

Supplementary information

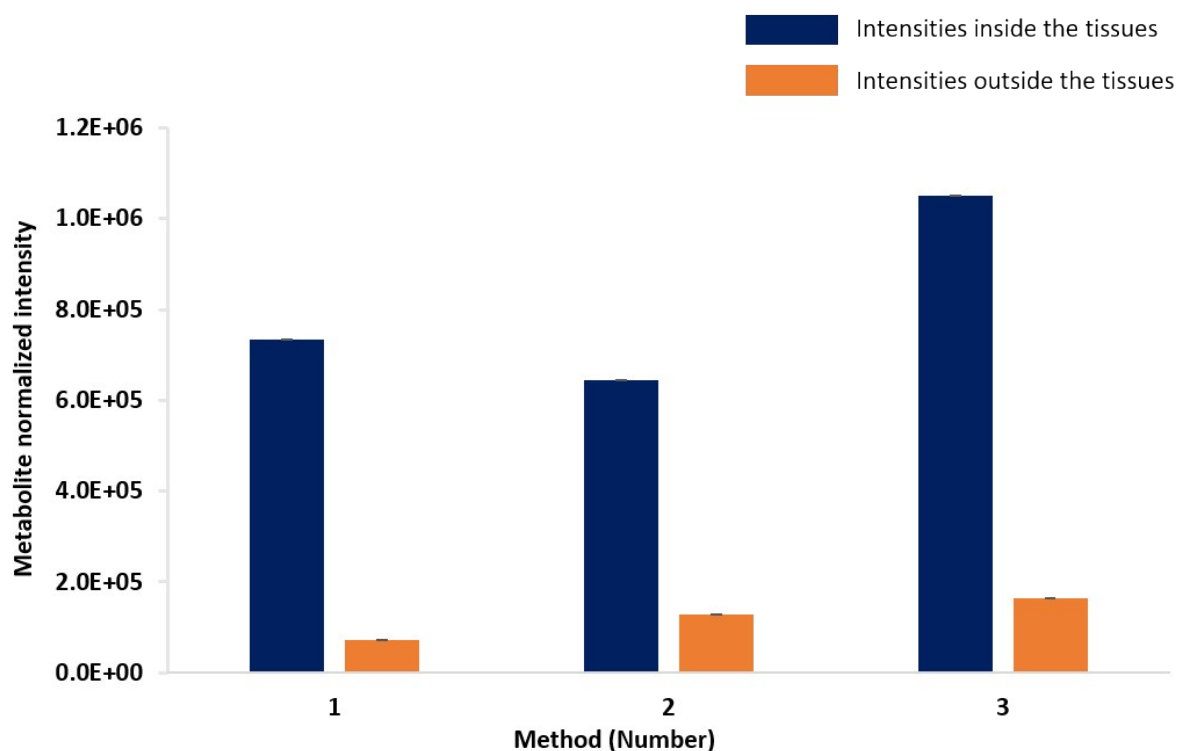
Supplementary table 1. List of detected metabolites. Five metabolites (in bold) were assigned with high confidence by their accurate mass (MS1) and their MS/MS information. Eleven (*) were assigned based on their accurate mass (MS1). HMDB and METLIN software were used for molecular assignments with a tolerance up to 1 ppm. Drugs and exogenous compounds were excluded during the search.

