

Final Response to referee comments on “ μ Dirac: An Autonomous Instrument for Halocarbon Measurements” by B. Gostlow et al.

Response to referee #1 comments:

Response to general comments:

We accept there is too much detail on the technical specifics and we will remove much of this in our revised manuscript. We will, however, include results of breakthrough volume and desorption efficiency tests / blank levels (possibly in tabular form). We will include additional non-linearity plots for other measured halocarbons, similar to that shown for C_2Cl_4 in figure 5. We will also discuss the possible cross-interferences (over lapping peaks) and their potential impact on measurement quality. Individual peaks were identified in test chromatograms by preparing dilutions (typically 10 to 50 pptv) in high purity nitrogen from single analyte solutions sourced commercially (Thames Restek UK Ltd, Sigma Aldrich Ltd). Although we have not yet had the opportunity to couple our system to a mass-spectrometer to look for interfering peaks (we hope to do this in the next few months) we have analysed our calibration gas on a GC-MS instrument from UEA. Work is ongoing to look for possible cross-interferences based on this analysis.

Response to specific questions / suggestions:

P 2127, section on sample adsorption / desorption: our revised manuscript will include an additional table detailing breakthrough volumes and desorption efficiencies for typical operating conditions. Breakthrough volume is highly compound dependent (high volatility compounds are hardest to trap quantitatively) and there is also a high dependency on trap temperature (lower breakthrough volume with increasing temperature). We aim for quantitative trapping of the compounds of interest but this has been marginal for CFC-11 and CFC-113, especially as we were only able to trap at room temperature. For this reason, we

intend to remove CFC-11 and CFC-113 from table 1. Our latest instruments are equipped with a Peltier cooled trap which will improve trapping of the CFCs.

P 2130, line 16: Our ECDs operate slightly lower than most (eg 300 °C in Bassford et al 1998). For a range of target compounds we examined the signal to noise ratio over the detector temperature range 200 to 300 °C and found a maxima around 260 °C (we will add this to the manuscript). The ECD is still hot enough at 260 °C to avoid the build-up of contaminants when run continuously for extended periods (months). The ECD oven requires ~10 watts of power at 260 °C which is manageable for battery operation. Running this at higher temperatures would not improve signal to noise ratio for our system but would incur additional power consumption.

P 2133, line 14: We tested standard grade Teflon for the inlet line but this produced a range of contaminant peaks in the chromatograms. However, when we zero air tested a 100 foot length of high purity PFA tubing we obtained low blank chromatograms, in addition, there was no obvious loss of halocarbons along the tube when we passed calibration gas through and compared the chromatogram to a normal, direct calibration run. We will add this to the manuscript.

P 2133 / 2134, standard / sensitivity drift with time: Had the MIR balloon flight remained aloft then we would have had the opportunity to look into this issue. The instrument was able to run any of seven different daily method sequences which could be user selected via the CNES tele-command system. One of these method sequences was designed to produce a 6 point response curve and another was designed to examine instrument precision (repeat calibration chromatograms and blanks). Sampling sequences would have obtained around 10 chromatograms during each ascent / decent profile, with a calibration at the start and at the end of each profile. We intended to use periodic response curve sequences to improve the calibration of the samples. We will add this information to the manuscript.

P2136, line 18, effect of ventilation on ECD performance: Although the ECD is highly sensitive to temperature variations we have not noticed an influence from the ventilation of

the housing. The detector is thermally isolated as it is fitted into an upturned stainless steel vacuum flask and only the electrometer connection head of the detector protrudes.

P2138, line 3: efficiency of the Nafion drier and blank chromatograms. In our lab tests the drier was able to reduce the relative humidity of the sample flow from 95% to 3% using a drying counter flow of just 5 ml min⁻¹.

