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# ***Interactive comment on “Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications” by M. R. Canagaratna et al.***

**Anonymous Referee #2**

Received and published: 5 October 2014

The manuscript reports the “improved-ambient method” for estimating elemental ratios (O:C and H:C) of organic aerosols (OA) from aerosol mass spectrometer (AMS) measurements. The standard calibration is well performed and covers a wide range of organics with different functionalities. There is no doubt that this work has a significant contribution to improve the accuracy of elemental analysis of ambient AMS dataset, which is largely based on the observations from Aiken et al (2008). In particular, the empirical equations determined in this study allow the AMS users to recalculate O:C, H:C, OM:OC and OSC of their existing dataset directly. Overall, it covers many aspects

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of elemental ratio determination in great detail. This manuscript is clear and well organized. However, it could be argued that this paper would be more suitable for AMT than for ACP as the main focus of the paper is rather on a technical (method) development. I recommend this manuscript to be published in ACP if the authors can better highlight the atmospheric implications and address the following comments.

Specific comments:

1. Introduction, second paragraph: Chemical ionization mass spectrometry (CIMS) with aerosol collection interface and high-resolution time-of-flight mass spectrometer has been recently deployed for determination of elemental ratios (i.e. O:C and H:C) of organic aerosols. Please add this information to the introduction with the support of some recent references.
2. Method, Page 19797, line 18-20: A complex mixture of organic aerosols generally retain water even though they are drying under a very low relative humidity condition. Can we ensure that condense-phase water in organic aerosols cannot be completely removed by silica gel diffusion dryer? What are the potential uncertainties due to this issue?
3. Figure 4 is a very good illustration of neutral CO<sub>2</sub>, CO, and H<sub>2</sub>O production via dehydration and decarboxylation of dicarboxylic acid upon thermal evaporation. It is recommended to add a few more examples (i.e. at least one for each class of organics in the supplement) to demonstrate that the same argument can be applied to different types of organics.
4. Page 19807, Line 19: How would the presence of aldehydes influence the use of fCHO<sup>+</sup> as a surrogate for alcohol content?
5. Section 3.6: Please specify the ranges of theoretical O:C and H:C of organic mixtures being investigated. Are they covering the typical ranges observed in ambient aerosols?

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6. Page 19812, line 5-8: Please add appropriate references to support the argument (e.g. isoprene and toluene SOA have a larger content of dicarboxylic acid and polyol functionalities).

7. Even though the focus of this manuscript is elemental analysis of OA, it is recommended to comment how the improved-ambient method may affect the total OA mass loading if the fragmentation table in Squirrel is modified accordingly.

Technical corrections:

1. Terminology: Both thermal vaporizer and oven are used. Please use either one in the manuscript.

2. Page 19806, line 9: Please change “Fig. S3” to “Fig S2”.

3. Page 19807, line 9: Please change “3.2 and 3.3” to “3.2”. Section 3.3 only demonstrates the production of CO<sub>2</sub>, CO and H<sub>2</sub>O fragments upon thermal evaporation.

4. Page 19808, line 24: The error of O:C shown in the Figure 1e (20%) is different to that reported in the text (28%). Please correct.

5. Page 19809, line 17: Please correct the reference to “Hildebrandt et al., 2014”. Please also update the information in the reference list (e.g., add the tentative title of the paper).

6. Equation 10 and Figure S4: The empirical relationship is slightly different between the figure (1.29) and the text (1.28)? Please correct.

7. Missing reference: Chen et al. (2014)

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