Review of Turnipseed et al., "Use of a Heated Graphite Scrubber as a Means of Reducing Interferences in UV-Absorbance Measurements of Atmospheric Ozone"

This paper describes a new alternative to conventional ozone scrubbing materials used within common UV-absorbance ozone analyzers. UV ozone analyzers, which are most commonly used for regulatory compliance monitoring, are susceptible to some degree of positive bias from interferents that both absorb at 253.7 nm and are scrubbed by the ozone scrubbing material for the Io measurement. With the tightening of the NAAQS ozone standard to 70 ppbv, it is prudent to works towards an improved ozone monitoring method that reduces the potential positive bias that could lead to false ozone non-attainment designations.

I view this current work as a first-step towards developing an improved UV-absorbance ozone monitor. This work demonstrates very well the much-improved performance of the new graphite scrubber in terms of reduced interferences from VOCs, water vapor, and mercury. The ability to omit a Nafion dryer is a definite benefit for ambient measurements. I have doubts regarding the real-world applicability of this method as it currently stands for compliance monitoring, primarily because dual-beam analyzers are overwhelmingly used for this application; however, I consider any incremental steps towards an improved method to be valuable in progressing the science. I also think that this method could have useful applications in laboratory studies, perhaps smog-chamber experiments, where VOC mixing ratios are typically much greater than ambient. Therefore, I do recommend publication of this work after addressing a few relatively minor concerns.

The primary complaint that I have with this manuscript is the somewhat misleading nature of the discussion regarding the potential positive biases with FEM ozone monitors. Although the authors do acknowledge that interferences in outdoor air normally cause only very small errors, "a few ppb at most", I think one who reads this paper without a background knowledge of ozone measurements or atmospheric science would draw the conclusion that most, or perhaps all, of the regulatory monitors are skewed high, and that a measurement error is resulting in non-attainment designations. Because EPA regulations, and associated non-attainment penalties, are an especially hot topic in today's political climate, the language used here needs to be cautious and make it clear that interferences of even a few ppb would be expected in only certain circumstances and in highly polluted environments. Ollison et al, 2013 reports positive biases of a few ppb from measurements conducted with the highly-industrialized Houston Ship Channel, a notoriously polluted location, though it's not discussed whether those few measurements from one location would be enough to designate the city as non-attainment. Other works cited in this manuscript present ambient measurement comparisons in Mexico City, a location with exceptionally high pollution relative to levels observed in the United States today. Although I know the authors are seeking to strengthen the motivation for this study, it is necessary to also acknowledge studies that have shown no discernible bias. Dunlea et al., 2006 is cited, but the "excellent agreement" they report between the UV monitor and the DOAS is not acknowledged. This manuscript should also cite Ryerson et al., 1998, in which no measurement bias was observed in concurrent O3 measurements by a chemiluminescence instrument and a UV monitor through 5 missions over 4 years, including within the Nashville urban plume. Parrish and Fehsenfeld, 2000, state "Even though significant evidence of interferences in the UV absorption technique has been reported, such interferences are not always observed, even in urban plumes."

The agreements in Figure 3a also suggest that the Hopcalite-srubbed 205 did not suffer any interferences in Boulder.

Along this same line, it is also essential to discuss quantitatively the levels of interferences one could reasonably expect from the compounds listed in Table 1 given typical ambient atmospheric mixing ratios. While I understand that laboratory studies and tests must use quite high VOC levels in order to generate the plots presented in Figure 7, it must be pointed out clearly that 1 ppm of xylene is not a realistic ambient atmospheric mixing ratio under normal circumstances. I'm stressing this strongly because AMT is an open-access journal, and one without an atmospheric science background likely is not aware of the normal atmospheric mixing ratios of these compounds. I would like to see two additional columns added to Table 1 that state the typical ambient mixing ratios of these compounds and then what that typical mixing ratio would equate to in "apparent" O3. I do appreciate that this is discussed in regards to mercury in ambient air on Lines 405-415. Pointing out the larger industrial emissions in the Houston Ship Channel, what compounds are enhanced there, and why this is a good example of a location where a positive bias has been shown to exist, would also be informative.

