APPLICATION NOTE 21

N_2Sense for Interference-Free Ultra-Trace Measurement of Nitrogen in Argon and Helium

The new reference for continuous nitrogen analysis

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ABSTRACT

Continuous measurement of ultra-trace level nitrogen in UHP argon and helium is a key application that requires highly sensitive and accurate instrumentation, especially in the semiconductor and air separation industries. 30 years ago, Yves Gamache, CEO of ASDevices, introduced the first plasma-based trace N_2 in argon analyzer named K2001, which was considered as a standard in the industry. In 2017, ASDevices released new technologies, including the enhanced plasma discharge (Epd), an improved plasma-based detection technology that is now used in the N_2Sense, leading to unprecedented sensitivity, stability and accuracy performances. Despite being the best technology at the time, the K2001 or variants based on Gamache 1990s design (LD8000, Servopro Plasma) were still suffering from some cross-interferences issues which have been addressed by ASDevices N_2Sense analyzer. Thanks to the spectral compensation capabilities of the Epd, interference from moisture and other permanent gases can be avoided, leading to more accurate and stable nitrogen quantification making the N_2Sense the new reference.

Introduction

Due to their inertness and many other desirable properties, ultra-high purity (UHP) argon and helium are frequently used for the fabrication of semiconductors, electronic components and many other industrial processes [1]. Constant purity monitoring of these gases with highly sensitive and accurate instruments is of utmost importance, as even low-ppb levels of impurities can cause irreversible damage to the materials [2]. Indeed, being the most abundant component of air, N_2 is one of the key impurities to monitor, as it can be indicative of leaks or malfunctions in a system. Other applications in which trace nitrogen analysis is of interest include separation plants, chemical plants, argon liquefaction plants, process control, the steel industry, gas management systems, specialty gas laboratories, leak testing systems, welding control, glove box control, cryogenic truck loading stations, etc.

The invention of the N_2 selective Plasma Emission Detector (PED) by Gamache was at the heart of the K2001, a major revolution in the 1990s. The K2001 relied on a selective bespoke narrow band interference filter to selectively measure the N_2 emission. Gamache's new method of doping the plasma with low-level moisture and adding a moisture trap before the analyzer sample inlet was paired with the PED sensor. This revolutionary method provided a major analytical improvement in reducing the impact of moisture contamination, which is common in this application. Even with this method, the best available at the time, the K2001 was still suffering from interference from other impurities such as H_2, O_2 and CH_4. 30 years later, Gamache and his team, renowned as world experts for that measurement, have further innovated by introducing an improved detector allowing the use a new proprietary method: the spectral compensation. This method removes interferences and allows ASDevices to offer the new market reference in a more compact form factor.

Sample Contamination

Impact of contamination and interfering impurities

All analytical systems are tuned and calibrated relative to the impurities to be identified and measured. In the case of the N_2Sense, only nitrogen is measured. The system is calibrated using different certified cylinders or a gas dilution system with high-purity gases to generate different concentration values, and to measure various performance parameters such as the limit of detection, repeatability, linearity, dynamic range, etc.

The system is qualified in ideal conditions, with clean gas. However, in practical conditions, the gas composition may have other impurities that are not on the list of the ones to measure and may cause interference, or measurement delay. In our case, we are mostly concerned with moisture, oxygen and organic compounds. Most trace N_2 analyzers on the market – including the N_2Sense - are based on plasma discharge technology. Plasma discharges are highly reactive and impurities can lead to unexpected chemical reactions that might have negative effects on the system performance. The Enhanced Plasma Discharge (Epd) technology, which is used in the N_2Sense, is capable of "spectral compensation", a unique feature that prevents such interference. More details about this feature will be presented below.

Sources of moisture contamination

When monitoring argon coming directly from an air separation process, the level of moisture is well below 1 ppm and will generally not interfere with the N_2 measurement. However, the same analyzer can be used to qualify cryogenic tankers. For such applications, some quick connections are used to connect the sampling line to the cryogenic tanker truck, or sometimes to the cryogenic train. The atmospheric moisture and air are momentarily introduced in the sample line. It is even worse during a rainy day.

