APPLICATION NOTE 24

Argon as Carrier and Discharge Gas for Measuring Ultra-Trace Level Impurities in Various Matrices

A cost-effective alternative to helium in gas chromatography

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ABSTRACT

Helium is a very common carrier gas used in chromatography (GC), due to its inertness and safe handling. It is also typically used as a discharge gas in plasma-based detectors, thanks to its high ionization and metastable state energy level that allow measurement of many molecules. However, due to its availability, high cost and variable purity, GC operators are now looking for alternatives. Over the past years, affordable inert carrier gases such as argon and nitrogen presented themselves as good alternatives to helium. However, most high-sensitivity detectors such as the Helium Ionization Detector (HID), the Discharge Ionization Detector (DID) and the Pulsed Discharge Ionization Detector (PDID) still rely on helium, because they use a specific high-energy photoionization mechanism that require this gas. The Enhanced Plasma Discharge (Epd) Technology, developed and patented by ASDevices, can be operated with various carrier and discharge gases, as the analytes are directly ionized in a plasma generated by DBD. The following application note intends to present how low-cost argon can be used as the carrier and discharge gas for GC with the Epd technology, for the analysis of various molecules at the ppm and ppb level. Chromatograms will be presented for trace and ultra-trace level permanent gases (H_2, O_2, N_2, CH_4, CO, CO_2), light hydrocarbons, H_2O, noble gases (Kr, Xe), N_2O, BTEX and sulfur compounds.

Introduction

Gas chromatography (GC) is one of the most reliable and cost-effective method for measuring low-level impurities in ultra-high purity (UHP) gases, as it allows separation of the various compounds from a sample, thus avoiding interference that could lead to false readings when attempting to measure them without separation. GCs require a continuous flow of carrier gas to push the injected sample through a column that separates the different components and also between each injection, to avoid column contamination and degradation. One of the most common carrier gas is helium, as it is safe to use and inert, preventing any undesired chemical interaction with the sample or the instrument. However, due to its increasing cost, GC operators are now looking for more affordable options [1]. This is especially important for process-oriented instruments that are designed to run continuously. Furthermore, the composition of helium is highly variable depending on the source, and the concentration of other noble gases such as argon and neon can vary significantly even after purification. This can lead to response variation on many types of detectors, depending on the helium source.

Hydrogen has been proposed as an alternative for multiple applications, but this gas also comes with significant safety hazards due to its high flammability [2]. Nitrogen and argon are also often used to replace helium, as they are inert and much less expensive than helium. Indeed, air contains 78% nitrogen and 0.9% argon, making both gases readily available. However, an important factor to take into consideration when choosing a carrier gas in GC is the type of detector used.

Thermal Conductivity Detectors (TCD) are often used in combination with GCs for measuring different impurities in the percent or high-ppm level. They can be operated with multiple carrier gases, but due to their low sensitivity, they cannot be used for low-ppm or ppb level analysis.

Over the past decades, detectors such as the Helium Ionization Detector (HID), the Discharge Ionization Detector (DID) and the Pulsed Discharge Ionization Detector (PDD/PDID) have been widely used for the analysis of UHP gases, as they are highly sensitive to permanent gases (H_2, O_2, N_2, CH_4, CO, CO_2) and light hydrocarbons. Indeed, these compounds can be challenging to measure, due to their high ionization energy level. In these detectors, the analytes are ionized via a photoionization mechanism that rely on helium [3]. Thanks to the high energy of the UV photons generated in the helium discharge, most compounds can be ionized and measured with an electrometer. The photons and metastable species generated in nitrogen or argon discharges are much less energetic, leading to very poor sensitivity with these gases. Furthermore, argon discharge could cause significant electrode etching, due to its high mass. Indeed, in these detectors, the electrode is directly in contact with the discharge, leading to frequent maintenance, even with helium discharge.

Plasma emission detectors (PED) have been introduced to the field of gas chromatography by Yves Gamache in 1992. This type of detector uses a photodiode to measure the light emitted from the analytes in a plasma generated by a dielectric

barrier discharge (DBD). Since the electrodes are protected by a dielectric material (typically quartz), the plasma can be generated from different gases such as argon without damaging the electrodes. Furthermore, the analytes are ionized directly in the plasma discharge, not from a photoionization mechanism. Therefore, this type of detector can be operated with various carrier and discharge gases with much better ionization efficiency and therefore sensitivity. In 2017, ASDevices released the Enhanced Plasma Discharge (Epd) technology, which is an improvement over the PEDs. It incorporated high-quality electronics as well as electron-injection and stabilisation electrodes, leading to unprecedented performances. Furthermore, it can measure and combine up to 4 different wavelengths in real-time, allowing unique measurement modes such as spectral compensation. The following document intends to present how GC-Epd can be used with low-cost argon carrier and discharge gas for the measurement of various analytes such as permanent gases, light hydrocarbons, water, noble gases, N_2O, BTEX and sulfur compounds.

