Mechanism and Elimination of a Water Vapor Interference in the Measurement of Ozone by UV Absorbance

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A water vapor interference in ozone measurements by UV absorption was investigated using four different ozone monitors (TEI models 49 and 49C, Dasibi model 1003-AH, and a 2B Technologies model 202 prototype). In the extreme case of step changes between 0 and 90% relative humidity (RH), a large interference in the range of tens to hundreds of ppbv was found for all instruments tested, with the magnitude and sign depending on the manufacturer and model. Considering that water vapor does not absorb at the wavelength of the Hg lamp (253.7 nm) used in these instruments, another explanation is required. Based on experimental evidence and theoretical considerations, we conclude that the water vapor interference is caused by humidity effects on the transmission of uncollimated UV light through the detection cell. The ozone scrubber acts as a water reservoir, either adding or removing water from the air sample, thereby modulating the detector signal and producing a positive or negative offset. It was found for the 2B Technologies ozone monitor that use of a 1-m length of Nafion tubing just prior to the entrance to the detection cell reduces the water vapor interference to negligible levels ($\pm$2 ppbv for step changes between 0 and 90% RH) while quantitatively passing ozone.

Introduction

No water vapor interference is expected for UV absorbance measurements of ozone since water vapor does not absorb at the wavelength of 253.7 nm used in commercial instruments. However, we have observed that rapid changes in water vapor concentration result in a false signal, which is either positive or negative depending on the instrument manufacturer. We first discovered this effect in vertical profiling field experiments where a prototype balloon-borne UV absorbance instrument would rapidly pass through alternately dry and wet atmospheric layers. For this miniature, single-beam instrument, apparent ozone swings of several hundred parts per billion by volume (ppbv) were observed. That observation led us to investigate water vapor effects on the 2B Technologies model 202 ozone monitor, which was under development at the time, and on larger, dual-beam instruments that have been used for monitoring of ozone for

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compliance of the Clean Air Act since about 1970. All of the UV absorbance instruments we tested exhibited a water vapor interference of several tens of ppbv upon rapid change of humidity.

Large changes in humidity can occur during passage of storm fronts with the effects being greatest in arid climates, in personal monitoring where the instrument is transported into and out of buildings, and during aircraft flight where alternating wet and dry layers are frequently encountered. During our investigation of the water vapor interference on ozone measurements by UV absorption, we learned anecdotally that some operators of instruments for compliance monitoring are aware that zeroing the instrument at a particular time of day (e.g., at night when the humidity is higher) will lead to lower ozone measurements the following day (and fewer exceedances of the ozone standard set by the EPA). The water vapor interference is of concern especially for vertical profiling using kites and balloons and for aircraft measurements where the instrument is exposed to frequent, abrupt changes in humidity.

Previous Studies of Water Vapor Effects on Ozone Measurements

Two peer-reviewed articles report studies of the effects of water vapor in UV-absorbance-based ozone instruments ([1], [2]) while only a few papers discussing anomalies that occur in ozone measurements have been presented at various scientific meetings ([3]–[8]). In these conference proceedings and reports, it is pointed out that UV ozone instruments often exhibit erratic behavior when sampling on hot, humid days; i.e., when the municipalities are most likely to be out of compliance. More interestingly, it was plausibly argued ([3]) that approximately half of the areas designated in 1993 as nonattainment may actually have been in compliance with the O_3 standard due to errors in ozone measurements. Additionally, the U.S. EPA has incorporated information from these conference reports into both draft ([9]) and official publications ([10], [11]) acknowledging a water vapor interference under certain circumstances, but, unfortunately, much like the non-peer-reviewed conference literature, the EPA reports provide no insight into the underlying physical mechanism responsible for the water vapor interference other than the possibility that water actually condenses within the instrument components.

The first ([1]) peer-reviewed published work utilized three commercial, dual cell, UV photometers: two from TECO (model 49) and one from Dasibi (model 1003-AH). These instruments were plumbed without their ozone scrubbers so that the solenoid which normally switches between ozone-rich and ozone-free air would now switch between ozone-free dry and humid air. Ambient air was used to produce dry, ozone-free air by passing it through a charcoal filter and molecular sieve. This initial air stream was split with one portion replacing what would be scrubbed air in the instrument. The other stream was split again to provide humidified air to what is normally the instrument's scrubber bypass tubing. The moist air stream was humidified to variable levels by bubbling one portion through a temperature controlled water bath and recombining with dry air by use of mass flow controllers to reach the desired humidity level. With these modifications, any interference from water vapor was measured as an apparent ozone mixing ratio.

