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Proton OnSite White Paper Series

The Effects of Hydrogen Purity on GC Analysis and Column Life

Abstract

Hydrogen has been widely adopted as a carrier gas to replace nitrogen and helium in GC applications for a variety of reasons. Superior advantages include faster analysis, lower cost and the reliability of supply that hydrogen (generated on-site) offers. The purity of carrier gas is crucial for higher performance, lower maintenance and the longevity of analytical instruments. High purity carrier gas lowers baseline noise and provides better sensitivity and longer column and gas trap life. The required purity for hydrogen carrier gas is 99.9999% (research grade) for trace work under 1 ppm, or at least 99.9995% for most normal analyses. Recent analyses from two third-party testing laboratories aid in understanding the importance of using research grade hydrogen gas generators to supply carrier gas to analytical instruments. This paper focuses on evaluating different hydrogen sources and addressing the benefits of using research grade hydrogen gas generators to meet the critical requirements of carrier gas for gas chromatography applications.

Introduction

It is widely acknowledged that the purity of carrier gas is critical for the performance, maintenance and longevity of analytical instruments - “contaminants in gases can significantly impact your analysis. Oxygen, hydrocarbons, and moisture can cause loss of sensitivity and accuracy of the GC and damage your column.” (1) Variations in samples’ sensitivities may cause laboratories performing normal analyses to experience high baseline noise- a result of water moisture and oxygen, which may distort sample results. Understanding the purity of various hydrogen supply methods is vital in identifying the appropriate hydrogen source for your operation, and will significantly impact the performance of analyses conducted. Using research grade (or better) high purity hydrogen can provide many benefits beyond stable results. “Oxygen is known for causing column stationary phase and inlet liner degradation in analytical instruments, further damaging the decomposition of labile analytes.” (2) Removal of contaminants, such as oxygen, is critical to GC performance because “as the column is heated, very rapid degradation of the stationary phase occurs. This results in the premature onset of excessive column bleed, peak tailing for active compounds and/or loss of efficiency (resolution) ... by the time oxygen damage is discovered, significant column damage has already occurred. In less severe cases, the column may still be functional but at a reduced performance level. In more severe cases, the column is irreversibly damaged.” (3)

Therefore, carrier gas purity is one of the most critical factors to consider when your sample results demand stability and you want to get the most useful life from the GC column. The supply of that gas, and the variability that is introduced to your process, must be understood.

Hydrogen is generally supplied to laboratories by two methods: bulk hydrogen delivery usually sourced from large natural gas reformation plants and packaged in cylinders or tube trailers for easier delivery; and on-site hydrogen generation via water electrolysis. The bulk delivery method has been in practice for decades and, in general, has proven to be a reliable source of hydrogen for the laboratory market. The purity content of bulk hydrogen and the price for guaranteed high purity are chief factors that must be understood when selecting a hydrogen source for gas chromatography applications. The most common contaminants associated with bulk hydrogen delivery that negatively affect analyses include water moisture, oxygen, hydrocarbon, carbon dioxide, carbon monoxide and nitrogen.(4) Proper measures must be taken to mitigate these contaminants in order to control the performance of analytical instruments and assure accurate results. Packaging, distribution, and purification methods are all factors that impact the purity of the gas that is provided to the customer.

The variability of purity, and in some cases reliability of supply, has caused a growing number of chemists and lab managers to consider generating their own hydrogen using water electrolysis. On-site hydrogen generation via water electrolysis provides the user with a research grade pure source of hydrogen for use as a carrier gas and gives the user complete control over cost and supply. Hydrogen produced via Proton Exchange Membrane (PEM) water electrolysis technology, does not contain any impurities other than trace amounts of water moisture, nitrogen and oxygen that are well below levels that negatively affect sample results or column life, and thus, allow the hydrogen to maintain a consistent level of purity.

Experiment

Testing was conducted by two third-party laboratories to analyze the output of a hydrogen gas generator producing 99.99999% pure hydrogen to be used as a carrier gas for GC analysis. As was previously stated, the purity of carrier gas is key as it impacts sample results in analytical testing as well as the longevity of analytical instruments used. O2 and water moisture output levels are of special concern and were the target contaminants in the experiment. The hydrogen generator used was a Proton OnSite® model G600-HP. O2 was measured by a Delta-F DF-550 Nanotrace Oxygen Analyzer (low-detection-level 0.2 ppb, resolution 0.1 ppb) and water moisture output was measured by a GE Moisture Monitor Series 35 IS.

