

Authors' Responses to Interactive Comments on "A gas chromatographic instrument for measurement of hydrogen cyanide in the lower atmosphere" by J. L. Ambrose et al.

We thank both reviewers for their helpful comments and suggestions. Our responses are provided below.

Referee #1:

Comment: Page 952, line 11 – missing an are measurements are presented to demonstrate....

Response: We have made the indicated correction.

Comment: Page 952, line 23 – Does when the construction of THF2 occurred have any relevance to this manuscript?

Response: In fact, this information is not relevant. We have removed the sentence "Construction of THF2 began during winter 2007–2008 and the station was brought on-line for atmospheric monitoring during the following summer".

Comment: Page 954, line 6 and Page 966, line 3 – Consider replacing sample integration time with either sample trapping or sample preconcentration time. My first thought of sample integration makes me think of peak area integration.

Response: We replaced "integration" with "preconcentration".

Comment: Overview of FTD – Consider adding a short section on the loss of sensitivity with operation time. I think it would be appropriate to move the 1st paragraph of section 3.1.2 to this section. This is a known result and is an important detail that needs to be addressed in the overview section.

Response: We agree that the loss of sensitivity which is characteristic of the FTD detector should be addressed in the overview section. We have moved the first paragraph of Section 3.1.2 to Section 2.2.2 as suggested by the reviewer.

Comment: Page 958, line 8-9 – what do you mean when you say you sampled the output for 5 cycles? That you did 5 calibrations per day? What was the time interval between calibrations?

Response: By "sampling the standard dilution system output for 5 cycles" we mean that 5 standard chromatograms were recorded each day. The standards were analyzed within a ~3.5 hour interval each day, typically between 13:00 and 18:00 local time, although we did not indicate this in the original manuscript. To better describe our calibration procedures we replaced the first sentence in Section 2.2.4 with the following:

“Instrument calibration was performed daily, typically between 13:00 and 18:00 local time (LT), by adding the HCN calibration gas (i.e., HCN in UHP N₂; Sect. 2.2.1) to the zero air generator output for ~3.5 hours, yielding 5 replicate standard chromatograms for each calibration.”

We indicated in Section 2.2.4 that “The instrument continuously stepped between sampling ambient air and the standard dilution system output”; based on the reviewers’ comments we find that this statement requires clarification. In the revised manuscript we moved the above sentence to Section 2.2.3 and added some details to clarify the description of our sampling protocol. The revised sentence reads as follows:

“The instrument continuously stepped between sampling ambient air and the standard dilution system output, thereby measuring HCN in ambient air and in zero air (or zero air + calibration gas; see Sect. 2.2.4) during odd and even numbered sample cycles, respectively.”

We have also reworded some of the text in Section 2.2.1 to further clarify our description of the calibration protocol. Specifically, the sentence “Standard samples of HCN were prepared in ultra-high purity (UHP) N₂ (Maine Oxy, Auburn, Maine) using an MKS type 1479A mass flow controller (MFC) (MKS Instruments, Inc., Andover, MA) coupled with an MKS type 247D digital readout” was replaced with the following:

“The HCN calibration gas was prepared in ultra-high purity (UHP) nitrogen (N₂) (Maine Oxy, Auburn, Maine) using an MKS type 1479A mass flow controller (MFC) (MKS Instruments, Inc., Andover, MA) coupled with an MKS type 247D digital readout.”

Comment: Page 960, lines 1-6 – As mentioned above, I think this information belongs in the Overview of FTD section.

Response: We have also moved the last paragraph of Section 3.1.2 to Section 2.2.2 as suggested by the reviewer.

Comment: Page 960, lines 24-25. I am confused by the statement that the day-to-day variability in the response of HCN appeared to be greater for more aged surfaces than shown in Fig 3. The data in Figure 3 extends throughout the entire measurement period doesn't it? Please clarify what you mean.

Response: In this analysis we focus on measurements made during March, but the instrument was operated from January to June as indicated in Section 1. In the above statement we were referring to some of the surfaces that were operated for extended periods at their threshold sensitivity during the measurement period not shown in Figure 3. In revising the manuscript we found that the statement in question and the paragraph containing it were somewhat distracting and not highly relevant to the rest of the information presented. We have therefore omitted this paragraph from the revised manuscript.

Page 961, lines 5-10. You indicate that bead lifetime is 2 months, so how do you arrive at a semi-continuous HCN measurement of 6 months? Couldn't one simply replace the bead every 2 months and stay in operation forever?

