APPLICATION NOTE 19

GC METHOD FOR MOISTURE ANALYSIS USING ARGON CARRIER AND DISCHARGE GAS

The most affordable option for moisture analysis by gas chromatography

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Authors:
Marc-Antoine Langevin, Ph.D.
André Lamontagne, Ing.
Yves Gamache, CEO, CTO

ASDevices

ABSTRACT

Nitrogen, hydrogen, oxygen and carbon dioxide samples containing trace-level moisture were generated and analyzed using a miniMOv GC platform equipped with a detector based on the Enhanced Plasma Discharge (Epd) technology configured in H_2O selective mode. This detection technology allows the use of argon instead of costly helium as the carrier and discharge gas. The method developed with this system was demonstrated to be reliable and highly sensitive for real-life application with various permanent gas matrices containing trace-level moisture. A limit of detection (LOD) in the ppb-level was calculated for moisture. The system developed by ASDevices offers many benefits compared to systems using Al_2O_3 detectors, Karl Fischer titration and other ionization-based detectors such as the PDHID, DID or BID. This method could be easily adapted for moisture analysis in solvents, oils and other petroleum products. A preconcentration method for ultra-trace level moisture in high-purity gases used in the semiconductor industry will also be presented. With this method, the LOD can be further pushed down to the ppt level.

Introduction

Measurement of trace-level moisture is a key analysis in permanent gases (H_2, O_2, N_2, CH_4, CO, CO_2). For example, according to the ISO standard for fuel-grade hydrogen (ISO 14687:2019), H_2O must be kept below 5 ppm to minimize formation of ice within the fuel cell system and to minimize entrainment of aerosols such as sodium and potassium ions [1]. Furthermore, the presence of trace-level moisture could cause catalyst poisoning or cause an unexpected chemical reaction, which could be problematic when inert gases like argon or nitrogen are assumed to be dry [2,3]. Therefore, moisture must often be monitored, especially in specialty high-purity gases.

Metal-oxide, more specifically Al_2O_3 detectors, are among the most popular moisture detectors for process analysis, as they are not very expensive. However, they are also known for their slow response time (wet to dry) because of Al_2O_3 surface roughness and their response drift over time. They are also highly sensitive to contamination and temperature variations and they require frequent calibration [4]. Therefore, this old technology suffers from a bad reputation due to reliability issues. Still, with a limit of detection (LOD) of 0.1 ppm its performance is deemed suitable for the most common applications.

For laboratory testing, Karl Fischer titration is a well-known standard method to measure water. While being fairly sensitive and accurate, this method requires mixtures of high-purity hazardous chemicals. Furthermore, common impurities such as ketones, carbonyl compounds, mercaptans, thio acids, hydrazines and peroxides can cause interference. Indeed, such interference can be avoided, but only with the use of even more chemicals [5]. While this is not very problematic for the analysis of high-purity gases, this must be considered when analyzing water in solvents or petroleum products. Karl Fischer titration can be automated and adapted for process analysis, but it is not optimal due to its complexity.

Gas chromatography (GC) is among the most reliable options for the analysis of trace-level impurities – for process or laboratory analysis - as interfering species can be separated with the right combination of columns. Furthermore, GCs are not affected by baseline drifts compared to inline analyzers. 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 optimized for the analysis of water in various solvents [6]. 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 costly helium as the carrier and discharge gas and this type of detector is not selective [7]. Other plasma-based technologies such as the Pulsed Discharge Ionization Detector (PDHID) would also be subject to the same limitations.

To overcome challenges associated with H_2O analysis by GC, ASDevices developed and

patented many new technologies that are making this measurement possible and reliable. Indeed, the level of sensitivity mostly depends on the detector used, but the reliability of the method also depends on a combination of all the technologies used for the analysis.

