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A method for analysis of vanillic acid in polar ice cores

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Abstract

Biomass burning generates a wide range of organic compounds that are transported via aerosols to the polar ice sheets. Vanillic acid is a product of conifer lignin combustion, which has previously been observed in laboratory and ambient biomass burning aerosols. In this study a method was developed for analysis of vanillic acid in melted polar ice core samples. Vanillic acid was chromatographically separated using reversed phase LC and detected using electrospray triple quadrupole mass spectrometry (ESI-MS/MS). Using a 100 µL injection loop and analysis time of 4 min, we obtained a detection limit (S : N = 2) of 58 ppt (parts per trillion by mass) and an analytical precision of ±10 %. Measurements of vanillic acid in Arctic ice core samples from the Siberian Akademii Nauk core are shown as an example application of the method.

1 Introduction

Biomass burning is an important part of the global carbon cycle and has a major impact on global atmospheric chemistry. Emissions include a wide range of compounds, including carbon dioxide, carbon monoxide, methane, volatile organic compounds, and aerosols. Emissions of CO and CH_4 affect the global abundance of hydroxyl radicals (OH) and influence the oxidative capacity of the troposphere (Crutzen and Andreae, 1990). Fire also influences climate by changing the albedo of the land surface (Randerson et al., 2006).

Several types of proxy records have been used to reconstruct change in biomass burning over time, but there is little consensus on regional/global trends or on the relationship between biomass burning and global climate. Evidence for historical rates of burning have been obtained from charcoal accumulation in lake sediments and dendrochronological evidence of fire scars on tree rings (Marlon et al., 2008; Whitlock and Larsen, 2001). Global burning histories have also been inferred from variations in the stable isotopic composition of ice core methane (Ferretti et al., 2005; Sapart et al., 2012). Ammonium, potassium, acetate, nitrate, oxalate, levoglucosan, and black carbon in ice cores have also been used as proxies for biomass burning emissions (Whitlow et al., 1994; McConnell et al., 2007; Gambaro et al., 2008; Kehrwald et al., 2012). Of these proxies, only levoglucosan is exclusively due to biomass burning. It is generated from combustion of all types of cellulose-containing plant matter, and thus is not specific to a particular plant type or ecosystem (Simoneit et al., 1999). There has been debate about the atmospheric reactivity of levoglucosan, and its suitability as a quantitative tracer for aerosol source apportionment (Hoffmann et al., 2010; Hennigan et al., 2010; Slade and Knopf, 2013).

Laboratory and field studies have shown that biomass burning aerosols contain a wide range of aromatic compounds whose chemistry is related to the structure of the precursor lignin material combusted (Simoneit, 2002). These lignin-derived methoxylated phenols, aldehydes, and acids have been used as tracers for the contribution of biomass burning to ambient aerosols on a local or regional basis (Nolte et al., 2001). Such compounds should be incorporated into polar ice cores and may contain information about climate-related variability in biomass burning and about the nature of the combusted material.

In this study we focus on vanillic acid, a product of combustion of conifer lignin. Kawamura et al. (2012) detected vanillic acid in a Kamchatka Peninsula ice core using preconcentration, derivatization and GC-MS, similar to techniques used for the analysis of biomass burning aerosols (Nolte et al., 2001; Simoneit et al., 2004; Fu et al., 2008). This method involves analysis of relatively large ice core samples (80–250 mL), with extensive sample handling that requires preconcentration by rotary evaporation, solvent extraction, heated derivatization to form trimethylsilyl derivatives, and dissolution in hexane. Our laboratory previously reported the observation of vanillic acid in a Greenland ice core using a continuous flow melter and analysis by electrospray ionization and mass spectrometric detection (ESI-MS/MS) (McConnell et al., 2007). That method is capable of high temporal resolution while relying on the selectivity of the ESI-MS/MS to insure the specificity of the analysis.

Here we report on the development of an analytical method for the rapid analysis of discrete ice core samples employing liquid chromatography with electrospray ionization and mass spectrometric detection (LC-ESI-MS/MS). The performance of the method is illustrated using synthetic aqueous solutions and natural samples from the Siberian Akademii Nauk ice core (Fritzche et al., 2005).