Purging moisture out of a stainless-steel sampling line takes a lot of time. For example, a 30-meters long ¼" O.D. 316 stainless steel sampling line can take as long as 24 hours to dry clean to below 1 ppm, after being contaminated with atmospheric moisture. It takes even longer if the line is made of copper, as it used to be in older air separation plants.

Another source of contamination comes from calibration cylinders. It is not uncommon to find moisture in a steel cylinder at a value exceeding 10 ppm. This value will increase when the cylinder pressure is going down. This is even worse when the cylinder has been in use for several years. Depending on where the calibration gas cylinder supplier is, the moisture level will be different. Aluminum or stainless-steel cylinder are usually better for this phenomenon, but we still have found various levels of moisture in these.

Another source of atmospheric moisture contamination could be from any Teflon seal used for the valve stem. We have often replaced such valves with stainless steel diaphragm or metal bellows valves, and moisture went down afterward. Any plastic or Teflon line or fitting is a risk of air and moisture diffusion or permeation into the gas sample.

Other Sources of Contamination

Aside from moisture, the sample may have some level of H_2, O_2, and CH_4. The N_2 measurement could be affected on a traditional plasma-based detector, but much more stable results are achieved with the Epd, thanks to its spectral compensation algorithm, as it will be presented below. Furthermore, the materials used for the fabrication of the plasma cell often contain some impurities that release OH radicals and other impurities in the discharge. This is why the materials used in ASDevices' detectors are carefully selected to avoid such interference [3].

Another source of contamination is Nickel Carbonyl or Iron Pentacarbonyl, $Fe(CO)_5$. Indeed, in some air separation plant designs, there is an argon purification step called Deoxo. It consists in flowing the argon having some level of O_2, normally not exceeding 2%, in a metal vessel reactor with a full wall nickel catalyst. Some H_2 is then added at the inlet of this reactor and a chemical reaction is triggered to react with O_2, reducing the final O_2 content in argon below the ppm level. This is a highly exothermic reaction that can reach as high as 450°C. There could be some levels of CH_4. The carbon part can react with the nickel catalyst or with the metal vessel and generate some metal compound. These contaminations will contribute to plasma cell contamination if they are not removed from the sample with filters or traps placed before the instrument.

Effect of Moisture on N_2 Measurement

Moisture in the sample will result in two negative effects on system performance. First, the accumulation of moisture into a sampling system line, valves, etc. will cause some N_2 adsorption that will result in a much longer response time. Furthermore, sampling system temperature change, for example between a sunny day and the night, will generate baseline or signal drift (Figure 1). In cold winters, like in Canada, we have found lower readings and faster response times during cold nights compared to warmer summer weather.

Also, introducing moisture into the detector will decrease the N_2 reading compared to a dry sample, as presented in Figure 2. Therefore, continuous N_2 analyzers that use the 1990s technology without adequate compensation methods will be affected by variations in the moisture content or other impurities that will inevitably occur in real-life applications.

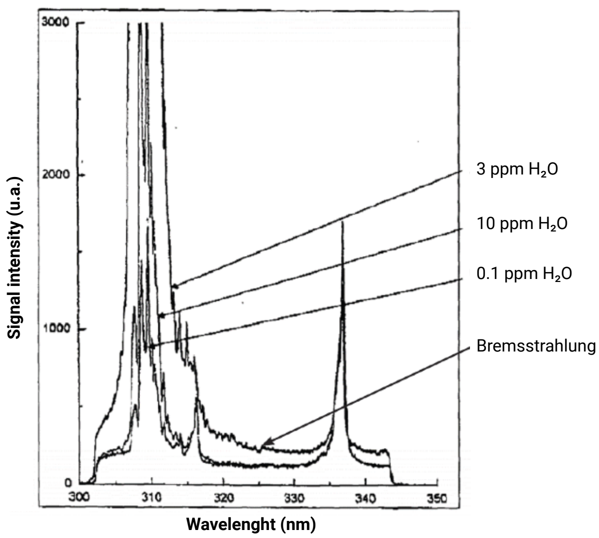

Figure 1 – Plasma baseline (Bremsstrahlung) offset due to various amounts of moisture [4]