Experimental Information

SePdd Detector[patented]

All the measurements were done with the SePdd from ASDevices. It is a fully scalable development kit for OEM and system integrators based on our Epd technology. With its versatility, ease of use, low maintenance cost, robustness and high sensitivity, this detector is the best alternative to other plasma-based technologies in laboratory and process-oriented applications.

Figure 1 - The SePdd detector

With its highly energetic stabilised and focused plasma discharge, most molecules are easily ionised and measured by monitoring specific wavelengths emitted from the plasma. It can be operated in helium, argon or nitrogen.

Since the carrier gas 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 stabilising electrodes, which significantly improve the ionization efficiency and decrease the background noise compared to the traditional PEDs. The Epd principle is presented schematically in Figure 2.

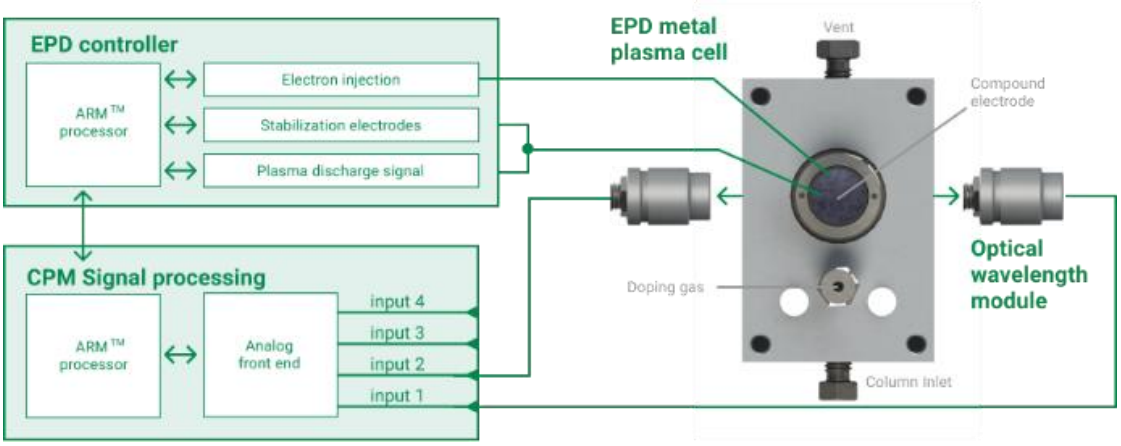

Figure 2 – Epd principle

All the results presented in this application note were obtained with a SePdd installed in ASDevices' iMOv GC platform. While this detector can also be installed on almost any other third-party platform, we can only recommend the use of ASDevices' high-quality components to reach the performances presented in this document. For each application, the platform was configured with the appropriate GC columns and valves combination for direct injection, heartcut or backflush to prevent matrix interference.

iMOv GC platform

The chromatographic platform also plays an important role in the overall performance of the system. From a mechanical standpoint, the iMOv platform offers many advantages. Its unique modular oven design allows easy integration of all the key analytical components. Its robustness and design make it ideal for process and field use. The iMOv platform is presented in Figure 3.

Figure 3 – The iMOv GC platform

For accurate measurements by GC, it is important to avoid any leaks or dead volumes, especially for ultra-trace level analysis. This is why the carrier gas and sample flows are always carefully designed using only high-quality treated tubing and fitting from ASDevices. LipLOK fittings are used for the gas inlets, as they have the leak integrity of a VCR fitting but are also compatible with Swagelok fittings [4]. All the GC valves used in the platforms are based on ASDevices' PLSV technology, which will be presented in the section below.

All the gas flows are controlled using our proprietary purged electronic pressure controllers (EPC) that prevents from any air ingress in the sample or carrier gas lines. Thanks to this unique purge feature, the EPC can be used inline for carrier gas control, instead of a bypass configuration, which is typically used in other similar platforms. This allows significant reduction of the gas flow consumption, which is especially important when working with expensive gases.

Purged Lip Sealing Valve Technology[Patented]

The Purged Lip Sealing Valve (PLSV) is a unique valve technology developed by ASDevices, which offers many advantages over the other chromatographic valve technologies [5-7]. For reactive samples such as sulfurs or moisture, it is necessary to treat the valve head with an inert treatment. Due to the sealing force required in typical conical rotary valves, such treatment cannot be used, as it would cause treatment peeling after only a few actuations. With the PLSV technology, thanks to its reduced surface sealing area and reduced sealing force, sulfinert-treaded valves can be used for more than 500,000 actuations without peeling. For untreated valves, their lifetime can even go up to 3,000,000 actuations for use in UHP gasses analysis.

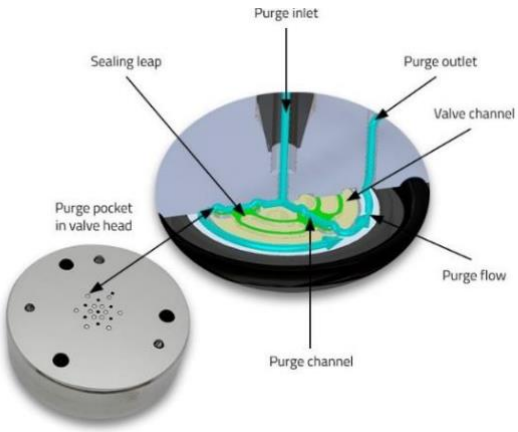

Figure 4 – PLSV Technology principle

The lifetime of diaphragm valves is also low compared to PLSV technology, since it suffers from pressure drops, as the flexibility of the diaphragm changes over time. This is a cause of peak shifting. Furthermore, this type of valves is known for containing dead volumes, which can trap air and also create ''ghost peaks'' due to re-injection [7].

