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Note: Plasma optical emission spectroscopy for water vapor quantification and detection during vacuum drying process

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A methodology involving plasma optical emission spectroscopy driven by a direct current (dc) plasma source is developed to quantify water vapor concentration in a gaseous stream. The experimental setup consists of a dc driven low-pressure plasma cell in which the emission from the plasma discharge is measured by using an optical emission spectrometer. The emission from H_α at 656.2 nm—the first transition in the Balmer series, was found to be the most sensitive to the water vapor concentration in the gas stream. Consistent linear trends of the emission signals with respect to variation in concentration of water are observed for multiple combinations of operating parameters. This method has been applied to a vacuum drying process of a mock nuclear fuel assembly to quantify the concentration of water vapor during the drying process. *Published by AIP Publishing.* https://doi.org/10.1063/1.5047210

Spent fuel rods from nuclear reactors are initially kept in spent fuel pools to allow radioactivity to decrease to levels so that they can be stored in a dry cask. The water acts as a heat sink for the decay heat. In the dry cask storage, these rods are sealed in a canister shrouded in inert gas and protected by an overpack of concrete that also serves as a radiation shield.[1] The purpose of drying is to remove the water left in the canister and fuel assemblies to ensure the long-term integrity and retrievability of the spent fuel assemblies. The drying is performed as a vacuum drying process or a forced gas recirculation process. Vacuum drying with pressure hold points, which indirectly relates to the available water vapor content in the fuel canister, is the most common industry practice to certify the "dryness" level of the system.[2] In-line moisture content detection and quantification in these fuel canisters is generally hindered by conventional humidity sensors posing several limitations,[3] like low sensitivity to moisture detection, inconsistency in ascertaining the end point of the drying process, and quantifying the absolute "mass" of water leaving the system and, therefore, remains a topic of research interest.

Among the different non-intrusive techniques of water vapor detection and quantification, non-thermal plasma discharge has the potential to overcome many of the limitations. An inductively coupled plasma (ICP) together with optical emission spectroscopy (OES) has been employed for *in situ* detection of moisture in a lyophilization chamber during the critical stages of a freeze-drying process.[4] Multipoint near-infrared (NIR) spectroscopy has also been applied for in-line moisture content quantification during the freeze-drying process.[5] However, the quantification was only reliable toward the end of the process. Andrawes[6] proposed a methodology for determining trace water contents in gaseous mixtures, utilizing gas chromatography together with a helium ionization source. A microwave plasma source and emission spectrometry were utilized to determine trace amounts of bound water in solid samples using peak areas of atomic oxygen (O) and hydrogen (H) emissions.[7] Radical species generated from plasma interaction with water vapor has been a topic of great interest as well with diagnostics conducted to quantify OH concentration.[8–10]

In this note, we propose a methodology that involves a direct current (dc) driven plasma discharge and optical emission spectroscopy for detecting and quantifying water vapor in a flowing gas stream under both trace and high-water vapor loading conditions. For the quantification of water content, the system was calibrated extensively and was then employed in a large scale mock nuclear fuel rod assembly drying experiments.

The schematic representation of the proposed plasma discharge cell setup for water vapor detection together with the ancillaries, i.e., calibration unit, diagnostics, and measurement tools, is presented in Fig. 1. The plasma cell consists of two solid cylindrical copper electrodes. A thin 0.34 mm insulation coating is provided on the outer periphery of the electrodes to prevent discharge initiation and formation on the cell wall and to further ensure that the discharge forms within the inter-electrode gap, providing the perfect/optimum view angle for the optical probe for recording the emission intensity. The inter-electrode separation is typically maintained at 4 mm. The emission from the plasma discharge is acquired by using an optical emission spectrometer (Ocean Optics HR 4000CG-UV-NIR) via an optical fiber, and the emission spectrum is acquired using the "Oceanview" spectroscopy software. The electrodes and the optical probe are housed inside a four-way stainless steel cross chamber. The flange, facing the discharge, is fitted with fused silica glass for visualization purpose.

