

UV-Absorption-Based Measurements of Ozone and Mercury: An Investigation on Their Mutual Interferences

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Abstract

Continuous mercury monitors (CMMs) have the advantage of performing real-time or near real-time measurement, although they are often vulnerable to measurement interferences. For example, CMMs based on atomic absorption spectrometry (AAS) are subject to interferences by components of the sample gas, such as ozone, if they happen to have strong absorption bands or lines overlapping the Hg absorption line. Studies on a selected commercially available CMM showed that 120 ppb of ozone could exert an interference of approximately 63 ng/m³ on Hg measurement. This interference may consequently affect the risk assessment of human exposure to Hg. On a similar basis, it was found that Hg can also result in significant interferences on an ozone analyzer based on UV absorption. Results showed that Hg at a concentration of 300 ng/m³ can potentially cause a bias in ozone measurement of approximately 35 ppb, comparable to the average ambient ozone concentration. It should be noted that interferences discussed in this paper are applicable only to UV-absorption-based Hg and ozone analyzers. It is also possible that certain models of such analyzers are not compromised by the reported interferences, and thus, the findings in this work should be considered as analyzer-specific.

Keywords: Measurement interference; Mercury; Ozone; UV adsorption; Atomic adsorption spectroscopy.

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INTRODUCTION

The 1990 United States Clean Air Act Amendments (CAAA) listed 189 hazardous air pollutants (HAPs), and among them, mercury (Hg) is believed to have a significant impact on human health (Brown *et al.*, 1999). The U.S. Environmental Protection Agency made a regulatory decision in 2000 that Hg should be controlled (USEPA, 2000), and finally issued the Clean Air Mercury Rule in 2005 to permanently cap and reduce Hg emissions from stationary sources (USEPA, 2005a). Consequently, Hg emission control technologies have developed rapidly in recent years (Pavlish *et al.*, 2003). Both Hg emission regulations and development of Hg control technologies require that reliable methods be used for accurate Hg measurement. Monitoring ground level of ozone, another significant air pollutant, is also required by the U.S. EPA. Control of ozone is expensive, with costs estimated in the billions of dollars (USEPA, 2005b). Hence, deployment of accurate ozone measurement is of great importance to demonstrate compliance with the National Ambient Air Quality Standard (NAAQS) for ozone.

Currently, the EPA-accepted methods for Hg measurement in the United States are manual procedures based on wet-chemistry, such as EPA Methods 29 and 101A (for total mercury) and the Ontario Hydro Method (for speciated mercury) (Laudal *et al.*, 2004). However, continuous mercury monitors (CMMs) have distinct advantages over these manual methods in that CMMs are able to provide a real-time or near-real-time response for Hg measurements and to perform long-term emission measurement to truly characterize a process' temporal emissions. On the other hand, a significant disadvantage of CMMs lies in their measurement interferences, which may vary depending on the principle of the Hg detection technique.

Atomic absorption spectrometry (AAS) is one of the major techniques applied to current CMMs. In the case of AAS, the concentration of elemental Hg in a gas sample is determined by measuring the light that is absorbed by Hg atoms at their characteristic wavelengths (usually at the resonance line of 254 nm). Thus, interferences can occur when other components of the sample gas possess strong absorption bands near this wavelength (254 nm). The EPA's Environmental Technology Verification (ETV) program (USEPA, 2001) identified sulfur dioxide (SO₂), nitrogen oxides (NO_x), hydrogen chloride (HCl), and chlorine (Cl₂) as interference gases by assessing the CMMs' responses to each gas, as well as to a mixture of the gases. Although pretreatment or conditioning systems can be used to remove or negate the effects of these interfering gases before sample delivery to the detectors (Laudal *et al.*, 2004), they may increase the complexity and cost of the instrumentation and impair the real-time feature of the CMMs. Consequently, many types of AAS-based CMMs do not have pretreatment systems.

Since the 254 nm Hg emission line also falls into the absorption spectra of ozone, which is capable of absorbing UV light below 290 nm, the presence of ozone in the sampling environment may impact the Hg measurement by AAS-based CMMs. Granite and Pennline (2002) studied

photochemical oxidation of Hg and speculated that photosensitized formation of ozone may interfere with Hg measurement by absorbing UV radiation. However, no quantitative data were reported on the magnitude of ozone interference. Therefore, the first objective of this study was to quantitatively investigate the interference of ozone on Hg measurement. This study may be of particular importance to ambient and indoor Hg measurement, because ozone and Hg coexist in these conditions.