2 Instrumentation

This study was carried out using a ThermoFinnigan TSQ Quantum System, consisting of an autosampler, a liquid chromatograph (LC), and an electrospray ionization-triple quadrupole mass spectrometer (ESI-MS/MS). Instrument control and data acquisition used the Xcalibur data system (ThermoFinnigan Corp.). The LC was operated isocratically using a mobile phase of 25 % methanol in water flowing at 200 µL min^{-1}, a C18 reversed phase analytical column, and a 100 µL injection loop. The electrospray ion source was operated using the following conditions: −3 kV spray voltage, 38 psi sheath gas pressure, and 15 psi auxiliary gas pressure. For instrument tuning and signal optimization, high concentration vanillic acid solutions (1–10 ppm) were introduced directly into the ESI-MS/MS via syringe pump (NE-300, New Era). Vanillic acid was detected using the mass spectrometer in the negative ion mode, with an ion inlet cone temperature of 350 °C.

3 Method optimization

3.1 Collision energy

MS/MS detection of vanillic acid was optimized using product scans with varying collision energies. Solutions containing 1 ppm vanillic acid in a 75 : 25 % water: methanol mixture were delivered directly to the electrospray source using the syringe pump. The vanillic acid $[\text{M}-\text{H}]^-$ (m/z 167) was used as the precursor mass and the collision gas pressure was 1.5×10^{-4} psi of Ar. Figure 1 shows a product scan at a collision energy of 30 eV. The major product fragments under these conditions are: $C_4H(O)$ (*m/z* 65), C_6H_3O (*m/z* 91), $C_6H_3(O)OH$ (*m/z* 108), $C_6H_3(OCH_3)OH$ (*m/z* 123), and $C_6H_3(O)(COO)OH$ (*m/z* 152).

Figure 2 shows the fragmentation pattern as a function of collision energy over the range of 0–40 eV. Maxima were found at a collision energy of 15 eV for fragments at *m/z* 152 (loss of CH_3) and *m/z* 123 (loss of CO_2). Maxima were observed at 25 eV for fragments at *m/z* 108 (loss of CH_3 and CO_2) and *m/z* 91 (loss of COOH and OCH_3). The highest response overall was obtained for the *m/z* 123 fragment at 15 eV. However, because less noise was observed at *m/z* 108 using a collision evergy of 30 eV, these were the conditions used in this study.

3.2 Chromatography

The Surveyor autosampler was programmed to inject 100 µL of sample onto a reversed phase Kinetex 2.6 µm particle size XB-C18 100A analytical column (100 mm × 2.2 mm, Phenomenex). The mobile phase was an isocratic solution of 25 % methanol in water, flowing at 200 $\mu L\,min^{-1}$. All of the column effluent was directed to the electrospray ionization source. Vanillic acid is eluted from the column with a retention time of 2.5 min and a peak width at half height of 0.2 min. Chromatograms of standard mixture of a 1 ppb vanillic acid standard (167→108) and a 1 ppb ^{13}C-labeled vanillic acid isotope standard (168→108) are shown in Fig. 3 (left side).

3.3 Standardization and limit of detection

Standards were prepared using vanillic acid (4-hydroxy-3-methoxybenzoic acid, 97 % purity, Sigma-Aldrich). The internal standard was ^{13}C labeled vanillic acid (Carboxyl-^{13}C, 99 % purity, Cambridge Isotope Laboratories). Stock solutions of 0.1 % vanillic acid and ^{13}C labeled vanillic acid were prepared monthly in HPLC grade methanol (J. T. Baker). Intermediate 1 ppm standards were prepared daily in methanol. Working standards ranging from 0–2 ppb were prepared by dilution in ultrapure water (Millipore Milli-Q) directly in 2 mL Surveyor autosampler vials. Samples and standards were spiked with ^{13}C-labeled vanillic acid (2 µL of 1 ppm internal standard in 2 mL) to generate a 1 ppb internal standard.

Calibration curves were constructed by analyzing vanillic acid standards ranging in concentration from 0–2 ppb. The calibration curves were based on the ratio of peak areas of the vanillic acid and isotope-labeled vanillic acid signals at their respective mass transitions, 167 → 108 and 168 → 108 (Fig. 4). Using linear least squares regression with a 95 % confidence interval, the uncertainty of the slope of the calibration curve was ±5.3 % and the uncertainty of the intercept is ±152 ppt. The detection limit is approximately 58 ppt, defined as two times the vanillic acid levels in distilled water blanks spiked with internal standard. The concentration of the ^{13}C ion attributable to the vanillic acid in the internal standard was below the limit of detection.

