

TN-05

The Power of Spectral Compensation for Fast Nitrogen Measurement in Oxygen with the Enhanced Plasma Discharge Technology



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ABSTRACT

The detection of trace impurities in UHP gases can be challenging with universal type detectors such as TCD, DID, HID and PDID, as complex and expensive chromatographic methods are often required to properly separate them from the sample matrix. Other selective technologies such as the plasma emission detector have been introduced, but they still suffer from instability in the presence of high levels of sample matrix gases such as oxygen. In this document, we demonstrate how the Enhanced Plasma Discharge (Epd) technology^{patent pending}, with its focusing/stabilising and electron injection electrodes and spectral compensation algorithm, was used with a simplified chromatographic setup to quantify trace nitrogen in UHP oxygen in less than 30 seconds.

INTRODUCTION

In many gas chromatographic (GC) applications, the analytes and impurities can be difficult to separate from the matrix. In the case of universal detectors such as thermal conductivity detectors (TCD), discharge ionization detectors (DID), pulsed DID (PDID), helium ionization detectors (HID) etc., no discrimination regardless of the molecule can be achieved. Furthermore, the high concentration of the matrix can cause instability to the detector, significantly increasing the background noise. Therefore, expensive and complex chromatographic methods such as heartcut valves and traps often have to be added to the GC systems [1,2]. Such configurations make the system more difficult to tune, more expensive and less stable in the long run.

A good example of complex matrix separation is the detection of trace nitrogen in UHP oxygen or crude argon (oxygen and argon mix) for air separation unit process control. Since high level oxygen and trace nitrogen are difficult to separate with most GC columns, this analysis can take many minutes per sample. However, it can be advantageous that the analysis time is shortened, especially in process optimisation.

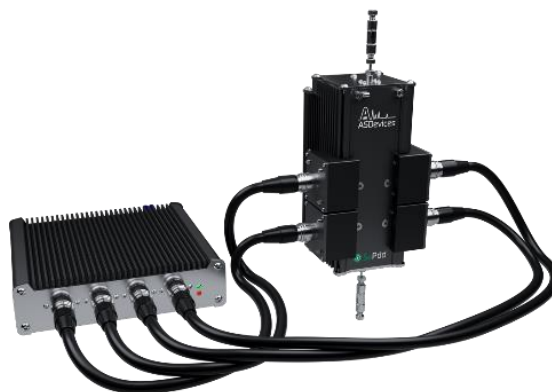


Figure 1 - The ASDevices SePdd™

Enhanced Plasma Discharge (Epd) detectors can be used as a replacement to most detectors on GC systems. With its unique stabilising and electron injection electrodes^{patent pending}, this technology is much more stable than traditional plasma detectors, even with high matrix concentrations. Such detectors use light emission from the excited and ionised elements in a plasma.

For this type of analysis, the power of our technology does not only reside in the high speed, high resolution and synchronous acquisition of multiple wavelengths. The breakthrough is in the proprietary processing algorithm and its feedback to the plasma discharge. The acquisition, which is done in oversampling mode, provides the proprietary

algorithm with a high-speed data stream. This algorithm, known as spectral compensation, performs high speed real-time computation in the frequency domain to reduce noise and perform arithmetic and compensation calculus between the two wavelengths. In parallel, the plasma discharge is maintained stable in the presence of high-level oxygen with our patent pending focusing/stabilising and electron injection electrodes. This is what makes this measurement possible and our technology unique.

Traditional plasma technologies are based on figure 2 architecture, which means that a single wavelength is measured while the plasma discharge is maintained by an open loop royer oscillator. This is the cause of instability. With our technology, figure 3, a much more advanced signal processing is done in real-time, in this case spectral compensation^{patent pending}, and the plasma is maintained stable in a closed loop feedback circuit^{patent pending}.

