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基于随机森林-多层感知机混合模型的激光诱导击穿光谱(LIBS)定量分析钢铁中的Mn和Cr

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摘　要　在钢铁工业中, 快速准确定量分析Mn、Cr等合金元素对成分控制与质量监测至关重要。激光诱导击穿光谱(LIBS)技术具备快速、制样简单、可多元素同步分析等优势, 但其光谱常存在冗余特征、噪声干扰以及光谱强度与元素浓度间的非线性关系, 从而限制了校正模型的预测精度。为提高LIBS对钢铁样品的定量分析性能, 本研究提出了一种基于特征筛选和二次残差校正的混合建模方法。首先采用变量重要性度量(VIM)对40 002维原始光谱特征进行降维, 并筛选关键光谱变量。完成特征筛选后, 建立随机森林(RF)模型作为主预测模型, 以获得目标元素质量分数的初始预测结果。随后, 计算参考值与RF预测值之间的预测残差。进一步引入多层感知机(MLP)神经网络学习残差信息, 并对RF模型的预测结果进行二次校正, 从而构建RF-MLP混合校正模型, 以进一步降低预测残差并提高模型精度。实验结果显示, 所提出的残差校正方法能够有效提升LIBS定量分析的预测性能。经过二次校正后, Mn的预测集决定系数(R_P^2)由0. 980 8提高至0. 987 6, 预测均方根误差($RMSE_P$)由0. 1425%降低至0. 1149%; Cr的R_P^2由0. 947 8提高至0. 967 8, $RMSE_P$由2. 4485%降低至1. 9240%。本研究提出的RF-MLP混合校正方法为提高钢铁合金元素LIBS定量分析精度提供了一种有效策略, 在钢铁冶炼过程中的快速元素检测和质量控制方面具有潜在应用价值。

关键词　激光诱导击穿光谱; 随机森林; 多层感知机; 钢铁; 定量分析

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要点

1）提出特征筛选结合残差校正的定量分析方法，预测钢铁元素含量。

2）LIBS技术无需复杂样品制备，具备快速多元素检测优势。

3）建立的方法能为钢铁中元素分析提供技术支持。

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钢铁工业作为国民经济的重要支柱，其产品性能与合金元素的精确控制密切相关[1]。其中，Mn是一种优良的脱氧剂和脱硫剂，可有效提升钢铁的强度、韧性与耐磨性[2]；Cr则是影响钢铁耐腐蚀性能的关键元素，同时能增强钢铁的硬度[3]。因此，快速、精准地检测钢铁中Mn和Cr的元素含量，对保证钢材质量具有重要意义。目前，电感耦合等离子体发射光谱法(ICP-OES)[4]和X射线荧光光谱法(XRF)[5]及传统元素分析方法[6]，具有较高的检测精度，但存在样品预处理复杂、检测周期长、仪器与维护成本高等问题。

激光诱导击穿光谱(LIBS)技术具备无需复杂制样、分析速度快及多元素同步检测等优势[7-13]，已成为冶金分析的重要工具[14-16]。近年来，偏最小二乘(PLS)、随机森林(RF)等机器学习方法，已被广泛应用于LIBS光谱分析[17-21]。针对LIBS光谱中变量冗余、噪声干扰及有效特征提取等问题，相关研究多通过特征筛选、光谱预处理和变量优化等方法提高模型预测性能[22-25]。杨淋玉等[16]提出的基于遗传算法优化的偏最小二乘(GA-PLS)策略用于LIBS检测钢铁中的Mn和Ni含量，结果显示其在Mn和Ni预测中的预测集决定系数(R_P^2)分别为0.999 0和0.999 5，预测均方根误差($RMSE_P$)分别为1.3473%和0.5254%，提高了预测精度。Wang等[26]提出变量重要性度量(VIM)结合RF的方法用于LIBS检测铁矿石酸度，预测精度R_P^2为0.910 3，$RMSE_P$为0.0554%。Hu等[27]基于LIBS技术开展中低合金钢硬度的检测研究，并采用无信息变量消除(UVE)、竞争性自适应重加权采样(CARS)和连续投影算法(SPA)等方法筛选有效光谱变量。结果显示，CARS-LS-SVM模型的R_P^2达到0.996 6，$RMSE_P$为9.480 0 HV。Wang等[28]提出最小绝对收缩和选择算子(LASSO)特征选择结合LightGBM回归和SHAP可解释性分析的方法，用于微合金钢中Mn、Cu、Ni、Mo和Ti的LIBS定量分析。结果显示，LASSO-LightGBM模型的交叉验证决定系数(R_{CV}^2)达到0.996，其中Cu的$RMSE_P$低至0.0053%。在模型构建与应用拓展方面，相关研究通过多变量建模提升LIBS在不同钢铁样品及多元素定量分析中的预测性能[29-33]。Traparić等[34]提出Gini重要性准则结合RF模型用于预测奥氏体不锈钢合金成分，经过优化，RF模型在Cr、Mn、Ni预测中的R_P^2分别为0.88、0.89和0.97，$RMSE_P$分别为3.68%、0.397%和1.77%。Li等[35]提出的基于交叉验证均方根误差($RMSE_{CV}$)和袋外误差优化的RF分析策略用于LIBS检测低合金钢中的碳元素，优化后的RF模型将$RMSE_P$降至0.023%，相比传统校准曲线法降低了32.4%。Ma等[36]提出基于全谱LIBS的多元素同步定量分析方法，用于不锈钢中Mn、Mo、Cr和Cu等微量元素检测。结果显示，Mn、Mo、Cr和Cu的R_P^2分别达到0.987 6、0.987 9、0.989 1和0.984 1。上述研究表明，基于特征筛选、光谱预处理和多变量建模的LIBS定量分析方法已取得较好效果，但现有研究多集中于光谱变量优化和主预测模型构建，对模型预测残差中潜在信息的进一步利用相对不足，限制了定量分析精度的进一步提升。为满足更高精度的应用需求，本研究在主模型预测的基础上，对其预测残差进行二次建模与校正，以降低残差影响并提升LIBS定量预测精度。