In 2017, ASDevices released the SePdd, based on Enhanced Plasma Discharge (Epd) detection technology. This technology measures light emitted at specific wavelengths by analytes in a stabilized argon, nitrogen or helium plasma using a highly sensitive photodiode and optical filters. To further stabilize the plasma and obtain better peak shapes, we have often been doping the discharge with a few ppm of moisture. With the use of a spectrometer, it is possible to measure specific emission wavelengths associated with the presence of moisture, as seen in Figure 1.

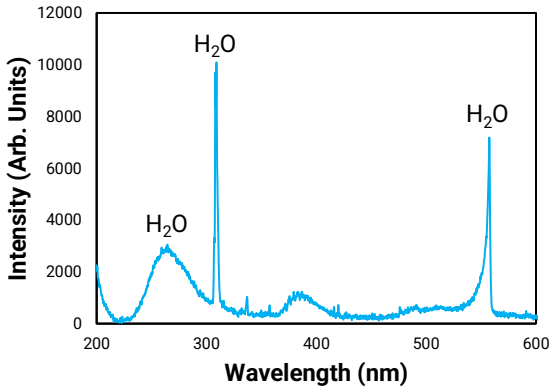

Figure 1 – Epd emission of 20 ppm moisture in argon plasma

From this observation, we concluded that the SePdd would be a good detector for trace-level moisture analysis using GC by monitoring specific emission wavelengths from H_2O. The following document intends to present how this detection technology can be used for moisture analysis in permanent gases with low-cost argon as the carrier and discharge gas. This method could easily be adapted for the analysis of trace-level water in other permanent gases and in solvents, oils or other petroleum products. Note that this document only presents preliminary results to demonstrate the high sensitivity of the Epd technology for moisture. Further application notes will be published for specific applications.

Experimental Information

SePdd Detector[patented]

Figure 2 - The SePdd detector

All the measurements presented in this document were done with the SePdd (see Figure 2). This detector is based on the Enhanced Plasma Discharge (Epd) technology developed by ASDevices. With its highly energetic stabilized and focused plasma discharge, water is easily ionized and measured by monitoring specific wavelengths emitted from the plasma. For this application, it can be operated with helium or low-cost argon as the carrier gas.

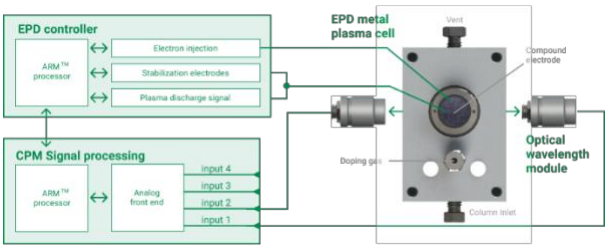

Figure 3 – Epd principle

Since the carrier gas used for chromatography 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 3.

Purged Lip Sealing Valve Technology[patent-pending]

The Purged Lip Sealing Valve (PLSV) is a unique valve technology developed by ASDevices, which offers many advantages over the other chromatographic valve technologies [8-10]. For moisture analysis, it is important to treat the valve head with an inert treatment, since water sticks to stainless-steel surfaces. 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, silconert-treaded valves can be used for more than 500 000 actuations without peeling. For untreated valves, their lifetime can even go up to 1 000 000 actuations for use in UHP gasses analysis. The PLSV technology also uses a unique purge system, presented in Figure 4, which makes leaks virtually impossible. Indeed, small molecules like hydrogen and helium 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. For trace-level H_2O analysis, it is especially important to avoid air ingress, which would have a significant impact on the measurement. The PLSV technology has been implemented in 6, 10 and 14 ports valves, as well as our unique Trap & Release (T&R) valve.