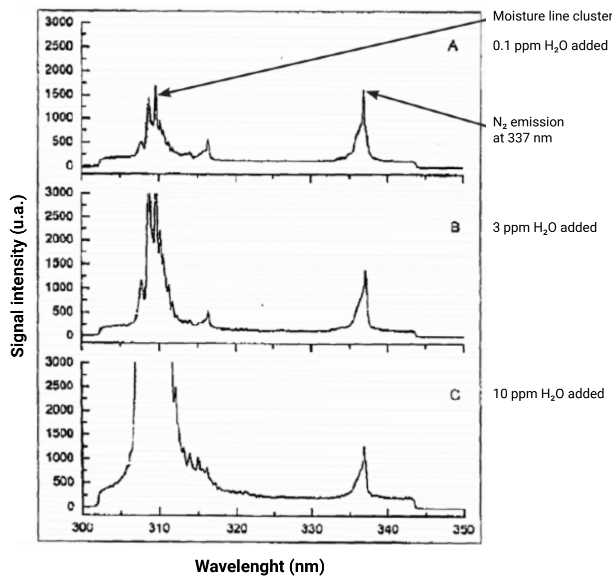

Figure 2 – Effect of moisture on N_2 response [4]

Technology Overview and Performance

N_2Sense Platform

The N_2Sense analyzer is presented in Figure 3. Thanks to the most recent developments in electronics miniaturization that were implemented, the N_2Sense is the most compact continuous nitrogen analyzer currenwtly available on the market. Furthermore, the large display screen and latest software interface were optimized to improve conviviality for the user.

With its IIoT capabilities, the N_2Sense can also be remotely accessed and controlled from any authorized computer or mobile phone, as shown in Figure 4.

When measuring low-ppb nitrogen levels, the leak integrity of the analytical system is extremely important. Therefore, the gas flow path was carefully designed to avoid any dead volumes. To achieve the best performance, we only use high-quality laser-cut stainless-steel tubes and analytical fittings from ASDevices. LipLOK bulkhead fittings are also used for the sample gas inlet, as they have the leak integrity of a VCR fitting while being compatible with Swagelok fittings.

ASDevices' purged Electronic Pressure Controller (EPC), shown in Figure 5, is another critical component in achieving remarkable leak integrity. Indeed, EPCs

Figure 3 – N_2Sense analyzer

Figure 4 – N_2Sense accessed from a mobile phone thanks to its IIoT capabilities.

Figure 5 – N_2Sense purged EPC

are active components that are susceptible to leaks, which can affect the baseline noise and lead to false readings. With its purge design, ambient air can't leak into the sample line through the EPC. Other N_2 sensing technologies use unpurged EPC, which has a significant negative impact on their performance.

As the world leader in continuous N_2 measurement in argon and helium, we also patented a method to avoid interference from moisture. This method combines the use of a moisture trap, placed before the sample inlet of the analyzer, with a moisture permeation tube to dope the plasma with a constant moisture level, well above the amount typically present in the sample. This has significantly reduced the moisture effect on the N_2 measurement and has made our technology a reference in the field. This method was the best option available when it was introduced in the 1990s, but with the Epd technology, much better performances can now be achieved. While plasma doping is still being used, the moisture trap is not needed anymore, despite still being a good practice.

Indeed, this method alone is not flawless, as most customers tend not to change the trap as often as they should, which may result in more moisture reaching the detector over time. Samples containing high moisture concentrations could also saturate the trap after only a few days or even hours, leading to measurement errors. Furthermore, moisture traps are permeable to other permanent gases, which could also cause interference.

Because of these interfering species, many users of the older technologies have preferred to perform offline N_2 analysis with GCs, as it separates N_2 from the other permanent gases. This is where the spectral compensation feature, unique to ASDevices' Epd technology, becomes useful in improving the system stability and accuracy of continuous inline N_2 measurement.