In this configuration a measurable water vapor effect ranging between 200 and 800 ppbv equivalent ozone was quantified; the authors explained the origins of the effect as

being due to optical differences in light scattering as water vapor interacted with contaminants and/or irregularities on the detection cell windows. The paper went on to say that this scattering only affected the instrument's noise and would only be problematic at times when rapid humidity changes occur at ground level or during vertical profiling in the atmosphere when the instrument passes through alternately wet and dry layers. The study did not mention any perturbation of water vapor on the instrument's calibration or zeroing offset nor the specific length of time that the effect persisted other than to state that the effect was not seen in the hourly averaged data.

The second peer-reviewed paper (*2*) further explored the possibility of humidity interferences in UV-based ozone instruments raised by Meyer et al. (*1*). Unlike the Meyer et al. experiments, the Kleindienst et al. (*2*) study kept the internal ozone scrubbers intact. Multiple instruments (two TEI 49, two Dasibi 1003-AH, and one Dasibi 1008-AH) were monitored simultaneously with the desired humidity and ozone concentrations mixed in a manifold system through the use of a temperature-adjusted water-bubbling system and a low-pressure mercury lamp, respectively. All instruments were calibrated immediately prior to their use against an EPA standard reference photometer with ozone in dry air.

A first set of experiments was run at three ozone concentrations of 85, 125, and 320 ppbv and three dew point temperatures of 11, 17, and 23 °C corresponding to relative humidity (RH) of approximately 40, 60, and 80%, respectively. This resulted in ozone readings with relative differences ranging from 0.64% to 7.5% with an average 2.9% relative difference from nominal ozone concentrations. Although the instruments were zeroed and spanned with dry air before each experiment, there was no attempt to independently verify the ozone concentrations during the humid air runs, which may explain the significant deviations of ozone from correct values. It must be further stressed that the "ozone/humid air mixtures were allowed to equilibrate for at least an hour before measurements were made" and that "following equilibration, readings were taken for a single ozone concentration at a single RH for 0.5 h". This is significant because measurements were not recorded for step changes in humidity nor for the 1 h or longer periods when the instruments were allowed to equilibrate before data collection commenced.

A second set of experiments in which ambient laboratory temperatures were kept approximately 5 °C lower than the air stream in the manifold system also was run. This was done in an attempt to replicate ambient monitoring during summer months where condensed water sometimes forms in the inlet tubing. The procedure was the same as for the first set of experiments, but this time the ozone concentrations were monitored throughout the procedure and calculated via dilution to give known concentrations. The same dew points were utilized as in the previous experiment, but this time only the two higher ozone concentrations of 200 and 325 ppbv were used. This set of experiments resulted in ozone readings with relative differences from nominal ozone concentrations ranging from 0.28% to 1.4% and an average relative difference of 0.53%; i.e., good agreement. Although Kleindienst et al. also saw both an initial 100−150 ppbv positive spike, followed by periodic 50 ppbv positive and negative spikes in some instruments and noisier operation in others during periods of humidity changes, the researchers concluded that these effects would have no effect upon the hourly averaged ozone readings.

As a result of the Meyer et al. and Kleindienst et al. papers and our field data using the prototype 2B Technologies ozone monitor, we investigated the effect of sudden humidity change on four different commercially available ozone monitors. Similar to the Meyer et al. and Kleindienst et al.

studies, we found a measurable water vapor interference in all ozone monitors tested. Even though all instruments were exposed to the same water vapor transients, the responses were of different magnitudes and direction depending upon the instrument evaluated.

Experimental Section

Four ozone instruments were used in this study: TEI model 49, TEI model 49C, Dasibi model 1003-AH, and a 2B Technologies model 202 prototype. No particle filter was used on the inlets of any of the ozone monitors in order to eliminate the filter as a variable in interpreting the experimental results. Particle filters provide an additional surface where water vapor can adsorb. Instead, the water vapor interference was quantified using zero air, which contains little or no particulate matter. All ozone monitors were calibrated immediately prior to their use against a standard reference photometer following the guidelines described in the EPA transfer standards manual (*12*). The ozone monitors sampled from an air stream which always exceeded the flow needed by the instruments, with the overflow venting into the laboratory. Ozone was not generated in these experiments. We used zero air containing no added ozone in order to study the effects of water vapor in the complete absence of ozone. Responses of these instruments were recorded as the humidity of zero air (Air Products, Ultrazero) was manipulated through the use of a temperature-regulated humidity generator. The humidity generator, described by Karbiwnyk et al. (*13*), consists of a microporous polytetrafluoroethylene (PTFE) tube surrounded by a thermally regulated water jacket. By adjustment of the water temperature and ratio of flow rates of zero air passing through the PTFE versus bypass tubing, any desired relative humidity could be attained. All experiments were carried out at an ambient temperature of 23 °C. Humidity measurements were made using a recently calibrated Cole Parmer model 37951-00 thermohygrometer.

