AN-16: FAST CRUDE ARGON ANALYSIS WITH THE µSENSE GC PLATFORM

TECHNICAL REPORT

SOLUTION FEATURES

- **Fastest cycle time -** Analysis in 30 seconds (15 seconds optional) due to Epd** and Spectral compensation*
- **Low maintenance**– No consumable, no O_2 trap
- **Most compact solution -** Only one GC valve, compact µSense GC platform

KEY SPECIFICATIONS

- **Limit of detection:** down to 50 ppb
- **Measurement range:** 1 ppm to 1000 ppm (Up to 1% possible)
- **Analysis time:** 30 seconds(15 seconds optional)
- **Carrier gas:** Argon

This report presents the results acquired for crude argon analysis (trace nitrogen in oxygen) using the **ASDevices' µSense** platform. The parameters were optimized for a measurement range of 0-1000ppm, but over-range N_2 concentrations can also be measured. The configuration of the **µSense** platform used for crude argon analysis is presented in Figure 1.

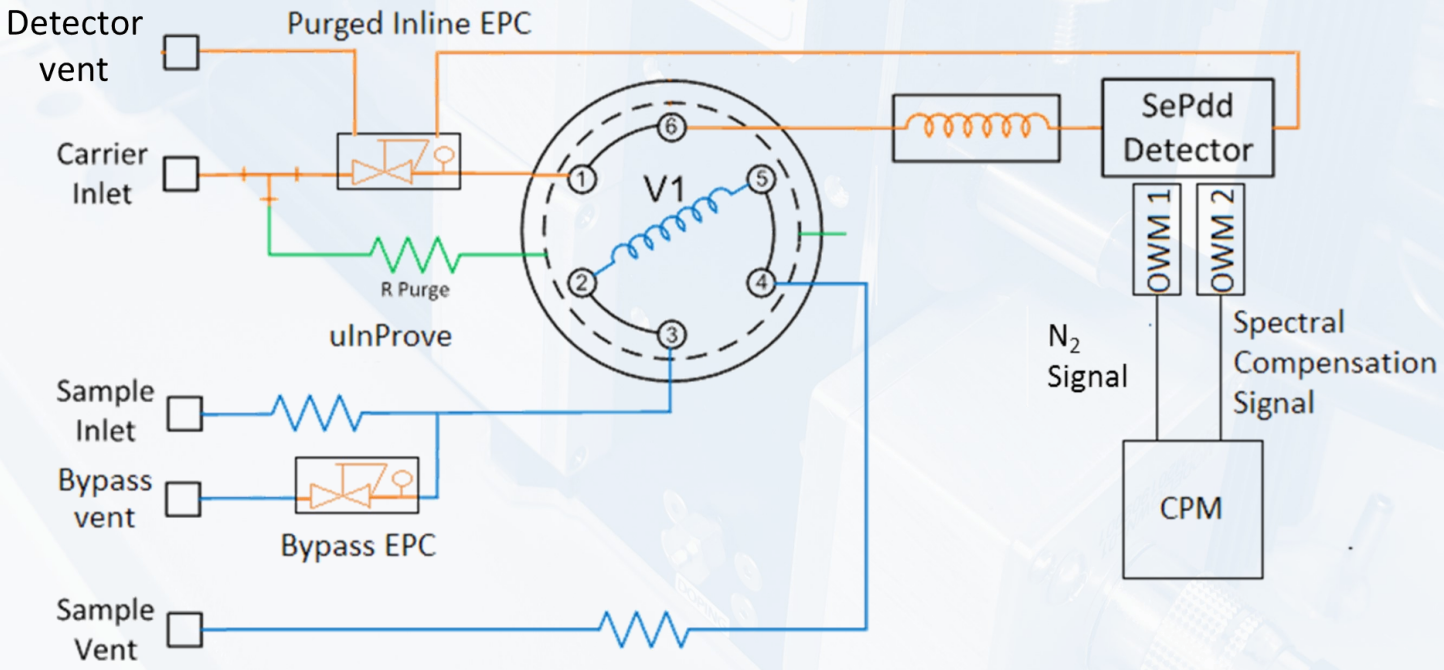

Figure 1— **µSense** platform configuration for crude argon analysis

Key features of this new GC platform include a purged inline electronic pressure controller (EPC), which consumes less carrier gas and allows precise gas flow control, a PLSV-based 6 ports injection valve and the Enhanced plasma discharge** (Epd) detection technology. Spectral compensation* is a measurement mode unique to this detection technology. Thanks to this mode, the N_2 peak can be accurately measured without separation from the matrix (oxygen). Therefore, shorter GC columns can be used and no expensive copper-based oxygen trap (consumable) is required. This results in significantly shorter analysis times, less expensive setup and more reliable results.

Spectral compensation*

The Epd technology allows simultaneous measurement of up to 4 different optical channels, which can then be combined to achieve spectral compensation. Since the effect of the matrix on the chromatogram background can be spectrally corrected, this method does not require a chromatographic separation of nitrogen and oxygen to achieve adequate and precise quantification. Therefore, crude argon analysis can be achieved in less than 30 seconds. Figure 2 shows a chromatogram acquired for 54 ppm of N_2 in oxygen.

