

## Electronic Supplementary Material of

Laser energy modulation in laser-induced breakdown spectroscopy of marine aerosols:  
unraveling energy-coupling pathways and improving quantitative analysis

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### 1. Emission intensities of solid-phase and liquid-phase aerosols

Table S1. Emission intensities of atomic sodium at 589 nm, atomic hydrogen at 656 nm  
and atomic nitrogen at 746 nm from solid-phase aerosols under different laser pulse  
energies.

Laser pulse energy ( $\mu$ J)	Peak Intensity		
	H I	Na I	N I
102.1	1455.861	715.037	558.145
118.4	1559.083	806.392	613.026
140.5	1599.428	1093.344	786.135
158.1	1817.793	1736.881	1157.360
178.8	2192.932	2806.211	1855.824
202.0	3188.267	5135.254	3263.564
225.0	3422.720	5615.800	3654.417
241.5	4316.294	7118.101	4622.705
261.2	5353.656	9265.294	5835.685
272.2	5267.273	9420.066	6160.780
283.1	5389.599	9385.436	6110.479
296.3	5535.215	9807.480	6405.737
320.6	6267.015	10430.788	6918.551
348.0	7327.637	12652.314	8275.199
374.3	7630.079	13369.302	9061.714
409.5	9417.159	16429.700	11196.418
432.5	10758.922	19081.309	13190.889
452.3	12298.885	20429.132	14215.320
467.6	12762.157	22459.402	15763.584
498.2	13584.421	23390.337	16586.658

505.0	14308.637	26008.405	18296.697
535.8	15210.027	26089.933	19302.861
557.7	17483.468	28669.114	20800.952
579.7	18718.227	31248.718	23224.208
632.4	19056.435	31319.058	23246.743
650	15737.244	25826.536	19248.629

Table S2. Emission intensities of atomic sodium at 589 nm, atomic hydrogen at 656 nm and atomic nitrogen at 746 nm from liquid-phase aerosols under different laser pulse energies.

Laser pulse energy ( $\mu$ J)	Peak intensity		
	H I	Na I	N I
102.1	2271.768	690.428	528.121
118.4	3021.746	752.910	650.289
140.5	4147.258	966.298	869.314
158.1	6123.958	1319.847	1251.911
178.8	8860.812	1835.120	1779.376
202.0	14289.609	2882.719	2810.831
225.0	17948.182	3762.009	3524.305
241.5	22999.605	4846.122	4448.263
261.2	27951.592	6034.524	5372.240
272.2	30941.139	6925.941	5977.041
283.1	33504.429	7651.451	6504.354
296.3	36004.554	8065.282	6878.089
320.6	40797.999	9124.816	7781.888
348.0	42405.792	9699.002	8181.415
374.3	46257.656	10404.263	8793.570
409.5	53021.345	11834.769	9997.532
432.5	57260.706	12769.473	10740.742
452.3	58878.765	12927.444	11008.734
467.6	62048.546	13455.230	11566.712
498.2	63724.510	14073.646	11917.435
505.0	65253.168	14564.074	12263.850
535.8	80244.357	18151.516	15399.289
557.7	91038.587	21197.055	18431.051
579.7	99413.475	23899.282	21249.438
632.4	100048.669	24052.038	21986.851
650	94784.314	23547.333	21459.916

## 2. Correlation intensities in the synchronous and asynchronous maps

Table S3. The correlation intensities of the typical cross-peaks in the synchronous and asynchronous maps of LIBS spectra with solid-phase aerosols.

Solid-phase aerosols		Correlation intensity in synchronous (asynchronous) map ( $\sim 10^6$ )				
Wavelength (nm)	Assignment	589.6	656.3	746.8	766.5	777.2
589.6	Na I	5.7	2.1(-0.2)	11.8(-0.7)	6.8(0.04)	42.3(-1.2)
656.3	H I		0.8	4.4(0.1)	2.5(0.2)	15.8(0.8)
746.8	N I			24.3	14.0(0.9)	86.9(2.3)
766.5	K I				8.2	50.5(-1.8)
777.2	O I					311.5

Table S4. The correlation intensities of the typical cross-peaks in the synchronous and asynchronous maps of LIBS spectra with liquid-phase aerosols.

Liquid-phase aerosols		Correlation intensity in synchronous (asynchronous) map ( $\sim 10^5$ )				
Wavelength (nm)	Assignment	589.6	656.3	746.8	766.5	777.2
589.6	Na I	21.2	89.3(14.2)	79.1(4.7)	4.6(-0.3)	261.0(37.7)
656.3	H I		391.5	338.2(-32.3)	19.1(-4.5)	1139.5(-11.7)
746.8	N I			297.1	17.1(-2.2)	987.6(82.0)
766.5	K I				1.01	55.9(12.4)
777.2	O I					3323.3

## 3. Results of quantitative analysis of liquid-phase aerosols

Table S5. Data of the calibration curve obtained using the original spectral intensity of Ca I, Na I and K I. Here, the blue-marked data represent the ones from the test samples.