P2140, line 6: The estimated accuracy (at the 95 % level) is based on that given by NOAA-ESRL in their analysis of the standard and includes errors associated with the preparation and analysis of the NOAA-ESRL gravimetric working standards as well as their analysis of our standard. In addition to the NOAA inaccuracies, we estimate our overall accuracy to be ~2 % for more stable (long lived) halocarbons and ~10 % for the less stable (shorter-lived) halocarbons as we have yet to quantify the errors (due to wall loss effects etc.) when decanting into portable Sulfinert calibration cylinders. This will be clarified in the revised manuscript.

P 2140, line 2, deviation from linearity in figure 5: We intend to add in figure 5 the deviations of the peak heights from linear behaviour as the referee suggests. We anyway believe we have a robust method for correcting for non-linearity in the response. In the field a response curve is routinely generated about every 2 days, the response curve is itself corrected for sensitivity drift over this period by using the precision calibrations runs (fixed volume of calibration gas). The corrected response curve is used to calculate the mixing ratio in the samples after the sample peak heights have also been corrected for sensitivity drift (in the same manner as the response curve calibrations). We will include a figure showing more response curves for other halocarbons and the fit curves used for the corrections.

P 2140 / table 1: Laboratory calibration precision is generally better than the field calibration precision because there are generally more environmental variations in the field (even in air conditioned rooms) which cause small changes in retention time, trapping efficiency and baseline interferences. The results presented from the Cape Verde Dornier campaign were

made with a non-optimised instrument and method sequence, resulting in lower precision compared to lab operation. We will state this in the revised manuscript.

P 2140 / table 1, effect of ECD temperatures on sensitivity. Yes, we have looked in detail on the effect of ECD temperature on sensitivity (see above reply for P 2130 line 16).

P 2140 line 13: we will make the chromatograms larger in figure 6 and include baseline blow-up, blank levels and an ambient air chromatogram, the manuscript will also discuss these in greater depth.

Broadness of peaks: we agree with the referee that our peaks are rather broad (for a 10 m long capillary column with i.d. of 0.18 mm). We believe much of this broadness results from both the sample introduction stage (desorption) and the detector stage rather than from the column itself. The internal volume of the trap is 0.044 ml but the desorption flow of 0.3 ml min⁻¹ is quite low so the residence time inside the trap tubing during heating is around 9 s (the trap is typically heated for 15 s). In most GC systems using thermal desorption much lower residence times are achieved for example by the use of wider bore capillary columns which have higher optimal carrier gas flow rates. In addition, our column does not refocus the more volatile compounds as we start the chromatogram at room temperature and so they tend to appear as broad peaks. There is also dead volume at the detector to consider, the ECD has an internal volume of ~0.15 ml. In order to extend the lifetime of the onboard nitrogen cylinder the detector make-up flow is kept to a minimum (5 ml min⁻¹) which means the detector is not flushed optimally and this contributes to peak broadness. Note however, that running with a low make-up flow improves sensitivity and therefore lowers the required target sample volume (allowing us to minimise the trap size).

Refocussing of the analytes: this would improve chromatographic resolution but would also require an additional form of cryogenic or Peltier cooling, thus dramatically increasing the power needs of the instrument and adding complexity (possibly at the expense of field reliability). Note that our new μ Dirac instruments include Peltier cooling of the trap to improve measurement precision and also use a 20 m long column to increase chromatographic resolution (this will help with the problem of overlapping peaks).