4 Ice core sample analysis

The ice core samples used to test the analytical method were obtained from the Akademii Nauk ice core (Fritzsche et al., 2005). This ice core was drilled on the Akademii Nauk ice cap covering Komsomolets Island in the Eurasian Arctic (80°31′ N, 94°49′ E). The site was 800 m a.s.l. with a mean annual temperature of −15.7 °C. The ice core was drilled to bedrock with a total depth of 723.91 m (Fritzsche et al., 2002, 2005; Weiler et al., 2005). The ice core samples analyzed for this study covered the time period AD 200–350. This is a provisional timescale (McConnell, personal communication). Samples were melted using a continuous melter, and collected in 8 mL HDPE vials using a peristaltic pump and fraction collector (McConnell et al., 2001).

The procedure used for analysis of ice core samples was as follows: 1 ppb of ^{13}C labeled vanillic acid was added to each ice core sample and standard. Occasional blanks without internal standard were also analyzed. A blank and/or standard was analyzed after every 5th ice core sample. Samples were typically analyzed in batches of

50–70 samples day^{-1} and typically calibration curves were based on all of the standards and blanks analyzed on the same day. An example of a chromatogram from an Akademii Nauk ice core sample is shown in Fig. 3 (right side).

The vanillic acid observed in 34 Akademii Nauk ice core samples, covering the time period from AD 200–350 is shown in Fig. 5. Each sample represents approximately one year. Vanillic acid concentrations ranged from 59 ppt to 698 ppt, with an overall mean of 226 ± 189 ppt (1σ) and a median of 156 ppt. All of the samples had vanillic acid levels above the detection limit (58 ppt). Duplicate analysis of ice core samples with vanillic acid above the detection limit gave a mean difference of ±6 % ($n = 5$ pairs).

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. 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. We did not observe any evidence of matrix effects in the Akademii Nauk samples, and similar results would have been obtained using external standards only.

There are few reports of previous ice core measurements of vanillic acid, but the levels reported in the literature are generally similar to those measured here. Kawamura et al. (2012) reported vanillic acid levels ranging from below detection (5 ppt) to 125 ppt for samples from the Ushkovsky ice core on the Kamchatka Peninsula covering the time period 1690–1997. McConnell et al. (2007) reported vanillic acid levels from 10–350 ppt in ice core samples from West Central Greenland ranging in age from AD 1788–2002.

5 Conclusions

This study demonstrates the feasibilty of analyzing small ice core samples using LC-ESI-MS/MS with minimal sample handling. The development of such rapid, low volume,

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high sensitivity analytical methods for analysis of organic compounds is needed in order to fully exploit the paleoenvironmental information stored in the polar ice archive. For organic biomass burning tracers such as vanillic acid, the potential exists to observe variations in the intensity and location of high latitude biomass burning over long time scales, with the caveat that such signals are influenced by atmospheric transport, chemical reactivity, and deposition.

The detection limit of 58 ppt achieved in this study using LC-ESI-MS/MS was sufficiently sensitive to detect vanillic acid in the Siberian ice core samples analyzed. The GC-MS method commonly used for aerosol analyses has a lower detection limit (5 ppt, Kawamura et al., 2012), but this method requires large samples (80–250 mL) and more extensive sample handling. Small samples make it possible to sample more frequently in time. Therefore, each sample represents a shorter period of time, and changes can be observed at decadal or even annual timescales. It is anticipated that detection limits will improve with further developments in chromatography. Application of the LC-ESI-MS/MS technique to other biomass-burning products will be a focus for future work.

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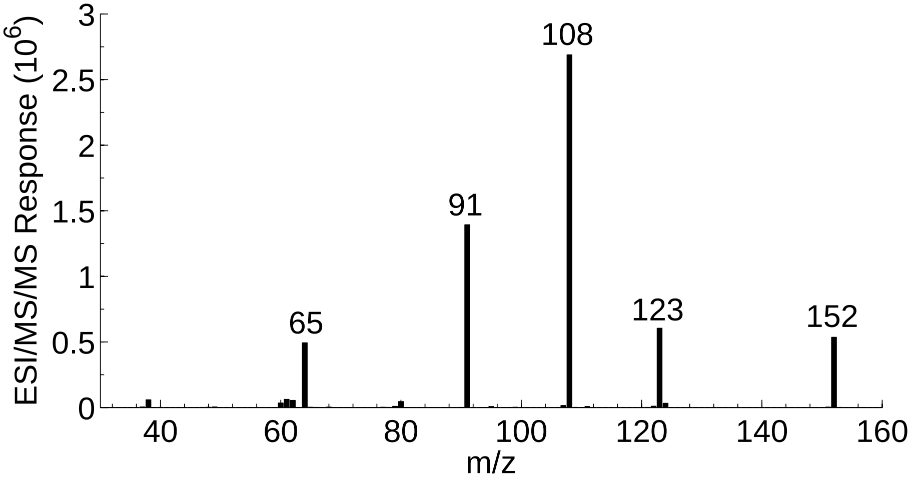

Figure 1. ESI-MS/MS product scan of vanillic acid using 30 eV collision energy.

