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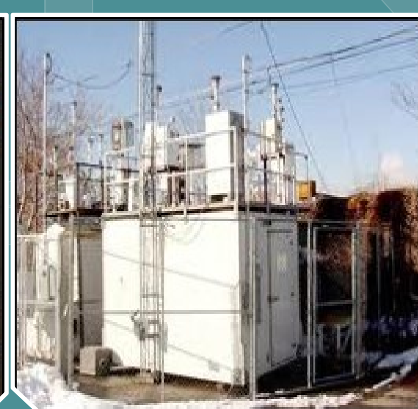
Recommendations for Nationwide Approval of Nafion™ Dryers Upstream of UV-Absorption Ozone Analyzers



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Recommendations for Nationwide Approval of Nafion™ Dryers Upstream of UV-Absorption Ozone Analyzers

by

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Abstract

Ultraviolet (UV) Photometry-based ambient Federal Equivalent Method (FEM) ozone (O_3) analyzers can experience significant water vapor interferences resulting in increased measurement noise, biased concentration measurements, and slow instrument response times. The magnitude and duration of these biases is particularly noticeable during sampling events where the O_3 analyzer experiences rapid changes in the sampled air's moisture content. The U.S. Environmental Protection Agency (EPA) implemented the use of a Perma Pure (Lakewood, NJ) Nafion™ tube dryer upstream of their Thermo Environmental Instruments LLC (Franklin, MA) Model 49i O_3 analyzers at 30 Clean Air Status of Trends Network (CASTNET) National Ambient Air Quality Standard (NAAQS) monitoring sites as part of a limited evaluation and has found that this approach minimizes spectroscopic water vapor interferences to an acceptable degree.

This document summarizes the pertinent qualitative and quantitative information to foster further discussion so that a consensus decision can be made whether to approve the routine use Nafion™ dryers on a nationwide basis. The operating principle of UV Photometer-based O_3 analyzers is presented along with a discussion of known measurement interferences, with a particular emphasis on atmospheric water vapor and approaches used to minimize the magnitude of this water vapor interference. Multiple studies are discussed which demonstrate that no inadvertent loss of O_3 occurs in the Nafion™ tube dryer. The design and operational specifications of CASTNET's Nafion™ dryer system are presented along with test results of the system's use since the Office of Air and Radiation's (OAR) approval to CASTNET evaluation. Based on the results of this investigation, the EPA Office of Research and Development (ORD) has determined that the use of Nafion™ dryers upstream of UV Photometric-based O_3 analyzers on a nationwide basis is a valid means to improve the data quality of O_3 compliance measurements.

Foreword

The EPA is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

EPA's Center for Environmental Measurement & Modeling (CEMM) within ORD conducts research to advance EPA's ability to measure and model contaminants in the environment, including research to provide fundamental measurement methods and deterministic models needed to implement environmental statutes. Specifically, CEMM characterizes the occurrence, movement, and transformation of contaminants in the natural environment through the application of measurement and modeling-based approaches. CEMM scientists develop, evaluate, and apply laboratory and field-based methods and approaches for use by EPA and its state, local, and tribal partners to characterize environmental conditions in direct support of implementation of EPA programs. CEMM scientists also provide scientific expertise and leadership related to the development and application of complex computational models that provide precise and detailed predictions of the fate and transport of priority contaminants in the environment to inform the environmental policies and programs at the EPA, state, local, and tribal level.

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Acronyms and Abbreviations

AAB	Ambient Air Branch
CASTNET	Clean Air Status and Trends Network
CAMD	Clean Air Markets Division
CEMM	Center for Environmental Measurement and Modeling
CO	Carbon Monoxide
DEQ	Department of Environmental Quality
EPA	Environmental Protection Agency
FEM	Federal Equivalent Method
FEP	Fluorinated ethylene propylene
FRM	Federal Reference Method
Hg^0	Elemental Gaseous Mercury
Lpm	Liters per minute
NAAQS	National Ambient Air Quality Standards
nm	nanometer
NO_2	Nitrogen Dioxide
O_3	Ozone
OAP	EPA Office of Atmospheric Programs
OAQPS	EPA Office of Air Quality Planning and Standards
OAR	EPA Office of Air and Radiation
ORD	EPA Office of Research and Development
ppb	Parts per billion
ppbv	Parts per billion by volume
ppt	Parts per trillion
RH	Relative Humidity (%)
SO_2	Sulfur Dioxide
TFE	Tetrafluoroethylene
UV	Ultraviolet
VOC	Volatile Organic Compounds

Acknowledgments

The authors acknowledge the useful comments from John Birks and Andrew Turnipseed of 2B Technologies Inc., those of Bob Judge of EPA Region 1, Joann Rice (OAQPS) and Matthew Landis (ORD). We also acknowledge the receipt of Nafion™ dryer performance data and information from Jeff Gobel (NC DEQ) and Timothy Sharac (EPA CAMD).

Executive Summary

Ultraviolet (UV) Photometry-based ambient ozone (O_3) analyzers can experience significant water vapor interferences resulting in increased measurement noise, biased concentration measurements, and slow instrument response times. The magnitude and duration of these biases is particularly noticeable during sampling events where the O_3 analyzer experiences rapid changes in the sampled air's moisture content. The U.S. Environmental Protection Agency (EPA) implemented the use of a Perma Pure Nafion™ tube dryer upstream of their Thermo Environmental Model 49i O_3 analyzers at 30 Clean Air Status of Trends Network (CASTNET) National Ambient Air Quality Standard (NAAQS) monitoring sites as part of a limited evaluation and has found this approach minimizes spectroscopic water vapor interferences to an acceptable degree.

The operating principle of UV Photmetric-based O_3 analyzers is presented along with a discussion of known measurement interferences, with a particular emphasis on atmospheric water vapor and approaches used to minimize the magnitude of this water vapor interference. Multiple studies are discussed which demonstrates that no inadvertent loss of O_3 occurs in the Nafion™ tubing. The design and operational specifications of the CASTNET implemented Nafion™ dryer system are presented along with test results of the system's performance. Based on the results of this investigation, the EPA Office of Research and Development (ORD) has determined that the use of Nafion™ dryers upstream of UV Photometric-based O_3 analyzers on a nationwide basis is a valid means to improve the data quality of O_3 compliance measurements.

1.0 Introduction

Water vapor interferences can bias ambient O_3 measurements in gas-phase UV absorption analyzers under certain sampling circumstances. In 2017, EPA's Office of Air and Radiation (OAR) approved the use of Nafion™ dryers upstream of designated Federal Equivalent Method (FEM) UV Photometric-based O_3 analyzers in the CASTNET. This approval was based on a request from EPA's Clean Air Markets Division (CAMD) and a review of pertinent information at the time. The use of the dryers was designed to help address instrument noise, response time issues, and bias issues observed in CASTNET's UV-based O_3 analyzers. These issues were due to the presence of excessive water vapor in the ambient air, particularly during events where the analyzer experiences rapid changes in the sampled air's water vapor concentrations.

EPA approved CASTNET's use of the Nafion™ dryer upstream of the instrument in the sampling train. EPA's approval, therefore, was not a modification of a previously designated O_3 analyzer per the 40 CFR Part 53 specifications but an interpretation of the specifications in Part 58 "Ambient Air Surveillance". Specifically, Section 9 of Part 58's Appendix E states that "…borosilicate glass, fluorinated ethylene propylene (FEP) Teflon® or their equivalent must be the only material in the sampling train (from the inlet probe to the back of the analyzer) that can be in contact with the ambient air sample…". As documented in Appendix A., OAR's June 2017 Nafion™ Dryer Approval Letter to CAMD, of this document, EPA's approved use of the Nafion™ dryer in the CASTNET network was based on its determination that Nafion™ represents a suitable "equivalent" material in the sampling train.

EPA's 2017 approval was deliberately designed to apply only to the CASTNET network. Since then, however, EPA has received inquiries from other monitoring organizations (e.g., NC Division of Air Quality) seeking the approved use of Nafion™ dryers in their own monitoring networks as a means of addressing UV-based O_3 measurement biases due to the presence of water vapor. As a result, EPA is now considering approving the use of a Nafion™ dryer upstream of all currently designated UV-based O_3 analyzers on a widespread basis, rather than on a case-by-case basis.

2.0 Operating Principle of UV-based O_3 Photometers

Figure 1 depicts the general design and operation of a UV-based O_3 photometer (2B Technologies, Model 106-L, 2014).