P 2141, effect of adsorption volume on chromatographic resolution: the target halocarbons are not truly immobilised on the adsorbent. It is better to consider the trap as a miniature packed column in which compounds of relatively high volatility pass through the adsorbent with higher velocities than compounds of lower volatility. The more volatile compounds (e.g. CFCs, CH₃I and CHCl₃) pass readily through the lightly adsorbing Carboxen 1016 bed but more slowly through the next bed of stronger adsorbing Carboxen 1001. Therefore, these compounds are distributed broadly along the length of the trap. On the other hand, the lower volatility compounds such as C₂Cl₄ and CHBr₃ have a high affinity even for the weakly adsorbing properties of the Carboxen 1016 bed and are therefore focussed in a relatively short length of the trap. When the trap is flash heated, the more volatile components take longer to desorb from the trap as they occupy sites across a large portion of the trap when compared to the lower volatile analytes which are adsorbed at the front end of the trap (only on the Carboxen 1016 bed). These factors together cause increased broadening of the peaks and result in lower resolution between peaks when increasing the volume of sample trapped. We have also modelled this process using breakthrough volume data (available from the Carboxen manufacturers) to look further into this effect. New versions of the instrument have Peltier cooled traps and will hopefully improve the resolution by focussing the analytes towards the front of the adsorbent bed.

P 2145, line 1: The μ Dirac CH₂Br₂ data are overestimated due to co-elution with CHBrCl₂ ... From the UEA instrument data the average levels of CH₂Br₂ and CHBrCl₂ (which co-elutes with CH₂Br₂ in μ Dirac chromatograms) were 1.20 pptv and 0.25 pptv respectively. On this basis we would expect the μ Dirac combined CH₂Br₂/CHBrCl₂ peak to be 83% due to CH₂Br₂ and 17 % due to CHBrCl₂ (assuming the ECD sensitivity is the same for both molecules). Taking this into account, the average μ Dirac CH₂Br₂/CHBrCl₂ level was actually 0.99 pptv (CH₂Br₂ 0.82 pptv, CHBrCl₂ 0.17 pptv), an underestimation of 32 % relative to the UEA instrument. It is therefore a little surprising that the μ Dirac CH₂Br₂ levels are lower than those of UEA when we expected them to be higher due to the coelution issue. Work is ongoing to find the cause of this difference and it is helpful that the μ Dirac calibration gas was measured by the UEA GC-MS instrument during the campaign. It is possible that there are changes in the μ Dirac calibration gas when decanted into the portable Sulfinert cylinder large enough to explain this ~0.5 pptv difference. It should be noted that

across the global science community there are differences in the calibration scales of many shorter-lived halocarbons. An inter-lab calibration comparison experiment will take place this year in the UK (led by York University) with the aim of reconciling some of these differences for UK measurement groups.

Response to referee #2 comments:

Response to general comments:

We take onboard the comments regarding under-emphasis of instrument performance and our revised manuscript will include more performance related description (as detailed in the response to specific comments below) and less description of the technical instrument detail.

Response to specific comments:

3.1 Calibration: Our revised manuscript will include the following detail on the standard gas: The standard consisted of Niwot Ridge air held in a 34 litre stainless steel cylinder at a pressure of 65 bar (the cylinder was humidified with 0.65 ml HPLC grade water prior to filling). The cylinder was also spiked with above background levels of CH₃I, CH₂Br₂ and CHBr₃. The cylinder was then calibrated for a range of halocarbons by NOAA-ESRL in December 2005 (as shown in footnote a of table 1).

P 2139, line 23: a blank chromatogram in the case refers to a chromatogram run after trapping a similar volume of helium carrier gas (instead of outside air or calibration gas). We use these blank runs as a check on desorption efficiency and as a check on the presence of unexpected contamination in the system. We add this to the revised text and will include such a blank chromatogram in a figure.

3.2 Accuracy and precision, P 2141 line 20: We will include an additional paragraph and table giving accuracy and in-flight precision data for an aircraft campaign (Cape Verde,

Dornier campaign). As the MIR balloon flight crashed before we were able to obtain any data (even calibrations) we are unable to provide such data in this case.