本研究针对钢铁中Mn、Cr的LIBS定量分析，提出了一种结合特征筛选与残差校正的混合建模方法。该方法首先通过特征筛选对光谱数据进行降维，以减少冗余信息，并使用RF算法构建主预测模型。随后，采用多层感知机(MLP)对预测残差进行校正，从而进一步提高定量分析的精度。

1　数据获取与分析

1.1　LIBS数据集获取与划分

本研究的LIBS钢铁数据来源于Képeš等[37]提供的光谱数据集。数据集共有42个钢靶材样品的光谱数据，每个样品50条光谱。为减小光谱波动的影响，本研究将每个样品中的光谱数据进行平均处理，平均后每个样品10条光谱，组成共420条光谱的实验数据集。本研究旨在对锰(Mn)和铬(Cr)两种元素进行定量分析，其参考浓度值汇总于表1。为验证模型性能，将所有光谱数据按8∶2的比例随机划分为训练集(336条)与测试集(84条)，分别用于模型的训练与测试。

表1 钢样中Cr和Mn含量

Table 1 Content of Cr and Mn in steel samples /%

No.	Cr	Mn	No.	Cr	Mn	No.	Cr	Mn	No.	Cr	Mn	No.	Cr	Mn
1	0.045	1.96	10	0.107	0.146	19	1.84	6.57	28	18.45	1	37	26.47	1.49
2	0.046 1	2.12	11	0.175	1.13	20	12.71	0.443	29	2.61	1.85	38	26.69	1.74
3	0.054 5	0.058 2	12	0.381	0.157	21	0.045	1.96	30	23.26	0.964	39	27.13	0.523
4	0.054 5	2.06	13	0.613	0.175	22	13.7	1.25	31	23.59	0.366	40	27.16	1.77
5	0.061 7	0.152	14	0.739	0.341	23	13.84	1.25	32	24	0.391	41	3.07	5.71
6	0.094 1	0.53	15	0.85	0.209	24	14.03	0.398	33	25.05	0.599	42	4.45	0.243
7	0.103	1.86	16	1.05	0.611	25	14.66	1.36	34	25.2	0.629			
8	0.104	1.37	17	1.32	0.607	26	15.34	0.811	35	25.69	0.497			
9	0.105	1.24	18	1.33	0.593	27	15.37	0.818	36	26.43	1.61			

1.2 建模方法

1.2.1 基于VIM特征筛选方法

本研究采用基于平均不纯度减少的VIM进行特征筛选。在定量任务中，节点的不纯度通常由方差来衡量。当一个特征被用于节点分裂时，其带来的方差减少量即为该次分裂的不纯度降低值。该特征的最终重要性得分，是其在RF所有决策树中每次分裂所贡献的不纯度降低值的累加总和。本研究将所有特征VIM得分的平均值设为筛选阈值，从而自动选择重要性得分高于该平均值的特征变量。

