Electronic Supplementary Information for

Enhanced Sensitivity and Metabolite Coverage with Remote Laser Ablation Electrospray Ionization-Mass Spectrometry Aided by Confined Coaxial Gas Flow

Jarod A. Fincher,[a] Andrew R. Korte,[a] Brent Reschke,[b] Nicholas J. Morris,[b] Matthew J. Powell,[b] and Akos Vertes*,[a]

[a] *Department of Chemistry, W. M. Keck Institute for Proteomics Technology and Applications, The George Washington University, Washington, DC 20052, USA*

[b] *Protea Biosciences, 955 Hartman Run Road, Morgantown, WV 26505,*

** Corresponding author. E-mail: vertes@gwu.edu, Phone: +1 (202) 994-2717, Fax: +1 (202) 994-5873.*

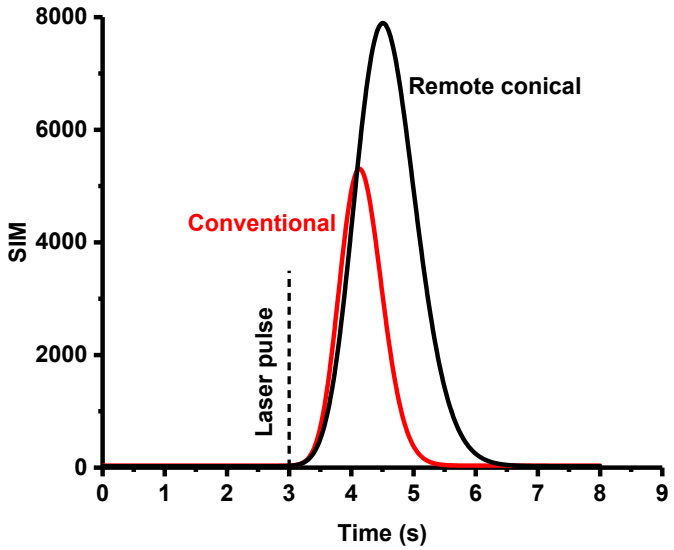

Figure S1: Signal profiles fitted by lognormal distributions from an ablation event in conventional LAESI-MS (red trace corresponding to verapamil molecular ion at *m/z* 455.29 from standard solution) and LAESI-MS in conical ablation chamber (black trace corresponding to disaccharide ion at *m/z* 381.06 from carrot tissue section).