Response: This is a very good point. In our experience, we recoated the FTD filament (bead) in order to recover sensitivity; we did not replace the filament assembly. Our estimate of a >6 month semi-continuous measurement period was derived from our experience with recoating the filament. Shimadzu Corporation markets the filament regeneration kit as a more economical alternative to replacing the filament assembly; however, as the reviewer pointed out the operating time of the instrument need not be limited by the filament recoating procedure since the filament assembly can in fact be replaced. We have clarified in the revised manuscript that our experience suggests that the instrument can be operated semi-continuously for >6 months “without replacing the filament assembly”.

Comment: Page 961, line 18 – You indicate that the precision of the zero air generator background is somewhat poorer, but on Page 962, line 5, you state the relative background level was remarkably constant. These two sentences seem to be contradictory. Please revise and clarify.

Response: The wording we used in the original manuscript is indeed somewhat confusing and does appear to be contradictory as noted by the reviewer. We have reworked Section 3.1.5 in order to clarify the discussion. Specifically, the first two paragraphs have been combined and rewritten as follows:

“As indicated above, the HCN level in the zero air diluent was non-zero. During 3–31 March, the ratio A_b/A_s for the 0.25 ppbv standards ranged from 0.20–0.29 with a mean value of 0.24 ± 0.03 . By comparison, the variability in the ambient HCN mixing ratio was significantly greater than that in the zero air background. For instance, the range of the ratio A_b/A_a was 0.18–0.55 with a mean value of 0.3 ± 0.1 . This suggests that incomplete chemical conversion of HCN within the catalytic converter may only partly have governed the background HCN level in the zero air diluent.”

Comment: Section 3.1.4 – I don't understand how you generated a multipoint calibration curve from data that spanned 8 days given that detector sensitivity changed. Please explain in detail how you generated the data in Figure 4.

Response: In response to the reviewer's preceding comments we have revised Section 2.2.4 to clarify how the calibrations were performed. Additionally, to the text in Section 2.2.5 we added the following for clarification:

“For each calibration, the value of A_s was calculated by averaging over the 5 replicate standard measurements (Sect. 2.2.4), while the value of A_b was calculated by averaging over 5 blank measurements which bracketed the standards.”

We also added the following text to Section 3.1.4 to clarify how the multipoint calibration curve was generated:

“The measurements presented in Fig. 4 have been “de-trended” (i.e., corrected for change in detector sensitivity (Sect. 3.1.2)) by normalizing to the sensitivity measured for the calibration on 18 March at $\text{VMR}(\text{HCN})_s=0.25\pm0.01$ ppbv. The calculation can be described by Eq. (4):

$$A^{\text{de-trended}} = A \cdot \left(\frac{\text{VMR}(\text{HCN})_s}{(A_s - A_b)^{\text{interpolated}}} \right) \cdot \left(\frac{(A_s - A_b)^{\text{reference}}}{\text{VMR}(\text{HCN})_s} \right) = A \cdot \left(\frac{(A_s - A_b)^{\text{reference}}}{(A_s - A_b)^{\text{interpolated}}} \right) \quad (4)$$

where A is the measured chromatographic peak area and $A^{\text{de-trended}}$ is the peak area corrected for sensitivity drift. The first bracketed term in Eq. (4) represents the instrument sensitivity (Sect. 2.2.5) interpolated to the time at which the value of A was measured, the second the instrument sensitivity measured for the “reference” calibration at $\text{VMR}(\text{HCN})_s=0.25\pm0.01$ ppbv (i.e., the 18 March calibration for the data shown in Fig. 4).”

Accordingly, Eq. (4) in the original manuscript has been renumbered as Eq. (5) in the revised manuscript.

Comment: Page 961, line 26 – The LOD is defined as $3\sigma b$ divided by the slope not the intercept.

Response: The reviewer is correct. We performed the LOD calculation correctly, but incorrectly substituted “intercept” for “slope” and “ b ” for “ m ” in our description in the original manuscript. This error carried over from an earlier version of the manuscript in which we had used a notation more similar to that used by Lavagnini and Magno (2007) with the slope denoted by “ b_1 ” rather than “ m ”. We have made the appropriate correction to the revised manuscript.

Comment: Page 962, lines 21-24. Please revise this sentence. Consider as a suggestion....therefore, the uncertainty of the HCN emission rate will be greater than.....

Response: We have revised this sentence as suggested by the reviewer.

Comment: Page 966, line 27 – Define RGD.

Response: We have defined RGD (reduction gas detector) as suggested. Although RGD was defined in the Introduction, a reminder here is certainly helpful since we use this acronym only twice.

Comment: Figure 1. Please indicate the Common, Normally Open and Normally Closed positions on the three-way valves.

Response: We have added the appropriate labels as suggested by the reviewer.

