

Environmental

Safe use of carrier hydrogen for air monitoring with Multi-Gas TD-GC-MS

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Keywords

Multi-Gas TD, TD100-xr, carrier hydrogen, TRACE 1610 GC, ISQ 7610 MS, NeverVent technology, GC-MS, VOC, air pollutants, HAPs

Goal

A comparative study was conducted between helium and hydrogen as carrier gas for the analysis of volatile organic compounds (VOCs) in air, evaluating the analytical performance (linearity, detection sensitivity), as well as data integrity when using spectral libraries originally developed using helium as carrier gas. This comparison helps in understanding potential differences in analytical results and ensures that the transition to hydrogen carrier gas does not compromise the accuracy or reliability of the data.

Introduction

Monitoring volatile organic air compounds, also known as hazardous air pollutants (HAPs), is crucial for maintaining air quality in urban and industrial environments due to their significant health risks. The growing concerns about these potentially dangerous volatile organic compounds in ambient air, particularly in urban areas and from industrial emissions, have led to the development of numerous national and international regulations. The use of Thermal Desorption (TD) coupled with GC-MS is the analytical technique of choice to enrich volatile organic compounds from air and quantify them at trace levels.¹

In gas chromatography, the choice of carrier gas is pivotal for the separation and detection of VOCs. Helium has traditionally been the preferred carrier gas for analyzing volatile organic air toxics due to its inertness and performance benefits. However, hydrogen is becoming increasingly popular due to economic and supply considerations. Each carrier gas has unique advantages and challenges, and the choice should be guided by specific analytical requirements, cost constraints, and safety protocols. As the demand for sustainable and cost-effective solutions grows, hydrogen is expected to play a more significant role in monitoring hazardous air pollutants in urban and industrial settings.

Thermal Desorption is an established way to analyze VOCs in a wide variety of sample types. This smart note highlights the use of the new Multi-Gas TD system (Markes International) that allows a safe use of carrier hydrogen for the analysis of VOCs in air, enhancing operational flexibility and supporting more sustainable laboratory practices.

Experimental

In this study, Markes TD100-xr™ Multi-Gas system, coupled with the Thermo Scientific™ TRACE™ 1610 gas chromatograph and Thermo Scientific™ ISQ™ 7610 single quadrupole mass spectrometer, was employed to accurately detect and quantify compounds for effective air monitoring. This combination leverages several technological advancements to optimize analytical performance and operational efficiency:

- 1. Multi-Gas flexibility:** Markes Multi-Gas enabled Thermal Desorber makes thermal desorption compatible with hydrogen in addition to helium and nitrogen. This flexibility enables laboratories to select the most suitable gas for their specific analytical needs, balancing factors such as cost, availability, and analytical performance.
- 2. Hydrogen carrier gas:** The system can be configured to work safely with hydrogen carrier gas. Hydrogen offers several benefits, including faster analysis times and improved separation for certain compounds, as well as being a more cost-effective and sustainable option compared to helium.
- 3. NeverVent technology:** The ISQ 7610 mass spectrometer is equipped with Thermo Scientific™ NeverVent™ technology, which allows users to quickly switch from helium to hydrogen and replace the most suitable source ion volume without breaking the vacuum. This unique feature ensures continuous operation, minimizing downtime and preserving the vacuum integrity of the mass spectrometer, critical for maintaining accurate and reliable analytical results.

The comparison between helium and hydrogen carrier gas was carried out using the same analytical column. The method conditions for all analytes could be easily transferred. Flow rates were adjusted using the split ratio calculator available in the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) Instrument Method Wizard (Figure 1) to maintain the same split level and therefore the same amount of transferred sample. A further factor facilitating rapid adoption of hydrogen carrier gas in laboratories is that existing columns and consumables can be used without restrictions.

