Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary Material

Polystyrene-Impregnated Paper Substrate for Direct Mass Spectro-metric Analysis of Proteins and Peptides in Complex Matrices

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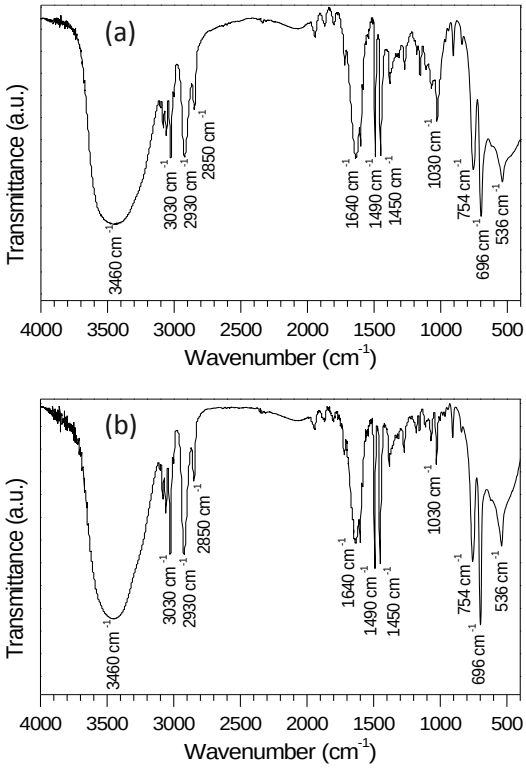

Figure S1. (a) FT-IR spectra of the collected product from the surface of PS-impregnated paper after baking at 180 °C for 30 min; (b) FT-IR spectra of PS microspheres from the reaction of 25 mL styrene, 1.0 g BPO and 1.0 g PVP in the presence of 80 mL ethanol.

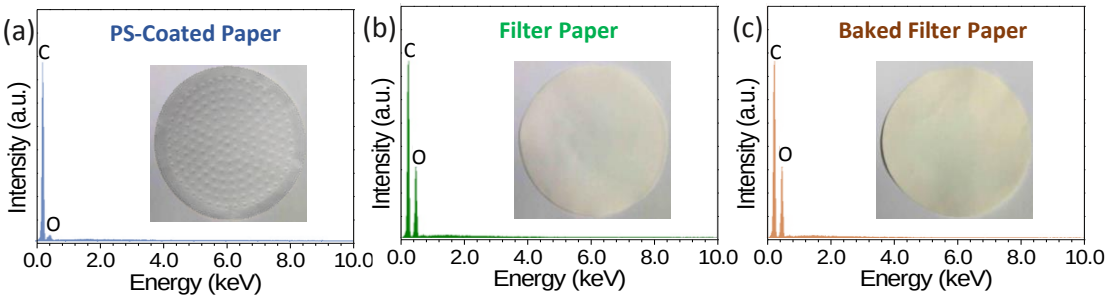

Figure S2. EDS analysis results of (a) PS-coated paper, (b) filter paper and (c) filter paper after baking at 180 °C for 30 min (the inserted parts in them are their corresponding photographic images).

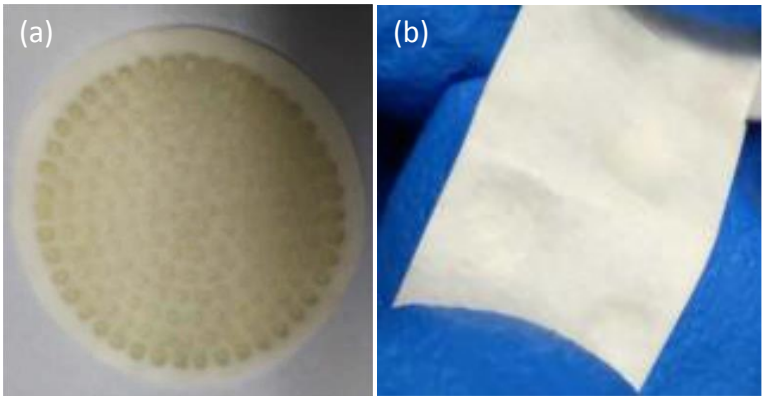

Figure S3. Photographic images of (a) obtained PS-impregnated paper and one piece of PS-impregnated paper during bending**.**

