

Nitrogen Monitor

Introduction

In the large liquid argon neutrino detector currently under consideration for construction at Fermilab,¹ neutrino interactions will result in tracks through the liquid argon. These “tracks” will consist of ionized argon atoms, electrons, and scintillation light. In order to detect the tracks, we need to ensure that light and electrons can pass through the liquid argon medium without being absorbed. In absolutely pure liquid argon, this is not a problem. However, contamination is ever present, and in our case one contaminant of concern is nitrogen: it is slightly electronegative and has a tendency to absorb scintillation light. Minimizing and controlling nitrogen levels in the liquid argon detector is one of the many tasks ahead. A first step in this direction is simply monitoring the nitrogen levels in the detector. In this paper, we explore the feasibility of using a particular meter to monitor nitrogen levels in gaseous argon.

The nitrogen meter we are considering operates by detecting the spectral emission lines of nitrogen. This type of detector was initially developed in the 1970s at Fermilab. The original technical memo is worth a look.² The intensity of the spectral emission lines is assumed to be proportional to the concentration of nitrogen in the gas. By monitoring the intensity of a specific spectral line of nitrogen, we can then monitor the concentration of nitrogen. For our purposes, we wish to monitor nitrogen concentration of 1-50ppm in an argon balance. (This range is set by assuming the effect of Nitrogen is about 1/1000 the effect of a similar amount of Oxygen - the factor of 1000 is just a guess.) The equipment necessary for this type of meter is available off the shelf: an arc cell or arc lamp, a monochromator, a photomultiplier tube, and a signal conditioning unit. See Figure 1 for a rough schematic.

Method

Arc lamps and emission spectra can be fairly complicated, and determining theoretically the best spectral line to use would be quite a challenge. Given the time constraints and limited ability of the authors, we choose to more or less completely ignore theory and determine a good spectral line to indicate nitrogen concentration using purely empirical means.

Activity

First, we gathered basic information on the emission spectrum of a sample with about 50 ppm nitrogen in argon balance. We then repeated the process with 1.2 ppm nitrogen in argon balance. The gathering process consisted of measuring the intensity of the arc after it passed through a

¹ For more information on the neutrino detector, please see Finley et. al. *A Large Liquid Argon Time Projection Chamber...* This is conveniently located on the web at <http://lartpc-docdb.fnal.gov/0000/000011/001/LArTPC.pdf>

² Walker, R. J. *Spectrographic Nitrogen Detector*. This document can be conveniently found here: http://lartpc-docdb.fnal.gov/0002/000260/002/nitrogen_in_helium_arc_cell_original_documentation_fermilab-tm-0742.pdf.

One should note, however, that Walker was trying to detect nitrogen in helium; we are trying to detect nitrogen in argon. Furthermore, the original meter was designed to detect one concentration of nitrogen in helium and trigger an alarm if this concentration was exceeded. In our case, however, we want to be able to accurately determine nitrogen concentrations in argon over a range, not a set point.

diffraction grating. The physical location of where we measure the light corresponds to a given wavelength. Our scanning monochromator selects which wavelength of light we measure with the photomultiplier tube allowing us to gather intensity information across a relatively broad spectrum. Table 1 presents the technical details of our two runs.

	Arc Cell Voltage	Arc Cell Current (mA)	PMT Voltage	Horiz. Pos. (mm)	Vert. Pos. (mm)	Run Time (min.)	Start λ (Å)	Stop λ (Å)	Flow (scfh)	Slit Width (microns)
50ppm	2000	19.5	450	12.48	15.75	997	3000	8436	3	203
1.2ppm	2000	19.5	450	12.48	15.75	426	3000	5322	3	203

Table 1: Scan Parameters. These parameters are fairly technical and are mainly included so someone using the same instrument can reproduce our data. The arc cell voltage and current describe how much the gas in the cell is being excited. The photomultiplier tube voltage determines the level of amplification given to the received signal. The horizontal and vertical positions refer to the relative location of the arc cell with respect to the monochromator. The runtime and the start/stop wavelengths describe the duration of the run. The flow rate describes how much gas was flowing through the arc cell. The slit width describes the diffraction grating of the monochromator. The rather large slit width we used provides for about a five angstrom resolution in the spectral lines (i.e. if two spectral lines differ by less than five angstroms, we see them as the same line, albeit one with a slightly odd shape).

The collected data are presented in Figure 2.

