J. Condensed Matter Nucl. Sci. 29 (2019) 298–308

Research Article

Development of a Sensitive Detection System for the Measurement of Trace Amounts of ^{4}He in Deuterium, Hydrogen, and Other Gasses

Malcolm M. Fowler*
McFarland Instrumentation Services Inc., Espanola, NM 87532, USA

Thomas N. Claytor†
High Mesa Technology, Los Alamos, NM 87544, USA

Abstract

Many LENR systems have been reported to generate small amounts of ^{4}He from experiments that employ deuterium as part of the experiment. There are few analytical methods that can detect trace amounts of ^{4}He in the presence of D_2. Most commercial magnetic sector mass spectrometers are large and expensive and, while they have excellent $\Delta m/m$ resolution, they still require some additional separation of He, such as a getter system to achieve ppb sensitivity. We have developed a lower cost, compact system that allows us to measure ^{4}He down to sub ppm levels in D_2 and other gasses. This system utilizes a column of activated carbon cooled with liquid nitrogen ($LN_{2)}$ that effectively absorbs everything but helium. Post absorption, the system uses an MKS Microvision residual gas analyzer (RGA) and a Stanford Research Systems (SRS) RS 100 RGA to check for helium purity. The helium eluted from the column is quantified by a small magnetic sector mass spectrometer tuned to mass 4. A typical sample size required to achieve ppb sensitivity to ^{4}He is 50 cm^3 at 50 Torr. Calibrations have been done with air, ^{4}He in D_2 at various concentrations and show a 3% variation from standard sample to standard sample. We will discuss the typical operation of this instrument and show results from various calibrations using different carrier gases.
 ISSN 2227-3123

Keywords: Chromatographic gas separation, Helium analysis, LENR product analysis, Mass spectrometry, Trace gas analysis

1. Introduction

We have been involved with many aspects of the "cold fusion" phenomena (LENR) since its announcement in 1989 and, for some time, we have gotten inquiries about analyzing for small amounts of helium in deuterium and/or hydrogen. About 2 years ago we started to look at what it would take to do these measurements and we present some of

*Corresponding author. E-mail: Malcolm-Fowler@zianet.com.
†E-mail: Claytor@att.net.

 ISSN 2227-3123

Table 1. Masses of light ion.

	Neutral mass	Positive ion mass
Atomic hydrogen	1.0078	1.0073
Molecular hydrogen	2.0157	2.0151
Deuterium	2.0141	2.0136
Tritium	3.0160	3.0155
HD	3.0219	3.0214
^{3}He	3.0160	3.0155
Molecular deuterium	4.0282	4.0277
^{4}He	4.0026	4.0021

the results of that development effort here. The separation and quantification of helium in the presence of hydrogen isotopes is quite difficult because the masses of the various species of interest are quite close in mass as is shown in Table 1. For instance, ^{4}He and D_2 differ in mass by only 0.025 mass units

We considered a variety of methods that would allow the measurements. Included were chemical removal of hydrogen isotopes. This approach included reacting the sample with excess oxygen, possibly with a catalyst. One can also pass the sample over hot copper oxide to produce water that is then trapped out or otherwise absorbed. Also considered was the use of a getter to absorb hydrogen and perhaps other constituents in the sample. Experience with the removal of tritium from He^3 has shown that the getter approach is not attractive as it is slow and requires circulation of the sample over the getter for some time to achieve quantitative separations. These methods all require consumable materials that make the methods somewhat unattractive. The sample often requires additional processing before final determination can be made. Several optical spectroscopic methods were considered, but it seemed that they did not have the required sensitivity and the methods were often compromised by other trace constituents in the sample.