1.2.2 残差校正方法

在由VIM筛选出的特征子集上，本研究构建了一个混合预测模型，先通过主模型完成初始预测，其预测值与真实值的差值构成残差，随后，残差校正模型根据残差进行补偿，从而提高整体的预测精度。

在第一阶段，选用RF算法作为主模型[38]，对经过变量重要性分析筛选出的光谱特征进行训练建模，用于元素浓度值的初步预测。

设真实值为y，则可以表示为：

$$y=\hat{y}+r \tag{1}$$

其中r为主模型的残差，单位为%；$\hat{y}$为RF模型输出的元素预测质量分数，单位为%。

第二阶段，残差校正的目标是学习映射$f(\cdot)$，使得

$$r\approx f_{\mathrm{NN}}\left(\boldsymbol{x},\hat{y}\right) \tag{2}$$

其中$\boldsymbol{x}$为与预测值对应的特征向量。

本研究引入MLP实现残差建模。MLP属于前馈神经网络，由输入层、若干隐藏层和输出层组成。MLP以主模型预测值$\hat{y}$与对应的特征x作为输入，经由两层全连接隐藏层(每层包含64个神经元，激活函数为ReLU)，最后通过一个线性输出层得到残差预测值$\hat{r}$：

$$\hat{r}=f_{\mathrm{NN}}\left(\boldsymbol{x},\hat{y};\theta\right) \tag{3}$$

其中θ为神经网络的可训练参数。

最终，混合模型的预测结果为：

$$y_{\mathrm{final}}=\hat{y}+\hat{r}=\hat{y}+f_{\mathrm{NN}}\left(\boldsymbol{x},\hat{y};\theta\right) \tag{4}$$

模型评估通过决定系数(R^2)、均方根误差(RMSE)等指标进行。R^2用于衡量模型拟合数据的能力，RMSE用于评估预测值与真实值之间的偏差。

图1展示了本研究所采用的LIBS定量分析混合建模流程。该流程依次包含数据预处理、基于VIM的特征筛选、主模型训练与初步预测、残差计算与校正、最终预测输出及模型性能评价。

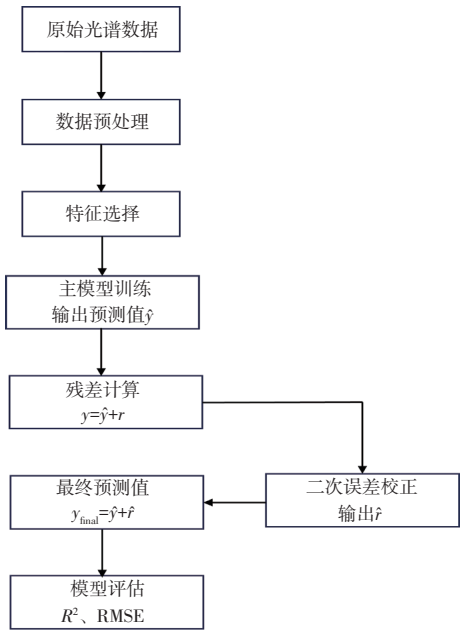


图1 LIBS定量分析混合建模流程图

Figure 1 Flow chart of hybrid modeling for LIBS quantitative analysis.

2　结果与讨论

2.1　不同模型预测性能的比较

本节在全谱数据上使用了PLSR与RF模型进行定量分析，通过5折交叉验证优化参数，并对模型性能进行了评估与对比。

对于PLSR模型，通过网格搜索寻优，确定Mn预测中最优主成分数为17，在Cr预测中最优主成分数为8。图2展示了$RMSE_{CV}$随主成分数变化的趋势，随着主成分数的增加，$RMSE_{CV}$逐渐下降，并在主成分数为17和8时分别达到最低值。对于RF模型，通过网格搜索寻优，确定Mn预测中最优决策树数为400，在Cr预测中最优决策树数为200。图3展示了$RMSE_{CV}$随决策树数变化的趋势，随着决策树数的增加，$RMSE_{CV}$明显下降，并在树数为400和200时分别达到了最小值。

