Electronic Supplementary Material (ESI) for Analytical Methods.

Different sample preparation methods for analysis of suspension fertilizers combining LIBS and liquid-to-solid matrix conversion: determination of essential and toxic elements

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Supplementary material

Table 1S Instrumental parameters for ICP OES analysis.

Instrument parameter	Operational conditions
Integration time (s)	15 s for low and 5 s for high wavelengths
Sample introduction flow rate (mL min^{-1})	2.1
Pump stabilization time (s)	5
Radio frequency (RF) applied power (kW)	1.15
Argon gas flow rate (L min^{-1})	12
Auxiliary gas flow rate (L min^{-1})	0.50
Nebulizer gas flow rate (L min^{-1})	0.70
Viewing mode	Radial
Elements and wavelengths (nm), I and II are atomic and ionic lines	B I 249.773, Ca II 317.933, Cu I 324.754, Fe II 240.488, K I 766.490, Mg I 285.213, Mn II 294.920, Na I 589.592, P I 178.284 and Zn I 481.053

Table 2S Operating parameters used in ICP-MS measurements.

Instrumental parameter	Operational conditions
Radio frequency generator (MHz)	27
Radio frequency (RF) applied power (kW)	1.55
Argon gas flow rate (L min^{-1})	14.0
Auxiliary gas flow rate (L min^{-1})	0.8
Nebulizer gas flow rate (L min^{-1})	1.18
Sampling depth (mm)	5.0
Integration time (s)	3.0
Sampling cone (mm)	Nickel 0.8
Skimmer (mm)	Nickel 1.2
Nebulizer	Glass concentric (MicroMist)
Spray chamber	Cyclonic
Replicates	3
Mass/charge ratios monitored	^{52}Cr, ^{75}As, ^{111}Cd and ^{208}Pb

Table 3S Concentrations (average, n = 3) and recoveries (%) for samples S1, S2 and S4 spiked with a standard solution of selected elements (Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn) by ICP OES.

Emission line (nm)	Added ($mg\ L^{-1}$)	Found ($mg\ L^{-1}$)			Recovery (%)		
		S1	S2	S4	S1	S2	S4
B I 249.773	50	47	46	41	95	92	82
Ca II 317.933	40	35	33	41	88	83	102
Cu I 324.754	80	86	91	71	107	114	88
Fe II 240.488	20	20	23	17	100	114	83
K I 766.490	6.0	6.6	6.4	6.8	111	107	113
Mg I 285.213	25	29	32	24	116	127	98
Mn II 294.920	30	28	30	35	94	100	116
Na I 589.592	4.0	3.3	4.8	3.6	82	119	91
P I 178.284	10	10	9	11	100	88	106
Zn I 481.053	40	37	49	46	94	124	115

Table 4S Concentrations (average, n = 3) and recoveries (%) for samples S2, S3 and S7 spiked with a 20 μg L^{-1} standard solution of selected elements (As, Cd, Cr and Pb) by ICP-MS.

Isotope	Found (μg L^{-1})			Recovery (%)		
	S2	**S3**	**S7**	**S2**	**S3**	**S7**
^{75}As	17	16	20	84	80	98
^{111}Cd	17	17	16	86	84	80
^{52}Cr	19	20	22	94	99	112
^{208}Pb	17	18	15	87	90	76

Figure caption

Figure 1S Emission signal intensities of (a) Cu, (b) K, (c) Mg, (d) Mn and (e) Zn preliminarily monitored in immobilized standard solution prepared for Doehlert design experiments (experiment 1 up to 15, optimization of LIBS system).

Figure 2S LIBS spectra and the identification of the main signals monitored for the eight samples studied: (a) S1, (b) S2, (c) S3, (d) S4, (e) S5, (f) S6, (g) S7 and (h) S8.

Figure 3S Study of polymer stability for the 5 analytes determined: (a) Cu, (b) K, (c) Mg, (d) Mn and (e) Zn.