The pressure inside the plasma chamber is varied by means of a two-stage mechanical vacuum pump and is measured with a digital pressure gauge. For calibration, the carrier helium gas (Praxair UHP 5.0) is mixed with water vapor and then injected into the vacuum chamber as a result of the negative pressure differential created by the vacuum to eliminate the possibility of gas/water vapor accumulation in

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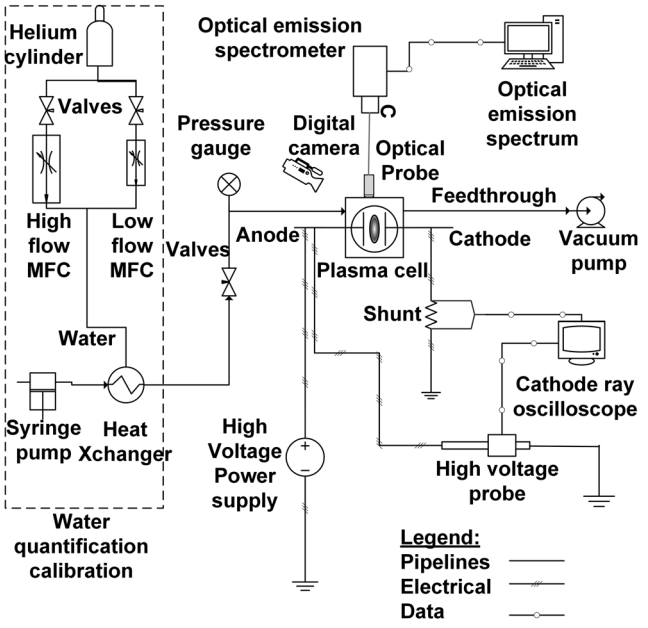

FIG. 1. Schematic representation of the proposed setup for water detection.

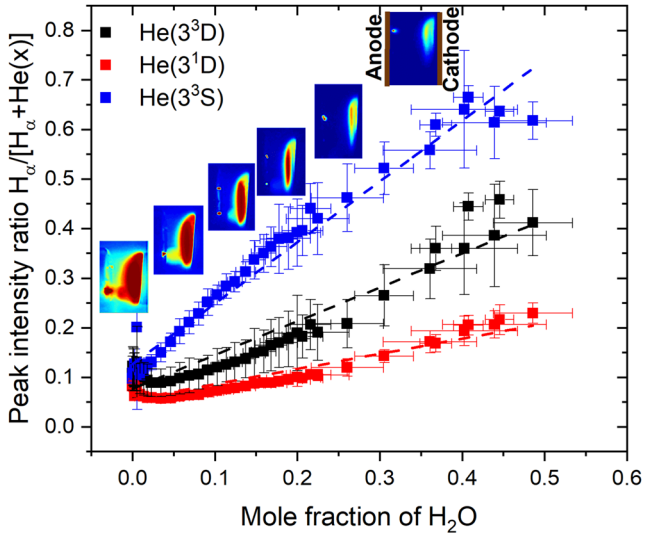

FIG. 2. Peak normalized emission intensity of H_α as a function of water mole fraction at an operating pressure of 16.6 Torr and discharge current of 2.0 mA. The H_α emission intensity is normalized by [H_α + He(3^3D)], [H_α + He(3^1D)], and [H_α + He(3^3S)] separately.

the piping network. The liquid water amount is regulated by using a programmable syringe pump, which injects water directly into the co-current heat exchanger where it undergoes flash vaporization and simultaneously mixes with the helium gas producing gaseous helium water mixture of known composition. Two calibrated mass flow controllers (MFCs), one from MKS Instruments (0-500 SCCM) and the other from Coastal Instruments (0-200 SCCM), were employed independently for varying mass flow rate of helium over two ranges. The plasma discharge is initiated and maintained via a Spellman (SL60P300) power supply unit. The voltage across the plasma discharge and that across the shunt for quantifying the discharge current are both measured with a cathode ray oscilloscope and a high voltage probe.

For detecting water vapor concentration, the emission from H_α at 656.2 nm was employed. The H_α emission is the red visible spectral line generated by a hydrogen atom when an electron falls from the third lowest to the second lowest energy level; this is the first transition in the Balmer series. The H_α is formed by the dissociation of water vapor to OH and H which undergoes further electronic excitation via electron impact reactions. The emission from H_α was chosen for water vapor detection purpose because of its very high sensitivity. Our experiments showed that even at a concentration of 2 ppm of water vapor, an emission from H_α was observed. The emission intensity of H_α was directly related to the water concentration level and thus was acquired for a range of water vapor concentration(s). In the calibration experiments, the water vapor concentration was systematically increased in the gas mixture by injecting a higher amount of water vapor into the helium stream.

