A METHOD FOR MEASURING TOTAL PROTIUM AND TOTAL DEUTERIUM IN A GAS MIXTURE CONTAINING HYDROGEN, DEUTERIUM AND HYDROGEN DEUTERIUM MIXTURE USING GAS CHROMATOGRAPHY

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Abstract

An analytical technique for measuring both total protium (H) and total deuterium (D) in a gas mixture containing hydrogen (H_2), deuterium (D_2), and hydrogen-deuterium (HD) has been developed. This technique uses a micro gas chromatograph uGC with two molecular sieve columns. The carrier gas for one column is deuterium and the second column uses protium as the carrier gas. Laboratory tests have shown that when used in this configuration the micro gas chromatograph can measure both total protium and total deuterium each with a detection and quantification limit of less than 20 ppm. This is a low-cost technology can be used to provide comparable results with the data generated from an expensive mass spectrometry with capabilities of high resolution at low mass.

Keywords

Hydrogen isotopes, protium, deuterium, gas mixture, detection limit, analytical technique.

1. Introduction

Hydrogen with its naturally occurring isotopes, protium (H) and deuterium (D) and man-made tritium (T), have been investigated for many decades for use in the medical field, for fusion energy, for defense programs and for energy storage applications.[1]

Fusion holds the promise of providing limitless, clean, sustainable energy capable of powering our society forever.[2] Fusion occurs when small amount of matter in the form of hydrogen isotopes, such as deuterium and tritium, fuse to form heavier nuclei of helium, neutrons while releasing huge amount of energy. Tritium, one of the hydrogen isotopes, is a vital component of nuclear weapons, fusion reactors and self-illuminating light sources. Tritium radioactively decays to helium-3, which has also become a precious analyte due to its use in neutron detection equipment that is used all over the world to protect our nation and its allies from terrorism. Additionally, the development of advanced nuclear signature collection (e.g. hydrogen isotopes) or detection technologies that enable advanced, in-field analysis methodologies for safeguarding and monitoring nuclear nonproliferation activities are highly sought. Potential occurrence of orthro and para isomers of hydrogen isotopes[3] coupled with the presence of hydrogen-deuterium species adds another degree of complexity to these processes which must be taken into consideration when developing these technologies. The composition and balance between the hydrogen isotopes is critical for many of these applications.[4] For example, less than 10% applied rate of deuterium and tritium is needed for operation, economy, and environmental safety of nuclear fusion reactions.

Therefore, a staggering amount of work has been focused on the development of hydrogen isotope separation, storage, purification, and quantification technologies. These are major undertakings as hydrogen isotopes have very similar physicochemical properties. The Thermal Cycling Absorption Process, an advanced technology was developed by Savannah River Site to separate hydrogen isotopes based on absorption, and temperature and pressure cycling.[5] Other technologies, namely cryogenic distillation, cryogenic adsorption, palladium alloy diffusion, thermal diffusion, localized electromagnetic thermal processes,[4] and laser separation have been explored for the separation of hydrogen isotopes for thermonuclear fusion reactors.[6] The presence of impurities, such as helium-3, argon, nitrogen, methane, carbon monoxide, zinc-65, hydrogen sulfide, moisture, etc., in a hydrogen gas stream impart additional challenges for hydrogen processing. To mitigate these issues the impurities from hydrogen streams prior to isotope separation. [7] Recently, an advanced nanomaterials[8] deposited on stainless steel wool as well as other substrates (copper coupons, bronze coupons and stainless-steel coupons) to capture the zinc vapors byproduct contaminants resulted in the tritium facilities was developed.[9] Once separated, hydrogen isotopes are stored in gas phase high pressure cylinders, a liquid phase at cryogenic temperature, or on solid-state materials, such as lanthanum-nickel-aluminum alloy materials.