Discussion

The data presented in Fig. 2 are fairly self explanatory: by viewing the differences between the two runs (50ppm and 1.2 ppm N₂), we can determine if an emission line is created by nitrogen or the balance. Notably, there are three rather high-intensity nitrogen spectral lines at approximately 4030, 4200, and 4400 angstroms. We see no high-intensity argon spectral lines. Yes, we see some spectral lines that are due to the balance gas, but these are not high-intensity or even necessarily argon. This is not horribly surprising: argon tends to emit light in longer wavelengths.³

Of the three rather intense nitrogen spectral lines previously mentioned, the 4200 Å candidate (hereafter referred to with the more exact value of 4221) seems to us to serve as the best indicator of nitrogen concentration. We claim this simply because the 4221 Å line is fairly isolated from other emission lines and yet has a relatively high intensity. Its isolation makes the background fairly constant, at least more so than the nitrogen spectral line at roughly 4030 angstroms. As one can see from Fig. 2, the 4030 spectral line has a nearby partner at a slightly longer wavelength. Moreover, with better resolution (i.e. smaller slit width; 100 microns is sufficiently small), one sees that the 4030 Å spectral line is actually a combination of a few distinct spectral lines. The 4221 line was chosen over the 4400 spectral line simply because it has a slightly higher intensity.

So we have identified a good peak for calibration (it's at least as good as any other peak as far as we can tell). However, there remains one obstacle for calibration and one general question. The obstacle: for a two-point calibration (which we can easily accomplish using the gain and zero of

³ One can explore the spectra of various elements using the National Institute of Standards and Technology website. http://physics.nist.gov/PhysRefData/ASD/lines_form.html. Viewing the argon emission spectrum reveals that lines in our area of interest (3000-5000 Angstroms) are far from intense.

our signal conditioning unit) to be of any use, we need the relationship between nitrogen concentration and the received signal to be (nearly) linear. We need to explore this in more detail. The general question⁴: we would expect the ratio of the nitrogen-induced signals to be 50:1.2 for the two separate runs once background is accounted for. Do we observe this ratio?

In order to probe these specific problems, we utilize a more focused measurement. First, as detailed below, we calibrate the nitrogen meter to the 4221.0 Å emission line. We then use this calibrated line to shed light on the relationship between nitrogen concentration and signal strength and on the signal ratios. Before we describe the calibration of the nitrogen monitor and the data we collected, let's discuss what data we can collect to bring this dawn.

First, the relationship between concentration and signal.⁵ In order to determine if this relationship is indeed linear, let's follow the path taken from concentration of nitrogen to signal. The arc cell is presumed to generate light in a linear fashion: if there are twice as many nitrogen molecules, then there will be about twice as many nitrogen electrons displaced, and so about twice as many photons emitted of the desired wavelength of 4221 Å. These photons are picked out by the monochromator and transmitted to the PMT, where they strike a photocathode. The photocathode, too, is presumed to be linear: if twice as many photons strike the photocathode, twice as many electrons are emitted. Not extraordinarily surprising. These electrons are then accelerated with an electric field, where they strike another material and create a shower of new electrons, which are then accelerated, et cetera. And so the initial light signal is amplified. Is this electron cascade linear? This we can check. We vary the voltage on the PMT. If the signals for the 50 ppm nitrogen and the 1.2 ppm nitrogen calibration gases both increase or decrease by the same factor, then the electron cascade does indeed behave linearly⁶. And if the PMT behaves linearly, then there is a very high probability that the relationship between nitrogen concentration and signal is linear.

Second, the ratios of the signals for 50 ppm and 1.2 ppm nitrogen. This is fundamentally an easy question to answer: we take readings with the nitrogen monitor with both the 50 and 1.2 ppm calibration gases. We subtract any signal induced by background light or noise in the PMT (we have to assume the background is constant with respect to time for this step), and then compare the values of the readings. While straightforward, if the ratio is not what we expect (i.e. not 50:1.2), then we are in somewhat of a jam. So we have taken a preemptive action: we know that our gas delivery system (i.e. how we get the calibration gas from the cylinder to the arc cell) may leak, and if such a leak exists, it will likely manifest itself in the form of raised nitrogen

⁴ I say general because it's not really a calibration issue, nor is it critical for meter functionality, but still it is of interest.

