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Supplementary information

TiO_2 nanocrystals - Assisted Laser Desorption and Ionization Time-of-Flight Mass Spectrometric Analysis of Steroid Hormones, Amino Acids and Saccharides. Validation and comparison of methods.

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Molecule Mm (g/mol)	Positive ion mode Calculated mass(g/mol)	Negative ion mode Calculated mass (g/mol)
E2, 272.4	407.6, molecule + $C_{10}H_{17}O$ - H_2O 423.6, molecule + $C_9H_{22}O$ - H_2O + Na^+ 439.7, molecule + $C_9H_{22}O$ - H_2O + K^+	328.9, molecule – H_2O + K^+ + Cl^-
T, 288.4	401.6, molecule + $C_8H_{18}O$ - H_2O + H^+ 423.6, molecule + $C_8H_{18}O$ - H_2O + Na^+	399.6, molecule + $C_8H_{18}O$ - H_2O - H^+
PRG, 314.5	315.5, molecule + H^+ 337.5, molecule + Na^+	313.5, molecule - H^+
L-Ala, 89.1	90.1, molecule + H^+ 112.1, molecule + Na^+ 128.2, molecule + K^+	88.1, molecule - H^+
L-Cys, 121.2	121.2, molecular ion 122.2, molecule + H^+ 144.2, molecule + Na^+ 167.1, molecule + $2Na^+$	120.2, molecule - H^+
DL-Met, 149.2	150.2, molecule + H^+ 172.2, molecule + Na^+ 188.3, molecule + K^+ 195.2, molecule + $2Na^+$	148.2, molecule - H^+
GSH, 307.3	308.3, molecule + H^+ 330.3, molecule + Na^+ 346.4, molecule + K^+ 353.3, molecule + $2Na^+$	306.3, molecule - H^+
D-(+)-Glu, 180.2	203.2, molecule + Na^+ 219.3, molecule + K^+	179.2, molecule - H^+
D-(+)-Malt, 342.3	365.3, molecule + Na^+	222.0, glucose unit - CHO + $2Cl^-$
β-CD, 1135.0	1158.0, molecule + Na^+ 1174.1, molecule + K^+	1134.0, molecule - H^+
Raff, 504.4	185.1, glucose unit - H_2O + Na^+ 203.2, glucose unit + Na^+ 365.3, maltose unit + Na^+ 384.3, molecule - glucose/fructose unit - $2H^+$ + Na^+ + K^+ 527.4, molecule + Na^+ 543.5, molecule + K^+	222.0, glucose unit - CHO + $2Cl^-$ 503.4, molecule - H^+
Ara, 150.1	173.1, molecule + Na^+ 189.2, molecule + K^+	149.1, molecule - H^+

Table S1: Identities of detected signals in SALDI TOF spectra with TiO_2 substrates.

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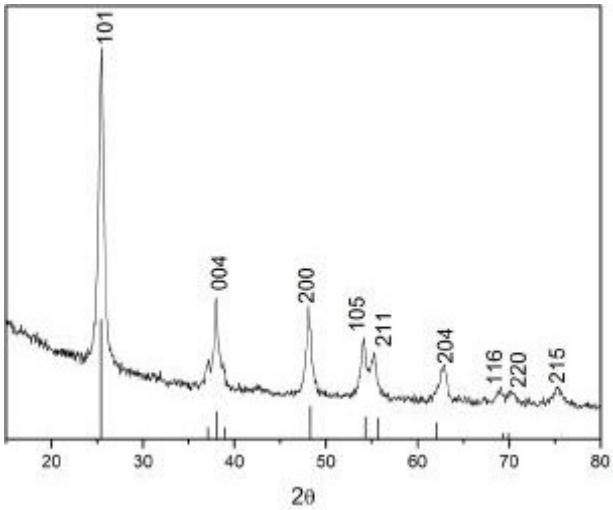

Figure S1: The X-ray diffraction pattern of TiO_2 prolate nanospheroids.

