Interference free detection for small molecules: Probing the Mn^{2+}-doped effect and cysteine capped effect on the ZnS nanoparticles for coccidiostats and peptide analysis in the SALDI-TOF MS

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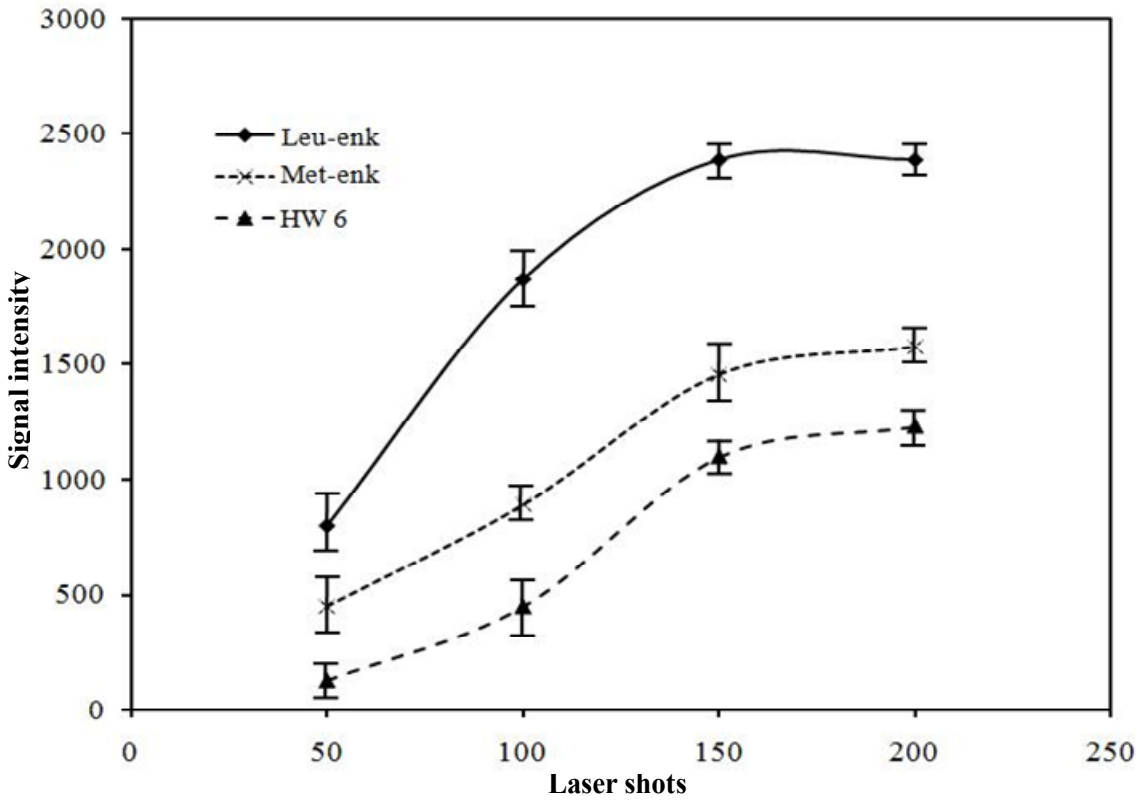

Figure S1. Effect of the signal intensity of the peptide mixtures (Leu-enk, Met-enk and HW6) with the number of laser shots by applying 64μJ laser fluence by using Mn^{2+}-doped ZnS@cysteine NPs as the matrix in the SALDI-TOF MS. The other conditions are same as those described in Figure 4.