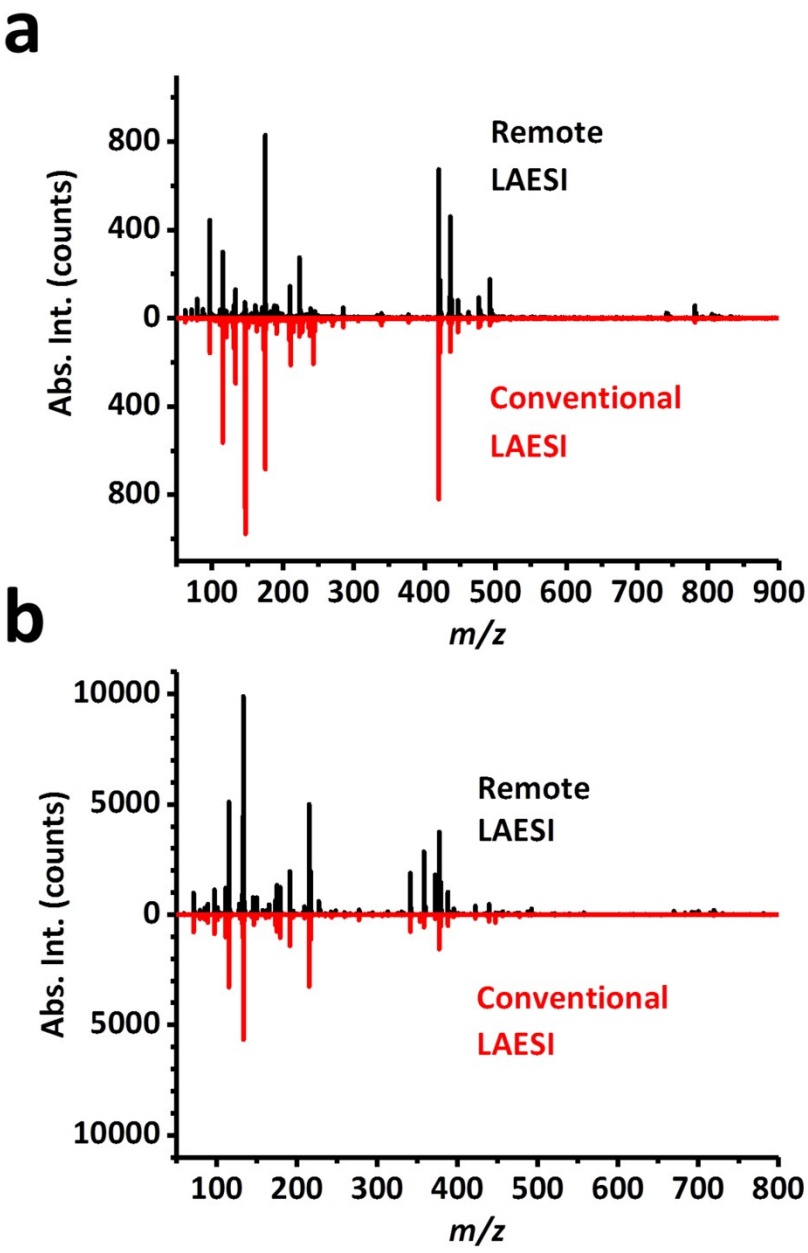

Figure S2: a) Negative ion mode mass spectra obtained from *Arabidopsis thaliana* leaves using remote LAESI-MS with a conical inner volume ablation chamber and conventional LAESI-MS. After deisotoping, 101 peaks were detected using remote LAESI-MS and 88 using conventional LAESI-MS. b) Negative ion mode spectra obtained from 60 µm thick Brussels sprout bud sections using remote LAESI-MS with a conical inner volume ablation chamber and conventional LAESI-MS. After deisotoping, 161 peaks were detected in remote LAESI-MS and 144 in conventional LAESI-MS.

