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## ***Interactive comment on “An analytical system for the measurement of stable hydrogen isotopes in ambient volatile organic compounds” by T. Meisehen et al.***

### **Anonymous Referee #2**

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This manuscript requires major revision and should be clearly marked as describing a proof-of-concept study since reported  $\delta^2\text{H}$  values fail to meet requirements for international comparability. There are number of technical corrections required prior to acceptance to ensure this manuscript meets IUPAC guidelines and recommendations. For example, heavy isotopes of hydrogen should be written as 2H rather than as D according to IUPAC: Nomenclature of Inorganic Chemistry. IUPAC Recommendations 2005, RSC Publishing, Cambridge, UK, 2005. So in all instances where D has been used instead of 2H, D must b replaced by 2H, e.g.  $\delta^2\text{H}$  instead of  $\delta\text{D}$ . Similarly, in equation (1) the factor 1000 has to be removed to meet the latest IUPAC guidelines

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and recommended terms of stable isotope ratio measurements and reporting results thereof (Coplen, T.B., 2011, Rapid Commun. Mass Spectrom., 25, 2538). The authors should note a H<sub>2</sub> cylinder gas cannot and must not be used as a 'reference gas' but at best as a monitoring gas. Since the H<sub>2</sub> cylinder gas is neither introduced into the IRMS directly nor meets the conditions of a reference material distributed by either the IAEA or NIST it does not meet the requirements of a 'reference gas', its sole purpose is that of a monitoring gas. For this reason sample  $\delta^2\text{H}$  values thus measured and calculated may not be reported v. VSMOW since they were not properly scale normalized on the VSMOW/SLAP scale on the basis of 2 contemporaneously analyzed reference materials. Pulses of H<sub>2</sub> 'reference gas' from a gas cylinder cannot be used for calibration of  $\delta^2\text{H}$  values, because such practice would violate the principle of identical treatment of sample and standard where all analyte gases must pass through the same preparative-analytical sequence. 'Reference gas' pulses from an H<sub>2</sub> cylinder are not generated in the same fashion as H<sub>2</sub> analyte gas from organic matter, do not pass through a GC prior to isotopic measurement, and thus are not subject to the same potential fractionations. The availability of a wide range of hydrogen stable isotope RMs for online analytical applications eliminates the justification of using outdated and indefensible 1-point calibration and the employment of H<sub>2</sub> 'reference gas' pulses except for monitoring IRMS performance and generation of raw  $\delta^2\text{H}$  values. Due to the wide range of the VSMOW/SLAP scale, for hydrogen isotopes only 2-point calibration can adequately account for the scale compression of individual isotope ratio mass-spectrometer systems. Therefore, 2-point calibration vs. calibrated Reference Materials is strongly recommended in order to achieve best accuracy and international comparability in hydrogen isotope analysis. In the light of the fact that determination of reported  $\delta^2\text{H}$  values does not meet the aforementioned IUPAC guidelines and recommended terms of stable isotope ratio measurements and reporting results thereof, this manuscript can only be accepted (after major revision) as a proof-of-concept paper reporting non scale normalized  $\delta^2\text{H}$  values. Presenting their  $\delta^2\text{H}$  values determined as described as  $\delta^2\text{H}$  v. VSMOW values is incorrect and, in fact misleading. On the sub-

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ject of reporting  $\delta^{2}\text{H}$  values properly scale normalized to VSMOW using 2 reference materials as scale anchors, more information is required detailing as to how independent  $^{2}\text{H}$  analysis was carried out by Agroisolab. For starters clarification is required if indeed as stated on page purce compounds were analysed for  $^{2}\text{H}$  abundance by elemental analysis (EA). Typically,  $^{2}\text{H}$  analysis of organic compounds requires high temperature conversion elemental analysis (TC/EA). On page 11 the authors state "at 1723 K themethane signal was below the lower limit of detection. This is in stark contrast to what is shown in Figure 7. In Fig. 7 at 1723 K a blue band/box is shown for the relative peak areas of a  $\text{CH}_4$  signal while on the other hand there is no grey band/box thus indicating there was no detectable  $\text{H}_2$  peak. Similarly, on the same page the authors state "below 1173 K no  $\text{H}_2$  is produced and this no  $\text{H}_2$  signal is detectable. Again this does not match what is shown in Figure 7. At 1173 K this figure shows a grey band representing the relative peak area range of detected  $\text{H}_2$  signals. Further down on page 7 the authors state "the same measurement series was analysed 'using'  $\text{H}_3^+$  factors of 5.0, 5.3 and 5.8". Were these  $\text{H}_3^+$  factors set arbitrarily, i.e. irrespective of what actual  $\text{H}_3^+$  factor was determined by the system? If so, this test makes no sense whatsoever. Correcting measurements for an  $\text{H}_3^+$  factor of e.g. 5.8 if the system test determined the current  $\text{H}_3^+$  factor to be e.g. 4.8 will of course affect results. One can only hope the way this sentence is phrased does not accurately reflect what actually happened.

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Interactive comment on Atmos. Meas. Tech. Discuss., 8, 7093, 2015.

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