

Author response to RC2 of Karu, E., Li, M., Ernle, L., Brenninkmeijer, C. A. M., Lelieveld, J., and Williams, J.: Atomic emission detector with gas chromatographic separation and cryogenic preconcentration (CryoTrap-GC-AED) for atmospheric trace gas measurements.

Thank you for your review and helpful feedback. The improvements as suggested have been carried out, helping to improve the manuscript. The responses to the review will follow below.

*Line 62: Is there any data to show that the adsorption to the Silonite-D layer to de-active surfaces is very low?*

Reference added:

Cardin, D.: Improving the Performance of Time Integrated Sampling of TO14 Compounds into Stainless Steel Canisters. Application Note: A-3725-02, 1999.

Added to the manuscript at L67.

*Figure 1: please say what part of the cycle this configuration is in, it took me a while to work out the flow regime in the valves. In the module 3, pre-concentration trap, does this contain packing or is it just a coated empty tube?*

The figure indicates the main sample trapping configuration through trap 1 and 2. The colors help to follow the flow path. The green color indicates the GC-AED column He flow and the blue color indicates the sample preconcentration flow pathway, starting from sample 1 inlet. Module 3 is just a part of 1/32" coated empty tube, no packing material inside.

To help clarify this we have inserted at line 371 the sentence "Blue color indicates the CryoTrap sample pre-concentration flow pathway through tarp 1 and 2, starting from sample 1 inlet position. Green color indicates the GC-AED He flow through to the column and leading to the He plasma."

To include the information on module 3 a further sentence was also added at line 76.

*Line 98: Can you be sure 100 % conversion to elements in the AED? Could this also be part of the reason for compound RF variability?*

Good point, the conversion to atoms in the He plasma may not be 100%. This can also play a role in the compound RF variability.

RF variability may stem from less than 100% conversion of molecules to atoms in the plasma. Added to the manuscript at L189.

*Line 105: What is element installation?*

This is an automatic process of calibrating CCD diode numbers to wavelengths according to the calibration table.

Element installation is an automated process of calibrating CCD diode numbers to wavelengths.

Added to the manuscript at L110.

*Line 113: This sentence is not very clear. Please consider rewording.*

Done. “Furthermore, at the beginning of the experimental design the highest calibration standard MR level carryover and retention potentials were tested for all of the compounds of interest with the zero-air measurement directly after as the sample measurement.”

Added to the manuscript at L119.

*Line 121: give details of the MFC*

Information added. “MFC, EL-Flow, Bronkhorst, the Netherlands”

Added to the manuscript at L129.

*Line 147: Why are the RFs for heteroatom containing species given as a per C RF? Does Table 1 consider solely the C signal and not the other wavelengths? I can see when reading further that this is the case. Perhaps just include a sentence to describe that you will first look at C only and then consider the other elements separately.*

Mistake corrected. The equation was written for the case of carbon emission line, but now written correctly in the general form. Table 1 is solely RF for per carbon atom, but Table 2 is RF per heteroatom.

Corrected in the manuscript at L156.

*Figure 1: Are all 84 species chromatographically separated in the C wavelength signal? This is essential if the C wavelength response is used. Also, how was the retention order determined? Was a GC-MS /retention indices used to determine the retention times prior to this detector being added?*

Most but not all of the 84 species are chromatographically separated in the carbon wavelength chromatogram. Co-eluting species that are detectable only in the carbon wavelength spectra are not reported. Retention times were determined with single species headspace “sniffing” tests and calibration gas mixtures.

*Table 2: Is there a trend in RF or RF variability based on whether a compound is a hydrocarbon or hetero-VOC?*

No clear trend was detected.

*Figure 4: I would like to see more discussion of the reproducibility for each compound. In some cases the standard deviation seem high and there is a significant discrepancy between the two standards.*

The discrepancy between two standards could have arisen from the extra dilution requirement of the 84 component nominal 50 ppbv Apel-Riemer-2015 calibration standard, which adds extra uncertainty. The nominal 4 ppbv NPL-2017 calibration standard needed no extra dilution.

The standard deviations of some compounds were higher than others, the Apel-Riemer standard being more variable. This was possibly the result of the extra dilution step required to dilute this standard to measurement level mixing ratios.

“In addition to the pre-concentration losses, the RF variability may also stem from less than 100% conversion of molecules to atoms in the plasma. As the per atom response factors determined to be compound specific, all the analytes of interest were always calibrated and quantified against a calibration standard, which was pre-concentrated and analyzed with exactly the same parameters as the samples. Therefore, all the losses and other effects in the analytical system leading to the variation in the RFs were accounted for.”

“The discrepancy between the two calibration standard determined RFs seen in Table 1 and 2 could rise from the point that the compounds in the NPL-2017 calibration standard are at nominal 4 ppbv

and could be pre-concentrated directly, but the Apel-Riemer-2015 compounds are nominally at 50 ppbv, thus requiring extra dilution before the trapping. The dilution with zero-air introduces further uncertainty for the RFs determined from the Apel-Riemer-2015 calibration standard.”

Added to the manuscript at L189 and L198.

*Line 196, Figure 2: It might be worth pointing out here that the high background is responsible for the higher LOD. The hetero-atom chromatograms show very useful selectivity and removal of the complex background signal. This is not really discussed here but seems like it would be useful in ambient samples, although only if the reduction in LOD is not an issue. Could you identify any other heteroatom containing species in the ambient samples, rather than just the targeted ones shown? It would be good to see the chromatograms for the other elements for a real sample, rather than just a gas standard. I can see this is where the technique could have advantages over an FID. As presented, the case studies don't really provide exciting new data that couldn't be achieved with more standard instrumentation.*

Great point. “Nevertheless, bromine emission line provides great selectivity, where the high background removes the complex background signal”

Added to the manuscript at L214.

Although we were always on the lookout for new heteroatom containing species in the ambient samples, we did not find any new compounds which were at a higher concentration than the LOD of the methods used.

“Unfortunately, no new exotic species (containing of iodine, bromine, nitrogen, silicon, mercury, selenium and arsenic) were revealed in any of the sampled environments to date.”

Added to the manuscript at L252.

“For the work presented here, a pre-concentrating GC-MS could have served as the same or better alternative for monitoring targeted species present in a calibration gas. Nevertheless, the AED system has advantages for searching exotic heteroatom molecules in the atmosphere, for the non-carbon elements which are in the detector wavelength range. For example, to analyze volcanic emissions.”

Added to the manuscript at L249.

*Line 236: perhaps direct reader that this information is about to be presented. When I first read this, I wondered why this information was given here.*

Done. “and will be presented in Chapter 4.1”

Added to the manuscript at L267.

*Line 258: extra space in 1400*

Done.

*Line 301: why was the NPL standard only used at 50 mL? This seems odd considering the Apel-Riemer is at much higher concentrations*

For routine measurements only one calibration MR was used for NPL-2017 standard (measured after every 5 unknown samples) for better statistics and time management.

*Line 325: should this say “marine OR volcanically”?*

You are correct, changed.