

激光诱导击穿光谱的近期发展与应用

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摘要 激光诱导击穿光谱作为分析科学领域里的一种新的光谱检测技术近年来得到了快速发展, 新的研究成果不断涌现, 应用范围逐渐扩大, 在分析物质成分元素方面越来越显现出巨大的应用潜力和勃勃生机. 本文在查阅近年来国内外最新文献的基础上, 进行分析归纳, 分为激光诱导击穿光谱的实验装置、方法研究以及在冶金分析、环境监测、生物医学、考古研究、地质探测、材料科学和其他领域的应用等几个部分做简要评述, 试图把各篇文章的新点和亮点呈现给读者, 以求共同促进激光诱导击穿光谱的繁荣与发展, 使这种新型的光谱检测技术日臻完善, 在科学研究和生产生活中发挥更大的作用.

关键词 激光诱导击穿光谱, 仪器装置, 元素分析

激光诱导击穿光谱(laser-induced breakdown spectroscopy, LIBS)是一种利用高能量脉冲激光烧蚀样品材料, 使材料表面的微量样品瞬间气化形成高温、高密度的等离子体, 测量等离子体原子发射光谱中的谱线波长和强度, 便可以完成样品材料所含化学元素的定性和定量分析的光谱检测技术. 自从1962年Brech等人^[1]首次提出采用激光烧蚀样品产生等离子体以来, 光谱工作者一直在探讨这项技术在分析科学领域中的应用, 尤其是近10年来LIBS的研究得到了快速发展, 相关研究论文逐年增多, 应用领域也逐渐扩大. 这项有别于其他光谱分析方法的激光光谱检测技术具备许多独特的优点, 如样品预处理简单或无需预处理; 适合于各种形态(气态、液态、固态、颗粒)物质的分析; 激光激发样品无二次污染; 近似于无损检测; 可进行快速实时现场分析; 能够完成表面和逐层原位检测; 可以实现非接触式远距离探测; 能够应对恶劣环境下的在线分析; 仪器操作简单方便等. 目前在环境监测、生物医学、空

间探测、考古鉴定、冶金分析和工业控制等许多领域得到了应用. 然而, LIBS的光谱检测灵敏度欠佳, 元素分析的检出限有待改善; 光谱定量分析的准确度和精密度较低, 易受样品基体成分的干扰.

经过光谱工作者的潜心研究和不懈努力, 取得了许多新的研究成果, 使得LIBS的检测能力逐渐提高, 应用领域不断扩大. 本文在查阅近些年来国内外最新文献的基础上, 进行分析归纳, 分几个部分简要评述, 试图把各篇文章的新点和亮点呈现给读者, 以求共同促进LIBS的繁荣与发展.

1 激光诱导击穿光谱的实验装置

基本的LIBS系统装置如图1所示, 主要由激光器、聚焦透镜、光导纤维、光谱仪、光检测器、微机和光谱数据处理软件等组成. 激光器是LIBS装置中的核心部件, 它基本上决定了激光诱导等离子体的特性. 目前多使用高能量的纳秒脉冲激光器, 包括固体激光器、气体激光器、准分子激光器等. 其次

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Chen J Z, Wang J, Song G J, et al. Recent development and application of laser induced breakdown spectroscopy (in Chinese). Chin Sci Bull, 2016, 61: 1086–1098, doi: 10.1360/N972014-01370

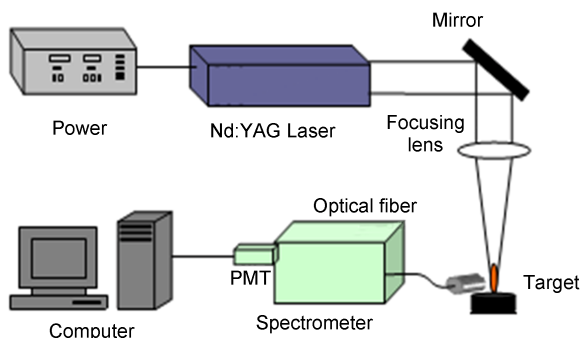


图1 (网络版彩色)LIBS实验装置示意图

Figure 1 (Color online) Schematic diagram of the LIBS experimental setup

是飞秒激光器,飞秒激光作用于样品产生的高光谱检测灵敏度已引起了光谱工作者的浓厚兴趣.聚焦透镜将脉冲激光汇聚于样品表面,用于烧蚀样品材料而产生等离子体;视激光输出能量大小和工作任务的不同,透镜焦距一般选择在40~140 mm,直径在25~45 mm.光导纤维(或加透镜装置)用于收集激光等离子体的光学辐射并传输到光谱仪;亦可用于传递激光能量,以实现远程探测和减少辐射伤害.配合LIBS多采用光栅光谱仪,常用装置为Czerny-Turner型,近年来中阶梯光栅(Echelle)光谱仪的使用逐渐增多,它产生的大色散率二维光谱给光谱测量带来了方便.光检测器主要有光电倍增管(PMT)和电荷耦合器件(CCD),将PMT用于扫描型光谱仪可以获得具有良好光谱信噪比的一维空间信息;以照相法记录光谱信息常用CCD或增强型CCD(即ICCD),亦可获得二维空间信息,尤其用ICCD可以设定延时和选通窗口来提高光谱信噪比或得到时间分辨光谱,不过ICCD的价格比CCD贵得多.由光检测器将光信号转换为电信号后传输到微机(PC),采用相关软件进行数据处理.如果用控制气氛法改善激光等离子体发射光谱质量,则将样品置于烧蚀室内,烧蚀室由石英、不锈钢或高分子聚合物制成,环境气体可以是惰性气体或氮气等.

2 激光诱导击穿光谱研究

与成熟的光谱分析方法如电感耦合等离子体原子发射光谱法(ICP-AES)、电热原子吸收光谱法(ETA-AAS)和电感耦合等离子体质谱法(ICP-MS)相比,LIBS作为一种强有力的物质成分检测方法在精确度和灵敏度方面尚显不足.目前的研究重点:(1)

对光谱信号的优化,如提高光谱强度,增大信噪比,改善元素检出限;(2)降低基体效应,提高信号稳定性,改善光谱定量分析准确度和精密密度.

2.1 纳秒激光诱导击穿光谱

近来研究与应用最多的是纳秒激光诱导击穿光谱(nanosecond-LIBS, ns-LIBS),由于纳秒激光器具有造价较低,操作便捷,维护简单等优点,ns-LIBS有着广阔的应用前景. Leme等人^[2]采用Nd:YAG激光器(1064 nm, 5 ns, 365±3 mJ),研究了脉冲重复率和脉冲数对聚丙烯和高密度聚乙烯样品的烧蚀坑影响,结果显示,重复率越高、脉冲数越大,则烧蚀坑越深,形状越规则,发射谱线越强.为了提高发射光谱强度和信噪比, Eschlböck-Fuchsa等人^[3]对铝合金、硅晶片和冶金渣样品进行加热,并用纳秒激光激发样品产生等离子体,发现等离子体的膨胀动力学和光学发射显著取决于样品温度,大多数元素发射谱线强度随着样品温度的升高而增强. Chen等人^[4]以土壤样品为靶,采用平面反射镜装置约束激光等离子体,获得元素Mg, Al, Fe和Ba发射光谱强度的增大幅度在93%~160%,光谱信噪比在17%~40%.用碳质空腔约束激光等离子体也可以有效提高发射光谱质量^[5].

2.2 飞秒激光诱导击穿光谱

随着激光技术进步,飞秒激光诱导击穿光谱(femtosecond-LIBS, fs-LIBS)逐渐受到关注.相对于ns-LIBS而言,fs-LIBS表现出高光谱信噪比.另外,纳秒激光能够使样品组分的化学键断裂,探测得到的是原子(或离子)光谱;而飞秒激光脉宽窄,光强较高,作用于样品表面的热效应范围小,使样品快速电离(非热过程将支配电离),从而保持了样品的分子结构,所以用fs-LIBS既可获得原子光谱,亦可得到分子光谱,进而辨别物质的组成和判断物质的种类.然而,fs-LIBS装置比较复杂,造价也高.

为了提高fs-LIBS检测灵敏度, Banerjee等人^[6]以Ti:Sapphire激光器(800 nm, 130 fs, 600 μJ)为激发源,对激光烧蚀的样品深度光谱灵敏度进行研究.结果显示,消融区表面的fs-LIBS强度很高,而深处的较低,由此表明fs-LIBS适合于表面污染物的高灵敏度检测. Ilyin等人^[7]采用Ti:Sapphire激光器(800 nm, 42 fs, 100 Hz, 1.1 mJ),研究海水表面的等离子体发射光谱和时间特性,证明了低发电位的原子谱线具有

更高的灵敏度. Bonis等人^[8]分别用Nd:YAG纳秒激光(532 nm, 7 ns, 1 Hz, 5.0 J cm⁻²)和Nd:glass飞秒激光(527 nm, 250 fs, 1 Hz, 4.2 J cm⁻²)激发青铜样品, 对比发现, fs-LIBS的谱线丰富, 连续辐射背景较低, 并且在80 ns延时得到了更好的光谱信噪比.

