Advantage Business Media

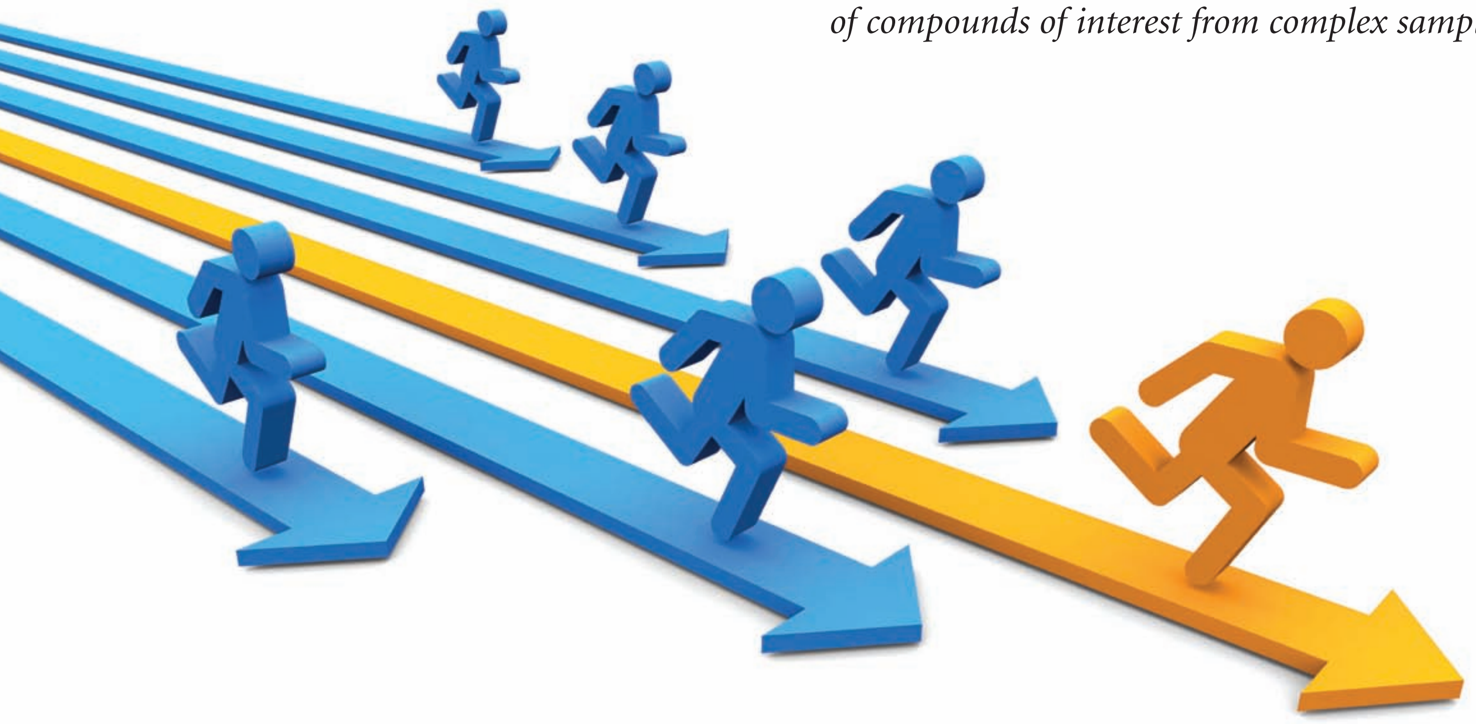
June 2010

Chromatography Techniques
Product Innovation for Chromatographers

A supplement to Laboratory EQUIPMENT

Hydrogen Gives GC Head Start

In-house generation of H_2 for head space gas chromatography provides effective extraction of compounds of interest from complex samples.



›› by Peter Froehlich, Peak Media, and Corky Belobraydich, Parker-Hannifin Corp.

