International Journal of Mass Spectrometry 404 (2016) 29–34

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

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

The investigation of the birch tar using ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry and Hydrogen/Deuterium exchange approach

Yury Kostyukevich[a,b,c,d], Alexander Zherebker[a,b,e], Alexey Kononikhin[b,d], Igor Popov[c,d], Irina Perminova[e], Eugene Nikolaev[a,b,c,d,*]

[a] Skolkovo Institute of Science and Technology Skolkovo Innovation Center, Building 3, Moscow 143026, Russia
[b] Institute for Energy Problems of Chemical Physics, Russian Academy of Sciences, Leninskij pr. 38 k.2, 119334 Moscow, Russia
[c] Emanuel Institute for Biochemical Physics, Russian Academy of Sciences, Kosygina St., 4, 119334 Moscow, Russia
[d] Moscow Institute of Physics and Technology, Dolgoprudnyi, 141700 Moscow, Russia
[e] Lomonosov Moscow State University, Department of Chemistry, Leninskie Gory 1-3, 119991 Moscow, Russia

ARTICLE INFO

Article history:
Received 15 January 2016
Received in revised form 31 March 2016
Accepted 31 March 2016
Available online 2 April 2016

Keywords:
Isotopic exchange
Dissolved organic matter
FT ICR
ESI

ABSTRACT

Birch tar was widely used since the Stone Age as adhesive, disinfectant, mosquito repellent etc. Despite of this, the chemical composition of the birch tar remains largely unknown. Here we implement the electrospray ionization ultrahigh resolution Fourier transform mass spectrometry for the determination of the molecular formulas of the birch tar constituents. It was found that in the positive ESI mode the compounds containing 2 nitrogen atoms dominates in the spectrum. Compounds containing 1 nitrogen atom were detected too but they are less abundant. In the negative ESI mode the compounds containing from 2 to 4 oxygen atoms were detected. Also, we used recently developed in-ESI source Hydrogen/Deuterium exchange approach for the structural characterization of the individual molecules. We observed the 1 H/D exchange for major O_3 compounds and did not observe H/D exchange for almost all O_2 compounds. Corresponding neutral molecules have 2 and 1 labile hydrogens and as a consequence –OH groups respectively.

1. Introduction

The birch tar is known to humankind since the Stone Age. It is widely used in traditional medicine as disinfectant, mosquito repellent, leather industry, agriculture etc. [1,2]. Birch tar is produced by heating the birch bark in the closed reactor without access of the air for several hours at the temperature around 200–300 °C. The previously performed investigation of the chemical composition of the birch tar revealed the presence of hundreds different compound [3]. This makes the wood tar a remarkable representative of the wide class of the natural complex organic mixtures. Fourier Transform Ion Cyclotron Resonance Mass-Spectrometry (FT ICR MS) [4–6] used with ambient ionization techniques (ESI, APPI and etc.) proved to be an important tool for the investigation of natural complex organic matter and the major attention received the investigation of the petroleum [7] and dissolved organic matter [8–11]. FT ICR allows identification of molecular weight and elemental composition, isolation, performing fragmentation and gas-phase reaction of individual molecules [8–10,12–15]. The FT ICR spectrum of natural complex organic mixtures contains thousands of peaks therefore visual analysis of the spectrum is usually performed using the Kendrick mass defect diagram and the Van Krevelen Diagram [13,16]. Only recently, the increasing interest in the biofuels have stimulated the investigation of the essential oils [17] and wood pyrolysis products using FT ICR [18,19].

Previously several groups have presented a simple approach for structural characterization of the individual compounds of the complex mixture by using isotope exchange reaction [20–22]. Indeed, hydrogen atoms from functional groups (–OH and –COOH) can be easily replace for deuterium simply by dissolving the substance in the D_2O and by use of the high resolution mass spectrometry the number of such groups in each molecule can be enumerated [23–29]. Oxygen atoms from keto-, aldehyde and carboxyl groups can be enumerated using acid catalyzed $^{16}O/^{18}O$

* Corresponding author at: Skolkovo Institute of Science and Technology Skolkovo Innovation Center, Building 3, Moscow 143026, Russia.
E-mail address: ennikolaev@rambler.ru (E. Nikolaev).

