

Electronic supplementary information (ESI)

**Biomolecule analysis and cancer diagnostics by negative mode probe
electrospray ionization**

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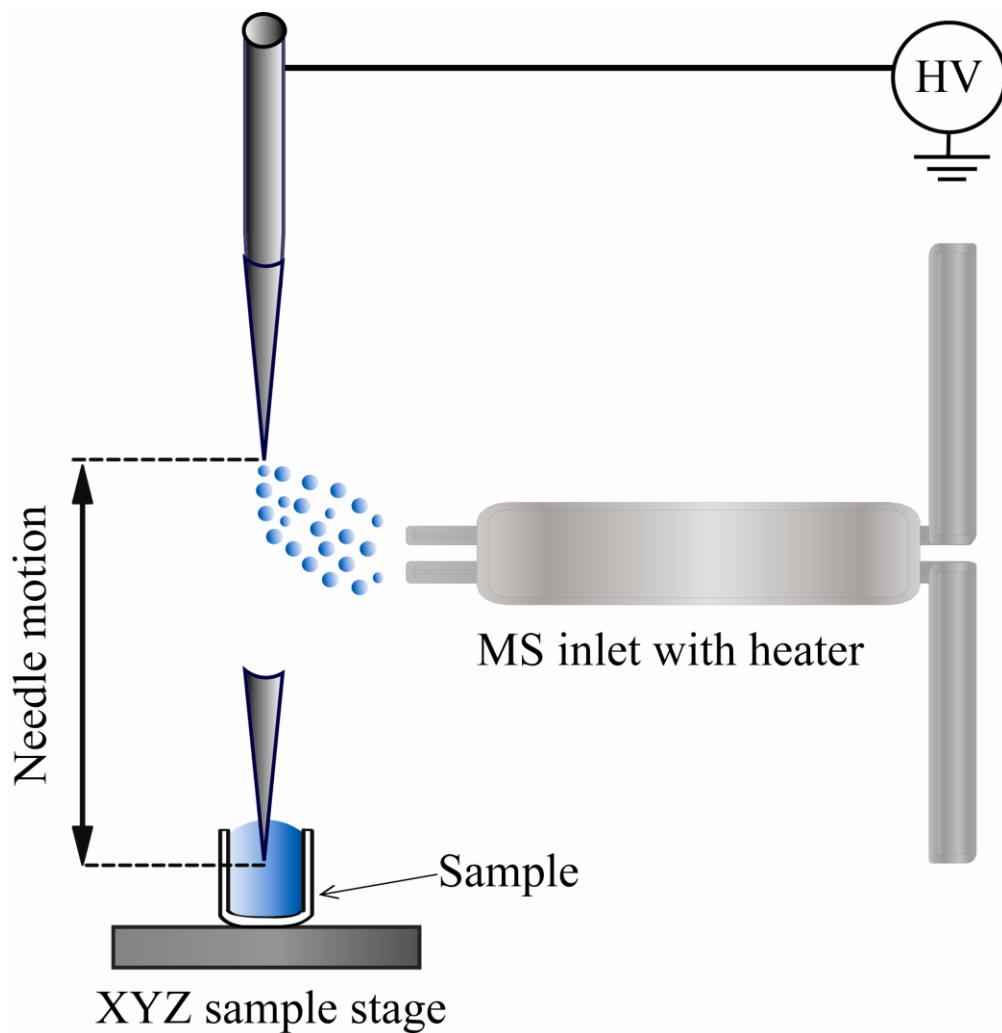
