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Atmospheric Measurement Techniques Discussions

Interactive comment on "A gas chromatographic instrument for measurement of hydrogen cyanide in the lower atmosphere" *by* J. L. Ambrose et al.

Anonymous Referee #1

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This manuscript describes an automated gas chromatographic instrument with flame thermionic detector for measuring HCN in the ambient environment. Few techniques exist for the continuous or semi-continuous measurement of ambient levels of HCN. While the flame thermionic detector provides good selectivity and sensitivity, its response decays with time. Characterization of the change in detector response requires regular calibration and filament lifetime limits the time the instrument can be used autonomously. Even with these caveats, this instrumental method provides a valuable tool to atmospheric scientists interested in measurement of organic nitriles.

There appears to be some uncertainty about the determination of the instrument backgrounds with respect to whether the zero air generator was capable of producing a HCN free sample stream. Since the calibration experiments were performed under the

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same concentration range as was found in the ambient, any over correction in the background appears to be compensated for in the calibration procedure. This result does raise some concerns about future experiments and the use of higher concentration calibrations standards.

One can't help but to lament that the authors didn't extend this study to do a comparative study with their PTR-MS instrument. A direct comparison of the two techniques for HCN and CH3CN would have been a very useful contribution.

Overall the manuscript is well presented. There are, however, some sections that I feel could use some additional clarification and a few places in the results section that appear to be contradictory. Below is a list of specific comments and/or recommendations:

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

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

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.

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.

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?

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

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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.

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?

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.

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.

Page 961, line 26 – The LOD is defined as 3σb divided by the slope not the intercept.

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 . . .. . .

Page 966, line 27 – Define RGD.

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

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 947, 2012.

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