Hydrogen Isotope Separation Using Gas Chromatography

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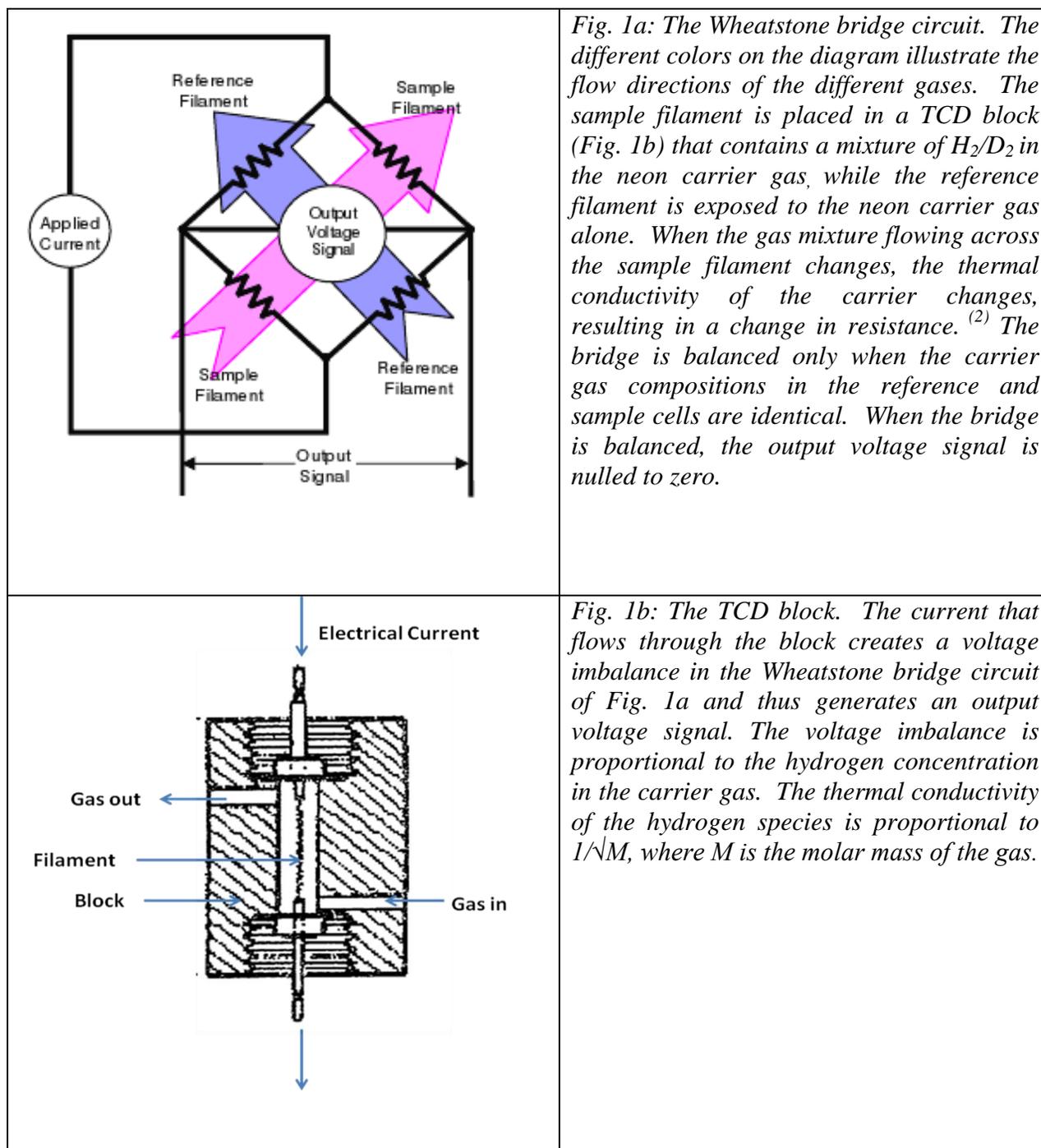Dec 2012

Abstract

A gas chromatograph (GC) system was commissioned to measure hydrogen isotope species. The GC system uses an iron-doped molecular sieve column held at 77 K to separate the hydrogen isotopes and a thermal conductivity detector (TCD) to analyze the separated species. The response of the TCD was shown to depend on the quantity of hydrogen injected, on the carrier flow rate, and on the temperature difference between a heated filament in the TCD and its housing. The instrument is very stable. Measurements are highly reproducible. Baseline separation is easily attained.

Introduction

The Laboratory for Laser Energetics (LLE) requires an in-house capability to monitor the composition of deuterium-tritium (DT) fuel. LLE is also in the process of designing an isotope separation system and requires a method of quantifying the purity of the tritium. To meet both these needs, LLE is developing a gas chromatograph (GC) system.

Gas chromatography is a physical method of separation where components are separated and distributed between a stationary phase and a mobile phase.[1] A Bruker CP-3800 gas chromatograph was configured and calibrated to measure hydrogen isotope concentrations. Gas chromatography with a thermal conductivity detector (TCD) is a good technique to measure the isotopic composition of hydrogen mixtures. The principle of the TCD is shown in figures 1(a) and (b). In figure 1(a), in the ideal case of four identical filaments and equal flow in each cell, the voltage drop across each filament is the same and a zero output voltage signal is recorded. When the sample gas flows, the voltage drops across the reference and sample filaments are

Fig. 1a: The Wheatstone bridge circuit. The different colors on the diagram illustrate the flow directions of the different gases. The sample filament is placed in a TCD block (Fig. 1b) that contains a mixture of H_2/D_2 in the neon carrier gas, while the reference filament is exposed to the neon carrier gas alone. When the gas mixture flowing across the sample filament changes, the thermal conductivity of the carrier changes, resulting in a change in resistance.[2] The bridge is balanced only when the carrier gas compositions in the reference and sample cells are identical. When the bridge is balanced, the output voltage signal is nulled to zero.