Results and discussion

Figure 2 presents a representative chromatogram of a 64-component VOCs mixture (75 ng in tube). Hydrogen, having a lower viscosity and higher diffusivity compared to helium, results in a faster linear velocity of the carrier gas leading to significantly faster separations. The last eluting compound, 1,2,3-trichlorobenzene, exhibits a notable difference in retention time when analyzed using helium and hydrogen carrier gas. Its retention time decreases from 42.15 minutes with helium to 25.41 minutes with hydrogen, providing a 60% reduction in analysis time. The insets of Figure 2 highlight the separation of *n*-butyl-benzene and 1,2-dichlorobenzene as an example of a critical pair. The comparison between the separation with helium and hydrogen as carrier gas demonstrates that the faster analysis time does not compromise the resolution of the chromatogram.

A linearity study was performed in the range of concentration from 1 ng to 150 ng in tube. A calibration curve was prepared to compare the linear response using the two carrier gases, since a different carrier may affect the MS detector's response and the overall analysis.

The Markes Calibration Solution Loading Rig (CSLR™) was used to create seven calibration levels. This device is chosen for its precision and reliability in preparing calibration, as demonstrated by the linearity obtained in this study. Including seven calibration points ranging from 1 ng to 150 ng in tube, the study ensures a comprehensive assessment of the linear response range, while the use of both helium and hydrogen carrier gas provides a robust comparison of analytical performance of the GC-MS under different conditions.

The resulting calibration curves, as shown in Figure 3, exhibit strong linearity with both carrier gases, evidenced by the high coefficient of determination (R^2). The confirmation of the linear response for all the tested VOCs demonstrates that the analytical system can accurately quantify compounds within the specified range, regardless of the carrier gas used.

The fidelity spectra were examined to rule out potential reactions that could occur with the use of hydrogen carrier gas because hydrogen is a reactive gas. As an example, Figure 4 compares the National Institute of Standards and Technology (NIST) helium library for two target compounds with mass spectra acquired with carrier hydrogen and helium. The library matching factors exceeded 90% for all analytes in the 64-component mixture, demonstrating that undesirable reactions were avoided.

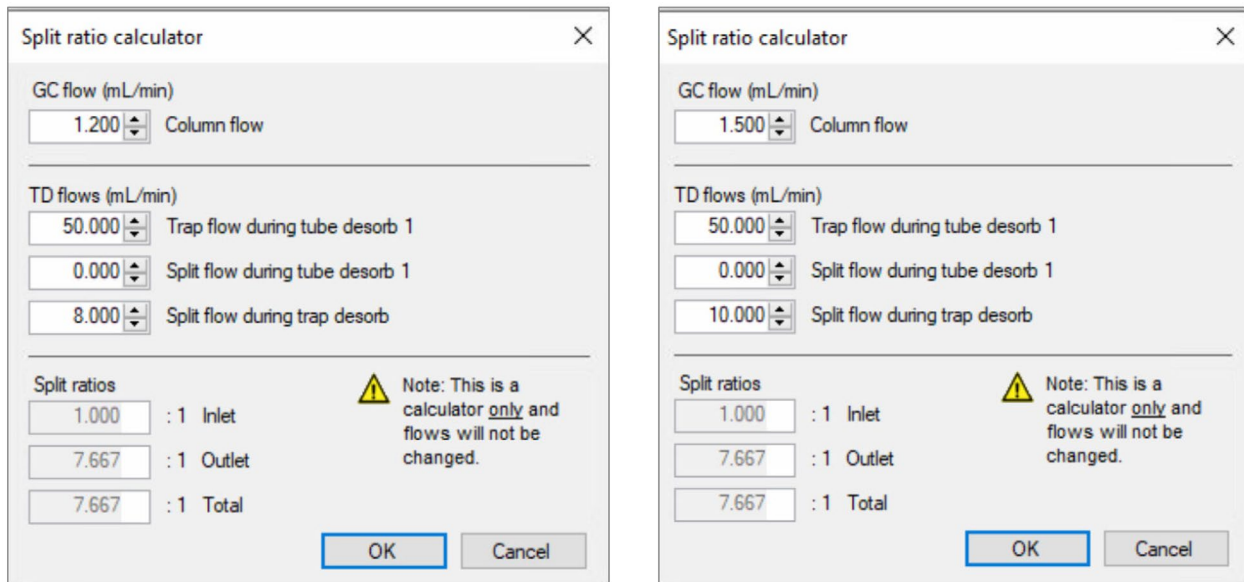


Figure 1. Split ratio calculator of the Chromeleon Instrument Method Wizard. Translation from helium carrier conditions (left) to hydrogen carrier conditions (right).