The PLSV technology uses a unique purge system, presented in Figure 4, which makes leaks virtually impossible. Indeed, small molecules

have a strong tendency to leaks between ports, but it can be prevented with this purge. Furthermore, the purge protects the sample integrity from inboard leaks, which is especially important for the measurement of ultra-trace level impurities. The PLSV technology has been implemented in 6, 10 and 14 ports valves, as well as our unique Trap & Release (T&R) valve configuration. We have also released a drop-in version of the PLSV with the same form-factor as conical rotary valves, as shown in Figure 5. This version can be easily integrated on third-party actuators and GC platforms.

Figure 5 – Drop-in PLSV with conical rotary valve form-factor*

*3 years warranty, 3,000,000+ actuations.

Carrier and Discharge Gas

Argon (5.0N) was used as the carrier and discharge gas for all the chromatograms presented in this document. Argon was further purified with a 1L/min ASDPure noble gas purifier installed before the GC platform. It is based on a double heated vessel design that provides gas with less than 1ppb total impurity. Indeed, it is well known in the field that traditional heated getter purifiers releases trace amounts of H_2 due to both hydrocarbon cracking and the metal being processed at high temperatures. With a second vessel operating at lower temperature, the hydrogen released by the first vessel is removed down to <1ppb. The use of a carrier / discharge gas purifier is important to prevent interference from impurities found in the gas and provide a stable baseline, leading to better analytical performances.

Results and Discussion

Important Note on Limit of Detection

The Limits of detection (LOD) presented in this document have been achieved for specific configurations where multiple compounds have to be separated from various matrices. These configurations have been designed to limit the number of valves and columns to optimize the cost of these standard instruments. Still, by optimizing the chromatography for each analyte separately, the LODs could be furthered improved. For example, the LOD for CO is often lower than for other permanent gases in standard instruments. This is not because the SePdd is less sensitive to CO, but because this molecule has a tendency to stick molecular sieves, leading to broader peaks in the conditions that are needed to achieve a good separation of the other compounds on the same channel. Using a channel specific to CO or column ramping will lead to better LODs for this compound. There are also many other ways to improve the sensitivity of the SePdd that have not been used here. For example, using a vacuum pump to reduce the internal pressure of the plasma chamber can increase the signal by more than 1/3 and significantly reduce the noise. Therefore, the results presented here should not be viewed as the SePdd detector sensitivity, but as typical performances that can be achieved for these specific standard configurations.

Measurement of Ultra-Trace Level Permanent Gases in Argon and Fuel-Grade Hydrogen

Permanent gases are among the most common impurities found in high purity gases, as they are some of the most abundant molecules in air. Since its release, the Epd technology has been widely used for the measurement of these impurities at the trace and ultra-trace level, thanks to its high sensitivity. For the semiconductor industry and other applications that require ultra-high purity gases, helium is typically used as the carrier and discharge gas, since its high ionization energy allows LOD of less than 100 ppt for all of these compounds [8]. However, for most

applications where sub-ppb LODs are not needed, using argon is often a good alternative. Indeed, while it strongly depends on the measurement range and the chromatographic front-end, a LOD in the low-ppb is achievable for all the permanent gases with argon as the carrier / discharge gas.

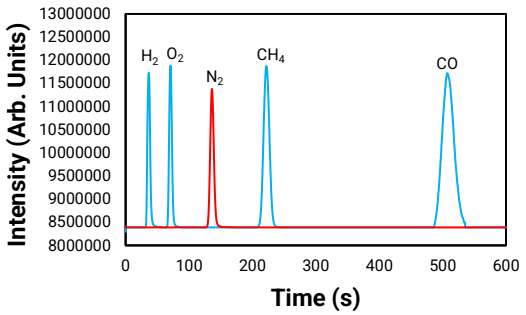

Figure 6 – 10ppm H_2, O_2, N_2, CH_4 and CO in Argon

Figure 6 presents a chromatogram acquired for 10 ppm H_2, O_2, N_2, CH_4, and CO in argon. Here, a single injection valve with a small 250 µL sample loop and 6ft molecular sieve 5A column maintained at 60°C was used, with 30mL/min argon as the carrier / discharge gas. Two different wavelengths were used: one highly sensitive and specific to N_2 and the other for measuring H_2, O_2, CH_4 and CO.