Gas chromatography and nuclear magnetic resonance spectroscopy have been used for detection and quantification of hydrogen isotope mixtures.[10,11] A common analytical method of identifying and quantifying isotopic species of hydrogen is mass spectrometry. However, a low mass, high resolution mass spectrometer with adequate sensitivity and stability to identify and quantify hydrogen isotopes in the low ppm range is expensive and is not readily available to all laboratories in the scientific community. It is a highly complex instrument that often requires sample preparation and post-data stream analysis and interpretation.

A novel analytical technique has been developed that measures both total protium (H) and total deuterium (D) in a gas mixture containing molecular hydrogen (H_2), molecular deuterium (D_2), and hydrogen-deuterium (HD) using a relatively inexpensive micro gas chromatograph (uGC). This technique uses two molecular sieve columns. One column uses molecular deuterium (D_2) as the carrier gas and the other uses molecular hydrogen (H_2) as the carrier gas.

2. Experimental Section

Materials and Instrumentation

The micro gas chromatograph used for testing the Thermal Cycling Absorption Process and subsequently to develop this new analytical technique is a model Fusion gas chromatograph from Inficon. This model micro gas chromatograph can be configured with two columns and two different carrier gases, which made it well suited for testing and developing this new analytical technique. Samples injected into the micro gas chromatograph are analyzed simultaneously by the two columns. Analysis time is approximately 45-60 seconds. A model M200 micro gas chromatograph was configured with two molecular sieve columns. One column was supplied with molecular hydrogen carrier gas and the other column supplied with molecular deuterium carrier. Both columns were equipped with thermal conductivity detectors. Gas mixtures containing (25% molecular hydrogen, 75% molecular deuterium), (50% molecular hydrogen, 50% molecular deuterium), and (75% molecular hydrogen, 25% molecular deuterium were prepared and analyzed with the gas chromatograph.

As anticipated each gas chromatograph column displayed only one peak and this peak amplitude varied as predicted. The maximum height of the peak for the gas chromatograph column with molecular hydrogen carrier gas was with the (25% molecular hydrogen, 75% molecular deuterium) mixture and the minimum peak height was produced by (75% molecular hydrogen, 25% molecular deuterium) mixture. This data meant that the peak represented molecular deuterium concentration. The maximum height of the peak for the gas chromatograph column with molecular deuterium carrier gas was produced by the (75% molecular hydrogen, 25% molecular deuterium) mixture and the minimum peak height was with the (25% molecular hydrogen, 75% molecular deuterium) mixture. This data meant that the peak represented molecular hydrogen concentration. A three-point calibration curve was generated for each gas chromatograph column based on the area under the curve for each analysis.

3. Results and Discussions

3.1. Initial Hydrogen Isotope Separation

The Thermal Cycling Absorption Process system is a thermal/cooling gas chromatograph technology used to separate hydrogen isotopes. The purpose of a Thermal Cycling Absorption Process system is to not only separate tritium from other hydrogen isotopes and minimize environmental releases of tritium, which is less than 5 atom ppm of tritium as hydrogen-deuterium, deuterium-tritium, or molecular tritium. The operation principle is based on heating and cooling approach of hydride material of interest, namely palladium coated kieselguhr that is housed in a column. Palladium is the material of interest as it readily absorbs hydrogen and provide an isotope effect as it preferentially absorbs the lighter hydrogen isotope.[12] A second column containing kieselguhr only assist with the pressure profiles. The temperature cycling generates the pressure and temperature gradients that provide the driving force to move and separate hydrogen isotopes.

A residual gas analyzer, a gas chromatograph, and a helium leak detector were used to monitor the Thermal Cycling Absorption Process during initial field testing. Each instrument has unique capabilities and limitations such as sensitivity, detection, quantification, specificity, reproducibility, etc. However, when used in conjunction, although cumbersome, these three instruments can trend the operation of the Thermal Cycling Absorption Process and demonstrate that it separates protium and deuterium.

