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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 #1

Received and published: 4 November 2009

There has been growing interest in atmospheric iodine chemistry recently due its possible role in aerosol nucleation and cyclic reactions between gas phase iodine radicals with ozone and HO. The latter processes may influence the oxidation capacity of the atmosphere by changing HO/HO₂ and NO/NO₂ ratios. The flux of molecular iodine appears to be significant in areas of high productivity and especially over macroalgae beds. Thus methods for I₂ quantification are vital to further our understanding of iodine chemistry. Chance et al. report on a simple method to quantify molecular iodine by trapping in a hexane bubbler and quantification by UV-Vis spectrometry. It is an independent method to those most often used to date (DOAS, BBCRS, LIF), and thus could be an important additional method for cross validation of the

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different techniques. The authors also demonstrate that problems may arise using the starch/amylose coated denuders previously suggested by Hongwei et al., (2006), and that further (inter)laboratory validation is required before wide spread use of this method. Thus the paper is suitable for publication after consideration of the following points.

Overall

The primary question that I have of the method is its selectivity. The authors state that it is selective; however they have only introduced molecular iodine in an N₂ atmosphere into the system. From the results presented in the paper it seems unknown if the method is only selective to I₂ or if other compounds present in the atmosphere (real or experimental) will also react with the hexane and cause absorption in the same wave length region. One possibility could be HOI, as this is likely to react with the hexane, or other dihalogen molecules (e.g. IBr, IC, Br₂ etc.). I would suggest running a few experiments with these (and perhaps other e.g. NO_x) compounds to determine if any interferences could be present. Note that even in experimental setups a number of iodine species could be in the gas phase such as IO, OIO and I₂O₂. The authors need to demonstrate that the method does not quantify such compounds as I₂.

The authors focus more attention on the 'prototype' hexane method than the modified method, giving a detailed account of replicates and detection limits. However, this 'prototype' is not all that satisfactory (data in Fig 4 does not match ideal recovery line, especially at high concentrations), compared to the modified method which seems to work very well. However, no replicate data is given for the modified method. I would like the authors to present some replicate data for each point in the modified method so that the reader can see how precise the method is at a given concentration. Also, it would be good if the authors provide both the spectrometer detection limit and the 3 σ value from traps filled with hexane and bubbled with iodine-free air. The authors should also include a quantification limit, as the detection limit only states if iodine can be detected or not. To assess the methods ability to be deployed in experiments and in the field,

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quantification is required, and thus a quantification limit needs to be presented.

The authors state that it is vital that the samples can be measured 'at a later date'. For the denuder samples they have tested the stability over two weeks, however for the hexane and ethanol traps there is no indication of how long the samples can be stored. Such considerations could be important for long field campaigns. Thus some experimental data on the stability of I2 in hexane would be beneficial.

Throughout the paper the authors seem to use the terms amylose and starch interchangeably sometimes stating 'starch coated denuders' when they have been coated with amylose. These are two separate substances, although amylose is part of starch in addition to amylopectin. I recommend use amylose only when it has been applied in the method and vice versa for starch.

The modified hexane method, as given, is only applicable to the very highest concentrations observed in the natural environment, mostly because of limitations in the sensitivity of the spectrometric method. I believe it is also possible to derivatise I2 to a volatile organic species (e.g. 4-iodo-N,N-dimethylaniline (Mishra et al., 2000) that could then be easily determined by GC-MS and thus gain much more sensitivity. This may lower detection limits to levels more applicable to natural environmental conditions.

Specific comments

P2192 In22: There are many references for I29I release in peer reviewed journals. I would suggest using some of these rather than 'British Nuclear Group'. Some examples could be (Moran et al., 1999; Raisback and Yiuo, 1999; Szidat et al., 2000; Snyder and Fehn, 2004; Reithmeier et al., 2006).

P2193 In8: As far as I can tell from ACPD, the paper by Saiz-Lopez and Box (2008) has never entered into accepted print (ACP). If this is so, caution needs to be taken when citing the reference.