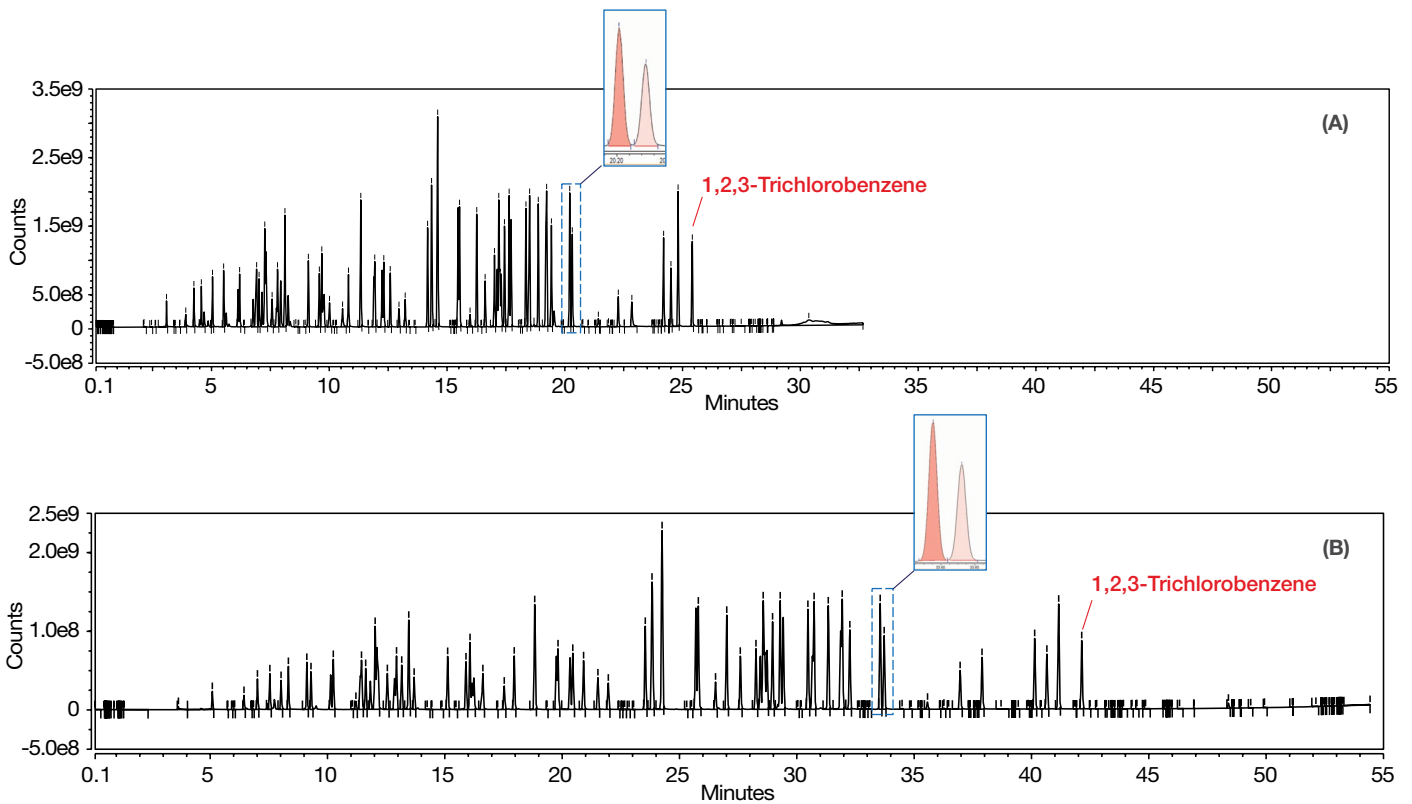
