

Figure S1. Boxplots showing the main metabolites varying in saliva (post-collection) at 22°C, up to 48h.

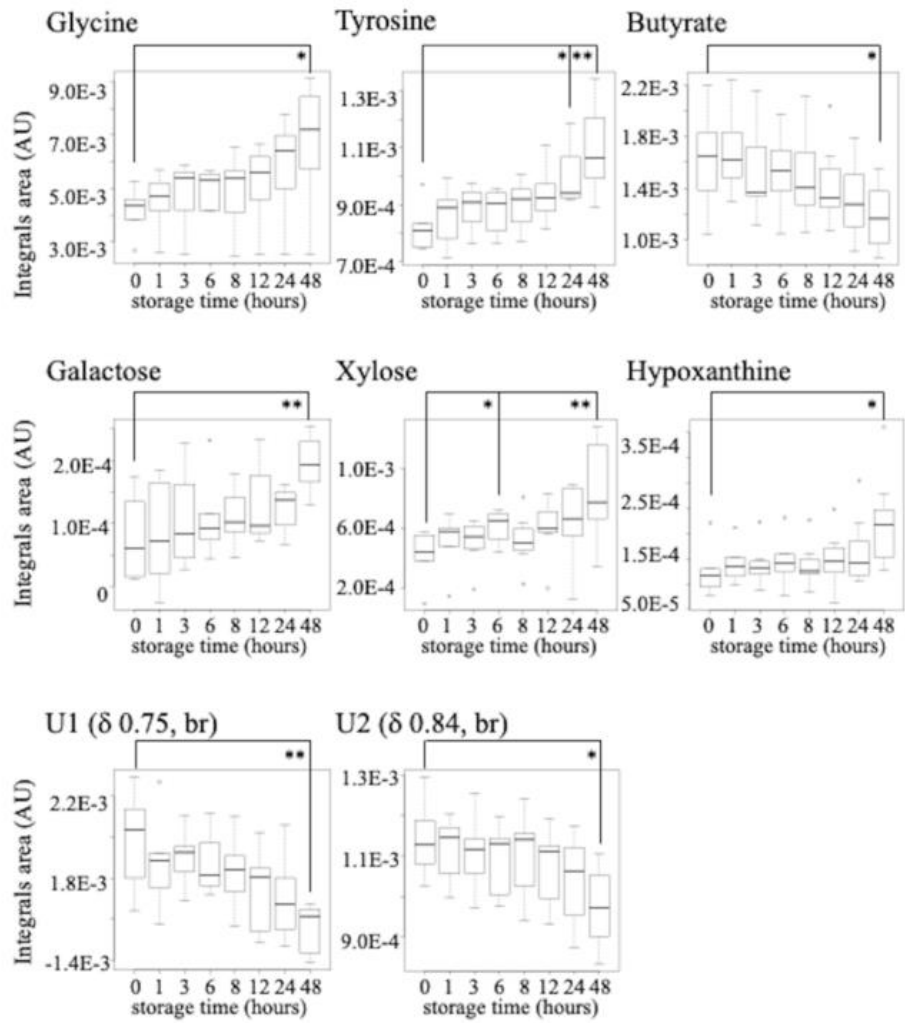


Figure S2. Boxplots showing the main metabolites varying in saliva (post-collection) at 4°C, up to 48h.