As for the measurement of ozone, many methods have been developed, and UV absorption and gas-phase chemiluminescence are the major techniques used nowadays. The UV-absorption method is based on the principle that, upon exposure to UV light, ozone will absorb some of the light, and the intensity difference is directly proportional to the concentration of ozone. Frequently, the UV light source is a 254 nm emission line from a Hg discharge lamp. Known interferences on this type of ozone detection method include gaseous hydrocarbons with strong absorption at 254 nm, such as aromatic hydrocarbons (i.e., benzene and substituted benzene rings) (NARSTO, 1999). Since 254 nm is exactly one of the Hg absorption lines, it is speculated that even a small amount of Hg in the sample gas may absorb a considerable amount of UV light. The U.S. EPA (1999a) reported that at a baseline ozone concentration of approximately 75 ppb, the addition of 0.04 ppb Hg (300 ng/m^3 at room temperature) caused an increase in measured ozone concentration by 12.8% at low humidity (RH = 20 ~ 30%) and 6.4% at high humidity (RH = 70 ~ 80%) using a UV photometric ozone monitor. The interferences of Hg using another two types of ozone monitors were above 30% at either low or high humidity. However, the interference data reported were only at one Hg level (0.04 ppb). More data at other levels of Hg are needed to determine the relationship between Hg concentration and its corresponding interference. Therefore, the second objective of this study was to quantitatively investigate Hg interference on ozone measurement. This is of importance in accurate ozone measurement in ambient and indoor conditions.

METHODS

Descriptions of Hg and ozone instruments

The CMM used in this study is a RA-915+ Hg analyzer (Ohio Lumex Co.), which is capable of recording Hg concentrations every second. It employs Zeeman AAS using High Frequency Modulated light polarization (ZAAS-HFM) (Sholupov *et al.*, 2004), which combines the approach of AAS with a simultaneous background correction provided by the Zeeman splitting of the Hg resonance line (254 nm). In the RA-915+ Hg analyzer, the emissions from a Hg discharge lamp are subjected to a strong magnetic field, which causes the three-fold splitting of the Hg resonance line (π , σ^+ and σ^- , respectively). Two of these components (σ^+ and σ^-) have identical

intensity when Hg is absent in the analytical cell. When Hg is present in the cell, the difference between the intensities of the two components is proportional to the Hg concentration. The calibration was conducted by the manufacturer using Dynacal[®] permeation device (VICI Metronics, Inc.) which is certified traceable to NIST (National Institute of Standards and Technology) standards. Two optical cells are available for different ranges of Hg concentration. A single-path cell is available for measuring higher Hg concentrations from 0.5 to 200 $\mu\text{g}/\text{m}^3$. A multi-path cell with an effective length of 9.6 m is used to enhance the sensitivity of analysis, and thus the detection limit can reach as low as 2 ng/m^3 . The RA-915+ Hg analyzer may not be suitable for ambient Hg measurement since the ambient Hg concentration has been reported to be approximately 1.5 to 1.9 ng/m^3 in the Northern Hemisphere (Ebinghaus *et al.*, 2002; Weiss-Penzias *et al.*, 2003), which is lower than the detection limit of this instrument. However, the RA-915+ Hg analyzer has been used for measurement in stationary sources, or Hg contaminated sites (including indoor areas) (Pogarev *et al.*, 2002; Kinsey *et al.*, 2004; Sholupov *et al.*, 2004).

A M146 dynamic gas calibration system (Thermo Electron Instrument) served as the ozone generating source using its internal ozonator. The precision of the ozone concentration that can be generated is 1 ppb. A M49 UV photometric ozone analyzer (Thermo Electron Instrument) was used to measure the ozone concentration in the sample gas. The UV light source in the ozone analyzer is a 254 nm emission line from a Hg discharge lamp. The full scale of the ozone analyzer was set to be from 0 to 500 ppb. Its precision is 2 ppb, while the noise is within ± 1 ppb. This type of ozone monitor is equipped with a standard (manganese-dioxide) scrubber, which was reported to suffer the lowest interference from Hg compared to two other types of ozone monitors (USEPA, 1999a). A M49-PS UV photometric ozone calibrator (Thermo Electron Instrument) was applied to calibrate both the ozone generator and analyzer.