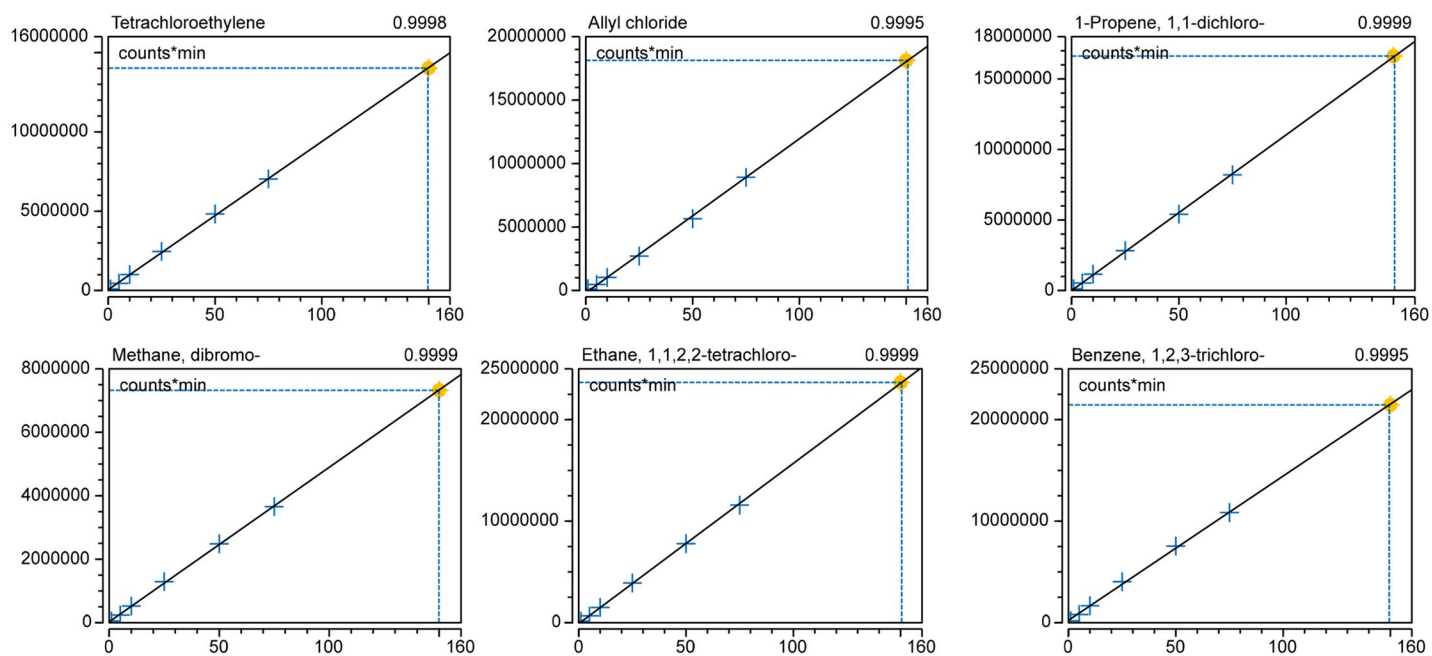


