

Reviewers' comments are in black, authors' response in blue and changes to the text in red.

Reviewer #2

This paper thoroughly details the trial of a deployable instrument for remotely measuring isoprene (the main focus of the manuscript) and similar VOCs. There is a great need for calibrated portable instruments that can monitor long term trends out in the field for campaigns and background measurements therefore the iDirac instrument is of great interest, as this can complement reference materials and satellite measurements to give a holistic overview of the atmospheric isoprene distribution. The paper thoroughly introduces the instrumentation and shows the breadth of measurements that have been performed to test it. However, despite the wealth of information specific quantification is often not provided (please see Specific comments). I recommend that this manuscript be accepted once these minor corrections have been addressed.

We thank the reviewer for their feedback and address their comments below.

General comments

In the introduction it would be useful to explain the importance of isoprene with regards to impact on the OH reservoir in the troposphere, as well as on SOA.

We added the following:

“As a result of its reactivity and the magnitude of its emission rates, determining the global abundance of isoprene is important to understand the oxidising capacity of the atmosphere (Squire et al., 2015) and the formation of SOA, which can affect the optical properties of the atmosphere and in turn impact the climate (Carslaw et al., 2010).”

I think that a bit more detail is required about the instrumentation, particularly with regards to the drier and breakthrough and poisoning of the trap.

Have any tests been performed to assess if the drier removes any VOCs?

Tests were carried out with and without the drier while feeding the instrument the same mixture. No statistically significant differences were observed. We added this sentence to the text:

“Laboratory tests found no statistically significant difference in isoprene peak area between runs using the drier and runs bypassing it.”

How do you recondition the trap, what if terpenes or heavy components stick and reduce trapping ability?

We run blank runs periodically to make sure heavier components are not carried over between runs. However we have not found evidence for carryover. We monitor the trap performance using plots such as the one shown in Fig. 16 and eventually replace it with a new one.

Figure 9

- breakthrough affected by flow rate
- how were the samples pumped into the system
- what happens if you vary the sampling rate?

Upon closer inspection, we now attribute the difference between the two instruments to peak tailing in the chromatograms from the Orange instrument (leading to an underestimate of the peak areas). We have amended this whole section to reflect this.

Similar questions arise from the results depicted in Figure 11.

– breakthrough affected by flow rate

The flow rate is held constant (~ 20 mL/min, the same flow used in the field) so the breakthrough volume obtained here is relevant to our field measurements.

– how were the samples pumped into the system

This is as described in Section 2.2

– what happens if you vary the sampling rate?

We have only investigated this using the sampling flow rate used routinely in the field. An in-depth investigation on the effect of flow rate on breakthrough volume would be valuable, but it is beyond the scope of this work.

It would also be helpful to have a clearer idea of what is meant by the trap becoming “poisoned” is this the result of moisture and what is the impact on uncertainties and sensitivity?

We believe the adsorbent degradation after repeated heat cycles is the principal cause of trap degradation. Typically thermal desorption tubes are replaced after 100 heat cycles. A week of continuous operation of the iDirac in the field consists of ~1000 heat cycles. We have added a second panel to Figure 16 to show the decrease in sensitivity as a function of time.

I strongly suggest that Figure 3 includes information about the isoprene concentration depicted and I would also like error bars added to all figures where required e.g. Figure 7.

Figure 3 has been amended to include a calibration, a sample and a blank chromatogram with peak fits. We also added additional information in the caption regarding the isoprene concentration for each run.

Error bars were added to Figure 7.

Volumes should have an associated uncertainty.

Refer to the answer to comment P10. Line 26.

Finally, I think it would be useful to know why was a Gaussian shape was used for the fitting, have you tried any other peak shapes for fitting e.g. Voigt or speed-dependent Voigt? These might optimise results.

We found that Gaussian curves provided the best fit to the observed chromatographic peaks. We found a marginal improvement with exponentially-modified Gaussians curves.

Specific comments

P1. Line 23. Please change to “Isoprene is an important nonmethane”

We prefer to stress the importance of isoprene relative to other non-methane VOCs, so we have not changed the text.

P1. Line 25. What is the impact of the SOA, please also add references

We added the following:

“As a result of its reactivity and the magnitude of its emission rates, determining the global abundance of isoprene is important to understand the oxidising capacity of the atmosphere

(Squire et al., 2015) and the formation of SOA, which can affect the optical properties of the atmosphere and in turn impact the climate (Carslaw et al., 2010).”

P2. Line 16. Grab samplers: please add example reference e.g. Robinson AD DOI: 10.5194/acp-5-1423-2005
Reference added.

P2. Line 36. What about trueness?
“Accuracy” includes trueness and precision according to ISO 5725.

P3. Table 1. Please specify nitrogen purity percentage
Text amended as follows:
High Purity Nitrogen (Grade 5.0, or 99.999%)

P4. Figure 1. Does the packaging and foam emit any VOCs?
Not to our knowledge. However the gas lines are never exposed to the internal packaging during a routine measurement sequence, so chances of VOCs from the foam or packaging affecting the measurement are very low.

P5. Paragraph 2. What is the volume sampled?
Details on this are given in the “Sample adsorption/desorption system” section further down P5.

P5. Line 30. Why can you not use a non-return valve?
We have more experience in the use of flow restrictors.

P5. Line 43. Specify the desired volume
This is specified by the user, and we’ve added the following to this:
“When the desired volume (as specified by the user in the configuration step – see Section 3) is reached...”

P6. Lines 11-14. Consider combining sentences.
We believe the paragraph reads better as two shorter sentences.

