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Laboratory Study to Explore Potential Interferences to Air Quality Monitors

EPA Disclaimer

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Section 1
Introduction

The ozone reference measurement principle and calibration procedure, promulgated in 1971 and amended in 1979, is based on detection of chemiluminescence resulting from the reaction of ozone with ethylene gas. When ultraviolet (UV) absorption photometric analyzers were first approved as equivalent methods in 1977, they gained rapid, almost universal acceptance. Today, users have their choice of many approved UV instruments from several manufacturers. The analytical principle is based on absorption of UV light by the ozone molecule and subsequent use of photometry to measure reduction of the quanta of light reaching the detector at 254 nm. The degree of reduction depends on the path length of the UV sample cell, the ozone concentration introduced into the sample cell, and the wavelength of the UV light, as expressed by the Beer-Lambert law. Any ozone analyzer used for routine ambient air monitoring must be calibrated against a suitable ozone primary standard or a secondary standard directly traceable to a primary standard. However, the chemiluminescence method is not problem-free.

Issues revolving around the UV measurements of ozone have been ongoing since 1989. Interferences due to water vapor, aromatic hydrocarbons, and mercury are acknowledged and procedures for minimizing these interferences are documented in the *Determination of Ozone by Untraviolet Analysis*, Draft May 1, 1997[1] and the *QA Handbook, Volume II*.[2] Oscillation or cyclic behavior of the UV analyzer output has been observed with the use of a strip chart recorder. If a strip chart recorder or high-resolution data logger is not used, the cycling problem may go unnoticed. The exact cause of the cycling baseline is still undetermined. Although the ozone scrubber of the analyzer appears to be involved, the cause is believed to be more complicated and may result from a combination of conditions possibly involving humidity, inlet lines, filters, ozone scrubber, other atmospheric pollutants or other unknown factors. From the information available, the problem is most likely to occur on hot and humid days. Interferences with the UV-based method are known,[1]

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[1]U.S. EPA (1997). Determination of Ozone by Ultraviolet Analysis. A New Method for Volume II, Ambient Air Specific Methods, QA Handbook for Air Pollution Measurement Systems, Final Draft, May 1, 1997. http://www.epa.gov/ttn/amtic/files/ambient/qaqc/ozone.pdf.

[2]U.S. EPA (1998). Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Part 1, EPA-454/R-98-004, August 1998. http://www.epa.gov/ttn/amtic/files/ambient/qaqc/redbook.pdf.

but it is unclear to what extent these interferences occur in real world monitoring and the quantitative effect on actual monitoring data is also not known.

Over the years a tremendous amount of work has been done by the U.S. Environmental Protection Agency, States (Connecticut, West Virginia, and Virginia), and the American Petroleum Institute to try to pinpoint and resolve the issues with the cycling and erratic baseline phenomenon. Researchers have documented water vapor interferences to chemiluminescence monitors using the ozone-ethylene reaction.[3] Others have reported UV photometric ozone monitor interferences due to some aromatic hydrocarbons.[4] Substances that interfere have strong absorbance at 253.7 nm wavelength of the UV lamp used in photometric monitors, and are also removed by the catalytic ozone scrubber. Some instrument manufacturers have recently developed a different scrubber for use with photometric ozone monitors.[5] The new scrubber design uses a heated metal surface to catalytically destroy ozone. The design is meant to minimize the uptake of potential ozone interferences.

This report describes two supplemental tasks that complement the ongoing research investigating potential interferences in ozone monitoring. The first task involves the investigation of potential H_2S poisoning of new heated catalysts used to scrub ozone in ozone monitors. These catalysts have been developed to replace conventional unheated manganese dioxide scrubbers that are presently being used. The second task focuses on determining long term potential monitor interferences with new heated scrubbers from mercury and select VOCs, that have not been previously tested.

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[3]Kleindienst,T.E., Hudgens, E.E., Smith, D.F., McElroy, F.F., and J.J. Bufalini, Comparison of Chemiluminescence and Ultraviolet Ozone Monitor Responses in the Presence of Humidity and Photochemical Pollutants. Journal Air and Waste Management Association. 43:213-222, February 1993.

[4]Kleindienst, T.E., McIver, C.D., and W.M. Ollison, A Study of Interferences in Ambient Ozone Monitors. Presented at the Air and Waste Management Association meeting in Research Triangle Park, N.C. May 1997.

[5]Maddy, J.A. Evaluating a Heated Metal Scrubber's Effectiveness in Preventing Ozone Monitor's Anomalous Behavior During Hot and Humid Ambient Sampling. Paper No. 99-451. Proceedings of the Annual Air & Waste Management Association Meeting, St. Louis, MO, June 1999.

Section 2
Technical Approach

Task 1. Laboratory Investigation of H_2S Poisoning of Heated Metal Catalyst

The first task undertaken was to determine the amount of H_2S uptake associated with the newly developed (heated catalyst) ozone scrubbers and to measure the effect of H_2S on scrubber efficiency. At this time there are two types of heated scrubbers being used: the Advanced Pollution Instruments (API) heated metal scrubber and the Horiba Instruments heated silver wool scrubber. Neither scrubber was commercially available at the start of testing. Because the proposed tests would likely result in poisoning the catalysts, the individual manufacturers were requested to donate a scrubber to this study with the knowledge that the scrubbers could be damaged. The scrubber provided by Advanced Pollution Instruments was selected for testing because the scrubber and heater were packaged as a separate unit and could be tested independent of any analyzer.

During the test, the scrubber was exposed to artificially high levels of H_2S (1000 ppb) for 16 days, which represents almost 8.5 years of exposure to ambient air with a H_2S concentration of 5 ppb. The mass of H_2S removed by the scrubber was measured. After exposure, the scrubber efficiency for ozone removal was tested at several ozone concentrations.

