Comparison of Ultraviolet Absorbance, Chemiluminescence, and DOAS Instruments for Ambient Ozone Monitoring

7 AUTHORS, INCLUDING:

E. J. Williams

National Oceanic and Atmospheric Administr…

142 PUBLICATIONS **7,564** CITATIONS

SEE PROFILE

Fred C. Fehsenfeld

503 PUBLICATIONS **25,295** CITATIONS

SEE PROFILE

Comparison of Ultraviolet Absorbance, Chemiluminescence, and DOAS Instruments for Ambient Ozone Monitoring

E. J. WILLIAMS,*,†,‡
F. C. FEHSENFELD,†,‡ B. T. JOBSON,†,‡,∥
W. C. KUSTER,† P. D. GOLDAN,†,‡
J. STUTZ,§ AND W. A. MCCLENNY⊥,#

Chemical Sciences Division, Earth System Research Laboratory, NOAA, Boulder, Colorado 80305, CIRES, University of Colorado, Boulder, CO, Department of Atmospheric Sciences, UCLA, Los Angeles, CA, and U.S. EPA, Research Triangle Park, NC.

This paper evaluates the accuracy of ozone measurements made by monitors that determine ozone concentrations in ambient air by UV absorption. These monitors are typically used to measure ozone for the purpose of establishing local compliance to air-quality standards. The study was predicated by the concern that commercially available UV absorbance O_3 monitors may be subject to interference from volatile organic carbon (VOC) species that absorb light at 254 nm. To test for these and other effects, we compared simultaneous O_3 measurements made by a commercial UV O_3 monitor with an O_3–NO chemiluminescence instrument, which is not subject to interference by VOC compounds. The comparisons were carried out in the summers of 1999 and 2000 at urban/industrial sites in Nashville and Houston, and in 2004 aboard a ship in the Gulf of Maine. In the two urban areas, we also compared the O_3 measurements from these two methods with O_3 measurements made by a long-path differential optical absorption spectrometer (DOAS). Our tests indicate that, with well-maintained monitors, there are no significant interferences even in areas with significant ambient concentrations of potentially interfering VOCs.

Introduction

Arguably, the most widely used instrument for the measurement of O_3 in the atmosphere is the UV absorbance monitor. These instruments are favored, especially in air quality monitoring networks, due to ease of operation, low maintenance, and because they have no need for reagent gases or solutions. However, the accuracy of the O_3 data provided by these instruments has come into question. Leston et al. (*1*) point out that there is accumulating evidence of measurement errors in UV absorbance monitors, apparently due to O_3 scrubber problems. These errors, which reportedly can be as high as 20–50 ppbv, are most likely to occur during

those hot and humid conditions that are also most likely to produce high O_3 levels. This is a serious issue since errors of this magnitude could falsely indicate that a monitoring region exceeded the 8-hour average O_3 air quality standard of 84 ppbv, potentially putting the region into noncompliance, which could require significant expenditures for remediation.

Leston et al. (*1*) cite evidence from ambient monitoring and smog chamber studies that shows significant differences in O_3 measurements from UV absorbance instruments compared to chemiluminescence instruments that do not use O_3 scrubbers. In Mexico City, the differences show distinct diurnal periodicity with the largest differences (UV instrument up to 50 ppbv higher) occurring near the times of peak O_3. Results from smog chamber studies at very high VOC loadings with three UV instruments and one chemiluminescence (CL) instrument showed that the UV instrument with the conventional (MnO_2) O_3 scrubber measured 14–40 ppbv more O_3 than the CL instrument. Kleindienst et al. (*2, 3*) have shown from laboratory work that interferences in the UV absorption instruments due to absorption by species other than O_3 are negligible, except in highly polluted environments. Arshinov et al. (*4*) reported a significant interference by fine aerosol (<0.2 μm diameter) on O_3 measurements from a UV instrument. Leston and Ollison (*5*) also showed an aerosol (<2.5 μm) interference in O_3 data from a UV instrument, although to a considerably lesser degree than the Arshinov et al. (*4*) results. Kauper (*6*) attributed reports of high wintertime O_3 measurements to a light leak in the monitor.

We address this issue of potentially erroneous O_3 measurements from UV monitors by reporting on simultaneous O_3 measurements with both UV and CL instruments at (1) an urban location, (2) a suburban/industrial location, and (3) aboard a ship in both polluted urban and clean marine air. These data cover a wide range of sampling conditions and thus provide a reasonable test of the susceptibility of our UV monitor to interferences due to environmental conditions or the presence of UV absorbing species in the sampled air. In all of these studies, additional measurements were made of important photochemical trace species, including VOCs. In the two land-based studies, O_3 was also measured by a long-path differential optical absorption spectrometer (DOAS). Although discrepancies in O_3 measurements beyond measurement error are seen in two brief instances, our conclusion is that a well-maintained and properly operated UV instrument will provide accurate O_3 mixing ratio data under a wide variety of conditions.

Experimental Section

Sampling Locations.. Additional measurements were made at all three locations. See the Supporting Information for details.

Nashville, TN (NV99). Measurements were made at the Cornelia Fort Air Park in Nashville, TN, from June 15 to July 15, 1999 (*7*). This urban/suburban site is located about 1 km west of Opryland and about 8–9 km northeast of downtown Nashville, and was selected to be at, or near, the point of maximum ozone formation rate in Nashville under normal summertime advection (winds 3–10 m s⁻¹). Ambient air was sampled at high flow (<1 s residence time) through 16 mm i.d. PFA Teflon tubing with the inlet located at the top of a ~10 m scaffolding tower. The O_3 instruments were inside an air-conditioned trailer at the base of the tower. The ~2 km long DOAS light beam path was oriented east-west and was ~0.5 km south of the tower (see the Supporting Information).

