Analytica Chimica Acta xxx (2018) 1–7

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

A rapid and sensitive method for the analysis of lignin phenols in environmental samples using ultra-high performance liquid chromatography-electrospray ionization-tandem mass spectrometry with multiple reaction monitoring

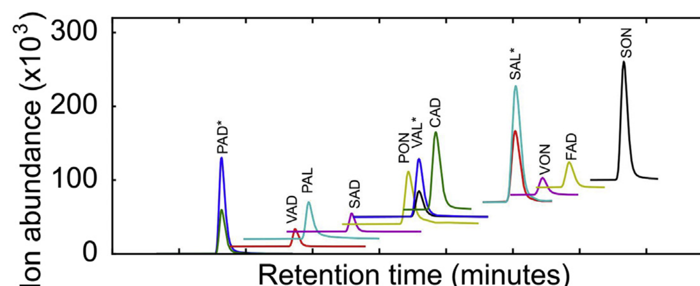
Ge Yan [a], Karl Kaiser [a, b, *]

[a] Department of Marine Sciences, Texas A&M University Galveston Campus, Galveston, TX, 77553, United States
[b] Department of Oceanography, Texas A&M University, College Station, TX, 77843, United States

HIGHLIGHTS

- Ultra-low concentrations of lignin phenols (<100 fmol) are analyzed by UHPLC-ESI-QqQ-MS.
- Samples are purified with polymer sorbent based solid-phase extraction.
- The matrix effects are compensated by ^{13}C-labeled surrogate standards.
- The method is fully validated by comparison with GC-EI-QqQ-MS.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 September 2017
Received in revised form
9 March 2018
Accepted 10 March 2018
Available online xxx

Keywords:
Lignin
Ultra-high performance liquid chromatography
Tandem mass spectrometry
Gas chromatography
^{13}C-labeled standards
Solid-phase extraction

ABSTRACT

A novel ultra-high performance liquid chromatography-electrospray ionization-tandem mass spectrometry method was developed to enable the analysis of ultra-low levels of lignin phenols (<100 fmol) in environmental samples. The method included a sample clean-up with a polymer sorbent based solid-phase extraction and reversed-phase chromatography that allowed separation of all lignin phenols with minimal interference from co-eluting matrix components. The application of ^{13}C-labeled surrogate standards effectively compensated for variability associated with sample preparation and ion suppression. The method was fully validated and compared to gas chromatography-electron impact ionization-tandem mass spectrometry for Suwannee River humic acid standard reference material and extracted riverine dissolved organic matter. The comparison demonstrated the robustness and suitability of the method for ultra-low lignin phenol concentrations and high matrix interference. The simple and fast sample preparation coupled to analysis without derivatization makes it feasible for routine and high-volume analyses.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Lignin is a phenolic heteropolymer (600–1000 kDa) primarily found in the secondary cell wall of vascular plants. The primary building units of lignin are *p*-coumaryl, coniferyl, and sinapyl

* Corresponding author. Department of Marine Sciences, Texas A&M University Galveston Campus, Galveston, TX, 77553, United States.
E-mail addresses: geyan@tamu.edu (G. Yan), kaiserk@tamug.edu (K. Kaiser).

https://doi.org/10.1016/j.aca.2018.03.054
0003-2670/© 2018 Elsevier B.V. All rights reserved.

Please cite this article in press as: G. Yan, K. Kaiser, A rapid and sensitive method for the analysis of lignin phenols in environmental samples using ultra-high performance liquid chromatography-electrospray ionization-tandem mass spectrometry with multiple reaction monitoring, Analytica Chimica Acta (2018), https://doi.org/10.1016/j.aca.2018.03.054

alcohols that are irregularly connected by carbon–carbon and diaryl–ether linkages. The proportions of specific units depend on vascular plant type and other criteria such as physiology and cytology [1].

Lignin analysis yields important information on the relative contributions of terrestrial organic matter in the marine environment [2,3], the distribution of dominant vegetation types (i.e., gymnosperm versus angiosperm and woody versus herbaceous), and the extent of decomposition of natural organic matter [4,5]. Lignin has therefore been extensively employed as a biomarker to investigate origins and cycling of terrigenous organic matter in various natural environments [6–8]. For example, lignin phenol analyses have established general distribution patterns and mechanisms of decomposition of terrestrial dissolved organic carbon in the global ocean [3]. Several studies have also shown the usefulness of lignin phenols for studying water mass formation and circulations in the oceans [6,9,10]. However, large scale generalizations are impossible due to difficulties and limitations associated with the present lignin phenol analysis method and the sensitivity of analytical instrumentation.

Mild oxidation with alkaline copper oxide (CuO) is the most common method for digestion of lignin polymers in aqueous, soil and sediment samples [11,12]. This method typically involves sample clean-up by liquid-liquid extraction (LLE) or solid phase extraction (SPE) before analysis by gas chromatography (GC) or high-performance liquid chromatography (HPLC) and detection using mass spectrometry (MS) or ultraviolet (UV) absorption spectroscopy [13–17]. Common clean-up procedures used for the analysis of lignin phenols have several drawbacks. Labor-intensive LLE leads to large volumes of solvent and non-specific extraction of a broad range of matrix components that interfere with quantification of phenols. Silica-based C_{18} sorbents are prone to drying out effects and irreversible trapping of phenols. Additional drawbacks of existing methods include the lack of selectivity of UV detection [15], time-consuming derivatization procedures for GC separation of lignin phenols [16,17], and inadequate correction of matrix interference [18].