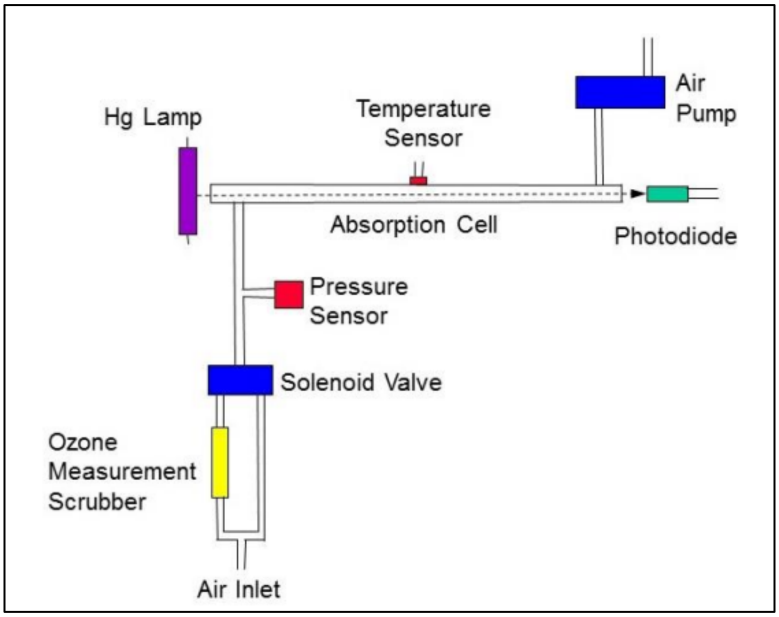

Figure 1. Schematic diagram of the 2B Technologies Model 106-L O_3 analyzer.

Ambient air is continuously drawn through the instrument's detection cell using a calibrated air pump, and the concentration of O_3 in the cell is determined by UV absorption. A mercury vapor lamp generates UV light at a wavelength of 253.7 nm, which corresponds to the peak absorption of O_3. The photodiode's response is inversely proportional to the concentration of O_3 in the detection cell. Upstream of the detection cell, a solenoid valve alternately directs the sample through and around a high efficiency solid-phase catalytic O_3 scrubber. The purpose of the scrubber is to convert O_3 molecules into oxygen molecules thus enabling matrix-matched background / reference measurements to be made in the absence of O_3. Scrubbers may be composed of potassium iodide, mixtures of magnesium dioxide and copper oxide (Hopcalite), metal-oxide coated screens, or heated silver wool (Turnipseed et al., 2017). The Beer-Lambert law is used to calculate O_3 concentration by comparing the measured intensity in the absence of O_3 (I_0, scrubbed sample) to that intensity in the presence of O_3 (I, unscrubbed sample):

$$Ozone\ concentration = \frac{1}{\sigma L}\left[\frac{Io}{I}\right]$$

where σ is the absorption cross section of O_3 and L is the path length of the detection cell. Dependent upon instrument design, I and I_0 values may be measured every few seconds, thus enabling an O_3 concentration determination approximately every 10 seconds. Some instruments have two cells and measure I and I_0 simultaneously, switching between the cells regularly to address any cell-specific biases. Temperature and pressure measurements within the air path enables measured concentrations to be expressed on a volumetric basis (i.e., ppbv). Although the O_3 concentration can theoretically be determined solely from the above equation, periodic instrument calibration is necessary to account for inlet losses, non-ideal scrubber efficiency, scrubber and cell condition, exact absorption cell geometry, and non-linearity in photodiode and amplifier response. A properly calibrated and operated O_3 compliance analyzer can measure O_3 concentrations with an accuracy and precision of approximately ±1 ppb.

2.1 Interference of Atmospheric Chemicals

Positive measurement interferences in UV photometric O_3 analyzers could occur from atmospheric species that absorb light in the region of 253.7 nm. The use of a two-channel UV photometric O_3 analyzer helps to mitigate the interference from volatile organic compounds (VOCs), with the assumption that the scrubber destroys O_3 but passes interfering VOC species. In particular, VOCs and elemental gaseous mercury (Hg^0) are noted to absorb in this range and positive measurement biases are well documented (Grosjean and Harrison, 1985; Huntzicker and Johnson, 1979; Kleindienst et al., 1993; Spicer et al., 2010). Birks et al. (2009) noted that the absorption cross section of Hg^0 was approximately 1600 times that of O_3 at a wavelength of 253.7 nm. At a baseline O_3 concentration of 75 ppb, laboratory tests (EPA 1999) showed that the presence or addition of 0.04 ppb (40 ppt) of Hg^0 would result in positive O_3 measurement biases in UV photometers of 12.8% and 6.4% at relative humidity (RH) values of approximately 25% and 75%, respectively. During this EPA study, no positive bias in Hg^0 concentrations were noted in chemiluminescent O_3 analyzers.

2.2 Interference of Atmospheric Water Vapor

While the chemical interferences previously mentioned would typically be of more significance in polluted environments rather than in clean environments, interferences due to atmospheric water vapor can be encountered under a range of sampling environments. Water vapor interferences have been reported by a variety of researchers and verified under both field conditions and in controlled laboratory tests (Meyer and Elsworth, 1991; Kleindienst et al., 1993; Leston and Ollison, 1993; Leston et al., 2005; Maddy, 1998; Parrish and Fehsenfeld, 2000; Wilson, 2005; Wilson and Birks, 2006; Spicer et al., 2010; Birks et al., 2016). These studies report that biases due to water vapor can be either positive or negative and can be significant in magnitude depending upon the sampling circumstances.

Unlike the interference mechanism mentioned for chemical interferents, water vapor does not significantly absorb wavelengths of 253.7 nm. As a result, the exact mechanism for the water vapor's interference was not immediately apparent when it was initially noted. Meyer et al. (1991) first reported O_3 measurement interferences during rapid changes in RH and associated it with the observed change in the transmission efficiency through scratched optical cells windows. Wilson and Birks (2006) conducted more focused tests and identified that rapid changes in sample moisture content can change the reflectivity of the detection cell's walls. Using a balloon-borne UV-based O_3 analyzer during vertical profiling tests, the magnitude of the bias was particularly significant when the O_3 analyzer rapidly passed through alternating wet and dry atmospheric layers. This bias mechanism of the interference of water vapor was later supported by Spicer et al. (2010) and explains why previous tests conducted under steady-state sampling conditions reported negligible effects of humidity on UV-based analyzers (Kleindienst et al., 1993).

Wilson and Birks (2006) further conjectured that it is the scrubber's interaction with the sampled airstream that accounts for variations in the detection cell wall's transmission efficiency. The O_3 scrubber can act as a water reservoir and can thus add or remove water from the sample air. Differences between I and I_0 values can occur even in the absence of O_3, depending upon recent sampling history, and explains why measurements biases can be either positive or negative and variable in magnitude. As will be discussed, Wilson and Birks later addressed this interference mechanism through incorporation of a Nafion™ tube upstream of the analyzer's absorption cell. To test this theory, Wilson and Birks conducted a series of tests using a Nafion™ tube purchased from Perma Pure LLC (Lakewood, NJ).

3.0 Characteristics of Nafion™ Tubes

Nafion™ membranes (Perma Pure LLC) are composed of a copolymer of perfluoro-3,6-dioza-4-methyl-7-octenesulfonic acid and polytetrafluoroethylene. In simpler terms, Nafion™ consists of tetrafluoroethylene (TFE) Teflon™ chemically bonded with sulfonic acid groups. The presence of sulfonic acid makes Nafion™ tubing selectively permeable to compounds (e.g., water, alcohol, and ammonia) that bind to sulfonic acids (Perma Pure, 2020). The selective permeability of Nafion™ makes it ideal for conditioning ambient air samples for subsequent pollutant analysis.

Although the term "Nafion™ dryer" is commonly used, a Nafion™ tube can either humidify or dry the tube's sampled air depending upon the differential moisture content across the membrane. If the moisture content of the air outside of the tube is higher than that inside the tube, the moisture content of the interior sample gas will increase (humidify). Conversely, if the moisture content of the air outside the tube is lower than that inside the tube, the moisture content of the interior sample gas will decrease (i.e., dehumidify). The magnitude of the change in the sampled air's moisture content will depend upon the difference in moisture content across the tube's wall and the residence time of the gas within the tube. As noted by Robinson et al. (1999), absorption and desorption of water can occur very rapidly, as evidenced by tests with a 1 m long Nafion™ tube of 1.07 mm inner diameter, 1.35 mm outer diameter operating a flow rate of 1 Lpm. Under these conditions, the Nafion™ tube sampled air was equilibrated with the surrounding air in a residence time of approximately 50 ms (0.05 sec).