Experimental Setup

The equipment setup used in the investigation of H_2S removal by heated metal catalyst is shown in Figure 1. A Metronic's Dynacalibrator with a Dynacal 4 cm H_2S permeation tube was used to generate H_2S at a rate of 2.04 micrograms per minute (µg/min) at 30EC. As shown, the H_2S air flow from the calibrator's permeation chamber and the calibrator's dilution air were mixed after the dilution air was humidified. This was done to prevent damage to the humidity monitor and to minimize H_2S loss from the sample stream.

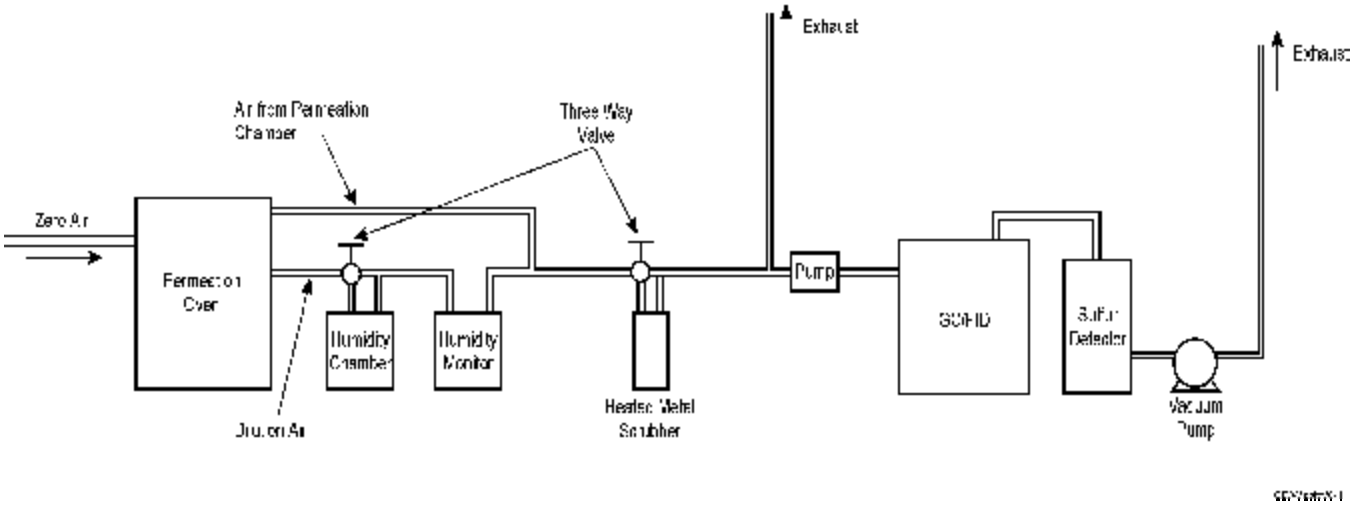

Figure 1. Equipment Setup for H_2S Experiment

H_2S concentrations were measured using a Siever Model 350B, sulfur chemi-luminescence detector interfaced to a Hewlett Packard Model 5890 gas chromatograph (GC) equipped with a flame ionization detector (FID). The Model 350B is a sulfur-selective detector based on a chemiluminescent reaction between ozone and combustion products of sulfur-containing analytes formed in a hydrogen/air flame provided by the Hewlett Packard GC/FID.

The heated metal scrubber was placed between the H_2S generation unit and the sulfur detector in a manner to allow the scrubber to be put in line or bypassed using a three-way valve. A stainless steel pump extracted a 60 cc/min sample from the manifold and pushed it through a 1/32 inch capillary tube to the hydrogen/air flame of the GC/FID. A ceramic probe positioned above the flame and attached to black PFA tubing collected and carried the combustion gases to the chemiluminescence reaction cell. H_2S and most other sulfur species are transformed to sulfur monoxide in the hydrogen flame of the FID. The sulfur monoxide is then reacted with ozone (from an ozone generator), and the resulting chemiluminescence is measured.

A Dell Optiplex GX5133 computer equipped with LabTech Notebook software was used to collect data in electronic form. Data points were recorded every 10 seconds with an Okidata Microline 321 nine pin printer.

Test Procedures

The purpose of this test was to pass a known quantity of H_2S through a heated metal scrubber, to determine how much H_2S would be collected and whether the H_2S would affect the scrubber's ability to remove ozone.

The original test plan called for exposing the heated metal scrubber to artificially high levels of H_2S (0.5-1.0 ppm) at approximately 50 percent relative humidity for up to 5 days, or until the scrubber no longer exhibits H_2S removal. However, during the preliminary setup of this experiment, a substantial decrease in the baseline (scrubber bypassed) H_2S concentration was observed as the relative humidity was increased above 10%. Decreases of up to 40% of the H_2S concentration occurred when the humidity was increased from 10% to 30%. Several attempts were made to determine if these losses were real or caused by moisture interference with the sulfur detector. All sample lines that H_2S passed through were shortened and/or changed to Teflon where possible. All metal parts except the GC supply pump were replaced. Efforts to control the problem were further complicated because the decrease in concentration was not consistent with humidity changes.

Since a reliable measurement of H_2S collected on the scrubber could only be verified at low humidities, it was decided to run the test at a low humidity and also to increase the length of exposure. This was done by increasing the scrubber's exposure time from 5 days to 16 days at a H_2S emission rate of 2.04 micrograms per minute. At a dilution air flow rate of 1390 cc/minute, this would produce a concentration of 1.053 ppm. To determine the H_2S uptake of the scrubber, the H_2S concentration measured as the sample stream passed through the scrubber was divided by the concentration of the sample air when in the bypass mode. This ratio is used in the following equation to calculate the rate of H_2S captured on the scrubber. By integrating the capture rate over the 16-day test period the total mass of H_2S collected on the scrubber is determined.

