AMT-2019-399: Portable Calibrator for NO Based on Photolysis of N_2O and a Combined NO_2/NO/O_3 Source for Field Calibrations of Air Pollution Monitors

Reply to the review by Anonymous Referee #2:

We appreciate the time and efforts of Referee #2. We would like to thank them for contributing their thoughtful comments. Their comments are listed below in **Bold** font followed by our responses in blue text. New text added is given in italics (quoted) along with page and line numbers within the new revised manuscript.

Reviewer #2:

This manuscript reports specifications and characterization tests for portable calibrators dedicated to the generation of NO and NO2/NO/O3 transfer standards. A special attention was put on assessing their performance in terms of stability, reproducibility, precision and accuracy. An originality of this work is the use of N2O photolysis to generate a known concentration of NO, which when combined to a previously described O3 generator, allows the generation of a known concentration of NO2 using the gas phase titration technique. The authors showed that these calibrators meet the US-EPA requirements for transfer calibration standards (based on the requirements for a level 4 ozone transfer standard).

This manuscript is well structured and well written but some clarifications need to be made about the different analyzers that were used to perform all the reported experiments. Different models of monitors were used and when the same model was used in different experiments, it is not clear whether it was the same monitor. In addition, the authors often indicate that the measurements were made using a "recently calibrated XXX monitor". How was the monitor calibrated? The authors should clarify these two points.

The different monitors for ozone and NO_x (NO and NO_2) used are described in Section 3.3 (page 12, lines 338-347). This paragraph also describes how these analyzers were calibrated and how these calibrations were traceable to NIST standards. Different actual analyzers were used throughout the various experiments; however, each analyzer was calibrated as described just prior to use.

The reviewer recommends publication in AMT after the authors address the other following comments:

Major comment:

Since these apparatus will be used for the calibration of NOx monitors based on chemiluminescence, the authors should address whether the use of a large concentration of N2O could lead to the quenching of the chemiluminescence.

This is an excellent point that we had not considered. Clyne et al., (1964) measured the relative quenching rate constants (relative to $O_2 = 1$) of the NO + O_3 chemiluminescent system and report: $N_2 = 0.9$ and $N_2O = 2.6$. (i.e., N_2O quenches 2.6 times more effectively than O_2 and 2.9 times more than N_2). Therefore the total relative quenching in pure air is:

$$kq(air) = (\%N_2)*0.9 + (\%O_2)*1 = 0.9122 \text{ (where } N_2 = 0.7808 \text{ and } O_2 = 0.2095).$$

Addition of 1.5% N_2O (typical of our calibrators) yields an effective quenching constant of

$$kq(eff) = (\%N_2O)*2.6 + (1 - \%N_2O)*0.9122 = 0.9375.$$

The ratio: kq(air)/kq(eff) = 0.973 suggests that the CL signal should be reduced by 2.7% (= 1 – 0.973). In practice, it is usually slightly less than this as CL-analyzers typically dilute the sample flow by addition of an O_3/air reagent (typically 10-25% of the total flow).

We also note here that the photolytic NO generator must initially be calibrated relative to a standard reference method (described in Section 3.1) using some type of NO analyzer. If that analyzer is a CL-analyzer, then the additional quenching by N_2O will be incorporated into the calibration curve of lamp intensity vs. NO output. We have added the following text at the end of Section 2.1 (page 6, lines 166-176) describing this:

"A final issue pertains specifically to CL NO analyzers where the presence of N_2O can lead to collisional quenching of the chemiluminescence signal. Clyne et al. (1964) report that N_2O quenches the NO/O_3 chemiluminescence 2.6 and 2.9 times more efficiently than O_2 and N_2, respectively. Therefore, a mixture of 1.5% N_2O in air (typical conditions – see Section 3) would be expected to reduce the observed chemiluminescent signal by ~ 2.7% relative to pure air. In practice, this is typically slightly less (2.2-2.4%) as the sample flow in a CL-analyzer is diluted by addition of a reagent O_3/air flow (10-25% of the total flow). This correction term can be explicitly calculated from the measured flows in the photolytic NO calibration source and the flow rates in the CL-analyzers (as in the example given here) or it can be eliminated depending upon the analyzer used during the initial calibration of the relationship between lamp intensity vs. NO output (see Section 3.1). If a CL-analyzer is used to determine this relationship, then quenching by N_2O is intrinsically included in the calibration of the photolytic source."