Various configurations and geometries of Nafion™ tubes are commercially available. In the tube depicted in Figure 2, the differential moisture content between the airstream inside the tube and the outside the tube dictates the actual direction of the moisture transfer. The configuration shown in Figure 3 enables the user to provide a counterflowing purge gas of known moisture content to actively control the direction and extent of the sampled gas' final moisture content. Figure 3 depicts the use of dry purge gas in a counterflow orientation to actively dry the moist sample gas.

Figure 2. Photograph of single Nafion™ tube.

Figure 3. Schematic of Nafion™ tube configured with active purge air for drying of sampled airstream.

For purposes of conditioning of ambient air samples, an important property of Nafion™ is its ability to provide moisture conditioning without the loss of the pollutant of interest. With respect to monitoring the four gaseous criteria pollutants carbon monoxide, sulfur dioxide, nitrogen dioxide, and O_3 (CO, SO_2, NO_2), all are expected to experience zero loss when sampled and transferred through Nafion™ tubing (Perma Pure, 2020). High transport efficiency of O_3 through Nafion™ tubes would also be expected based on the similarity between PTFE Teflon™ and the chemically inert fluorinated ethylene propylene (FEP) Teflon™. This theoretical transport efficiency of O_3 was verified in the laboratory by Wilson and Birks (2006) at an RH of 39% using O_3 mixing ratios in the range of 0 to 350 ppbv. Linear regression of O_3 transport measurements with the Nafion™ tube present versus those measurements without the Nafion™ tube present yielded a slope of 0.9967, an intercept of 0.27 ppbv, and a correlation coefficient of 1.0000. The authors concluded that there was no loss of O_3 with the Nafion™ tube within experimental measurement uncertainty. Similar transport efficiency test results were obtained during three separate field studies using Nafion™ dryers upstream of designated O_3 analyzers.

3.1 2B Technologies Nafion™ - Equipped O_3 Analyzers

Wilson and Birks (2006) conjectured that modulation of the sampled stream's humidity by the scrubber is responsible for changing the reflectivity of the UV analyzer's absorption cell, thus accounting for noted variabilities in instrument performance during rapid changes in ambient moisture content. They proposed that equilibration of humidity of the scrubbed and unscrubbed air upstream of the absorption cell would ensure that I and I_0 values were measured at the same RH level. To test this theory, a Nafion™ tube was installed immediately upstream of a 2B Technologies Model 202 O_3 analyzer's absorption tube (Figure 4). Note that active purge air was not provided to the outside of the Nafion™ tube because achieving a specific moisture content is not actually required. Instead, the Nafion tube equilibrated the sample air with the room air in the analyzer's sampling location. This ensured that the I and I_0 measurements were conducted at the same humidity levels, minimizing the O_3 bias caused by rapidly changing ambient humidity levels.

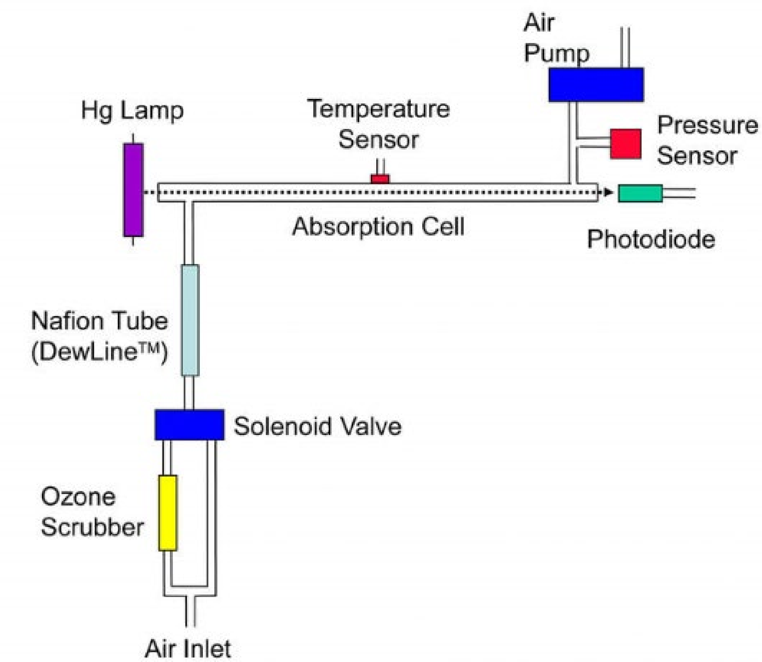

Figure 4. Schematic diagram showing location of "DewLine" Nafion™ tube upstream of the absorption cell

Wilson and Birks (2006) conducted three tests to verify the effectiveness of the system, one in dry tank air, one using room air of 39.2% RH, and one using humidified air with a RH of 93.0%. The RH of the sample air exiting the Nafion™ tube during these three separate tests was measured to be 39.3%, 39.2%, and 39.4%, respectively. These test results demonstrated the Nafion™ tube's ability to condition the incoming air to the humidity level of the analyzer's location (e.g., shelter), independent of the initial moisture content of the sampled (outdoor) airstream. A video demonstration of the DewLine's ability to moderate humidity effects under very rapid and dramatic changes in the sampled air's moisture content is available at 2B Technologies' website: https://www.youtube.com/watch?v=8Hk9w7kskDI *(last accessed 10/19/2020)*.

2B Technologies incorporates its "Dewline™" Nafion™ assembly in its EPA-designated FEM O_3 analyzers (Models 106, 106-L, 202, 205, 211 OEM-108-L, 211, 211G, and POM) as well as its EPA-designated Model 405 nm NO_2 FEM analyzer. 2B Technologies recommends that each O_3 analyzer's Dewline™ assembly be replaced during the instrument's annual scrubber replacement.

4.0 EPA's Review and Approval of CASTNET's Nafion™ Dryer Request

In early 2017, OAR received a written request from the EPA CAMD to add Nafion™ dryers upstream of Thermo 49i UV-absorbance O_3 analyzers operating in the CASTNET monitoring network. The purpose of the Nafion™ dryer's addition was to address increased instrument noise and decreased measurement response, which typically occurred during hot and humid days. The Thermo 49i instrument problems were noted when ambient dew points reached or exceeded nominal shelter temperatures of 25 °C. In such circumstances, the zero, span, and quality control (QC) checks showed slow (>30 minutes) response times.

To support their request, CAMD provided the results of field tests conducted by CASTNET's contractor (Amec Foster Wheeler) in Gainesville, FL from October 2016 through 2017. Specifically, the collocated performance of a Thermo 49i analyzer equipped with a 1.2 m long Nafion™ tube upstream of analyzer was compared to the performance of a collocated Thermo 49i analyzer without the Nafion™ tube.

