Electronic Supplementary Material (ESI) for Analytical Methods.

Sheath-flow probe electrospray ionization (sfPESI) mass spectrometry for the rapid forensic analysis of human body fluids

Stephanie Rankin-Turner, Satoshi Ninomiya, James C. Reynolds and Kenzo Hiraoka

Supplementary Information

Tab. S1 Selected compounds of interest detected in urine, saliva and blood, with possible identifications based on accurate mass, molecular formulae, and characteristic fragment ions in comparison to previous literature and the Human Metabolome Database.

Body Fluid	Possible Identification	Molecular Formula	Experimental *m/z*	Theoretical *m/z*	ppm Error	Characteristic Fragment Ions
Urine	Creatinine	C4H8N3O	114.0666	114.0662	3.507	114, 86, 44
Urine	Urea	C2H9N4O2	121.0725	121.0720	4.130	121, 61, 44
Urine	1-methylhistidine	C7H12N3O2	170.0931	170.0925	3.527	170, 124, 109, 96, 83
Urine	Creatine	C4H10N3O2	132.0772	132.0767	3.786	132, 90, 72, 44
Urine	Proline betaine	C7H14NO2	144.1021	144.1019	1.388	144, 98, 84
Urine	Dibutylformamide	C9H20NO	158.1546	158.1540	3.794	158, 116, 102
Urine	Propionylcarnitine	C10H20NO4	218.1394	218.1387	3.209	218, 144, 85
Urine	Isovalerylcarnitine	C12H24NO4	246.1704	246.1700	1.625	246, 187, 85
Urine	Acetylcarnitine	C9H18NO4	204.1239	204.1231	3.919	204, 158, 145, 85, 60
Saliva	4-aminobutyric acid	C4H10NO2	104.0709	104.0707	1.922	104, 86, 69, 42
Saliva	5-aminopentanoic acid	C5H12NO2	118.0866	118.0863	2.541	118, 101, 100, 83, 59, 55
Saliva	Methylimidazoleacetic acid	C6H9N2O2	141.0661	141.0659	1.418	141, 123, 95, 81
Saliva	Proline	C5H10NO2	116.071	116.0707	2.585	116, 70
Saliva	Threonine	C4H10NO3	120.0657	120.0656	0.833	120, 102, 56
Saliva	Phenylalanine	C9H12NO2	166.0869	166.0863	3.613	166, 120, 103
Blood	Glucose	C6H12O6Na	203.0535	203.0527	3.940	203, 188
Blood	C16:1 Sphingomyelin	C39H79N2O6PNa	725.5595	725.5568	3.721	725, 666, 542
Blood	Cholesteryl linoleic acid	C45H76O2Na	671.5759	671.5738	3.127	N/A*
Blood	20:4 Cholesteryl ester	C47H76O2Na	695.5754	695.5730	3.450	N/A*

NA* In some instances fragment ions could be not observed due to the low concentration of the analyte.

