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基于激光诱导击穿光谱技术的录井岩屑 多元素定量分析方法(特邀)

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摘 要:利用自行研制的台式激光诱导击穿光谱仪,采集了岩石样品的光谱图,将数据划分为训练集和测试集,然后结合主成分回归算法对 Si、Al、Ca、Mg 和 K 元素建立了定量分析模型,将测试集数据应用于模型评估,五种元素预测的决定系数(R^2)分别为 0.974 5、0.941 1、0.984 3、0.990 1、0.811 4。最后,将定量模型集成到仪器上,对 97 个来自我国西南某钻井现场的岩屑样品进行了分析,并与该批样品的实验室 X 射线荧光检测结果进行了对比。结果表明,五种元素的激光诱导击穿光谱预测值与 X 射线荧光检测值之间的决定系数(R^2)分别达到 0.971 9、0.960 4、0.947 9、0.965 2 和 0.924 5,整体趋势基本一致,说明集成了定量模型的仪器能够实现快速、有效的岩屑元素含量分析,在油气勘探开发领域具有良好的应用潜力。

关键词:光谱学;激光诱导击穿光谱;岩石分析;定量分析;主成分回归

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0 引言

现代社会的快速发展使人类对于各种能源的需求和消耗日益增加,油气资源勘探活动日渐频繁,而岩屑录井是油气勘探过程中的基础工作之一^[1]。在录井现场,工作人员需要测定和记录不同井深岩屑的元素组成和含量信息,以此来绘制录井图。准确的元素录井图能够为正确地识别岩性、判断地层层位、预测将要钻遇的地层、选择合适的钻井施工参数和降低钻井工作风险提供关键的基础资料。

传统的元素分析技术通常是基于实验室的技术,如:原子吸收光谱法、电感耦合等离子体发射光谱法、电感耦合等离子体质谱法等,它们的分析准确度虽然较高,但是检测装置昂贵、操作流程复杂、分析时间较长,无法满足录井现场的实际需求。小型化的 X 射线荧光(X-ray Fluorescence Spectrometry, XRF)分析仪因其便携、样品需求量较少、检测速度较快和满足元素录井要求的检出限等特点,被广泛应用于录井现场进行实时、在线的元素分析^[2-4]。但是基于其技术原理,XRF 分析仪具有一定的辐射风险,而且对轻元素(原子序数 <11)的检测效果欠佳,难以全面地获得样品的元素信息。

激光诱导击穿光谱(Laser-induced Breakdown Spectroscopy, LIBS)技术作为一种原子发射光谱分析检测技术,具有结构简单、无需复杂的样品前处理、分析速度快、能够同时检测多种元素等特点^[5],已经被广泛应用于合金^[6-8]、土壤^[9-11]、食品^[12-14]、爆炸物^[15-16]等多种物质的分析。在岩石分析方面,国内外研究人员进行了大量的研究。HARMON R S 等^[17]利用商业化的实验室 LIBS 系统对美国中部大陆地区宾夕法尼亚晚期的黑色页岩样品进行了分析,样品中富含 V、Fe、Cu、Zn 等元素。SOBRON P 等^[18]采用实验室 LIBS 系统对智利北部阿塔卡马沙漠地区的沉积岩样品中的 Li、Na、Mg、Al、Si 等元素进行了半定量分析,研究结果

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展现了LIBS技术在野外进行快速、半定量分析的应用潜力。SANGHAPI H K等^[19]利用实验室的LIBS系统对北美东部马塞勒斯组的岩石样品进行了分析,使用偏最小二乘法(Partial Least Squares Regression, PLSR)对Mg、Al、Si、Ca和Ti元素进行了定量分析。汪家升等^[20]使用LIBS技术对岩石标准样品中的Ca和Mg元素进行了分析,研究表明使用强度归一化的方法在一定程度上可以提升测量的准确度。中国科学院空间主动光电技术重点实验室使用中国火星探测计划所使用的LIBS系统结合卷积神经网络算法(Convolutional Neural Network, CNN)对23个岩石标准样品中的SiO₂、Fe₂O₃、CaO等8种主要成分进行了分析,其结果表明CNN在定量分析方面具有良好的准确性^[21]。

本文针对录井现场的实际需求,利用团队自行研制的台式激光诱导击穿光谱仪,采集了66个岩石样品的LIBS光谱数据,提出了基于主成分回归(Principle Component Regression, PCR)的系数校正法,建立了Si、Al、Ca、Mg和K五种元素的定量分析模型。随后将该模型安装到所使用的仪器上,对来自我国西南地区某钻井现场的97个岩屑样品的元素含量进行了预测,并与实验室XRF仪器的检测结果进行了对比。

1 实验与方法

1.1 实验仪器及样品

本实验使用团队自主研制的台式激光诱导击穿光谱仪。该仪器采用Nd:YAG激光器,激光脉冲能量为100 mJ,激光波长为1 064 nm,脉冲宽度为10 ns,频率为1 Hz,延时时间设置为1.5 μs,曝光时间为1 ms,使用三台2 048通道光谱仪(180~345 nm, 340~570 nm, 565~780 nm),光栅刻线密度分别为2 400 lines/mm、1 800 lines/mm和1 800 lines/mm,光谱分辨率分别为0.1 nm、0.15 nm和0.15 nm,光谱仪的入射狭缝宽度均为10 μm。仪器的实物图如图1所示。