References

Lavagnini, I., and Magno, F: A statistical overview on univariate calibration, inverse regression, and detection limits: Application to gas chromatography/mass spectrometry technique, Mass Spectrom. Rev., 26, 1–18, 2007.

Referee #2:

Comment: Please check that throughout the text every chemical species is spelled before the correspondent acronym is used.

Response: We have confirmed that all chemical symbols and formulas are defined when introduced as suggested by the reviewer.

Comment: Page 954 line 6: the wording integration time makes the reviewer think about area integration of the chromatographic peak, consider changing it with preconcentration time.

Response: We replaced “integration” with “preconcentration” as suggested by the reviewer.

Comment: Section 2.2.4: the reviewer would like this section to be slightly reworked including more details about the multi-concentration calibration. Instead of just saying periodically, a more precise description of this calibration seems to be required. Also, how was the zero air background subtracted? Did you do a measurement of the zero air background after each standard analysis?

Response: We have revised Sections 2.2.3, 2.2.4, 2.2.5, and 3.1.4 to clarify how the calibrations were performed and how the multipoint calibration curve was generated. To better describe our calibration procedures we replaced the first sentence in Section 2.2.4 with the following:

“Instrument calibration was performed daily, typically between 13:00 and 18:00 local time (LT), by adding the HCN calibration gas (i.e., HCN in UHP N₂; Sect. 2.2.1) to the zero air generator output for ~3.5 hours, yielding 5 replicate standard chromatograms for each calibration.”

Additionally, we replaced the sentences “The standard HCN mixing ratio was usually set to 0.25±0.01 ppbv. Additionally, it was periodically varied over four levels within the range 0.101±0.005 to 0.75±0.04 ppbv to quantify the system linearity” in Section 2.2.4 with the following in the revised manuscript:

“During two periods (7–15 and 18–26 March) the standard HCN mixing ratio was varied over three additional levels within the range 0.101±0.005 to 0.75±0.04 ppbv to quantify the system linearity; during these periods the standard mixing ratio was set to a level that differed from the common level of 0.25 ppbv typically every other day.”

We indicated in Section 2.2.4 that “The instrument continuously stepped between sampling ambient air and the standard dilution system output”; based on the reviewers’ comments we find that this statement requires clarification. In the revised manuscript we moved the above sentence

to Section 2.2.3 and added some details to clarify the description of our sampling protocol. The revised sentence reads as follows:

“The instrument continuously stepped between sampling ambient air and the standard dilution system output, thereby measuring HCN in ambient air and in zero air (or zero air + calibration gas; see Sect. 2.2.4) during odd and even numbered sample cycles, respectively.”

We have also reworded some of the text in Section 2.2.1 to further clarify our description of the calibration protocol. Specifically, the sentence “Standard samples of HCN were prepared in ultra-high purity (UHP) N₂ (Maine Oxy, Auburn, Maine) using an MKS type 1479A mass flow controller (MFC) (MKS Instruments, Inc., Andover, MA) coupled with an MKS type 247D digital readout” was replaced with the following:

“The HCN calibration gas was prepared in ultra-high purity (UHP) nitrogen (N₂) (Maine Oxy, Auburn, Maine) using an MKS type 1479A mass flow controller (MFC) (MKS Instruments, Inc., Andover, MA) coupled with an MKS type 247D digital readout.”

Additionally, to the text in Section 2.2.5 we added the following for clarification:

“For each calibration, the value of A_s was calculated by averaging over the 5 replicate standard measurements (Sect. 2.2.4), while the value of A_b was calculated by averaging over 5 blank measurements which bracketed the standards.”

We also added the following text to Section 3.1.4 to clarify how the multipoint calibration curve was generated:

“The measurements presented in Fig. 4 have been “de-trended” (i.e., corrected for change in detector sensitivity (Sect. 3.1.2)) by normalizing to the sensitivity measured for the calibration on 18 March at VMR(HCN)_s=0.25±0.01 ppbv. The calculation can be described by Eq. (4):

$$A^{\text{de-trended}} = A \cdot \left(\frac{\text{VMR(HCN)}_s}{(A_s - A_b)_{\text{interpolated}}} \right) \cdot \left(\frac{(A_s - A_b)^{\text{reference}}}{\text{VMR(HCN)}_s} \right) = A \cdot \left(\frac{(A_s - A_b)^{\text{reference}}}{(A_s - A_b)_{\text{interpolated}}} \right) \quad (4)$$

where A is the measured chromatographic peak area and $A^{\text{de-trended}}$ is the peak area corrected for sensitivity drift. The first bracketed term in Eq. (4) represents the instrument sensitivity (Sect. 2.2.5) interpolated to the time at which the value of A was measured, the second the instrument sensitivity measured for the “reference” calibration at VMR(HCN)_s=0.25±0.01 ppbv (i.e., the 18 March calibration for the data shown in Fig. 4). ”

Accordingly, Eq. (4) in the original manuscript has been renumbered as Eq. (5) in the revised manuscript.