We finally chose to look at a procedure based on gas chromatography. In this method, there is one or more columns, cooled with liquid nitrogen, that absorb essentially all components of the gas sample except for helium. Initially, we started with two columns, supplied by Hewlett-Packard [1], a molecular sieve column filled with MS-5A sieve followed by a second column filled with activated charcoal. The MS-5A column contained 100 g of 45/60 mesh molecular sieve 5A, while the activated charcoal column contained about 20 g of activated charcoal. Both columns were about 0.5 in. in diameter by 20 in. long. The normal procedure is to pump out the traps while being heated to about 200°C. At this temperature both water and carbon dioxide can be removed from the MS-5A molecular sieve trap. Once the pressure in the traps is below 0.001 Torr, the traps are cooled with liquid nitrogen (LN) and the sample is bled into the traps where most gasses are absorbed. Helium from the sample is not absorbed and is pushed through the traps by the incoming sample gas and ultimately is fed directly into the Residual Gas Analyzer (RGA) system. After some time, we found that a single activated charcoal column was adequate for the separations we wanted.

2. Experimental

Initially, data were collected from the SRS RGA operating in the mode where the partial pressures of several trace constituents were recorded as a function of time. The integral of the ^{4}He signal, over the time that the helium was eluting from the cooled columns, gives a result that is proportional to the ^{4}He concentration in the sample. In this mode, the minimum detectable signal is about 5×10^{-10} Torr. After operating in this mode for a while, it became clear that the RGA did not have the sensitivity to make the low-level measurements that were desired. We then turned to the Alcatel ASM-110 leak detector which had much lower background and higher sensitivity. The shortcoming of this instrument is that it only measures mass 4 with poor resolution. The low-level analog output from the ASM-110 leak detector was recorded as a function of time using a Tektronix TDS-744 digital scope. Typically, measurements were made at a rate of 5 per second with a total record length of 5000 s, resulting in 25 000 points per measurement

run. The scope was also run in the "high resolution" mode. In this mode the signal is averaged for the time between measurement samples resulting in about 12-bit resolution as opposed to 8-bit resolution in the normal mode. To improve the data acquisition, we switched from the TDS-744 scope to a Tektronix DPO-7254. The DPO scope has four input channels, much better I/O capabilities, and a fully capable windows computer on board. Another RGA, made by MKS, was added to the system that has a range of only 0–6 amu, but with about 50 times the mass resolution of the SRS RGA. This RGA has good resolution and can distinguish between D_2 and ^{4}He. Short comings for this RGA are relatively slow mass scan and mass tailing to the low side of a mass peak. In the case of D_2 and ^{4}He, the deuterium is the heavier mass and that peak tails to lower mass and overlaps the helium peak. If the deuterium is at a greater concentration relative to the helium, it quickly becomes very difficult to measure the helium. Notwithstanding these shortcomings, the MKS RGA is quite useful in looking for contamination in ^{4}He samples to be analyzed.

Once we started using both the RGA and the leak detector at the same time it became clear that the background of the leak detector was lower than the RGA, resulting in greater sensitivity. One difficulty with the leak detector was that the analog signal was small (25–50 mV) and the output followed range changes on the leak detector. This meant that careful records had to be kept so that after the run the recorded data could be properly scaled to give a smooth curve. In addition, the small signal made the data more susceptible to noise and the records often had to be noise filtered prior to analysis.

As a further development, it was discovered that there was a high-level output (0–100 V) available from the ASM-110 leak detector. In addition, this output does not change if the range of the ASM-110 is changed. To make use of this output, we paralleled all four inputs of the DPO7254 scope and operated the four inputs at 0.1, 0.5, 2.0, and 10 V/division. In this way I could record signals as large as 100 V yet retain good precision for signals as small as a few 10's of mV. The result is that the recording system has more than three orders of magnitude dynamic range without changing ranges. A final addition was to replace the DPO7254 scope with a Keysight 34465A 6.5-digit voltmeter. This voltmeter logs the data and can directly output the data to an Excel workbook.

3. Runs with Large Nitrogen and Air Samples

We have looked at pure nitrogen to verify that there is no helium signal from the nitrogen or from background in the RGA. Initially, 10 cm^3 samples of nitrogen that were at local atmospheric pressure (635 Torr) were analyzed to verify that there was no leakage through the traps. We injected three successive 10-cm^3 samples with no evidence of leakage through the traps. The traps were regenerated by heating the traps to 200–250°C while pumping on them. It was surprising that, even with heating, it took several hours to remove most of the absorbed gas. In cases of air samples, H_2O and CO_2 were the last to come off and this was presumably from the molecular sieve trap. In an effort to speed up the elution of the ^{4}He from the columns, we removed the MS-5A column, leaving only the activated charcoal column. We found that the absorption of sample gasses was still quantitative. In addition, the time for elution was decreased, improving background uncertainty.

