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ELECTROLYTIC CONDUCTIVITY DETECTOR FOR TRACE ANALYSIS OF H₂, HD, D₂, AND NEON IN HYDROGEN AND DEUTERIUM*

E. L. Garwin and A. Roder

Stanford Linear Accelerator Center Stanford University, Stanford, California 94305

Abstract

A gas chromatograph has been developed to detect traces of H_2 , HD, D_2 , and neon in hydrogen or deuterium. It uses a stainless steel column packed with ferric chloride-treated alumina, hydrogen-doped helium carrier gas, palladium chloride to convert the eluted components into their corresponding chlorides, and an electrolytic conductivity cell to measure the chloride concentration. The detection limits of the instrument are 0.01% H_2 in D_2 , 0.02% D_2 in H_2 , and 0.02% HD in either gas.

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Introduction

The evaluation of experimental results obtained from deuterium targets at the Stanford Linear Accelerator Center requires that the gas be periodically analyzed for its HD and H_2 impurity content at levels ranging from 0.1% to 3%. This analysis has traditionally been performed at great expense and difficulty by mass spectrometry.

The literature shows that gas chromatography has been used by others to separate H_2 , HD, and D_2 , using various types of columns and detectors. Glass capillary columns with internally etched surfaces are reported (1-4) to perform the best separation of isotopic molecules, but are very difficult to fabricate and procure, expensive, and fragile. Columns packed with molecular sieve materials or etched glass beads have also been used with varying degrees of success (5-9), but require careful activation and cryogenic temperature control, with no apparent advantages over alumina.

The selection of ferric chloride-treated alumina for our application was dictated by this material's reported (10-12) reliability and reproducibility, and by the fact that it was readily available and could be packed into columns using conventional techniques.

The detection of hydrogen in a helium carrier gas by means of thermal conductivity detectors is limited in sensitivity by the small difference in the conductivities of the two gases. This problem has been circumvented by some of the authors cited above (1,2,4,6,8,10), either by using neon instead of helium as a carrier gas or by oxidizing the eluted hydrogen isotopes over hot copper oxide and monitoring the resulting water with thermal conductivity detectors. A third approach (13-16) has been to convert the eluted components into inorganic gas compounds, dissolving these compounds in water, and

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measuring the changes in the water conductivity. For our purposes, these electrolytic conductivity detectors offered the advantages of having a higher sensitivity than thermal conductivity detectors, while being able to respond only to specific gases, determined by the choice of converters.

Drawing from this store of information, we have developed a gas chromatograph for the separation of H_9 , HD, and D_9 , whose salient features are:

- 1. Detector response specific to H_2 , HD, and D_2 .
- 2. Detectability limits of 0.01% H_2 in D_2 , 0.02% D_2 in H_2 , and 0.02% HD in either gas.
- 3. Optional capability of detecting neon at 0.1% levels during analysis.
- 4. Reproducibility of $\pm 3\%$ of the signal strength for any given sample.

System

Figure 1 shows a block diagram of the system whose components are identified in the figure caption. The function of these components and, wherever pertinent, novel details about their operation will be described below.

All the components are interconnected with Swagelok fittings, the metal ferrules of which are replaced with Viton O-rings at glass or plastic connections.

Carrier Gas

Helium containing 10 ppm hydrogen is used as carrier gas [1] at a typical flow rate of 45 cc/min. The hydrogen doping is added in order to stabilize the response of the palladium chloride converter and reduce tailing, and will be discussed further in the section devoted to the converter.

The carrier gas flows through a conventional pressure regulator [2], and a differential constant flow controller* [3]; it is then purified through a 13X *Moore Products Co., Spring House, Pa. 19477, Model 63 BU-L. molecular sieve trap [4] maintained at liquid nitrogen temperature, and passed through a 0.22 μ m filter [5] to remove entrained particles.

A sampling value* [6] is used to introduce $10 \ \mu l$ samples of hydrogen or deuterium [7] into the chromatographic column.