Discussion

Guaranteed Ultra High Purity & Consistent Results

The enabling feature of Proton's water electrolysis system is the proton exchange membrane (PEM), which only allows water and positive ions to cross between compartments. The membrane also serves as the electrolyte in the cell, eliminating the need for hazardous liquid electrolytes such as concentrated potassium hydroxide. PEM water electrolysis simply splits pure deionized water (H2O) into its constituent parts, hydrogen (H2) and oxygen (O2), on either side of this membrane. When a DC voltage is applied to the electrolyzer, water fed to the anode, or oxygen electrode, are oxidized to oxygen and protons, while electrons are released. The protons (H+ ions) pass through the PEM to the cathode, or hydrogen electrode, where they meet electrons from the other side of the circuit, and are reduced to hydrogen gas. The two reactions that occur in the cell are as follows:

$2H_2O \rightarrow 4H^+ + 4e^- + O_2$

$4H^+ + 4e^- \rightarrow 2H_2$

Thus, the only possible components of the streams are hydrogen, oxygen and water moisture, as shown in Figure 1 below.

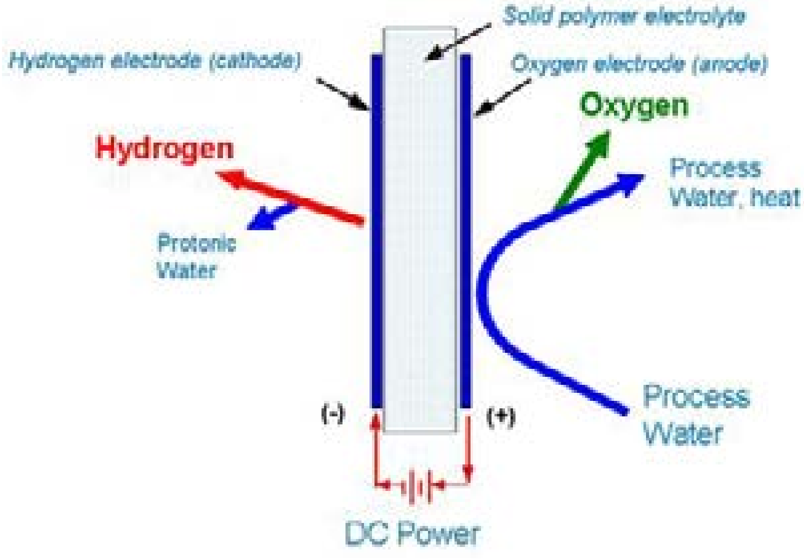

Figure 1. Proton Exchange Membrane (PEM) Illustration.

The hydrogen generator used in this analysis utilizes Proton Exchange Membrane (PEM) technology with a high differential pressure design to safely and efficiently generate hydrogen at 8 barg and oxygen at ambient pressure. This significant pressure difference eliminates the possibility of oxygen entering the hydrogen stream- not only providing superior unit safety, but also guaranteeing hydrogen of ultra high purities for analytical applications.

As illustrated below in Figure 2, the O2 levels measured from the hydrogen gas generator averaged below 0.55 ppb after a stable baseline was achieved. The water content testing results depicted in Figure 3, show the hydrogen gas generator performance at approximately 20 ppb. With O2 less than 1 ppb and water moisture content less than 20 ppb, the total impurities are less than 50 ppb and the hydrogen gas purity of the G600-HP is approximately 99.999995%, approaching 99.999999%.

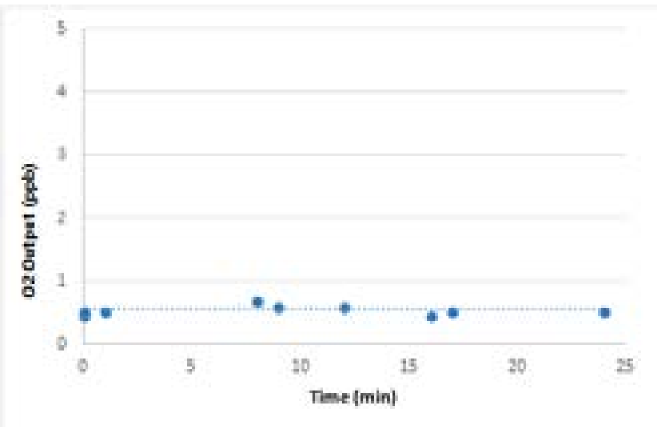

Figure 2: O2 output results from G600-HP.

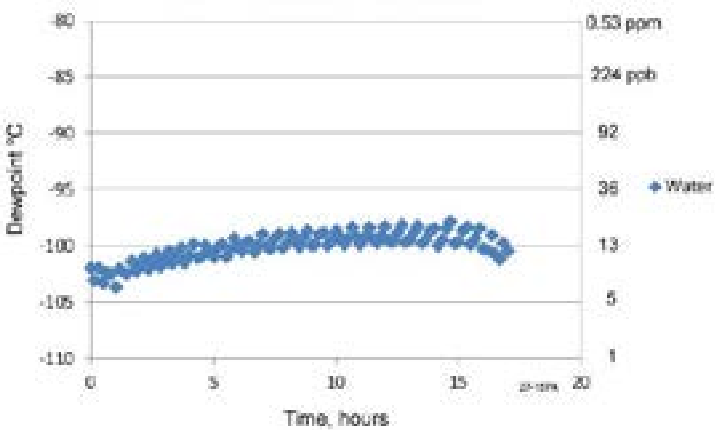

Figure 3: Water content results from G600-HP.