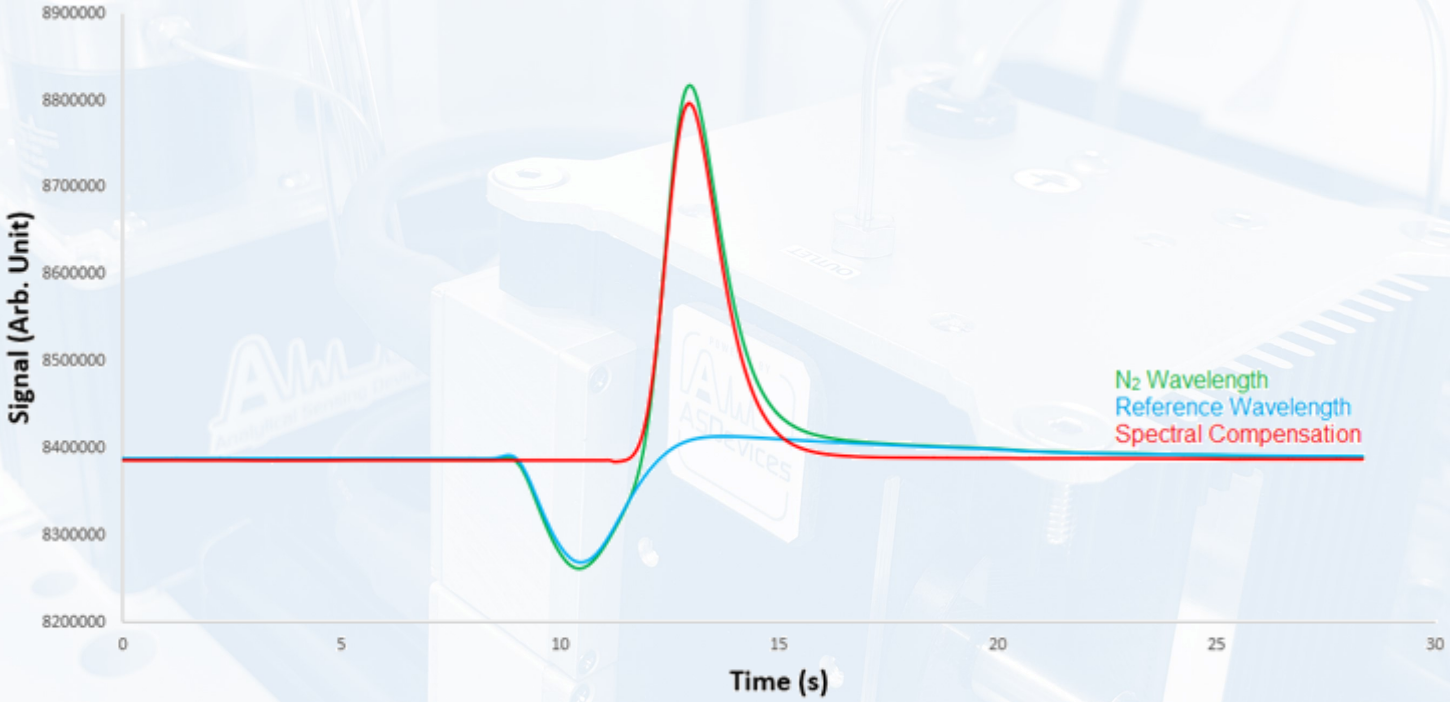

Figure 2— Chromatogram acquired for 54 ppm of N_2 in oxygen

The green line is the response acquired with a wavelength specific to N_2. However, its background is also affected by the large amount of oxygen from the matrix, which makes this signal unusable for accurate N_2 quantification in these conditions. This is why typical crude argon setups require longer GC columns and/or an oxygen trap, which makes the analysis longer and more expensive. The blue line is recorded at a wavelength affected only by the oxygen matrix and not by N_2. Therefore, this wavelength is used to cancel the effect of oxygen on the background of the N_2 signal. The resulting spectrally compensated measurement is shown as the red line. Signal processing is done by the chromatographic processing module at the same time as the signal acquisition. No additional processing time is required.