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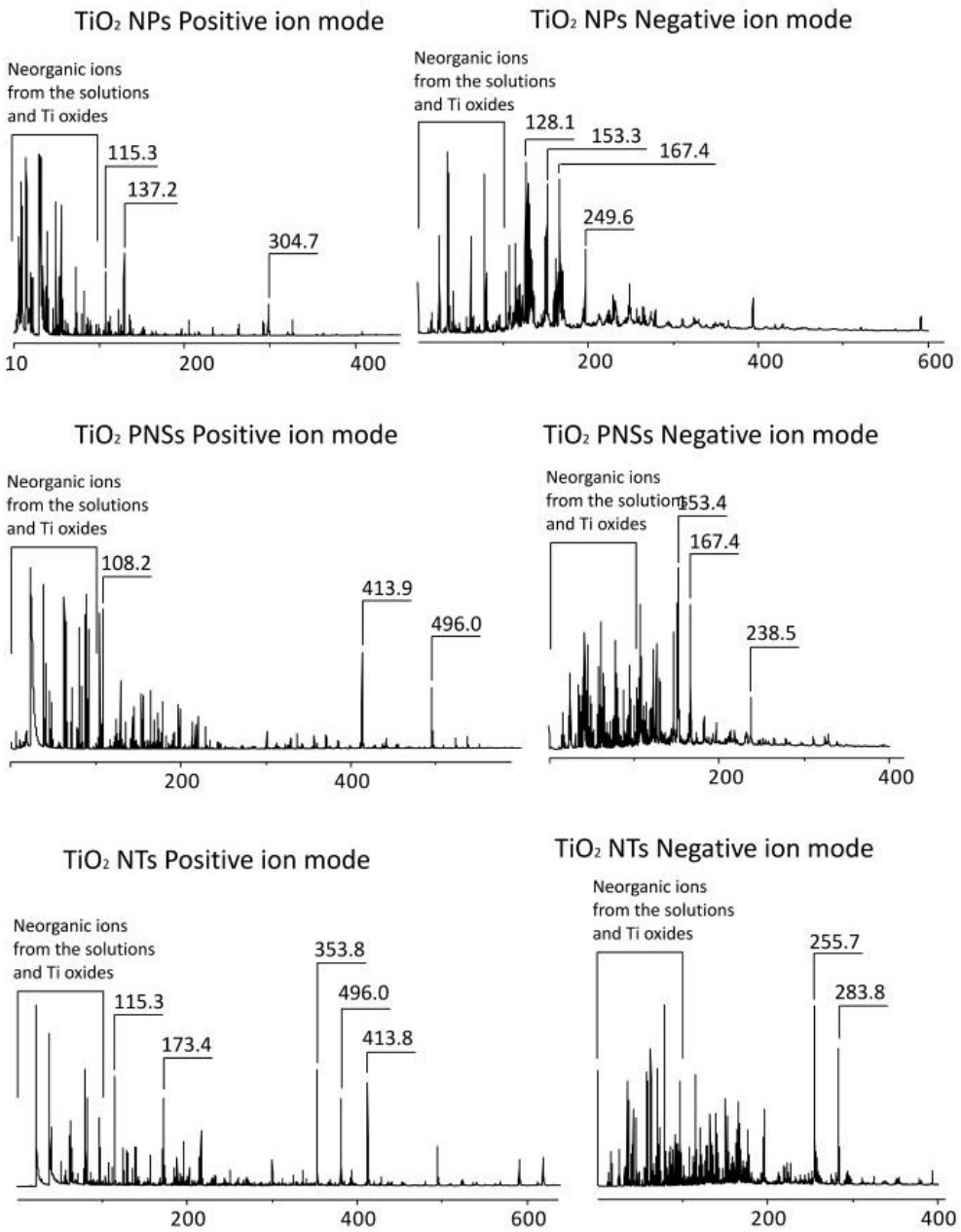

Figure S2: Positive and negative ion mode LDI TOF mass spectra of TiO_2 NPSs, TiO_2 PNs and TiO_2 NTs.

