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Atmospheric Measurement Techniques Discussions

Interactive comment on "Improved Methodologies for Continuous Flow Analysis of Stable Water Isotopes in Ice Cores" *by* Tyler R. Jones et al.

J. Rudolph (Referee)

rudolphj@yorku.ca

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The paper presents a description and detailed characterisation of a semi continuous, automated system for analysis of hydrogen and oxygen isotope ratios in ice cores. This is a highly relevant subject for studying past changes in the hydrological cycles. I assume that this method will be used for analysis of a substantial number of ice cores in the future and a paper presenting details of its performance will be important for a realistic evaluation of uncertainty in such measurement and thus their interpretation. In addition to the description of the method the authors provide a detailed characterisation and a substantial numbers of tests. In my opinion the experimental work and a considerable part of the data analysis is excellent. Therefore the paper ultimately merits publication in ACP. Nevertheless, the paper has a few issues that need to be addressed before it can be published.

1) The authors do not always clearly (and consistent with established terminology) identify different types or errors. Reproducibility (repeatability, precision) should be used for the standard deviation of repeat measurements, independent of the type of measurement. The qualifier has to the identification of the type of measurement. Accuracy should be used for the estimate of the deviation between the result of the measurement (if applicable including corrections) and the (unknown) true value. Accuracy includes all potentially relevant sources of error and can never be smaller than any of the individual contribution to uncertainty. For a systematic difference between result and true value the term bias should be used. Information on linearity is extremely sparse.

2) Connected to accuracy, there is a lack of evaluation of error propagation from calibrations, corrections etc. Sometimes it may be justified to neglect some contributions, but this needs to be demonstrated based on a quantitative evaluation.

3) The authors provide substantial details relevant for evaluating accuracy, precision, mixing. However, there is no overall evaluation. The various pieces of information are presented separately and summarizing overviews (e.g. in tables or bar graphs) are missing.

4) The authors often use narrative to explain calculations. In my opinion this adds unnecessary length and creates the risk of a lack of clarity. Any calculation can be clearly and unambiguously described by giving the formulas and identifying the variables and parameters used in the calculation. If a calculation is trivial (such as using Gaussian error propagation for simple calculations) it generally is sufficient to state this unless it is an extremely complex calculation which may not be obvious.

5) The structure of the paper is confusing. The method section contains results and discussions, the results and discussion part contains method description. This makes it very difficult for the reader to compare results and follow the logic behind results and conclusions that are presented.

6) The paper contains a fair amount of comparison between the newly developed method and existing methods. However, these comparisons can be found in many different parts of the paper (method, results and discussion, conclusions). Moreover, several of these comparisons are only qualitative. I also have to admit that, since these comparisons are spread throughout the paper, I am not sure if all other relevant methods are included in the comparisons. There should be one subchapter (last subchapter before conclusions) which presents a comparison of performance characteristics of different methods based primarily on quantitative information. In summary the paper merits publication in AMT after revision. Here are some specific points related to the previously mentioned problems as well as some other details that need to be changed.

Some details:

i) There should be a clearer distinction between the directly measured H and O isotope ratios and the deuterium excess, which is calculated from the two isotope ratios (Eq.2.) and therefore is to some extent redundant as far as analytical techniques are concerned.

ii) The last statement in 1.1 (p3, L21-24) is a result/conclusion and does not belong there.

iii) I do not understand “and normalized to Standard Light Antarctic Precipitation (SLAP)” (P4, L$). Eq. 1 is the standard definition of the isotope ratio relative to VSMOW and contains no reference to a normalization relative to SLAP.

iv) The statement “The precise measurement of dxs (‰ has historically been challenging because IRMS methodology requires that oxygen and hydrogen water isotope ratios be analyzed on separate systems, which increases uncertainty. The CRDS-CFA technique removes multi-system uncertainty because both isotopic values are measured simultaneously on a single sample with the same system.” (P4, L10-13) may be correct, but at this point it is unproven and speculative. It should either be backed-up by references or phrased as a possibility that is evaluated later based on results.

Furthermore, when looking at the measurement uncertainties in Table 5 it seems that the preparation creates (not surprisingly) some correlated errors for oxygen and hydrogen isotope ratio measurements (uncertainty for dxs is lower than expected from error propagation) while the errors for CRDS measurement seem to be independent (uncertainty for dxs exactly matches a Gaussian/ independent error propagation).

v) The heading “Data and results” is not clear. Data would include results, but there is a separate section results and discussion. Should it be “Data processing (or evaluation) and method? There are indeed several results and to some extent a discussion of these results, which I find confusing given that there is also a results and discussion section.

vi) P4, L21: “bolted with thermal paste” needs rephrasing

vii) P4, L22-23:” This method is preferable to proportional-integral-derivative controlled resistive heaters used in most systems, which introduce small temperature fluctuations that can result in varying melt rates.” is an evaluation of the method not based on presented facts and does not belong into the method section.