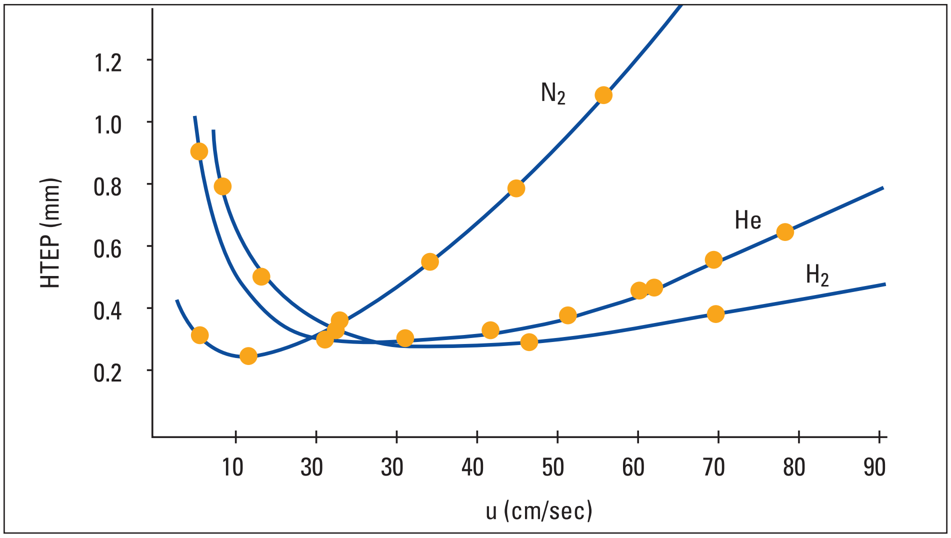


FIGURE 1. Van Deemter Plot for N_2, He and H_2. While N_2 provides the highest chromatographic efficiency, the optimum velocity for H_2 is considerably greater, so the use of H_2 as the carrier gas can lead to analysis times that are four times faster than when N_2 is used.

Introduction

Headspace techniques are commonly used to extract compound(s) of interest from a complex matrix to prepare samples for gas chromatography (headspace GC) and a variety of other analytical techniques. Typical applications of headspace technology include the extraction of ethanol from blood samples in a forensic laboratory, the analysis of arson samples, the extraction of volatile aromatic hydrocarbons from environmental samples such as soil, and the extraction of residual solvents used in pharmaceutical processing. These matrices include materials that may be deleterious to the GC column and/or complicate the separation and/or detection.

When headspace GC is employed, the sample is placed in a vial with an appropriate gas, sealed, and heated for a period of time to optimize the concentration of the compound(s) of interest in the vapor phase. The vapor phase is then injected into the GC, separated and detected. A critical issue is the selection of the gas; it must not react with the compound(s) of interest, and it must be compatible with their separation and detection.

Historically, He has been used for headspace GC. However, He supplies are diminishing, and its availability and price have become significant issues. He is obtained from the fractional purification of natural gas; in recent years, the use of He has been greater than the production of the gas, and chromatographers are preparing for the time when He is no longer economically reasonable to use. In the following, we describe the use of H_2 for headspace analysis and discuss the safety, convenience and cost reduction that is obtained by in-house generation of H_2.

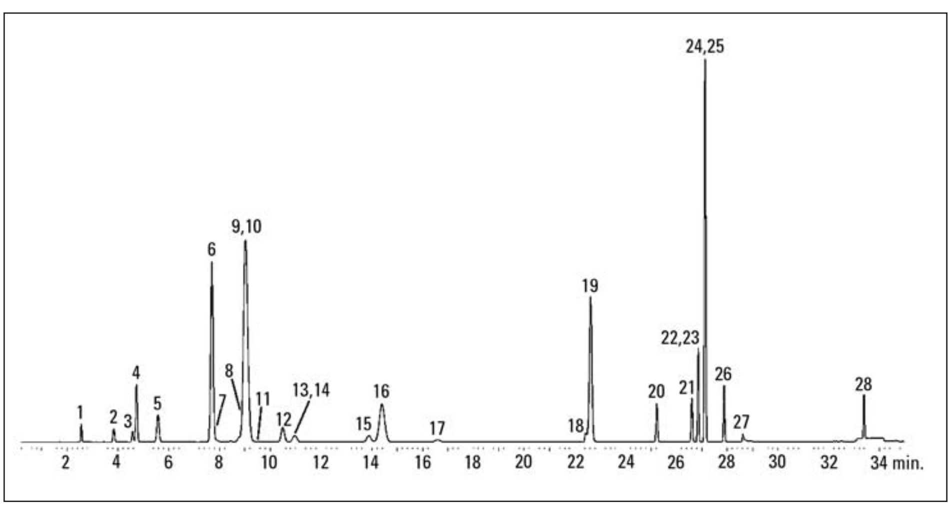


FIGURE 2. Headspace GC separation of 28 Class 1 and Class 2 residual solvents for pharmaceutical processing. Gas = H_2. Samples shaken and heated at 80 C for 15 min; 1 mL used for headspace injection. Photo: Restek, Inc.

Hydrogen, preferred carrier gas for headspace GC

H_2 and N_2 are commonly used for headspace GC. These gases are compatible with GC separations, do not react with the compounds of interest, are readily available and are inexpensive. While either gas is acceptable, H_2 leads to a considerably greater level of efficiency than N_2.