Column

The column [8] consists of a stainless steel tube, 3.28 mm OD \times 1.75 mm ID \times 1 meter long (.125" \times .069" \times 39.4"), packed with 60/80 mesh alumina treated with ferric chloride according to a process described by Shipman (10); this consists of dampening a quantity of alumina with a 1.8M solution of ferric chloride, titrating the slurry with 6M ammonia to a pH of 7, filtering and washing the mixture to a pH of 6, and drying the coated alumina at 120^oC for 24 hours.

Column efficiency is highly sensitive to this treatment; we have obtained best results with Shipman's C packing, in addition to which we have taken special precautions to classify our final product in the 60/70 mesh range in order to remove fines and the dark brown residues precipitated during the treatment.

Before it is used for the first time, and after it has been in standby condition for several weeks, the column is reactivated by baking in situ for 12-16 hours at 120° C, while maintaining a flow of a few cc/min of pure helium. The procedure consists of removing the dewar which normally surrounds the column, and replacing it with a suitable temperature-controlled heating coil.

Because the column is also capable of separating neon from H_2 or D_2 , a conventional thermal conductivity detector**, installed as shown in Fig. 1, can be used to measure the neon content of the sample.

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^{*}Carle Instruments, Inc., Fullerton, CA 92631, Model 2015 P. **Carle Instruments, Inc., Fullerton, CA 92631, Model 1000.

Converter

A palladium chloride converter [9] was used by Mohnke <u>et al.</u> (15) to transform hydrogen isotopes into their corresponding chlorides. The converter consists of a quartz tube, 3 mm OD \times 1 mm ID \times 4 cm long (.118" \times .039" \times 1.5"), packed with palladium chloride* and surrounded by a heater. The packing covers the central 4 mm (.157") of the tube, with quartz wool plugs placed at each end of the packing. The palladium chloride packing is buttressed at its downstream end by a constriction in the quartz tube, which effectively prevents the material from being blown out into the detector during gas pressure surges.

Several aspects of the converter's operation merit comment at this point: its efficiency as a function of temperature, its reaction mechanism, and its lifetime.

All other things being equal, the signal strength obtained increases as a function of converter temperature, and then remains constant from 80° C to 200° C. We maintain a temperature of 150° C by means of a $1000-\Omega$, 10-watt, wire-wound hollow ceramic resistor slipped over the quartz tube and connected to a voltage source variable from 0-120V.

During our early tests, we observed that following a period during which the chromatograph had been on prolonged standby, the first hydrogen samples introduced into the column yielded no signal, and that the first peaks which were eventually produced were smaller than those of subsequent samples. Introducing closely spaced samples, we further observed that peak height increased until it reached a maximum value, which then decreased by 1% after a 20-minute time delay between successive samples.

*Engelhard Industries, Newark, NJ 07114.

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These observations are consistent with the well-known affinity of palladium for hydrogen and with the postulated reaction mechanism of the converter, which is

$$Pd Cl_2 + H_2 \rightarrow 2HCl + Pd$$
.

As the leading edge of the eluted hydrogen isotope enters the converter, it reduces a portion of the dichloride to palladium, which then immediately absorbs the remainder of the sample. At a temperature of 150° C and atmospheric pressure, palladium absorbs approximately 100 times its volume of hydrogen (17), eventually reaching an equilibrium concentration which is maintained for as long as sufficient hydrogen is available at the surface of the metal.

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With this in mind, and in order to eliminate the need for the precursor samples which were used to bring the palladium chloride into a reproducible response condition, we doped the helium carrier gas with trace amounts of hydrogen. In effect, the doping saturates the palladium and thus serves to pre+ vent absorption of the eluted sample. The level of doping was determined empirically by mixing increasingly higher amounts of hydrogen into the helium carrier gas and observing the signal produced by a sample of known concentration. Our most satisfactory results were obtained with 10 ppm H₂ in He; peak heights obtained with lower doping levels were not reproducible, while higher concentrations had a tendency to shift the baseline after elution of the sample.

