

Supplementary Material for Fusion Strategies of Internal Standard Method based on Image Feature for Enhanced Quantitative Analysis of Steel Alloy Elements by LIBS

1. Internal standard method

The internal standard method is widely used in LIBS analysis due to its excellent stability and relative insensitivity to spectral line interference and self-absorption effects. However, traditional internal standard methods rely heavily on manual experience and require the presence of a high-concentration, stable internal standard element within the sample. Although selecting an appropriate internal standard spectral line can yield satisfactory quantitative results, the process is often time-consuming and labor-intensive. Therefore, to simplify and improve the efficiency of internal standard selection, we also attempted a straightforward approach by selecting the peak spectral line of Fe at 404.582 nm as the internal standard.

Table S1 details the results for the traditional internal standard method (Int1) and the simplified internal standard method (Int2) for five elements: Si, Cr, Mn, Ti, and V. After optimization, we selected Fe spectral lines at 263.59 nm, 425.089 nm, 400.535 nm, 340.746 nm, and 322.193 nm as internal standards for Si I 288.17 nm, Cr I 425.433 nm, Mn I 403.067 nm, Ti II 334.94 nm, and V I 311.29 nm.

Table S1 indicates that when Fe peak lines were simply used as internal standard lines, an R^2 value of 0.9663 was achieved, outperforming the manually selected internal standard method ($R^2 = 0.9480$). The RSD was also lower, indicating that when an inappropriate internal standard line is chosen in the conventional method, the quantification of V becomes less accurate compared to the simplified approach. It is noteworthy that, as shown in Figure S1, as many as 12 Fe spectral lines are available for selection within the 343–406 nm wavelength range.

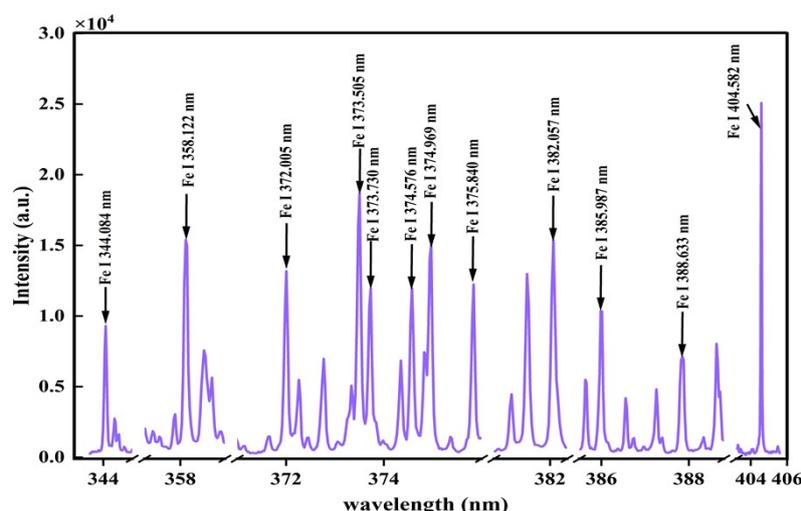


Fig S1. Available Fe spectral lines for internal standard selection in the range of 343–406 nm

Although the use of image features as an internal standard (IFIS) results in a lower R^2 (0.9174) for Cr quantification compared to conventional methods, its performance is comparable to that of manually

selected internal standards for Si and Mn. Moreover, for Ti and V, the IFIS method achieves higher R^2 values, approaching those of manual methods. These findings demonstrate that the image feature-based approach is effective for most elements and can achieve performance close to that of manual selection. Additionally, plasma images are easy to acquire, and the four image features used—area, intensity, area-intensity, and max-intensity—are straightforward to extract, thereby reducing the reliance on expert judgment.

2. Image assisted method and spectral normalization method

Compared to the original spectra, the image-assisted method demonstrates a relatively balanced improvement in the performance of LIBS quantitative analysis. However, as shown in Table S1, the enhancement is rather modest. Taking Si as an example, the R^2 value increased from 0.9069 to 0.9338, while the RSD_P decreased from 19.66% to 17.79%, representing a limited improvement. In contrast, the spectral normalization method significantly enhances stability. The RSD_P values for Si, Cr, Mn, Ti, and V decreased from 19.66%, 16.22%, 11.00%, 23.06%, and 17.34% to 7.07%, 4.73%, 6.34%, 10.30%, and 6.13%, respectively. Notably, the RSD for Ti improved by 55.33%. It is noteworthy that when spectral normalization was employed, Si exhibited an R^2 value of merely 0.8410. This may be attributed to our use of concentration c as the standard during the fitting calculations, which resulted in suboptimal linearity along the concentration-axis for Si. As illustrated in Figure S2, its linearity is comparable to that achieved by spectral normalization.