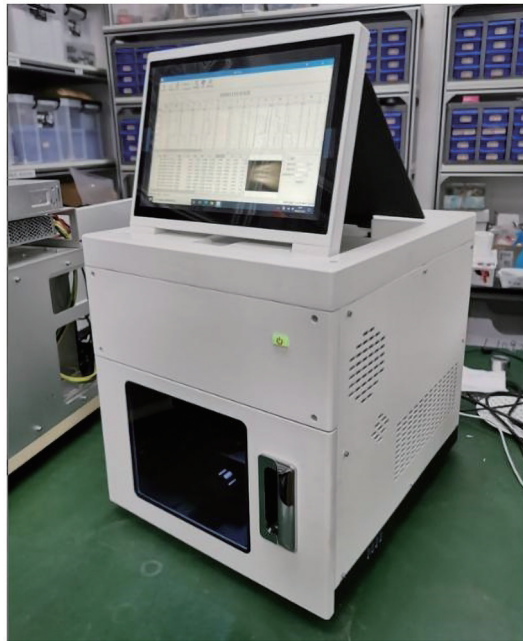


图1 激光诱导击穿光谱仪实物图

Fig. 1 Picture of laser induced breakdown spectrometer

本实验使用的岩石样品包括49个国家标准岩石样品,17个补充样品和97个来自我国西南地区某钻井现场的岩屑样品。补充样品是将国家标准样品按照一定的比例混合,经涡旋混匀器搅拌均匀后制得,编号为GBA #01~GBA #17;97个取自钻井现场的样品及其元素含量由成都艾立本科技有限公司提供,编号为LJ #01~LJ #97。所有样品都是均匀的岩石粉末,每个样品的Si、Al、Ca、Mg和K元素含量详见补充材料中的表1和表2。样品经过烘干后,称取1 g,放置到压片机(8 Mpa压强持续20 s)中压制成直径为20 mm的圆片,代表性样本如图2所示。

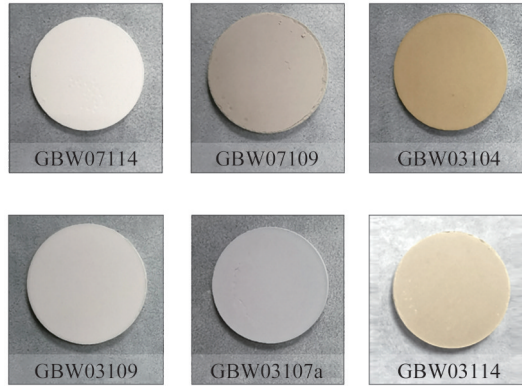


图2 代表性岩石样品压片实物图
Fig. 2 Pictures of representative rock tablet samples

1.2 光谱数据采集

由于样本是由固体的岩石粉末压制而成,光谱的精度容易受元素分布不均匀性的影响,所以随机地在样本表面20个不同的位置采集LIBS光谱。为了减少激光脉冲能量波动的影响,提高谱线的信噪比,通过累计采集4次光谱信号取平均值代表该位置的光谱,最终每个样本获取20张光谱数据。

1.3 数据分析流程

本文把49个国家标准样本的光谱数据作为训练集,以此为基础来建立定量分析模型。然后把17个补充样本的光谱数据作为测试集,不参与模型的训练,来验证模型的有效性。最后用97个取自钻井现场的样本进行应用测试,预测目标元素的含量,对比LIBS技术和目前广泛使用的XRF技术对于录井岩屑元素分析的差异。

数据分析流程如图3所示。首先,采用不同的方法对光谱数据进行预处理,针对每个元素,筛选出合适的预处理方式。然后,针对每个元素分别建立峰强与含量的定标曲线,以该曲线为基础,计算出不同含量所对应的理想峰强,将理想峰强除以实际峰强,计算出峰强的校正系数。接下来,采用主成分回归算法,以全谱数据为输入,建立计算校正系数的PCR模型。最后,针对每个元素分别建立经过系数校正之后的峰强和含量之间的定标曲线,确定定量模型。

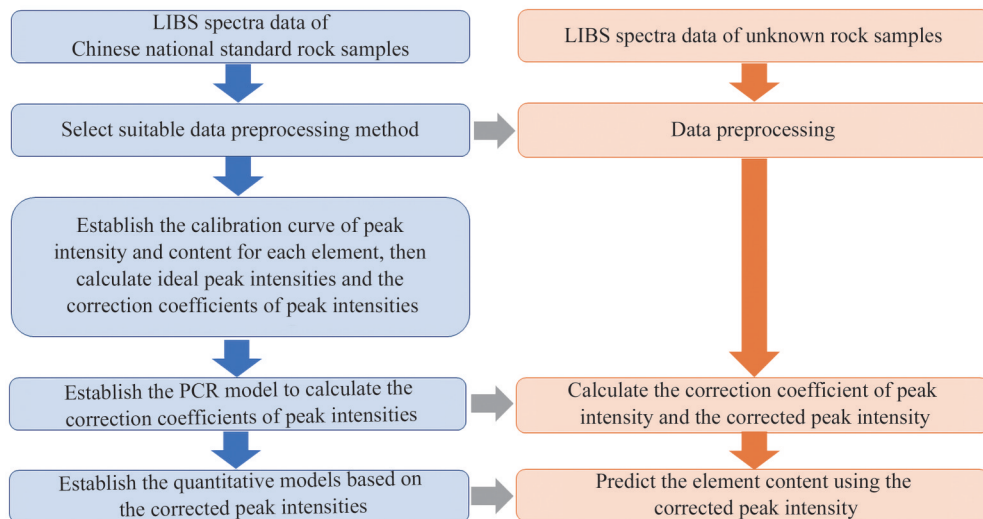


图3 数据分析流程示意图
Fig. 3 Schematic diagram of data analysis process

对于未知样品,首先按照选定的最优预处理方法对其光谱进行预处理,然后计算峰强的校正系数,再将校正后的峰强带入定量模型,得到目标元素的预测结果。

1.4 PCR算法

PCR是一种将主成分分析(Principal Components Analysis, PCA)和多元线性回归(Multiple Linear Regression, MLR)相结合的方法。

PCA是一种通过矩阵运算来对原始数据进行降维的方法。实验中所采集到的岩石国家标准样本的LIBS光谱数据可以表示为向量 $I_i=(I_{i1}, I_{i2}, \dots, I_{i6144})$,每个岩石样本的光谱包含6144维光谱特征,其中 $i=1, 2, \dots, 49$ 。对原始LIBS光谱进行预处理之后,可得到原始数据矩阵 X 。通过奇异值分解(Singular Value Decomposition, SVD)的方法^[22-23]提取出光谱数据中的主成分(Principal Components, PCs),每一个PC都是没有关联、单独存在的。在本文中,我们选取对原始数据的累积解释率达到99.95%的前 n 个PC带入MLR来构建PCR模型。