2.3 双脉冲激光诱导击穿光谱

单脉冲LIBS(single pulse LIBS, SP-LIBS)的探测偏差通常在5%~10%, 偏差较大主要归因于激光脉冲稳定性较差、探测器有噪声信号、易受样品基体效应干扰等因素. 双脉冲LIBS(dual pulse LIBS, DP-LIBS)在一定程度上弥补了SP-LIBS的不足, 不仅增大了光谱强度, 提高了检测灵敏度, 而且光谱信号比较稳定, 改善了分析准确度. 但是, DP-LIBS的设备较为复杂.

为了提高光谱强度, Yurdanur-Tasel等人^[9]采用2台Q开关Nd:YAG激光器, 一台Big Sky-Quantel型(532 nm, 6 ns, 1~100 Hz, 25 mJ), 另一台为Focus Eng. IR-(100)型(1064 nm, 20 ns, 1~100 Hz, 40~50 mJ), 对晶体Si(111)和Si(100)进行光谱分析. 结果显示, 在双脉冲之间任何延迟时间下产生的等离子体光谱强度都比单脉冲的高, 1~2 μs时达到最大; Si(100)的光谱强度高于Si(111)的, 因为晶体结构不同. Jiang等人^[10]分别用SP-LIBS和DP-LIBS对低气压环境下钢样品的真空紫外光谱进行研究, 结果也证明, 双脉冲激光方法能够显著提高谱线强度, 并在两脉冲延迟为100 ns得到了最强的谱线. Lazic等人^[11]以液体样品为靶材, 采用2台Nd:YAG纳秒激光器, 研究两脉冲之间的延时对DP-LIBS信号的影响. 结果发现, 在第1个激光脉冲产生的气泡完全展开时发送第2个激光脉冲可以得到最强的光谱信号.

为了比较LIBS的测量精度, Gaft等人^[12]采用2台Nd:YAG纳秒激光器, 分别用SP-LIBS和DP-LIBS研究Zr元素在短紫外波段的发射光谱, 从获得的228.0~247.0 nm的光谱可知, 用DP-LIBS得到的测量精度高于SP-LIBS的. 在提高LIBS的检测速度方面, Gurell等人^[13]把LIBS系统与计算机软件相结合, 以现有认证的参考物质和已知元素组成为根据, 制作出一个可以遥控的自动化元素分析系统, 能够瞬时确定元素组成.

2.4 激光诱导击穿光谱定量分析

LIBS定量检测物质成分的常用方法是校准曲线

法, 即借助一套已知待测元素浓度的标样的光谱数据绘制校准曲线, 然后用测得的待测样品中未知元素的光谱数据从校准曲线查出元素浓度. 此方法的准确度易受设备及操作条件、环境条件和样品组分(基体效应)的影响. 作为探讨, Cong等人^[14]以铅黄铜合金为靶, Nd:YAG 激光器为激发源, 分别用偏小二乘法(PLS)和校准曲线法(CC)做定量分析, 研究表明, 无论是主要元素还是微量元素的分析, PLS都要好于CC, 认为PLS更适用于铜冶炼行业中不同元素的同时定量分析.

目前研究认为一种比较有希望的定量检测方法是无定标激光诱导击穿光谱(calibration free-LIBS, CF-LIBS), 它快速、简单, 无需标准参考物质, 所以不存在基体效应的影响. 采用CF-LIBS的假设: 激光诱导等离子体符合局部热平衡(LTE)条件, 其成分代表样品成分, 并且为光学薄的. 例如, Horňáčková等人^[15]采用Nd³⁺:YAG激光器(532 nm, 4 ns, 10 Hz, 165 mJ), 由CF-LIBS测定3种沸石(丝光沸石、Y型沸石和ZSM-5)的Si/Al摩尔比, 所得结果与古典湿化学分析法的一致, 认为CF-LIBS可用作沸石和类沸石材料的定量分析, 而无需再用有害的化学物质的定性和半定量分析方法, 也提高了分析速度.

2.5 环境条件对激光诱导击穿光谱特性影响

产生激光等离子体的环境条件会明显影响LIBS光谱特性. Mateo等人^[16]采用KrF准分子激光器(248 nm, 450 fs, 900 μJ), 分别以空气、氩气和氦气为缓冲气体, 研究黄铜、紫铜、铝合金和硅样品的光谱特性. 结果表明, 氩气和氦气在500 hPa气压时光谱强度最大, 并有相对较高的光谱分辨率. Sreedhar等人^[17]利用Ti:sapphire激光器(800 nm, 40 fs, 1 kHz, 2.5 mJ), 分别在空气、氮气和氩气环境下研究了3种高能材料的发射光谱, 获得了C元素的光谱在空气、氮气、氩气中的衰减时间分别为 54±3, 43±3和121±16 ns, 即在氩气中得到了更高的光谱强度. 另外, De Giacomo等人^[18]研究比较了气体和液体环境下的激光等离子体发射光谱.

3 激光诱导击穿光谱的应用

虽然早在20世纪60年代就提出了LIBS, 但其广泛应用是近年来的事情. 激光技术和光学探测技术的快速发展促使LIBS技术日臻完善.

3.1 激光诱导击穿光谱在冶金分析领域的应用

钢铁工业是一个国家的主导产业,钢铁中元素成分及含量对材料本身的工艺性能和应用性能起着决定性作用,因此,快速、准确地检测钢铁中的元素种类与含量是研究和评价材料性能的科学依据. Xin等人^[19]采用Nd:YAG激光器(1064 nm, 10 ns, 140 mJ),在聚焦透镜($f=150$ mm)与样品表面之间距离为145 mm、延时0.83 μ s的优化条件下,定量分析低合金钢样品.研究表明,元素含量与光谱强度之间有较好的线性关系,大多数元素的相对误差小于10%,确立了LIBS快速多元素同步分析合金样品的可行性. Legnaioli等人^[20]用2台Nd:YAG激光器(1064 nm, 8 ns, 20 Hz, 120 mJ)组成双光路系统,激光束与法线呈45°角入射到样品,分析了多种贵金属合金,其检出限达到了0.2 mg/g;浓度在20 mg/g(黄金)时的最大偏差为1 mg/g. Pedarnig等人^[21]采用Nd:YAG激光器(1064 nm, 6 ns, 5~10 Hz, 100 mJ),由CF-LIBS分析钢生产中的炉渣和混合氧化物.结果显示,测得氧化物的浓度值与参考值一致,大部分氧化物组分的相对误差在2%以下;大范围改变测定参数值时,浓度值保持稳定.邵妍等人^[22]利用波长为1064 nm的脉冲激光烧蚀合金钢样品,由ICCD探测光谱信号,实验表明,激光的脉冲能量、聚焦位置以及ICCD探测器的延时等对光谱有较大影响,通过优化实验条件,获得了高光谱强度和信背比.为了发挥LIBS的高空间分辨率性能, Lopez-Quintas等人^[23]用Nd:YAG激光器研究了发动机阀门的成分分布,通过测定元素铁、钴、镍和锰,建立了阀门成分分布的三维立体模型,证明LIBS能够完成机械零件成分立体分布的能力.潘从元等人^[24]为了实现真空冶金炉内样品成分的LIBS检测,采用真空泵和中频感应电炉设计和搭建系统,成功获得了钢样品的LIBS光谱,为研究真空环境下熔融金属成分奠定了基础.

降低LIBS仪器成本,减少样品检测费用,这是科学研究和生产应用中一个现实而重要的问题. Gonzaga等人^[25]把被动Q开关Nd:LSB微片激光器(1062 nm, 800 ps, 2 kHz, 12 μ J)和常用的Czerny-Turner型摄谱仪结合,设计了一种紧凑的低成本分析仪,分析了铬和镍含量为5%~26% w/w的标准钢样品,并建立了2个偏最小二乘法(PLS)校正模型.结果表明,测定铬和镍的平均相对误差分别是3.7%和6.7%,此结果类似或优于采用单变量校正的高配置光谱仪的结果,

证明多元校正可以克服低配置仪器的灵敏度低、分辨率低和脉冲能量低的问题.

3.2 激光诱导击穿光谱在环境监测领域的应用

由于工业“三废”大量排放、农用化肥和农药过度施用、城市垃圾和废弃物缺少无害化处理等原因,环境污染问题日趋严重,与人类生活息息相关的空气、水和土壤受到了不同程度的污染,直接威胁人身健康.而方便快捷的LIBS已成为环境质量监测领域强有力的分析技术.