I have no doubts regarding the improved performance of the graphite scrubber, and I do believe that it could find valuable use in lab or smog-chamber studies where VOC mixing ratios are typically very high. However, going back to applicability to real-world monitoring, I wonder whether the uncertainty associated with the analyzer itself is even sufficient to discern any potential improvement by this scrubber. My personal experience with using the 202 Single-Beam, and that of others I have worked with who have had independent experiences, is that this monitor is generally very noisy and variable, making 1-min or less data essentially useless. The agreements shown in Figure 3 suggest that 5-min averaged data doesn't suffer to the same degree, but I still want to know what the measurement uncertainty is for the 5-min data. This is especially important to discuss given the statements on lines 490-494 that: "concentration levels of interfering VOCs were quite low in the Spicer et al (2010) study, ranging from 7.6 to 14 ppb and their measured apparent ozone mixing ratios were <15 ppb. At these levels, small signal drifts, or even the typical precision of ±1 to 2 ppb in the ozone analyzers impart significant measurement uncertainty." I would argue that 7.6 to 14 ppb is actually very high relative to typical atmospheric mixing ratios of these compounds; so, can any standard FEM analyzer even distinguish a potential bias from these VOCs within its measurement uncertainty (barring exceptional emissions events)? I understand that this work is about the performance of the scrubber and not the monitor, but my question is about whether this new scrubber actually improves the ozone measurement in practice in typical ambient measurements given the limitations of the monitor itself. I recommend addressing this issue somewhere in the manuscript and quantifying the uncertainty of the monitors used.

Additional comments:

- Line 75: The authors state that desorption at a later time would cause a measured negative absorbance. This is only true in ozone-free air (or perhaps ODEs?); in ambient air this would be a negative *bias*. Please clarify.
- I understand that there was not a mercury analyzer available to quantify what concentrations of mercury vapor were tested, but would it be possible to at least provide

an estimate of the range of mercury tested given the temperature, vapor pressure of mercury, and flow rates?

- In regards to the scrubber degradation discussion (pages 7 and 8), the laboratory degradation tests appear to have been conducted with relatively high O3 (150-250 ppb and then 300-700 ppb), and from this it was concluded that this scrubber isn't feasible for the dual-beam. Sampling ambient levels in Boulder, the scrubber lasted 38 days at 130° in the single-beam. So how long does the scrubber last at 130° sampling ambient air in the dual-beam? I would assume it must be better than the "overnight" time period deduced from the lab test at high O3 levels.
- Line 211: Define "adequate" in quantitative terms. What is the ozone destruction efficiency of the graphite and how does that compare to conventional scrubbers?
- Line 238" Define "high".
- Lines 244-246: How long is "overnight" exposure?
- Lines 246-247: Quantify "faster temporal decay." What is the decay rate?
- Line 248: Define "periodically." How often would one have to recharge the scrubber if operating under ambient conditions? Is it too often to make it worthwhile? Is it possible to just shut off the flow to the Io channel of a dual-beam monitor every so often for a few minutes to let it recharge? Or use two scrubber channels and switch between the two to continuously do an Io measurement in a dual-beam?
- Line 260-261: Is the competition also dependent upon the mixing ratio of O3 being sampled?
- Lines 427-430: Clarify that the "positive absorbance measurement" and "negative absorption" only apply to ozone-free air; or else change to the wording to *bias* rather than absorbance.
- Lines 473-474: Do you mean that error tends to *decrease* with volatility? It should be more difficult to desorb the less-volatile compounds, meaning the high-volatility compounds would have less error, if I'm understanding this correctly.
- Line 481: Since these selectivity ratios are calculated based upon an assumption and not directly measured, I suggest changing "were measured" to "were estimated."
- Lines 590-592: The concentrations of these species are a factor of what higher than typical ambient mixing ratios?
- Table 1: Besides the suggestion above, I suggest also adding naphthalene to the table since it is discussed in some of the cited references (e.g, the Spicer papers).
- Figure 3: Based on this agreement, is it fair to conclude that, at least for Boulder, no actual benefit is observable in ambient measurements using the new scrubber? For follow-up work, I suggest doing this comparison in a more polluted environment, like the Houston Ship Channel perhaps, where the benefit could be observed.

References:

Parrish, D.D. and Fehsenfeld, F.C.: Methods for Gas-Phase Measurements of Ozone: Ozone Precursors, Aerosol Precursors; Atmos. Environ. 34, 1921-1957, 2000.

Ryerson, T.B., et al.: Emissions lifetimes and ozone formation in power plant plumes. Journal of Geophysical Research 103, 22569-22583, 1998.