Pulsed Discharge Helium Ionization Detector for Highly Sensitive Aquametry

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Trace moisture quantitation is crucial in medical, civilian and military applications. Current aquametry technologies are limited by the sample volume, reactivity, or interferences, and/or instrument size, weight, power, cost, and complexity. We report for the first time on the use of a pulsed discharge helium ionization detector (PDHID-D2) (~196 cm³) for the sensitive (limit of detection, 0.047 ng; 26 ppm), linear (r² >0.99), and rapid (< 2 min) quantitation of water using a small (0.2 - 5.0 μL) volume of liquid or gas. The relative humidity sensitivity was 0.22% (61.4 ppmv) with a limit of detection of less than 1 ng moisture with gaseous samples. The sensitivity was 10 to 100 to fold superior to competing technologies without the disadvantages inherent to these technologies. The PDHID-D2, due to its small footprint and low power requirement, has good size, weight, and power-portability (SWAPP) factors. The relatively low cost (~$5000) and commercial availability of the PDHID-D2 makes our technique applicable to highly sensitive aquametry.

Keywords Pulsed discharge helium ionization detector, PDHID-D2, water quantitation, aquametry, gas samples, humidity measurements

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Introduction

Due to its ubiquitous presence, water is a major contaminant in anhydrous applications, requiring stringent dehumidification and quantitation of moisture traces.1 Water is a polar molecule and physisorbs to a broad range of surfaces,2 making it difficult to be completely eliminated from moisture-sensitive reagents during anhydrous reactions.3 Moisture contamination can lead to corrosion, aging and catastrophic failures, such as in the case of nuclear weapon and/or nuclear fuel components.4 The electrical properties of cables, connectors and insulators are affected by water traces. For example, the electrical properties of Kapton, a polyimide component of electrical cables, are affected by humidity.5 Water causes the oxidative degradation of lubricants and hydraulic oils by combining with H₂S or CO₂, forming acids and ultimately corroding machinery.6 Moisture-free ultra-high purity (UHP) gases are required for accurate determinations by TCD. Gravimetry, based on the weight difference of a sample before and after volatilization, estimates the total volatiles in a sample, not just water. There were reports of aquametry in the 1970’s and 1980’s using gas chromatography (GC) with a helium ionization detector (HID); however this detector utilized a tritium foil for ionization.7 The detector used here was a non-radioactive version, first described in 1992.8 The aquametry of headspace vapor has been demonstrated by pulsed discharge helium ionization detector (PDHID); however that system was more complex, and used larger sample volumes9 relative to the volume (0.25 μL) reported here. With respect to methods using a fixed sample size, the method described here enables the use of smaller sample volumes; also, the detector has been shown to be robust upon exposure to a wide variety of other chemical species (organics, inorganics, chlorinated, sulfur-containing compounds, etc.).10 Aquametry methods that typically use a flowing sample configuration include mass spectrometry (MS), near infrared (NIR), Cavity Ring-Down Spectroscopy (CRDS), Fourier transform infrared (FTIR), and tunable diode laser absorption spectroscopy (TDLAS).8,9,10 Although such technologies can achieve ppb (parts per billion) sensitivity, they require a...
continuous sample flow and/or sample volumes of 100 μL or more.10 Some require laboratory-sized, bench-scale equipment, which is unsuited for field aquametry or applications in which only a small sample volume is available for analysis. In addition, commercially available sensors used for flowing samples are not configured for liquid aquametry.

We describe for the first time, a commercially available pulsed discharge helium ionization detector (PDHID-D2), for highly sensitive, quantitative aquametry with a limit of detection (LOD) of 0.047 ng water. The same detector was used for both liquid and gas aquametry. A flowing gas was not required, and the method utilized significantly smaller sample sizes (100 to 1000-fold lower) than many competing technologies. The PDHID-D2, due to its small footprint and low power requirement, has excellent SWAPP factors that could be combined with fully portable GC systems.15,16 The relatively low cost (~$5000)10 and commercial availability of the PDHID-D2 makes our technique applicable to field aquametry and/or applications that have limited sample size.