Figure 2 shows the H_α intensity normalized by the intensity of three different He excited states [He(3^3D) 587.6 nm, He(3^1D) 667.8 nm, and He(3^3S) 706.5 nm] separately for a plasma discharge operating at 16.6 Torr pressure and having 2.0 mA discharge current. Four independent experiments were conducted, and the error bars represent the standard deviation among the four experimental data set(s). For sensitivity purpose, the emissions from the three different excited states of helium were investigated. It can be seen that all three normalized H_α intensity signals increase linearly with increasing water vapor content. This suggests that the normalized H_α intensity can be used as a marker for water vapor detection and quantification. Despite the linear trend in all three of the emission intensity signals, it is apparent that as the water mole fraction is increased beyond 0.5 the uncertainty in the measurements increases. This is due to the fact that at high water vapor loading, there is the possibility of condensation taking place inside the plasma cell. It should be noted that a slight nonlinearity in the emission is observed for the low water mole fraction range (i.e., 0–0.025). Presumably, this is related to the heavy particle reactions between helium and water (e.g., Penning ionization and charge transfer). A definitive understanding of this behavior is still being pursued at this stage. Exemplar false-colored images of the plasma discharge are also presented in Fig. 2 as insets. It is apparent that with an increase in the water vapor content, the discharge radially constricts and its emission intensity decreases owing to both transport and electronegative behavior of water. Introduction of water in plasma reduces the electron density via attachment reactions which also act as an energy sink and reduce the electron temperature, leading to reduced emission. In addition, compared to helium, water has lower diffusivity, which contributes to the observed constriction as well. However, the emission intensity of H_α decreases at a lesser gradient than that of excited states of helium, thus rendering the fractional intensity ratio of H_α to that of [H_α + He(x)] to attain a positive slope. The radial constriction of the discharge also increases the current density for the same discharge current. It is observed that for a constant discharge current the discharge constricted almost by a factor of ~4.0 for the entire range of moisture loading. To increase the maximum limit of water loading without possible condensation taking place, additional experiments were conducted at

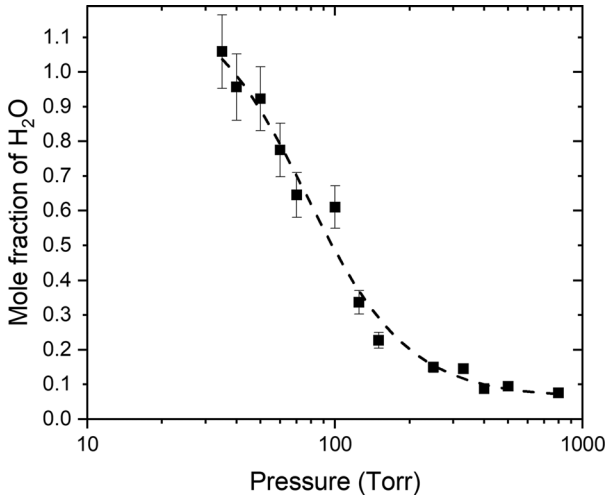

FIG. 3. Variation of water concentration with pressure observed inside the fuel casket during the vacuum drying process.

2 Torr for 2.0 mA discharge current. The water vapor mole fraction was increased up to ~0.65, and similar linear trends of the emission intensity ratios were observed.

To determine if the emission signals have similar linear trends for different discharge parameters, a range of experiments were conducted for different discharge currents and operating pressures. It was found that the normalized intensity signals of $H_\alpha/[H_\alpha + He(3^3D)]$ at different discharge parameters collapsed on top of each other (not shown here) and still maintained a linear trend. Since the plasma discharge that is used as the source for the different excited states is operated in the "normal glow" mode, an increase in the current does not increase the current density but only the discharge cross-sectional area. This is because, in the "normal glow" regime of operation, the discharge maintains a constant electron, ion, and excited state number density value.[11] A larger cross-sectional area/volume of the discharge results in a higher spatially averaged emission intensity acquired by using the optical probe, but the relative increase in the intensity of H_α with respect to that of each of $He(3^3D)$, $He(3^1D)$, and $He(3^3S)$ is similar. Consequently, the normalized intensity still maintained a linear trend as a function of the water content for the different operating pressures and discharge currents.

