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Review

Review of recent developments and applications in low-pressure (vacuum outlet) gas chromatography

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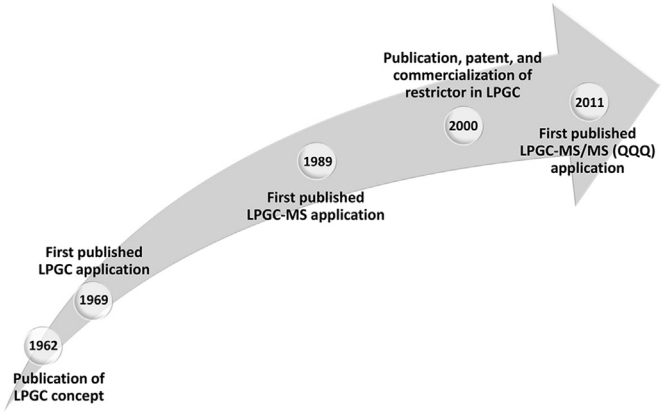
HIGHLIGHTS

- This review provides an updated overview of low-pressure gas chromatography (LPGC) and its applications.
- Previously unpublished information and chromatograms comparing LPGC with standard GC-MS are presented.
- The reader will gain insight regarding the benefits, and limitations, of LPGC in different applications.

GRAPHICAL ABSTRACT



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ABSTRACT

The concept of low pressure (LP) vacuum outlet gas chromatography (GC) was introduced more than 50 years ago, but it was not until the 2000s that its theoretical applicability to fast analysis of GC-amenable chemicals was realized. In practice, LPGC is implemented by placing the outlet of a short, wide (typically 10–15 m, 0.53 mm inner diameter) analytical column under vacuum conditions, which speeds the separation by reducing viscosity of the carrier gas, thereby leading to a higher optimal flow rate for the most separation efficiency. To keep the inlet at normal operating pressures, the analytical column is commonly coupled to a short, narrow uncoated restriction capillary that also acts as a guard column. The faster separations in LPGC usually result in worse separation efficiency relative to conventional GC, but selective detection usually overcomes this drawback. Mass spectrometry (MS) provides highly selective and sensitive universal detection, and nearly all GC-MS instruments provide vacuum outlet conditions for implementation of LPGC-MS(/MS) without need for adaptations. In addition to higher sample throughput, LPGC provides other benefits, including lower detection limits, less chance of analyte degradation, reduced peak tailing, increased sample loadability, and more ruggedness without overly narrow peaks that would necessitate excessively fast data acquisition rates. This critical review summarizes recent developments in the application of LPGC with MS and other detectors in the analysis of pesticides, environmental contaminants, explosives, phytosterols, and other semi-volatile compounds.
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Contents

1. Introduction

In 1962, Giddings introduced the concept of applying a vacuum to the column in gas chromatography (GC) to generate a greater pressure drop than possible with the outlet at atmospheric pressure, thereby speeding the separation [1]. In essence, the viscosity of the carrier gas is reduced at lower pressure than at higher pressure conditions, which acts to shift the optimum average linear flow velocity ($\bar{u}_{opt}$) in the van Deemter equation to a higher flow rate. Thus, higher carrier gas flow may be employed in low pressure gas chromatography (LPGC) to achieve the same degree of separation with all other factors being equal. LPGC with He as the carrier gas can be likened to using H_2 in conventional GC. A typical optimal flow rate is 2 mL/min He in LPGC rather than 1 mL/min at common GC conditions. Higher flow rate yields shorter retention time (t_R) and thereby faster analyses. Chromatographic peak broadening from diffusion and tailing is also reduced in shorter separations, thus gains in peak height and signal/noise ratio also result (leading to lower detection limits if matrix is not the limiting source of noise).

The first published application of LPGC was in 1969, when Palamand and Thurow reported use of a vacuum outlet for a packed stainless steel GC column with conductivity detection [2]. They compared the GC behavior of 9 room temperature liquids (formic acid, water, acetic acid, isooctane, propionic acid, 2-octanol, phenylethanol, n-dodecane, and phenylethyl acetate) under normal and LPGC conditions. LPGC achieved the separation in half the time and gave taller and narrower chromatographic peaks.

Despite the benefits of LPGC, few other chromatographers for many years entertained this notion of gaining speed in GC analysis by using vacuum outlet column conditions [3–5]. LPGC advantages remained largely unrealized in part due to the practical complexity of the instrumental set-up with respect to need for a vacuum source, tight seals, and vacuum operation of detectors and injectors. In 1991, Puig and Sacks revisited LPGC using photo-ionization detection and compared linear gas velocities of He and H_2 as carrier gases under conventional and LPGC setups [6]. They demonstrated that for 0.32 mm inner diameter (i.d.) capillary columns, the optimum gas velocities for H_2 and He increased from 70 cm/s to approximately 300 cm/s under LPGC conditions, consequently leading to faster separations.

Because mass spectrometry (MS) nearly always requires low pressure by its nature, the vast majority of GC-MS methods entail vacuum outlet conditions. However, the standard GC-MS column is 30 m, 0.25 mm i.d., and the sub-atmospheric outlet pressure only extends a short way up the analytical column. The distinguishing aspect of LPGC-MS(/MS) is analyst intent to speed the analysis by placing the entire (or nearly entire) analytical column under vacuum. The first published study of LPGC-MS was in 1989 to compare theory with observations in practical application [7]. In 1993, Vanysacker et al. reported a study applying LPGC-MS in the separation of polychlorinated biphenyls (PCBs) using an ion trap instrument [8]. The authors performed the LPGC-MS method using a 7 m, 50 μm i.d. column to separate a mixture of Arochlor 1248 in 4 min, compared to 30–40 min using conventional GC.

Until 2000, the overwhelming limitation in LPGC-MS was that the vacuum extended all the way to the inlet, which required specially designed injectors to control carrier gas flow and allow reproducible introduction of the sample [5,7]. In an elegant solution to this problem, de Zeeuw et al. patented [9] and published [10] the idea to attach a short, narrow restriction capillary at the inlet and couple the other end of this restrictor to the wider analytical column terminating at the MS ion source. In this design, the analytical column is at similar vacuum pressure as the MS source, while the restrictor keeps the inlet at normal GC operating conditions (see Fig. 1).

This concept was named "Rapid-MS™," which was commercialized by Varian-Chrompack at the time. The Rapid-MS column consisted of a 0.1 m, 0.1 mm i.d. deactivated capillary restrictor preconnected to a 10 m, 0.53 mm i.d. column with 5% phenyl, 95% dimethylpolysiloxane (5 ms) stationary phase of 0.12, 0.25, 0.5, or

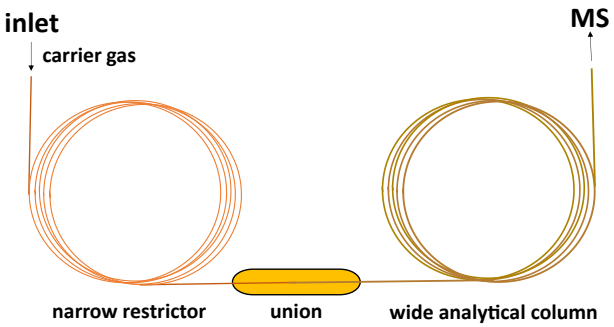

Fig. 1. Column arrangement for LPGC-MS.