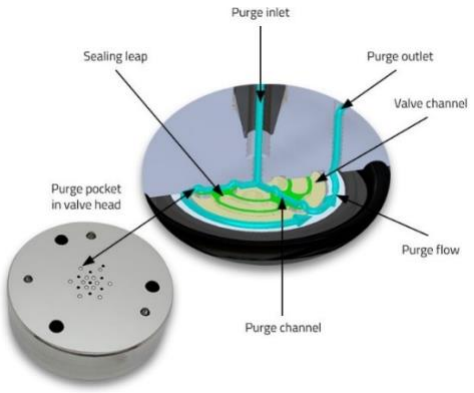

Figure 4 – PLSV Technology principle

Diaphragm valves could also be treated with silconert coatings. However, this type of valve contains dead volumes, which causes two issues for this application. Moisture can be trapped in these volumes, which would lead to measurement errors and peak tailing. Furthermore, dead volumes are known to create "ghost peaks" due to re-injection [10]. This technology is also susceptible to pressure drops, which may cause peaks shifting over time. Therefore, the PLSV technology is the best option for moisture analysis.

GC Platform and Method

The following tests were all performed using the miniMOv GC platform. It is the latest benchtop GC platform released by ASDevices (Figure 5). It beneficiated from our three decades of expertise in designing robust and reliable process-oriented instruments for the analysis of ultra-high purity gases in the field of semiconductors, air separation and other specialty gases. The miniMOv contains one ramping oven and one isothermal oven. The platform can be equipped with up to 10 purged electronic pressure controllers (EPC), 3 valves and two detectors. It was optimized for the use of ASDevices' detectors (SePdd, eFID, FePID and TCD), but it is also compatible with almost any other third-party detector. The same performance as presented here could also be achieved using the iMOv GC platform, as it uses the same high-quality components. This platform would only be more suitable for continuous industrial process analysis due to its mechanical design.

Figure 5 - ASDevices' miniMOv GC platform

The detector inlet, as well as all the valves, tubes and unions in contact with the sample were all

silconert-coated to avoid losing moisture by adsorption on the surface of the various components. Furthermore, the GC valves and sample line were maintained in an isothermal oven to further prevent water from sticking to the components.

The samples were generated from 5.0N N_2, H_2, O_2 or CO_2 (Messer Canada). The high-purity gases were further purified using a moisture trap, as a few ppm could still be present in the bottles. The gas flow was then directed to a certified Teflon permeation tube containing water (Kin-Tek). The permeation tube was previously calibrated to generate 28 ppm at 45°C with a gas flow rate of 75 mL/min. The moisture concentration was modified by changing the gas flow with a restrictor in front of the permeation tube. The sample was injected from a 410 µL sample loop, but larger volume could be used for improved sensitivity.

A Watercol 1910 30m x 0.25mm x 0.2µm film thickness (Supelco) was used to separate moisture from the matrix. Argon was purified using ASDevices' Pure purifier, which removes trace of permanent gases and moisture down to 1 ppb. The carrier gas pressure in front of the column was set to 35 psi. Due to the low carrier gas flow through the column, 25 mL/min argon make up gas was also added to the detector. The SePdd was connected to a vacuum pump to improve the peak shape. Since hydrogen has a strong tendency to stick to the column material, the temperature was ramped from 40°C to 80°C at a rate of 5°C/min for better peak separation. For the other gas matrices, the oven was set to 80°C.

For measuring moisture, the photodiode on the SePdd was equipped with an optical filter made specifically for ASDevices, centered at a wavelength that is highly sensitive to H_2O. While high-concentration matrix still affects the measurement from this wavelength, it is almost not sensitive to most trace impurities that could be found in such sample.

Results and Discussion

Trace-level Moisture in N_2

First, a sample containing 26 ppm H_2O in nitrogen was generated and analyzed, as presented in Figure 6.