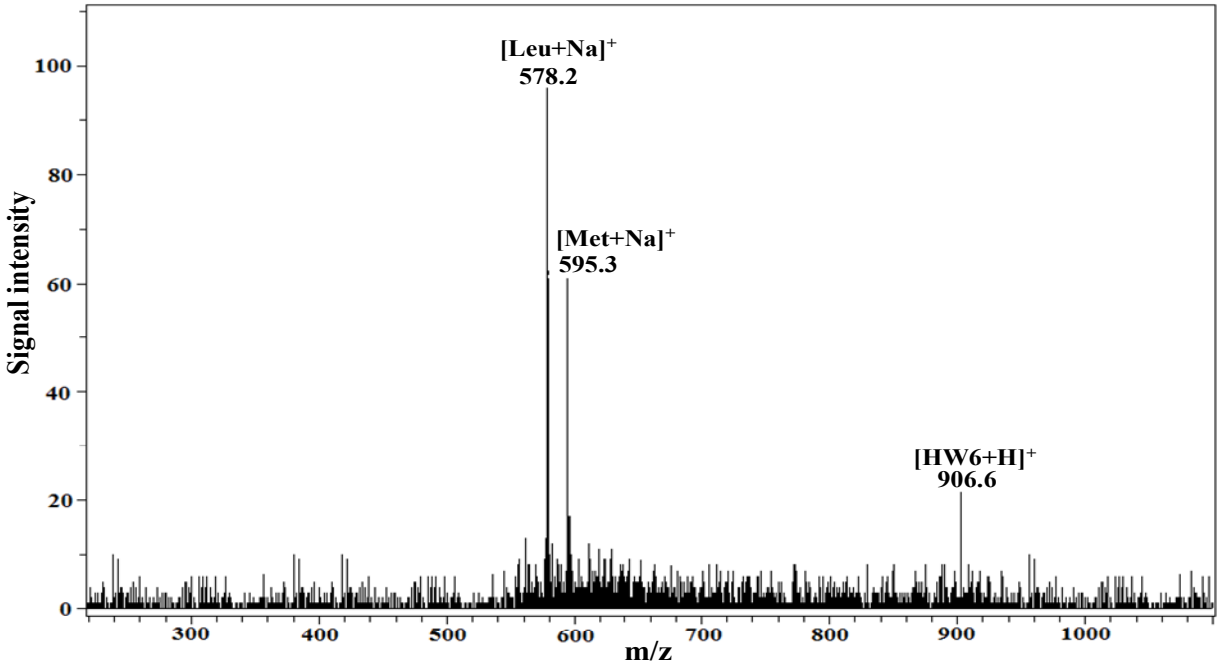

Figure S2. SALDI-TOF mass spectra of peptide mixtures (Leu-enk, 65 nM; Met-enk, 78 nM and HW6, 57 nM) by using the Mn^{2+}-doped ZnS@cysteine NPs as the matrix. The other conditions are same with those described in Figure 4.