A Van Deemter plot (Figure 1) presents the efficiency (Height equivalent to a theoretical plate [HETP]) of a separation as a function of the linear velocity of the carrier gas and shows that hydrogen allows for a higher flow rate than nitrogen for the optimum separation. The higher flow rate leads to a shorter separation time, thereby increasing laboratory efficiency. The maximum efficiency for N_2 is obtained at a linear velocity of 8 to 10 cm/sec while the maximum efficiency for H_2 is obtained at approximately 40 cm/sec. In addition, the use of H_2 frequently allows for a lower temperature for the separation, thereby increasing column life and system longevity and reducing the possibility that the analyte will undergo thermal decomposition.

A chromatogram showing the separation of a standard reference mix of solvents used in pharmaceutical processing via headspace GC is presented in Figure 2. A 1-mL sample of 28 residual solvents at the regulatory limit concentration was sealed in a vial with H_2, shaken and heated at 80 C for 15 min, and then injected onto an RTx-1301 capillary column (Restek Corporation). A very satisfactory extraction and separation can be obtained with H_2 as the headspace gas and carrier gas.

Providing hydrogen for headspace GC

H_2 is obtained by the electrolysis of water as shown in equation 1 using a metallic electrode or an ionomeric proton exchange membrane using an in-house generator:

Equation 1: $2H_2O + 2e^- \rightarrow 2H_2 + O_2$

Water electrolysis of using metal electrode

The traditional method of generating H_2 via the electrolysis of water involves a metal anode (i.e., Pd), a metal cathode and a strong, water soluble electrolyte (i.e., 20% NaOH) because water does not conduct an electric current very effectively.

A cathode consisting of a bundle of palladium tubes is used to provide high purity gas (only H_2 and its isotopes pass through the cathode, oxygen and other impurities collect at the anode).

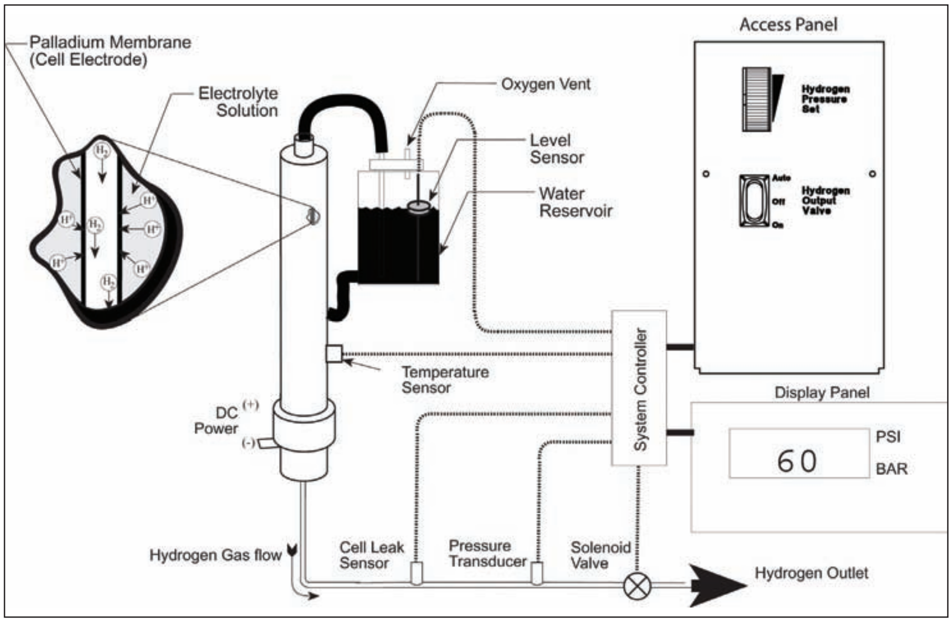


FIGURE 3. Overall design of a system for the generation of hydrogen via the electrolysis of water using a metal catalyst. Photo: Parker Hannifin Corp., Haverhill, MA

The design of a typical system for the in-house generation of hydrogen via the electrolysis of water using a metal electrode is presented in Figure 3 (Parker Balston Model H2PD-300 hydrogen generator, Parker Hannifin Corporation). This system generates H_2 with a purity of 99.99999+ %, oxygen content of <0.01 ppm and moisture content of 0.01 ppm at a maximum flow rate of 300 cc/min with a maximum outlet pressure of 60 psig. Once the H_2 is generated, it can be directly ported to the instrument.