Figure 2. Full scan chromatograms of 64 VOC components (75 ng in tube) using hydrogen (A) and helium (B) carrier gas. Insets show the preserved separation of n-butyl-benzene and 1,2-dichlorobenzene.

(A)



(B)

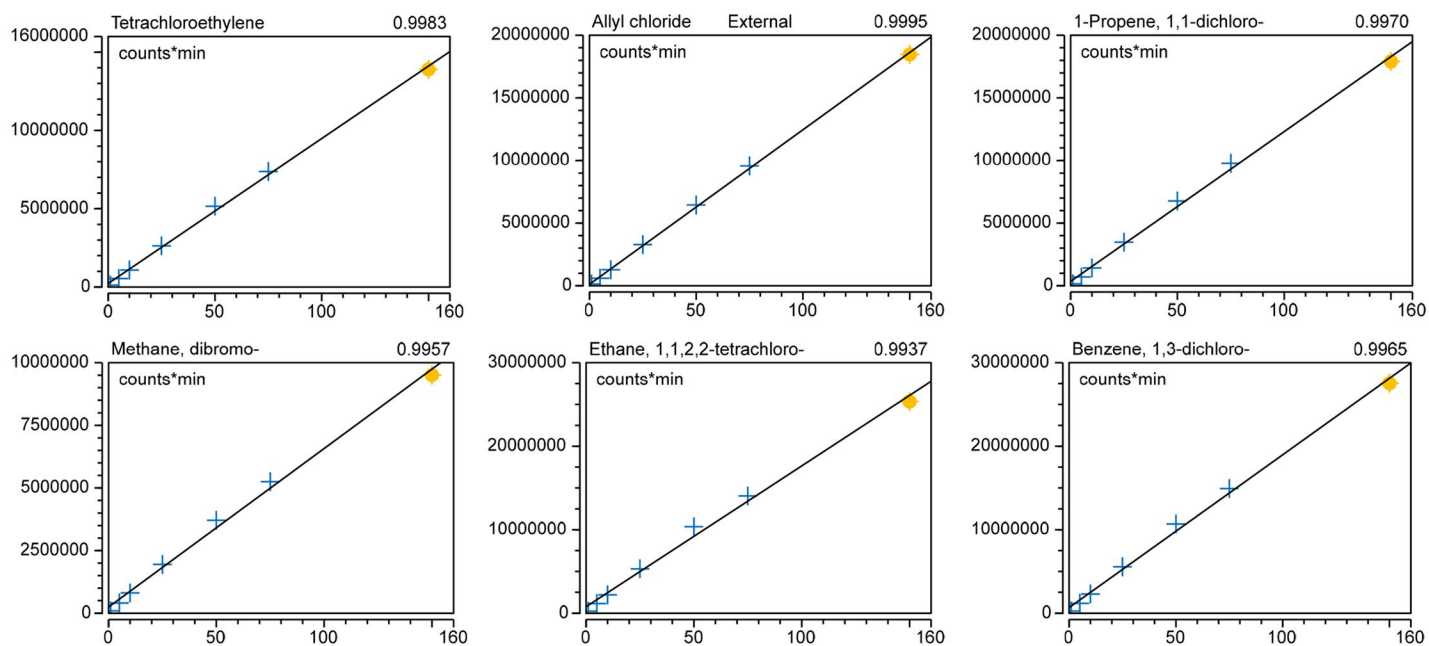


Figure 3. Examples of calibration curves from 1 ng to 150 ng in tube using hydrogen (A) and helium (B) carrier gas