Next, we investigated the capacity of the traps and for this, we used 1725 cm^3 of nitrogen at 1001 Torr for a total of 2.27 l-atm. of nitrogen. This amount of sample is far larger than anticipated for most samples, but we wanted to verify that the traps had adequate capacity to trap and retain the bulk of the sample.

Again, the absorption of the nitrogen was quite rapid and there was no leakage through the traps. In Fig. 1 is shown the absorption of the 2.27 l-atm. of nitrogen, starting at a pressure of 1001 Torr. It is interesting to note that more than 90% of the nitrogen sample was absorbed in less than ten minutes and 99.9% was absorbed in about 20 min.

Next, we analyzed air samples and tried to detect helium in air. The sample size was 1725 cm^3, but the pressure was 636 Torr, so that sample (1.44 l-atm.) was only about 63% of the size of the pure nitrogen sample. This air sample contained 2.03×10^{17} atoms of helium (0.007593 atm.cm^3 of He). When this sample was bled into the cooled traps, I observed a good helium signal in the RGA less than 5 min after start of introduction of the sample into the traps.

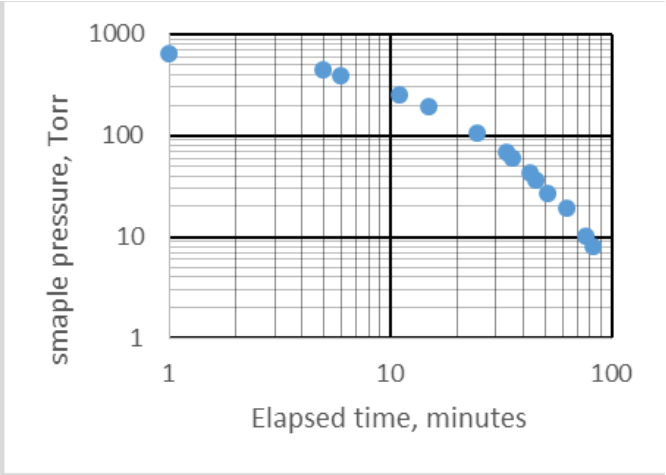

Figure 1. Absorption of pure nitrogen in cold traps.

Figure 2 shows the absorption of the air sample in the cooled traps. It is of interest here that the absorption of air is quite a bit slower than for the absorption of pure nitrogen. In this case, it took about 100 min to absorb 90% of the sample while it took only about 10 min for the pure nitrogen sample. The precise reason for this is not known at this time.

Next, we ran two air samples that were each 350 cm^3 @ 200 Torr. Each of these samples were much smaller than the earlier samples. These samples each contained 0.000485 atm. cm^3 of helium. In Fig. 3 is shown the time history of the partial pressure of helium and several other gasses that make up the background in the RGA. The introduction of the air sample was started at about 8 min and the helium elution was essentially complete by about 25 min after the

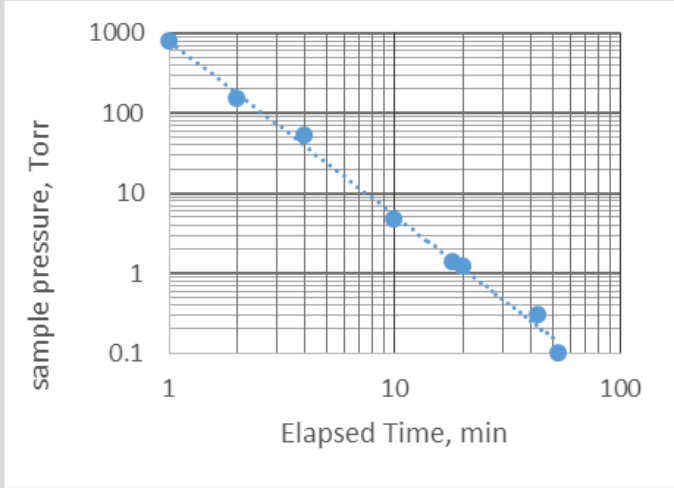

Figure 2. Absorption of air in cold traps.