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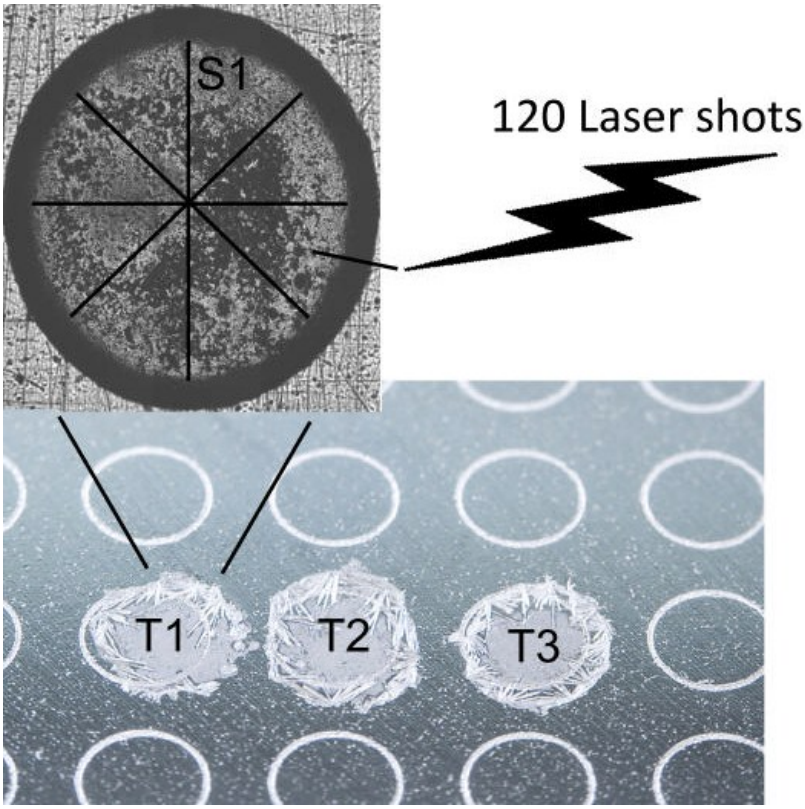

Figure S3: Illustration of experiment in which we tested the homogeneity of the system. One sample spot was divided into eight sectors (S1-S8). Each sector was shot with 120 lasers shots (in total, 960 shots per one spot) and each analyte/substrate combination was run in triplicate (T1, T2, T3). The same procedure was repeated for three consecutive days.

The overview of the statistics

The effects of different substrates (NPs, PNSs and NTs) on the S/N ratios of amino acids (L-Cys, L-Ala, DL-Met), tripeptide (GSH), hormones (E2, T, PRG) and carbohydrates (D-(+)-Glu, D-(+)-Malt, Raff, Ara, β-CD) were also investigates in order to test the possibility of potential use of substrates for quantitative analyses of small molecules. Overview of the results obtained by the statistical analysis of the obtained results is presented in Figure 2, using the box and whisker plots. The "box" contains the middle half of S/N data points (summary 72, data points per one combination of molecule with one substrate). Lines extending vertically from the boxes (whiskers) indicate variability outside the upper and lower quartiles. Box and Whiskers plots are very useful for descriptive comparison of detectability and precision of measurements of molecules with substrates and allow us to visually compare and select a pair(s) of molecule/substrate with the respect of goal that want to achieve.

For E2 with PNSs and NTs similar results were obtained, whereas PNSs gives a slightly higher S/N values and deviation than NTs for the major signal (*m/z* 407.6). Testosterone yielded the highest S/N values and deviations with NTs, very low S/N values with NPs, but with PNs it had the optimal parameters and very high S/N values with significantly smaller deviations in comparison to other two substrates.