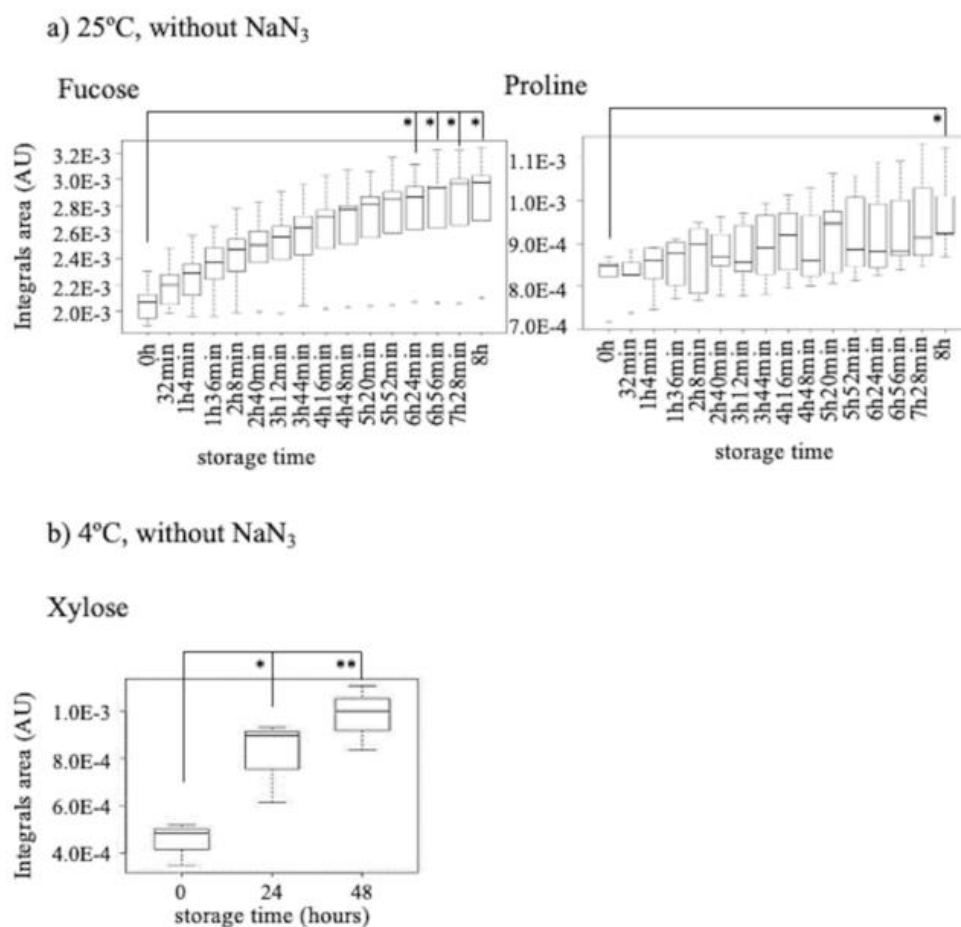


Figure S3. Boxplots of metabolite variations noted post-preparation, in the absence of sodium azide and at 25°C.

Table S1. Peak assignments in the ¹H NMR spectrum of saliva of healthy adult female subjects. s: singlet, d: doublet, t: triplet, q: quartet, dd: doublet of doublets, m: multiplet, br: broad signal. SCFA, short chain fatty acids; ^{a,b,c,d} compounds previously reported in NMR studies of unstimulated saliva of healthy adults in references [38] to [41], respectively; ^e compound detected by NMR in saliva of children [12]. *U_i*: unassigned resonances *i*, for which significant variations were noted at least in one of the conditions considered. HMDB ID: compound ID number according to the Human Metabolome Database [62].

Metabolite	HMDB ID	δ _H ppm (multiplicity)
<i>Amino acids</i>		
alanine ^{a, b, c}	HMDB0000161	1.48 (d), 3.76 (q)
aspartate ^{a, c}	HMDB0000191	2.69 (dd), 2.83 (dd), 3.90 (dd)
glycine ^{a, b, c}	HMDB0000123	3.56 (s)
glutamate ^{a, c}	HMDB0003339	2.04 (m), 2.11 (m), 2.34 (m), 3.74 (dd)
glutamine ^{a, c}	HMDB0000641	2.12 (m), 2.44 (m), 3.76 (t)
histidine ^{a, b, c}	HMDB0000177	3.02 (m), 3.15 (s), 7.05 (s), 7.75 (s)
isoleucine ^{a, c}	HMDB0000172	0.92 (t), 0.99 (d), 1.24 (m), 1.45 (m), 1.96 (m), 3.66 (d)
leucine ^{a, b, c}	HMDB0000687	0.94 (t), 1.7 (m), 3.72 (m)
lysine ^{a, c}	HMDB0000182	1.46 (m), 1.71 (m), 1.89 (m), 3.02 (t), 3.74 (t)
phenylalanine ^{a, b, c}	HMDB0000159	3.19 (m), 3.98 (dd), 7.32 (d), 7.36 (m), 7.42 (m)
proline ^{a, c}	HMDB0000162	1.99 (m), 2.06 (m), 2.35 (m), 3.33 (dt), 3.41 (dt), 4.16 (dd)
sarcosine ^{a, b, c}	HMDB0000271	2.74 (s), 3.60 (s)
taurine ^{a, b, c}	HMDB0000251	3.27 (t), 3.42 (t)
threonine ^{a, c}	HMDB0000167	1.32 (d), 3.57 (d), 4.26 (m)

