

Interactive comment on “A 5-channel cavity ring-down spectrometer for the detection of NO₂, NO₃, N₂O₅, total peroxy nitrates and total alkyl nitrates” by N. Sobanski et al.

Anonymous Referee #2

Received and published: 27 August 2016

General comments:

Sobanski et al. describe a 5 channel instrument based on cavity ring down spectroscopy for measurement of NO₂, peroxy nitrates, alkyl nitrates, NO₃ and N₂O₅. The first three are measured directly as NO₂ or by thermal conversion to NO₂, where NO₂ is measured using CRDS at 405 nm. The latter two are measured directly as NO₃ or by thermal conversion to NO₃ using 662 nm CRDS. Although all measurements have been described previously by this group, this paper summarizes the performance characteristics of an instrument that detects all 5 simultaneously. It also adds to and augments the thorough description from this group of the radical chemistry and wall loss corrections required for measurement of this set of 5 reactive trace gases. I rec-

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commend publication following attention to the specific comments below.

Specific comments:

Page 2, lines 23-25: Reference should be made to CIMS techniques developed more recently that can detect speciated organic nitrates.

Page 5, line 19: “ms” presumably means microseconds, not milliseconds?

Page 5, line 22: does “zero signal” mean with continuous NO added or under a flow of zero air?

Page 5, line 31: Comment on the potential for thermal dissociation of N₂O₅ or PAN at the elevated 305 K temperature in the NO₂ channel.

Page 6, line 2: Why is the optical isolator unnecessary at 405 nm? Empirically determined, or is there a clear reason for it?

Page 7, line 27: Suggest replacing the phrase “essentially calibration free” with “absolute measure of concentration within the optical cavity” or equivalent phrase. Calibration free implies no requirement for standard additions, which is never the case in practice, even for non-reactive trace gases measured using optical instruments.

Page 8, line 4: Is the uncertainty in the NO₃ transmission through the filter and housing really as low as 3%, even for sampling ambient air with aerosol accumulation on the filter? Some further comment here is warranted.

Page 11, bottom: How significant is the reaction sequence leading to, for example, alpha lactone production? Perhaps this is discussed further in Thieser 2016, but there is no referencing given in this paragraph to justify what appears to be a somewhat arbitrary sequence of radical reactions.

Section 3.2.4. Two comments. First (minor), the approximation $k_{16}[\text{O}_2] \gg k_{17}[\text{NO}_2]$ should be noted with respect to equation (3). Second (more important), is this treatment realistic for ambient air, in which there may be reactions of atomic O with other

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species that reduce the effect of R17? The authors should comment.

Page 13, lines 27-28: Confusing sentence structure.

Section 3.2.5: How is NO + O₃ affected by thermal dissociation of O₃ referenced above? Presumably this reduces the influence of the NO + O₃ reaction directly, but then requires accounting of O + NO → NO₂? Please comment.

Page 16, lines 15-16: The derived equilibrium constant agrees to within the combined uncertainty, but the field determination is systematically larger. Give the average deviation of this difference and note that the field data do not scatter around the center line of either recommendation.

Page 16, line 11: Remove the characterization of the correction as “rather small” (arbitrary here, a subset of values exceed 50%) but instead give only the center value and the width of the distribution, which is visually symmetric enough that a Gaussian fit may be appropriate.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-191, 2016.