Fig. 1b: The TCD block. The current that flows through the block creates a voltage imbalance in the Wheatstone bridge circuit of Fig. 1a and thus generates an output voltage signal. The voltage imbalance is proportional to the hydrogen concentration in the carrier gas. The thermal conductivity of the hydrogen species is proportional to $1/\sqrt{M}$, where M is the molar mass of the gas.

different and an output voltage signal will be observed. In figure 1(b), the applied current is chosen to heat the filament to the desired operating temperature in the presence of gas flow. This current will depend on the thermal conductivity of the gas, as this affects the loss of heat from the filament to the block. The resistance of the filament depends on its temperature. If the current is held fixed and the gas changes to a gas with a different thermal conductivity, the resistance of the filament will change.

Preparation of Sample Cylinders

Six calibration standard sample cylinders were filled using a gas handling system capable of high vacuum in order to calibrate the GC. The cylinders were evacuated and then filled with half of the primary component gas pressure required to achieve 1000 torr total pressure. The cylinders were then filled with all of the secondary component gas required to achieve 1000 torr total pressure. The cylinders were then pressurized with the second half of the remaining primary component gas required to achieve the 1000 torr gas standard. The composition ratios of the cylinders were 1/99%, 20/80%, 40/60%, 60/40%, 80/20%, and 99/1% H_2/D_2. After it was discovered that the 1000 torr cylinders did not have enough gas pressure in them to achieve a high signal-to-noise ratio from the TCD, cylinders of 10/90%, 90/10%, and 46/54% H_2/D_2 were created at 5000 torr.

Configuration and Calibration of the Gas Chromatograph Setup

Figure 2 shows a schematic of the GC setup. The primary flow is that of the neon carrier gas. Either the unknown sample or the gas from one of the standard cylinders can be added to the flow.
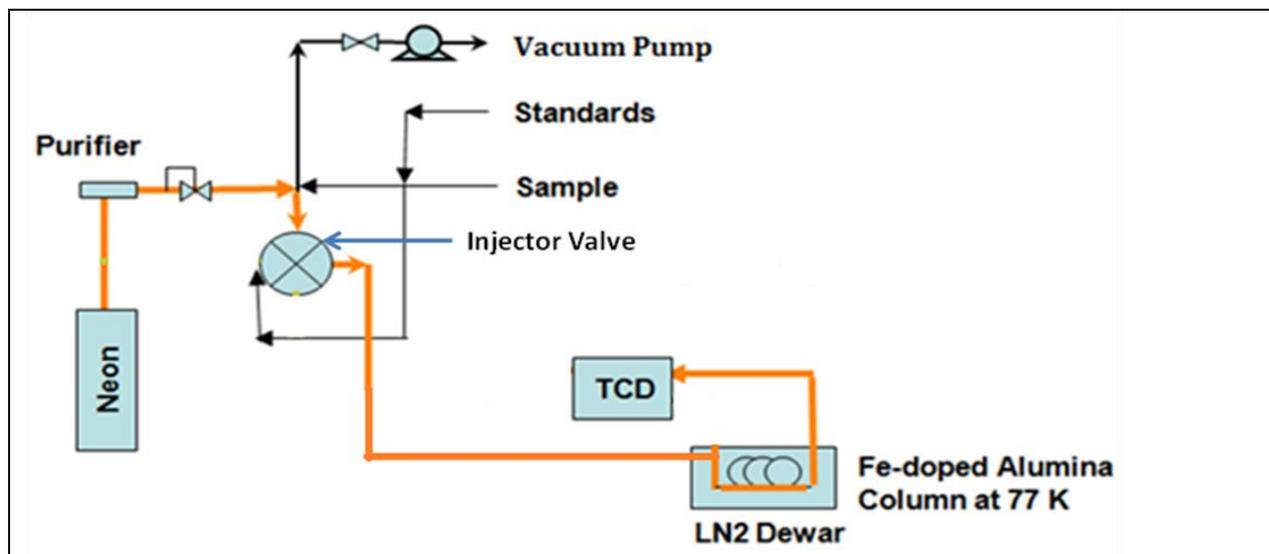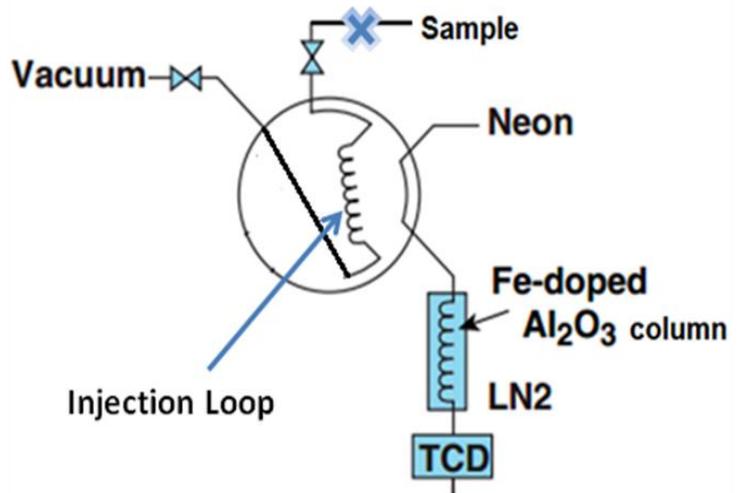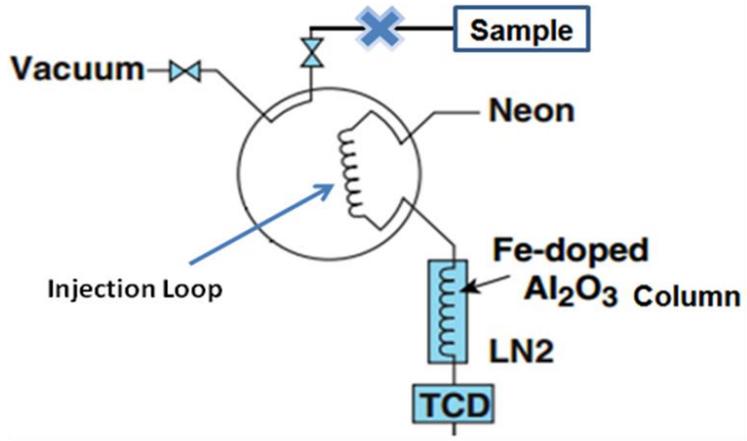

Fig 2: Schematic of the GC setup. The GC comprises the alumina column and the TCD. The injector valve allows different gases to flow into the GC. The orange arrows represent the carrier gas flowing through the GC.