P6. Line 21. Are there any other VOCs with similar ionisation values or boiling points?
Most VOCs have ionisation energies in the 8-10 eV range, so they can be detected by the PID (notable exceptions: methanol and formaldehyde). The boiling point is key to determine elution order and potential co-elution, and we have tested for these potential interfering species in Section 5.1.

P6. Figure 3. What concentration does this peak represent? What’s the S/N ratio?
We have now amended Figure 3 to include a blank, a calibration and a sample peak, with additional information on the gas sampled in the cation. The S/N ratio for the calibration run is 51.8.

P7. Line 7. Should read “in a nitrogen balance”
Amended.

P7. Line 9. Is the calibration gas purchased or decanted, if the latter please specify how.
As stated in the text, these details are given in Section 4.1 and the reader is referred to that Section for further information on the calibration routine.

P7. Line 20. Please specify the reduced pressure
This is stated on line 23 on the same page (20 kPa below ambient).

P7. Line 23. I think that you mean “nominally” not “typically”?
Agreed and amended.

P7. Line 38. Is the clock calibrated?
The clock is not calibrated but we found negligible drift (1-2 seconds) over a 5 months field deployment.

P9. Line 15. What are the criteria for insufficient/sufficient (how many?)

P9. Line 16. What is the criteria for “too great”

In order to capture the fluctuations in elution time brought about by the variations in oven temperature, we recommend having a calibration run at least every six hours. We have amended the text as follows:

“When there are insufficient calibration chromatograms to determine the isoprene peak retention time (e.g., less than 4 calibration runs in a day)...”

P9. Line 26. What is the stability period of the gas standard?

Studies (Rhoderick et al., 2019) have shown that VOC mixtures in Air Products Experis cylinders have a stability of at least 2 years. We have added this to the text.

P10. Line 13. Replace “good practice” with “essential”!
Amended.

P10. Line 14-19. Please give numbers.

The following text was added:

Typically, a calibration run is performed every 35 sample runs. As the mean duration of a 150 mL sample run is approximately 9 min (consisting of 7.5 min of sampling and 1.5 min of chromatographic run), a calibration run is performed approximately every 5.25 hours.

P10. Line 26. What is the error on the volumes?

We have added the following sentence (and error bars in the relevant plots):

The error in the sampled volumes is dominated by the dead volume in the gas lines before the trap (approximately 1.6 mL), combined with the uncertainty in the measurement of flow rates (1%) and sampling times (0.05%). The overall uncertainty in the volumes is estimated as 50% for 3 mL, 13% for 12 mL, 3% for 48 mL and 1% for 200 mL.

P11. Paragraph 1. Are we talking about intermediate precision or reproducibility?

This is over the timescale of 1 week to 1 month, so strictly speaking it is intermediate precision.

P12. Line 13. What is the lowest volume used – this may impact uncertainty and S/N as the sensitivity is likely to vary with volume size

The volume in the sample runs is held constant throughout a deployment.

P12. Line 31. “the grey and the grange instruments” I think you mean “orange”; please clarify (explain what the difference is before section 5.5).

“Grange” was a typo and has been amended. We have added a reference to Section 5.1 where the two instruments are described more in detail.

P13. Line 11. Specify uncertainty of BOC mixture and add the word “balance” to describe the matrix gas.

Amended.

P13. Line 12. Do you have an offset from losses to the chamber wall?

Potentially, but the point is that both instruments were sampling the same air. So if there were wall losses within the chamber, they would affect both instruments

P13. Line 15. Should be “tee-piece”

Amended.

P13. Line 17. “high” Specify above 8 ppb.

Amended.

P13. Line 22. What happens if you switched the trap? Have you considered the impact of breakthrough at high flow rates?

The rate of gas flows through the trap is roughly constant (20 mL/min \pm 2%), Switching the traps between the 2 instruments would be an interesting experiment, and would definitely allow to quantify the impact of the traps on the overall instrument performance. However we now attribute the difference between the two instruments to peak tailing in the chromatograms from the Orange instrument (leading to an underestimate of the peak areas). We have amended this whole section of the manuscript to reflect this.

P15. Line 8. Rephrase “pure substance”. Surely there will be impurities in the raw materials? Perhaps state the purity of the reagent?

Rephrased as follows:

“... from the “pure” substance (Sigma Aldrich, purity typically > 98%)...”

P16. Figure 12. What does a blank run look like?

A typical blank run was added to Figure 3.

P17. Line 7. Please resolve “Error! Reference source not found: : :”

Amended.

P17. Line 12. How has this been addressed in subsequent versions?

We implemented an “idle” setting for when the instrument is not used in between measurements. This way, once warmed up, the iDirac can be left on stand-by without requiring another warm-up period when measurement is resumed.

P19. Figure 16. Can you please use a wider colour range?

We have amended the colour palette.

P19. Line 4. Is the poisoning moisture? What impact does this have on the sensitivity and uncertainties attributed?

We believe the adsorbent degradation after repeated heat cycles is the principal cause of trap degradation. Typically thermal desorption tubes are replaced after 100 heat cycles. A week of continuous operation of the iDirac in the field consists of ~1000 heat cycles. We have added a second panel to Figure 16 to show the decrease in sensitivity as a function of time.

P19. Line 20. “can be run autonomously for months” Assuming the trap is not degraded? Even as the trap degrades progressively, the instrument can run on the same trap for up to 19 weeks as shown in Figure 16. We have added the following sentence to the text:

“provided the performance of the trap is assessed periodically”