

Interactive comment on “Identification of Gas-phase Pyrolysis Products in a Prescribed Fire: Seminal Detections Using Infrared Spectroscopy for Naphthalene, Methyl Nitrite, Allene, Acrolein and Acetaldehyde” by Nicole K. Scharko et al.

Anonymous Referee #2

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Overall this paper presents a useful extension of FTIR analysis for VOCs in samples taken from challenging environments. The paper is well written and requires few, if any, typographical corrections.

However, I do have some suggestions that I believe would increase the readability and utility of the paper.

The term "Seminal Detections" is correct but, unfortunately, the term is much more

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commonly associated with seminal fluid detection and may reduce the “searchability” of the paper. Perhaps "First Detections" could be used in the title and in equivalent places within the body of the manuscript.

Lines 16/17 (first sentence in abstract): split into two sentences at the semicolon.

Line 29 "significantly": in a measurement and analysis paper the term "significantly" should be retained for use only in the statistical context. While clear enough here, it is best to avoid it and use, perhaps, "profoundly", "strongly", etc.

Line 31 "however, prescribed ...": "however" implies "in contrast to", but this sentence seems more to be about additional sources of VOCs. Perhaps "Additionally, prescribed ..."

Line 55 "thermal decomposition (pyrolysis)": the technical definition of pyrolysis seems to be something like physical and chemical transformation induced by high temperature INERT atmosphere (absence of oxygen). I am not sure that wildfire processes meet that definition. Perhaps the authors can expand upon this section slightly to make it clear that this is actually pyrolysis and not simply emission due to pressure increases (gas expansion), vapourisation, etc.

Line 85-90 Table 1: The order in which the compounds are presented in the table is not justified. A statement regarding this would be appreciated.

Line 114 "Beer's Law": should not be possessive - "a Beer Law plot". Preferable would be "a Beer-Lambert Law plot" (the Beer law is concentration only, Lambert Law is path-length only, Beer-Lambert Law incorporates both)

Line 118-122: Some further details on the calibration would be appreciated. There is no intercept reported - was the regression constrained to a zero-intercept? What is the uncertainty in the slope/pathlength?

Line 126/127: Dry-air generators are not necessarily CO₂-free generators. I assume that this system does produce dry, CO₂, CO and hydrocarbon-free air, but a statement

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to that effect should be included.

Line 184 Figure 2: This comment applies to all figures containing stacked spectra. The colours are not easily distinguishable and colour-blind people may have some difficulty identifying the correct trace. It would be better to label each trace with a letter, (a), (b), (c), etc, and include the legend in the figure caption.

Line 191 and following: The authors use the term “Limit of Detection” or “Detection Limit” in the sense of being the lowest concentration for which they can provide a value. However, the LoD is the limit at which the analyte can be reasonably stated as being present, but without quantification. The Limit of Quantification, the lowest concentration for which it is acceptable to provide value, is generally given as $10 \times \text{StdDev}$. The authors should clarify and confirm what concept they are employing.

Line 258 Figure 3 and accompanying text: The inclusion of naphthalene in the fit has not only improved the fit in the wavenumber range of the naphthalene peak ($785 - 775 \text{ cm}^{-1}$) but also in the $770 - 760 \text{ cm}^{-1}$ range. While a minor point, it is probably worth commenting that the fitting process will result in poorer values for other species without all the contributors to the spectrum being included, as the intensities of those other components are distorted to try to compensate for the missing component. This observation holds for most of your spectra.

Line 275 – 279 Table 3: This table seems to be somewhat misplaced, being in the “3.1 Naphthalene” but referring to all compounds. It would perhaps be better placed in “3.5 Comparison to Other Sections” (the section can be renamed to something like “Limits of Detection and Comparison to Other Methods”).

Line 280-287 and corresponding text for other compounds: Each section on a compound finishes with a paragraph of health aspects and atmospheric chemistry of the compound. This feels to be tacked-on and does not directly relate to the science being discussed. It would be better if these sections, if included at all, were collected and condensed to a single space, perhaps in the introduction.

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Line 309 – 312: In the discussion of the conformers of methyl nitrate, it is not obvious if two spectra, one for the cis- and one for the trans-isomer, were employed. It would be appreciated if this was discussed.

Line 451 and following Section 3.5: In this section, it would be appropriate to include indicative limits of quantification

Line 464-466 Table 4. The way the units are presented in the header row (in parentheses) and the way the uncertainty of the values are presented in the table body (in parentheses) caused some confusion. IUPAC requires that parentheses are NOT used for units, rather the solidus (divide-by symbol) is used. However, I suspect that this is too radical-a-step for the journal. The uncertainty in the table would be clearer if expressed in the form “ $a \pm \varepsilon$ “. Note that ppb/ppm is the same as per mille (‰).

It would be appreciated if here, or perhaps earlier, the justification for using emission ratios is given.

Section 3.5: It would be appropriate in this section to present the LoDs or LoQs of other techniques and compare this with your FTIR method. In addition, it would be appropriate to include a short comparison of sample-handling requirements, the time required, and other advantages/disadvantages of FTIR over other methods.

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