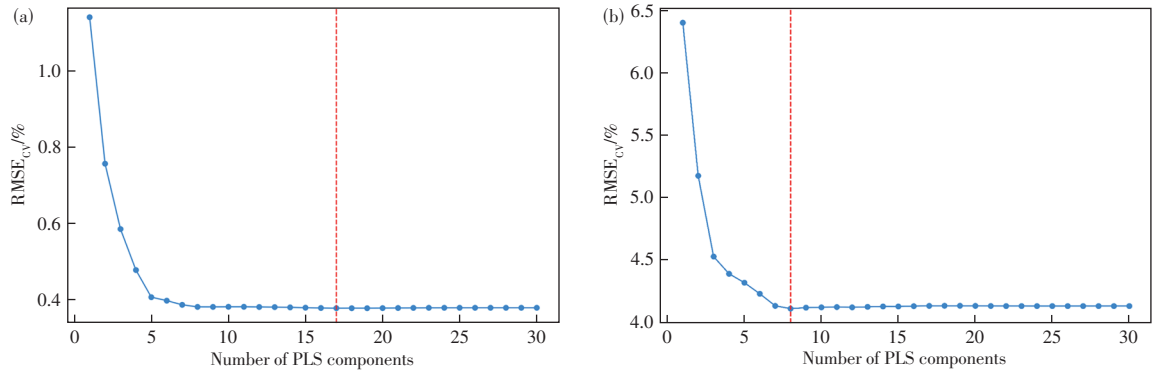


图2　PLSR主成分数优化图：(a)Mn；(b)Cr

Figure 2　PLSR components selection plot: (a)Mn; (b)Cr.

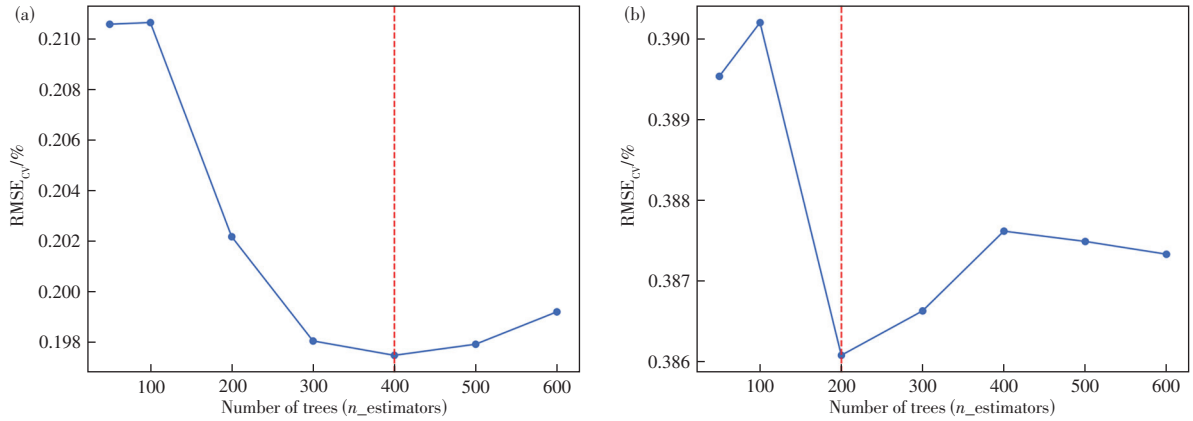


图3　RF决策树个数优化图：(a)Mn；(b)Cr

Figure 3　Random forest tree count optimization plot: (a)Mn; (b)Cr.

在确定各自最优参数后，两个模型的最终性能对比如表2所示。从表2中可以看出，RF模型在两个元素的预测上均优于PLSR模型。对于Mn，RF模型的R_{CV}^2为0.969 0，高于PLSR的0.913 9；其$RMSE_{CV}$为0.2337%，优于PLSR的0.3894%。对于Cr，RF模型的R_{CV}^2为0.853 9，高于PLSR的0.844 9；其$RMSE_{CV}$为4.0565%，优于PLSR的4.1803%。结果表明，RF模型在本次分析中表现更优，因此选择RF模型作为最终模型。

表2　不同模型的Mn、Cr定量分析性能对比

Table 2　Comparative analysis of quantitative performance for Mn and Cr using different models

Methods	Mn				Cr			
	R_{CV}^2	$RMSE_{CV}$/%	R_P^2	$RMSE_P$/%	R_{CV}^2	$RMSE_{CV}$/%	R_P^2	$RMSE_P$/%
PLSR	0.913 9	0.389 4	0.900 1	0.325 6	0.844 9	4.180 3	0.917 3	3.082 0
RF	0.969 0	0.233 7	0.963 4	0.197 0	0.853 9	4.056 5	0.931 4	2.806 5