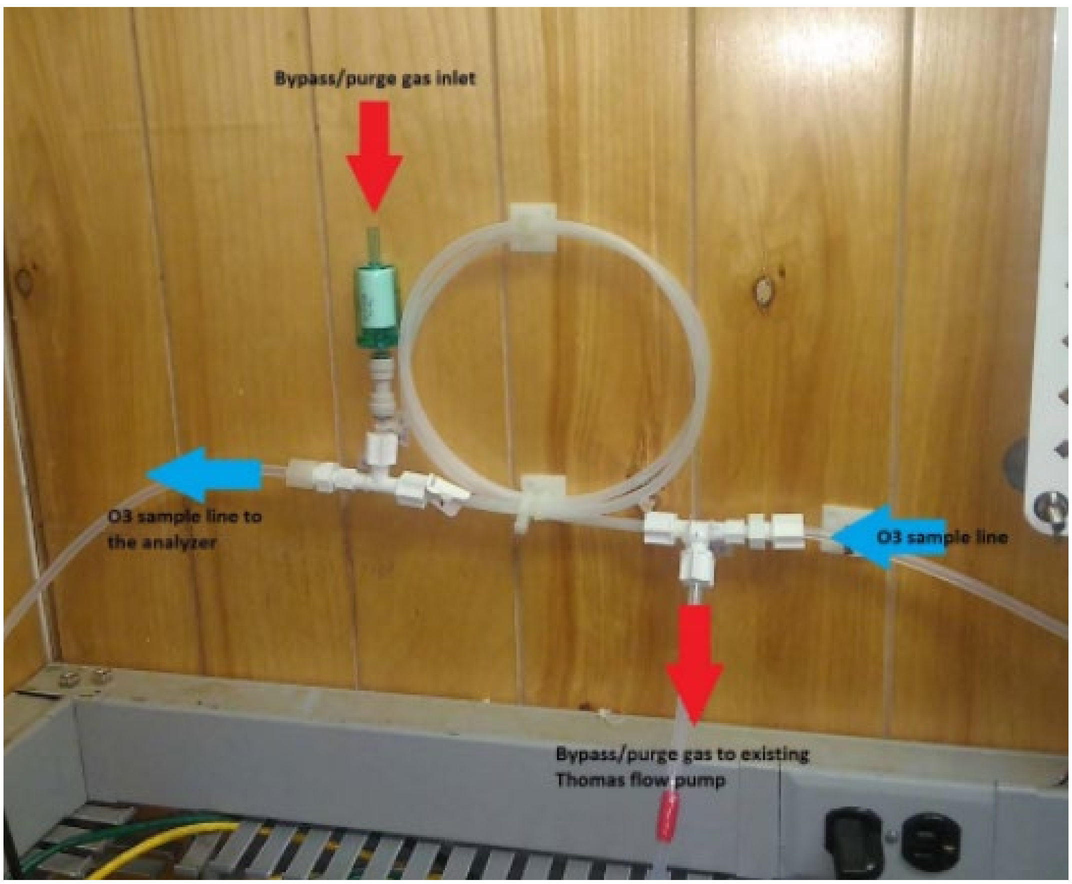

Figure 5. Photograph of CASTNET's Nafion™ assembly showing sample and purge air paths.

The configuration of CASTNET's Nafion™ assembly (Figure 5) matches that of Figure 3, with an active purge flow of shelter indoor air is provided in addition to the sampled ambient air flow. Purge flow is provided using a 20 Lpm capacity vacuum pump and the 1.3 Lpm purge air flow rate is controlled by an orifice downstream of the depicted purge air filter. The resulting 1:1 ratio of purge air flow rate to sampled air flow rate meets Perma Pure's recommended ratio of 1.0 to 3.0. The sampled air's 2.1 second residence time is expected to be more than sufficient for the sampled air's moisture content to be equilibrated to that of the purge air.

The purge air in this configuration originates from the shelter's interior air rather than from a totally dry air source. This approach avoids the additional cost, complexity, and maintenance of a provided dry air source for the purge air. Because the shelter's air naturally has some degree of moisture associated with it, there is no expectation that the sampled air exiting the Nafion™ dryer will be totally dry. Instead, use of the Nafion™ dryer is intended to reduce the sampled air's moisture content such that the resulting water vapor interference to the 49i O_3 analyzer will be acceptably low. Table 1 provides the Nafion™ dryer's design and operating specifications.

Table 1. Design and operating specifications of CASTNET's Nafion™ Dryer

Parameter	Specification
Tested UV-based O_3 analyzer	Thermo 49i FEM (EPA designation EQOA-0880-047)
49i sample flow rate	1.3 Lpm
Nafion™ tube	Perma Pure, Model # MD-110-48P-4
Nafion™ tube length	48 inches (1.2 m)
Nafion™ sample air tube's ID	0.086" (0.218 cm)
Nafion™ sample air residence time	2.1 seconds
Purge air flow rate	1.3 Lpm (nominal)
Purge air to sample air flow ratio	Approx. 1:1
Purge air inlet filter	Parker – Balston, #9933-05-DQ
Purge air flow control orifice	McMaster-Carr, size 0.010", Model #6349T42
Vacuum pump	Thomas, Model # 107CA18

4.1 October 2016 to January 2017 Evaluation Tests

Tests conducted in Gainesville, FL during this time period involved the use of two identical Thermo 49i O_3 FEM analyzers (EPA designation EQOA-0880-047). Data collected during these tests included 1-minute and 1-hour O_3 concentrations, 1-minute shelter temperatures, and 5-minute measurements of ambient temperature, RH, and dew point. The configuration of one 49i analyzer "Control Analyzer" did not change during these tests. The other 49i analyzer "Evaluation Analyzer" was not equipped with a Nafion™ dryer during the Control period nor the Post-Evaluation period but was equipped with the Nafion™ dryer during the Evaluation period. Although the October to January period is not the humid season at this location, there were a few days in which the ambient air's dew point was sufficiently close to the shelter temperature to evaluate the Nafion™ dryer's effectiveness.

4.1.1 Control Period (Oct. 21 to Nov. 27, 2016)

During this Control period, the Control Analyzer and the Evaluation Analyzer were configured identically (the Evaluation Analyzer was not equipped with the Nafion™ dryer). As shown in Figure 6, atmospheric conditions during this time period were such that the ambient air's dew point was not within 2 ºC of the shelter temperature. This test period, therefore, provided an opportunity to compare the inherent O_3 measurement performance of the two collocated Thermo 49i O_3 analyzers.

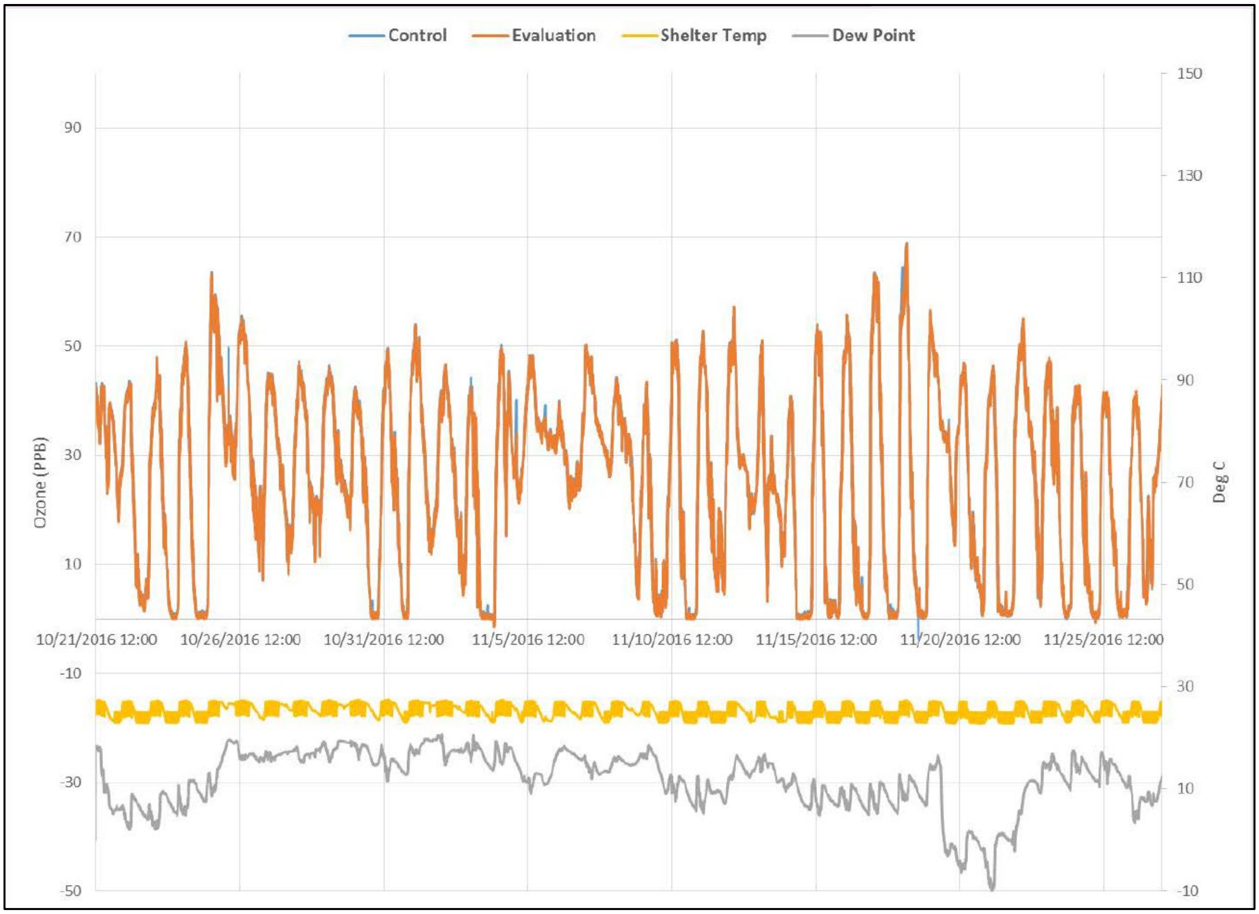

Figure 6. Control period timeline showing response of the two Thermo 49i O_3 analyzers

Visual inspection shows that the two identically configured 49i analyzers agreed well with each other during each of the test days. Linear regression of 1-minute data for the Evaluation Analyzer versus the Control Analyzer resulted in slope, intercept, and coefficient of determination (R^2) values of 0.998, -0.14 ppbv, and 0.9996, respectively. Linear regression of hourly data for the Evaluation Analyzer versus the Control Analyzer resulted in slope, intercept, and R^2 values of 0.999, -0.15 ppbv, and 0.9999, respectively. Under identical test conditions, therefore, the two Thermo 49i O_3 analyzers agreed well with each other on both a 1-minute and an hourly basis.