Filling Phase

Vacuum

Sample

Neon

Fe-doped Al₂O₃ column

LN2

TCD

Injection Loop

Fig 3: The GC in the filling phase. This stage is where the gas is expanded into the injection loop (the coil). The injector valve is rotated into the filling position. The first step to analyze a sample is to open the sample cylinder valve to pressurize the injection loop then close the valve. Next, all of the valves in the system are opened. As a result, the sample pressure is reduced in a repeatable fashion and is sustained under a static vacuum within the injection loop.

Measurement Phase

Vacuum

Sample

Neon

Fe-doped Al₂O₃ Column

LN2

TCD

Injection Loop

Fig 4: The GC in the measurement phase. In this stage, the components of the sample gas in the injection loop are separated as they flow through the Fe-doped Al₂O₃ column and diagnosed in the TCD. [3]
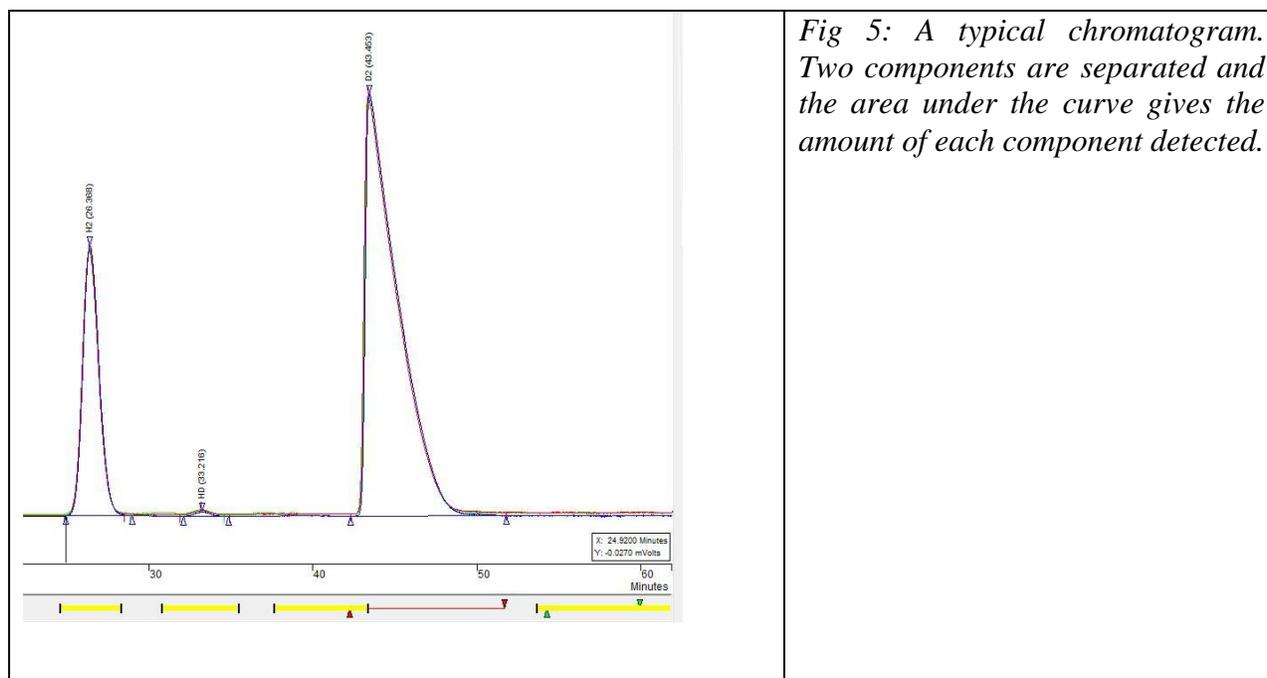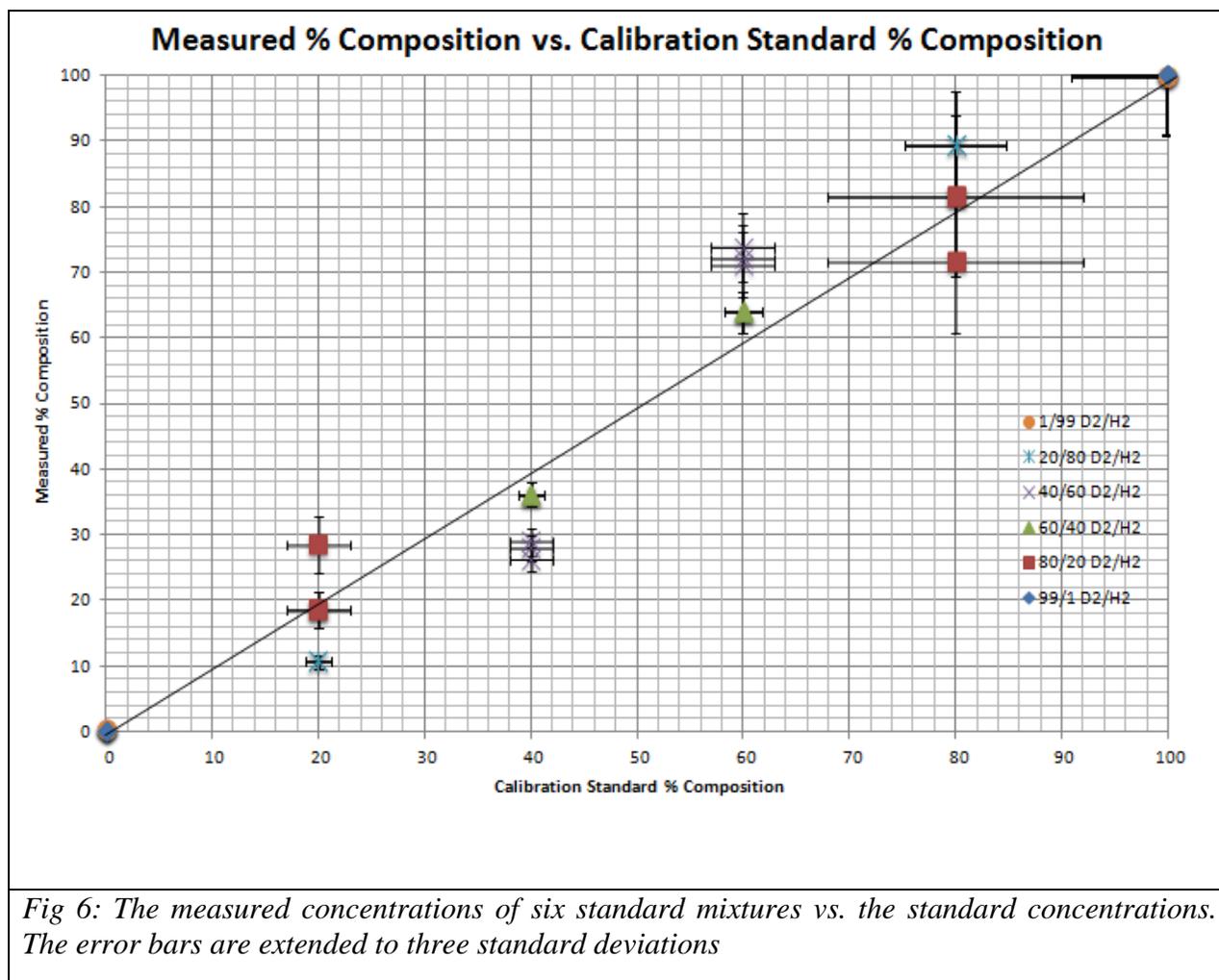
Fig 5: A typical chromatogram. Two components are separated and the area under the curve gives the amount of each component detected.