H_2S uptake (µg/min) =

$$\textit{Permeation output } (\mu g / min) \; \frac{1 - H_2S \text{ concentration from scrubber (ppb)}}{H_2S \text{ concentration bypass scrubber (ppb)}}$$

During exposure, flow rates and scrubber temperatures recommended by the manufacturer were maintained. H_2S was measured first in the bypass mode to establish baseline concentrations and then with the scrubber in line to assess uptake (and possibly scrubber poisoning). Periodic baseline measurements taken throughout the test were used to determine H_2S uptake. After the first 9 days of H_2S exposure, the scrubber efficiency in removing ozone was measured by passing a sample of 100 ppb ozone in air through the scrubber at a flow rate of 3 lpm. No reduction in scrubber efficiency for ozone was observed. The H_2S exposure was then conducted for an additional 8 days. At that time (16 days) the scrubber ozone removal efficiency was again measured. This time the efficiency test was conducted over a period of 5 days at 100 ppb. of ozone.

Task 2. Laboratory Investigation of Potential Ozone Monitor Interferences

An investigation of potential interferences was conducted on the following ozone monitors:

- Thermal Electron Model 49 UV Photometer equipped with a manganese-dioxide scrubber
- Dasibi Model 1008-PC UV Photometer equipped with a heated metal scrubber
- Bendix Model 8002 chemiluminescent analyzer
- Horiba Model APOA-360 UV Photometer equipped with a heated silver wool scrubber.

All analyzers were simultaneously exposed to individual concentrations of o-nitrotoluene, o-cresol, and mercury at low and high relative humidities.

Experimental Setup

The equipment setup used to investigate potential interferences to the ozone monitors is shown in Figure 2. This system is composed of two parts, a concentration generating section (A) and a measurement section (B). In the concentration generating section, clean hydrocarbon free air from an Aadco clean air system was delivered (20 psig) to the equipment setup at point (1). From this point clean air was supplied to an Environics Series 100 ozone generator (2), a Metronics Model 340 Dynacalibrator (3) and two Tylan mass flow controllers (4) and (5). The Metronics Dynacalibrator's temperature controlled oven was used with calibrated permeation tubes to generate known concentrations of individual interferants. A controlled source of ozone was provided by the Environics ozone generator. A mass flow controller at point (4) provided clean air to the humidifier, while the controller at point (5) provided dilution air. The water trap (7) positioned after the humidifier removed any water droplets from the gas stream. A glass mixing chamber and Teflon filter holder were placed between the generation section and the measurement section to assure a well mixed gas stream and to remove any water droplets that may have formed due to condensation.

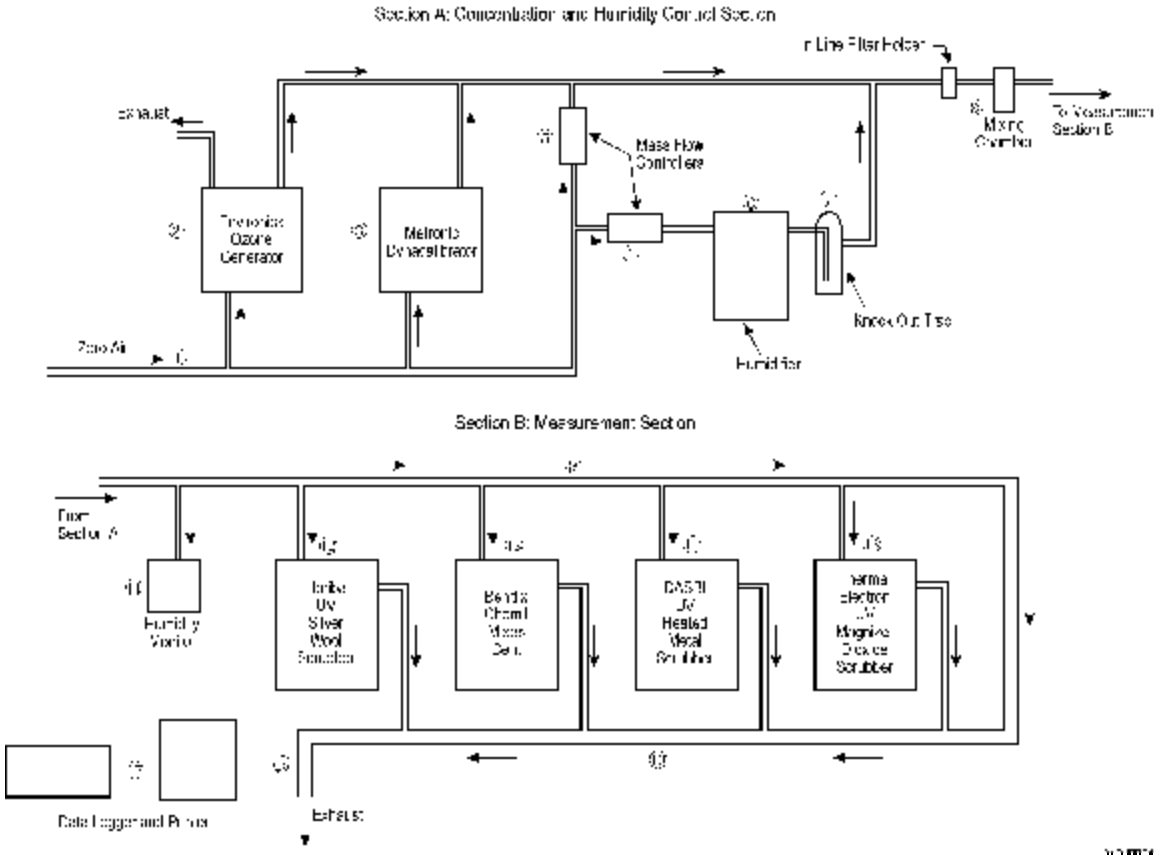

Figure 2. Schematic of System to Test Scrubber Absorbance of H_2S Over the 16-Day Test Period

The measurement section consisted of an Ace Glass 25 mm glass sampling manifold with six sample ports (9). Excess sample air from the sampling manifold flowed into a 51 mm PVC exhaust manifold (10) which exhausted to the outside (16). Relative humidity of the sample air was measured at the first port of the sampling manifold using an Edge Tech Model 911, Dew-All Digital Humidity Analyzer (11). The individual ozone analyzers consisted of a Horiba UV photometer (12), a Bendix chemiluminescent analyzer (13), a Dasibi UV photometer (14), and a Thermal Electron UV photometer (15). These were attached to the next four ports. The sixth port was blanked off. The exhaust port of each of the analyzers was attached to the exhaust manifold. The exhaust gases along with the excess sample air were vented outside the laboratory.