4.1.2 Evaluation Period (Dec. 5 to Dec. 26, 2016)

During this time period, the Evaluation Analyzer was configured with the Nafion™ dryer upstream of the analyzer. Visual inspection of the timeline during this 22-day evaluation period in Figure 7 shows that there were several days during which the shelter's interior temperature was close to the dew point. The timeline in this figure indicates that these days corresponded to noted difference in O_3 measurement response between the Control Analyzer and the Evaluation Analyzer.

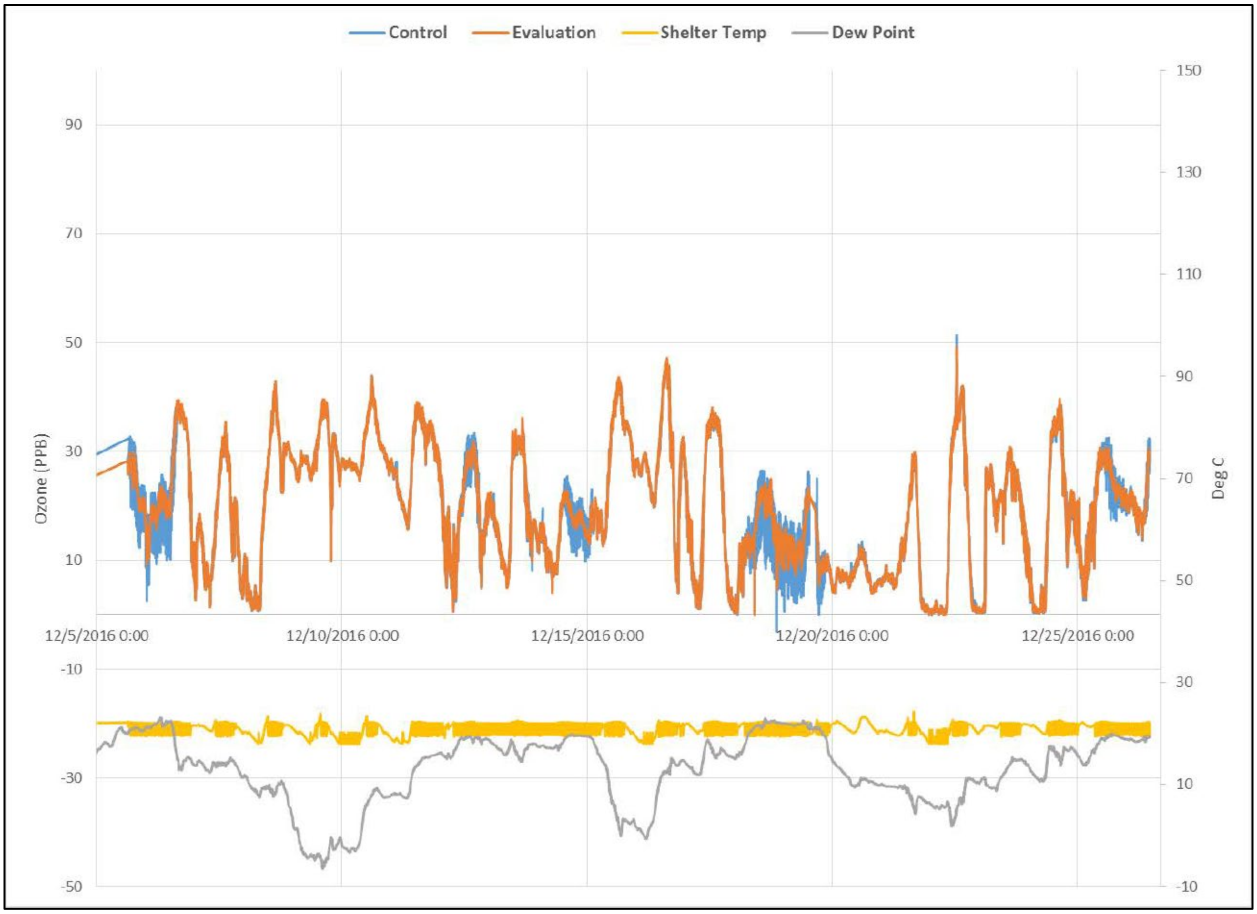

Figure 7. Evaluation period timeline showing response with the Evaluation Analyzer equipped with an upstream Nafion™ dryer.

If one considers the measurement comparability only during "dry" periods (defined as those days when shelter temperature was greater than 2 °C above the dew point), the regression of 1-minute data between the Evaluation Analyzer and the Control Analyzer resulted in slope, intercept, and R^2 values of 1.001, 0.096 ppbv, and 0.9983, respectively. This is an important observation because it supports both theoretical predictions and previous experimental results (Wilson and Birks, 2006) which concluded that there is no measurable transport loss of O_3 within the Nafion™ tube.

Regarding measurement data only during "wet" periods (defined as those where shelter temperature is within 2 °C of the dew point), the regression of 1-minute data between the Evaluation Analyzer and the Control Analyzer resulted in slope, intercept, and R^2 values of 0.859, 2.913 ppbv, and 0.8562, respectively. Compared to the data collected on "dry" days, this is a significant reduction in slope and a significant increase in intercept. The R^2 value of 0.8562 indicates that there is far less consistency in the measurement response between the Control Analyzer and Evaluation Analyzer than occurs during dry periods. This is expected if the presence of the Nafion™ dryer improves the measurement response of the Thermo 49i analyzer, as intended.

4.1.3 Post-Evaluation Period (Dec. 27, 2016 to Jan. 13th, 2017)

Following the Evaluation period, the Nafion™ dryer assembly was removed from the Evaluation Analyzer's configuration and the identically configured Control Analyzer and Evaluation Analyzer were concurrently operated for a 17-day time period. Linear regression of 1-minute data for the Evaluation

Analyzer versus the Control Analyzer resulted in slope, intercept, and R^2 values of 0.998, -0.17 ppbv, and 0.9984, respectively. These regression coefficients are similar to those obtained during the 5-week Control period using this same configuration of analyzers. Linear regression of hourly data for the Evaluation Analyzer versus the Control Analyzer resulted in slope, intercept, and R^2 values of 0.999, -0.19 ppbv, and 0.9995, respectively. As in the case of the 1-minute data, these hourly regression coefficients were similar to those obtained during the 5-week Control period.

Although the measurement comparability between the two Thermo 49i analyzers without Nafion™ dryers was noted to be similar during this Post-Evaluation period, Figure 8 shows that short-term differences between the two instruments was noted on Jan. 3, 2017 during a period where shelter temperatures were very close to the dew points. This illustrates that somewhat different short-term response between identically configured instruments can result in substantial differences. It is expected that use of a Nafion™ dryer upstream of the Evaluation Analyzer would have appreciably reduced the noted measurement response during this humid episode. Following consideration of the theoretical and empirical information mentioned in this report by staff from ORD and OAR, EPA formally approved the Nafion™ dryer's use for Thermo 49i analyzers in CASTNET's monitoring networks. A copy of this approval letter is presented in Appendix A. OAR's June 2017 Nafion™ Dryer Approval Letter to CAMD.