2.2 基于变量重要性的RF模型建立

为了提升LIBS定量分析模型的预测精度与运算效率，本研究引入了基于VIM的特征筛选算法。VIM方法通过计算每个特征对RF模型预测的贡献度，筛选出对模型预测有较大影响的特征，剔除冗余的特征。图4展示了特征筛选前后光谱特征的分布变化，图5则展示了各波长特征的VIM得分，结果表明，光谱中不同特征对RF模型的重要性差异显著。少数特征具有较高的VIM得分，表明这些特征在模型中起到了关键作用，而大部分特征的VIM得分较低，说明它们对目标元素浓度的预测贡献较小。本研究采用了VIM得分的平均值作为筛选阈值，保留了高于该阈值的特征，最终筛选出320个特征用于Mn定量分析，686个特征用于Cr定量分析。

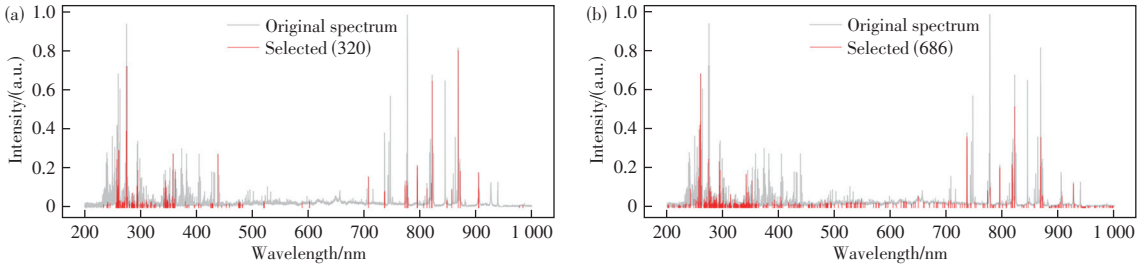


图4 特征筛选前后光谱图：(a)Mn；(b)Cr

Figure 4 Spectra before and after feature selection: (a) Mn; (b) Cr.

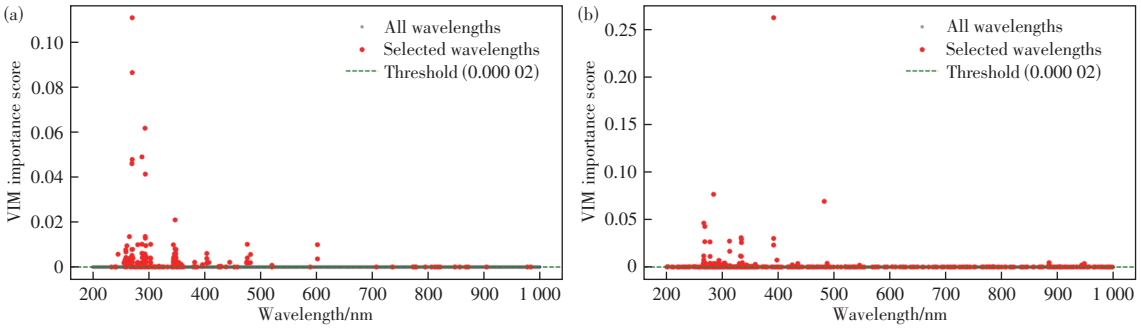


图5 特征重要性得分图：(a)Mn；(b)Cr

Figure 5 Feature importance score plot: (a) Mn; (b) Cr.

通过对特征筛选前后模型的预测性能进行比较，表3、图6展示了全谱模型与VIM特征筛选模型在Mn和Cr上的性能对比。结果显示，经过VIM特征筛选后，Mn的模型R_{CV}^2由0.969 0提升至0.988 0，$RMSE_{CV}$由0.2337%降至0.1497%，预测集R_P^2从0.963 4提升至0.980 8，$RMSE_P$从0.1970%降至0.1425%；Cr的模型R_{CV}^2由0.853 9提升至0.908 8，$RMSE_{CV}$由4.0565%降至3.2046%，预测集R_P^2从0.931 4提升至0.947 8，$RMSE_P$从2.8065%降至2.4485%。图6进一步展示了VIM特征筛选后RF模型预测值与真实值之间的关系。此外，特征筛选提升了模型的计算效率，缩短了RF模型的训练时间和预测时间。优化后的模型在提高预测精度的同时有效降低了计算开销，使LIBS分析系统更适用于工业现场的快速检测需求。这验证VIM特征筛选策略在去除冗余特征、提升模型精度和运算效率方面的有效性。

表3 特征筛选前后模型预测性能指标的对比

Table 3 Model performance comparison before and after feature selection

Elements	Methods	Number of features	5-fold cross-validation			Test set		
			R_{CV}^2	$RMSE_{CV}$/%	Time/s	R_P^2	$RMSE_P$/%	Time/s
Mn	RAW	40 002	0.969 0	0.233 7	4.366 4	0.963 4	0.197 0	1.665 5
	VIM	320	0.988 0	0.149 7	0.901 5	0.980 8	0.142 5	0.142 5
Cr	RAW	40 002	0.853 9	4.056 5	5.260 1	0.931 4	2.806 5	1.191 7
	VIM	686	0.908 8	3.204 6	3.235 9	0.947 8	2.448 5	0.067 4