Figure 3 shows the GC in the filling phase. After this, the valves are closed and the injection loop moves into the inject position shown in figure 4. In both stages, the neon carrier gas flows through the alumina column and the TCD. A typical chromatogram is shown in figure 5: this is a graph showing the voltage across the Wheatstone bridge as a function of time. The two pulses correspond to two substances that pass through the chromatography column at different rates. The area of each pulse gives the amount of the substance detected. An earlier calibration relates the measured area in volts*time to the mass of the substance measured conveniently in torr*cc (from the ideal gas law, mass is proportional to pressure times volume).

Measurements Using Six Mixed Standards

The sample cylinders consisting of 1/99%, 20/80%, 40/60%, 60/40%, 80/20%, and 99/1% H_2/D_2 were examined first. The results are shown in figure 6. Each run produces two

points; one for the D_2 concentration and one for the H_2 concentration. Three runs were made for each cylinder, producing 36 points on figure 6. Some of these points are coincident.

Fig 6: The measured concentrations of six standard mixtures vs. the standard concentrations. The error bars are extended to three standard deviations
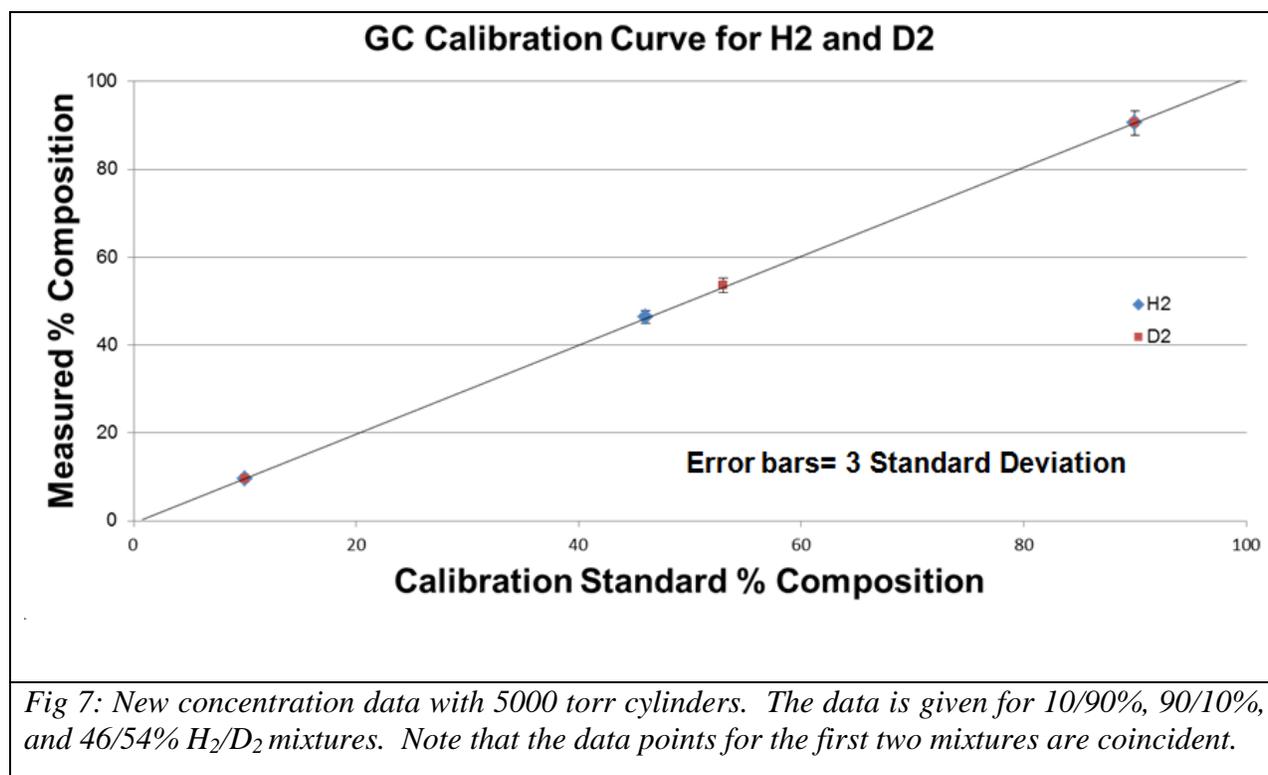
As seen on figure 6, most of the mixed concentrations don't match the measured concentrations. For example, the standard created at 40/60% H_2/D_2 was measured by the GC at 36%/64% H_2/D_2. In addition, even with the error bars at 3 standard deviations, the measured amounts don't match the mixed standard. The y error bar is three times the rms of the three runs.