⁵ Perhaps the most straightforward way to examine this question is to simply acquire a number of gas cylinders with a variety of nitrogen concentrations. If the nitrogen spectral line at 4221 Å can be calibrated to report the correct value for all the nitrogen concentrations using only a gain and zero adjustment, then the relationship between nitrogen concentration and signal is indeed linear. In our case, we only had two cylinders with known nitrogen concentrations. So we resort to the method above, which is (as one may note) somewhat dubious. But we think it works: none of the relationships described (e.g. nitrogen concentration and light emission) will be perfectly linear, but as long as they are pretty close to linear, then a two-point calibration still has some value.

⁶ [Reading at Voltage 1]=[Constant 1]*[Reading at Voltage 2] for any nitrogen input if the PMT is linear. Also, if the entire signal transducer is linear, then [Reading at 50 ppm]=[Constant 2]*[Reading at 1.2 ppm] for any PMT voltage. Using these two relations, we find that [Reading at Voltage 1 for 50 ppm]/[Reading at Voltage 1 for 1.2 ppm]=[Constant 2]=[Reading at Voltage 2 for 50 ppm]/[Reading at Voltage 2 for 1.2 ppm].

concentrations. Now, a leak would likely admit nitrogen from the atmosphere to the apparatus at a (more or less) constant rate. This means that as we change the flow rate through the nitrogen monitor, a leak would cause the ratios of the 50 ppm signal to the 1.2 ppm signal to vary. A short hypothetical example: if atmosphere leaks into our piping system at a rate of 5×10^{-6} scfh, then with a flow rate of 2 scfh through the arc cell, the leak adds 2.0 ppm nitrogen to the gas in the arc cell.⁷ The ratio of the signals is no longer 50:1.2, but rather 52:3.2, a rather large difference (41.7 compared to 16.25). But if we increase the flow rate through the nitrogen monitor to 4 scfh, then the leak only increases the nitrogen concentration in the arc cell by 1.0 ppm. Now the ratio of the signals would be 51:2.2 (or 23.2). So by comparing the signal strengths at different flow rates for the 50 and 1.2 ppm calibration gases, we can probe whether our piping system has any leaks.

More Activity

We calibrated the meter on the 4221 Å spectral line to 1.2 and 50 ppm nitrogen in argon balance using as variables the slit width, PMT voltage, and the zero point and gain adjustments of our signal conditioning device. The final calibration parameters are presented in Table 2.

Arc Cell Voltage	Arc Cell Current (mA)	PMT Voltage	Horizontal Position (mm)	Vertical Position (mm)	Flow Rate (scfh)	Slit Width	Wavelength (Å)
2000	19.5	425	12.48	15.75	3	83	4221.0

Table 2: Calibration Parameters. Columns have the same meaning as in Table 1. One should note, however, that future calibration will undoubtedly be necessary. Fortunately, calibration is a rather simple procedure. It only requires a bit of patience.

We then collected readings for a variety of different settings; namely, we varied the flow rate, the PMT voltage, the input gas, and the wavelength of the light incident on the PMT. These data are presented in Table 3.

Input Gas (ppm N ₂ in Ar)	Flow (scfh)	Nominal PMT Voltage	Wavelength (Angstroms)	ppm N ₂ per Monitor	ppm Reading above Background	Wavelength (Angstroms)	ppm N ₂ per Monitor
1.2	3	450	4221	1.3	3.3	4231	-2
1.2	2	450	4221	2.4	4.4	4231	-2
1.2	4	450	4221	0.8	2.8	4231	-2
1.2	3	550	4221	16.8	16.8	4231	0
1.2	2	550	4221	22.8	22.8	4231	0
1.2	4	550	4221	13.8	13.9	4231	-0.1
1.2	3	650	4221	73.3	66.4	4231	6.9
1.2	2	650	4221	96.7	89.8	4231	6.9
1.2	4	650	4221	61.8	54.9	4231	6.9
50	3	450	4221	50	51.6	4231	-1.6

⁷ These numbers are calculated using the idea that amount/time equals flow rate times concentration. So the amount of nitrogen going through the monitor per unit time equals [flow from cylinder]*[concentration of nitrogen in cylinder]+[flow from leak]*[concentration of nitrogen in atmosphere]. To find the concentration of nitrogen in the monitor, we simply divide the amount of nitrogen at the monitor by the flow rate.