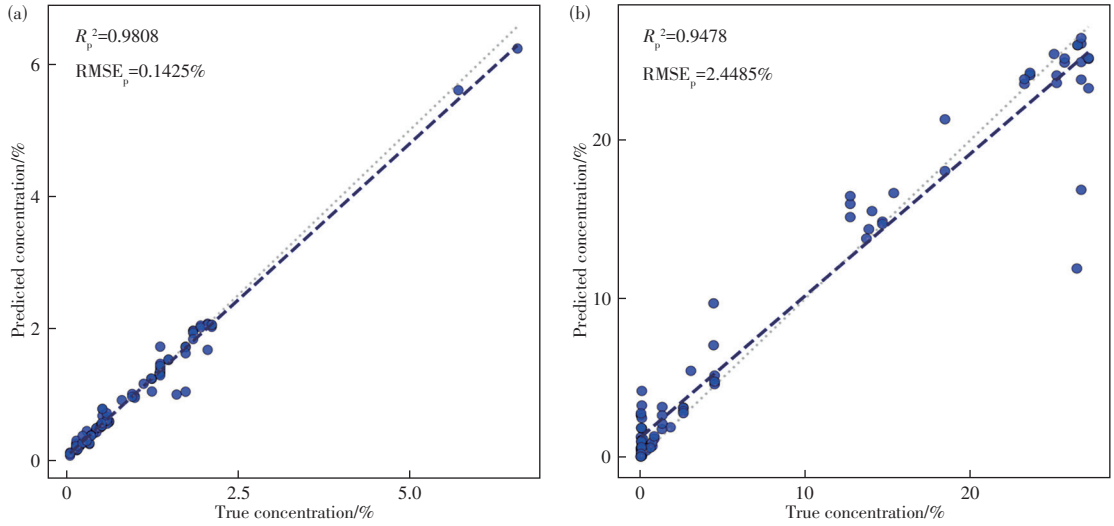


图6　特征筛选后模型的预测性能：(a)Mn；(b)Cr

Figure 6　Predictive performance of the model after feature selection: (a) Mn; (b) Cr.

2.3　混合模型的性能评估

为降低预测残差提升预测精度，在利用VIM完成特征筛选后，本研究进一步引入MLP网络对RF模型的预测残差进行校正。为验证校正模型的训练效果，对训练过程进行了监控，如图7所示，Mn(图7a)损失在训练初期快速下降，Cr(图7b)则呈较为平缓的下降趋势。随着迭代推进，两者损失均在约60个Epoch后收敛于零附近。

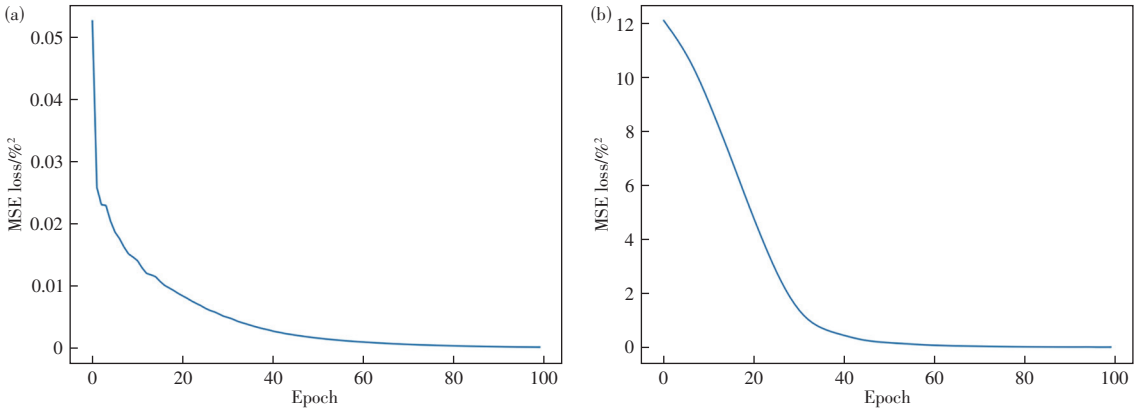


图7　残差校正网络的训练损失收敛曲线：(a)Mn；(b)Cr

Figure 7　Training loss convergence curve of the residual correction network: (a) Mn; (b) Cr.