P2193 In29: the authors state that the hexane trap is specific to I2, however I have not

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been able to find any evidence of this or detailed research on possible interferences from other atmospheric constituents.

P2194 heading 2.1: add molecular iodine not just iodine. This could mean single iodine atoms.

P2194l18: perhaps present the lower number followed by the higher number. i.e. 190ppt to 285ppb.

P2196 In14-20: Please list the concentration range of gases used in the experiments and also the concentration intervals.

P2198: General question to this section: in what range was the photometer calibrated (i.e. concentration range of standard solutions) and what was the detection limit just of the spectrometric method compared to blank hexane bubbled with iodine free air. Also, how many blank replicates were used for calculating the detection limit ($n=?$). Is there any memory effect between samples?

P2198: the authors present a figure of the basic hexane trap. Since the modified method functions significantly better than the prototype, I would suggest changing the figure to the new method using the midget bubblers. If anyone wants to repeat the method then they will use the modified version and thus a diagram of the modified version would be most helpful.

p2199 In 23: what is 'appropriate precautions'? Does this include doing all work in a fume hood? I guess that in your group there is a lot of volatile iodine measurements being conducted, including the one described in this paper. Therefore there may be significant 'contaminants' in the laboratory air. Conducting all experiments in a fume hood could solve this problem.

P2200In24: the denuders were coated with amylose not starch. P2200In27: 'ICP-MS determination step was well validated' how was it validated? Was a standard reference material analysed? Where samples quantified by both external and standard addition

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methods etc.?

P2201 In1-25: This section makes it clear that there are some differences between the denuder method employed by Chance et al. and Hongwei et al., although the authors note that using starch as per Honwei et al gave 'poor results'. What is classified as poor results? It might be useful to include this information in the paper as it more accurately copies the method of Hongwei et al.

P2202: The paper would be clearer if the basic hexane method was called 'prototype' or something similar to differentiate it from the modified method. This then needs to be used systematically throughout.

P2203 In1-10: Why is it not possible to simply purge the ethanol with He for a few hours and use this as the standard? Has this been tested?

P2203 In14-27: The authors set 10% hexane loss to the maximum amount of time that a trap can be deployed. This assumes that iodine is also lost from the trap over time and that it is somehow proportional to hexane loss (i.e. 10% hexane loss= $\pm 10\%$ variation in iodine loss). Have any tests been conducted to see if iodine is lost from the bubblers at all? If so, is it lost systematically over the sampling time or does it appear to be random? Does 10% hexane loss represent $\pm 10\%$ iodine loss? This could be simply tested by spiking hexane with some I₂ and bubbling with zero air (or iodine free compressed air) over a number of time periods. It would be very interesting to see this as a new figure.

P2204 In1-7: it was an interesting idea to derivatise the molecular iodine using leuco crystal violet. This obviously significantly increases detection potential. Can the authors provide any explanation why the standard deviation is so large? Perhaps the reaction needs longer than 1 min to run to completion?

P2204 In20-25: The authors note that water vapour may cause problems for field application due to freezing of water in the glass frit. They state that no suitable means

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of removing the water has been found. What have they tried to use to remove the water so far? Have they tried a cold trap upstream of the sample remove water but not I2? Molecular sieves can also be rather selective to water vapour. Perhaps a slightly heated molecular sieve would keep the I2 volatile but trap the water vapour. Some test data would be interesting for anyone wanting to develop the method further.

P2204 In23: the authors state the recovery using the modified method was close to 100%. Please give exact recovery with standard deviation.

P2205 In6: The method used amylose not starch.

Technical comments

The authors need to standardise units. In some sections concentrations are given in mass/volume (e.g. ng/ml) whereas in other sections concentrations are given on a molar basis (μM e.g. p2204). I would suggest that the authors choose one unit and use this consistently throughout the paper.

With a little more work I believe the hexane trap could be a valuable additional method for I2 quantification in both lab experiments and in the field. This is especially true due to its simplicity and cost efficiency.

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