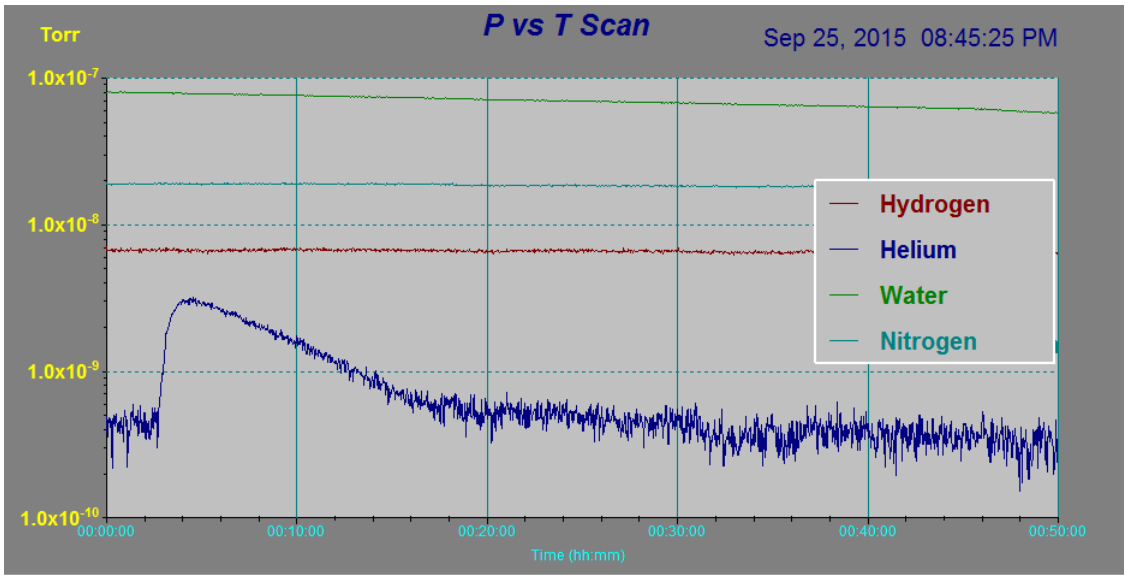

Figure 3. RGA analysis of effluent from cooled traps injected with air.

start if the introduction of the air. Figure 4 shows the net helium signal for the air sample after subtracting the averaged background. The integral of this curve is related to the helium concentration in the air sample. For this sample, the partial pressure was sampled every 2 s and the first 250 samples (500 s) were averaged to get the "before" background of 2.697×10^{-10} Torr. The "after" background was obtained by averaging 250 samples starting at 2000 s and gave a value of 2.75×10^{-10} Torr. If one sums up the data before background subtraction to get the uncorrected gross

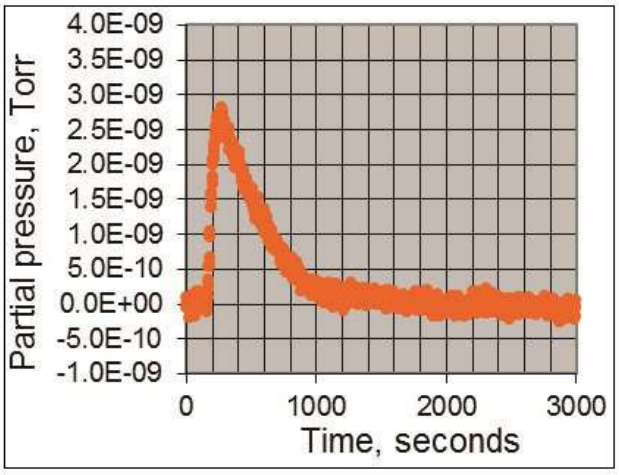

Figure 4. Net ^{4}He signal from 350 cm^3 of air at 200 Torr measured with an RGA.

signal, one obtains 6.71×10^{-7} Torr sample. The unweighted average of these two values (2.723×10^{-10} Torr) was then subtracted from each of the data points. The net data points were then summed to get the net helium signal, and this gave a value of 4.68×10^{-7} Torr sample and the difference between this and the net signal is the background contribution of 2.03×10^{-7} Torr sample. Thus, the background represents about 30% of the total signal for this run. The uncertainty associated with the background is about 28% so this contributes an uncertainty in the net signal of 8.4%.