2 结果与讨论

2.1 数据预处理

使用团队自主研发的台式激光诱导击穿光谱仪所采集到的岩石压片样本的代表性光谱图如图4所示,该光谱图中包含了丰富的元素特征谱线,基线较为平稳,信噪比也较好,说明该仪器的光谱采集性能可以满足分析的需求。

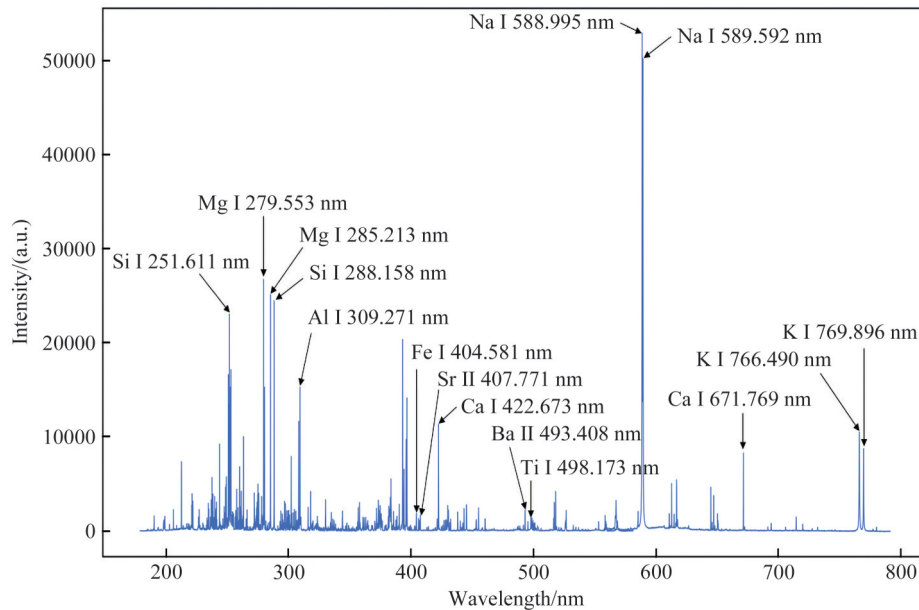


图4 代表性岩石样品(GBW07111)的LIBS光谱图

Fig. 4 LIBS spectrum of representative rock samples (GBW07111)

但是,在光谱数据采集过程中,岩石样品粉末的均匀度、压片表面的平整度、岩石中复杂的基质效应和仪器性能等因素会影响光谱信号的稳定性。为了提升数据的稳定性和重复性,可以对光谱数据进行归一化^[24],常用的归一化方法主要有最大最小强度归一化(Min-Max Normalization)^[25]、总面积归一化(Total Area Normalization)^[26]、标准正态变化(Standard Normal Variate, SNV)^[27]等。总面积归一化能够减少由于样品烧蚀量不一致所导致的光谱差异,但是在光谱发射的过程中,不同元素的发射谱线数量和总强度是有差异的。以Fe元素为例,当岩石样品中的Fe元素含量较高时,它们的LIBS光谱中存在几十甚至数百条Fe的特征谱线,数量远远高于其他元素的特征谱线。如果采用总面积归一化,将全部谱线的强度相加,会在一定程度上削弱其他元素的谱线强度和含量之间的映射关系,反而放大了基质效应的影响。因此针对岩石样品,根据其中元素分布的特点,本文基于总面积归一化提出了利用代表性元素进行部分面积归一化(Part Area Normalization)的方法,既能减少由于烧蚀量不一致导致的光谱差异,又能兼顾元素谱线强度与含量之间的映射关系,减小基质效应的影响。

首先挑选出岩石中主要成岩元素的18根代表性特征峰:250.690 nm (Si I)、390.552 nm (Si I)、308.215 nm (Al I)、309.271 nm (Al I)、259.940 nm (Fe II)、404.581 nm (Fe I)、422.673 nm (Ca I)、714.815 nm (Ca I)、285.213 nm (Mg I)、516.732 nm (Mg I)、766.490 nm (K I)、769.896 nm (K I)、337.280 nm (Ti II)、368.521 nm (Ti II)、455.403 nm (Ba II)、493.408 nm (Ba II)、407.771 nm (Sr II)、421.552 nm (Sr II),然后将这些特征峰的强度求和作为分母,对整个光谱中每个像素的强度进行归一化。具体的归一化公式为

$$I'_i = \frac{I_i}{\sum I_{\text{select}}}$$

式中, I_i 为每个像素的谱线强度, $\sum I_{\text{select}}$ 为挑选出的特征峰的强度之和, I'_i 为归一化之后的每个像素的谱线强度。

本文首先分别采用最大最小强度归一化、总面积归一化和部分面积归一化三种方法对采集到的49个国家标准样品的LIBS光谱数据进行预处理,然后与NIST数据库进行对比,选择目标元素信号较强而且周围干扰较少的一些特征峰,确定每个元素用于建模的特征峰:288.158 nm (Si I)、308.215 nm (Al I)、445.478 nm (Ca I)、516.732 nm (Mg I)和769.896 nm (K I)。