Assignment	Designation	Theoretical m/z value	Experimental m/z value	PPM error	Chemical Formula	MS/MS fragments
CMP*	[M-H] ⁻	322.0446	322.0448	0.70	C ₉ H ₁₄ N ₃ O ₈ P	-
UMP*	[M-H] ⁻	323.0286	323.0288	0.65	C ₉ H ₁₃ N ₂ O ₉ P	-
AMP*	[M-H ₂ O-H] ⁻	328.0452	328.0458	1.70	C ₁₀ H ₁₄ N ₅ O ₇ P	-
AMP	[M-H] ⁻	346.0558	346.0558	0.02	C ₁₀ H ₁₄ N ₅ O ₇ P	78.95 96.96 134.05 210.99
GMP*	[M-H] ⁻	362.0507	362.0507	0.06	C ₁₀ H ₁₄ N ₅ O ₈ P	-
UDP*	[M-H ₂ O-H] ⁻	384.9844	384.9848	1.15	C ₉ H ₁₄ N ₂ O ₁₂ P ₂	-
UDP	[M-H] ⁻	402.9949	402.9948	0.30	C ₉ H ₁₄ N ₂ O ₁₂ P ₂	78.95 158.91
ADP*	[M-H ₂ O-H] ⁻	408.0116	408.0118	0.55	C ₁₀ H ₁₅ N ₅ O ₁₀ P ₂	-
UDP*	[M+Na-2H] ⁻	424.9769	424.9778	2.20	C ₉ H ₁₄ N ₂ O ₁₂ P ₂	-
ADP	[M-H] ⁻	426.0221	426.0228	1.50	C ₁₀ H ₁₅ N ₅ O ₁₀ P ₂	78.95 96.96 134.04 158.92 290.96 328.05
GDP*	[M-H] ⁻	442.0171	442.0170	0.12	C ₁₀ H ₁₅ N ₅ O ₁₁ P ₂	-
ADP*	[M+Na-2H] ⁻	448.0041	448.0048	1.60	C ₁₀ H ₁₅ N ₅ O ₁₀ P ₂	-
UTP*	[M-H] ⁻	482.9612	482.9620	1.66	C ₉ H ₁₅ N ₂ O ₁₅ P ₃	-
ATP	[M-H] ⁻	505.9885	505.9888	0.65	C ₁₀ H ₁₆ N ₅ O ₁₃ P ₃	78.95 96.96 134.04 158.92
GTP*	[M-H] ⁻	521.9834	521.9840	1.15	C ₁₀ H ₁₆ N ₅ O ₁₄ P ₃	-
ATP*	[M+Na-2H] ⁻	527.9704	527.9708	0.73	C ₁₀ H ₁₆ N ₅ O ₁₃ P ₃	-
ADP-Ribose	[M-H ₂ O-H] ⁻	540.0538	540.0538	0.06	C ₁₅ H ₂₃ N ₅ O ₁₄ P ₂	158.91 408.01
Sodium ATP*	[M+Na-2H] ⁻	549.9524	549.9528	0.80	C ₁₀ H ₁₅ N ₅ NaO ₁₃ P ₃	-
UDP-Glucose/Galactose*	[M-H] ⁻	565.0477	565.0484	1.20	C ₁₅ H ₂₄ N ₂ O ₁₇ P ₂	-
UDP-N-Acetyl Glucosamine/Galactosamine*	[M-H] ⁻	606.0743	606.0754	1.80	C ₁₇ H ₂₇ N ₃ O ₁₇ P ₂	-

Supplementary table 2. List of TM-SPRAYER™ settings. According to the experiments performed in step 1, the matrix concentration, the temperature, the number of layers and the flow rate were defined as non-significant parameters. Only the percentage of solvent used to dissolve the matrix was defined as a significant setting. Drying time was added to step 2 to confirm the non-significance of this setting.

		STEP 1			STEP 2		
TM-SPRAYER™ Settings	Unit	Lower value	Center value	High value	Lower value	Center value	High value
Matrix Concentration	mg/mL	7	8.5	10	fixed value: 10		
Solvent	%	60	65	70	50	75	100
Temperature	°C	65	72.5	80	fixed value: 80		
Number of layers	N	4	5	6	fixed value: 10		
Flow rate	mL/min	0.12	0.135	0.15	fixed value: 0.1		
Drying time	Sec	22	26	30	2	31	60

Supplementary figure 1. Validation of the experimental design model. Intensities of ATP, ADP and UDP were normalized by root mean square (RMS) for each experiment performed in duplicate.



Supplementary figure 2. Spatial distribution of GTP and UTP.