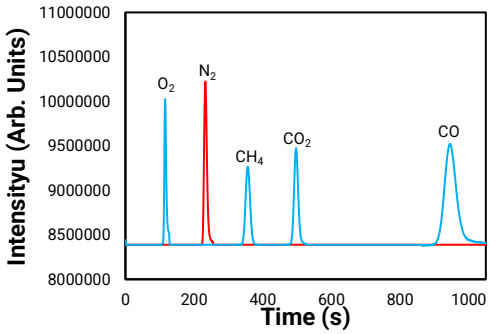

Figure 7 – 2ppm Permanent Gases in Fuel-Grade Hydrogen

With the adequate chromatographic front-end, similar results could also be achieved in almost any gas-phase matrix. For example, Figure 7 presents a chromatogram acquired for 2 ppm permanent gases in fuel-grade hydrogen. Here, the injection valve was configured with a 1mL sample loop and two 6ft molecular sieve 5A columns maintained at 60°C in a heartcut configuration to improve the separation between the analytes and the hydrogen matrix. A second chromatographic channel using a backflush configuration and a porous polymer column was configured for measuring CO_2. Argon was also used as the carrier / discharge gas with a flow rate of 30mL/min.

The ISO 14687:2019 standard for fuel-grade hydrogen requires that all permanent gases are kept in the low-ppm level. The results show that ASDevices' GC platform, in combination with the Epd technology using argon as the carrier / discharge gas can therefore be used to measure the permanent gases impurity in fuel-grade hydrogen. By adjusting heartcut timing, the same GC configuration could also be used to measure trace-level permanent gases in oxygen, nitrogen, methane, carbon monoxide and air. Table 1 presents the LODs achieved for permanent gases on a 0-20 ppm range with a standard instrument using argon as the carrier / discharge gas at ambient pressure. The performance presented here is adequate for the most common applications that require monitoring permanent gases in various matrices. Different ranges and LODs can also be obtained with different analytical conditions, such as a different sample loop or column.

Table 1- LOD calculated for permanent gases using argon as carrier / discharge gas at ambient pressure

Analyte	Range (ppm)	LOD (ppb)
H_2	0-20	20
O_2	0-20	9
N_2	0-20	1
CH_4	0-20	20
CO	0-20	50
CO_2	0-20	9

Another key advantage of using argon as the carrier / discharge gas is that **oxygen can be measured without GC separation from trace (or matrix) argon present in the sample**. Indeed, on most GC columns, argon and oxygen will co-elute at temperatures above room temperature [9]. Therefore, analysers using helium plasma-based detectors can only measure $Ar+O_2$ as a single peak. It is often assumed in fuel-grade hydrogen and other matrices that the amount of argon is

negligible compared to oxygen, but it is often not the case. Furthermore, the maximum allowable limit of oxygen in high-purity gases is usually much lower than for argon, as it a highly reactive molecule. For example, the ISO 14687:2019 standard for fuel-grade hydrogen allows 300 ppm N_2+Ar, but only 5 ppm O_2. Using argon as the carrier / discharge gas is therefore the best option for accurate oxygen measurement in samples that contain some argon.

Ultra-Fast Crude Argon Analysis

Argon is produced in air separation plants using a distillation process. In order to maintain the optimum argon extraction efficiency, the argon draw-off mixture must be properly controlled. At the extraction point, the argon bubble will typically contain around 90% oxygen and 10% argon with nitrogen traces. If the nitrogen concentration reaches >2000 ppm, the process will stop working, as nitrogen ice will block the crude argon column and eliminate the reflux. Therefore, the nitrogen content must be known in real-time to optimize argon extraction and avoid shutdown.

Ultra-fast crude argon analysis is a good tool to improve argon recovery in air separation plants. It consists of measuring trace-level nitrogen in a mixture of argon and oxygen. Indeed, argon is the carrier / discharge gas of choice here, as nitrogen will not have to be separated from argon, allowing simpler GC configuration and method. However, high oxygen concentration from this mixture is difficult to separate from trace nitrogen. In typical crude argon analyzers, a long molecular sieve 5A column is used in combination with an oxygen trap in a heartcut configuration to prevent oxygen reaching the detector. This configuration leads to long cycle times of >5 minutes and the expensive copper-based trap must often be changed.

Thanks to spectral compensation, a measurement mode unique to the Epd technology, crude argon analysis can now be done in less than 30 seconds (15 seconds option also available) with a single GC valve and only a short molecular sieve column. This is done by measuring and combining two different wavelengths at the same time. A typical chromatogram acquired with ASDevices' crude argon analyzer is presented in Figure 8.

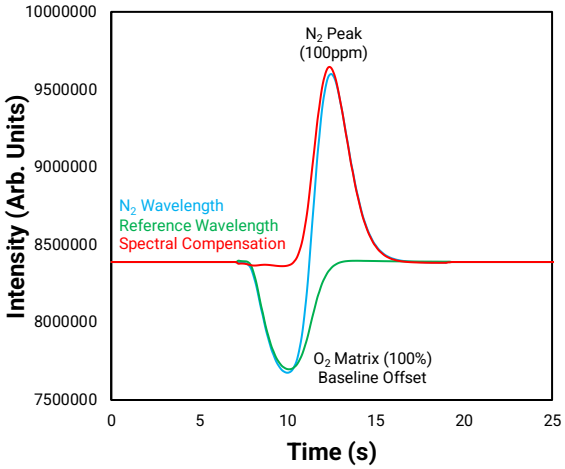

Figure 8 – Crude argon chromatogram acquired for 100 ppm N_2 in oxygen with the N_2 wavelength (blue line), reference wavelength (green line) and spectral compensation (red line).