Furthermore, a comparison between Table S1 and Table 2 indicates that the fused IFIS-IA and IFIS-SN methods substantially outperform the standalone IA and SN methods, respectively, in terms of the coefficient of determination (R^2), with all R^2 values showing improvement. Despite this enhancement, the fused methods exhibit slightly higher RSD , attributable to the inherently higher initial RSD of the IFIS approach. Nevertheless, their consistently superior R^2 and lower $RMSE$ values conclusively demonstrate the efficacy of the data fusion strategy.

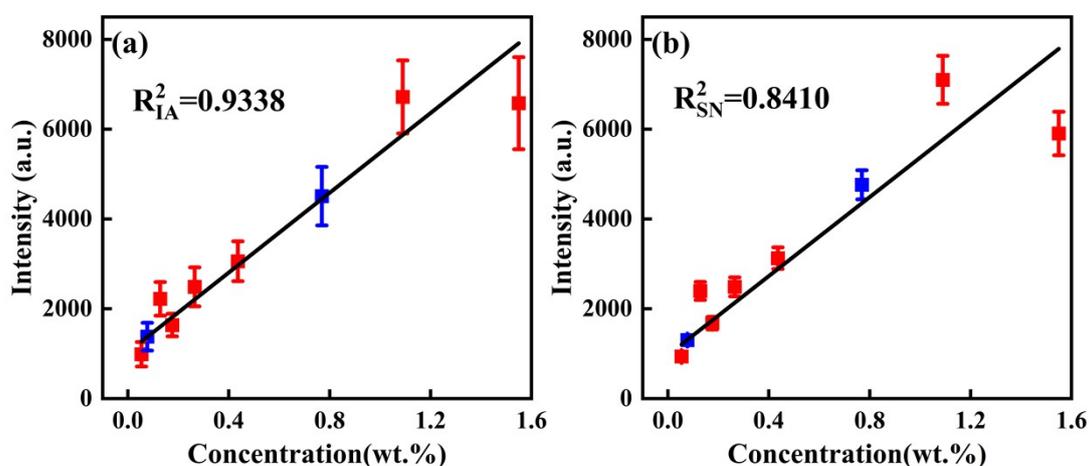


Fig S2. Calibration of Si with the spectral line at 288.17 nm using (a) image-assisted method, (b) spectral normalization method.

Table S1. Comparisons of R², RSD, RMSE and ARE between two new methods of combination

Element (nm)	Method	R ²	RSD (%)		RMSE (wt.%)	
			C	P	C	P
Si I 288.17	Ori ^a	0.9069	19.46	19.66	0.1666	0.0734
	Int1 ^b	0.9908	11.08	13.43	0.0529	0.0197
	Int2 ^c	0.9118	24.07	23.12	0.1573	0.1028
	ISIF ^d	0.9831	19.12	19.04	0.0705	0.0348
	IA ^e	0.9338	17.14	17.79	0.1421	0.0471
	SN ^f	0.8410	7.67	7.07	0.2156	0.1115
Cr I 425.433	Ori ^a	0.9154	14.07	16.22	0.2193	0.0791
	Int1 ^b	0.9923	8.58	11.17	0.0650	0.0334
	Int2 ^c	0.9166	16.36	15.56	0.2195	0.0596
	ISIF ^d	0.9174	13.66	15.54	0.2138	0.1024
	IA ^e	0.9203	12.40	15.22	0.2133	0.0721
	SN ^f	0.9385	4.65	4.73	0.1874	0.0628
Mn I 403.067	Ori ^a	0.9738	12.10	11.00	0.0962	0.1332
	Int1 ^b	0.9856	6.06	5.07	0.0823	0.0610
	Int2 ^c	0.9684	8.11	7.82	0.1240	0.0804
	ISIF ^d	0.9767	12.62	11.37	0.0972	0.1069
	IA ^e	0.9802	9.16	8.04	0.0890	0.1002
	SN ^f	0.9724	5.24	6.34	0.1067	0.1136
Ti II 334.94	Ori ^a	0.9616	30.58	23.06	0.0122	0.0207
	Int1 ^b	0.9414	24.66	17.53	0.0162	0.0230
	Int2 ^c	0.9388	25.32	18.27	0.0167	0.0231
	ISIF ^d	0.9858	32.08	25.76	0.0084	0.0101
	IA ^e	0.9599	27.72	21.29	0.0134	0.0189
	SN ^f	0.9757	8.45	10.30	0.0111	0.0130
V I 311.29	Ori ^a	0.9734	16.18	17.34	0.0155	0.0122
	Int1 ^b	0.9480	23.07	23.26	0.0231	0.0090
	Int2 ^c	0.9663	20.40	21.05	0.0186	0.0069
	ISIF ^d	0.9817	15.82	14.80	0.0133	0.0078
	IA ^e	0.9739	14.21	13.41	0.0148	0.0144
	SN ^f	0.9521	6.21	6.13	0.0201	0.0193

^a original spectral intensities. ^b internal standard method with manual selected lines. ^c internal standard method with max intensity of Fe at 404.582 nm. ^d internal standard method based on image feature. ^e image assisted method. ^f spectral normalization method.