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Atmospheric Measurement Techniques Discussions

Interactive comment on "Caution with Spectroscopic NO_2 Reference Cells (Cuvettes)" *by* Ulrich Platt and Jonas Kuhn

Anonymous Referee #2

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In this submission, Platt and Kuhn describe how optics and chemistry alter the effect of reference cells, particularly the NO2 reference cell. Such cells are commonly used in DOAS and gas correlation spectroscopy for wavelength calibration and absolute calibration of column densities. Although the authors show that the influence of optical factors can be appreciable, the most important outcome of this work is that it draws attentions to the complexity of the chemical composition in the reference cell when exposed to light. Changes in chemical composition can be very large indeed, and inattention to these effects will compromise measurements.

The underlying reactions are well-known and relatively easily modelled and this work presents nothing new in this respect. From the practical point of view, such factors may not be widely appreciated. Therefore, from the instrument operator's perspective, the

authors offer a cautionary information about such cells, as well as practical suggestions to improve the stability of the chemical composition in these cells. The use of such cells and their influence on standard trace gas measurements by a widely used technique could make this work a valuable practical contribution to the literature. However, there are several aspects of this work that should be clarified and improved before publication can be recommended.

I found the manuscript unnecessarily convoluted and hard to read. A direct presentation of the calculations and simulation results would be clearer to the reader. In particular, the approach of gradually ramping up the complexity of the underlying reactions and analytical approximations seems unhelpful to this reviewer. Why not just present the full simulations? Limiting conditions could be examined separately.

1. Introduction

- The introduction is unusually short. The authors should explain how these reference cells are used in terms of calibration and column density, how this could lead to errors, and what sort of errors could arise. Would errors be expected for the wavelength calibration, for instance, even if the NO2 concentration in the cell changes? More equations in this part of the paper would be helpful.

- 44-45: Other cells and gases are mentioned; real-world examples should be provided. NO2 is relatively unusual as a strongly absorbing gas in the actinic region of the solar terrestrial spectrum.

2. Optics

- Section 2.1 is unclear whether it refers to a cell containing absorbing gas or not. This should be explicit, and the Beer-Lambert dependence on pathlength for the single and multiple passes should be clearly described.

- 16: The authors explain in the figure caption, but not the text, where the figure of 2% enhanced SCD comes from. It is unclear how this relates to the absorption coefficient

of the gas in the cell. In the case of strong absorption, the contribution of the multiple reflection becomes negligible even at relatively modest absorptions (e.g., exp (-a L) < 0.5 means the first multiple pass of three times through the cell is < 12% of the original value. Values for other column densities would be instructive here.

3. Chemistry

- p.3, 43: A J value is provided for R1 but it is unclear where this comes from. The formula describing the photolysis rate and relationship to the actinic flux, quantum yield, and absorption spectrum should be provided. There is no recognition in the text that this key parameter, which drives all the subsequent chemistry, can be highly variable. It depends on whether this is direct sunlight, and how it depends on season, latitude, time of day, etc. It is also unclear how this J could relates to values for an active DOAS system with an artificial light source, or even whether such cells are used in this case.

- The text does not describe whether the beam diameter completely or only partially fills the reference cell diameter. If the latter, then there is a more complex spatial dependence on the chemistry. Fortunately in this case, such a situation reduces the impact of the chemical reactions.

- The text should clarify that the value for k5 pertains to ambient pressures.

- Example 2 has limited value because it excludes R5 (which has approximately the same rate as R4). In the limit, reformed NO2 will eventually photolyse until NO is the sole product, but this process becomes increasingly slow. This is surely an important practical issue in the use of these cells.

- P6, 18: While the point made is correct, the time to attain equilibrium should be stated less precisely. The half-life is about 5 us.

- Fig. 3 may be simplified, but it seems odd to leave out these reactions: O + NO, O3 + NO2, and 2NO2 + H2O –> HONO + HNO3

- P.10, 35: State that this is a slow reaction in the gas phase

- P11,21: “??” ??

- 2NO2 + H2O –> HONO + HNO3 is an important heterogeneous reaction and would certainly be expected to occur in reference cells, including under dry conditions as it is very difficult to get a completely dry well. This should be included in the simulations.

4. Simulations

- I find little value in Figs 4 & 5 which simulate simplified chemistry. What’s the point? Simplifying cases of the full chemical system can be discussed in the text.

- In contrast, Fig.6 could be split into several figures for presentation clarity.

- The effect of changing J values was not investigated, though this would strongly influence the chemistry in the cells.

5. Summary and conclusions

Another possibility is to use wedged windows for the cell (which would halve the reflections assuming internal window are parallel) or parallel windows angled sufficiently to avoid multiple passes.

Minor comments:

Abstract:

21: “at” → “using” / “for” etc. Awkward sentence.

25: particularly

p.3, 4: “oft” → “of”

p3, 23: sentence fragment needs clarification

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