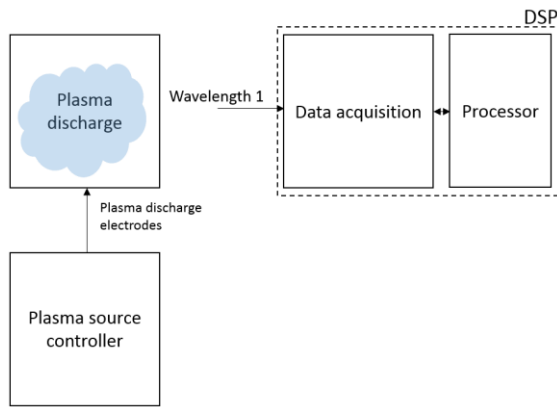


Figure 2 - Traditional plasma emission detector

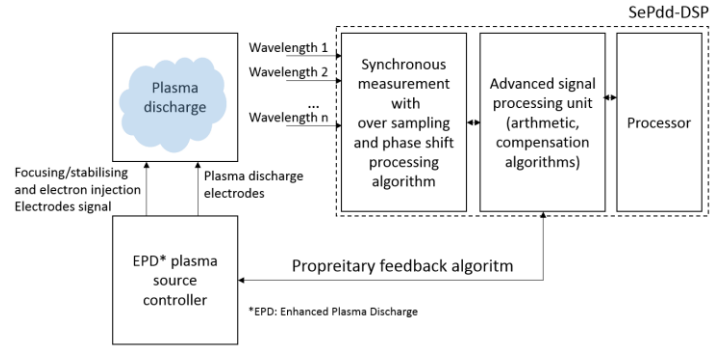


Figure 3 - Enhanced Plasma Emission detector with feedback algorithm

By using spectral compensation measurement, the effect of oxygen on the baseline can be subtracted to the specific emission of nitrogen, resulting in fast and accurate quantification, even if the matrix is not properly separated. In this technical note, we will present how spectral compensation with the Epd technology was used to quickly measure nitrogen impurity in UHP oxygen with a simple GC injection configuration, without heartcut or oxygen trap.

EXPERIMENTAL INFORMATION

Enhanced Plasma Discharge (Epd)

All the measurements were done with the SePdd™ from ASDevices (See Figure 1). It is a fully scalable development kit for OEM and system integrators based on our Enhanced Plasma Discharge Technology. Due to its high sensitivity, versatility, ease of use and low maintenance cost, Epd is an interesting alternative to DID, PDID, HID, FPD, FID and TCD on most GC systems.

With its highly energetic stabilised and focused plasma discharge, most molecules can be ionised and consequently measurable. It can be operated with argon, helium, nitrogen, oxygen, hydrogen and CO₂ carrier gas. Multiple measurement modes are available (emission, tracer, power balance), allowing detection and quantification of various analytes from the ppb to the percent range. The sensitivity of the Epd is further increased thanks to the presence of electron injection and stabilising electrodes, which significantly reduce the background noise (See Figure 4) Patent Pending.

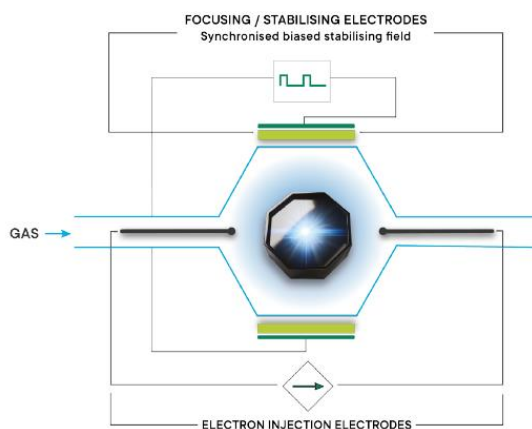


Figure 4 - Schematic representation of the SePdd™ stabilising and electron-injection electrodes

The digital signal processing (DSP) platform is equipped with 4 (8 optional) independent measurement channels, allowing simultaneous measurements of 4 or 8 different optical wavelengths. With our plug and play philosophy in mind, the platform can be easily integrated to any GC platform. The platform is also equipped with Ethernet communication ports and is Industrial Internet of Things (IIoT) Ready.

Experimental Parameters

Here, a simple configuration with a GC valve, a sample loop of 62 µL, a 4ft molecular sieve 5A GC column at 100°C and the Epd detector was used, as presented in Figure 5. The leak integrity of the system was confirmed with the method presented in our previous technical note (TN-01) [3]. The sample was high-purity oxygen (5N) containing 1.5 ppm of nitrogen. Other samples containing 30 ppm, 76 ppm and 467 ppm of N₂ were also analysed. Argon was used as the carrier gas with a flow rate of 55 mL/min.