* Patent pending ** Patented

Signal Stability and Limit of Detection

The **ASDevices' µSense** platform configured for crude argon analysis allows highly stable and accurate nitrogen quantification. A sample containing 340 ppm of N_2 in oxygen was analysed every 30 seconds on a 24h period. A good standard deviation of 0.5% on the value or 0.17% on the full range was achieved. The results are presented in Figure 3.

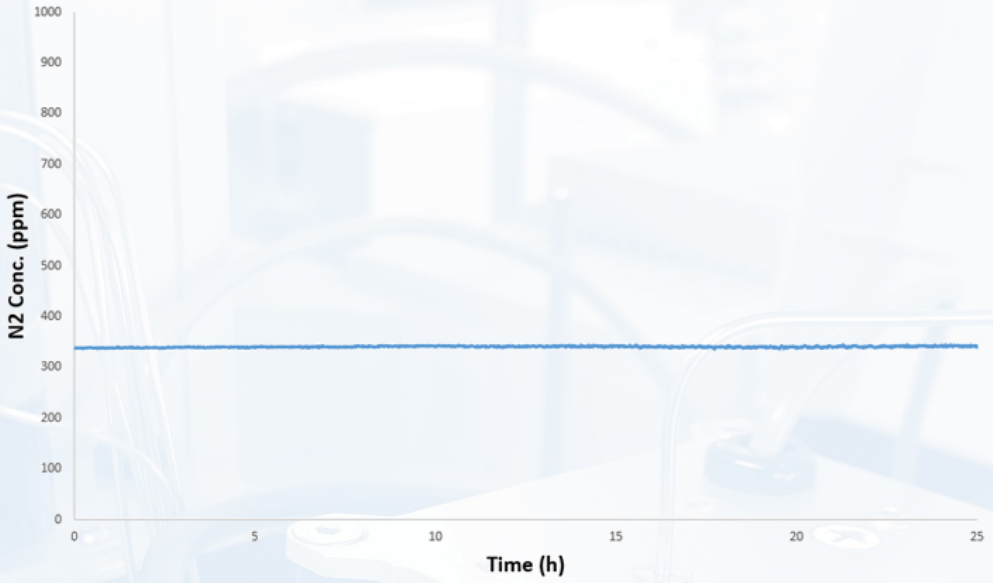

Figure 3— N_2 concentration measured with the **µSense** platform for a sample containing 340 ppm N_2 in oxygen on a 24h period with an acquisition every 30 seconds

This test has been extended for a period of 4 days. A good stability and accuracy, with a standard deviation of 1.1% on the value or 0.37% on the full range has been achieved, as seen in Figure 4.