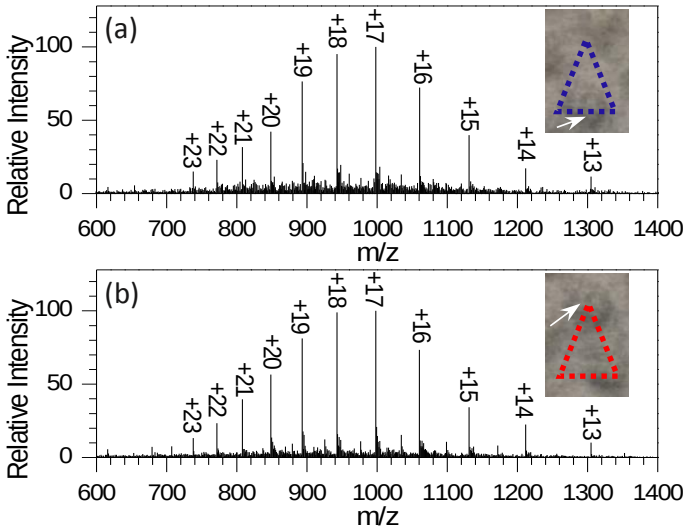

Figure S4. Mass spectra of myoglobin using PS-impregnated paper as substrate for paper spray mass spectrometry, in which the paper was cut into a triangle (a) with the paper tip far away from the generated dot formed in preparation as shown in the inserted photograph and (b) with the paper tip just inside the generated dot as shown in the inserted photograph (sample: 5 µL of 50 µg mL^{-1} myoglobin; spray solvent: 25 µL 1:1 methanol/water; spray voltage: 3.5 kV).

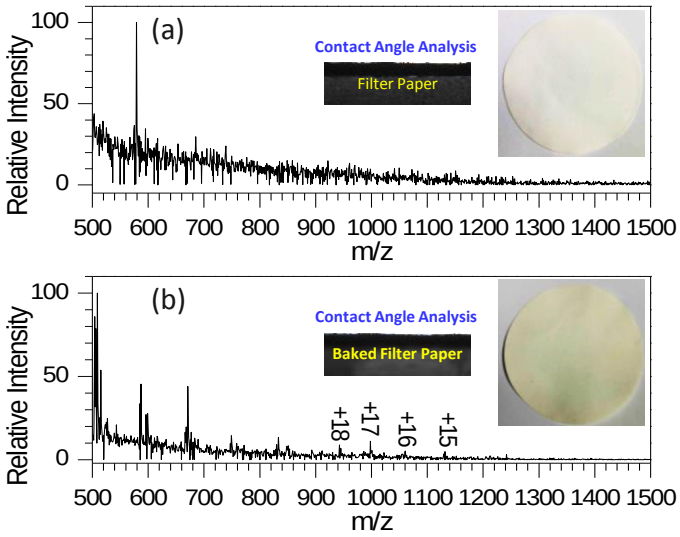

Figure S5. Mass spectra of myoglobin using filter paper (a) before and (b) after baking at 180 °C for 30 min as substrates for paper spray mass spectrometry (the inserted parts are their corresponding contact angle analysis and photographic image, respectively; sample: 5 µL of 50 µg mL^{-1} myoglobin; spray solvent: 25 µL 1:1 methanol/water; spray voltage: 3.5 kV).

