

Interactive comment on “Development and validation of a portable gas phase standard generation and calibration system for volatile organic compounds” by P. Veres et al.

P. Veres et al.

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Comment 1: Discussion on the conversion efficiency to CO₂ for differing VOC types. In this study CH₄, benzene, formic acid and HCHO are all individually tested directly. Other VOCs are indirectly assessed through mixtures, but here one or more VOCs could have poor response whilst the overall result still lay within the combined gas cylinder and MOCCS uncertainty. Is there any experimental or literature evidence on the types of VOCs that will efficiently convert?

Answer: The following has been added to section 2.1 Mobile Oxidative Carbon Calibration System (MOCCS) “Conversion efficiencies of C1-C7 compounds on a

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Pd/aluminum catalyst has previously been shown to be quantitative (Roberts et al., 1998).”

Comment 2: In particular does the presence of a halogen or nitrogen atom create deviations?

Answer: Halogen and nitrogen containing species have not been analyzed in this study. However, in response to this comment as well as one contained in the second review, the following text has been added to the conclusions section. “While we have shown this technique to be effective for pure hydrocarbons and simple oxy-hydrocarbons, studies of VOCs containing heteroatoms, such as nitrogen, must be performed to validate the efficacy of this method for those compounds. MOCCS is somewhat limited in its applicability as S- and Cl- containing compounds are known to have the potential of deactivating such oxidation catalysts and as such may not be amenable to this technique.”

Comment 3: Independent calibration of the GC-MS for response to benzene. The paper refers to it being independently calibrated with over 20 different cylinder gas standards. Was this really done in one measurement cycle before testing against MOCCS? Or rather is this that over the GC-MS lifetime it has observed an internally and self-consistent calibration from this number of different cylinders. If this is the case which was the ‘current’ VOC standard used?

Answer: To address this point of confusion the following has been added to the text in section 2.2 GC-MS: “Benzene measured by the GC-MS was independently calibrated using more than 20 single- and multi-component VOC mixes over the lifetime of the GC-MS. The GC-MS response to benzene as determined from all 20 calibration mixes has an overall measurement uncertainty of $\pm 20\%$.”

Comment 4: Table 1 could be made clearer by labeling the 4th column as ‘measured Carbon by MOCCS’ and including an additional column that indicated the nominal carbon as derived from the cylinder values. I appreciate these appear in figure 5 but

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they would be useful here also.

Answer: The fourth column is in fact the nominal carbon as derived from the cylinder content. The header has been slightly changed to read “calculated nominal carbon after dilution” for clarity.

Comment 5: Figure 3 shows a large number of replicate measurements of benzene as derived from the total carbon measured by MOCCS. It would be interesting to have some assessment of whether the authors believed this variability to be due to variability in the ability to generate a consistent amount of vapor from the permeation or variability in the CO₂ conversion / CO₂ measurement. E.g. would this graph have less scatter if the Li-COR instrument had been used?

Answer: We believe that the variability in the CO₂ signal is a result of fluctuations in temperature, pressure, and flow over the permeation housings. The use of crimped capillaries leaves the system slightly susceptible to flow changes as ambient pressure and temperature change. Mass flow controllers can be used in place here and would be expected to greatly improve the stability of the measured signal; however, capillaries were chosen to limit the overall costs. The LI-COR indirectly reduces the uncertainty in the individual measurement of these sources as it reports a 30 second running average of the measured signal, and is a generally quieter, more precise instrument.

Comment 6: There appears to be some inconsistency in the uncertainties associated with the NOAA VOC cylinder standards. P 431 line 1 gives 20% but later on p 342 line 17 this is given as 10%.

Answer: The confusion is the result of a typo in the error associated with the nominal carbon as derived from cylinder values. The single component error in the NOAA VOC cylinders is 20%. As a result, the error in the calculated nominal carbon varies based on the number of components in a specific mixture. To clarify the text has been edited where necessary.

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Comment 7: Figure 4b y axis should be labelled MOCCS I think.

Answer: This typo has been addressed and the y-axis label on figure 4b has been changed from GC-MS to MOCCS.

Comment 8: For the fire intercomparison, can the language around line 20 be tightened up. – A good R2 value for the comparison tells us nothing about whether the calibrations are within uncertainties. This is only derived from the slope of the data.

Answer: The section to which you are referring contains both the slope data referred to as the fit ratio as well as the R2 value. We make a generalized comment after listing the ratios (i.e. fit slope) that the measurements compare well to within the instrument uncertainties and thus the calibrations must be valid. However, to avoid further confusion the text has been modified to read “A scatter plot of the data shown gives a slope of an orthogonal distance regression of 0.91 ± 0.02 with a correlation (R2) of 0.91.”

Comment 9: Figure 6 for the purposes of this paper would be much better as an x/y correlation rather than two overlaid time series.

Answer: The figure was altered from a time trace to an x/y correlation plot of the data contained within the original figure submitted. Text within the body of the paper was edited when necessary with respect to this change.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 333, 2010.

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