图5展示了选定的特征峰根据原始峰强和三种预处理之后的峰强与元素含量所建立的标准曲线。在

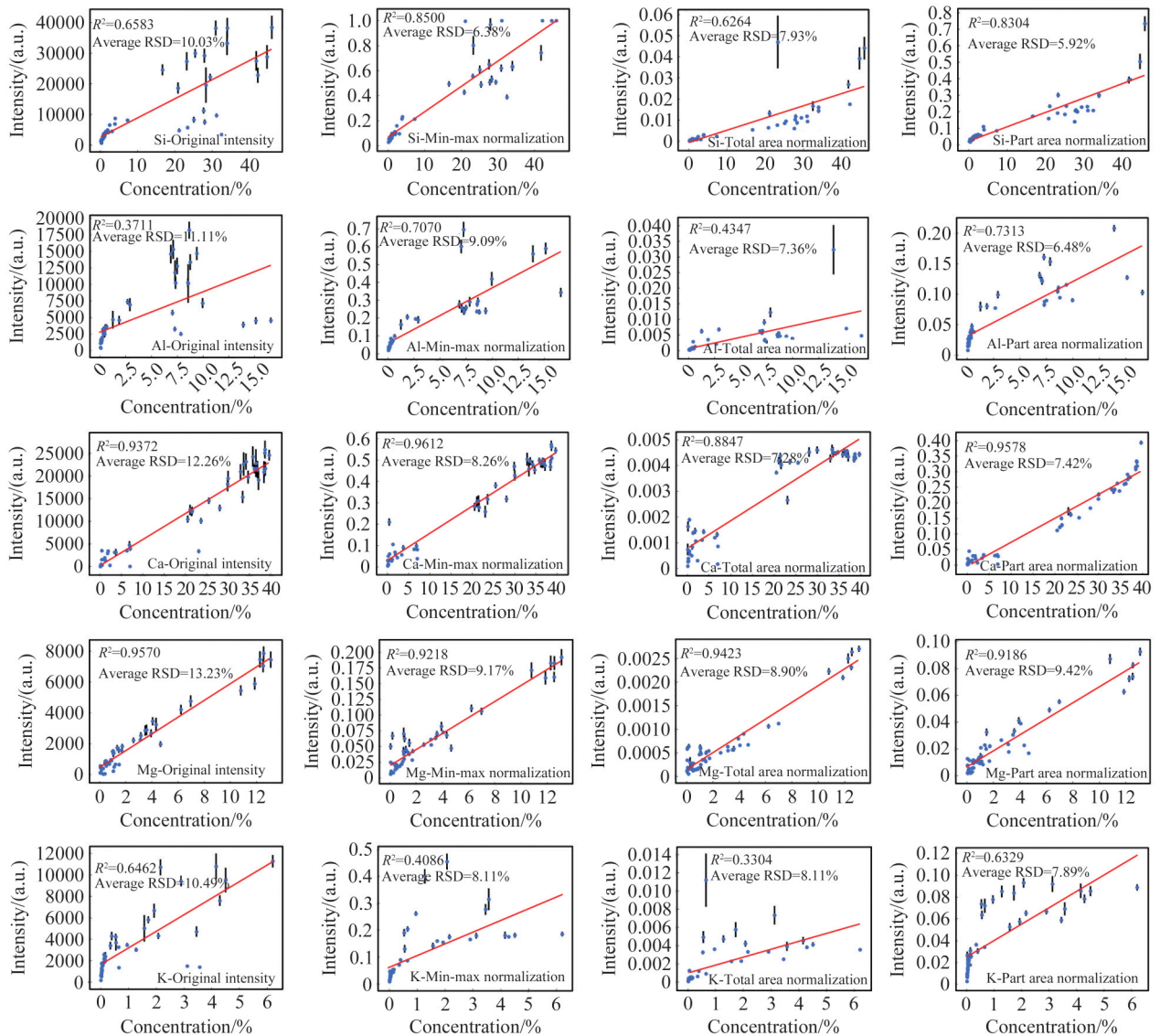


图5 五种元素根据原始峰强和三种不同预处理之后建立的定标曲线对比

Fig. 5 Comparison of the calibration curves of five elements based on the original peak intensity and three different pretreatment methods

49个国家标准样品中,5个元素的原始数据特征峰的平均RSD在11%左右,说明该LIBS仪器的稳定性和重复性是比较可靠的。归一化之后,数据的稳定性和重复性得到了不同程度的提升。综合考虑定标曲线的线性度、样本的整体离散程度和数据的稳定性,以此来确定每种元素的最优归一化方式。对于Si、Al和K元素最优的归一化方式是部分面积归一化,其中Si元素的 R^2 从0.6583提升到0.8304,平均RSD从10.03%下降为5.92%,Al元素的 R^2 从0.3711提升到0.7313,平均RSD从11.11%下降为6.48%,K元素的 R^2 变化不大,平均RSD从10.49%下降为7.89%;Ca元素的最优归一化方式是Min-Max归一化, R^2 从0.9372提升到0.9612,平均RSD从12.26%下降为8.26%;Mg元素的最优归一化方式是总面积归一化, R^2 变化不大,平均RSD从13.23%下降为8.90%。

2.2 定量模型的建立与验证

针对每种元素,需要分别建立定量的模型。Ca元素通过Min-Max归一化以后,定标曲线的 R^2 超过了0.95,达到了比较理想的状态,以此为基础构建了Ca元素的定量方程。其余四种元素在归一化之后,虽然元素含量和选定的特征峰强度之间总体呈现出正相关趋势,但是 R^2 仍然不够理想。为了进一步的提升定量的准确性,本文提出了基于主成分回归(Principal Component Regression, PCR)的系数校正法来进一步校正光谱强度。

基于数据预处理的结果,可以根据拟合出的定标曲线来计算国家标准样品中的Si、Al、Mg和K元素在不同含量时所对应的理想峰强。如图5所示,Al元素和K元素虽然特征峰强度和含量总体上呈现出正相关的趋势,但是在不同的含量范围呈现出了不同的趋势,为了更好地拟合强度随含量变化的趋势,采用分段拟合的方式,用两个方程来计算理论峰强。图6展示了49个国家标准样品的理想峰强和实际峰强以及理想峰强的计算公式。计算出理想峰强以后,用理想峰强除以实际峰强就可以得到每个样品中各元素的校正系数。