The use of a Pd tube cathode provides a considerable improvement in the purity of the generated H_2, compared to systems that use a desiccant as the final drying agent. Figure 4 presents gas chromatograms for hydrogen gas prepared by the two techniques and monitored via a discharge ionization detector. The large black peaks indicate the presence of a combined concentration of 12 ppm of O_2 and N_2 in the H_2 that was dried with a desiccant. These peaks are not present in the H_2 that was generated via the tubular Pd cathode.

In a typical application, Pd-based hydrogen generators (H2PD-150 and 300) are used to provide H_2 for headspace GC at the Department of Forensic Sciences at West Virginia Univ. Dr. Suzanne Bell of WVU reports that her group analyzes a broad range of samples by headspace GC, including blood (alcohol) and burnt materials such as wood in arson investigations in these laboratories, and a chromatogram from a spiked blood sample is presented in Figure 5. The headspace extraction was carried out using H_2 at 65 C. Similarly, Dr. Bell reports that a series of terpenes from wood samples can be readily extracted from wood samples using a 20 min extraction using H_2 at 120 C for 20 min.

In recent years, the use of a proton exchange membrane (PEM), an ionomeric (ionic polymer) membrane such as Nafion (a sulfonated tetrafluoroethylene polymer) or polybenzimidzole (PBI) that is designed to conduct protons while being impermeable to gases such as hydrogen and oxygen has been used to electrolyze water. While PEM's are commonly used in fuel cells to create an electric current (and form water) from hydrogen gas and oxygen gas, when an appropriate potential is applied to a PEM in the presence of water, the reverse process occurs, and the water is dissociated to form O_2 and H_2. A significant benefit of this approach for the generation of hydrogen is that DI water can be employed instead of the caustic 20% NaOH solution. A Pd membrane is included to further purify the H_2 by removing O_2 to <0.01 ppm and moisture down to <1.0 ppm.

The general design of the Parker Model H2PEM-510 hydrogen gas generator, which is based on PEM membrane technology, is capable of generating 99.9995% pure H_2 at a flow rate of 510 mL/min at pressures up to 100 psi.

While high-purity H_2 can be generated using an in-house generator, some labs obtain H_2 from a pressurized cylinder from a commercial source. This approach has a number of disadvantages including safety, convenience and cost issues. An in-house, benchtop H_2 generator can provide the gas at a purity, pressure and flow rate that meets the needs of the GC laboratory, and is considerably safer, more convenient and less expensive than the use of cylinder H_2 (or He) gas.

Benefits of in-house-generated H_2

Safety

In-house generation of H_2 allows the required volume of gas to be generated on demand at a low pressure and is considerably safer than cylinder gas. In contrast, when cylinder gas is used, a cylinder may contain a considerable amount of hydrogen gas at high pressure. If a leak were to occur (i.e., the valve was compromised), a large quantity of gas would be released into the laboratory and would displace the air, leading to the potential of asphyxiation and/or explosion. Because in-house H_2 generators typically have a maximum output of 1,200 mL/min at a pressure of 100 psig, the volume of gas that could escape in the lab due to a leak in the system is small and presents a minimal hazard.

The in-house H_2 generators described above include a variety of safety features to minimize the possibility of hazardous situations. For example, if an overpressure or pressure loss of the system is observed, H_2 production will be immediately terminated and a diagnostic message will be generated. In addition, the message can trigger an audible alarm and/or send a signal to an external controller or operator.

In-house H_2 generating systems are designed to meet the standards of a broad range of safety requirements, including NFPA, OSHA 1910.103. The systems are designed to meet the requirements of other regulatory agencies, including IEC, CSA, UL and cUL.

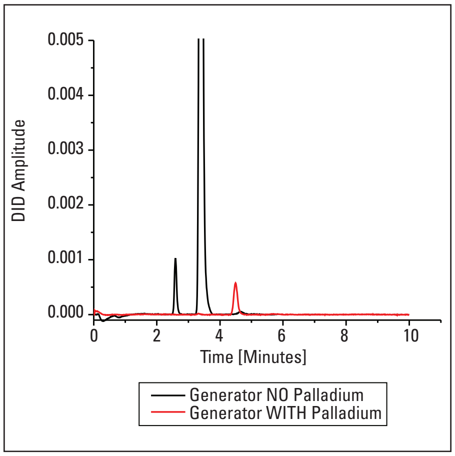


FIGURE 4. GC-FID chromatogram. Black line—generation of hydrogen with a system with palladium membrane as the final purifier. Red line—generation of hydrogen with a generator using a desiccant as the final purifier.

