

# The Vacuum Outlet GC-MS Technique

A Versatile Technique for Fast GC Separations

Prof. Dr. Erwin Rosenberg | Chrysoula Kanakaki

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

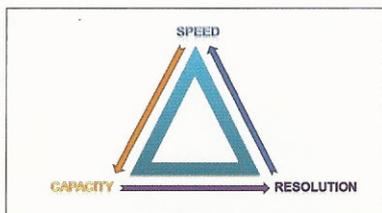


Fig. 1: The magic triangle of chromatography, with the three most important parameters for chromatographic separations that never can be maximized at the same time [3].

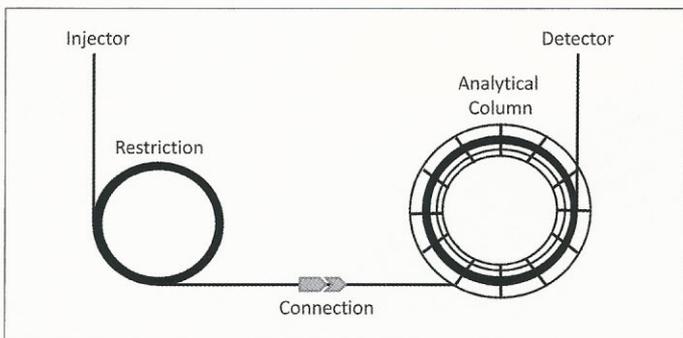


Fig. 2: Typical vacuum outlet column setup using a longer, small inner diameter uncoated pre-column as a restrictor.

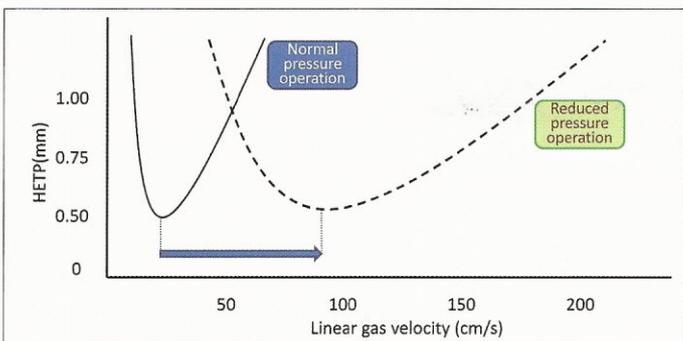


Fig. 3: Sketch of the Van Deemter plots of 0.53 mm columns operated under atmospheric outlet (continuous line) and vacuum outlet (dashed line) conditions for He as carrier gas [9].

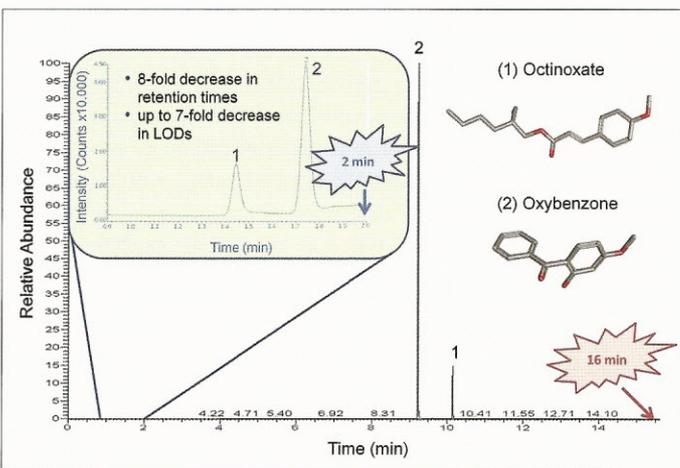


Fig. 4: DI-SPME-LP-GC-MS chromatogram of swimming pool water, spiked with octinoxate (1) and oxybenzone (2) at 5 µg/L (inset) and comparison with separation at normal conditions (large chromatogram). [12]

whole column length, providing a higher analysis speed than the same column operated at atmospheric outlet pressure. To enable vacuum operation through coupling a wide-bore column to a mass spectrometer, the use of a restriction at the head of the column is necessary (Figure 2). Direct coupling