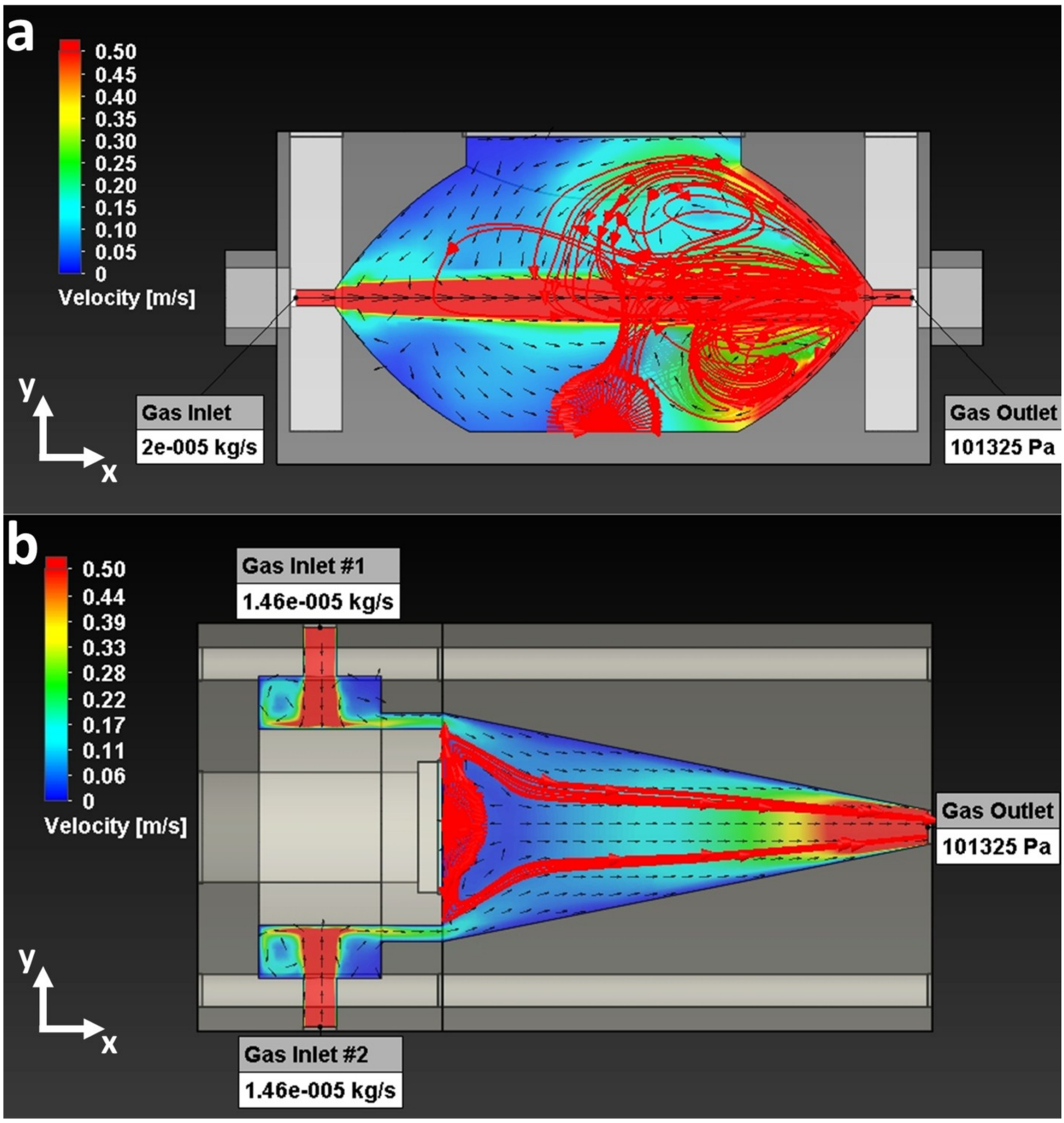

Figure S3: Overlay of particle trajectories (red traces) with carrier gas flow contour plots and black arrows for a) prolate spheroid ablation chamber and b) conical inner volume ablation chamber.

Table S1: Glucosinolates detected in 8-week-old *Arabidopsis thaliana* plant leaf by conventional and remote LAESI-MS in negative ion mode. Glucosinolate identities were verified by tandem MS.

Compound Name	Chemical Formula	Measured *m/z*	Calculated *m/z*	Δm (mDa)
Glucoerucin	$[C_{12}H_{23}NO_9S_3\text{-}H]^-$	420.0447	420.0457	-1.0
Glucoraphanin	$[C_{12}H_{23}NO_{10}S_3\text{-}H]^-$	436.0406	436.0406	-
Glucobrassicin	$[C_{16}H_{19}N_2O_9S_2\text{-}H]^-$	447.053	447.0532	-0.2
7-Methylthioheptyl glucosinolate	$[C_{15}H_{29}NO_9S_3\text{-}H]^-$	462.0932	462.0926	0.6
8-Methylthiooctyl glucosinolate	$[C_{16}H_{31}NO_9S_3\text{-}H]^-$	476.107	476.1083	-1.3
Neoglucobrassicin	$[C_{17}H_{21}N_2O_{10}S_2\text{-}H]^-$	477.0645	477.0638	0.7
Glucohirsutin	$[C_{16}H_{31}NO_{10}S_3\text{-}H]^-$	492.1042	492.1032	1.0

Table S2: Glucosinolates detected in 60-µm-thick Brussels sprout bud tissue sections in conventional and remote LAESI-MS negative ion mode. Glucosinolate identities were verified by tandem MS.

Compound Name	Chemical Formula	Measured *m/z*	Calculated *m/z*	Δm (mDa)
Sinigrin	$[C_{10}H_{17}NO_9S_2\text{-}H]^-$	358.0272	358.0272	0.0
Gluconapin	$[C_{11}H_{19}NO_9S_2\text{-}H]^-$	372.0438	372.0429	0.9
Progoitrin	$[C_{11}H_{19}NO_{10}S_2\text{-}H]^-$	388.0392	388.0372	2.0
Glucoiberin	$[C_{11}H_{21}NO_{10}S_3\text{-}H]^-$	422.029	422.0249	4.1
Glucobrassicin	$[C_{16}H_{19}N_2O_9S_2\text{-}H]^-$	447.053	447.0532	-0.2
Glucohirsutin	$[C_{16}H_{31}NO_{10}S_3\text{-}H]^-$	492.1049	492.1032	1.7