viii) P5,L4 and L8: Typical ranges of flow rate should be explicitly be given, as well as the typical actual water levels in the 2mL vial. This is important to understand to which extent this reservoir may contribute to mixing occurring in the liquid phase of the CRDSCFA system.

ix) P5,L11: The flow rate should be given. The suction effect does not depend on pressure, but on flow velocity.

x) P5,L29-30: I do not fully understand how 25 samples for 1m of ice core can give a 2.5 cm resolution. Is the resolution given calculated from mixing effects? xi) The last paragraph in 2.2 is a discussion/conclusion and does not belong into the method description.

xii) P6, L16-17 : unclear meaning.

xiii) P7, L19: “can” or “was” or “routinely is” verified. What is (was) actually done?

xiv) P7, L20-30: This detailed explanation of the amount of data connected to computing resources is unnecessary. The authors simply should state the type of computer used and the time needed for processing. Any qualitative explanation that a more powerful computer will speed up processing is trivial. Statements about time savings and resolution of different methods should be moved to the end of the discussion into a sub chapter presenting a systematic comparison of different methods.

xv) P8, L15-20: The definition of accuracy seems to differ from the typical definition of analytical accuracy. Analytical accuracy includes all sources of error and thus cannot be lower than the precision of a measurement. What is presented as accuracy seems to be the bias of the measurement. Bias can be corrected, but the overall accuracy needs to consider (in addition to all other sources of uncertainty) the uncertainty of the correction.

xvi) P8,L20-21: This statement is out of place and somewhat speculative since it does not present any quantitative comparison of precision and accuracy. If correctly determined accuracy and precision of different methods can be compared directly.

xvii) P9, L5-6: Table 3 and Figure 3 are redundant. Furthermore, they are results and should be presented and discussed in Chapter 3.

xviii) P9,L18: At this point there is no explanation how the vapor phase mixing is determined. Furthermore, this is a result.

xix) P9, L20-P10, L6: The description of the mixing correction is not clear. It seems to be based on the deviation from the expected value. This works for a sample with known isotope ratios, but not for ice cores with a priori unknown isotope ratios (and it would not be necessary if the correct isotope ratios were known). The correct procedure would be to solve Eq. 5 for ct (as function of t) for tests with known “correct” isotope ratios and then use ct as function of t as described in Eq. 5. Is this what has been done?

Clarification is needed. Furthermore, corrections have uncertainties which will impact the accuracy of the result. There is no information on the uncertainty of this correction, except that it “can only be applied at ct>0.65”, which implies a (not explained) threshold for error introduced by the correction. There is no information about magnitude or uncertainty of ct, let alone an evaluation how this impacts the final result.

xx) Subchapter 2.6 in general: This subchapter also contains a mixture of method description and results. Here a clear description of the procedure should be given, results should be presented and discussed in Chapter 3.

xxi) P9,L29: “at time t-1” needs rephrasing. Here t is the number of a given time interval, not really a time (an index needs to be a number). Probably better to use n

xxii) P10, L20 “We modified”

xxiii) P10, last line: “to maximize the fit” is not clear.

xxiv) Chapter 2.7 in general: Again there is a mixture of method description and results, especially P11, L16 to P12 L6 contain mainly results and discussion/conclusions.

xxv) Chapter 2.6 and 2.7: The isotope step correction and mixing length are tightly connected, here it seems that they are separate issues. However, the necessity for a correction is the consequence of mixing. The order in which the two subchapters are presented should be reversed and the correction be identified as procedure to correct for the impact of mixing.

xxvi) Chapter 3 contains not only results and discussion, it includes method description such as the origin and handling of ice cores analyzed as well as description of tests. The chapter presents three evaluations by comparing results for “real samples” using different methods (including the method presented here). This is excellent work. Unfortunately the value of this is difficult to see and understand for the reader due to the “parallel presentation and discussion”. I find it very difficult to compare performance data (e.g. precision and accuracy, mixing length etc.) for different types of samples (ar-

tificial mixtures, water, ice cores and firn etc). To do this the reader has to go back and forth not only between the three subchapters of Chapter 3, but also between chapter 2 and 3. The authors should present a clear comparison between performance parameters under different conditions, for example as Table (or bar graph). This would provide the reader with the possibility to understand differences in performance between artificial samples, water, different ice or firn cores. This would also would provide a solid basis for a straightforward comparison of the newly developed method with existing methods, which should be combined in one subchapter.

xxvii) P12, L9-10: I find the use of the terms “external precision” or repeatability as specific goals of this test somewhat confusing. The authors should stick to clearly defined criteria such as accuracy, reproducibility, bias, mixing length etc. If the performance criteria are different for different types of samples, then this is something that needs discussion and (ideally) explanation.

xxviii) The conclusion contains a significant amount of detailed repetitions from chapters 2 and 3 as well as performance comparison with other methods. This results in a rather long (especially for a measurement technic paper) conclusion. This can be avoided by a better structure (see above) which will also give the reader a much better chance to form an own opinion.

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