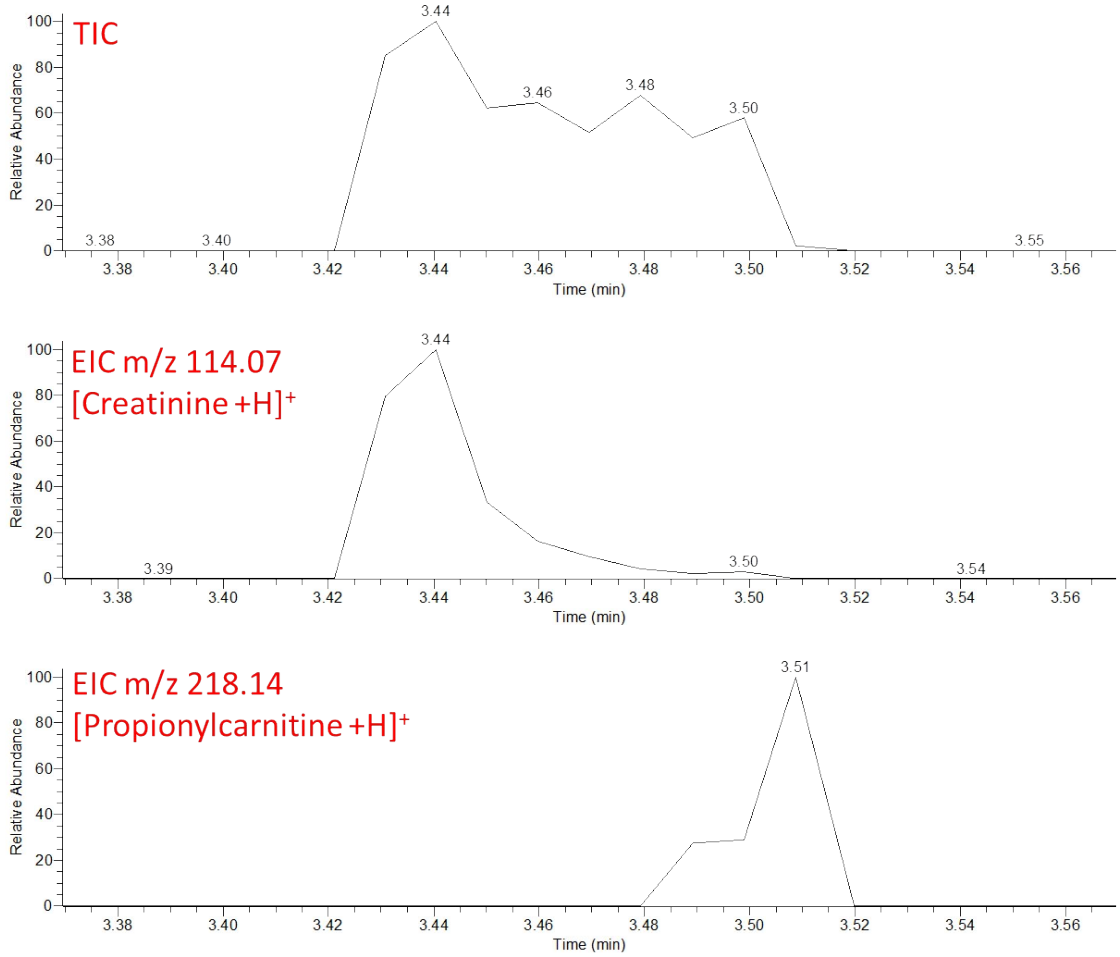

Fig. S1 Extracted ion chromatogram (EIC) of creatinine and propionylcarnitine in comparison to the total ion chromatogram from fresh urine, demonstrating the change in the detection of these compounds throughout the electrospray.