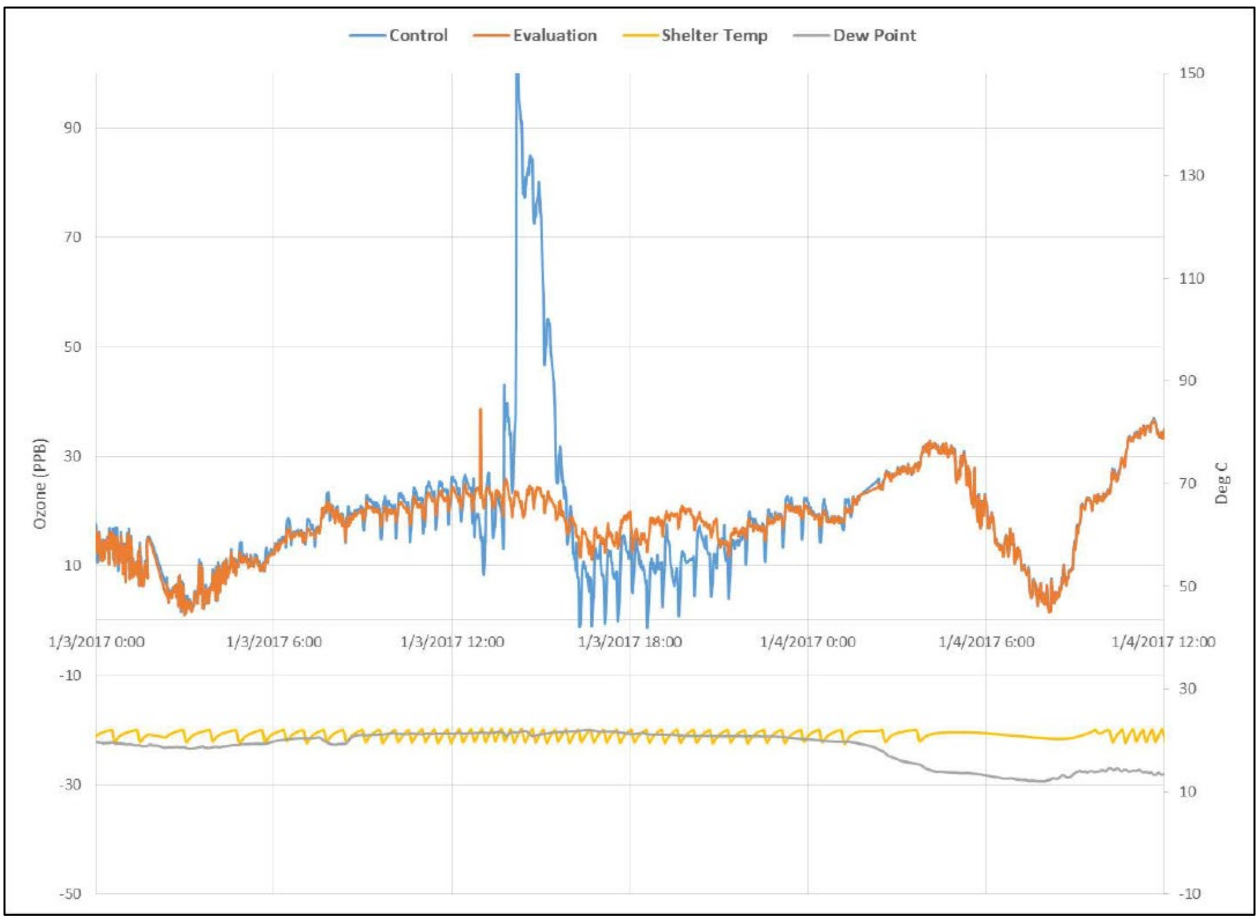

Figure 8. Post-Evaluation period timeline during the Jan. 3, 2017 humid sampling event.

OAR's June 15, 2017 approval letter to the EPA CAMD reiterated that the approval was <u>not</u> a formal modification to existing designated UV-based instruments because the approved Nafion™ dryer's use is upstream of the O_3 analyzer itself, rather than internally as in the case of 2B Technologies' O_3 FEM analyzers. Instead, it was EPA's technical judgement that Nafion™ represents an acceptably "equivalent" material regarding probe materials in Section 9 of 40 CFR Part 58 Appendix E. Approval was specifically intended for use solely in the CASTNET monitoring network.

4.2 Nafion™ Dryer Issues Since EPA's 2017 Approval to the Clean Air Markets

Since the time of EPA's 2017 approval to use a Nafion™ dryer in CASTNET's monitoring system as a means of improving O_3 monitoring performance, EPA has received several inquiries from various monitoring organization inquiring about the possibility of using Nafion™ dryers to address O_3 monitoring issues in their own networks.

4.2.1 EPA Region 1

In 2018, Peter Kahn (EPA Region 1) contacted EPA (P. Kahn, personal communication to Robert Vanderpool, August 21, 2018) for information regarding the potential use of a Nafion™ dryer in Rhode Island's Thermo 49i O_3 analyzers. Darren Austin of Rhode Island's Department of Environmental Management later became involved and provided data to Joann Rice showing that some O_3 network data has been flagged during very high dew point days (D. Austin, personal communication to Joann Rice, August 24, 2018). Darren mentioned that the O_3 analyzer was subsequently audited and found to function nominally. It was also mentioned, though, that the analyzer's calibration was conducted using dry air and thus the audit may not be representative of the analyzer's actual sampling situation under consideration. Bob Judge later communicated that some sampling sites in Region 1 were experiencing water vapor issues as evidenced by visible condensation in sampling lines upstream of the Thermo 49i O_3 analyzer (R. Judge, personal communication to Lewis Weinstock, Sept. 13, 2018). Recommended efforts to mitigate the problem (e.g., insulating sampling lines, heating sampling line, increasing shelter temperature) were apparently only partially successful at addressing the water vapor issue. Bob Judge also raised question about the potential use of Nafion™ dryers in Rhode Island's O_3 analyzers.

4.2.2 North Carolina Department of Environmental Quality (NC DEQ)

In late 2019, Jeff Gobel (NC DEQ) contacted Richard Guillot (Region 4) and requested use of Nafion™ dryers at some monitoring sites in NC which had been experiencing ongoing moisture problems with their Thermo 49i O_3 analyzers (J. Gobel, personal communication to Richard Guillot, Nov. 26, 2019). NC DEQ was not seeking statewide permission to use the Nafion™ dryer but only requested use of the dryers at NC's Monroe and Linville Falls sites. Previous efforts to address analyzer performance issues at these sites included insulating probe lines and filter assemblies, using heat tape on sample lines, installing and operating dehumidifier within the analyzer's shelter, and raising shelter to 30 °C. Richard subsequently requested assistance from Joann Rice regarding this issue (R. Guillot, personal communication to Joann Rice, Nov. 26, 2019).

As supporting evidence for approval of the Nafion™ dryers in NC's networks, Jeff Gobel provided results of preliminary beta testing of Nafion™ dryer assemblies at the Monroe and Linville sites. Nafion™ dryers were installed on Sept. 26, 2019 and Oct. 2, 2019 at the Linville and Monroe sites, respectively. The design of the Nafion™ assemblies exactly matched those currently operated by CASTNET, based on technical input received from CASTNET's contractor. These specifications match those previously mentioned in Table 1 of this document. The two sites were audited before, during, and after the Nafion™ dryer installations. Comparison of the audit data showed that no O_3 loss occurred in the Nafion™ dryers at either site. These test results are thus in agreement with those previously mentioned (Wilson and Birks, 2006) and from tests conducted in Gainesville, FL.

As of May 2020, these two sampling sites are just now entering the O_3 season and instrument performance data will be provided to EPA as it becomes available. NC DEQ also intends to install meteorological systems at each site for the recording of ambient wind speed, wind direction, temperature, and RH. In conjunction with plans to install RH sensors inside the shelters, these measurements will help assess the performance of the installed Nafion™ dryer systems at both sites.

4.2.3 CASTNET

At ORD's request, Timothy Sharac (OAR/OAP/CAMD) provided an update on CASTNET's experience with the Nafion™ dryer installation and operation since EPA's June 2017 approval (T. Sharac, personal communication to Robert Vanderpool, May 20, 2020). CASTNET's contractor (John Wood Group PLC) reported two notable improvements in Thermo 49i O_3 analyzer performance following installation of the Nafion™ dryer assembly upstream of the analyzer.

The first improvement related to instrument noise which resulted during short-term shelter temperature cycles in the trailer. Prior to the Nafion™ dryer installation, O_3 measurement deviations of ±10 ppb were noted to occur due to short-term temperature cycling. Although subsequent installation of the Nafion™ dryer did not completely eliminate the problem, these measurement deviations were reduced from ±10 ppb to ±1 ppb when tests were conducted at the same ambient air dew point.

The second noted improvement related to results obtained during analyzer QC checks conducted using dry air. Figure 9 depicts the results of zero tests conducted at a Tennessee CASTNET site (Site SPD111, Speedwell Co., TN) over a 4-year period (January 2016 to April 2020). Note that the plot represents unvalidated data so that negative data can be seen. For this Thermo 49i analyzer operated without a Nafion™ dryer installed, large deviations from zero periodically occurred. In particular, numerous measurements in the range of -4 ppb to -10 ppb were noted during high humidity events.

