

Interactive comment on “A method for analysis of vanillic acid in polar ice cores” by M. M. Grieman et al.

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Response to reviewer comment by Referee 2

Referee 2 raised several issues regarding the manuscript. These points are well taken and we appreciate the comments. The manuscript has been modified to take them into account.

Issue 1. Number of transitions

“In terms of selectivity, it is good practice when developing a LC/MS/MS method to use

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at least two transitions (Trace Quantitative Analysis by Mass Spectrometry Robert K. Boyd, Cecilia Basic, Robert A. Bethem, 2008 John Wiley & Sons, pg 471.) for each target compound. It seems that the method presented in the paper uses only one transition for unlabeled vanillic acid (167/108 m/z) and another for labeled vanillic acid (168/108 m/z). The use of more transitions would have allowed the authors to check the relative intensity of ions and exclude the possible interference of other compounds.”

We agree that monitoring at least two transitions is desirable. Unfortunately, background noise levels at other transitions were much higher than those at 167/108. As a result, it was difficult to confirm the relative intensities at the very low vanillic acid levels of these ice core samples. We have subsequently confirmed the identity of the vanillic acid peak in these ice core samples using ion chromatography/ESI/MS/MS. However, those results are beyond the scope of this paper.

The end of section 3.1 (Collision Energy) will be changed to:

“However, solvent noise at the 167/123 transition was too high to allow detection of vanillic acid in ice core samples. The optimal signal to noise was obtained at the 167/108 transition at a collision energy of 30 eV. These conditions were used in this study.”

Issue 2. Increasing baseline noise

“...an isocratic elution at 25% of methanol is not able to clean the column of the hydrophobic compounds present in the samples, and these will progressively accumulate in it. In term of robustness, the authors should therefore explain how they addressed the ensuing increase of baseline noise.”

We agree this can sometimes be an issue in analysis of natural samples. However, we did not observe progressive accumulation of baseline noise in this study.

Issue 3. Accuracy

“Accuracy: the paper presents no evaluation of accuracy regarding the determination

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of vanillic acid in real samples. The validation must be integrated.”

We added the following to section 3.3 (Standardization and limit of detection):

“The accuracy of these standards is estimated to be $\pm 4\%$.”

Issue 4.

“I think that the following passages should be clarified/corrected: ‘We did not observe any evidence of matrix effects in the Akademii Nauk samples.’ Which test did you perform? Explain better. ‘and similar results would have been obtained using external standards only.’ I think this part needs to be carefully proved. The statement should also be explained or corrected in relation to a previous statement, namely that ‘the presence of strong acids or bases (nitrate, sulfate, ammonia, etc.) could be the source of matrix effects. This is of particular concern for organic acids such as vanillic acid which are weakly retained on the HPLC column.’ Have you tried external calibration? Have you quantified samples using both approaches? Did you study, for example, the slope of the calibration curve prepared in the matrix?” The use of isotope-labeled standards is a rigorous way of assessing matrix effects. The response of the isotope was the same in ice core standards as in standards, indicating that matrix effects were negligible.

We modified the paragraph at line 10 of p2811 as follows:

“The rationale for using stable isotope-labeled internal standards in this study was to account for potential matrix effects that might suppress or enhance analyte response in an ice core sample compared to that in a pure water standard. The response to the isotope-labeled standard in ice core samples was identical to that in standards prepared in pure water. This indicates the absence of significant matrix effects in the Akademii Nauk samples.”

Issue 5. Proxies

“Figure 5 shows an increasing trend in the concentration of vanillic acid in samples C1381

dating from AD 200-350. Have you tried to compare these levels with those of other proxies of biomass burning, e.g. black carbon? Have you tried to explain this trend?”

We intentionally did not introduce comparisons with other paleofire proxies. This paper is intended to validate the methodology for measuring vanillic acid, not its use as a proxy. That is a far more complex task that will require considerable additional data from numerous sources. We are continuing to work on this issue, but are not prepared to make a statement about the relationship between vanillic acid and other proxies at this time.

Interactive comment on *Clim. Past Discuss.*, 10, 2805, 2014.