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## ACCEPTED MANUSCRIPT

## On-line electrochemistry/electrospray ionization mass spectrometry (EC-ESI-MS) system for the study of nucleosides and nucleotides oxidation products

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#### Highlights

- Electrochemical oxidation of nucleosides, nucleotides was performed using EC-ESI-MS.
- Type, concentration, pH influences oxidation process in electrochemical cell and MS.
- Positive and negative ionization modes should be used to identify oxidation products.
- Urine analysis confirmed possibility of using EC-ESI-MS to simulate the metabolism.

#### Abstract

The main aim of present investigation was to study the oxidation products of nucleosides and nucleotides with the use of on-line electrochemistry/electrospray ionization mass spectrometry (EC-ESI-MS) system. The conditions applied in the system were optimized in complex manner, involving study of the impact of working electrodes or sample solvent on the oxidation of tested compounds and their ionization in mass spectrometry. Finally 5 mM of ammonium acetate was used selected and pH 3 was used for positive ionization mode, while pH 7 was applied for negative ionization in mass spectrometry. It was shown that utilization of both ionization modes is indispensable in order to detect and identify all of oxidation products. Furthermore the identification

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