Experimental setup and procedures

A schematic diagram of the experimental system is shown in Fig. 1. All experiments were carried out at room temperature ($25 \pm 1^\circ\text{C}$). To test the ozone interference on Hg measurement (Fig. 1a), zero air was produced using a zero air supplier (M111, Thermo Electron Instrument) and then passed through the ozone generator to provide designated ozone concentrations. The total air flow rate at the outlet of the ozone generator was controlled at 5 L/min. The ozone-laden air was then divided into two streams and connected to the RA-915+ Hg analyzer and the ozone analyzer, respectively. The reading from the Hg analyzer would indicate potential interference caused by ozone. The interferences from a designated range of ozone concentrations were measured. Each time before changing the ozone concentration, the entire system was purged by ozone-free air until the readings from both Hg and ozone analyzers were zero. This was to

minimize the experimental error from residual ozone in the system. Finally, the sample gas was cleaned through an activated carbon trap before being exhausted through the vent hood.

Fig. 1b shows the experimental setup for testing Hg interference on ozone measurement. The incoming zero air with a flow rate of 5 L/min was split into two streams. One stream was passed through the surface of a liquid Hg reservoir, which was placed in an ice-water bath to maintain a constant Hg vapor pressure. By doing this, saturated Hg vapor was introduced into the system. The other stream served as dilution air and was used to adjust the Hg concentration. Both air streams were controlled by mass flow controllers (MFC, Model. FMA 5400/5500, Omega Engineering, Inc.). The RA-915+ Hg analyzer was used to measure the Hg concentration in the sample gas while the ozone analyzer was used to detect the potential interference caused by Hg. Similarly, the interferences from a designated range of Hg concentrations were measured, and each time before changing the Hg concentration, the entire system was cleaned until the readings from both Hg and ozone analyzers were zero.

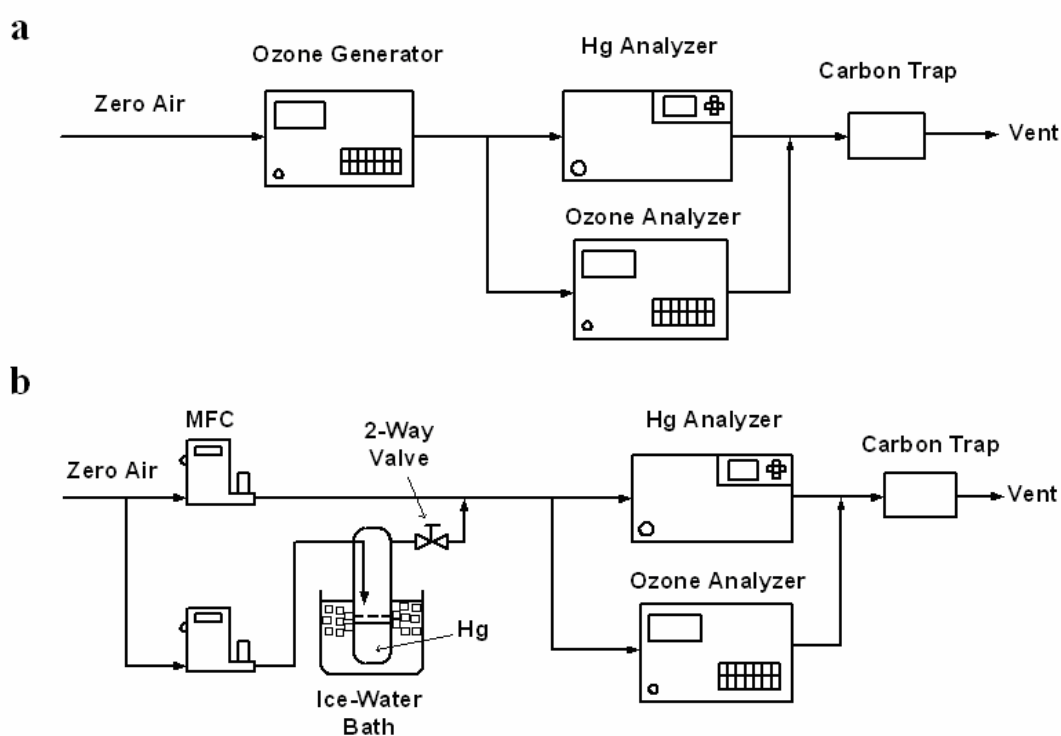


Fig. 1. Schematic diagram of the experimental setup.
(a) Ozone interference on Hg measurement;
(b) Hg interference on ozone measurement.