图8展示了模型在测试集上对Mn和Cr两种元素的定量分析残差分布情况。图8中横坐标代表元素的真实浓度，纵坐标代表预测残差。红色圆点表示RF模型的预测残差，蓝色圆点表示经MLP残差校正后的预测残差，两者之间的灰色线段反映了MLP对RF模型预测残差的调整幅度。对于Mn，其浓度范围较低，基础RF模型的残差分布相对分散，有少数样本存在较大残差。引入MLP残差校正后，蓝色散点明显向零残差虚线集中，且多数灰色线段较长，表明原先偏离较大的样本得到有效校正，整体预测残差显著降低。Cr的浓度范围较宽(约0～27%)。在低浓度区，两种模型的预测结果差异较小；而在高浓度区(>15%)，基础RF模型残差整体偏负，对Cr含量存在低估。引入MLP残差校正后，高浓度样本多得到正向修正，蓝色散点整体更接近零线，预测残差得到有效减小。

图9展示了预测值与真实值的散点分布及拟合趋势。从图9中可以看出，经过残差校正后，Mn与Cr的散点整体更加集中并贴近拟合线，反映了模型预测精度的提升。通过RF-MLP两阶段混合建

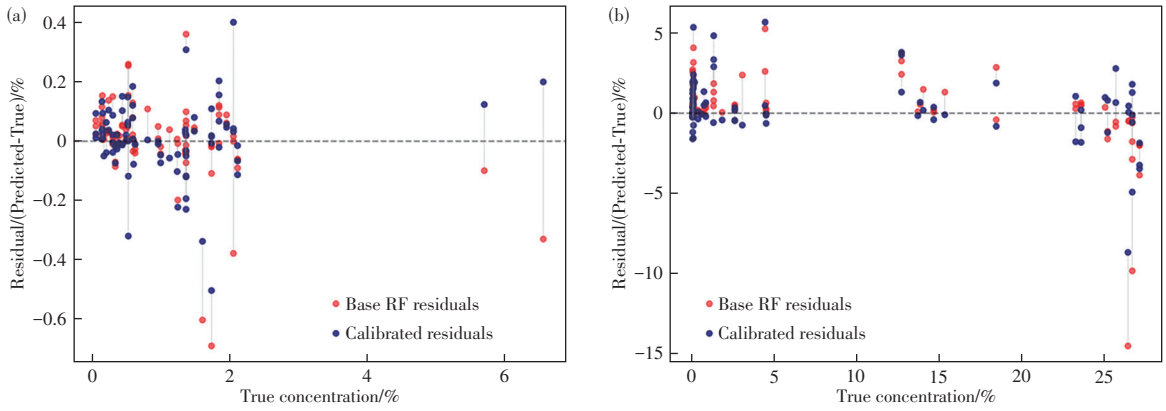


图8 残差校正后的预测残差分布对比图：(a)Mn；(b)Cr

Figure 8 Comparison of the prediction residual distribution before and after residual correction: (a)Mn; (b)Cr.

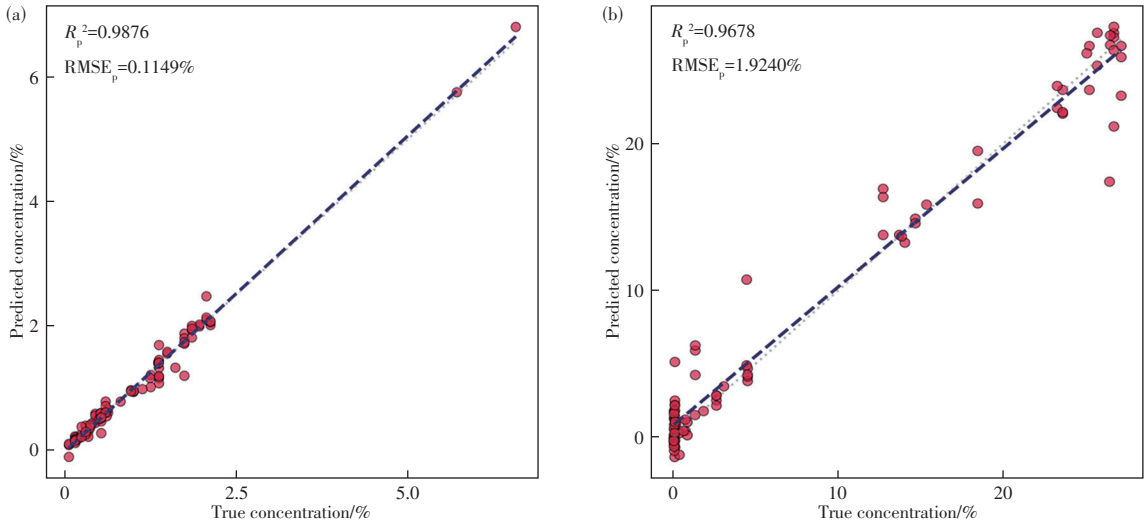


图9 残差校正后模型的预测性能：(a)Mn；(b)Cr

Figure 9 Prediction performance of the model after residual correction: (a)Mn; (b)Cr.

