The Vacuum Outlet GC-MS Technique
A Versatile Technique for Fast GC Separations

The vacuum outlet technique offers a simple approach to gain both speed and sensitivity in gas chromatographic separations without requiring dedicated instrumentation or a complicated experimental set-up.

Gas chromatography (GC) is one of the most powerful analytical techniques, providing the separation of several ten to a few hundred volatile or semi-volatile compounds in one chromatographic run. Its separation efficiency exceeds the one of high-performance liquid chromatography (HPLC) with peak widths in the range of few seconds and typical separation times ranging from 10 – 60 min. This results in a peak capacity of more than 100, however at the expense of extended run times.

Approaches to fast GC separation
For this reason, a number of approaches have been developed over the years that are aiming at increased separation speed while maintaining the separation efficiency and the loadability (capacity) of the chromatographic system [1]. The ‘magic triangle’ of chromatography (Figure 1), however, indicates that with current chromatographic systems and typical operating conditions, it is impossible to optimize all three parameters at the same time. Most solutions nowadays offered for fast GC represent a compromise with respect to at least one of the three parameters. Many of the currently successful methods for fast GC exploit scaling laws for GC, that is, they employ relatively short, small inner diameter columns with a thin film of stationary phase (typically 10 m x 0.1 mm x 0.1 µm) which are run at high heating rates (up to 60°C/min). These high heating rates are attained by very powerful GC heaters, by customized column ovens of reduced thermal mass, or by direct resistive heating [2]. While this method offers high separation efficiency and reduced separation time, sample capacity is also decreased significantly due to the low amount of stationary phase present, and method translation from regular-dimension systems requires particular consideration [3]. Moreover, the decreased peak widths obtained with such columns make the use of a fast duty cycle mass spectrometer (MS), such as a fast-scanning quadrupole MS or the time-of-flight (TOF) MS, mandatory.

Completely different approaches for fast GC have also been devised, such as the supersonic molecular beam (SMB) GC/MS technique, initially proposed by Amirav et al. [4] which relies on adding a large make-up flow of He after the GC separation at conventional flow rates. When expanding into the vacuum, the large carrier gas stream forms a supersonic molecular beam. This has, together with the special design of the fly-through electron ionization (EI) ion source, the advantage that the molecular ions of vibrationally cold analytes can be detected by this technique even for very labile compounds. Another original approach for GC with high time resolution (although not necessarily with very fast individual GC runs) is the so-called multiplex-GC technique in which the sample is repeatedly introduced in a pseudo-random sequence into an isothermally operated GC system in time intervals much shorter than the individual GC run time. The resulting overlay of chromatograms preserves the time resolution of the sample introduction sequence, but the individual original chromatograms have to be reconstructed from the complex data matrix through the use of the Hadamard transform [5].

A further interesting and largely underrated alternative fast GC-MS technique involves, in a rather counter-intuitive way, the use of short wide-bore capillaries operated at reduced pressures. This so-called low pressure (LP) or vacuum outlet GC approach is a very appealing one, as it does not require any particular modification of the separation system.

Practical aspects of the vacuum outlet GC technique
Performing the separation under low-pressure leads to a number of advantages, as was first recognized by Giddings in 1962 [6], and coupling with a mass spectrometer has made LP-GC very easy to implement. Under vacuum-outlet conditions and by using a short, wide-bore column (e.g. 5 to 10 m x 0.53 mm inner diameter) the vacuum extends across almost the
of such columns to the MS is difficult, since the GC inlet would have to be
operated at sub-ambient pressures and the high column flow might exceed
the tolerable level for stable operation of the ion source of the mass spec-
trometer. If instead a restriction at the column head is used, the flow is restric-
ted to an acceptable level, the injection system can operate at above-atmos-
pheric pressures and low-pressure conditions do still prevail throughout the
entire analytical column. Various types of restrictions have been suggested.
The most practical ones are either very short (1-10 cm) capillaries of small
inner diameter (e.g. 20 μm i.d.) or longer capillaries (of 0.5 - 5 m length and
0.05-0.15 mm i.d.), which at the same time also may serve as a guard column
[7]. Optimization of the restriction dimensions can be performed, with the
longer and wider restrictions providing column setups with a slightly better
chromatographic performance in terms of separation efficiencies [8].