Figure 1Sa

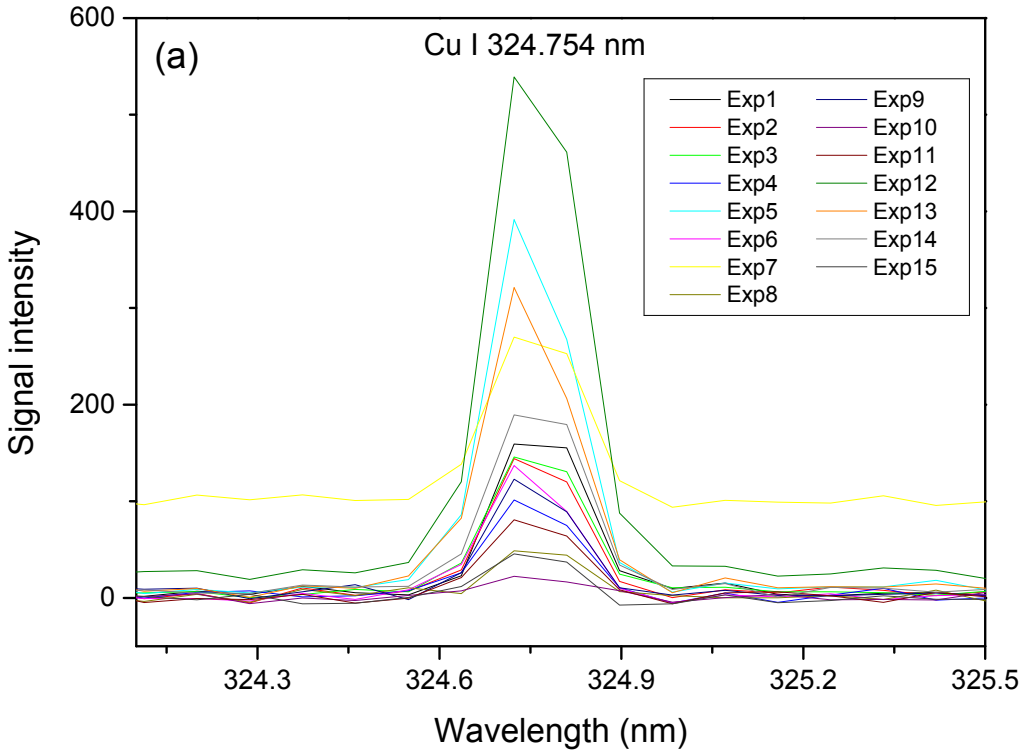

(a)
Cu I 324.754 nm
Exp1
Exp2
Exp3
Exp4
Exp5
Exp6
Exp7
Exp8
Exp9
Exp10
Exp11
Exp12
Exp13
Exp14
Exp15
Signal intensity
600
400
200
0
324.3
324.6
324.9
325.2
325.5
Wavelength (nm)

Figure 1Sb

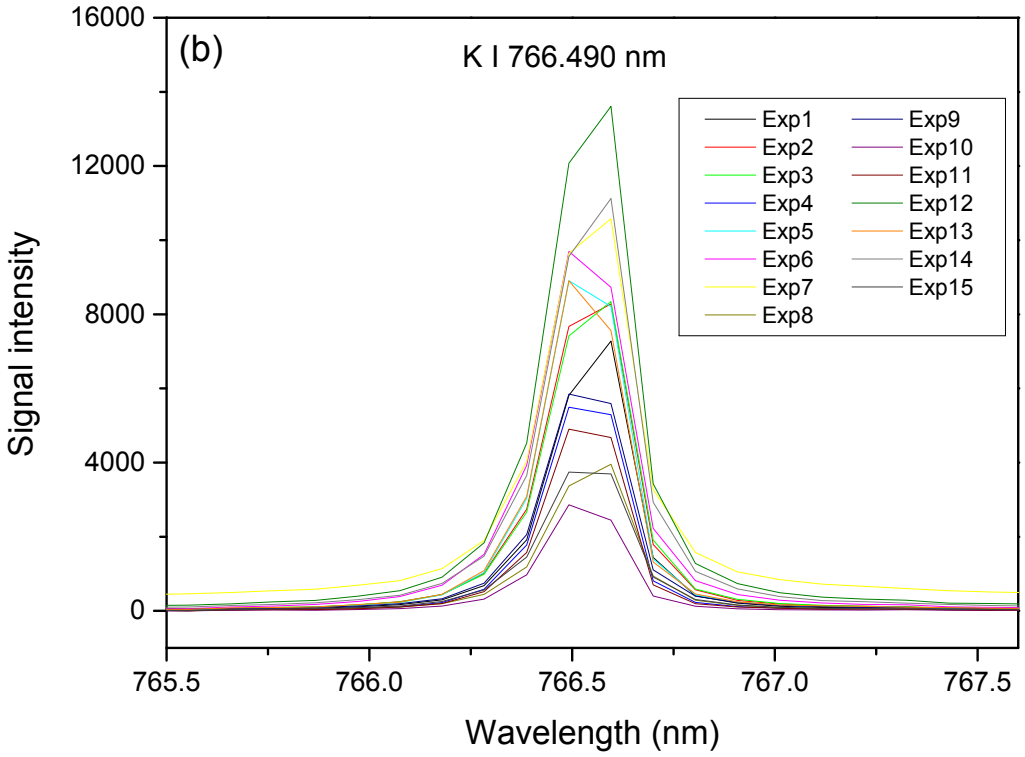

(b)
K I 766.490 nm
Exp1
Exp2
Exp3
Exp4
Exp5
Exp6
Exp7
Exp8
Exp9
Exp10
Exp11
Exp12
Exp13
Exp14
Exp15
Signal intensity
16000
12000
8000
4000
0
765.5
766.0
766.5
767.0
767.5
Wavelength (nm)