**Experimental**

**Reagents and chemicals**

Helium (He) (99.999% pure) was purchased from Mattheson Tri-Gas (Albuquerque, NM), and purified further with a He gas purifier before using it as the carrier gas with the PDHID-D2 (VICI, Valco Instruments Co. Inc., Houston, TX). Salts, including potassium hydroxide, calcium bromide, potassium acetate, magnesium chloride, sodium bromide, sodium chloride, potassium chloride, and potassium sulfate, and solvents used in the preparation and dilution of gas chromatography (GC) samples, as well as all other chemicals were of reagent grade and purchased from Sigma-Aldrich (St. Louis, MO).

**Sample preparation**

Commercial benzene was dried using a 3-angstrom molecular sieve desiccant purchased from Sigma-Aldrich. The desiccant itself was pre-dried immediately before use. Solvent drying was by either allowing the benzene to stand over the desiccant under nitrogen or by passing the solvent over a column of the desiccant, as described previously. Water was then gravimetrically back-added to the benzene samples in order to construct the moisture standards calibration chart.

In the case of gas samples, saturated salt solutions were used to generate headspace samples with a wide range of relative-humidity (RH) values for subsequent analysis using the GC-PDHID-D2. Various RH salt standards were used in the creation of the humidity calibration curves as follows: KOH, 7.38% RH; CaBr2, 16.50% RH; CH3COOK, 21.61% RH; MgCl2, 32.44% RH; NaBr, 56.03% RH; NaCl, 75.09% RH; KCl, 83.62% RH and K2SO4, 97.00% RH. The autosampler had a heated agitator and a 6890N GC oven with DB-5 GC column (30 m × 0.32 mm × 0.25 μm film coating. Agilent Technologies, Santa Clara, CA) were used in the analyses. The GC oven was maintained at 30°C, the inlet to 250°C, a column pressure of 82.7 kPa with a split ratio of 10:1. A volume of 5 μL from the headspace of the RH salt standards was injected into the GC column with He being the carrier gas. The hold time for each GC run was 2 min, and the retention time for water was ~96 s. For each RH salt standard, ten separate sample injections were made in order to calculate the average and standard deviation values of the various measurements.

The data acquisition system was setup with the PDHID-D2 attached to the outer wall of the GC oven with the column running from the 6890N oven into the PDHID-D2. The flows for the system had an exit rate of 31.8 mL/min, a purge flow rate of 2.68 mL/min, and a split flow rate of 29.8 mL/min. The PDHID-D2 was linked to a VICI Valco Instrument Pulsed Discharge Controller, which controlled the PDHID-D2, and this was set to 275°C. The VICI was linked to an Agilent E3630A 0–6 V, 2.5 A power supply and to an NI_USB 6281 NIDAQ system (National Instruments Corporation, Austin, TX) for data acquisition. Data were acquired using the LabVIEW 2013 software program (National Instruments Corporation) in the differential mode. The entire setup allowed for an automatic trigger from the autosampler, which separated the data runs into individual data loops.

Other instrumentation for moisture content analyses of the spiked benzene solutions and room temperature RH analyses included a capillary GC column (Thermo Finnigan Corp., San Jose, CA), liquid injection autosampler (CTC Analytics, Model A200S, Lake Elmo, MN), and heated transfer line (Clayborn Labs, Truckee, CA). The signal response from the PDHID-D2 control unit electrometer was streamed into a LabVIEW data acquisition logger (NI_USB-6251, 16 bit) and control program. The peak area and the peak height were calculated as nA·s and nA, respectively. Each sample was injected at least in triplicate during sensitivity determinations. The linearity was determined by the correlation coefficient, r2 values. Additional GC operational details as well as detection using the PDHID-D2 and the calculation techniques for sensitivity (LOD) were comprehensively described previously.

**Data calculations**

Briefly, calibration data were used to create a X/Y scatter plot with a regression line. Standard errors of slope and the y-intercept were calculated from the residuals (difference
between the measured y value and calculated y) from the equation \( y = bx + a \), where \( b \) is the slope of the regression line, \( x \) is the unknown analyte concentration, and \( a \) is the y-intercept. The LOD was considered to be a theoretical value of the lowest peak area that the PDHID-D2 could detect based on the baseline noise. To determine this value, the LabView program was used to determine the peak area of the baseline before any species eluted, (80 – 85 s). The average (\( \mu \)) and standard deviation (\( \sigma \)) of these values were also determined. The LOD was then determined to be \( \geq \mu + 3\sigma \), as this encompasses 99.7% of the noise.\(^{19} \) The limit of quantitation (LOQ) would be the LOD multiplied by a factor of three.\(^{19} \) Linearity calculations were carried out using Kaleidagraph software (Ver. 2.0, Synergy Software, Reading, PA).