An ion chamber can be used to monitor the Thermal Cycling Absorption Process during normal tritium isotope operation. It is relatively inexpensive, simple to operate, and has sensitivity equivalent to less than 1 ppm. Theoretically, an ion chamber can detect the decay of one tritium atom. Therefore, monitoring for small quantities of tritium and other isotopes in the final product and raffinate is relatively simple. Note: raffinate is the component which had a component removed from its mixture (**Figure 1**).

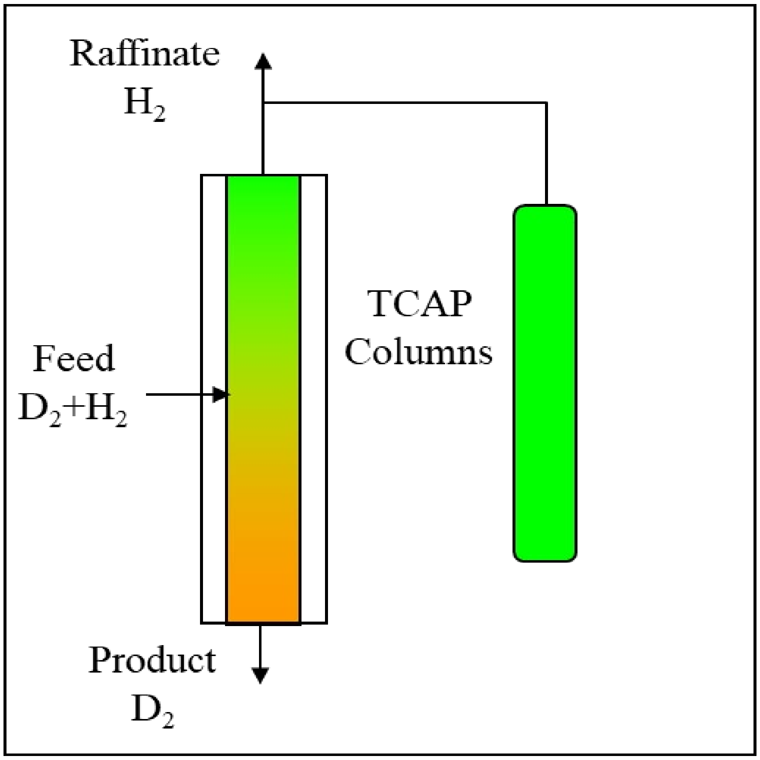

Figure 1. Thermal Cycling Absorption Process schematic.

One could monitor a decreased in concentration of deuterium in the column raffinate, while in the same time an increasing concentration of deuterium in the column product. Final determination of Thermal Cycling Absorption Process performance was accomplished by collecting resulting separated samples from the column raffinate and column product and analyzing them using a low mass high resolution mass spectrometer. While successful, this process is operational complex and require a number of steps that may add uncertainty to the accuracy of the final result.

Moreover, when tritium was substituted with deuterium, monitoring the columns raffinate and product for isotope separation and differentiation of small amounts of deuterium in protium posed a significant analytical challenge. To further complicate matters the Thermal Cycling Absorption Process will also produce hydrogen-deuterium (HD) which could contaminate either the raffinate or product (**Figure 2**). Therefore, the analytical challenge for the test was to provide instrumentation to measure both total deuterium in the column raffinate, and total hydrogen (protium) in the column product.

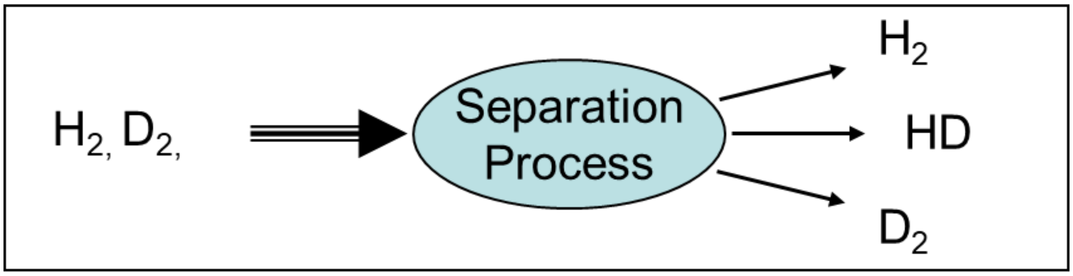

Figure 2. Schematic showing hydrogen separation process.

