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Supplement for

GHCTWNNM: A Gradient Histogram Constraint Truncated WNNM Denoising Algorithm for LIBS with Spectrum-to-Image Conversion

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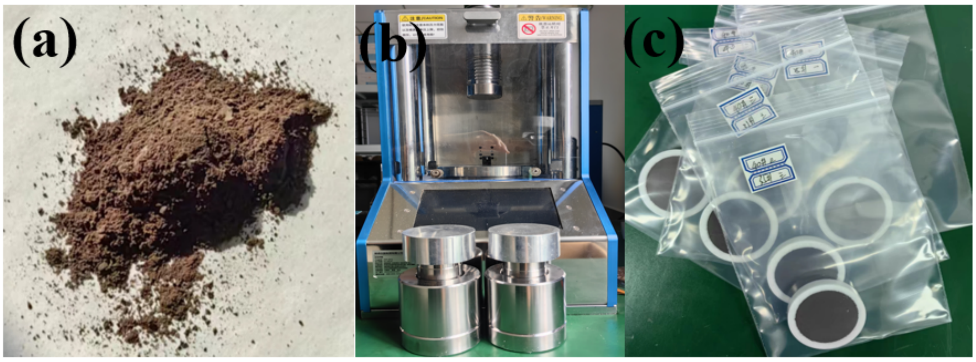

Fig.S1 Process of samples preparation. (a) is the powdery steel slag sample, (b) is the the tablet press produced by Shanghai Xinnuo Instrument Equipment Co., Ltd. And (c) is sample after tablet pressing.

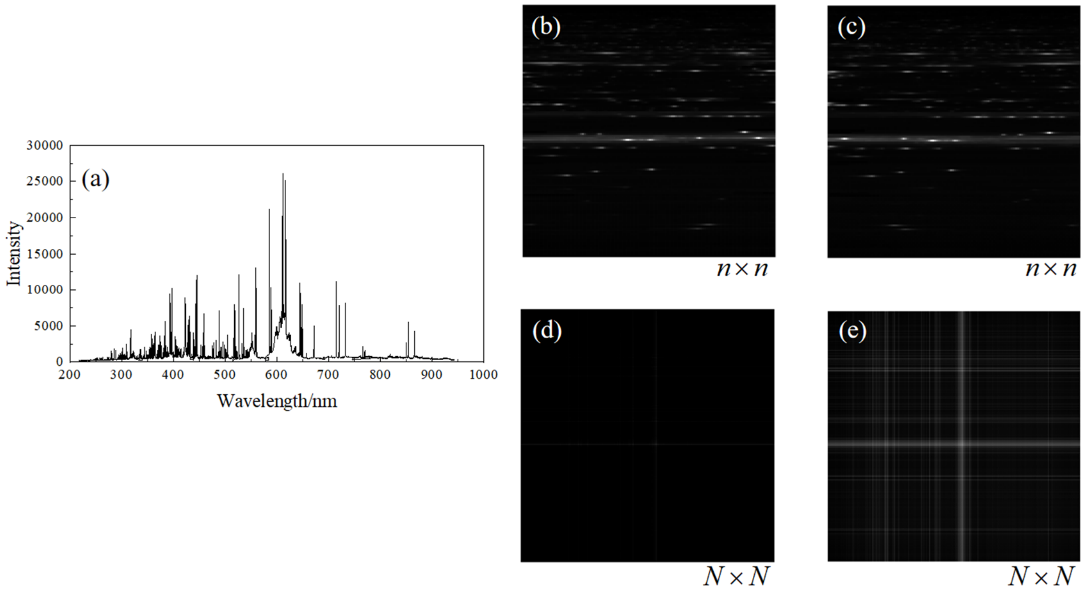

Fig.S2 The grayscale images of Fig.4. (a) is the raw LIBS spectrum, and (b)-(e) are the 2D LIBS images obtained using the methods in Fig.3(a), (b), GASF, and GADF, respectively.

Tab.S1 The concentration of the major components in steel slag samples.