RESULTS AND DISCUSSION

Interference of ozone on Hg measurement

The NAAQS for ozone is 80 ppb for an 8-hour average and 120 ppb for a 1-hour average (USEPA, 1997). Thus, the ozone concentration generated in this work ranged from 0 to 120 ppb. The corresponding interference on the RA-915+ Hg analyzer is shown in Fig. 2. The blank test showed that no interference was detected when no ozone was fed into the gas stream. As the ozone concentration increased, the reading on the Hg analyzer was almost linearly elevated. At each ozone concentration level, tests were repeated three times. For ozone concentrations at 80 and 120 ppb, the interferences on Hg measurement reached approximately 46 and 63 ng/m³, respectively. The relationship between ozone concentration and its corresponding interference can be approximated as:

$$C_{Hg,e} = 0.5559 \times C_{O_3} \quad (1)$$

where $C_{Hg,e}$ is the equivalent Hg concentration; i.e., the interference on Hg analyzer (in units of ng/m³) and C_{O_3} is the ozone concentration (in units of ppb). 1 ng/m³ of Hg is equivalent to 1.22×10^{-4} ppb at room temperature. For a convenient understanding of the significance of the interference magnitudes, units used in Eq. 1 and Eq. 2 are in line with the EPA standards (USEPA, 1997; 1999b).

This observed ozone interference may have an important effect on Hg measurement. For example, Ferrara (1999) used the RA-915+ Hg analyzer to measure the Hg distribution over the area of Idria, where one of the largest European Hg mines was located. The Hg concentration was reported to range from 50 to 170 ng/m³ in the central part of Idria near the Hg mines and dumps. Suppose that 40 ppb ozone existed in that local atmosphere, an overestimate of Hg concentration at about 22 ng/m³ would have been involved according to the results from this work.

Indoor Hg measurement can also be affected by ozone interference. Although indoor ozone levels are typically less than those outdoors (Weschler, 2000), they can be much greater when strong ozone-generating sources are present, such as photocopiers, electrostatic filters, and ozone generators (Godish, 2001). In addition, the use of ozone for the removal of indoor air contaminants has been widely promoted in the United States (Li *et al.*, 2002). In those areas with elevated ozone concentrations, the interference of ozone on Hg measurement may result in a significant overestimate of Hg concentrations when using RA-915+ or other similar Hg analyzers.

It has been indicated by Singhvi *et al.* (2001) that water vapor can have positive interference on UV Hg analyzers. The magnitude of this interference was not reported, and it could vary for different UV Hg analyzers. If this positive interference of water vapor were applied to the RA-

915+ Hg analyzer used in this study, the total interference on Hg measurement (caused by both ozone and water vapor) could be even larger.

The interference of ozone on Hg measurement can also impact the risk assessment of human exposure to Hg. The Reference Concentration (RfC) for elemental Hg specified by the EPA is 300 ng/m³ based on central nervous system (CNS) effects in humans (USEPA, 1999b). Hg concentrations above this level may result in a further investigation of hazardous exposure. According to the findings in this work, an ozone concentration in the range of 0-120 ppb can exert a positive bias in Hg measurement up to 21% (63 ng/m³) of the EPA RfC (300 ng/m³). The interference may be especially critical for conditions where the measured Hg concentration is slightly above the RfC level, because after subtracting the bias caused by ozone interference, the actual Hg concentration may not exceed the RfC any more. Therefore, eliminating ozone from sample gas is essential to obtain accurate Hg concentration and thus is important for risk assessment of human exposure to Hg. Helmig (1997) reviewed ozone removal techniques in sampling of atmospheric volatile organic trace gases. These techniques may be applicable to ozone removal in Hg sampling as long as they do not tamper with Hg concentrations.