Figure 1Sc

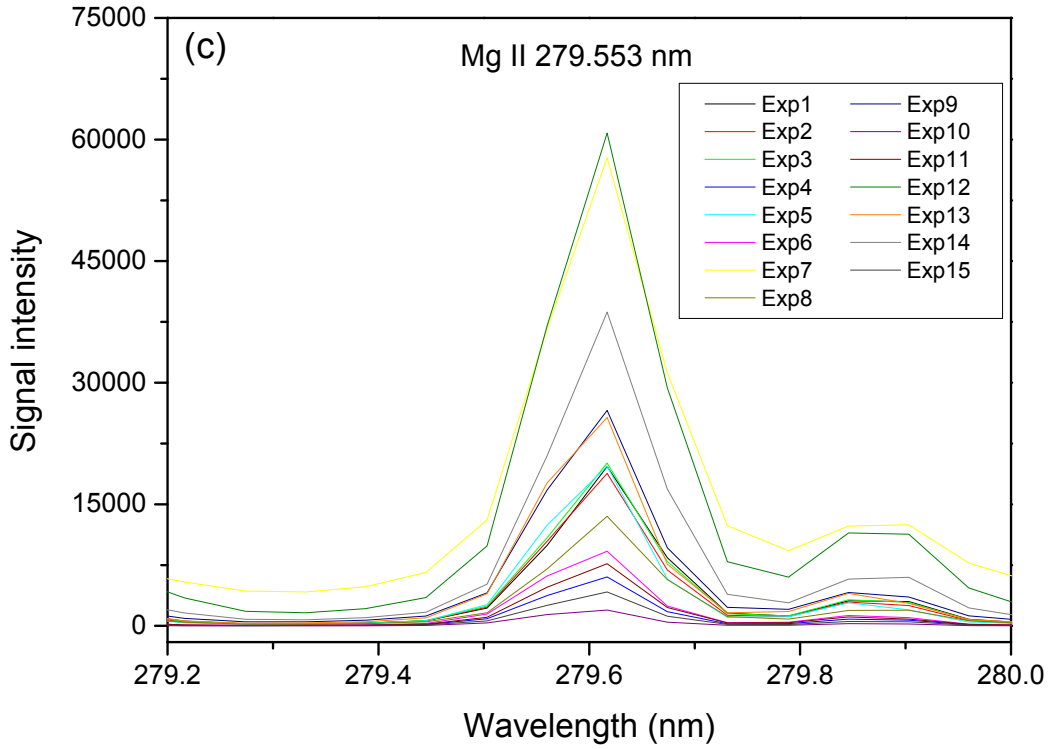

(c)
Mg II 279.553 nm
Exp1
Exp2
Exp3
Exp4
Exp5
Exp6
Exp7
Exp8
Exp9
Exp10
Exp11
Exp12
Exp13
Exp14
Exp15
Signal intensity
75000
60000
45000
30000
15000
0
279.2
279.4
279.6
279.8
280.0
Wavelength (nm)

Figure 1Sd

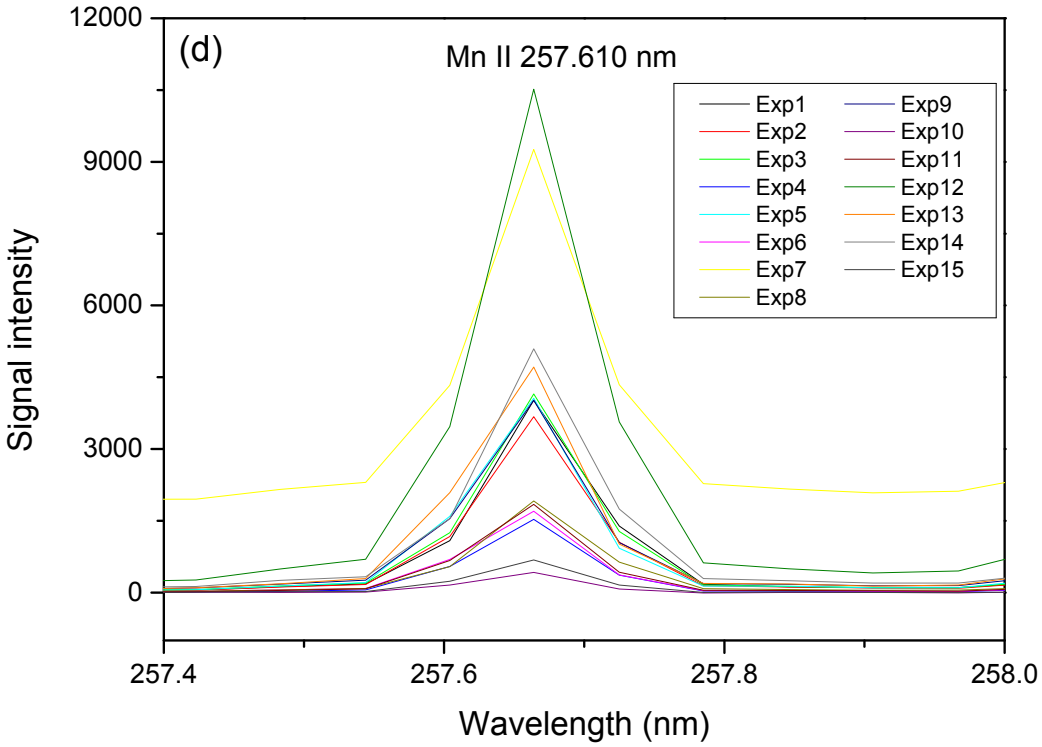

(d)
Mn II 257.610 nm
Exp1
Exp2
Exp3
Exp4
Exp5
Exp6
Exp7
Exp8
Exp9
Exp10
Exp11
Exp12
Exp13
Exp14
Exp15
Signal intensity
12000
9000
6000
3000
0
257.4
257.6
257.8
258.0
Wavelength (nm)