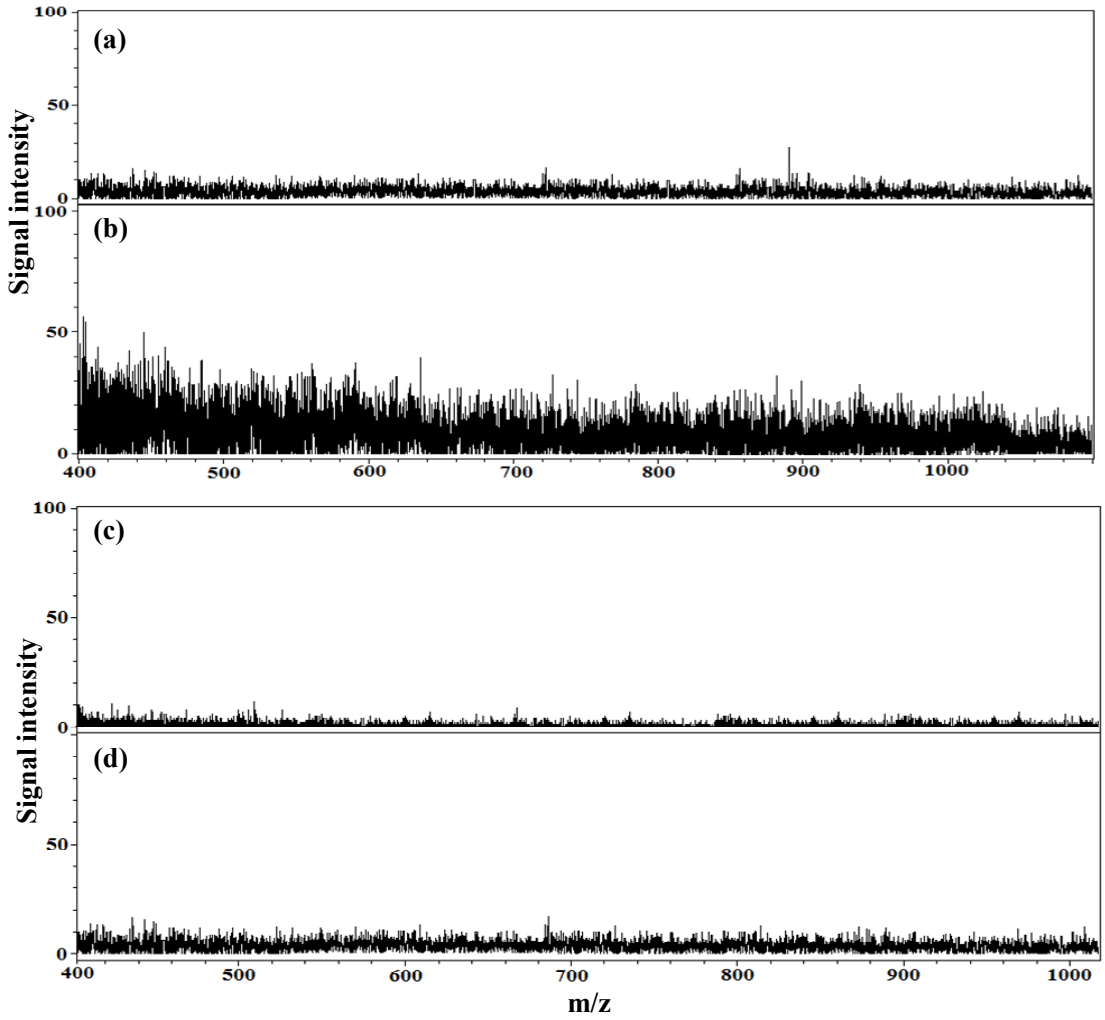

Figure S3. LDI-TOF mass spectra of (a) blank urine samples without NPs (b) blank extracts of egg samples without NPs (c) blank urine samples with the Mn^{2+}-doped ZnS@cysteine NPs as the matrix (d) blank extractes of egg samples with the Mn^{2+}-doped ZnS@cysteine NPs as the matrix. The mass spectra were generated at 200 pulsed laser shots by applying 64 μJ laser fluence.