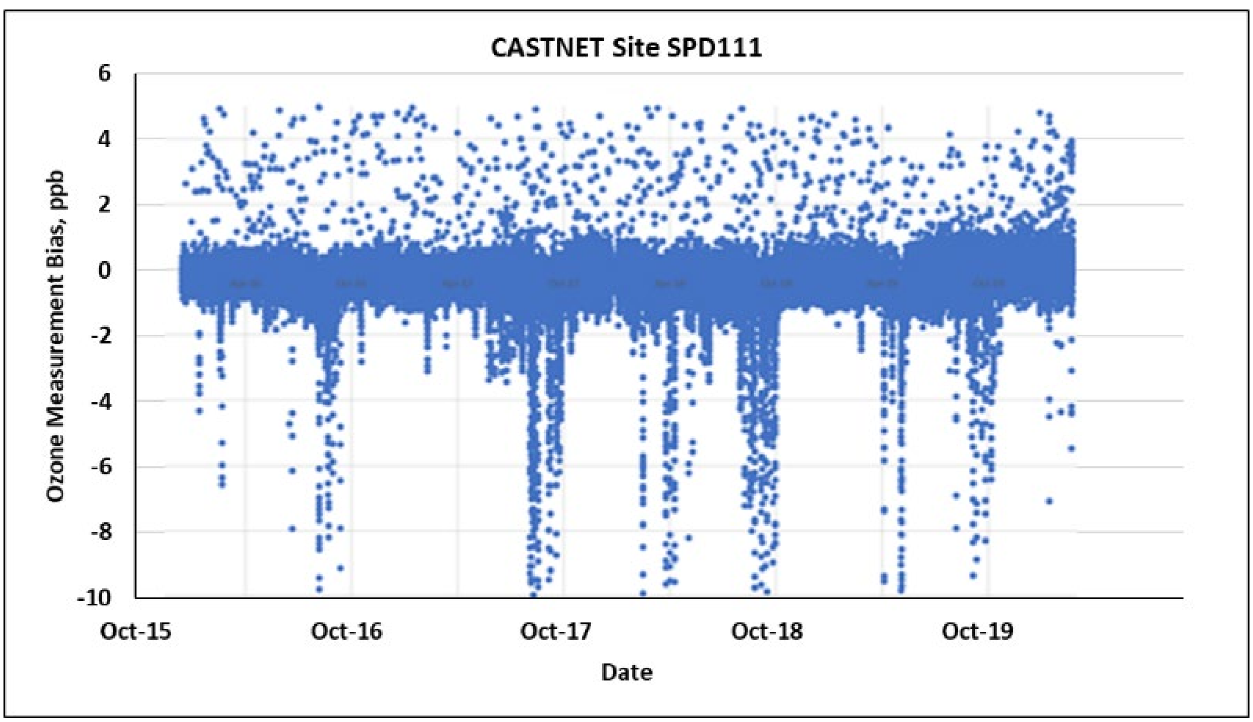

Figure 9. Results from zero tests of a Thermo 49i O_3 analyzer at a TN CASTNET site. This analyzer was not equipped with a Nafion™ dryer during this 3-year period.

Similar zero test results of the Thermo 49i O_3 analyzer were observed at an east Texas CASTNET site (Site ALC188, Polk Co) prior to a Nafion™ dryer's installation on July 14, 2017. In the Figure 10 timeline of ALC188 zero test data, the vertical orange line represents the Nafion™ dryer's installation date. Use of the Nafion™ dryer at this site minimizes the incidence of concentration data below –4 ppb.

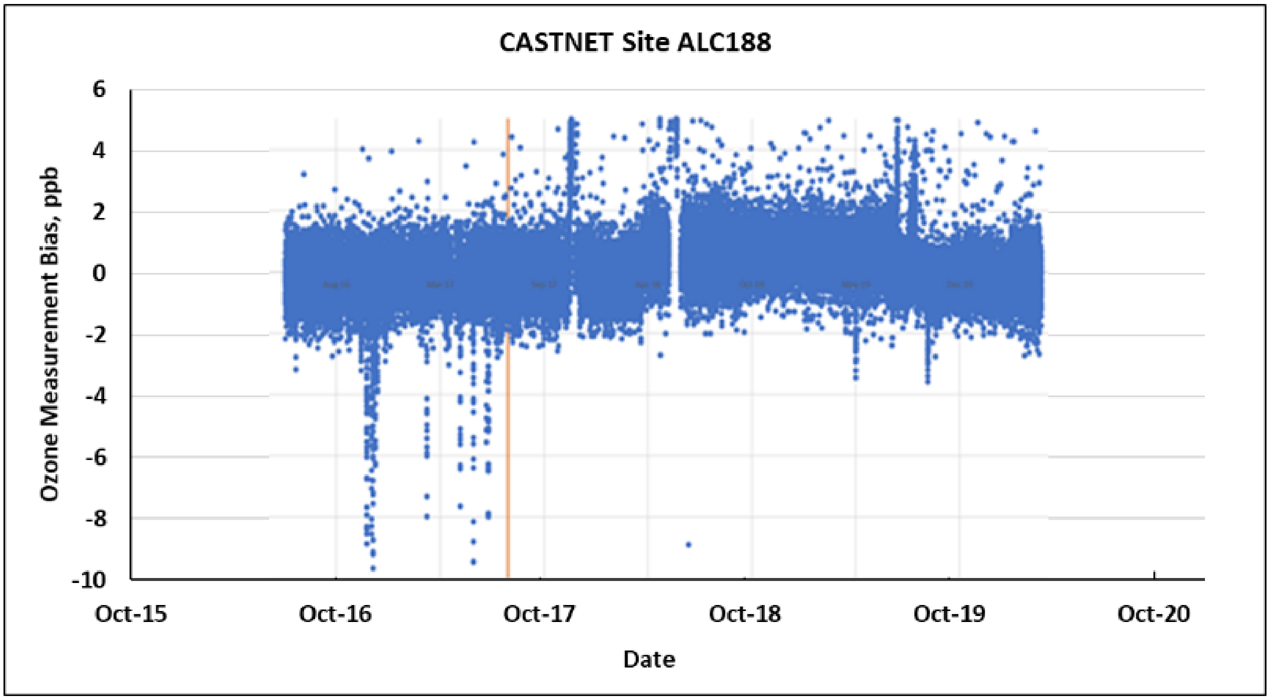

Figure 10. Results from zero tests of a Thermo 49i O_3 analyzer at an east TN CASTNET site. This analyzer was equipped with a Nafion™ dryer in July 2017, at the time indicated by the orange vertical line.

CASTNET suggested that improved performance of the Nafion™ system could be obtained using drier purge air (e.g., using a nitrogen cylinder) but acknowledged that increased operational and maintenance costs would be required. It was also suggested that improved moisture control under network conditions might be obtained using higher purge flow rates, increased purge vacuum, and/or by increasing the Nafion™ tube length from 48 in (1.2 m) to 72 in (1.8 m). An increase to a 72 in length would equate to a 50% increase in transfer area at a marginal increase in cost (i.e., \$305 versus \$358).

5.0 Summary and Conclusions

O_3 analyzers based on UV-absorbance are widely deployed and generally provide reliable measurement results under routine operating conditions. While some measurement interferences (e.g., VOCs and Hg^0) can exist in polluted environments, measurement interferences due to atmospheric water vapor can occur in both polluted and unpolluted airsheds. These interferences can increase instrument noise, slow instrument response, and bias measurements.

While the exact mechanism of water vapor's interference was not initially known, the problems were observed to frequently occur when shelter temperatures were at or near the dew point and when rapid fluctuations of atmospheric moisture occurred. With varying degrees of success, efforts to address the issue included insulating sampling lines, heating sampling lines, and/or raising shelter temperatures.

Wilson and Birk (2006) experimentally identified that O_3 scrubbers can act as sinks for water vapor and can absorb or desorb water vapor depending upon specific sampling circumstances. Because variations in water vapor downstream of the scrubber can alter the reflectivity of the detection cell's wall, variations in humidity during the analyzer's measurement cycle can produce uncertain results. The introduction of a Nafion™ tube immediately downstream of the analyzer's scrubber was found to effectively eliminate this measurement bias mechanism. It should be reiterated that the Nafion™ tube in this configuration does not actually dry the sampled gas stream but ensures that the moisture content remains stable during the measurement cycle. 2B Technologies' suite of approved FEM O_3 analyzers each are equipped with an internal Nafion™ tube to minimize the water vapor interference. The manufacturer recommends that the internal Nafion™ tube be replaced annually during the instrument's scrubber replacement procedure.