No.sample	TFe	SiO_2	CaO	MgO	Al_2O_3	S	P_2O_5	TiO_2	MnO	Fe_2O_3
1	18.12	11.55	43.15	8.53	1.97	0.08	2.47	1.12	3.56	
2#	16.78	13.49	42.26	8.02	1.71	0.06	3.07	1.16	3.91	
3	18.43	11.53	41.70	8.83	2.00	0.08	2.55	1.20	3.77	
4#	25.97	10.21	37.41	7.77	1.91	0.09	2.33	1.13	3.54	
5	17.08	13.72	42.24	7.93	1.70	0.07	3.11	1.19	3.98	
6	19.49	11.42	41.05	8.66	2.60	0.07	2.49	1.17	3.80	
7	18.55	13.38	41.33	7.36	1.70	0.06	3.02	1.20	4.07	
8	17.65	13.24	42.06	8.16	1.74	0.06	3.05	1.13	3.98	9.84
9#	20.52	11.78	40.93	8.08	1.85	0.06	2.41	1.05	3.66	12.22
10#	17.88	13.89	41.96	7.84	1.83	0.07	3.07	1.26	4.16	
11	17.86	13.49	42.01	7.82	1.85	0.05	3.03	1.18	4.09	
12#	19.12	12.09	41.22	8.65	2.14	0.08	2.55	1.20	3.71	12.97
13#	20.45	10.67	41.35	7.67	1.93	0.08	2.46	1.12	3.68	
14	32.44	9.22	31.51	2.82	1.96	0.11	1.66	0.73	3.89	
15	21.51	10.77	39.71	7.89	1.69	0.06	2.41	1.05	3.97	
16	29.29	10.71	33.54	3.18	2.50	0.10	1.97	0.89	4.35	
17	31.54	10.05	31.29	2.79	2.62	0.10	1.76	0.90	4.07	
18#	23.04	12.05	38.13	6.65	1.73	0.05	2.64	1.12	3.68	16.73
19	18.23	13.22	41.26	7.82	1.92	0.05	3.05	1.16	3.91	
20#	18.39	13.00	41.24	7.83	1.93	0.06	2.96	1.16	3.86	
21	17.43	13.04	42.21	7.55	1.95	0.07	3.01	1.18	3.87	
22	22.27	10.86	39.69	8.34	1.78	0.05	2.48	1.16	3.85	
23	21.29	10.65	40.99	8.31	1.71	0.06	2.52	1.14	3.81	
24#	17.73	13.71	42.87	7.49	1.80	0.06	3.16	1.22	4.07	
25	22.68	10.03	41.12	8.19	1.49	0.08	2.63	0.93	3.78	
26	19.87	12.50	41.69	7.47	1.74	0.06	3.12	1.17	3.97	
27	22.26	12.08	39.11	6.83	1.73	0.06	2.82	1.23	3.87	
28	31.99	9.54	30.87	2.73	2.34	0.11	1.76	0.90	4.21	18.77
29	20.20	10.66	42.5	8.38	1.53	0.07	2.71	0.99	3.91	
30	30.49	10.01	32.41	2.81	2.50	0.10	1.90	0.93	4.42	
31	29.47	10.27	33.00	2.81	2.65	0.10	1.94	0.96	4.42	
32	35.56	9.46	28.88	2.79	2.41	0.09	1.67	0.88	3.89	
33	30.93	9.64	31.88	2.68	2.46	0.10	1.75	0.91	4.11	
34	29.51	10.42	32.76	3.16	2.60	0.11	1.86	0.89	4.29	
35	29.31	10.38	32.41	3.02	2.50	0.10	1.87	0.91	4.38	
36	20.98	10.83	40.31	8.16	1.53	0.07	2.47	1.04	3.86	
37	21.58	12.21	38.77	7.64	1.64	0.06	2.74	1.17	3.71	
38	29.47	10.21	33.06	3.09	2.39	0.10	1.91	0.90	4.29	
39#	29.72	10.30	33.03	3.01	2.51	0.11	1.87	0.90	4.28	13.02
40	31.81	9.95	31.58	2.81	2.46	0.10	1.81	0.88	4.20	

Tab.S2 The model, parameters and other information of the LIBS experiment instruments.

Experiment instruments	Model, parameters and other information
Laser	The laser is produced by Changchun New Industries Optoelectronics Technology, the model is DPS-1064-BS-D, the wavelength is 1064nm, the laser energy is adjustable in 0-100mJ, the frequency is 10Hz, the pulse width is 10ns.
DG645	Model number is Stanford DG645 Digital Delay Pulse Generator, which is a precision 8-channel delay generator that can output arbitrary delays from 0 to 2000 s with 5 ps resolution and typical rms jitter of 12 ps.
Spectrometer	The spectrometer is the AvaSpec Multi-Channel optical fiber spectrometer with a spectral resolution of 0.14-0.18nm.
ICCD	The model is the DH334T camera produced by Andor in the UK, with 1024*1024 pixels.
Lens	The focal length is 75mm.

Tab.S3 SNR value of characteristic spectral lines at Al396.15nm after adding noise with different variances.

σ^2	0.2	0.4	0.6	0.8	1
SNR/dB	16.00	13.93	11.07	9.81	7.13

The principle of GAF and inverse GAF

For the LIBS spectrum sequence, we should first normalize the spectra intensity to the range of [-1,1]. Considering that there will be a one-to-many mapping relationship when performing the inverse GAF transformation, we choose to normalize the spectra intensity to the range of [0,1]. Assuming the LIBS spectra sequence is $y=[y_1,y_2,...,y_N]$, the normalization form can be expressed as

$$\tilde{y}_i = \frac{y_i - \min(y_i)}{\max(y_i)-\min(y_i)} \tag{S1}$$

Subsequently, we represent the spectra sequence in polar coordinates, and we can have