为了监测空气质量, Kwak等人^[26]采用Nd:YAG激光器(1064 nm, 5 ns, 2 Hz, 90 mJ),由LIBS测定空气中可吸入颗粒物中重金属含量.研究显示,粉尘中的重金属可分为地壳的(Al, Ca, Mg)和人为的(Cr, Ni, Zn),当粉尘经过工业污染地区时Cr, Ni和Zn的含量明显升高. Awan等人^[27]采用Nd:YAG激光器(1064 nm, 10 ns, 10 Hz, 89.5 mJ)激发空气中的颗粒物,在延时4.5 μ s、镜头距离样品表面70 mm、用金属滤盘收集样品的优化条件下,定标曲线在50~500 ppm的元素浓度范围有良好线性, R^2 在0.992~0.998,测得Cd, Zn和Pb的检测限为29~48 ppm,证明了LIBS检测空气中重金属的能力.

水是生命之源.李敏等人^[28]用LIBS测定湖水中的铜,建立了铜浓度与谱线强度的定标曲线, R^2 为0.99;测得铜的检出限为1.14355 mg/L. Al-Adel等人^[29]通过将水样品冻结和优化Nd:YAG激光器参数(266 nm, 6 ns, 10 Hz, 30 mJ)降低了元素检出限,提高了分析灵敏度. Bukhari等人^[30]用吸收纸提取水样品中杂质,采用Nd:YAG激光器(1064 nm, 10 ns, 10 Hz, 146.7 mJ-铬, 89.5 mJ-镉)检测制革废水中重金属铬和镉,在延时4.5 μ s、样品表面距离镜头70 mm、采光系统距离样品表面7 mm的优化条件下,得到了信噪比最好的光谱. Faye等人^[31]应用LIBS对含有硼硅玻璃颗粒的受污染水进行监测,也取得了理想效果.

目前用LIBS检测土壤成分被认为是最直接最有效的方法.杜闯等人^[32]用Nd:YAG激光器的二倍频和基频、脉冲能量分别为70和100 mJ组成正交DP-LIBS系统检测土壤中重金属,得到双脉冲之间延时为20 μ s时 MnI 406.4 nm谱线增强幅度可达2.75倍. Kim等人^[33]用Nd:YAG激光器(1064 nm, 4~5 ns, 1 Hz, 90 mJ)分析土壤中的重金属和油类污染物,结果显示,重金属污染土壤、油类污染土壤和非污染土

壤的检测正确率分别为100%, 100%和95%, 证明用LIBS分析土壤成分可行. 为了进一步提高LIBS的检测能力, Liu等人^[34]把LIBS与微波辅助技术相结合, 在探测土壤样品中30 mg kg⁻¹的铜和23.3 mg kg⁻¹的银时发现, 单一用LIBS未探测到铜和银, 而微波辅助LIBS技术却可以探测到. 另外Srungaram等人^[35]分别用LIBS和火花诱导击穿光谱(SIBS)对土壤中的汞进行分析, 研究得出LIBS和SIBS的分析检出限分别为483和20 ppm, 它们分别适用于高浓度和低浓度汞检测, 也说明LIBS的检测能力有待进一步提高. Farooq等人^[36]用Nd:YAG激光器(1064 nm, 6 ns, 10 Hz, 50 mJ)检测化肥中的元素成分, 得出其中含有镉、镍、铅等有害人体健康的元素, 这是土壤污染源之一.

在用LIBS分析固体废弃物成分方面, Peng等人^[37]以Nd:YAG 激光器(1064 nm, 8 ns, 10 Hz)为激发源, 测定废锌锰电池中的重金属和其他元素, 得出正极中存在Mn 58.17%, Zn 31.41%, Fe 12.42%, Cr 3.85%, V 4.36%, Cu 0.14%, Al 0.3%, Si 1.71%, Mg 2.62%和Ca 0.08%; 负极一端含有Pb 6.04%, Fe 11.03%, Al 0.26%, Mg 0.22%, Si 0.32%, C 1.99%和Ca 0.03%等. Aguirre等人^[38]用Nd:YAG激光器(1064 nm, 10 ns, 180 mJ), 光谱检测废电器和电子设备成分, 得出一些聚合物部件和涂料中含有重金属Cr, 白片中主要是Al, Ba和Ti. Rabasovic等人^[39]采用YAG激光激发电器废物, 发现了钢的光谱线, 证明了LIBS可用于废弃电器回收利用的可行性.

材料的分类是处理废弃物过程中一项重要工作. 如图2所示, Huber等人^[40]用Nd:YAG激光器(1064 nm, 7 ns, ≤100 Hz, 80 mJ)激发废弃的含氯聚合物, 研究表明, 把LIBS用作工业材料的分拣设备, 可快速鉴定PVC废物, 根据Cl的浓度能够将废弃材料分成几类. Barbier等人^[41]也研究了用Nd:YAG激光器组成的LIBS系统在塑料识别上的应用, 以氦气作缓冲气体

时, 用波长为266 nm激光能够获得最高的光谱分析灵敏度; 根据元素含量的不同将塑料样品分成了四类, 证明LIBS可以胜任废弃塑料回收当中的分拣工作.

3.3 激光诱导击穿光谱在生物医学领域的应用

日趋严重的环境污染造成了生物样品中重金属含量超标. Yao等人^[42]采用Nd:YAG激光器(1064 nm, 8 ns, 0.1~10 Hz, ≤200 mJ), 由LIBS检测赣南脐橙中重金属元素Cr, 证明了LIBS实时快速测定水果中重金属元素含量的可行性. 张旭等人^[43]通过LIBS测定了赣南脐橙中重金属元素Cd, 用偏最小二乘法(PLS)对Cd元素的39个样品建立定量分析模型, 拟合曲线的 R^2 为0.9806, 其余12个样品的验证结果的相对误差为10.94%, 检测限为3 μg/g. 万雄等人^[44]用由Nd:YAG 激光器组成的LIBS系统检测受污染鱼体内各器官中重金属元素分布及含量, 得出鱼的肝脏和口腮等部位重金属较多, 而鱼肉中重金属含量极低.

LIBS在医学研究领域有着广阔的应用前景. Diaz等人^[45]采用高功率CO₂激光器(10.591 μm, 64 ns, 25~70 J/cm²)研究DNA碱基鸟嘌呤和腺嘌呤的光谱, 得出了DNA碱基鸟嘌呤和腺嘌呤的等离子体光谱的时间分布特性. Dhar等人^[46]用Nd:YAG激光器研究补骨脂种子提取物中有降糖和降脂作用的微量元素, 得出钙和镁的浓度与提取物的降糖和降脂能力有关系, 证明用LIBS检测中药中的主要和次要元素及浓度可行. Emara等人^[47]采用Nd:YAG 激光(1064 nm, 8 ns, 10 Hz, 100 mJ)激发人的头发, 发现头发中微量元素Na, K, Ca, Mg, Fe和Si的含量能够反映人的健康状况.

在法医学研究方面, Manzoor等人^[48]以Nd:YAG激光器(1064 nm, 4 ns, 1 Hz, 20 J/cm²)为激发源, 通过对猪的肌肉进行LIBS分析, 来确定猪的死亡时间. 研究表明, H α 谱线随时间变化明显, 由H α 谱线可以确定死亡时间, 误差为7%, 此方法可用于法医学对死亡时间的鉴定. Kula等人^[49]采用由Nd:YAG激光器(1064 nm, 6 ns, 150 mJ)组成的LIBS系统对不同品牌、颜色、类型的墨水进行分析, 研究对象是油墨中常见的9种元素: Ba, Cr, Cu, Fe, Li, Mo, Mn, Ni 和W, 建立了常用墨水的元素组成, 证明了LIBS用于油墨的鉴定可行, 能够用于法医鉴定.