Figure 1Se

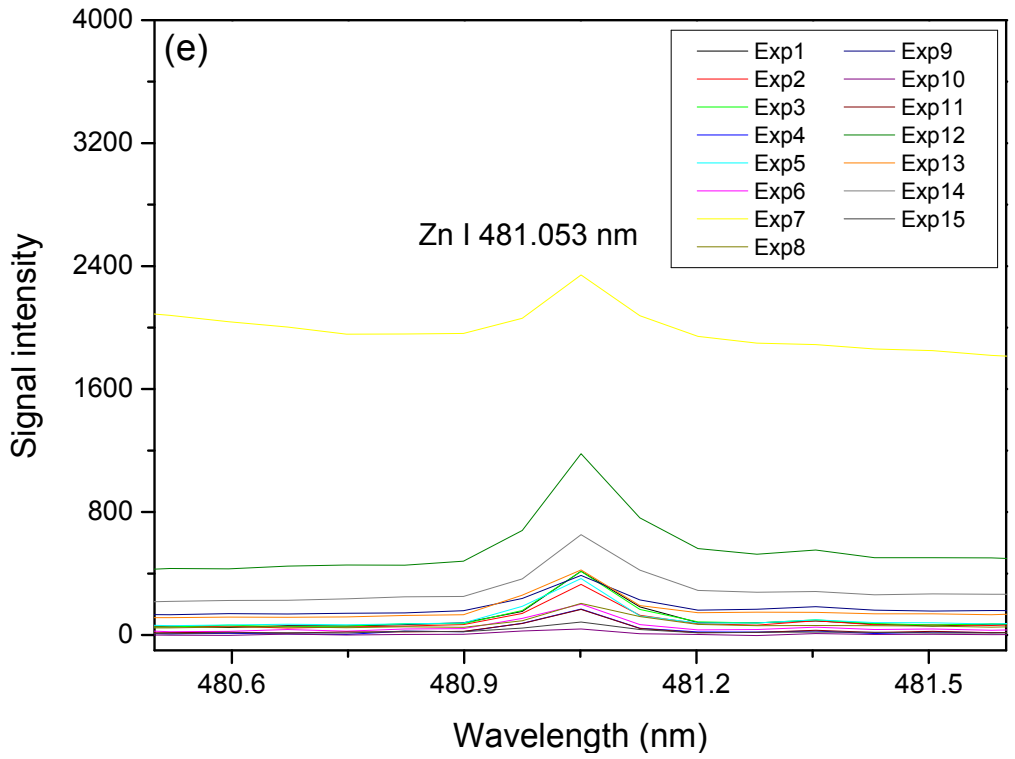

(e)
Zn I 481.053 nm
Exp1
Exp2
Exp3
Exp4
Exp5
Exp6
Exp7
Exp8
Exp9
Exp10
Exp11
Exp12
Exp13
Exp14
Exp15
Signal intensity
4000
3200
2400
1600
800
0
480.6
480.9
481.2
481.5
Wavelength (nm)

Figure 2Sa

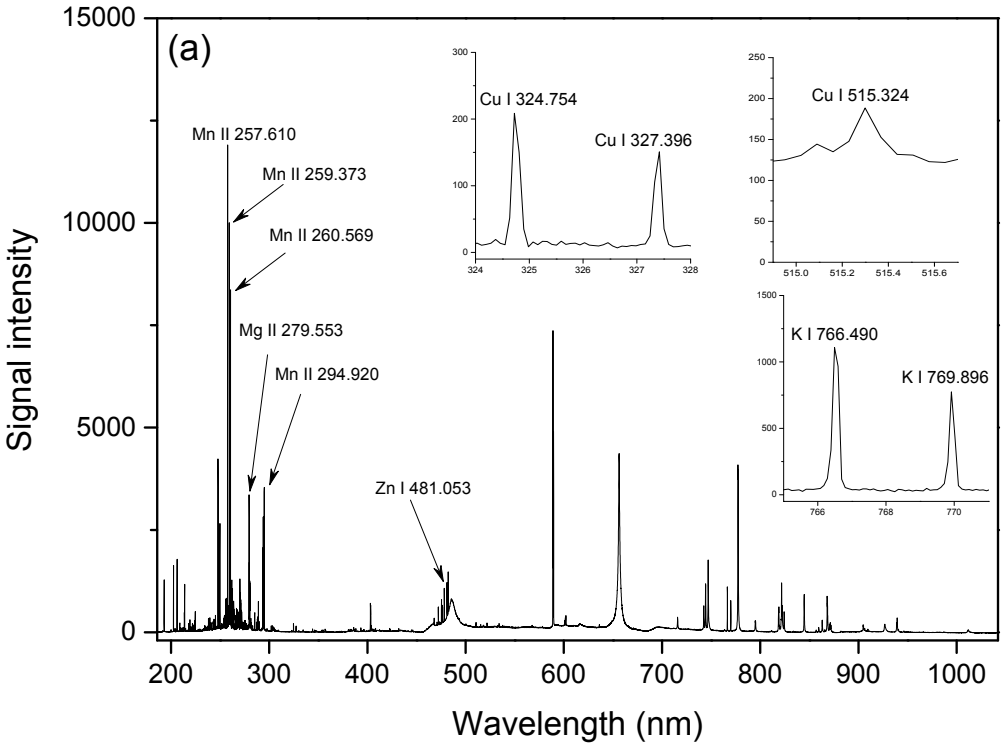

(a)
Mn II 257.610
Mn II 259.373
Mn II 260.569
Mg II 279.553
Mn II 294.920
Zn I 481.053
Cu I 324.754
Cu I 327.396
Cu I 515.324
K I 766.490
K I 769.896
Signal intensity
Wavelength (nm)