3.2. Development and Testing of a New Analytical Method for Hydrogen Isotope Separation

A new analytical technique was developed to provide unique analytical instrumentation to measure the protium and deuterium concentrations at several process points during initial testing of new Thermal Cycling Absorption Process columns.

The typical configuration of a gas-chromatograph to detect hydrogen gas is a molecular sieve column that uses argon carrier gas and a thermal conductivity detector. However, the limitation of this configuration for testing the hydrogen isotope separation via Thermal Cycling Absorption Process is the inability of the molecular sieve column to separate the hydrogen isotopes of interest, namely molecular hydrogen, molecular deuterium, and hydrogen-deuterium (HD). This is due to the fact that all of these species co-elute at similar times which makes it impossible, to identify and quantify each isotope.

In order to eliminate these shortcomings, a replacement gas carrier system was proposed and developed: hydrogen or deuterium. Specifically, argon carrier was replaced with molecular hydrogen carrier. This change allows one to detect only deuterium in a sample mixture containing both molecular hydrogen and molecular deuterium while masking the signal contribution of molecular hydrogen. As expected, when molecular deuterium was the selected carrier gas in a sample mixture containing both molecular hydrogen and molecular deuterium, hydrogen signal would be easily detectable while the contribution of molecular deuterium would be masked. and leave only the hydrogen signal. What was unknown was how this gas chromatograph configuration would respond to the presence of hydrogen-deuterium (HD) in the sample mix.

The gas chromatograph was configured with two molecular sieve columns. One column supplied with molecular hydrogen carrier gas and the other column supplied with molecular deuterium carrier. Both columns were equipped with thermal conductivity detectors.

Initially gas mixtures containing (25% molecular hydrogen, 75% molecular deuterium), (50% molecular hydrogen, 50% molecular deuterium), and (75% molecular hydrogen, 25% molecular deuterium) were produced and analyzed. As anticipated each gas chromatograph column displayed only one peak and this peak amplitude varied as predicted. The maximum height of the peak for the gas chromatograph column with molecular hydrogen carrier gas was with the (25% molecular hydrogen, 75% molecular deuterium) mixture and the minimum peak height was produced by (75% molecular hydrogen, 25% molecular deuterium) mixture. This result support our hypothesis and the peak were attributed to the molecular deuterium concentration. The maximum height of the peak for the gas chromatograph column with molecular deuterium carrier gas was produced by the (75% molecular hydrogen, 25% molecular deuterium) mixture and the minimum peak height was with the (25% molecular hydrogen, 75% molecular deuterium) mixture. Each gas sample was analyzed three times. This result meant that the peak represented molecular hydrogen (H_2) concentration (**Table 1**).

Table 1. Gas chromatography data collected on deuterium and hydrogen (protium) mixtures.

	Analysis # 1	**Analysis # 2**	**Analysis # 3**	**Average**
Mixture 50% D_2 50% molecular hydrogen	(Area Counts Under Curve)			
Column A (H_2 carrier Gas) D_2=	69,140,528	69,140,658	69,149,321	**69,143,502**
Column B (D_2 Carrier Gas) H_2=	48,541,600	48,541,455	48,545,632	**48,542,896**
Mixture 75% D_2 25% molecular hydrogen				
Column A (H_2 carrier Gas) D_2=	100,414,040	100,464,512	100,593,056	**100,490,536**
Column B (D_2 Carrier Gas) H_2=	24,483,564	24,507,014	24,551,368	**24,513,982**
Mixture 25% D_2 75% molecular hydrogen				
Column A (H_2 carrier Gas) D_2=	36,488,572	36,493,176	36,531,768	**36,504,505**
Column B (D_2 Carrier Gas) H_2=	71,972,384	72,009,008	72,042,288	**72,007,893**

A three-point calibration curve was generated for each gas chromatograph column based on the area determined under the curve for each analysis: % D_2 = 7.813E^{-07}*X - 3.69 X = Area Counts, and %H_2 = 1.053E^{-06}*X - 0.904 X = Area Counts.