The first wavelength (blue line) is highly sensitive to nitrogen. However, high oxygen concentrations will disturb the baseline. Since oxygen is co-eluting with nitrogen, the resulting N_2 peak cannot be integrated for quantification. Therefore, a reference wavelength (green line) is also used to measure the plasma baseline disruption from oxygen, but not the light emission from nitrogen. The spectrally compensated reading (red line) is generated in real-time by the Digital Signal Processing (DSP) unit, by combining the signal from the two wavelengths. The resulting peak can then be integrated for accurate N_2 quantification. More information and performance results for this application are available in our documents TN-05, AN-16 and AN-23 [10-12].

This application also highlights the importance of the PLSV valve technology developed by ASDevices. Indeed, in the crude argon analyzer, the valve is actuated twice every 30 seconds. This results in more than 1,000,000 actuations after one year. Therefore, long-term continuous use of such analyzer is only possible thanks to the excellent robustness of the PLSV, leading to longer lifetime and reducing the need for maintenance. At the time of writing this document, we have multiple on-site crude-argon analyzer that have been used continuously for more than 3 years without any need of maintenance, proving the robustness of this analytical system.

Measurement of CO_2 and Light Hydrocarbons Without Methanizer

The Epd technology is also highly sensitive to light hydrocarbons. Therefore, it presents itself as a robust and safe alternative to flame ionization detectors (FID). Indeed, FIDs must be fueled with high-purity air and hydrogen to generate the flame, which is not needed with the Epd technology. Only the carrier gas, argon here, is used as the discharge gas.

FIDs can only measure analytes that are flammable in the hydrogen flame. While it results in high sensitivity to most hydrocarbons, highly oxidized or halogenated compounds are more challenging to measure. As they are non-flammable, CO and CO_2 cannot be measured with FIDs, unless they are first converted into methane with a methanizer. This device is often based on a nickel catalyst that can be deactivated by common gases such as air, water, oxygen, hydrogen sulfide (H_2S) and unsaturated hydrocarbons, which greatly reduce the methanization process [13]. To avoid the catalyst poisoning, heartcut or backflush valves often have to be added, thus increasing the complexity and cost of the system.

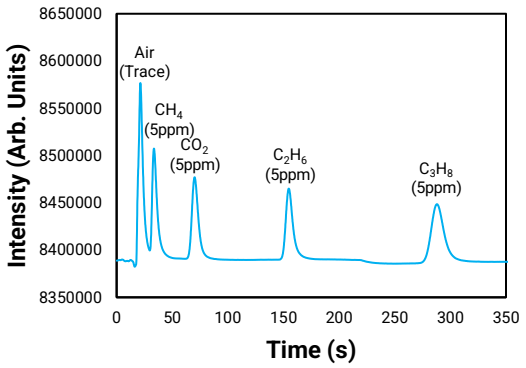

Figure 9 – Chormatogram acquired for 5ppm CH_4, CO_2, C_2H_6 and C_3H_8 in Ar with traces of air using the Epd technology.

Figure 9 presents a chromatogram acquired for 5 ppm methane (CH_4), CO_2, ethane (C_2H_6) and propane (C_3H_8) in argon, with traces of air using the Epd technology. Here, a single injection valve with a 250 µL sample loop and a 8ft PoraPak Q column were used. The column was ramped from 25°C to 100°C with a rate of 30°C/min to optimize the separation between the light hydrocarbons and CO_2. Argon was used as the carrier / discharge gas, with a flow rate of 30mL/min. Furthermore, the plasma was doped with moisture from a permeation tube to enable the "tracer mode". This measurement mode allows monitoring of new emission wavelengths that are generated from the interaction between the analytes and a doping gas. Here, the same wavelength was used to measure CO_2 and the light hydrocarbons. This result shows that argon can be used as the carrier / discharge gas to measure CO_2 and light hydrocarbons in the low-ppm, down to the ppb level.

Trace Moisture Analysis in industrial and UHP Gases

The measurement of trace-level moisture is a key analysis in most industrial and UHP gases, as it could cause the formation of damaging ice crystals and poison catalysts. For process analysis, moisture is typically measured inline with metal-oxide detectors such as Al_2O_3, thanks to their low cost. However, despite being used inline, they are known for their slow wet-to-dry response time because of Al_2O_3 surface roughness. This also causes signal drifting over time. They are also highly sensitive to contamination and temperature variations [14]. Therefore, this old technology suffers from a bad reputation due to reliability issues.

Gas chromatography can be used to overcome most of these issues, such as baseline drift and interferences. However, the measurement of moisture by GC has notoriously been considered extremely difficult or impossible, as it sticks to most column materials and stainless steel from the valves and tubes. In the past few years, Supelco released a new type of GC column based on ionic liquids, which has been optimised for the measurement of water in various solvents [15]. Using a TCD, they were able to cover a concentration range between 0.05% and 1%. More sensitive methods have since been developed using a Barrier Discharge Ionization Detector (BID), but this type of detector only rely on helium as the discharge gas and this type of detector is not selective [16].