4. Run with a 10 cm^3 air sample at 2585 Torr

This sample was one of the smaller air samples run to date and is similar in size to those expected from LENR experiments. For this run the Alcatel AMS-110 leak detector was used it to provide the backing pump for the RGA turbo. In this way, relatively quantitative helium measurements as the leak detector could be calibrated with a known helium leak and we could monitor the signals from both the RGA as well as the leak detector.

Figure 5 shows the net helium signal from the RGA after subtracting the averaged background. For this sample, the partial pressure was sampled every 2 s. We averaged 100 s of data just before the sample was injected to get a "before" background of 4.79×10^{-10} Torr. The "after" background was obtained by averaging 100 s of data samples starting at 1900 s and gave a value of 5.35×10^{-10} Torr. The unweighted average of these two values (5.066×10^{-10} Torr) was then subtracted from each of the data points. The net data points were then summed from 500 to 1500 s to get the net helium signal and this gave a value of 9.63×10^{-8} Torr sample. Each sample was 2 s so to convert "Torr Samples" to Torr s one need to multiply by 2, and this gives a net He signal of 1.93×10^{-7} Torr s. If one sums up the data shown in Fig. 5 to get the uncorrected gross signal, one obtains 3.50×10^{-7} Torr sample and the difference between this and

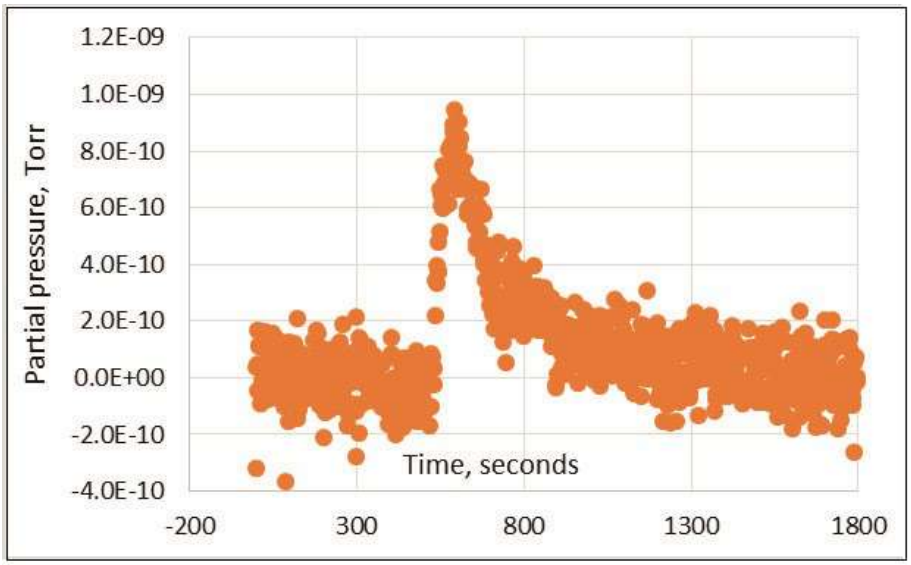

Figure 5. Net He-4 RGA signal from 10 cm^3 of air at 2585 Torr.

the net signal is the background contribution of 2.53×10^{-7} Torr sample. The background represents about 72% of the total signal for this run. These data are quite noisy and that limits the accuracy as well as the detection limit for helium. We have estimated that the uncertainty in the net signal is on the order of 50%. It seems that for this size of sample the detection limit is on the order of 6×10^{-8} Torr s corresponding to about 2 ppm of helium.