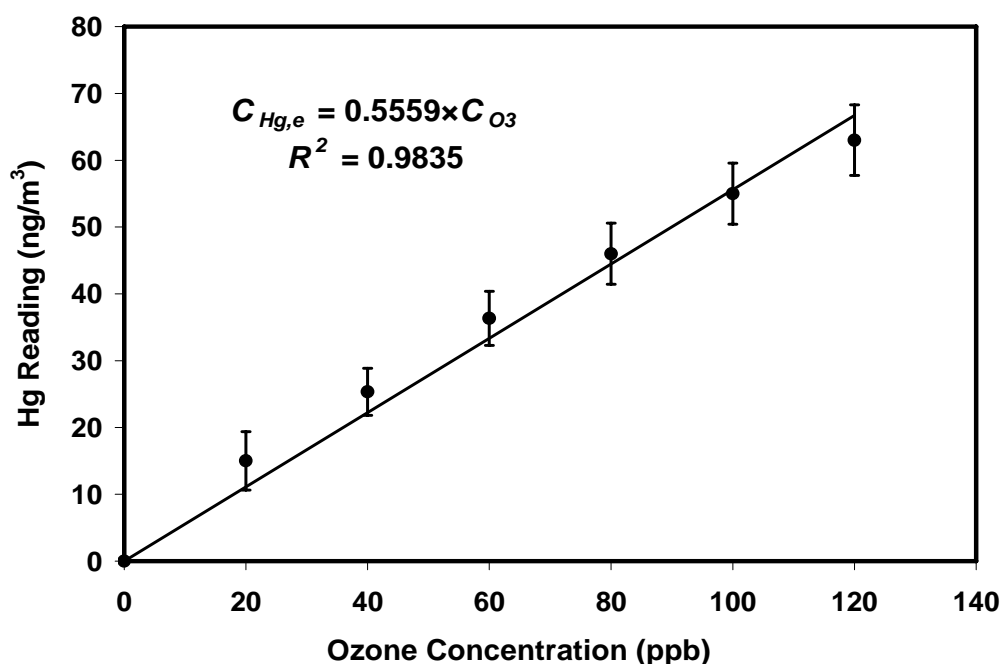


Fig. 2. Measurement interference of ozone on the RA-915+ Hg analyzer as a function of ozone concentration (error bars represent one standard deviation).

Interference of Hg on ozone measurement

A designated range of Hg concentrations was fed into the gas stream to investigate the possible Hg interference on ozone measurement. Due to the limitation of the Hg vapor-generating unit used in this work (the dilution ratio was relatively small compared with the saturated Hg vapor concentration), the minimum Hg concentration introduced was about 2300 ng/m³. In addition, Hg levels were controlled so that the interferences on ozone readings were within the measurement range of the ozone analyzer (0-500 ppb). A blank test showed no interference when no Hg was present. As the Hg concentration in the sample gas increased, the corresponding reading on the ozone analyzer also increased (as shown in Fig. 3). An approximately linear relationship can be obtained as expressed in the following equation:

$$C_{O_3,e} = 0.1165 \times C_{Hg} \quad (2)$$

where $C_{O_3,e}$ is the equivalent ozone concentration; i.e., the interference on ozone analyzer (in unit of ppb) and C_{Hg} is the Hg concentration (in unit of ng/m³).

Eq. 2 implies that Hg can exert a significant interference on ozone measurement, which is very likely due to the UV absorption by Hg when passing through the ozone analyzer (USEPA, 1999a). Although the Hg level in the ambient and indoor environment is typically lower than the minimum Hg concentration (2300 ng/m³) tested in this work, the results obtained can be used as a reference to predict the practical conditions. It should be noted that extrapolation beyond the tested concentration range might involve errors that could impact the accuracy of the prediction. However, given the high value of R^2 (0.9957) in the regression analysis which has incorporated the origin point, it is suggested that the error associated with the extrapolation to the range of 0 to 2300 ng/m³ may not be significant. Carpi and Chen (2001) reported that the highest Hg concentration measured at 12 indoor sites in New York City was 523 ng/m³. This Hg level would result in 61 ppb interference on ozone measurement using a UV-absorption-based ozone analyzer, provided that Eq. 2 is valid at lower Hg concentration levels. The interference, 61 ppb, added to the normal ambient ozone concentration (0-50 ppb) (Lim and Turpin, 2002), may have many chances to exceed the NAQQS for ozone (80 ppb). In the case when Hg concentration is equal to the EPA RfC (300 ng/m³), an interference of 35 ppb would be involved, which is comparable to the average ambient ozone concentration.