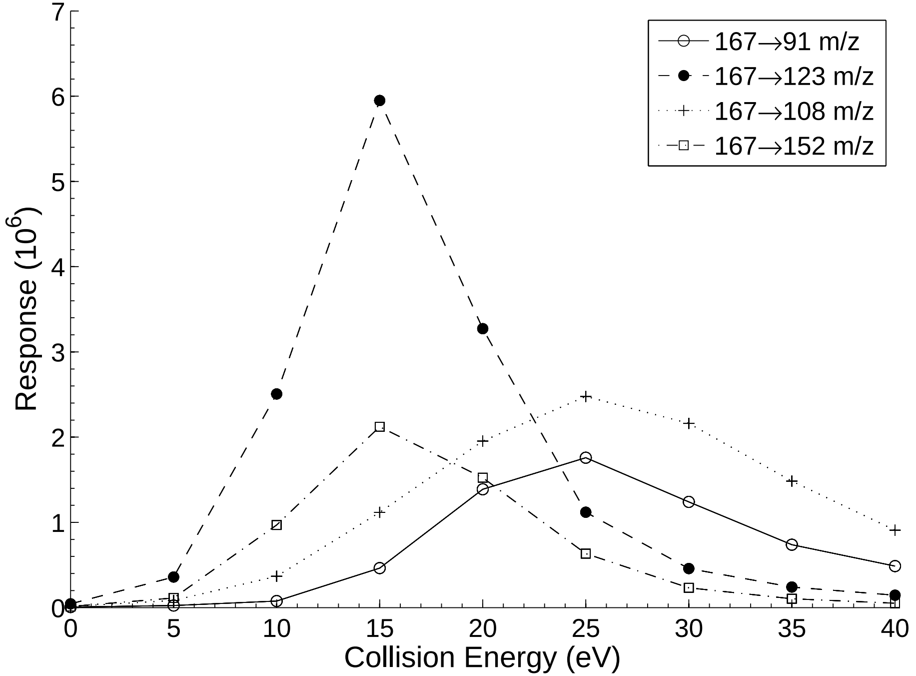

Figure 2. Instrument response to a 1 ppm vanillic acid solution at varying collision energies using the 167 → 91 *m/z*, 167 → 123 *m/z*, 167 → 108 *m/z*, and 167 → 152 *m/z* mass transitions.

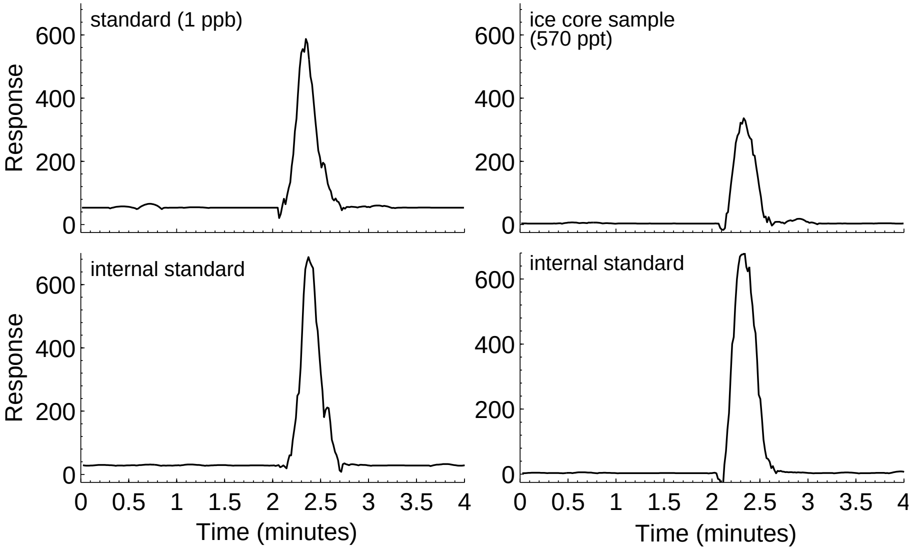

Figure 3. Vanillic acid chromatograms. Left: 1 ppb vanillic acid standard in milli-Q water (^{12}C, 167 → 108 *m/z*) (upper) with 1 ppb internal standard (^{13}C-labelled vanillic acid, 168 → 108 *m/z*) (lower). Right: Akademii Nauk ice core sample containing 570 ppt vanillic acid (325 m depth, AD 286) (^{12}C, 167 → 108 *m/z*) (upper) with with 1 ppb internal standard (^{13}C-labelled vanillic acid, 168 → 108 *m/z*) (lower).