The prototype 2B Technologies model 202 ozone monitor is a single beam photometer with a schematic diagram identical to other single beam ozone monitors such as the Dasibi model 1003-AH also used in this work. The 2B Tech instrument differs from other ozone monitors primarily in its small size (9 × 21 × 29 cm), weight (2.1 kg with case, 0.7 kg without case), and power requirement (4 W). It was designed for measurements from kites, balloons, and light aircraft where size, weight, and power requirements are critical. Like other ozone monitors, the instrument makes use of a low-pressure mercury lamp as the light source. The lamp emission is detected using a photodiode having a built-in interference filter that isolates the 254-nm line from other Hg lamp emissions. The absorption path length is 15 cm, approximately half that of the other instruments used in this study. A miniature solenoid valve switches every 5 s, allowing either sample air or ozone-scrubbed air to enter the detection cell. Ozone concentration is calculated from the Beer−Lambert Law in exactly the same way as in other ozone monitors. The instrument uses a miniature air pump on the outlet of the detection cell to draw sample air through the instrument at a nominal volumetric flow rate of 1 L/min.

The prototype 2B Technologies model 202 ozone monitor made use of a freshly prepared hopcalite (Supelco) scrubber. This is ultraclean material marketed for preconcentration of trace gas species via adsorption at room temperature followed by thermal desorption. The material was thermally desorbed at a temperature of approximately 100 °C prior to use as an ozone scrubber to be certain that it did not contain measurable quantities of adsorbed UV-absorbing compounds. Hopcalite is a mixed oxide of copper and manganese and is chemically similar to the proprietary materials used in the ozone scrubbers of the other ozone monitors evaluated

(a) TEI Model 49

(b) TEI Model 49C

(c) Dasibi Model 1003-AH

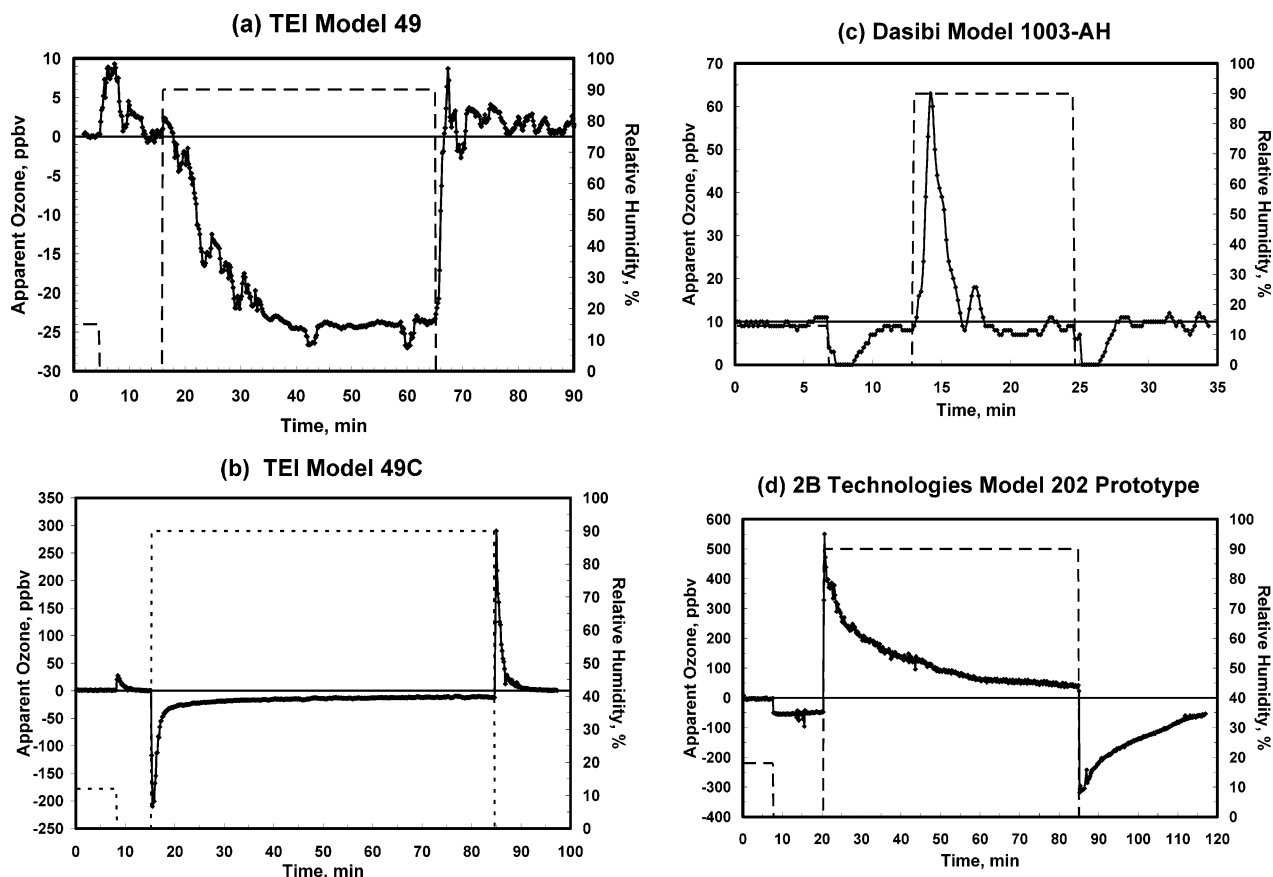## (d) 2B Technologies Model 202 Prototype

