Atmos. Meas. Tech. Discuss., 3, C1630–C1632, 2010
www.atmos-meas-tech-discuss.net/3/C1630/2010/

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.

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Received and published: 5 October 2010

Review of "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.

This paper describes the design, calibration, and operation of a new instrument that detects atomic and molecular iodine using atomic resonance fluorescence and molecular fluorescence. The authors provide a very thorough and detailed description of the fluorescence detection technique including characteristics of the iodine lamp used to

excite iodine atoms and molecular iodine. This section is especially informative and will be a valuable contribution to the scientific literature. The operation of the instrument including the calibration method that uses a combination of photolysis and broadband cavity ringdown is described completely and effectively. Overall, this is a well written paper that meets all of the requirements for publication. I recommend this paper for publication after these minor comments are addressed.

General comments:

It is not clear in the paper how the loss of I atoms on the wall of the flow tube or on the orifice affects the calibration and the measurement. There is a brief mention of the loss of I atoms on the smallest pinhole on page 3819 lines 1-3. The fact that I atom recombination is observed on the smallest pinhole suggests that the same process is occurring elsewhere in the system, on walls of tubing and solenoid valves, especially. This loss could be significant - from the drawing, there are lots of surfaces for this recombination to occur. Is it significant? What evidence do you have that this recombination is understood?

Even if the recombination has a small effect on the calibration, can you be sure that it also has a small effect in the measurement of I atoms in ambient air? What about the conversion of other Iodine species (e.g. IO)? Are they converted to I or I_2 in the sample inlet?

Another concern that I have is the loss of I atoms to species other that molecular iodine. If any oxidizer is present (O, O_3, OH, etc) iodine oxides will be produced. These species are notorious for sticking to flow tube walls. In the calibration system, the use of the Xe lamp could easily produce these oxidizers, especially if there is UV light present. Is the lamp filtered? These species are not included in Equation 4. Do you have any evidence to support the absence of these species? If not, how big of an effect might you expect from their presence?

Detailed comments:

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p. 3807 ln 4-12 and p. 3825 ln 3 -12. The lamp self-absorption will also decrease the sensitivity of the 178 nm line. In fact, this could be a major part of the reason that the resonance fluorescence of I is so much less sensitive than Cl in your case. Have you tested to see if the 178 nm line is self-absorbed? I would expect that the fluorescence in Ar shown in Fig 3 would have a peak at a lower temperature than in air if the 178 nm line were not already self-absorbed.

p. 3821 ln 15-22. This is the first (and only?) mention of measurement uncertainty that I found. It should be expanded here or elsewhere in the paper. What is the relative error from these individual terms? What is the typical uncertainty in the calibration? Is an estimate of wall loss included?

p. 3825 ln 8 – 14. Have you adjusted the pressure to show that it is the O_2 absorption that removes the 178 nm signal? If so, just state this. This paragraph is too wordy. Also, the emission line at 178 nm is about 6 times weaker than the emission at 184 nm.

Miscellaneous:

You might be interested to know about similar detection method for Cl and Cl_2: Wilmouth et al, J. Phys. Chem., 2009.

I_2 adsorbed on molecular sieves provides a low vapor pressure source for I atom resonance lamps. It can operate above 300 K without running the lamp deep.

Typos:

p3825 ln 3; 2825 ln 14; 3827 ln 7; Table 1 the superscript “g” should be “h”

Fig. 1 is too small. It has a lot of good information, but it is hard to read. Consider splitting it into two figures.

Fig. 2. Indicate where the sample intake is.

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