

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

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We would like to thank referee#1 for their detailed and constructive comments, our responses to which are given below.

Overall:

Method selectivity

We are confident the hexane trap technique is selective for I₂ (absorption maxima at 520 nm in hexane) against most other volatile iodine compounds which might be

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present, with the exception of the interhalogens IBr, and to a lesser extent ICl (see below). The absorption cross sections of ICl and IBr are however red-shifted and weaker than that of I₂, so that their concentrations would have to be similar to or in excess of I₂ to comprise a significant interference. However, care would need to be exercised in experiments or environments where relatively high concentrations of the interhalogens are expected to be present.

Possible halogen interferences: (a) Organoiodines: the most red shifted bands of iodoform (CHI₃) absorb at 350 nm in cyclohexane (Wall et al., 2003). Other organoiodine compounds absorb more strongly in the UV. (b) HOI and I₃⁻: As shown in figure 1b, I₃⁻ has strong UV-Vis absorption bands at 350 nm and 285 nm (Palmer and Lietzke, 1982). The absorption wavelength of HOI also falls at 285 nm (Paquette, 1985). (c) Interhalogens (ICl, IBr): The gas and solution phase absorption spectra of ICl and IBr overlap with I₂. In CCl₄, I₂, IBr and ICl have absorption peaks at 517, 492 and 465 nm respectively (Augdahl and Klaeboe, 1965).

We have added the following paragraph to the discussion section, P2203, Ln27: “The trap is thought to be selective for molecular iodine over volatile organohalogens, HOI and I₃⁻, which all have absorption maxima at shorter wavelengths (Wall et al., 2003; Palmer and Lietzke, 1982; Paquette, 1985). However, there may be some overlap in absorption spectra between I₂ and the dihalogens IBr and ICl, which absorb 492 and 465 nm respectively in CCl₄ (Augdahl and Klaeboe, 1965). However, the absorption cross sections of ICl and IBr are red-shifted and weaker than that of I₂, so that their concentrations would have to be similar to or in excess of I₂ to comprise a significant interference. Nevertheless care would need to be exercised in experiments or environments where relatively high concentrations of the interhalogens are expected to be present.”

Replicate data for modified solvent trap

Each time point in figure 6 represents a separate experiment using the solvent trap

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for a given length of time; each experiment was only conducted once under the final, optimized conditions, so replicate data is not available for individual time points. However, the linearity of the response indicates good reproducibility. Note that for each time point, spectrophotometric scans were made in triplicate.

Solvent trap Blank LoD

Unfortunately we do not have any measurements made on hexane traps bubbled with iodine free air or N₂ with which to calculate the LoD of the overall trapping method as suggested by reviewer#1. However, we note that, during determination of the trapping efficiency of the optimized trap, scans of hexane from the second solvent trap yielded absorbance values indistinguishable from the hexane blank baseline. This suggests that the overall trap blank would be very low and might be close to or the same as the solvent blank.

Quantification limit

The quantification limit (LoQ) of the optimized solvent traps has been calculated using the formula $LoQ = 10 \times \text{standard deviation of the blank}$. It is now presented in section 3.2.2 as follows:

P2205; Ln3: For a trapping time of 10 hours 45 minutes (10% solvent loss), the atmospheric LoD is of 69 pptv and the limit of quantification (LoQ; calculated using 10 times the standard deviation of the blank) is 230 pptv.

Measurement of samples 'at a later date'

We do not state that it is “vital” that samples can be measured “at a later date”, only mention it as a potential advantage when referring to the denuder tube method specifically. As the ICP-MS instrument is not portable and cannot be taken to the field or experimental location, and the TMAH elution and subsequent analysis requires laboratory facilities and is fairly time consuming, the ability to store denuder tube samples until such time they can be analysed is very useful. Conversely, a spectrophotometer is

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a relatively portable instrument and the analysis is relatively quick and straightforward, so it is less important solvent trap samples can be stored. Therefore, we have not investigated the stability of molecular iodine trapped in hexane specifically as part of this work. However we have observed that I₂ in hexane standards remain stable for periods of a few weeks and so storage of solvent trap samples may be possible if required. To clarify this we have altered the text in section 1 as follows:

P2194, Ln1: “if using denuders” added after “Additionally”

Starch vs amylose

We have replaced the word “starch” with “amylose” where appropriate in the manuscript – see response to specific comments

Derivatisation

Our manuscript includes a brief foray into the derivatisation of molecular iodine trapped in hexane (section 2.3.3) which is discussed further below. The referee's suggestion of derivatisation followed by GC-MS detection may well allow the LoD of the trapping technique to be reduced further as the LoD for molecular iodine given by Mishra et al., 2000, is approximately 200 times lower than that achieved using a spectrophotometer with a 10 cm cell. However, this LoD is based on reactions occurring in aqueous phase rather than organic solvent and includes a solvent extraction step that would not be possible when using the solvent traps, as the iodine is dissolved in organic solvent from the outset. There may be potential to adapt the derivatisation step so it works in organic solvent and still gives good reproducibility, specificity and a low LoD, but we feel this is beyond the scope of the current manuscript. To reflect this we have added the following text:

P2204, Ln7. “With further work, it may be possible to develop a derivatisation method that yields reproducible results in organic solvent and a lower LoD.”

Specific comments

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P2192, Ln22: The reference for ¹²⁹I release has been changed to Raisbeck and Yiou, 1999, as suggested by the reviewer.

P2193, Ln8: Although Saiz-Lopez and Boxe (2008) has not been accepted for ACP, it is publically available online in ACPD and so can be cited, especially given that the citation is for a suggested mechanism of molecular iodine formation rather than for an established fact. We have changed the phrase “proposed as the source” to “suggested as a source” to emphasise this.

P2193, Ln29: See above comments relating to specificity of the method.

P2194, Ln7: ‘Molecular’ has been inserted before ‘iodine’, ‘an’ has been changed to ‘a’.

P2194, Ln18: The order of the numbers has been changed such that the lower number is now presented before the higher number.

P2196, Ln14-20: The concentrations used and exposure durations are given in table 1. We have also inserted the concentration range used into the text and made reference to table 1 in the paragraph.

P2198: The concentration range used to calibrate the spectrophotometer was typically 500 to 5000 nM. Three standard replicates were used to calculate the spectrophotometric LoD. The spectrophotometric cuvettes were thoroughly rinsed with solvent between each sample or standard, and blanks were run between each set of replicate analyses. Following this protocol, we found that memory effects in the spectrophotometer and solvent traps were not a problem. Text has been added as follows:

Ln6 “the concentration range used was typically 500 to 5000 nM”; Ln6: “To avoid any memory effects, the spectrophotometer cuvettes were rinsed thoroughly with solvent between each scan and solvent blanks were run between each sample or standard.”
Ln7 “(n=3)”

P2198, Ln25: Figure 2 has been changed to show the optimized trap set-up, reference C1094

to this figure has been moved from section 2.3.1 to section 2.3.2 and now refers specifically to the optimized set-up (“The optimised solvent traps were set up as shown in Fig. 2”).

P2199, Ln23: As the reviewer suspects, our work at the University of York involves a number of volatile iodine species and so there is a risk of contamination from these compounds. We therefore did not use TMAH in our own laboratories at the University of York and instead used those of other research groups. However, we suspect that background iodine levels may also have been high in these laboratories due to the widespread use of iodine compounds as a chemical reagent etc within the Department of Chemistry. As we mention in the manuscript, we believe the trace analysis facilities available at CSL had lower background iodine levels and this was supported by the lower blanks we could achieve there. Precautions against contamination included storing the TMAH in an air tight box and using dedicated acid cleaned glass ware and clean plastic ware when handling it. We have inserted the following text to provide more detail on this: “(e.g. storing in an air-tight box away from known sources of iodine compounds, using dedicated, acid-washed glassware)”. TMAH was handled in a fume hood because of its corrosive nature; as a fume hood draws air in from the laboratory it would not offer much protection from contamination. A laminar flow hood with a chemical filter would be a better solution, but unfortunately no such facility was available to us at the time of this work.

