Interactive comment on “Stack emission monitoring using non-dispersive infrared with optimized nonlinear absorption cross-interference correction algorithm” by Y.-W. Sun et al.

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Dear Anonymous Referee #2: Thanks for your comments, our point-to-point responses to your comments are listed as follows. Your comments: General comments: This paper presented an analysis algorithm for non-dispersive infrared to solve the non-linear absorption problem, which is very common in infrared field. The author presented a complex way to show how to resolve the problem of non-linear absorption. The author just mentioned concentration of the gases, which can cause non-linear absorption, but in my opinion, I think, not only the concentration, but also the optical path which can cause non-linear absorption, i.e. it is the optical depth (optical density) that cause the
non-linear absorption. In the most part of the paper, the author wanted to show his method is better than commercial instrument, but in the last part of the text (section 5), a commercial NDIR multi-gas analyzer Model 60i manufactured by Thermo Fisher Scientific Inc. was used to validate the CO and CO2 results measured by the NDIR analyzer prototype. The results showed there was no obvious difference between two analyzers, for readers, it is hard to say which one is better. The author should present enough data to show his prototype is better than the commercial one. And the authors should consider a few points in their analysis to make sure that their conclusions are robust. Current manuscript contains some major deficiencies and thus would require several major revisions before I would consider this paper for publication.

Response: We have seriously considered your comments, especially those major deficiencies that you mentioned in the AMTD. We have given the corresponding corrections or, alternatively, explanations in the revised paper. Besides that, some new contents used to prove our points are also presented in the revised paper (please see line 56~58, line 166~168, line 461~468 and section 4.3 for details). So the revised paper can avoid these problems. In detail: 1. There is no doubt that it is the optical depth (optical density) that cause the non-linear absorption. That means not only the concentration, but also the optical path can cause nonlinear absorption. However, for a specified NDIR analyzer, the optical path length (controlled by multi-pass cell) is constant. Thus, only gases concentration can cause nonlinear absorption. The experiments and discussions of this paper are all based on this precondition which has been presented in the revised paper (please see line 56~58, 104/105 and line 569 for details). 2. Actually, we want to show that the optimized algorithm is better than the classical one when nonlinear absorption appears. The classical algorithm only works when there is no nonlinear absorption for all gases (i.e., including the target gases and the interference gases). Once nonlinear absorption appears, error of the classical algorithm increases and the measurement accuracy would decline. On the contrary, the optimized algorithm can correct cross interference no matter linear absorption or non-linear absorption. Thus, dynamic measurement range of a NDIR analyzer is expanded.
That means whether the optimized algorithm is better than the classical one depends on the gas absorption condition of an analyzer. These points can be fully proved by the mathematical derivations and discussions in the revised paper, i.e., in section 2, 3, 4.2 and 4.3. On the one hand, we actually didn’t mention that the optimized algorithm is better than the classical one when all gases exhibit linear absorption. In fact, the classical algorithm offers a faster processing speed than the optimized one because of relative simpler equations to be solved. On the other hand, the optimized algorithm is a generalization of the classical algorithm and they can be derived from each other. The classical algorithm can be derived from the optimized one, if (1) all gases (i.e., including the target gases and the interference gases) exhibit linear absorption, and (2) a linear model “y=kx” is used to model the gas to gas interference during least-squares fitting. Please see section 4.3 in the revised paper for details. This section, with new contents compared with the original paper, presents a conceptual comparison of the two algorithms. Model 60i uses the classical algorithm to correct cross interference among different gases, i.e., interferences between any two gases are quantified by using a constant factor. Model 60i can correct cross interference well in this manner because all gases concentrations (during the whole field experiment) lie within its linear dynamic range. Thus, five target gases (i.e., CO2, CO, NO, NO2 and SO2) can be retrieved with a high accuracy (<± 2%). However, the classical algorithm is not suitable for the prototype because CO2 concentration may beyond its linear dynamic range (17%). Hence, the optimized algorithm has to be used. From this perspective, using Model 60i for NDIR analyzer prototype (in which an optimized cross interferences correction algorithm is embedded) measurements validation is a reasonable choice. In fact, not only Model 60i, but also many other instruments can be used to validate the prototype measurements as long as they have high accuracy for CO and CO2. The good agreement between the two analyzers is not to prove that the prototype is better than the commercial one, but to show that the prototype exhibits the same cross interference correction effect as the commercial one or, in other words, the optimized algorithm still has a good cross interference correction effect even when nonlinear absorption appears. Please
see line 429/430 and 443~449 in the revised paper for details. What this paper really cares about is the algorithm which still works for nonlinear absorption and thus can expand the dynamic measurement range of a NDIR analyzer. It does not give any judgment to the commercial instrument. In fact, we do admit that the accuracy provided by the manufacturers is reliable if all gases concentrations lie within the linear dynamic range of a commercial instrument (that’s why we select Model 60i for comparison).