We looked at the data from the leak detector for the same sample and found it to be much less noisy as well as having a very small background. Figure 6 shows the data from the leak detector. The background for the leak detector when connected to the RGA and the traps is about 1×10^{-10} atm cm^3/s. If the signal is integrated from about 450 to 2000 s the result is 1.5×10^{-7} atm. cm^3. When the helium signal is integrated over the same period, the result is 3.73×10^{-5} atm. cm^3. In this case, the background is only about 0.4% of the total signal. From these data, we estimate we could measure a much lower concentration of helium with the leak detector than with the RGA. We estimate that we could easily detect 20 ppb of helium in a 10 cm^3 sample at 2585 Torr pressure.

5. Calibration

We can verify that the calibration of the helium leak detector is correct using a known calibrated leak. Figure 7 shows the response of the leak detector to a calibrated leak that has a leak rate of 4.0×10^{-8} atm. cm^3/s. The integral of the measured sample "leak rate" over time gives the number of atm. cm^3 of He that have "leaked" into the system. The ratio of this to the total number of atm. cm^3 in the sample gives the concentration of helium in the sample.

We can also prepare known standards of helium that are similar in concentration to that expected in the samples and then analyze the sample and standard using the same volumes and pressures for both. Figure 8 shows the measured peak area for several different pressures of the 12.8 ppm standard in the 50 cm^3 sample volume. The concentration of helium in the sample is given by the ratio of the integrated signal, over time for the standard, to that for the sample. Several standards were prepared that have equal amounts of hydrogen and helium. The hydrogen allows a check to be made that no hydrogen isotopes are leaking through the chromatographic procedure.

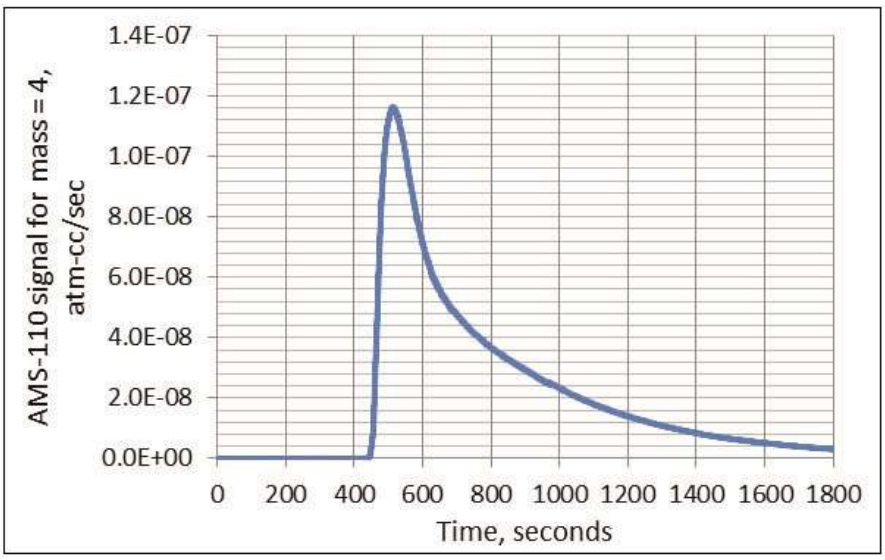

Figure 6. AMS-110 signal for mass=4 from 10 ^{3} of air at 2585 Torr.

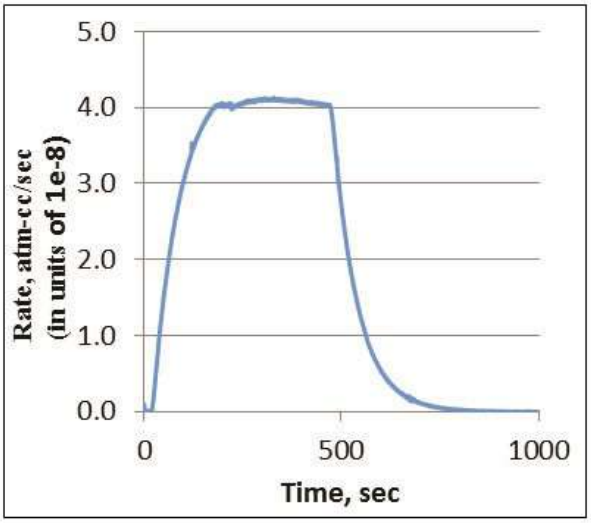

Figure 7. Measured He signal from standard leak vs. time.