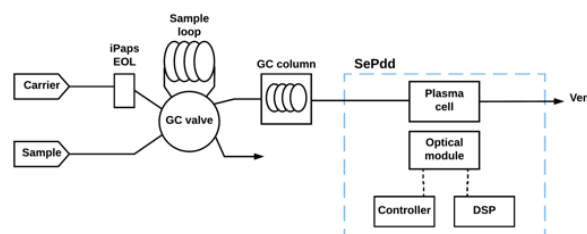


Figure 5 - Configuration of the GC system

The results were acquired simultaneously with three different optical modules linked to the DSP. A broadband optical filter was added to the first optical module to show the typical response of a universal detector. A narrow optical filter centered at 357nm (±3nm) was added to the second optical module, as

it corresponds to a strong emission line from nitrogen (see Figure 6). Another narrow optical filter centered at 345nm (± 1 nm) was added to the third optical module as a reference wavelength. This wavelength was chosen because there is no emission line from nitrogen or other common impurities at this wavelength. Therefore, any signal variation at this wavelength can be attributed to the oxygen matrix disturbing the plasma. Thanks to our real-time correction algorithm, the spectrally compensated measurement was instantly traced by the software without post-processing. The pre-amplification and gain of each optical module were optimised to cancel the influence from the oxygen matrix.

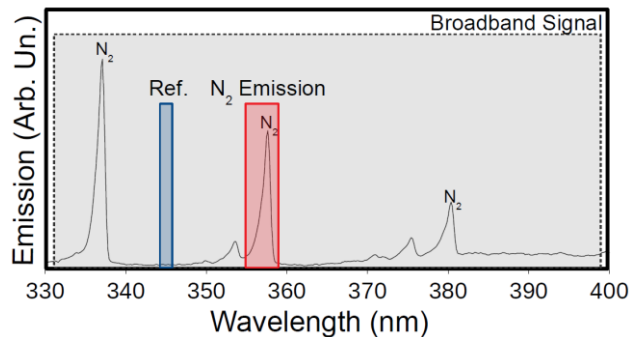


Figure 6 - Epd emission spectrum of Nitrogen in Argon. The rectangles represent the broadband signal (grey) and the optical filters of N₂ emission (red) reference wavelength (blue)

RESULTS AND DISCUSSION

Measurement with the universal mode

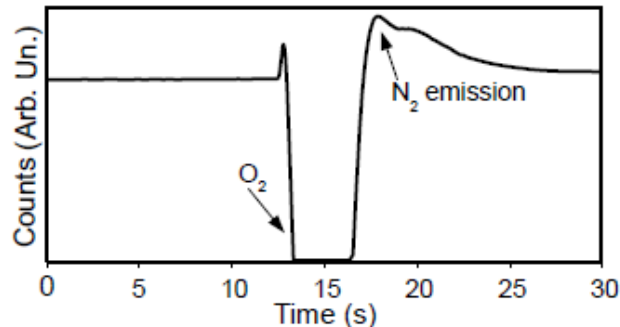


Figure 7 - Chromatogram acquired for the universal signal

First, a chromatogram was recorded for the universal mode signal (see Figure 7). 13 seconds after injection of the sample, a strong disturbance of the plasma caused by oxygen was observed, as it is by far the major component of the matrix. Since the emission from nitrogen is a small component of the universal signal, its contribution is almost unnoticed. Only a small kink around 18 seconds can be seen. Therefore,

such signal cannot be used for quantification of impurities in UHP oxygen. It shows the limitation of universal type detectors such as DID, HID and PDHID and highlights why more complex chromatographic methods and traps are usually required for such analysis.

