**Supporting Information**

Parallel headspace extraction onto etched sorbent sheets prior to ambient-ionization mass spectrometry for automated, trace-level volatile analyses

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Figure S-1: (top) Dissembled components of SPMESH apparatus. Top right – 24-well plate, bottom right – Teflon gasket, bottom left – bottom stainless steel plate, top left – top stainless steel plate with butterfly nuts and bolts
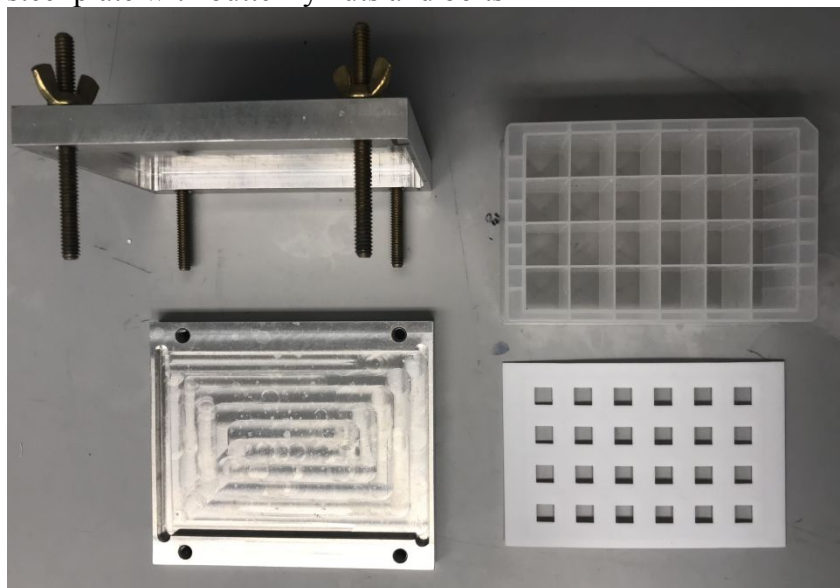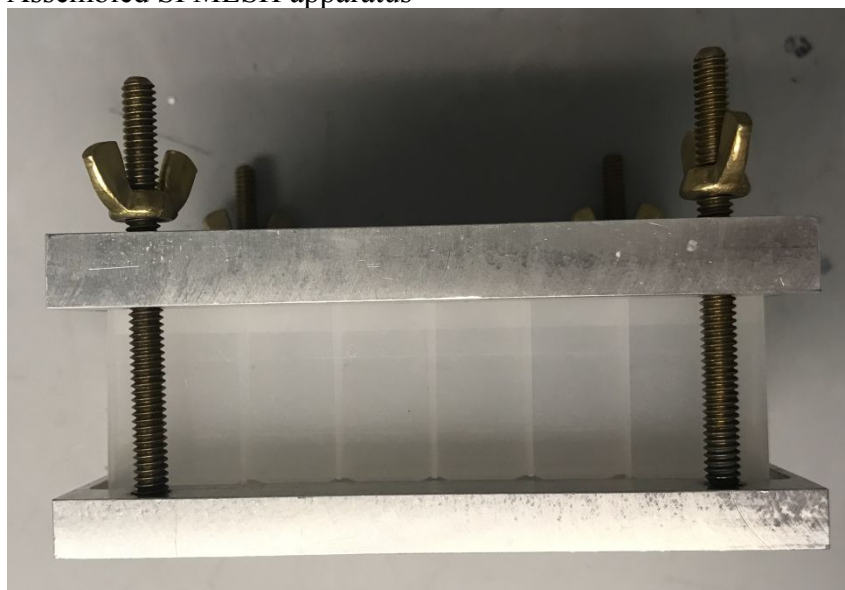

Assembled SPMESH apparatus

Figure S-2: SPMESH sheet and stainless steel frame, loaded in automated positioning stage in front of the DART source.

Table S-1: Response surface experimental design for extraction and desorption optimization

Extraction Temperature (°C)	Extraction Time (min)	Desorption Temperature (°C)	Scan Speed (mm/s)
30	15	200	1
60	15	450	0.5
30	15	450	2
60	15	200	0.5
50	60	450	2
50	60	200	0.5
60	15	400	2
50	30	400	1
30	60	450	0.5
40	30	400	1
50	30	300	1
40	60	250	1
30	60	350	2
60	60	350	0.5
40	30	400	1
40	60	250	1
40	30	200	2
60	30	250	1
50	15	250	2
60	60	200	2
40	15	350	0.5
30	30	250	0.5
50	30	400	1

Table S-2: Distribution of blanks and standards in 24 well platers for calibration curves &
recovery experiments.