The plasma discharge cell and the associated diagnostics are connected to a mock nuclear fuel rod assembly to acquire and detect real-time gas composition data, representative of a vacuum drying process (Fig. S1 of the supplementary material). Details of the mock nuclear fuel rod drying experiment are provided in Ref. 12. The fuel rod assembly cask (484 l in volume) is wetted with a known amount of water. The cask is then purged and pressurized to 1 atm with helium and then progressively vacuumed in multiple stages to promote the drying process. A small stream of outflow gas from the cask is bled off into the OES cell, maintained at a pressure of 2 Torr in which the emission intensity is measured. Exemplar OES signals are also provided in the supplementary material (Fig. S2).

Figure 3 shows the water vapor concentration as a function of vacuum pressure in the mock fuel rod assembly. The water concentration was determined from the extensive database of the water vapor emission signals for ranges of current and pressure showing the variation of H_α to $[H_\alpha + He(3^3D)]$. It is observed that up to 200 Torr, the concentration of water vapor remains mostly unchanged but increases exponentially thereafter. The plot also shows that below 30 Torr, the resulting pressure is predominantly the partial pressure of water vapor, reconfirmed by measurements by using relative humidity sensors. It is to be noted that even though the existing signal marker database accounts for a maximum of 0.65 mol fraction of water, this database has been extrapolated to quantify mole fraction as high as 1.0. The validity for this extrapolation stems from the strong linear correlation between the normalized ratio of the signal intensity and the concentration of water.

In summary, a plasma based optical emission spectroscopy technique has been developed for detecting and quantifying water vapor concentration in moisture enriched flow conditions. The normalized fractional intensity of H_α was identified to have a strong linear dependency on the water vapor content in the gas stream and therefore was selected as a detection and quantification marker. It was further found that the normalized intensity was independent of the plasma discharge current conditions in the "normal glow" regime of operation of the discharge as well as the vacuum operating pressure. The proposed methodology has been applied to effectively characterize outflow gases from vacuum drying of a mock nuclear used fuel assembly.

See supplementary material for the schematic of the setup of mock nuclear fuel rod drying experiments and exemplar OES signals.

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[1]USNR Commission, Standard Review Plan for Dry Cask Storage Systems (Office of Nuclear Material Safety and Safeguards, Washington, DC, 20555-0001, 1997).
[2]L. Miller, D. Basu, K. Das, T. Mintz, R. Pabalan, and G. Walter, Prepared for US Nuclear Regulatory Commission Contract NRC-02-07-006, 2013.
[3]X. He, R. Benke, Y.-M. Pan, L. Caseres, P. Shukla, K. Chiang, R. Pabalan, G. Willden, and D. Vickers, ML14323A067, US Nuclear Regulatory Commission, Washington, DC, 2014.
[4]Y. Mayeresse, R. Veillon, Ph. Sibille, and C. Nomine, "Freeze-drying process monitoring using a cold plasma ionization device," PDA J. Pharm. Sci. Technol. **61**, 160–174 (2007).
[5]A. Kauppinen, M. Toiviainen, O. Korhonen, J. Aaltonen, K. Järvinen, J. Paaso, M. Juuti, and J. Ketolainen, Anal. Chem. **85**, 2377–2384 (2013).
[6]F. F. Andrawes, Anal. Chem. **55**, 1869–1872 (1983).
[7]S. Hanamura, B. Kirsch, and J. D. Winefordner, Anal. Chem. **57**, 9–13 (1985).
[8]F. P. Sainct, D. A. Lacoste, M. J. Kirkpatrick, E. Odic, and C. O. Laux, J. Phys. D: Appl. Phys. **47**, 075204 (2014).
[9]S. Yonemori, Y. Nakagawa, R. Ono, and T. Oda, J. Phys. D: Appl. Phys. **45**, 225202 (2012).
[10]T. Verreycken, N. Sadeghi, and P. Bruggeman, Plasma Sources Sci. Technol. **23**, 015009 (2014).
[11]T. Farouk, B. Farouk, D. Staack, A. Gutsol, and A. Fridman, Plasma Sources Sci. Technol. **15**, 676 (2006).
[12]T. W. Knight, J. Khan, T. Farouk, and J. Tulenko, in *Proceedings of International High-Level Radioactive Waste Management Conference* (American Nuclear Society, 2017).