La Porte, TX (TX00). Measurements were made at the La Porte municipal airport near Houston, TX, from August 19

* Corresponding author e-mail: eric.j.williams@noaa.gov.
† Earth System Research Laboratory, NOAA.
‡ University of Colorado.
§ UCLA, Los Angeles.
⊥ U.S. EPA.
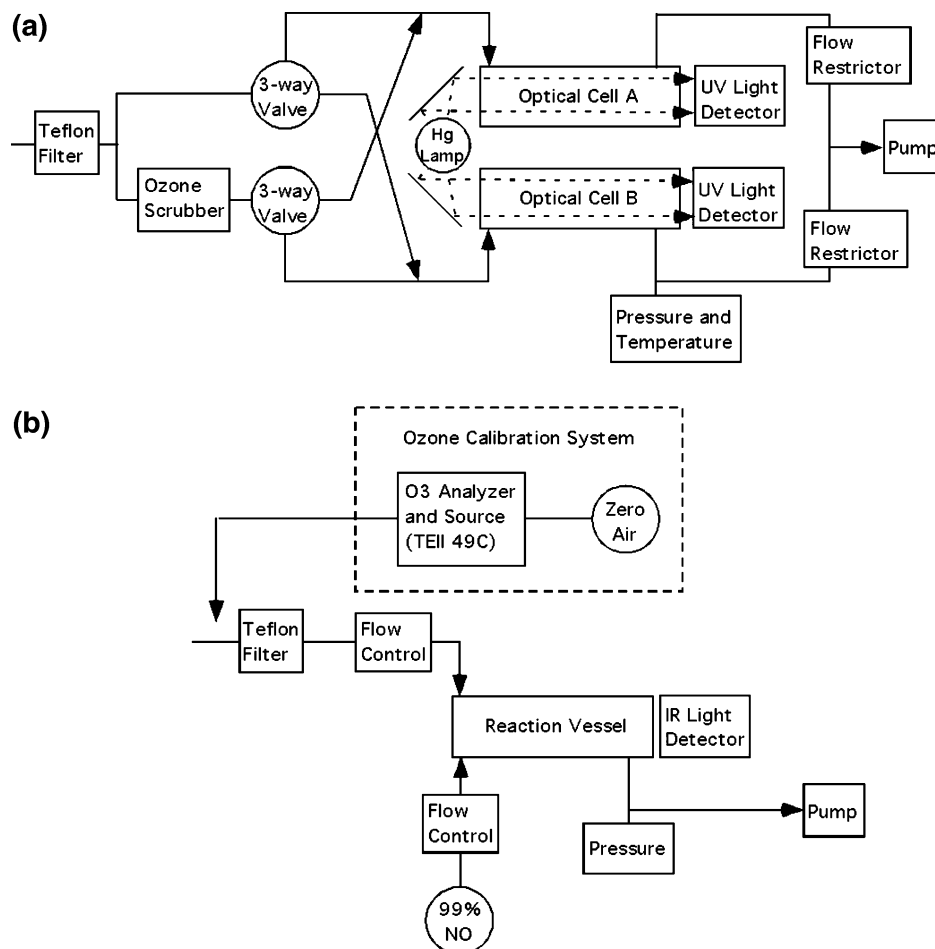∥ Now at Washington State University, Pullman, WA.
Now retired.

FIGURE 1. Diagrams of the O₃ instruments. (a) UV absorbance system; (b) chemiluminescence system.

to September 14, 2000 (*8*). Although the area immediately around the airport is retail−residential, much of the industrial capacity of the Houston Ship Channel region lies within a 25 km radius of this suburban site. Ambient air was sampled from the top of a ~10 m tower at high flow (residence time: <1 s) through 16 mm i.d. PFA Teflon tubing. The O₃ instruments were located in an air conditioned trailer at the base of the tower. The ~2 km long DOAS light beam path was oriented northwest−southeast and was located about 0.5 km east of the tower (see the Supporting Information).

Gulf of Maine, 2004 (NQ04). The ship-based measurements took place on the NOAA research vessel *Ronald H. Brown* from July 9 to August 13, 2004. The ship was based in Portsmouth, NH, but sailed throughout the Gulf of Maine, including excursions into the harbors of Boston, MA, and Portland, ME. Ambient air was sampled through an unheated PFA Teflon manifold (16 mm i.d. tubing) at high flow (<1 s residence time) from an inlet near the top of a 10 m tower (~26 m above waterline). For the first half of the study a 90 mm Teflon filter (5 um pore size) was placed at the tubing inlet; this filter was removed during the second half. The O₃ instruments were inside an air conditioned laboratory on the forward deck of the ship.

Instrumentation. *Ultraviolet light absorbance instrument (UV).* The primary instrument used to measure O₃ in these studies was a commercial UV absorbance system (Model 49C; Thermo Environmental Instruments). A schematic diagram of this instrument is shown in Figure 1a. Differences exist among manufacturers of these UV absorbance instruments. For example, some use a single cell as opposed to the twin cell design described below. There may also be differences in the optical components and scrubbers. How-

ever, in all cases the same analytical principle, Beer's Law, is used,

$$I/I_0 = \exp(-a \times L \times [O_3]) \tag{1}$$

where a is the O₃ absorption cross-section (308 cm⁻¹ atm⁻¹ at STP) and L is the optical path length of the absorption cell (38 cm). For this model 49C instrument (see the Supporting Information for a history of this unit), the air sample is drawn through twin optical cells that are illuminated by 254 nm light from a low-pressure mercury discharge lamp. While ambient air is sampled by one of the cells (I in Beer's Law), an ozone scrubber is used to remove O₃ from the air sample going to the other cell (I_0 in Beer's Law). This provides an absolute measurement of the O₃ concentration in the sample cell; conversion to mixing ratio units uses the measurement of temperature and pressure in the absorption cell. After 10 s the air flows are reversed, and the cell that did measure I then measures I_0 and another O₃ measurement is made. These two separate measurements are then averaged and output with a response time on the order of 10−20 s. During the studies reported here the data were averaged to 1 min values. This instrument is always operated with a 5 micrometer pore-size Teflon filter on the inlet.

If other species that absorb or scatter light at the 254 nm wavelength are present in the sample and are removed by the scrubber, then the ratio of I/I_0 will not reflect the O₃ concentration, and the O₃ measurement will be in error. Species known to absorb are certain aromatic volatile organic compounds and elemental Mercury. The level of interference will depend on the species absorption cross-section at 254 nm and its concentration in sampled air. Although water

vapor does not absorb 254 nm light, it has been shown (*9*) to interfere with light transmission in optical cells with damaged or dirty windows. Increased scattered light from aerosols present in the sample air but not in the scrubbed air can produce false readings (*4*). There are also reports of oscillating output that have been attributed to damaged optical components or damaged or poorly performing O_3 scrubbers (*1, 10*). Other factors that commonly induce erroneous O_3 data include leaks and dirty or contaminated tubing, valves, or optical components.