Minor comments:

P8 L233: Please indicate what types of O3 and NOx scrubbers were used

We have noted that the scrubbers were "…*a mixture of Carulite® and activated carbon*…)

P9 L249-250: The authors indicate that it is important to maintain a constant ratio of lamp emission between 184.9 and 253.7 nm. How is this ratio changing with the lamp aging? In addition, it is mentioned that NO is varied by adjusting the lamp emission. How is it done? If the current or the voltage applied to the lamp is varied, the authors should comment on the impact on the 184.9nm/253.7nm emission ratio?

The lamp emission is varied by changing the pulse-width modulated duty cycle to the Hg lamp. We have added the sentence at pg10, line 265:

"*NO output is varied by changing the pulse-width modulated duty cycle to the Hg lamp while monitoring its intensity with a photodiode*."

Our experience has shown that the ratio of the 184.9nm/253.7 nm emission is mainly dependent on the lamp temperature. Therefore, we control the temperature at 40°C in both our NO and O_3 photolysis cells. As the duty cycle to the lamp is varied (which can cause slight heating or cooling), the temperature control compensates to maintain a constant temperature – thus a constant ratio of 184.9/253.7 nm. The observation that the NO or O_3 output is strictly linear as one varies the duty cycle strongly suggests that the 184.9/253.7 nm does not change significantly. To clarify this, we have added the sentence at pg 10, line 272:

"…*Even as the duty cycle is varied, the temperature regulation maintains a constant lamp temperature, thus ensuring a stable 184.9/253.7 nm output."*

Lamp aging is addressed in the following comment concerning long-term repeatability.

P16 Fig.6: The repeatability for NO generation tested over 6 days is excellent. Based on their practical experience, could the authors comment on the repeatability over a longer period? Weeks? Months?

We recommend that the photolytic NO generator should be re-calibrated at least annually (however, note that a Level 4 EPA transfer standard which is a generator-only is required to be re-calibrated quarterly - see US-EPA, 2013 in manuscript). For our ozone generators (for which we have more experience), we have observed that their calibration typically changes by < 2-3% over a yearly period. We would expect similar performance for the NO generator since it uses the same lamp and electronics. This exact cause of the small observed calibration drift is not explicitly known, but small changes in the 184.9/253.7 nm ratio of the lamp could play a role.

Technical corrections:

P6 L172-173: "O" should read "O(^{3}P)"
Corrected as suggested.

P5 L173: M is missing on the right hand side of the equation
Corrected as suggested.

P8 L226: "photolytic NO converter" should read "photolytic NO2 converter"
Corrected as suggested.

P18: L436: "the NO calibrator of ambient pressure" should read "the NO calibrator on ambient pressure"
Changed to: "*…dependence of the NO calibrator with ambient pressure…*"

P 21 L476-494: This section should be moved in 3.2 when the calibration sources are first described.
We agree with Reviewer #2 that this section is repetitive and have incorporated this text into Sections 2.2 (pg 7, lines 200-208) and Section 3.2 (pg. 11, lines 303-307, pg. 12, lines 316-318) while removing any redundancies in the information presented.

P22 L 539: Section 3.2.3 does not exist. Should it read "section 3.3"?
Corrected to "Section 3.3" as suggested.

P24 Fig. 10: Please add the O3 setpoints in the table.
Corrected as suggested.

P26 L588: Please replace "NO_{meas}" by "$NO_{meas,O3>0}$" and "$NO_{O3=0}$" by "$NO_{meas,O3=0}$
Corrected as suggested.