### Results and Discussion

#### Liquid aquametry

The PDHID-D2 can ionize and detect all compounds with an ionization potential (IP) of \(< 19.8 \text{ eV}^{14,21} \). Since the IP of water is \( 12.6 \pm 0.01 \text{ eV}^{22} \), it was considered to be possible to quantitate water using the PDHID-D2. We first demonstrated the sensitivity and linearity of aquametry in experiments involving liquid samples conducted under ambient temperature and pressure conditions (Fig. 1). We used the direct injection of 0.2 \( \mu \)L of dried benzene containing various quantities of back-added water for these experiments, since water was reported to be a frequent contaminant of organic solvents.\(^{23} \) The tests were also conducted in accordance with the five-point calibration recommended by the United States Environment Protection Agency (US-EPA) method.\(^{24} \) Increasing concentrations of water spiked into benzene produced increasingly larger water peaks emerging from the GC column at ~96 s post-sample injection as detected by the PDHID-D2 (Fig. 1). The peak observed at 91 s is due to ambient air (consisting of nitrogen, oxygen, carbon dioxide, etc., that are typical for our location in Albuquerque, NM, USA) in the autosampler needle and/or dissolved in the benzene that was also injected. Because it was impractical to completely dry the benzene, the smallest water peak in Fig. 1 represents the baseline water remaining in the benzene. The technique demonstrated excellent linearity (\( r^2 > 0.99 \)) regardless of whether the PDHID-D2 response was analyzed as peak height (nA) or peak area (nA·s) (Fig. 2). The sensitivity profile was determined to yield an LOD value of 0.047 ng of water. This is equivalent to 26 ppm with the split ratios used here for benzene injections. A lower split ratio would allow for the detection of moisture at lower liquid concentrations.

#### Gaseous aquametry

The mass sensitivity determined above can be put into context for gaseous aquametry by observing the signal obtained for 1.0 \( \mu \)L volume gas injections of RH salt standards shown in Fig. 3. Under the conditions used, these injections correlated to the following ng of water per microliter (\( \mu \)L) at 23°C: 23% RH, 4.7 ng/\( \mu \)L; 75% RH, 15.5 ng/\( \mu \)L and 98% RH, 20.2 ng/\( \mu \)L.

![Fig. 1](image1.png)

Fig. 1 Elution profiles of air (91 s) and water spiked in benzene (96 s). Indicated and increasing concentrations of water spiked into benzene were eluted from the GC and detected using the PDHID-D2. The solid tracing is the zero-spike background and the various broken, dotted or dashed tracings with increasing peak heights represent the following amounts (nanograms to detector) of water spiked into benzene: 0.12, 0.16, 0.22, 0.33, and 0.83.

![Fig. 2](image2.png)

Fig. 2 Water calibration profiles with the detector response being shown in peak height (open circles, nA) or peak area (open squares, nA·s). Panel A shows the detector response to water spiked into benzene (mg/mL) and Panel B shows calculated nanograms (ng) of water reaching the detector. The linearity (correlation coefficient, \( r^2 \)) of the various calibration tracings was greater than 0.99.
using a polymer wire quartz tuning fork sensor for aquametry.25

calculated using the expression to the 40% RH at which the first inflection point occurred when 6 s longer, eluting between 103 to 104 s (Fig. 3), compared to frost point of –46.2

Retention time for water in gaseous aquametry was about 96 s for liquid aquametry (Fig. 1), due to slightly different column flow rates and split flow conditions. The estimated detection limit of 0.22% RH is approximately equal to 61.4 ng/L moisture in the sample; broken/dashed line, 78% RH corresponding to 20.2 ng/L sample. The experiments were carried out at room temperature (~23°C).

