

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

### **Anonymous Referee #2**

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The article is very interesting: it respects the objectives of CPD, and shows high throughput and sensitivity. The approach it presents can provide useful indications about the presence of a biomass burning tracers such as vanillic acid in ice cores. However: – The method in itself is not innovative: the application of HPLC/MS to the determination of phenolic compounds in plant and food analysis using a C18 column is a well-established approach. The innovation, if any, could be in the matrix analyzed. – The development and validation of the analytical method present a number of shortcomings that could invalidate the data obtained. They will therefore require a careful and thorough review. In terms of selectivity, it is good practice when developing a LC/MS/MS method to use 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

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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. I do appreciate the importance of high throughput when hundreds/thousands of samples must be analyzed, and 50-70 samples/day is indeed a remarkable result. However, 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. Accuracy: the paper presents no evaluation of accuracy regarding the determination of vanillic acid in real samples. The validation must be integrated. Matrix effect: while I agree that the usage of isotope labeled internal standard can correct (or alleviate) uncertainties due to matrix effect, and that polar ice generally provides matrices that are quite clean, 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? Figure 5 shows an increasing trend in the concentration of vanillic acid in samples 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?

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

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