After approximately 150 hours of operation with doped carrier, all the palladium dichloride will have been converted to palladium, at which time the baseline level will suddenly shift. In order to extend the lifetime of the converter, the doped gas is valved off and pure helium flowing at a few cc/min is used while the instrument is on standby.

Detector

A gas-water mixing tee, a capillary tube, and a gas-water separator (Figure 2) deliver the chlorinated eluted sample to a conductivity cell (Figure 3).

Our first conductivity cells were similar to Piringer's (14) design. Despite several modifications, they proved to be capricious in their ability to separate gas from liquid, and to maintain a constant flow of liquid past the electrodes. We therefore adopted the Hall (18) design which, with only the improvements which will be described below, produced chromatograms with the required sensitivity and reproducibility.

The deionized water is pumped from a bottle [10] using a Masterflex Model 7013 pump and a variable speed drive* [11] to deliver 1.0 ml/min to the mixing tee [12]. In the plexiglas mixing tee two orthogonal channels enable the chlorinated isotope gas produced in the converter to blend with water, changing the conductivity of the water in proportion to the concentration of the eluted component. The mixture then flows through a capillary tube, in which discrete amounts of water are maintained separated by menisci. The capillary tube discharges into the conductivity cell through a Teflon tube which acts as a gas-water separator.

The separation action inside the Teflon tube takes advantage of the fact that Teflon is hydrophobic, forcing the water to form discrete beads which adhere to the wall of the tube, allowing the gas to flow past them and exhaust into the atmosphere. As they reach the tip of the tube, the water beads are collected on a glass rod whose surface has been roughened by sandblasting with a fine grit, and which leads into the conductivity cell. While a polished, chemically clean glass surface could also be used, the frosting resulting from

*The Barnant Corporation, Barrington, Ill. 60010

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the sandblasting significantly improves the affinity of the surface for water and reduces splashing. We have also observed that the Teflon separator gradually loses its hydrophobic quality with use, and must be replaced after several hundred injections.

The electrolytic conductivity cell [13] is a modified Hall detector (18) which consists of two concentric electrodes, a water delivery rod, a syphon drain, and a capillary wick. While respecting the principle that the greatest electrode area per volume is obtained with concentric electrodes, several features of the Hall design were modified to improve the signal-to-noise ratio and the ease of operation.

In the Hall design the separation of the gas-liquid phase occurs within the cell, the gas being vented through the hollow center electrode. In our experience, the performance of this design was often marred by water entering the vent and causing violent fluctuations in the recorded signal; in our design the separation occurs outside the cell, thereby eliminating this problem.

A major difficulty associated with the concentric design is that of maintaining the electrodes exposed to a constant level of water. The solution to this difficulty resulted in three other improvements: a syphon drain, a capillary wick, and an insulating sleeve.

As described by Hall, the inside diameter or the length of the drain has to be adjusted to provide sufficient back pressure to maintain a constant level within the cell; this adjustment is not readily achieved in practice, requiring time-consuming trial and error. On the other hand, a syphon which would automatically maintain a constant level fails to do so because the surface tension of the water leads to the formation of drops at the upper end of the syphon, causing pulses in the recorded signal every time a drop separates from the cell. The use of an absorbent paper wick eliminates the latter problem by decoupling the syphon outlet from the drops which inevitably form at very low water flow rates.

Despite all these improvements, the water level still fluctuated in rhythm with the addition of each droplet from the separator, introducing significant noise in the output signal. The remedy for this last inconvenience was to limit the conductive portion of the outer electrode to a height equal to that of the center electrode, by inserting an insulating sleeve into the upper portion of the outer electrode.

For the cell dimensions shown in Figure 3, the cell constant is calculated to be 0.122 cm^{-1} , a figure confirmed by actual conductance measurements of distilled water of known resistivity. The volume of the cell shown in Fig. 3 is 0.0618 ml.