3.4 激光诱导击穿光谱在考古领域的应用

考古工作是通过实物材料来直接了解历史, 可

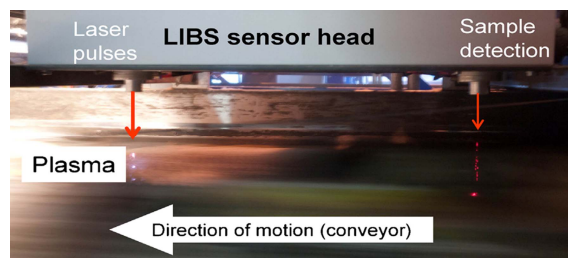


图2 (网络版彩色)LIBS用于工业材料分拣

Figure 2 (Color online) LIBS is applied to industrial materials sorting

以帮助人类把握现实, 预知未来. Kokkinaki等人^[50]分别采用LIBS和质谱(MS)对文化遗产资料进行分析, 研究对象是锌钡白、柠檬黄和酞菁蓝. 结果显示, LIBS能够快速进行涂料元素特别是金属元素的识别, 对环境条件要求低; 而质谱提供包括S和Cl的敏感检测、有机分子和分子碎片的认定. Palomar等人^[51]利用由Nd:YAG激光器(266 nm, 5 ns, 10 Hz)组成的LIBS系统对罗马的古董玻璃的退化进行研究, 样品是7个玻璃珠, 测量确定了色团和不透明元素的成分. Blagoev等人^[52]通过ns-LIBS对考古发掘的陶瓷碎片进行分析, 得出了陶瓷的化学成分, 并由此了解了陶瓷的制作工艺. Pardini等人^[53]分别采用由Nd:YAG激光器(1064 nm, 8 ns, 10 Hz, 80 mJ)组成的DP-LIBS装置和X射线荧光光谱仪对两千多年前的罗马金币进行现场元素测定, 确定了硬币的主要成分和浓度, 并探测了硬币的组合物及其走线, 否定了锯齿硬币理论, 对硬币的鉴别有重要意义.

古生物化石可以为研究生命起源和演化、地质地貌成因、环境气候变迁等提供可靠依据. Roberts等人^[54]采用Nd:YAG激光器(1064 nm, 8 ns, 3 mJ, 1 Hz), 由LIBS分析从南非的Malapa人类文化遗址中发现的古人类化石时, 试图通过找到一条光谱线作为控制信号, 当用高能量激光去除化石上的岩石包裹时, 可自动控制保护化石. 他们发现, 中性的磷谱线可以在单脉冲LIBS系统中用作控制线, 因为在限定的光谱区内岩石成分的谱线是硅、铁和锰的谱线, 而古人类骨骼却是很强的磷谱线. 这样的操作对化石的破坏很小, 达到了保护化石之目的.

传统的考古鉴定是极其缓慢而繁琐的, 特别是在考古发掘前期的考古发现和定位方面, 在没有历史数据的情况下, 古老文明的发掘是非常困难的. 而采用LIBS可以实现远程现场探测, 使得考古工作变得容易. Vítková等人^[55]利用线性判别分析(LDA)和人工神经网络(ANN)技术, 分别对LIBS在未发掘地区的远程探测光谱进行了快速识别分析, 在检测的8种考古材料中, 用LDA鉴定出了其中的6种, 而用ANN鉴定出了其中的7种, 这是一个相当优秀的鉴定成绩. 用这种方法, 可以加快和简化考古中的采样过程, 便于部分出土样品的初步分析, 有助于确定值得再次挖掘的方位和面积. 2014年, 该课题组分别采用远程型LIBS装置和桌上型LIBS装置, 将主成分分析法(PCA)和线性判别分析法(LDA)相结合用于本实验中,

对7个不同地点的29块砖样品进行快速分类, 通过精确对比研究表明, 远程LIBS装置用于考古现场的实地测量有着巨大潜力, 为完成考古挖掘和砖建筑物及不同砖结构的修复工程奠定了基础^[56].

LIBS也可用于水下作业, 如图3所示. 为了完成水下的考古工作, Guirado等人^[57]利用由Nd:YAG激光器(1064 nm, 7 ns, 20 Hz, 100 mJ)组成的远程LIBS系统探测了位于地中海水下30 m深处的考古材料. 实验用一根45 m长的光纤将激光束传输至样品表面, 光束与材料表面的夹角为0°~40°; 利用与此处海水压强差大于1 bar的空气流吹开海水, 在激光烧蚀之前产生一个海水-样品界面, 以减少海水导纳对LIBS系统的影响, 保证激光诱导等离子体的质量, 获得最佳光谱. 在优化的实验条件下, 对地中海水下不同氧化程度的青铜器进行了现场分析, 获得的光谱的标准偏差小于10%. 这种考古材料的海底原位分析技术对于保持考古资料的原来形态具有重要的意义.

3.5 激光诱导击穿光谱在地质领域的应用

开展地质学方面的研究, 对于人类了解地球的物质组成、内部构造、外部特征、各层圈之间的相互作用和演变历史的知识具有重要意义, 也是满足人类物质需求的前提与基础. Hanif等人^[58]利用由Nd:YAG激光器(1064和532 nm, 5 ns, 10 Hz)组成的LIBS系统研究了硫矿石产生的等离子体, 结果表明, 沿着等离子体高度距离样品表面0.05 nm处的电子密度和温度值最大, 后随距离的增大而降低, 随激光强度的增大而提高. Giacomo等人^[59]在局部热动力学平

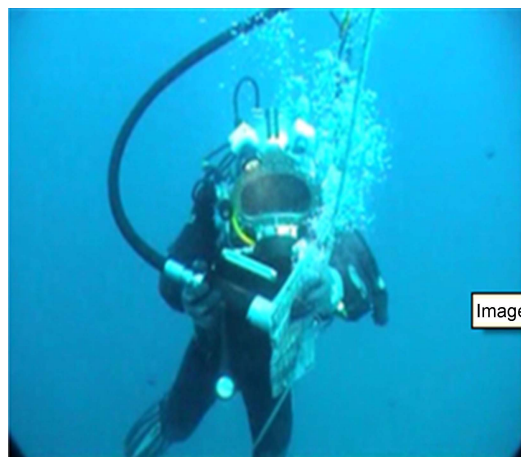


图3 (网络版彩色)LIBS用于水下作业

Figure 3 (Color online) LIBS is applied to underwater operation

衡(LTE)条件下,用Nd:YAG激光(1064 nm, 7 ns, 10 Hz)激发紫翠玉宝石,测定了宝石的主要和次要元素,误差分别为1%和5%,展示了LIBS在宝石鉴定领域的应用潜力.

通过探讨与改进分析方法来提高LIBS检测水平是研究热点之一. Horňáčková等人^[60]利用由调Q Nd:YAG激光器(532 nm, 4 ns, 10 Hz, 165 mJ)组成的LIBS系统,建立有序结构的微孔晶体硅铝酸盐(沸石)的不同Si/Al摩尔比的校准曲线,以分析不同类型沸石. 实验利用测量谱线峰值下面积加上背景的方法,使得校准曲线的线性回归系数拟合度达到0.97以上,提高了LIBS可靠性. Kim等人^[61]在试验中以Nd:YAG激光器为激发源,对经过标准加入法处理的铀矿石进行定性和定量分析,获得铀的检出限为158 ppm,与其他检测方法相比, LIBS具有更好的稳定性. Mukhono等人^[62]利用由Nd:YAG激光器组成的LIBS系统研究土壤和岩石样品中痕量元素Cr, Cu, Pb和Ti的光谱,采用偏最小二乘法(PLS)和人工神经网络(ANN)做定量分析,结果表明,多元校准能够显著提高分析的精度. Hark等人^[63]利用由Nd:YAG激光器组成的LIBS系统,对来自北美、南美、非洲和亚洲的37个地区的57种钽铌样品进行检测,用偏最小二乘判别分析法(PLSDA)对光谱进行分析,结果准确率在90%以上. 这在矿物的发现以及珍贵稀缺矿产的国家归属鉴定上具有重要意义.

依据LIBS在远程探测和实时现场分析的显著优势,美国宇航局(NASA)在发射的“好奇”号火星车上携带LIBS探测器“ChemCam”已于2012年8月6日成功登陆火星,图4是ChemCam在火星上进行地质分析的实拍画面^[64].

为了使LIBS在外星地质探测方面更为成熟,模拟外星上工作过程的实验研究不断涌现. Pavlov等人^[65]采用由Nd:YAG激光器(1064 nm, 8 ns, 0.8~47 mJ)和Nd:YLF激光器(1053 nm, 5 ns, 2.7 mJ)组成的DP-LIBS系统,模拟了行星表面上的元素探测. 研究发现,用多个激光脉冲累积光谱的方法提高了信噪比,而且只需能量大于1 mJ的激光脉冲就能激发产生等离子体,实验测得多个元素的检测精度达到了重量的0.02%~1%.

