

Interactive comment on “A comparison of spectrophotometric and denuder based approaches for the determination of gaseous molecular iodine” by R. J. Chance et al.

Anonymous Referee #2

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The manuscript describes the comparison of a solvent-trap and a denuder based approach for the measurement of gaseous molecular iodine. I agree with the authors that to date measurement techniques for ambient molecular iodine are still remarkably scarce, especially when the measurements should be single point in situ measurements.

In the present paper the authors investigate the recovery, reproducibility, stability and blank of a starch-coated denuder sampling system, which was first described by Chen et al. and concluded that the starch-coated denuders are not suitable for the determination of molecular iodine due to a low and highly variable recovery. In contrast to the

C792

starch-coated denuder, hexane and ethanol solvent traps in combination with UV/VIS detection of iodine species were shown to give better performance in terms of recovery and reproducibility. However, a trapping time of greater than 10 hours is required to get a detection limit of 70 ppt and the trap has to be kept at extremely low temperature (-50°C) to minimize the solvent evaporation during the sampling period. At such low temperatures the gas stream entering the trap has to be completely dry to avoid the freezing of moisture on the inlet, as stated by the authors. This certainly limits the application of the hexane trap for ambient molecular iodine measurements. Nevertheless, the solvent trap could be still useful for laboratory-based iodine research. Therefore, I suggest to publish the paper with the revisions and clarifications as described below.

1. How stable is the test gas source? It would be helpful if the authors could report the reproducibility (standard deviation) since it also determines the accuracy of the recovery test.
2. Do other halogen species like dihalogens ICl, IBr, Br₂ interfere with the solvent trap measurements of I₂? The authors should test or at least comment the potential spectrometric overlapping.
3. In page 5 line 2, the authors mention that gaseous molecules will diffuse to the inner surface of the denuder under the condition of laminar flow. However, from the experimental part it is not clear if a laminar flow is guaranteed. The recovery of the denuder will decrease if turbulent air is sampled into denuder.
4. Page 5: A brief description of the measurement procedures by Chen et al. should be given since it is the basis of the denuder experiments reported.
5. Page 6: From which company was the TMAH used in the study? Did the authors test the iodine blank value of TMAH? It should be mentioned that different sources of TMAH can contain variable amounts of iodine as contamination.
6. Page 11, paragraph 2: The authors discuss that the mass of coating material in

C793

the denuder is present in excess and should be sufficient for the target molecule collection. In fact, if same amount of coating materials as used in the denuder is dissolved in aqueous solution, it may finally form the inclusion complex with as much as 1 mg iodine. However, it should be recognized that for denuder collection the complex formation takes place between gas phase I₂ and solid phase starch. Therefore, the complex formation rate or even equilibrium constant may significantly differ from those in aqueous solution. Furthermore, the residence time of gaseous I₂ in the denuder (50 cm) is in the order of a second or even smaller. Therefore, simple stoichiometric estimations are useful but probably not completely valid to apply them to a denuder technique. Consequently, in general an excess of coating materials should be applied for efficient denuder operation.

7. Page 15 lines 2-4 and the 2nd paragraph of the conclusion: The authors state that the LOD of the solvent trap is below the upper limit of I₂ concentrations in the coastal marine atmosphere (e.g., Mace Head). However, it should be realized that the upper limit of 93 ppt reported by Saiz-Lopez et al. is a peak value during low tide, which is probably higher than the average concentration levels. Furthermore, the low tide period typically lasts for around 4-6 hours for one tidal cycle, which is around half of the trapping time used in this work. Therefore, the LOD of the solvent trap technique is probably often not sufficient for ambient measurements. However, the method still can be useful for laboratory-related studies such as seaweed chamber experiments. I suggest the authors emphasizing these points.

8. Table 1 and Fig. 4: The temperature used in solvent traps should be mentioned.

Minor points:

1. Page 11 line 21: "as per the method" should be " as the method "

2. " Chen " is the first name and " Hongwei " is last name, the citation related should be corrected.

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C794