More recently, ASDevices developed a method with this column for measuring trace-level moisture in various gas matrices using the Epd technology and argon as the carrier / discharge gas. An example of chromatogram acquired for 26 ppm H_2O in nitrogen is presented in Figure 10. More detailed results acquired for trace-level moisture in various matrices are presented in our application note AN-19 [17]. Furthermore, we are currently working on the development new methods for measuring trace-level moisture in petrol-based products and ppt-level moisture in semiconductor gases. These results will be published in future application notes.

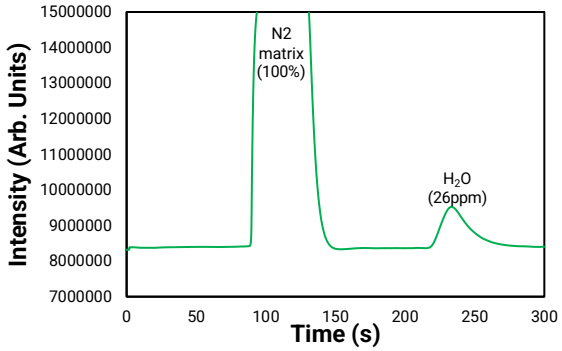

Figure 10 - Chromatogram acquired for a sample containing 26 ppm moisture in Nitrogen

Another advantage of using argon instead of helium for moisture analysis is the faster stabilization time. Indeed, moisture sticks to the stainless-steel components. Since argon is a much heavier molecule, trace moisture sticking on tubing surface is removed much faster, compared to helium. With argon carrier, this type of GC can be up and running in only a few hours.

Measurement of Trace Kr and Xe in Argon

Ambient air contains 1.1 ppm krypton and 0.09 ppm xenon [18]. Therefore, they are common impurities that can be found in argon produced in air separation plants. Argon is often used as an inert gas in many industrial processes such as the fabrication of semiconductor materials. While Kr and Xe are generally considered inert, they are the most reactive of the noble gases. They can even react and generate defects in semiconductor materials during their fabrication, due to the exotic conditions required for their production [19]. Therefore, the measurement of Kr and Xe in argon might be needed for many applications.

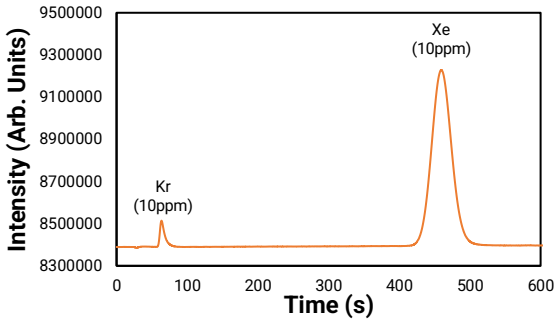

Figure 11 - Chromatogram acquired for 10 ppm Kr and Xe in argon.

Figure 11 presents results that were acquired for the injection of 410µL of 10 ppm Kr and Xe in argon using the Epd technology. The gases were separated using a 1 m x 1 mm Shincarbon column maintained at 60°C. Kr and Xe were measured with the same wavelength that showed excellent response for both gases.

With its lower ionization energy, signal from Xe is approximately 10x more intense than for Kr. Still, thanks to the good signal to noise ratio, Kr can be measured down to 100 ppb in argon plasma, while Xe can be measured down to 15 ppb. Indeed, this is not as sensitive as helium plasma, but such performance is still excellent and could be used for the analysis of high-purity gases. Additional heartcut or backflush valves and columns could also be used to measure Kr and Xe in different backgrounds. For lower LODs, down to 0.5 ppb, helium could be used as the carrier / discharge instead of argon. More information about the measurement of noble gases in various matrices is presented in our application note AN-22 [20].

Measurement of Trace N_2O and SF_6

Nitrous oxide (N_2O) and Sulfur Hexafluride (SF_6) are two of the most potent greenhouse gases. As for CO_2, their concentration in the atmosphere have been constantly increasing since the beginning of the industrial era [21,22]. While atmospheric N_2O concentration is now above 310 ppbv, SF_6 is still in the low-ppt. Despite their

low concentration, they already have a significant effect on the global climate. Furthermore, these two compounds are often concentrated when producing some gases from air separation.

This is especially problematic for the production of UHP Kr and Xe. Indeed, due to their low concentration in atmosphere, many ultra-trace atmospheric contaminants are also concentrated during their production [23]. N_2O and SF_6 concentrations can even be increased up to the high-ppm level in Kr and Xe. While N_2O can be easily degraded with the use of catalysts, SF_6 is much harder to remove due to its inertness. Therefore, monitoring of these two compounds is important, especially in UHP Kr and Xe produced for the semiconductor industry, as they can lead to unexpected side-reaction that could damage the materials.