3.3. Generating Hydrogen-Deuterium (HD) Components and Testing the New Analytical Method for Hydrogen Isotope Quantification

Palladium silver diffusers are integral components for generation the tritium gas processing systems for separation of hydrogen isotopes from various inert species.[13] The process is based on the sorption/desorption of hydrogen molecules on the membrane. Inside the diffuser, the hydrogen molecules dissociate and form hydrogen atoms which subsequently diffuse through the diffuser's wall and re-combinate outside the once passed the diffuser. The hydrogen gas streams permeate at different rates, depending on the composition and characteristics, through the wall of the diffuser tubing into the lower pressure cavity of the diffuser shell.

The mass transfer mechanism of hydrogen through dense metal lattice follows the following (equation 1): [14]

$$F = \Phi \frac{\left(p_{\mathrm{up}}^{\mathrm{n}} - p_{\mathrm{down}}^{\mathrm{n}}\right) A}{t} \qquad \text{Equation 1}$$

where F is the hydrogen permeation flow rate (mol/s), Φ is the hydrogen permeability (mol/m^{-1} s^{-1} Pa^{-n}), p_{up} and p_{down} (Pa) are the hydrogen partial pressures upstream and downstream, respectively, n is the pressure factor, A is the membrane area (m^2), and t is the membrane thickness (m). the n factor is assumed to be 0.5 for palladium alloy membranes.

Hydrogen-deuterium (HD) was generated by passing a 50% mixture of molecular hydrogen and molecular deuterium through a palladium silver diffuser **(Figure 3)**. The permeation of hydrogen isotope through a palladium-silver membrane have been developed by us and others.[15]

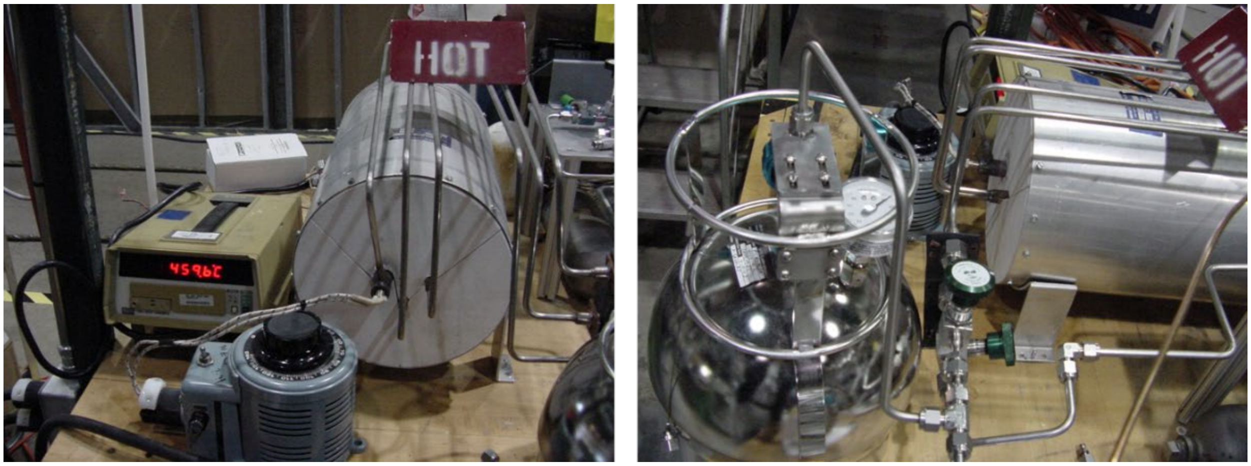

Figure 3. Photograph of palladium silver diffuser used to produce protium-deuterium species.