Before and after the studies in Nashville and Houston, the field instrument (TEII model 49C) was compared using zero air with our Dasibi 1008 laboratory standard. The ozone mixing ratios over a range from 0 to ~400 ppbv determined in these zero air tests agreed with a discrepancy <2%. In 2004, our Dasibi O_3 laboratory standard failed due to a faulty circuit board and valve. Consequently, after the 2004 study on the ship, the field UV instrument was compared to a reference UV instrument maintained by NOAA/CMDL (now NOAA/ESRL/GMD) that is referenced to a NIST standard reference photometer. Our field instrument was found to be about 3% low compared to the CMDL standard. This difference was attributed to O_3 wall losses in our field instrument after constant exposure to marine air.

Since all UV absorbance instruments provide an absolute determination of O_3, there should be agreement of any instrument with any other to within the total instrument uncertainties of 1−2%. These uncertainties principally arise from the O_3 cross section (~1%), the path length (≪1%), the pressure and temperature corrections (~1%), and the measurement precision (~1 ppbv). In the laboratory, there are also sampling uncertainties that arise from providing exactly equivalent O_3 air samples to the instruments being compared. Any disagreement beyond the 1−2% level should be investigated, the cause determined, and the instrument repaired. It is not good practice to adjust the electronic span or calibration factor in these instruments. This is also pointed out in the operating manual for the TEII model 49C.

Chemiluminescence Instrument (CL). The CL technique used in this work relies on chemiluminescence from electronically excited NO_2 produced via reaction of NO with O_3 and can be used to detect either NO or O_3 (*11*). A schematic diagram of this type of instrument is shown in Figure 1b. Air is drawn into the reaction vessel where it is mixed with pure NO to a concentration of ~0.1%. The resulting light is measured by a red-sensitive PMT operated in photon-counting mode. Other molecules that oxidize NO will also produce a response, but these are present in ambient air at levels at least 100 times less than O_3. Since water vapor quenches the excited NO_2 molecules, this method is subject to interference from large changes in absolute humidity, but it is not sensitive to UV absorbing molecules such as aromatic compounds. The instrument has very high sensitivity, very low background, and fast time response (1 s or less). Data were acquired at 1 Hz and averaged to 1 min. This instrument is always operated with a 5 micrometer pore-size Teflon filter on the inlet.

Unlike the absolute measurement of O_3 by the UV absorbance system, the CL instrument requires external calibration. In the Nashville study, the CL instrument was calibrated by plotting the counting rate against the ozone mixing ratio measured by the UV instrument for all one-minute periods that the instruments were simultaneously operated. The slope of the linear fit to this correlation provided a single calibration factor (4100 Hz ppbv^{-1}) that was used to normalize the counting rates of the CL measurements to ozone mixing ratios. No attempt was made to apply additional corrections to the Nashville CL data to account for variations in the water vapor mixing ratio.

In the Houston and Gulf of Maine studies calibration factors for the CL instrument were determined by using the UV instrument with zero air to supply known amounts of ozone to the former. The counting rate data were corrected for coincident photon pulses via the following calculation:

$$Hz_{corr} = Hz_{meas}/(1 - t \times Hz_{meas}) \qquad (2)$$

where t is the total photon detection system deadtime. The parameter, t, was determined from the zero air calibration data by adjusting t in eq 2 until the maximum squared correlation coefficient was obtained from the linear fit between the counts data and the O_3 mixing ratios. For both studies, $t = 25$ ns, which is consistent with the two principal sources of deadtime in this instrument. The maximum correction was ~3%. The average slope of the linear least-squares fits (multiple independent calibration curves were determined for each study) was used to obtain dry air O_3 mixing ratios from the corrected counting rate data of the CL instrument. Finally, the CL data were corrected (*11*) to account for variations in quenching at different levels of ambient absolute humidity:

$$O_{3\ corr} = O_{3\ meas} \times (1 + 0.0043 \times WV) \qquad (3)$$

where WV is the water vapor mixing ratio in parts per thousand and the factor 0.0043 was derived from laboratory studies. The maximum correction was ~15%, compared to dry air.

Differential Optical Absorption Spectrometer (DOAS). The DOAS instruments used in these studies are similar to the ones described by Alicke et al. (*12*). This DOAS technique measures the spectrally resolved absorption features in a beam of white light that is folded once by an array of retroreflectors located at some distance from the instrument (see the Supporting Information for additional details). The absorption features measured in the returning light beam correspond to a convolution of all the absorption bands in that wavelength region due to absorbing molecules that are present at any point in the beam path. The instrument uses a double Newtonian telescope to send and receive a beam of white light from a Xe-arc lamp through the atmosphere. The receiving part of the telescope is coupled to a Czerny−Turner spectrograph with a focal length of 0.5 m ($F = 6.9$, 600 grooves/mm grating, temperature controlled at +30 ± 0.3 C) by a 200-um diameter quartz fiber. A photodiode array detector was used for the detection of the spectra from 300 to 380 nm which were recorded at a spectral resolution of 0.55 nm. Sophisticated computer software extracts, simultaneously from each measured spectrum, the identity and concentration of all the absorbing species present in the path of the beam solely based on well-characterized published absorption cross-section data. A calibration of the instrument is not necessary. These instruments have variable data collection rates (5−30 min), depending on atmospheric opacity and O_3 mixing ratios. The accuracy of the DOAS system for O_3 is 3% due to uncertainties of the absorption cross section, ~1% (*13;* comparable to the uncertainty at 254 nm), and straylight in the spectrometer (~2−3%). Stutz and Platt (*14*) show for the DOAS technique that noise and unexplained spectral structures determine errors and detection limits (2−4 ppbv), which scale inversely with the path length.