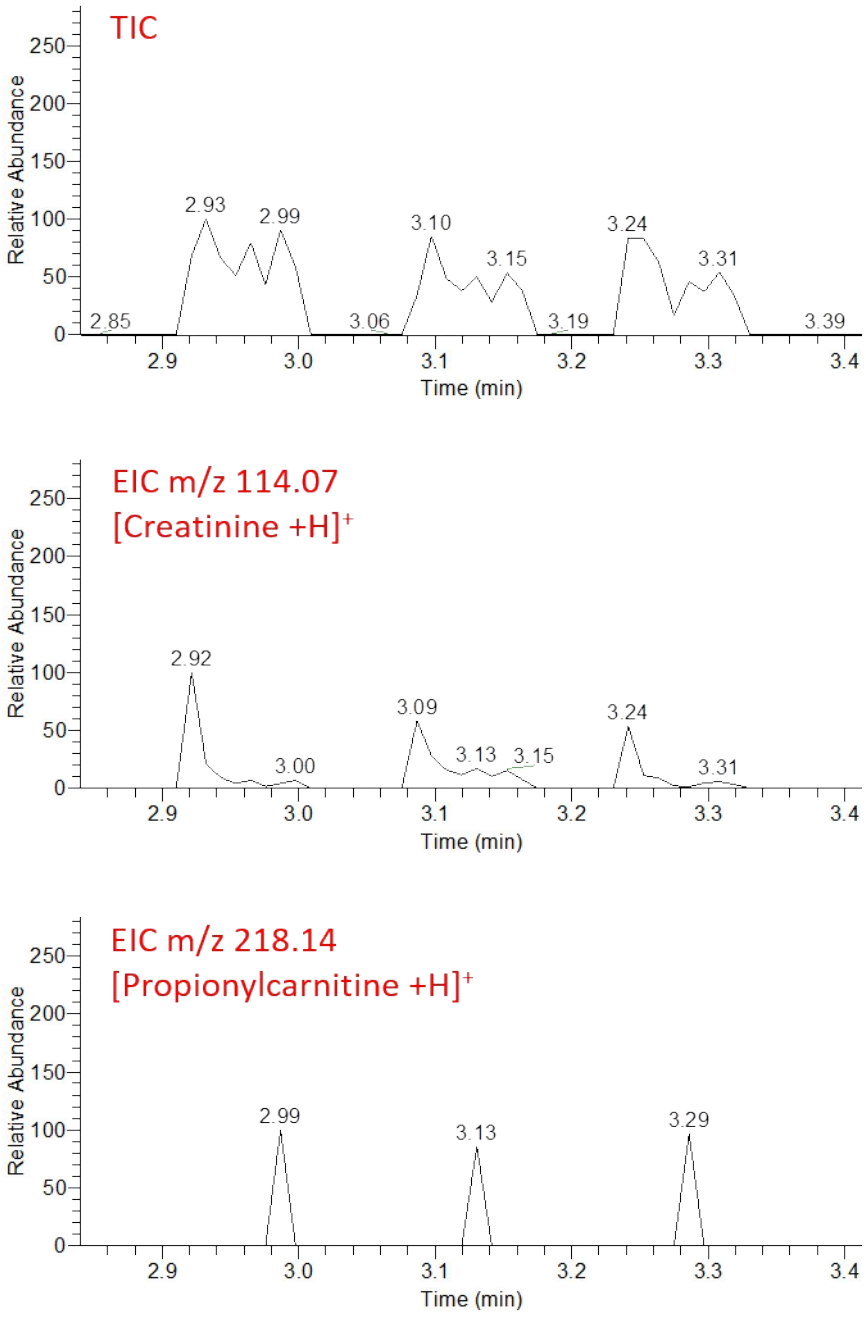

Fig. S2 Repeated extracted ion chromatogram (EIC) of creatinine and propionylcarnitine, demonstrating the reproducibility of the sequential ionisation effect (%RSD of creatinine = 29.3% and %RSD of Propionylcarnitine = 8.3%).

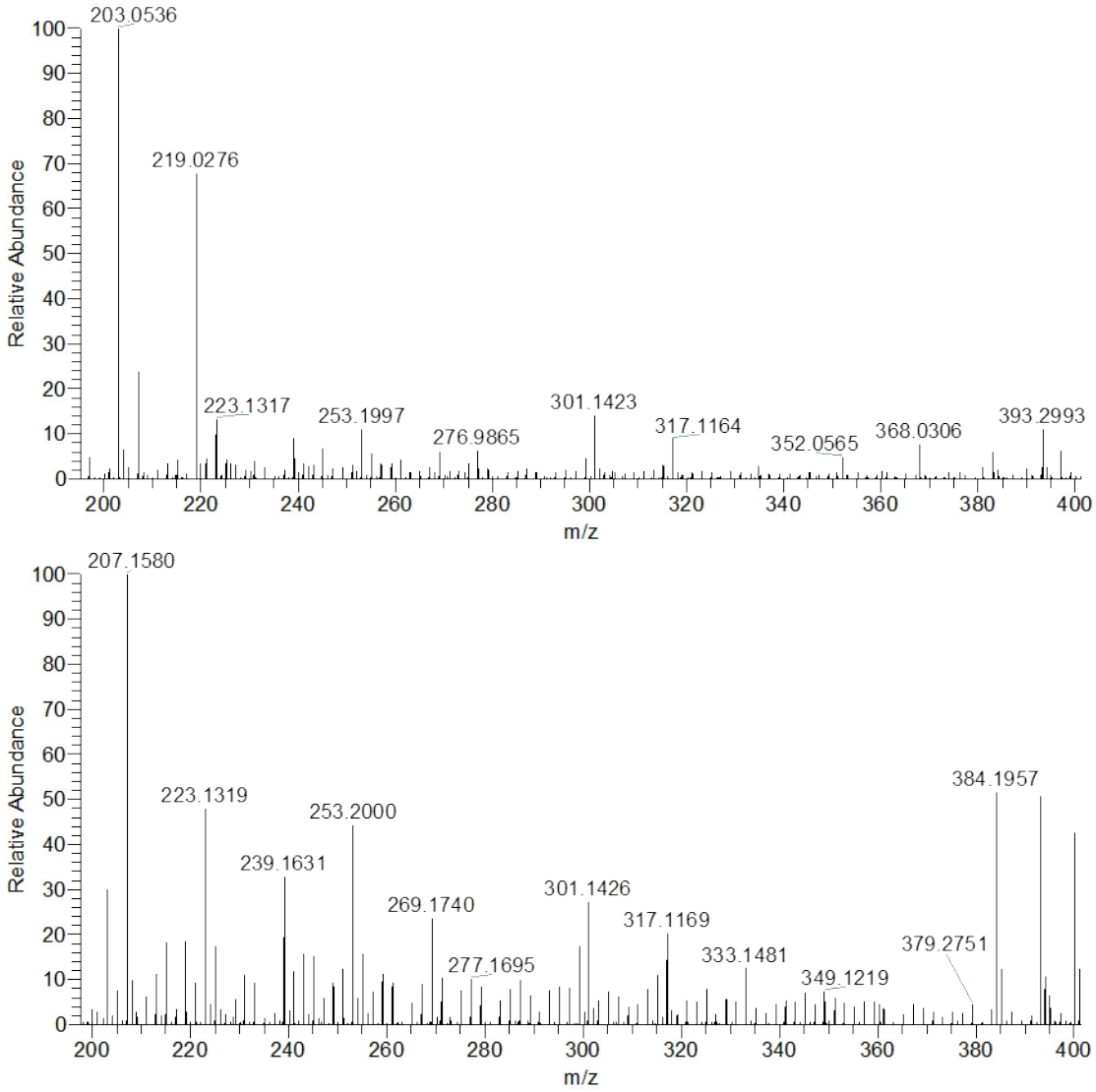

Fig. S3 Mass spectra of fresh (above) and one month old (below) blood on glass slides, demonstrating chemical changes observed over time.