Since indoor ozone concentration is typically lower than that outdoors (Weschler, 2000) and indoor Hg concentrations generally higher than that outdoors due to various indoor Hg contamination sources (such as accidental spills of Hg from natural gas meters, Hg thermometers, fluorescent light bulbs, etc.) (Carpi and Chen, 2001), the impact of Hg interference on indoor

ozone measurement may be much greater. These results indicate that it is essential to eliminate the Hg interference to obtain correct ozone concentration at Hg contaminated places.

Once the linear relationship between Hg concentration and corresponding interference on ozone measurement was successfully established, it was necessary to compare the results with those by the EPA (1999a) where the same type of ozone monitor was used. At a Hg concentration of 0.04 ppb (328 ng/m³ at 25°C), Eq. 2 predicts an ozone interference of 38 ppb, whereas the EPA (1999a) reported approximately 10 ppb at low humidity (RH = 20 to 30%) and 5 ppb at high humidity (RH = 70 to 80%). Since in this work the experiments were conducted using dry zero air, comparison of the above results suggests that higher humidity may diminish the interference caused by Hg. A possible reason is the deposition of water vapor in the optical cell attenuates the incident UV light, causing a negative interference by water vapor itself. The finding also suggests that the reported interference may not be so significant in ambient and indoor air as in the dry air used in this work. Further research is needed to verify this hypothesis.

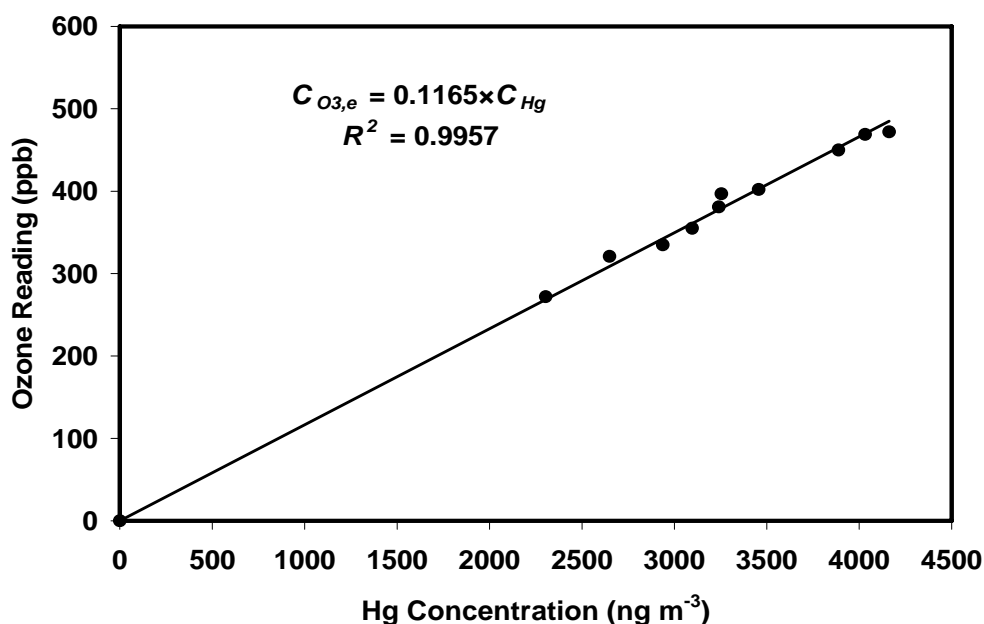


Fig. 3. Measurement interference of Hg on the ozone analyzer as a function of Hg concentration.

CONCLUSIONS

Mutual interferences of UV-absorption-based measurements of ozone and Hg were investigated in this study. It was found that ozone in the range of 0 to 120 ppb can exert an interference of up to 63 ng/m³ on an AAS-based Hg analyzer. A linear relationship was established between the ozone concentration and corresponding interference on Hg measurement.

On the other hand, it was found that Hg can also result in significant interferences on an ozone analyzer based on UV absorption. Results showed that Hg at a concentration of 300 ng/m³ can potentially cause a bias in ozone measurement of approximately 35 ppb. These mutual interferences may consequently affect the risk assessment of human exposure to both Hg and ozone. It should be noted that the results were obtained from relatively small set of instrumentation (only one Hg and one ozone analyzer). There are many different types of Hg and ozone analyzers based on principle of UV absorption. It is possible that certain types of analyzers are not compromised by the interferences found in this work. Thus, the findings in this work should be considered as analyzer-specific. Further investigation is needed to determine whether the trends observed in this work can be extended to other types of analyzers.

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