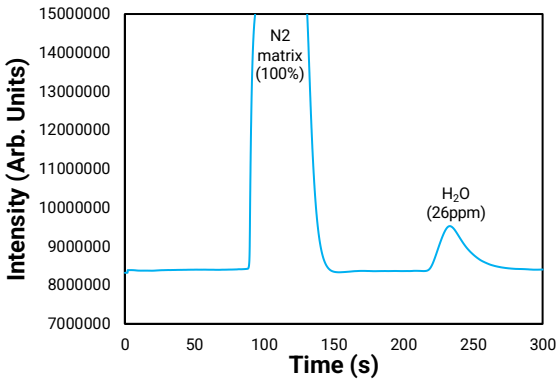

Figure 6 – Chromatogram acquired for a sample containing 26 ppm moisture in Nitrogen

The linearity response for moisture in nitrogen as a function of concentration is presented in Figure 7. A good linearity with a R^2 of 0.999 was obtained and a LOD of 0.1 ppm was calculated from the results acquired with a small sample loop of 410 µL. Much lower LODs can be expected by increasing the sample loop size.

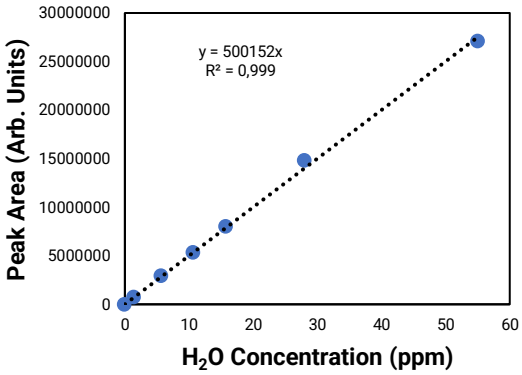

Figure 7 – Peak area as a function of H_2O concentration in Nitrogen

The repeatability of the analysis was also evaluated by injecting a sample containing 26 ppm H_2O every 5 minutes over a period of one hour. The results, presented in Figure 8, show a good repeatability with a variation of only 1.4%.

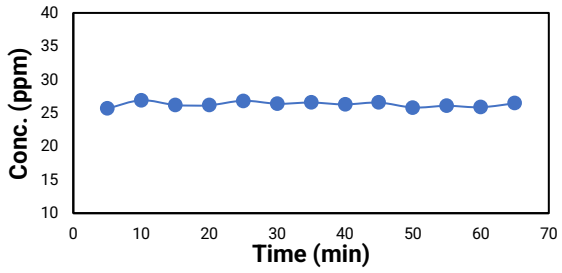

Figure 8 – Calculated concentration for a sample containing moisture in Nitrogen over one hour

Trace-level Moisture in H_2

Then, a sample containing 30 ppm H_2O in hydrogen was generated and analyzed with the miniMOv GC platform. The result is presented in Figure 9.

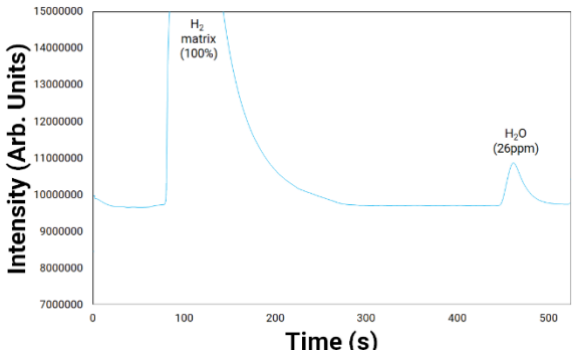

Figure 9 – Chromatogram acquired for a sample containing 30 ppm moisture in Hydrogen

The linearity of the response for moisture as a function of the concentration was evaluated, as presented in Figure 10.

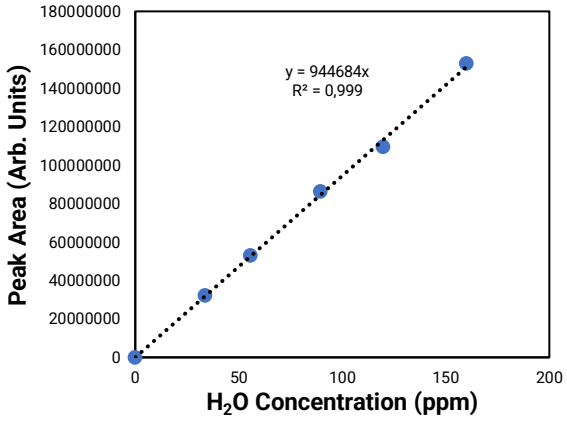

Figure 10 – Peak area as a function of H_2O concentration in Hydrogen

The chromatograms also showed a good linearity with a R^2 of 0.999 for the moisture response as a function of concentration. From the results acquired, a LOD of 0.1 ppm was also calculated here.