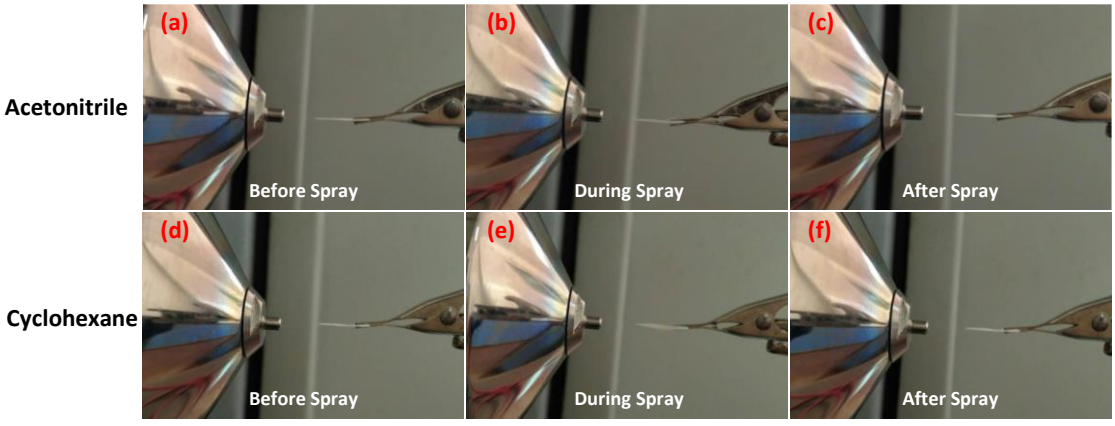

Figure S6. Photographic image of a PS-impregnated paper triangle placed on an ionization source (a) and (d) before spray, (b) and (e) during spray and (c) and (f) after spray using (a)-(c) acetonitrile and (d)-(f) cyclohexane as spray solvent (spray voltage: 3.5 kV).

