Accelerated benzene polycarboxylic acid analysis by liquid chromatography–time-of-flight–mass spectrometry for the determination of petrogenic and pyrogenic carbon

Benjamin Hindersmann, Christine Achten*

Institute of Geology and Palaeontology—Applied Geology, University of Münster, Corrensstr. 24, 48149 Münster, Germany

ABSTRACT

Pyrogenic carbon species are of particular interest due to their ubiquitous occurrence in the environment and their high sorption capacities for nonpolar organic compounds. It has recently been shown that the analysis of the molecular markers for complex aromatic carbon structures, benzene polycarboxylic acids (BPCA), has a high potential for aid in the identification of different carbon sources.

In this study, the first LC method using mass spectrometry (MS) for reliable and accelerated (<24 h) quantification of pyrogenic and petrogenic carbon by BPCA analysis has been developed. The main advantage of LC–MS compared to previous methods is the higher sensitivity, which is important if only small sample amounts are available. Sample pre-treatment could be reduced to a minimum. Deuterated phthalic acid was introduced as internal standard due to its structural similarity to BPCA and its lack of occurrence in the environment. Linear quantification with $r^2 \geq 0997$ was accomplished for all BPCA. Method validation showed an excellent quantification reproducibility (mean CV < 5%) which is comparable to LC-DAD methods and more reliable than GC-FID measurements (CV 16–23%). In summary, the presented BPCA method is more economic, efficient and presumably attractive to use.

Besides reference materials, various pyrogenic and petrogenic samples were analyzed to test if the sources were indicated by BPCA analysis. In addition to pyrogenic carbon, large amounts of petrogenic carbon species can also be present in urban soils and river sediments, especially in mining regions. They also to a large degree consist of aromatic carbon structures and therefore have an impact on source identification by BPCA analysis. Comparison of petrogenic and pyrogenic carbon samples shows similarities in the BPCA concentrations and patterns, in their aromaticity and degree of aromatic condensation. Thus, a differentiation between petrogenic and pyrogenic carbon only by BPCA analysis of samples with unknown carbon sources is not possible. For reliable source identification of the carbon species, the combination with other methods, such as e. g. analysis of polycyclic aromatic hydrocarbons may be successful.

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1. Introduction

Organic matter in soils is of particular interest due to its contribution to the carbon cycle, its partially high resistance to degradation and its effective sorption properties for hydrophobic organic contaminants [1–4]. Numerous methods have been developed to measure carbon species of varying stability in different compartments, although many of these methods focus on particular ranges of the carbon continuum [5]. Until today there are still uncertainties regarding the choice of an optimal method, because of the wide range of carbon species and possibly increased time expenditure with suitable methods for the analysis of particularly pyrogenic carbon (black carbon, BC) [6,7]. Therefore, fast and reliable methods suitable for different sample types such as soot, atmospheric particulate matter, uncontaminated and contaminated soil, sediment and suspended matter, etc. are targeted.

Organic matter in soils and sediments is either of biogenic, petrogenic or pyrogenic origin. Carbon species herein that contain complex aromatic carbon structures are more persistent against degradation. These higher molecular carbon species can be mainly assigned to combustion or coalification [7]. Particularly in urban areas, soils can be heavily enriched by petrogenic and/or pyrogenic carbon from anthropogenic activities.

Depending on temperature, time, oxygen availability and type of biomass, residues of combustion range from partly charred biomass to highly condensed aromatic structures [8–10]. These parameters

together with pressure influence the process of coalification of biomass as well, albeit over longer time scales and at lower temperature than combustion [11]. Although coalification and combustion are different processes, both lead to a reduction of the H/C and O/C ratios as well as (i) an increase in the proportion of aromatic carbon structures (aromaticity) and (ii) an increase in the size of aromatic structures (degree of aromatic condensation) [12–17].

In 2012, different methods for the quantitative analysis of the carbon continuum in various matrices were compared [7] and it was concluded that, of the tested methods, the molecular marker method using benzene polycarboxylic acids (BPCA) showed the highest potential for qualitative and quantitative analysis of different carbon types in soils and sediments [7]. Moreover, BPCA analysis provides additional information on the degree of aromatic condensation and aromaticity [14]. Recently, it has been proven that the ratio of BPCA to total carbon content (TOC) is an indicator of aromaticity and that of the acid containing six carboxylic acid groups, mellitic acid (1,2,3,4,5,6-B6CA) to total BPCA content corresponds to the degree of aromatic condensation [14].

BPCA analysis was first used in 1998 by Glaser et al. [18] to identify and quantify BC in soils. The aromatic carbon structures of BC are converted into BPCA by oxidative HNO_3 digestion at high pressure and temperature followed by analysis using gas chromatography (GC) coupled to flame ionization detection (FID) [18]. In 2005, an overestimation caused by artificially formed BPCA during the pre-sample treatment was revealed and the method was reviewed and improved [19]. Since then, BPCA analysis has been used to identify and quantify pyrogenic carbon structures in different types of samples such as soils [18–21], marine sediments [22,23], pure combustion residues [7,24,25] and dissolved organic matter [26–28]. Commonly, BPCA analysis is performed by GC-FID [7,21,25,29–34]. However, sample preparation for this method of about 4–5 days is very time-consuming and prone to losses caused by the many different processing steps [20,24]. The use of a cation-exchange column within the extraction step for GC analysis of BPCA is indispensable due to the interaction of polyvalent cations with the derivatisation reagents and can therefore lead to losses.