A Dell Optiplex GX5133 computer equipped with LabTech Notebook software was used to collect data in electronic form. Data points were recorded every second with an Okidata Microline 321nine pin printer.

Test Procedures

Nitrotoluene, cresol, and mercury were selected as three chemicals that had a potential to interfere with ozone measurements. Each of these interferants was evaluated under conditions of both high (70 to 80%) humidity and low (20 to 30%) humidity to determine if any discernable differences in effects could be seen. Prior to the start of the test series, a multi-point calibration was conducted on each analyzer using the Environics ozone generator and dry air. Although numerous zero and span checks were conducted during the tests, no additional adjustments were made to the analyzers. Data sets for each test were corrected for each individual analyzer's zero and span drift.

The step sequence followed for each test series is shown in Table 1. At the beginning of each test instrument zero and span checks (Steps 1 and 2) were made on all four analyzers. These checks were done at the same relative humidity at which the tests were to be conducted. Once the span reading had stabilized, a known concentration of the chemical being investigated was introduced into the system (Step 3). Care was taken to assure that the total air flow remained constant thus preventing dilution of the ozone concentration. This was done by reducing the dilution air flow by the same amount that was added by the flow from the permeation chamber of the Metronic's Dynacalibrator. Once the interferant was introduced, the test was continued for at least 8 hours. After 8 hours, the interferant concentration was reduced to zero, and the test continued for an additional 8 hours (Step 4). This was done to determine what, if any, recovery time would be required for those analyzers that showed interference. A zero and span check was conducted at the end of Step 4 to determine instrument drift. These steps were then repeated under conditions of low humidity (Steps 6 through 10).

The following Dynacal permeation tubes were used in the generation of interferants for individual tests.

- o-Cresol: 12 cm tube with a permeation rate of 110 ng/min/cm at 90EC
- o-Nitrotoluene: 20 cm tube with a permeation rate of 80 ng/min/cm at 90EC
- Mercury: 0.5 cm tube with a permeation rate of 4 ng/min at 30EC.

Table 1. Test Cycle Used for Nitrotoluene, Cresol, and Mercury

Step	Purpose	Interferant Concentration	Ozone Concentration	Relative Humidity
1	Establish ozone analyzers' zero at high RH	None	None	High
2	Establish ozone analyzers' span at high RH	None	High	High
3	Investigate potential interference on individual analyzers over 8 hours	High	High	High
4	Investigate recovery time for analyzers with indication of interference and verify instrument span (8-hour test)	None	High	High
5	Verify analyzers' zero at high RH	None	None	High
6	Verify analyzers' zero at low RH	None	None	Low
7	Verify analyzers' span at low RH	None	High	Low
8	Investigate potential interference on individual analyzers over 8 hours	High	High	Low
9	Investigate recovery time for analyzers with indication of interference and verify instrument span (8 hours test)	None	High	Low
10	Verify analyzers' zero at low RH	None	None	Low

Section 3
Test Results

H_2S Poisoning of Heated Metal Scrubber

The primary purpose of this study was to determine if H_2S in the ambient air would degrade the ozone scrubbing ability of a heated metal scrubber. Such damage could result in ozone passing through the scrubber, thus causing a falsely high baseline. This high baseline in turn would result in the analyzer generating measured ozone concentrations that would be biased low. To determine if poisoning could occur, a heated metal scrubber was exposed to an artificially high concentration of H_2S (1053 ppb) for a period of 16 days. Exposure to this high concentration of H_2S is equivalent to almost 9 years of ambient air exposure to H_2S at 5 ppb. During the exposure test, concentrations of H_2S passing through the scrubber were continuously measured while baseline concentrations were recorded periodically. The measured rate of H_2S absorbed by the heated metal scrubber over time is presented in Figure 3. As shown in Figure 3, the rate of H_2S removal decreased rapidly from 100 to 40% over the first few hours and then decreased slowly over the next 6 days for an average of 36% removed. On the seventh day, the vacuum pump for the sulfur detector failed and had to be replaced. During the period when the sulfur detector was not operating, the heated scrubber continued to be purged with H_2S. When the detector was brought back on line on Day 8, the amount of H_2S being absorbed had increased to 41%. This change in removal remained relatively constant for the remainder of the test.