SePdd Detector (patented)

The SePdd, presented in Figure 6, is based on the Enhanced Plasma Discharge (Epd) technology developed by ASDevices in 2017. With its highly energetic stabilized and focused plasma discharge, nitrogen is easily ionized and measured by monitoring specific wavelengths emitted from the plasma. For continuous N_2 analysis, it can be operated in a helium or argon matrix.

Figure 6 - The SePdd detector

Since the sample matrix is also used as the plasma discharge gas, there is no need for any additional UHP gas to operate the detector. The sensitivity of the detector is further increased thanks to the presence of electron injection and stabilizing electrodes, which significantly improve the ionization efficiency and decrease the background noise. The Epd principle is presented schematically in Figure 7.

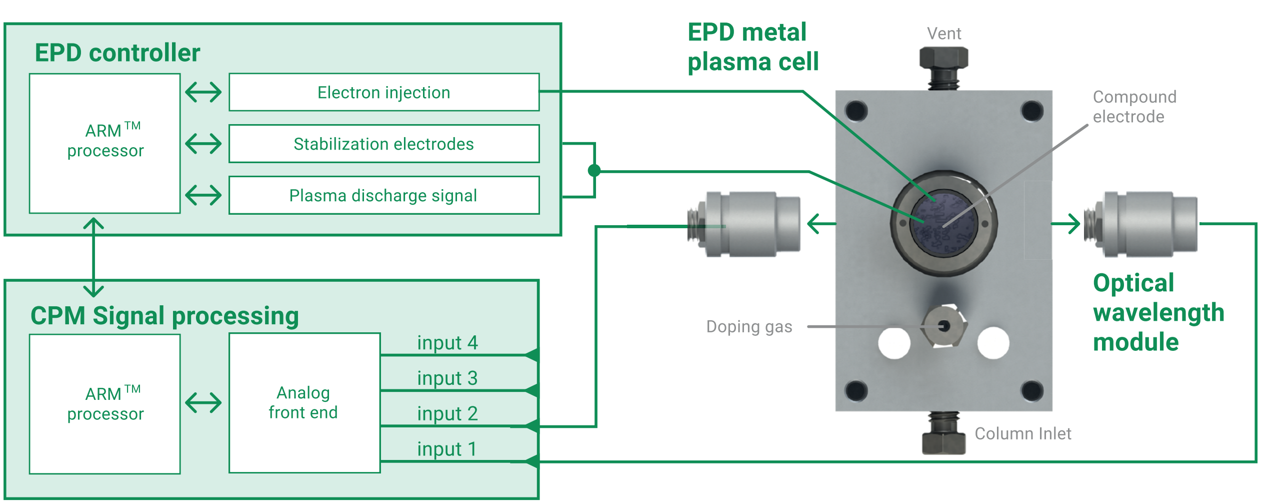

Figure 7 – Epd principle

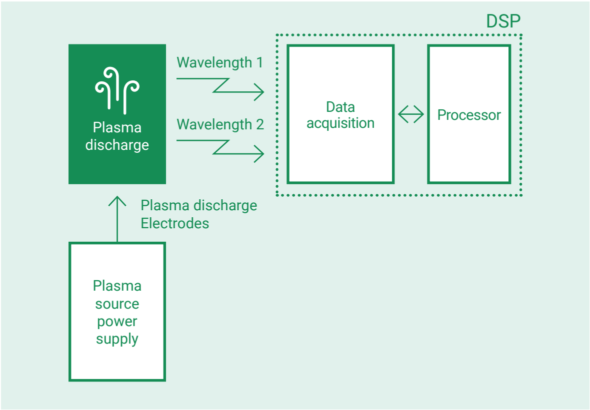

Figure 8 – Traditional plasma emission detector

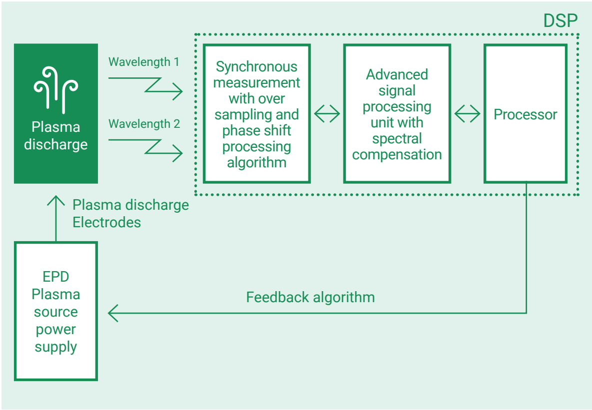

Figure 9 – Enhanced Plasma Emission detector with feedback algorithm

Despite these features, as discussed previously, the introduction of impurities in the plasma could still cause variations in the Bremsstrahlung and therefore affect the N_2 readings. This is why ASDevices developed a unique processing algorithm, spectral compensation. The data acquisition, which is done in oversampling mode, provides the proprietary algorithm with a high-speed data stream. This algorithm performs high-speed real-time computation in the frequency domain to reduce noise and perform arithmetic and compensation calculus between two wavelengths that are measured simultaneously. One wavelength is highly sensitive to N_2, while the second is only sensitive to Bremsstrahlung variations from impurities such as moisture, oxygen and methane. This is what makes our technology so stable and provides the most accurate N_2 measurement.