P2200, Ln24: ‘Starch’ has been changed to ‘amylose’.

P2200, Ln24: The iodine concentration in the eluates was quantified using a set of external calibration standards (potassium iodate). Tellurium and antimony internal standards are used to correct for any drift in signal over the duration of the measurement run. This is described in section 2.2.3. Certified reference materials (CRMs) were not analysed as part of this work as no suitable liquid CRM is available. However, the ICP-MS method used at CSL has been thoroughly validated using solid CRMs (typically NIST1549 and NIST8435 milk powders) extracted into TMAH. The method is UKAS

accredited to ISO 17025 and the uncertainty of measurement (95% confidence) calculated to be 13% from the results of cross-laboratory proficiency exercises (FAPAS). Details of this validation have now been added to section 2.2.3.

P2201, Ln1-25: We have not included more details of the preliminary trials mentioned here because they were rather limited. Additionally, they were slightly different in set up to the experiments reported (e.g. different iodine test gas source) and subject to a number of other problems (e.g. blank contamination) and so we felt to include them would cause confusion. However, as the results of these preliminary trials led to us using amylose rather than starch in the more comprehensive tests we report here, we have made mention of them. In this context, 'poor results' means 'low and poorly reproducible' results - we have amended the text to state this as follows: "poor results" replaced with "low recovery and poor reproducibility"

P2202: The words 'prototype' or 'optimised' have been inserted before mention of the solvent traps as applicable to make it clearer which is being talked about in each section. In section 2.3.1, P2198, Ln11 now begins "Initial trials used a prototype solvent trap consisting of a 100 mL round bottomed flask containing 50 mL of solvent."

P2203, Ln1-10: We did attempt to purge the ethanol solvent with inert gas (N_2 rather than He) prior to using it to make up calibration standards, and found this enhanced the iodide signal at 225 nm. This is described in lines 6-8, P2203. In order to make it more obvious what we are describing, the text has been altered slightly to read: "Comparison of calibration curves prepared using pre-purged and unpurged ethanol suggested that the iodine signal at ~ 225 nm (iodide) in purged ethanol may be 1.2 to 1.8 fold greater than in unpurged ethanol, resulting in overestimation of the amount of iodine trapped." The need to pre-purge the solvent was one of the reasons that we chose hexane above ethanol, so we did not do any further tests using pre-purged ethanol in this work.

P2203, Ln14-27: We did compare evaporative losses of I_2 and hexane using a test similar to that described by the reviewer. We found that evaporative losses of I_2 (ex-

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pressed as % loss) were approximately 50% of the evaporative loss of hexane (see figure 1 below). We considered it better to minimize I_2 losses by limiting the amount of solvent evaporation to no more than 10% (equivalent to iodine losses of no more than 5%), rather than correct for them in this case. The sentences "As some fraction of the trapped iodine evaporates with the solvent, evaporation cannot simply be corrected for and instead must be minimized to a level predetermined as acceptable" has been deleted and the following text has been added: "A fraction of the trapped iodine evaporates with the solvent. By evaporating iodine in hexane solutions under a stream of gently warmed N_2 (to simulate the warm gas stream produced by the permeation oven), we found that the ratio of % I_2 loss to % solvent loss was 0.47 ± 0.03 ($n=3$). Therefore, 10% hexane loss equates to approximately 5% iodine loss, a level considered sufficiently low as to not be corrected for in this work."

P2204, Ln1-7: Why the leucocrystal violet method gave unexpectedly poor reproducibility remains unclear, despite attempts to investigate this. The method gave promising results at first, so we do not believe that the reaction time was insufficient for the reaction to go to completion. Fresh reagent solutions were made up daily so the problem is not thought to be due to these degrading. However, as the response of the method became progressively worse over a period of time we believe the problem may be related to the stability and/or solubility of the reagents in conjunction with the need to use them in hexane miscible solvents.