x (ppm)	y_Ca	Error bar	y_Na	Error bar	y_K	Error bar
250	3290	3290 $\pm$ 517.7	1823	1823 $\pm$ 243.1	1170	1170 $\pm$ 138.2
476	4267	4267 $\pm$ 459.6	2249	2249 $\pm$ 203.0	1406	1406 $\pm$ 119.2
682	4900	4900 $\pm$ 611.0	2516	2516 $\pm$ 275.5	1554	1554 $\pm$ 153.7
870	5291	5291 $\pm$ 535.2	2664	2664 $\pm$ 242.9	1630	1630 $\pm$ 138.1
1042	5560	5560 $\pm$ 553.9	2767	2767 $\pm$ 253.7	1679	1679 $\pm$ 140.3

1200	5898	5898±641.1	2883	2883±280.0	1743	1743±153.6
1481	6169	6169±659.0	2963	2963±281.4	1768	1768±153.9
1724	6670	6670±765.2	3159	3159±321.7	1870	1870±175.2
1935	6608	6608±675.7	3084	3084±284.7	1810	1810±154.4
2121	6903	6903±710.2	3190	3190±295.6	1859	1859±159.9

Table S6. The detailed parameters of the figures-of-merit of the calibration curves obtained using the original spectral intensity.

	Ca	Na	K
Train_R <sup>2</sup>	0.939	0.901	0.866
Test_MAPE (%)	9.8	8.9	8.3
LOD (ppm)	338.3	355.6	369.7

Table S7. Data of the calibration curves obtained using the correlation intensities of auto-peaks of the Ca I, Na I and K I in synchronous maps. Here, the blue-marked data represent the ones from the test samples.

x(ppm)	y_Ca(~10 <sup>6</sup> )	y_Na(~10 <sup>3</sup> )	y_K(~10 <sup>2</sup> )
250	4.2	9.3	3.3
476	6.1	14.6	10.9
682	7.9	25.1	29.7
870	8.3	28.9	39.1
1042	9.1	34.7	55.6
1200	10.3	42.1	77.5
1481	14.6	68.3	148.8
1724	14.2	68.5	169.3
1935	15.3	80.4	215.2
2121	16.1	87.6	240.4

Table S8. The detailed parameters of the figures-of-merit of the calibration curves obtained using the correlation intensities.

	Ca	Na	K
Train_R <sup>2</sup>	0.962	0.974	0.957
Test_MAPE (%)	7.3	4.3	7.2
LOD (ppm)	66.1	158.1	225.4

Table S9. Data of the calibration curves obtained using the single-energy dataset with the MLP-ANN model. Here, the blue-marked data represent the ones from the test samples.

x(ppm)	y_Ca	Error bar	y_Na	Error bar	y_K	Error bar
250	298	298±66.7	311	311±103.8	356	356±87.1
476	458	458±89.2	547	547±161.6	630	630±221.1
682	690	690±130.7	723	723±228.3	871	871±257.1

870	901	901 ± 102.5	869	869 ± 194.7	966	966 ± 172.4
1042	1048	1048 ± 128.4	1008	1008 ± 203.4	1073	1073 ± 227.8
1200	1250	1250 ± 157.1	1194	1194 ± 224.2	1217	1217 ± 329.7
1481	1568	1568 ± 161.3	1497	1497 ± 219.7	1411	1411 ± 313.2
1724	1681	1681 ± 150.2	1723	1723 ± 218.9	1714	1714 ± 249.3
1935	1856	1856 ± 178.3	1800	1800 ± 190.3	1734	1734 ± 266.9
2121	2033	2033 ± 121.4	1973	1973 ± 142.9	1907	1907 ± 209.8

Table S10. The detailed parameters of the figures-of-merit of the calibration curves obtained using the single-energy dataset with the MLP-ANN model.

	Ca	Na	K
Train_R <sup>2</sup>	0.954	0.902	0.841
Test_MAPE (%)	11.2	16.5	24.1
Test_Mean_RSD (%)	13.2	20.4	25.6

Table S11. Data of the calibration curves obtained using the multi-energy dataset with the MLP-ANN model. Here, the blue-marked data represent the ones from the test samples.

x(ppm)	y_Ca	Error bar	y_Na	Error bar	y_K	Error bar
250	252	252 ± 17.3	264	264 ± 27.6	261	261 ± 23.8
476	474	474 ± 23.1	472	472 ± 44.2	473	473 ± 53.4
682	713	713 ± 29.1	765	765 ± 75.1	798	798 ± 80.9
870	871	871 ± 24.3	874	874 ± 46.4	880	880 ± 47.6
1042	1041	1041 ± 24.8	1038	1038 ± 42.9	1033	1033 ± 62.6
1200	1225	1225 ± 35.7	1152	1152 ± 55.9	1209	1209 ± 91.3
1481	1488	1488 ± 29.1	1491	1491 ± 50.1	1483	1483 ± 52.9
1724	1715	1715 ± 42.5	1724	1724 ± 61.7	1727	1727 ± 71.1
1935	1989	1989 ± 42.6	1987	1987 ± 79.1	1922	1922 ± 100.2
2121	2119	2119 ± 18.7	2111	2111 ± 40.7	2108	2108 ± 49.4

Table S12. The detailed parameters of the figures-of-merit of the calibration curves obtained using the multi-energy dataset with the MLP-ANN model.

	Ca	Na	K
Train_R <sup>2</sup>	0.998	0.995	0.993
Test_MAPE (%)	3.8	7.2	8.3
Test_Mean_RSD (%)	3.2	4.6	6.6