Calibration Curve -
Well Plate Setup Run 1:

B	IS 1	B	5.1	B	2.4
IS 3	B	5.3	B	3.4	B
B	1.1	B	5.2	B	3.3
3.2	B	4.1	B	2.2	B

Well Plate Setup Run 2:

B	4.3	B	4.4	B	1.4
4.2	B	2.3	B	3.1	B
B	5.4	B	2.1	B	IS 4
1.3	B	IS 2	B	1.2	B

Recovery -
Well Plate Setup:

B1	1.2	B2	IS 1	B3	IS 2
IS 4	1.3	2.4	1.4	GB 3	3.1
B4	3.4	3.2	GB 2	IS 3	3.3
1.1	2.3	2.2	2.1	GB 4	GB 1

B = blank (water)
GB = matrix blank (grape macerate)
IS = internal standard (grape macerate)

Figure S-3: Cartoon of etched SPMESH sheet indicating parallel (a, gray) vs. perpendicular (b, white) edge area.
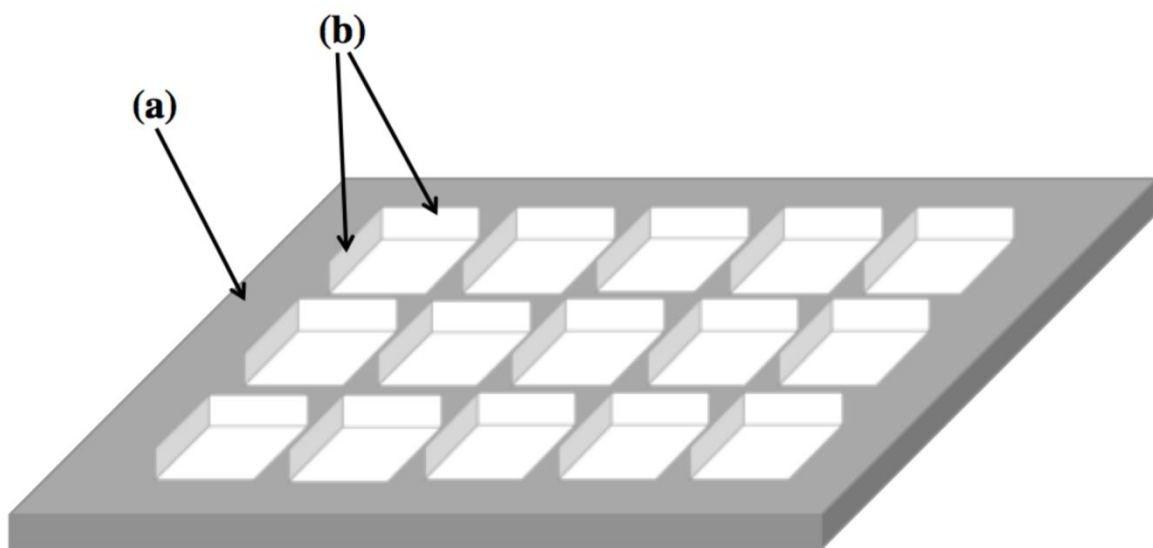
Figure S-4: Results from determining optimum mesh bakeout time at 250 °C. Columns depict average IBMP signal from three replicate runs; error bars indicate the average standard deviation of three replicate runs of three samples; a total of nine replicates.
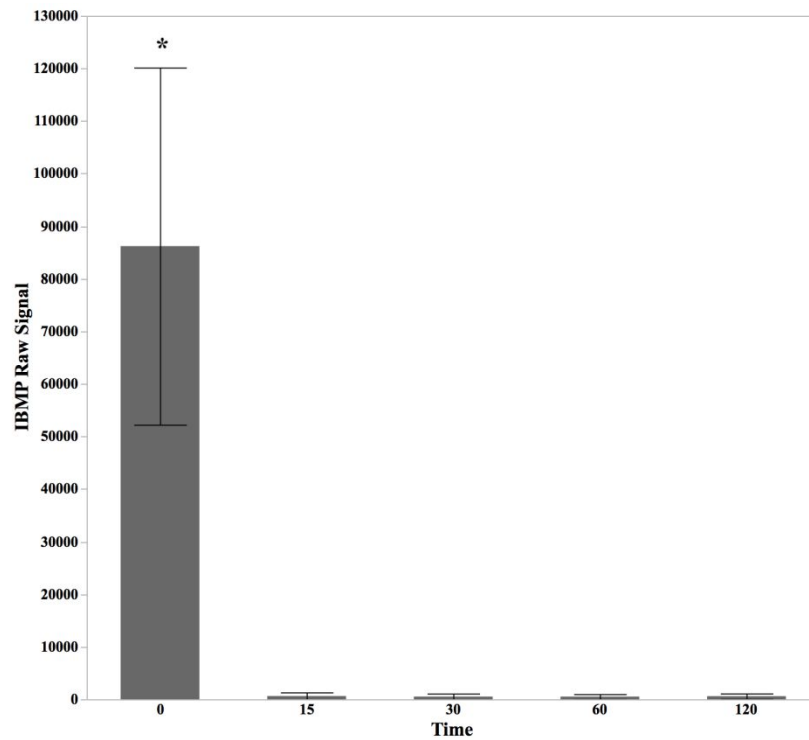*Indicates significant difference ($p < 0.0001$)