Figure 2Sb

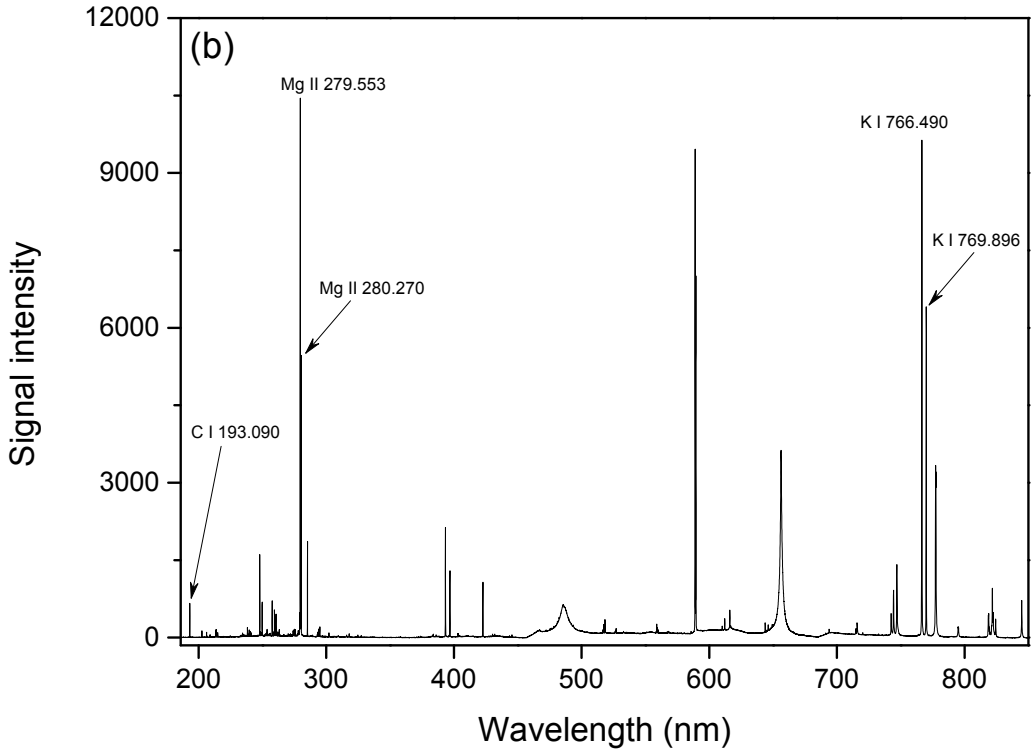

(b)
Mg II 279.553
Mg II 280.270
C I 193.090
K I 766.490
K I 769.896
Signal intensity
Wavelength (nm)
12000
9000
6000
3000
0
200
300
400
500
600
700
800

Figure 2Sc

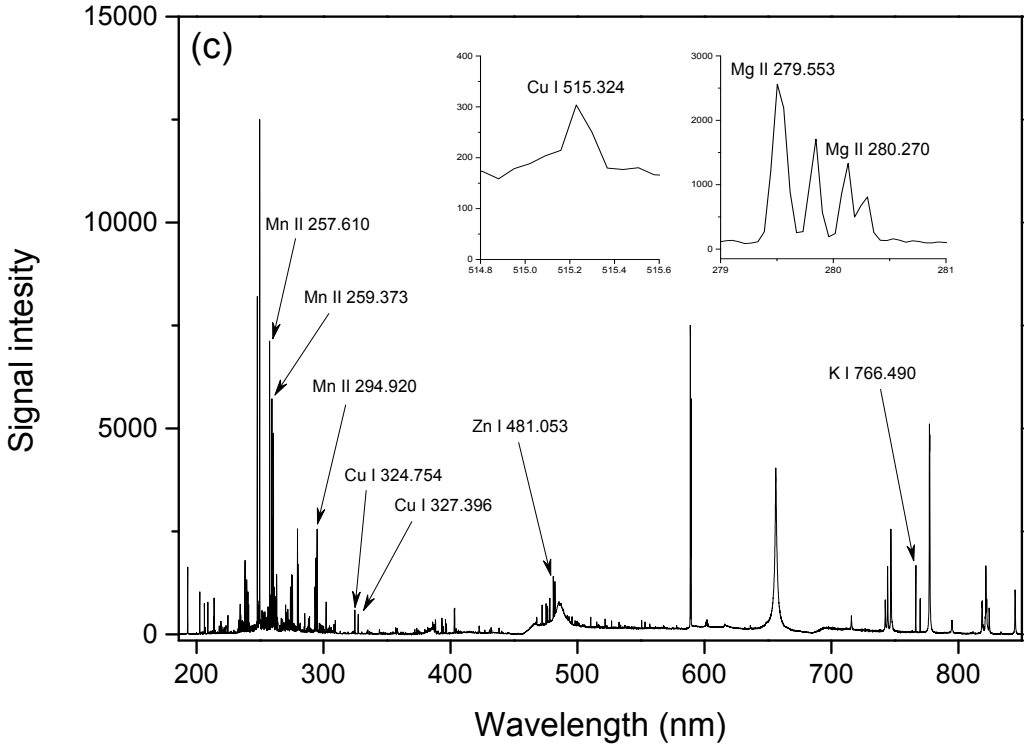

(c)
Cu I 515.324
Mg II 279.553
Mg II 280.270
Mn II 257.610
Mn II 259.373
Mn II 294.920
Cu I 324.754
Cu I 327.396
Zn I 481.053
K I 766.490
Signal intesity
Wavelength (nm)
15000
10000
5000
0
200
300
400
500
600
700
800

