Referee Comment AMT-2011-125

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.

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 (deriviatization methods are not results, in my opinion).

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.

Introduction: p. 6008, line 26 – the authors write, "as illustrated by two examples below." I cannot figure out what the examples are. Please clarify.
p. 6010, line 20 – this almost looks like a formatting error, but I see the following "X = $NR^1$ $R^2$ , OR)". I cannot make sense of this.

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.

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

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.