FIGURE 1. Effect of step changes in RH on apparent ozone reading for (a) TEI model 49, (b) TEI model 49C, (c) Dasibi model 1003-AH, and (d) prototype 2B Technologies ozone monitor prior to modifications. The dashed line is a plot of relative humidity. Step changes are from 13% (ambient) to 0% (dry tank air) to 90% (humidified tank air), and finally to 0% RH. A solid line is drawn at the baseline ozone mixing ratio (10 ppbv for the Dasibi instrument and 0 ppbv for the other instruments.)

in these studies. Unlike activated carbon, hopcalite destroys ozone by a catalytic mechanism; i.e., the scrubber material is not consumed in its reaction with ozone.

Some experiments made use of a 1-m long, 1.07 mm i.d., 1.35 mm o.d. Nafion membrane tube (Perma Pure, Toms River, NJ) just prior to the absorbance cell of the 2B Technologies model 202 ozone monitor.

Results and Discussion

Responses to Step Changes in Humidity. The four ozone monitors were equilibrated to the laboratory ambient humidity (13 ± 1% RH) by sampling ambient air for at least 4 h prior to commencement of each experiment. Each run consisted of first obtaining a baseline by sampling ambient air drawn through a Mersorb Indicator Chemical Cartridge (3M, Minneapolis, MN) as an external ozone scrubber. This was followed by rapid valve switching to tank zero air at 0% RH, next switching to zero air adjusted to 90 ± 1% RH, and finally switching again to 0% RH air. (Throughout this paper, "ambient air" refers to ozone-scrubbed ambient air at 13 ± 2% RH, "dry air" refers to zero air direct from the cylinder (0% RH), and "90% RH air" refers to zero air humidified to 90% RH at 23 °C.) This experiment simulates the expected results for calibration using dry zero air followed by sampling of a humid atmosphere. Sudden changes in humidity also occur during aircraft or balloon flights—for example during passage through stratospheric folds or during flight in and out of clouds. Results for cycling between ozone-scrubbed ambient air at 13% RH, dry air, and 90% RH air are shown in Figure 1 for the four ozone monitors tested. Relative humidity is indicated by the dashed lines in those figures.

The four instruments had quite different responses to the humidity changes. For the TEI model 49 ozone monitor

(Figure 1a), positive spikes on the order of 8 ppbv occurred when changing from ambient to dry air and persisted for 5−10 min. A negative excursion of about −25 ppbv ozone occurred over the course of 35 min when changing from dry to 90% RH air and flattened out, showing no signs of recovery even a full hour following the humidity change. The instrument responded rapidly (~2 min) to a change from 0% to 90% RH, leveling off with an offset of about +2 ppbv within a total time of 10 min. The noise of the instrument also increased over that of its normal operation as a result of the humidity changes, the standard deviation of the baseline increasing from ~4.2 ppbv for ambient air at the beginning of the experiment to ~13.6 ppbv for dry air at the end of the experiment.

Humidity cycling had a different effect on the response of the newer TEI model 49C ozone monitor (Figure 1b). Although the direction of the peaks remain the same, in this case they are sharper and of a greater magnitude. A positive spike of ~30 ppbv occurred when switching from 13% RH to dry air, with recovery to zero occurring after 5 min. A negative spike of ~210 ppbv resulted from a switch from dry to 90% RH air, but the instrument response never fully recovered; 70 min after switching to dry air, the instrument still had a negative offset of ~13 ppbv. Switching from 90% RH to dry air resulted in a positive spike of ~295 ppbv, but within 10 min the instrument completely recovered to the baseline of 0 ppbv. Note the scale differences for the two TEI instruments. The baseline noise increased from a standard deviation of ~0.3 ppbv for sampling of ambient air at the beginning of the experiment to ~1.5 ppbv for dry air at the end of the experiment.