After 9 days of H_2S exposure, the heated metal scrubber was placed in line between the ozone generator and the ozone analyzer. Sample air containing 100 ppb of ozone was passed

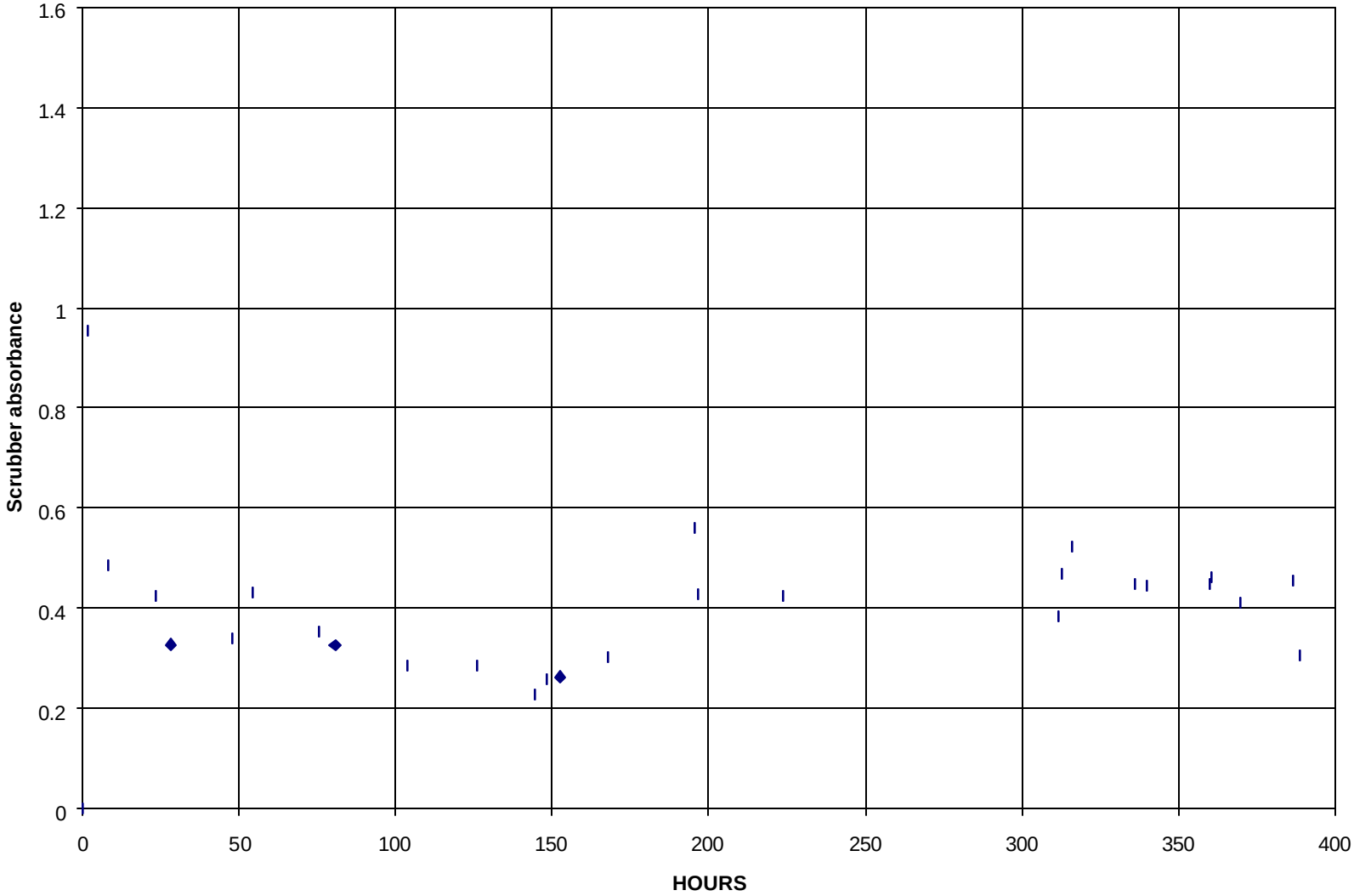

Figure 3. H_2S Absorbance by Heated Metal Scrubber

through the scrubber and the removal efficiency was found to be 100%. Results of the ozone scrubber efficiency test are shown in Table 2.

After the 16 days of H_2S exposure, the heated metal scrubber was again placed in line between the ozone generator and the ozone analyzer. Sample air containing 100 ppb of ozone was passed through the scrubber and the removal efficiency was found to be 100%.

Sample air containing 100 ppb of ozone was then passed through the scrubber for an additional 6 days. At the end of the sixth day the scrubber efficiency for ozone was still at 100%. At this time the scrubber heater was turned off. Sixteen hours later no decrease in efficiency was observed. The ozone concentration was then increased several times from 100 ppb, to 200 ppb, then 500 ppb, and finally to 1000 ppb to see if breakthrough could be forced. No break through was observed and the scrubber efficiency remained at 100%.

Table 2. H_2S Removal by Heated Metal Ozone Scrubber and Effect on Scrubber Efficiency

Time (days)	Total H_2S Exposure (µg)	Total H_2S Removed by Scrubber (µg)	Ozone Concentration (ppb)	Ozone Scrubber Efficiency (%)	Scrubber Heater
Day 1	0	0	100 ppb	100	on
Day 9	23,990	8,706	100 ppb	100	on
Day 16	47,614	18,432	100 ppb	100	on
Day 22		18,432	100 ppb	100	on
Day 23		18,432	100 ppb	100	off
Day 24		18,432	200 ppb	100	off
Day 24		18,432	500 ppb	100	off
Day 24		18,432	1000 ppb	100	off

The results of those tests indicate that ozone analyzers equipped with heated metal ozone scrubbers are unlikely to suffer scrubber efficiency loss due to H_2S poisoning.

Potential Monitor Interference

Three potential interferants, o-nitrotoluene, o-cresol and mercury were selected as chemicals that had a potential to interfere with ozone measurements made by UV photometry. Each of these interferants was evaluated under conditions of both high (70 to 80%) humidity and low (20 to 30%) humidity to determine whether the ozone response was biased by the interferant over 1-hour and 8-hour averaging times. Two concerns that had to be addressed in evaluation of the test data were ozone concentration changes do to changes in sample air flow rates and instrument drift.

It was necessary to make several air flow adjustments at four points (the ozone generator, permeation oven, humidified air, and dry dilution air) in the generation system in order to obtain the proper humidity, interferant, and ozone concentrations needed for each test. Once the equilibrium was established, care had to be taken to assure that the total sample flow did not change during the test. Any changes in the total flow would be reflected in similar changes in the generated concentrations. Every effort was made to measure and document flow changes to minimize this error.