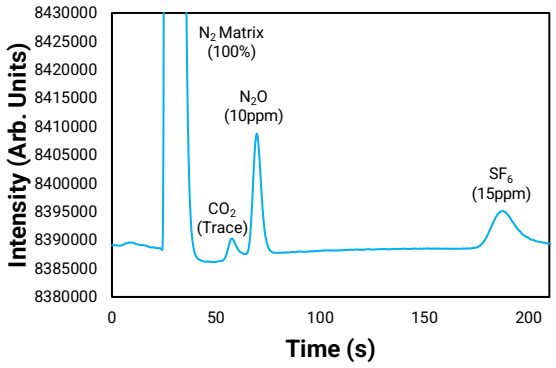

Figure 12 – Chromatogram acquired for 10ppm N_2O and 15ppm SF_6 in N_2.

Figure 12 presents a chromatogram for the injection of 410µL 10 ppm N_2O and 15 ppm SF_6 in N_2. Here, a single 1m x 1mm ShinCarbon column maintained at 150°C was used to separate N_2O and SF_6 from the N_2 matrix. The same highly sensitive wavelength was used for the measurement of both compounds.

In the conditions presented above, a LOD of 35 ppb was calculated for N_2O and 200 ppb for SF_6. The LOD could also be further improved by increasing the sample injection volume. Therefore, this method using GC-Epd with argon carrier / discharge gas would be sensitive enough for measuring trace N_2O in ambient air. The method would also be suitable for measuring SF_6 in UHP gases down to the low-ppm level. Again, the sensitivity could also be improved by replacing Ar with He as the carrier / discharge gas.

Measurement of Trace BTEX

BTEX (Benzene, Toluene, Ethylbenzene, Toluene and Xylenes) are volatile molecules often found in gasoline and other petroleum-based products. Therefore, they are common contaminants found in UHP gases, especially when they are extracted or synthesized from hydrocarbons. Furthermore, due to their high volatility, they can easily contaminate soil, water and air. According to the World Health Organization (WHO), BTEX are highly toxic and carcinogenic molecules. Even low-ppm level of these molecules in air could cause long-term health issues [24]. Therefore, highly sensitive detectors are required to assess the high purity standard of specialty gases and strict environmental regulations.

FIDs are among the most common detectors for the measurement of volatile hydrocarbons. However, as previously discussed, they must be fueled with UHP air and hydrogen, which is not allowed in many classified areas. Photoionization detectors (PID) are very sensitive to BTEX and other aromatic compounds, but they require expensive xenon lamp (9.6 eV) that must be changed every 1 to 2 years. Due to their low ionization energy, such lamp can only be used for molecules with low ionization potentials. Argon lamps (11.7 eV) can be used instead to measure other molecules with higher ionization potentials, but due to their instability, they are generally not recommended [25]. PDHID is also often used for BTEX measurement, with a LOD around 10 ppb for benzene.

The Epd technology is an excellent alternative to these two types of detectors, as it is also highly sensitive to BTEX, but there is no need for any flammable gas or long-term maintenance. Figure 13 presents a chromatogram acquired for the injection of 4mL sample containing 950 ppb BTEX in air. The column used was a Rxi-5SilMS 30m x 0.52mm maintained at 50°C with an argon carrier / discharge gas flow rate of 15 mL/min.

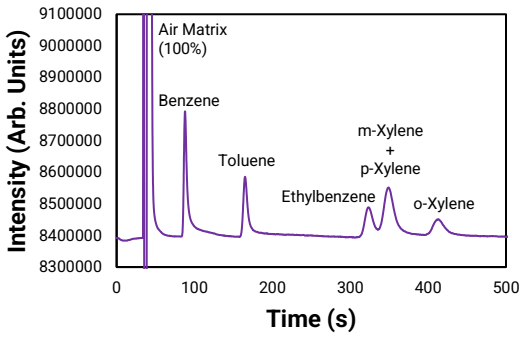

Figure 13 – Chromatogram acquired for 950ppb BTEX in Air.

Here, a LOD of 10 ppb was calculated for Benzene and between 20 ppb and 50 ppb for the other compounds. These results are comparable to the PDHID performance, but without the use of helium or need for maintenance. While such sensitivity is satisfactory for many applications, the LOD could also be pushed down further to the sub-ppb level by combining this system with ASDevices' sample preconcentration system (SCS).

Measurement of Trace Level Sulfurs and Light Hydrocarbons

Due to their reactivity, sulfur compounds are key impurities to monitor in high-purity gases for many applications. For example, along with hydrocarbons, they are known to poison catalysts or cause undesirable byproducts in various processes [26]. Therefore, they must often be kept in the low-ppm or even the ppb-level.