NTs appeared to be the substrate of choice for the detection of PRG (*m/z* 337.5), L-Ala (*m/z* 112.1), GSH (*m/z* 330.3), and Ara (*m/z* 173.1) according to box and whiskers graphs with high S/N and low deviations. For L-Cys in the positive ion mode (*m/z* 144.2) the best substrate was NPs, and in the negative ion mode (*m/z* 120.2) PNSs. DL-Met had high S/N values and low deviations with PNSs for the peak at *m/z* 172.2. Therefore, PNS was the substrate of choice for the analysis of DL-Met. PNSs were also good substrate for the D-Glu, D-Malt, β-CD, and Raff considering the peaks at *m/z* 203.2, 365.3, 1158.0, and 365.3, respectively.

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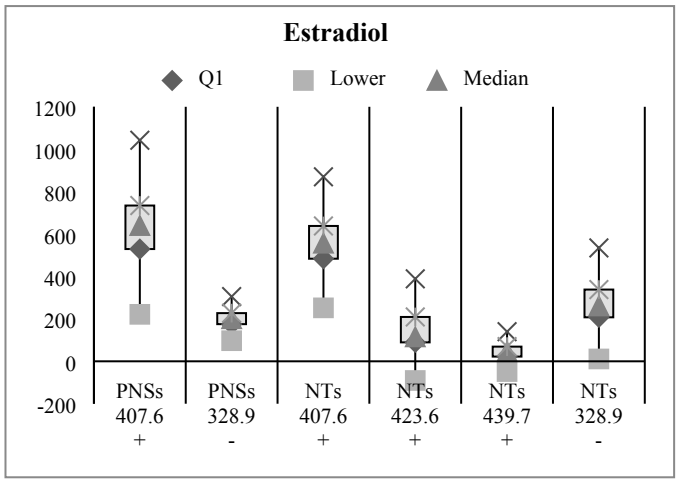

