

## ***Interactive comment on “A new comprehensive approach to characterizing carbonaceous aerosol with an application to wintertime Fresno, California PM<sub>2.5</sub>” by P. Herckes et al.***

**P. Herckes et al.**

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The general comment of the reviewer that liquid state NMR is more sensitive than solid state NMR is not correct. CPMAS <sup>13</sup>C-NMR is about two orders of magnitude more sensitive than liquid state <sup>13</sup>C-NMR for a given magnetic field strength because of cross polarization of carbon by hydrogen in organic structures. However, the resolution of liquid state NMR is much greater than solid state NMR. We used solid state NMR because of its greater sensitivity for the very small sample amounts in our study. In addition solid state NMR is able to address all atmospheric aerosol matter and is not limited by solubility considerations.

Test separations using model compounds have been performed and are detailed in

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Leenheer and Huffman (1976) and Leenheer (1981). The distinct differences in both NMR and IR spectra indicate little compound class overlap. In other words, this fractionation procedure gives discrete fractions of different compound class composition

We agree with the reviewer's concern that volatile compounds will be distilled off; therefore, we mention that part of our carbon losses are from volatiles because we will not be able to isolate these species as salts after the freeze-drying. These species will most likely be lost as they will evaporate in the freeze-drying process. However, given that the focus of our study is investigation of non-volatile aerosol material, the overall fraction is likely small.

Figure 4 has been updated, following the suggestions of the reviewer, in the final version of the manuscript.

A dialysis step was performed to expose the quartz fiber substrates with the aerosol sample to hydrofluoric acid. The acid reacts with silica to  $\text{H}_2\text{SiF}_6$ , which then is removed through dialysis while the particulate aerosol organic matter remains inside the dialysis bag.

The inorganic salts that are isolated in the fractionation procedure, for which the reviewer questions an atmospheric origin, are not salts that are initially present in the aerosol. These salts reform from the ionic species that have been extracted and then passed over ion exchange columns and rinsed and eluted with HCl or NaOH. The remaining ionic components precipitate out during the azeotropic distillation as these salts and hence are removed in this form.

The reviewer voiced a concern regarding the co-precipitation of organic material with barium sulfate. This issue was extensively addressed in the Leenheer et al. (2000) reference. The use of acetic and formic acid during precipitation followed by an HCl resin eliminated the co-precipitation problem.

Quantification using solid state  $^{13}\text{C}$ -NMR is certainly challenging. However, a detailed

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study has investigated the quantification issues and solutions. The results of this study are published in the cited paper by Wershaw et al. (2000). Discussing these issues will go far beyond the scope of the current paper; therefore, we only refer the interested reader to this study.

The reviewer appropriately questions the assignment of the aromatic carbon peak in NMR as "elemental". The elemental carbon component of aromatic carbon detected by  $^{13}\text{C}$ -NMR cannot be differentiated; therefore, we have eliminated the reference to "elemental"; and changed the formulation of this discussion in the text.

We further agree with the reviewer that we cannot reach the conclusions stated p13 and p14 based solely on the FT-IR and NMR spectra. These spectra, however, were obtained for isolated fractions and, given the fractionation and isolation procedure, we can exclude the presence of many alternative compound possibilities and improve confidence in the peak assignments we suggest. Consequently, we do not believe we are over-interpreting the data. In particular, in the example questioned by the reviewer (the presence of acids) ketones (peak at  $> 200$  ppm) were not detected in the  $^{13}\text{C}$ -NMR spectra and with the exception of the base fraction, amides were not detected in the FT-IR spectra. The broad shoulder near  $2500\text{ cm}^{-1}$  for the acid fractions is caused by H-bonded OH groups in carboxylic acids. Esters may well be a small component of the carbonyl groups in the acid fractions.

We agree with the reviewer that the "substructures" of the aliphatic peak in the NMR spectrum of the "volatile acid" fraction are not clearly distinguishable from the noisy background and therefore we have removed this part of the discussion

## References

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