50	2	450	4221	50.4	52	4231	-1.6
50	4	450	4221	49.5	51.1	4231	-1.6
50	3	550	4221	267.9	265.7	4231	2.2
50	2	550	4221	269.6	267.5	4231	2.1
50	4	550	4221	266.4	264.2	4231	2.2
50	3	650	4221	1070.8	1055.4	4231	15.4
50	2	650	4221	1081.2	1066.5	4231	14.7
50	4	650	4221	1061.6	1045.7	4231	15.9

Table 3: Nitrogen readings from calibrated peak and background with varied operational parameters. Concentrations recorded at 4231 Angstroms are considered background. The PMT voltage is *very* nominal, but this nominal value is repeatable to a sufficient degree. Interestingly, our monitor can only read a maximum of about 124 ppm nitrogen. As one may note, we report much higher ppm readings. In these cases, we scaled back the current input to our signal conditioning unit by a known amount using a resistor placed in parallel. Crude, but functional.

We are really interested in the ratios of the signals at 50 ppm N₂ and 1.2 ppm N₂. Table 4 presents these ratios for each of the operating conditions.

Flow (scfh)	Nominal PMT Voltage	Signal Ratio ([50ppm]/[1.2ppm])
2	450	11.8
3	450	15.6
4	450	18.3
2	550	11.7
3	550	15.8
4	550	19.0
2	650	11.9
3	650	15.9
4	650	19.0

Table 4: Signal Ratios and their associated conditions.

First we note that the signal ratios as the PMT voltage varies (and the flow is not changed) remain more or less constant, indicating that the PMT is linear. This in turn indicates that nitrogen concentration is transduced to a signal in a (nearly) linear fashion if the amount of light is indeed proportional to the amount of nitrogen. We, however, would still like to test this linear relationship in the more direct way noted in Footnote 5. Perhaps not surprisingly, the signal ratio as we vary the flow rate does not remain constant. Is this variation in the signal ratio created by a leak, and if it is, how big is the leak?

In order to determine if a leak causes these flow-induced ratio variations, it first makes sense to leak-check our gas delivery system. We didn't bother. Our system leaks if for no other reason than some of the materials involved, such as the plastic tubing.

To check that a leak is the dominant source of the variation we observe in the signal ratios, we can do the following: assume that the proper ratio is 50:1.2 and that the leak adds a constant concentration of nitrogen for a given flow rate. We can write this as:

$$\frac{[Signal @ 50 ppm] - [LeakSignal]}{[Signal @ 1.2 ppm] - [LeakSignal]} = \frac{50}{1.2} \quad (1)$$

Since we know the signal at 50 and 1.2 ppm, we can solve for the leak signal. The leak signal is proportional to the concentration of nitrogen that is introduced to the arc cell by the leak. This step is only tricky because we presume to know the proper signal ratio. There could, in fact, be other forces at work that change the signal ratio, so the leak may not be solely responsible for deviation from the desired ratio.

Table 5 presents the leak signal for each combination of parameters (flow and PMT voltage). The leak signal is also converted to an amount per unit time by multiplying by the flow rate. Of course, it is crucial to note that the signal added by the leak cannot readily be converted to a nitrogen concentration because the monitor is only calibrated to one of the nine scenarios listed (3 scfh flow and 450 nominal PMT voltage). And even in this one case where we might convert signal to concentration, we still need to add in a proper portion of the background to change the signal into an accurate indication of nitrogen concentration. This means that the “amounts” listed in Table 5 are only proportional to the actual amount in scfh of nitrogen that goes through the nitrogen meter.

Flow (scfh)	Nominal PMT Voltage	" concentration of N2 " added by leak	"amount of N2 " added by leak
2	450	3.2	6.5
3	450	2.1	6.3
4	450	1.6	6.4
2	550	16.8	33.6
3	550	10.7	32.0
4	550	7.7	31.0
2	650	65.8	131.6
3	650	42.1	126.2
4	650	30.5	122.1

Table 5: Leak Information. The values in the third column are calculated using equation (1). The amount added by the leak is calculated by multiplying the signal added by the flow rate.

We immediately notice that the leak "amounts" are quite constant⁸ over a given PMT voltage. This is exactly what we would expect if there were indeed a leak: it would be constant over variations in flow. Don't fret over the apparent discrepancies in the amount added as we change the PMT voltage. This is simply due to the fact that by increasing the PMT voltage, we amplify the signal and so we also amplify the signal that is due to the leak.

⁸ Sure, there is a little variation. One might be slightly curious about the 550 and 650 nominal PMT voltages, simply because the leak amount seems to decrease as flow increases. Such a relationship is somewhat expected as an increased flow rate causes a slight pressure increase which may indeed slightly slow the amount of nitrogen leaked into the piping system.

