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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.

J. Severinghaus (Referee)

jseveringhaus@ucsd.edu

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The authors show convincingly that krypton (specifically, low-energy doubly-charged Kr-86 ions appearing in the tail of the beam) interferes with methane measurements in atmospheric samples that are analyzed as CO2 in the mass/charge 44, 45, and 46 Faraday cups. The paper is very well documented, treats the subject thoroughly, and is written very clearly. It is relevant to the journal and is appropriate for the readership.

Overall, this is an excellent paper and should be published with only very minor revi-

sions.

It would be interesting to explore a little further why such a large tail exists for krypton. The authors mention interaction with the helium in the source, and point out that pure krypton has a much narrower peak. This is probably a correct hypothesis.

I suspect that the basic reason for the big tail has to do in some way or other with low-energy ions, which are more strongly deflected by the magnetic field than ions having the nominal accelerating energy. It would be good to mention "low-energy ions" in the paper. [By the way this suggests that one possible solution might include an electrostatic analyzer, to eliminate low-energy ions.]

I once had a problem with graphite ferrules adsorbing krypton, and wonder if the systems discussed by the authors have any of these ferrules. Not that this would explain the interference - rather, this adsorption led to a very large memory effect lasting many hours after putting pure krypton into the machine. But it might exacerbate the problem by boosting the amount of krypton above what would normally be encountered in air.

Another idea for dealing with the issue might be to put a m/z=43 cup in the mass spec so that the krypton problem could be monitored in real time.

This problem is reminiscent of a problem we have long been dealing with in the lab, the fact that the large low-energy tail of the argon-40 beam falls into the m/z = 38 cup. It adds to the mass 38 peak by about 1%, which makes the delta values about 1% too small (too near zero). For precise 40/38 measurements it is necessary to make a correction for this issue, much as the earlier generation of mass spectrometrists corrected for the CO2 tails.

minor edits:

pg 1424, line 17 "inferred" rather than "derived" pg 1425, line 24 "an AV scan" pg 1428, line 16 "account for or eliminate" pg 1431, line 17 LN2 (it looks like lN2 at present)