(Fig. 3). These values assume ideal gas behavior and are calculated using the expression \( A = \frac{C \times p_w}{T} \), where \( A \) is the absolute humidity (g/m³), \( C \) is the molar mass of water over the gas constant, \( p_w \) is vapor pressure in kPa, and \( T \) is the temperature in K. Based on this and the liquid aquametry LOD of 0.047 ng, we were able to estimate a vapor detection limit of 0.22% RH in our laboratory (Albuquerque, NM, barometric pressure conditions 620 torr and 23°C). This corresponds to an estimated frost point of –46.2°C for an injection volume of 1.0 mL. The retention time for water in gaseous aquametry was about 6 s longer, eluting between 103 to 104 s (Fig. 3), compared to 96 s for liquid aquametry (Fig. 1), due to slightly different column flow rates and split flow conditions. The estimated detection limit of 0.22% RH is approximately equal to 61.4 parts per million by volume (ppmv) at one atmospheric pressure and 20°C.\( \text{This value was more than 150-fold lower compared to the 40% RH at which the first inflection point occurred when using a polymer wire quartz tuning fork sensor for aquametry.}^{25}

The PDHID-D2 detection limit was comparable to the RH values of 0.075 to 1.20% reported using a perfluorosulfonate ionomer composite.\( \text{26}

Early detection and prevention of moisture-induced damage is critical to the oil and natural gas industry, where an LOD of 10 to 50 ppmv is desirable with the chosen aquametry technology. The aquametry sensitivity using the PDHID-D2 is near to this range (using only 1.0 μL of gas) for gaseous aquametry and 100 to 500-fold below this range for liquid aquametry, as applicable to the oil and natural gas industry. Although, a detection limit of 1 – 10 ppm was achievable using KFT,26 but without the disadvantages of these latter techniques.\( \text{In KFT, there is a requirement for large (5 - 15 g) samples. It is essential to have some prior knowledge regarding the water level in a given sample in order to choose the proper analytical method.}^{27}

These disadvantages are eliminated by the PDHID-D2 aquametry. Although the moisture LOD obtained using the PDHID-D2 did not match the higher sensitivity reported using TDLAS/NIR,\( \text{TDLAS hygrometers are expensive.}^{10}

The range of RH values over which the PDHID-D2 was used overlapped with the range reported using competing technologies.

The results generated by injecting 1.0 μL of gas with different RH values demonstrated both the linearity (\( r^2 >0.99 \)) and the suitability of the PDHID-D2 for aquametry of gaseous samples (Fig. 3) in addition to liquid samples (Fig. 1). The results also confirmed the need for extremely small sample volumes in order to conduct aquametry using the PDHID-D2. Similar results were obtained by injecting either 5.0 or 0.2 μL of gaseous samples under 620 Torr ambient atmospheric pressure demonstrating flexibility in the facile handling of at least one order of magnitude sample volume (data not shown). At these injection volumes, the 22 to 98% RH values corresponded to 0.91 to 101 ng of water quantitation, which equaled 2 orders of magnitude water concentration range that could be detected using the PDHID-D2. Extrapolation of the calibration tracing using the curve fit option of the software showed that less than 1% RH quantitation was possible using the PDHID-D2 (Fig. 3). This technique was thus once again found to be superior to the tuning fork aquametry.\( \text{25 Since the system uses a smaller flow/}

volume than commercial flow-through systems, this makes it relevant to our small-analysis volume measurements described in this paper. Overall, the PDHID-D2 data were similar to the RH measurements with the perfluorosulfonate ionomer or KFT,\( \text{but without the disadvantages of these latter techniques.}

Humidity aquametry

Using a second GC system with better temperature control of the samples but with the same PDHID-D2 detector, humidity measurements were made using the headspace of saturated RH
salt standard solutions and the results are shown in Fig. 4. An eight-point linear calibration curve was constructed from ten independent headspace (vapor) injections of samples in the range of 7.38 to 97.00% RH. The data showed that aquametry performed using the PDHID-D2 was indeed applicable to extremely sensitive RH determinations. The calibration profile (Fig. 4) showed excellent linearity ($r^2 > 0.99$) and the sensitivity (LOD) was down to 1 ng of water, using only 5.0 μL of gas. Even lower levels of moisture traces were potentially detectable using the PDHID-D2, while still utilizing volumes significantly smaller than those required by typical flowing-gas techniques.

Although water had been detected using PDHID previously, these reports were limited to preliminary observations, and presented no quantitative/sensitivity data. Thus, various publications have reported that water could be detected using PDHID or incidentally reported on RH impacting the detection of another compound such as toluene.32 Only Jalbert et al. quantitated water in oil and reported a detection limit of 0.1 μg/g (0.1 ppm) for dissolved water using two regular sized PDHID units (PDHID D-3-I-HP, VICI Valco Instruments) instead of the single PDHID-D2 used in the present study and with a better LOD outcome (Fig. 1). Furthermore, the PDHID D-3-I-HP occupies a minimum volume of approximately 702 cm³, whereas the PDHID-D2 is nearly one quarter of the size of the D3 unit. Thus, to the best of our knowledge, the present report is the first of its kind reporting on the use of a PDHID-D2 for highly sensitive aquametry that was supported by quantitative analyses.