Major issues: 1) In section 5 (Field applications), the authors should classify the carbon dioxide volume-mixing ratio (the data in Fig. 11) into two groups, one is below 17% and the other is larger than 17%, and analyze the differences between prototype and Model 60i to make sure the optimized algorithm is better than the classical algorithm. If the differences are not obvious, section 5 is not necessary;

Response: We didn’t classify the carbon dioxide volume-mixing ratio (the data in Fig. 11, section 5) into two groups (to make sure the optimized algorithm is better than the classical algorithm when nonlinear absorption appears) because this point has been fully proved by the mathematical derivations and discussions in section 2, 3, 4.2 and 4.3. We treat it in this manner is to avoid repetition. In section 4.2, we classify the carbon dioxide volume-mixing ratio (the data in Fig. 7) into two groups, one is below 17% and the other is larger than 17%, Fig.7 shows that CO2 interference can be effectively corrected by both algorithms if CO2 concentration is lower than 17%. Measurement errors calculated after interference correction by both algorithms are less than 1%. However, interference correction results with the optimized algorithm are obviously better than those with the classical algorithm if CO2 concentration exceeds 17%. In this case, the CO measurement errors for interference correction using the optimized algorithm change by less than 1%, whereas those for interference correction using the classical algorithm increase with increasing CO2 concentration. In fact, the point of this manuscript won’t be change even if section 5 is deleted. However, we keep section 5 for two reasons. First, section 5 describes field application of the prototype, which is consistent with the title of this manuscript (i.e., stack emission monitoring. . .).
Second, whether CO2 is larger than 17% or not, the good agreement between two analyzers shows that the optimized algorithm not only works in laboratory but also works in field application (where the interference is much complex than laboratory experiments).

2) Please give measurement range of Model 60i, and the authors should make sure Model 60i works in linear absorption within the measurement range; Response: The measurement range of Model 60i please see table 4 and all gases concentrations (during the whole field experiment) lie within its linear dynamic range. Please see line 445 to 447 in the revised paper, where the detailed description document of Model 60i was inserted as a reference.

3) The authors said “the upper measurement range of this analyzer prototype for CO2 and CO is only 17% and 850 ppmv, respectively, if cross-interference is corrected by a constant factor”, why? Please give the criterion of this; Response: We select 17% and 850 ppmv as the upper measurement range of this analyzer prototype for CO2 and CO, respectively, because when CO2 (CO) is lower than 17% (850ppmv), the CO2 (CO) interference to CO (CO2) can be effectively modeled by a constant factor. However, when CO2 (CO) is larger than 17% (850ppmv), using a constant factor to model the CO2 (CO) interference to CO (CO2) would result in great error, and the error increases with the concentration. Please see line 276∼285, figures 5 and 7 in the revised paper for details.

Detailed comments: 1) What does the “a specified NDIR analyzer” mean? If a NDIR analyzer with constant optical path length is called “specified”, please tell us what is “common NDIR analyzer”? Response: a specified NDIR analyzer means a NDIR analyzer with constant optical path length. Common NDIR analyzer is no special meaning, just donate a NDIR analyzer. “common NDIR analyzer” has been revised as “NDIR analyzer” in the revised paper.

2) In equation (3), the “i” has different means in left and right of the equation, it is very easy to make the readers confused, please avoid this. Response: Actually, the “i” has
the same means in left and right of the equation, it represents gas i. In this manuscript, all notations are consistent.

3) There are some mistakes in equation (5) and (6), please check them carefully. Response: We have re-solved equation (3) and (4), and checked equation (5) and (6) carefully. We found that equation (5) and (6) are right. Thanks for your comments.

4) Please combine section 3.1 and 3.2. Response: section 3.1 and 3.2 are combined in the revised manuscript, please see section 3 of the revised paper for details.

5) In page 2019, line 22-23, why the measurement error caused by the gas distribution system ignored? Response: Gas concentrations from 10% to 90% of nominal value can be obtained with a high precision of ±0.5% by varying the voltages of the two mass flow meters. So the measurement error caused by the gas distribution system can be ignored compared with the error caused by cross interference. For simplify the analysis, we neglect the error of the gas distribution system. Please see line 218∼222 in the revised paper for details.

6) In page 2020, line 8, “only fitting correlation coefficients are shown for linear fittings” should be “only fitting correlation coefficients are shown for nonlinear fittings”, I guess. Response: Actually, what we want to say is that “only fitting correlation coefficients and no fitting parameters are shown for linear fittings”. Please see line 230∼231 and figure 3∼4 in the revised paper for details.

7) In Fig. 3, there are just 11 data points, but in Fig. 5, there are much more data points than in Fig.3, I can’t understand this from the paper (section 3.1 and 3.2). Response: This is because the data processing methods for figure 3 and 5 are different. For a NDIR analyzer, the calibration curve determination is very important, so we start to save data till the analyzer reading for a specific concentration level is stable, and then the mean value of the whole sampling period is used for least squares fitting. The 11 data points (in figure 3) which represent 11 different concentration levels are mean values of 11 different sampling periods, respectively. However, the data processing
method for figure 5 is different. The procedure is as follows. Firstly, 1 L CO2 of 25% concentration is pumped into the sample cell. Secondly, 0.95 L 25% CO2 and 0.05 L pure N2 (99.999%) are mixed (by using the gas distribution system) and then pumped into the cell. Thirdly, the mixture of 0.9 L 25% CO2 and 0.1 L pure N2 is pumped into the cell, etc. Finally, 1 L pure N2 is imported. During this whole period, the CO2 concentrations in the sample cell vary from 0% to 25%, we save data once a time on every 5s. Thus, the data points in figure 5 are much more than figure 3.

8) The description of instruments and field campaign in section 5 is tedious, please simplify it. Response: We have simplified them in the revised paper. Please see the description of instruments and field campaign in section 5 of the revised paper for details.

Thanks for your comments and the detailed corrections please see the last upload documents.

Please also note the supplement to this comment: http://www.atmos-meas-tech-discuss.net/6/C1067/2013/amtd-6-C1067-2013-supplement.pdf