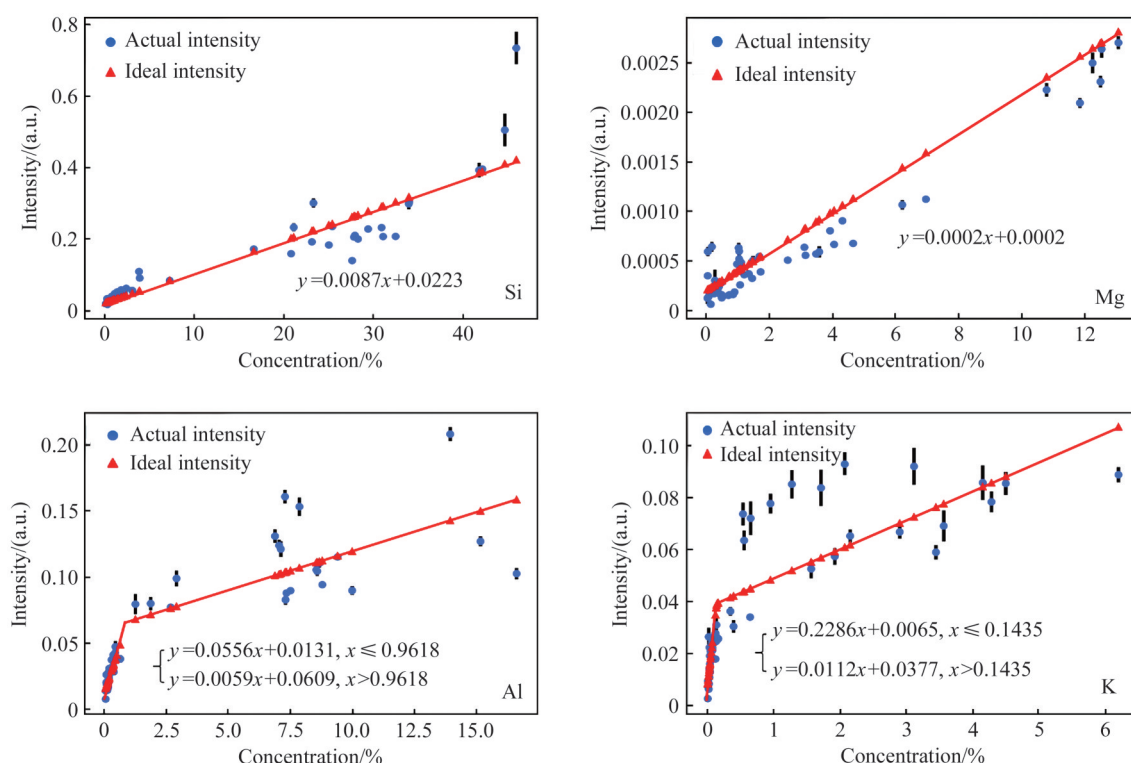


图6 理想峰强与实际峰强

Fig. 6 Ideal and actual peak intensities

要建立整个光谱数据和校正系数之间的PCR模型首先需要确定合适的PC数量。对于Si、Al和K元素,选用的是部分面积归一化,而Mg元素选用的是总面积归一化,在采用两种不同预处理方法对光谱数据进行归一化之后,通过主成分分析(PCA)对数据进行降维。如图7所示,对于两种预处理之后的数据,当PC

数分别为 11 和 15 时,累积数据解释率都超过了 99.5%,说明此时的 PC 数量已经可以代表岩石国家标准样本光谱数据中的大部分信息,我们基于此建立了校正系数和主成分之间的 PCR 模型。

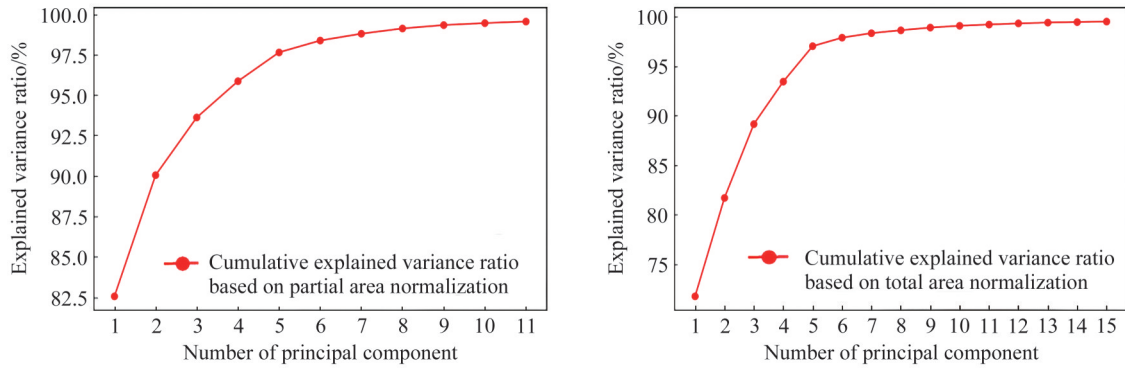


图 7 基于两种预处理之后的累积主成分数据解释率

Fig. 7 Cumulative interpretation rates of PCs based on two different pretreatment methods

建立了 Si、Al、Mg 和 K 元素的系数校正模型以后,使用该模型计算校正系数,然后用校正系数乘以实际峰强就可以计算出校正后的峰强,根据校正后的峰强和对应的含量建立了定量分析模型,如图 8 所示。

