Review…Karu et al.

The authors have clarified a number of my questions regarding the operations of the current version of the AED III. I appreciate that the authors wish to present an accurate characterization of their analytical system…"warts and all", and they do this to a certain extent. However, there are mixed messages remaining in the paper that I think can be clarified. The authors first sentence presents the AED as providing equimolar responses of elements (among other advantages). However, they show that when the AED is combined with the cryo-GC-MS inlet that the responses are not equimolar, and the responses depend on many factors. At several places in the manuscript, the authors will ascribe the variable response to either losses/artifacts in the inlet system or to inefficiencies of compound ionization in the AED plasma, or both. So I don't know what the authors think they have learned about the AED, or about their inlet system. Did they determine that there was a variable response to compounds in the AED plasma? Did they determine there was an inlet problem? Was it from the preconcentration step? Was it from the GC column? Did they determine that there were artifacts in the standard tanks or standard delivery system? Various test could have been done to evaluate these potential issues, and more interpretation of the results is needed. I don't think the authors provided any particular insight into how their system operated. Instead, the authors rely on doing what is necessary under these conditions: they use a multicomponent standard to account for all of the unknown factors that affect the system response to different compounds. This is the practical solution, but not one which provides much useful information for the analytical chemist. It seems that the authors treat the Cryo-GC-AED system as a black box that can be calibrated to measure certain compounds within a relatively large standard deviation if one has appropriate standards. To be fair, the manuscript reasonably describes the operation of the system which has been used for some field research. It is useful to have this system documented in the literature. It is a bit disappointing, though, since my own experience with an older version of the AED was much more inline with the advertised equimolar response, even with cryogenic or adsorbent preconcentration/GC separation prior to the detector. This paper suggests otherwise and I think it is necessary for the authors to at least acknowledge that they have not been able to do the required testing to sort out reasons for the observed results. I have seen a GC/AED respond to simple hydrocarbons from C3 – C8 with a constant response, which is also consistent with C response from various heteroatom compounds that were tested. It's troubling that the authors find something very different from their system. My main suggestion for further revision is to more clearly discuss the "warts" and not gloss over the inconsistencies that were observed.

Below are some additional comments/suggestions:

L20 suggest "is reported to provide"…

L22 suggest "may be attainable"

L28 change to "The first AED…

L35 here is an example that suggest inlet artifacts are minimized, but can't be true if AED is equimolar response as stated in L20.

L38 suggest change "pseudo-unknown" to "unidentified compound"

L40 note that previous AED systems also had sufficient sensitivity for ambient air, at least for C and for Cl in major CFCs and CH_3Cl.

L46 actually MS can provide semiquantitative data on identified compounds without a specific standard

L55 probably should list the make/model of the tank regulators used in standard delivery system.

L139 I can see that the system is reasonably linear from the plots provided and from the good R^2. Still, I would like some uncertainty attached to that statement of linear over 4 orders of magnitude. I suggest a table in the supplement that shows the response factor for standards over those 4 orders of magnitude for at least a major selection of compounds, if not all of them.

L160-170 Please specify in the manuscript if the SD is one SD or 2 SD? And if this description is the same throughout the text and tables.

It seems unfair to compare the overall C response factor in the Riemer mix, which contains many heteroatom compounds, with the NPL mix of all hydrocarbons. Could you do the comparison also of C response of just the hydrocarbons in the different mixes?

Given the difference between NPL and Riemer toluene response, can you say how you quantified toluene in ambient samples? One or the other, or average?

Do you think that the generally increasing variability of C response with increasing C number for hydrocarbons provides some insight into inlet vs AED issues?

L190 Here is an unsubstantiated claim that the AED response may not be 100% for different compounds. At least note that you did not test this hypothesis, and that it is not consistent with manufacturer claims.

L198 but the observed difference for a few outliers can't be explained by dilution vs no dilution. It seems to me that the NRL standard was compromised during the testing somehow. Looking at C response for hexane, benzene, toluene, ethylbenzene in the 2 standards suggests some issue with the NRL standard at least for toluene. Why not evaluate this difference rather than dismiss it?

Standard	Hexane	Benzene	Toluene	EthylBenzene
Riemer	643-+41	671-+53	643-+68	610-+92
NRL	701-+71	695-+65	913-+77	743-+101

L210 Not sure of the point of providing average S response if that is never used in practice. Can you comment on the usefulness of a -+15% single standard deviation for trace gas analysis?

L230 Here is another example of the excessively optimistic presentation of AED characteristics. I don't agree that a "great advantage" of an expensive, difficult to use AED is that it is more sensitive to OCS than the FID. If the only alternative to OCS measurement was an FID, then this is an advantage, but other options for much better OCS measurements are available, including direct, high resolution cavity ring down direct measurements.

Field measurement performance Given the authors comments on the plasma tube degradation issue, I think it is important to document the actual performance in continuous field operation. I would like to see a discussion of typical changes in C or S response vs time over the course of the experiments. This could provide additional useful comparison to the performance of other detectors.

L348. Here again I don't know what the take-home message is. The authors state: "however, the application of the equimolarity feature of the detector is limited by pre-concentration and transmission losses." Earlier the authors suggested the inlet was configured to minimize adsorption and losses, and that there could be <100% efficiency of ionization in the AED. Here it seems that the authors do not question the "equimolarity feature" of the AED, but point to the inlet. So what is the reader to believe? And the authors might also want to consider testing several different standard tanks to evaluate various multicomponent mixes.