

IMPROVEMENTS IN PEAK CAPACITY OF AND MOLECULAR FORMULA ASSIGNMENT TO FTICR MS DATA ATTAINED ON FRACTIONS OF HUMIC ACIDS

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Humic substances (HS) are complex mixtures formed during decay of plant and animal residues. HS are operationally classified into fulvic acid (FA) and humic acid (HA) fractions according to their solubility in weak acids and bases: HA precipitates at pH < 1–2 and represents higher molecular weight, carbonized fraction of HS, while FA is more oxygenated, lower molecular weight fraction of HS. Ultrahigh resolution FTICR mass spectrometry is the most powerful tool for complex mixtures analysis and its use can be particularly advantageous for revealing differences between HA and FA on the level of molecular formulas. It is known in the art that the FTICR MS spectra of HA are much more depleted in peaks as compared to FA, which can contain thousands of peaks in the same mass range. The goal of this research was to maximize peak capacity of and to improve molecular formula assignment to FTICR data on HA fractions from different sources

FT ICR mass spectra were acquired using 7 Tesla ESI LTQ FT (Thermo Fisher). Selected ion monitoring (SIM) and narrow mass scanning was implied to improve sensitivity and resolution of FTICR data. HA from different sources (river and peat) as well as corresponding FA and non-fractionated dissolved organic matter (DOM)) were used as humic samples. 1:4 water-acetonitrile solution was used to prepare solutions of humic samples at 25 mg/l. Kendrick mass plots, van Krevelen diagrams and total mass difference statistics (TMDS) were used to define best descriptors for HA data. Self-made FIRAN software was used for mass spectra processing.

It was found that electrospray ionization efficiency of the humic fractions studied differed significantly in positive and negative ionization modes. Major part of FA seemed to be ionized with negative mode, whereas HA were much better ionized upon using positive mode. This was observed for the humic samples from all sources studied. This observation was confirmed by determination of elemental compositions based on molecular formulas assigned to the obtained FTICR MS data. The elemental compositions determined from mass spectra acquired in negative ESI mode and from direct elemental analysis data were in good agreement for FA, but differed greatly in case of HA.

Most of negative ions were deeply oxidized, depleted with hydrogen and enriched with double bonds (C=C and C=O). Positive ions seemed to be provided by pretty saturated and less oxidized structures (lower O/C ratio). The differences in O/C and H/C ratios between HA and FA fractions could be visualized using the van Krevelen diagrams but they are getting obvious only upon plotting both positive and negative ions on the same diagram. A use of a single ionization mode led to reduced number of detected ions (especially in case of peat HA) and yielded smaller differences in average O/C and H/C ratios.

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