3.6 激光诱导击穿光谱在材料分析领域的应用

各种材料的组成与其应用性能和工艺性能密切

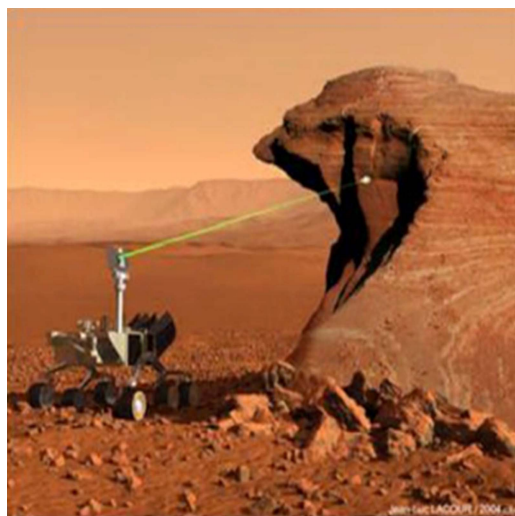


图4 (网络版彩色)“好奇”号火星车上携带LIBS探测器

Figure 4 (Color online) The Curiosity Mars Rover is equipped with LIBS detector

相关,通过检测和控制材料的成分及含量能够达到不同的应用目的. Apostol等人^[66]采用由Nd:YAG激光器(355 nm, 6 ns, 10 Hz)组成的LIBS装置定量分析了一种纳米颗粒,其主要成分为Al, O和Si, 归属于硅酸盐材料. Kim等人^[67]使用Nd:YAG激光(1064和532 nm, 5 ns)激发太阳能电池薄膜,研究发现,波长为1064 nm的激光烧蚀样品依赖于Ga的浓度,而532 nm激光烧蚀样品能够稳定地输出LIBS信号,可以实现连拍分析. Darwiche等人^[68]采用Nd:YAG激光器(266 nm, 4 ns, 20 Hz, 10 mJ),以氦气或氩气作为缓冲气体(压力在100~500 mbar),由LIBS检测固体硅和熔融硅中的杂质. 结果显示,固体硅中硼的检测限达到0.2 ppm (1 ppm=1 mg/kg),而熔融硅中则是6 ppm. 硅晶体的结构不同,使得激光等离子体发射光谱强度有差异^[9].

建筑材料是否达标关乎建筑物的安全使用性能. Gondal等人^[69]利用Nd:YAG激光器的基频和四倍频组成的DP-LIBS系统对钢筋混凝土样品中的硫离子进行检测,以硫的S II 545.38 nm谱线为标记线,以相邻铝的Al II 559.3 nm谱线作为参照. 比较发现,随着硫离子浓度的增大, S II 545.38 nm的峰值相对于Al II 559.3 nm的峰值会慢慢变大;其检出限可达到38 mg/g.

在液体材料检测方面, Rosado等人^[70]在用Nd:YAG激光器(266 nm, 4 ns, 20 Hz, 15 mJ)分析液体中Al₂O₃颗粒大小对LIBS的影响时发现,随着Al₂O₃颗粒尺寸的增大,校准曲线的斜率会显著减小,即大的Al₂O₃颗粒会明显减弱LIBS的信号强度. 另外,大部

分激光能量被用于气泡的产生,液体表面的晃动也会影响元素检测的准确性和灵敏度. Sovago等人^[71]研究组合了拉曼-LIBS实验装置,在线监测溶液中纳米颗粒浓度. 实验证明,组合拉曼-LIBS装置可以用于纳米粒子合成的在线监测,最小可检测粒径为5 nm的纳米颗粒. 为了提高LIBS的检测能力, Sobral等人^[72]用冷冻技术把液体样品转化为固体后进行LIBS检测,这样增加了样品表面的烧蚀率,使得检测灵敏度提高了6倍. 溶液冷冻技术将对液体样品的LIBS检测产生深远影响.

3.7 激光诱导击穿光谱在其他领域的应用

研究诊断激光诱导等离子体的特性,是为了提高LIBS的检测水平. Sherbini等人^[73]采用Nd:YAG激光激发含有Si 1.16%的铁合金,测量了等离子体的温度和电子密度. 研究显示, Si谱线的强度和线宽度分别对应等离子体温度和电子密度,经过对Si I谱线的自吸收修复以后可用于温度和电子密度测量. 实验进一步证明, Mg I, II谱线的自吸收被校准后也可用于等离子体温度测量^[74]. Aguilera等人^[75]采用由Nd:YAG激光器(1064 nm, 4.5 ns, 20 Hz, 100 mJ)组成的LIBS装置记录并测量Ni II谱线的Stark宽度,测得结果与文献记载一致;实验还测定了Ni II谱线的跃迁几率,通过优化实验方条件有效避免了自吸收的影响,第1次得到17%的实验结果^[76]. Diaz等人^[77,78]采用CO₂激光(10.591 μm, 64 ns)激发LiF和TiO₂样品,研究得出了LiF和TiO₂的激光诱导等离子体的时间分辨特性,其中Ti²⁺和Ti³⁺衰变速度比Ti和Ti⁺快, Li⁺, F²⁺和F³⁺衰变速度比Li和F⁺快.

LIBS具有高空间分辨率的独特优势,能够胜任微区、微量、薄层和细丝样品的分析任务. Siozos等人^[79]利用由Nd:YAG激光器组成的LIBS系统检测工业生产中机器上的沉积物成分,得知其污垢按主要成分可分为富含钙、富含钡和富含铁3类,为工业除垢提供了参考. Kumar等人^[80]利用Nd³⁺:YAG激光激发风力涡轮机叶片上的沉积物,准确地分析出了沉积盐的含量,证明此技术可用于监测偏远地区风力涡轮机叶片的沉积污染程度. Maurya等人^[81]采用由Nd:YAG激光器组成的LIBS装置分析了法兰表面和托卡马克光学窗口表面上的杂质,结果显示,所含杂质为Fe, Ni, Cr, Mo, Mn, Cu和C. Yang等人^[82]采用LIBS、扫描电子显微镜/能谱仪(SEM/EDS)和电子探

针显微分析(EPMA)3种方法对2类不同焊缝的熔合线区域进行线扫描分析,结果表明,对于含量较低且焊缝和母材成分差别较小的元素C和Si而言,只有用LIBS能够清晰展现出2区域的成分差异,证明LIBS的检测灵敏度明显高于SEM/EDS和EPMA.

一些气体混合物的最佳混合比可以用LIBS进行研究确定. Zhang等人^[83]通过LIBS研究高压背景下煤油和空气混合物的超声速燃烧的煤油/空气当量比,建立了不同气压下的发射强度比H/O和H/N与煤油/空气当量比的关系图,完成了压强与H α 谱线半高全宽度的关系图. Lee等人^[84]利用LIBS研究液化石油气(LPG)和电解氢氧(EOH)的火焰,在波长为532 nm激光的200 mJ脉冲能量(LPG 50 ccm, LPG 50 ccm-EOH 10 ccm, LPG 50 ccm-AIR 10 ccm)和500 mJ脉冲能量(EOH 500 ccm, EOH 500 ccm-LPG 70 ccm)条件下,记录了延迟时间为2 μs时的光谱线. 设定CN LIBS信号代表液化石油气燃料的浓度, H/O LIBS信号代表燃料/空气当量比,由此得出了显示火焰信息的二维图. Kotzagianni等人^[85]用钛宝石激光器(800 nm, 100 fs, 10 Hz)分析空气和甲烷的混合气体,结果表明CNB² Σ^+ -X² Σ^+ , $\Delta v=0$ 线是最强谱线,其光谱特征和甲烷含量呈线性关系,可以利用LIBS监测混合气体中的甲烷含量.

在工业过程控制方面, Reyhani等人^[86]采用Q开关Nd:YAG激光器(1064 nm, 10 ns, 5 Hz, 50 mJ),由LIBS监测甲烷在Pd催化下的不同气压下的分解. 研究证明, Pd能够有效地催化甲烷的分解,可以通过LIBS监测甲烷分解过程来控制压强,提高效率. Parvin等人^[87]采用ArF准分子激光器(193 nm, 10 ns, 50 mJ),把LIBS与激光诱导荧光光谱(LIFS)手段相结合,研究变压器中油的老化问题,通过使用油基纸代替液态油来获得更好的检测限. 研究表明,通过谱线强度可以确定油的老化程度,并且灵敏度很高.

张曦等人^[88]将LIBS用于煤粉颗粒流的直接检测,采用自行搭建的实验台架重点研究了不同收光角度下煤粉颗粒的等离子体光谱特性. 通过测量元素C, Si和Al的谱线强度和相对标准偏差表明,收光角度在30°~45°之间得到的等离子体光谱信号更强且稳定.