Ultra-high performance liquid chromatography (UHPLC) in combination with tandem mass spectrometry (MS/MS) is a promising candidate for lignin phenol analysis. Lignin phenols are soluble in aqueous solutions and can be separated without prior derivatization. High peak capacity allows for efficient separation of lignin monomers from matrix components at short analysis times. MS/MS enables unparalleled specificity of detection in multiple reaction monitoring (MRM) mode with high signal-to-noise ratios and minimal co-elution interferences, both of which are important attributes for robust quantification of lignin phenols in environmental samples associated with complex matrices. Few methods describe the analysis of common phenols by LC-MS/MS, but none adequately address ion suppression for accurate quantification [18,19].

Here we present a novel analytical method for analysis of lignin in environmental samples after alkaline oxidation by UHPLC-triple quadrupole mass spectrometry (QqQ-MS). Sample clean-up was achieved using a polymer-based SPE sorbent prior to chromatography. UHPLC with QqQ-MS detection in dynamic MRM (DMRM) mode coupled with isotopically-labeled surrogate standards yielded much improved sensitivity and selectivity, and accurate quantification of lignin phenols. Validation by parallel measurements with a separately developed GC-QqQ-MS method indicated the robust performance of the novel method for environmental samples with ultra-low lignin concentrations and matrix interference.

2. Materials and methods

2.1. Materials

Standards of monomeric lignin phenols for calibration, ^{13}C labeled surrogate standards, and methyl acetate were purchased from Sigma-Aldrich Co. (St. Louis, MO). Sulfuric acid was from EMD Chemicals (Darmstadt, Germany). LC-MS grade methanol and acetonitrile were obtained from J. T. Baker (Phillipsburg, NJ). LC-MS eluent additive formic acid was from Thermo Scientific (Rockford, IL). Ultra-pure water was obtained with a Milli-Q water purification system (Millipore, Bedford, MA). Oasis HLB cartridges (30 mg, 1 mL) were purchased from Waters (Milford, MA). A 12-port vacuum manifold used for extraction and drying was purchased from Supelco (St. Louis, MO). Stock calibration standard mix and surrogate standards prepared in acetonitrile/water (20/80 v/v%) were portioned into 2 mL glass vials and kept frozen at −20 °C. Working standards were prepared for each set of samples using stock and surrogate standards by dilution with water. All the chemicals were of the highest grade commercially available. All glass (combustion for 5 h at 500 °C) and plastic (acid-rinsed) ware were cleaned prior to use.

A 40 L water sample was collected from the Brazos River in Freeport, Texas. After collection, the sample was filtered through a Whatman Polycap 75AS capsule filter (0.2 μm) and acidified to a pH of 2.5 with 12 mol L^{-1} sulfuric acid. Extraction was performed with Agilent PPL cartridges (5 g), and ~13 L were extracted at a flowrate of 50 mL min^{-1} per cartridge. Each cartridge was conditioned with 50 mL of methanol and 100 mL of water at pH = 2.5. After extraction each cartridge was flushed with 50 mL of water at pH = 2.5 and dried for 30 s to remove residual water. Retained compounds were extracted with 50 mL of methanol, combined in a glass bottle and stored at −20 °C until analysis. Suwannee River humic acid standard reference material (SRM-2S101H) was obtained from the International Humic Substance Society (IHSS, St. Paul, MN).

2.2. Sample oxidation and clean-up

Dried aliquots of the Brazos River methanol extract and humic acid reference material were oxidized following the method described in Kaiser and Benner [20]. After oxidation a surrogate standard mixture of *p*-hydroxybenzoic acid-$^{13}C_7$ (PAD-$^{13}C_7$), vanillin-$^{13}C_6$ (VAL-$^{13}C_6$), and syringaldehyde-$^{13}C_6$ (SAL-$^{13}C_6$) was added into reaction vessels. The amount of surrogate standards added was matched to levels of their analogues in samples. The closed reaction vessels were thoroughly mixed, and the solutions were transferred to glass tubes. After rinsing reaction vessels with 2 × 0.5 mL of argon-sparged 1 M NaOH, the combined sample solutions in glass tubes were centrifuged to remove any particulates. The supernatant was then transferred to another glass tubes and acidified to pH ~2.5 with 12 M sulfuric acid. Waters HLB cartridges (30 mg, 1 mL) were attached to the extraction manifold and conditioned with 2 × 1 mL of methanol followed by rinsing with 2 × 1 mL of water. The acidified samples were loaded onto the cartridges under gravity flow. Cartridges were washed with 3 × 300 μL of methanol/water (20/80 v/v%) to remove inorganic ions and weakly retained compounds. The cartridges were covered with aluminum foil and dried under vacuum for 10 min. Lignin phenols retained on the resin were then eluted with 2 × 300 μL of methanol/methyl acetate (30/70 v/v%) into 2 mL autosampler glass vials at gravity flow. Residual eluent remaining in the cartridges was collected by a short (5 s) burst of vacuum. The eluate was evaporated to near dryness under a gentle flow of argon gas directly in the extraction manifold [20]. The manifold lid was slightly lifted with a foil shim to create an air gap for enhanced evaporation.

Please cite this article in press as: G. Yan, K. Kaiser, A rapid and sensitive method for the analysis of lignin phenols in environmental samples using ultra-high performance liquid chromatography-electrospray ionization-tandem mass spectrometry with multiple reaction monitoring, Analytica Chimica Acta (2018), https://doi.org/10.1016/j.aca.2018.03.054

Download English Version:

https://daneshyari.com/en/article/7553645

Download Persian Version:

https://daneshyari.com/article/7553645

Daneshyari.com