The Dasibi instrument showed opposite effects from the two TEI instruments to the same humidity changes (Figure

1c). Transitions from humid to dry air resulted in negative excursions, and transitions from dry to humid air gave positive excursions. The negative excursions were not fully quantified because the analog output of the instrument does not allow for negative ozone measurements. This deficiency was partially overcome by applying a +10 ppbv offset to the instrument output, but the negative excursions exceeded this value. A positive ~50 ppbv spike occurred when changing from 0% to 90% RH. Although the Dasibi did recover from the humidity changes in approximately 5 min, its readings were noisier as a result of the sudden humidity change. The baseline noise increased from a standard deviation of ~0.8 ppbv for sampling of ambient air at the beginning of the experiment to ~1.1 ppbv for sampling of dry air at the end of the experiment.

The prototype 2B Technologies model 202 instrument exhibited the largest deviations from zero in apparent ozone readings of the four instruments tested (Figure 1d). Like the Dasibi, it produced a positive spike (~550 ppbv) when changing from dry to humid air and a negative spike (~300 ppbv) when switching from humid to dry air. As with the TEI instruments, the prototype 2B Technologies ozone monitor did not fully recover from the humidity change from 0% to 90% RH even after an hour. The baseline noise for the 2B Technologies instrument increased from a standard deviation of ~1.6 ppbv measured for ambient air at the beginning of the experiment to ~1.8 ppbv for dry air at the termination of the experiment. In this case, it was necessary to detrend the data at the end of the experiment before calculating the standard deviation since the baseline had not yet leveled off. Based on the discussion that follows, the larger interference in the 2B Technologies prototype instrument probably can be attributed to the shorter path length (15 cm vs 30 cm) and higher surface to volume ratio. Because of the shorter path length, a given change in light intensity reaching the detector is interpreted as twice the ozone concentration.

These experiments clearly demonstrate a large humidity interference in all of the ozone monitors tested. This interference exists despite the fact that water does not absorb at 254 nm. One possible explanation for the effect is that water vapor displaces adsorbed UV-absorbing organics from the surface of the ozone scrubber. This almost certainly occurs to some extent, especially if the ozone monitor has been exposed to air pollution for a significant length of time. However, this effect cannot be the complete explanation since two of the instruments displayed negative interferences when sampling was switched from dry air to 90% RH air (TEI models 49 and 49C), while two instruments displayed positive interferences (Dasibi and 2B Technologies). We hypothesized that the humidity effect is primarily due to physical interactions of water with the absorption cell surface. All of the ozone monitors tested make use of an ozone scrubber that can modulate the water vapor concentration by adsorption/ desorption at the scrubber surface during measurements of light intensity during scrubbed (I_o) and unscrubbed (I) measurement cycles. Modulation of water vapor in the cell will, in turn, modulate the amount of water vapor adsorbed to the cell surface, which could significantly affect the reflectivity of the cell surface. Ozone monitors make use of an uncollimated light source with much of the light reaching the detector via reflection from the cell wall surface. Changes in cell wall reflectivity need not be large to account for the water vapor interference since a change in light intensity by a factor of only 3×10^{-6} corresponds to 1 ppbv ozone for a 15-cm cell length. Experiments described below were designed to test this hypothesis and to provide a means for eliminating the interference in the 2B Technologies instrument. Based on these results, it is expected that other ozone monitors can be modified to remove the water vapor interference as well.
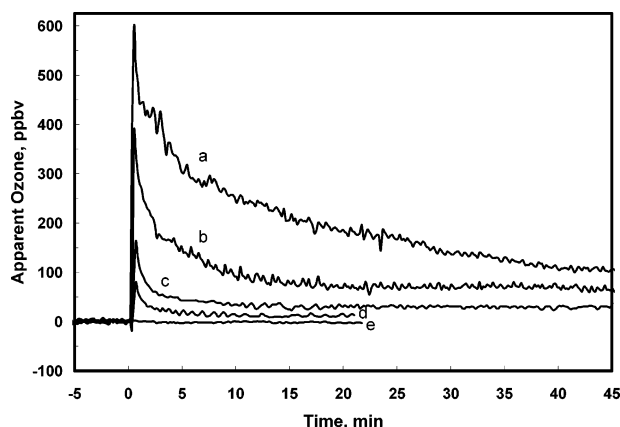

FIGURE 2. Water vapor effect on apparent ozone reading for prototype 2B Technologies ozone monitor resulting from a step change from 0% to 90% RH at time equals zero for (a) no modification, (b) decrease in ozone scrubber size, (c) switch from a borosilicate to a fused quartz cell, (d) increase of cell temperature by 10 °C, and (e) cleaning the cell with methanol, in order of decreasing maximum positive ozone interference.

