## Combination of high resolution mass-spectrometry (FT-ICR) and nuclear magnetic resonance (NMR) for analysis of mumijo (shilajit)

<u>Gleb Vladimirov</u><sup>1</sup>, Anton Grigoryev<sup>1,5</sup>, Alexey Kononikhin<sup>1,2</sup>, Norbert Hertkorn<sup>4</sup>, Andrey Konstantinov<sup>3</sup>, Irina Perminova<sup>3</sup>, Igor Popov<sup>1,2</sup>, Eugene Nikolaev<sup>1,2</sup>

<sup>1</sup>Institute For Energy Problems of Chemical Physics RAS, Moscow, Russia

<sup>2</sup>Institute of Biochemical Physics RAS, Moscow, Russia

<sup>3</sup>Lomonosov Moscow State University, Moscow, Russia

<sup>4</sup>Helmholtz-Zentrum Muenchen-German Research Center for Environmental Health, Munich, Germany

<sup>5</sup> Institute for Systems Analysis RAS, Moscow, Russia

Native Mumijo is a blackish-brown exudation, of variable consistencies, obtained from steep rocks of different formations found in the Himalayas at altitudes between 1000-5000 m, from Arunachal Pradesh in the East, to Kashmir in the West. Mumijo also is found in other mountain ranges of the world, e.g. Afganisthan (Hindukush, Badakh-Shan), Australia (Northern Pollock Ranges), and in the former USSR (Tien-Shan, Pamir, Caucasus, Ural). There are several regional synonyms for mumijo, the second-most common one being Shilajit (in Sanskrit "destroyer of weakness") [1]

Currently available methods based on mass spectrometric study of complex mixtures (crude oil, humic substances) allow to characterize the sample by determining the molecular formulas for mixture components based on exact mass measurement. [2]. However, this analysis will be more effective if we supplement the mass-spectrometric data with quantitative and structural information obtained by NMR [2].

Altai mumijo sample in the form of food supplement "Purified Altaj mumijo" produced by Company "Evalar" was studied. In-house software «Transhumus» was used for data processing.

In addition to brutto formulas of the components of the sample, FT-ICR mass spectrometry allows to obtain information on regular structures and building blocks of the mixture by the mass difference statistics analysis. Comparison of this structural information with quantitative NMR structural information may be used to validate the semi-quantitative data from FT-ICR spectra, and also to assess the ionization efficiency of different components of the mixture.

**Results:** 

1) Part of total ion current corresponding to ions of NMR structural units series and corresponding to structural units series for mass differences statistic was determined. Abundance of structural groups discovered by NMR and by mass difference statistics was compared

2) NMR structural groups and component formulas from mass-spectrometric data were used to construct a graph of structure-group relationships for components of the complex mixture. Connectivity degree of the graph was estimated, and possible explanation of observed graph structure was given.

[1] Suraj P. Agarwal, Rajesh Khanna, Ritesh Karmarkar, Md. Khalid Anwer and Roop K. Khar Phytother. Res. 21, 401–405 (2007)

[2] Hertkorn N., M. Meringer, R. Gugisch, C.Ruecker, M. Frommberger, E. M. Perdue, M. Witt ,Ph. Schmitt-Kopplin, Bioanal. Chem. (37), 389, 1309-1310 (2007)