Results and Discussion

In all three cases, the scatterplots (see the Supporting Information) of coincident 1-minute average O_3 measurements made by the UV instrument and the CL instrument show linear least-squares fitted slopes to be within <1% of unity and intercepts less than 1 ppbv. The fits are robust, with small standard errors for the slopes and intercepts and large (>0.995) squared correlation coefficient.
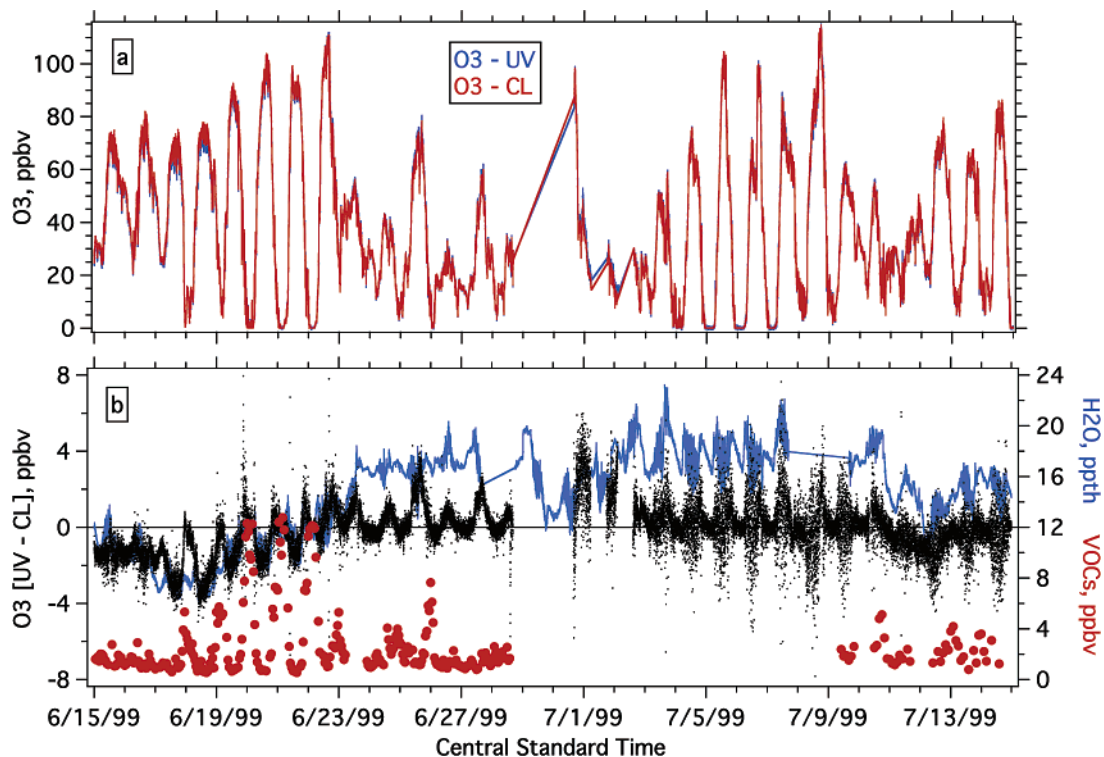
FIGURE 2. O₃ comparison data from Nashville, 1999. (a) One minute data: blue trace is UV; red trace is CL. (b) Absolute O₃ difference (UV−CL) shown as black dots (left axis); one-minute averaged water vapor mixing ratio shown by the blue line (right axis); sum of hourly averaged measured aromatic VOC species shown as red dots (right axis).
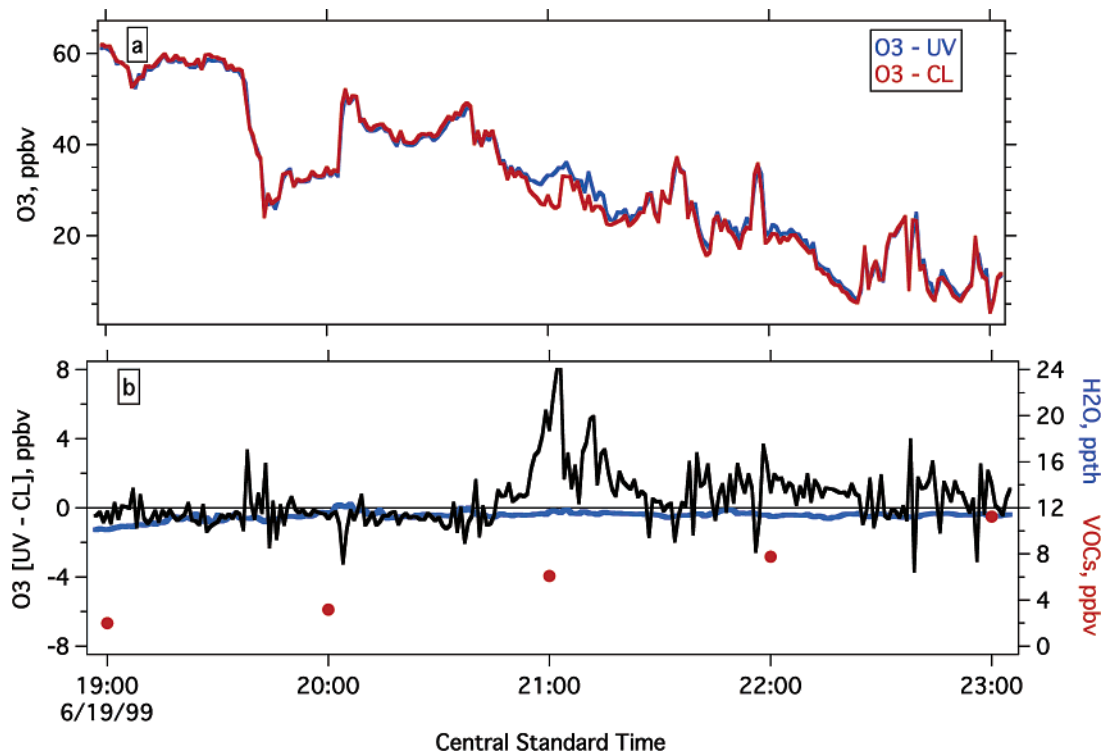

FIGURE 3. Similar to Figure 2, but limited to 1900−2300 CST on June 19, 1999.

Comparisons of In Situ CL and UV Instruments. *Nashville, 1999.* The NV99 O₃ data (Figure 2a) exhibit a strong diurnal variation with daytime maxima approaching 120 ppbv and levels near zero on many nights. This latter effect is typical of a ground measurement location where the nocturnal inversion isolates the surface layer from O₃-rich air aloft and induces loss of O₃ due to slow deposition to the surface and titration by emissions of NO. The O₃ difference

plot (Figure 2b) shows that 99.6% of the data (39 816 points) span the range −4 to 4 ppbv with 93.1% in the −2 to 2 ppbv range. The relatively large negative excursion of the differences early in the time period is because the CL data were not corrected for ambient water vapor changes.