Effects of Instrument Modifications on the Humidity Interference. In order to test the hypothesis that the observed water vapor interference is caused by differences in amounts of water adsorbed to the cell surface during I_o and I measurement cycles, we made the following sequential modifications in the prototype 2B Technologies ozone monitor that would be expected to reduce the modulation of adsorbed water vapor: (1) the mass and surface area of ozone scrubber material was reduced in order to reduce the amount of water adsorbed to the catalyst surface; (2) the Pyrex (borosilicate glass) absorption cell was replaced with a quartz cell; (3) the cell was heated to 10 °C above ambient; and (4) the cell was cleaned with methanol. The results of those changes are shown in Figure 2 where the ozone instrument was cycled between dry and moist air, as in the experiments described by Figure 1. Figure 2 shows only the data for step changes from 0% to 90% RH, as this produced the largest excursion in the 2B Technologies prototype instrument. All data are adjusted to read an average of zero ppbv on dry air. With no modifications to the instrument (control experiment), a positive spike of ~600 ppbv apparent ozone resulted, which decayed over a period of more than 40 min. The decay is not described by single-exponential decay, most likely due to adsorption sites on the scrubber material and Pyrex cell having different binding energies. In the first modification of the instrument, the volume of scrubber material was reduced from 16 to 0.07 cm³ (minimal amount of material needed to destroy more than 99% of ozone at a flow rate of ~1 L/min). As seen in Figure 2, this resulted in an approximate 33% reduction (from ≈600 to 400 ppbv) in the peak of the apparent ozone deviation. The modified instrument with the smaller scrubber does not fully recover to zero within the 40 min monitored following the humidity change, but compared to the unmodified instrument, the decay rate is faster, and the plateau of ≈80 ppbv ozone equivalent is reached more quickly, at ~15 min. Consistent with our hypothesis, this can be explained as being due to the reduced catalyst surface area becoming equilibrated more rapidly with the 90% RH air. However, even though the scrubber surface area was decreased to less than 1% of the original value, the magnitude of the humidity spike decreased by only about one-third.

The smaller ozone scrubber was used in all subsequent experiments, and as the next modification, the cell composition was changed from borosilicate glass to fused quartz. Borosilicate glass substitutes boron oxide in place of some

of the alkali oxides (most commonly sodium and potassium) found in soft glass. Although borosilicate glass, commonly sold under the trade name Pyrex, has fewer impurities as contrasted to soft glass, its residual alkali salts still provide many hydrophilic surface sites for water absorption. Fused quartz, however, is a highly pure form of silicon dioxide with a low occurrence of impurities (typically less than 50 ppm). Of course, quartz is still hydrophilic due to the presence of Si−OH functional groups on the surface. As seen in Figure 2, an additional 60% reduction (from ≈400 to 160 ppbv) in the peak apparent ozone spike occurred as a result of this change in cell material. The fused quartz cell also resulted in a ∼5 min faster decay to a plateau at half the value for the borosilicate glass cell (∼40 ppbv ozone after only 10 min).

The quartz cell was next heated by wrapping it in copper foil and heat sinking the 5-V voltage regulator used to power the lamp and an additional 100 resistor to the foil, for a total heat dissipation of ∼1.5 W. The copper foil was held in place and thermally insulated by the use of silicone tape. The heat from the resistor and waste heat from the voltage regulator raised the cell temperature to 33 °C or ∼10 °C above ambient. Under these conditions, air having a relative humidity of 90% is reduced to approximately 51% within the detection cell. As seen in Figure 2, mild heating of the cell resulted in an additional 50% reduction (from ≈160 to 80 ppbv) in peak apparent ozone deviation. Although significantly improved relative to the unheated cell, the ozone excursion again did not decay completely to zero during 40 min of monitoring. A similar decay rate of ∼10 min was found for the heated cell to that of the unheated cell, but a lower plateau of ∼15 ppbv, as compared to ∼40 ppbv, apparent ozone was reached. Use of higher cell temperatures (e.g., 20 °C) provided minimal improvement at the cost of additional power; minimization of power is a requirement for most of the applications of this small, light weight, portable instrument. Also, at much higher temperatures ozone will decompose on the cell surface. A cell temperature of 10 °C above ambient serves the additional function of preventing condensation of liquid water within the cell from air supersaturated in water vapor.