P2204, Ln23: "close to 100%" has been replaced with " 105 ± 6 %"; this value is the average recovery (\pm standard deviation) for the 5 different time points shown in figure 6. As noted earlier, we do not have replicate recovery data for a single trapping time.

P2204, Ln20-25: We tried a number of means of removing water vapour but not I_2 from the gas stream, these were as follows: 1. A Nafion box dryer (Nafion membrane in airtight box containing molecular sieve) - this caused a 60% I_2 loss. 2. Chemical drying agents such as K_2CO_3 , Drierite and molecular sieve - these all resulted in approx 50-80% I_2 loss from the gas stream. 3. Two spiral condensers in series (at 0 and -10

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°C respectively) to physically strip out the water vapour. Using these condensers I₂ losses still occurred but were less than with the chemical methods above. We have added the following text to the manuscript detailing these measures: Ln21 "Use of a Nafion box drier upstream of the solvent traps led to 60% I₂ loss, while chemical drying agents such as K₂CO₃, Drierite and molecular sieve gave 50 to 80% I₂ loss. The most suitable means of removing moisture but not molecular iodine from the gas stream identified to date has been two spiral condensers in series held at 0 and -10°C, but some iodine losses were still incurred" Note that drying the gas stream was not required for the recovery tests using the permeation oven, so these measures are not included in figure 2.

P2205, Ln6: 'Starch' has been changed to 'amylose'.

Technical comments

Units

We have used the following units in the manuscript:

Gas phase concentrations have been given in ppbv or pptv. We have changed the gas phase concentration units given on P2201, Ln11 and Ln12, from ng L⁻¹ to ppbv for consistency.

Gas flow rates are given in L min⁻¹. The flow rate given in sccm on P2204, Ln11, and the flow rate units in figure 5, have been converted to L min⁻¹ for consistency.

The amylose suspension and LCV reagent are described using g L⁻¹ and elution solvents and acid wash solutions in % (v/v) as these are the most practical units to use when preparing these mixtures.

ICP-MS calibration standards and eluate concentrations are given in g iodine L⁻¹. These units are used in the place of molar units because the measurement gives the total amount of iodine present regardless of chemical speciation (i.e. total number of iodine atoms, rather than I₂ molecules or IO₃⁻ ions). We feel that citing these results

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in terms of moles of potassium iodate, or iodine atoms, would lead to confusion when converting to molecular iodine concentrations. In some cases, e.g. contamination of the blanks, the original chemical speciation of the iodine detected by ICP-MS is not known, so conversion to molar units of anything other than iodine atoms or equivalents of molecular iodine molecules is not possible.

Solvent trap iodine concentrations are given in molar units because they relate directly to molecular iodine concentrations in solution (see above comments on specificity), and can be converted directly to gas phase units, which are also effectively molar.

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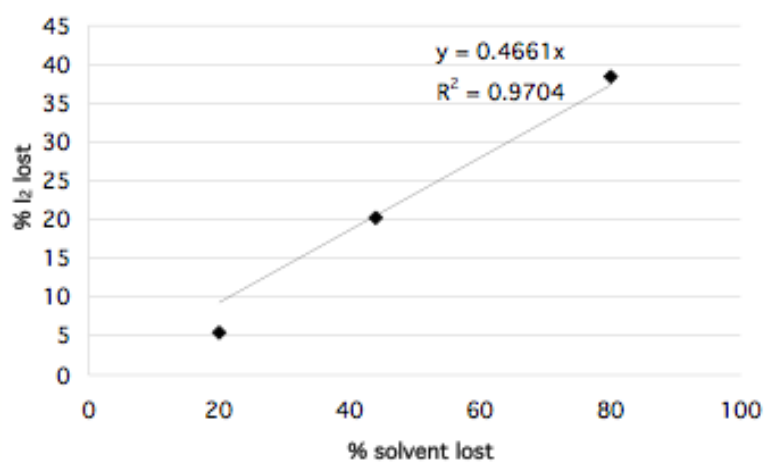


Fig. 1. Percentage molecular iodine lost during evaporation of a molecular iodine in hexane solution under trapping conditions.

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