**Supplementary: Figures**



Fig. S1 Schematic representation of the applied LIBS apparatus for the analysis of *Senna* leaves.



Fig. S2 Preparation of*Senna*leaves samples, a) purchased dried leaves, b) crushed leaves, and c) pelletized powdered leaves.



Fig. S3 Representative time delay influence on LIBS emission line intensities using Ca at 422.6 nm.

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Fig. S4 The representative influence of pulse energy on emission line intensities using of Ca lines peaking at 422.6 nm.

**Supplementary: tables**

Table S1. The spectroscopic data of different Ca lines used for the electron temperature (Te) determination.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Wavelength****(nm)** | **Element** |  **Signal Intensity** |  **Configurations** | **Statistical weight** | **Transition probability****Aik x10 8(S-1)** | **Energy of the upper** **level** |
| **gi** | **gk** | **Ei****(eV)** | **Ek****(eV)** |
| 428.9 | Ca I | 5533 | *3p64s4p* 3Po0$\rightarrow $*3p64p2* 3P1 | 1 | 3 | 0.6 | 1.879  | 4.769 |
| 429.8 | Ca I | 4550 | *3p64s4p* 3Po1$\rightarrow $*3p64p2* 3P1 | 3 | 3 | 0.466 | 1.885  | 4.769 |
| 430.7 | Ca I | 5936 | *3p64s4p* 3Po1$\rightarrow $*3p64p2* 3P0 | 3 | 1 | 1.99 | 1.885  | 4.763 |
| 442.5 | Ca I | 4989 | *3p*6 *4s4p*  3Po0$\rightarrow $ *3p*6 *4s4d* 3D1 | 1 | 3 | 0.498 | 1.879 | 4.68 |
| 527.0 | Ca I | 5746 | *3p*6 3d4s 3D3$\rightarrow $*3p*6*3d4p* 3Po2 | 7 | 5 | 0.5 | 2.526 | 4.878 |
| 585.7 | Ca I | 5431 | *3p*6 4s4p 1Po1$\rightarrow $*3p*6 *4p2* 1D2 | 3 | 5 | 0.66 | 2.933 | 5.049 |
| 616.2 | Ca I | 6972 | *3p*6 *4s4p* 3Po2$\rightarrow $ *3p*6 *4s5s* 3S1 | 5 | 3 | 0.477 | 1.899 | 3.91 |
| 649.3 | Ca I | 6422 | *3p*6*3d4s*  3D1$\rightarrow $*3p*6*3d4p* 3Fo2 | 3 | 5 | 0.44 | 2.521 | 4.43 |