The gas mixtures data listed in **Table 2** and **Table 3** that were passed through a palladium diffuser to generate the mixtures containing hydrogen-deuterium (HD). These mixtures were also subsequently analyzed by two different techniques to provide accurate analysis of the hydrogen-deuterium (HD) component. Data collected by the high-resolution mass spectrometer and gas chromatograph analysis were included in **Table 2** and **Table 3**, respectively.

Table 2. High resolution mass spectrometer data collected on hydrogen isotope mixtures passed through the palladium-silver gas diffuser (diffuser output).

Diffuser Input 25%D_2 75%H_2	Molecular Hydrogen (H_2)	Hydrogen-Deuterium (HD)	Molecular Deuterium (D_2)
Mass Spec Analysis of Output	56.67%	36.69%	6.64%
Diffuser Input 75%D_2 25%H_2	Molecular Hydrogen (H_2)	Hydrogen-Deuterium (HD)	Molecular Deuterium (D_2)
Mass Spec Analysis of Output	6.82%	36.97%	56.22%
Diffuser Input 50%D_2 50%H_2	Molecular Hydrogen (H_2)	Hydrogen-Deuterium (HD)	Molecular Deuterium (D_2)
Mass Spec Analysis of Output	26.36%	48.73%	24.89%

Table 3. Gas chromatograph analysis data collected on hydrogen isotope mixtures passed through the palladium-silver gas diffuser.

Mixture Analyzed	Gas Chromatograph Analysis
H_2 (26.36%), HD (48.73%), D_2 (24.89%)	
Column A (D_2 carrier Gas)	H_2=51.36%
Column B (H_2 Carrier Gas)	D_2=48.51%
Mixture Analyzed	
H_2 (6.82%), HD (36.97%), D_2 (56.22%)	
Column A (D_2 carrier Gas)	H_2=26.12%
Column B (H_2 Carrier Gas)	D_2=73.70%
Mixture Analyzed	
H_2 (56.67%), HD (36.69%), D_2 (6.64%)	
Column A (D_2 carrier Gas)	H_2=75.87%
Column B (H_2 Carrier Gas)	D_2=23.94%

Half of the hydrogen-deuterium value from the mass spectrometry analysis was added to either the molecular hydrogen or molecular deuterium value. These calculated values were then compared to the results generated from the gas chromatograph analysis (**Table 4**).

Table 4. Comparison of gas chromatograph and mass spectrometry analysis.

Mass Spectrometry Analysis	1/2HD + (D_2 or H_2)	Gas Chromatograph Analysis
D_2= 24.89%		
H_2=26.36%	1/2 HD+D_2 = 49.25%	D_2 = 48.51%
HD=48.73%	1/2 HD+H_2 = 50.72%	H_2 = 51.36%
D_2=56.22%		
H_2=6.82%	1/2 HD+D_2 = 74.70%	D_2 = 73.70%
HD=36.98%	1/2 HD+H_2 = 25.30%	H_2 = 26.12%
D_2=6.64%		
H_2=56.67%	1/2 HD+D_2 = 24.99%	D_2 = 23.94%
HD=36.69%	1/2 HD+H_2 = 75.01%	H_2 = 75.87%

Testing to evaluate the new analytical was performed with a mixture containing molecular hydrogen, hydrogen-deuterium, and molecular deuterium to determine the efficiency of this technology in the presence of hydrogen-deuterium upon isotope separation in the Thermal Cycling Absorption Process system. The results showed that the gas chromatograph column with deuterium carrier gas measured a value of approximately 50% molecular hydrogen (**Figure 4a**) and the gas chromatograph column with hydrogen carrier gas measured a value of approximately 50% molecular deuterium (**Figure 4b**). These results (**Table 5**) are in agreement previous results.[15] Gas chromatography method for the determination of the ratio of hydrogen and deuterium in gas mixtures is typically due to the difference in the thermal conductivity of these isotopes. Moreover, in an equilibrated mixture of molecular hydrogen, molecular deuterium, and hydrogen-deuterium (HD), the thermal conductivity of hydrogen-deuterium (HD) is half of each component, molecular hydrogen or molecular deuterium, respectively. The detection limit of the collected data is included in **Table 6**.