A chromatogram was also recorded for the emission line centered at 357 nm specific to nitrogen (Figure 8 (a), red line). Since the optical filter selected has a narrow bandwidth, most of the recorded signal can be attributed to nitrogen and a peak can be seen around 18 seconds. However, an important disturbance of the plasma by oxygen is still measured. This has been a limitation of other currently exiting plasma technologies. In these experimental conditions, oxygen and nitrogen are not well separated. Therefore, the disturbance from oxygen deforms the nitrogen peak, making it impossible to use for proper quantification, unless a more complex heartcut method is used to improve separation [1,2]. Still, this result highlights the

importance of our stabilising electrodes, as the plasma is only slightly quenched and light-emission from nitrogen is still measurable. With other types of detectors, such oxygen concentration may completely extinguish the signal or even cause damages to the detector.

Measurement with spectral compensation

A chromatogram showing only the effect of oxygen on the plasma was recorded by using an optical filter centered at 345 nm, since there is no spectral line from nitrogen or any common impurity at this wavelength (Figure 8 (a), blue line). The spectrally compensated measurement, obtained from our proprietary algorithm, can be instantly traced by the recording software. The high-speed processing is done in real-time by the SePdd™ DSP embedded algorithms. The resulting chromatogram is presented in Figure 8 (b). The result is a Gaussian peak with an improved signal to noise ratio thanks to the algorithm. Such signal can easily be used for fast and accurate quantification of nitrogen in high-purity oxygen. In this example, the measurement was done in less than 30 seconds, compared to traditional methods which can take 3 to 5 minutes [2]. This is due to the more complex heartcut method used and longer columns. In our experimental conditions, this signal corresponds to 1.5 ppm of nitrogen, as expected for this 5N oxygen sample.

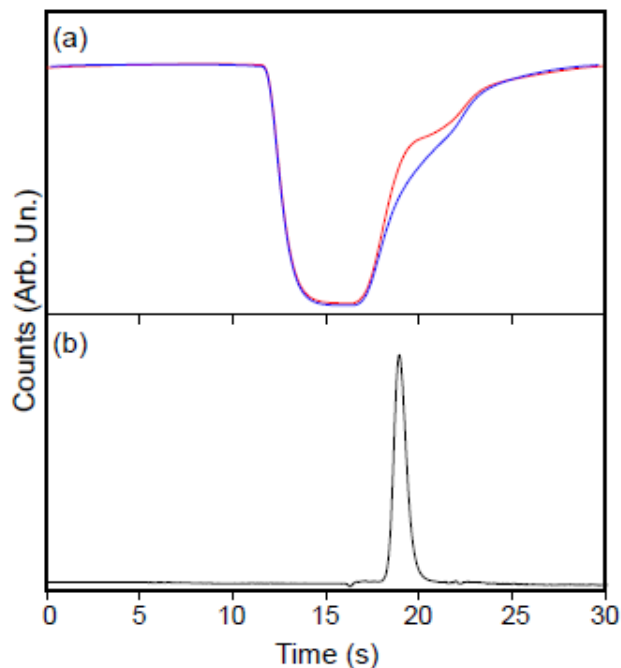


Figure 8 - Chromatograms acquired for (a) Red line: nitrogen emission at 357 nm, Blue line: disturbance from oxygen at 345 nm and (b) the spectrally compensated measurement

To show the high speed of this method and reliability of the results, samples containing 30 ppm, 76 ppm and 467 ppm of N₂ in oxygen were injected 5 times every 30 seconds. The chromatograms acquired are presented in Figure 9. The results acquired are reproducible and the peak intensity is proportional to the N₂ concentration, at least for a range of 1 to 500 ppm.