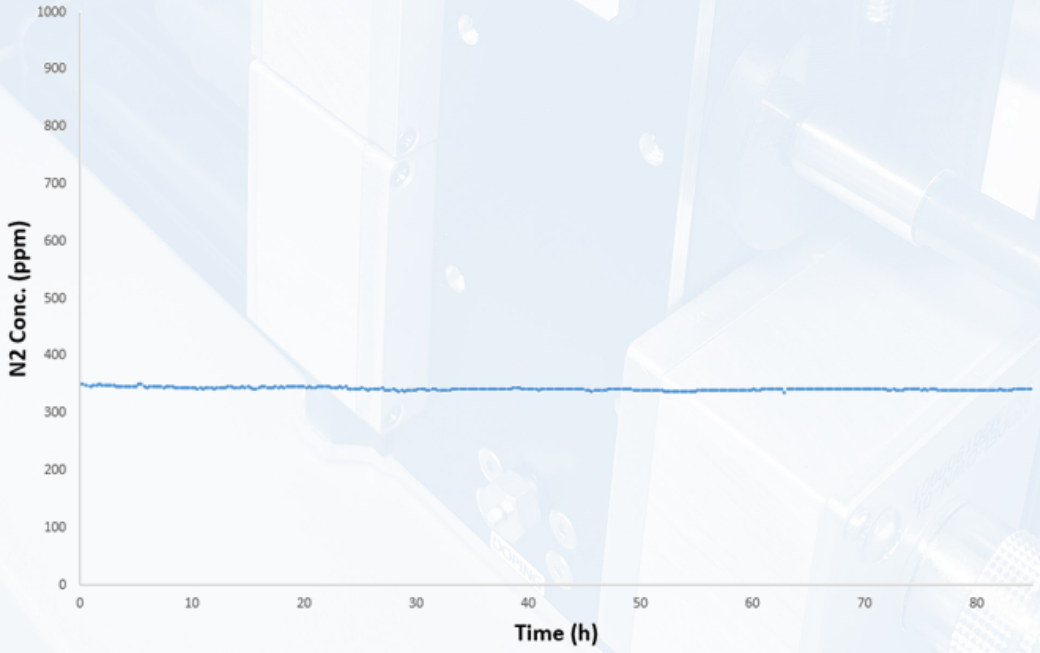

Figure 4— N_2 concentration measured with the **µSense** platform for a sample containing 340 ppm N_2 in oxygen on a 4 days period.

To show the accuracy of the system, 30 consecutive acquisitions of a low concentration dilution (54ppm) of N_2 in oxygen are presented in Table 1. From these 30 points, a standard deviation of 2.1 ppm or 0.21% of the full measurement range was calculated.

Table 1— Measured concentration for 30 consecutive acquisitions with a 54 ppm of N_2 in oxygen dilution

Acquisition	1	2	3	4	5	6	7	8	9	10
N_2 Conc. (ppm)	55,255	53,075	54,752	49,079	51,983	55,180	53,991	59,040	49,947	57,256
Acquisition	11	12	13	14	15	16	17	18	19	20
N_2 Conc. (ppm)	51,579	53,236	55,269	54,379	52,895	54,007	54,289	56,066	55,559	52,777
Acquisition	21	22	23	24	25	26	27	28	29	30
N_2 Conc. (ppm)	54,942	55,770	55,643	52,125	50,935	52,863	55,149	54,868	53,571	51,961

The limit of detection (LOD) of this system was determined as 3 times the signal to noise ratio on a chromatogram acquired for 54 ppm of N_2 in oxygen (Figure 2). A LOD of 500 ppb was calculated, and a LOD of 50 ppb can even be reached using a larger sample loop.

Signal Linearity

The signal intensity as a function of N_2 concentration was shown to be linear, at least for a range of 0 to 1000ppm N_2 in oxygen. The following chromatograms were acquired by diluting a certified sample of N_2 in oxygen with various amounts of UHP oxygen. Figure 5 shows 8 chromatograms acquired with spectral compensation at different N_2 concentrations in oxygen.