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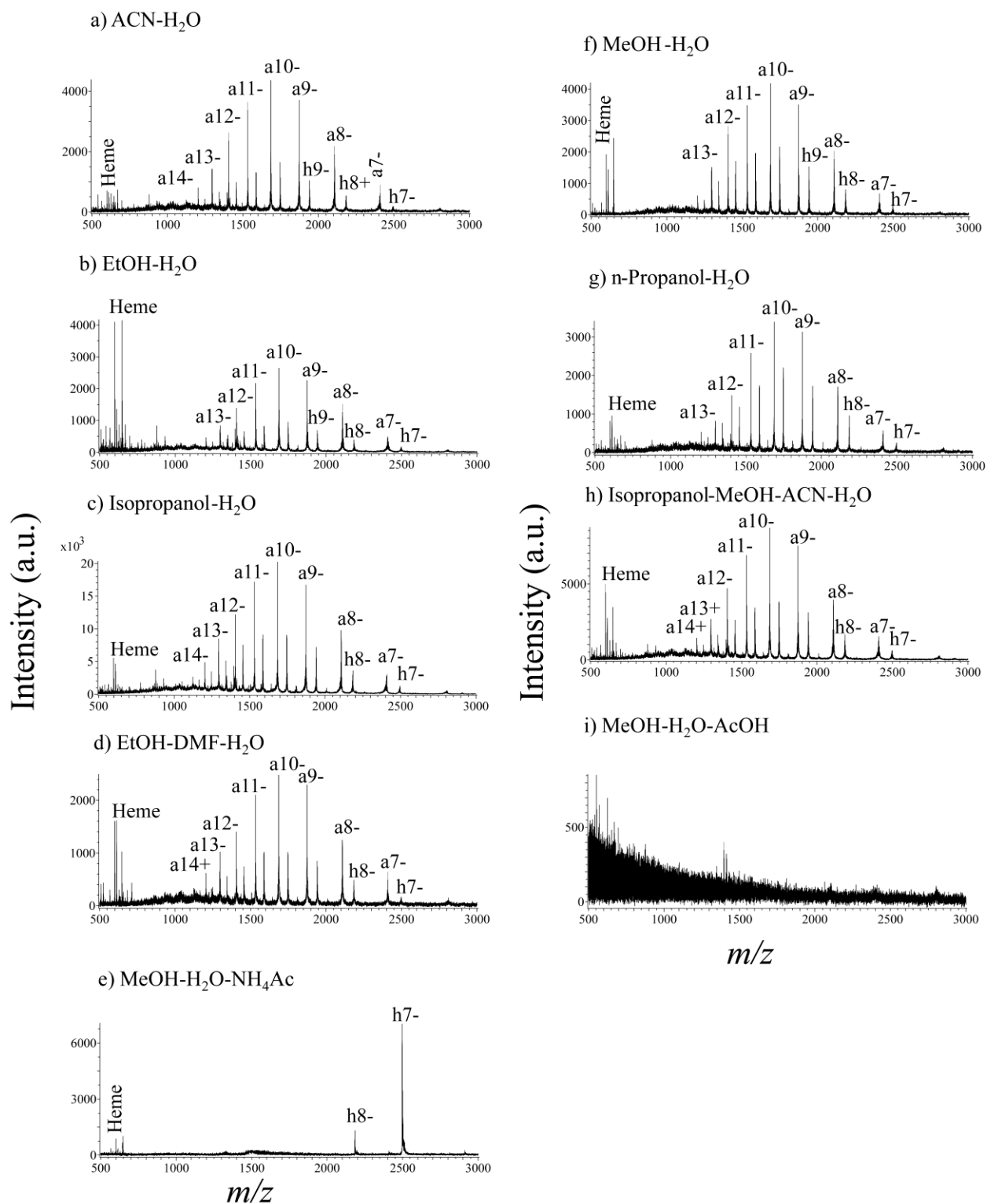
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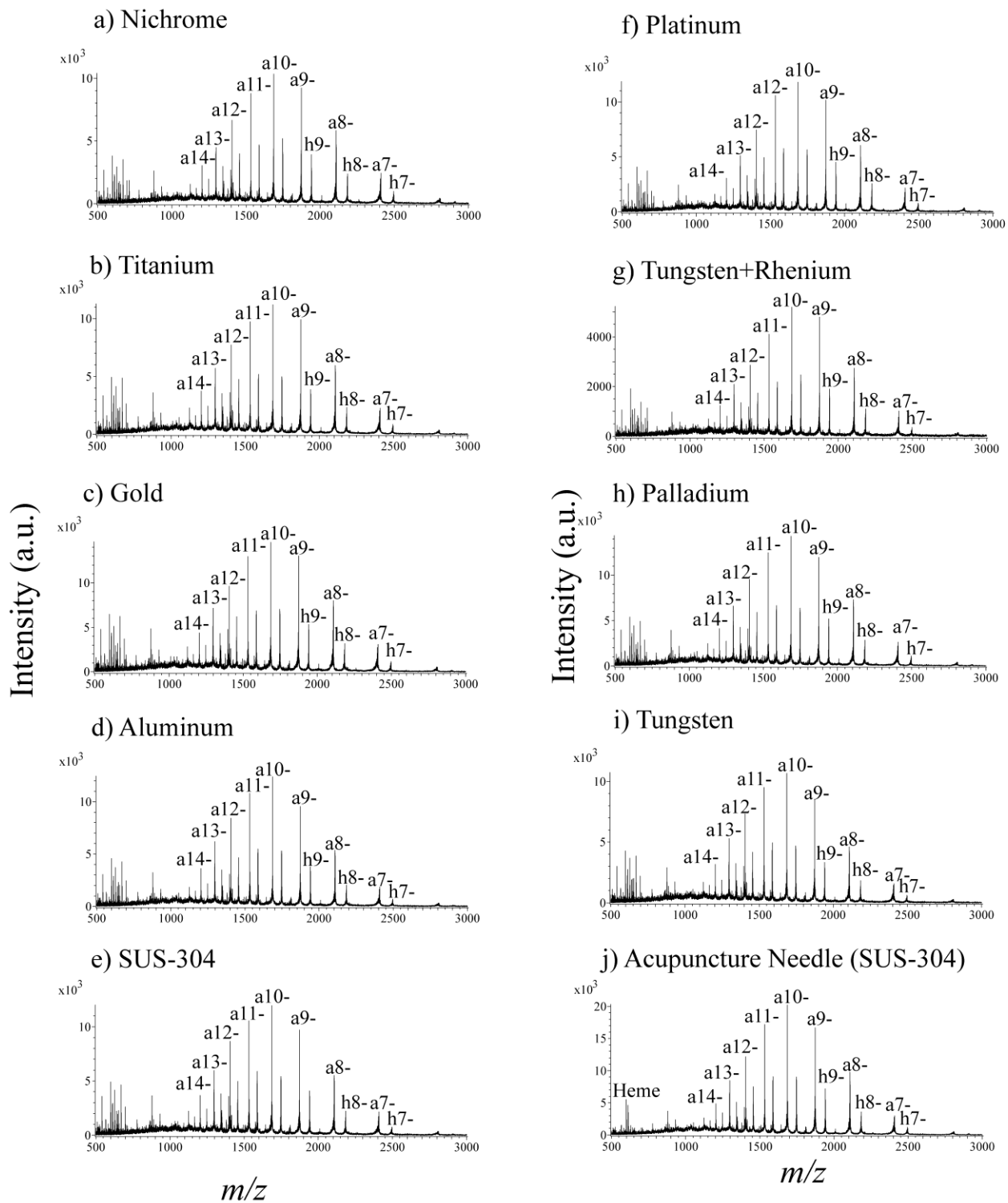