Advantages of vacuum outlet GC-MS
Lowering the pressure inside the capillary results in faster diffusion in the gas
phase, shifting the optimal flow rate of the van Deemter curve to greater li-
near velocities (Figure 3). In addition, when He is used as a carrier gas, the
viscosity of the He is reduced at reduced pressure, leading to H₂-like proper-
ties. This translates to higher efficiencies over a wider range of flow rates and
temperatures. Because of the higher linear velocities, the analytes are elu-
ting earlier, which leads to narrower and consequently also relatively higher
peaks, and results in a better signal to noise ratio (S/N) and correspondingly
lower detection limits [9]. Another advantage of the vacuum outlet GC-MS is
that the sample components elute at significantly lower temperatures (by ca.
50-70 K) from the GC column as compared with normal pressure operation,
This feature also enables the analysis of thermally labile compounds, whose
degradation is strongly reduced under higher flow rates and shorter time of
residence in both the injector and in the column. Also, the analysis of heavier
sample components is facilitated by the lower elution temperatures, which
result in shorter elution times. The lower elution temperatures furthermore
reduce stationary phase bleed, providing mass spectra with lower noise, cor-
responding to a higher signal to noise ratio, and reduced risk of pollution of
the ion source [10]. As discussed before, any chromatographic method has to
be a balanced compromise between speed, capacity, and resolution as
illustrated in Figure 1 [3]. Distinctly different from the other approaches dis-
cussed before, the low pressure GC/MS technique does not suffer from re-
duced sample capacity: Due to the use of large inner diameter columns with
relatively thick stationary phases (up to 5 μm film thickness), there is hardly
the danger of column overload. In the case of the vacuum outlet GC, howe-
ever, by increasing both speed and sample capacity, the resolution is partially
sacrificed. The selectivity of the MS is then used to overcome that sole short-
coming of the technique.

Applications of the vacuum outlet GC-MS technique
The past few years have seen an increasing interest in the vacuum outlet GC/
MS technique. Successful applications of vacuum outlet GC/MS have been
developed for the rapid analysis of various types of organic environmental
pollutants [11]. Most examples refer to the determination of pesticides in dif-
f erent matrices, but also polycyclic aromatic hydrocarbons (PAHs) and other
hydrocarbons, plant and flower oils, organotin compounds, pharmaceutical
products, steroid estrogens, polybrominated diphenyl ethers (PBDEs), po-
lychlorinated biphenyls (PCBs) and other semi-volatile compounds (VOCs)
have been investigated. In the most recent application of the technique, our
group has combined solid phase microextraction (SPME) with the vacuum
outlet GC-MS for the identification and quantification of UV filters in swim-
mong pool waters [12]. In that particular case, octinoxate and oxybenzone,
two of the most widely used chemicals in sunscreen lotions and suspected
endocrine disrupters, were analyzed by direct immersion (DI) SPME followed
by low pressure GC-MS analysis (Figure 4) and the results were compared
to a conventional GC-MS method. In accordance with our expectations, the
proposed fast gas chromatographic approach proved to increase speed and
whole column length, providing a higher analysis speed than the same co-

Fig.1: The magic triangle of chromatography, with the three most important parameters for chromatographic separations that never can be maximized at the same time [3].

Fig.2: Typical vacuum outlet column setup using a longer, small inner diameter uncoated pre-
column as a restrictor.

Fig.3: Sketch of the Van Deemter plots of 0.53 mm columns operated under atmospheric outlet
(continuous line) and vacuum outlet (dashed line) conditions for He as carrier gas [9].

Fig.4: DI-SPME-LP-GC-MS chromatogram of swimming pool water, spiked with octinoxate (1)
and oxybenzone (2) at 5 μg/L (inset) and comparison with separation at normal conditions (large
chromatogram). [12]
sensitivity over the standard GC-MS method, showing an 8-fold reduction in
the total analysis time and leading at the same time to a 7-fold improvement
in the detection limit of both compounds.

Conclusions
From the fast GC techniques available, vacuum outlet- or low pressure-GC-
MS has proven to be a highly favorable choice, particularly due to its simplic-
ity and ease of application, since it does not entail the use of additional ins-
strumentation. Its numerous advantages, like the shorter run times, increased
sample loading and greater sensitivity, earlier elution of less volatile com-
pounds and reduced thermal degradation, justify its selection for the analy-
sis of various classes of organic compounds. It can thus be expected that the
field of applications for the LP-GC-MS technique will significantly increase,
responding to the ubiquitous requirement for fast and sensitive detection


Authors | Contact
Prof. Dr. Erwin Rosenberg | Chrysoula Kanakaki
Vienna University of Technology
Institute of Chemical Technologies and Analytics
Getreidemarkt 9/164 AC | A-1060 Vienna | Austria
www.cta.tuwien.ac.at

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