Figure 2Sd

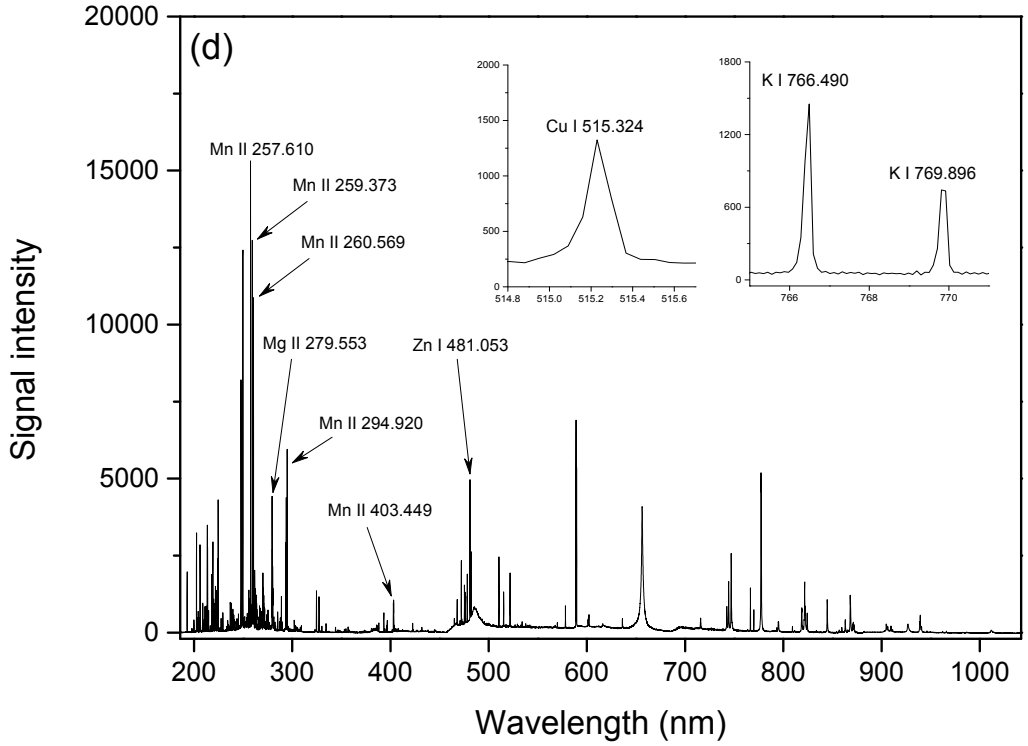

(d)
Mn II 257.610
Mn II 259.373
Mn II 260.569
Mg II 279.553
Mn II 294.920
Mn II 403.449
Zn I 481.053
Cu I 515.324
K I 766.490
K I 769.896
Signal intensity
Wavelength (nm)

Figure 2Se

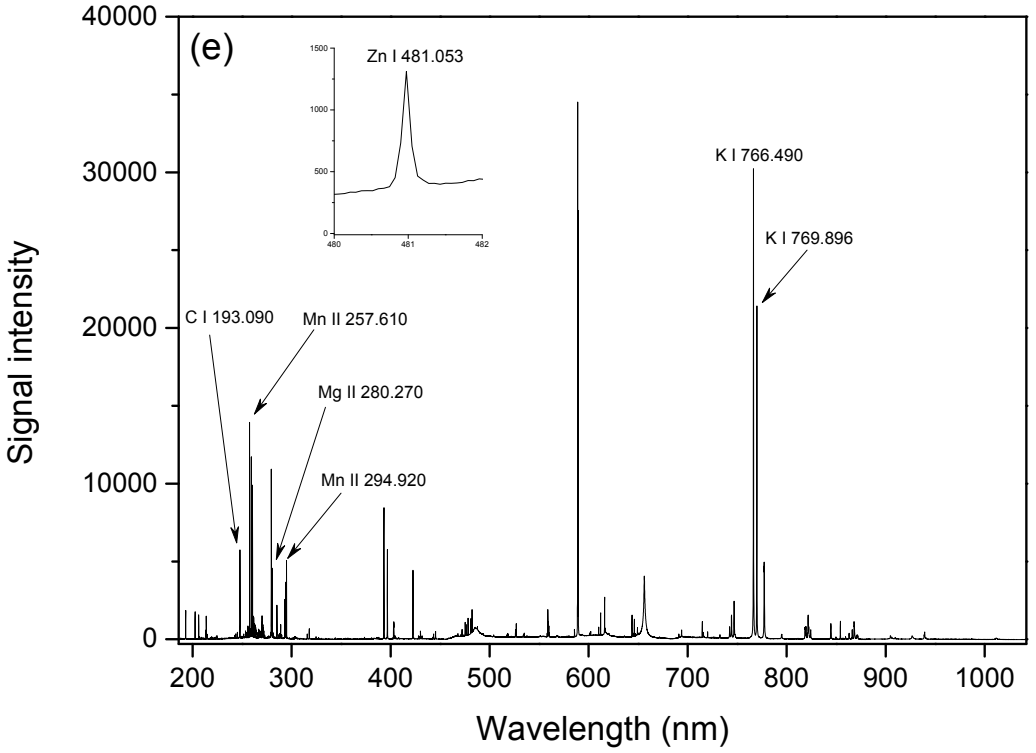

(e)
Zn I 481.053
K I 766.490
K I 769.896
C I 193.090
Mn II 257.610
Mg II 280.270
Mn II 294.920
Signal intensity
Wavelength (nm)
40000
30000
20000
10000
0
200
300
400
500
600
700
800
900
1000
1500
1000
500
0
480
481
482

