**Table S1.** Spectral preprocessing parameters used in this work

| Parameter | Value |
|---|---|
| Dark-current acquisition | Avantes AvaSoft built-in routine, laser blocked |
| Baseline algorithm | Asymmetric least squares (AsLS); Eilers & Boelens |
| AsLS smoothness λ | $10^5$ |
| AsLS asymmetry p | 0.001 |
| Smoothing filter | Savitzky–Golay |
| Smoothing window | 7 points |
| Smoothing polynomial order | 3 |
| Peak-detection routine | scipy.signal.find_peaks (SciPy v1.13) |
| NIST line-match tolerance | ±0.07 nm |
| Line profile fit | Lorentzian (least-squares) |
| Instrumental broadening | 0.07 nm (subtracted in quadrature for Stark) |
| ML cross-validation | Leave-One-Group-Out (per pellet) |
| Spectra per class | 100 (5 pellets × 20 shots) |

**Figure S1.** Representative raw-to-processed LIBS spectra showing dark-current/background correction, baseline subtraction, smoothing, and final processed spectrum.

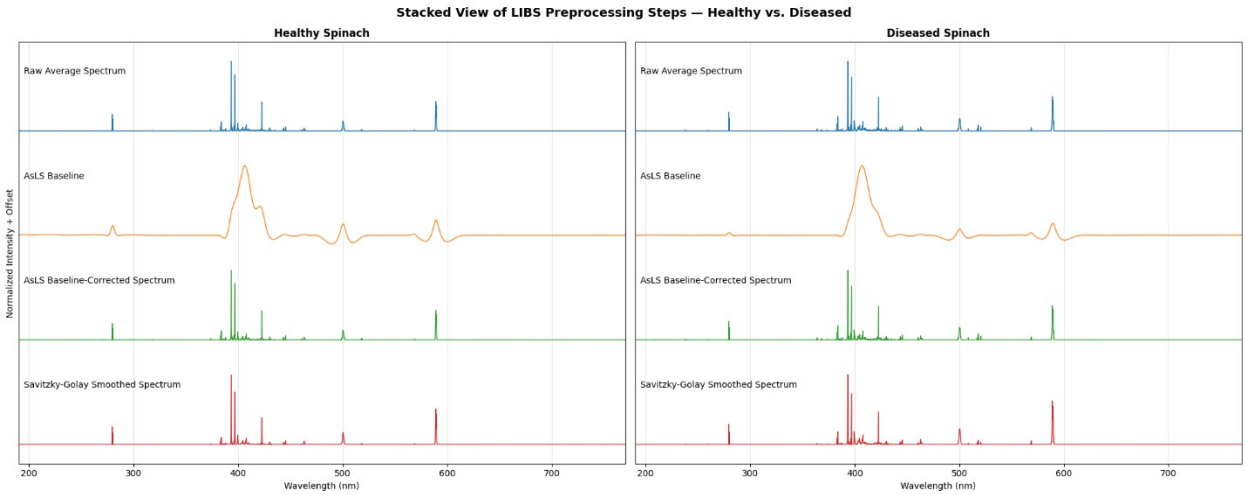

**Table S2.** Observed LIBS emission lines and NIST assignments within ±0.07 nm.

| Line | NIST wavelength (nm) | Observed wavelength (nm) |
|---|---|---|
| B I 249.67 | 249.67 | 249.632 |
| P I 253.56 | 253.56 | 253.513 |
| Mg II 279.55 | 279.55 | 279.497 |
| Mn I 279.83 | 279.83 | 279.764 |
| Mg II 280.27 | 280.27 | 280.198 |
| Si I 288.15 | 288.15 | 288.126 |
| Ca II 317.93 | 317.93 | 317.978 |
| Pb I 363.96 | 363.96 | 363.966 |
| Pb I 368.35 | 368.35 | 368.340 |
| Ca II 373.69 | 373.69 | 373.711 |
| Mg I 383.23 | 383.23 | 383.187 |
| Mg I 383.83 | 383.83 | 383.774 |
| Hg II 391.92 | 391.92 | 391.925 |
| Ca II 393.37 | 393.37 | 393.304 |
| Ti I 395.63 | 395.63 | 395.590 |
| Al I 396.15 | 396.15 | 396.134 |
| Ca II 396.85 | 396.85 | 396.821 |
| Mn I 403.31 | 403.31 | 403.320 |
| K I 404.41 | 404.41 | 404.436 |
| Fe I 407.17 | 407.17 | 407.166 |
| Fe I 407.62 | 407.62 | 407.620 |
| V I 409.54 | 409.54 | 409.587 |
| V I 409.97 | 409.97 | 409.965 |
| Ag II 411.18 | 411.18 | 411.25 |
| Ca I 422.67 | 422.67 | 422.698 |
| Cr I 425.43 | 425.43 | 425.362 |

| | | |
|---|---|---|
| Cr I 428.97 | 428.97 | 428.930 |
| Cr I 430.11 | 430.11 | 430.120 |
| Hg I 435.83 | 435.83 | 435.785 |
| V I 443.45 | 443.45 | 443.428 |
| Ca I 445.48 | 445.48 | 445.410 |
| Ni I 460.62 | 460.62 | 460.626 |
| Zn I 462.98 | 462.98 | 463.009 |
| Zn I 468.01 | 468.01 | 468.032 |
| Zn I 481.05 | 481.05 | 481.071 |
| Fe I 500.20 | 500.20 | 500.195 |
| Cd I 508.58 | 508.58 | 508.592 |
| Mg I 517.27 | 517.27 | 517.210 |
| Mg I 518.36 | 518.36 | 518.330 |
| Cr I 520.45 | 520.45 | 520.470 |
| Na I 568.82 | 568.82 | 568.831 |
| Na I 588.99 | 588.99 | 588.970 |
| Na I 589.59 | 589.59 | 589.529 |

**Table S3.** Lorentzian fitting parameters pre and post IRSAC correction.

| **Line** | **Sample** | **self-absorbed center (nm)** | **Self-absorbed peak intensity** | **IRSAC-corrected peak intensity** | **IRSAC-corrected /self absorbed intensity ratio** |
|---|---|---|---|---|---|
| Na I 588.99 | Healthy | 588.93667 | 11418.42 | 16275.03 | 1.43 |
| Na I 588.99 | Diseased | 588.91655 | 10391.90 | 20538.96 | 1.98 |
| Na I 589.59 | Healthy | 589.56211 | 8996.25 | 10870.95 | 1.21 |
| Na I 589.59 | Diseased | 589.56595 | 9029.08 | 16972.09 | 1.88 |

| | | | | | |
|---|---|---|---|---|---|
| Mg II 279.553 | Healthy | 279.49035 | 2239.87 | 3442.17 | 1.54 |
| Mg II 279.553 | Diseased | 279.48980 | 2586.35 | 3237.73 | 1.25 |
| Ca II 393.366 | Healthy | 393.32175 | 46747.04 | 77782.62 | 1.66 |
| Ca II 393.366 | Diseased | 393.31831 | 38111.23 | 70272.80 | 1.84 |

**Figure S2.** Representative self-absorbed line profiles of (a) Na I 588.99/589.59 nm, (b) Ca II 393.366 nm and (c) Mg II 279.553 nm used to evaluate line-shape distortion before IRSAC correction.