The x error bar is the accuracy with which the % fill is measured. In order for the GC method to be robust and the instrument properly calibrated, the mixed standard and the measured concentration results must be within 3 standard deviations of each other. Results within 3 standard deviations represent 99.7% of all the results, so GC analysis results within 3 standard deviations would be highly reproducible. The poor correlation between the measured and expected results may be due to inaccuracies in filling the standard cylinders to the correct concentrations. Figure 6 shows a lack of agreement between standard and measured, and a large variability between the three runs with a given standard. The larger error bars are because the pressure injected into the GC was insufficient. As a result, there are weaker signals and hence greater variability.
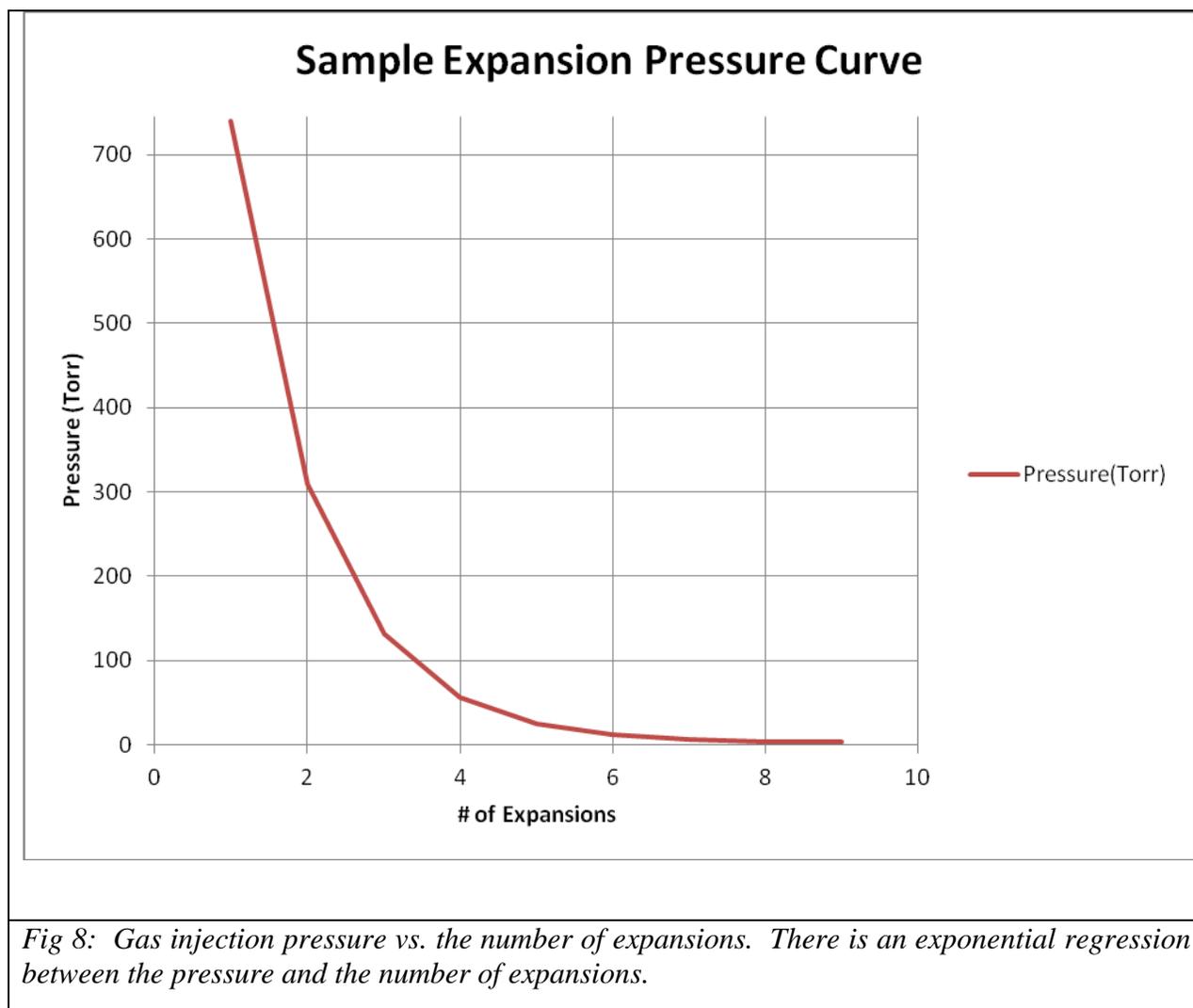
To remedy this problem, three new sample cylinders were prepared with a higher pressure of 5000 torr. The cylinders had H_2/D_2 ratios of 10/90%, 90/10%, and 46/54% H_2/D_2.