Traditional plasma technologies – which are used in other continuous N_2 analyzers - are based on Figure 8 architecture, where a single wavelength is measured, while the plasma discharge is maintained by an open loop Royer oscillator. This is a cause of instability. With our technology shown in Figure 9, the plasma is maintained stable in a closed loop feedback circuit thanks to spectral compensation. By using spectral compensation, the effect of impurities on the baseline can be compensated by the specific emission of N_2, resulting in accurate real-time quantification.

Demonstration of Spectral Compensation

A demonstration was made to show the impact of trace-level moisture on continuous N_2 quantification. A certified sample containing 0.1 ppm N_2 in argon was analyzed using an N_2Sense, with and without the spectral compensation feature activated. At some point in the test, the sample stream was directed to a permeation tube that increases moisture concentration by 10 ppm. Here, no moisture trap was used in front of the analyzer. The results are presented in Figure 10. Without spectral compensation, which is equivalent to the 1990s competitors' technologies, the N_2 measurement increased to 1 ppm after adding 10 ppm moisture. With spectral compensation, the N_2 measurement remained constant at 0.1 ppm.

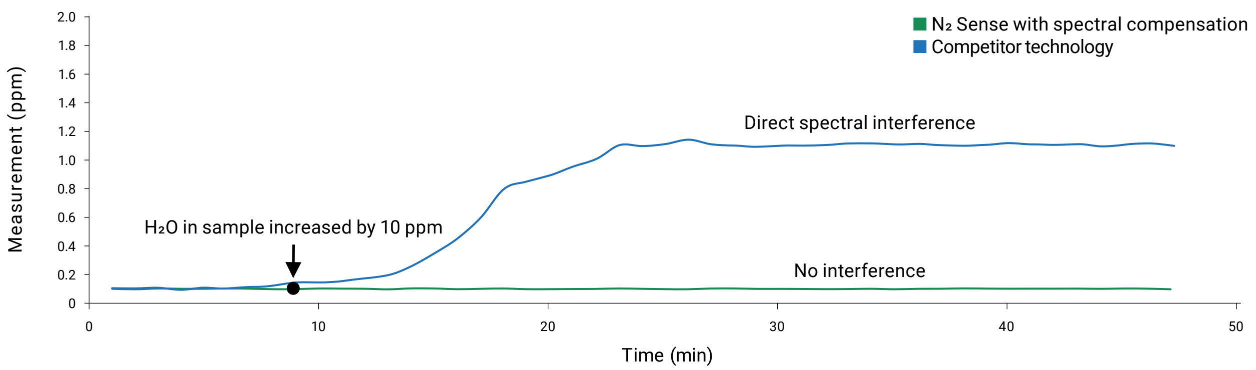

Figure 10 – Baseline offset caused by moisture

This might seem in contradiction with the results presented in Figure 2 since moisture should lower the N_2 signal. However, as presented in Figure 1, moisture also causes a Bremsstrahlung offset that can be wrongfully measured as N_2 increases. Thanks to spectral compensation, this baseline variation on the N_2 signal is canceled, leading to more accurate measurements. Other impurities such as oxygen, methane and hydrogen can cause similar positive or negative baseline offsets that can be canceled using spectral compensation.