Figure 2Sf

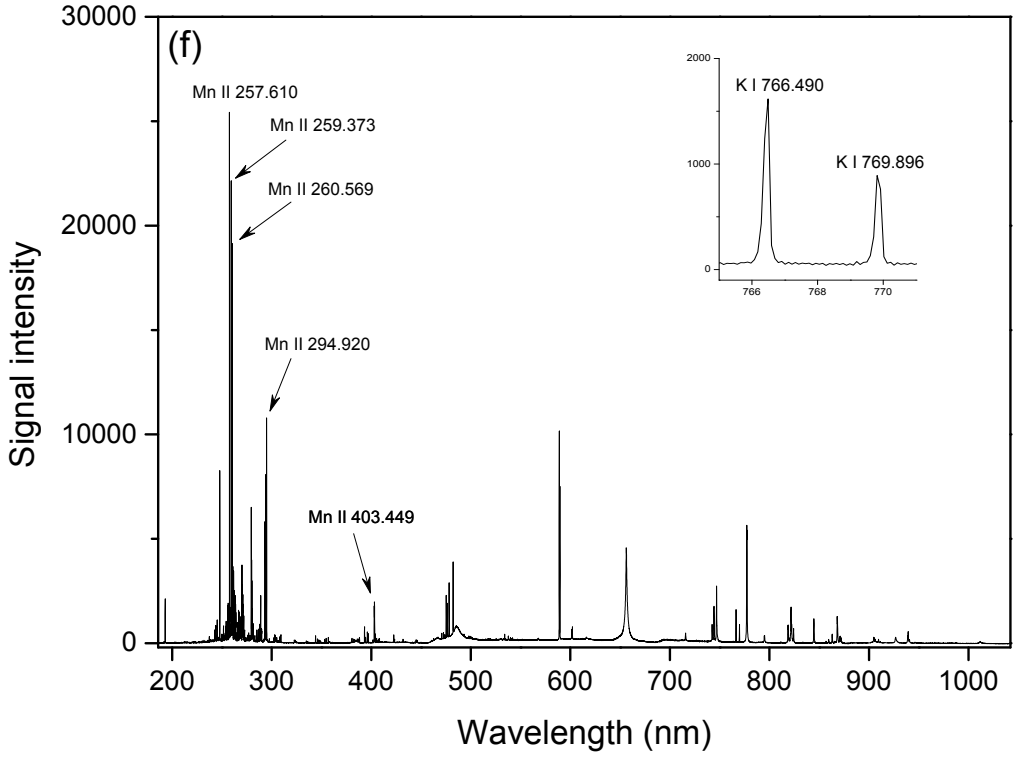

(f)
Mn II 257.610
Mn II 259.373
Mn II 260.569
Mn II 294.920
Mn II 403.449
K I 766.490
K I 769.896
Signal intensity
Wavelength (nm)
30000
20000
10000
0
200
300
400
500
600
700
800
900
1000
2000
1000
0
766
768
770

Figure 2Sg

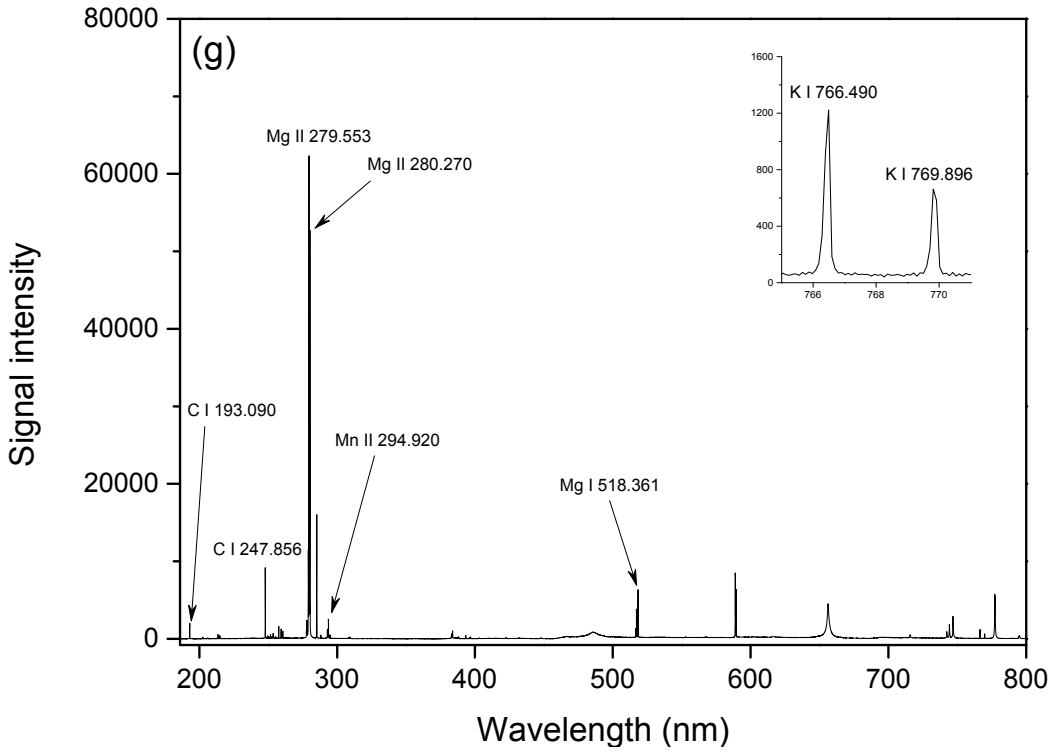

(g)
Signal intensity
Wavelength (nm)
Mg II 279.553
Mg II 280.270
C I 193.090
C I 247.856
Mn II 294.920
Mg I 518.361
K I 766.490
K I 769.896