Use of liquid chromatography (LC) coupled to a diode array detector (DAD) for quantitative BPCA analysis needs less sample preparation and leads to higher reproducibility compared with GC-FID [20,24,26]. The LC-DAD method developed by Dittmar [26] and Schneider et al. [24] requires minimum sample preparation steps time but was only tested for polycyclic aromatic hydrocarbons (PAHs), dissolved organic matter and charcoals at different combustion conditions. Furthermore, an analytical runtime of more than one hour per sample is required. For another method by Wiedemeier et al. [20], an analysis time of only 30 min is needed but more comprehensive sample preparation steps are necessary. Aiming at fast, reproducible and sensitive methods, we hypothesize that use of mass spectrometry (MS) may lead to higher sensitivity compared with DAD which is of particular interest if only small sample amounts e. g. of soot or particulate matter are available. Additionally, superimposition may be detected to a larger extent. Existing methods are not compatible with LC–MS analysis because of the non-volatile buffers used as mobile phases such as orthophosphoric acid [15] or tetrabutylammonium bromide [19,21] which can lead to deposits in the MS, source blockages, decreased signal-to-noise ratios and losses in signal intensities [30]. Therefore, in this study, a method for the quantification of BPCA by LC–MS was developed for the first time. The main requirements of this method beside reliability, easy and rapid feasibility and good peak separation were a short analysis time and the suitability for electrospray ionization (ESI). BPCA reference materials and a set of petrogenic (including coals) and pyrogenic samples were used. To our knowledge, neither has the used range of petrogenic source samples of this study been analyzed before, nor have the resulting BPCA concentrations

and patterns as well as the aromaticity and degree of aromatic condensation of petrogenic and pyrogenic carbons of such a set been compared before.

2. Material and methods

2.1. Reference materials and environmental samples

Three certified reference materials (CRM) and four other reference materials (RM) all of which had been used in other studies before [5,7,20,24,35–37], as well as sixteen samples from original carbon sources (O) were used for method development and validation (Table 1). CRM were diesel particulate matter (SRM 2975 NIST, USA), urban dust (SRM 1649b NIST, USA) and organics in marine sediment (SRM 1941b NIST, USA). RM consisted of charred rice straw (*Oryza sativa*, UHZ Zürich, CH), charred chestnut wood (*Castanea sativa*, UHZ, Zürich, CH), haplic chernozem soil (2013, UHZ, Zürich, CH) and *n*-hexane soot (own production in the laboratory).

All reference materials were analyzed in triplicate to estimate reproducibility and standard deviations. The total sample set encompassed petrogenic and pyrogenic source materials: lignite, sub-bituminous coal, bituminous coal, anthracite and crude oil (petrogenic), and charcoal, tar oil, coke and soot (pyrogenic). Environmental samples were "non/low"-contaminated soil and sediment as well as urban dust.

All source samples were freeze dried and milled to analytical grade. The total organic carbon content of the samples was determined by a CS-MAT 5500 elemental analyzer (Ströhlein Instruments, Germany) prior to BPCA analysis.

2.2. BPCA analysis by LC–MS

LC–MS was performed using a Prominence XR UFLC (Shimadzu, Germany) with a Poroshell 120 SB-C18 column (2.7 μm, 2.1 mm × 150 mm, Agilent, Germany) coupled to an ultrahigh resolution–time of flight–mass spectrometer Maxis 3G (Bruker Daltonik, Germany) operated in negative ESI mode at a nebulizer pressure of 2.0 bar. Capillary voltage was set to 5000 V with an end plate offset of −500 V. A dry gas flow of 6.5 l/min at dry gas temperature of 250 °C was used. The monitored masses ranged from 100–800 *m/z* at a spectra rate of 1.0 Hz. Further parameters of the TOF-MS setting are listed in the supplementary information (Supplementary information 1: Fig A1).

The Poroshell 120 SB-C18 column was chosen due to its good separation performance [20] at acidic conditions. Ionization and chromatographic separation of the BCPA were tested for various acidic solutions, including acetic acid (100% Roth, Germany), amidosulfonic acid (≥99.5%, AnalaR Normapur®, VWR, Germany), formic acid (98–100%, Merck, Germany) and trifluoroacetic acid (≥99.9%, Roth, Germany). The acids were diluted with ultrapure water (TOC <5 ppb, Milli-Q, Germany) at different concentrations and pH values within the range of pH 1.2–pH 7.0 depending on the minimum possible pH value. For this purpose, in the first step, the extent of ionization of the BPCA dissolved in the acidic solutions (100 ng/μL) was determined by direct injection. In the second step, the acidic solutions showing the highest ionization yields for BPCA were used to test the chromatographic separation performance. Acetonitrile (HPLC–MS grade, VWR, Germany) was additionally used as mobile phase.

The BPCA compounds 1,3,5-tricarboxylic acid (trimesic acid, 1,3,5-B3CA), 1,2,4-tricarboxylic acid (trimellitic acid, 1,2,4-B3CA), 1,2,3-tricarboxylic acid (hemimellitic acid, 1,2,3-B3CA), 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid, 1,2,4,5-B4CA), benzenepentacarboxylic acid (1,2,3,4,5-B5CA) and 1,2,3,4,5,6-benzenehexacarboxylic acid (mellitic acid, 1,2,3,4,5,6-B6CA, all