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Atmospheric Measurement Techniques Discussions

Interactive comment on "In situ detection of atomic and molecular iodine using resonance and off-resonance fluorescence by lamp excitation: ROFLEX" *by* J. C. Gómez Martín et al.

Anonymous Referee #2

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General Comments: This manuscript describes the design and performance of a new instrument to make in situ measurements of atomic and molecular iodine. The instrument design is focused in particular on observations in the marine boundary layer. In general, the paper is well written, thorough and contains a significant amount of detailed information about the technique, its development and implementation. The content of the manuscript seems entirely appropriate for publication in AMT and I recommend publication after the authors address the comments below.

Specific Comments:

p. 3805-6: The discussion of previous uses of resonance fluorescence for detection of atmospheric halogen species seems to imply an analogy between the measurements of Cl and Br and that of I. To my knowledge, there have been no measurements of ambient halogen atoms in the troposphere; those reported in the literature were for observations made in the middle stratosphere [Anderson et al., 1977 and Anderson et al., 1980].

p. 3807 and Figure 1: There has been considerable work done in the past on the effects of self-absorption in atomic resonance light sources. I recommend that the authors look at the work of, for example, Linevsky and deHaas (J. Chem. Phys., 77, 6060, 1982) and Braun and Carrington (J. Quant. Spectrosc. Radiat. Transfer, 9, 1133, 1969). These authors discuss the theoretical basis of self-absorption and also provide a framework for characterizing it. In particular, I am concerned that the authors are using a lamp temperature of 243 K for their calculations. This may be the external temperature of the lamp, but it is not likely to be the temperature of the emitters within the lamp, so the Doppler width and overlap with the absorbers in the flow system will be incorrect. Figure 1, panel b: There are quite large differences among the three I2 absorption cross-sections shown here. What are the implications of those differences for the measurement technique?

p. 3808: Can the atomic I lamp photolyze I2?

p. 3810: Is it more advantageous to keep the I atom resonance axis at a vacuum (via pump) than to purge it with some gas (such as N2 or Ar)?

p. 3814: I am not clear on the procedure for calibrating the absorption path reduction. How well can this be done? That is, the authors quote a reduction of 14%, but how well is that value known?

p. 3820: The calibrations described here are carried out at very large mixing ratios compared to those measured in the atmosphere. How have the authors established that these calibrations are linear and absolute?

p. 3824, lines 14-17: It would seem that the differences in optimal pressure are related to the use of different atomic lines whose line broadening characteristics vary.

p. 3824, lines 18-19: Note that there may only be one prior in situ measurement for BrO (not Br atoms), but there are numerous observations of tropospheric and boundary layer BrO made by DOAS. Also, there is recent work by Greg Huey at Georgia Institute of Technology to use CIMS for measuring BrO (in situ) from airborne platforms.

Section 5.2: While I think it is useful to talk about the potential importance of interferences in a measurement, I think this section is unnecessary. In section 4.2, the authors state that they have found no interference from water vapor or nitrogen oxides. Why then spend more than two pages discussing the theoretical background of how these species might interfere?

Section 5.3: This section also seems redundant with information presented earlier in the manuscript.

Figure 8: In the manuscript text, the authors note the size of their background signals (a few hundred counts each for I and I2). So, how in the calibration procedure can the signals be zero (or even negative) at zero concentration of I (and I2)?

Technical Comments:

p. 3804, line 17 – write out “marine boundary layer (MBL)”, since this is the first time the term is used.

p. 3805, lines 8-9 – this sentence is awkwardly written and the meaning is not very clear.

p. 3805, lines 26-28 – this sentence is redundant with information given earlier in the paragraph.

p. 3806, line 2 – the phrase “for the detection of atomic iodine” is redundant and can be removed.

p. 3810, line 13 – “below” not “bellow”

p. 3818, line 5 – I am not sure what the “factor of 4 increase” relates to

p. 3818, line 8 – “major” not “mayor”

p. 3822, line 19 – “major” not “mayor”

p. 3825, line 3 – “below” not “bellow”

p. 3825, line 13 – no “d” on Schumann

p. 3829, line 5 – “major” not “mayor”

Figure 3: write out “SBT” in this caption

Figure 4: The figure caption and the labels on the top panel do not seem to agree.

Figure 10: It is difficult to discern which line is meant by the “thick line” – in my copy, it looks like the spectrum for the old lamp is thicker than for the new one.

Table 1: The final footnote should be “h” not “g”.

Table 1: The Br atom reference here should probably be to Brune et al., 1989, where the RF technique was first described.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 3803, 2010.