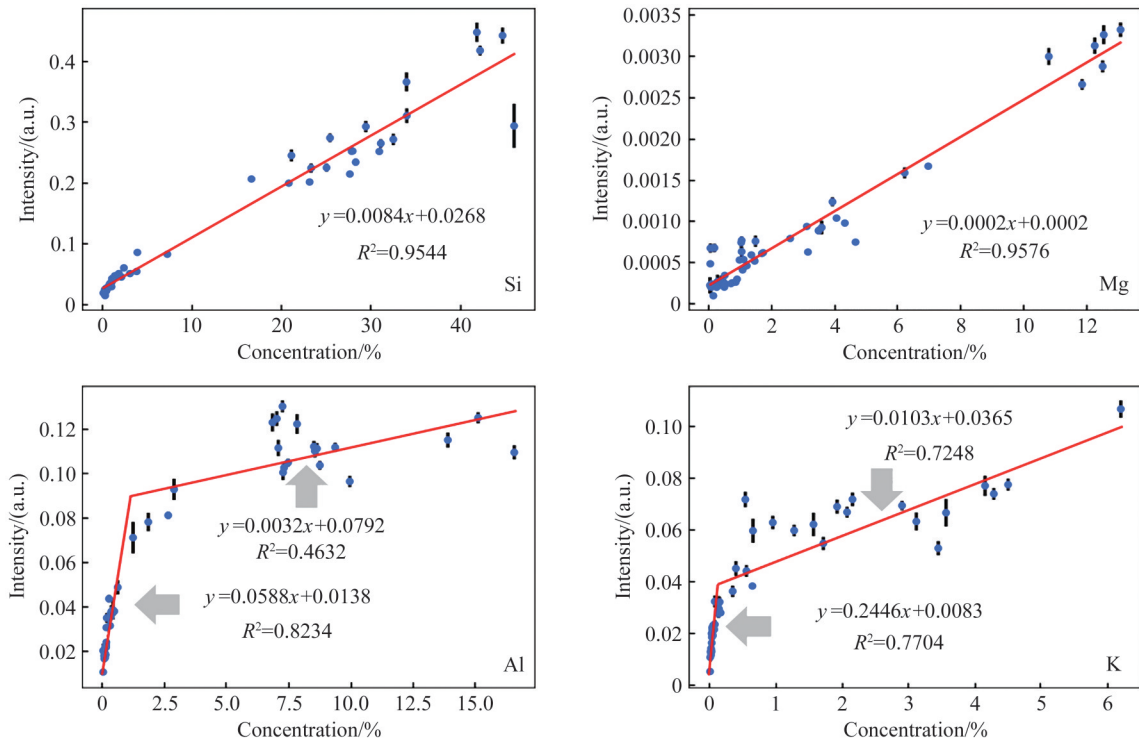


图 8 Si、Mg、Al、K 元素的定量模型

Fig. 8 Quantitative models of Si, Mg, Al and K

利用所建立的定量方法,对测试集的 17 个补充样品中的五种元素含量进行了预测,结果如图 9 所示, Si、Mg、Ca 元素的预测结果与标准含量之间的 R^2 分别为 0.974 5、0.990 1、0.984 3, Al 元素的 R^2 也接近 0.95, 说明了该方法的有效性。在五种元素中, K 元素的预测结果相对较差,是因为当 K 元素含量比较高时,由于受到自吸收效应的影响,降低了定量分析的准确性。

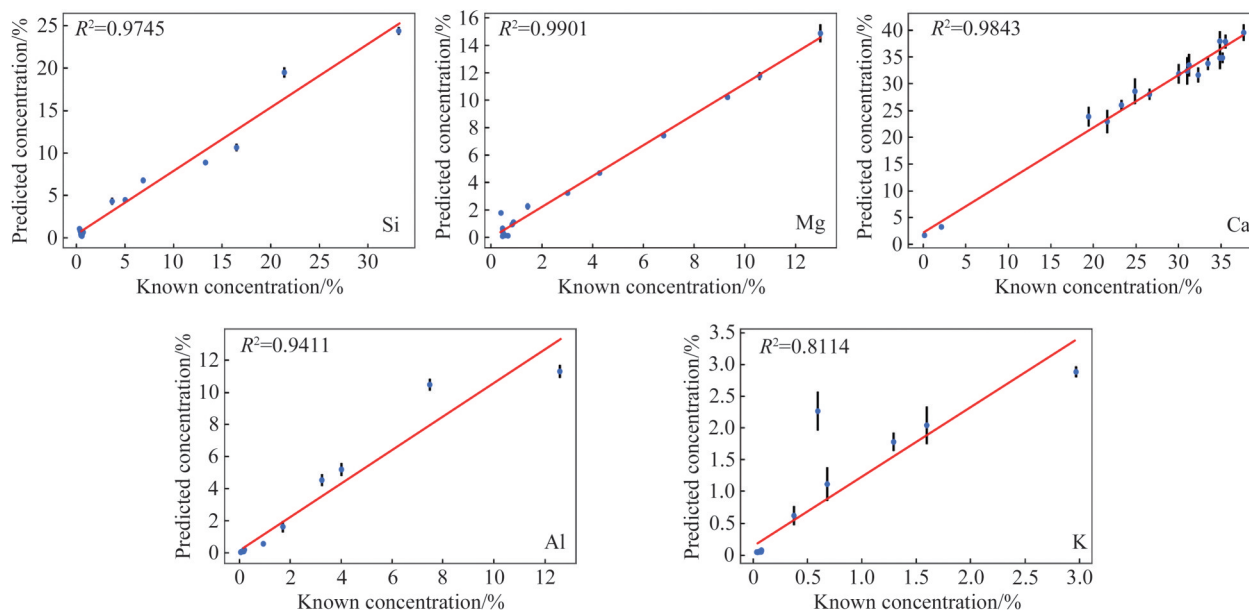


图9 测试集样品的五种元素含量预测效果

Fig. 8 Predictive performance of quantitative analysis for the five target elements on test data

2.3 应用测试

为了验证本方法应用于录井现场岩屑元素分析上的可行性,本文将所建立的定量模型集成到团队自主研发的LIBS仪器上,对来自我国西南地区某钻进现场所采集到的同一口井不同深度的97个岩屑样品进行了分析。我们将LIBS的预测值和实验室XRF仪器的检测值进行了对比,结果如图10所示,Si、Mg、Ca、Al和K五种元素的预测值与XRF检测值之间决定系数(R^2)分别达到0.9719、0.9652、0.9479、0.9604和0.9245。