Table 5 essentially shows that there is a leak (which we already knew) and that we can detect its presence with the monitor. Still, we would like to know the leak rate. This is a rather tricky business. We can figure out the leak rate if we have a solid reading of the concentration using the following equation:

$$(F - X) * A + X * B = F * C \quad (2)$$

where F is the total flow rate (including the leak) at the arc cell, X is the leak rate, A is the concentration of nitrogen in the cylinder, B is the concentration of nitrogen in the atmosphere, and C is the concentration of nitrogen at the arc cell. And here is the problem: we don't know the concentration of nitrogen at the arc cell. We calibrated the monitor, yes, but only so that when we input 50 or 1.2 ppm N_2 gas, the monitor reads just that. Our monitor, in other words, already accounts for the leak rate. Which is no good. There is a way around this, however. Let's trust that our nitrogen meter is calibrated fairly well for when the PMT voltage is nominally 450, at least so that we accurately detect changes in the nitrogen concentration. So while we do not know the nitrogen concentration at the monitor, we do know the difference in nitrogen concentration at the monitor created when we change the flow rate. By changing the flow rate at the cylinder, we can use the following equations:

$$(F_1 - X) * A + X * B = F_1 * C_1 \quad (3)$$

$$(F_2 - X) * A + X * B = F_2 * C_2 \quad (4)$$

where the variables all have similar definitions to those in equation (2). This gives us two equations and three unknowns (X , C_1 , and C_2). But, if we trust our calibration of the nitrogen meter to a limited extent, then we know the difference between C_1 and C_2 . With minor rearranging, we have:

$$X = \text{Leak Rate} = \frac{[C_1 - C_2]}{\left[\frac{(B - A)}{F_1} + \frac{(A - B)}{F_2} \right]} \quad (5)$$

The important thing is that equation 5 is solvable for the leak rate X . Moreover, we have six different chances to calculate the leak rate. For 1.2 ppm nitrogen input at nominal 450 PMT voltage, we can compare between the three different flow rates. The same goes for 50 ppm nitrogen input at nominal 450 PMT voltage. Table 6 shows the leak rate calculated with different flow rates.

Input Gas (ppm N_2 in Ar)	Leak Input (approx ppm N_2 in Air)	Flow Rate 1 (scfh)	Flow Rate 2 (scfh)	Difference in Concentration (ppm N_2)	Calculated Leak Rate (scfh)
1.2	800000	2	3	1.1	8.3×10^{-6}
1.2	800000	2	4	1.6	8.0×10^{-6}
1.2	800000	3	4	0.5	7.5×10^{-6}
50	800000	2	3	0.4	3.0×10^{-6}
50	800000	2	4	0.9	4.5×10^{-6}

50	800000	3	4	0.5	$7.5 \cdot 10^{-6}$
----	--------	---	---	-----	---------------------

Table 6: Calculated Leak Rates. The values in column six are calculated using equation (5).

Interestingly, the leak rate seems to vary quite a bit when we use the differences in the 50 ppm flow readings. While not expected, this is not entirely surprising: in order to successfully calculate the leak rate, we need to detect changes in the nitrogen concentration of less than one part per million. With the low nitrogen input gas, such a change is much more dramatic than with the high nitrogen input gas. So we have more faith in the leak rates calculated using differences in the readings of the 1.2 ppm input gas.

It's important to note, however, that the change in signal ratios may not be completely caused by a leak. The best way to check this is simply to improve our gas delivery system and repeat the measurements.

Even More Activity

We improved our setup. We now have a high-purity regulator, stainless steel tubing, and metal-seal fittings. These should work to reduce the leak rate to near zero. Since the signal seems linear with respect to the PMT voltage, we only check the signal as we change the flow rate. We calibrated the meter with the following specifications.

Arc Cell Voltage	Arc Cell Current (mA)	PMT Voltage	Horizontal Position (mm)	Vertical Position (mm)	Flow Rate (scfh)	Slit Width	Wavelength (Å)
2000	19.5	425	12.48	15.75	3	71	4221.0

Table 7: Calibration Parameters with Improved Gas Delivery System.