Measurements using the new Mixed Standards

Fig 7: New concentration data with 5000 torr cylinders. The data is given for 10/90%, 90/10%, and 46/54% H_2/D_2 mixtures. Note that the data points for the first two mixtures are coincident.

The same procedure for loading the GC with the sample gas was implemented except for the pressure adjustments. The results, shown in figure 7, are much more promising. The 10/90% H_2/D_2 was measured to have an average composition of 9.6/90.4% H_2/D_2. The standard deviation within the three runs that were made with this composition was only 0.45%, indicating that the GC is accurate and consistent. The 90/10% and 46/54% H_2/D_2 compositions support the performance of the GC. The 10/90% H_2/D_2 was measured to have an average composition of 90.5/9.5% H_2/D_2, and the standard deviation within the three runs that were made with this composition was 0.06%. The 46/54% H_2/D_2 was measured to have an average composition of 46.4/53.6% H_2/D_2, and the standard deviation within the three runs that were made with this composition was 0.25%.

The results of figure 7 show that the measured amount is accurate within 1% of the mixed standard. In addition, the error bars are significantly smaller than on figure 6 and show that the GC is highly reproducible and accurate.

Fig 8: Gas injection pressure vs. the number of expansions. There is an exponential regression between the pressure and the number of expansions.

Since the pressure transducer measuring sample pressure attached to the GC can only read up to 1000 torr, the instrument can't read a 5000 torr gas sample. As a result, multiple expansions had to be made in order to bring the pressure down to a readable pressure. An expansion is performed when the sample gas is first injected into the GC, and then placed under

a static vacuum with all the valves opened for a specified amount of time. Figure 8 shows how the pressure decreases exponentially with each expansion. With numerous expansions, the pressure becomes low enough that it can be measured. The original 5000 torr pressure is then inferred by moving the pressure down on each expansion. Expansions were used to investigate the dependence on sample size.

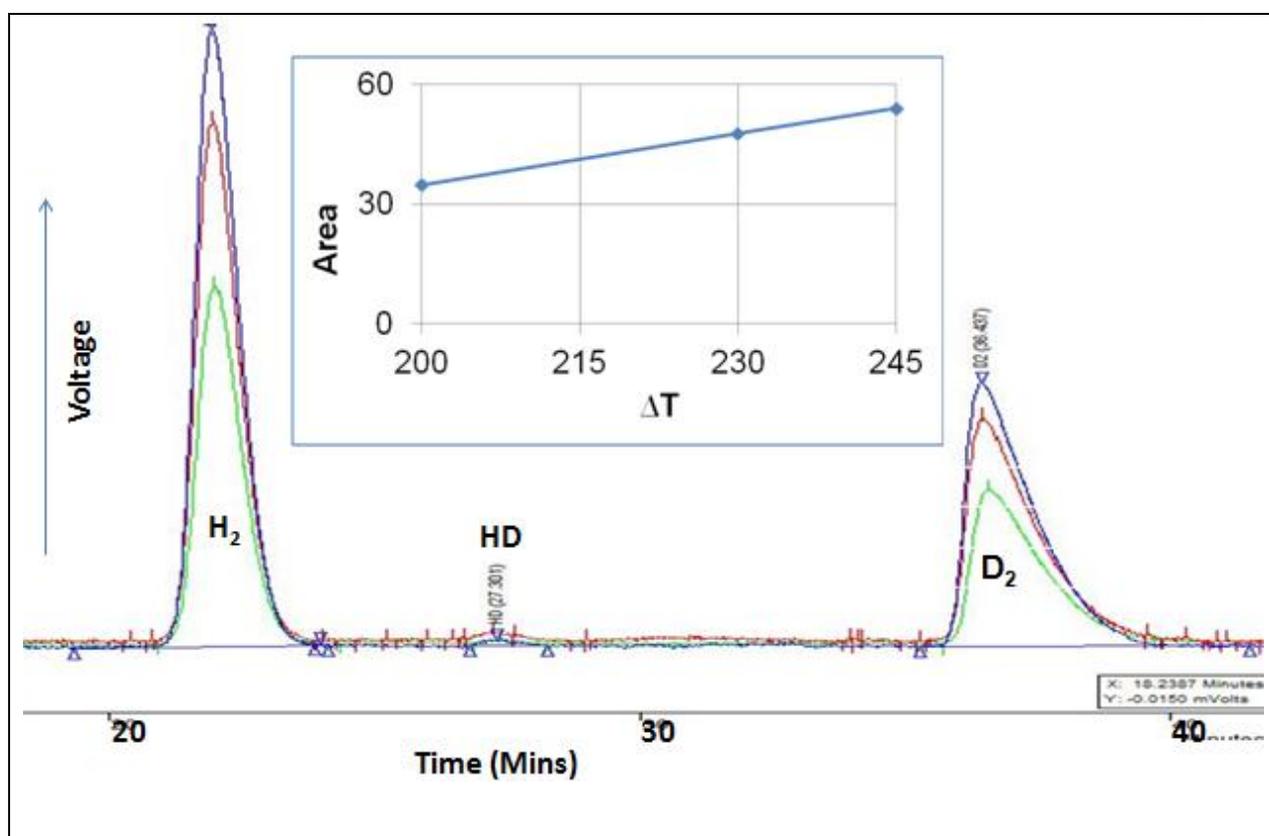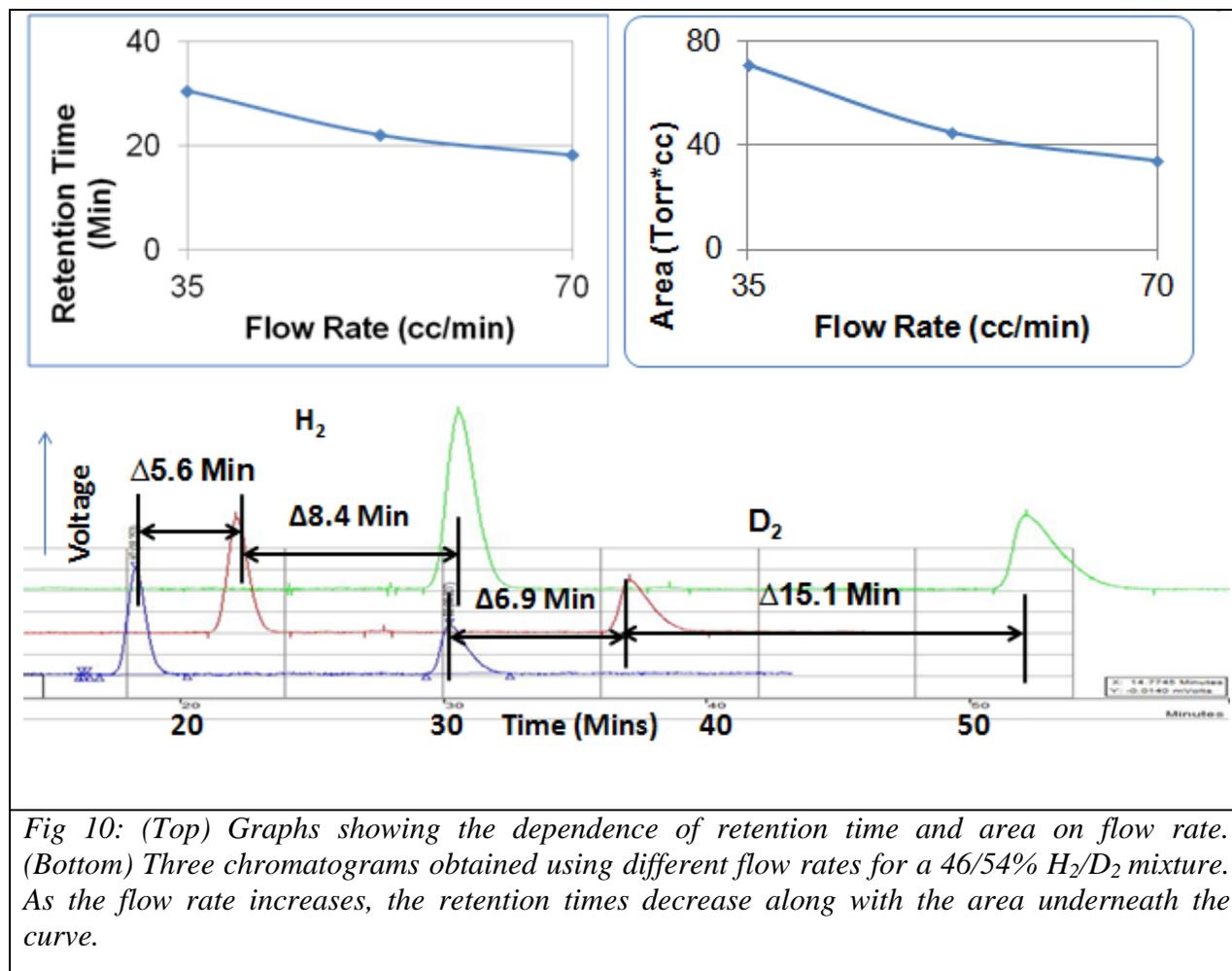**Dependence on Block and Filament Temperature Differences**