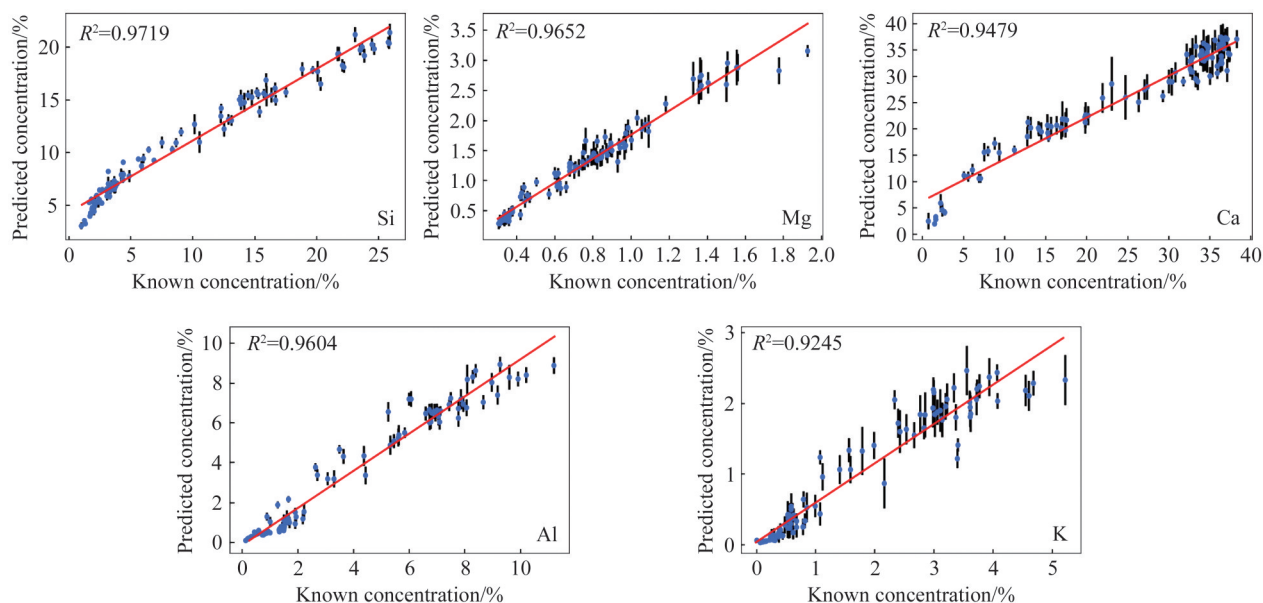


图10 岩屑样品的五种元素含量预测效果

Fig.10 Predictive performance of quantitative analysis for the five target elements of samples of cuttings

根据分析结果绘制了各元素含量变化曲线图,如图11所示,LIBS预测值和XRF检测值整体趋势基本一致,从图中各元素变化的趋势能够分析出岩性及地层的变化。例如,LIBS对LJ#22~LJ#30样品的Si元素含量预测值在20%左右,Al元素含量预测值在7%左右,Ca元素含量的预测值普遍低于10%,说明这部

分样品属于黏土岩(如:泥岩、页岩);对LJ#31~LJ#64样品的Si元素含量预测值低于10%,Mg元素含量预测值低于1%,Ca元素含量预测值高于30%,说明这部分样品属于石灰岩。根据LIBS的预测值,可以分析出从LJ#31样品开始样品所属的岩性和地层出现了明显的变化,这一结论与录井现场的真实情况一致,证明了本方法的有效性,也表明该LIBS仪器在油气勘探开发领域的应用潜力。但是,从图中也可以看出,Mg元素的LIBS预测值比XRF检测值整体偏高,K元素的LIBS预测值比XRF检测值整体偏低,而且本次所分析的元素种类有限,因此后续的工作研究重点需要建立更加全面的元素定量分析模型,开发定量准确性更高的数据处理算法。