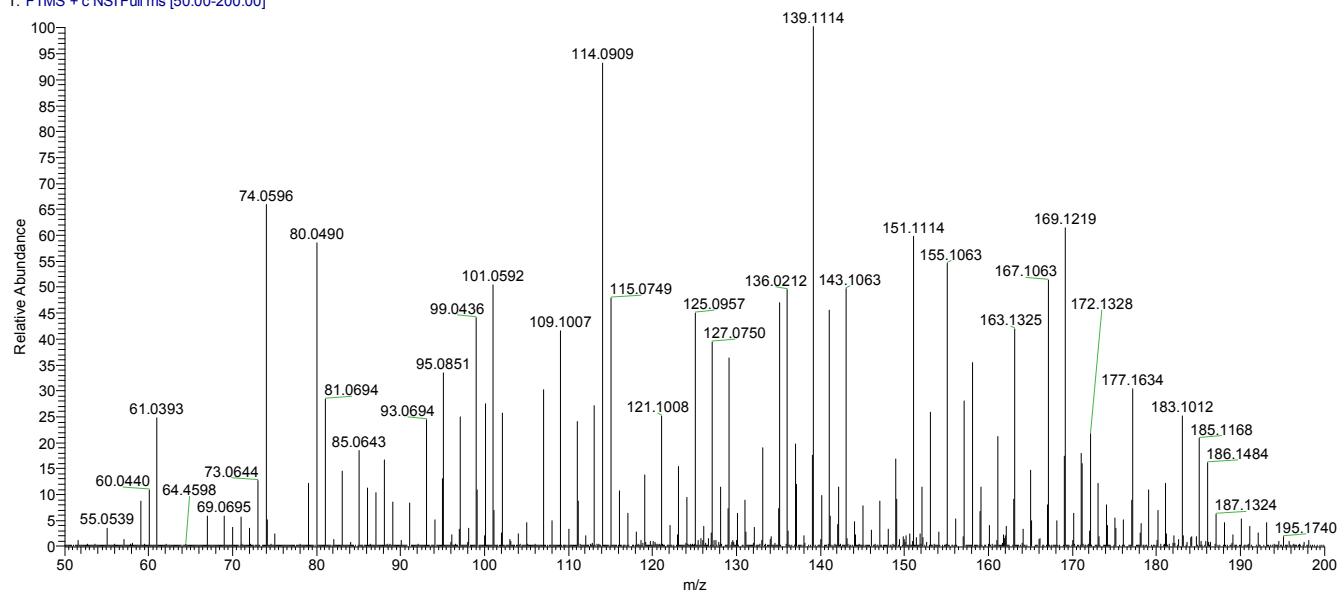Figure S-5: Full mass spectrum of a single well over mass range 50-200 *m/z* for a blank mesh

Table S-3: ANOVA tables for RSM models from extraction and optimization experiments.

IBMP:

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	14	1888511299	134893664	87.9728
Error	8	12266848.5	1533356.1	Prob > F
C. Total	22	1900778148		<.0001*

Linalool:

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	14	1.4283e+10	1.0202e+9	4.6605
Error	8	1751213408	218901676	Prob > F
C. Total	22	1.6034e+10		0.0174*

Methyl anthranilate:

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	14	7.9601e+10	5.6858e+9	77.3056
Error	8	588396020	73549503	Prob > F
C. Total	22	8.0189e+10		<.0001*