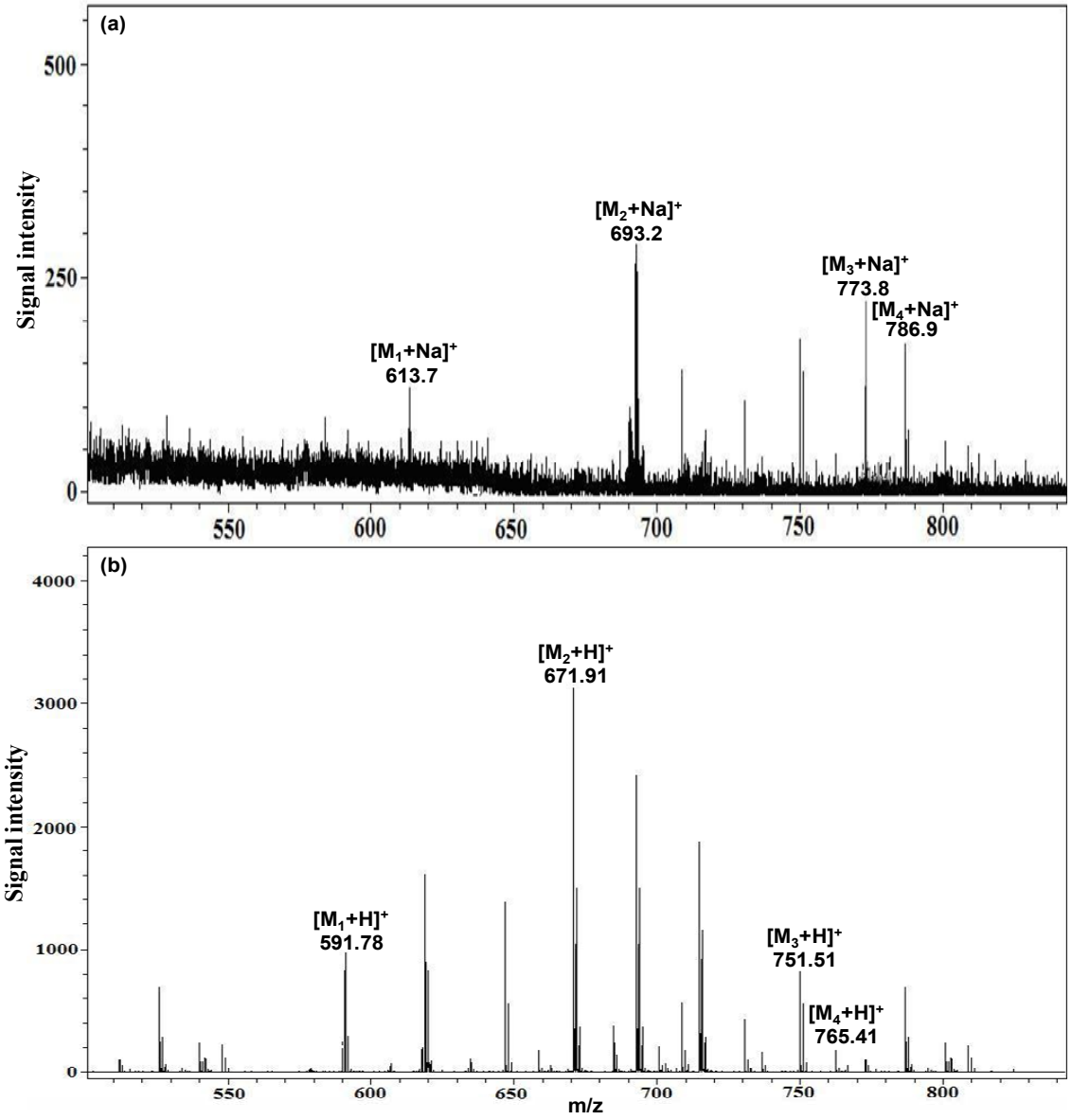

Figure S4. Mass spectra of mixtures of lasalocid (M_1, 250 nM), monensin (M_2, 1.79 μM), salinomycin (M_3, 0.26 μM) and narasin (M_4, 0.16 μM) obtained from aqueous solutions of (a) LDI-TOF MS (without using any matrix) (b) using CHCA as the matrix. Peak identities: *m/z* 613.7, 693.2, 773.8 and 786.9 are assigned as the $[M_1+Na]^+$, $[M_2+Na]^+$, $[M_3+Na]^+$ and $[M_4+Na]^+$. Mass spectra were generated at 200 pulsed laser shots by applying 64 μJ laser fluence.

Calculation of Mn^{2+}-doped ZnS@cysteine NPs concentration

Number of Mn^{2+}-doped ZnS@cysteine NPs and concentration of Mn^{2+}-doped ZnS@cysteine NPs were calculated by the reported methods.[S1 – S5] To calculate Mn^{2+}-doped ZnS@cysteine nanoparticle concentration, the average diameter of the particle is ~6.5 nm by TEM. The Mn^{2+}-doped ZnS particle having 2660 atoms per particle,[S5] in this particle 4 Mn atoms can be found in each ZnS particle.[S4-S5] Therefore, we can be calculated the number of surface atoms, N_s on a single Mn^{2+}-doped ZnS nanoparticle by using following equations

$N_s = 4\ N^{2/3}$
N is the number of the atoms ($ZnS:Mn^{2+}$) per nanoparticle
N_s is the number of the surface atoms

$N_s = 4 \times (2660)^{2/3}$

$N_s = 768$ $ZnS:Mn^{2+}$ atoms per nanoparticle

From the above calculations, the molecular weight (M_w) of a single nanoparticle can be calculated by using the relative molecular mass of the single Mn^{2+}-doped ZnS@cysteine ($M_{Mn^{2+}\text{-doped ZnS@cysteine}}$).

$M_w = M_{Mn^{2+}\text{-doped ZnS@cysteine}} \times N$

$M_w = 273.5 \times 2660$

$M_w = 727510$ Da

Calculation of the amount of nanoparticles (N_{NP}; 1.0 M of NPs) were formed when 1.0 M of $Zn(NO_3)_2.6H_2O$, 0.25 M L-cysteine, 0.01 M $Mn(NO_3)_2.4H_2O$ and 1.0 M $Na_2S.9H_2O$ solutions were mixed in the reaction flask; we can expect that 1.0 M of Mn^{2+}-doped ZnS@cysteine NPs could be produced from the above solutions.

Number of the Mn^{2+}-doped ZnS@cysteine particles in the solution is
$= 1 \times N_A$
$= 1 \times 6.022 \times 10^{23}$
$= 6.022 \times 10^{23}$

$N_{NP} = N_{atom}/N$
$N_{NP} = (6.022 \times 10^{23}) / (2660)$
$N_{NP} = 2.264 \times 10^{20}$ nanoparticles are formed from the above concentrations.

Hence, the final concentration of the Mn^{2+}-doped ZnS@cysteine NPs (C_{NP}) was estimated by dividing N_{NP} by Avagadro's number (N_A)

$C_{NP} = N_{NP} / N_A$

$C_{NP} = (2.264 \times 10^{20}) / (6.022 \times 10^{23})$

$C_{NP} = 0.3759 \times 10^{-3}$ mol

Reference

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