Table S2. LIBS signal intensities of the viewed spectral transitions for the elemental analytes featuring the dried leaves samples of *Senna* and their concentration results using ICP-OES.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  **Elements** | **Wavelength** **(nm)** | **Transition Configuration** | **LIBS Signal Intensity****(a.u.)** | **ICP-OES concentration (mg/kg)** |
| **Ca** |  393.3 | *3p64s* 2S1/2$\rightarrow $ *3p64p* 2Po3/2 | 10871 | 26193.35 |
| 396.8 | *3p64s*  2S1/2$\rightarrow $ *3p64p* 2Po1/2 | 10322 |
| 422.6 | 3*p*6*4s*2 1S0$\rightarrow $ 3*p*6*4s4p* 1P°1 | 9812 |
| 445.4 | 3*p*6 *4s4p* 3Po2$\rightarrow $ 3*p*6 *4s4d* 3D3 | 6624 |
| 527.0 | *3p*6 3d4s 3D3$\rightarrow $ *3p*6*3d4p* 3Po2 | 5746 |
| 616.2 | *3p*6 *4s4p* 3Po2$\rightarrow $ *3p*6 *4s5s* 3S1 | 6972 |
| 646.2 | *3p*6*3d4s* 3D2$\rightarrow $ *3p*6*3d4p* 3Fo3 | 6795 |
| **K** | 404.7 | 3*p*6 4*s* 2S1/2$\rightarrow $ 3*p*6 5*p* 2P°1/2 | 5411 | 9829.17 |
| 580.1 | 3*p*6 4*p* 2P°1/2$\rightarrow $ 3*p*6 7s2S1/2 | 5305 |
| 766.4 | 3*p*6 4*s* 2S1/2$\rightarrow $ 3*p*6 4*p* 2P°3/2 | 6034 |
| 769.8 | 3*p*6 4*s* 2S1/2$\rightarrow $ 3*p*6 4*p* 2P°1/2 | 5812 |
| **Mg** | 279.5 | 2*p*6 3*s* 2S1/2$\rightarrow $ 2*p*6 3*p* 2P°3/2 | 5068.5 | 3499.54 |
| 280.2 | 2*p*6 3*s* 2S1/2$\rightarrow $ 2*p*6 3*p* 2P°1/2 | 3856.5 |
| 285.2 | 2*p*6 3*s2* 1S0$\rightarrow $3*s3p* 1P°1 | 5305 |
| 448.1 | 2*p*6 3*d* 2D5/2$\rightarrow $2*p*6 *4f* 2F°7/2 | 652 |
| 518.3 | 3s3*p* 3P2$\rightarrow $3*s4s* 3S1 | 1316 |
| **S** | 543.2 | 3*s*2*3p2(3P) 4s* 4P3/2$\rightarrow $ 3*s*2*3p2(3P) 4p* 4Do5/2 | 2533 | 2311.49 |
| 545.3 | 3*s*2*3p2(3P) 4s* 4P5/2$\rightarrow $ 3*s*2*3p2(3P) 4p* 4Do7/2 | 2778 |
| 563.9 | 3*s*2*3p2(3P) 4s* 2P3/2$\rightarrow $ 3*s*2*3p2(3P) 4p* 2Do5/2 | 1918 |
| **P** | 253.5 | 3*s*2*3p3* 2Po3/2$\rightarrow $ 3*s*2*3p2(3P) 4s* 2P3/2 | 2576 | 1516.95 |
| 255.3 | 3*s*2*3p3* 2Po1/2$\rightarrow $ 3*s*2*3p2(3P) 4s* 2P1/2 | 2604 |
| 650.3 | 3*s*2*3p3d* 3Fo3$\rightarrow $ 3*s*2*3p4p* 3D2 | 1546 |
| **Na** | 328.5 | 2*s*2 2*p5 3s* 1Po1$\rightarrow $2*s*2 2*p5 3p* 1D2 | 3334 | 968.37 |
| 330.1 | 2*s*2 2*p5 3p* 3P1$\rightarrow $2*s*2 2*p5 (*2Po3/2*) 3d* 2[3/2]o2 | 3148 |
| 588.9 | 2*p*6 *3s* 2S1/2$\rightarrow $2*p*6 *3p* 2Po3/2 | 3207 |
| 589.5 | 2*p*6 *3s* 2S1/2$\rightarrow $2*p*6 *3p* 2Po1/2 | 2341 |
| **Al** | 281.6 | 3*s3p* 1Po1$\rightarrow $ 3*s4s* 1S0 | 2414 | 574.85 |
| 394.4 | 3*s*2*3p* 2Po1/2$\rightarrow $ 3*s*2*4s* 2S1/2 | 2111 |
| 396.1 | Fe3*s*2*3p* 2Po3/2$\rightarrow $ 3*s*2*4s* 2S1/2 | 2686 |
| **Si** | 251.6 | 3*s*2*3p2* 3P2$\rightarrow $ 3*s*2*3p4s* 3Po2 | 2124 | 550.66 |