Another demonstration of the power of spectral compensation is presented for oxygen. For this test, a 2 mL pulse of UHP oxygen containing a certified N_2 concentration of 100 ppm was injected through a short chromatographic column and measured with a SePdd detector. Here, the column did not allow full O_2/N_2 separation. The detector was equipped with the same wavelengths as the ones used in the N_2Sense: One wavelength that is highly sensitive to N_2 and a reference wavelength that is only sensitive to plasma baseline variations. The signal trending from this injection is presented in Figure 11. The figure also displays the spectrally compensated signal resulting from the real-time combination of these two wavelengths.

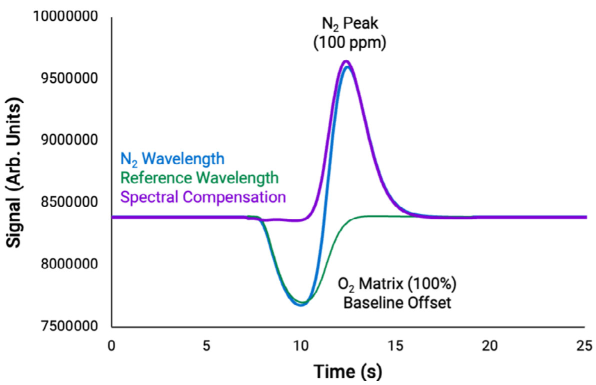

Figure 11 - Signal trending of a 2 mL O_2 pulse in a SePdd for the N_2 wavelength (blue line), reference wavelength (green line), and spectral compensation (red line)

From this data, it is obvious that a pulse of oxygen has a very strong impact on the plasma baseline, even for the wavelength that is selective to N_2. Indeed, in real-life applications, the amount of impurities will most likely be in the ppm or ppb range. Still, this is enough to cause interference that will lead to inaccurate N_2 readings.

In our example, the nitrogen signal is affected by the drift caused by the oxygen pulse. Despite this, using spectral compensation – by combining the signal from the N_2 wavelength and a reference wavelength – the real contribution of N_2 to the signal can be extracted, allowing its accurate measurement. This principle is therefore exploited in the N_2Sense. It allows accurate real-time correction of the nitrogen signal when other impurities are introduced in the sample line.

N_2Sense Performance

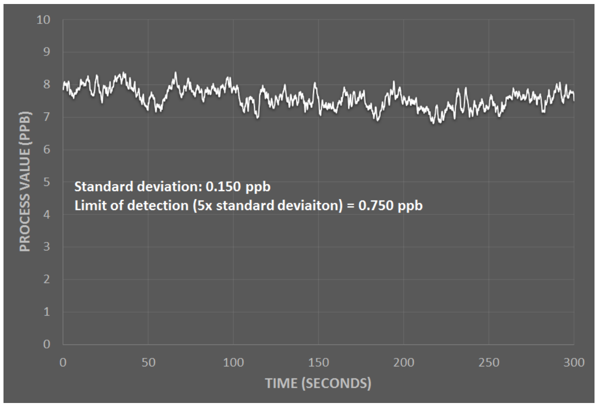

Figure 12 – N_2Sense noise trending over 5 minutes

Figure 12 presents the measured concentration for a sample containing 8 ppb N_2 in helium over a period of 5 minutes with the N_2Sense. From this data, we calculated a standard deviation of 0.150 ppb. A limit of detection of 0.750 ppb was then calculated, as specified in the IEC 61207-1:2010 standard.