Figure S-6: Additional response surface plots for extraction and desorption optimization experiments
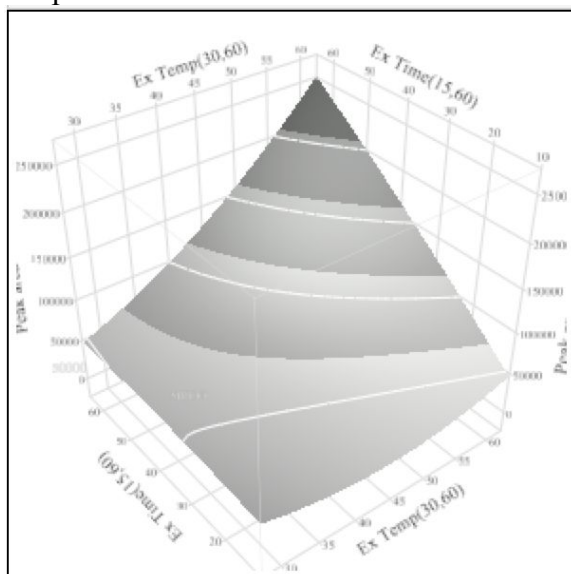
IBMP – scan speed vs. desorption temperature
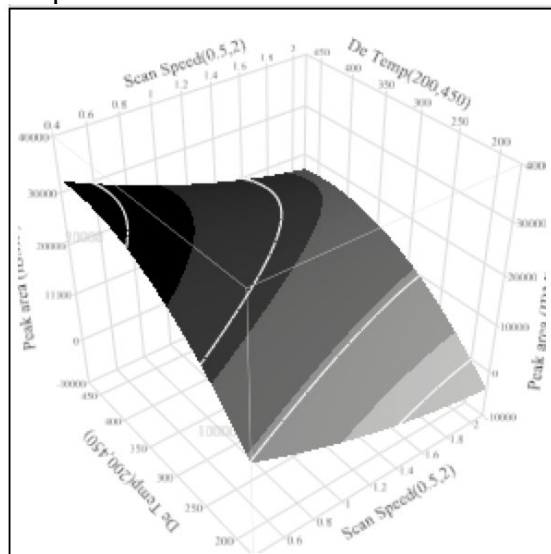
Linalool – extraction time vs. extraction temperature
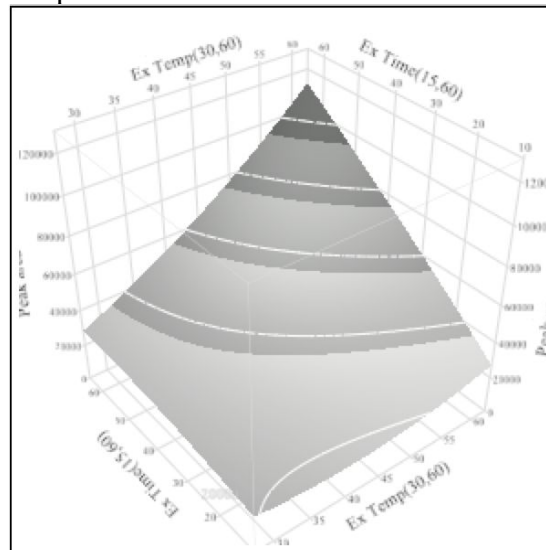
MA – extraction time vs. extraction temperature
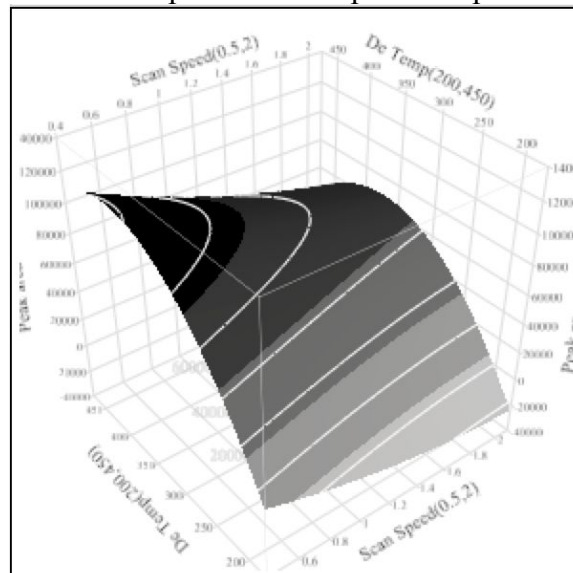

MA – scan speed vs. desorption temperature

Figure S-7: Sheet-based SPMESH-DART-MS calibration curves for aqueous samples. The internal standard ratio = (peak area of standard)/(peak area of matched internal standard). Points represent the average of four replicates; error bars represent the standard deviation for each level.