模，Mn的R_P^2从0.980 8提升至0.987 6，RMSE$_P$从0.1425%降低至0.1149%。对于Cr，R_P^2从0.947 8上升至0.967 8，RMSE$_P$从2.4485%降至1.9240%。

上述结果表明，引入MLP网络能够有效挖掘并修正了RF模型的预测残差，提升了定量分析能力。

3 结论

本研究提出了一种结合特征筛选与残差校正的LIBS定量分析方法。首先，通过VIM计算变量重要性，从原始高维光谱中筛选出最具代表性的特征子集，减少了冗余信息。在特征筛选后，对于Mn，筛选后变量数减少至320个，R_P^2从0.963 4提升至0.980 8，RMSE$_P$从0.1970%降至0.1425%；对于Cr，筛选后变量数为686个，R_P^2从0.931 4提升至0.947 8，RMSE$_P$从2.8065%降至2.4485%。随后，构建了RF模型对元素浓度进行初步预测，并引入MLP网络对RF模型的残差进行建模，实现了对初步预测结果的二次补偿。经过残差校正后，Mn的R_P^2由0.980 8提高至0.987 6，RMSE$_P$从0.1425%降低至0.1149%；Cr的R_P^2从0.947 8上升至0.967 8，RMSE$_P$由2.4485%下降至1.9240%。结果表明，该方法能够有效应用于钢铁中多种合金元素的光谱定量分析，为冶金工业中的成分控制与质量监测提供了可靠的技术参考。

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Quantitative Analysis of Mn and Cr in Steel by LIBS Based on a Random Forest-multi-layer Perceptron Hybrid Model

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Abstract In the steel industry, rapid and accurate quantitative analysis of alloying elements such as Mn and Cr is crucial for composition control and quality monitoring. Laser-induced breakdown spectroscopy (LIBS) offers advantages including fast analysis, simple sample preparation, and simultaneous multi-element detection. However, LIBS spectra often suffer from redundant features, noise interference, and nonlinear relationships between spectral intensity and elemental concentration, which limit the predictive accuracy of calibration models. To improve the quantitative performance of LIBS for steel samples, this study proposes a hybrid modeling method based on feature selection and secondary residual correction. In the proposed method, variable importance measurement (VIM) was first used to reduce the dimensionality of the 40 002-dimensional original spectral features and select key spectral variables related to the prediction of target elements. After feature selection, a random forest (RF) model was established as the primary prediction model to obtain the initial predicted mass fractions of Mn and Cr. Subsequently, the prediction residuals between the reference values and the RF-predicted values were calculated. A multilayer perceptron (MLP) neural network was further introduced to learn the residual information and perform secondary correction on the RF prediction results. In this way, an RF-MLP hybrid correction model was constructed to further reduce prediction errors and improve the prediction accuracy of LIBS quantitative analysis. The results show that the proposed residual correction strategy effectively improves the predictive performance of LIBS quantitative analysis. After secondary correction, the prediction-set coefficient of determination (R_P^2) for Mn increased from 0.980 8 to 0.987 6, while the root mean square error of prediction ($RMSE_P$) decreased from 0.1425% to 0.1149%. For Cr, the R_P^2 increased from 0.947 8 to 0.967 8, and the $RMSE_P$ decreased from 2.4485% to 1.9240%. The proposed RF-MLP hybrid correction method provides an effective strategy for improving the accuracy of LIBS-based quantitative analysis of alloying elements in steel. It shows potential application value for rapid elemental detection and quality control in steelmaking.

Keywords laser-induced breakdown spectroscopy (LIBS); Random Forest; multi-layer perceptron; steel; quantitative analysis

HIGHLIGHTS

1) A quantitative analysis method combining feature selection and residual correction was proposed to predict the elemental content in steel.
2) LIBS technology requires no complex sample preparation and offers the advantage of rapid multi-element detection.
3) The established method provided technical support for elemental analysis in steel.