

Interactive comment on “Online technique for isotope and mixing ratios of CH₄, N₂O, Xe and mixing ratios of organic trace gases on a single ice core sample” by J. Schmitt et al.

Hinrich Schaefer (Referee)

hinrich.schaefer@niwa.co.nz

Received and published: 31 March 2014

The authors describe an analytical system that measures certain isotope ratios and mixing ratios of a suite of trace gases that influence climate and atmospheric chemistry. The documented performance of the system is comparable to existing techniques for the more widely used parameters, but in addition offers completely new analyses and allows for combined interpretation of the measured parameters. This has large potential in both modern atmospheric and ice core studies. The development pushes the boundary of what is technically feasible. The method has been extensively tested and is well described in the manuscript. Two points where the manuscript should be

C323

improved concern calibrations and blank measurements. Both are notoriously difficult because isotopically calibrated reference gases and ice samples, as well as truly gas-free ice are not be available. However, I think that the current description does not provide enough detail and discussion of the limitations. It seems to me that all relevant tests have been carried out, but the findings are in some cases not reported in a way that they could be assessed by the reader. Overall, this is a valuable contribution to the field of trace gas analysis.

Please see the following for a list of comments and suggestions:

Page 2019; 8-13: the use of isotope terminology here leaves to be desired. Please specify which isotopologue is enriched or depleted in the three examples.

Page 2021; paragraph 2.1.2.: would you consider it worthwhile to briefly discuss similarities and differences to the sublimation line described in Schmitt et al. (2011) and why the current set-up is better suited to the presented analyses?

Page 2022; 2-4: how are temperature and melt rates controlled?

Page 2022; 2-4: Is it correct that the vessel is connected to the vacuum pump during the melting step? If so, please state this in the text.

Page 2022; 28-29: in addition, this also strips remaining dissolved gas from the melt water.

Page 2023; 19-25: is the same purification applied to the He-purge gas described in the previous paragraph?

Page 2024; 1: can you quantify “most of the bulk air”? This seems important for the concentration calculations.

Page 2024; 3-7: could you provide details on the cryofocus trap? How is its temperature controlled?

Page 2024; 10-11: how long and to what final temperature is the GC ramped up?

C324

Page 2024; 18 (and throughout the manuscript): I find the name Boulder for this tank confusing, given that it is also simply a location. In my opinion, consistently using quotation marks ("Boulder") would make it easier to follow.

Paragraph 2.2.1 presents interesting information, but could arguably be shortened.

Page 2027; 3-8: this is a little confusing, as the CO₂-N₂O run precedes the ones with altered magnet current (which would be worthwhile stating here). What about disequilibrium effects during runs 3 through 5?

Page 2027; 10-12: this sentence should be moved to the description of the GC.

Page 2028; 6-7: is this done mechanically; e.g. with a band saw?

Page 2028; 14-15: are all flow rates controlled by head pressure, pump rate and restrictions?

Page 2028; 17-19: how does purging 2 ml/min for 24 min result in only 15-17 ml? Is the flow diluted with He?

Paragraph 3.1.2: it would be very helpful to have a table listing all assigned values for the various tanks and indicating which values are calibrated back to primary standards. For other values, e.g. all species in "Saphir" as well as CCl₂F₂, Xe and δ Xe it should be explained how the assigned values were derived. A further point that is relevant here and for Section 4.6. is the problem of single point calibrations. This seems to be the case for all isotope ratio analyses as well as the higher hydrocarbons. The limitations imposed by this should be discussed.

Paragraph 3.2.1: using Helium blanks is the most direct way of detecting blanks, however, the quantification is complicated by low signal-to noise ratios and, in the presented set-up, uncertainties in the air volume measurements. An alternative way to quantify sample contamination from extraction procedures are standard gas transfers. It seems that you should be able to use the "over-ice" measurements of your reference gases to quantify elevated values. How do "over-ice" and "bypass" measurements of Saphir

C325

compare to your blank results? Another point is that none of the He-blanks mimics the complete extraction procedure, i.e. including the melting step. I understand that it is impossible to do this properly without truly gas-free ice. However, the authors don't discuss the possibility that the heating of the flask and the first contact between water and flask surface increases the blank. Tests with bubble-free ice would give an upper limit for such contributions (acknowledging that at least part of the signal would be gas released from the "blank" ice). The implications of a potentially higher blank should also be discussed in Section 4.1, which currently only addresses blanks in mixing ratios, but not isotope analysis.

Page 2030; 21: is 0.1 g the mass of ice lost?

Page 2032; 21-24: this is unclear. Do you compare runs for the same species (e.g. CH₄ mixing ratio or δ ¹⁵N-N₂O) from several days? Does this apply to samples as well as standard runs? Are trends based on reference runs?

Page 2032; 26-27: technically, the blank would affect mostly the accuracy of the measurement, unless you can quantify the variability in the blanks. Do you have information how blank values vary over time?

Page 2033; 15: which m/z trace (minor 1 or 2) would show 600 fA for air?