Figure 2b also shows (red dots) the hourly averaged sum of aromatic VOCs, which includes benzene, toluene, C2-benzenes (i.e., xylenes and styrene) through C4-benzenes,
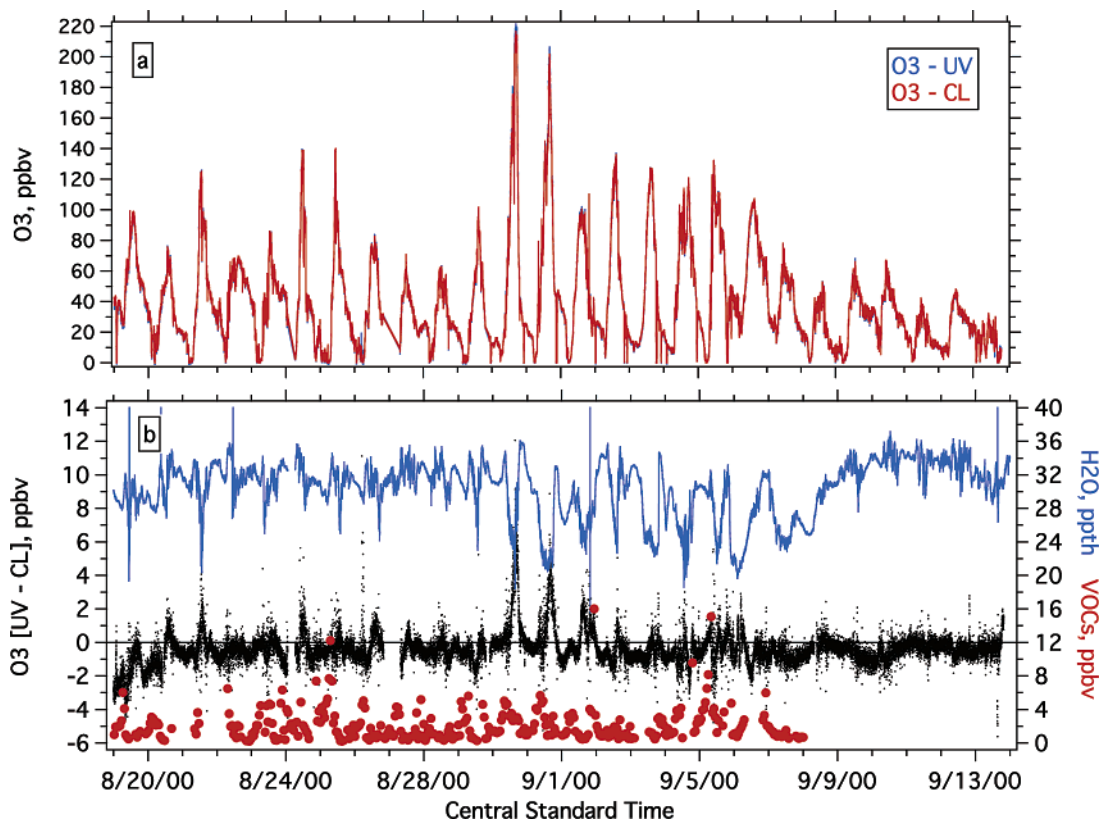
FIGURE 4. O$_3$ comparison data from La Porte, 2000. (a) One minute data: blue trace is UV; red trace is CL. (b) Absolute O$_3$ difference (UV−CL) shown as black dots (left axis); one-minute averaged water vapor mixing ratio shown by the blue line (right axis); sum of ten-minute averaged measured aromatic VOC species shown as red dots (right axis).

chlorinated benzenes, and oxygenated aromatics such as benzaldehyde. Although these compounds can cause an interference in the UV absorbance determination of O$_3$, there is no relationship between the presence of high levels of aromatic VOCs and the absolute difference in these O$_3$ measurements.

The short-term excursions of O$_3$ differences in most cases can be attributed to poor time correlation between the measurements. Figure 3a shows an expanded view of Figure 2a for the period 1900−2300 CST on June 19. First examine the O$_3$ peak at about 2200 in the upper panel. Although it is clear that the short-term O$_3$ variations between the instruments track very well, there is a slight time offset between the two traces that shows up as a ±2 ppb difference in the lower plot. This is an unavoidable consequence of dealing with ambient data taken under field conditions and is responsible for virtually all of the short-term variations seen in Figure 2b.

The one period in the NV99 data that we could identify as an O$_3$ difference of possible significance is also shown in Figure 3a. The short time period spanning 2100 (∼32 min; 0.08% of total data) shows the two O$_3$ traces diverging and with different fine structure. The lower panel shows that there were no measured changes in water vapor but some increase in the VOCs. Although the 1-h average VOC data may mask shorter term fluctuations, other gas-phase and meteorological data indicate that the conditions were not rapidly changing at this time (∼2000−2200 CST): wind speed dropped from ∼2 mps to calm; wind direction was variable; temperature dropped steadily from 24 to 18°C; and the relative humidity increased from 50 to 90%. One possible cause for the increasing VOC (and CO) mixing ratios during this time is a decrease in the nocturnal boundary layer height, an explanation that is consistent with the meteorological data. Also, the levels of the aromatic VOCs relative to one another

do not change significantly during this time, which suggests that the sampled air mass did not change. While the cause of this discrepancy between the O$_3$ instruments remains unknown, the structure of the data traces suggests more of a short-term instrument malfunction rather than the transient presence of an interfering species.

La Porte, 2000. The TX00 O$_3$ data (37 665 points) are shown in Figures 4 and 5. Though the scales are different than the NV99 data, the structure of the O$_3$ differences is similar with the majority of the differences in the same range: 95.2% within ±2 ppbv; 99.4% within ±4 ppbv. Similarly, most of the short-term excursions in the differences here are due to noncoincidence in the data; however, for one period this is clearly not the case (Figure 5). For an approximately 1-h period on August 26, the UV absorbance O$_3$ system indicated short-term spikes in O$_3$ of up to 10 ppbv that were not present in the CL data. In contrast to the discrepancy noted in the NV99 data, the structure of these data seem to indicate the presence of interfering species. While there is no indication of changes in either water vapor or the sum of the aromatic VOCs (substantially the same group of compounds as was measured in Nashville), there was a significant correlation of the UV O$_3$ spikes with spikes in the CO data at this time. CO will not cause an interference in the UV measurement of O$_3$, but it is likely that the source of the CO was also a source of some unmeasured species that did cause an interference with the UV O$_3$ measurement.