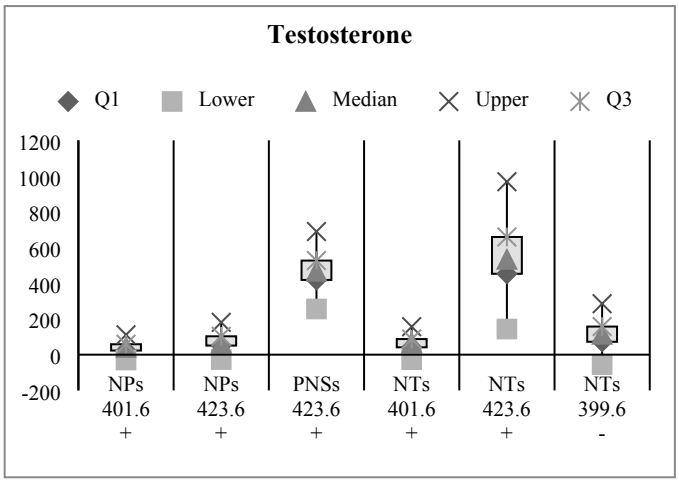

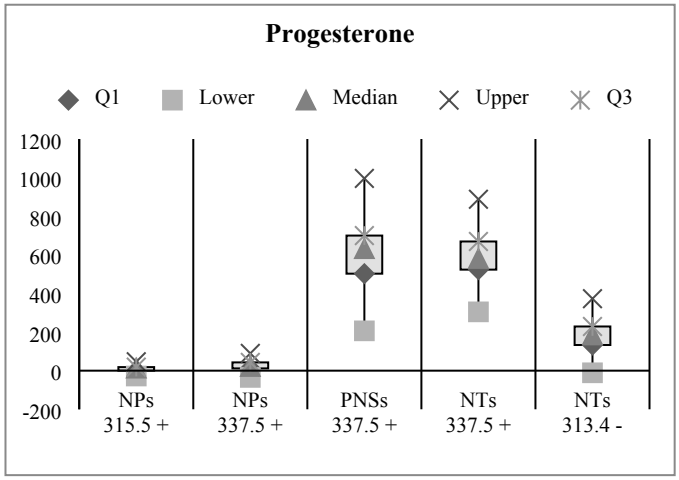

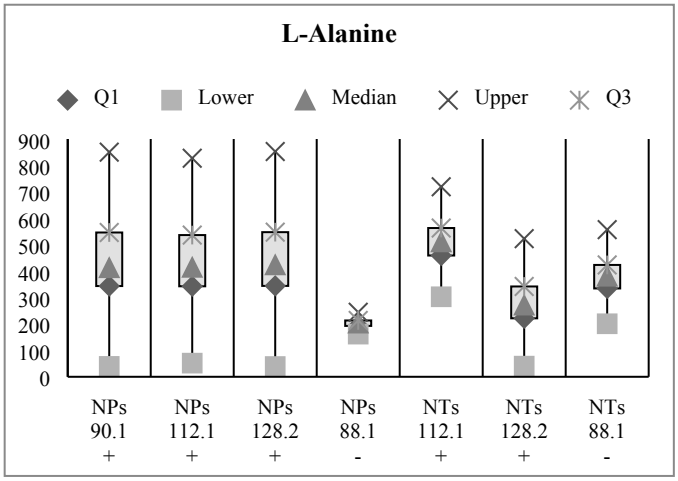

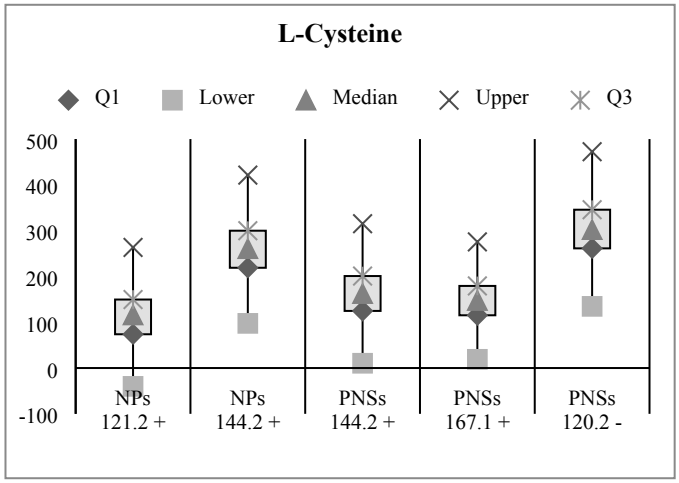

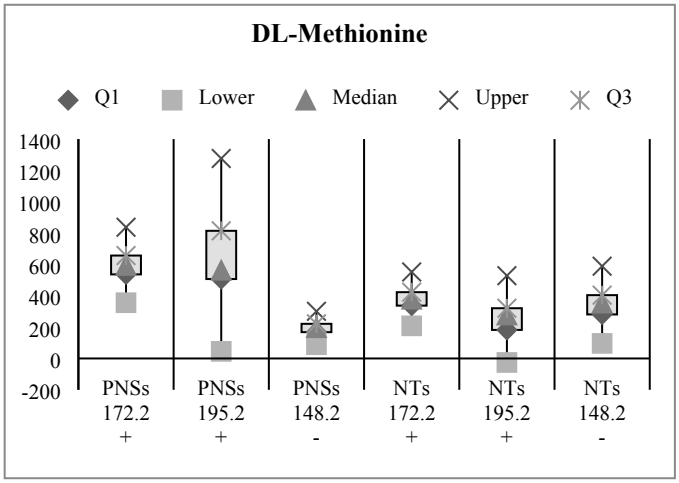

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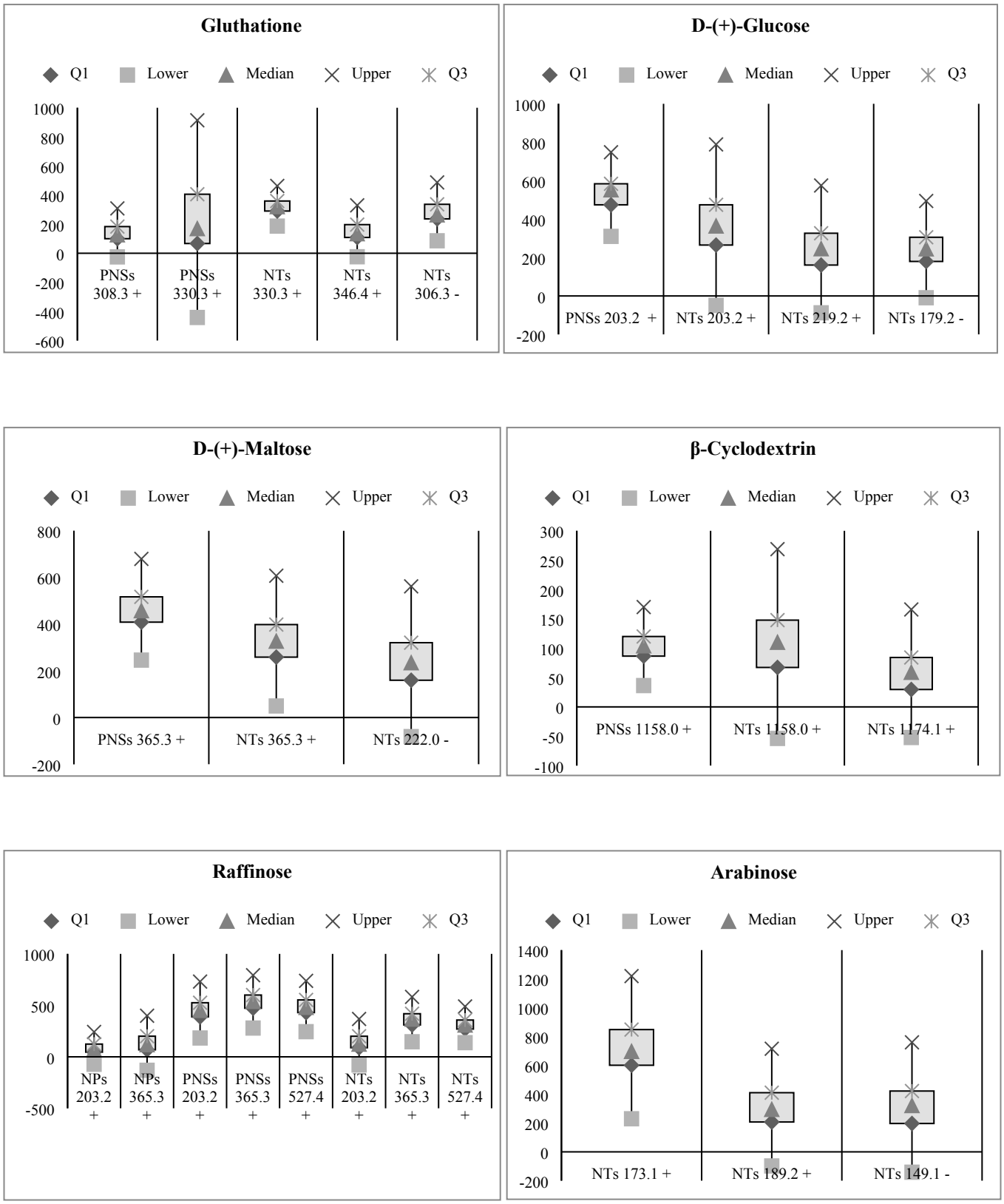

Figure S4: The Box and Whiskers plots for all combinations of molecules and substrates. All detectable signals in positive and negative ion mode, which are marked as "+" and "-", respectively, are presented. The “box” contains the middle half of S/N data points (summary 72, data points per one combination of molecule with one substrate).

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