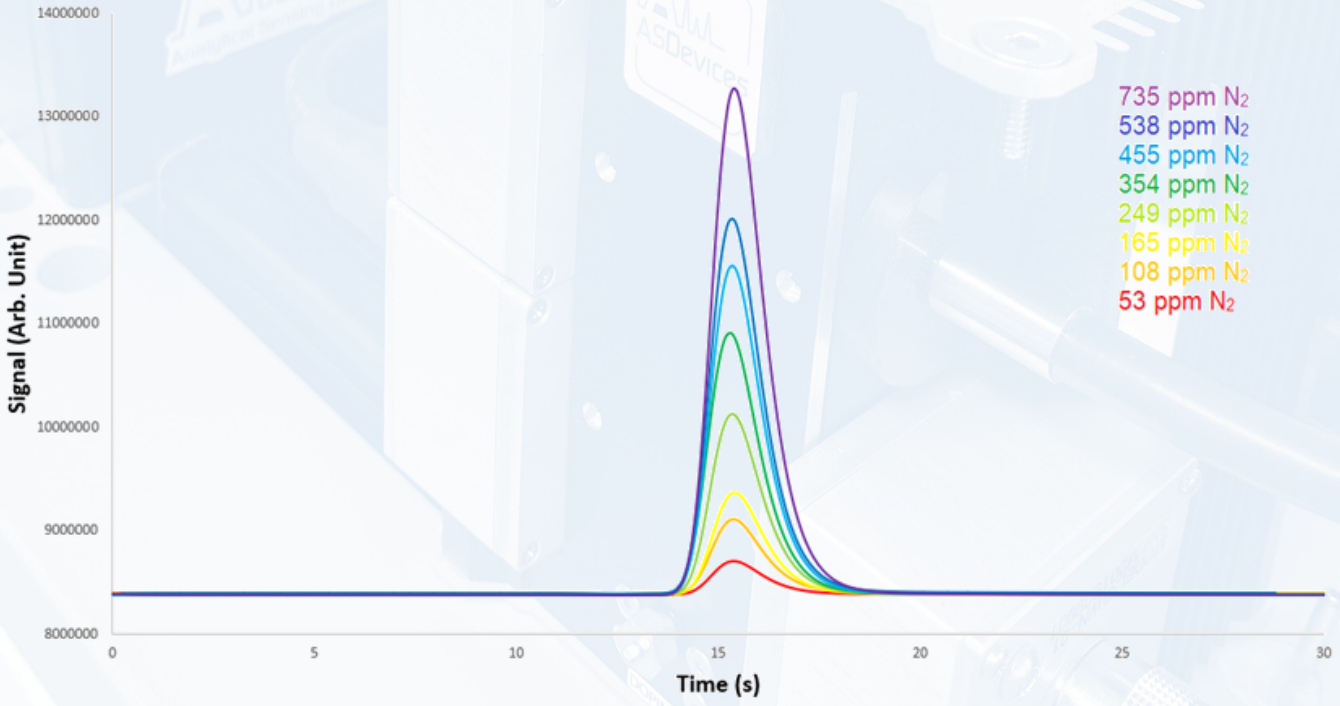

Figure 5— Chromatogram acquired for 8 different concentrations of N_2 in oxygen (spectral compensation)

The linearity of the response is presented in Figure 6. A good R^2 of 0.999 was reached for a range of at least 0-1000ppm. The error bars represent the uncertainty on the sample concentration from to the dilution system used.