In the refinery and petrochemical plant dominated environment of the La Porte site, such compounds may be present. Jobson et al. (*15*) report maximum values of aromatic VOCs for the La Porte site during this study as benzene: 8.2 ppbv (93 L/mol-cm); toluene: 7.6 ppbv (137 L/mol-cm); ethylbenzene: 2.3 ppbv; xylenes (sum): 17 ppbv (140−200 L/mol-cm); trimethylbenzenes (sum): 2.6 ppbv (162 L/mol-cm); styrene: 1.5 ppbv (3600 L/mol-cm). The values in
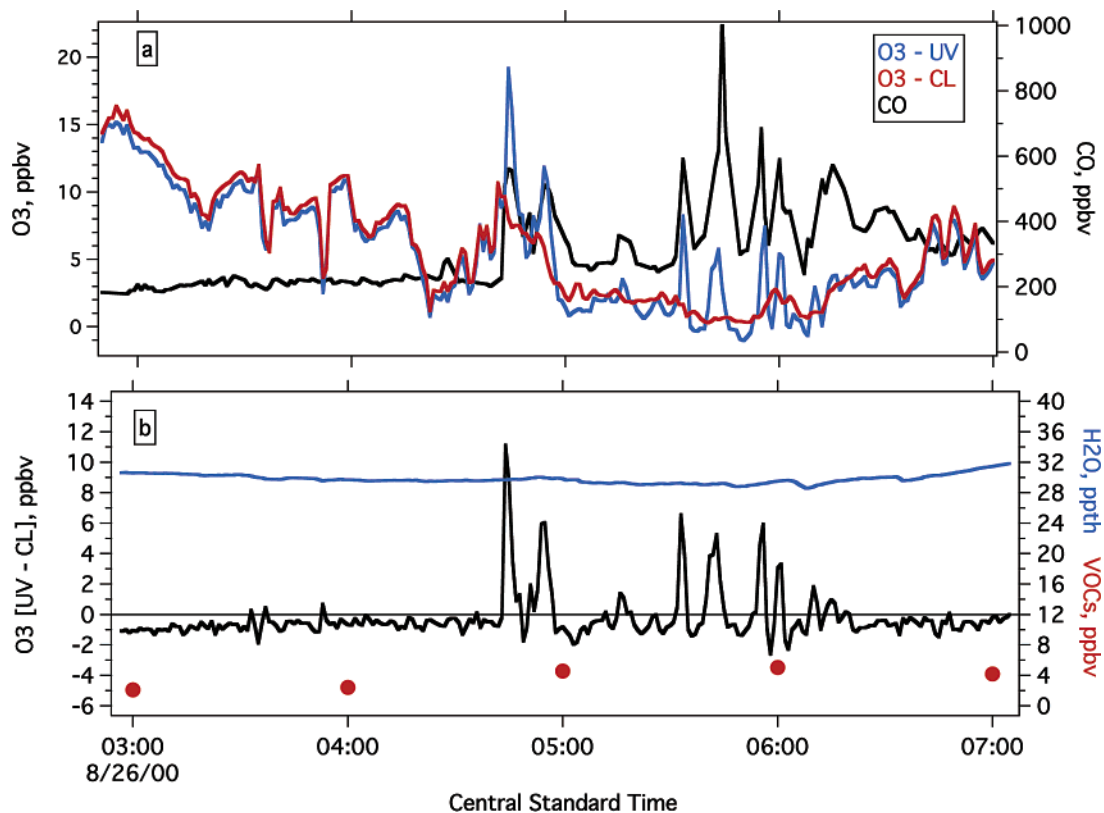
FIGURE 5. Similar to Figure 4, but limited to 0300–0700 CST on August 26, 2000. CO data (right axis) are added to the upper panel.
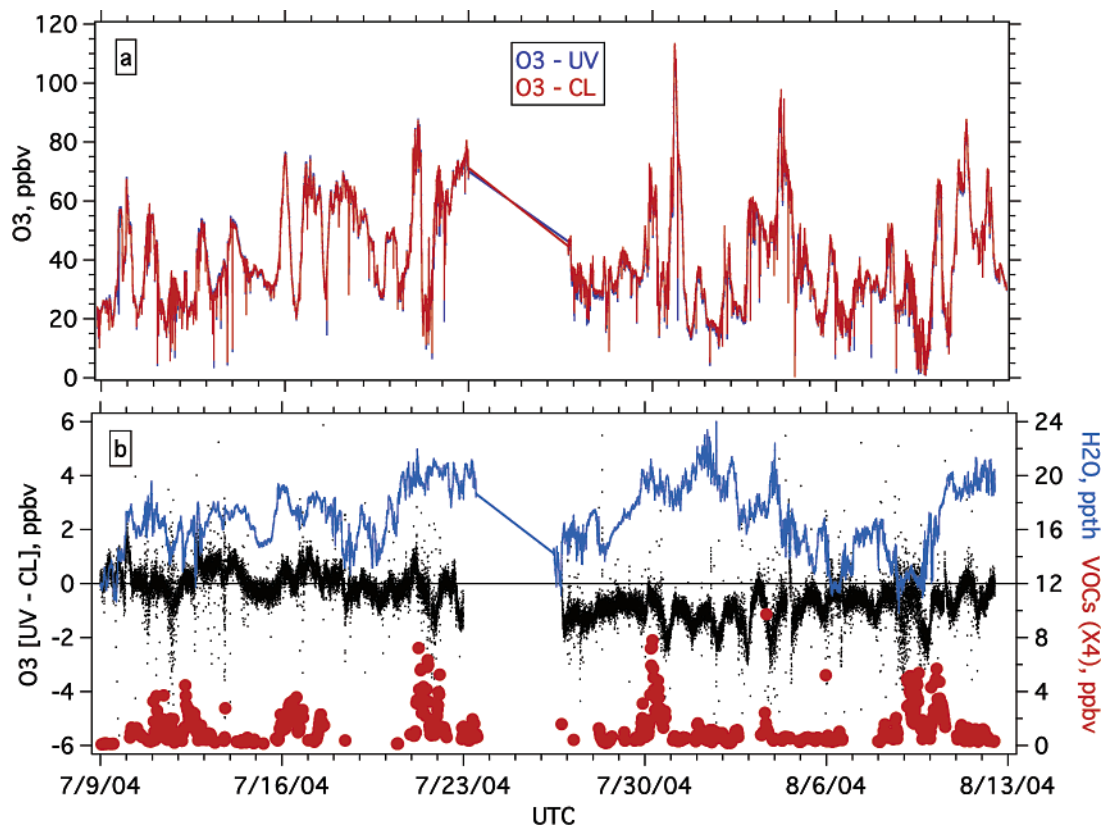

FIGURE 6. O_3 comparison data from Gulf of Maine, 2004. (a) One minute data: blue trace is UV; red trace is CL. (b) Absolute O_3 difference (UV−CL) shown as black dots (left axis); one-minute averaged water vapor mixing ratio shown by the blue line (right axis); sum of five-minute averaged measured aromatic VOC species shown as red dots (right axis).

parentheses are the absorbance data from Kleindienst et al. (*3*), where the absorbance of ozone is 3200 L/mol-cm. The average mixing ratios reported were 20−100 times lower than the maxima. However, with the reported maximum VOC values and the absorptivity data provided by Kleindienst et al. (*3*), this mix of VOCs would present at most a 3−4 ppbv

interference to a UV O_3 monitor. This assumes that these compounds were present all at the same time at the maximum reported levels and that they all were scrubbed with 100% efficiency by the O_3 trap in the instrument.