Trace-level Moisture in O_2 and CO_2

Preliminary results were also acquired for moisture in O_2 and in CO_2. The chromatograms acquired are presented in Figure 11 and Figure 12 respectively.

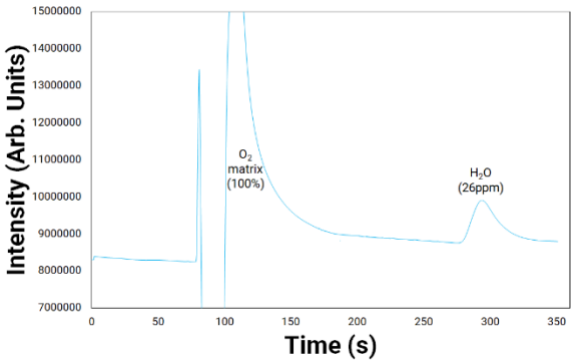

Figure 11 – Chromatogram acquired for a sample containing 26 ppm moisture in Oxygen

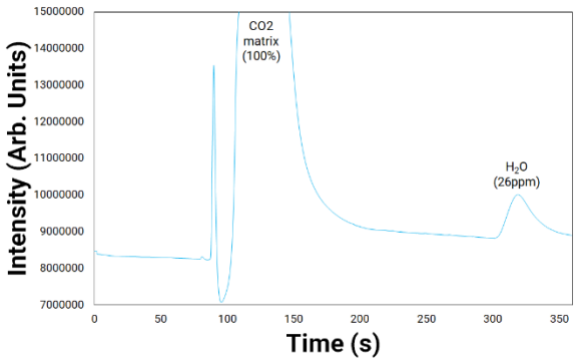

Figure 12 – Chromatogram acquired for a sample containing 26 ppm moisture in Carbon Dioxide

Highly linear and stable are expected after optimization of the chromatography.

Ultra-Trace Level Moisture for Semiconductor Industry

The semiconductor industry requires ultra-high purity gases, as only a few ppb of impurities could cause irreversible damage to the materials. Therefore, we developed a new method that uses

a proprietary trapping material for moisture preconcentration and the T&R PLSV, unique to ASDevices. This system is schematically represented in Figure 13.

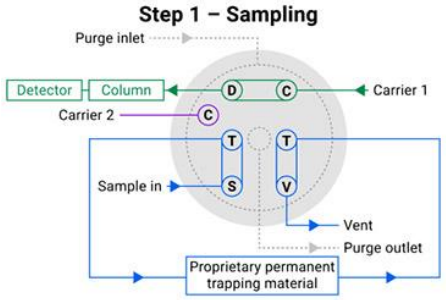

Figure 13- Schematic representation of the T&R PLSV in sampling position, used for moisture preconcentration.

In this representation, a GC column is used, which might be needed for the analysis of complex matrices. However, for the analysis of simple matrices such as the permanent gases, moisture can be preconcentrated on our proprietary trapping material, while the matrix is eliminated thanks to the trap's purge position. Moisture can then be directly injected to the detector, without any GC column. ASDevices' unique T&R PLSV and pre-concentration methods are presented in more details in the document AN-11 – New Method Using Argon as an Alternative to Helium for Sub-ppb Level Measurement of Permanent Gases with the T&R PLSV and the Epd Technology (2020). Figure 14 presents a chromatogram acquired for 10ppb H_2O in pure argon. Here, no GC column was used.

From this result, a LOD below 1ppb was obtained for H_2O in argon. Other results acquired with permanent gas matrices showed that H_2O can be well retained on ASDevices' proprietary trapping material while the matrix can be well removed from the trap when the T&R PLSV is set in purge position.