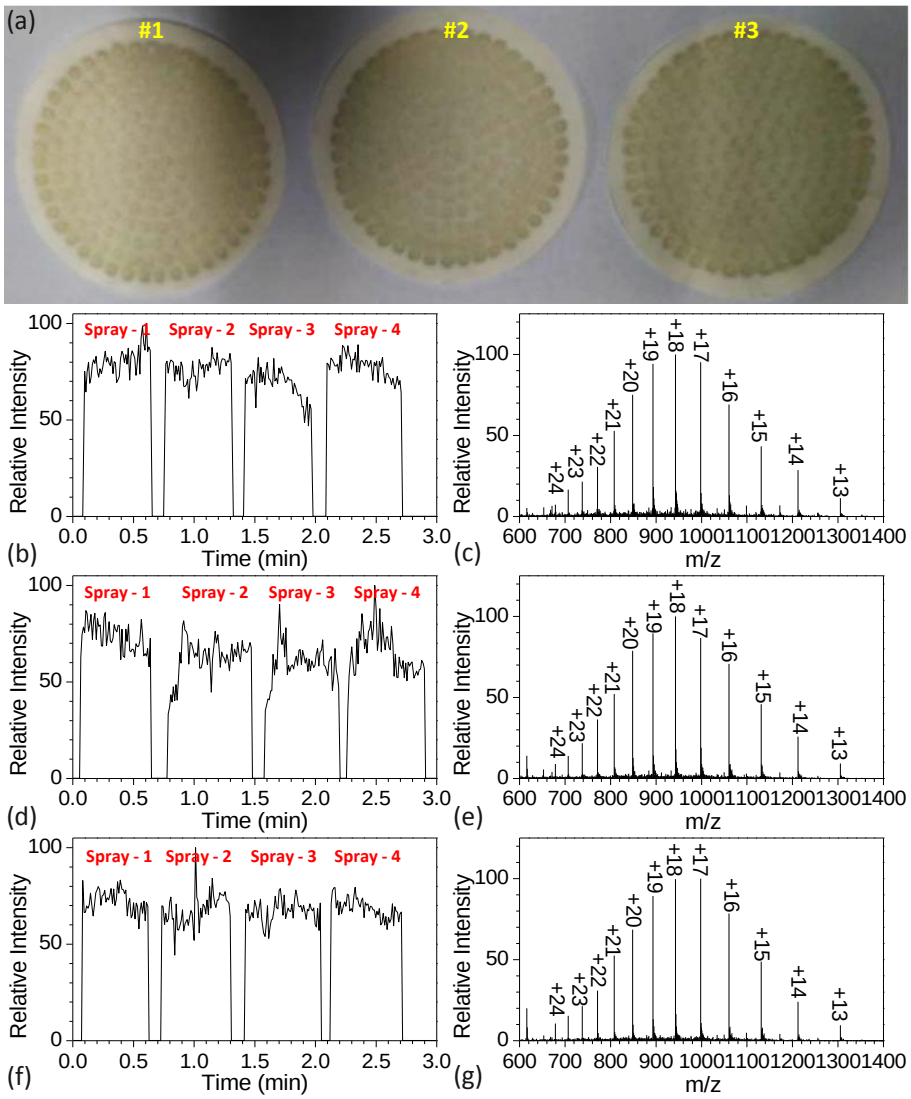

Figure S7. (a) Photographic image of three continuously prepared PS-impregnated papers; Total ion current chronograms (signal *versus* time) for the sequential analysis of myoglobin using (b) #1 paper, (d) #2 paper, (f) #3 paper as substrates for paper spray. Each peak in the chronogram was from the analysis of a different PS-impregnated triangle; (c), (e) and (g) Typical mass spectra of myoglobin using (b) #1 paper, (d) #2 paper, (f) #3 paper for paper spray, respectively (sample: 5 µL of 50 µg mL^{-1} myoglobin; spray solvent: 25 µL 1:1 methanol/water; spray voltage: 3.5 kV).