Instrument drift was documented by conducting a zero and span check at the beginning and end of each test. An incremental correction factor, based on a linear relationship between the initial and final zero and span, was then applied to the hourly averages to correct for instrument drift. The downside of this approach is that it is based on the assumption that instrument drift is linear over the test period, which may not always be the case. Hourly averages for each of the six tests are presented in Tables 3 through 7.

Table 3 presents the o-cresol data from the high humidity test. The first and second columns give the lapsed time in hours from the start of a test and whether the interferent was present (on/off) in the sample stream. Columns 3 to 6 present the average hourly measured ozone concentrations corrected for calibration and instrument drift. The first row at the top of these columns is the ozone concentration generated during the test. This value provides the instrument baseline. Average concentrations (normally 8 hours) for each on/off segment are

Table 3. Results of Ozone Interference Test with 25 ppb o-Cresol at High Humidity

Interferent Addition	Hours	UV Photometer with Standard Scrubber (A) (ppb)	UV Photometer with Silver Wool Scrubber (B) (ppb)	UV Photometer with Heated Metal Scrubber (C) (ppb)	Chemiluninescence Monitor (D) (ppb)		% Difference for A and D	% Difference for B and D	% Difference from C and D
		75.6	75.6	75.6	75.6				
On	1	77.3	74.8	73.7	74.0		4.4	1.0	-0.4
	2	77.1	73.5	73.9	74.6		3.4	-1.5	-0.9
	3	77.0	73.3	73.9	74.8		2.9	-2.1	-1.3
	4	77.0	73.2	74.2	74.4		3.5	-1.7	-0.2
	5	76.8	73.3	77.4	74.4		3.2	-1.5	3.9
	6	76.6	73.3	75.9	74.0		3.6	-0.8	2.7
	7	76.8	73.7	75.7	74.1		3.7	-0.6	2.2
	8	76.9	73.9	75.7	73.7		4.4	0.3	2.7
	9	76.9	74.3	75.3	73.9		3.9	0.5	1.8
Off	10	76.0	75.8	77.6	75.1		1.2	0.8	3.2
	11	76.2	76.2	77.3	75.2		1.3	1.3	2.9
	12	76.4	76.6	77.3	74.9		2.0	2.3	3.2
	13	76.3	76.5	75.4	74.9		1.8	2.1	0.6
	14	76.0	76.2	76.1	75.9		0.2	0.4	0.4
	15	75.9	76.0	75.6	76.2		-0.4	-0.2	-0.7
	16	75.7	76.0	75.8	76.2		-0.7	-0.3	-0.6
	17	75.8	76.2	75.5	76.4		-0.8	-0.2	-1.1
	18	76.0	76.3	75.3	76.1		-0.2	0.2	-1.1
	19	75.6	76.2	74.0	75.9		-0.4	0.3	-2.6
	20	75.6	76.5	74.1	75.9		-0.3	0.8	-2.3
	21	75.5	76.2	76.4	75.4		0.1	1.0	1.3
	22	75.4	76.2	74.3	75.5		-0.1	1.0	-1.5
	23	75.4	76.1	73.0	75.7		-0.3	0.6	-3.5
On	Avg	76.9	73.7	75.1	74.2		3.7	-0.7	1.2
Off	Avg	75.9	76.2	75.6	75.7		0.3	0.7	-0.1

Table 4. Results of Ozone Interference Test with 24 ppb o-Nitrotoluene at Low Humidity

Interferent Addition	Hours	UV Photometer with Standard Scrubber (A) (ppb)	UV Photometer with Silver Wool Scrubber (B) (ppb)	UV Photometer with Heated Metal Scrubber (C) (ppb)	Chemiluminescence Monitor (D) (ppb)		% Difference for A and D	% Difference for B and D	% Difference from C and D
		75.9	75.9	75.9	75.9				
On	1	111.6	76.8	82.5	74.2		50.4	3.4	11.2
	2	83.1	76.2	82.9	74.7		11.3	2.1	11.0
	3	76.5	76.6	82.5	74.9		2.1	2.3	10.2
	4	77.3	76.5	82.8	74.8		3.3	2.2	10.7
	5	74.1	76.3	82.1	75.3		-1.5	1.4	9.2
	6	75.7	76.4	81.7	75.0		1.0	1.9	9.0
	7	75.9	76.0	81.5	74.7		1.6	1.6	9.0
	8	75.9	75.9	80.6	74.5		1.8	1.9	8.1
	9	76.5	75.7	80.4	74.6		2.5	1.5	7.8
Off	10	36.3	75.2	75.4	77.6		-53.2	-3.0	-2.8
	11	65.4	76.7	75.8	76.9		-15.0	-0.4	-1.5
	12	77.2	77.2	77.8	76.7		0.6	0.6	1.4
	13	77.4	77.2	78.0	76.8		0.8	0.6	1.6
	14	77.1	77.1	78.1	76.6		0.6	0.7	2.1
	15	76.9	76.8	77.5	76.6		0.4	0.3	1.2
	16	76.6	76.7	75.8	76.1		0.7	0.9	-0.3
	17	76.7	76.5	75.7	76.2		0.7	0.5	-0.6
	18	76.3	76.3	76.1	76.0		0.4	0.4	0.1
	19	76.4	76.3	75.7	76.0		0.6	0.4	-0.4
	20	76.3	76.3	76.5	76.4		-0.1	-0.1	0.1
On	Avg	80.7	76.3	81.9	74.7		8.1	2.0	9.6
Off	Avg	72.1	76.6	76.6	76.5		-5.8	0.1	0.1

Table 5. Results of Ozone Interference Test with 24 ppb o-Nitrotoluene at High Humidity

