Review of "New technique for high-precision, simultaneous measurements of CH_4*,* N_2O *and* CO_2 *concentrations, isotopic and elemental ratios of* N_2*,* O_2 *and Ar, and total air content in ice cores by wet extraction" by Oyabu, I. et al. AMTD.*

General:

The manuscript discusses a significantly improved extraction method for sample size without compromising precisions of several important paleo-proxy parameter. The multi-proxy approach is very helpful for improving not only the resolution due to the lower sample amounts necessary, but also regarding the comparison among the different parameters analysed. This again improves the issues with timing, since all the parameters are measured on the same sample, as well as the intercomparison of parameter because only one laboratory and one method is used.

The manuscript is very nicely written with detailed information how the method works and how it is used for standard and sample analyses. Furthermore, the authors show tests that only a very limited number of corrections are necessary which is obviously due to the in depth selection and preconditioning of all materials used in the extraction, split and measurement lines. They further state how the values are calibrated.

It was easy to read the manuscript and I would like to congratulate the authors. I have only a few rather minor comments and suggestions. I suggest to publish it once these comments have been taken into consideration.

Thank you very much for your review. Our replies are in Blue.

Minor points:

You often used subscripts rather than superscripts in the text. This need to be changed, i.e. $\delta^{15}N$ *rather than* $\delta^{15}N$*, or cm3 rather than cm3. Please check any such issues.*

They were due to unexpected errors of MS Word application when the word file was converted to the PDF file. We will use a different conversion software to solve the issue and check all the descriptions.

Line 137: New header (Description of method and manipulations)

We will add a new header there, and we will also add two more headers under section 2.1., as the following.

2.1.1 Extraction line and its pre-treatment

Line 93 (current manuscript) "A schematic diagram of our extraction system is…….".

2.1.2 Preparation of apparatus and ice samples

Line 110 (current manuscript) "For routine air extraction, the sample tubes and extraction line are……….".

2.1.3 Manipulations for air extraction

Line 137 (current manuscript) "Up to six vessels, thus prepared, are brought to our laboratory room at……..".

Line 211: Flame Ionization Detector not Frame

We will correct it.

Line 293: How are the coefficients d, e, and f calculated, how do they relate to a, b and c?

For the FIDs, the relationships between peak area and pressure (for a same standard gas) are found to be almost linear over a wide pressure range, but it is slightly nonlinear towards lowest pressures within the range of the ice core measurements. Also, the response of ECD detector is generally nonlinear. We thus interpolate the three calibration points for each of three standard gas by a quadratic fit (the determination of a, b, and c for each gas). The relationship between the concentration and area at any given pressure is also slightly nonlinear, and thus we interpolate the three calibration points on the area-concentration space (from three standard gases, at the pressure of the sample gas) also with a quadratic fit (the determination of d, e, and f). A three-point calibration with quadratic fit is a common practice in precise atmospheric observations. The a, b, and c should be closely related with d, e, and f (after compensating for different units, for the same molar abundance of a gas of interest) because they both represent the same nonlinear responses of the same detectors. However, the coefficients would not necessarily be identical because of uncertainties unrelated with the detector characteristics, such as those from pressure measurement, standard gas scale, and deviation of actual pressure-area relationship from the quadratic function.

We will add some more description to the text based on the above explanation, together with a figure below.

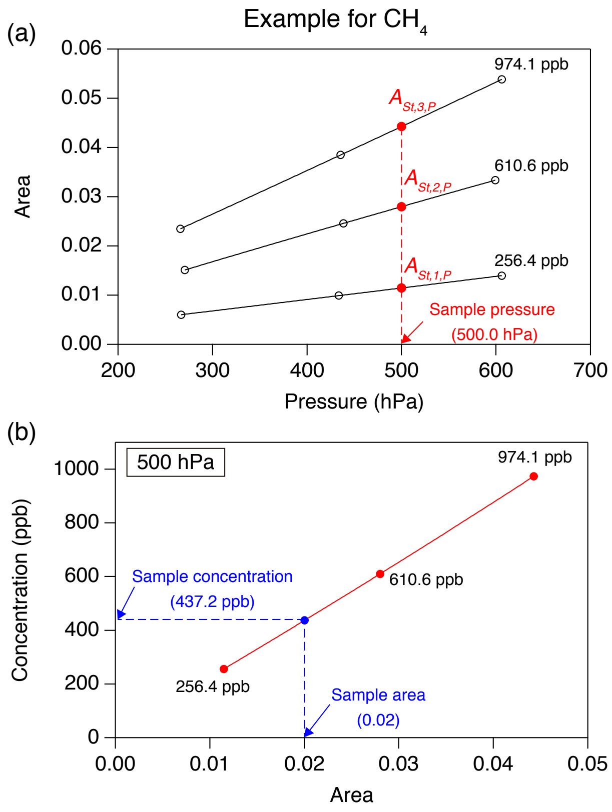

Figure: Example of calibration procedure for CH_4 concentration. (a) Black lines are quadratic fits to the peak area versus pressure for the three standard gases. Peak areas of the standard gases at the sample pressure are estimated by substituting the sample pressure on the fitted curves (red points, $A_{St,1,P}$, $A_{St,2,P}$, and $A_{St,3,P}$). (b) Red line is the calibration curve for the sample, which is a quadratic fit through the three red points from (a).

Eq. 6, lines 380ff: what about the sample loss during the first evacuation after loading the sample? Is this neglectable?

We indeed take into account the sample loss during the evacuation as follows, although it is small. After all the extractions for a day, the mass of Trap 1 is measured to obtain the total mass of sublimated ice during the first-stage evacuations. The typical amount of ice is 0.5 – 1.5 g for four to six samples (each with ~90-min evacuation). To account for the additional loss during the second evacuation after switching the line to the transfer line (~30 min), the mass of ice in Trap 1 is multiplied by 4/3 (120 min/90 min). The ice loss for each sample is estimated by simply dividing the total ice loss by the number of samples, and it is typically 0.1 – 0.3 g. We will add this explanation to the text.

Eq. 8: Why is the normalization made to direct atmospheric air and not to a standard that is well linked to the outside air at a given time.

The normalization of the sample is indeed made to the reference can, which is determined against atmosphere from time to time. Perhaps the current equation gave the wrong impression that the sample is directly normalized against atmosphere. We will re-write the equation in an expanded form, so that the readers can immediately see (without looking for the previous equations) that all the measurements are made against the reference can.

Line 548: …is impossible to be of atmospheric origin…

We will correct it.

Line 603ff: you might cite Huber et al., EPSL 2006

We will add Huber et al. (2006, EPSL) and Severinghaus et al. (2009, Science).