

Interactive comment on “Continuous measurements of methane mixing ratios from ice cores” by C. Stowasser et al.

Anonymous Referee #2

Received and published: 6 March 2012

General Comments:

In this contribution, Stowasser et al. discuss the development of a new system to make continuous measurements of methane extracted from ice cores. The system utilizes a Continuous Flow Analysis (CFA) front-end to melt the core extract air and residual water from the ice core. This mixture is then further debubbled and the air is extracted using a hydrophobic membrane. The extracted air is dried (Nafion) and then its methane content is quantified using a modified version of a commercially-available methane analyzer.

The work represents an advance in the field of quantifying gases in ice cores and continuous, in-field measurements of such cores. It is well-suited for publication in Atmospheric Measurement Techniques Discussion and the text is clear and well-written.

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However, there are several major points that should be clarified and discussed before this paper is finally published. All of these points are presented below. Most importantly, the calibration issues require clarification and explanation (Point #6 below).

Specific Comments

1. Page 212, Lines 19 – 25 (Introduction). Can you please indicate the required analytical parameters (e.g. accuracy, precision, dynamic range, time response) for continuous ice core measurements of methane?
2. Page 215, Lines 21 – 25. If possible, please quantify the dependency of the membrane extraction on water pressure, air pressure, and temperature. Likewise, please quantify the dependence of the dissolved methane concentration on these parameters (e.g. P, T). This is critical in assessing how well the pressures and temperature must be controlled to obtain adequate precision and minimal bias.
3. Page 215 – Page 216. Can you quantify the efficiency of the membrane extractor at your flow rates and conditions?
4. Page 216, Line 12. Please confirm that the sample is dried to 0.003 % (30 ppmv). Typically, Nafion does not dry to below 300 ppmv using the configuration described in the text.
5. Page 217, Line 5. Do the calibration gases also contain Argon? Argon significantly broadens the methane absorption spectra and should be included in the calibration source. If not, this may be one source of the observed bias offset.
6. Page 217 – 218, Figure 2. The text should be revised to explain several aspects of these calibration curves: a. Figure 2b. Please add a residual to the fit so that discrepancies from the line can be clearly seen. Moreover, the fit seems highly linear, thus, the large uncertainty in the slope (0.7941 ± 0.3561) is almost impossible. I assume that this is a typographical error? b. Figure 2a. There is a LARGE discrepancy between the slope in Figure 2b and Figure 2a. The instrument reads almost 16 % less methane

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than it should based on the pure gas calibrations. It is critical to discuss the sources of this low reading. Is the membrane extractor inefficient? Is there a substantial amount of methane still left in the water? Is it an instrument issue? Likewise, it is almost impossible for these spectroscopic instruments to have a non-zero intercept (the intercept is typically < 1 ppbv). Thus, the observed 12 ppbv offset is highly improbable, suggesting that the calibration response is non-linear and more standards are required. Please discuss these issues and possible reasons for this behavior in the text. c. The authors conclude that the data presented in Figure 2b are more accurate partially due to the wider dynamic range of calibration. This is not true. The instrument calibration should span the measurement range as closely as possible. This accounts for the slightly non-linear response of the analyzer over a wider dynamic range. Thus, although there is less uncertainty in the slope of the fit line with a wider dynamic range, the accuracy of the instrument over the measurement range is worse. So, it is not true that using larger differences in the CH₄ mixing ratios in the field would improve the instrument accuracy. d. Was the instrument zero checked (e.g. on dry nitrogen or similar)? If so, why weren't the calibration curves in Figure 2a and 2b forced through zero? e. Please note that it is critical to address these calibration issues (specifically point 6b above) in order for rest of the data to be interpreted.

7. Page 219 – 220 (Figure 3). Please add a few more details to the stability plot and discussion: a. The noise present in Figure 3a is clearly not “white noise” and shows discrete “drop-out” behavior. Why do you observe these sporadic, low readings? b. Can you please overlay the pure gas data discussed on Page 219 (Line 22 onwards) onto Figure 3? This would help the reader see the differences in the Allan variances and raw data. c. You conclude that the instabilities are due to the “gas extraction module”. . . can you elaborate on this conclusion? Is it due to a change in the membrane efficiency? d. Since the calibration interval is 24 hours, can you estimate the 24 hour precision of the setup? It seems that providing a short-term Allan Variance (e.g. < 1 hour) is not relevant to the actual measured data presented in this paper. e. You also conclude that the WS-CRDS is using software signal smoothing to improve the

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short-term precision to below the Allan variance limit. Did the manufacturer provide any further information about this point? How does this smoothing affect linearity?

8. Page 222, Line 9. Can you estimate the orifice size of the needle valve?

9. Page 222, Line 24. Please note that CH₄ does NOT interact with the cavity surfaces in any significant way. The observed smoothing is largely dominated by flow response time and dispersion.

10. Page 223, Line 7. Cavity-enhanced absorption spectrometry techniques must retain very clean flows to prevent fouling of the cavity mirrors. Yet, you removed the inlet filter. Was the gas prefiltered in another manner? Did the cavity foul (i.e. get dirty)? What happens if it does?

11. Page 224, Lines 18 – 27 (Figure 4b). The +25 ppbv bias is disturbing and well-discussed in the paper. However, it is critical that this bias remain constant for this technique to be adopted. Is there any longer-term data suggesting that this bias remains at +25 ppbv? If not, does the setup need to be calibrated using a GC system during every run?

12. General – It should be noted that the WS-CRDS instrument only measures 12CH₄ and does NOT measure 13CH₄. Thus, changes in the isotope ratio of methane will lead to erroneous methane readings. Please discuss this effect and its potential magnitude for ice core studies.

13. Figure 1 – Please clarify to better describe the debubbler and pressure decoupling unit. I realize that these are discussed in some of the references; however, a more detailed picture (and discussion) in this paper would be very beneficial to describing the system.

Technical Corrections

1. Page 214, Line 5: Change “is to a high degree automated,” to “is, to a high degree, automated,”

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2. Page 217, Line 5: Change “for in the field day to day calibration. . .” to “for day-to-day calibration of the system in the field. . .”

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 211, 2012.

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