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Interactive comment on “Detailed characterizations of a Comparative Reactivity Method (CRM) instrument: experiments vs. modelling” by V. Michoud et al.

Anonymous Referee #1

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Michoud et al. (2015) present the new Mine Douai Comparative Reactivity Method (CRM) instrument to determine the atmospheric total OH reactivity. This publication focusses on instrumental development, and the detailed characterization of the new instruments performance. Various tests are shown that determine and examine corrections needed for good and reliable total OH reactivity measurements. Hence, the manuscript covers topics that match the scope of AMT.

Many aspects of the CRM are presented in greater detail and depth than it can be found in previous publications. However, the original CRM publication (Sinha et al., 2008) introduced already most of the concepts and corrections that are presented by

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Michoud et al. (2015). New are the NO₂-tests and the proposed correction, as well as the attempt to simulate in detail the chemistry within the instrument. Also, in this manuscript several improvements are proposed, such as the humid pyrrole measurement without OH using propane as a scavenger (C1) and the experimental alternative for a correction to pseudo first order conditions.

Overall, text, references, figures and supplementary material presented are clear, well-structured and conclusive. Hence, I recommend the paper to be published in AMT, after addressing the following comments:

Novelty: As this study describes a new instrument which is built based on an existing concept, you need to be careful to highlight strongly the new achievements of this presentation compared to previous work. In particular title and abstract should illustrate what is new, what is different to previous CRM instruments and publications, and what is the impact of the new findings.

Title: The manuscript-title neither tells the reader anything about the newly build Mine Douai instrument nor it explains what is addressed by “experiment vs. modelling”. May I suggest to formulate it more precisely? (E.g. “Detailed characterizations of the new Mine Douai Comparative Reactivity Method instrument via experiment and model”)

Abstract: Until line 24 the reader finds nothing really new in the abstract. It would help to comprise this part of the abstract keeping all the interesting and important facts, on the one hand. And on the other hand, the new aspects and achievements of the presented study can be added, e.g. the new Mine Douai instrument, and the relative magnitude of the corrections (as examined in this paper). The second part of the abstract reads rather lengthy and may be shortened for the benefit of summarizing actual results. Similar to what is written in the introduction (p. 3808, l. 17-22) it could be more informative for the reader describing precisely what kind of model was used for what purpose. In general, I think the abstract should have information about the new instruments performance (LOD, uncertainty), about the relative importance of the examined

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and applied corrections (e.g. which correction has the greatest impact on the result? does it correct towards higher/lower values?), and about the results of the model compared to the experimental tests (e.g. what can you learn from the comparison?) What is the benefit of your study for other researchers and CRM users?

p. 3804, l.16: I find the description of this first correction not precise, or even confusing. It is not very clear, if you are talking about the humidity dependence of the PTR-MS sensitivity or the OH production inside the reactor. I believe that you mean the latter one. Please, could you modify the sentence accordingly?

p. 3804, l. 18: HO₂, NO: Abbreviations are commonly introduced for the first time by spelling out the entire word or phrase.

p. 3806, l. 4-6: Volatile organic compounds (VOC) are of particular interest for the OH chemistry not only because they are present in the atmosphere in large numbers, but because they are often highly reactive to OH. Please, add this important detail.

p. 3806, l. 9: "... orders of magnitudes lower than expected in the atmosphere."

p. 3806, l. 28-29: There are many more references. Either list them all or insert "e.g."

p.3807, l. 4-5: Please, include the original publications for the different techniques here. It seems that the given reference is not published yet.

p.3808, l. 10: Correction (iii) is not mentioned in the abstract. Please be consistent.

p. 3809, l. 6: Again, Hansen et al. (2015) is cited, even though the reference is not published yet. In this context either another publication that describes the CRM in detail may be mentioned or you present your manuscript as the first which discusses the MD-CRM in detail.

p. 3809, l. 8: Again, the abbreviation should be spelled out for the first time mentioned.

p. 3810, l. 23: As far as I can see, this manuscript is published before Hansen et al. (2015). Please, modify the text accordingly.

p. 3811, l. 7: Please, be precise and list the entire list of chemicals or refer to Table S1 directly.

p. 3813, l. 2-5: In the PTR-TOF-MS on m/z 19 the signal of primary ions and on m/z 37 the first water cluster are monitored. Due to their high abundance these two peaks are often saturated in such instruments and do not follow a linear behavior anymore. Could you please comment on your instrument's behavior? Since you use the $m37/m19$ ratio for correction, their accurate determinations seem to be critical for the OH reactivity measurement.

p. 3813, l. 15-19: When reading this paragraph for the first time, I wondered if you did the NO-sensitivity experiment only for zero OH reactivity or also for different OH reactivities introduced by different test-compounds? Later in your manuscript (p.3820, l. 11-14), you mention that you did these tests. That is why I think that you should extend the description here and include a sentence about tests with various compounds and different levels of OH reactivities.

p. 3813, l. 25: Why did you not test for NO₂ interference below 60 ppbV of NO₂? Typical atmospheric levels are often lower. In your results it looks like the OH reactivity correction in this region (Figure 4, 0-60 ppbV NO₂) is very sensitive to changes in NO₂. It would be beneficial for the manuscript to include some measurements at these critical NO₂ levels.

p. 3816, l. 11: typo: "extracted"

p. 3815, l. 24 - p. 3816, l. 4 (Table S2): Could you please explain the choice of the reaction rate constants used in the simple model mechanism? Can you comment, in particular, on the slow rates attributed to the peroxy radical reactions (RO₂+NO, RO₂+RO₂, RO₂+HO₂)? How much does the choice of these rate coefficients affect the agreement between simulation and measurement? Please, provide a reference for pyrrole+OH (Dillon et al., 2012).