IBMP
*One outlier removed from the highest concentration (5000 ng/L) IBMP analyses, determined by quantile range outliers in JMP, with tail quantile of 0.1 and Q of 3.
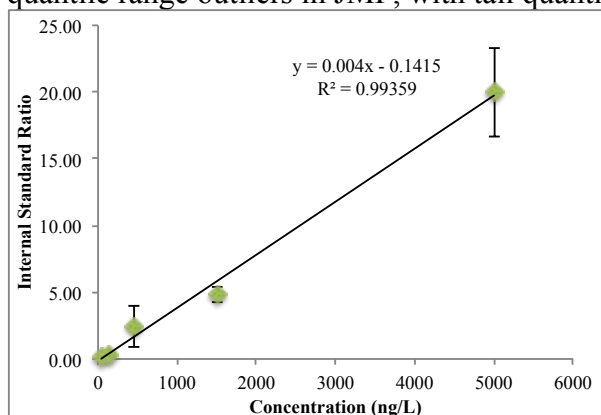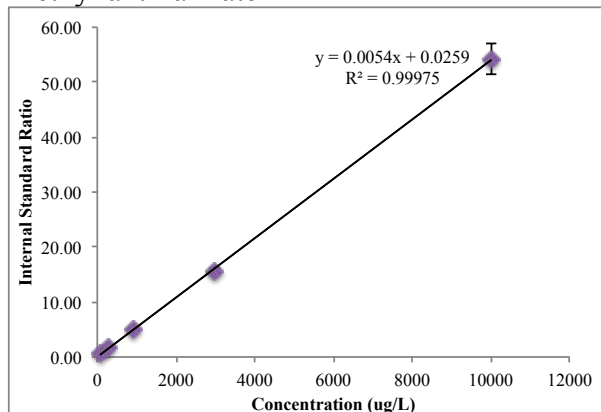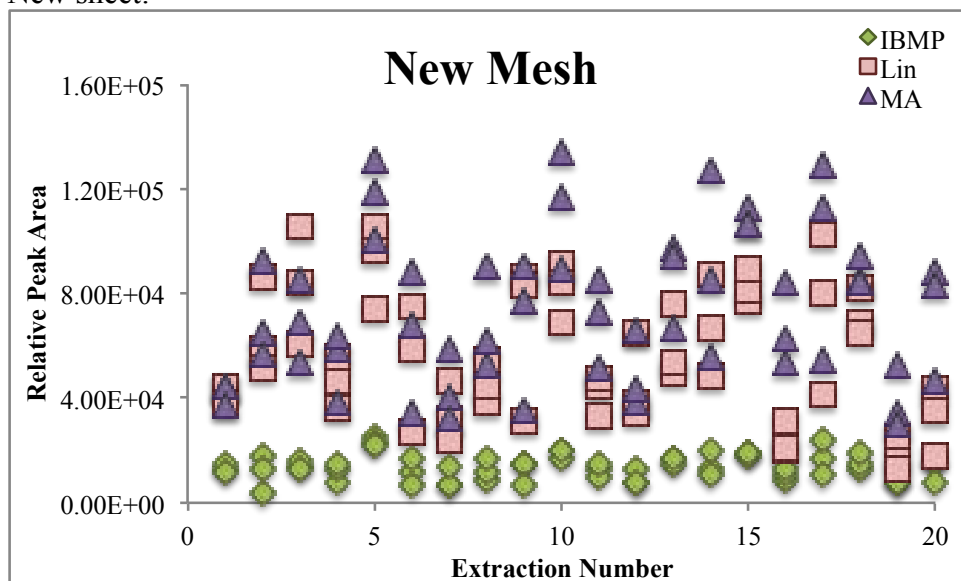

Linalool
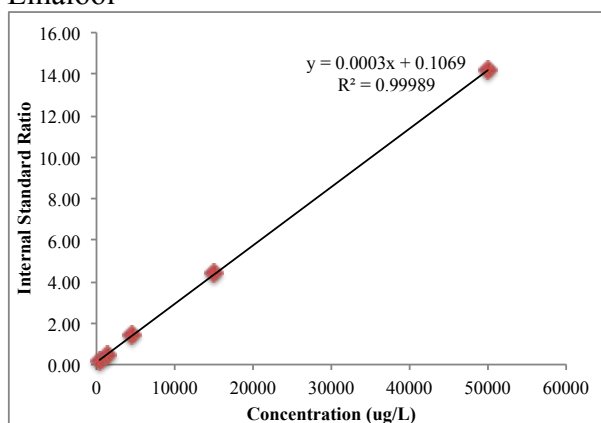
Methyl anthranilate

Figure S-8: SPMESH-DART-MS robustness over 20 extractions; raw signal. Wells were loaded with 500 ng/L IBMP, 100 μg/L linalool, 100 μg/L MA, and their deuterated analogs, and samples were run once per day for the first 12 extractions (n = 3 each day); the remaining eight analyses were run on the final day.

New sheet:

Previously used sheet (~75 extractions):