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Atmospheric
Measurement
Techniques
Discussions

Interactive comment on “Atomic emission detector with gas chromatographic separation and cryogenic pre-concentration (CryoTrap-GC-AED) for atmospheric trace gas measurements” *by* Einar Karu et al.

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The manuscript by Karu et al. describes a newly developed trace gas measurement system based on cryogenic enrichment of ambient air samples followed by gas chromatographic separation prior to compound detection and quantification based on atomic emission spectrometry. The novel aspect of the manuscript is the use of an atomic emission detector. As this detector has seen little use for routine trace gas analysis, this paper would be of interest to the atmospheric sciences community. However, the paper needs substantial modification before publication.

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Discussion paper

The authors wish to present the case that the features of atomic emission detection (equimolar atomic response independent of compound and specific atom detection) provide new capabilities for atmospheric chemical measurements. However, the authors undermine their case by demonstrating that, in fact, their combined analytical system produces a compound specific response, presumably related to the enrichment and pre-separation protocols. Thus, individual compound standards must be used for quantitation. Also, the examples of field measurements shown by the authors might have been done more easily with a GC/FID or GC/MS system. No advantage to the AED is demonstrated, nor is it compared to other techniques to show that it is at least equivalent to “standard” methods. It would have been valuable to see how the multi-atom capabilities of the AED could be used, for example, to identify unknowns by determining composition of a mixed halocarbon compound (or other hetero atom compound) from response factors of the component halogens (heteroatoms) and of carbon. Similarly, could the AED capability to measure oxygen be used to better identify oxygenated VOC that may co-elute in a complex air sample?

Other comments are listed below

L33. Even though “great care” was taken to minimize compound specific effects, such effects are later reported. Here the authors claim that a single RF could be applied to an unknown compound, but they don’t indicate how they choose this RF, or if they use some average.

L41 The authors show a range of 161 – 211 nm for the range of the JAS AED III HR instrument. It seems from the literature of JAS that higher wavelengths are also accessible. Earlier AED models did have a much wider range. Can the authors clarify if this limited range is all that is available? Improved responses for some elements might be found at higher wavelengths. If the instrument is limited in wavelength range, perhaps the authors could comment on the advantages or disadvantages of a limited range versus an extended range instrument.

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L47 The authors state that the performance of atomic emission lines for multiple compounds is discussed. However, no information is provided if the authors characterized different potential atomic emission lines for each atom. Why were these particular lines chosen? Or if different ratios of combustion gases were tested to evaluate the impact of plasma conditions on the results.

L56 Are the sample inlet lines temperature controlled? Is an internal standard used? Did you determine the maximum sample size possible before the most volatile measured compound breaks through the trap?

L64 Could you specify the sample and other flows used during sample collection/transfer?

L96 Perhaps also specify purity requirements for the H2 and O2.

L114 Could you specify what backflush and bakeout times were required based on the carryover experiments? What level of carryover is observed from ppb level to zero level samples?

L116 Only two standards are described, but it says that three were used. Please clarify. Later a NOAA ambient air calibration standard was mentioned. Is this number 3? If so, how does this compare with dilutions of the Riemer or NPL standards?

L131 Not really sure what linear up to 4 orders of magnitude means? Could you please provide a table of response factors determined for a range of different classes of compounds over the 4 orders of magnitude that were tested. Can you also do a similar table for the calibration levels used for the characterization experiments (e.g. 50 – 1000 pptv).

L137 I am curious how the instrument drifted under normal use. Is there a significant drift in system response over time?

L144 The LOD determination can be done in a variety of ways. In a system that is free of adsorption or other arifacts, the equation 1 might be a reasonable extrapolation to determine detection limit. However, the system described does have some compound specific characteristics, so it would be helpful to verify the reported LODs with actual measurements near that LOD (e.g., within a factor of 3).

L152 It is not clear how the average RF that is calculated was actually used for quantitation.