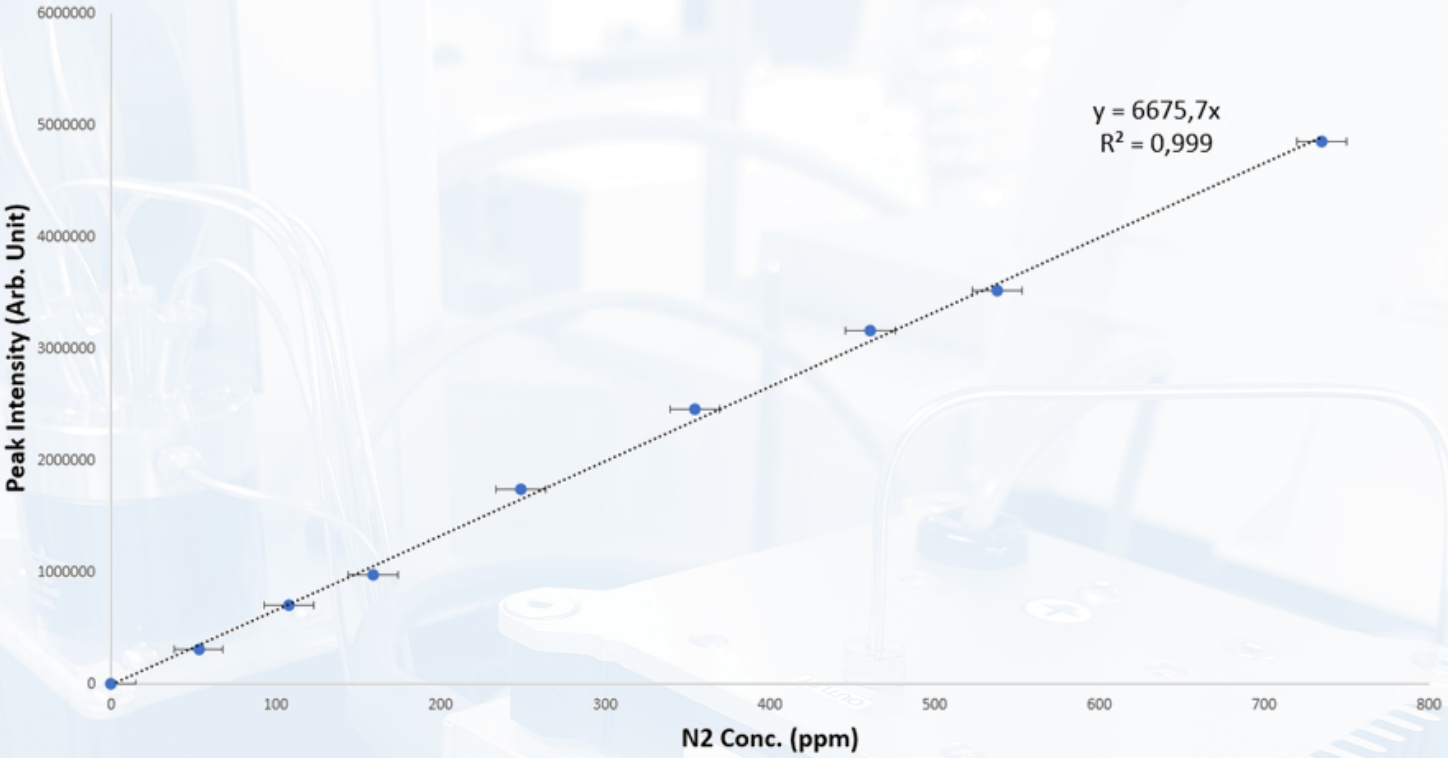

Figure 6— Peak intensity as a function of N_2 concentration in oxygen

Effect of Oxygen Concentration on N_2 Measurements

The previous results were all acquired for N_2 in oxygen matrix. As seen in Figure 2, high amounts of oxygen will disturb the baseline. This disturbance strongly depends on the oxygen concentration and this is another reason why oxygen must be well separated and/or trapped in typical crude argon setup. Indeed, changes in O_2 concentration can have a significant impact on the measurement if the peak is not well separated. Since nitrogen and oxygen are co-eluting in our method and Ar/O_2 mix in crude argon can vary, we tested N_2 measurements with various O_2 concentrations to show that it has no impact on the N_2 measurements. For this test, we used a certified sample containing N_2 in argon and diluted it with various amounts of UHP oxygen. The results are presented in Figure 7. The percentage of oxygen in the matrix is indicated below each point.

Results similar to those presented in Figure 6 with a good R^2 of 0.999 were obtained here, despite the large variation in oxygen concentration. This shows that the spectral compensation can indeed be used for accurate N_2 measurement, regardless of the oxygen concentration in the matrix, without increasing measurement inaccuracy.