http://dx.doi.org/10.1016/j.ijms.2016.03.012
1387-3806/

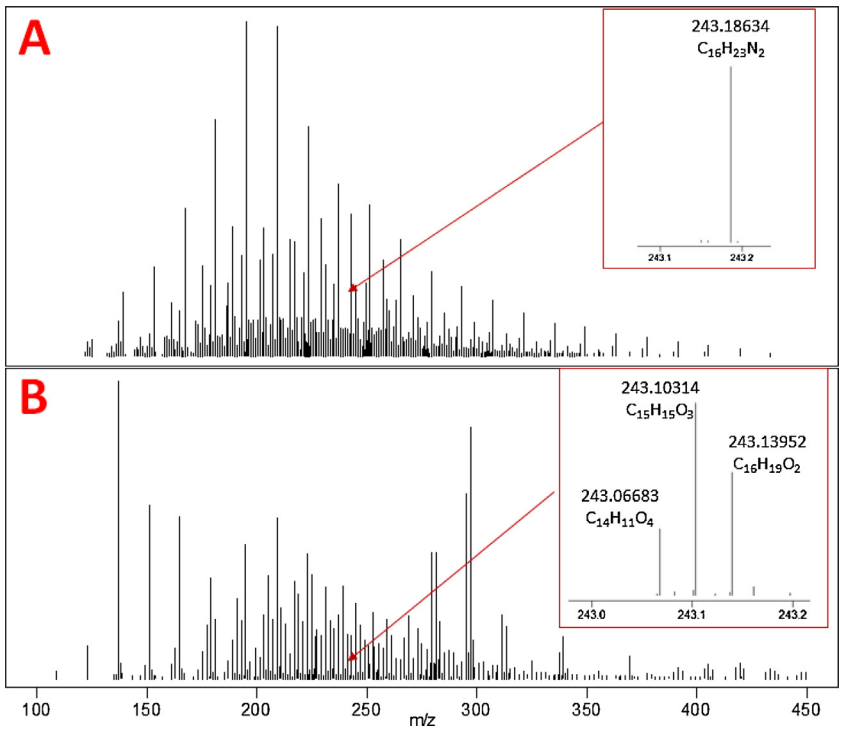

Fig. 1. The FT ICR spectrum of the birch tar. (A) positive ESI mode, (B) negative ESI mode. Temperature of the desolvating capillary was equal to the 200 °C.

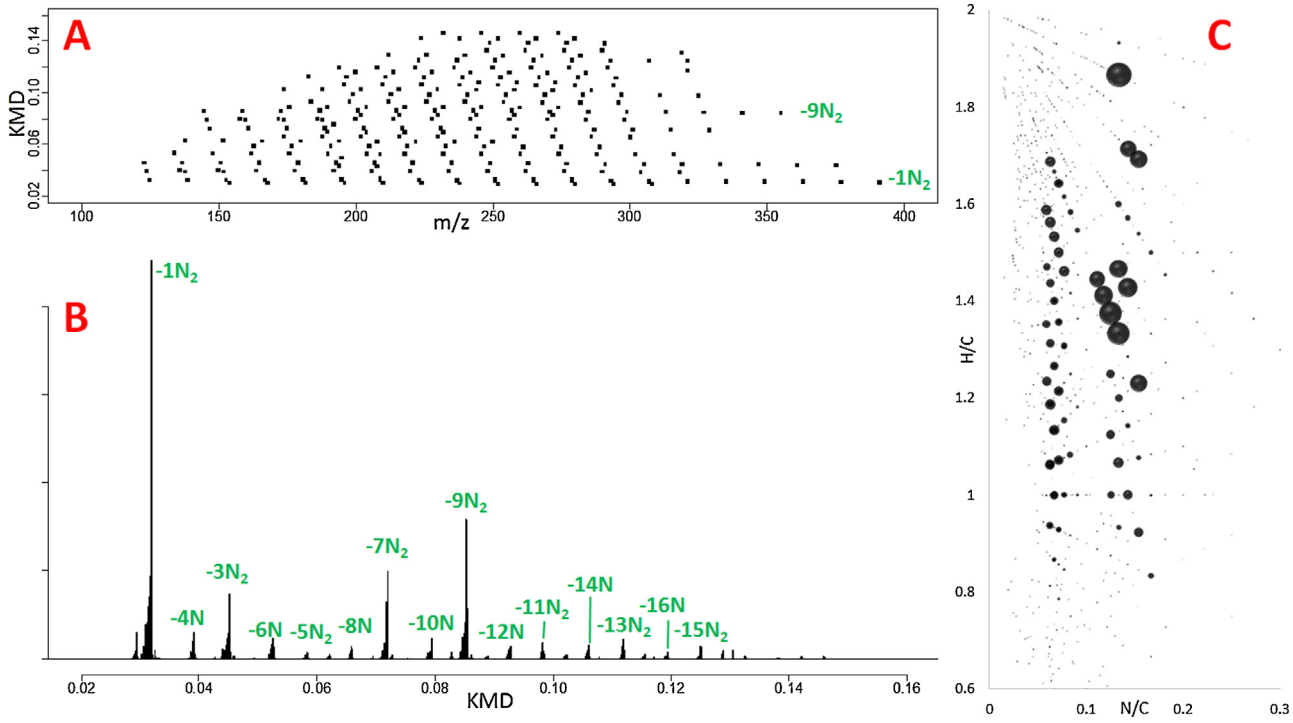

Fig. 2. The visual analysis of the positive ESI FT ICR spectrum of the birch tar. (A) Kendrick mass defect diagram, (B) weighted Kendrick mass defect histogram. Temperature of the desolvating capillary was equal to the 200 °C. (C) the Van Krevelen diagram. The size of the bubble correspond to the intensity of the peak.

exchange [30,31]. The number of active –CH hydrogens also can be enumerated using acid or base catalyzed H/D exchange [32,33].

Here we report the use of the Hydrogen/Deuterium exchange performed in the ESI source coupled with the ultrahigh resolution mass spectrometry for the investigation of the chemical composition of birch tar.

2. Methods

2.1. Samples and instruments

The birch tar was purchased from the “Biolit” company. D_2O was purchased from “Neogaz” company. Other chemicals were