Another approach would be to use He^3 as a spike and then use isotopic dilution to get at final sample concentration, but we have not implemented this yet.

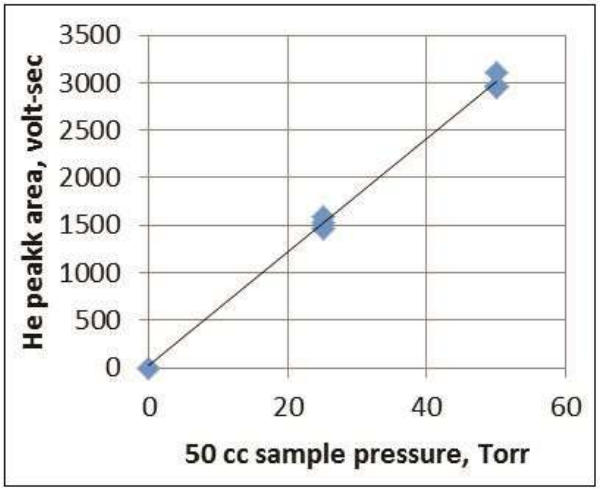

Figure 8. Calibration curve for 12.8 ppm He standard.

6. Current Performance

Figure 9 shows the current system response to a sample that was 1250 Torr cm^3 with a ^{4}He concentration of 12.8 ppm. This sample drives the output to nearly 80% of full scale, so if we wanted to measure more concentrated samples, we would need to use a smaller sample (lower pressure). The background of the ASM-110 leak detector corresponds to about 1×10^{-10} atm. cm^3/s and that gives a signal of about 10 mV, so with a full-scale range of 100 V, we have a dynamic range of four orders of magnitude. With a background "leak rate" of 1×10^{-10} atm. cm^3/s and an ^{4}He elution time of about 100 s, we can estimate that the minimum amount of ^{4}He we can detect is about 1×10^{-8} atm. cm^3, or 2.5×10^{11} atoms of ^{4}He in a sample that is 1250 Torr cm^3. This would correspond to about 6 ppb in the sample. This is a lower estimate compared the earlier estimate of 20 ppb, due mainly to the shorter elution time.

Certainty more modern mass spectrometers could lower this detection limit by quite a bit, but it does not seem necessary for LENR investigations especially when one considers that ambient air is about 5 ppm ^{4}He. Many, if not most, experiments are not well isolated from air. This is also true for the components and chemicals that are used, so it is not surprising that small amounts (ppm) of ^{4}He are found in most samples. As of late 2018, we have run nearly 200 samples, most of which were standards, pure gasses, and backgrounds. We have recently run several samples of pure argon and pure nitrogen. The argon samples gave an average value for ^{4}He of 0.202 ± 0.006 ppm while the hydrogen samples gave an average value of 0.033 ± 0.007. The quoted uncertainties are estimates of the statistical uncertainties. The total uncertainty is probable larger due to the uncertainty in the background for measurements close to the detection limit.

7. Summary

A system has been developed that can measure small amounts of helium in air samples. Currently, we can measure the amount of helium in air at ambient levels (5.26 ppm) with an uncertainty of about 10% with a sample of about 100 cm^3 at 1 atm. pressure to make the measurement. The minimum detectable amount of helium is estimated to be

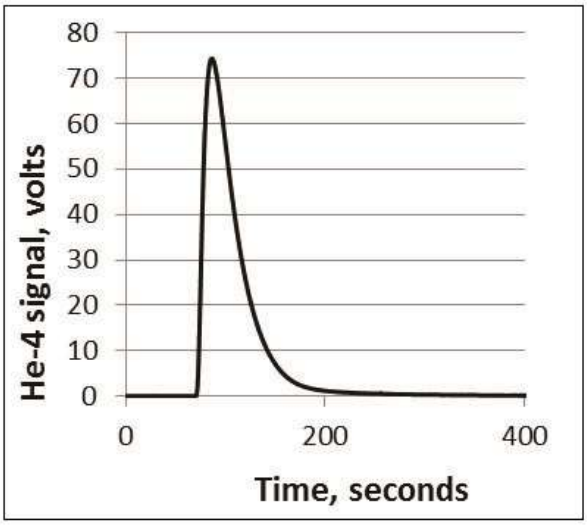

Figure 9. ASM-110 signal from 50 cm^3 of 12.8 ppm ^{4}He at 25 Torr.