**PDHID-D2 advantages**

Trace water quantitation (aquametry) has important civilian, medical, and military applications. Current aquametry technologies suffer from one or more disadvantages of SWAPP factors, interfering compounds, cost and complexity. We report, for the first time, on the highly sensitive (LOD, 0.047 ng, linear ($r^2 > 0.99$)) detection and quantitation of water using 0.2 – 5.0 μL of liquid or gas samples within 2 min using a commercially available PDHID-D2 detector. The LOD was 10- to 500-fold lower than previously reported sensitivity values using competing technologies with fixed volume samples such as the thermal conductivity detector (TCD) or a polymer-based tuning fork water sensor or KFT. Unlike KFT for moisture analysis, our technique directly and specifically detected and quantitated the target analyte (moisture) and the measurements were unaffected by the presence of interfering substances because they are separated out chromatographically. Recently, both TCD and barrier ion discharge detector (BID) were used to detect water at the micrograms level using headspace gas chromatography (HSGC). The authors claimed that 100 μg of water was “easily determined.” These data were 50 000-fold less sensitive compared to our LOQ of 0.046 ng water. Ionic liquids (ILs) were employed by Frink et al. for headspace sampling unlike saturated salt RH standards (Fig. 4). The difference in sensitivity may also be due to the choice of detectors employed (BID and TCD in the cited work) or vis-à-vis PDHID-D2 of the present work. As discussed below, PDHID is more sensitive compared to TCD. The sample volumes required are also significantly smaller than those utilized by techniques with flowing sample configurations. The PDHID-D2 has a small footprint (~196 cm³), and requires lower power for operating with a portable He gas canister. Furthermore, since the PDHID-D2 is commercially available, it is immediately applicable to a broad range of aquametry or dehumidification situations, such as UHP gas analyses for the semi-conductor industry or preventing moisture-induced corrosion in nuclear weapon or nuclear fuel systems. The PDHID-D2 is also unlike other aquametry technologies that involved large, bench-top instruments or remained laboratory curiosities and have not transitioned into the commercial realm. Furthermore, in a study involving direct comparisons with other applications, the PDHID matched the performance of the flame ionization detector (FID), and was more sensitive than the TCD, during high speed gas chromatography. The PDHID is also advantageous, since it does not involve radioactive and toxic elements (radium, beryllium) used in neutron scattering for indirect aquametry or the mandatory frequent servicing of tensiometers for aquametry. Additional advantages of the present technology include an approximately 50% lower cost of the PDHID ($<$5000) compared to other aquametry instruments that have been characterized as “low” due to a price point of below $100 000.

**Conclusions**

Aquametry is critical to a broad range of applications. Although a variety of techniques for aquametry have been reported in the literature, only a few have been adopted widely. Several lab-scale detection techniques have been reported with ppbv to pptv levels of sensitivity. However, these have remained bench-sized instruments or laboratory curiosities, and have not transitioned into a commercially viable product for widespread use. Nor are these alternate techniques readily portable for applications with small or limited sample volume and/or field use. We report, for the first time, on a commercially available PDHID-D2 for highly sensitive (ng detection of moisture; ppbv to ppb range) quantitative aquametry using both liquid and gas samples. The technique is fast (less than 2 min), requires small sample volume (0.2 to 5.0 μL), and is immediately applicable due to the availability of a low cost commercial detector, the PDHID-D2. The PDHID is one of the most sensitive universal detectors for GC applications. Our technique overcomes the disadvantages posed by competing technologies in the area of SWAPP factors. We are also fabricating a micro-PDHID (μ-PDHID) with an even better SWAPP, cost, and performance factors. We will integrate the μ-PDHID with our previously reported μGC and micro-sample preconcentrator (μPC), both of which will be coupled to a portable He gas canister, to enable a low cost, hand-portable, field aquametry instrumentation package, for onsite chemical and biological vapors and moisture measurements, in a variety of civilian, medical, and military applications. Progress in these directions is also being enabled by recent reports of other micro-discharge photoionization detectors for μGCS.

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