More highly derivatized aromatic VOCs have much higher absorptivities than the simpler aromatics shown above. For example, 2-methyl-4-nitrophenol absorbs 254 nm light about 1.5 times more efficiently than does O_3 (3). However, such species can present a nonnegligible interference to a UV absorbance O_3 monitor only if they are present in the atmosphere at high mixing ratios. This is not likely to be the case, as a recent review (16) of nitrophenol compounds in the atmosphere reports polluted urban maximum values on the order of 300−350 ng m^{-3}, or considerably less than 1 ppbv.

Gulf of Maine, 2004. The NQ04 data (43 485 points; Figure 6) exhibit different trends than the previous two data sets. There is little diurnal pattern evident due to few NO sources and considerably diminished O_3 surface deposition loss over the ocean. The O_3 differences are smaller: 98.9% are within ±2 ppbv and 99.9% are within ±4 ppbv. The sum of aromatic VOCs is much smaller here (note the factor of 4 scale change) primarily because these compounds are reactive and have been removed during transit over the water. The ship anchored overnight in the harbors of Boston and Portland and, on departure from each, was within the urban plumes during rush-hour. No deviations were found between UV and CL data during either of these periods.

Discussion of In Situ Comparisons. The O_3 comparisons from these three studies demonstrate the agreement between the UV and CL data to within <1% with no significant nonlinearity nor unexpected scatter, although correction of the CL data for absolute humidity improves the correlation. Nor were systematic deviations seen in plots of diurnal trends, either in all the data or with only high ozone (>80 ppbv) data (see the Supporting Information). No positive deviations were seen in the UV O_3 data compared to the CL data from the NQ04 study, which is consistent with the low levels of potentially interfering aromatic VOCs measured over the Gulf of Maine. For the NV99 study, the UV and CL data were consistent despite significant concentrations of strongly UV absorbing aromatic VOCs. For the TX00 study, a short episode of positive deviation of UV data from CL data was seen. The period (~90 min; 5−10 ppbv) correlated with enhanced pollution transported to the site from nearby sources. However, the identity of the interfering pollutant was not determined. Because the UV and CL detection methods are completely different, the similarity of the results indicates that, within the precision of the data and with the exception of a single incident, only O_3 is being detected by the two instruments.

The point should be made here that, although the UV instrument provides accurate data for the vast majority of urban and rural monitoring locations, there are areas where this may not be the case. In a region like La Porte, where industrial processes use, produce, and emit a vast array of chemical products, compounds that cause an interference in the UV instrument can be present. However, since these interfering compounds tend to be aromatic species with multiple functional groups, they are very reactive or of low vapor pressure, both of which will significantly reduce their concentration in the atmosphere except near sources. In these near-source locations, it may be prudent to have additional measurements, such as a CL O_3 monitor, to preclude false positive data.

Comparison of In Situ UV and Remote Sensing DOAS Instruments. At the two urban locations, DOAS instruments provided independent absolute O_3 measurements. Robust comparison of DOAS and in situ data can reveal the presence of systematic errors that affect the latter, such as loss of O_3
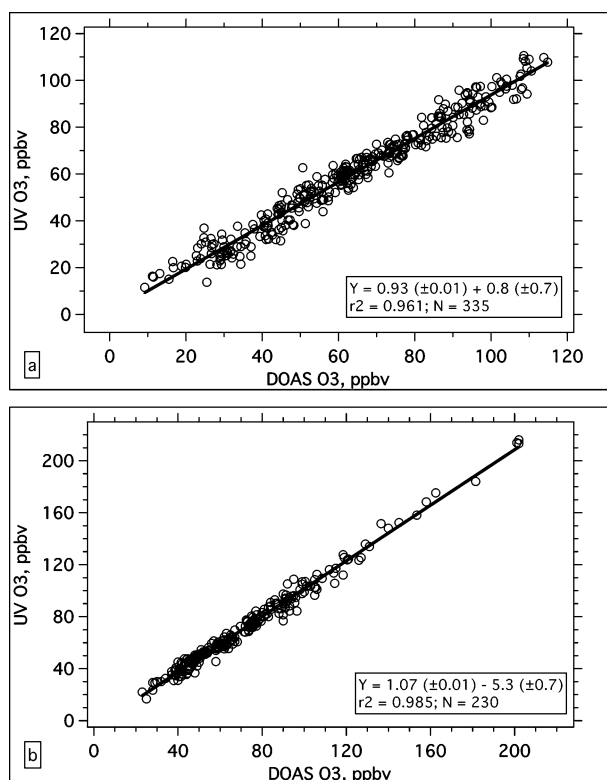

FIGURE 7. Comparison of in situ UV and DOAS O_3 data. (a) Scatterplot of the NV99 data. The black line is the one-sided linear least-squares fit to the data shown as circles. The fitting parameters (±1 standard error) are shown in the inset. (b) Similar to Figure 7a, except for TX00 data.
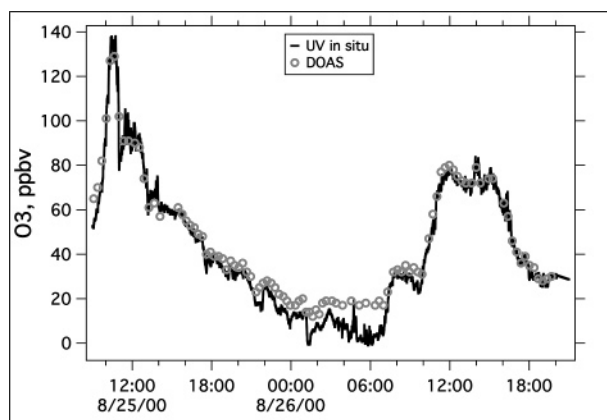

FIGURE 8. Time series of DOAS (circles) and UV absorbance (line) O_3 data from the TX00 study, limited to 0900 CST on August 25 to 2100 CST on August 26, 2000.

during transit down sample tubing or through filter media or via gas-phase reactions that can diminish O_3 levels during plumbing transit. On the other hand, comparison of long-path data to in situ data can be compromised due to spatial and temporal atmospheric inhomogeneities.