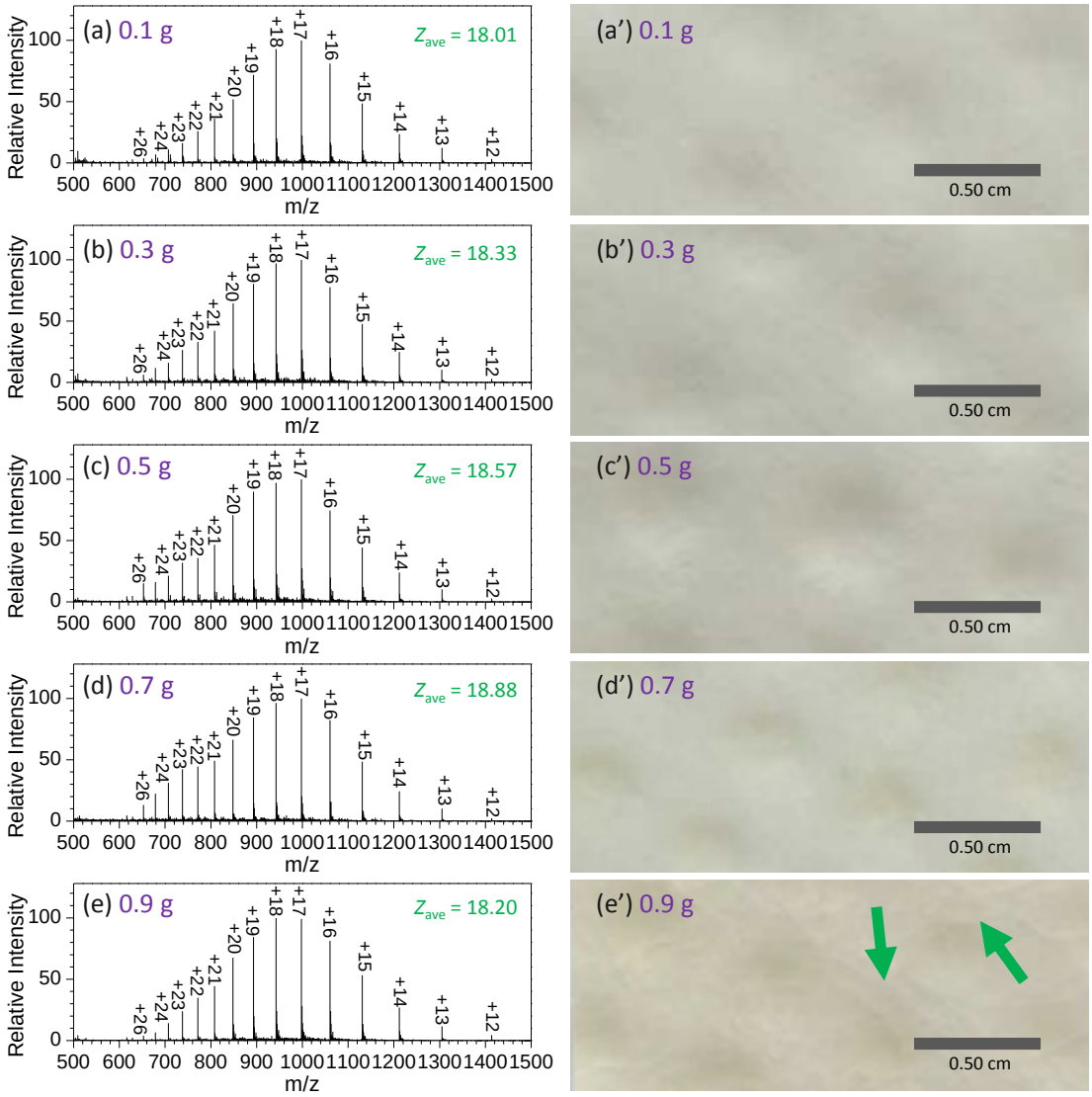

Figure S8. (a)-(d) Effect of coating amount of PS particles on the performance of generated paper substrates in analysis of myoglobin: (a) 0.1 g, (b) 0.3 g, (c) 0.5 g, (d) 0.7 g and (e) 0.9 g (Note: solution volume for coating: 100 mL; baking temperature and time: 180 °C for 30 min; sample: 5 µL of 50 µg mL^{-1} myoglobin; spray solvent: 25 µL 1:1 methanol/water; spray voltage: 3.5 kV); (a') – (e') Surface structures of the corresponding paper substrates as indicated in the figures.

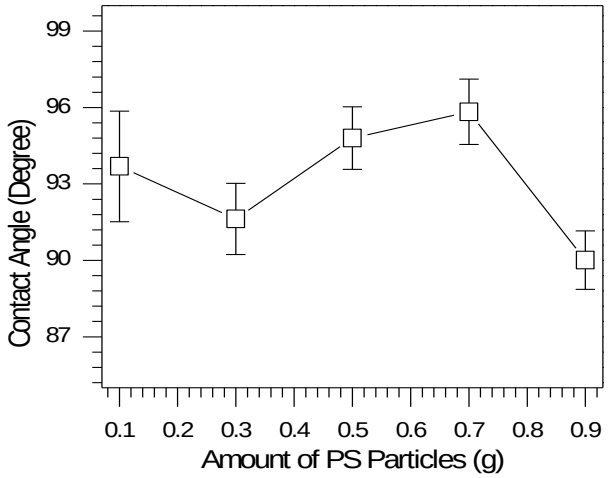

Figure S9. Correlation between the contact angle of water at the surface of obtained papers and the coating amount (0.1 – 0.9g) of PS particles for preparation of various PS-impregnated papers**.**