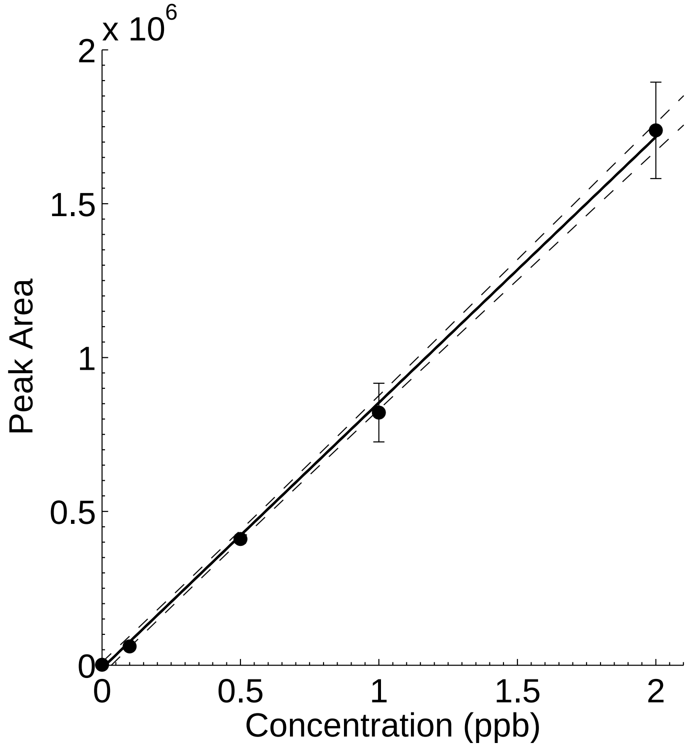

Figure 4. Calibration curve constructed from analysis of vanillic acid solutions prepared in milli-Q water with 1 ppb of ^{13}C-labeled vanillic acid as an internal standard. Results are shown as the ratio of the peak areas from the ^{12}C and ^{13}C isotopomers at mass transitions 167 → 108 and 168 → 108, respectively. Error bars represent standard deviation of the peak areas at each concentration, with the number of measurements given.

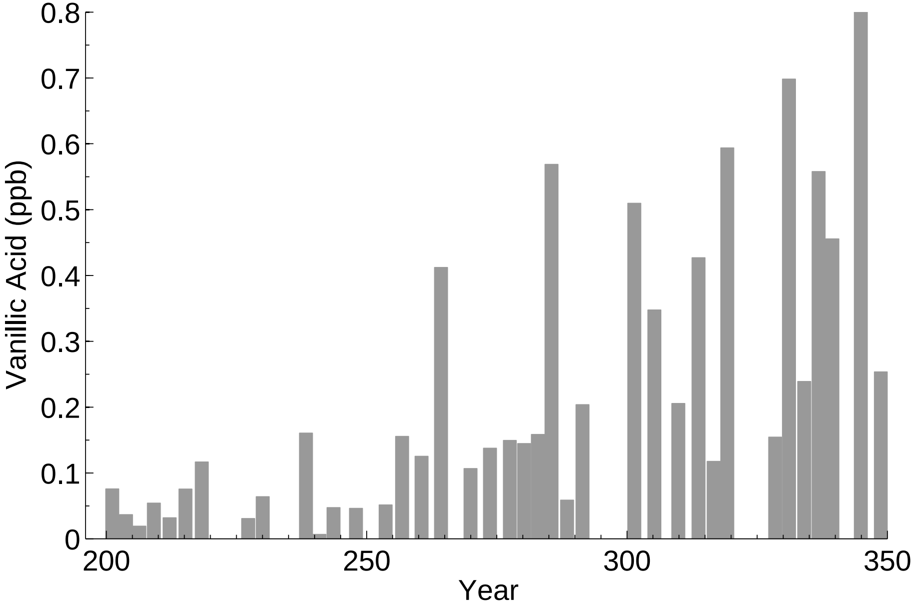

Figure 5. Vanillic acid concentrations in Akademii Nauk ice core samples plotted against ice age for the years AD 200–350.