Fig 9: Chromatograms (output voltage from the TCD vs. time) for three different filament-to-block temperature differences ΔT (200°C (green), 230°C (red), 245°C (blue)). As the difference in temperature increases, the area underneath the curve (shown in torr*cc) increases, meaning that the sensitivity of the GC increases.

With Varian detectors, the filament temperature is between 350°C and 490°C. A higher filament temperature setting results in bigger peaks on the chromatogram but the lifetimes of the filament are shorter. To avoid burning out the filament, a moderate filament temperature was used and the block temperature was lowered in order to create the optimum temperature difference. The difference in temperature between filaments and the detector block provides much of the control over the sensitivity of the detector. The block temperature should be high enough to prevent potential condensation of the major sample constituents. The block has a large thermal mass to maintain a consistent temperature, which provides a stable baseline.[2]

The filament temperature stayed at a consistent 350°C with the 46/54% H_2/D_2 sample, while the block temperature was changed twice. The block typically runs at a temperature of 120°C, but it was altered to be 105°C and 135°C. With a 105°C block temperature, the area count is approximately 53.97 torr*cc, while a 135°C block temperature results in an area count of 34.89 torr*cc. Since a higher block temperature decreases the temperature difference between the block and the filament, there is a decreased sensitivity and therefore a lower area count.

Dependence on Carrier Flow Rate

Fig 10: (Top) Graphs showing the dependence of retention time and area on flow rate. (Bottom) Three chromatograms obtained using different flow rates for a 46/54% H_2/D_2 mixture. As the flow rate increases, the retention times decrease along with the area underneath the curve.

The optimum carrier flow rate is a compromise between reasonable analysis time and detector sensitivity. Lower flow rates will maximize detector sensitivity, but will significantly lengthen the overall measurement time. Higher flows, however, achieve fast separations, but will deteriorate performance as the analytes do not reside long enough in the cell to effectively cool the filaments. The TCD is a concentration-dependent detector and its response is critically dependent on the retention time, i.e., how long an analyte spends inside the detector.[2]

Figure 10 shows chromatograms for the 46/54% H_2/D_2 sample, used with flow rates of 35 (green), 52.5 (red), and 70 (blue) cc/min. With 35 cc/min, the retention times for H_2 and D_2 are 30.6 mins and 52.2 mins, respectively. A 52.5 cc/min flow rate has retention times of 22.1 mins for H_2 and 37.1 mins for D_2. With 70 cc/min, the retention times for H_2 and D_2 are 18.3 mins and 30.2 mins, respectively. The 35 cc/min flow rate has an H_2 area underneath the curve around 76.5 torr*cc. The 52.5 cc/min and 70 cc/min flow rates have H_2 areas of 42.13 and 34.29 torr*cc, respectively. Both the area counts and the retention times decrease with flow. As a result, figure 10 illustrates how smaller retention times decrease the area underneath the curve.

