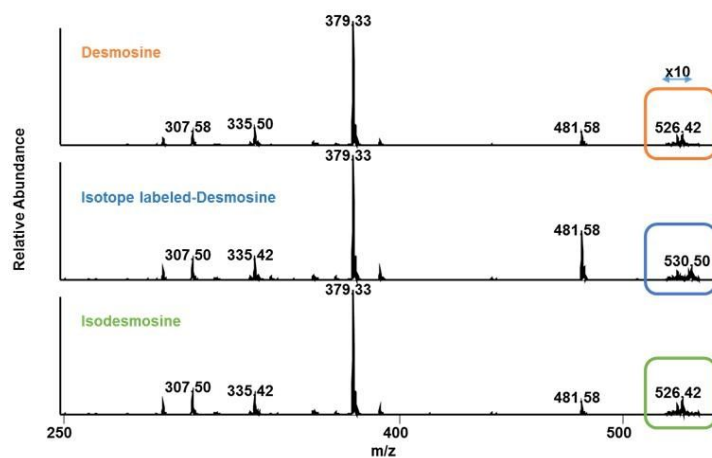


## **Analytical and Bioanalytical Chemistry**

### **Electronic Supplementary Material**

#### **Quantification of desmosine and isodesmosine using MALDI-ion trap tandem mass spectrometry**

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**Fig. S1** Full MS spectra of Des, Labeled-Des, and Isodes are shown as top, middle, and bottom panel. 10X magnification was applied to detect the molecular ion of each of these molecules

**Table S1** Average peak area obtained from the two sets of linearity study using MALDI-MS<sup>2</sup> quantification method is listed below. Various concentrations of Des were mixed with 25 ng/ $\mu$ L of Labeled-Des. RSD from 0.17% to 4.7% was obtained for the entire concentration range

Des Conc (ng/ $\mu$ L)	Average Peak Area	SD	%RSD
3.125	0.07	0.000	0.382
6.250	0.14	0.004	3.076
12.50	0.50	0.001	0.251
25.00	1.00	0.007	0.695
31.25	1.23	0.058	4.673
43.75	1.74	0.068	3.920
50.00	2.03	0.058	2.851
62.50	2.42	0.068	2.797
80.00	3.23	0.014	0.422
105.0	4.16	0.053	1.269
125.0	4.78	0.008	0.166

**Table S2** Normalized peak area ratios (Des:Labeled-Des) for serial dilutions of desmosine were used to calculate LOQ using standard  $10\sigma/s$  method. These are the same samples used for the lower four concentrations in Table 1. For each series, the Des:Labeled-Des signal intensity was normalized to the amount of Labeled-Des present

<u>Desmosine</u> (ng/ $\mu$ L)	<u>Relative Signal Intensity</u>	
	<u>Urine</u>	<u>Serum</u>
0.50	111	99.4
0.10	23.3	19.6
0.020	4.59	3.86
0.0040	1	1
	$\sigma = 0.490$	$\sigma = 0.204$
	s = 221.4	s = 198.8

**Table S3** Average peak area obtained from the three sets of linearity study using MALDI-MS<sup>2</sup> quantification method is listed below. Various concentrations of Des were mixed with 25 ng/ $\mu$ L of Labeled-Des. RSD from 0.46% to 4.3% was obtained for the entire concentration range

<b>Desmosine</b> (ng/ $\mu$ L)	<b>Trial 1</b>	<b>Trial 2</b>	<b>Trial 3</b>	<b>Average</b>	<b>SD</b>	<b>%RSD</b>
	<b>Peak area</b>	<b>Peak area</b>	<b>Peak area</b>	<b>Peak area</b>		
3.125	0.07	0.07	0.08	0.07	0.003	4.313
6.250	0.14	0.13	0.14	0.14	0.004	2.587
12.50	0.50	0.50	0.50	0.50	0.003	0.517
25.00	1.00	0.99	0.98	0.99	0.010	1.049
31.25	1.29	1.17	1.24	1.24	0.047	3.830
43.75	1.67	1.81	1.76	1.75	0.057	3.240
50.00	1.98	2.09	2.00	2.02	0.050	2.495
62.50	2.35	2.48	2.51	2.45	0.070	2.852
80.00	3.22	3.25	3.21	3.23	0.015	0.456
105.0	4.22	4.11	3.97	4.10	0.099	2.419
125.0	4.77	4.79	4.67	4.74	0.050	1.063

**Table S4** Comparison of 5 minute and 1 minute scan times. Comparison of scan times for Des at 6.25 ng/ $\mu$ L shows that reducing the analysis time to 1 minute does not substantially compromise accuracy or reproducibility

	<b>Urine</b>		<b>Serum</b>	
	<b>Peak Area</b>	<b>%RSD</b>	<b>Peak Area</b>	<b>% RSD</b>
<b>5 min</b>	0.69	1.49	0.77	1.89
<b>1 min</b>	0.72	4.46	0.77	2.54

**Fig. S2**  $^1\text{H}$  NMR spectra of UV-irradiated Des at different time intervals (0, 5, 15, 30 and 60 min)