吴鼎等人^[89]利用LIBS对常见食用油和地沟油进行鉴别比较,检验结果良好,测试数据识别率高达98.1%. 数据结果为进一步推广LIBS在农副产品、药

品、食物等检测领域的应用提供了依据。

为了比较光谱仪器的分析性能, Arab等人^[90]采用由Nd:YAG激光器(1064 nm, 10 ns, 90 mJ)组成的LIBS系统研究比较2台分光计(Maya2000Pro和USB 4000)的性能, 分别对KBr溶液中的Pb和Cu做光谱分析, 结果表明, Maya2000Pro具有低检测限和高重复性, 性能比较好。就我国在LIBS仪器的研究方面, 2015年4月14日, 国家重大科学仪器设备开发专项项目“激光诱导等离子体光谱分析设备开发和应用项目”在京全面启动, 旨在研制出具有自主知识产权的LIBS设备, 实现其在冶金领域的生产应用, 制定出

针对LIBS设备研制的技术及产业化规范, 形成批量生产能力。

4 结论

LIBS自1962年诞生至今已走过50多年的历程, 经过不断的创新与发展, LIBS已日渐成熟, 获得了显著的理论与技术成果, 并广泛用于多个科研和生产领域, 成为了一种炙手可热的快速便捷、准确可靠的元素检测方法。基于LIBS成功的实验基础, 相信经过广大光谱工作者的不懈努力, LIBS将在更多的领域创造出更高的应用价值。

参考文献

- Brech F, Cross L. Optical microemission stimulated by a ruby laser. *Appl Spectrosc*, 1962, 16: 59–64
- Leme F O, Godoi Q, Kiyataka P H M, et al. Effect of pulse repetition rate and number of pulses in the analysis of polypropylene and high density polyethylene by nanosecond infrared laser induced breakdown spectroscopy. *Appl Surf Sci*, 2012, 258: 3598–3603
- Eschlböck-Fuchsa S, Haslinger M J, Hinterreiter A, et al. Influence of sample temperature on the expansion dynamics and the optical emission of laser-induced plasma. *Spectrochim Acta Part B*, 2013, 87: 36–42
- Chen J Z, Bai J N, Song G J, et al. Enhancement effects of flat-mirror reflection on plasma radiation. *Appl Opt*, 2013, 52: 6295–6299
- Chen J Z, Chen Z Y, Sun J, et al. Effect of cavity confinement on the soil plasma radiation characteristics (in Chinese). *Chin Sci Bull*, 2014, 59: 2065–2070 [陈金忠, 陈振玉, 孙江, 等. 空腔约束对土壤等离子体辐射特性的影响. *科学通报*, 2014, 59: 2065–2070]
- Banerjee S P, Fedosejevs R. Single shot depth sensitivity using femtosecond laser induced breakdown spectroscopy. *Spectrochim Acta Part B*, 2014, 92: 34–41
- Ilyin A A, Sokolova E B, Golik S S, et al. Time evolution of emission spectra from plasmas produced by irradiation of seawater surfaces by a femtosecond laser. *J Appl Spectrosc*, 2012, 78: 861–866
- Bonis A D, Filippo B D, Galasso A, et al. Comparison of the performances of nanosecond and femtosecond laser induced breakdown spectroscopy for depth profiling of an artificially corroded bronze. *Appl Surf Sci*, 2014, 302: 275–279
- Yurdanur-Tasel E, Berberoglu H, Bilikmen S. Investigation of materials of different crystal structure under various time delays using double pulse laser induced breakdown spectroscopy. *Spectrochim Acta Part B*, 2012, 74–75: 74–79
- Jiang X, Hayden P, Laasch R, et al. Inter-pulse delay optimization in dual-pulse laser induced breakdown vacuum ultraviolet spectroscopy of a steel sample in ambient gases at low pressure. *Spectrochim Acta Part B*, 2013, 86: 66–74
- Lazic V, Laserna J J, Jovicevic S. Insights in the laser induced breakdown spectroscopy signal generation underwater using dual pulse excitation—Part II: Plasma emission intensity as a function of interpulse delay. *Spectrochim Acta Part B*, 2013, 82: 50–59
- Gaft M, Nagli L, Gornushkin I. Laser-induced breakdown spectroscopy of Zr in short ultraviolet wavelength range. *Spectrochim Acta Part B*, 2013, 85: 93–99
- Gurell J, Bengtson A, Falkenström M, et al. Laser induced breakdown spectroscopy for fast elemental analysis and sorting of metallic scrap pieces using certified reference materials. *Spectrochim Acta Part B*, 2012, 74–75: 46–50
- Cong Z B, Sun L X, Xin Y, et al. Comparison of calibration curve method and partial least square method in the laser induced breakdown spectroscopy quantitative analysis. *J Comput Commun*, 2013, 1: 14–18
- Horňáčková M, Horňáček M, Rakovský J, et al. Determination of Si/Al molar ratios in microporous zeolites using calibration-free laser induced breakdown spectroscopy. *Spectrochim Acta Part B*, 2013, 88: 69–74
- Mateo M P, Piñon V, Anglos D, et al. Effect of ambient conditions on ultraviolet femtosecond pulse laser induced breakdown spectra. *Spectrochim Acta Part B*, 2012, 74–75: 18–23
- Sreedhar S, Rao E N, Kumar G M, et al. Molecular formation dynamics of 5-nitro-2, 4-dihydro-3H-1, 2, 4-triazol-3-one, 1, 3, 5-trinitroperhydro-1,3,5-triazine, and 2,4,6-trinitrotoluene in air, nitrogen, and argon atmospheres studied using femtosecond laser induced breakdown spectroscopy. *Spectrochim Acta Part B*, 2013, 87: 121–129
- Giacomo A D, Dell'Aglio M, Gaudioso R, et al. Effects of the background environment on formation, evolution and emission spectra of

- laser-induced plasmas. *Spectrochim Acta Part B*, 2012, 78: 1–19
- 19 Xin Y, Sun L X, Cong Z B, et al. In deep UV quantitative analysis of multi-element low alloy steel by laser-induced breakdown spectroscopy. *J Comput Commun*, 2013, 1: 19–22
 - 20 Legnaioli S, Lorenzetti G, Pardini L, et al. Laser-induced breakdown spectroscopy application to control of the process of precious metal recovery and recycling. *Spectrochim Acta*, 2012, 71-72: 123–126
 - 21 Pedarnig J D, Johannes H, Bernhard P, et al. Analysis of oxide materials in steel industry by calibration-free laser-induced breakdown spectroscopy. *Metall Anal*, 2012, 32: 9–12
 - 22 Shao Y, Gao X, Du C, et al. The LIBS experiment condition optimization of Alloy steel (in Chinese). *Spectrosc Spect Anal*, 2013, 33: 531–534 [邵妍, 高勋, 杜闯, 等. 合金钢的激光诱导击穿光谱实验条件优化. *光谱学与光谱分析*, 2013, 33: 531–534]
 - 23 Lopez-Quintas I, Mateo M P, Piñon V, et al. Mapping of mechanical specimens by laser induced breakdown spectroscopy method: Application to an engine valve. *Spectrochim Acta Part B*, 2012, 74-75: 109–114
 - 24 Pan C Y, Du X W, An N, et al. Laser-induced breakdown spectroscopy system for elements analysis in high-temperature and vacuum environment (in Chinese). *Spectrosc Spect Anal*, 2013, 33: 3388–3391 [潘从元, 杜学维, 安宁, 等. 真空环境熔融金属成分检测的激光诱导击穿光谱系统. *光谱学与光谱分析*, 2013, 33: 3388–3391]
 - 25 Gonzaga F B, Pasquini C. A compact and low cost laser induced breakdown spectroscopic system: Application for simultaneous determination of chromium and nickel in steel using multivariate calibration. *Spectrochim Acta Part B*, 2012, 69: 20–24
 - 26 Kwak J H, Kim G, Kim Y J, et al. Determination of heavy metal distribution in PM10 during Asian dust and local pollution events using laser induced breakdown spectroscopy (LIBS). *Aerosol Sci Technol*, 2012, 46: 1079–1089
 - 27 Awan M A, Ahmed S H, Aslam M R, et al. Determination of heavy metals in ambient air particulate matter using laser-induced breakdown spectroscopy. *Arab J Sci Eng*, 2013, 38: 1655–1661
 - 28 Li M, Zhu X Y, Xu Y, et al. Quantitative determination of Cu in lake water by laser induced breakdown spectroscopy (in Chinese). *Laser Optoelectron Prog*, 2013, 50: 013001 [李敏, 朱心勇, 徐媛, 等. 应用 LIBS 技术定量检测湖水样品中的铜. *激光与光电子学进展*, 2013, 50: 013001]
 - 29 Al-Adel F F, Dastageer M A, Gasmi K, et al. Optimization of a laser induced breakdown spectroscopy method for the analysis of Liquid samples. *J Appl Spectrosc*, 2013, 80: 767–770
 - 30 Bukhari M, Awan M A, Qazi I A, et al. Development of a method for the determination of chromium and cadmium in tannery wastewater using laser-induced breakdown spectroscopy. *J Anal Methods Chem*, 2012, 2012: 823016
 - 31 Faye C B, Amodeo T, Fréjafon E, et al. Sampling considerations when analyzing micrometric-sized particles in a liquid jet using laser induced breakdown spectroscopy. *Spectrochim Acta Part B*, 2014, 91: 5–11
 - 32 Du C, Gao X, Shao Y, et al. Analyses of heavy metals by soil using dual-pulsed laser induced breakdown spectroscopy (in Chinese). *Acta Phys Sin*, 2013, 62: 045202 [杜闯, 高勋, 邵妍, 等. 土壤中重金属元素的双脉冲激光诱导击穿光谱研究. *物理学报*, 2012, 62: 045202]
 - 33 Kim G, Kwak J, Kim K R, et al. Rapid detection of soils contaminated with heavy metals and oils by laser induced breakdown spectroscopy (LIBS). *J Hazard Mater*, 2013, 263: 754–760
 - 34 Liu Y, Bousquet B, Baudelet M, et al. Improvement of the sensitivity for the measurement of copper concentrations in soil by microwave-assisted laser-induced breakdown spectroscopy. *Spectrochim Acta*, 2012, 73: 89–92
 - 35 Srungaram P K, Ayyalasamayajula, Fang Y Y. Comparison of laser induced breakdown spectroscopy and spark induced breakdown spectroscopy for determination of mercury in soils. *Spectrochim Acta Part B*, 2013, 87: 108–113
 - 36 Farooq W A, Al-Mutairi F N, Khater A E M, et al. Elemental analysis of fertilizer using laser induced breakdown spectroscopy. *Opt Spectrosc*, 2012, 112: 874–880
 - 37 Peng L L, Sun D X, Su M G, et al. Rapid analysis on the heavy metal content of spent zinc – manganese batteries by laser-induced breakdown spectroscopy. *Opt Laser Technol*, 2012, 44: 2469–2475
 - 38 Aguirre M A, Hidalgo M, Canals A, et al. Analysis of waste electrical and electronic equipment (WEEE) using laser induced breakdown spectroscopy (LIBS) and multivariate analysis. *Talanta*, 2013, 117: 419–424
 - 39 Rabasovic M S, Sevic D, Pejcev V, et al. Detecting indium spectral lines using electron and laser induced breakdown spectroscopy. *Nucl Instrum Methods Phys Res Sect B*, 2012, 279: 58–61
 - 40 Huber N, Eschlböck-Fuchs S, Scherndl H, et al. In-line measurements of chlorine containing polymers in an industrial waste sorting plant by laser-induced breakdown spectroscopy. *Appl Surf Sci*, 2014, 302: 280–285
 - 41 Barbier S, Perrier S, Freyermuth P, et al. Plastic identification based on molecular and elemental information from laser induced breakdown spectra: A comparison of plasma conditions in view of efficient sorting. *Spectrochim Acta Part B*, 2013, 88: 167–173
 - 42 Yao M Y, Huang L, Zheng J H, et al. Assessment of feasibility in determining of Cr in Gannan Navel Orange treated in controlled conditions by laser induced breakdown spectroscopy. *Opt Laser Technol*, 2013, 52: 70–74