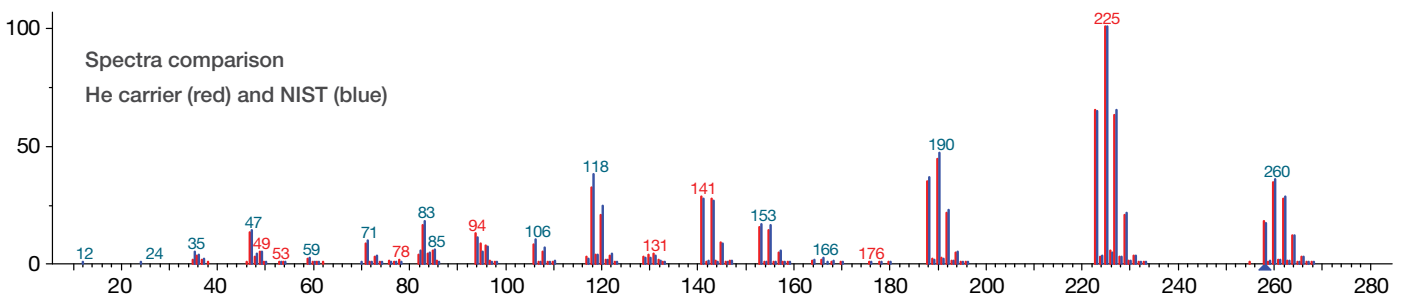
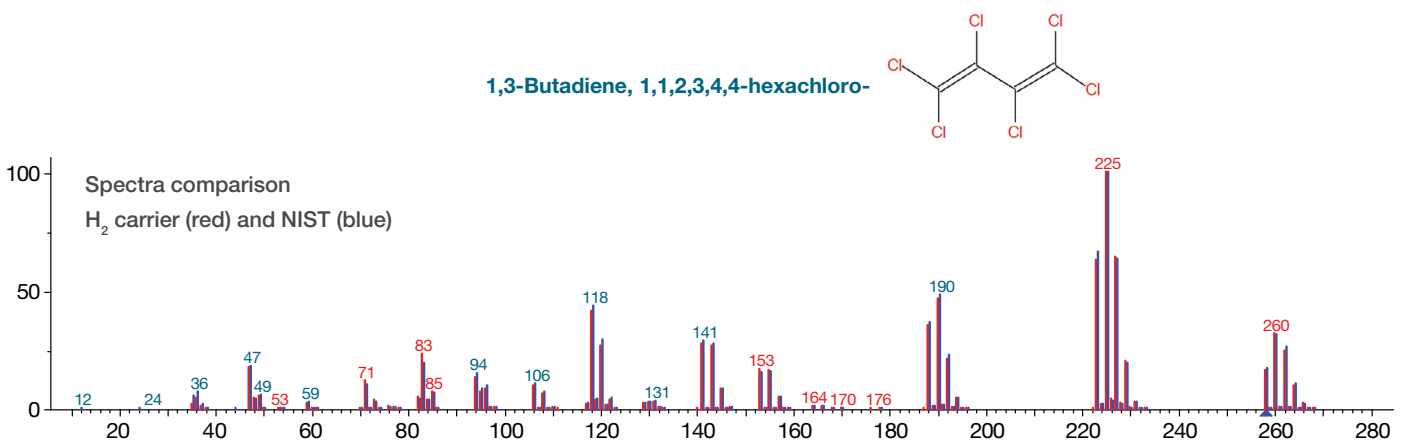
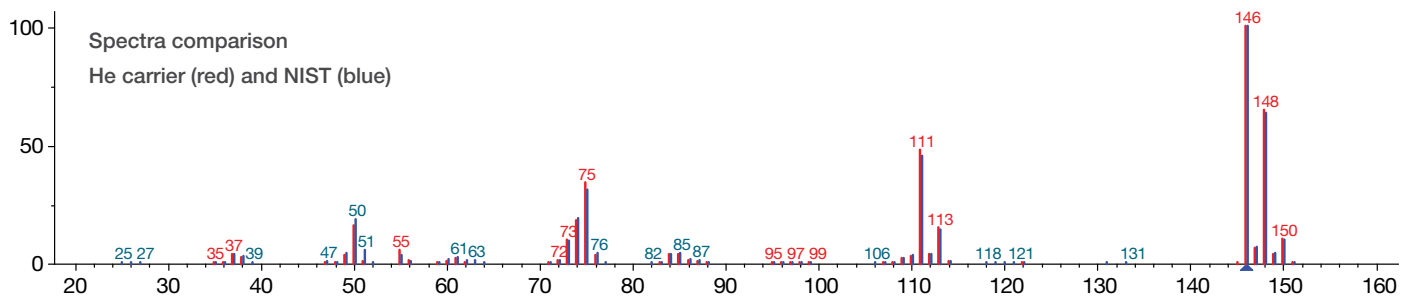
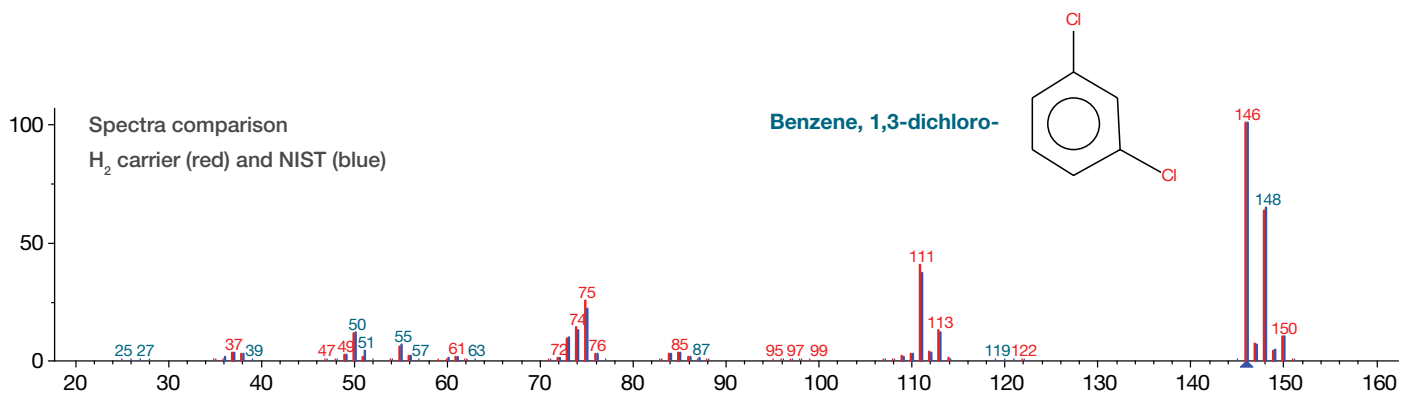