tyrosine ^{a, b, c}	HMDB0000158	3.06 (dd), 3.12 (dd), 3.95 (dd), 6.90 (d), 7.20 (d)
valine ^{a, c}	HMDB0000883	0.99 (d), 1.05 (d)
SCFA		
acetate ^{a, b, c}	HMDB0000042	1.92 (s)
butyrate ^{a, c}	HMDB0000039	0.89 (t), 1.56 (m), 2.14 (t)
formate ^{a, b, c}	HMDB0000142	8.46 (s)
propionate ^{a, b, c}	HMDB0000237	1.06 (t), 2.18 (q)
Organic acids		
4-hydroxyphenyllactate ^c	HMDB0000755	2.87 (dd), 3.04 (dd), 4.35 (dd), 6.85 (d), 7.17 (d)
5-aminopentanoate ^c	HMDB0003355	1.65 (m), 2.23 (t), 3.00 (t)
ascorbate ^a	HMDB0000044	3.76 (m); 4.01 (m); 4.52 (d)
lactate ^{a, b, c}	HMDB0000190	1.32 (d), 4.11 (q)
pyruvate ^{a, b, c}	HMDB0000243	2.38 (s)
succinate ^{a, c}	HMDB0000254	2.41 (s)
Carbohydrates		
α -fucose ^c		1.21 (d), 1.25 (d), 3.45 (dd), 3.64 (dd), 3.79 (m), 4.56 (d)
α -galactose ^{a, c}	HMDB0000143	3.48 (dd), 3.64 (dd), 3.72 (m), 3.82 (m), 3.92 (d), 3.96 (d), 4.07 (t), 5.27 (d)
α -glucose ^{a, b, c}	HMDB0000122	3.23 (dd), 3.39 (m), 3.45 (m), 3.52 (dd), 3.72 (m), 3.82 (m), 3.88 (dd), 4.63 (d), 5.23 (d)
sucrose ^{b, c}	HMDB0000258	3.46 (t), 3.55 (dd), 3.67 (s), 3.75 (t), 3.82 (m), 3.87 (dd), 3.89 (dd), 4.04 (t), 4.21 (d), 5.42 (d)
xylose ^e	HMDB0000098	3.23 (dd), 3.33 (dd), 3.42 (t), 3.53 (dd), 3.63 (m), 3.93 (dd), 4.58 (d), 5.21 (d)
Amines		
dimethylamine ^{a, c}	HMDB0000087	2.73 (s)
hypoxanthine ^{a, c}	HMDB0000157	8.19 (s), 8.20 (s)
methylamine ^{a, c}	HMDB0000164	2.61 (s)
trimethylamine ^{a, c}	HMDB0000906	2.89 (s)
Other compounds		
acetone ^{a, b, c}	HMDB0001659	2.23 (s)
acetoin ^d	HMDB0003243	1.39 (d)
allantoin ^a	HMDB0000462	5.39 (s)
choline ^{a, c}	HMDB0000097	3.20 (s), 3.52 (m), 4.07 (m)
dimethyl sulfone ^c	HMDB0004983	3.15 (s)
ethanol ^{a, b, c}	HMDB0000108	1.19 (t), 3.65 (q)
methanol ^{a, b, c}	HMDB0001875	3.36 (s)
methylguanidine ^{a, c}	HMDB0001522	2.83 (s), 3.36 (s)
<i>N</i> -acetyl-glycoproteins ^a		2.06 (s)
propylene glycol ^{b, c}	HMDB0001881	1.15 (d), 3.43 (dd), 3.53 (dd), 3.87 (m)
<u>putrescine</u>	HMDB0001414	3.04 (m), 1.76 (m)
uracil ^c	HMDB0000300	5.79 (d), 7.52 (d)
urea ^{b, c}	HMDB0000294	5.78 (br)
Unassigned resonances		
U1		0.75 (br)
U2		0.84 (s)
U3		3.22 (s)