The recovery time of the cell was measured by introducing into the cell a small amount of HCl of various concentrations while maintaining a constant flow of distilled water. The time required for the conductivity to reach 1/e of the initial value ranged from 60 sec when the HCl concentration was 10^{-1} N, to 3 sec when the concentration was 10^{-5} N. We conclude therefore that the cell response time is not a limiting factor in the total response of the system for the retention times of this separation.

The cell linearity was determined by measuring the conductivities of known HCl concentrations and comparing them to conductivities calculated on the basis of published conductance values (19) (Figure 4). At high concentrations the cell does become nonlinear, but since our analysis is concerned with trace amounts this is not a matter for concern.

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Similarly, by comparing the calculated conductivity expected from a 10 μ l sample of D₂, and the conductivity which was actually measured following an injection of 10 μ l of pure D₂, the conversion efficiency was estimated to be approximately 50%.

The electronic signal to the electrolytic cell is supplied by a current source consisting of a 1000-Hz oscillator [14] with a series-connected 4.7-M Ω resistor. Before being fed into a suitable recorder [16] the detected signal is processed through an operational amplifier, a precision rectifier, and an optional zero suppression circuit which allows the recorder scale to be expanded for low conductivity signals [15] (Figure 5).

Operation

Since the voltage measured at the conductivity cell electrodes is inversely proportional to the conductance of the water flowing through the cell, the electronic system is calibrated before operation by disconnecting the cell and substituting resistances of known values; the oscillator signal is then adjusted so that the voltage detected for the highest resistance (lowest water conductance) anticipated does not saturate the operational amplifier.

The calculation procedure consists of converting the voltages detected for an injected sample to conductance values and of subtracting the baseline conductance during steady-state operation from the maximum conductance obtained for a peak. The conductance thus obtained is divided by the conductance of reference samples of 1% H_2 and 1% D_2 to obtain the concentration of the unknown. The calibration value for HD is the average of the H_2 and D_2 values. The calibration curve is linear from zero to 15% H_2 ; at 100% H_2 the conductivity is 48% of the value it would have if the curve were linear. In addition, it has been experimentally determined that for our column parameters, no significant differences exist between the concentrations calculated from maximum peak heights and those calculated from integrated peak areas.

Results

The sensitivity of the system is determined by two factors: the separation factor of the column and the inherent sensitivity of the detector.

With a carrier gas flow of 45 cc/min, H_2 is eluted after 10 minutes, HD after 13 minutes, and D_2 after 19 minutes. For low hydrogen content in deuterium, baseline separation is possible, but, as the hydrogen percentage increases, the tailing of the H_2 eluted peak extends into the elution range of HD and D_2 , with the result that separation is less complete and the sensitivity for the latter isotopes is reduced. At concentrations below 0.1% H_2 , the signal from the conductivity cell is indistinguishable from the noise level of the baseline.

Figure 6 shows the chromatographic analysis of a typical gas sample. Reproducibility for successive samples of the same gas was found to be $\pm 3\%$ of the signal strength.

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Figure Captions

 Block diagram of chromatographic system. [1] Carrier gas; [2] Pressure regulator; [3] Flow controller; [4] Gas purifier and dewar; [5] Gas filter;
 [6] Sampling valve; [7] Sample gas; [8] Column and dewar; [9] Palladium chloride converter and heater; [10] Deionized water; [11] Pump and variable speed drive; [12] Gas-water mixing tee and separator; [13] Electrolytic conductivity cell; [14] 1000-Hz oscillator current source; [15] Operational amplifier, rectifier, and zero-suppression; [16] Recorder;

[17] Thermal conductivity detector (optional for neon detection); [18] Thermal conductivity detector power supply and bridge (optional for neon detection); [19] Recorder (optional for neon detection).

- 2. Mixing tee and separator.
- 3. Electrolytic detector assembly.
- 4. HCl conductivity as a function of concentration.
- 5. Electrolytic detector wiring diagram.
- 6. Chromatogram of deuterium containing 0.52% H₂ and 0.91% HD.









Fig. 3



Fig. 4



OUTPUT = 4V DC WITH 0.13 V P-P INPUT.

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Fig. 6