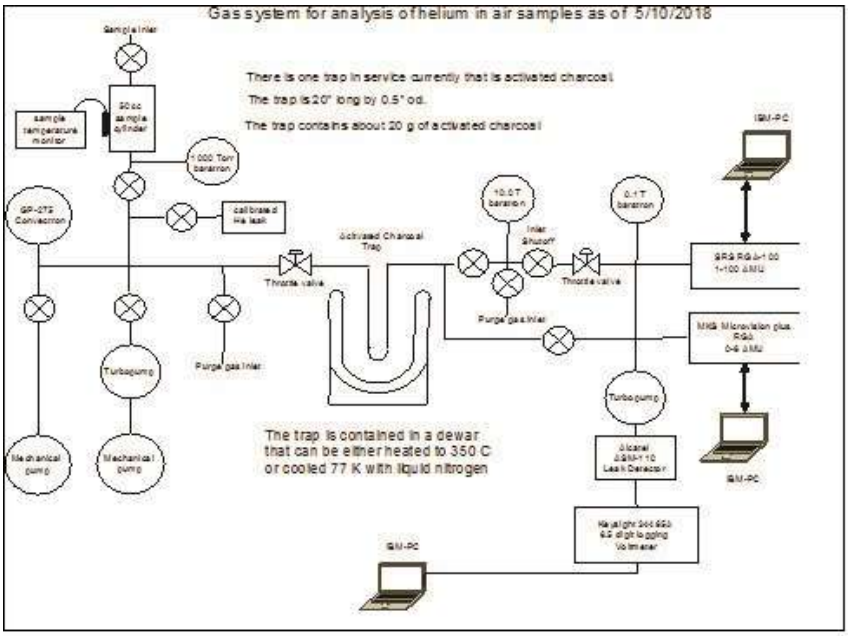

Figure 10. Diagram of the system for trace analysis of helium in gas samples as of 1/1/2019.

about 0.3 ppm for the same size sample. The measurement requires about 1 h to complete, but then requires several hours to warm and regenerate the traps to prepare for the next sample. So far, we have demonstrated that we can detect and measure helium in nitrogen and other gasses with sensitivities quite a bit better than the goal of 1 ppm. Uncertainties are driven mainly by the relatively long time that one must integrate the signal. If there is a relatively stable background, the relative contribution of this background to the total signal increase with time and eventually dominates the overall uncertainty. Efforts to improve uncertainty are centered around two areas; first, one could, in theory, decrease the elution time of the He and thereby reduce the time required for signal integration. At this time, this does not seem too feasible, but changing the geometry of the columns should help here. Next, we can be more rigorous in preconditioning the columns to reduce the overall background. If this can be done in a reproducible manner, then this could lead to considerable improvement. Another approach would be to model the shape of the elution curve. If this could be done, then one might be able to extract a few shape parameters from the recorded data that would allow estimation of the area of the elution curve. I have investigated this a bit and, so far, this does not seem too promising.

8. Future Efforts

We have fabricated a tube furnace that is connected to the analysis system with the goal of being able to heat foil samples to desorb and measure contained helium. What we have found so far is that above about 300°C the quartz tube becomes sufficiently permeable that we see significant signal from atmospheric helium. This is also true for 304 stainless steel at higher temperatures. 316 stainless steel might perform better but we have not tried this yet. We are now investigating methods to protect the heated tube from atmospheric air with coaxial tubes that are either evacuated or filled with some inert gas such as argon.

Acknowledgements

We would like to acknowledge the continued support and encouragement for this work by: Mr. Thomas Francis Darden II, J.D, Mr. J.T. Vaughn, and Mr. Dewey Weaver of Industrial Heat, LLC, 111 East Hargett Street, Suite 300, Raleigh, NC 27601 USA.

References

[1] Hewlett-Packard, MS-5A part number 5060-9084, Activated Charcoal part number 5060-9094.