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p. 3816, l. 15-23: As stated in your manuscript, the model approach is a very crude one. The surrogate 2(5H)-Furanone might have a very different oxidation chemistry than pyrrole. Did you test your mechanism as well for other potential pyrrole surrogates? Are there significant differences? What advantage do you think you gain by using the MCM with a surrogate for pyrrole instead of using the simple mechanism? Can you use this model study to distill any significant result for the usage of CRM or the understanding of pyrrole chemistry?

p. 3817, l. 8: typo: “Preliminary results of OH reactivity measurements. . .”

p. 3817, l. 13-18: Could you specify what kind of inlet and flow you used for the measurements? Was it insulated/heated/flushed?

p. 3818, l. 4-13: Several points in this paragraph are unclear to me and should be clarified: You corrected the detected C2 pyrrole levels for the relative humidity which you determined via m37/m19 ratio. Did you do this for every single measurement point during C2? Or for the average of C2? Or for the interpolated C2 values that match the times of the C3 measurement points? Depending on your approach, I wonder if the noise of m/z 19 and m/z 37 may affect your corrected pyrrole levels? How do you account for rapidly changing humidity during C3 between two C2 measurements? Why did you chose to correct the C2 pyrrole measurements and not the C3 values?

p. 3818, l. 17: typo: “black”

p. 3818, l. 18-20: Could you please give typical numbers for the amplitude of the correction? How much variability did you find in the pyrrole mixing ratios, how much is this in OH reactivity, and how big is the average relative correction of the OH reactivity data?

p. 3822, l. 5-13: In this section it is very important to clearly define: What are “apparent ratios”? What has been measured? What was modeled? Could you please rephrase?

p. 3822, l. 14-20: You describe in the SI how you derive experimentally the OH mixing

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ratios inside the glass reactor. I find this information very important and would encourage you to include it in the main manuscript. Additionally, I was wondering how did you determine the model OH mixing ratio?

p. 3824, l. 27: typo: “through”

p. 3826, l. 26: Are you talking about the “full range of reaction rate constants” of OH reactive compounds in your sample?

p. 3827, l. 9-12: During your tests of the influence of the pyrrole-to-OH ratio on the correction, that you need to apply to account for pseudo-first order assumptions, you find that (as expected) the correction decreases for higher ratios. From your experiments you conclude that for higher ratios than 2.3 a correction factor smaller than unity was observed. However, “this tendency is only significant for one experiment”. Since this observation is such a puzzling result, not easy to explain, the scatter of the data generally looks quite high (Fig. 7), and only one experiment has been carried out in this region of ratios, it seems logic to me to add a few more experiments in that region. The additional data will definitely tell you if you are converging to unity or some number below unity. Subsequently, you may try to explain the puzzle or find that the experiments actually show what was expected.

p. 3827, l. 27 (Figure 7): You conclude that the relationship between pyrrole-to-OH ratio and the correction factor (experimentally determined) is linear. However, theory expects a converging relationship (p. 3827, l.12). This can be seen as well by the model-runs presented in Figures S8-S11 or Figure 9. So, why do you use a linear regression rather than a polynomial one?

p. 3832, l. 19-27: It would be great if you could give numbers (absolute and relative) about how much is the impact of each of the previously discussed corrections on the measured total OH reactivity?

Figure 1: For better visibility of the insert, please frame it.

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Figure 2: Please include error bars. Like this the reader can see how big is the variability for both the C2 signal (pyrrole mixing ratio) and the m37/m19 (tracer for humidity).

Figure 3: The labels and legends of the two lower graphs were too small to be readable on my print-out. Is the outlier point for the highest pyrrole-to-OH ratio the dry experiment? Was it included in the data to determine the fit?

Figure 4: Unfortunately, there are no experiments performed for NO₂ mixing ratios between 0 and 60 ppbV. It would be great to include a couple of experiments in that region, since these are atmospherically relevant mixing ratios of NO₂. Why are the green experiments (pyr/OH=2.0) so different from the other two experiments? These data points seem to be significantly lower.

Please, check all your graphs to be consistent with the use of ppb or ppbV.

Figure 5: The labels and legends of the two lower graphs were too small to be readable on my print-out. Also, the legend does not help to distinguish between the simple and the MCM simulations, because not the markers make the difference but the line appearance.

Table S2: The given values for the bimolecular rate constants are missing a multiplication sign. Why is there nothing written behind the equal sign for RO₂+RO₂ and RO₂+HO₂? It would be important to highlight that both of these reactions are terminating steps. Could you explain your choice of rate constants in more detail, please?

Figure S4: You explain that you derived experimentally the OH mixing ratio inside the glass reactor by using isoprene as scavenger. Could you please be more precise on this description? Did you add isoprene instead or additionally to pyrrole to the reactor? Why is isoprene a better scavenger than pyrrole? They both have very similar reaction rate coefficients with OH. How did you observe a significant difference (larger than noise) between isoprene mixing ratios with and without OH, having in mind that isoprene is about 3 ppmV and OH about 50 ppbV? Maybe it would make it easier

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to understand if you showed the data of the experiment (e.g. isoprene and pyrrole as detected by the PTR-TOF-MS)? Did you try other scavengers? Did you get to the same result? How big is the effect of OH recycling (e.g. in the isoprene chemistry)?

Figure S6: Why don't you add the experiments for comparison to the model results (shown in Fig. S2)?

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 3803, 2015.

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