L154 Were other carbon emission lines tested? If so, what were the different characteristics? Section 3.1 This section describes results that begs further investigation and discussion. The range of reported response for carbon in different compounds is very troubling. What is reported is not the equimolar response that is claimed for the system, and it suggests big problems somewhere. A factor of >2 between benzyl chloride and butyl nitrate seems to me to be a big problem that needs to be evaluated further. To me, the differences suggest issues of stability or standard drift, though system artifacts can't be ruled out. The observed differences could be checked with independent standards, or at least compare calculations of mixing ratios based on both carbon and heteroatoms in the molecule. Further, the large variability within each response factor also seems to be a problem (36% for butyl nitrate, 43% for benzyl chloride). It is not clear to me how these variations are useful for quantitative analysis. Overall, the response factor uncertainty (to 1 sigma) is quite variable, from reasonable few percent to much higher values depending on compounds.

The authors also note that the standard deviations from the Apel-Riemer standard is about 2 x that of the NPL standard. The authors speculate that this may result from changing discharge tubes, though one could also speculate that the dilution system used for the Apel-Riemer tests had some stability problems. If the problem is from discharge tubes, wouldn't this suggest a significant problem for routine application?

Paragraph beginning L178. This paragraph describes the crux of the problem with this paper and with the proposed method. The nominal advantage of the equimolar response of an AED is not found in this system, presumably because of sample prepa-

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ration/separation issues. I don't think it lies with the AED, but this could be checked by additional testing. My suggestion would be to locate the source of the problems and determine what needs to be fixed to improve the accuracy and precisions of the whole instrument. As presented, the analytical system described has some basic flaws. It can, as the authors point out, be used if one calibrates each compound. But this is essentially no different from use of an FID, which is substantially less complicated. (I would be interested to know if the cryo-enrichment unit was tested using an FID detector, and how this might compare.) The average RF is precise to about 10% (only 1 SD), and this offers no advantage over other common analytical systems.

Section 3.2 Why is chlorine not included in this section? Was this not measured due to wavelength limitations? If available, please add Cl atom responses to this Table 2, and discuss in this section. It would have been great to also have Cl responses for the Apel Riemer standard to help diagnose the system. Also, I was trying to compare relative C and halogen, N, or S responses, but couldn't match all compounds between Table 1 and Table 2. For example, bromodichloromethane and acrylonitrile are in Table 2, but not listed in Table 1. Why?

L204. This sentence further explains the fundamental problem with the proposed method. "The different element count scales were non-related to each other." It seems to me that this negates the advantages of AED over other methods. Note for example CS2 and OCS. Ratio of C response between compounds (OCS/CS2): C ratio = 637/696 = 0.915; S ratio=342/476 = 0.718. How these differences are handled in practice needs clarification. It is not specified in the later examples, for example, if C or S emission lines are both used for the CS2 and OCS measurements, or one or the other. The authors might also wish to check on influence of CO2 on the response factors. I found a 1994 reference (Swan and Ivey, DOI: 10.1002/jhrc.1240171203) that discuss use of AED for ambient S compound analysis. Interestingly, their S ratio response between OCS and CS2 was 2932/1745 = 1.68, something quite different from that reported here (note: should add this reference to Introduction).

Section 3.3 The authors compare the advantages/disadvantages of the AED system to other common analytical systems. Given the problems outlined, the main advantage seemed to be the detection of compounds with low FID response, particularly COS. This is not particularly compelling, as other (simpler) options are available. The calculated detection limits are useful for ambient measurement of the NMHC, OCS, and perhaps several oxygenated species. LODs of halogenated species is too low for ambient measurement in most environments. The authors further argue that the multi-element capabilities of the system are useful for screening gas samples. I would agree, but the selective transmission of compounds through their system would make quantitative estimations problematic, especially for exotic compounds. It would have been much more interesting to see how this system might be used to measure volatile arsenic, selenium or silicon compounds, which are not routinely done by other methods. Furthermore, the issue of the deterioration of the plasma tube and potential effects on atomic emission would also seem to be a big disadvantage for routine analysis. Given that the instrument has been in use for several years, the authors may be able to comment on that in more detail.

Section 4 Case Studies. The case studies presented show that the AED system can produce data that appears reasonable. It would be important to help validate the analytical system if it was compared to currently validated techniques, or if the instrument was used in some sort of multi-lab comparison study. The forest study was mostly for terpenes and sulfur species. Were any new S species (or other heteroatom) species found in this environment? For the CARIBIC flights, one might get a better sense of sample to sample reproducibility if the data were presented in a graphical time series that also included flight altitude and perhaps ozone as a secondary tracer. Or, if the samples were measured in more than one lab, a comparison of the data for OCS would be of interest.

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