Figure 2Sh

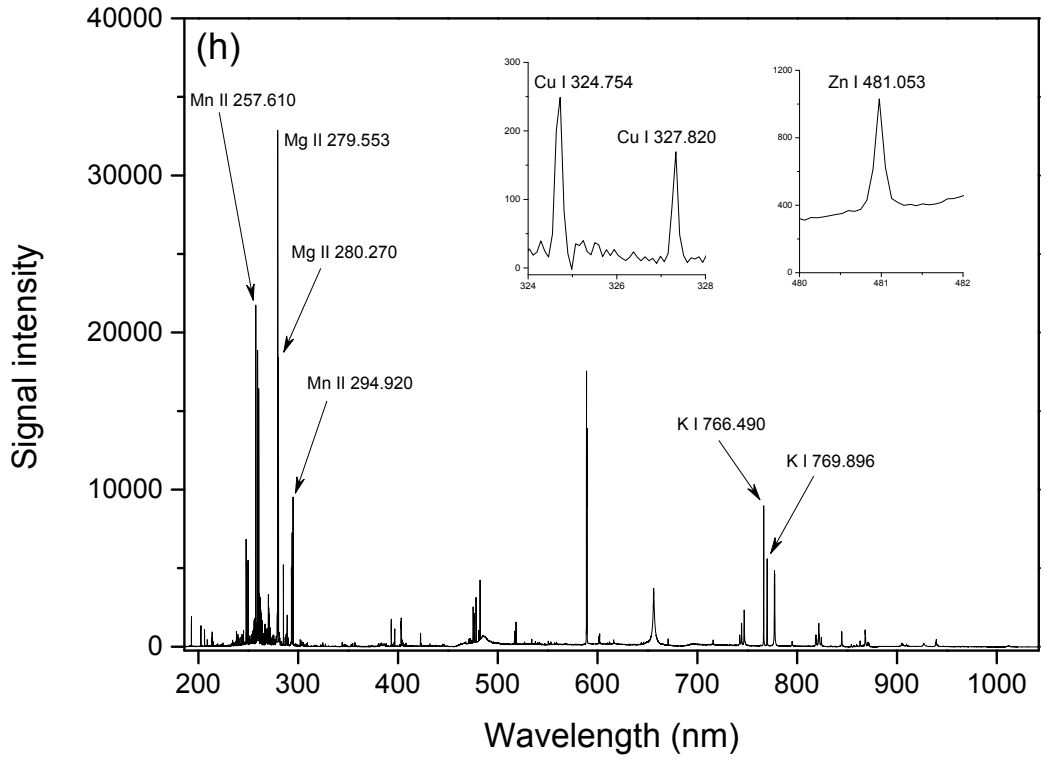
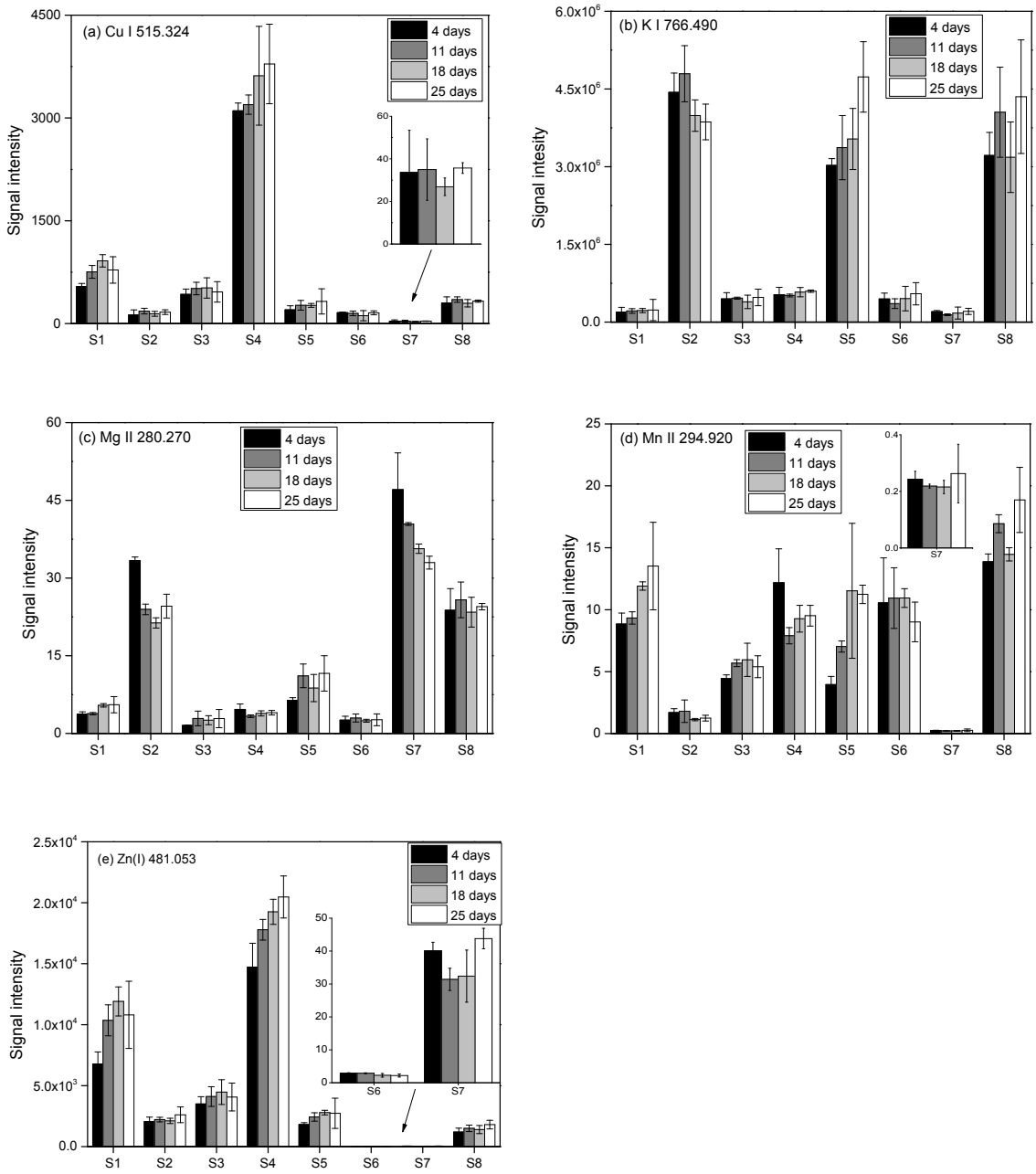

(h)
Mn II 257.610
Mg II 279.553
Mg II 280.270
Mn II 294.920
K I 766.490
K I 769.896
Cu I 324.754
Cu I 327.820
Zn I 481.053
Signal intensity
Wavelength (nm)
40000
30000
20000
10000
0
200
300
400
500
600
700
800
900
1000

Figure 3S


(a) Cu I 515.324
4 days
11 days
18 days
25 days
Signal intensity
4500
3000
1500
0
S1
S2
S3
S4
S5
S6
S7
S8
(b) K I 766.490
6.0x10^6
4.5x10^6
3.0x10^6
1.5x10^6
0.0
Signal intesity
(c) Mg II 280.270
60
45
30
15
0
(d) Mn II 294.920
25
20
15
10
5
0
(e) Zn(I) 481.053
2.5x10^4
2.0x10^4
1.5x10^4
1.0x10^4
5.0x10^3
0.0