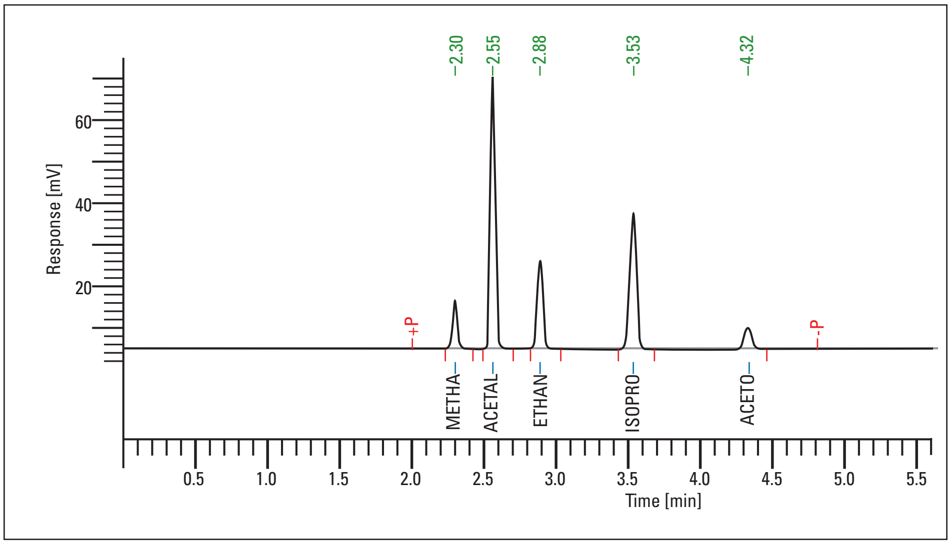


FIGURE 5. Headspace GC analysis: HS conditions - Oven 60 C, needle 65 C, pressurization time 3 min, injection time 0.04 min, 110 C transfer line temperature. Purge and carrier gases are hydrogen. GC: 40 C for 5 min, 25 C/min to 100 C hold 1 min; 25 C/min to 200 C. Column flow is 1.50 mL/min and injector is 200 C. Compounds are methanol, acetaldehyde, ethanol, isopropanol, and acetone. Photo: Restek, Inc.

It should be noted that vials containing hydrogen gas for headspace analysis can safely withstand fairly extreme conditions; for example, the West Virginia group reports that they heat vials containing H_2 for 20 min at 120 C to extract the compounds of interest.

Convenience

When an in-house hydrogen generator is employed, the gas is readily available on a continuous or on-demand basis. The operator simply needs to add DI water manually. Full-flow operation on a 24/7 basis requires approximately 4 L of water a week and can be automatically filled by installing a continuous source of DI water to ensure continuous operation. The conductivity of the water used for a PEM-based system is continuously monitored (ionic materials in the water could foul the electrode, and the system will shut down if the conductivity reaches a preset level). If a PEM-based system is employed, the deionizer and filter are replaced every six months. A typical user reports that their in-house systems are reliable, and provides the required hydrogen as needed.

In contrast, when a hydrogen cylinder is employed, the operator must make certain that it contains a sufficient amount of gas for the desired operation. In many facilities, replacement cylinders are frequently stored in a remote (outdoor) location for safety reasons, and specially qualified personnel may be required to perform cylinder replacement. This certainly would be an inconvenience in inclement weather and could lead to a hazard in earthquake-prone zones of the world. When bottled gas is employed, it is necessary to maintain a supply of spare cylinders and order/return cylinders on a periodic basis.

Eliminating contamination

When a bottle is used to deliver H_2, the connection between the source of the gas and the chromatograph must be broken when the cylinder is replaced. This can lead to the introduction of contaminants such as moisture and other materials that may be present in the lab atmosphere into the system. This may have an effect on the column and/or separation. In contrast, when an in-house H_2 generator is used, a direct connection is made between the generator and the chromatograph that need not be broken, eliminating the possibility of contamination.

Cost

The overall cost of operation of an in-house hydrogen generator is considerably lower than the use of hydrogen cylinders. The operating costs for an in-house generator are for electricity and DI water. For example, the power consumption for the 500 mL/min system is 235 W, so if the generator is used for 40-hr cycle on a 52 week basis, approximately 5000 Kwh would be used (at 10 c/kwh, the annual operating cost would be $500). The cost of maintenance and replacement of the deionizer and desiccant of an in-house H_2 generator is about $500/yr. While the payback period of the hydrogen generator clearly depends on the amount of gas that is consumed and the local cost of the gas cylinders, the H_2 generator pays for itself in a year or two in many facilities. When cylinders are used to supply the gas, the time cost of ordering the gas and bottle demurrage should be included; these costs are not present with an in-house H_2 generator. CT

For more information, please contact Peter Froehlich at pfpeakmedia@msn.com.