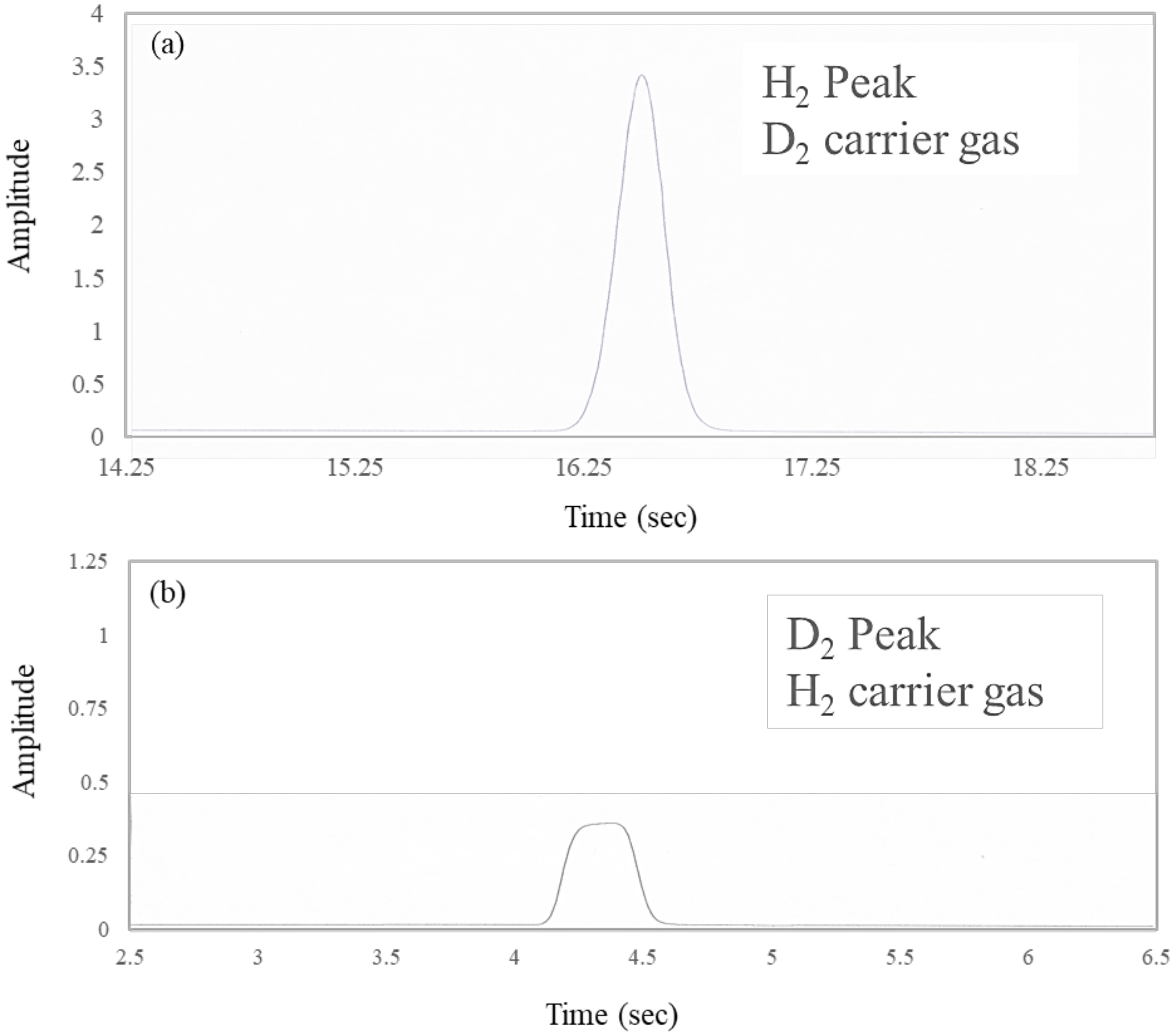

Figure 4. Gas chromatograph analysis on a mixture of molecular hydrogen (H_2), molecular deuterium (D_2), hydrogen-deuterium (HD) with **(a)** deuterium carrier gas measured a value of approximately 50% molecular hydrogen, and **(b)** hydrogen carrier gas measured a value of approximately 50% molecular deuterium.

Table 5. Comparison of gas chromatograph and mass spectrometry data collected upon isotope separation in the Thermal Cycling Absorption Process system.

Mass Spec Total Deuterium [Deuterium (D_2) +1/2 Hydrogen-Deuterium (HD)] %	Gas Chromatograph Total Deuterium %
18.798	20.582
0.021	0.022
0.248	0.314
0.023	0.022
23.536	25.832
0.024	0.024
0.005	0.002
0.318	0.373
6.127	6.336
0.211	0.22

Table 6. Limit of detection collected with the new gas chromatograph analytical tool.

Dilution	Theoretical Values (parts per million - ppm)	Gas Chromatograph Analysis (parts per million - ppm)
0	747,000	734,910
10	74,643	74,980
100	7,464	7,658
1001.0	746.4	776.5
10009.6	74.6	78.4
20038.0	37.3	39.8
40722.0	18.4	19.4
81688.2	9.2	8.2

While high-precision isotope measurements are of high interest in the scientific community the field still relies heavily of the use of mass spectrometry for decades. Over the years, a number of analytical advances have been developed, namely continuous-flow techniques to isotope ratio mass spectrometry (IRMS) instrumentation, capillary gas chromatography interfaced to isotope ratio mass spectrometry via on-line microchemistry to facilitate routine analysis of H isotopes after chromatographic separation.[16] For example, isotope ratio monitoring techniques, such as isotope ratio monitoring gas chromatography/mass spectrometry have been used for on-line D/H measurements.[17] The technique required the modification of the technique by introduction of a retardation lens into the Faraday cup of a 3 kV isotope ratio mass. These modifications allowed detection of sub-micromole amounts of H-bearing material with very high precision in helium as the carrier gas.[18] Cryogenic distillation (CD) columns for hydrogen isotope separation have been used in the fuel cycle of nuclear fusion reactors,[19] fission reactors,[20] and others.

