Clim. Past Discuss., 10, C1177–C1179, 2014
www.clim-past-discuss.net/10/C1177/2014/

Climate of the Past Discussions

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

Anonymous Referee #3

Received and published: 28 July 2014

The paper describes the optimisation of a method in HPLC-MS/MS for the direct analysis of vanillic acid in ice cores. The method itself is not innovative, only the application to ice cores is. The paper can be much improved on the methodology, validation and citation of proper references. Some significant technical shortcomings should be addressed before considering it for publication.

Introduction section: one important reference is missing (Zangrando et al., 2013) in which HPLC-MS/MS analysis is used to quantify vanillic acid (together with other biomass burning tracers) in arctic aerosol. The method optimised by Zangrando et al. (2013) is similar to the one here presented and it includes isovanillic acid, homovanillic acid, syringic acid, ferulic acid, coniferyl aldehyde, syringaldehyde and p-coumaric acid in addition to vanillic acid. Why wasn't any attempt made to include other biomass

burning tracers in this study as well?

Section “2 instrumentation” and “3.2 chromatography” present some redundancies. I suggest merging the two section.

Page 2810, line 10-12: “The detection limit is approximately 58 ppt, defined as two times the vanillic acid levels in distilled water blanks spiked with internal standard.” I find the calculation of the LOD not very robust and somewhat unconventional. Often LOD is calculated as 3 times the standard deviation of the blank (Gambaro et al., 2008) or following IUPAC recommendation (Currie, 1999).

Method optimisation: although ice cores samples are very clean I think that the accuracy of the method should be tested with matrix-matched standards or samples spiked with known amounts of vanillic acid.

Page 2811, line 8-9: “Duplicate analysis of ice core samples with vanillic acid above the detection limit gave a mean difference of $\pm$6% (n = 5 pairs).” Were the samples analysed always in duplicates but only 5 were above LOD? It would be nice to expand this to more samples and include a figure in which the precision is plotted against concentration levels of real samples.

Page 2811, lines 12-15: “In ice core analysis, 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.” This can be avoided/minimised by controlling the pH of the mobile phase. If this was not necessary it should be explained in the text.

Discussion of the results obtained on real samples is limited. Do you have the possibility to compare the results obtained with other proxies? I think that this would be a nice addition because the method itself is not innovative.

Figure 4 is not informative and can be removed. Values of slope, intercept and r2 of the linear regression (including uncertainties) would be more informative.

CPD
10, C1177–C1179, 2014

References: Currie, L.A., 1999. Nomenclature in evaluation of analytical methods including detection and quantification capabilities. Anal. Chim. Acta 391, 105–126. doi:10.1016/S0003-2670(99)00104-X Gambaro, A., Zangrando, R., Gabrielli, P., Barbante, C., Cescon, P., 2008. Direct determination of levoglucosan at the picogram per milliliter level in Antarctic ice by high-performance liquid chromatography/electrospray ionization triple quadrupole mass spectrometry. Anal. Chem. 80, 1649–55. doi:10.1021/ac701655x Zangrando, R., Barbaro, E., Zennaro, P., Rossi, S., Kehrwald, N.M., Gabrieli, J., Barbante, C., Gambaro, A., 2013. Molecular markers of biomass burning in arctic aerosols. Environ. Sci. Technol. 47, 8565–74. doi:10.1021/es400125r

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