Interferent Addition	Hours	UV Photometer with Standard Scrubber (A) (ppb)	UV Photometer with Silver Wool Scrubber (B) (ppb)	UV Photometer with Heated Metal Scrubber (C) (ppb)	Chemiluminescence Monitor (D) (ppb)		% Difference for A and D	% Difference for B and D	% Difference from C and D
		75.8	75.8	75.8	75.8				
On	1	79.6	74.8	74.9	75.7		5.1	-1.2	-1.1
	2	76.4	74.5	73.5	75.6		1.0	-1.5	-2.8
	3	76.4	74.6	77.6	75.7		1.0	-1.4	2.6
	4	76.4	74.7	74.1	75.8		0.8	-1.5	-2.3
	5	76.5	74.4	75.1	75.4		1.6	-1.3	-0.3
	6	76.3	74.4	75.0	75.1		1.5	-0.9	-0.2
	7	76.1	74.3	77.3	75.1		1.3	-1.0	2.9
	8	76.1	74.3	78.6	75.1		1.3	-1.1	4.6
Off	9	73.3	75.7	77.8	77.2		-5.0	-1.9	0.8
	10	77.1	75.8	74.8	76.8		0.4	-1.3	-2.7
	11	77.2	76.3	77.3	76.9		0.3	-0.8	0.4
	12	77.3	76.2	80.0	76.7		0.7	-0.6	4.2
	13	77.0	76.1	80.5	76.6		0.5	-0.7	5.0
	14	76.7	76.1	79.5	76.4		0.4	-0.3	4.0
	15	76.5	75.9	77.5	76.1		0.6	-0.3	1.9
	16	76.2	76.0	76.4	76.1		0.3	-0.1	0.5
	17	76.0	75.8	74.7	75.7		0.4	0.2	-1.4
On	Avg	76.7	74.5	75.8	75.4		1.7	-1.3	0.4
Off	Avg	76.8	76.0	77.6	76.4		0.4	-0.5	1.5

Table 6. Results of Ozone Interference Test with 0.04 ppb Mercury at Low Humidity

Interferent Addition	Hours	UV Photometer with Standard Scrubber(A) (ppb)	UV Photometer with Silver Wool Scrubber (B) (ppb)	UV Photometer with Heated Metal Scrubber (C) (ppb)	Chemiluminescence Monitor (D) (ppb)		% Difference for A and D	% Difference for B and D	% Difference from C and D
		75.9	75.9	75.9	75.9				
On	1	82.9	92.5	96.3	75.4		9.9	22.6	27.7
	2	86.4	104.5	112.2	74.1		16.6	41.1	51.5
	3	85.5	104.0	107.3	73.7		16.1	41.2	45.7
	4	84.4	103.1	103.7	73.8		14.4	39.8	40.6
	5	83.8	100.8	101.0	74.6		12.4	35.2	35.5
	6	83.4	96.4	98.2	75.0		11.2	28.6	31.0
	7	83.2	92.9	99.1	75.2		10.7	23.5	31.8
	8	83.2	91.3	96.4	74.7		11.4	22.2	28.9
	9	84.1	93.2	98.7	74.3		13.1	25.4	32.7
Off	10	76.3	69.6	63.3	76.2		0.1	-8.7	-16.9
	11	76.1	71.6	66.4	76.2		-0.1	-6.0	-12.8
	12	76.1	73.0	71.1	75.8		0.4	-3.7	-6.2
	13	76.2	74.7	73.3	75.9		0.5	-1.5	-3.4
	14	76.4	75.2	75.0	76.0		0.5	-1.0	-1.3
	15	76.1	75.4	75.6	77.0		0.1	-0.8	-0.6
	16	76.6	76.4	78.4	75.7		1.2	0.9	3.5
On	Avg	84.1	97.6	101.4	74.5		12.8	31.1	36.2
Off	Avg	76.3	73.7	71.9	76.0		0.4	-3.0	-5.4

Table 7. Results of Ozone Interference Test with 0.04 ppb Mercury at High Humidity

Interferent Addition	Hours	UV Photometer with Standard Scrubber (A) (ppb)	UV Photometer with Silver Wool Scrubber (B) (ppb)	UV Photometer with Heated Metal Scrubber (C) (ppb)	Chemiluminescence Monitor (D) (ppb)		% Difference for A and D	% Difference for B and D	% Difference from C and D
		75.6	75.6	75.6	75.6				
On	1	78.54	101.46	107.09	73.87		6.3	37.3	45.0
	2	78.53	101.94	101.60	74.11		6.0	37.5	37.1
	3	78.40	103.00	101.13	73.76		6.3	39.6	37.1
	4	78.32	103.39	99.18	73.44		6.6	40.8	35.0
	5	78.09	103.22	99.64	73.60		6.1	40.2	35.4
	6	78.33	103.27	100.48	73.44		6.7	40.6	36.8
	7	78.33	103.34	102.71	73.53		6.5	40.5	39.7
	8	78.42	103.35	104.27	73.69		6.4	40.3	41.5
	9	76.23	76.90	66.03	75.33		1.2	2.1	-12.3
Off	10	76.74	77.27	69.87	74.91		2.4	3.1	-6.7
	11	76.69	77.36	70.97	74.61		2.8	3.7	-4.9
	12	76.14	76.96	73.56	75.44		0.9	2.0	-2.5
	13	75.92	76.70	73.27	76.06		-0.2	0.8	-3.7
	14	75.70	76.55	74.42	76.09		-0.5	0.6	-2.2
	15	75.65	76.12	76.21	75.99		-0.4	0.2	0.3
	16	76.71	75.87	75.10	75.97		-0.3	-0.1	-1.1
	17	75.52	75.78	75.49	75.92		-0.5	-0.2	-0.6
On	Avg	78.37	102.87	102.01	73.68		6.36	39.62	38.44
Off	Avg	76.03	76.61	72.77	75.59		0.59	1.36	-3.75

provided in the last two rows. The last three columns on the right side of the table provide a comparison between the three UV photometers and the chemiluminescent analyzer. Looking at the measured concentrations in Table 3, little or no effect from adding cresol to the sample stream can be observed. The standard UV photometer equipped with manganese-dioxide scrubber shows a small increase of 1 or 2 ppb as compared to the other analyzers. This can also be seen in the seventh column which shows a 3 to 4% difference as compared to the chemiluminescent analyzer. These differences however have little impact on the longer (8 hour) averages shown in the last two rows. The cresol data for low humidity is not presented in this report. Problems with flow changes and instrument drift during the test proved to be uncorrectable; therefore, the test results are not reported.