Improved Efficiency

When laboratories test a sample, efficiency is key. Hydrogen, especially at high purities, can benefit analyses. High purity carrier gas enables lower detection limits based on its ability to reduce band broadening. High purity hydrogen also produces sharp peaks that simplify the process and improve performance.

When performing a trace analysis on samples with extremely low concentrations, one must rely on a high purity carrier gas to ensure a stable reading. There are many advantages to introducing a high purity carrier gas into GC testing. Other than high sensitivity, lowered baseline noise and faster analysis, hydrogen produced on-site with a high purity hydrogen generator yields additional benefits. “Ensuring gas hygiene is one of the most important steps you can take to optimize GC system performance. Impure gases can introduce contaminants, or cause installation delays, premature instrument failure, and flawed results.”(5)

“All but the 6.0 grades of gas are qualified by statistical quality control. Generally, 10% or fewer of the cylinders in a fill batch will be analyzed to verify gas quality....The problem with per cylinder guarantees is that the analytical costs incurred by the gas supplier to ensure the gas quality of each cylinder are passed along to the customer.” (4) When it is determined that a

laboratory requires certified high purity gas, the cost associated with this requirement becomes a concern. “The inefficient use of increasingly expensive and rare gas can go right to your bottom line.” (5) Alternatively, many laboratories choose to purchase uncertified cylinder gases. In doing so; gas chromatography manufacturers often suggest that the laboratories source gas traps, such as oxygen traps, moisture traps, hydrocarbon traps and combination traps, as a final line of defense, to filter impurities and purify the inlet carrier gas, leading to additional consumable expenses. In both cases, certified and uncertified gas cylinder sourcing, laboratory professionals can benefit from producing high purity hydrogen on-site, allowing further control of their gas purity and costs associated with the supply of hydrogen to their GC analyses.

“The general principle is that your GC gases should be free of the impurities that would interfere with your specific analysis or would degrade your chromatographic equipment.” (4) On-site hydrogen generators, employing PEM technology, only use DI water and electricity and will not contain any impurities other than water moisture and trace amounts of nitrogen and oxygen. In fact, the research grade hydrogen produced by the G600-HP, with oxygen less than 1 ppb and water moisture less than 20 ppb, eliminates the need for laboratories to secure purification tools, such as gas traps, that add additional cost to their processes. “This reduces the risks of column damage, sensitivity loss, and instrument downtime.” (1)

Extended Column Life

The use of hydrogen, as a carrier gas for gas chromatographs can be very beneficial, specifically, in extending column life, because it allows for a faster analysis (a result of hydrogen’ higher linear velocity). Hydrogen can also keep column temperature low due to the speed of the separations. Column life is a quintessential aspect of maintaining sound analytical instruments and ensuring stable readings. Columns can be susceptible to many contaminants if the proper carrier gas is not identified. Contaminants not only threaten the condition of the analytical instruments, but also make for problematic testing results. “With extended use, columns may accumulate absorptive debris or experience a loss of surface deactivation that leads to increased polar peak tailing and subsequent loss of resolution as well as compromised minimum detectable levels,” (6) making it critical for laboratory professionals to secure a safe and dependable high purity carrier gas for analytical testing. The purity of the carrier gas employed is directly related to the performance and lifespan of analytical instruments. Aimed to prevent column damage, extend detector life and improve the quality and consistency of GC separations, research shows that high purity hydrogen supports analytical testing while greatly reducing the chance of column degradation. In fact, research grade hydrogen removes common contaminants such as oxygen and moisture from the sample. Constant exposure to moisture and oxygen, especially at high temperatures, results in rapid and severe capillary column damage.

Thus, many laboratory professionals rely on oxygen and moisture traps to extend column life and protect their analytical instruments. (2) The purity requirements depend on the function of the gas, the sensitivity of the analysis and the specific detector. For example, – oxygen in the carrier gas will shorten the life of your column by contributing to stationary phase degradation. To select the appropriate gas, you have to know what impurities exist and at what levels these impurities will interfere with your analysis. “Packed and capillary columns may respond differently to the active impurities in the carrier gas. This difference in response depends on the extent of cross-linking, phase loading, age and condition of the column, and typical temperatures the column is exposed to.” (4)

Conclusion

As analytical data presented in this paper supports, the purity of carrier gas is crucial for laboratory operations conducting GC sample analyses. On-site gas generators producing research grade hydrogen offer many benefits to gas chromatographers in their analyses. Specifically, these generators provide faster analyses, improved efficiencies and lower operational expenses. Additionally, the reliability of supply and the extended column life these generators provide are of great value to laboratories conducting GC analytical testing. Proton OnSite’s G600-HP is a cost-effective solution that eliminates the hassles experienced by laboratory professionals when supplying their GC with high purity carrier gas sourced from delivered cylinders. Thus, the G600-HP is an advantageous source of research grade hydrogen to support analytical testing and improve analysis performance.

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