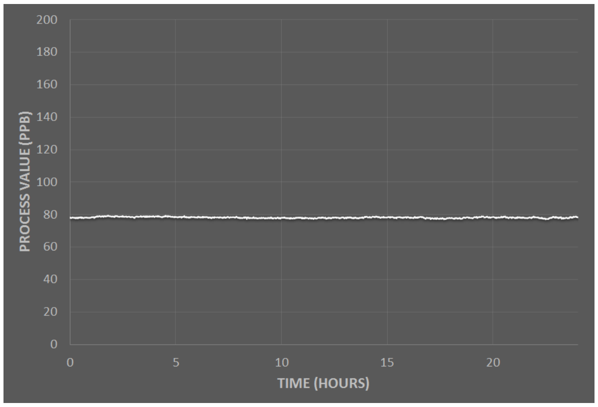

Figure 13 – N_2Sense 24-hour drift

Figure 13 presents the 24-hour drift for a sample containing 80 ppm N_2 in hydrogen. Such stability can only be achieved thanks to the combination of the new features introduced in the Epd technology, including spectral compensation, and the use of ASDevices' high-quality components.

Figure 14 presents the response time of the N_2Sense. Here, the sample was switched from purified helium to a sample containing 8.8 ppm N_2 at Time = 45s. After less than 5 seconds, the N_2Sense already reached the expected value.

Finally, the step-response of the N_2Sense was evaluated. A sample containing initially 4 ppb N_2 in helium was measured. Then, every 30 seconds, the N_2 concentration was increased by 1 ppb. The results are presented in Figure 15.

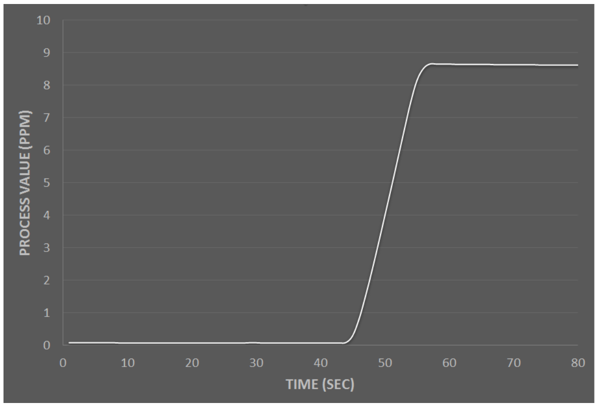

Figure 14 – N_2Sense response time

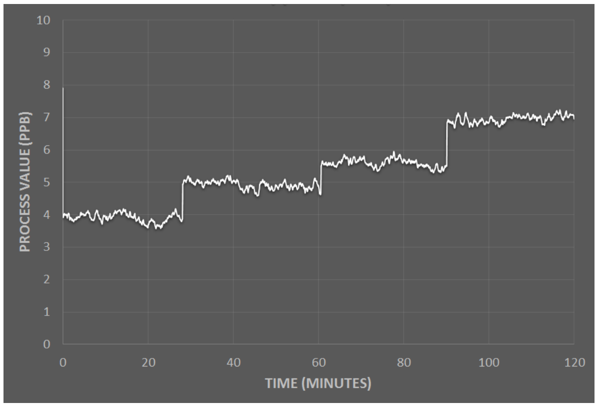

Figure 15 – N_2Sense 1 ppb step response

Conclusions

In conclusion, the N_2Sense benefits from over 30 years of development and expertise in the field of ultra-trace analysis. With the recent introduction of the Epd technology, unprecedented limits of detection of >1 ppb can now be reached for continuous N_2 measurement in argon and helium. Furthermore, the use of spectral compensation, unique to the Epd technology, allows the cancellation of the impact of impurities such as moisture, hydrogen, methane and oxygen. Combined with the use of ASDevices' high-quality hardware, this leads to the highest stability and the most accurate N_2 quantification currently available on the market.

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Related Documents

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- TN-05 – The Power of Spectral Compensation for Fast Nitrogen Measurement in Oxygen with the Enhanced Plasma Discharge Technology, ASDevices, 2019.

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