3.4 Comparison with UEA GC-MS instrument: We will move this section to the end of section 4 in the revised manuscript which will improve the flow of the paper and eliminate repetition. At the time of the campaign, UEA samples were referenced to a NOAA-ESRL 2003 scale whereas the μ Dirac samples were referenced to a 2005 scale. Referee 1 raised the same question regarding the difference in CH_2Br_2 between μ Dirac and UEA which we repeat here for the benefit of referee 2:

From the UEA instrument data the average levels of CH_2Br_2 and CHBrCl_2 (which co-elutes with CH_2Br_2 in μ Dirac chromatograms) were 1.20 pptv and 0.25 pptv respectively. On this basis we would expect the μ Dirac combined $\text{CH}_2\text{Br}_2/\text{CHBrCl}_2$ peak to be 83% due to CH_2Br_2 and 17 % due to CHBrCl_2 (assuming the ECD sensitivity is the same for both molecules). Taking this into account, the average μ Dirac $\text{CH}_2\text{Br}_2/\text{CHBrCl}_2$ level was actually 0.99 pptv (CH_2Br_2 0.82 pptv, CHBrCl_2 0.17 pptv), an underestimation of 32 % relative to the UEA instrument. It is therefore a little surprising that the μ Dirac CH_2Br_2 levels are lower than those of UEA when we expected them to be higher due to the coelution issue. Work is ongoing to find the cause of this difference and it is helpful that the μ Dirac calibration gas was measured by the UEA GC-MS instrument during the campaign. It is possible that there are changes in the μ Dirac calibration gas when decanted into the portable Sulfinert cylinder large enough to explain this ~ 0.5 pptv difference. It should be noted that across the global science community there are differences in the calibration scales of many shorter-lived halocarbons. An inter-lab calibration comparison experiment will take place this year in the UK (led by York University) with the aim of reconciling some of these differences for UK measurement groups.

P 2142, line 20: For CHCl_3 the μ Dirac measurements are on average 3.6 pptv higher (70.7 % higher) higher than those of UEA. For CH_3CCl_3 the μ Dirac measurements are on average 1.7 pptv lower (16 % lower) than those of UEA. For CCl_4 the μ Dirac measurements are on average 6.4 pptv lower (6.7 % lower) than those of UEA. We will add this to the manuscript.

Ongoing work, further collaboration with UEA and the inter-lab calibration comparison (York University) will hopefully help us identify the cause of these differences.

4.1 Attempted MIR long duration balloon flight: We feel it is important to state in the manuscript that μ Dirac was flown on a MIR balloon despite it not succeeding in producing data as the underlying design of μ Dirac was entirely based on the requirement for autonomous, long duration balloon flights. The subsequent deployment and autonomous operation of the instrument at ground based sites has only been possible as a result of the MIR instrument development. We accept that the paragraph in section 4.1 seems out of place in the results section (as there are no MIR results to report) and we therefore move it to the end of section 2.2 (requirements for MIR balloon deployment) where we feel it would improve the continuity of the MIR deployment description. We hope that this, coupled to the reduction in the technical description of the MIR instrument is sufficient to meet the referees concerns.

P 2144, line 13-14: It is true that the values of CHCl_3 at Weybourne are up to 50 % higher than the baseline values for Mace Head for the same time period. The reason for this is not known (could be due to calibration differences) but we also note that Weybourne is not a true background site in the same sense as Mace Head and may be influenced by anthropogenic sources along the air mass back trajectory more so than Mace Head. As this manuscript is an instrument description paper, the focus of the results section is merely to demonstrate instrument performance in the field. Furthermore, as there are no corroborative halocarbon observations from Weybourne over the measurement period and as this deployment was done with a prototype version of μ Dirac, we have decided to remove section 4.3 (and Figure 9) from the manuscript. We will leave the results from the Cape Verde (Dornier aircraft) and Malaysian Borneo (ground based) campaigns in the manuscript as these relate to final version μ Dirac instruments.

4.4 Operation in Malaysian Borneo, P 2144 Lines 25 / 26 and P 2145 Lines 1-3: Please see reply above for 3.4 (comparison with UEA GC-MS instrument) where these issues are addressed.