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 spectrometer. If instead a restriction at the column head is used, the flow is restricted to an acceptable level, the injection system can operate at above-atmospheric 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 linear 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 H<sub>2</sub>-like properties. This translates to higher efficiencies over a wider range of flow rates and temperatures. Because of the higher linear velocities, the analytes are eluting 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, corresponding 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 discussed before, the low pressure-GC/MS technique does not suffer from reduced 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, however, by increasing both speed and sample capacity, the resolution is partially sacrificed. The selectivity of the MS is then used to overcome that sole shortcoming 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 different matrices, but also polycyclic aromatic hydrocarbons (PAHs) and other hydrocarbons, plant and flower oils, organotin compounds, pharmaceutical products, steroid estrogens, polybrominated diphenyl ethers (PBDEs), polychlorinated 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 swimming 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

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 simplicity and ease of application, since it does not entail the use of additional instrumentation. Its numerous advantages, like the shorter run times, increased sample loading and greater sensitivity, earlier elution of less volatile compounds and reduced thermal degradation, justify its selection for the analysis 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

- [1] E. Matisová, M. Dömötörövá, *J. Chromatogr. A*, 1000 (2003) 199–221.
- [2] A. Wang, H.D. Tolley, M.L. Lee, *J. Chromatogr. A*, 1261 (2012) 46–57.
- [3] M. S. Klee, L. M. Blumberg, *J. Chromatogr. Sci.* 40 (2002) 234–247.
- [4] A.B. Fialkov, M. Moragn, A. Amirav, *J. Chromatogr. A*, 1218 (2011) 9375–9383.
- [5] O. Trapp, *Angew. Chem. Int. Ed.* 46 (2007) 5609–5613.
- [6] J. Calvin Giddings, *Anal. Chem.* 34 (1962) 314–319.
- [7] M. van Deursen, H.-G. Janssen, J. Beens, P. Lipman, R. Reinierkens, G. Rutten, C. Cramers, *J. Microcol. Sep.*, 12 (2000) 613–622.
- [8] C. Kanakaki, Dissertation, Vienna University of Technology, in preparation (2015).
- [9] J. de Zeeuw, S. Reese, J. Cochran, S. Grossman, T. Kane, *C. English: J. Sep. Sci.* 32 (2009) 1849–1857.
- [10] J. de Zeeuw, J. Peene, H.-G. Jansen, X. Lou, *J. High Resol. Chromatogr.* 23 (2000) 677–684.
- [11] K. Ravindra, A.C. Dirtu, A. Covaci, *Trends Anal. Chem.*, 27 (2008) 291–303.
- [12] Ö. Yilmazcan, C. Kanakaki, B. Izgi, E. Rosenberg, *J. Sep. Sci.* (2015) DOI:10.1002/jssc.201401250.



## 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](http://www.cta.tuwien.ac.at)

# New IKA® Recirculating Chillers

# IKA®



Recirculating  
Chiller RC 2  
basic | control

More  
information on  
[www.ika.com/  
thermostats](http://www.ika.com/thermostats)



**Handling**  
Safe and ergonomic handling  
due to a well thought-out design.  
Transport casters on the rear of  
the device enable easy transport  
and set up



**Energy efficiency**  
Up to sixty percent lower  
energy consumption during  
standard operation than  
comparable devices from  
competitors



Detachable wireless  
controller (WiCo) for simple  
and safe remote access from  
up to 10m (30 ft.)

## Safety. Power. Intelligence.

- >> Sophisticated method of handling cooling fluids, handles and castors for easy transportation
- >> 400 W cooling power and excellent temperature constancy of  $\pm 0.05$  K (control) while using up to 60 % less energy
- >> Interfaces for external temperature sensor, RS 232 and USB, unique wireless controller (control)

designed  
for scientists



[www.ika.com](http://www.ika.com)



Mixing



Crushing



Temperature  
Control



Separation



Laboratory  
Reactors



Analytical  
Technology



Software