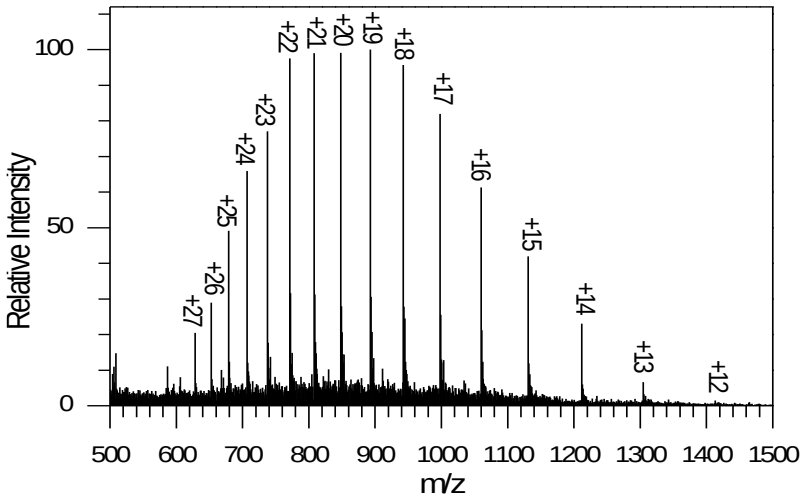

Figure S10. Mass spectra of myoglobin using PS-impregnated paper as substrate for paper spray (sample: 5 µL of 200 µg mL^{-1} myoglobin; spray solvent: 25 µL water; spray voltage: 3.5 kV).

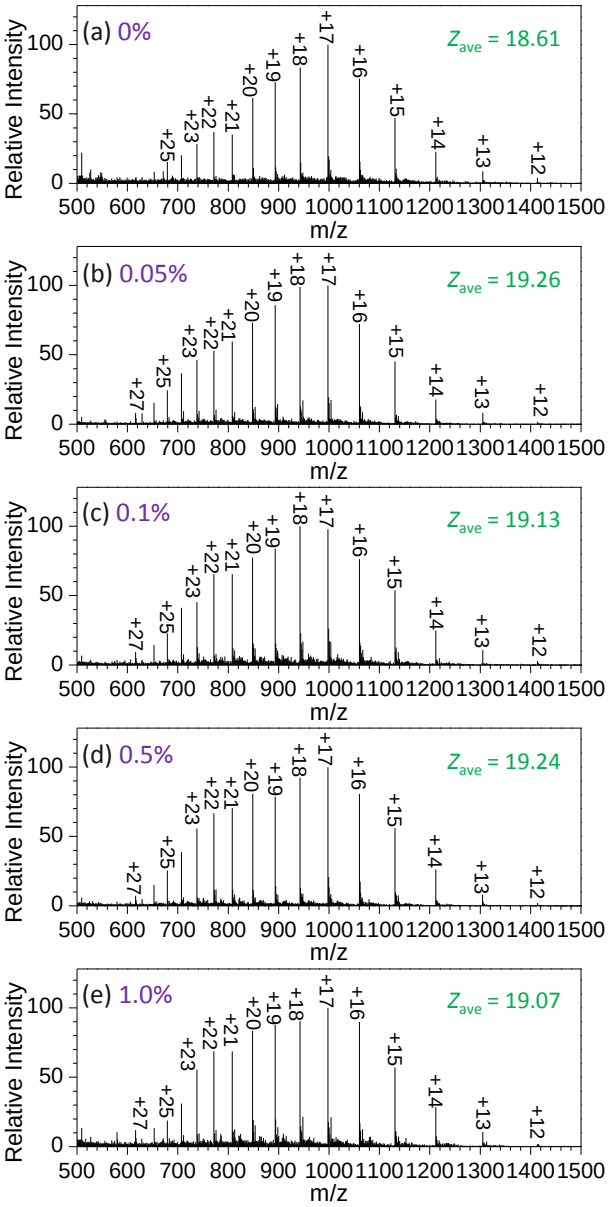

Figure S11. Effect of spray solvent (5:5 water/methanol) with different contents of acetic acid on the performance of paper spray in analysis of myoglobin using PS-impregnated paper: (a) 0%, (b) 0.05%, (c) 0.1%, (d) 0.5% and (e) 1.0% (Note: sample: 5 µL of 50 µg mL^{-1} myoglobin; spray solvent: 25 µL 1:1 methanol/water; spray voltage: 3.5 kV).