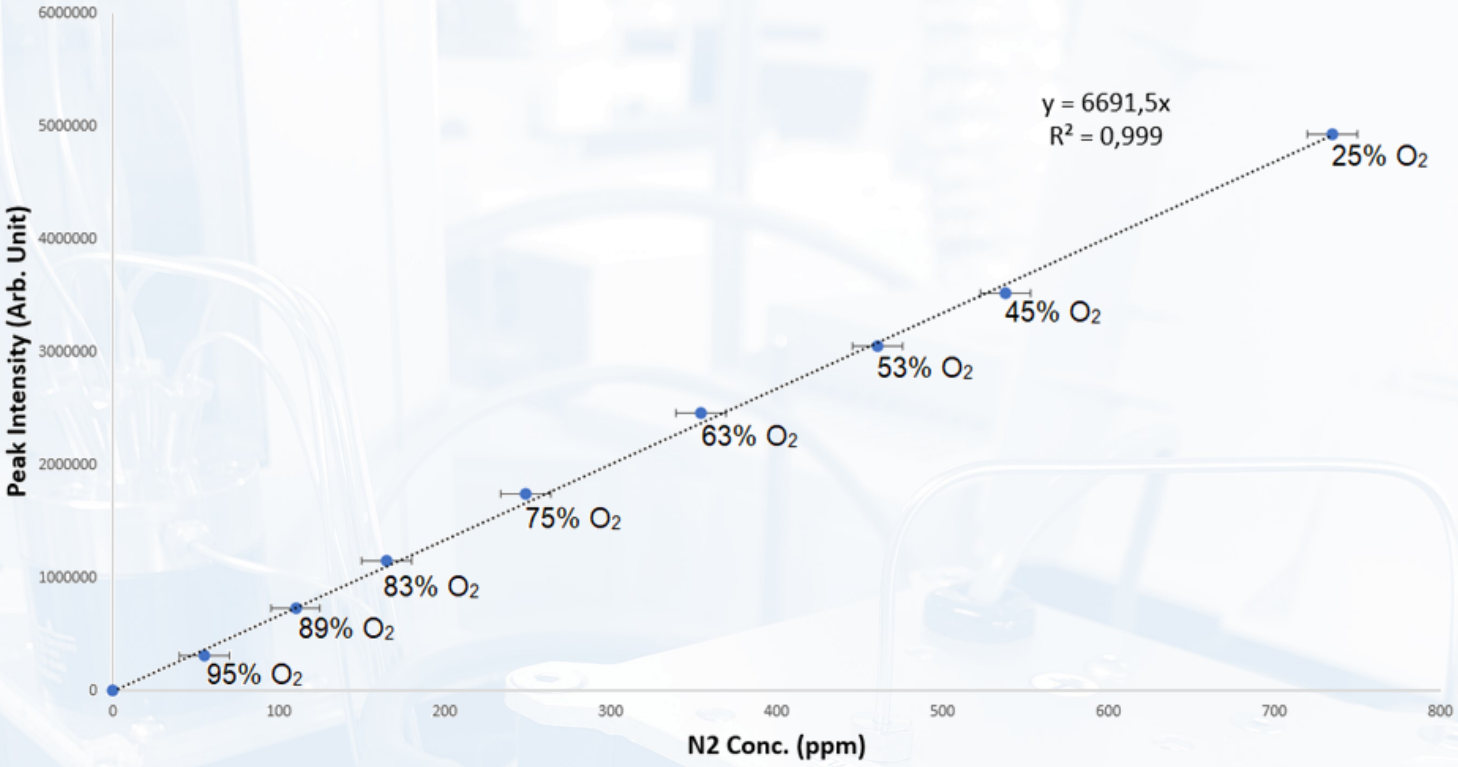

Figure 7— Peak intensity as a function of N_2 concentration with various oxygen concentration in the matrix

Conclusions

In conclusion, the **µSense** platform is ideal for crude argon analysis. Thanks to the Epd technology**, spectral compensation* can be used to measure N_2 peaks that are co-eluting with the oxygen matrix. This allows faster and more accurate N_2 quantification without the use of expensive oxygen traps. The system has shown excellent repeatability and stability over a 4-day period and a LOD of 500 ppb was determined. A good linearity, with a R^2 of 0.999 was determined for a range of at least 0-1000 ppm N_2 in oxygen and over-range quantification can also be achieved. The same level of accuracy was also achieved with various oxygen concentrations in the matrix.

* Patent pending ** Patented