Table 4 presents low humidity test data for nitrotoluene. These data show a marked increase of 36 ppb in the measured ozone concentration for instrument A (the manganese-dioxide scrubber), with a lesser increase of 1 and 6 ppb for the other two UV instruments during the first hour. In the second hour the concentration for instrument A decreases significantly from 111 ppb to 83 ppb. By the third hour the hourly average is down to 76 ppb. Instrument C, equipped with a heated metal scrubber, shows 5 ppb positive difference for the first 8 hours.

Instrument C (heated silver wool scrubber) showed no difference when compared to the chemiluminescence monitor. When the nitrotoluene was turned off, instrument A showed an hourly ozone concentration decrease from 76.5 to 36.3 ppb for the first hour. By the second hour the readings had recovered to 65.4 ppb. By the third hour the readings were within 1% of the other analyzers. Instrument C showed a much smaller 5 ppb drop in the hourly average. The other two analyzers did not appear to be affected by the presence or absence of nitrotoluene. In the long-term averages shown at the bottom of the table, instrument A has a positive bias of 4 ppb when nitrotoluene was present and a negative bias of 4 ppb during the period after the nitrotoluene was discontinued. Instrument C showed a positive bias of 5 ppb with nitrotoluene present but none after it was removed.

Surprisingly during the high humidity test only a 3.8 ppb positive increase was noted in instrument A for the first hour after the nitrotoluene was added and a negative 2.6 ppb upon its removal. The other analyzers did

not seem to be impacted by the presence of nitrotoluene. As seen at the bottom of the page, none of the analyzers' long-term averages seem to be affected.

The mercury test data presented in Tables 6 (low humidity) and 7 (high humidity) show a marked increase in ozone concentrations measured by the UV photometers. This positive bias is not discernable in the chemiluminescence analyzer ozone measurements. This bias was especially noticeable for the two UV analyzers equipped with the new heated scrubbers. These two analyzers show concentration increases of 18 to 20 ppb during the first hour and 29 to 36 ppb over the second hour at low humidity. At high humidity similar high increases of 26 to 31 ppb were seen over the same period. Using the chemiluminescence analyzer as the baseline measurement, the average percent increase in 8-hour average ozone concentration for the two UV analyzers showed an increase of 13 and 31% at low humidity and 39 and 38% at high humidity. The photometer equipped with the manganese-dioxide scrubber also showed a positive bias but to a lesser extent. The first hour measured ozone concentration increased to 9.9% of the chemiluminescence analyzer for the first hour and 16.6% over the second hour. At high humidity the increase was 6% for both the first and second hour. The overall increase for the 8-hour average concentration was 12.8% at low humidity and 6.4% at high humidity. While all three UV analyzers returned to near normal readings within the first hour after the mercury was turned off, a negative bias was noted for the two UV analyzers with heated scrubbers at low humidity and the Dasibi at high humidity. After 8 hours the three UV analyzers were again within 1 to 5% of the chemiluminescence analyzer. This is within the noise level expected between the individual analyzers. It should be noted that in both cases the Dasibi with the heated metal scrubber was still showing a negative bias after 8 hours.

The positive bias caused by mercury had been anticipated in that mercury vapor absorbs UV light at the same wavelength as that produced by the mercury lamp light source used by the UV analyzer. The high affinity of mercury to silver makes the heated scrubbers excellent in removing mercury vapor from the sample stream. Since mercury would be present in the sample air during the measurement cycle but not during the zero reference cycle, the absorbance of UV light would include both ozone and mercury, thus, causing a positive bias. Once the mercury is removed from the sample stream there is a period when the mercury continues to desorb from the heated scrubbers. During this period the mercury would be in the reference cycle but not in

the sample cycle, thus, causing the zero baseline to be high. Subtraction of the high reference signal from the sample absorbance would result in a negative bias.

Conclusions

This report described two supplemental tasks that complement the ongoing research investigating potential interferences in ozone monitoring. The first task involved the investigation of potential H_2S poisoning of new heated catalysts used to scrub ozone in ozone monitors. The results of this investigation indicate that ozone analyzers equipped with heated metal ozone scrubbers are unlikely to suffer scrubber efficiency loss due to H_2S poisoning. The second task focused on determining long term potential monitor interferences to new heated scrubbers from mercury and select VOCs that have not been previously tested. Of primary concern is the possible impact on 1-hour and 8-hour ozone averages. Of the two VOCs investigated (o-cresol and o-nitrotoluene), o-cresol did not interfer with the 1-hour or 8-hour ozone concentration measurements of the analyzers tested. Nitrotoluene at low humidity, however, had a major impact on the first two 1-hour ozone measurements for the UV photometer with the standard scrubber. This was true when it was first introduced and then when it was removed from the sample stream. This bias was also reflected in the 8-hour averages for that instrument. The heated metal scrubber showed a small increase during the time when o-nitrotoluene was present but not after its removal. During the test at high humidity, no bias in ozone measurements was noted.

Low levels of mercury vapor show a marked impact on all three UV photometers at both low and high humidity. The two UV photometers with the heated scrubbers were affected the most. While heated metal scrubbers helped to reduce instrument bias for some VOCs, they seemed to increase bias due to mercury vapors.