$$\begin{cases} \varphi = \arccos(\tilde{y}_i) \\ r = i/N \end{cases} \tag{S2}$$

The Gramian Angular Difference Field (GADF) can be expressed as

$$\begin{aligned}
&GADF \\
&=[\sin(\varphi_i-\varphi_j)] \\
&=\begin{bmatrix} \sin(\varphi_1-\varphi_1) & \sin(\varphi_1-\varphi_2) & \ldots & \ldots & \sin(\varphi_1-\varphi_N) \\ \sin(\varphi_2-\varphi_1) & \sin(\varphi_2-\varphi_2) & \ldots & \ldots & \sin(\varphi_2-\varphi_N) \\ . & & & & . \\ . & & & & . \\ . & & & & . \\ \sin(\varphi_N-\varphi_1) & \sin(\varphi_N-\varphi_2) & \ldots & \ldots & \sin(\varphi_N-\varphi_N) \end{bmatrix} \\
&=\left[\sin\left(\arccos(\tilde{y}_i)-\arccos(\tilde{y}_j)\right)\right] \\
&=\sin\left(\arccos(\tilde{y}_i)\right)\cos\left(\arccos(\tilde{y}_j)\right)-\cos\left(\arccos(\tilde{y}_i)\right)\sin\left(\arccos(\tilde{y}_j)\right) \\
&=\sqrt{1-\tilde{y}_i^{\,2}}\,\tilde{y}_j-\tilde{y}_i\sqrt{1-\tilde{y}_j^{\,2}} \\
&=\sqrt{\boldsymbol{I}-\tilde{\boldsymbol{y}}^2}^{\,T}\,\tilde{\boldsymbol{y}}-\tilde{\boldsymbol{y}}^T\sqrt{\boldsymbol{I}-\tilde{\boldsymbol{y}}^2}
\end{aligned} \tag{S3}$$

And the Gramian Angular Summation Field (GASF) can be expressed as

$$
\begin{aligned}
&GASF \\
&=[\cos(\varphi_i+\varphi_j)] \\
&=\begin{bmatrix}
\cos(\varphi_1+\varphi_1) & \cos(\varphi_1+\varphi_2) & \dots & \dots & \cos(\varphi_1+\varphi_N) \\
\cos(\varphi_2+\varphi_1) & \cos(\varphi_2+\varphi_2) & \dots & \dots & \cos(\varphi_2+\varphi_N) \\
. & & & & . \\
. & & & & . \\
. & & & & . \\
\cos(\varphi_N+\varphi_1) & \cos(\varphi_N+\varphi_2) & \dots & \dots & \cos(\varphi_N+\varphi_N)
\end{bmatrix} \\
&=\left[\cos\left(\arccos(\tilde{y}_i)+\arccos(\tilde{y}_j)\right)\right] \qquad\qquad\qquad\qquad \text{(S4)} \\
&=\cos\left(\arccos(\tilde{y}_i)\right)\cos\left(\arccos(\tilde{y}_j)\right)-\sin\left(\arccos(\tilde{y}_i)\right)\sin\left(\arccos(\tilde{y}_j)\right) \\
&=\tilde{y}_i\tilde{y}_j-\sqrt{1-\tilde{y}_i^{\,2}}\sqrt{1-\tilde{y}_j^{\,2}} \\
&=\tilde{\boldsymbol{y}}^T\tilde{\boldsymbol{y}}-\sqrt{\boldsymbol{I}-\tilde{\boldsymbol{y}}^2}^{\,T}\sqrt{\boldsymbol{I}-\tilde{\boldsymbol{y}}^2}
\end{aligned}
$$

For the Inverse Gramian Angular Summation Field (IGASF) transformation, according to Eq.(S4), we can have $GASF_{i,i}=2\tilde{y}_i^{\,2}-1$, then the result of the IGASF can be expressed as $\tilde{y}_i=\sqrt{\dfrac{GASF_{i,i}+1}{2}}$.

The information of four different wavelet thresholding strategies

Thresholding strategy	The threshold value
Sqtwolog	$\lambda_1 = \sigma\sqrt{2\ln N}$ $\sigma = \frac{median(\lvert w \rvert)}{0.6745}$, w is the wavelet coefficient to scale j.
MiniMaxi	$\lambda_2 = \begin{cases} \sigma\left[0.3936 + 0.10829(\ln N / \ln 2)\right], & N > 32 \\ 0, & N \le 32 \end{cases}$
Heursure	$\lambda_3 = \begin{cases} \lambda_1, & \eta > \mu \\ \min(\lambda_1, \lambda_0), & \eta < \mu \end{cases}$, $\lambda_0 = \sigma\sqrt{w_b}$, $\eta = \frac{(W-n)}{n}$, $\mu = (\log_2 n)^{3/2}\sqrt{n}$
Birge Massart	The coefficients $K_j = \begin{cases} K_{J-1}, & J > J_0 \\ \frac{m}{(J_0 + 1 - J)\alpha}, & 1 < J < J_0 \end{cases}$ J is the decomposition level, m is the length of the coarsest approximation over 2, the suggested value of α is 1