Page 2034; 1-5: this is impossible to understand without the explanation given in the caption of table 2. I suggest moving the description of how mixing ratios in blank air are calculated and how that is translated into a sample contamination into the text.

Page 2034; 1-21: there is no discussion on the differing blanks between "over-ice", "bypass" and "melt water". Why are the "bypass" values for blank air mixing ratios listed in Table 2 higher than "over-ice" but result in the same or lower sample contamination? What can be learned from the "melt water" runs?

Page 2035; 7-8: This loss is important when air content is interpreted as indicator of sample quality or for palaeo-environmental information. However, for the determination

C326

of mixing ratios it is irrelevant because the analysed species is lost as well.

Page 2035; 9-10: this sentence is incomplete. What is “0.5”?

Page 2035; 10-11: is it not possible to calibrate the volume by measuring the pressure reduction when expanding gas from a precisely known volume?

Page 2036; 13-14: I am missing some information here. How was the precision of 0.05‰ determined; Table 4 lists a variety of values (see also page 2038; 14 where it's listed as 0.04‰? Also, the wording is ambiguous. The precision is determined for the δXe measurement with its 4 mass unit difference. I agree that this uncertainty should then apply to the gravitational correction, but the current wording may be misunderstood.

Page 2036; 13-26: there is inconsistent use of the three terms “ δXe ”, “ $^{136}\text{Xe}/^{132}\text{Xe}$ ” and “ $\delta^{136}\text{Xe}/^{132}\text{Xe}$ ”. It would be better to define the one you are using and then refer to it consistently. There are further instances throughout the text that should be unified.

Equations (1) and (3): the term “ $A(\text{species})_{\text{ref}}/A(^{136}\text{Xe})_{\text{ref}}$ ” should be in the denominator, shouldn't it?

Page 2039; 13-14: what is the reference for ^{136}Xe and how is it tied to primary standards?

Page 2040; 4-9: I am not sure I agree with this argument. Melt layers would present themselves as outliers from the values of the unaffected sequence and these outliers should be more clearly detectable with better analytical precision, even though the baseline value is subject to the mentioned influences.

Page 2041; 8-12: I don't follow this: what exactly is the “correction”? Is it the difference to the square peaks? If it is, has the working gas been calibrated against primary standards? Else the difference between the two in its magnitude is meaningless and cannot serve as an indication on fractionation or lack thereof in the system.

C327

Page 2041; 23-25: Firstly, Saphir indeed extends the range covered by the working standards, but the expected values for ice core air lie outside that range. Secondly and more importantly, is Saphir calibrated independently of “Boulder”? If it is not, you still have a single-point calibration. This problem is relevant to section 4.6.2 as well, where the amount effects are quantified using both “Boulder” and Saphir, but it is not demonstrated that deviation of sample isotopic signature from the references is not skewing the results. Overall, the problem of single-point calibrations should be discussed in detail; with the current documentation it is not possible to assess the true calibration range for the various species. Where single point calibrations are used, the limitations of the approach must be discussed.

Page 2042; 4: please provide details how the anomalies are calculated. Is each gas calculated relative to a chosen standard amount and what is that amount?

Section 4.6.2: if both Saphir and “Boulder” are calibrated relative to primary standards a correction for the analytical bias due to sample-reference isotope difference should be applied (see Ferretti et al., 2005; SOM for a description of such a correction). It is true that even with independently calibrated references the samples would lie outside the calibration range, but the extrapolation would give an estimate of how large the bias may be.

Page 2043; 7: technically, your results show that a potential memory effect is not changing over time, but I don't think they rule out that a memory effect occurs.

Page 2043; 21: For $\delta^{13}\text{CH}_4$ the standard deviations double, is this adequately described as “similar”?

Page 2043; 25 and following: throughout the manuscript, the only measurements of Saphir that are mentioned are “over ice”. The reader therefore cannot follow the argument whether there is an offset or not. Is there a comparison between “over ice” and “bypass” runs of Saphir?

C328

Section 5.3: the main question is not discussed in this section: how do ice core replicates compare to sequences of air runs and what do the differences tell about system performance?

Page 2045; 23-26: just out of curiosity, do you think that these species could be better analysed using sublimation techniques?

Page 2046; 3-11: without robust correction for the Kr-effect these results remain qualitative and are not very informative. Given that there are good results for intercomparison with IMAU from the firn air samples I would drop this section.

Table 1; caption: do you have an estimate of the time difference between elution from the GC and analysis in the IRMS (i.e., how well does the GC temperature at the time of the IRMS represent the elution conditions for that gas?

Table 3: is n for "Boulder" not known?

Table 4: If Air Control as the reference is only measured periodically, how does the referencing work?

Table 5: in the current table it doesn't become clear that the FA32 values are from OSU. The main text mentions that FA32 was also measured at CIC, how do those values compare?

Fig. 6: how do the raw values compare to the calibrated ones? It would be interesting to see them plotted as well.

Fig. 8: this plot suggests that the isotope offset is calculated for each reference gas independently, therefore the experiment does not give information on a bias introduced by differences in isotopic signature between sample and reference (see the comment to the relevant section in the text).

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 2017, 2014.