To reduce the effect of these inhomogeneities, for both urban sites the UV and DOAS data sets were averaged to common 30-minute measurement periods and then filtered to retain data between 1000 and 1800 CST, which is when the boundary layer is expected to be well-mixed. Figure 7 shows scatterplots of these comparisons (see the Supporting Information plots of all data). Both data sets show a high degree of correlation, but with different slopes. The overall ±7% variations from unity seen in the slopes likely reflect characteristics of the sampling locations and meteorology.

From these data we can conclude that the UV instrument systematically varies no more than ±7% from the completely independent DOAS technique.

Finally, the short time period of the discrepancy seen between the UV and CL instruments at the La Porte site is shown in Figure 8. During the day there is excellent agreement between the two systems, but at night the DOAS data are systematically higher than data from the in situ UV monitor. This is due to the DOAS beam scanning over a path that is higher in altitude than the sampling point of the UV instrument, thus measuring the higher O_3 levels that are aloft than those at the surface. This difference in sampling prevents use of the DOAS data to resolve the discrepancy seen in the in situ data (see Figure 5). However, the excellent daytime agreement with the DOAS data provides additional confidence in the veracity of data from the UV monitor. Thus, it is our conclusion that a well-maintained and properly operated UV photometric O_3 analyzer provides accurate O_3 measurements at urban as well as at remote sites.

Supporting Information Available

Additional information about the UV instrument and measurements at the three locations. Also, supplementary figures that show additional experimental details and data analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Leston, A. R.; Ollison, W. M.; Spicer, C. W.; J. Satola, J. Potential interference bias in ozone standard compliance monitoring *J. Air Waste Manage. Assoc.,* **2005**, *55*, 1464−1472.

(2) Kleindienst, T. E.; Hudgens, E. E.; Smith, D. F.; McElroy, F. F.; Bufalini, J. J. Comparison of chemiluminescence and ultraviolet ozone monitor responses in the presence of humidity and photochemical pollutants *J. Air & Waste Manage. Assoc.*, **1993**, *43*, 213−222.

(3) Kleindienst, T. E.; McIver, C. D.; Ollison, W. M. A study of interferences in ambient ozone monitors. In *Proceedings of a Specialty Conference: Measurement of Toxic and Related Air Pollutants*, VIP-74; Air and Waste Management Association: Pittsburgh, PA, 1997; pp 215−225.

(4) Arshinov, M. Yu.; Belan, B. D.; Krasnov, O. A.; Kovalevskii, V. K.; Pirogov, V. A.; Plotnikov, A. P.; Tolmachev, G. N.; Fofonov, A. V. Comparison of ultraviolet and chemiluminescent ozonometers *Atmos. Oceanic Opt.* **2002**, *15*, 656−658.

(5) Leston, A. R.; Ollison, W. M. The impact of ambient aerosols on ozone as measured by ultraviolet photometry. In *Measurement of Toxic and Related Air Pollutants*, VIP-100/CD, September 12−14, RTP, NC; Air and Waste Management Association: Pittsburgh, PA, 2000.

(6) Kauper, E. K., Ozone measurements over snow *Atmos. Environ.* **1978**, *12*, 1287−1288.

(7) Thornton, J. A.; Wooldridge, P. J.; Cohen, R. C.; Williams, E. J.; Hereid, D.; Fehsenfeld, F. C.; Stutz, J.; Alicke, B. Comparison of in situ and long path measurements of NO_2 in urban plumes, *J. Geophys. Res.* **2003**, *108* (D16), 4496, doi: 10.1029/2003JD003559.

(8) Stutz, J.; Alicke, B.; Ackermann, R.; Geyer, A.; White, A.; Williams, E. Vertical profiles of NO_3, N_2O_5, O_3, and NO_x in the nocturnal boundary layer: 1. Observations during the Texas Air Quality study 2000 *J. Geophys. Res.*, **2004**, *109*, D12306, doi: 10.1029/2003JD004209.

(9) Meyer, C. P.; Ellsworth, C. M.; Galbally, I. E. Water vapor interference in the measurement of ozone in ambient air by ultraviolet absorption *Rev. Sci. Instrum.* **1991**, *62*, 223.

(10) Maddy, J. A. A test that identifies ozone monitors prone to anomalous behavior while sampling hot and humid air, paper 98-MBP.02P. In *Proceedings of the Air and Waste Management Association,* 91st Annual Meeting, June 14−18, 1998, San Diego, CA; Air and Waste Management Association: Pittsburgh, PA, 1998.

(11) Ridley, B. A.; Grahek, F. E.; Walega, J. G. A small, high-sensitivity, medium- response ozone detector suitable for measurements from light aircraft *J. Atmos. Oceanic Technol.*, **1992**, *9*, 142−148.

(12) Alicke, B.; Platt, U.; Stutz, J. Impact of nitrous acid photolysis on the total hydroxyl radical budget during the Limitation of Oxidant Production/ Pianura Padana Produzione di Ozono study in Milan *J. Geophys. Res.*, **2002**, *107* (D22), 8196, doi: 10.1029/2000JD000075.

(13) Orphal, J. A Critical Review of the Absorption Cross Sections of O3 and NO2 in the 240−790 nm Region, Part I: Ozone. In *ESA Technical Note MO-TN-ESA-GO*-0302; European Space Agency: Noordwijk, 2002; pp 126.

(14) Stutz, J.; Platt, U. Numerical analysis and estimation of the statistical error of differential optical absorption spectroscopy measurements with least-squares methods *Appl. Opt.*, **1996**, *35*, 6041−6053.

(15) Jobson, B. T.; Berkowitz, C. M.; Kuster, W. C.; Goldan, P. D.; Williams, E. J.; Fehsenfeld, F. C.; Apel, E. C.; Karl, T.; Lonneman, W. A.; Riemer, D. Hydrocarbon source signatures in Houston, Texas: Influence of the petrochemical industry *J. Geophys. Res.*, **2004**, *109*, D24305, doi: 10.1029/2004JD004887.

(16) Harrison, M. A.; Barra, J. S.; Borghesi, D.; Vione, D.; Arsene, C.; Olariu, R. I. Nitrated phenols in the atmosphere: a review *Atmos. Environ.* **2005**, *39*, 231−248.