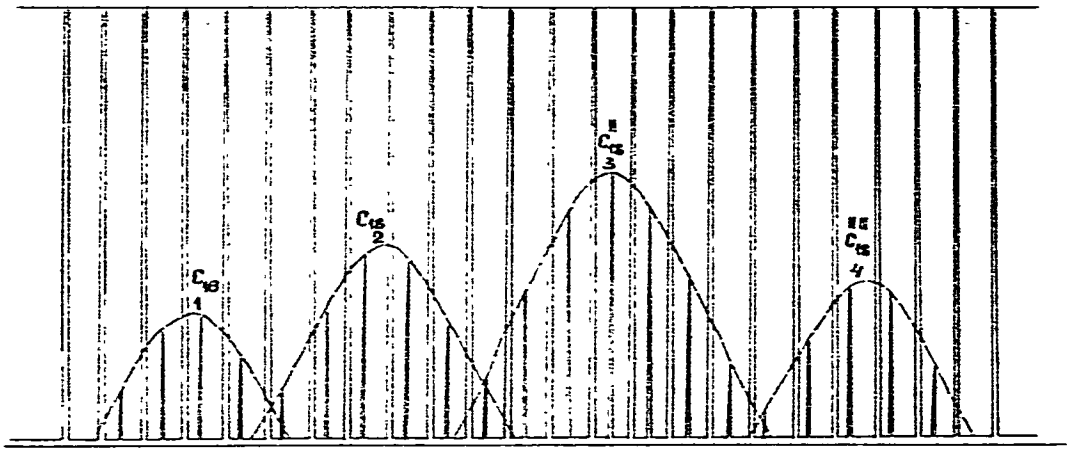

Fig. 2. Compound chromatogram obtained from preparative separation of methyl esters of fatty acids. Separation conditions: the LC column (50 cm × 6.7 mm I.D.) is packed with silica gel treated with $AgNO_3$; eluent, benzene; flow-rate, 30 ml/h; room temperature; sample volume, 600 μl. Detection conditions: the GC column (30 cm × 2 mm I.D.) is packed with Chromosorb W with 10% SH-550; column temperature, 265°; vaporizer temperature, 350°; carrier gas (helium) flow-rate, 50 ml/min; detector, flame-ionization. Substances: 1 = methyl palmitate; 2 = methyl stearate; 3 = methyl oleate; 4 = methyl linoleate.

chromatogram, by a corresponding variation in the solvent peak height because the volume of the injected sample is virtually the same. The area of the resulting vacancy (see Fig. 1b) serves as a measure of the amount of sample introduced into the LC column.

If the compound of interest is non-volatile, its peak will not be registered because this compound will be precipitated in the vaporizer and therefore will not enter the column. However, the variation in the solvent peak height, corresponding to the variation in the concentration of the non-volatile compound in the eluate in the form of a vacancy, will indicate the amount of the non-volatile compound in the sample. The proposed method for detecting non-volatile compounds is extremely simple and does not require any additional devices, except for a vaporizer with a replaceable element for precipitation of non-volatile compounds. However, a serious limitation of the vacanto detection method as applied to non-volatile compounds is its restricted sensitivity.

In assessing the extent of application of compound chromatography it should be pointed out that it is as broad as LC in combination with mass spectrometry, which is being steadily improved at present[12]. Naturally, the informative value of compound chromatography is substantially lower than that of column LC in combination with mass spectrometry. This factor, however, is of importance primarily for research and analysis of mixtures with an unknown composition. For routine analysis compound chromatography is highly advantageous owing to its simplicity and low cost.

Its limitations notwithstanding, compound chromatography is highly promising in two respects —instrumentation and technique developments. Some areas in which improvements can be made are as follows: (1) a unit for transforming the liquid eluate to the vapour phase; the development of a specially designed vapoirzer with a

replaceable element for the analysis of an eluate containing non-volatile compounds; (2) a system for processing the initial separation data; (3) the use of selective detectors, such as electron-capture or mass-spectrometric detectors; (4) the development of instruments and methods for the rapid separation of the eluent from the component of interest; (5) extension of applications, *e.g.*, in petrochemistry the group separation of various oil fractions, in biochemistry for the determination of fatty acids in vegetable oils, fats and products of their processing; and (6) enhancing the detection sensitivity by intermediate concentration of trace amounts[13].

In conclusion, the combination of column LC and GC seems to hold much promise and it would be particularly worthwhile to develop GC detectors as attachments to liquid chromatographs.

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