Ultimately, the new analytical configuration tool provided measurement of the total amount of deuterium and the total amount of protium in the sample mixture. Various other mixes of (molecular hydrogen, hydrogen-deuterium (HD), molecular deuterium) were analyzed and each time values of total deuterium and total protium were correctly quantified. The sensitivity to both protium and deuterium was determined to be less than 20 ppm. This is significantly better sensitivity than the high-resolution mass spectrometers used in the scientific community which have a detection limit of 100 ppm for molecular hydrogen and molecular deuterium. The simplicity and accuracy of this technique makes this a very useful process that can be implemented in laboratory and industrial settings.

4. Conclusions

A new micro gas chromatograph analytical tool configured with two molecular sieve columns was designed and developed. The new technology was used to separate, differentiate and quantify a number of hydrogen isotopes, namely molecular hydrogen, molecular deuterium and hydrogen-deuterium (HD). Detection and quantification of protium or deuterium using this technique is at least 20 ppm including protium and total deuterium in a gas mixture containing molecular hydrogen, molecular deuterium and hydrogen-deuterium (HD). This is the first time that a low cost, fast technology was developed that is comparable with the costly mass spectrometry. Samples containing tritium have not been analyzed with this method. Results of such analysis would be of great interest and could possibly lead to a simple analytical method for tritium.

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