Electronic supplementary information Figure1 (ESI Fig. 1): Schematic of the PESI source with modified ion sampling capillary. The original ion sampling orifice is replaced with 5 cm custom made ion sampling capillary with inner diameter of 0.5 mm. The temperature is regulated by an external heater mounted on the ion sampling capillary.

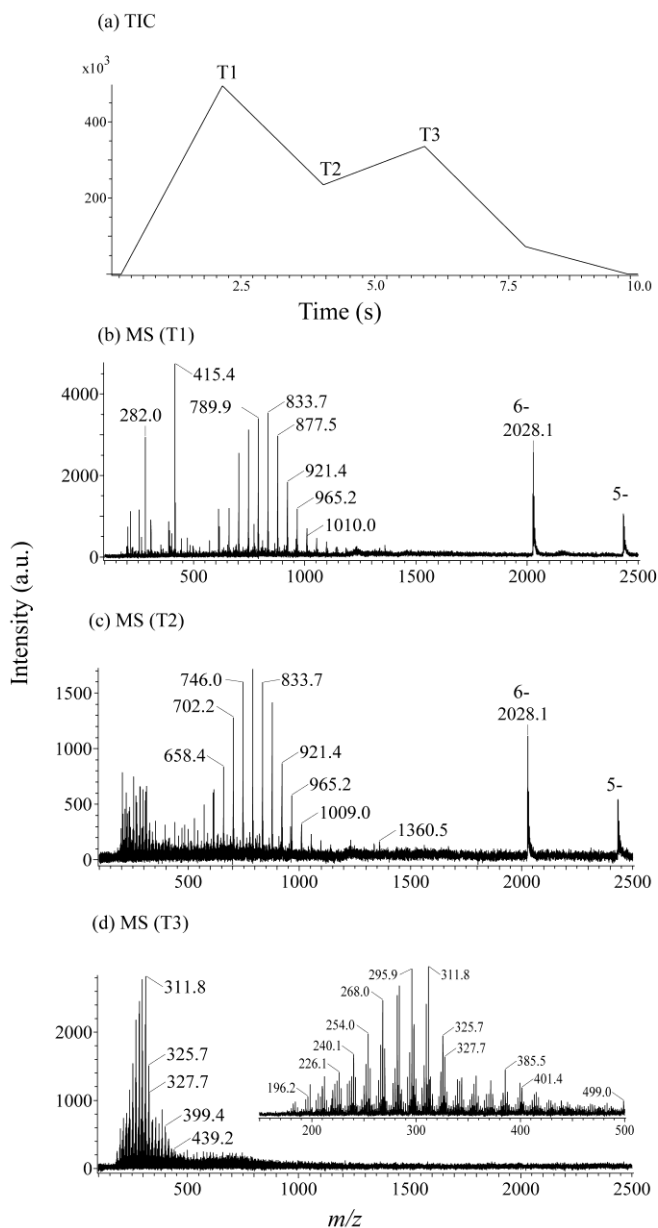


Electronic supplementary information Figure 2 (ESI Fig. 2): Negative mode PESI mass spectra of 10^{-5} M myoglobin using (a) ACN-H₂O (1/1), (b) EtOH-H₂O (1/1), (c) isopropanol-H₂O (1/1), (d) EtOH-DMF-H₂O (1/1/2), (e) MeOH-H₂O (1/1) in 10 mM NH₄Ac, (f) MeOH-H₂O (1/1), (g)

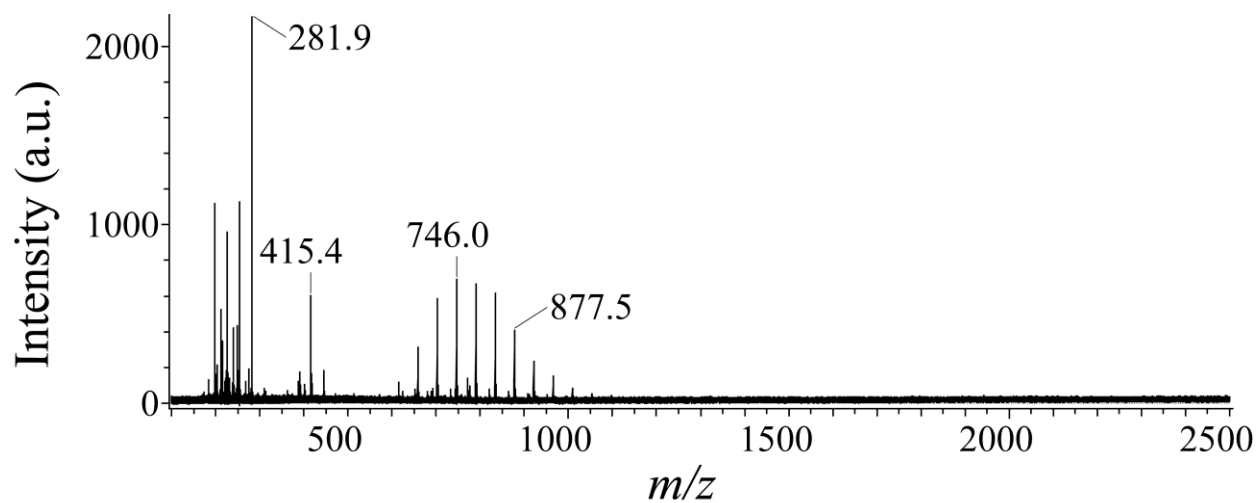
n-propanl-H₂O (1/1), (h) isopropanol-MeOH-ACN-H₂O (1/1/1/3) and (i) MeOH-H₂O-AcOH (50/49/1).



Electronic supplementary information Figure 3 (ESI Fig. 3): Negative mode PESI mass spectra of 10^{-5} M myoglobin using (a) nichrome, (b) titanium, (c) gold, (d) aluminum, (e) SUS-304, (f) platinum, (g) tungsten and rhenium (9/1), (h) palladium, (i) tungsten and (j) acupuncture needle (SUS-304) with sharp tip. Solvent: isopropanol- H_2O (1/1).



Electronic supplementary information Figure 4 (ESI Fig. 4): Negative mode PESI experimental results for 10^{-4} M Triton X100 and 10^{-5} M cytochrome c and 10 mM NH_4Ac in isopropanol- H_2O (1/1) solvent. Tangentially cut surface modified 0.5 mm Ti wire was used. (a) Total ion chromatogram (TIC); (b) mass spectrum at T1; (c) mass spectrum at T2 and (d) mass spectrum at T3.



Electronic supplementary information Figure 5 (ESI Fig. 5): Negative mode nanoESI experimental results for 10^{-4} M Triton X100, 10^{-5} M cytochrome c and 10 mM NH_4Ac in isopropanol- H_2O (1/1) solvent.