As a further test of the role of the absorption cell surface, the quartz cell was cleaned by flushing with HPLC grade methanol and dried with zero air. The cell had been cleaned prior to use in the instrument, but the instrument had been operated for several hours prior to carrying out the previous experiments. Any chemical species and particles collected on the cell surface from the atmosphere could provide additional hydrophilic sites to which water would absorb. Figure 2 shows the results obtained for the 0% to 90% step change in RH immediately after cleaning the absorption cell. At the scale shown the water vapor effect appears to have completely vanished; actually there is a small 5 ppbv peak distinguishable above the ∼2 ppbv noise, which decays to zero over about 10 min. This would be an acceptable level of interference in most applications, considering that an abrupt change for 0% to 90% RH would almost never occur. Unfortunately, however, within 2 h of sampling ambient air, the water vapor interference increased to approximately the same level as measured prior to cleaning, apparently due to contamination of the cell by species present in ozone-scrubbed room air.

In other work we tried using hydrophobic polymer cells (PTFE and polyvinylidene fluoride) but obtained no better results than with quartz. This is likely due to the fact that even these materials adsorb some water and are limited by adsorption of atmospheric contaminants, which can increase the polarity of the surface. Although we considered silanization of the quartz surface with a hydrophobic functionality, the cleaning experiments described above strongly indicated that any surface, no matter how hydrophobic, will soon become sufficiently contaminated to cause a significant water vapor interference.

All of the experiments described above are consistent with our hypothesis that the water vapor interference results from a difference in the amounts of water present on the absorption cell surface during measurements of I and I_o. The water vapor concentration in the ozone-scrubbed air stream is modified by the ozone scrubber; the RH may be either higher or lower during measurement of the reference intensity I_o, depending on the humidity history of the scrubber, which, in turn, depends on the humidity history of the air being sampled.

Theoretical Considerations. An analysis of the effect of a microscopic water layer on the detection cell wall is provided in the Supporting Information and in the Ph.D. thesis of Kevin Wilson (14), where the opposite sign of the interference for the TEI and 2B Tech instruments is predicted by simple refractive index considerations. In summary, a water layer on the quartz cell of the 2B Tech instrument reflects less light than dry quartz and thus increases the amount of light lost to the black paint on the exterior of the cell, thereby *decreasing* the light intensity at the detector. In contrast, a water layer on the polyvinylidine fluoride (PVDF) interior coating of the highly reflective aluminum TEI cell reduces the amount of total internal reflection within the PCDF layer, thereby *increasing* the intensity of light at the detector. These effects, when combined with modulation of water vapor concentration by the scrubber, result in a modulated light intensity which is interpreted as a false positive or negative ozone signal.

Elimination of the Water Vapor Interference by Use of a Nafion Tube. If our hypothesis that the water vapor interference in UV absorbance instruments is due to modulation of humidity of the sample stream by the ozone scrubber, then equilibration of humidity of scrubbed and unscrubbed air after the scrubber and prior to the absorption cell should eliminate the interference entirely. This was confirmed in experiments described below by insertion of a Nafion membrane tube just prior to the absorbance cell of the 2B Technologies model 202 ozone monitor. Nafion is a copolymer consisting of a tetrafluoroethylene backbone with perfluoro-3,6-dioxa-4-methyl-7-octenesulfonic acid side chains (15). Nafion has the desirable properties of exhibiting a high permeability to water while retaining the property of Teflon of being highly resistant to attack by strong oxidants such as ozone. The sulfonic acid groups impart ionic properties to the bulk polymer matrix, allowing absorption of up to 13 waters of hydration per sulfonate group and a water content of up to 22% by weight (15). Furthermore, the adsorption and desorption of water is very fast, with the result that an air stream passing through the interior of a 1-m long, 1.07 mm i.d., 1.35 mm o.d. Nafion tube at a flow rate of 1 L/min is equilibrated with the humidity of exterior air within the ∼50 ms residence time (16).