| 252.4 | 3*s*2*3p2* 3P1$\rightarrow $ 3*s*2*3p4s* 3Po0 | 2243 |
| 288.1 | 3*s*2*3p2* 1D2$\rightarrow $ 3*s*2*3p4s* 1Po0 | 2629 |
| **Fe** | 248.3 | 3*d*6 *4s*2 5D4$\rightarrow $ 3*d*6*(5D)4s4p* (1Po) 5F°5 | 2544 | 477.72 |
| 259. 9 | 3*d*6 *(5D) 4s* 6D9/2$\rightarrow $ 3*d*6*(5D) 4p* 6Do9/2 | 2338 |
| 275.5 | 3*d*6 *(5D) 4s* 4D7/2$\rightarrow $ 3*d*6*(5D) 4p* 4Fo9/2 | 2043 |
| 358.1 | 3*d*7 *(4F) 4s* 5F5$\rightarrow $ 3*d*7*(4F) 4p* 5Go6 | 2095 |
| **Sr** | 407.7 | 4*p*6 *5s* 2S1/2$\rightarrow $ 4*p65p* 2Po3/2 | 2054 | 182.63 |
| 421.5 | 4*p*6 *5s* 2S1/2$\rightarrow $ 4*p65p* 2Po1/2 | 1900 |
| **B** | 249.6 | 2s2 *2p* 2Po1/2$\rightarrow $ 2s2 *3s* 2S1/2 | 893 | 43.56 |
| 249.7 | 2s2 *2p* 2Po3/2$\rightarrow $ 2s2 *3s* 2S1/2 | 1528 |
| 345.1 | 1s2 *2s2p* 1Po1$\rightarrow $ 1s2 *2p2* 1D2 | 954 |
| **Ba** | 553.5 | 6*s*2 1S0$\rightarrow $*6s6p* 1Po1 | 1499 | 35.16 |
| 614.1 | 5d2D5/2$\rightarrow $*6p* 2Po3/2 | 628 |
| **Mn** | 403.0 | 3*d*5*4s*2 6S5/2$\rightarrow $ 3*d*5*(6S) 4s4p* ( 3P°) 6Po7/2 | 1169 | 34.20 |
| 257.6 | 3*d*5*(6S)4s* 7S3$\rightarrow $ 3*d*5*(6S) 4p* 7Po4 | 1467 |
| 259.3 | 3*d*5*(6S)4s* 7S3$\rightarrow $ 3*d*5*(6S) 4p* 7Po3 | 930 |
| **Ti** | 334.9 | 3*d*2 *(3F) 4s* 4F9/2$\rightarrow $ 3*d*2*(3F) 4p* 4Go11/2 | 1505 | 21.95 |
| 336.1 | 3*d*2 *(3F) 4s* 4F7/2$\rightarrow $ 3*d*2*(3F) 4p* 4Go9/2 | 776 |
| 365.3 | 3*d*2*4s*2 3F4$\rightarrow $ 3*d*2*(3F) 4s4p (*1Po*)* 3Go5 | 847 |
| 399.8 | 3*d*2*4s*2 3F4$\rightarrow $ 3*d*2*(3F) 4s4p (*1Po*)* 3Fo4 | 1280 |
| **Zn** | 255.7 | 3*d*10*4p* 2Po3/2$\rightarrow $ 3*d*10 *5s* 2S1/2 | 424 | 9.36 |
| 334.5 | 3*d*10 *4s4p* 3Po2$\rightarrow $ 3*d*10 *4s4d* 3D3 | 565 |
| **Cr** | 425.4 | 3*d*5 *(6S) 4s* 7S3$\rightarrow $ 3*d*5*(6S) 4p* 7P°4 | 488 | 3.54 |
| 357.8 | 3*d*5 *(6S) 4s* 7S3$\rightarrow $ 3*d*4*(5D) 4s4p* ( 3P°) 7P°4 | 453 |
| 520.8 | 3*d*5 *(6S) 4s* 5S2$\rightarrow $ 3*d*5*(6S) 4p* 5P°3 | 367 |
| **Cu** | 324.7 | 3*d*10*(1S) 4s* 2S1/2$\rightarrow $ 3*d*10*(1S) 4p* 2P°3/2 | 428 | 3.23 |
| 327.3 | 3*d*10*(1S) 4s* 2S1/2$\rightarrow $ 3*d*10*(1S) 4p* 2P°1/2 | 564 |
| **Ni** | 341.4 | 3*d*9*(2D) 4s* 3D3$\rightarrow $ 3*d*9*(2D) 4p* 3F°4 | 355 | 1.94 |
| 352.4 | 3*d*9*(2D) 4s* 3D3$\rightarrow $ 3*d*9*(2D) 4p* 3P°2 | 382 |
| 356.6 | 3*d*9*(2D) 4s* 1D2$\rightarrow $ 3*d*9*(2D) 4p* 1D°2 | 257 |
| **V** | 437.9 | 3*d*4*(5D) 4s* 6D9/2$\rightarrow $ 3*d*4*(5D) 4p* 6F°11/2 | 325 | 1.5 |
| 440.8 | 3*d*4*(5D) 4s* 6D3/2$\rightarrow $ 3*d*4*(5D) 4p* 6F°3/2 | 250 |
| **As** | --- | --- | ND | ND |
| **Se** | --- | --- | ND | ND |
| **Cd** | --- | --- | ND | ND |
| **Co** | --- | --- | ND | ND |
| **Pb** | --- | --- | ND | ND |

ND: Not detected