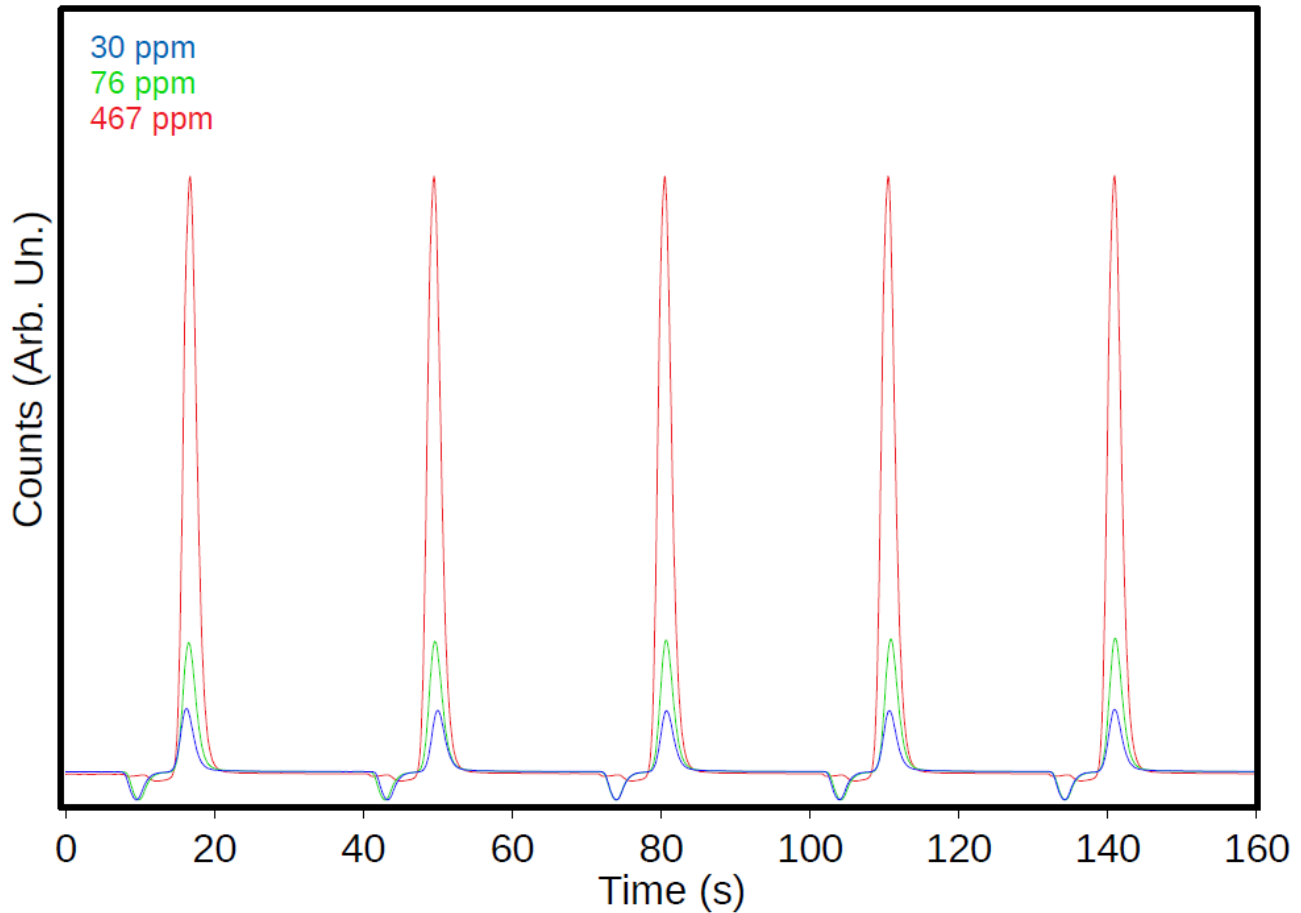


Figure 9 - Chromatograms acquired for samples of oxygen containing 30 ppm (blue line), 76 ppm (green line) and 467 ppm (red line) of N₂. Each sample was injected 5 times every 30 seconds

CONCLUSIONS

In conclusion, universal detectors cannot be used for the quantification of trace impurities, unless they were properly separated from the matrix. Other currently available plasma emission technologies can be used, but still require additional hardware such as longer columns and heartcut valves, which add complexity and cost to the system and result in longer analysis time.

The Epd technology exploits the unique spectral signature of the compounds in the plasma, allowing spectral compensation. Such method allows real-time subtraction of the effect of the matrix on the plasma, resulting in easily quantifiable peaks from the impurities with a simple injection GC configuration, even if they are not properly separated from the matrix. It allows significant cost

and time savings compared to the traditional analytical methods. With spectral compensation, trace nitrogen in UHP oxygen can be measured in less than 30 seconds, while other methods can take 3 to 5 minutes per sample. This application is only one example of the great versatility of spectral

compensation. It could easily be implemented to further improve other chromatographic methods.

REFERENCES

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