In order to measure the degree of humidity equilibration, air of varying RH was drawn through the Nafion tube. The pump of a 2B Tech ozone monitor was used for this to ensure identical flow rates to those found in an instrument, ∼1 L/min. Dry tank air, room air (39.2% RH), and humidified air (93.0% RH) were drawn through the Nafion tube, and the humidity of the effluent was measured. The results were 39.3%, 39.2%, and 39.4%, respectively. Neither the beginning relative humidity nor the order in which the various air streams were measured affected the outcome within the estimated ±0.2% measurement error. In each case the air stream was equilibrated to the relative humidity (39.2 ± 0.2%) of the ambient air surrounding the Nafion tube, demonstrating the ability to equilibrate the often different humidity levels found in both the ozone-scrubbed and bypass air streams present in all UV ozone monitors.
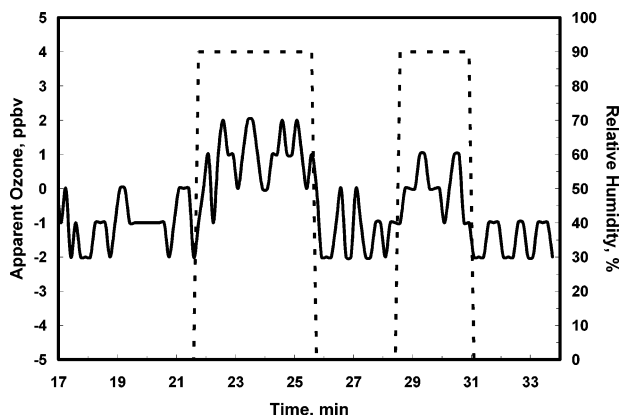
FIGURE 3. Apparent ozone measurement for 2B Tech ozone monitor resulting from changes in the relative humidity of zero air with a Nafion tube used to equilibrate the humidity level just prior to the absorption cell.

In an effort to check for the possibility of ozone loss within the Nafion tube, ozone was generated in ambient air (0.8 bar, 39% RH) in the mixing ratio range of 0−350 ppbv and measured with the Nafion tube present and absent. Linear regression of a plot of ozone measurements made with the Nafion tube present versus those made in the absence of the Nafion tube gave a slope of 0.9967, intercept of 0.27 ppbv, and correlation coefficient of 1.0000. Within measurement error, the slope of the plot obtained is not significantly different from unity; i.e., there is no measurable loss of ozone within the Nafion tube.

A replication of the humidity experiments described above and summarized in Figure 2 was carried out. A humidity generator was again used to create a 90% RH zero air stream, and the 2B Technologies ozone monitor with the modifications described earlier (small scrubber, quartz cell, heated) was rapidly switched between sampling dry and moist zero air. As seen in Figure 3, apparent ozone increases by ∼2 ppbv when switching from 0% to 90% RH air. Furthermore, the ozone monitor undergoes this change in one instrument reading (10 s). Results for the water vapor interference in all four instruments investigated are compared in Figure S1 of the Supporting Information. Compared to other instruments, which undergo −200, +80, +60, and +25 ppbv changes in ozone signal when relative humidity increases under the same experimental conditions and require up to an hour to equilibrate after changes in relative humidity, the Nafion-tube modified 2B Technologies ozone monitor is an order of magnitude superior with respect to the magnitude of ozone offset (±2 ppbv). Although not tested, the use of a Nafion tube is expected to eliminate the water vapor interference in other UV instruments as well, but because of their higher sampling flow rates a longer Nafion tube may be required.

It should be noted that the magnitude of the water vapor interference reported here could easily cause a metropolitan area to be either in or out of compliance with EPA regulations (e.g., 8-h average of ozone not to exceed 80 ppbv rounded to the nearest 10 ppbv). Also, measurements for research purposes using balloons and aircraft could also be in error due to passage through alternately wet and dry air parcels. For these reasons we recommend the use of a Nafion tube in all UV-based ozone monitors.

In this work, a significant and sometimes large water vapor interference inherent in all commercially available ozone monitors tested (TEI, Dasibi, 2B Technologies) was positively identified for the first time. Prior knowledge of this interference was mostly anecdotal, with the only published studies dismissing it as being solved in newer instruments. Here the mechanism of the interference was elucidated, the interfer-ence being caused by changes in the transmission efficiency of light through the UV detection cell as a result of adsorption of water molecules to the cell surface. The water vapor concentration within the cell and therefore light transmission of the cell is modulated by the ozone destruction catalyst, which acts as a water vapor reservoir. Consistent with this mechanism, a number of factors were found to reduce or eliminate the water vapor effect. These include heating the absorption cell, changing the composition of the absorption cell, reducing the nature and/or surface area of the ozone destruction catalyst, and, finally, using a Nafion tube to equalize the humidities of scrubbed and unscrubbed air.

The use of a Nafion tube for elimination of the water vapor interference, elucidated in this work, was introduced as an option in 2B Technologies ozone monitors in early 2004 under the trade name DewLine. To date, DewLines have been installed in more than 100 2B Technologies ozone monitors with no reported adverse effects such as loss of ability to equilibrate water vapor, decreased sensitivity to ozone, or large shifts in the instrument zero.

Supporting Information Available

Comparison of step changes in humidity on different ozone analyzers, proposed model of the effect of a water layer on light interaction with the cell's surface, reflection efficiences of various interfaces in 2B Tech and TEI ozone monitors (Table S1), comparison of water vapor effect on apparent ozone reading (Figure S1), and representation of light paths in TEI model 49 optics cell (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

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