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Review

Extending the molecular application range of gas chromatography

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Abstract

Gas chromatography is an important analytical technique for qualitative and quantitative analysis in a wide range of application areas. It is fast, provides a high peak capacity, is sensitive and allows combination with a wide range of selective detection methods including mass spectrometry. However, the application area of GC is limited because the molecules to be analysed have to be thermally stable and sufficiently volatile. Numerous molecules do not meet these requirements and hence are not amenable to direct GC analysis. Recent research has resulted in better chromatographic columns and methods for sample preparation that enable a significant expansion of the molecular application range of GC. The strategies exploited include conversion of (macro)molecules into smaller species and approaches to reduce the polarity of molecules. In this review we identify four generic routes for extending the applicability of GC. These include high-temperature GC, derivatisation, pyrolysis and thermochemolysis. The principles, recent developments and future perspectives of these routes are discussed and examples of applications using the different options will be shown. Life sciences, metabonomics and profiling strategies for sample characterization are identified as important future drivers for the continued development of GC.

Keywords: Gas chromatography; High-temperature GC; Derivatisation; Pyrolysis; Thermochemolysis; Applications; Application range; Future developments

Contents

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1. Introduction

Chromatographic separation methods are without any doubt the most frequently employed analytical techniques for compositional analysis. Both gas chromatography (GC) and liquid chromatography (LC) are widely used in a huge number of application areas in laboratories all over the world. LC and GC are complementary yet at the same time competing techniques. There is a significant number of applications that can equally well be solved by GC as by LC. For other applications clearly one of the techniques is to be preferred over the other. Which technique to select depends on numerous objective parameters such as the physico-chemical properties of the analytes, matrix properties, the presence of similar analytes, the required sensitivity and selectivity, etc., next to more subjective personal preferences. In practice the process of selecting between LC and GC is a process of multi-criteria decision making where incomparable properties have to be compared. Would I prefer the faster method running on the more expensive instrument, or the more reliable and selective method that unfortunately requires slightly more maintenance? As always when making a difficult choice a consequence of taking a decision is that the attractive features of the other option are lost. When resorting to LC one no longer benefits from the merits of GC. In this sense it is interesting to think about options for transferring applications from the LC to the GC domain.

The general consensus when comparing LC and GC is that GC is faster, provides higher separation efficiency, has better properties for combination with a wide range of sensitive and selective detectors and, finally, allows easier mass spectrometric identification. LC is generally stated to require less sample preparation, provide a better selectivity, have a much wider application range and be more rugged. Given these complementary advantages it is logical that in the past decades several attempts have been made to combine the advantages of LC and GC. One of the major justifications for research into supercritical-fluid chromatography (SFC) in the 1980s and 1990s was in fact the possibility to combine the advantages of LC and GC [1]. Right now SFC has secured itself a clear, albeit small position between LC and GC as is evidenced by the small and stable number of SFC papers appearing in scientific literature. Other examples of trying to combine the strengths of LC and GC include research directed towards LC with GC detectors [2], hyphenated LC–GC [3], comprehensive two-dimensional LC × GC [4], and unified chromatography [5,6]. Similarly to SFC, most of these attempts have been more or less successful, yet the methods have not (yet) gained widespread acceptance.

The main question that determines whether a compound can be eluted from a GC column is whether it can reach a sufficiently high concentration in the gas phase in the GC column at a realistic temperature. For very high molecular weight compounds this is evidently not possible. Polymers are thermally decomposed long before they reach a measurable vapour pressure. The same holds for highly polar molecules. Due to the strong intermolecular forces high temperatures are needed to vapourize polar molecules and the molecules might decompose on the GC column. It is for this reason that small but highly polar molecules, such as amino acids and sugars, cannot be analysed using GC. A possible solution is the use of chemical derivatisation techniques where the polar groups of the target molecules are converted into less polar moieties, which favourably affects the vapour pressure and the adsorption characteristics. Clearly the two factors that determine whether a compound can be analysed using GC are size and polarity. Only a limited range of relatively small and non-polar molecules is accessible for direct analysis by GC. By increasing the temperature at which the GC column is operated this range can be extended slightly, but at some point thermal stability of the compounds and/or the GC column becomes a limiting factor. Samples containing molecules outside the GC range have to be analysed using another technique, very often LC, or have to be pretreated first to make size and polarity compatible with GC. Derivatisation has already been mentioned as a method to convert polar species into less polar, GC-amenable analytes. Pyrolysis is a method to convert high molecular weight species into smaller fragments that fall within the application range of GC. Pyrolysis with simultaneous derivatisation, known as thermochemolysis, can be used for converting polar polymers into species suitable for subsequent GC analysis.

The application range of GC and the routes available to bring more molecules into the scope of GC are schematically depicted in Fig. 1. In the first route, high-temperature GC, the molecules in the sample are not changed. The chromatographic conditions are adapted to allow elution of the compounds that at lower maximum temperatures would be fully retained. The other routes, derivatisation, pyrolysis and thermochemolysis alter the properties of the molecules either slightly (derivatisation) or completely (pyrolysis and thermochemolysis). In Fig. 1 and in the rest of this review we will restrict ourselves to a discussion of these four generic routes for extending the applicability of GC. For certain specific applications alternative methods might be