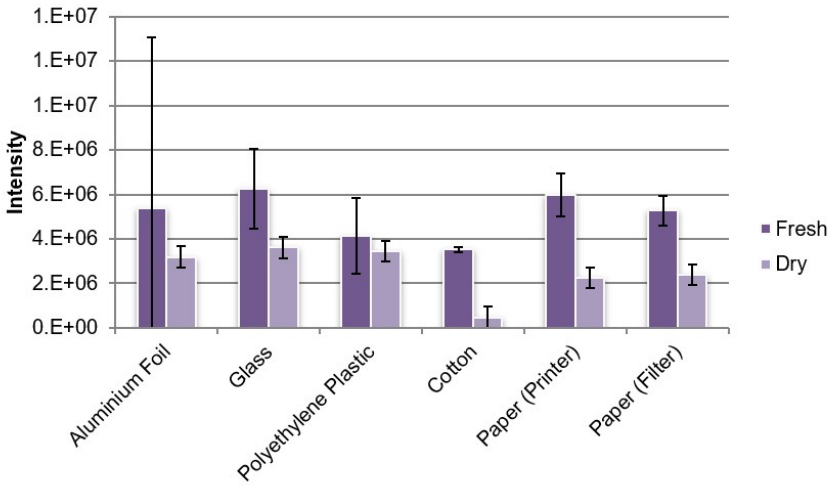

Fig. S4 Sodiated fructose/glucose signal intensity in fresh and dried blood spots analysed on a range of surface materials

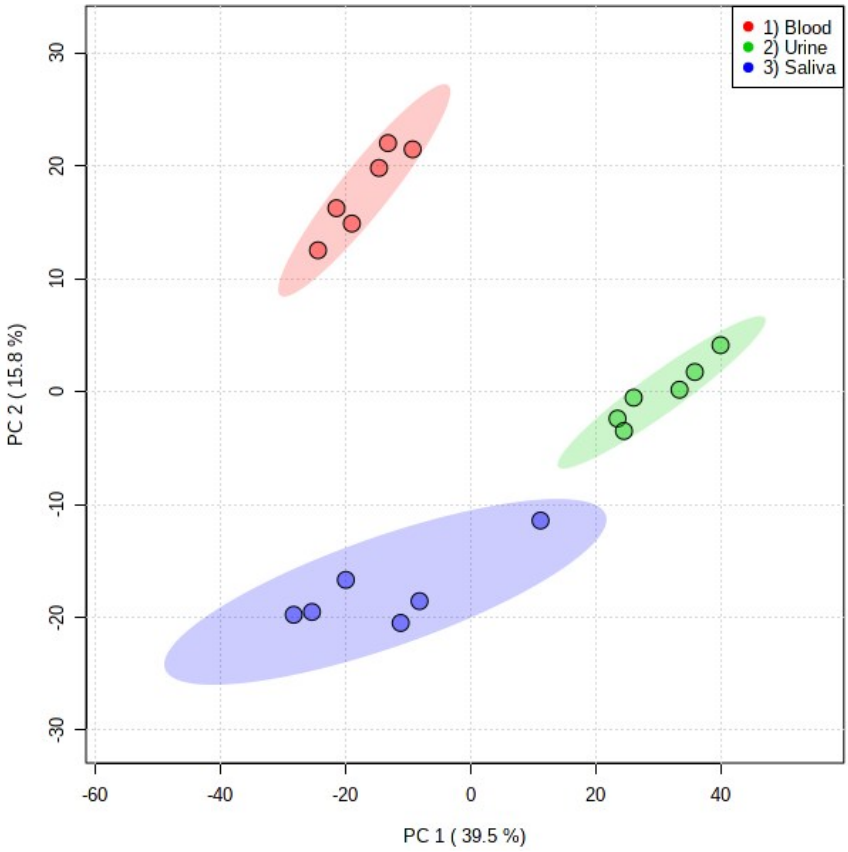

Fig. S5 Principal component analysis scores plot of fresh blood, saliva and urine sampled from glass slides, with log transformation and Pareto scaling. Ellipses depict 95% confidence regions.