In order to check performance, we monitored the signal as we changed the sample gas flow rate. Ideally, a change in flow rate would not result in a signal change. [currently working on this]

Conclusion

We've successfully calibrated the nitrogen monitor using a spectral emission line at 4221 Å. Furthermore, we've determined with some certainty that the nitrogen monitor behaves linearly, meaning that this monitor should accurately indicate the concentration of nitrogen in the arc cell with its current calibration. Finally, we've discovered that our original setup probably leaked with a rate between $2.5 \cdot 10^{-6}$ and $1 \cdot 10^{-5}$ scfh. We are currently trying to correct this. Overall, however, the nitrogen monitor functions quite well. With some further tweaking (namely an improved sample gas delivery system), we believe it can have accuracy to 0.1 ppm N₂.

Figure 1: Simple Schematic of Nitrogen Detector. Niceties such as a regulator and a flow meter are omitted. The load resistor serves to keep the current through the arc cell relatively constant. Important when one considers that the emitted light intensity is a function of the current, and the resistance across the arc may vary seemingly randomly as the gas particles move about.

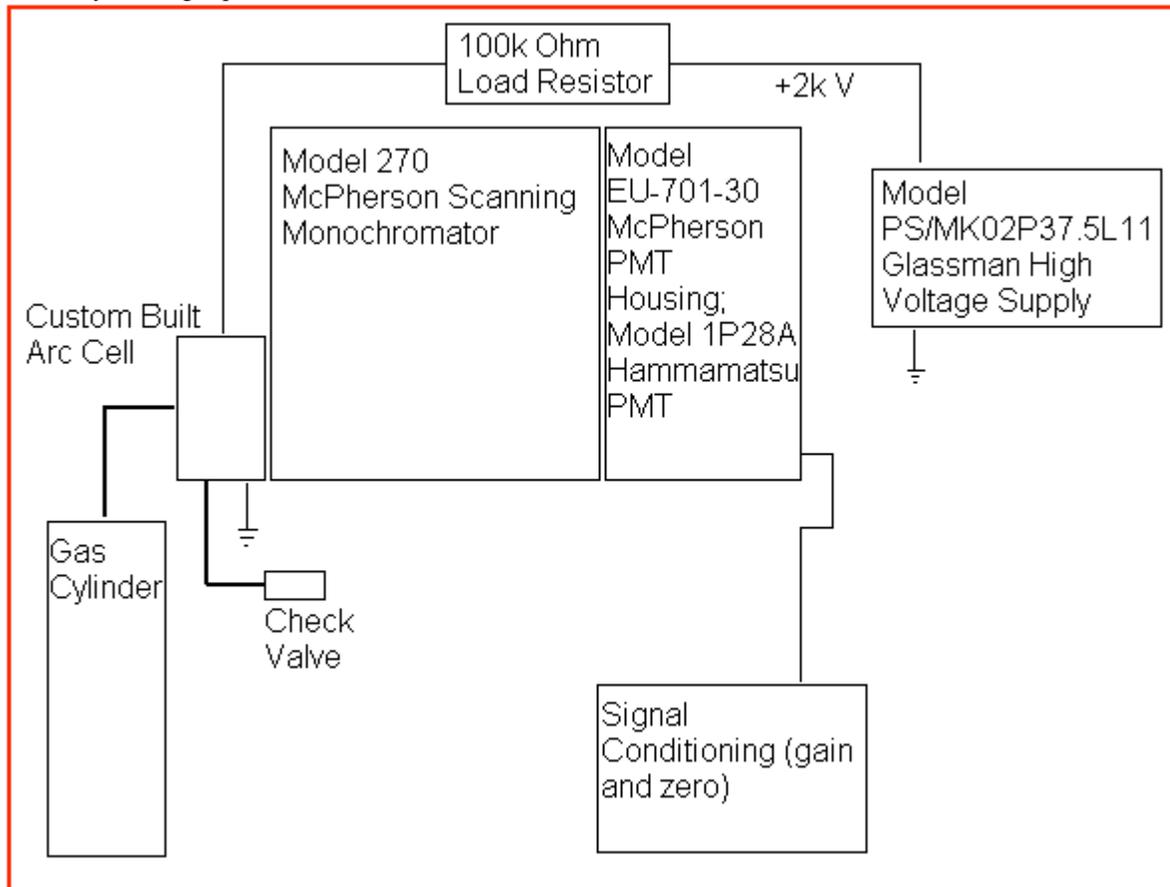


Figure 2: Intensity vs. Wavelength for Spectral Lines of Nitrogen and Argon Balance. As mentioned previously, we used our monochromator to scan emission lines over a range of wavelengths. The intensity of each wavelength was recorded.