Existing UV-based O_3 analyzers which do <u>not</u> contain an internal Nafion™ tube could be retrofitted to contain this feature. Such a retrofit, however, changes the terms of the instrument's original FRM or FEM designation and the analyzer's manufacturer would need to submit a formal Modification Request to EPA for review and approval in order to retain the designation. The Request would need to contain supporting rationale along with results of experimental tests demonstrating that the retrofit successfully addresses the humidity issues without compromising the inherent measurement quality of the analyzer. Submittal of such a Modification Request is voluntary, and manufacturers must decide whether the retrofit financially justifies the resources required to develop and submit the Request. To date, none of these manufacturers have submitted a Modification Request of this type to EPA for review.

Installation of a Nafion™ tube upstream of the O_3 analyzer does not violate the terms of the analyzer's original FRM or FEM designation. Because an external Nafion™ tube does not address the interference mechanism in the same manner as an internal Nafion™ tube, its degree of effectiveness depends on how well moisture can be removed from the sampled airstream prior to the airstream's entry into the analyzer. A continuous supply of dry air to the Nafion™ drier would ensure the airstream's moisture removal but this approach is considered too complicated and costly during routine monitoring. Instead, air inside the shelter is used as the Nafion™ dryer's counterflowing purge air. Because the shelter's internal air will possess some degree of moisture, the incoming airstream will not be fully dried under all sampling situations. However, the degree of water removal may be sufficient to eliminate much of the O_3 measurement bias which ambient air of high ambient moisture content can produce.

As part of CASTNET's request to EPA to allow incorporation of Nafion™ dryers in the CASTNET network, field tests were conducted in Gainesville, FL during the 2016/2017 wintertime season. In agreement with theory and with experimental tests conducted by Wilson and Birks (2006) and Perma

Pure's literature. Results of these tests showed no measurable transport loss of O_3 in the Nafion™ tube. During periods when the shelter's temperature was not near the dew point, a Thermo 49i configured with a Nafion™ dryer upstream provided results which agreed closely to a collocated, concurrently operated Thermo 49i which did not use a Nafion™ dryer. However, during periods when the shelter temperatures were close to the dew point, a significant difference in measurement response between the two Thermo 49i O_3 analyzers was noted. On average, the Thermo 49i equipped without the Nafion™ appeared to over-measure the O_3 concentration compared to the Nafion™ dryer-equipped unit.

Based on review of theoretical considerations and of the Gainesville, FL tests data, EPA concluded that Nafion™ represented an acceptably "equivalent" sampling material, as defined in Appendix E to 40 CFR Part 58. As a result, EPA approved the use of Nafion™ dryers in the CASTNET network on June 15, 2017. Although this approval was limited to sites in the CASTNET network, other monitoring organizations have since expressed interest in implementing a Nafion™ dryer at some of their own sites which experience moisture interference issues.

In considering whether to approve the use of Nafion™ dryers on a widespread use, rather than on a case-by-case basis as was the CASTNET approval, there are generally two technical questions for which consensus by ORD is required. First: <u>Is the inherent transport efficiency of O_3 molecules through Nafion™ tubing sufficiently high to ensure that negative O_3 measurement biases would not occur?</u> From a theoretical perspective, the chemical composition of Nafion™ and its similarity to FEP Teflon is such that little or no O_3 loss would be expected to occur in Nafion™ tubes. As discussed in previous sections, the results of multiple laboratory and field tests of Nafion™ tubing strongly support this hypothesis. Therefore, there appears to be more than sufficient rationale for the use of Nafion™ tubing for the intended purpose of O_3 sampling and transport.

The second question for which consensus is required relates the ability of Nafion™ dryers to minimize water vapor to an acceptable degree in UV-absorption O_3 analyzers. Specifically: <u>Is there sufficient rationale to conclude that use of Nafion™ dryers under field conditions improves data quality of UV-based O_3 analyzers to an acceptable degree?</u> Field tests conducted in Gainesville, FL using Thermo 49i analyzers equipped with Nafion™ dryers demonstrated that the dryer's use reduced short-term measurement noise during periods where shelter temperatures approached the dew points. Following EPA's approval in 2017 of Nafion™ dryers in CASTNET sites, Nafion™ dryers have been installed and operated at 30 separate CASTNET sites. While analysis of the resulting data has not been fully conducted, data presented in this report for two CASTNET sites indicated that that the Nafion™ dryer's installation reduced measurement uncertainties during short-term fluctuations in shelter temperature and also improved results obtained during zero checks of the O_3 analyzer. Although these field test results are obviously limited, there appears to be sufficient supporting evidence to conclude that the Nafion™ dryers effectively reduce UV-based O_3 measurement uncertainties associated with interferences caused by ambient water vapor.

Based on the above considerations, ORD recommends that the use of Nafion™ systems upstream of UV-based O_3 analyzers be approved on a nationwide basis for all NAAQS compliance networks. From both theoretical predictions and laboratory experiments, there is no evidence that significant loss of O_3 occurs in Nafion™ systems. Other than the cost and maintenance requirements of the Nafion™ systems, there appears to be no downside of the system's use from a data quality perspective. In sampling circumstances where ambient moisture content undergoes rapid, short-term changes, the Nafion™ systems has been shown to significantly reduce measurement noise, concentration measurement biases, and slow instrument response times. By reducing the amount of water vapor experienced by the UV-based analyzer's scrubber, use of the Nafion™ system may also provide the added advantage of increasing the scrubber's service life.

Regarding a site's implementation of the Nafion™ system, ORD recommends that the system be based on CASTNET's operating and design specifications which are provided in Table 1 and Figure 5. The only recommended revision to the design specifications might be increasing the Nafion™ tubing length from 48 in to 72 in. At a nominal increase in purchase price (i.e., $305 versus $358), the increased tubing length provides a 50% increase in the sampled air's residence time and may thus provide more effective water vapor transfer than does the 42 in model when using counter current purge air. Because the 72 in tubing provides 50% more surface area than the shorter tube, the service life of the longer tube might be longer since contamination by impurities (e.g., VOCs) may not occur as rapidly. The 72 in tube does, however, have a 50% greater pressure drop than the 48 in tube, so tests should be conducted to ensure that O_3 analyzer can maintain the rated sampling flow rate under the additional pressure drop conditions. It may also be necessary to modify the purge air system to ensure the purge air flow rate is at least equal to the sample air flow rate.

As a final operational consideration, ORD recommends that O_3 calibration gases be introduced at the inlet to the Nafion™ system rather than directly into the O_3 analyzer. This will ensure that the calibration gas is conditioned to the shelter's humidity level and thus avoid excessive measurement noise which can occur during use of dry calibration gases.

6.0 References

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Appendix A. OAR's June 2017 Nafion™ Dryer Approval Letter to Clean Air Markets Division

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

June 15, 2017

AIR QUALITY OFFICE **PLANNING** OF

AND STANDARDS

Richard Haeuber, Branch Chief
Assessment and Communications Branch (ACB) Clean Air Markets Division (CAMD) Office of Atmospheric Programs (OAP)

Dear Rick:

This letter transmits our approval of your request to add Nation™ dryers to the ozone sampling lines at select Clean Air Status and Trends Network (CASTNET) sites. Specifically, you are requesting the approval to add a Nation™ dryer at the back of the ozone analyzer inside the monitoring station. We understand that this request is being made because the CASTNET ozone network uses Thermo 49i ozone analyzers which do not include a dryer for humidity control as part of the FEM approval, and that you have observed instrument noise problems and slowed response.

In considering the request, the Office of Research and Development (ORD) and the Ambient Air Monitoring Group (AAMG) of the Office of Air Quality Planning and Standards (OAQPS) have discussed this issue and determined that this is not a request for modification to the Thermo 49i FEM analyzers used in the network, but rather a decision regarding the use of acceptable materials in sampling probes as covered in Appendix E to 40 CFR part 58.

After careful consideration of your request, we agree that the addition of Nafion™ dryers to the ozone analyzer in the CASTNET is compliant with Part 58 and that the Nafion™ will not interfere with the transmission of ozone.

For technical questions, you may contact Joann Rice at rice.joann@epa.gov and 919-5413372.

Sincerely,

Lewis Weinstock, Group Leader
Ambient Air Monitoring Group (AAMG)
Air Quality Assessment Division (AQAD)
Office of Air Quality Planning and Standards (OAQPS)

cc: Joann Rice (OAQPS/AQAD/AAMG)
Tim Sharac (OAP/CAMD/ACB)
Melissa Puchalski (OAP/CAMD/ACB)
Robert Vanderpool (ORD/National Exposure Research Lab (NERL)) Mike Papp (OAQPS/AQAD/AAMG)

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