- 43 Zhang X, Yao M Y, Liu M H. Quantitative analysis of cadmium in navel orange by laser-induced breakdown spectroscopy combined with partial least squares (in Chinese). *Acta Phys Sin*, 2013, 62: 044211 [张旭, 姚明印, 刘木华. 激光诱导击穿光谱结合偏最小二乘法定量分析脐橙中 Cd 含量. *物理学报*, 2013, 62: 044211]
- 44 Wan X, Wang J Y, Ye J H, et al. Analysis of distribution and contents of heavy metal pollution in fish body with laser-induced breakdown spectroscopy (in Chinese). *Spectrosc Spect Anal*, 2013, 33: 206–209 [万雄, 王建宇, 叶建华, 等. 激光诱导击穿光谱对污染鱼体内重金属元素分布与含量的分析. *光谱学与光谱分析*, 2013, 33: 206–209]
- 45 Diaz L, Rubio L, Camacho J J. Time evolution of the infrared laser induced breakdown spectroscopy of DNA bases Guanine and Adenine. *Appl Phys A*, 2013, 110: 847–851
- 46 Dhar P, Gembitsky I, Rai P K, et al. A possible connection between antidiabetic & antilipemic properties of psoralea corylifolia seeds and the trace elements present: A libS based study. *Food Biophys*, 2013, 8: 95–103
- 47 Emara E M, Imam H, Hassan M A, et al. Biological application of laser induced breakdown spectroscopy technique for determination of trace elements in hair. *Talanta*, 2013, 117: 176–183
- 48 Manzoor S, Moncayo S, Navarro-villoslada F, et al. Determination of the postmortem interval by laser induced breakdown spectroscopy using swine skeletal muscles. *Spectrochim Acta Part B*, 2013, 88: 186–191
- 49 Kula A, Wietecha-Poslusznny R, Pasione K, et al. Application of laser induced breakdown spectroscopy to examination of writing inks for forensic purposes. *Sci Justice*, 2014, 54: 118–125
- 50 Kokkinaki O, Mihasan C, Velegrakis M, et al. Comparative study of laser induced breakdown spectroscopy and mass spectrometry for the analysis of cultural heritage materials. *J Mol Struct*, 2013, 1044: 160–166
- 51 Palomar T, Oujja M, García-Heras M, et al. Laser induced breakdown spectroscopy for analysis and characterization of degradation pathologies of Roman glasses. *Spectrochim Acta Part B*, 2013, 87: 114–120
- 52 Blagoev K, Grozeva M, Malcheva G, et al. Investigation by laser induced breakdown spectroscopy, X-ray fluorescence and X-ray powder diffraction of the chemical composition of white clay ceramic tiles from Veliki Preslav. *Spectrochim Acta Part B*, 2013, 79–80: 39–43
- 53 Pardini L, Hassan A E, Ferretti M, et al. X-ray fluorescence and laser-induced breakdown spectroscopy analysis of roman silver denarii. *Spectrochim Acta B*, 2012, 74–75: 156–161
- 54 Roberts D E, Plessis A D, Steyn J, et al. An investigation of laser induced breakdown spectroscopy for use as a control in the laser removal of rock from fossils found at the Malapa hominin site, South Africa. *Spectrochim Acta*, 2012, 73: 48–54
- 55 Vítková G, Novotny K, Prokes L, et al. Fast identification of biominerals by means of stand-off laser-induced breakdown spectroscopy using linear discriminant analysis and artificial neural networks. *Spectrochim Acta*, 2012, 73: 1–6
- 56 Vítková G, Prokes L, Novotny K, et al. Comparative study on fast classification of brick samples by combination of principal component analysis and linear discriminant analysis using stand-off and table-top laser-induced breakdown spectroscopy. *Spectrochim Acta*, 2014, 101: 191–199
- 57 Guirado S, Fortes F J, Lazic V, et al. Chemical analysis of archeological materials in submarine environments using laser-induced breakdown spectroscopy. On-site trials in the Mediterranean Sea. *Spectrochim Acta*, 2012, 74–75: 137–143
- 58 Hanif M, Salik M. Optical emission studies of sulphur plasma using laser induced breakdown spectroscopy. *Opt Spectrosc*, 2014, 116: 315–323
- 59 Giacomo A D, Dell’Aglio M, Gaudio R, et al. A laser induced breakdown spectroscopy application based on local thermodynamic equilibrium assumption for the elemental analysis of alexandrite gemstone and copper-based alloys. *Chem Phys*, 2012, 398: 233–238
- 60 Horňáčková M, Grolmusová Z, Horňáček M, et al. Calibration analysis of zeolites by laser induced breakdown spectroscopy. *Spectrochim Acta*, 2012, 74–75: 119–123
- 61 Kim Y S, Han B Y, Shin H S, et al. Determination of uranium concentration in an ore sample using laser-induced breakdown Spectroscopy. *Spectrochim Acta*, 2012, 74–75: 190–193
- 62 Mukhono P M, Angeyo K H, Dehayem-Kamadjeu A, et al. Laser induced breakdown spectroscopy and characterization of environmental matrices utilizing multivariate chemometrics. *Spectrochim Acta Part B*, 2013, 87: 81–85
- 63 Hark R R, Remus J J, East L J, et al. Geographical analysis of “conflict minerals” utilizing laser-induced breakdown spectroscopy. *Spectrochim Acta*, 2012, 74–75: 131–136
- 64 Li W, Liu L, Su Y, et al. The detect of Mars component based on femto-LIBS technology (in Chinese). Article 26 the 2nd national conference on space exploration, 2013. 703–713 [李维, 刘励, 苏云, 等. 基于 femto-LIBS 的火星矿物岩石成分探测技术. 第二十六届全国空间探测学术研讨会, 2013. 703–713]
- 65 Pavlov S G, Schroder S, Rauschenbach I, et al. Low-energy laser induced breakdown spectroscopy for *in-situ* space missions to solar system bodies without atmospheres. *Planet Space Sci*, 2012, 71: 57–63
- 66 Apostol I, Damian V, Damian R, et al. Laser induced breakdown spectroscopy surface analysis correlated with the process of nanoparticle production by laser ablation in liquids. *Hyperfine Interact*, 2013, 216: 139–143