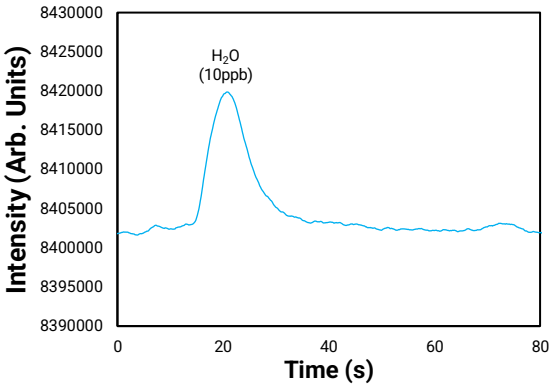

Figure 14 – Chromatogram acquired for 10 ppb H_2O in argon preconcentrated on ASDevices' proprietary trapping material.

Conclusions

In conclusion, ASDevices' SePdd is a highly sensitive detector for moisture analysis by gas chromatography, even using argon as the carrier and discharge gas, which is not possible with other ionization-based detectors.

The use of argon is a significant advantage compared to helium, not only because of its lower cost, but also because it is much more efficient in purging a system from residual moisture, as argon is also heavier than helium.

When using a Supelco Watercol 1910 GC column, a LOD of 0.1 ppm can be easily reached. Thanks to the high reliability of this method, which is only possible thanks to the use of high-quality components from ASDevices, it is already offered as an option and used by customers in our complete analytical system for fuel-grade hydrogen analysis. The LOD can be further pushed down below 1 ppb using ASDevices' preconcentration method with the T&R PLSV and our proprietary trapping material for moisture.

While the current results show the high sensitivity of the Epd technology for moisture analysis, future work will be done to improve the performance of the GC method down to the ppt level.

References

[1] US Department of Energy. Hydrogen Fuel Quality Specifications for Fuel Cells in Road Vehicles, 2016.

[2] W. B. Burford III, *et al.* The Poisoning of Nickel Hydrogenation Catalyst by Water Vapor, J. Am. Chem. Soc. 1945, 67 (2), 331-332.

[3] K.B. Sravan Kumar *et al.* Water Poisons H_2 Activation at the Au-TiO_2 Interface by Slowing Proton and Electron Transfer Between Au and Titania, J. Am. Chem. Soc. 2020, 142(12), 5760-5772.

[4] S. Gleissner, Sensor Technologies Used in Dew Point Transmitters Advantages / Disadvantages, Compressed Air Best Practices.

[5] J. Mitchell Jr., Karl Fischer Reagent Titration, Anal. Chem. 1951, 23(8), 1069-1075.

[6] L. M. Sidisky *et al.* Mixing Water and Gas : The Quantitative Measurement of Water by Gas Chromatography Using Ionic Liquid Capillary Columns, Chromatography Today, 2016.

[7] Shimadzu. Analysis of Trace Water in Petroleum Products by GC, 2017.

[8] ASDevices. AN-08 – PLSV Technology – A Quantum Leap for Chromatographic Valves, 2019.

[9] ASDevices. AN-10 – PLSV Improved Valve Technology for Ultra-trace Sulfur Analysis, 2019.

[10] ASDevices. AN-13 – PLSV Pressure Drop Dead Volume: PLSV Against Diaphragm Valve, 2020.

C. Xu *et al.* Analytical Progress of Trace Impurities in Hydrogen for Fuel Cell Vehicles, Chem. Ind. Eng. Prog., 2021, 40 (2), 688-702

Related Documents

AN-11 – New Method Using Argon as an Alternative to Helium for Sub-ppb Level Measurement of Permanent Gases with the T&R PLSV and the Epd Technology.

AN-15 – Trace Sulfur in H_2 Analysis Without SCD, FPD and Thermal Desorber.

AN-17 – PLSV Valve Purge Technology Explained – Leak Management Principle.

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