Common detectors for sulfur analysis include the Sulfur Chemiluminescence Detector (SCD) and the Flame Photometric Detector (FPD) [27,28]. Despite being very sensitive, the SCD is not adapted for process monitoring, due to its complexity and constant need for maintenance. Furthermore, it is specific to sulfur and cannot be used to monitor other impurities. The FPD is similar to FID, but it monitors a specific emission wavelength from S_2 radicals, instead of an electric current. Due to the light-emission mechanism, the detector output is proportional to the square of the sulfur mass flow rate [28]. Furthermore, as for FID, the FPD requires UHP hydrogen and air to fuel the detector. The FPD can be equipped with a second wavelength to detect phosphorus compounds, but other impurities cannot be measured with this detection technology. In the past years, the Epd was shown to be very sensitive to sulfur compounds [29-31]. It was also shown that the detector signal is proportional to sulfur concentration [29]. Therefore, the Epd technology presents itself as the best alternative to SCD and FPD for sulfur analysis, especially in process-GCs, thanks to its high sensitivity and ease of use.

Figure 14 presents a chromatogram acquired for 490µL of 10 ppm sulfur compounds (H_2S, CH_3SH, CS_2, C_2H_6S, $C_2H_6S_2$) and light hydrocarbons (C_1-C_4) in argon using the Epd technology. All the compounds were measured using the same emission wavelength.

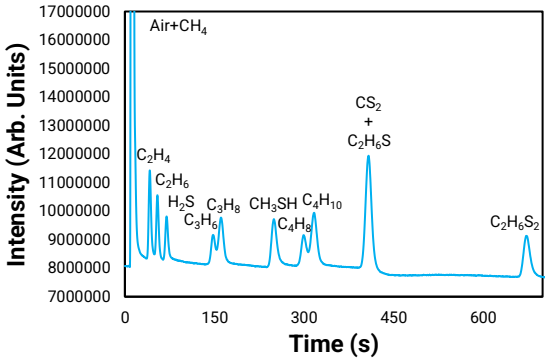

Figure 14 – Chromatogram acquired for 10ppm Sulfur and light hydrocarbons in argon.

Here, a single Rt-XLSulfur 1m x 1mm column was used for the separation of the sulfur compounds and hydrocarbons, but different column and valve combinations can be used for other matrices. Indeed, due to the interaction between sulfur and stainless-steel, all the components in contact with the sample – including the tubing and injection valve – must be Sulfinert-treated to avoid trace sulfur losses. This highlights the importance of using the PLSV valve technology, as typical conical rotary valves cannot be inerted, because the friction would cause surface treatment peeling during actuation. In the conditions presented above, a LOD between 20 ppb and 40 ppb was calculated for all the sulfur compounds (35ppb for H_2S), which is sensitive enough for multiple applications.

The measurement of total sulfur is also a key analysis in food-grade gases such as CO_2. Due to the distinctive taste and odor of these compounds, the International Society of Beverage Technologists (ISBT) Carbon Dioxide Guidelines limits total sulfur concentration to 0.1ppm v/v [32]. One way to simplify total sulfur analysis is to convert all the compounds into H_2S using a heated metal catalyst and a low hydrogen flow. Figure 15 presents a chromatogram acquired for a total sulfur concentration of 78 ppb in CO_2. The sample contained 13 ppb H_2S, COS, CH_3SH, CS_2, C_2H_6S, $C_2H_6S_2$ which were all converted into H_2S with the catalyst. The results presented here demonstrate that GC-Epd with argon carrier / discharge gas can indeed be used for the monitoring of total sulfur in food-grade CO_2.

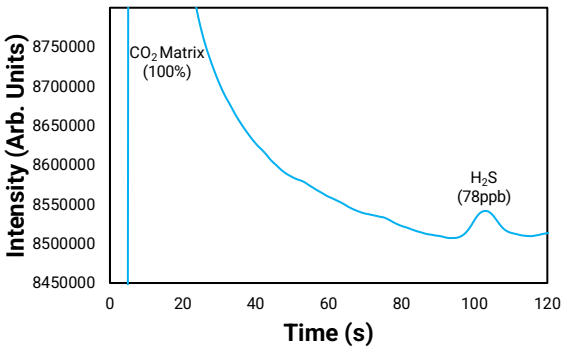

Figure 15 – Chromatogram acquired for 75 ppb total sulfur converted into H_2S in food-grade CO_2.

More information about the use of the Epd technology for measuring sulfur compounds, especially in fuel-grade hydrogen, is presented in our application notes AN-09, AN-15 and AN-18 [29-31].

Conclusions

In conclusion, argon has been successfully used as an alternative to helium carrier and discharge gas with the Epd technology for the measurement of permanent gases (H_2, O_2, N_2, CH_4, CO, CO_2), light hydrocarbons, H_2O, noble gases (Kr and Xe), N_2O, SF_6, BTEX and sulfur compounds. Argon even offers many advantages compared to helium and other carrier gases. For example, it allows accurate O_2 measurement without the interference from trace argon present in most samples and the GC tubing can be purged much faster than with helium. The results presented in this application note show that Epd using argon as the carrier / discharge gas offers performances that are good for most applications that require the measurements of trace impurities in the low-ppm or high-ppb measurement ranges. The sensitivity of the SePdd detector could also be further improved by optimizing the chromatography for each compound and by reducing the plasma chamber pressure.

These were only a few examples of applications that could be achieved using argon as the carrier and discharge gas. As long as the impurities are ionized in the argon discharge, they can be detected and quantified. Therefore, the possibilities are almost limitless.

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