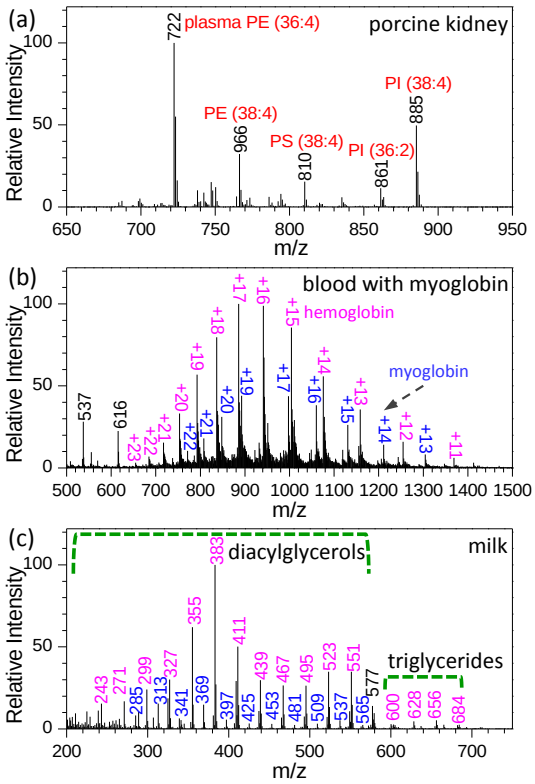

Figure S12. (a) Mass spectrum of tissue samples from the porcine kidney surface (plasma PE: plasmalogens; PE: glycerophosphoethanolamines; PS: phosphatidylserine; PI: phosphatidylinositol; spray solvent: 25 µL methanol; spray voltage: -3.5 kV); (b) Mass spectrum of bovine whole blood containing 200 µg mL^{-1} myoglobin (Note: The blood samples were diluted 100 times to decrease the viscosity; sample volume: 5 µL; spray solvent: 25 µL 1:1 methanol/water containing 0.5% acetic acid; spray voltage: 3.5 kV); (c) Mass spectrum of milk sample (sample volume: 25 µL; spray voltage: 3.5 kV).

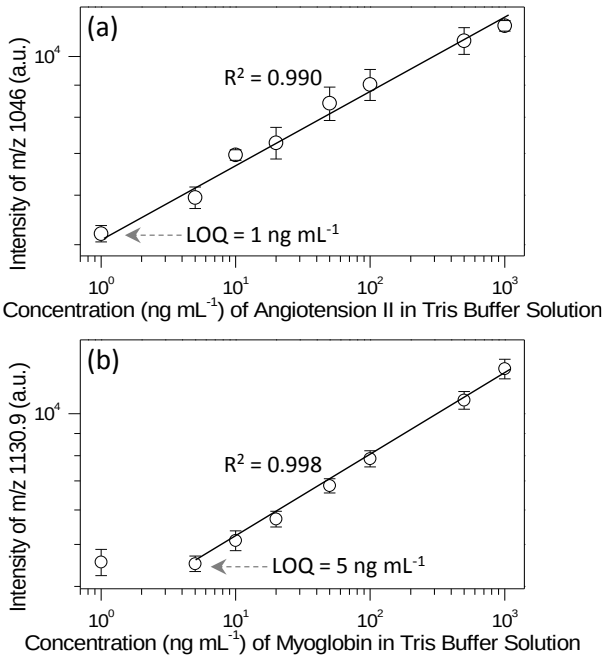

Figure S13. Quantitative analysis of 0.01 mol L^{-1} Tris buffer solution spiked with (a) angiotension II and (b) myoglobin using PS-impregnated paper (concentration: 1 - 1000 ng mL^{-1}, pH = 8.5, sample solution: 5 µL, spray solvent: 25 µL 1:1 methanol/water containing 0.5% acetic acid, spray voltage: 3.5 kV, detection mode: selected ion monitoring (SIM)).