

Anonymous Referee #2

“General Comments

In my opinion, this paper is perhaps better suited for publication in a different journal, as it is very heavy with laboratory chemistry, and the atmospheric connection is only as an application of the chemistry. I see the paper as more appropriate to a journal like “Analytical Chemistry”. It is not entirely inappropriate for AMT, but it seems to be well out of the mainstream of papers published in this journal.”

We respectfully disagree with this assessment. According to AMT guidelines, our manuscript is appropriate for publication in the journal. “Laboratory Measurement” is one of the three techniques that are listed under AMT’s Journal Subject Areas and “Validation” is listed as a topic. The methods described in our article were developed and validated with the specific goal of measuring atmospheric bases in two significantly different field study settings, and were supported by the corresponding field measurements. We therefore contend that the manuscript meets the criteria for publication in AMT.

With regard to the paper itself, my basic criticism is the organization of the manuscript. After the introduction there is a section labeled “Experimental”. There is no description of sampling here (the discussion there is on this topic is toward the end, in sections 3.4 and 3.5), so the reader does not know where the samples came from or what medium they are in. Then the very detailed methods developed during the project are presented. Then, later in the paper (section 3.2, p. 6017, lines 14-16) the authors write, “A significant amount of effort was dedicated towards improving the conditions, leading to the optimized method presented above. The most important modifications are described below.” Huh? The authors seem to say that they are not presenting the information in a logical order – that some is above, and some is below, and these lines are the roadmap to interpret the flow. I am sure that was not their intent, but that is how this reader interprets it. Suffice it to say that the experimental section should describe the details related to making the measurements (including how they improved conditions, yields, sensitivity, etc.) and the results section should present results (derivatization methods are not results, in my opinion).

The revised manuscript was reorganized according to the structure proposed by the Editor to address these comments, as well as those from Referee #1.

“Specific Comments

Abstract: There is no mention of example compounds here. It would seem at least ammonia, methylamine, ethylamine, and diethylamine should be mentioned here, probably with the optimized LODs for these compounds.”

The abstract has been modified to include this information.

Introduction: p. 6008, line 26 – the authors write, “as illustrated by two examples below.” I cannot figure out what the examples are. Please clarify.

The two examples are described in the following two sentences. The sentence has been re-written in the revised manuscript as follows:

“Emerging technologies in the stationary and mobile source sectors will potentially constitute new sources of atmospheric nitrogenous bases. For example, carbon-dioxide-capture technologies...”

p. 6010, line 20 – this almost looks like a formatting error, but I see the following “X = NR¹ R², OR)”. I cannot make sense of this.

These are standard notations in organic chemistry where the X group can be either a N-atom with two different alkyl/aryl groups (R¹ and R²), or an O-atom with one alkyl/aryl group (R).

“Results and discussion: p. 6015, lines 4-6 – The authors use terms like “routine measurement”, “easy to apply”, and “low-cost ... instrumentation”. These are all exaggerations at best, and border on the laughable! Easy, routine, and low-cost is an ozone analyzer that is turned on, calibrated and left to run. For “routine” measurement, this method requires someone to change a sample every three hour (or eight samples every 24 hours, etc). This is technician time and logistics. Then there is sample preparation – a very exacting and time-intensive process. Very few people would read the sections on derivatization and come away using the words “easy to apply”! Finally, the instrumentation – I estimate a few hundred thousand dollars of equipment was used in the analyses. Again, not exactly “low-cost”. If the authors were to add together the total cost for the full process (including chemicals, scientist/technician time for denuder/impinge cleaning, preparation, installation and retrieval, and for derivatization and analysis; and finally for time on the instruments), I am quite sure that the cost would be moderately high.”

We understand the Referee's position, but there seems to be some context missing in the above comments. Ozone is a routinely measured single analyte for which dedicated analyzers are available commercially. We are discussing a new method of measuring a large family of compounds for which there are currently is no convenient alternative. The two scenarios are very different. A more appropriate comparison would be the atmospheric monitoring of carbonyl compounds or peroxides. Considering the challenges associated with measuring nitrogenous bases in the atmosphere, our methods are relatively easy to apply and compare favorably to methods used by numerous groups in the atmospheric science community to measure, for example, carbonyl compounds or peroxides. The scientist/technician cost associated with using our methods also compares favorably with these kinds of field measurements. Most research groups active in our field already have access to either a GC/MS or an LC/MS, which is why we developed methods that are compatible with both. No expensive instrumentation such as a dedicated laser system or a specialized mass spectrometer needs to be purchased expressly to use our methods. In summary, while we disagree with the Referee that the above statements are ludicrous exaggerations, we have made an effort to tone them down in the revised manuscript to avoid any perceived misrepresentation.

“Technical Corrections

p. 6012, line 16 – the acronym “THF” is not defined.”

The acronym has been defined in the revised manuscript.

“P 6015, line 17 – the term “AU” is not defined. It might mean “Absorption Units”, which is a purely relative unit. IN that case the standard deviation is purely relative as well, since it is not referenced to any other reported measurements.”

“AU” indeed stands for “absorbance units” and has been defined in the revised manuscript.