**Atmospheric
Measurement
Techniques
Discussions**

Interactive comment on "On the interference of ^{86}Kr^{2+} during carbon isotope analysis of atmospheric methane using continuous flow combustion – isotope ratio mass spectrometry" *by* J. Schmitt et al.

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Schmitt et al. report on the problem of interference from Kr during measurements of stable carbon isotope ratios of methane (δ13CH4). The study covers the complete process from detection of an interference to the identification of the "contaminant", and finally technical solutions to eliminate the problem during analysis and providing correction strategies for affected data series. The discovery of the problem has already sparked discussions in the atmospheric measurements community so that it is more than timely for this work to be published. Since my institute hosts an analytical system

that is subject to the problem I have put the manuscript through its paces regarding the practical tests and solutions. I don't see reasons against publication of the manuscript as presented, as it provides a robust and comprehensive treatment of the issue. The manuscript is well structured and clearly written. I have noticed a few instances where I recommend clarification or minor corrections as detailed below. None of those concerns are of major importance. The only small point where I see room for improvement is to communicate the potential importance of the findings to other research fields. For instance, the list of affected studies could be moved from the conclusions section and discussed already in the introduction, which currently focuses only on ice core research. The implications for other mass spectrometry studies is discussed only briefly; it seems that the issue would be of interest to isotope chemists working in different fields as well. A list of good, relevant key words may be a way to bring the findings to their attention. However, I wonder if a more general title would be more effective. One suggestion would be to mention the low-energy tailing in the title. Overall, I recommend this manuscript for publication in Atmospheric Measurement Techniques.

Specific comments:

Page 2; Line 8: Kai et al. and Levin et al. should be references for the preceding sentence (lines 3-5) as they don't report palaeo-data but modern atmospheric time series.

Page 3; Lines 18 & 19: quoting the actual deviation of δ13CH4 values is helpful for the reader to understand the scale of the problem, yet such values are not provided in the manuscript except for a statement on page 6, lines 25 &26, and the AWI correction factors which amount to max. $\sim$1.3‰ . A short report, maybe as a table, of the deviations observed during the round-robin exercise would be of interest to the reader.

Page 5; line 29: it may be preferable to introduce the abbreviations "PI", "GLA", and "PD" in this line, so that the reader easily sees what they stand for.

Page 8; line 16: I think that the IMAU tests provide robust evidence for Kr as the

interfering agent already at this point, so "believe" is very conservative wording.

Page 8; line 26: while using the manuscript as a manual to conduct the described test I got hung up on the magnitude of the accelerator voltage (AV) shift, here 55 V. This is less than the 85 V that are later quoted as needed to shift a given m/z beam to the next cup and the evidence for the Kr tailing across an AV range has not yet been mentioned or presented. Therefore, it is not clear at this point why the m/z 43 and 45 beams would be detectable in the major and minor 2 cups, respectively. It is true that lengthy explanations will distract from the simple and very useful test. Possibly, Section 4.1. should be moved to the end of Section 4. This would provide the reader with a better understanding how the test exploits the tailing and cup characteristics. The reader could be referred to Fig. 6, which illustrates the positioning of beams and cups very clearly. The one point that Section 4.1. currently provides in the logical flow of the argument is the demonstration of peak positions. These features can also be shown using Figs. 2 and 4 although I admit that peak overlap is not explicitly shown in those figures. Using the proposed order, readers would be armed with all information on the behaviour of Kr and CH4-CO2 before they explore their own set-up. This is a suggestion only .

Page 9; lines 15 & 16: as m/z is defined as mass to charge ratio (page 2; line 22) it is unclear what is meant by "m/2z (for doubly charged ions)".

Page 10; line 12: do you mean that the signal is 10x higher at the same run time (as opposed to the max. minor 2 signal of the air run with ∼350 mV)?

Page 11; line 6: What is the m/z 43 beam proximal to?

Page 12; line 27: should this be Fig. 6?

Page 18; line 29: the wording "Kr now elutes 25 s before…" invokes the lead to be an inherent characteristic of the set-up. In contrast,using the trap one should be able to place the CH4-CO2 peak at any desired time in the window between Kr and N2O.

Maybe this is worth clarifying?

Page 20; lines 14 & 15: it seems this should be Fig 5b (instead of Fig. 4b).

Page 21; lines 8 & 9: one detail that is not explicitly discussed is the temporal offset between the peak of the Kr elution on one hand and the peaks of the ion current ratios on the other. Making this point would illustrate how the calculated Kr excess is different from the ion current ratio peaks and may be helpful for the reader.

Page 21; lines 10 and 11: please provide some details on the fitting procedure.

Page 22; line 4: what is the reported average standard deviation? Is it the pooled standard deviation of replicate measurements (n=?) for each tank? Or is this some measure of corrected versus measured values? Please provide more detail.

Page 23; lines 12 & 13: although the peak cut-off correction is close in magnitude to the algorithm, it is systematically higher. I wonder if this reflects the fact that the heavier isotopes tend to elute slightly later than the lighter ones (as the authors allude to in the previous paragraph), so the former would be more strongly affected by the peak cut-off. If this is the case the algorithm would not only provide more consistent but also more accurate results.

Page 26; line7: If I am not mistaken Kr's higher solubility should lead to higher CH4/Kr ratios (not lower as currently stated) as proportionally more CH4 is extracted into the head space.

Page 12; line 12: it seems important to complete the argument and state that the Kr bias related to CH4 concentration will lead to erroneous assessments of alpha.