Comment: Page 960, lines 24-25. Day-to-day variability in the response of HCN appeared to be greater for more aged surfaces coatings than shown in Fig 3. This sentence is not clear, please rephrase.

In the above statement we were referring some of the surfaces that were operated for extended periods at their threshold sensitivity. By “day-to-day variability” we were referring to the precision of the daily calibrations. In revising the manuscript we find that the statement in question and the paragraph containing it are somewhat distracting and not highly relevant to the rest of the information presented. We have therefore omitted this paragraph from the revised manuscript.

Comment: Section 3.1.4 – This section needs to be clarified. The multipoint calibration curve was performed over a period of 8 days. Does every data point represent the standard concentration for a certain day (minus the zero air concentration for the correspondent point)? If so, when was the calibration exactly carried out? Were the dates equally spaced? How does this calibration compare to other calibrations during the field campaign?

Response: In response to the reviewer’s preceding comments we have revised Sections 2.2.3, 2.2.4, 2.2.5 and 3.1.4 to clarify how the calibrations were performed and how the multipoint calibration curve was generated.

We performed two sets of multipoint calibrations during the January–June measurement period, both during March (7–15 and 18–26). Both calibrations were in good agreement and therefore we presented data for one (18–26 March) as an example. We note that when both sets of calibrations are normalized to the same “reference” calibration (the calibration on 18 March at $\text{VMR}(\text{HCN})_s=0.25\pm0.01$ ppbv; see our responses to the reviewer’s preceding comments), the slopes agree to within 10%. In order to describe the comparability of the two calibrations we added the following sentence to Section 2.2.5 of the revised manuscript:

“The results of the multipoint calibrations performed during 7–15 and 18–26 March were in good quantitative agreement. When normalized to the instrument sensitivity on 18 March, the slope of the calibration curve for the 7–15 March data was within 10% of that for the 18–26 March data ($r^2=0.995$).”

To further clarify our description of the data presented in Figure 4 we added the following to the figure caption:

“Each group of data points at $\text{VMR}(\text{HCN})>0$ ppbv represents the 5 replicate standard measurements from a single daily calibration; the chromatographic peak areas have not been corrected for the corresponding blanks. The group of data points at $\text{VMR}(\text{HCN})=0$ ppbv represents the mean values of the 5 replicate blanks measured in conjunction with each calibration. The group of data points at $\text{VMR}(\text{HCN})=0.25$ ppbv corresponds with the “reference” calibration on 18 March.”

Comment: Do calibration curve change for different filaments? It would be very useful to see how the different type of calibrations carried out by the authors compare over the four months of the deployment.

Response: In response to the reviewer’s preceding comments we demonstrated that for the same filament, the calibration curves did not appear to change significantly over a large sensitivity range. Specifically, the slopes of the calibration curves for the 7–15 and 18–26 multipoint

calibrations agreed to within 10%, while the FTD sensitivity decreased by ~50% from the beginning of the first set of calibration measurements on 7 March to the beginning of the second set on 18 March. To emphasize this point, we added the following to Section 3.1.4 of the revised manuscript:

“During the period from 7–18 March the instrument sensitivity decreased by ~50%. Thus, the instrument linearity does not appear to have been significantly affected by sensitivity drift.”

Since we did not perform additional multipoint calibrations during the January–June deployment, we cannot be certain that the calibration curves were consistent for the different filaments that were worked with during this time period. However, we did perform an additional multipoint calibration under similar operating conditions during a brief deployment of the instrument at THF2 during 2–9 April, 2009. During this time period a different filament was used and the FTD sensitivity was ~20-fold higher than that on 18 March, 2010. This calibration was performed at three concentration levels: 0.126 ± 0.006 ppbv, 0.25 ± 0.01 ppbv and 0.50 ± 0.03 ppbv. When this calibration is normalized to the 18 March, 2010 “reference” calibration, its slope agrees with that of the 18–26 March, 2010 calibration to within 10% ($r^2=0.993$). When the 2–9 April, 2009 and 7–15 March, 2010 calibrations are both normalized to the 18 March, 2010 “reference” calibration, their slopes agree to within 1%. This further suggests that the instrument linearity is consistent for different filaments. However, it would be best to verify this for each filament in the future.