- 67 Kim C K, In J H, Lee S H, et al. Influence of laser wavelength on the laser induced breakdown spectroscopy measurement of thin $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ solar cell films. *Spectrochim Acta Part B*, 2013, 88: 20–25
- 68 Darwiche S, Benrabbah R, Benmansour M, et al. Impurity detection in solid and molten silicon by laser induced breakdown spectroscopy. *Spectrochim Acta Part B*, 2012, 74-75: 115–118
- 69 Gondal M A, Dastageer A, Maslehuddin M, et al. Detection of sulfur in the reinforced concrete structures using a dual pulsed LIBS system. *Opt Laser Technol*, 2012, 44: 566–571
- 70 Rosado J C D, Hermite D L, Levi Y, et al. Effect of particle size on laser-induced breakdown spectroscopy analysis of alumina suspension in liquids. *Spectrochim Acta*, 2012, 74-75: 80–86
- 71 Sovago M, Buis E J, Sandtke M. Nanoparticle detection in aqueous solutions using Raman and laser induced breakdown spectroscopy. *Spectrochim Acta Part B*, 2013, 87: 182–187
- 72 Sobral H, Sanginés R, Trujillo-vázquez A, et al. Detection of trace elements in ice and water by laser-induced breakdown spectroscopy. *Spectrochim Acta*, 2012, 78: 62–66
- 73 Sherbini A M E, Aamer A A S A. Measurement of plasma parameters in laser-induced breakdown spectroscopy using si-lines. *World J Nano Sci Eng*, 2012, 2: 206–212
- 74 Sherbini A M E, Aamer A A S A, Hassan A T, et al. Measurements of plasma electron temperature utilizing magnesium lines appeared in laser produced aluminum plasma in air. *Opt Photonics J*, 2012, 2: 278–285
- 75 Aguilera J A, Aragon C, Manrique J. Measurement of Stark widths of Ni II spectral lines by laser induced breakdown spectroscopy. *J Quant Spectrosc Radiat Transfer*, 2013, 114: 151–156
- 76 Manrique J, Aguilera J A, Aragon C. Transition probabilities of Ni II spectral lines measured by laser induced breakdown spectroscopy. *J Quant Spectrosc Radiat Transfer*, 2013, 120: 120–124
- 77 Diaz L, Camacho J J, Sanz M, et al. Temporal evolution study of the plasma induced by CO_2 pulsed laser on targets of titanium oxides. *Spectrochim Acta Part B*, 2013, 86: 88–93
- 78 Camacho J J, Diaz L, Cid J P, et al. Time-resolved study of the plasma-plume emission during the nanosecond ablation of lithium fluoride. *Spectrochim Acta Part B*, 2013, 88: 203–210
- 79 Siozos P, Philippidis A, Hadjistefanou M, et al. Chemical analysis of industrial scale deposits by combined use of correlation coefficients with emission line detection of laser induced breakdown spectroscopy spectra. *Spectrochim Acta Part B*, 2013, 87: 86–91
- 80 Kumar V S, Vasa N J, Sarathi R. Detecting salt deposition on a wind turbine blade using laser induced breakdown spectroscopy technique. *Appl Phys A*, 2013, 112: 149–153
- 81 Maurya G S, Jyotsana A, Pathak A K, et al. Spatial analysis of impurities on the surface of flange and optical window of the tokamak using laser induced breakdown spectroscopy. *Opt Lasers Eng*, 2014, 56: 13–18
- 82 Yang C, Zhang Y, Jia Y H, et al. Element distribution analysis of welded fusion zone by laser-induced breakdown spectroscopy (in Chinese). *Spectrosc Spect Anal*, 2014, 34: 1089–1094 [杨春, 张勇, 贾云海, 等. 激光诱导击穿光谱对焊缝熔合区的元素成分分布分析. *光谱学与光谱分析*, 2014, 34: 1089–1094]
- 83 Zhang S H, Yu X L, Li F, et al. Laser induced breakdown spectroscopy for local equivalence ratio measurement of kerosene/air mixture at elevated pressure. *Opt Lasers Eng*, 2012, 50: 877–882
- 84 Lee S H, Hahn H T, Yoh J J. Towards a two-dimensional laser induced breakdown spectroscopy mapping of liquefied petroleum gas and electrolytic oxy-hydrogen flames. *Spectrochim Acta Part B*, 2013, 88: 63–68
- 85 Kotzagianni M, Couris S. Femtosecond laser induced breakdown spectroscopy of air-methane mixtures. *Chem Phys Lett*, 2013, 561-562: 36–41
- 86 Reyhani A, Mortazavi S Z, Parvin P, et al. Simultaneous laser induced breakdown spectroscopy and Pd-assisted methane decomposition at different pressures. *Spectrochim Acta Part B*, 2012, 74-75: 124–130
- 87 Parvin P, Shoursheini S Z, Khalilinejad F, et al. Simultaneous fluorescence and breakdown spectroscopy of fresh and aging transformer oil immersed in paper using ArF excimer laser. *Opt Lasers Eng*, 2012, 50: 1672–1676
- 88 Zhang X, Lu J D, Pan G, et al. Investigation on laser-induced coal particle flow plasma properties acquired with different collection angles (in Chinese). *Spectrosc Spect Anal*, 2013, 33: 1473–1476 [张曦, 陆继东, 潘刚, 等. 不同收光角度下煤粉颗粒流的 LIBS 光谱特性研究. *光谱学与光谱分析*, 2013, 33: 1473–1476]
- 89 Wu D, Hai R, Liu P, et al. Preliminary study of identifying trench oil based on laser-induced breakdown spectroscopy (in Chinese). *Chin Sci Bull*, 2014, 59: 2071–2076 [吴鼎, 海然, 刘平, 等. 基于激光诱导击穿光谱地沟油鉴别的初步探究. *科学通报*, 2014, 59: 2071–2076]
- 90 Arab M, Bidin N, Rizvi Z H, et al. Comparison study of two commercial spectrometers for heavy metal analysis of laser induced breakdown spectroscopy (LIBS). *Photonic Sensors*, 2014, 4: 63–69

Recent development and application of laser induced breakdown spectroscopy

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Laser-induced breakdown spectroscopy (LIBS) is a spectroscopy detection technology. As sample is ablated by high-energy pulse laser, trace amounts of sample material gasify to form high temperature and density plasma. Qualitative and quantitative analysis of chemical elements in the sample can be achieved through measuring wavelengths and spectral line intensity of plasma atomic emission spectrum. As a new spectroscopy detect technology in the field of analytical science, LIBS has developed rapidly in recent years, and new research results constantly emerging, the application scope expanding gradually. It shows more and more potential and vitality in terms of analysis of material composition elements.

Since the method of using laser as excitation source of atomic emission spectrum was first put forward by Brech and Cross in 1962, spectrum researchers have being kept exploring in this regard. Especially during the last decade, LIBS have got the fast development. Relevant papers are increasing year by year. Compared with traditional methods of spectral analysis, such as Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Atomic Absorption Spectroscopy (AAS) and X-ray Fluorescence spectrometry(XRF), LIBS has many unique advantages: Strong ability to adapt to all kinds of phase states: gaseous, liquid, solid or particles. As pretreatment is simple or no sample pretreatment is needed, operating time is saved. As for laser excitation, there is no secondary pollution. LIBS is a pure elemental analysis technology. Similar to nondestructive examination reduce the losses of standard samples and test samples. LIBS is suitable for fast, real-time and in-field analysis, and therefore, it avoids the difficulties of sampling, packaging and transport. Through the surface determination and layers-in situ detection, it could be concluded the spatial distribution of analysis elements in the sample. Non-contact, remote probing and online analysis could be achieved, even in harsh environments. The operation of LIBS device is simple and convenient, and so forth. Due to its marked superiority in determination of material composition, spectrum researchers are interested in researching and applying LIBS increasingly.

According to the latest related reports at home and abroad, the experimental apparatus, research methods and the applications of metallurgical analysis, environmental monitoring, biological medicine, archaeological researchs, geological exploration, materials science and other areas of LIBS are analysed and summarized in this paper. In order to jointly promote the prosperity and development of LIBS, the paper tries to present the new and light points of each article to the readers, making this new type of spectral detection technology gradually perfect, playing more important role in the scientific research, production and living.

laser-induced breakdown spectroscopy, experimental apparatus, elemental analysis

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