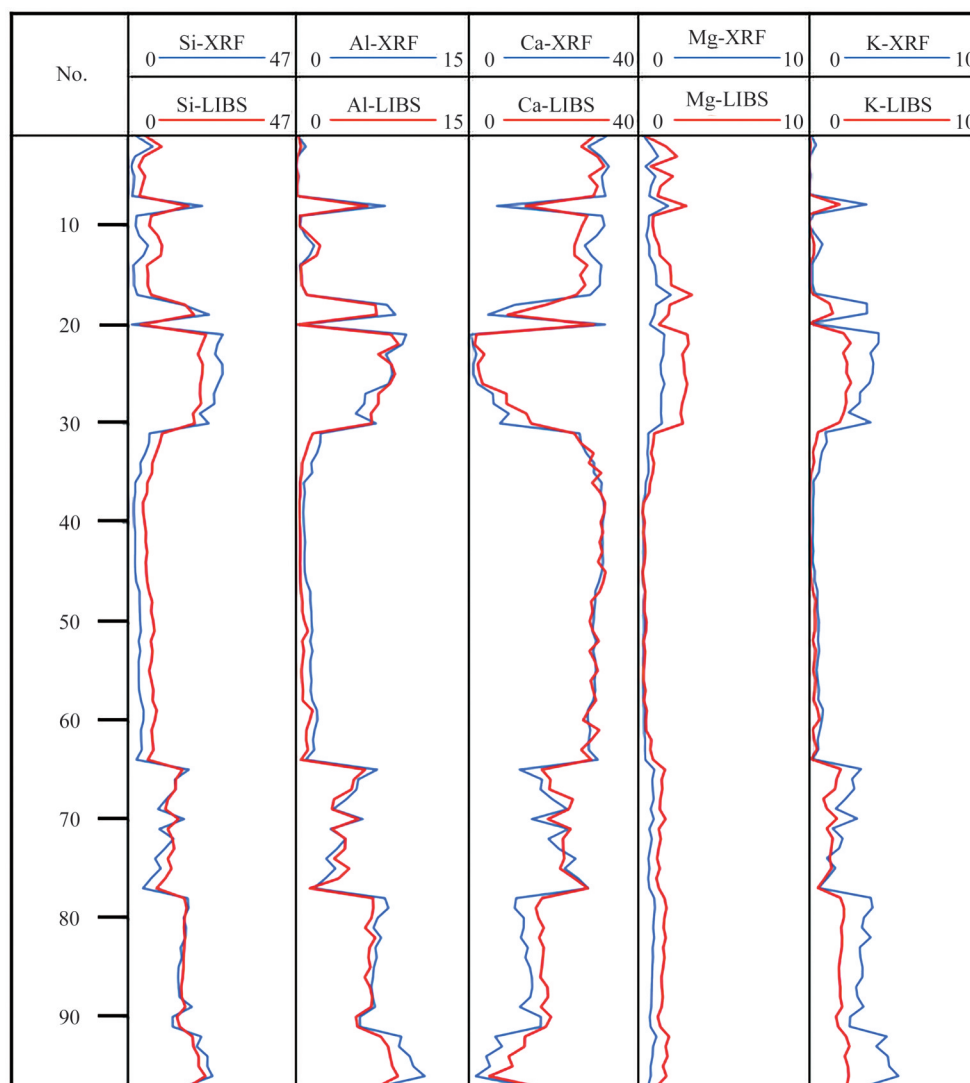


图11 岩屑样品的五种元素含量变化曲线图

Fig. 11 The content change curves of five elements in the samples of cuttings

3 结论

本文基于岩石国家标准样品的LIBS光谱数据,针对Si、Al、Ca、Mg和K五种元素选择了合适的数据处理方法和用于定量分析的特征峰,为了提高定量准确性,提出了基于PCR的系数校正法,对特征峰的强度进行进一步的校正,根据校正后的峰强数据建立了定量分析模型。以测试集数据验证了该方法的有效性之后,将定量模型集成到团队自主研发的LIBS仪器上,对来自录井现场的岩屑样品进行了分析,并与实验室XRF的检测值进行了对比。结果表明,基于两种方法检测结果所绘制的元素含量变化图整体趋势基本一致,说明该仪器能够对录井岩屑样品进行有效的分析。本文证明了所建立的定量分析模型结合团队自主研发的LIBS仪器在油气勘探开发领域具有良好的应用前景。

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Quantitative Analysis Method of Multi-elements for Logging Cuttings Based on LIBS Technology (Invited)

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Abstract: It is one of the basic works to determine the elemental contents of cuttings' samples from different depths in the process of oil and gas exploration and development. An accurate element logging map can provide significant information for identifying lithology, predicting the formation to be drilled, selecting suitable drilling parameters and reducing drilling risks. With the disadvantages of complex operation processes, complicated sample pretreatment and long analysis time, most traditional element analysis technologies are difficult to meet the requirements of rapid analysis for cuttings at the logging site. In recent years, X-ray fluorescence spectrometry technology has been widely used in the logging field for real-time online element analysis due to its portability, low sample demand and fast detection speed. However, based on its technical principles, XRF has a certain radiation risk, and it is poor to detect light elements (atomic number < 11). As a promising analytical technology, laser-induced breakdown spectroscopy technology has the advantages of real-time, in-situ, simple structure and multi-element simultaneous analysis, which meets the actual need of rapid analysis for cuttings logging. The experimental system used in this study was a self-developed benchtop laser-induced breakdown spectrometer, mainly consisting of a Nd: YAG laser, three spectrometers, a digital delay generator and several optical fibers and lenses. A total of 1320 LIBS spectra of 66 rock samples, including 49 Chinese national standard rock samples as training samples and 17 supplementary samples as test samples, were collected by the instrument. The characteristic peaks including 288.16 nm (Si I), 308.22 nm (Al I), 445.48 nm (Ca I), 516.73 nm (Mg I) and 769.90 nm (K I) were selected as target peaks for quantitative analysis. To improve the data stability and repeatability, a part area normalization was proposed. Different from total area normalization, only considering 18 characteristic spectral lines of 9 main elements in rocks, part area normalization could take into account the mapping relationship between the spectral line intensity and content of the element, reduce the spectral difference caused by the inconsistent ablative amount and weaken the influence of matrix effect. Based on the training data set, the appropriate data pretreatment method was selected from three normalization methods (including min-max normalization, total area normalization and part area normalization) for each element.

To improve the quantitative accuracy, a coefficient correction method based on a principal component regression algorithm was proposed to correct the characteristic peak intensity. On the basis of the calibration curve of peak intensity after normalization and content established for each element, the ideal peak intensity and correction coefficient between peak intensity corresponding to different content could be calculated. PCR algorithm was used to establish models for calculating correction coefficients with the input of the full spectrum data. Then, the quantitative analysis models for five target elements were established upon the corrected peak intensity data. The test data set was applied to evaluate the quantitative models. The coefficients of determination (R^2) of the Si, Al, Ca, Mg and K between LIBS predicted values and known contents were 0.974 5, 0.941 1, 0.984 3, 0.990 1 and 0.811 4, respectively, which proved the effectiveness of quantitative models. Finally, to verify the feasibility of application in logging site, the quantitative models were integrated into the self-developed instrument to analyze 97 cuttings samples from the same well at different depths, which were collected from a drilling site in southwest China and provided by Chengdu Aliben Science & Technology Co., LTD. The predicted results were compared to the detection values obtained by using the laboratory XRF. The coefficient of determination (R^2) between LIBS predicted values and XRF detected values of Si, Al, Ca, Mg and K were 0.971 9, 0.960 4, 0.947 9, 0.965 2 and 0.924 5, respectively, which indicates that the instrument integrated with the quantitative models can rapidly and effectively analyze cuttings element content. In the light of the analysis results, the variation curves of contents for five target elements were plotted, which demonstrated the overall variation trends of element contents obtained by LIBS and XRF were basically consistent. Based on the variation trends of LIBS predicted values, the changes of lithology and formation could be analyzed, which were consisted with the real situation at the logging site. The research results showed that this instrument integrated with the developed quantitative models is expected to achieve rapid and effective quantitative element analysis for cuttings, and has good potential application value in the field of oil and gas exploration and development.

Key words: Spectroscopy; Laser-induced breakdown spectroscopy; Rock analysis; Quantitative analysis; Principal component regression

OCIS Codes: 300.2140; 300.6210; 300.6365