Figure 4. Examples of spectra comparison acquired with hydrogen and helium carrier gas versus NIST helium-based library, for two target compounds

Conclusion

The use of the Markes TD100-xr Multi-Gas system combined with the ISQ 7610 GC-MS for the analysis of VOC in air allows for a safe use of carrier hydrogen, making it a viable alternative to helium and offering an effective solution for laboratories facing the challenges of helium scarcity and rising costs, while maintaining the accuracy and reliability of VOC detection and quantification.

- The comparative analysis clearly confirmed that using hydrogen carrier gas in gas chromatography offers substantial benefits over helium. The significant reduction in retention time, as shown by the 60% decrease for 1,2,3-trichlorobenzene, leads to faster analysis without compromising the separation efficiency.
- Enabling shorter analysis time, hydrogen enhances laboratory productivity, reduces costs, and contributes to more sustainable practices.

- The results also indicate that both helium and hydrogen can be used effectively as carrier gases without impacting the response linearity for the VOC compounds under evaluation. Laboratories can confidently use hydrogen as an alternative to helium for quantitative analysis, ensuring accurate and reliable analytical results.
- When using multiple carrier gases, the ISQ 7610 NeverVent technology is key to easily switching from helium to hydrogen and back to helium with no venting required, making this operation very quick and safe.

In conclusion, coupling the Markes TD100-xr Multi-Gas system with the ISQ 7610 single quadrupole GC-MS offers a robust and flexible solution for air monitoring. This integration enhances operational efficiency, reduces costs, and maintains high data integrity, making it an invaluable tool for modern analytical laboratories.

Reference

1. Ramírez, N. et al. Comparative study of solvent extraction and thermal desorption methods for determining a wide range of volatile organic compounds in ambient air, *Talanta*, **2010** Jul 15, *82*(2), 719–27. DOI: 10.1016/j.talanta.2010.05.038

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