Dependence on Sample Size

Fig 11: A chromatogram and two charts showing the differences in sample size. As the sample size increases, the area increases in an approximately linear relation.
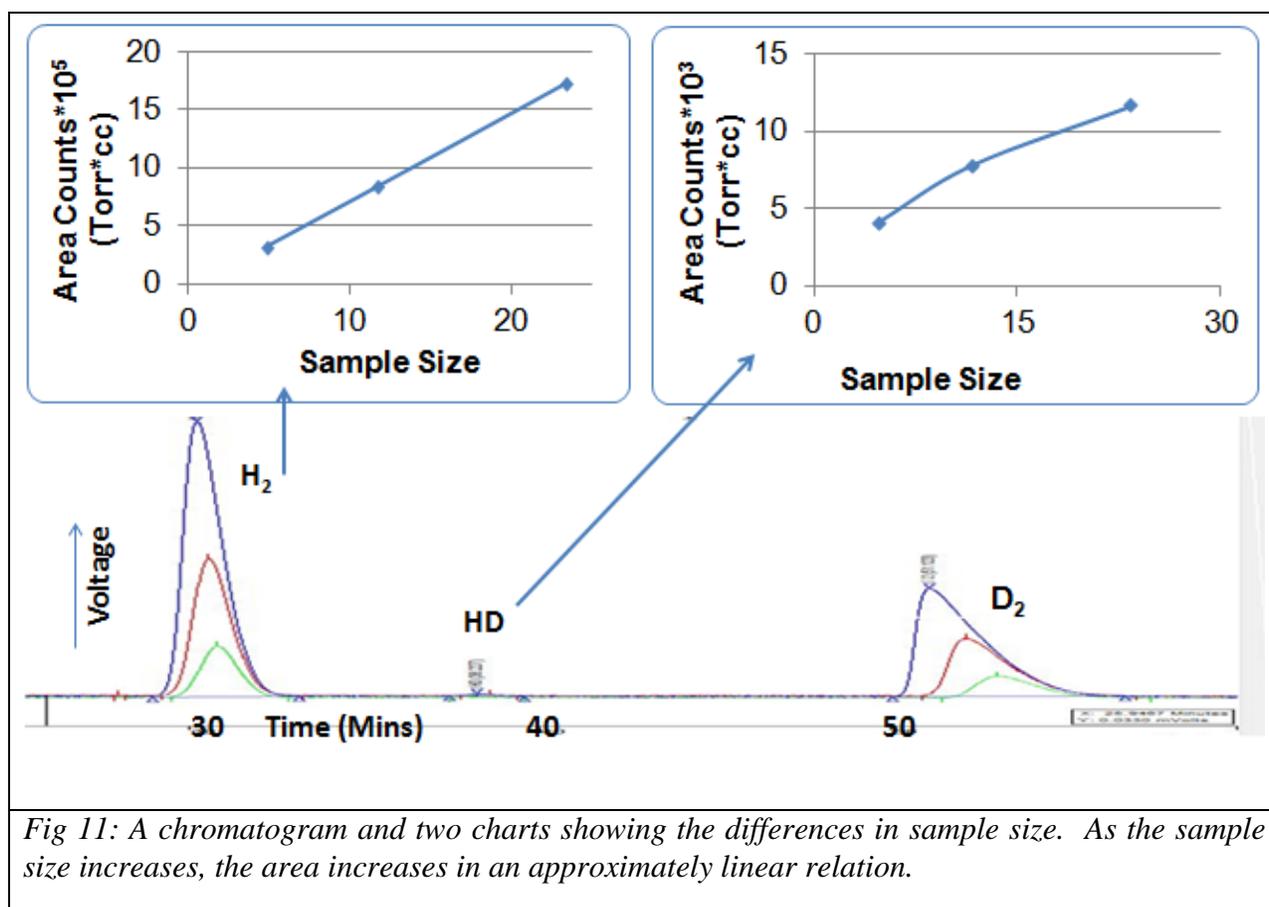
Figure 11 shows three chromatograms with different sample sizes and a different number of expansions. A sample size refers to how much sample is injected into the GC. As more expansions are made, the sample size decreases. The green chromatogram represents 6 expansions, while the red and blue chromatogram represents 5 expansions and 4 expansions, respectively.

With H_2, the area underneath the curve after 4 expansions is 17.28 torr*cc. After 5 and 6 expansions, the areas are 8.31 torr*cc and 3.09 torr*cc, respectively. Based on the data, as the number of expansions increases, the sample size decreases, as does the area underneath the curve.

In order to find the detection limit of the GC for hydrogen isotopes, serial expansions were made and the injection pressure was monitored for each injection. After 9 expansions the area underneath the H_2 curve was 0.085 torr*cc. The injection pressure at the 9th expansion was 3.39 torr. However, the 10th expansion didn't provide enough detector response for the GC to integrate the H_2 peak.

Conclusions

Gas chromatography with a TCD has been demonstrated to be a good technique to measure the isotopic composition of hydrogen mixtures. Using a Bruker CP-3800 GC, it was shown that hydrogen isotope concentrations can be measured to an accuracy of 1%. Best results were obtained for 5000 torr gas samples. The detection limit of this GC configuration for hydrogen isotopes was quantified. Sensitivities of the technique to temperature, carrier rate, and sample size were all measured. Increasing the temperature difference between the TCD block

and filament increases sensitivity. Decreasing the carrier flow rate and increasing the sample size both increase sensitivity.

References [4]

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Acknowledgments